Supporting Information

for

Propylene Polymerization and Deactivation Processes with Isoselective {Cp/Flu} Zirconocene Catalysts

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MATERIALS AND METHODS

General. All manipulations were performed under a purified argon atmosphere using standard Schlenk techniques or in a glovebox. Solvents were distilled from Na/benzophenone (THF, Et_2O) and Na/K alloy (toluene, hexane, and pentane) under nitrogen, degassed thoroughly and stored under nitrogen prior to use. Deuterated solvents (benzene-d_6, toluene-d_8; >99.5% D, Deutero GmbH and Euroisotop) was vacuum-transferred from Na/K alloy into storage tubes. $CDCl_3$ and CD_2Cl_2 were dried and kept over 4Å molecular sieves and vacuum-transferred before use.

The ligand precursors 3,6-di-*tert*-butyl-fluorene, 2,7-di-*tert*-butyl-fluorene were generously provided by Total Petrochemicals or synthesized according to literature protocols.[1] The precursors *tert*-butyl-cyclopentadiene (mixture of isomers),[2,3] 6,6'-dimethyl-fulvene,[4] 3-*tert*-butyl-6,6'-dimethyl-fulvene,[4] 3-*tert*-butyl-6,6'-diphenyl-fulvene,[2] 6,6'-di-(*n*-butyl)-fulvene [5] and (2,7-di-*tert*-butyl-fluorenyl)chlorodiphenylsilane,[6] 2.7-$(cumyl)_2$–fluorene, 2,7–$(mesityl)_2$-fluorene [7] and 1,1,4,4,7,7,10,10-octamethyl-1,2,3,4,7,8,9,10-octahydrodibenzo[*b*,*h*]fluorene ("Oct"), [2,8] were prepared according to literature protocols. Other starting materials were purchased from Acros, Strem and Aldrich, and used as received. MAO (30 wt% solution in toluene, Albermale; contains ca. 10 wt% of free $AlMe_3$) was used as received.

NMR spectra of complexes were recorded on Bruker AM-400 and AM-500 spectrometers in Teflon-valved NMR tubes at 25 °C, unless otherwise indicated. ^1H and ^{13}C NMR chemical shifts are reported in ppm vs. $SiMe_4$ (δ 0.00) as determined by reference to the residual solvent peaks. ^{19}F NMR chemical shifts were determined by external reference to an aqueous solution of $NaBF_4$. The resonances of organometallic complexes were assigned from 2D ^1H–^{13}C HSQC and HMBC NMR experiments. Coupling constants are given in Hertz.

^{13}C NMR analyses of iPP samples were run in the research center of Total Petrochemicals in Feluy (Belgium), on a AM-500 Bruker spectrometer using the following conditions: solutions of ca. 200 mg of PP polymer in trichlorobenzene/C_6D_6 mixture at 135 °C in 10 mm tubes, inverse gated experiment, pulse angle 90°, delay 11 sec, acquisition time 1.25 sec, number of scans 6000.

Elemental analyses (C, H, N) were performed using a Flash EA1112 CHNS Thermo Electron apparatus and are the average of two independent determinations.

ASAP-HRMS spectra were recorded on a Bruker Daltonics - maXis 4G - UHR-TOF spectrometer. iASAP-HRMS were recorded on hybrid quadripole time of flight mass spectrometer (Synapt G2, Waters Corp. Wilmslow, UK) using the iASAP technique described here: [9]

DSC measurements were performed on a SETARAM Instrumentation DSC 131 differential scanning calorimeter at a heating rate of 10 °C/min; first and second runs were recorded after cooling to 30 °C; the melting temperatures reported in tables correspond to the second run.

GPC analyses of iPP samples were carried out in 1,2,4-trichlorobenzene at 135 °C in the research center of Total Petrochemicals in Feluy (Belgium), using polystyrene standards for universal calibration.

Synthesis of proligand precursors.

Synthesis of 6-methyl-6'-*tert*-butyl-fulvene (1a). A 1L round bottom flask was charged with cyclopentadiene (45 mL, 0.54 mol), sodium methoxide (34 g, 0.63 mol) and 3,3-dimethyl-butan-2-one (80 mL, 0.63 mol). The resulting brown slurry was stirred thoroughly for three days. HCl (37 wt% aq, 20 mL) and water (100 mL) were added under ice cooling. The resulting mixture was diluted with Et_2O (100 mL), and the aqueous layer was extracted with Et_2O (2 × 100 mL). The combined organic phases were washed with $NaHCO_3$, dried with $MgSO_4$, and evaporated under vacuum. The crude orange oil was distilled twice under reduced pressure (3 Torr, 45–50 °C) to yield **1a** as a bright orange oil (29.0 g, 36 %). ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C): δ 6.77 (d, *J* = 5.4, 1H, H_{Cp}), 6.57 (dt, *J* = 5.4, 1H, H_{Cp}), 6.49 (m, 1H, H_{Cp}), 6.40 (d (br), *J* = 5.4, 1H, H_{Cp}), 2.28 (s, 3H, C*H*$_3$), 1.37 (s, 9H, C(C*H*$_3$)$_3$). ^{13}C{^{1}H} NMR (CD_2Cl_2, 100 MHz, 25 °C): δ 162.5 (C^q), 141.6 (C^q), 131.0 (C_{Cp}), 128.7 (C_{Cp}), 123.2 (C_{Cp}), 122.2 (C_{Cp}), 39.1 (*C*(CH$_3$)$_3$), 32.2 (C(*C*H$_3$)$_3$), 20.3 (*C*H$_3$). ESI-MS (CH_3OH/CH_2Cl_2 90/10, *m/z*) $[M+H]^+$ Calcd for $[C_{11}H_{17}]^+$:149.1330. Found: 149.1325.

Synthesis of 1-(dimethyl-*tert*-butyl)-cyclopentadiene (mixture of isomers). To a solution of 6-methyl-6'-*tert*-butyl-fulvene (15.3 g, 0.1 mol) in Et_2O (200 mL) was added dropwise MeLi (98 mL of a 1.6 M solution in Et_2O, 0.16 mol) at 0 °C. The resulting solution was stirred overnight. The white suspension obtained was hydrolyzed with sat. NH_4Cl (50 mL) and water (100 mL), and diluted with Et_2O (100 mL). The aqueous phase was extracted with Et_2O (100 mL) and the combined organic phases were dried over $MgSO_4$, filtered and evaporated under reduced pressure. The crude product was distilled under vacuum (0.8 Torr, 45 °C) to yield the product as a bright yellow oil (6.58 g (mixture of isomers), 39%). ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C): δ 6.05–6.72 (3H, multiple signals, H_{Cp}), 3.04–2.96 (2s, 2H, CH_2(Cp)), 1.19 (s, 6H, CH_3), 0.89 (s, 9H, $(CH_3)_3$). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz, 25 °C): δ (isomer 1): 154.06 (C^q), 135.7 (C_{Cp}), 131.3 (C_{Cp}), 127.0 (C_{Cp}), 40.8 (CH_2), 40.5 (C^q), 35.8 (C^q). δ (isomer 2): 156.9 (C^q), 131.9 (C_{Cp}), 130.6 (C_{Cp}), 126.7 (C_{Cp}), 44.1 (CH_2), 41.4 (C^q), 36.3 (C^q) and for both isomers: 26.6 (-C(*C*H$_3$)$_3$, 23.9 (-*C*H$_3$).

Synthesis of 6, 6'-diphenyl-3-(2,3,3-trimethylbutan-2-yl)fulvene (1b). To a solution of 1-(dimethyl-(*tert*-butyl))-cyclopentadiene (6.5 g, 39.5 mmol) was added *n*-BuLi (23 mL of a 2.3 M

solution in hexanes) at 0 °C. After 2 h at RT, a solution of benzophenone (7.55 g, 42 mmol) in Et_2O (15 mL) was then added dropwise and stirring was continued overnight. The orange reaction mixture was hydrolyzed with 20% aqueous HCl (50 mL) and stirred overnight. The organic phase was washed with $NaHCO_3$, dried over $MgSO_4$, and the volatiles were removed under vacuo. The orange/red residue was taken up in methanol and recrystallized to afford **1b** as an orange powder (5.77 g, 44 %). ^{1}H NMR (CD_2Cl_2, 400 MHz, 25 °C): δ 7.43-7.30 (m, 10H, H_{Ph}), 6.65 (dd, *J* = 6.0, *J* = 2.0 , 1H, H_{Cp}), 6.20 (dd, *J* = 6.0, *J* = 2.0, 1H, H_{Cp}), 6.00 (t, *J* = 2.0, 1H, H_{Cp}), 1.19 (s, 6H, C*H*$_3$), 0.94 (s, 9H, C(C*H*$_3$)$_3$). ^{13}C{^{1}H} NMR (CD_2Cl_2, 100 MHz, 25°C): δ 156.4 (C^q), 149.2 (C^q), 144. (C^q), 142. (C^q), 135.6 (C_{Cp}), 132.3 (C_{Ph}), 132.2 (C_{Ph}), 128.7(C_{Ph}), 128.8(C_{Ph}), 128.2(C_{Ph}), 128.1 (C_{Ph}), 123.3 (C_{Cp}), 119.7 (C_{Cp}), 41.2(*C*Me$_2$*t*Bu), 36.6 (*C*(CH$_3$)$_3$), 26.8 (C(*C*H$_3$)$_3$), 23.8 (2C, *C*H$_3$).

Synthesis of 1-(tri-*n*-butyl)cyclopentadiene. In a 1L flask, 6,6'-dibutylfulvene (31 g, 0.16 mol) was diluted in Et_2O (200 mL) and cooled to 0 °C. MeLi (80 mL of a 2.2M solution in Et_2O, 0.18 mol) was added dropwise at 0 °C. After one night of stirring, the mixture was hydrolyzed with saturated NH_4Cl (50 mL) at 0 °C, diluted with water (100 mL) and Et_2O (100 mL). The organic phase was washed with brine and dried over Na_2SO_4. The volatiles were removed *in vacuo* and the resulting yellow oil was distilled under reduced pressure to afford the desired cyclopentadiene as a yellow liquid (12.4 g, 48 %). ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C). (At least two sets of H_{Cp} signals/isomers were detected. As the signals of isomers are overlapping, all the chemical shifts are given hereafter): δ 6.56-6.51, 6.50-6.46, 6.45-6.38, 6.30-6.26, 6.16, 5.97 (m, 3H, H_{Cp}), 2.97 (d, *J* = 1.1, 1H, CH_{2Cp}), 2.83 (d, *J* = 1.1 , 1H, CH_{2Cp}), 1.49-1.44 (m, 6H, CH_2), 1.30-1.22 (m, 6H, CH_2), 1.11-1.02 (m, 6H, CH_2), 0.91-0.86 (m, 9H, CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz, 25 °C) (only major isomer shifts are given): δ 154.1 (C^q), 133.1 (C_{Cp}), 132.8 (C_{Cp}), 125.7(C_{Cp}), 40.9 (*C*(*n*Bu)$_3$), 37.3 ($CH_{2\ Cp}$) 36.1 (CH_2), 25.9 (CH_2), 23.7 (CH_2), 14.3 (CH_3).

Synthesis of 6,6'-diphenyl-2-(tri-*n*-butyl)-fulvene (1c). Using a similar procedure established for **1b**, **1c** was obtained from *n*-Buli (11.3 mL of 2.5 M solution in hexanes, 28 mmol), 1-(tri-*n*-butyl)-cyclopentadiene (6.4 g, 25.8 mmol) and benzophenone (5.2g, 28.3 mmol). Workup afforded **1c** as an orange powder (3.6 g, 34 %). ^{1}H NMR (CD_2Cl_2, 400 MHz, 25 °C): δ 7.41-7.36 (m, 6H, H_{Ph}), 7.34-7.28 (m, 4H, H_{Ph}), 6.59 (dd, *J*= 5.5, *J*= 2.0, 1H, H_{Cp}), 6.59 (dd, *J* = 5.5, *J* = 2.0, H_{Cp}), 5.93 (t, *J* = 2.0, 1H, H_{Cp}), 1.49-1.45 (m, 6H, C-C***H***$_2$-CH_2-), 1.27 (hex, *J* = 7.3, 6H, -C***H***$_2$-CH_3), 1.16-1.08 (m, 6H, CH_2-C***H***$_2$-CH_2), 0.89 (t, *J*= 7.3, 3H, CH_3). ^{13}C{^{1}H} NMR (CD_2Cl_2, 100 MHz, 25 °C): δ 156.8 (C^q) , 148.3 (C^q), 144.5 (C^q), 142.1 (C_{Ph}), 142.0 (C_{Ph}), 132.9 (C_{Cp}), 132.2 (C_{Ph}), 132.2 (C_{Ph}), 128.7 (C_{Ph}), 128.6 (C_{Ph}), 128.1 (C_{Ph}), 128.0 (C_{Ph}), 125.1 (C_{Cp}), 118.6 (C_{Cp}) , 41.7(*C*(*n*Bu)$_3$), 36.3 (C-*C*H_2-CH_2-), 26.3 (CH_2-*C*H_2-CH_2), 23.9 (***C***H_2-CH_3), 14.4 (*C*H_3).

Synthesis of 1-(cyclohexyl-methyl-)cyclopentadiene. MeLi (100 mL of a 1.6M solution in Et_2O, 0.16 mol) was added dropwise at 0 °C on a solution of 6,6'-cyclohexylfulvene (24 g, 0.16 mol) in diethyl ether (250 mL) and the resulting solution was slowly warmed up at room temperature. After one night of stirring, the mixture was slowly hydrolyzed at 0 °C with sat. NH_4Cl (50 mL). The organic phase was washed with brine, dried over Na_2SO_4 and the solvent was removed under reduced pressure. The yellow liquid obtained was distilled under reduced pressure (80 °C, 1 Torr) to yield 1-(cyclohexyl-methyl)-cyclopentadiene as a yellow oil (9.4 g, 35 %). ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C) (at least two isomers were detected; as the isomers signals overlapped, the chemicals shifts for both isomers are given hereafter): δ 6.62-659, 6.47-6.42, 6.29-6.2, 6.21-6.20 and 6.03-6.01(m, 3H, H_{Cp}), 2.98 and 2.93 (2 q, *J* =1.5, 2H, $CH_{2\ Cp}$), 1.80-1.75 (m, 2H, CH_{2Cyclo}), 1.56-1.35 (m, 8H, CH_{2Cyclo}), 1.11 and 1.13 (s, 3H, CH_3). ^{13}C{^{1}H} ($CDCl_3$, 100 MHz, 25 °C): δ 158.9 and 156.0 (C^q) 133.5 (C_{Cp}), 132.8 C_{Cp}), 132.3 130.3 124.8 123.9(C_{Cp}), 41.2 and 39.9 ($CH_{2\ Cp}$), 38.4 and 37.5 (2C,CH_2), 29.4 and 27.7 (br, *C*H_3), 26.6 and 26.5 (CH_2), 22.8 and 22.7 (2C, CH_2), aliphatic quaternary carbon not observed. ASAP-MS (50 °C, *m/z*) $[M+H]^+$ Calcd for $[C_{12}H_{19}]^+$ 163.1481. Found:163.1482.

Synthesis of 6,6'-diphenyl-(2-cyclohexyl-methyl)fulvene (1e). Using a similar protocol than that for **1b**, **1e** was obtained from *n*-BuLi (24 mL of a 2.5M solution in hexanes, 61 mmol), 1-(cyclopenta-1,4-dien-1-yl)-1-methylcyclohexane (9.0 g, 56 mmol) and benzophenone (11.2 g, 61 mmol) as an orange powder (6.8 g, 37 %). ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C): δ 7.39-7.29 (m, 10H, H_{Ph}), 6.64 (dd, *J* = 5.4, *J* = 1.7, 1H, H_{Cp}), 6.27 (dd, *J* = 5.4, *J*= 1.7, 1H, H_{Cp}), 1.82-1.71 (m, 2H, CH_2), 1.46(m, 8H, CH_2), 1.13 (s, 3H, CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz, 25 °C): δ 157.9 (C^q), 148.9 (C^q), 144.2 (C^q), 141.8 (C^q), 141.7 (C^q), 132.4 (C_{Cp}), 132.1(C_{Ph}), 132.0 (C_{Ph}), 128.4 (C_{Ph}), 128.3 (C_{Ph}), 127.8 (C_{Ph}), 127.7(C_{Ph}), 125.2 (C_{Cp}), 116.2 (C_{Cp}) 37.3 (2C, CH_2), 35.9 (C^q), 27.5 (*C*H_3), 26.5 (CH_2), 22.8 (2C, CH_2). ASAP-MS (95 °C, *m/z*) $[M+H]^+$ Calcd for $[C_{25}H_{27}]^+$: 327.2107. Found: 327.2103.

Synthesis of 9-(4-(*tert*-butyl)-2-methylcyclopenta-2,4-dien-1-ylidene)-9*H*-fluorene (1i). To a solution of 3-methyl-*tert*-butyl-cyclopentadiene (1.0 g, 7.1 mmol) in THF (15 mL) was added *n*-BuLi (3.4 mL of 2.4 M solution in Et_2O, 8.1 mmol) at 0 °C. After two days of stirring at room temperature, a solution of fluorenone (1.4 g, 7.7 mmol) in THF (15 mL) was added dropwise and the reaction was heated at reflux for two days. HCl (10 wt% aq, 30 mL) was added slowly and stirring was continued for 4 h. The mixture was diluted with Et_2O and the organic phase was washed with sat. $NaHCO_3$ and brine and dried on Na_2SO_4. Volatiles were removed *in vacuo* to give a dark brown orange oil. The mixture was filtrated on a silica pad (Pet. ether: CH_2Cl_2/ 90:10 *v/v*) and the solvent removed under reduced pressure to afford **1i** (1.4 g, 70 %) as a dark orange tar. ^{1}H NMR (CD_2Cl_2 , 25 °C, 400 MHz): δ 7.95 (d, J = 7.4, 1H, H_{Ph}), 7.92 (d, J = 7.9, 1H, H_{Ph}), 7.68 (d, J = 7.4, 2H, H_{Ph}), 7.38-7.24 (m, 6H, H_{Ph}) , 6.55 (p, J = 1.7, 1H, H_{Cp}), 6.40 (d, J =1.6, 1H, H_{Cp}), 2.36 (d, J = 1.6, 3H, CH_3), 1.25 (s, 9H, $C(CH_3)_3$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 100 MHz, 25 °C): δ 159.9 (C^q), 148.1(C^q), 142.6 (C^q), 142.4 (C^q), 142.0 (C^q), 140.5 (C^q), 137.4(C^q), 136.7 (C_{Cp}), 132.4 (C^q), 130.0, 129.5, 129.1, 128.9, 127.9, 127.2, 120.4, 120.3, 115.1 (C_{Cp}), 32.9 ($C(CH_3)_3$), 29.6 ($C(CH_3)_3$), 17.7 (CH_3). ASAP-MS (110°C, *m/z*) $[M+H]^+$ Calcd for $[C_{23}H_{23}]^+$: 299.1794. Found: 299.1791.

Synthesis of 9-(3-(*tert*-butyl)cyclopenta-2,4-dien-1-ylidene)-9*H*-fluorene (1j). Using a protocol similar to that described for **1i, 1j** was obtained from 3-*tert*-butyl-cyclopentadiene (0.9 g, 7.4 mmol), *n*-BuLi (3.4 mL of 2.4 M in Et_2O, 8.1 mmol)) and fluorenone (1.4 g, 7.7 mmol). Workup afforded **1j** as a dark orange tar (0.56 g, 23 %). ^{1}H NMR (CD_2Cl_2, 400 MHz, 25 °C): δ 8.09 (d, J = 7.7, 1H, H_{Ph}), 8.06 (d, J = 7.7, 1H, H_{Ph}), 7.69 (dt, ^3J = 7.5, 1H, H_{Flu}), 7.40-7.35 (m, 2H, H_{Flu}), 7.33-7.27 (m, 2H, H_{Flu}), 7.20 (dd, J = 5.5, J = 2.2, 1H, H_{Cp}), 6.79 (t, J = 1.7, 1H, H_{Cp}), 6.79 (dd, J = 5.5, J = 1.7, 1H, H_{Cp}), 1.29 (s, 9H, CH_3). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 100 MHz, 25 °C): δ 161.7 ($C^q{}_{Cp}$), 144.6 ($C^q{}_{Cp}$), 142.5 (C^q), 142.3 (C^q), 140.4 (C^q), 139.3 (C^q), 139.2 (C^q), 134.9 (C_{Cp}), 130.0 (C_{Flu}), 129.9 (C_{Flu}), 128.0 ($2C_{Flu}$), 127.5 (C_{Flu}), 127.4 (C_{Flu}), 123.8 (C_{Cp}), 120.4 (2 C_{Flu}), 113.8 (C_{Cp}), 33.1 ($C(CH_3)_3$), 29.6 ($C(CH_3)_3$).

Synthesis of proligands

Synthesis of 2,7-di-*tert*-butyl-9-((3-(*tert*-butyl)cyclopenta-1,3-dien-1-yl)diphenylmethyl)-9*H*-fluorene (2a). To a solution of **1a** (1.21 g, 4.2 mmol) in Et_2O (10 mL) was added dropwise at 0 °C to a solution of 2,7-(di-*tert*-butyl)-fluorenylithium (prepared from 2,7-(di-*tert*-butyl)-fluorene (1.06 g, 3.8 mmol) and *n*-BuLi (1.9 mL of a 2.2 M solution in hexanes, 4.2 mmol)). The resulting mixture was stirred for 7 days at 90 °C in an autoclave, then cooled to room temperature, quenched with a saturated aqueous solution of NH_4Cl (30 mL) and diluted with Et_2O (30 mL). The organic phase was separated and dried over $MgSO_4$. Volatiles were removed under reduced pressure. The residue was triturated in

and washed with MeOH, then dried under vacuum to afford **2a** as an off-white powder (1.58 g, 74 %). ^{1}H NMR (CD_2Cl_2, 400 MHz, 25 °C): δ 7.6–6.8 (m br, 16H, H_{arom}), 6.5–5.5 (br m, 3H, H_{Cp}, and H9-Flu), 3.5–2.0 (br s, 2H, $CH_{2\ Cp}$), 1.25–0.75 (br m, 27H, $C(CH_3)_{3\ Cp}$ and $C(CH_3)_{3\ Flu}$). $^{13}C\{^{1}H\}$ NMR (CD_2Cl_2, 100 MHz, 25 °C) (due to a substantial broadening and overlapping, some resonances could not be observed): δ 149.1 (C^q), 148.9 (C^q), 145.4(C^q), 144.9 (C^q), 139.88 (C^q), 139.7 (C^q), 130.5 (C^q), 130.3 (C^q), 127.6 (br m, C^q), 126.9 (C^q), 126.2 (C_{arom}), 124.9 (C_{arom}), 124.0 (C_{arom}), 123.9 (C_{arom}), 122.1, 118.4 (C_{arom}), 118.3 (C_{arom}), 59.9 ($Ph_2\mathit{C}$), 35.1 ($\mathit{C}(CH_3)_{3)}$, 35.0 ($\mathit{C}(CH_3)_{3)}$, 31.6 ($C(\mathit{C}H_3)_3$), 31.6 ($C(\mathit{C}H_3)_3$), 30.8 (br m), 29.9 ($C(\mathit{C}H_3)_3$). ASAP-MS (160 °C, *m/z*) $[M+H]^+$ Calcd for $[C_{43}H_{49}]^+$: 565.3829. Found: 565.3638. Anal. Calcd for $C_{43}H_{48}$: C, 91.43; H, 8.57. Found: C, 91.54; H, 8.53.

Synthesis of 2,7-di-*tert*-butyl-9-(diphenyl(3-(2,3,3-trimethylbutan-2-yl)cyclopenta-1,3-dien-1-yl)methyl)-9*H*-fluorene (2b). Using a protocol similar to that described above for **2a**, compound **2b** was obtained from **1b** (1.38 g, 4.2 mmol) and 2,7-(di-*tert*-butyl)-fluorenylithium (prepared from 2,7-(di-*tert*-butyl)-fluorene (1.15 g, 4.13 mmol) and *n*-BuLi (1.98 mL of a 2.3 M solution in hexanes, 4.5 mmol)). Workup afforded **2b** as an off-white powder (1.71 g, 68 %). ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C) (due to substantial broadening and overlapping, some resonances could not be observed): *δ* 8.12-6.58 (br, m, 16H), 6.53-5.42 (br m, 3H, (2 H_{Cp}+1H_{Flu})), 3.36-2.21(br m, 2H, (CH_2)), 1.30 - 0.49 (br m, 33H, (($CH_3)_3$) + CH_3). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz, 25 °C) (Some carbon signals were not observed): *δ* 149.10 (C^q), 148.9 (C^q), 145.4(C^q), 139.8(C^q), 139.7(C^q), 131.4, 130.3, 127.6, 126.23, 126.1, 125.0, 124.0, 123.9, 118.5, 59.5 ($Ph_2\boldsymbol{C}$), 35.9, 35.1 ($\mathit{C}(CH_3)_3$), 35.0 ($\mathit{C}(CH_3)_3$), 31.7 ($C(\mathit{C}H_3)_3$), 31.6 ($C(\mathit{C}H_3)_3$), 30.4, 26.7($C(\mathit{C}H_3)_3$), 24.6, 23.9. ESI (CH_3OH/CH_2Cl_2, *m/z*) $[M+Na]^+$ Calcd for $[C_{46}H_{54}Na]^+$: 629.4118. Found: 629.4118. Anal. Calcd for $C_{46}H_{54}$: C, 91.03; H, 8.97. Found: C, 91.68; H, 8.87.

Synthesis of 2,7-di-*tert*-butyl-9-((3-(5-butylnonan-5-yl)cyclopenta-1,3-dien-1-yl)diphenylmethyl)-9*H*-fluorene (2c). Using a protocol similar to that described above for **2a**, compound **2c** was obtained from **1c** (1.49 g, 3.6 mmol) and 2,7-(di-*tert*-butyl)-fluorenylithium (prepared from 2,7-(di-*tert*-butyl)-fluorene (1.0 g, 3.6 mmol) and *n*-BuLi (1.72 mL of a 2.3 M solution in hexanes, 4.0 mmol)). Workup afforded **2c** as an off-white powder (1.78 g, 72 %). ^{1}H NMR (CD_2Cl_2, 400 MHz, 25 °C) (due to substantial broadening and overlapping, some resonances could not be observed): *δ* 8.22-6.22 (br m, 16H, H_{arom}) , 6.10-5.37 (br m, 2H, H_{Cp}) , 5.00-4.75 (br s, 1H, H_{Flu}), 3.46-2.16 (2H, br m, -CH_2-Cp), 1.41-0.57 (br m, 45H, $C(CH_3)_{3\ Flu}$, 6-CH_2-, 3-CH_3). $^{13}C\{^{1}H\}$ NMR (CD_2Cl_2, 100 MHz, 25 °C): *δ* 149.1, 145.8, 140.1, 130.7 (br), 130.2 (br), 128.3(br), 126.4, 125.1(br), 124.0, 118.7, 59.6(br) ($Ph_2\mathit{C}$), 37.03(br), 35.2, 31.8 $(CH_3)_3$, 26.0 (br), 24.0, 14.6(CH_3). ESI-MS (CH_3OH/CH_2Cl_2 (90/10 *v/v*), *m/z*) $[M+Na]^+$ Calcd for $[C_{52}H_{66}Na]^+$: 713.5056. Found: 713.5059. Anal. Calcd for $C_{52}H_{66}$: C, 90.37; H, 9.63. Found: C, 90.29; H, 9.68.

Synthesis of 3,6-di-*tert*-butyl-9-((3-(5-butylnonan-5-yl)cyclopenta-1,3-dien-1-yl)diphenylmethyl)-9*H*-fluorene (2d). Using a protocol similar to that described above for **2a**, compound **2d** was synthesized from 3,6-(di-*tert*-butyl)-fluorenyllithium (prepared from 3,6-(di-*tert*-butyl)-fluorene (1.25 g, 4.5 mmol) and *n*-BuLi (2.2 mL of 2.3 M in hexanes, 4.9 mmol)) and **1c** (1.97 g, 4.8 mmol). The product was isolated as a pale orange powder (2.05 g, 66 %). ^{1}H NMR (CD_2Cl_2, 400 MHz, 25 °C): δ 7.80-6.58 (br m, 16H, H_{Ph}), 6.52-6.37 (br m, 3H, $2H_{Cp}$ + H9-Flu), 1.48-1.02 (br m + br s, 36 H, CH_2+ $C(CH_3)_3$), 0.98-0.78 (m, 9 H, $(CH)_3$). $^{13}C\{^{1}H\}$ NMR (CD_2Cl_2, 100 MHz, 25°C) (some carbon signals were not observed or were very broad, the signals of carbons from the butyl arms are somehow doubled): δ 153.8 (C^q), 150.7 (C^q), 150.4 (C^q),143.3 (C^q), 142.6 (C^q), 142.6 (C^q), 130.8 (C^q), 130.7 (C^q), 130.2 (C^q), 128.3, 128.2, 127.0, 126.2, 126.1 (C^q), 125.2, 123.8, 123.6, 116.1, 116.0, 60.8 (Ph_2C), 59.5, 53.9 (C9-Flu), 42.3 (C^q), 41.5 (C^q), 37.2 (CH_2), 36.1 (CH_2), 35.1 ($C(CH_3)_3$), 35.1 ($C(CH_3)_3$), 31.9 ($C(CH_3)_3$), 31.8 ($C(CH_3)_3$), 26.4 (CH_2), 26.2 (CH_2), 24.1 (CH_2), 24.0 (CH_2), 14.6 (CH_3), 14.6 (CH_3). ASAP-MS (160 °C, *m/z*) $[M+H]^+$ Calcd for $[C_{52}H_{67}]^+$: 691.5237. Found: 691.5234. Anal. Calcd for $C_{52}H_{66}$: C, 90.37; H, 9.63. Found: C, 90.63; H, 9.56.

Synthesis of 2,7-di-*tert*-butyl-9-((3-(1-methylcyclohexyl)cyclopenta-1,3-dien-1-yl)diphenylmethyl)-9*H*-fluorene (2e). Using a protocol similar to that described above for **2a**, proligand **2e** was synthesized from 2.7-(di-*tert*-butyl)-fluorenyllithium (prepared from 2.7-(di-*tert*-butyl)-fluorene (1.55 g, 5.6 mmol) and *n*-BuLi (2.4 mL of a 2.5 M solution in hexanes, 5.6 mmol)), and **1e** (2.0 g, 6.1 mmol). The product was obtained as an off-white powder (2.17 g, 63 %). ^{1}H NMR (CD_2Cl_2, 400 MHz, 25 °C): δ 8.10-6.58 (br m, 16H, H_{arom}), 6.51-5.37 (br s, 3H, $H_{Cp)}$, 5.23-4.71 (br s, 1H, H_{Flu}), 3.31-2.12 (br m, 2H, $CH_{2\ Cp}$), 1.78-0.60 (br m, 31H, CH_3, $C(CH_3)_3$, CH_2). $^{13}C\{^{1}H\}$ NMR (CD_2Cl_2, 100 MHz, 25 °C) (some carbon signals were not observed): δ 148.9 (C^q), 145.4, 139.8, 130.2, 128.6, 126.2, 124.9, 123.8, 118.4, 59.7 (Ph_2C) , 38.3(CH_2), 36.7 (C^q), 35.0 (C^q), 31.5 (($CH_3)_3$), 26.8 (CH_2), 23.0 (CH_2). ASAP-MS (210 °C, *m/z*) ($C_{46}H_{53}$) $[M+H]^+$ Calcd for $[C_{46}H_{53}]^+$ 605.4142. Found: 605.4142. Anal. Calcd for $C_{46}H_{52}$: C, 91.34; H, 8.66. Found: C, 91.11; H, 8.49.

Synthesis of (3-*tert*-butyl-cyclopenta-1,4-dienyl)-diphenylethyl-octamethyloctahydrodibenzofluorene (2f). Using a protocol similar to that described above for **2a**, compound **2f** was obtained from 6,6'-diphenyl-(2-*tert*-butyl)fulvene (2.04 g, 7.1 mmol) and octamethyloctahydrodibenzofluorenyllithium (prepared from 6-octamethyloctahydrodibenzofluorene (2.5g, 6.4 mmol) and *n*-BuLi (5.4 mL of 2.5 M solution in hexanes, 13.4 mmol)).Workup afforded **2f** as an off-white powder (3.4 g, 78 %). ^{1}H NMR (CD_2Cl_2, 400 MHz, 25 °C) (broad signals): δ 7.97-5.37 and 5.27-4.66 (br m, 16+1H, H_{arom}+H_{Cp}+H9-Flu), 3.32-2.16 (br m, 2H, $CH_{2\ Cp}$), 1.73-1.55 (br m, 8H, $CH_{2\ Oct}$), 1.28 (br s, 6H, $CH_{3\ Oct}$), 1.28 (br s, 6H, $CH_{3\ Oct}$), 1.21-0.55 (br m, 9H +12 H, $C(CH_3)_3$ + $CH_{3\ Oct}$). $^{13}C\{^{1}H\}$ NMR (CD_2Cl_2, 100 MHz, 25 °C) (some carbon signals were not observed): δ 143.8,

142.6, 130.5, 128.2, 127.1, 126.3, 125.8, 125.2, 116.5, 60.3 (Ph_2C), 35.9 (CH_2), 35.7 (CH_2), 34.8 (C^q), 34.7 (C^q), 32.3(CH_3), 32.3 (CH_3), 32.3 (CH_3), 32.0 (CH_3). ASAP-MS (210 °C, *m/z*) $[M+H]^+$ Calcd for $[C_{51}H_{61}]^+$ 673.4768. Found: 673.4770. Anal. Calcd for $C_{51}H_{60}$: C, 91.01; H, 8.99. Found: C, 91.65; H, 8.94.

Synthesis of 9-((3-(*tert*-butyl)cyclopenta-1,3-dien-1-yl)diphenylmethyl)-2,7-bis(2-phenylpropan-2-yl)-9*H*-fluorene (2g). Using a protocol similar to that described above for **2a**, compound **2g** was obtained from 6,6'-diphenyl-(2-*tert*-butyl)-fulvene (1.8 g, 6.5 mmol) and 2,7-(di-cumyl)-fluorenylithium (prepared from 2,7-(di-cumyl)-fluorene (2.0 g, 5.0 mmol) and *n*-BuLi (2.3 mL of a 2.5 M solution in hexanes, 5.5 mmol)). Workup and a purification by column chromatography (SiO_2, Petroleum Ether/ CH_2Cl_2 (80:20 *v/v*), R_f = 0.4) afforded **2g** as a light-yellow solid foam (1.39 g, 41 %). ^{1}H NMR (CD_2Cl_2, 400MHz, 25 °C): δ 8.42-5.41 and 5.28-4.69 (br, 26+1H, H_{Arom}+H_{Flu}), 3.08-2.23 (br, 2H, $CH_{2\ Cp}$)), 1.84-0.62 (br m, 21H, $CH_{3\ cumyl}$ + $C(CH_3)_{3\ Cp}$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 100 MHz, 25 °C) (some carbon signals were not observed): δ 151.6 (C^q), 148.9 (C^q), 148.8 (C^q), 130.5, 128.4, 128.4, 127.2, 126.3, 125.9, 125.7, 118.5, 59.9 (Ph_2C), 43.4 (C^q), 43.4 (C^q), 31.2 (CH_3), 31.1 (CH_3), 31.0 (CH_3), 31.0 ($C(CH_3)_3$), 30.9 (CH_3),30.9 (CH_3). ASAP-MS (250 °C, *m/z*) $[M+H]^+$ Calcd for $[C_{53}H_{54}]^+$: 641.4147. Found: 641.4141. Anal. Calcd for $C_{53}H_{53}$: C, 92.39; H, 7.61. Found: C, 92.88; H, 7.61.

Synthesis of 9-((4-(*tert*-butyl)-2-methylcyclopenta-1,3-dien-1-yl)diphenylmethyl)-2,7-di-mesityl-9*H*-fluorene (2h). Using a protocol similar to that described above for **2a**, compound **2h** was obtained from 6,6'-diphenyl-(2-*t*Bu-5-Me)fulvene (0.81 g, 2.7 mmol) and 2,7-(dimesityl)-fluorenyllithium (prepared from 2,7-(dimesityl)-fluorene (0.78 g, 1.9 mmol) and *n*-BuLi (0.85 mL of a 2.5M solution in hexanes, 2.1 mmol)). Workup afforded **2h** as an off white solid (0.63 g, 48 %). ^{1}H NMR (CD_2Cl_2, 400 MHz, 25 °C): *δ* 7.86-6.54 (br m, 21H, H_{arom}+H_{Cp}), 5.91-5.60 (br m,1H, H9-Flu), 3.07-2.61 (br m , 2H, CH_2), 2.35-1.80 (br m, 21H), 1.04 (s, 9H, $C(CH_3)_3$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 100 MHz, 25 °C): *δ* 145.5, 140.0, 136.7, 136.3, 136.3, 128.5, 128.0, 119.1, 46.9, 33.4, 30.8, 21.3, 21.2, 21.1, 17.5. ASAP-MS (180 °C, *m/z*) $[M+H]^+$ Calcd for $[C_{54}H_{55}]^+$: 703.4298. Found: 703.4308. Anal. Calcd for $C_{54}H_{54}$: C, 92.26; H, 7.74. Found: C, 92.05; H, 7.49.

Synthesis 9-(4-(*tert*-butyl)-2-methylcyclopenta-2,4-dien-1-yl)-9*H*,9'*H*-9,9'-bifluorene (2i). Using a protocol similar to that described above for **2a**, compound **2i** was obtained from **1i** (1.5 g, 5.0 mmol) and fluorenyllithium (prepared from fluorene (0.55g, 3.3mmol) and *n*-BuLi (1.5 mL of a 2.4 M solution in hexanes, 3.6 mmol)). After 2 weeks reaction, workup and purification by chromatography (Pet ether: CH_2Cl_2 / 90:10 *v/v*), R_f = 0.2, afforded **2i** as an off-white solid (0.66 g, 44 %). ^{1}H NMR (CD_2Cl_2, 400 MHz, 25 °C) (broad signals): δ 8.07-5.43 (br m, 17H, 16 H_{Flu} + H_{Cp}), 5.30 (s, 1H, H9-Flu), 3.44-2.70 (br m, 2H, CH_2), 1.41-0.78 (br m, 12H, $C(CH_3)_3$ + CH_3). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 400

MHz, 25 °C) (some aromatic carbon signals were not observed): δ 156.9 (C^q), 156.5 (C^q), 141.1 (C^q), 137.5 (C^q), 136.9 (C^q), 134.9(C^q), 130.8 (HC_{Cp}), 127.8, 127.7, 127.1, 126.9, 125.8 (C^q), 125.5 (C^q), 120.1, 119.7, 59.5 (Flu*C*), 54.2 (C9-Flu), 47.3 (CH_2), 33.7 (***C***$(CH_3)_3$), 31.2 (C(***C***$H_3)_3$), 31.1 (CH_3). ASAP-MS (160 °C, *m/z*) $[M+H]^+$ Calcd for $[C_{36}H_{34}]^+$ *:* 465.2577. Found: 465.2577. Anal. Calcd for $C_{36}H_{33}$: C, 93.06; H, 6.94. Found: C, 92.96; H, 6.85.

Synthesis 9-(3-(*tert*-butyl)cyclopenta-2,4-dien-1-yl)-9*H*,9'*H*-9,9'-bifluorene (2j). Using a protocol similar to that described above for **2a, 2j** was prepared from **1j** (0.55 g, 1.9 mmol) and fluorenyllithium (prepared from fluorene (0.28 g, 1.7 mmol) and *n*-BuLi (0.8 mL of a 2.3 M solution in Et_2O, 1.8 mmol)). Workup and chromatography (same conditions as **2i**) afforded **2j** as a white powder (0.141 g, 20 %). ^{1}H NMR (CD_2Cl_2, 400 MHz, 25 °C) (At least two isomers were detected in a 1:3 ratio): δ 7.61-7.57 (m, 5H, H_{Flu}), 7.33-6.95 (br m, 14H, H_{Flu} + H_{Cp}), 5.06 (min)/5.04 (maj) (s, 1H, H9-Flu), 3.41(min)/3.38 (maj) (s, 2H, CH_2), 1.26(min)/1.15(maj) (s, 9H, C$(CH_3)_3$). ^{13}C{^{1}H} (CD_2Cl_2, 100 MHz, 25 °C) (peaks from both isomers are reported and identified when possible): δ 159.0(min)/156.6(maj) (C^q_{Cp}), 149.8(maj)/146.6(min) (C^q_{Cp}), 143.9 (C^q), 143.8 (C^q), 141.8 (C^q), 140.5 (C^q), 140.4 (C^q), 130.7(maj)/129.7 (C_{Cp}), 127.4, 127.3, 127.2, 126.7, 126.7, 126.1, 126.0, 125.2, 125.1, 125.0, 124.9, 124.9, 123.0/ 121.3(maj) (C_{Cp}), 119.7, 119.7, 119.1, 119.1 60.1(maj)/60.0 (Flu*C*), 54.9(maj)/54.8 (C9-Flu) 41.7(maj)/41.0 (CH_2), 33.3/32.1 (maj) (*C*$(CH_3)_3$), 30.7(min)/29.3(maj) (C**(***C*$H_3)_3$) . ASAP-MS (190 °C, *m/z*) $[M+H]^+$ Calcd for $[C_{35}H_{31}]^+$*:* 450.2420. Found: 451.2421. Anal. Calcd for *(*$C_{35}H_{30}$): C, 93.29; H,6.71. Found: C, 93.09; H, 6.74.

Synthesis of (4-(*tert*-butyl)-2-methylcyclopenta-1,3-dien-1-yl)(2,7-di-*tert*-butyl-9*H*-fluoren-9-yl)diphenyl -silane (2k). A solution of 5-methyl-3-*tert*-butylcyclopentadiene (0.106 g, 0.78 mmol) in Et_2O (10 mL) was cooled to 0 °C and *n*-BuLi (32 mL of a 2.3 M solution in hexanes, 73.6 mmol) was syringed in dropwise. To the resulting white suspension, CuCN (28 mg, 0.37mmol) was added and the reaction turned black. After 10 min, a solution of chloro(2,7-di-*tert*-butyl-9*H*-fluoren-9-yl)diphenylsilane (0.35g, 0.71 mmol) and TMEDA (0.4 mL, 2.7 mmol) was added dropwise; the reaction was stirred for 3 days protected from light. The mixture was filtered on a silica pad and eluted with CH_2Cl_2. The solvent was removed under vacuum and the residue was purified by column chromatography (SiO_2, petroleum ether/DCM (90:10 *v/v*), R_f = 0.4) to yield **2k** (0.22 g, 47 %). ^{1}H NMR (CH_2Cl_2, 400 MHz, 25 °C) (at least two isomers (**1**) and (**2**) were detected in a ca. 1:1 ratio): δ 7.76-7.70 (m, 6H, H_{Ph}), 7.57 (s, 1H, H_{Flu}), 7.49-7.23(m, 17H, H_{Ph} +H_{Flu}), 7.22-7.16 (m, 2H, HPh), 7.11-7.06(m, 2H, 2H_{Flu}+2H_{Ph}), 6.95 (s, 2H, H_{Flu}), 6.16 (s,1H, H_{Cp}), 6.10(s, 1H, H_{Cp}), 6.45 (**1**) (s, 1H, H9-Flu), 4.57 (**2**) (s,1H, H9-Flu), 4.01 (s, 1H, Si-$C_{Cp}H$), 2.10 (s, 3H, CH_3), 2.04 (br s, 2H, CH_2), 1.31 (s, 9H, C$(CH_3)_{3\ Flu}$), 1.24 (s, 9H, C$(CH_3)_{3\ Flu}$) 1.16 (s, 18H, C$(CH_3)_{3\ Flu}$), 1.00(1) (s, 9H, C$(CH_3)_{Cp}$), 0.99(**2**) (s, 9H, C$(CH_3)_{3\ Cp}$). ^{13}C{^{1}H} NMR (CH_2Cl_2, 100 MHz, 25 °C): δ 167.1(**1**) (C^q_{Cp}), 158.0 (**2**) (C^q

$_{Cp}$), 157.4 (**1**) (C^q $_{Cp}$), 149.4($C(CH_3)_3$ $_{Flu}$), 149.3(2 C^q), 149.3(C^q), 145.5(C^q), 145.1(C^q), 144.5(C^q), 144.4(C^q), 139.2(C^q), 139.0(C^q), 138.8(C^q), 136.6 (C^q),136.5 136.1, 136.0, 131.1(C^q), 130.9(C^q), 130.0 (**2**)(HC_{Cp}), 129.9, 129.8, 129.6, 129.3 (**1**)(HC_{Cp}), 128.5, 127.3, 127.1, 126.0 (**1**)(C^q_{Cp}), 123.4, 1231, 123.0, 1227, 122.4, 120.6 (**2**)(HC_{Cp}), 119.3, 119.3, 119.2, 47.0(2) (Ph_2Si-C_{Cp}), 45.6 (**1**)(CH_2), 40.9 (**1**) (C9-Flu), 40.8 (**2**) (C9-Flu), 35.2 ($C(CH_3)_3$), 35.2 ($C(CH_3)_3$), 35.1 ($C(CH_3)_3$), 33.7 ($C(CH_3)_3$), 32.5($C(CH_3)_3$), 31.9 (C(CH_3)$_3$), 31.8(C(CH_3)$_3$), 31.8(C(CH_3)$_3$), 31.0 (**1**) (Cp-C(CH_3)$_3$), 30.2 (**2**) (Cp-C(CH_3)$_3$), 18.2 (**2**) (CH_3), 18.1 (**1**) (CH_3). ESI-MS (MeOH, *m/z*) $[M+Na]^+$ Calcd for $[C_{43}H_{50}NaSi]^+$ 617.3574. Found: 617.3574. Anal. Calcd for $C_{43}H_{50}Si$: C, 86.81; H, 8.47. Found: C, 86.97: H, 8.42.

Synthesis of metallocene complexes.

Synthesis of {Ph_2C(2,7-*t*Bu_2-Flu)(3-*t*Bu-Cp)}$ZrCl_2$ (3a). To a solution of **2a** (0.98 g, 1.73 mmol) in Et_2O (20 mL) was added *n*-BuLi (1.55 mL of a 2.25 M solution in hexanes) at 0 °C under stirring. After 12 h, anhydrous $ZrCl_4$ (0.405 g, 1.74 mmol) was added to the sample in the glovebox. The resulting pink reaction mixture was stirred at room temperature for 6 days. Volatiles were evaporated *in vacuo*, and the residue was taken up in CH_2Cl_2 (20 mL) and *n*-heptane (10 mL) was added. The mixture was filtered over celite and concentrated in vacuum. Complex **3a** crystalized from heptane; it was separated and dried in vacuum to afford an orange powder (0.503 g, 39 %). ^{1}H NMR (CD_2Cl_2, 400 MHz, 25 °C): δ 8.06–8.04 (m, 3H, H_{Ph} +H_{Flu}), 7.98 (d, *J* = 7.8, 1H, H_{Ph}), 7.89 (t, *J* = 7.0, 2H, H_{Ph}), 7.64 (dd *J* = 8.8, *J* =1.5, 1H, H_{Flu}), 7.61 (dd, *J* = 8.8, *J* =1.5, 1H, H_{Flu}), 7.49 (dq, *J* = 7.8, *J* = 1.0, 2H, H_{Ph}), 7.37 (t, *J* = 7.5, 2H, H_{Ph}), 7.33–7.28 (m, 2H, H_{Ph}), 6.31(s, 2H, H_{Flu}), 6.19 (t, *J* = 2.9, 1H , H_{Cp}), 5.64 (t, *J* = 2.9, 1H, H_{Cp}), 5.55 (t, *J* = 2.9, 1H, H_{Cp}), 1.17 (s, 9H, ($C(CH_3)_3$)$_{Cp}$), 1.03 (s, 9H, ($C(CH_3)_3$)$_{Flu}$), 1.02 (s, 9H, ($C(CH_3)_3$ $_{Flu}$). ^{13}C{^{1}H} NMR (CD_2Cl_2, 100 MHz, 25 °C): δ 150.8 (C^q_{Flu}), 150.7 (C^q_{Flu}), 146.1 (C^q_{Cp}), 145.5 (C^q $_{Ph}$), 145.4 (C^q_{Ph}), 130.1 (C_{Ph}), 129.8 (C_{Ph}), 129.5 (C_{Ph}) , 129.4 (C_{Ph}), 129.4 (C_{Ph}), 129.3 (C_{Ph}), 127.5 (C_{Ph}), 127.4 (C_{Ph}), 127.2 (C_{Ph}), 126.9 (C_{Ph}), 125.0 (C_{Flu}), 124.9 (C_{Flu}), 124.4, 124.1 (C_{Ph}), 121.9 (C^q_{Flu}), 121.7 (C^q_{Flu}), 121.6 (C^q_{Flu}), 121.1 (C^q_{Flu}), 120.6 (C_{Flu}), 119.8 (C_{Flu}), 114.6 (C_{Cp}), 108.9 (C^q_{Cp}), 105.2 (C_{Cp}), 100.6 (C_{Cp}), 77.6 (C9-Flu), 58.0 (Ph_2C), 35.3($C(CH_3)_3$), 35.2($C(CH_3)_3$), 33.5 ($C(CH_3)_3$), 30.8 (C(CH_3)$_3$), 30.7 (C(CH_3)$_3$), 30.2 (C(CH_3)$_3$). iASAP-MS (toluene, *m/z*) $[M]^+$ Calcd for $[C_{43}H_{46}Cl_2Zr]^+$: 722.2023. Found: 722.2022. Anal. Calcd for $C_{43}H_{46}Cl_2Zr$: C, 71.24; H,6.40. Found: C,70.65; H,6.58.

Synthesis of {Ph_2C(2,7–*t*Bu_2-Flu)(3-Me_2*t*BuC-Cp)}$ZrCl_2$ (3b). Using a procedure similar to that described above for **3a**, complex **3b** was obtained from **2b** (1.0 g, 1.65 mmol), *n*-BuLi (1.52 ml of a 2.3M solution in hexanes, 3.5 mmol) and $ZrCl_4$ (0.384 g, 1.65 mmol). The complex was obtained as a red-orange microcrystalline powder (1.2 g, 95 %). ^{1}H NMR (CD_2Cl_2, 400 MHz, 25 °C): δ 8.05 (t, *J* =

9.0, 2H, H_{Flu}), 8.01 (d, *J* = 7.1, 1H, H_{Ph}), 7.92-7.87 (m, 3H, 2 H_{Flu} + H_{Ph}), 7.65 (dd, *J* = 1.6, *J* = 8.8, 2H, H_{Flu}), 7.60 (dd, 1H, *J* =8.8, *J* = 1.6, H_{Flu}), 7.50-7.46 (m, 2H, H_{Ph}), 7.40-7.35 (m, 2H, H_{Ph}), 7.33-7.29 (m, 2H, H_{Ph}), 6.32 (s, 2H, H_{Ph}), 6.20 (t, *J* = 3.0, 1H, H_{Cp}), 5.62 (t, *J* = 3.0, 1H, H_{Cp}), 5.56 (t, *J* = 3.0, 1H, H_{Cp}), 1.22 (s, 3H, CH_3), 1.04 (s, 9H, $C(CH_3)_{3\ Flu}$), 1.03 (s, 9H, $C(CH_3)_{3\ Flu}$), 0.84 (s, 9H, $C(CH_3)_3$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 100 MHz, 25 °C): δ 151.0 (C^q), 145.8 (C^q_{Ph}), 145.5 (C^q_{Ph}), 144.1 (C^q), 130.3(C_{Ph}), 129.9(C_{Ph}), 129.7(C_{Ph}), 129.6 (C_{Ph}), 129.5 (C_{Ph}) 129.4 (C_{Ph}), 127.7 (C_{Ph}), 127.7 (C_{Ph}), 127.2(C_{Ph}), 127.0 (C_{Ph}), 125.2 (C_{Flu}), 125.1 (C_{Flu}), 124.7 (C_{Flu}), 124.2(C_{Flu}), 122.2 (C^q), 121.9 (C^q), 121.7(C^q), 121.2 (C^q), 121.0 (C_{Flu}), 119.6 (C_{Flu}), 116.5 (C_{Cp}), 108.3 (C^q_{Cp}), 104.5 (C_{Cp}), 103.6 (C_{Cp}), 78.0 (C9-Flu), 57.8 (Ph_2***C***), 41.8 (C^q), 38.2 (C^q), 35.5 (*C*$(CH_3)_{3\ Flu}$), 35.4 (*C*$(CH_3)_{3\ Flu}$), 30.9 (C(*C*$H_3)_{3\ Flu}$), 30.9 (C(*C*$H_3)_{3\ Flu}$), 26.5 (C(*C*$H_3)_3$), 21.2 (*C*H_3), 19.7 (*C*H_3). iASAP-MS (*m/z*) $[M]^+$ Calcd for $[C_{46}H_{52}Cl_2Zr]^+$: 764.2493. Found 764.2490. Anal. Calcd for $C_{46}H_{52}Cl_2Zr$: C, 72.03; H, 6.58. Found: C, 72.27; H, 7.30.

Synthesis of {Ph_2C(2,7–*t*Bu_2-Flu)(3-*n*Bu_3C-Cp)}$ZrCl_2$ (3c). Using a procedure similar to that described above for **3a**, complex **3c** was obtained from **2c** (1.08 g, 1.56 mmol), *n*-BuLi (1.3 ml of a 2.3M solution in hexanes) and $ZrCl_4$ (0.384 g, 1.65 mmol). The complex was obtained as a pink microcrystalline powder (0.311 g, 25 %). ^1H NMR (CD_2Cl_2, 400 MHz, 25 °C): δ 8.02 (d, *J* = 8.8, 2H, H_{Flu}), 7.97 (d, *J* = 8.0, 1H, H_{Ph}) , 7.93 (d, *J* = 8.0, 1H, H_{Ph}), 7.88 (t, *J* = 7.0, 2H, H_{Ph}), 7.64 (dd, *J* = 8.8, *J* =1.6, 1H, H_{Flu}), 7.59 (1H , dd, *J* = 8.8, *J* =1.6, H_{Flu}), 7.48 (tt , *J* = 7.7, *J* =1.6, 2H, H_{Ph}), 7.40-7.5 (m, 2H, H_{Ph}), 7.33-7.28 (m, 2H, H_{Ph}), 6.31 (s, 2H, H_{Flu}), 6.16 (t, *J* = 3.0, 1H, H_{Cp}), 5.64 (t, *J* = 3.0, 1H, H_{Cp}), 5.53 (t, *J* = 3.0, 1H, H_{Cp}), 1.63-1.55 (m, 2 H, -CH_2-), 1.49-1.41 (m, 2H, -CH_2-), 1.27-1.10 (m, 12H, -CH_2-), 1.04 (s, 9H , $C(CH_3)_{3\ Flu}$), 1.03 (s, 9H, $C(CH_3)_{3\ Flu}$), 0.85 (t, *J* = 7.0, 9H, CH_3). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 100 MHz, 25 °C): δ 150.7 (*C*$C(CH_3)_3$), 150.6 (*C*$C(CH_3)_3$), 145.6 (C^q), 145.5 (C^q), 144.4 (*C*C(*n*Bu)$_3$), 130.0 (C_{Ph}), 129.9 (C_{Ph}), 129.5 (C_{Ph}), 129.4 (C_{Ph}), 129.3 (C_{Ph}), 129.2 (C_{Ph}), 127.5 (C_{Ph}) 127.5 (C_{Ph}), 127.0 (C_{Ph}), 126.9 (C_{Ph}), 125.1 (C_{Flu}), 124.9 (C_{Flu}), 124.5 (C_{Ph}), 124.0 (C_{Ph}), 122.3 (C^q), 121.8 (C^q), 121.3 (C^q), 121.2 (C^q), 120.6 (C_{Flu}), 119.8 (C_{Flu}), 116.8 (C_{Cp}), 108.7(C^q_{Cp}), 104.5 (C_{Cp}), 101.9(C_{Cp}), 77.4 (C9-Flu), 57.6 (Ph_2C), 42.8 (*C*(*n*Bu)$_3$), 37.7 (CH_2), 35.3 (*C*(CH_3)), 35.2 (*C*(CH_3)), 30.8(C(*C*H_3)), 30.7(C(*C*H_3)), 26.8 (*C*H_2), 23.9 (*C*H_2), 14.31(*C*H_3). iASAP-MS (*m/z*) $[M+H]^+$ Calcd for $[C_{52}H_{64}Cl_2Zr]^+$: 848.3432. Found: 848.3426.

Synthesis of {Ph_2C(2,7–*t*Bu_2-Flu)(3-*n*Bu_3C-Cp)}$ZrMe_2$ (4c). To a solution of **3c** (282 mg, 0.33 mmol) in toluene (20 mL) was added MeMgBr (0.41 mL of a 2.85 M solution in Et_2O, 1.2 mmol) and the mixture was heated for 4 h at 80 °C. The reaction was cooled down to RT and evaporated to dryness. The yellow residue was dissolved in heptane (4 x 10 mL) and filtrated by cannula. Volatiles were evaporated *in vacuo* affording **3d** as a yellow powder (0.160 g, 60 %). ^1H NMR (C_6D_6, 500 MHz, 25 °C): δ 8.16 (dt J^{ortho} = 8.0 J^{meta} = 1.5, 1H, H_{Ph}), 8.07 (dt, J^{ortho} = 8.0 J^{meta} = 1.5, 1H, H_{Ph}), 8.03 (d,

J^{ortho} = 8.7, 1H, Flu-H_5), 8.01 (d, J^{ortho} = 8.7, 1H, Flu-H_5), 7.73 (dt, J^{ortho} = 8.0, J^{meta} = 1.5, 1H, H_{Ph}), 7.68 (dt, *J* = 8.0, *J* = 1.5, 1H, H_{Ph}), 7.52 (dd, J^{ortho} = 8.7, J^{meta} = 1.7, 1H, Flu-H_3/ Flu-H_6), 7.46 (dd, J^{ortho} = 8.7, J^{meta} = 1.7, 1H, Flu-H_3/ Flu-H_6), 7.24 (td, *J* = 7.7, *J* = 1.5, 1H, H_{Ph}), 7.13 (td, *J* = 7.7, *J* = 1.5, 1H, H_{Ph}), 7.05 (m, 2H, H_{Ph}), 6.95 (m, 2H, H_{Ph}), 6.49 (d, *J* = 1.5, 1H, Flu-H_1 / Flu-H_8), 6.42 (d, *J* =1.5, 1H, Flu-H_1 / Flu-H_8), 6.26 (t, *J*= 2.7 , 1H, H_{Cp}) , 5.69 (t, *J* = 2.7, 1H, H_{Cp}), 5.60 (t, *J*= 2.7, 1H, H_{Cp}), 1.69 (m, 6H, -C***H***$_2$-CH_2-),1.41 (m, 6H, -CH_2-C***H***$_2$-), 1.31 (h, *J* = 7.3, 6H, -C***H***$_2$-CH_3-), 0.95 (t, *J* = 7.3, 9H, -CH_2-*C****H***$_3$) , –0.99 (s, 3H, Zr-CH_3), –1.09 (s, 3H, Zr-CH_3). $^{13}C\{^1H\}$ NMR (C_6D_6, 125 MHz, 25 °C): δ 148.5 (*C*C(CH_3)$_3$), 148.4 (*C*C(CH_3)$_3$), 146.7 (C^q_{Ph}), 146.5 (C^q_{Ph}), 137.6 (C^q_{Cp}), 130.3 (C_{Ph}), 130.2 (C_{Ph}), 128.9 (C_{Ph}), 128.7 (C_{Ph}), 128.6 (C_{Ph}), 127.0 (C_{Ph}), 126.8 (C_{Ph}), 126.7 (C_{Ph}), 126.6 (C_{Ph}), 124.0 (C_{Flu}), 123.7 (C^q_{Flu}), 123.6 (C_{Flu}), 123.1 (C^q_{Flu}), 121.64 (C_{Flu}), 121.58(C_{Flu}), 120.18 (C_{Flu}), 119.3 (C_{Flu}), 119.1 (C^q_{Flu}), 118.2 (C^q_{Flu}), 111.4 (C_{Cp}), 103.5 (C_{Cp}), 103.3 (C_{Cp}), 101.4 (C_{Cp}), 75.1 (C9-Flu), 57.6 (Ph_2***C***), 42.6 (***C***(nBu)$_3$), 38.7 (-***C***H_2-CH_2), 37.3 (Zr-CH_3), 35.2 (***C***(CH_3)$_3$), 35.1 (***C***(CH_3)$_3$), 33.3 (Zr-CH_3), 31.3 (C(*C*H_3)$_3$), 31.2 (C(***C***H_3)$_3$), 27.2 (-CH_2-***C***H_2-), 24.0 (-***C***H_2-CH_3), 14.5 (***C***H_3). Satisfactory iASAP-MS and elemental analysis data could not be obtained for this compound due to its high sensitivity.

Synthesis of {Ph_2C(3,6-*t*Bu_2-Flu)(3-*n*Bu_3C-Cp)}$ZrCl_2$ (3d). Using a procedure similar to that described above for **3a**, complex **3d** was obtained from **2d** (1.5g, 2.1 mmol), *n*-BuLi (2.0 mL of a 2.3M solution in hexanes, 4.6 mmol) and $ZrCl_4$ (0.505 g, 2.17 mmol). The desired complex was obtained as a red microcrystalline powder (0.138 g, 7 %). ^{1}H NMR (C_6D_6, 400 MHz, 25 °C): δ 8.33 (d, J^{meta} = 2.1, 1H, H5/H4$_{Flu}$), 8.32 (dd, J^{meta} = 2.1, H5/H4$_{Flu}$, 1H), 8.14 (dt, *J* = 8.0, *J* =1.5, 1H, H_{Ph}) , 7.96 (dt, *J* = 8.0, *J* = 1.5, 1H, H_{Ph}), 7.76 (dt, *J* = 8.0, *J* = 1.5, 1H, H_{Ph}), 7.72 (dt, ^3J = 8.0, *J* = 1.5, 1H, H_{Ph}), 7.26 (td, *J* = 7.7, *J* =1.4, 1H, H_{Ph}), 7.13 (td, *J* = 7.7, *J* =1.4, 1H, H_{Ph}), 7.07-7.02 (m, 2H, H_{Ph}), 7.00-6.95 (m, 2H, H_{Ph}), 6.92 (dt, *J* = 9.1, *J* = 2.1, 2H, H1+H8 $_{Flu}$), 6.59 (d, *J* = 9.1, 1H, H2/H7$_{Flu}$), 6.47 (d, *J* = 9.1, 1H, H2/H7$_{Flu}$), 6.34 (t, *J* = 3.0, 1H, H_{Cp}), 5.89 (t, *J* =3.0, 1H, H_{Cp}), 5.84 (t, *J* =3.0, 1H, H_{Cp}), 1.86-1.64 (m, 6H, -CH_2-), 1.49-1.37 (6H, m, CH_2), 1.34 (s, 9H, C(CH_3)$_3$), 1.33 (s, 9H, C(CH_3)$_3$, 1.31-1.24 (m, 6H, CH_2), 0.94 (t, *J* = 7.2, 9H, CH_3). $^{13}C\{^1H\}$ NMR (C_6D_6, 100 MHz, 25 °C): δ 150.8 (***C***C(CH_3)$_3$)), 150.5 (***C***C(CH_3)$_3$), 146.0 (C^q_{Ph}), 145.9 (C^q_{Ph}), 143.8(C^q_{Cp}), 130.1(C_{Ph}), 130.0 (C_{Ph}), 129.4 (C_{Ph}), 129.3 (C_{Ph}), 129.1 (C_{Ph}), 128.9 (C_{Ph}), 127.9 (C_{Flu}), 127.8(C_{Flu}), 127.4(C_{Ph}), 127.2 (C_{Ph}), 126.9 (C_{Ph}), 126.8 (C_{Ph}), 124.3 (C^q_{Flu}), 124.1 (C_{Flu}), 123.5 (C_{Flu}), 123.3(C^q_{Flu}), 121.0(C^q_{Flu}), 120.1 (C^q_{Flu}), 120.1 (C_{Flu}), 119.5 (C_{Flu}), 117.3 (C_{Cp}), 109.9 (C^q_{Cp}), 105.0 (C_{Cp}), 102.6 (C_{Cp}), 78.0 (C9-Flu), 58.1 (Ph_2*C*), 43.0 (*C*(*n*Bu)$_3$), 38.1 (*C*H_2), 35.2 (*C*(CH_3)$_3$), 35.1 (*C*(CH_3)$_3$) , 31.8 (C(*C*H_3)$_3$), 27.0 (*C*H_2), 24.0 (*C*H_2), 14.5 (*C*H_3). iASAP-MS (*m/z*) $[M]^+$ Calcd for $[C_{52}H_{64}Cl_2Zr]^+$: 848.3432. Found: 848.3432. Anal. Calcd for $C_{43}H_{46}Cl_2Zr$: C, 73.37; H, 7.58. Found: C, 73.73; H, 7.82.

Synthesis of {Ph_2C(2,7-*t*Bu_2-Flu)(3-Me(Cyclo)-Cp)}$ZrCl_2$ (3e). Using a protocol similar to that described above for **3a, 3e** was obtained from **2e** (0.502 g, 0.83 mmol). *n*-BuLi (0.7 mL of a 2.5 M solution in hexanes, 1.74 mmol) and $ZrCl_4$ (0.211 mg, 0.91 mmol). The bright orange powder recovered was dried under vacuum and identified as complex **3e** (142 mg, 22%). ^{1}H NMR (C_6D_6, 500 MHz, 25 °C): δ 8.00 (dt, *J* = 8.0, *J* = 1.5, 1H, H_{Ph}), 7.96 (d, *J* = 9.0, 1H, H_{Ph}), 7.93 (d, *J* = 9.0, 1H, H_{Flu}), 7.86 (dt, *J* = 8.0, *J* = 1.5, 1H, H_{Flu}), 7.67 (dt, *J* = 8.0, *J* = 1.5, 1H, H_{Ph}), 7.64 (dt, *J* = 8.0, *J* = 1.5, 1H, H_{Ph}), 7.58 (td, *J* = 9.0 , *J* = 1.6, 2H, H_{Flu}), 7.19-7.13 (m, 2H, H_{arom}), 7.09-7.04 (m, 2H, H_{arom}), 6.98-6.95 (m, 2H, H_{arom}), 6.53 (s, 1H, H_{Flu}), 6.50 (s, 1H, H_{Flu}), 6.29 (t, *J* = 2.9, 1H, H_{Cp}), 5.84-5.82 (m, 2H, 2 H_{Cp}), 1.80-1.68 (m, 4H, CH_2), 1.50-1.19 (m, 14H, CH_2), 1.28 (s, 3H, CH_3), 1.13 (s, 18H, C(CH_3)$_3$). ^{13}C{^{1}H} NMR (C_6D_6, 125 MHz, 25 °C): δ 150.4 (*C*C(CH_3)$_3$, 150.0 (*C*C(CH_3)$_3$, 147.3(C^q_{Cp}), 145.8 (C^q_{Ph}), 145.6 (C^q_{Ph}), 130.2 (C_{Ph}), 129.9 (C_{Ph}),129.2 (C_{Ph}), 129.1(C_{Ph}), 129.0 (C_{Ph}), 129.0 (C_{Ph}), 127.1(C_{Ph}), 127.1(C_{Ph}), 127.0 (C_{Ph}), 126.8 (C_{Ph}), 124.9(C_{Flu}), 124.9 (C_{Flu}), 124.8 (C_{Flu}) , 124.5 (C_{Flu}), 122.2 (C^q_{Flu}), 121.9 (C^q_{Flu}), 121.8 (C^q_{Flu}), 121.2 (C^q_{Flu}), 120.6 (C_{Flu}), 119.8 (C_{Flu}), 114.4 (C_{Cp}), 109.1 (C^q_{Cp}), 104.9 (C_{Cp}), 100.0(C_{Cp}), 77.8 (C9-Flu), 58.0 (Ph_2*C*), 38.4(CH_2), 37.2(CH_2), 36.4(*CC*(Cyclo)(CH_3)), 35.3(*C*(CH_3)$_3$), 35.2(*C*(CH_3)$_3$), 30.9 (C(*C*H_3)$_3$), 30.8 (C(*C*H_3)$_3$), 26.2 (-CH_2-), 22.6(*C*H_3), 22.5 (CH_2), 22.4 (CH_2). iASAP-MS (*m/z*) [M]$^+$ Calcd for [$C_{46}H_{50}Cl_2Zr$]$^+$: 762.2336. Found: 762.2336.

Synthesis of {Ph_2C(Oct)(3-*t*Bu-Cp)}$ZrCl_2$ (3f). Using a procedure similar to that described above for **3a, 3f** was obtained from **2f** (0.98, 1.5 mmol), *n*-BuLi (1.3 mL of a 2.5 M solution in hexanes, 3.1 mmol) and $ZrCl_4$ (0.373 g, 1.6 mmol). The red/pink powder obtained was dried under vacuum and identified as complex **3g** (0.140 g, 12 %). ^{1}H NMR (C_6D_6, 500 MHz, 25 °C): δ 8.40 (s, 1H, H_{Flu}), 8.40 (s,1H, H_{Flu}), 8.01 (dt, *J* = 8.0, *J* = 1.5, 1H), 7.86 (dt, *J* = 8.0, *J* = 1.5, 1H, H_{Ph}), 7.73 (td, *J* = 7.3, *J* = 6.6, 1.5, 2H, H_{Ph}), 7.18-7.14 (m (overlaped with solvent), 2H, H_{Ph}), 7.12–7.08 (m, 2H, H_{Ph}), 7.00–6.96 (q, *J* = 7.3 , 2H, H_{Ph}), 6.46 (s, 1H, H_{Flu}), 6.43 (s, 1H, H_{Flu}), 6.20 (t, *J* = 3.0, 1H, H_{Cp}), 5.77 (t, *J* = 3.0, 1H, H_{Cp}), 5.70 (t, *J* = 3.0, 1H, H_{Cp}), 1.67-1.57 (m, 8H, CH_2), 1.53 (s, 3H, CH_3), 1.50 (s, 3H, CH_3), 1.36 (s, 3H, CH_3), 1.35 (s, 3H, CH_3), 1.29 (s, 9H, C(CH_3)$_3$), 1.10 (s, 3H, CH_3), 1.08 (s, 3H, CH_3), 1.06 (s, 3H, CH_3), 1.02 (s, 3H, CH_3). ^{13}C{^{1}H} NMR (C_6D_6, 125 MHz, 25 °C): δ 146.5 (C^q_{Oct}), 146.5 (C^q_{Oct}), 146.4 (C^q_{Oct}), 146.3 (C^q_{Oct}), 145.7 (2C^q_{Ph}), 145.2 (C^q_{Cp}), 130.1 (C_{Ph}), 130.0 (C_{Ph}), 129.2 (C_{Ph}), 129.0 (C_{Ph}), 127.1 (C_{Ph}), 127.0 (C_{Ph}), 126.9 (C_{Ph}), 122.5 (C^q_{Oct}), 122.4 (CC_{Oct}), 122.4 (C_{Oct}), 122.2 (C_{Oct}), 121.8 (C_{Oct}), 121.6 (C^q_{Oct}), 120.6 (C^q_{Oct}), 120.3 (C^q_{Oct}), 114.6(C_{Cp}), 108.2 (C^q_{Cp}), 104.2 (C_{Cp}), 99.6(C_{Cp}), 74.5 (C9-Flu), 57.8 (Ph_2***C***), 35.5 (br, 2CH_2), 35.1(7) (C^q_{Oct}), 35.1(6) (C^q_{Oct}), 35.1(1) (CH_2), 35.0(9) (CH_2), 35.0(8) (C^q_{oct}), 35.0(6) (C^q_{Oct}), 34.0 (CH_3), 33.9 (CH_3), 33.4 (*C*(CH_3)$_3$), 32.9 (CH_3), 32.8 (CH_3), 32.5 (CH_3), 32.4 (CH_3), 32.3 (CH_3), 31.6 (CH_3), 30.5 (C(*C*H_3)$_3$). iASAP-MS (*m/z*) [M]$^+$ Calcd for [$C_{51}H_{58}Cl_2Zr$]$^+$: 830.2963. Found: 830.2963.

Synthesis of {Ph_2C(2,7-(cumyl)$_2$-Flu)(3-*t*Bu)}$ZrCl_2$ (3g). Using a procedure similar to that described for **3a**, complex **3g** was obtained from **2g** (0.20 g, 0.30 mmol), *n*-Buli (2.4 mL of a 2.4 M solution in hexanes, 0.72 mmol) and $ZrCl_4$ (0.074 g, 0.4 mmol) as an orange powder identified as the heptane adduct (**6c**. heptane) (0.032 g, 12 %). ^{1}H NMR (C_6D_6 , 500 MHz, 25 °C): δ 7.86 (dt, *J* = 8.0, *J* =1.5 , 1H, H_{Ph}), 7.75 (s, 1H, H_{Flu}), 7.74 (s, 1H, H_{Flu}), 7.64 (dt, *J* = 8.0, *J* = 1.5, 1H, H_{Ph}), 7.49 (dt, *J* = 8.0, *J* = 1.5, 1H, H_{Ph}), 7.46 (dt, *J* = 8.0, *J* = 1.5, 1H, H_{Ph}), 7.37 (dd, *J* = 8.8, *J* = 1.6 , 1H, H_{Flu}), 7.30 (dd, *J* = 8.8, *J* = 1.6 , 1H, H_{Flu}), 7.22-7.20 (m , 8H, H_{Ph}), 7.09-7.06 (m, 2+1H, H_{Ph}), 7.03-7.00 (td, *J* = 7.7, *J* = 1.3, 1H, H_{Ph}), 6.97 (tt, J= 7.7 and 1.8, 2H, H_{Ph}), 6.90-6.85 (m, 2H, H_{Ph}), 6.47 (s, 1H, H_{Flu}), 6.30 (t , *J* = 3.0, 1H, H_{Cp}), 6.26 (s, 1H, H_{Flu}), 5.57 (t, *J* = 3.0, 1H, H_{Cp}), 5.52 (t, *J* = 3.0, 1H, H_{Cp}), 1.47 (s, 6H, CH_3), 1.43 (s, 6H, CH_3) 1.39 (s, 6H, CH_3) 1.32 (s, 9H, $C(CH_3)_3$). $^{13}C\{^1H\}$ NMR (C_6D_6, 125 MHz, 25 °C): δ 150.6 (C^q_{Flu}), 150.3 (C^q_{Flu}), 150.3 (C^q_{Ph}), 150.0 (C^q_{Ph}), 145.6 (C^q_{Cp}), 145.3 (C^q_{Ph}), 145.3 (C^q_{Ph}), 129.9 (2C_{Ph}), 129.0 (C_{Ph}), 128.9 (C_{Ph}), 128.9 (C_{Ph}), 128.8 (C_{Ph}), 128.4 (2 C_{Ph}), 128.3 (overlaped with solv., 2C_{Ph}), 127.5 (2 C_{Ph}), 127.3 (2 C_{Ph}), 127.2 (C_{Ph}), 127.1(C_{Ph}), 126.8(C_{Flu}) 126.6 (C_{Ph}), 126.5 (C_{Ph}), 126.2(C_{Ph}), 126.1 (C_{Ph}), 126.0 (C_{Flu}), 124.7 (C_{Flu}), 124.4 (C_{Flu}), 122.6 (C^q_{Flu}), 122.1 (C^q_{Flu}), 122.0 (C^q_{Flu}), 121.5 (C^q_{Flu}), 121.2 (C_{Flu}), 121.0 (C_{Flu}), 115.1 (C_{Cp}), 109.6 (C^q_{Cp}), 105.5 (C_{Cp}), 100.6 (C_{Cp}), 78.6 (C9-Flu), 58.0 (Ph_2C), 43.7(C^q_{Cumyl}), 43.6 (C^q_{Cumyl}), 33.5 ($C(CH_3)_3$), 30.6 (CH_3), 30.6 (CH_3), 30.6 (CH_3), 30.5 ($C(CH_3)_3$), 30.3 (CH_3). iASAP-MS (*m/z*) $[M]^+$ Calcd for $[C_{53}H_{50}Cl_2Zr]^+$: 846.2337. Found: 847.2337.

Synthesis of {Ph_2C((2,7-(Mesityl)$_2$-Flu)(5-Me-3-*t*Bu-Cp)}$ZrCl_2$ (3h). Using a procedure similar to that described above for **3a**, complex **3h** was obtained from **2h** (0.20 g, 0.30 mmol), *n*-BuLi (0.25 mL of a 2.5 M solution in hexanes, 0.60 mmol) and $ZrCl_4$ (75 mg, 0.30 mmol). Workup (with hexane instead of heptane) afforded the desired complex as an orange microcrystalline powder (0.020 g, 8 %). ^{1}H NMR (CD_2Cl_2, 400 MHz, 25 °C) (one aromatic hydrogen overlaped with the solvent signal): δ 7.98 (d, *J* = 8.5, 1H, H_{Flu}), 7.90 (d, *J* = 8.5, 1H, H_{Flu}), 7.85 (t, *J* = 8.6, 2H, H_{Ph}), 7.61 (d, *J* = 8.2, 1H, H_{Ph}), 7.34 (d, *J* = 8.0, 1H, H_{Ph}), 7.27 (dd, *J* = 8.5, *J* = 1.3, 1H, H_{Flu}), 7.22 (dd, *J* = 8.5, *J* = 1.3, 1H, H_{Flu}), 7.04 (td, *J*= 7.6, *J* = 1.3, 1H, H_{Ph}), 6.99 (m, 2H, H_{Ph}), 6.90 (td, *J* = 7.8, *J* = 1.4, 1H, H_{Ph}), 6.86-6.74 (m, 5H, H_{Ph}+H_{Flu}), 6.45 (s, 1H, H_{Flu}), 6.24 (d, *J* = 3.0, 1H, H_{Cp}), 5.83 (d, *J* = 3.0, 1H, H_{Cp}), 2.40 (s, 3H, $CH_{3\ Mes}$), 2.26 (s, 3H, CH_{3Mes}), 2.20(s, 3H, $CH_{3\ Mes}$), 2.11 (s, 6H, 2$CH_{3\ Mes}$), 2.10 (s, 3H, $CH_{3\ Mes}$), 1.79 (s, 3H, CH_{3Cp}), 1.25 (s, 9H, $C(CH_3)_3$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 400 MHz, 25 °C): δ 147.9 (C^q), 145.5 (C^q), 144.6 (C^q), 141.4 (C^q), 139.1(C^q), 138.9(C^q), 136.9 (C^q), 136.8 (C^q), 136.6 (C^q), 136.6 (C^q), 135.8 (C^q), 135.6 (C^q), 135.5 (C^q), 129.8, 129.2, 128.7, 129.1 129.1, 129.0, 129.0, 128.9, 128.6, 128.5, 128.4, 128.4, 127.2, 126.8, 126.1, 125.1 (2C), 125.0 (C^q), 124.7, 124.6 (C^q), 124.1 (C^q), 122.3 (C^q), 121.9 (C^q), 121.9 (C^q), 121.0, 120.9 (C_{Cp}), 106.9 (C^q_{Cp}), 102.8 (C_{Cp}), 80.8 (C9-Flu), 60.4 (Ph_2C), 30.2 ($C(CH_3)_3$), 29.5 ($C(CH_3)_3$), 22.5 (CH_3), 22.0 (CH_3), 21.6 (CH_3), 21.5 (CH_3), 21.0 (CH_3),

21.0(CH_3), 20.7 (CH_3). Since only a very small amount of pure compound was isolated, mass spectrometric and elemental analyses data could not be obtained for this complex.

Synthesis of {Ph_2Si(2,7-*t*Bu_2-Flu)(5-Me-3-*t*Bu-Cp)}$ZrCl_2$ (3k). Using a procedure similar to that described for compound **3a**, complex **3k** was prepared from proligand **2k** (0.28 g, 0.46 mmol) *n*-BuLi (0.4 mL of a 2.5 M solution in hexanes, 0.98 mmol) and $ZrCl_4$ (0.12 g, 0.51 mmol). **3k** was obtained as a yellow powder (0.137 g, 40 %). ^{1}H NMR (CH_2Cl_2, 400 MHz, 25 °C): δ 8.11-8.08 (m, 2H, H), 8.00-7.97 (m, 2H, H_{Ph}), 7.95 (d, *J* = 8.8, 2H, H_{Flu}), 7.89(d, *J* = 8.8, H, H_{Flu}), 7.64 (d, *J* = 8.8, *J* = 2.7, H, H_{Flu}), 7.60 (dd, *J* = 8.8, *J* = 1.7, 2H, H_{Flu}), 7.42 (br s, 1H, H_{Flu}), 7.26-7.17 (m, 6H, H_{Ph}), 6.93 (br s, 1H, H_{Flu}), 6.46 (d, *J* = 2.5, 1H, H_{Cp}), 5.87 (d, *J* = 2.5, 1H, H_{Cp}), 2.10 (s, 3H, CH_3), 1.24 (s, 9H, C(C*H*$_3$)$_3$), 1.15 (s, 9H, C(C*H*$_3$)$_{3\ Flu}$), 1.09 (s, 9H, C(C*H*$_3$)$_{3\ Flu}$). ^{13}C{^{1}H} NMR (CH_2Cl_2, 100 MHz, 25 °C): δ 153.1(C^q), 151.1 (C^q) 150.4 (C^q), 135.6(C^q), 135.4 (2C_{Ph}) 134.7(2C_{Ph}), 132.4(C^q), 130.7(C^q), 130.6(C_{Ph}), 130.5(C_{Ph}), 130.0 (C^q), 129.0 (2C_{Ph}), 128.6 (2C_{Ph}), 127.2 (C^q), 126.9 (C^q), 126.4 (C_{Flu}), 126.1 (C_{Flu}), 124.8 (C_{Flu}), 124.5 (C_{Flu}), 124.0 (C_{Flu}), 123.5(C_{Cp}), 120.2 (C_{Flu}), 107.2 (C_{Cp}), 96.0 ($C_{Cp–Si}$), 63.2 (C9-Flu), 35.3 (***C***CH_3), 35.1 (***C***CH_3) 34.1 (***C***CH_3), 31.1 (C***C***H_3), 30.9 (C***C***H_3), 30.1 (C***C***H_3), 19.2 (CH_3). iASAP-MS (*m/z*) $[M]^+$ Calcd for $[C_{43}H_{48}Cl_2SiZr]^+$: 752.1949. Found: 752.1949.

NMR scale reaction between {Ph_2C(2,7-*t*Bu_2-Flu)(3-(*n*Bu_3C)-Cp)}$ZrMe_2$ (4c) and $B(C_6F_5)_3$. In the glovebox, a Teflon-valved NMR tube was charged with **4c** (40 mg, 49.4 μmol) and $B(C_6F_5)_3$ (27 mg, 54.3 μmol). Then, toluene-d_8 was vacuum-transferred in at −50 °C and the NMR tube was rapidly introduced in the spectrometer probe (kept at −50 °C) for analysis. The ^{1}H NMR spectroscopy analysis revealed that the activated ion-pair formed quantitatively. ^{1}H NMR (tol-d_8, 500 MHz, −50 °C): δ 8.08 (d, *J* = 8.0, 2H), 7.70 (d, *J* = 8.8, 2H) 7.46–7.41 (br m, 2H), 7.31 (d, *J* = 8.9, 1H), 7.15 (s, 2H), 6.98–6.82 (br m, 7H), 6.30 (s, 1H, H_{Flu}), 6.11 (s, 1H, H_{Flu}), 5.61 (s, 1H, H_{Cp}), 5.30 (s, 1H, H_{Cp}), 4.62(s, 1H, H_{Cp}), 1.49–1.35 (br m, 8H, CH_2), 1.25–1.13 (br m, 10H, CH_2) , 1.04 (s, 9H, C(C*H*$_3$)$_3$), 0.90 (br s, 9H, C(C*H*$_3$)$_3$), 0.80 (br s, 9H, CH_3), −0.22 (br s, 3H, BC*H*$_3$), −0.38 (s, 3H, Zr-CH_3). ^{13}C{^{1}H} (tol-d_8, 125 MHz, −50 °C) (many aromatic carbon signals overlapped with those of the solvent): δ 152.5, 150.2, 148.3 (br d, ^1J = 246.7, *o*-C_6F_5), 143.6. 143.5, 143.5, 139.3 (br d, *J* = 249.1, *p*-C_6F_5), 137.4, 137.3 (br d, *J* = 255.0, *m*-C_6F_5), 126.3, 125.8, 125.6, 123.6, 123.4, 122.4, 121.6, 121.6, 119.3, 117.8, 108.7 , 105.2, 104.9, 101.5, 76.5 (C9-Flu), 57.2 (Ph_2***C***), 47.8 (Zr–C*H*$_3$), 41.6, 36.9, 35.2, 35.0, 32.5, 30.4, 29.3, 26.9, 23.7, 14.4 (CH_3). ^{11}B{^{1}H} NMR (tol-d_8, 128 MHz, −50 °C): δ −14.0. ^{19}F{^{1}H} NMR (tol-d_8, 376 MHz, −50 °C): δ −132.0 (d, ^3J = 23, 6F, *o*-F), −160.2 (t, ^3J = 23, 3F, *p*-F), −165.0 (t, ^3J = 23, 6F, *m*-F).

Propylene polymerization. Polymerizations were performed in a 300 mL high-pressure glass reactor equipped with a mechanical stirrer (Pelton turbine) and externally heated with a double mantle

with a circulating water bath. The reactor was filled with toluene (80 to 150 mL) and MAO (1.5 mL of a 30 wt-% solution in toluene) and pressurized at 5 atm of propylene (Air Liquide, 99.99%). The reactor was thermally equilibrated at the desired temperature for 30 min. The propylene pressure was decreased to 1 bar and a solution of the catalyst precursor in toluene (ca. 2 mL) was added by syringe. The propylene pressure was immediately increased to 5 bar (kept constant with a back regulator) and the solution was stirred for the desired time (typically 30 min). The temperature inside the reactor was monitored using a thermocouple. The polymerization was stopped by venting the vessel and quenching with a 10% HCl solution in methanol (ca. 3 mL). The polymer was precipitated in methanol (ca. 200 mL) and 35 % aqueous HCl (ca. 1 mL) was added to dissolve possible catalyst residues. The polymer was collected by filtration, washed with methanol (ca. 500 mL), and dried under vacuum overnight.

Crystal Structure Determination of 2a-c, e-k and 3b-d, e, g, h. Diffraction data were collected at 150 K with a D8 VENTURE Bruker AXS diffractometer equipped with a (CMOS) PHOTON 100 detector, [MoKα] radiation (λ = 0.71073 Å, multilayer monochromator). The structure was solved by dual-space algorithm using the SHELXT program [10], and then refined with full-matrix least-squares methods based on F2 (SHELXL) [11]. For **3c, f** and **h**, the contribution of the disordered solvents to the calculated structure factors was estimated following the BYPASS algorithm[12], implemented as the SQUEEZE option in PLATON [13]. All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. H atoms were finally included in their calculated positions and treated as riding on their parent atom with constrained thermal parameters. Crystal data and details of data collection and structure refinement for the different compounds are given in **Table S1** and **S2**. Crystal data and details of data collection and structure refinement for the different compounds are given in **Table S1**. Crystal data, details of data collection and structure refinement for all compounds (CCDC 2068317–2068330) can be obtained from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Computational Studies. The calculations were performed using the Gaussian 09 [14] program employing B3PW91 [15,16] functional, and using a standard double-ξ polarized basis set, namely the LANL2DZ set, augmented with a single polarization f function on zirconium (0.875). The solvent effects, in our case for toluene, were taken into account during all the calculations by means of the SMD model.[17] All stationary points were fully characterized via analytical frequency calculations as either true minima (all positive eigenvalues) or transition states (one imaginary eigenvalue). The IRC procedure was used to confirm the nature of each transition state connecting two minima. [18] Zero-point vibrational energy corrections (ZPVE) were estimated by a frequency calculation at the same level of theory, to be considered for the calculation of the total energy values at T = 298 K in the same way as in the approach used by Castro et *al*.[19]

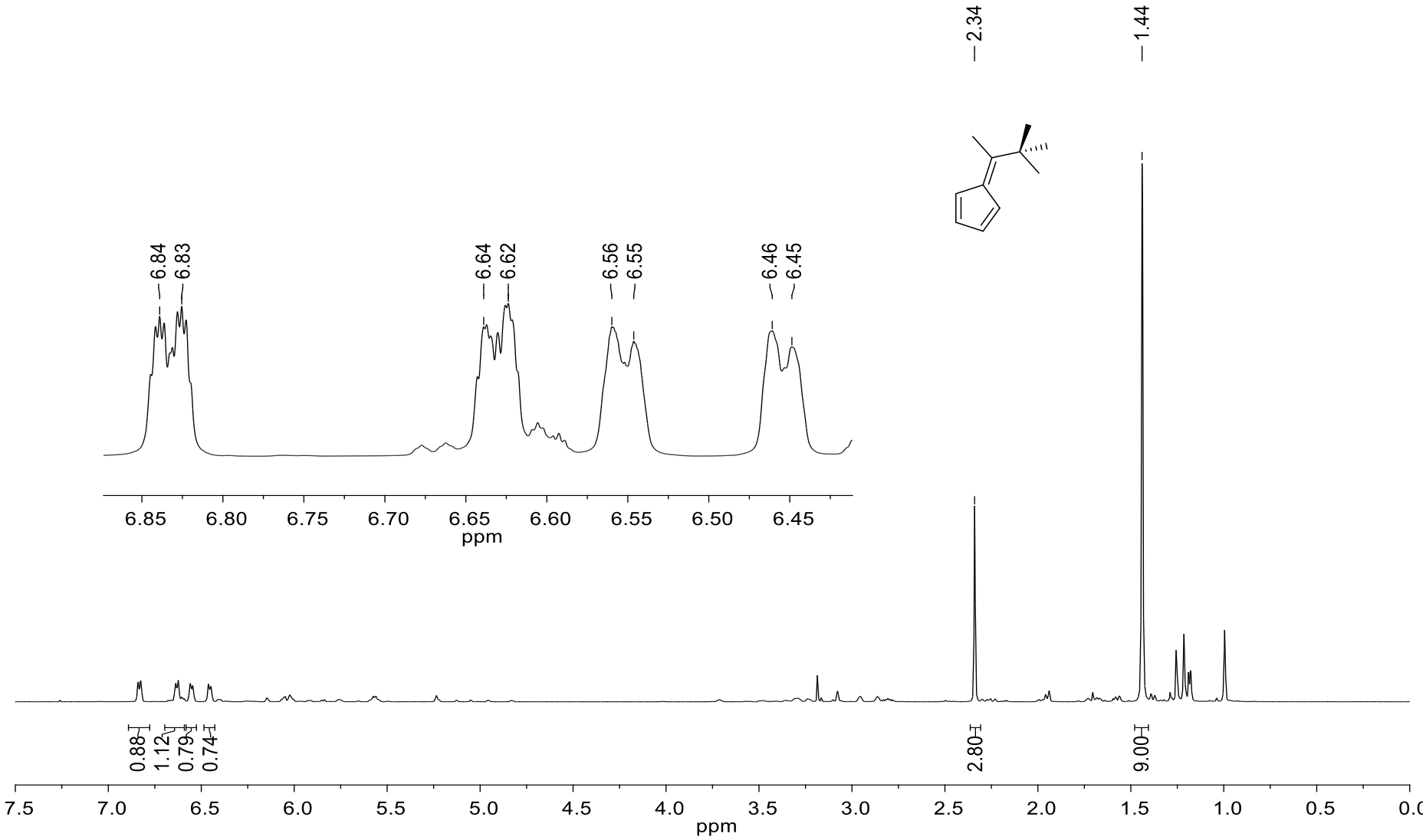

Figure S1. ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C) of **6-methyl-6'-*tert*-butylfulvene**.

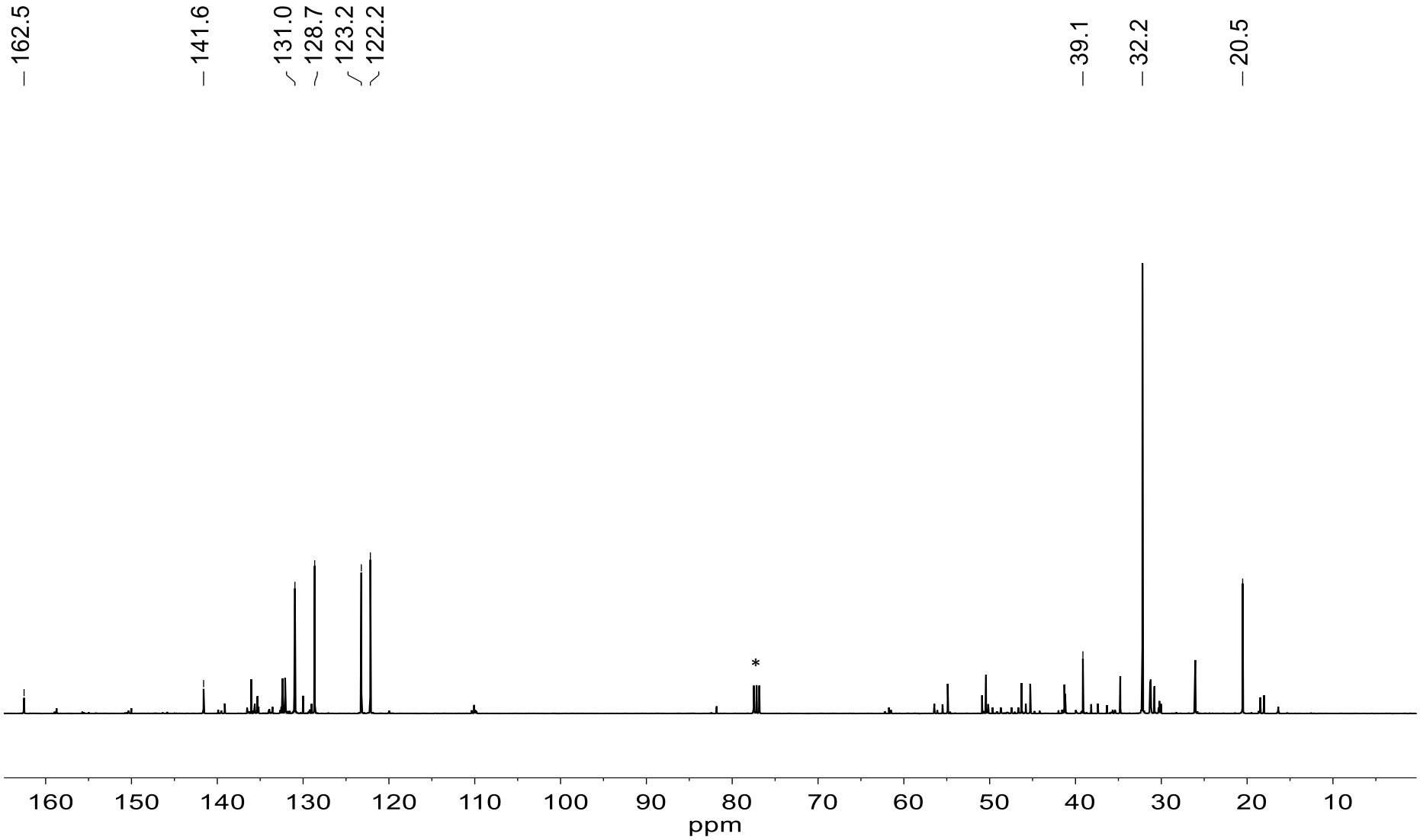

Figure S2. $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 100 MHz, 25 °C) of 6-methyl-6'-*tert*-butylfulvene (mixture of isomers). * stands for residual NMR solvent signals.

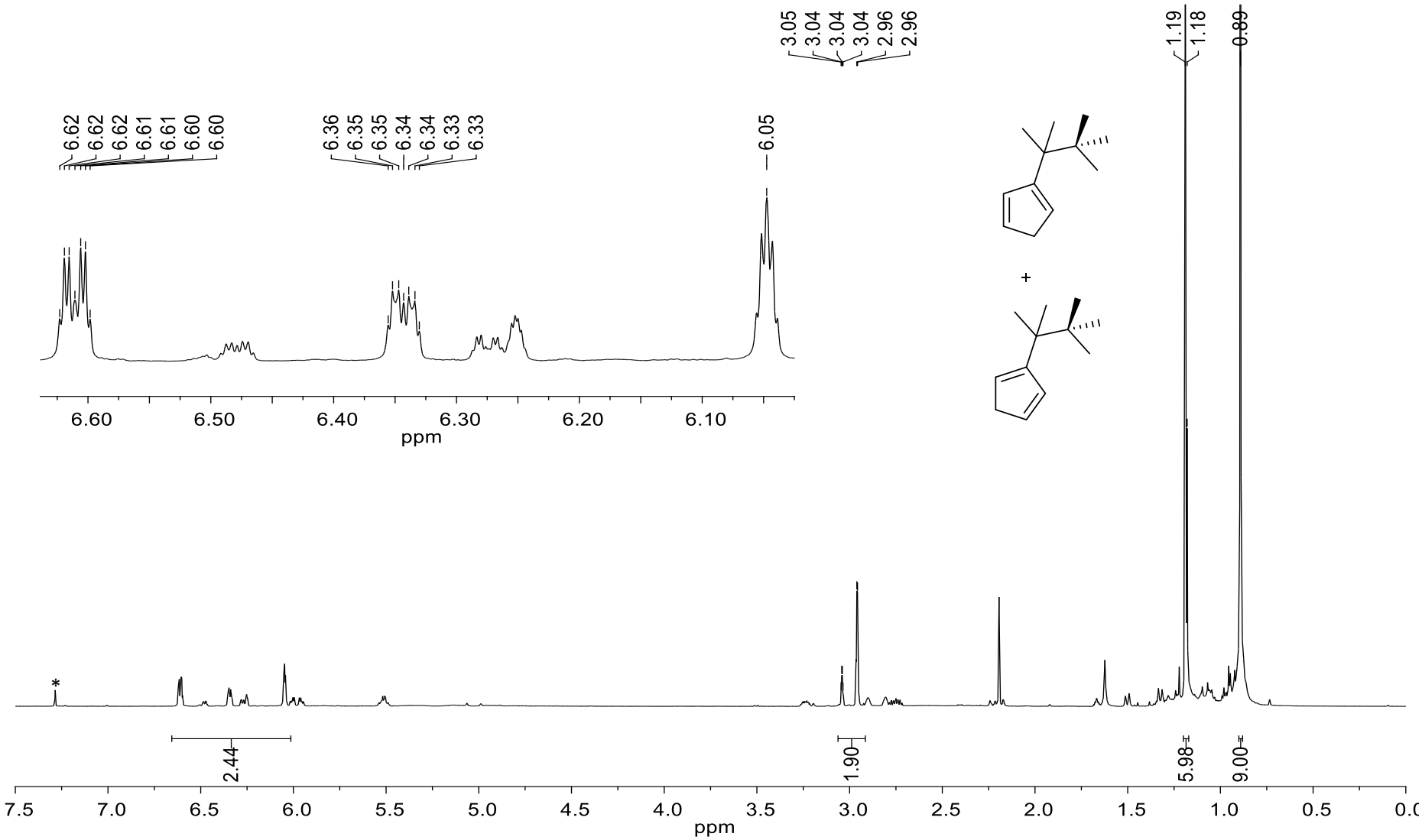

Figure S3. ^{1}H NMR spectrum (CD_2Cl_2, 400 MHz, 25 °C) of **2-(2,3,3-trimethylbutan-2-yl)cyclopentadiene** (mixture of isomers). *stands for residual NMR solvent signals.

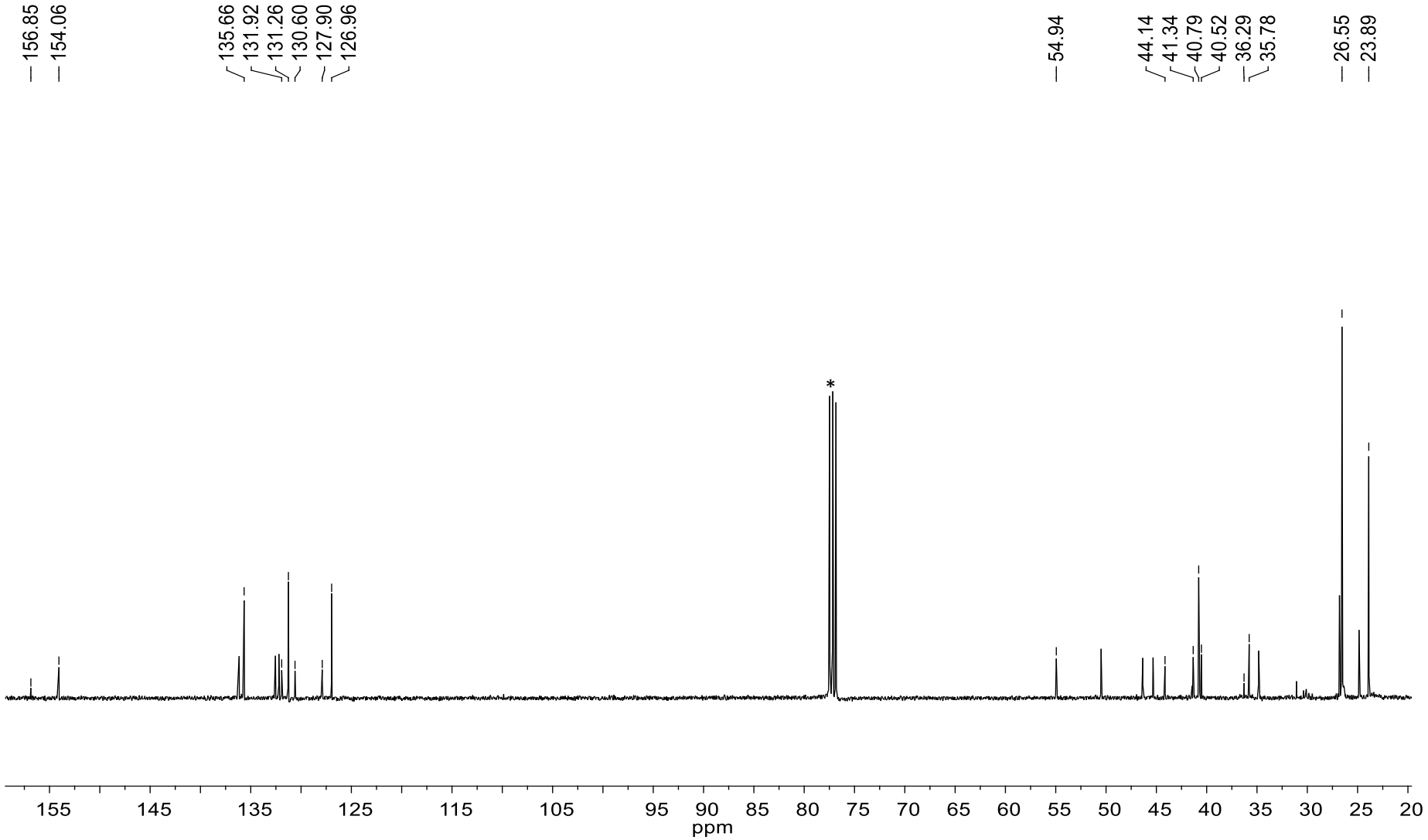

Figure S4. $^{13}C\{^{1}H\}$ NMR spectrum (CD_2Cl_2, 100 MHz, 25 °C) of **2-(2,3,3-trimethylbutan-2-yl)cyclopentadiene** (mixture of isomers). * stands for residual NMR solvent signals.

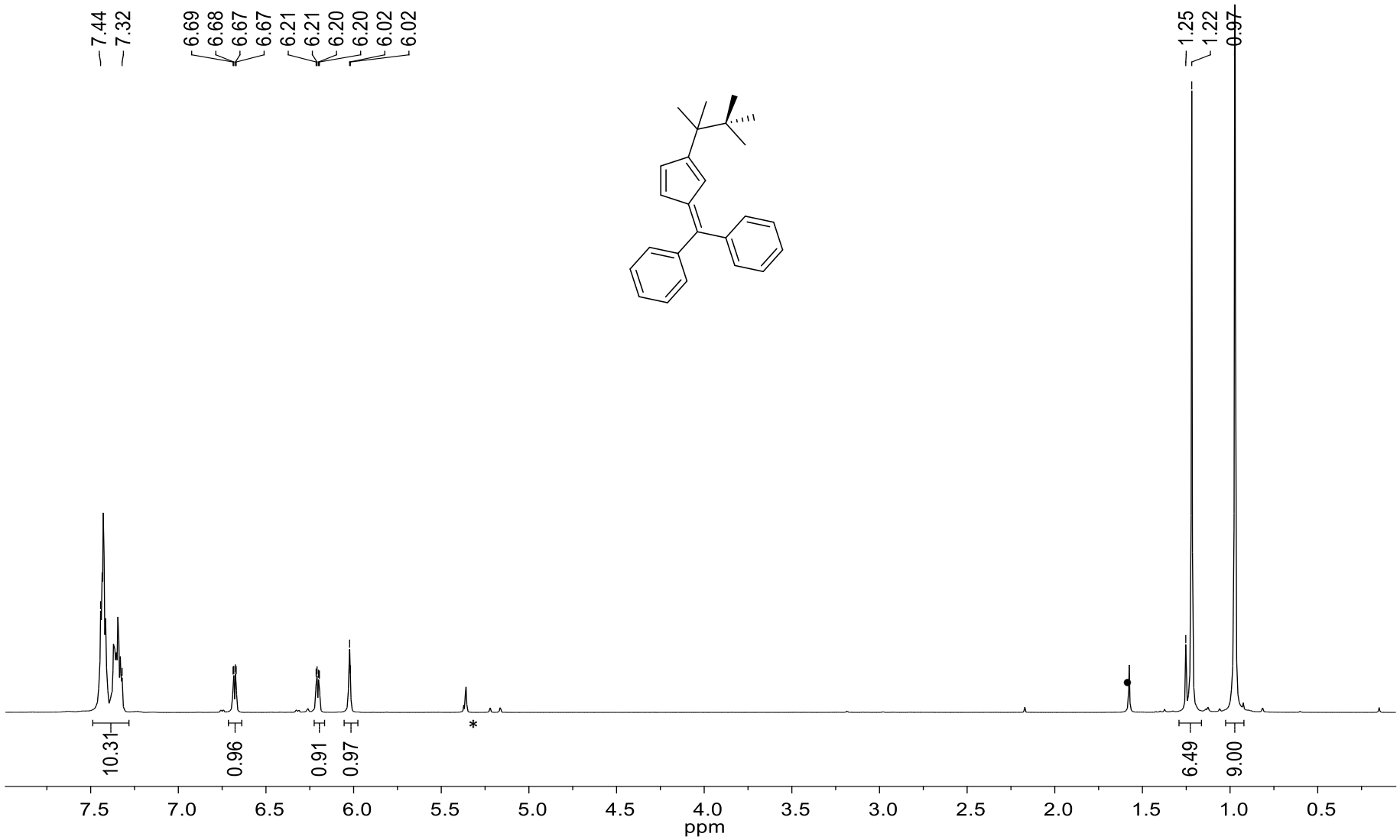

Figure S5. ^{1}H NMR spectrum (CD_2Cl_2, 400 MHz, 25 °C) of fulvene **1b**. *stands for residual NMR solvent signal. ● stands for signal of residual water from NMR solvent.

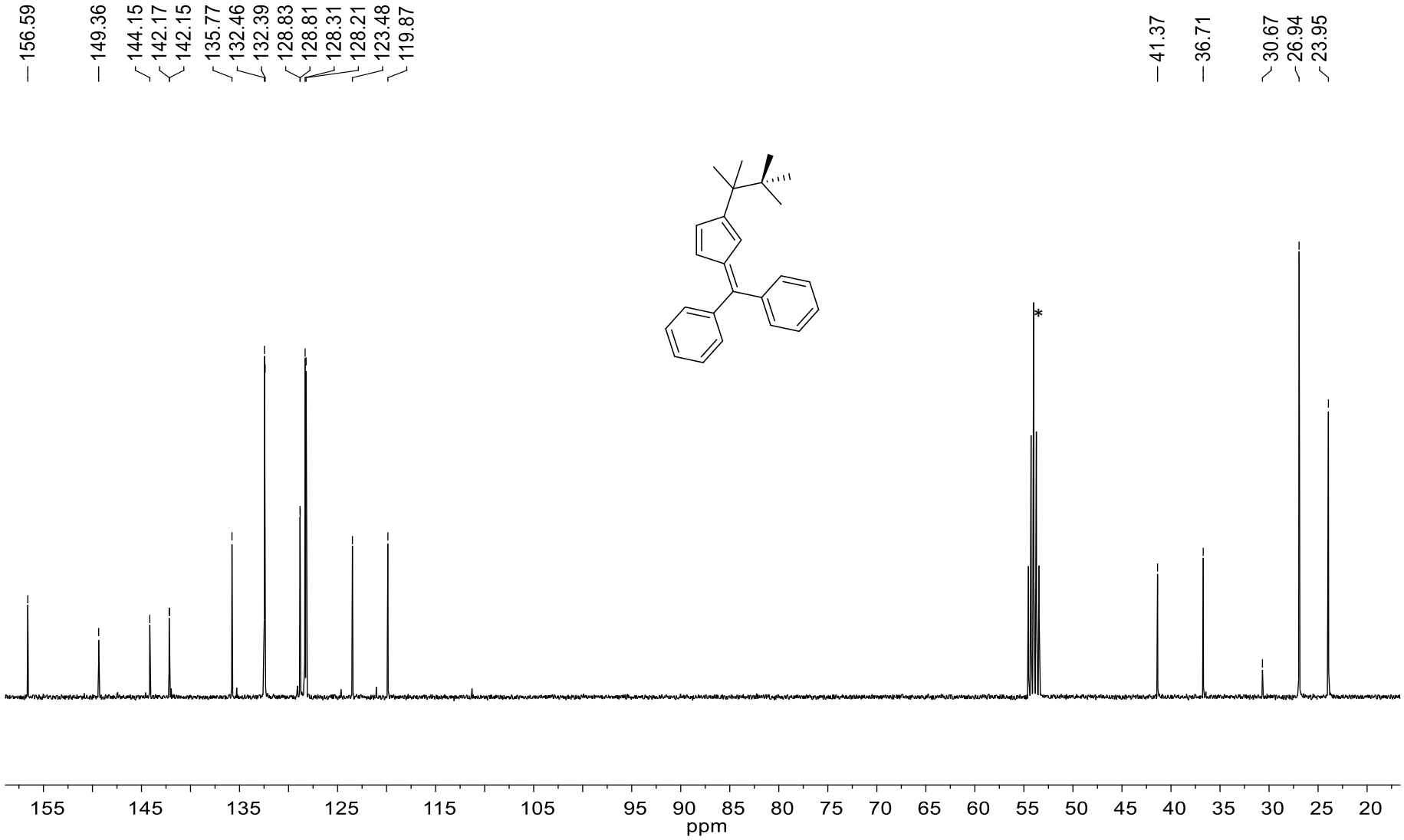

Figure S6. $^{13}C\{^{1}H\}$ NMR spectrum (CD_2Cl_2, 100 MHz, 25 °C) of fulvene **1b**. * stands for residual NMR solvent signals.

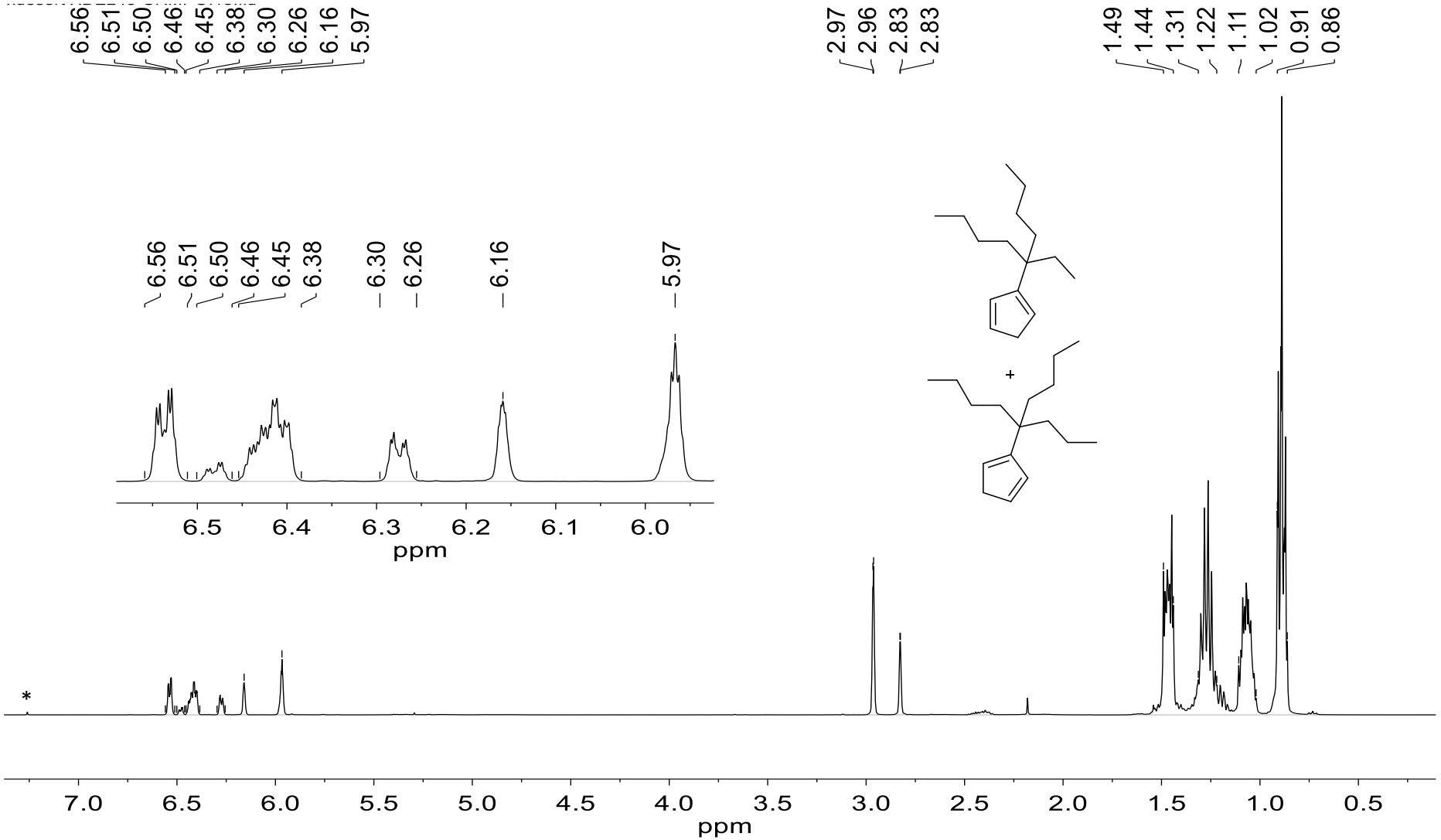

Figure S7. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, 25°C) of **1-(tri-*n*-butyl)-cyclopentadiene** (mixture of isomers). * stands for residual NMR solvent signal.

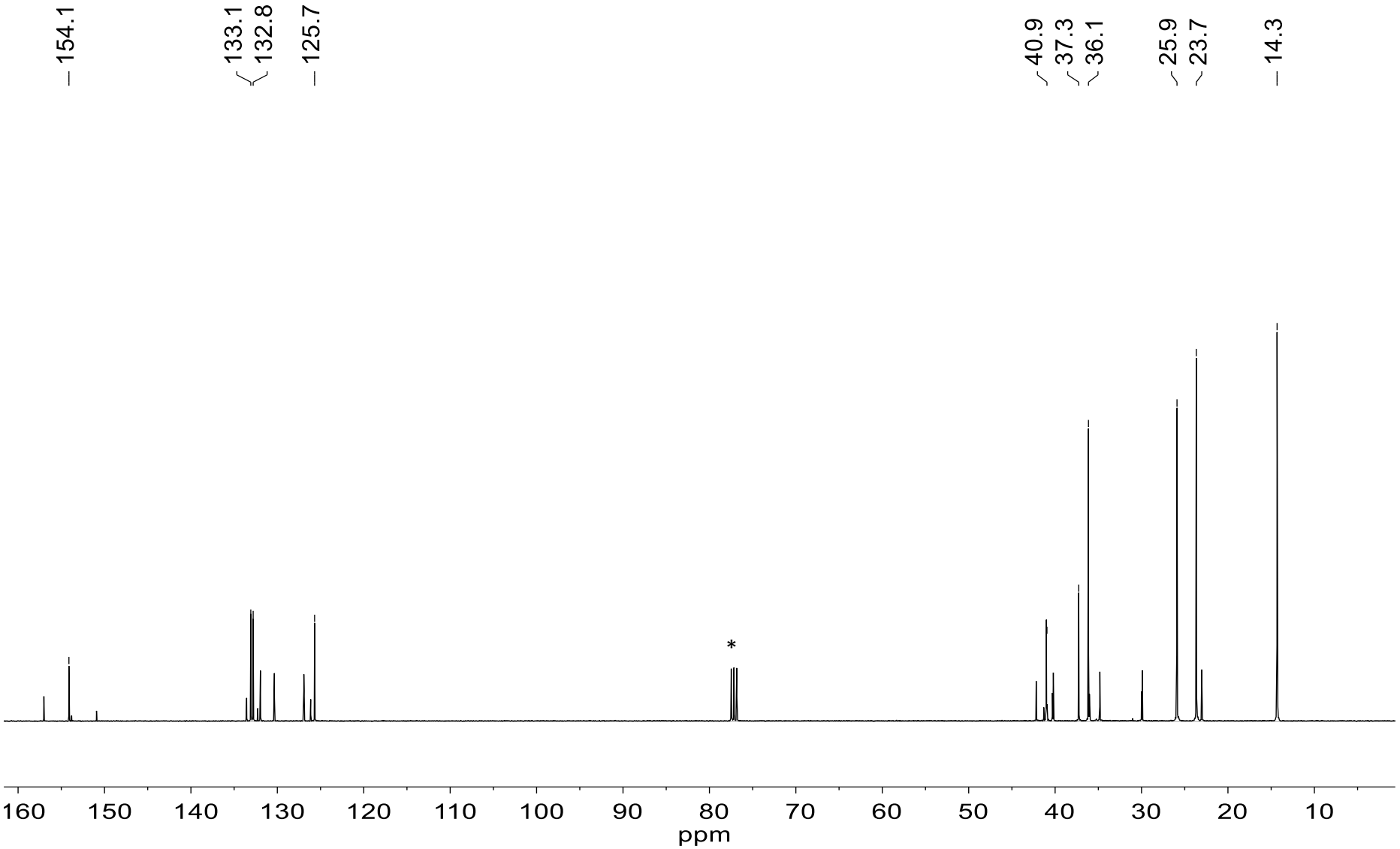

Figure S8. $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 100 MHz, 25 °C) of **1-(tri-*n*-butyl)-cyclopentadiene** (mixture of isomers). * stands for residual NMR solvent signals.

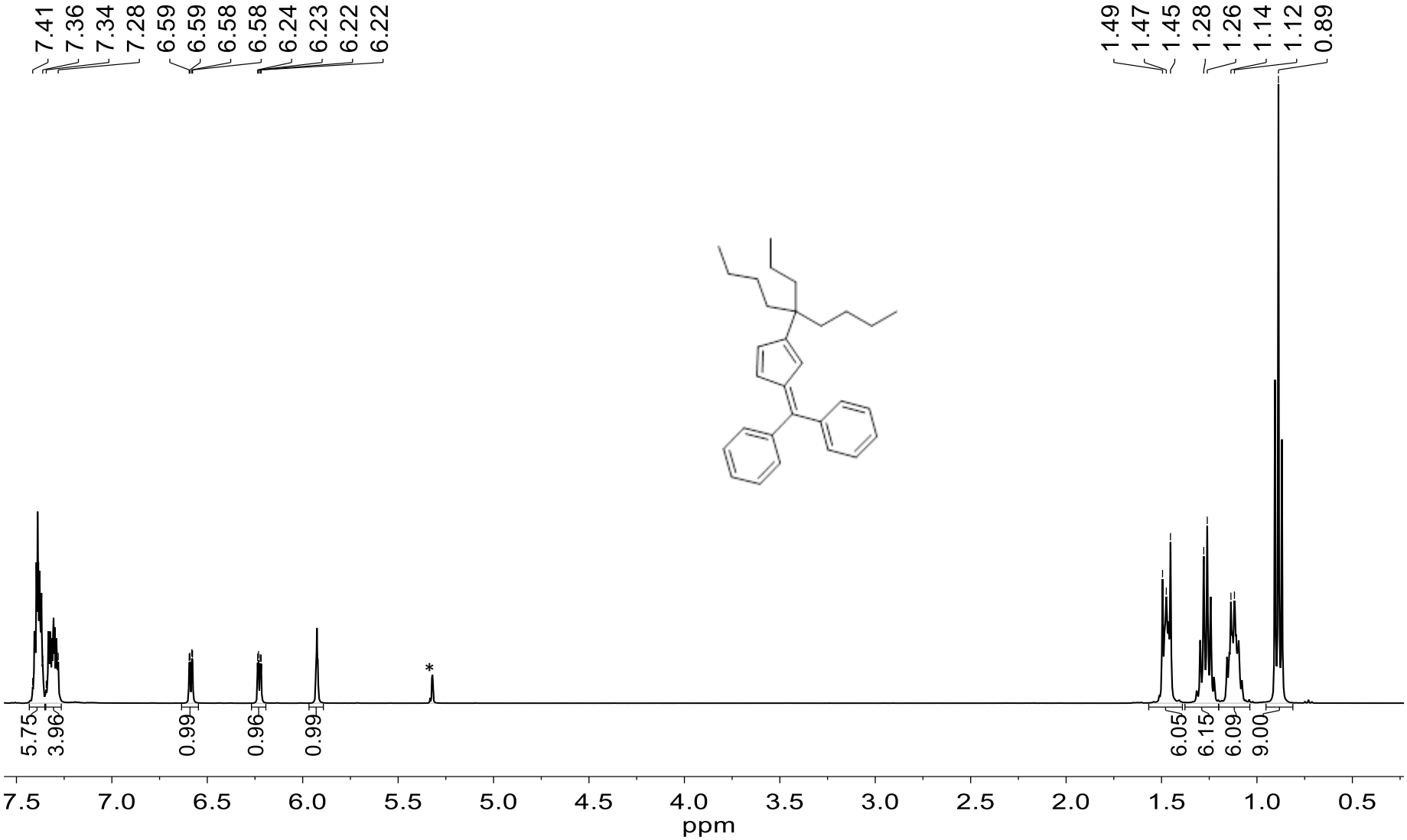

Figure S9. ^{1}H NMR spectrum (CD_2Cl_2, 400 MHz, 25 °C) of **1c**. * stands for residual NMR solvent signal.

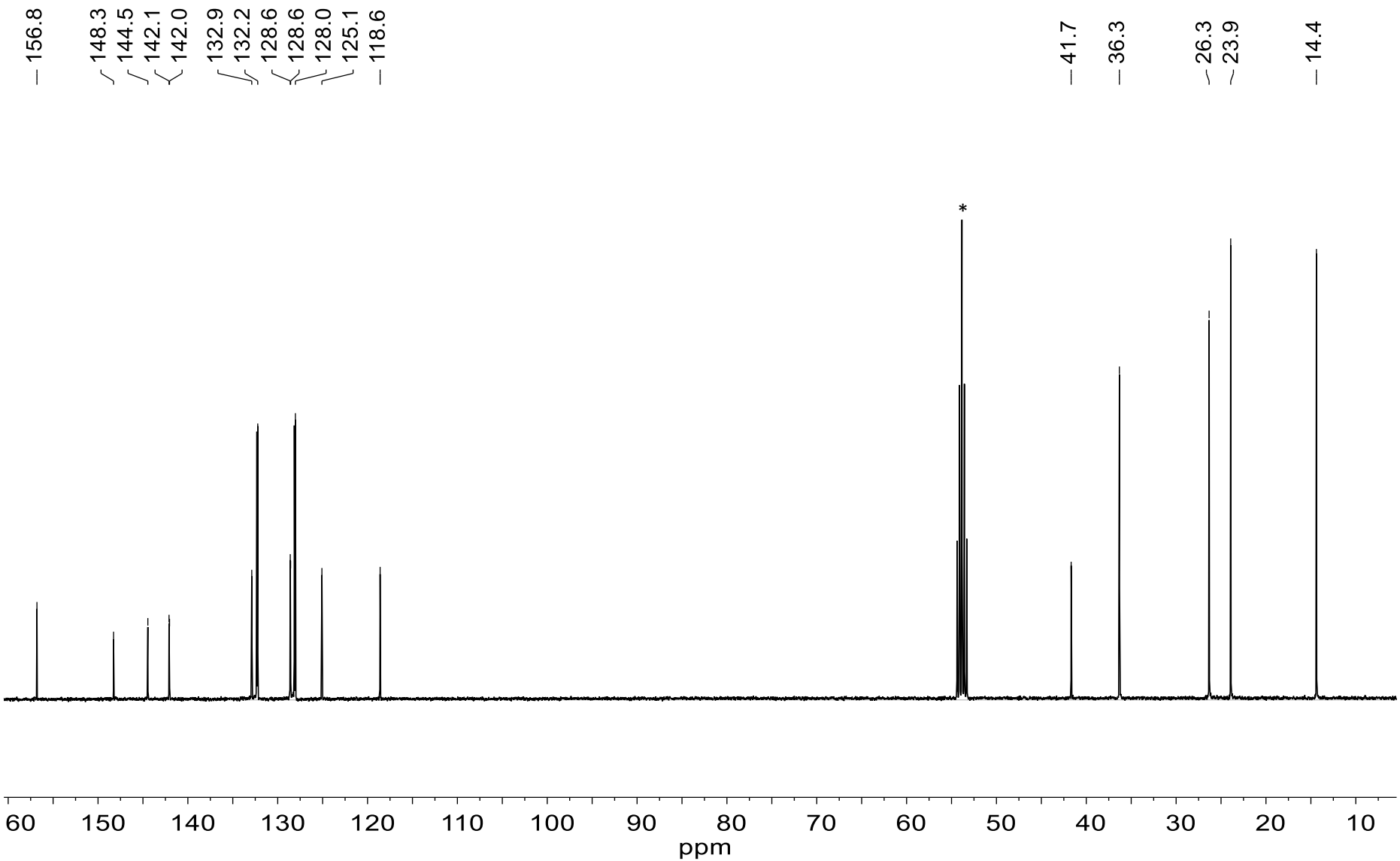

Figure S10. $^{13}C\{^{1}H\}$ NMR spectrum (CD_2Cl_2, 100 MHz, 25 °C) of **1c**. * stands for residual NMR solvent signals.

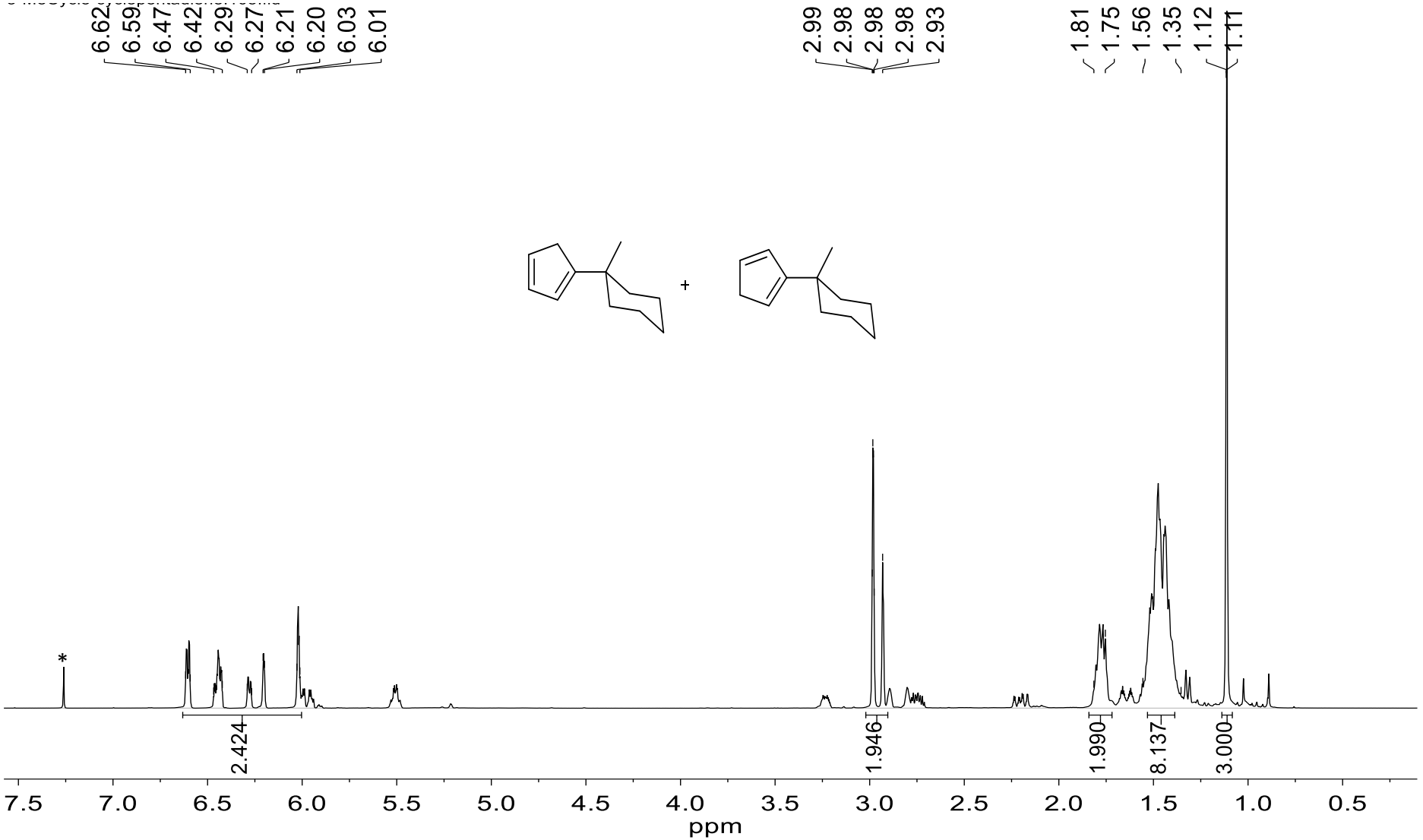

Figure S11. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, 25 °C) of **1-(methyl-cyclohexyl)-cyclopentadiene** (mixture of isomers). * stands for residual NMR solvent signal.

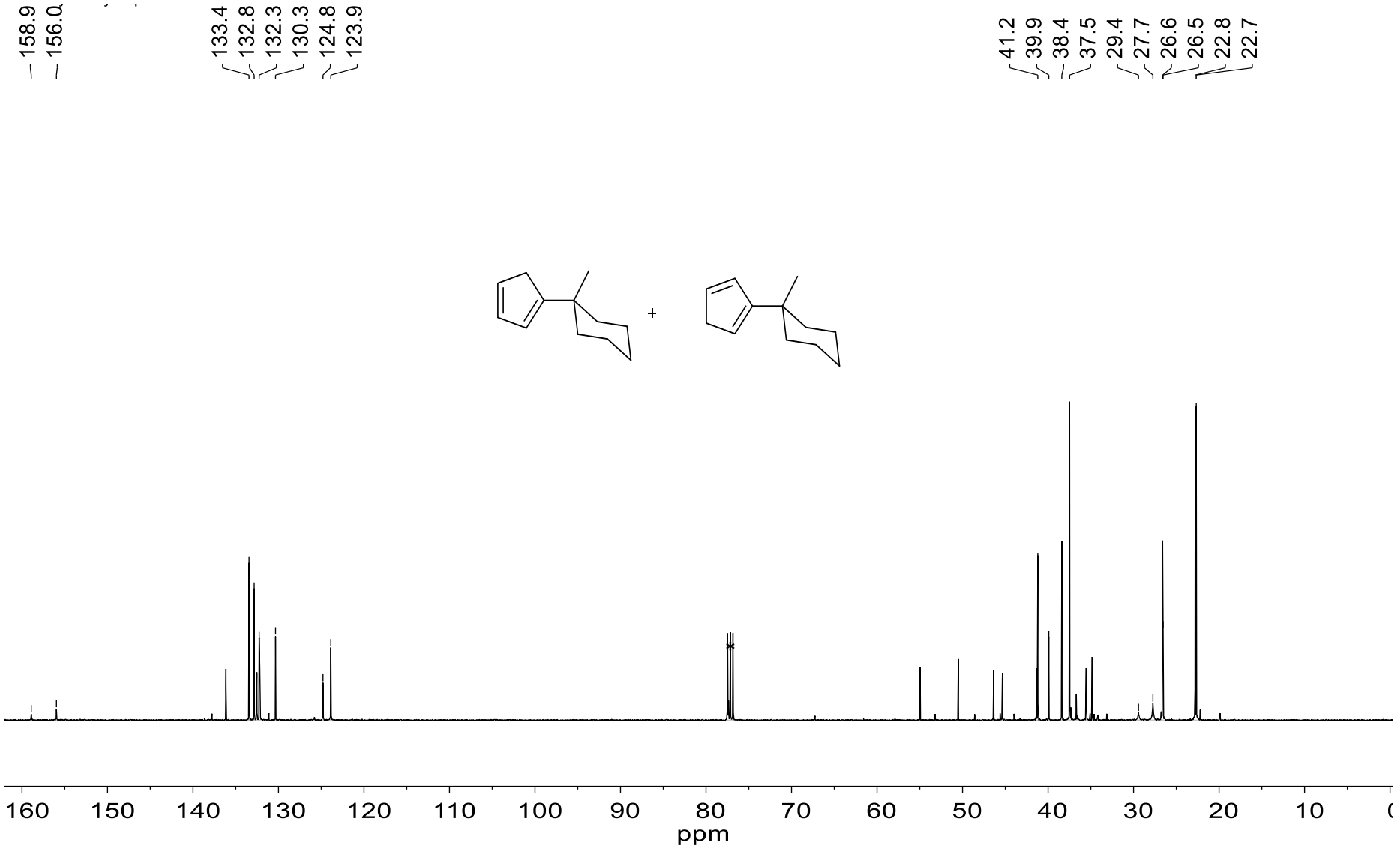

Figure S12. $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 100 MHz, 25 °C) of **1-(methyl-cyclohexyl)-cyclopentadiene**. * stands for residual NMR solvent signals.

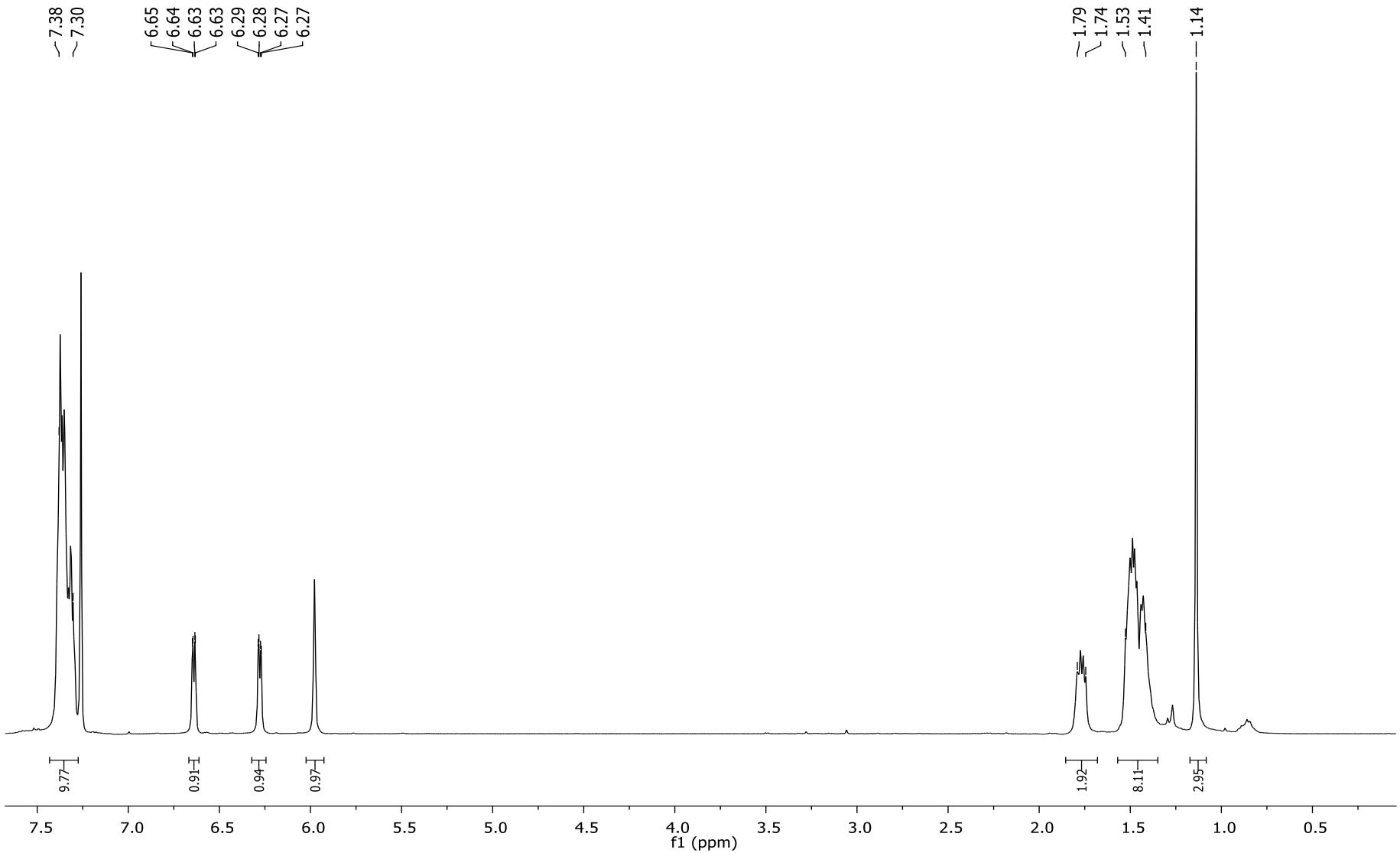

Figure S13. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, 25 °C) of **1e**.

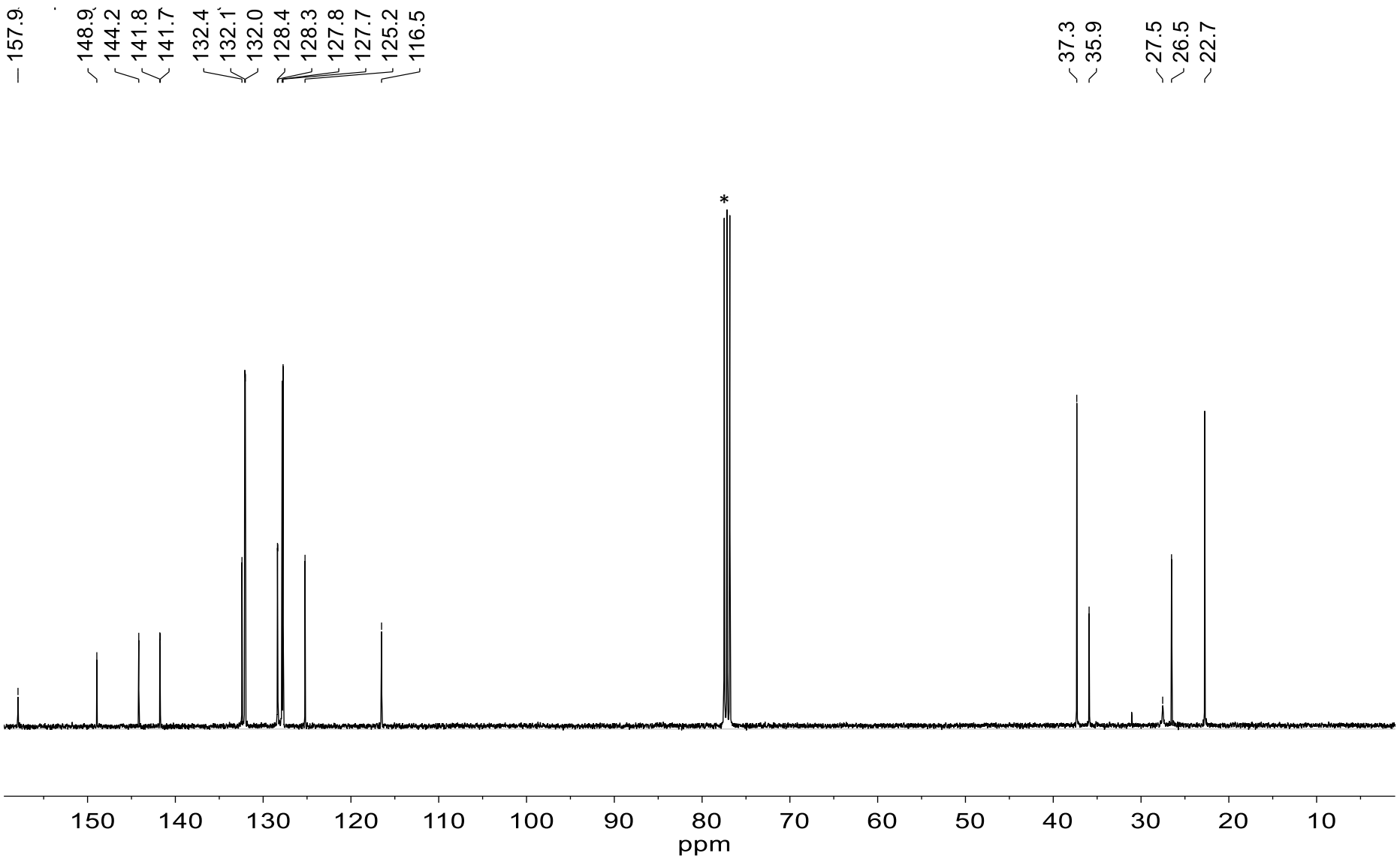

Figure S14. $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 100 MHz, 25 °C) of **1e**. *stands for residual NMR solvent signals.

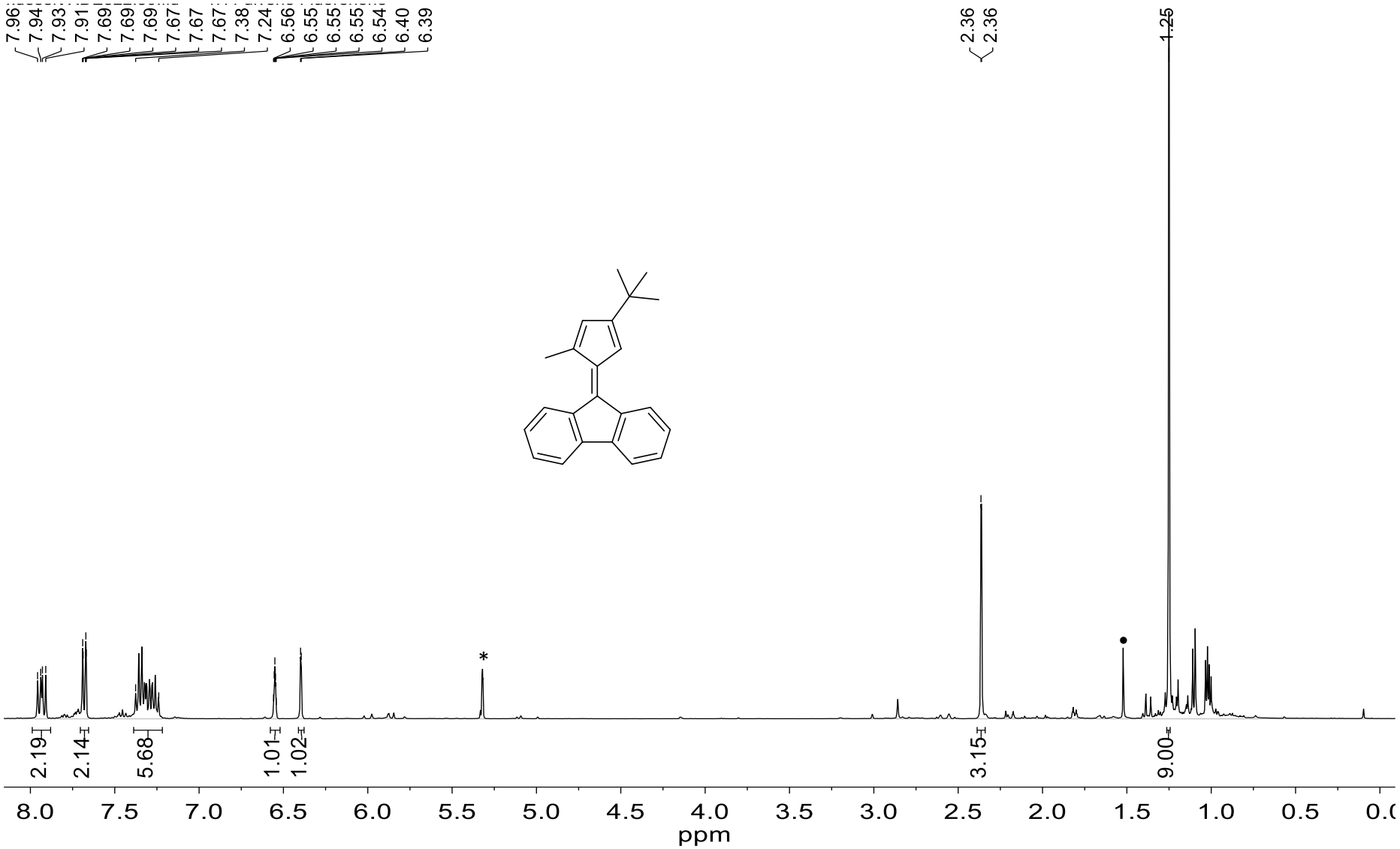

Figure S15. ^{1}H NMR spectrum (CD_2Cl_2, 400 MHz, 25 °C) of **1i**. * stands for residual NMR solvent signal. ● stands for residual water from the NMR solvent.

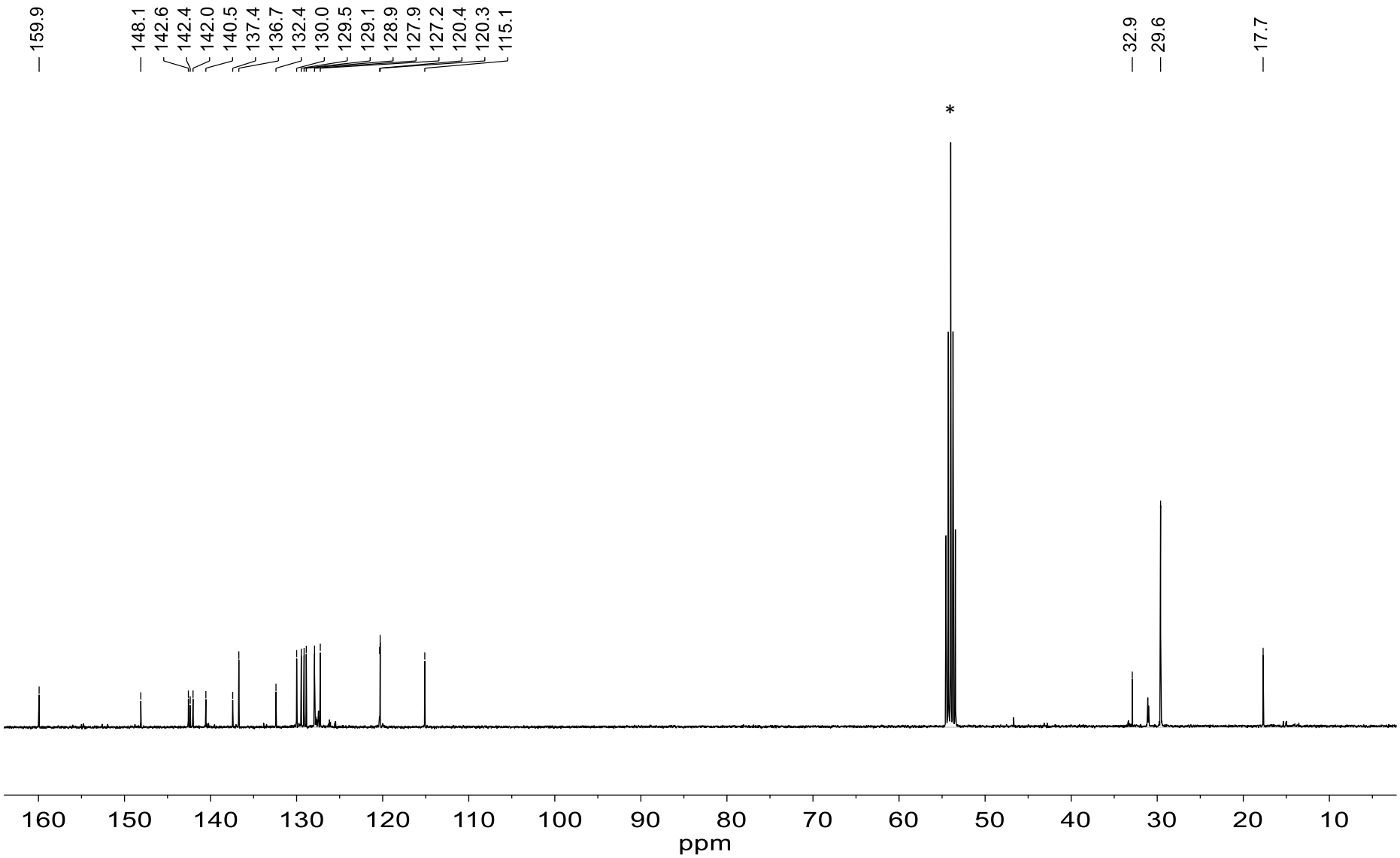

Figure S16. $^{13}C\{^{1}H\}$ NMR spectrum (CD_2Cl_2, 100 MHz, 25 °C) of **1i**. * stands for residual NMR solvent signals.

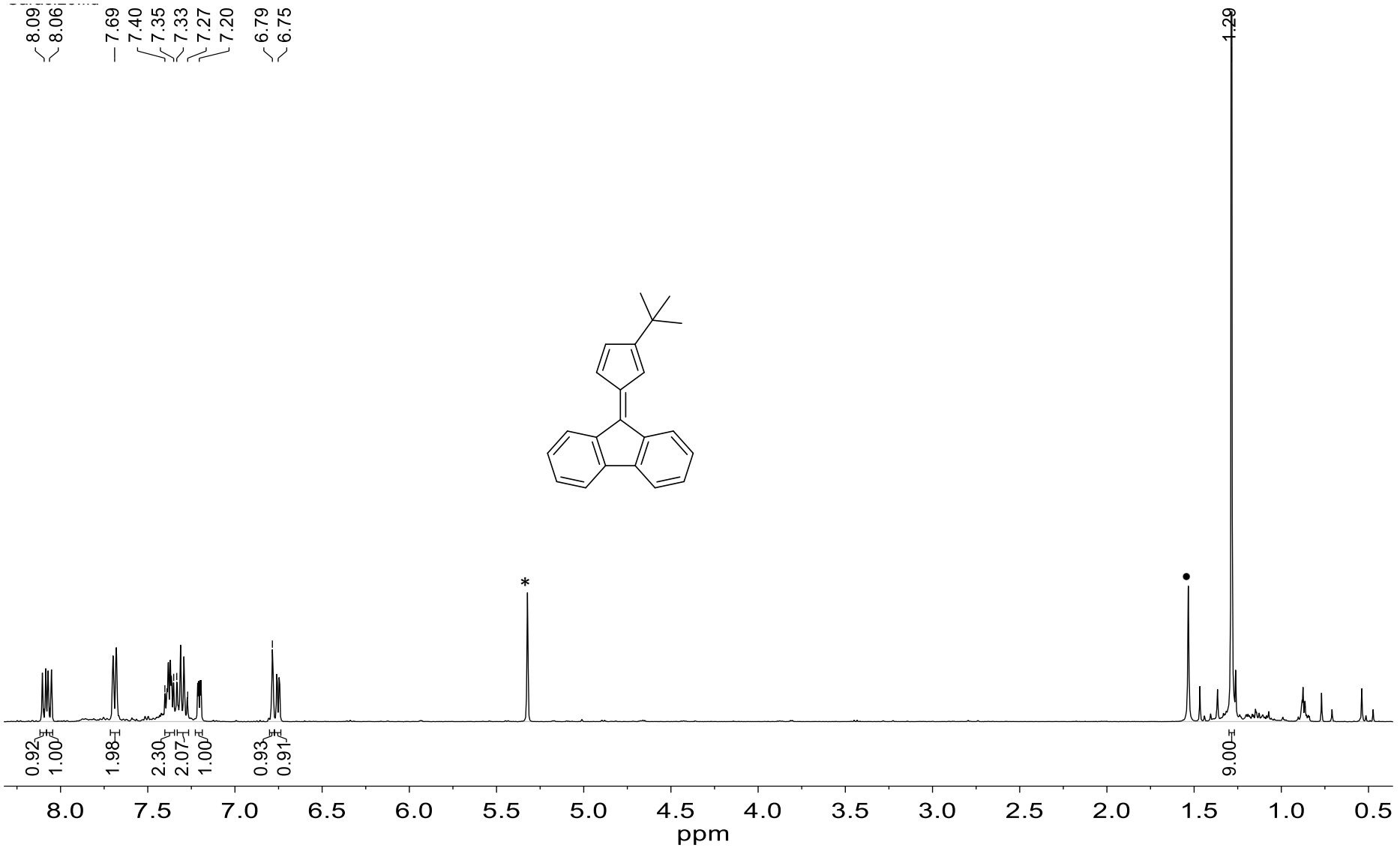

Figure S17. ^{1}H NMR spectrum (CD_2Cl_2, 400 MHz, 25 °C) of **1j**. * stands for residual NMR solvent signal. ● stands for NMR solvent residual water signal.

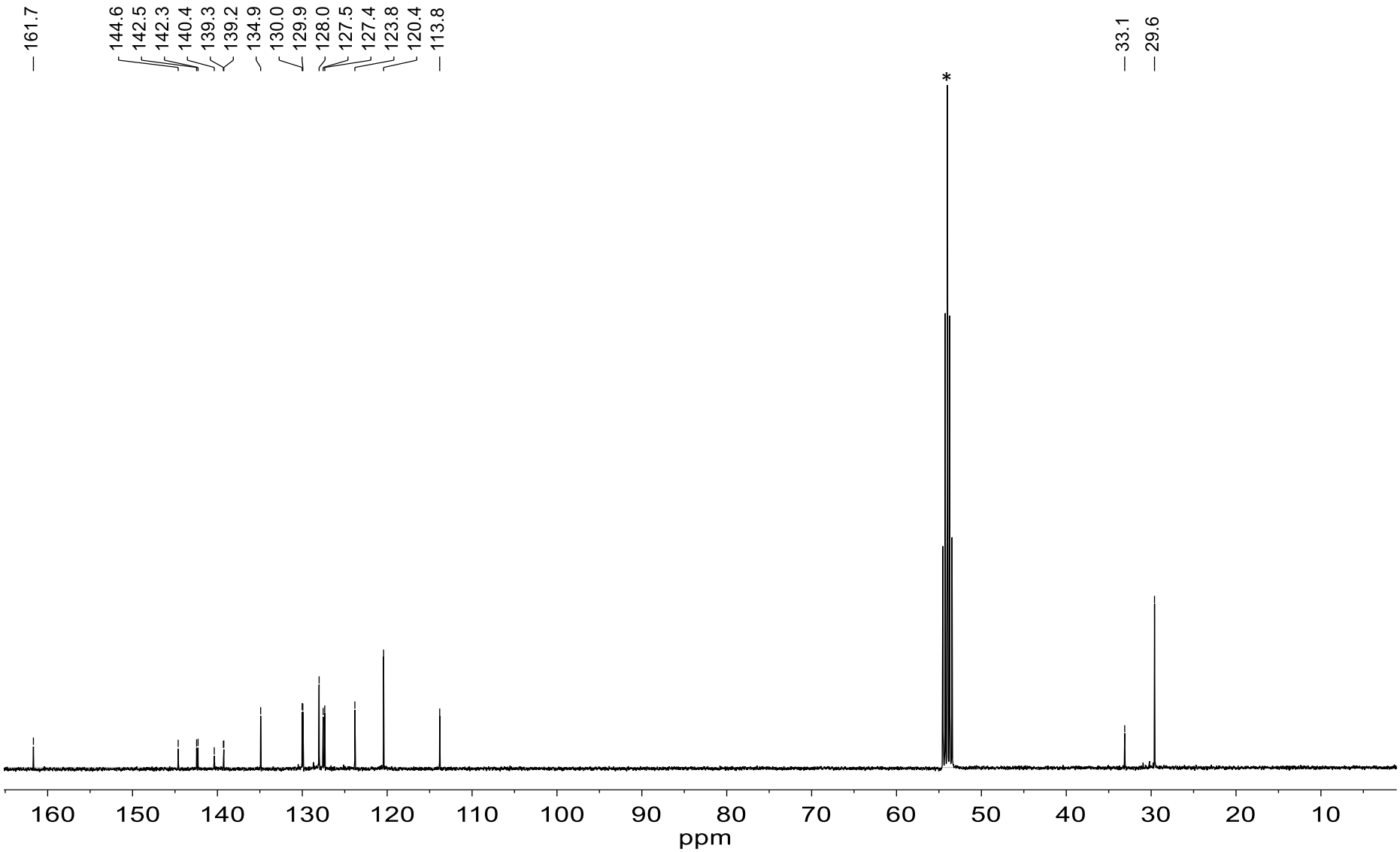

Figure S18. $^{13}C\{^{1}H\}$ NMR spectrum (CD_2Cl_2, 100 MHz, 25 °C) of **1j**. * stands for residual NMR solvent signals.

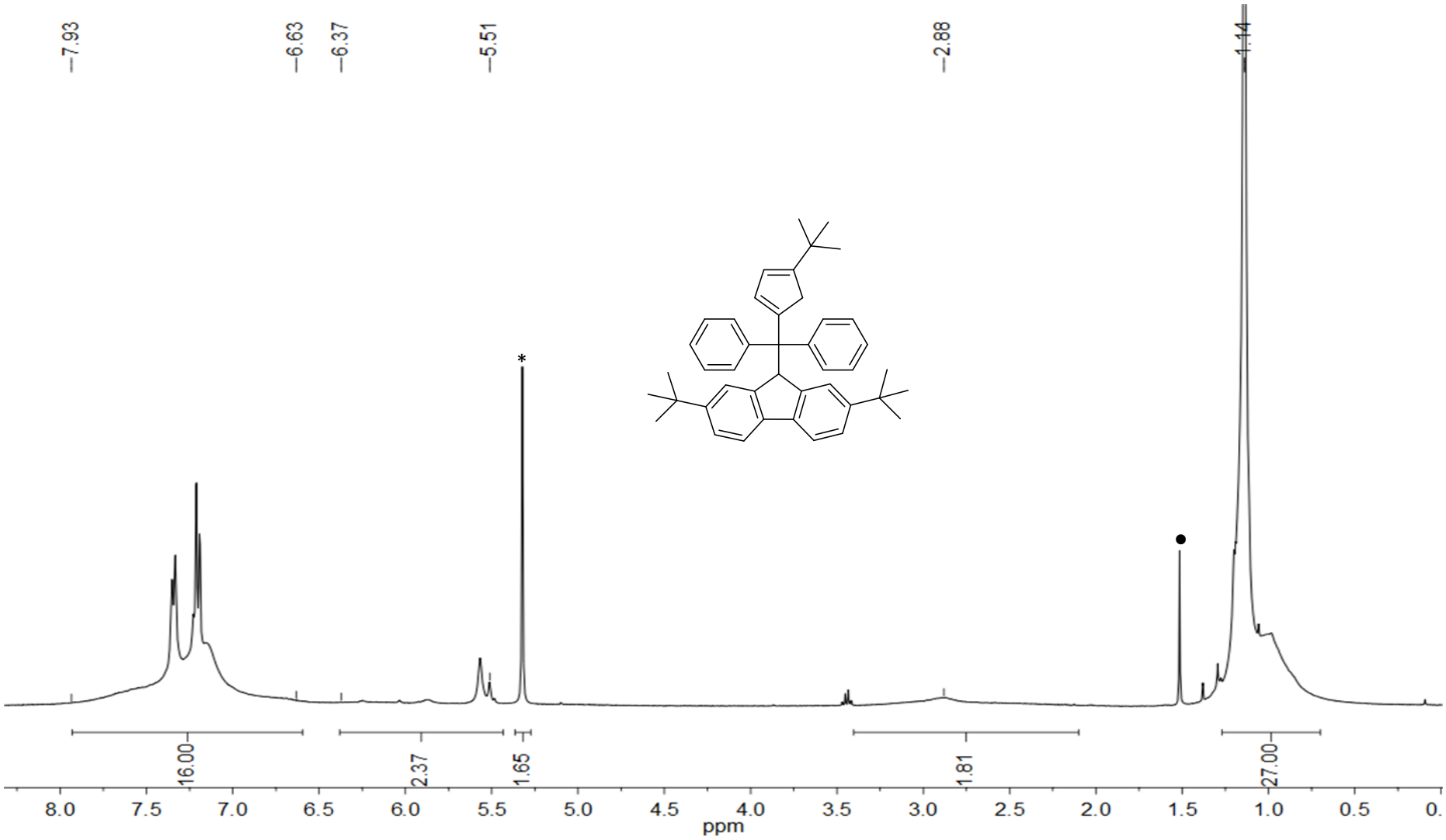

Figure S19. ^{1}H NMR spectrum (CD_2Cl_2, 400 MHz, 25 °C) of **2a**. * stands for residual NMR solvent signal, ● stands for NMR solvent residual water signal.

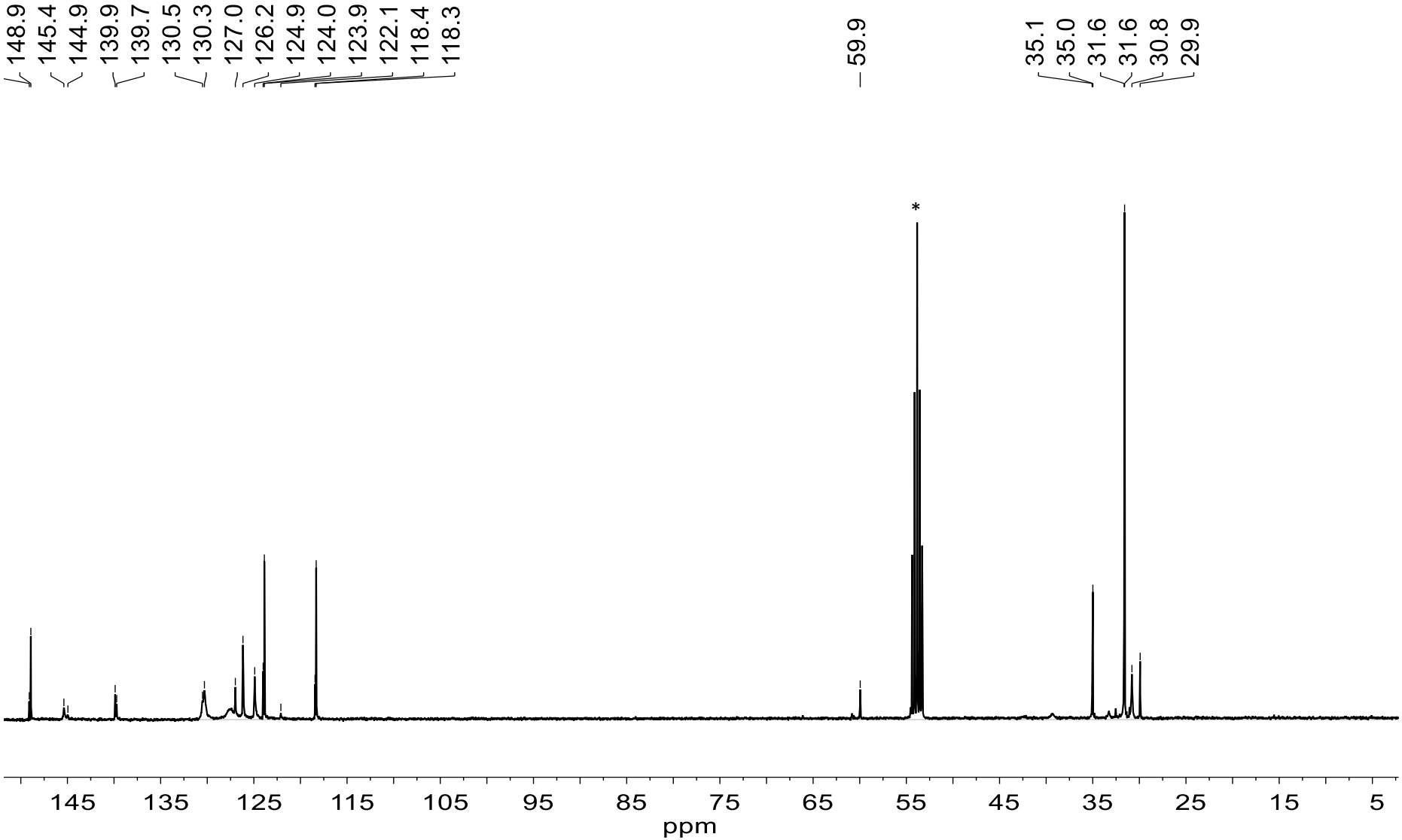

Figure S20. $^{13}C\{^{1}H\}$ NMR spectrum (CD_2Cl_2, 100 MHz, 25 °C) of **2a**. * stands for residual NMR solvent signals.

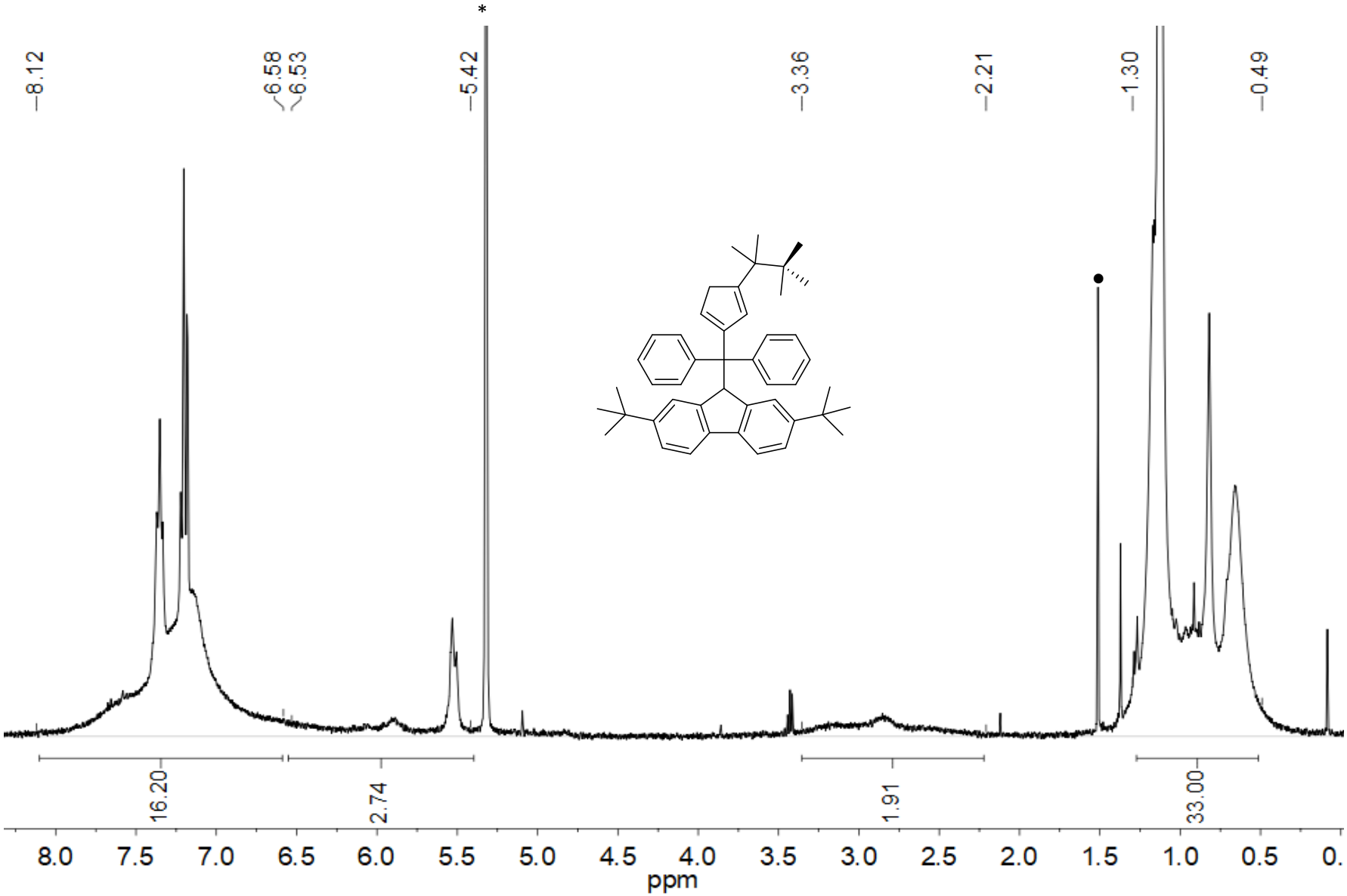

Figure S21. ^{1}H NMR spectrum (CD_2Cl_2, 400 MHz, 25 °C) of **2b.** * stands for residual NMR solvent signal. ●stands for NRM solvent residual water signal.

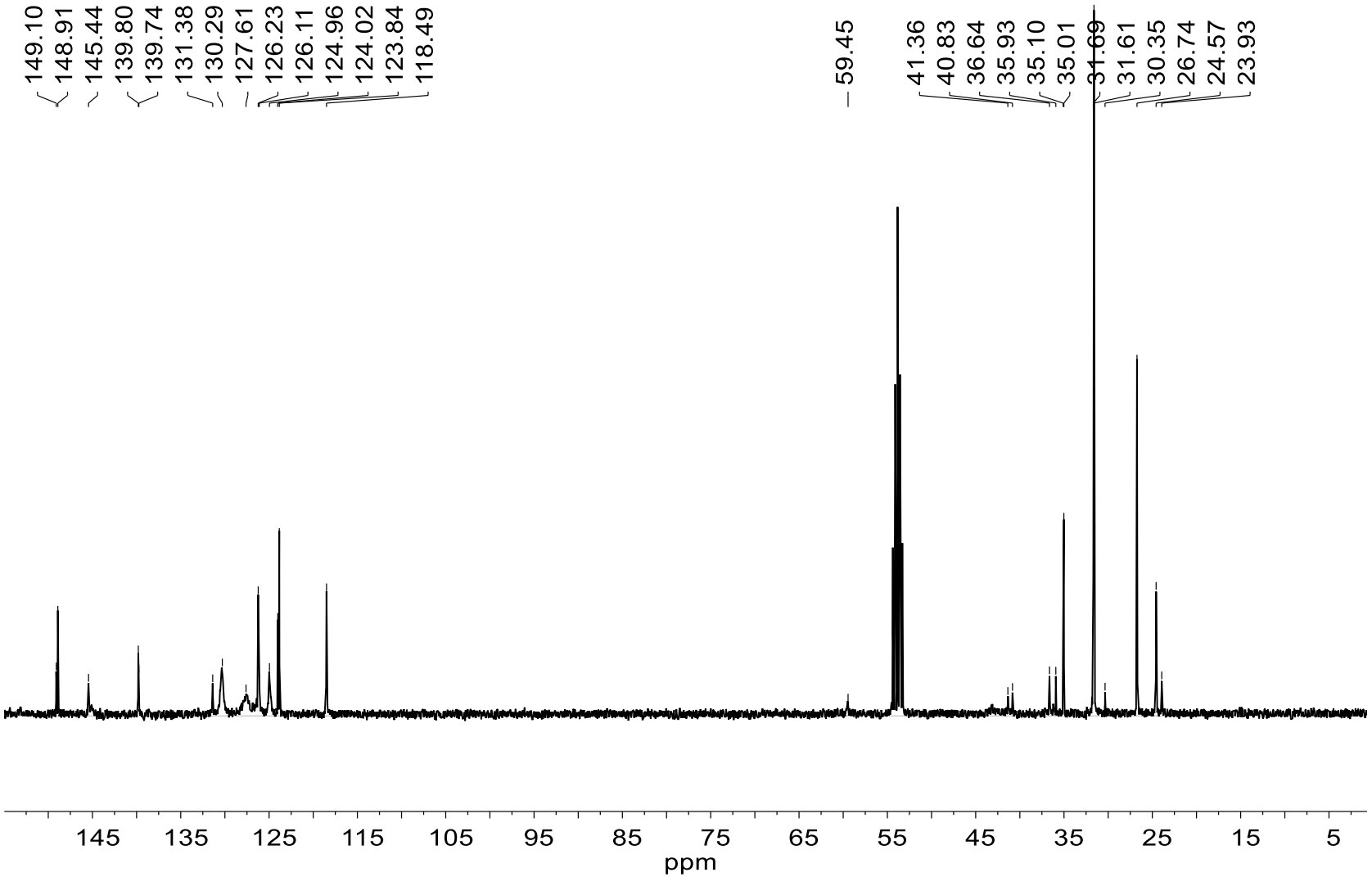

Figure S22. $^{13}C\{^{1}H\}$ NMR spectrum (CD_2Cl_2, 100 MHz, 25 °C) of **2b**. *stands for residual NMR solvent signals.

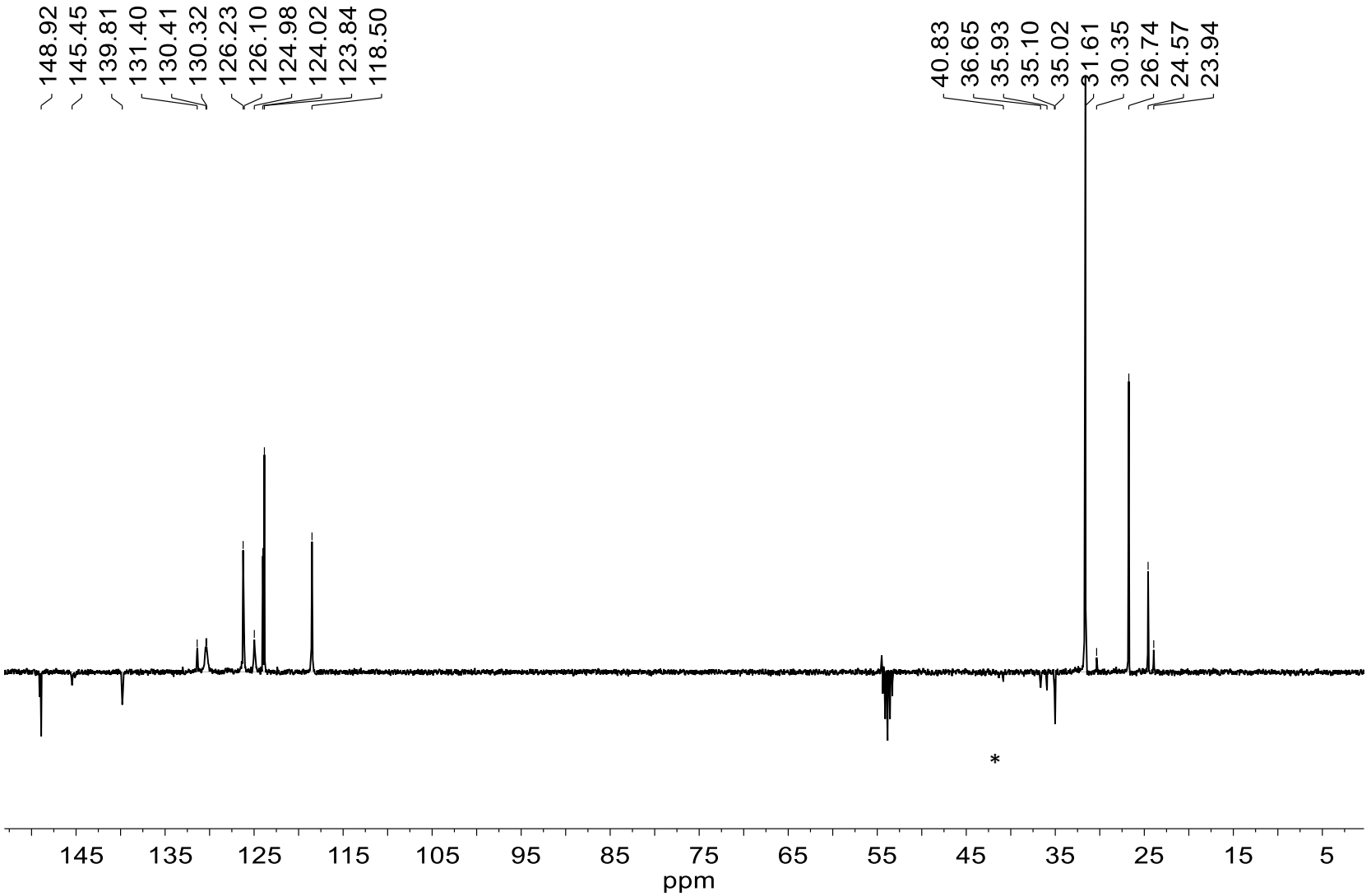

Figure S23. $^{13}C\{^{1}H\}$ NMR JMOD experiment (CD_2Cl_2, 100 MHz, 25 °C) of **2b**. * stands for residual NMR solvent signals.

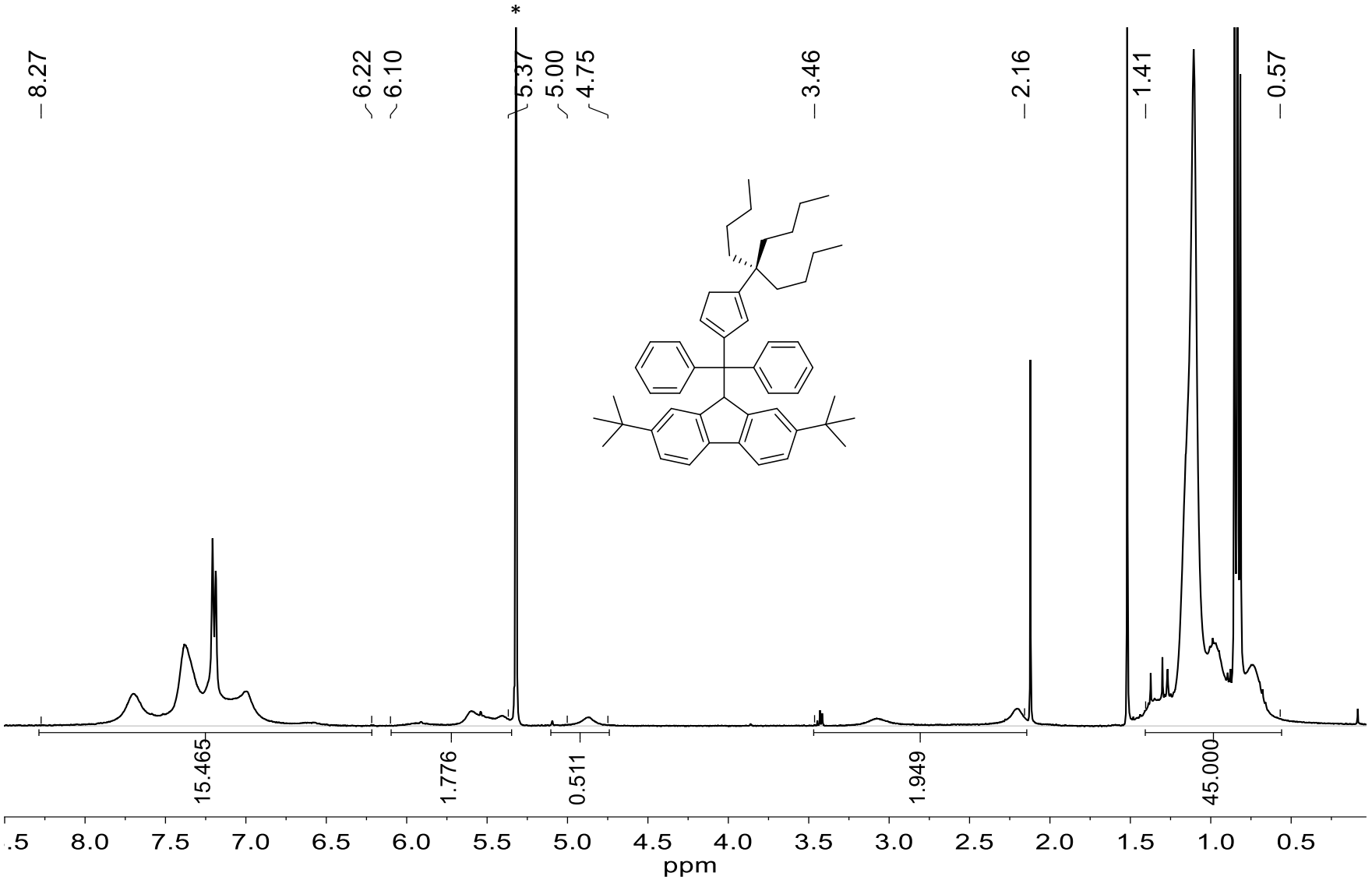

Figure S24. ^{1}H NMR spectrum (CD_2Cl_2, 400 MHz, 25 °C) of **2c**. * stands for residual NMR solvent signal**.** ● stands for NRM solvent residual water and acetone signal**.**

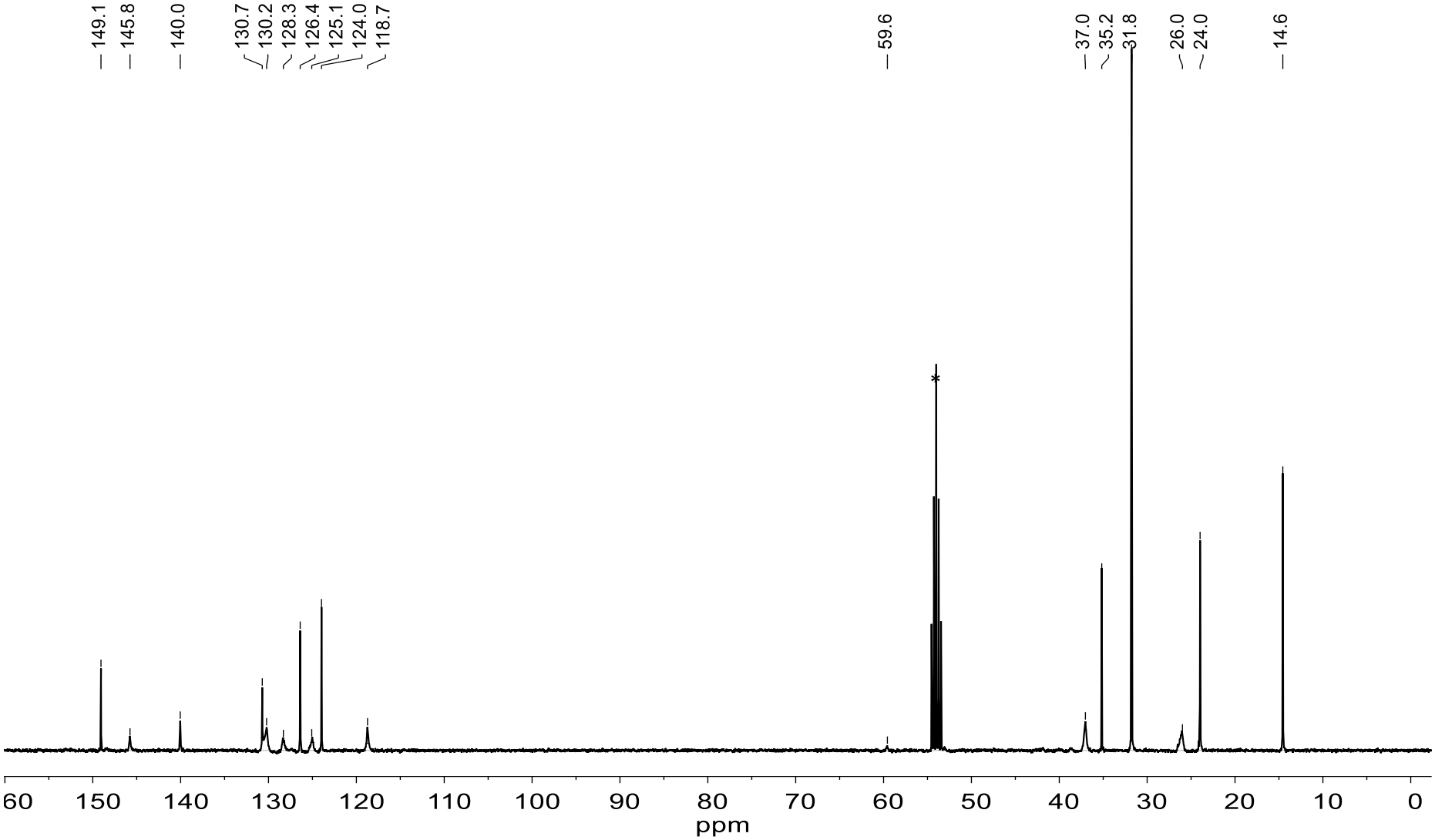

Figure S25. $^{13}C\{^{1}H\}$ NMR spectrum (CD_2Cl_2, 100 MHz, 25 °C) of **2c**. * stands for residual NMR solvent signals.

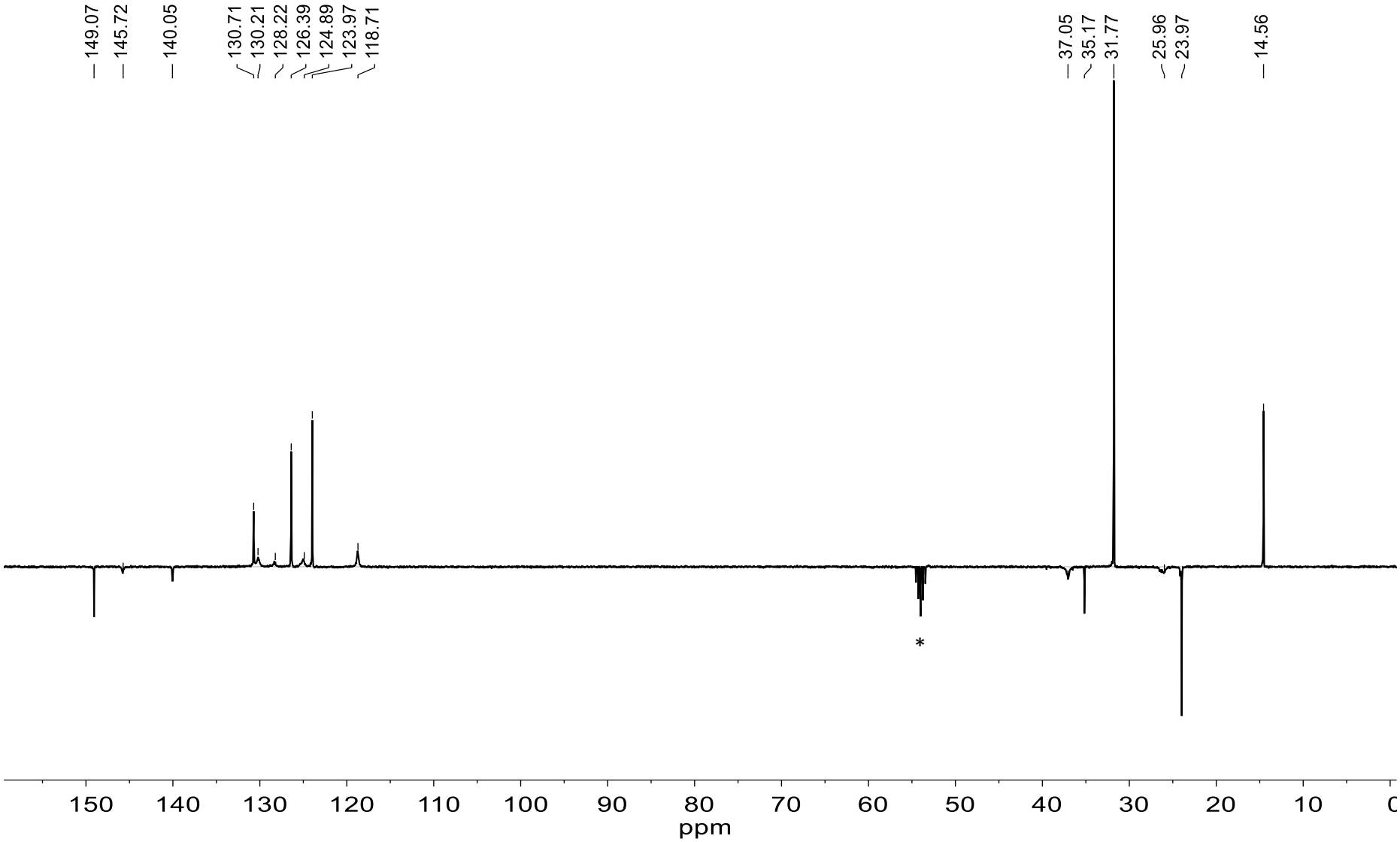

Figure S26. $^{13}C\{^{1}H\}$NMR JMOD spectrum (CD_2Cl_2, 100 MHz, 25 °C) of **2c**. *stands for residual NMR solvent signals.

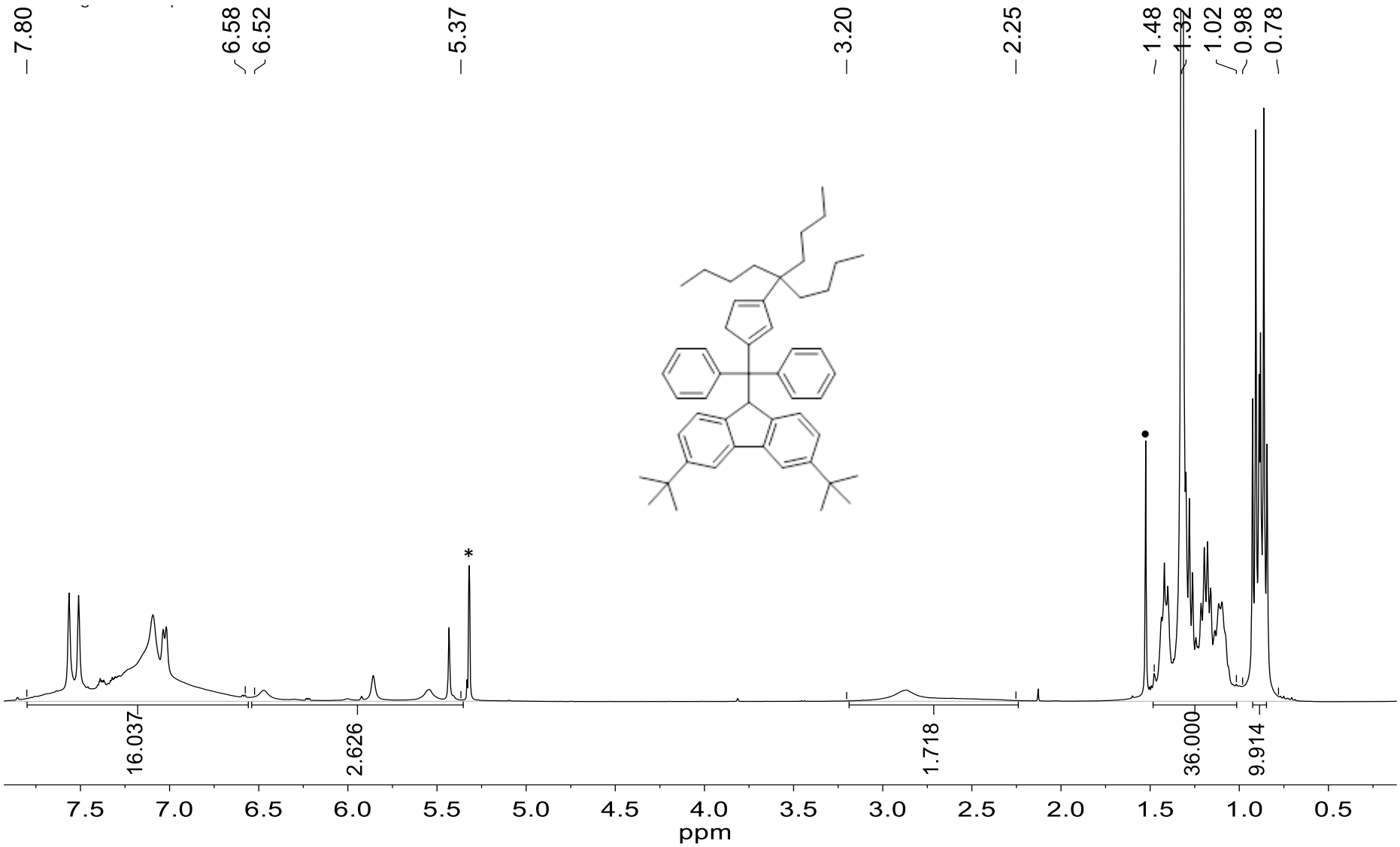

Figure S27. ^{1}H NMR spectrum (CD_2Cl_2, 400 MHz, 25 °C) of **2d**. * stands for residual NMR solvent signal. ● stands for NMR solvent residual water signal.

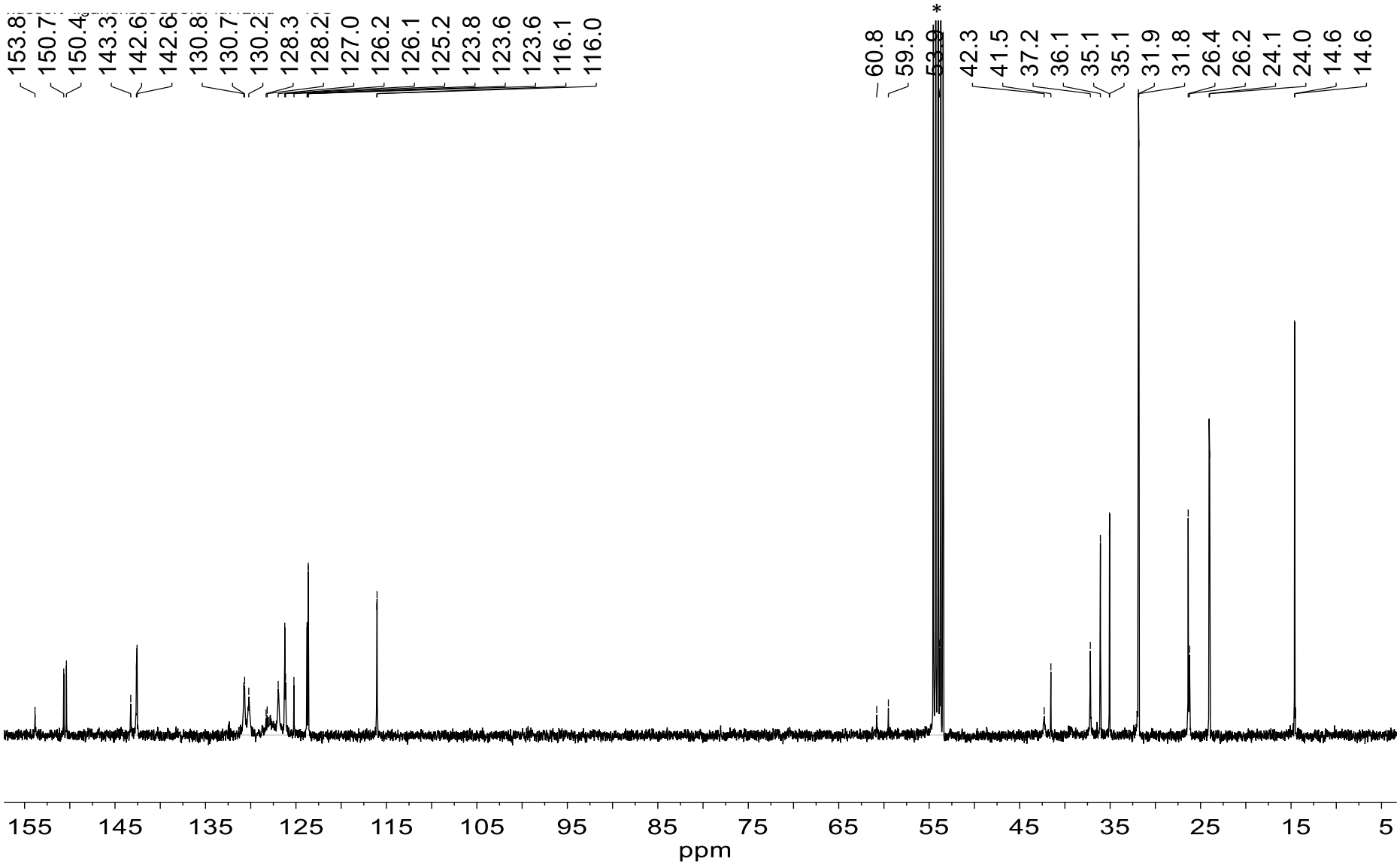

Figure S28. $^{13}C\{^{1}H\}$ NMR spectrum (CD_2Cl_2, 100 MHz, 25 °C) of **2d**. * stands for residual NMR solvent signals.

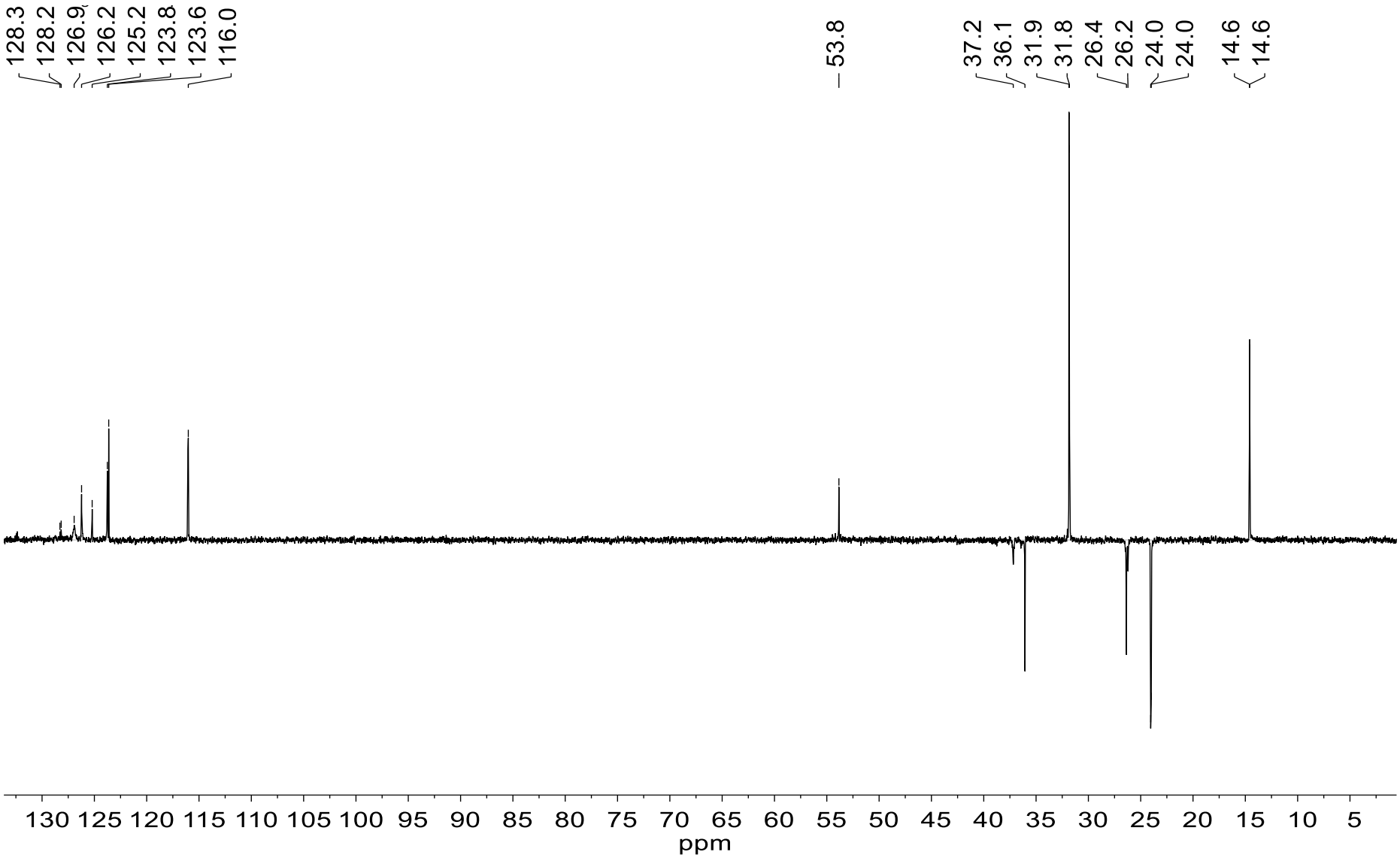

Figure S29. ^{13}C DEPT135 experiment (CD_2Cl_2, 100 MHz, 25 °C) of **2d.**

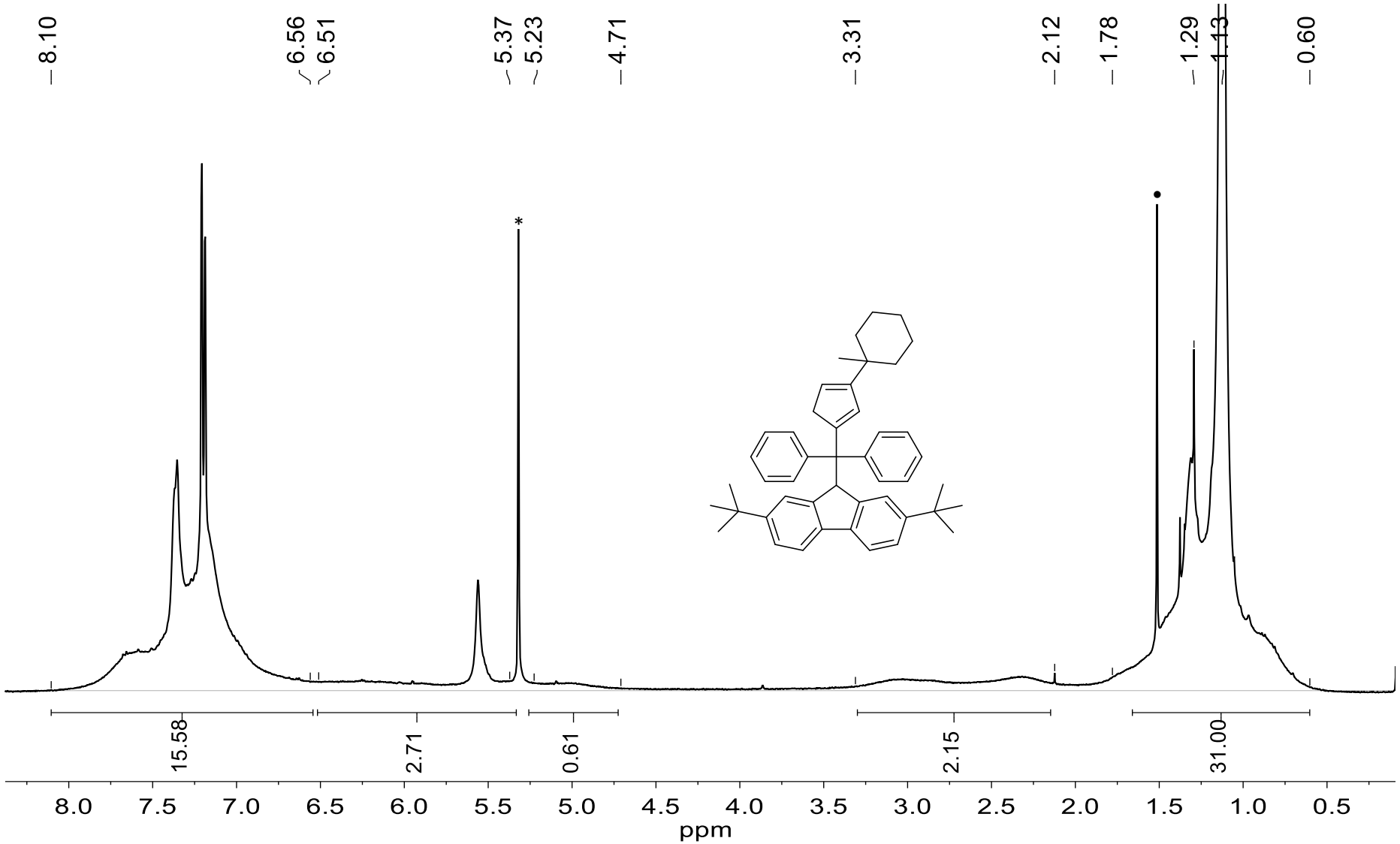

Figure S30. ^{1}H NMR spectrum (CD_2Cl_2, 400 MHz, 25 °C) of **2e**. * stands for residual NMR solvent signal. ● stands for NMR solvent residual water signal.

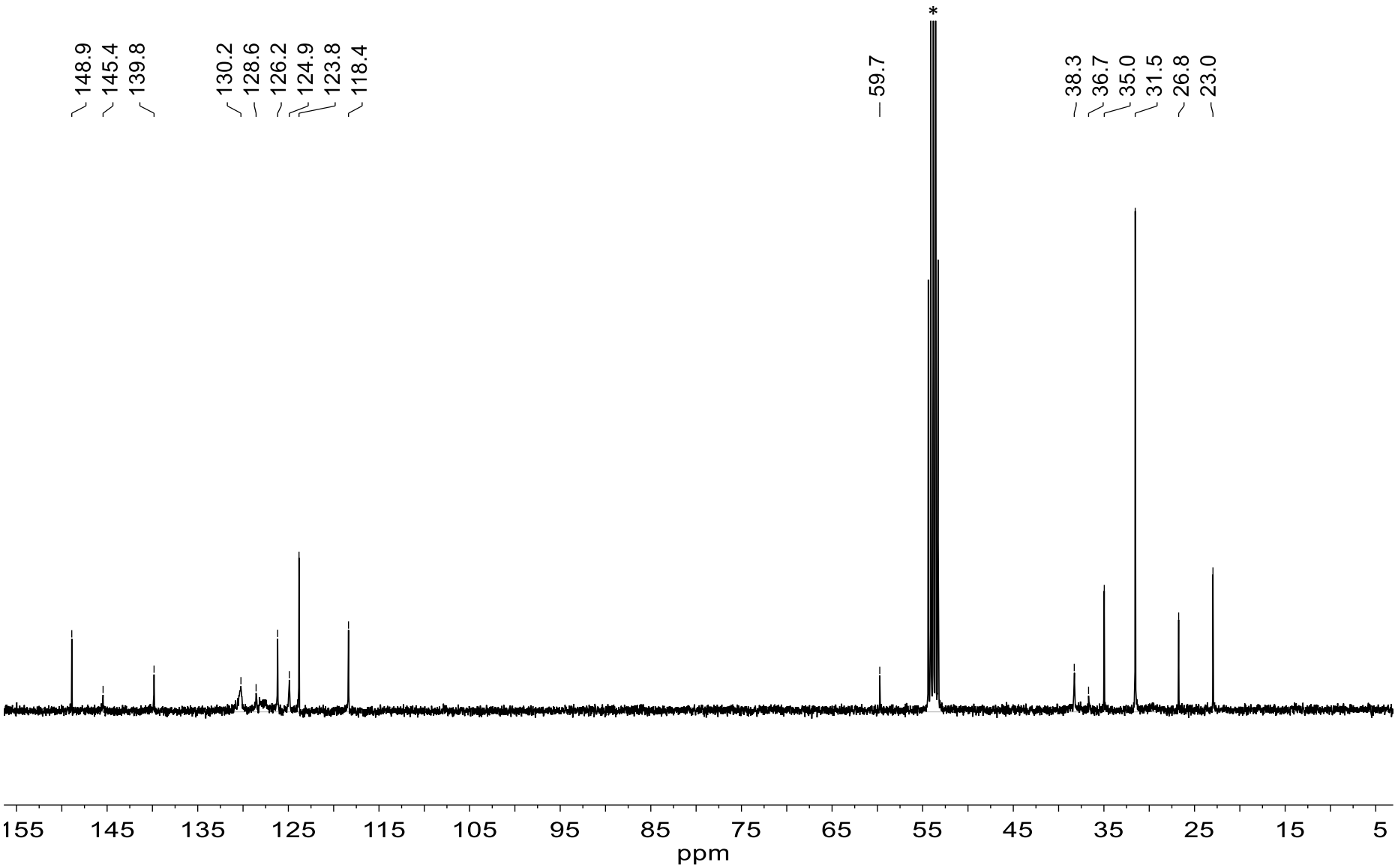

Figure S31. $^{13}C\{^{1}H\}$ NMR spectrum (CD_2Cl_2, 100 MHz, 25 °C) of **2e**. * stands for residual NMR solvent signals.

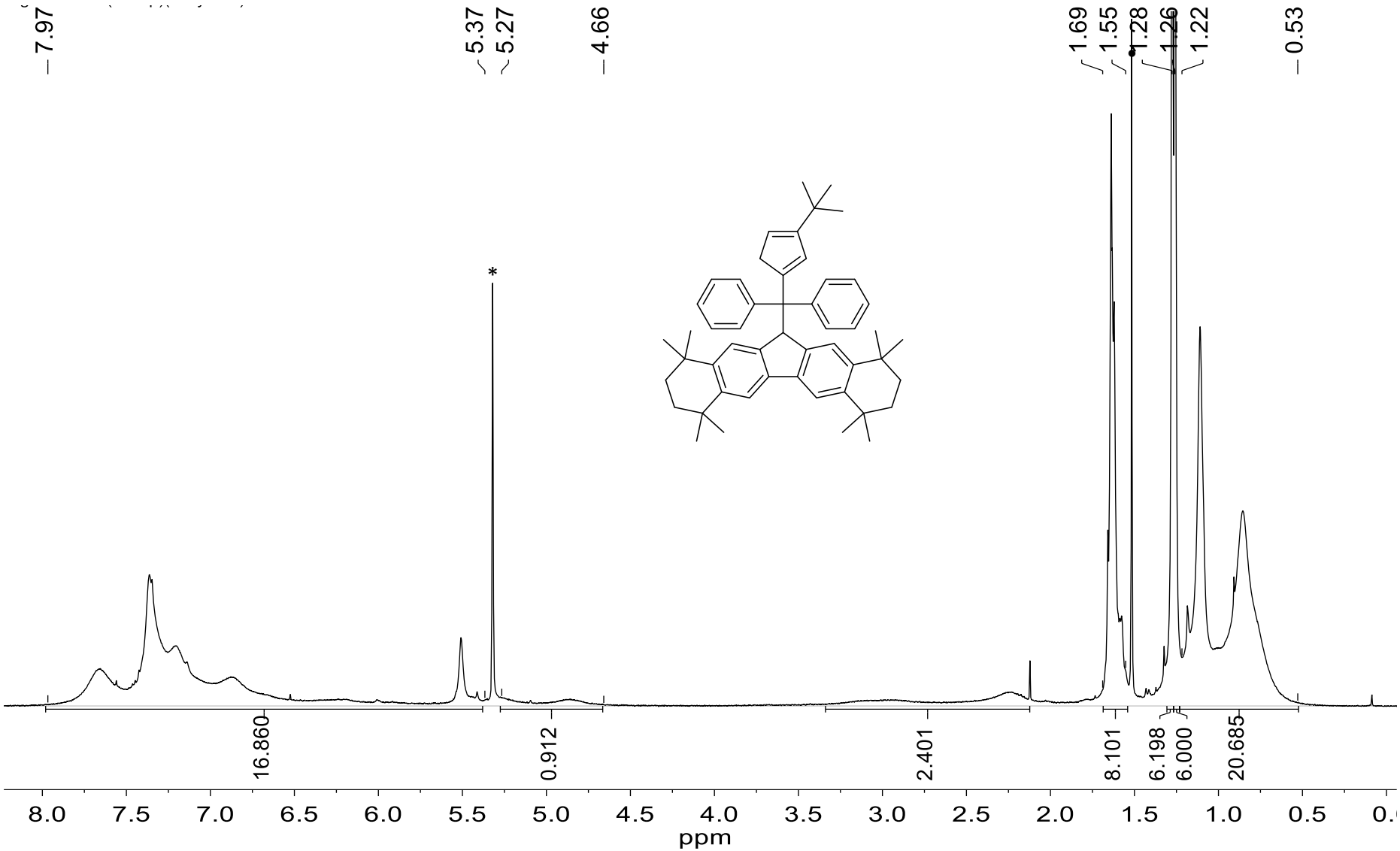

Figure S32. ^{1}H NMR spectrum (CD_2Cl_2, 400 MHz, 25 °C) of **2f**. * stands for residual NMR solvent signal. ● stands for NMR solvent residual water signal.

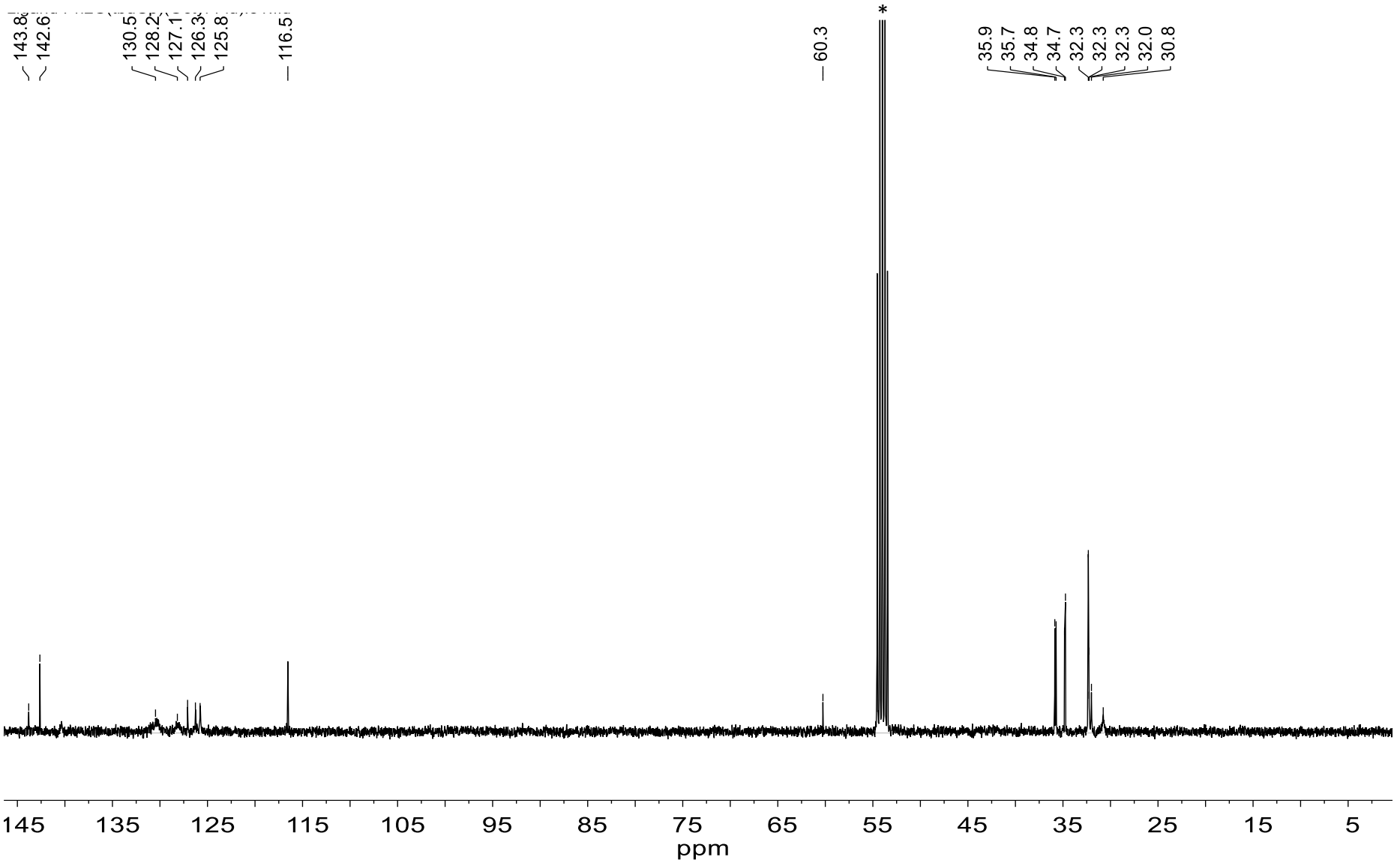

Figure S33. $^{13}C\{^{1}H\}$ NMR spectrum (CD_2Cl_2, 100 MHz, 25 °C) of **2f**. * stands for residual NMR solvent signals.

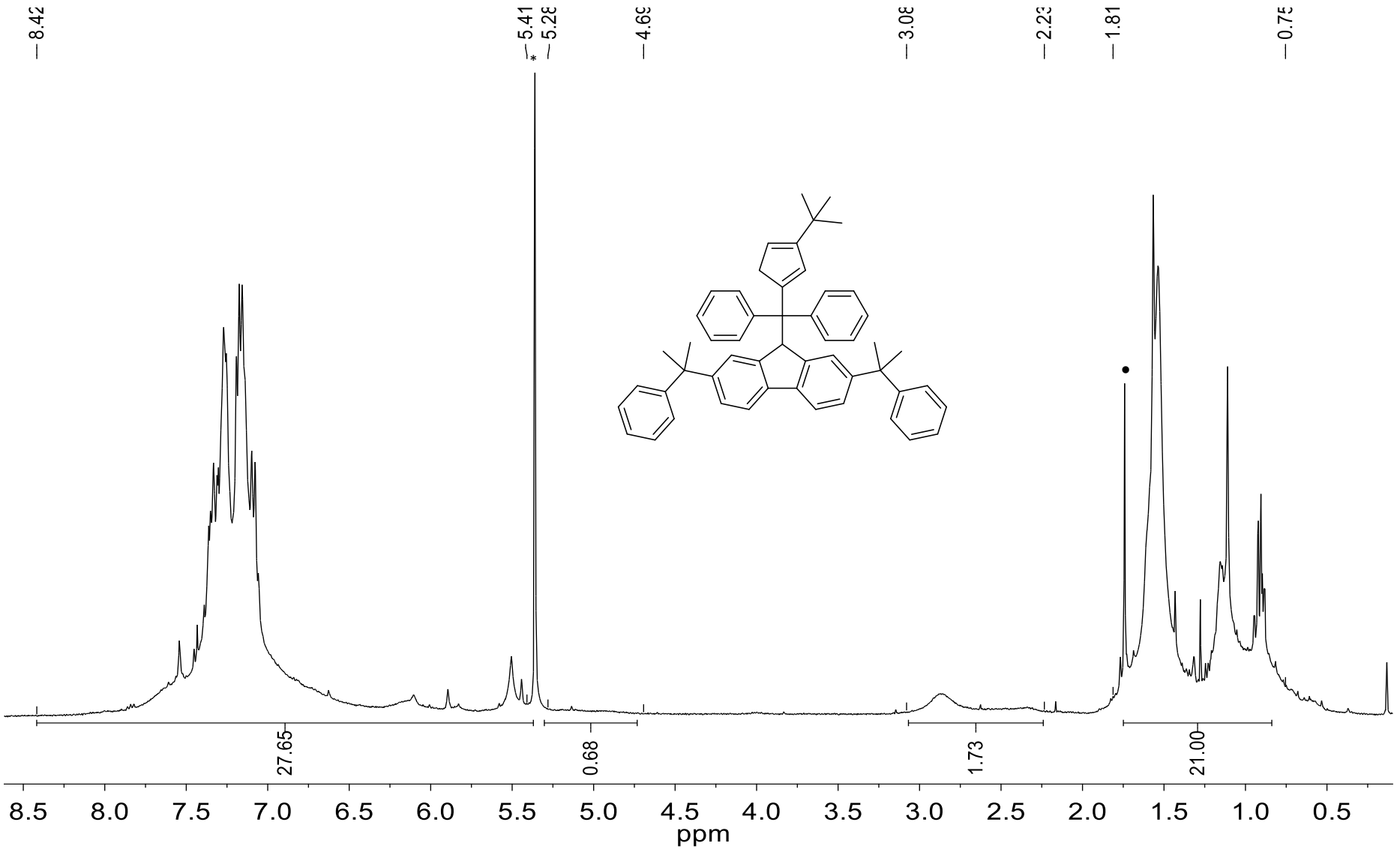

Figure S34. ^{1}H NMR spectrum (CD_2Cl_2, 400 MHz, 25 °C) of **2g**. * stands for residual NMR solvent signal. ● stands for NMR solvent residual water signal

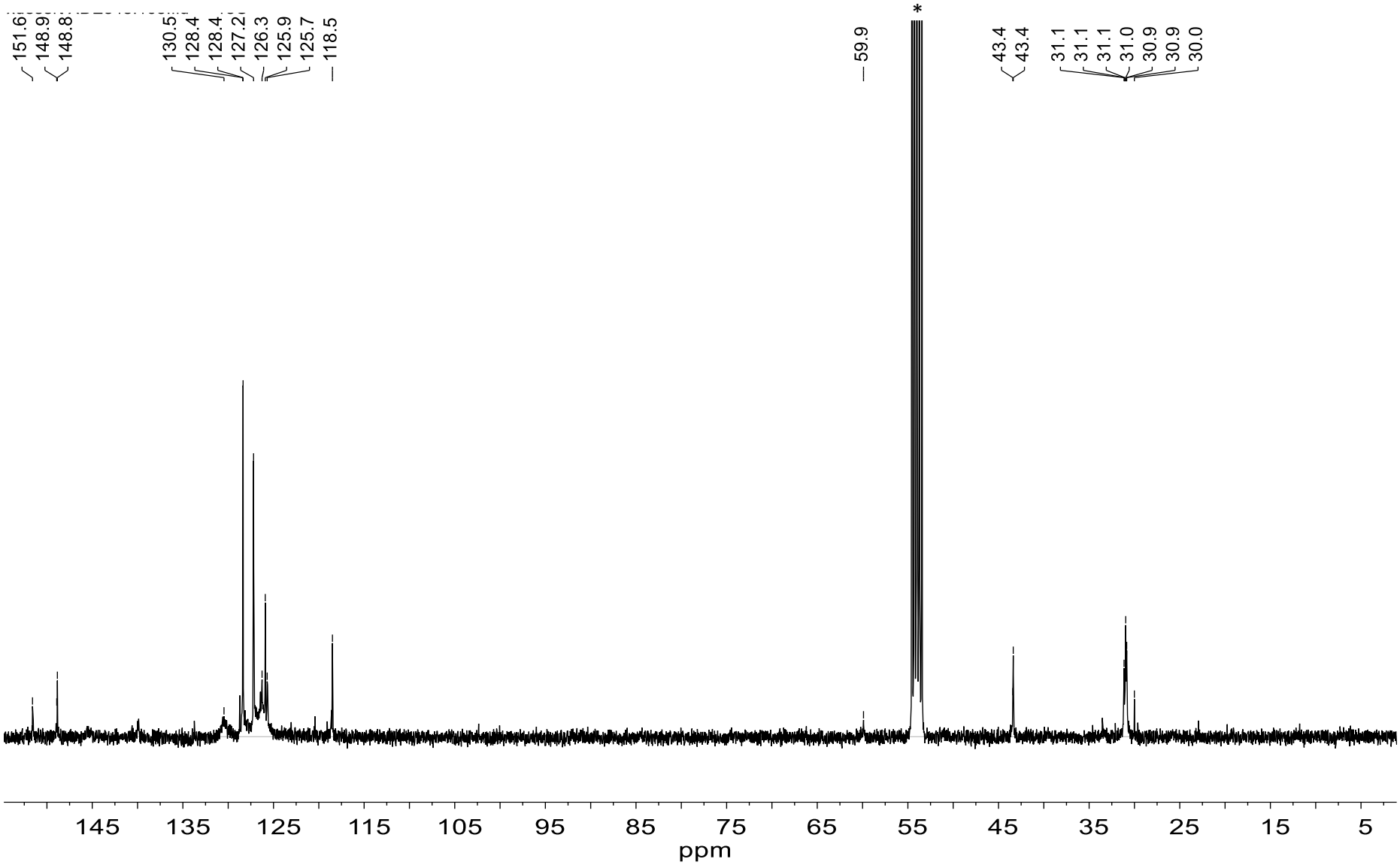

Figure S35. $^{13}C\{^{1}H\}$ NMR spectrum (CD_2Cl_2, 100 MHz, 25 °C) of **2g**. * stands for residual NMR solvent signals.

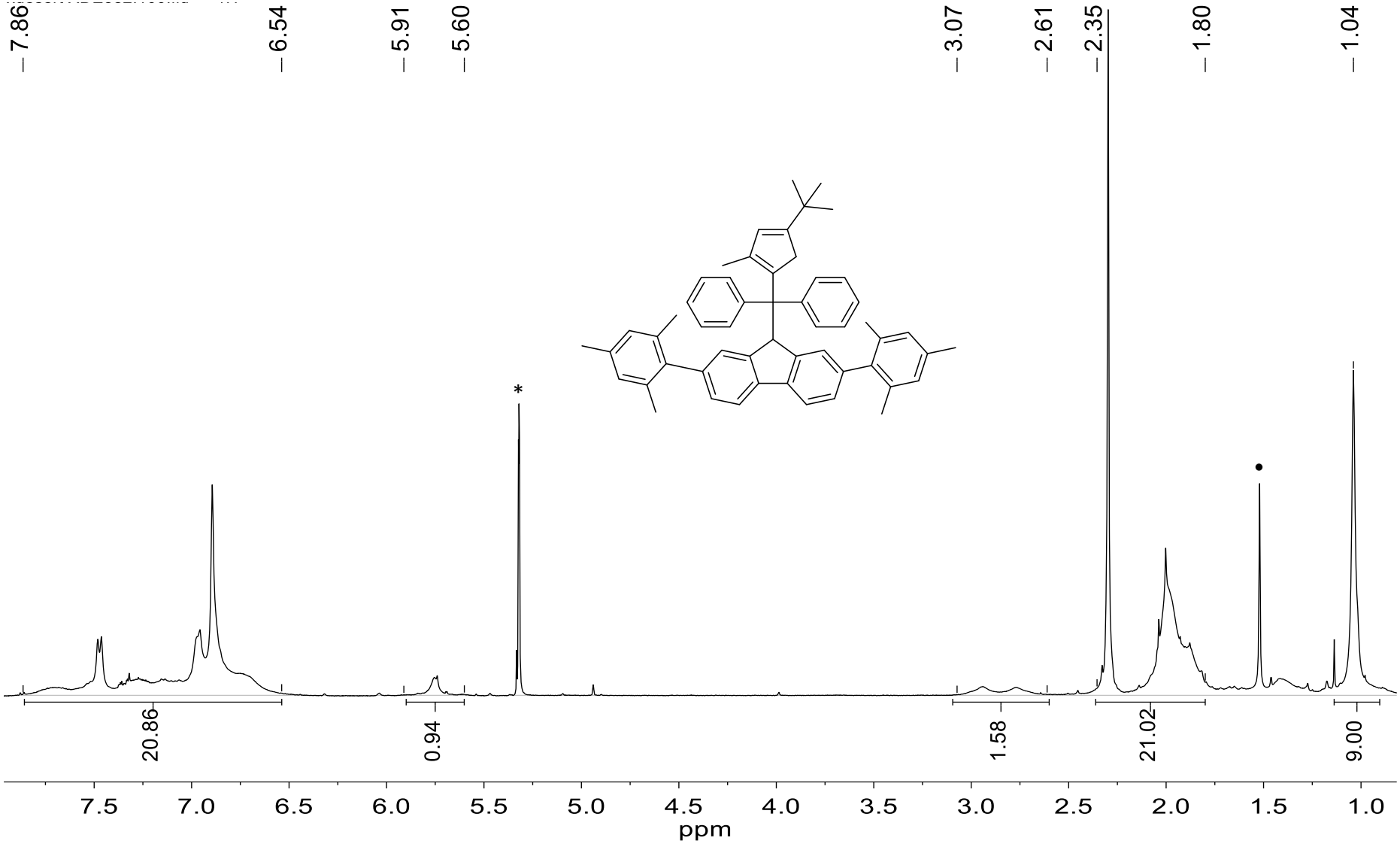

Figure S36. ^{1}H NMR spectrum (CD_2Cl_2, 100 MHz, 25 °C) of **2h**. * stands for residual NMR solvent signal. ● stands for NMR solvent residual water signal.

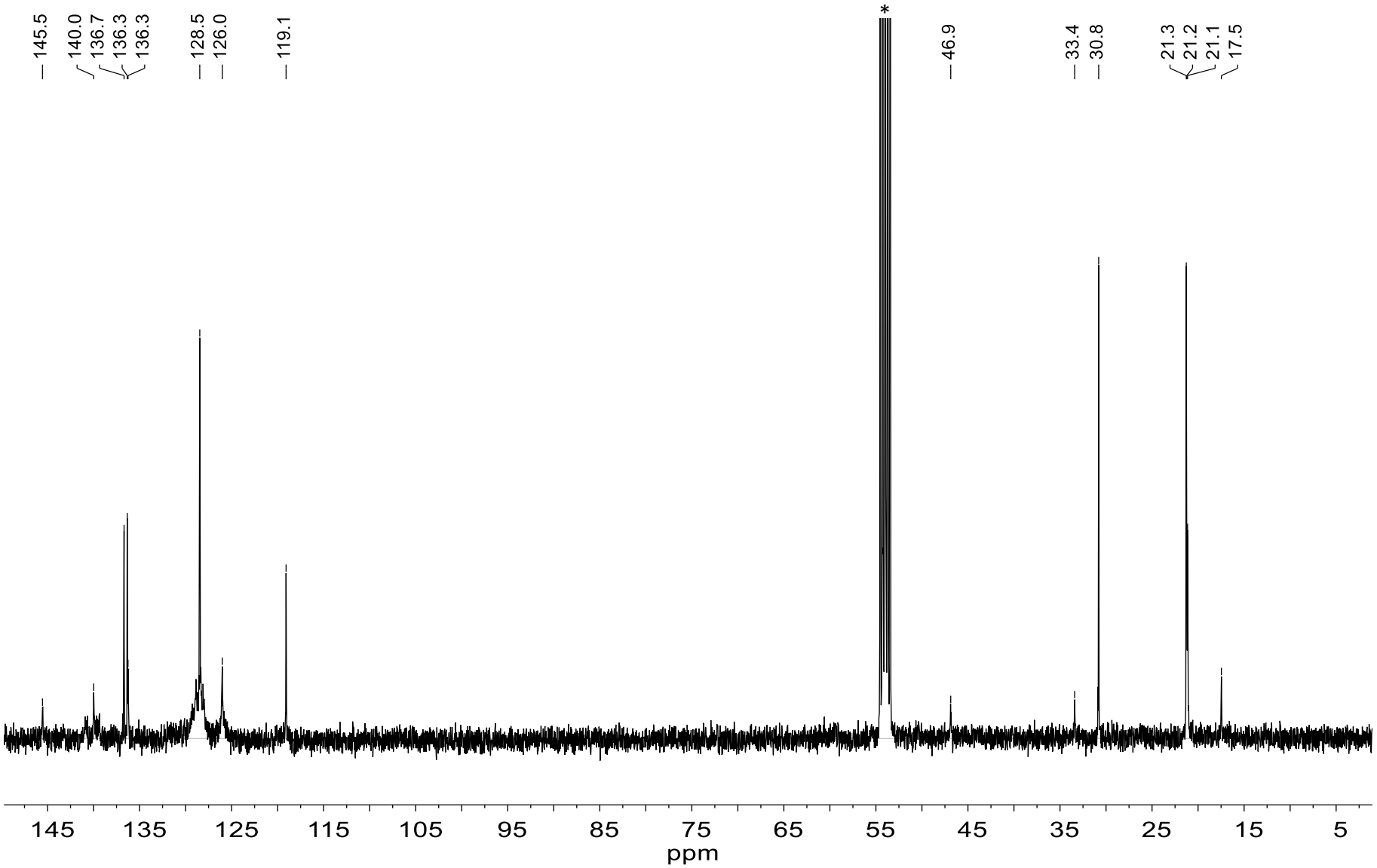

Figure S37. $^{13}C\{^{1}H\}$ NMR spectrum (CD_2Cl_2, 100 MHz, 25 °C) of **2h**. * stands for residual NMR solvent signals.

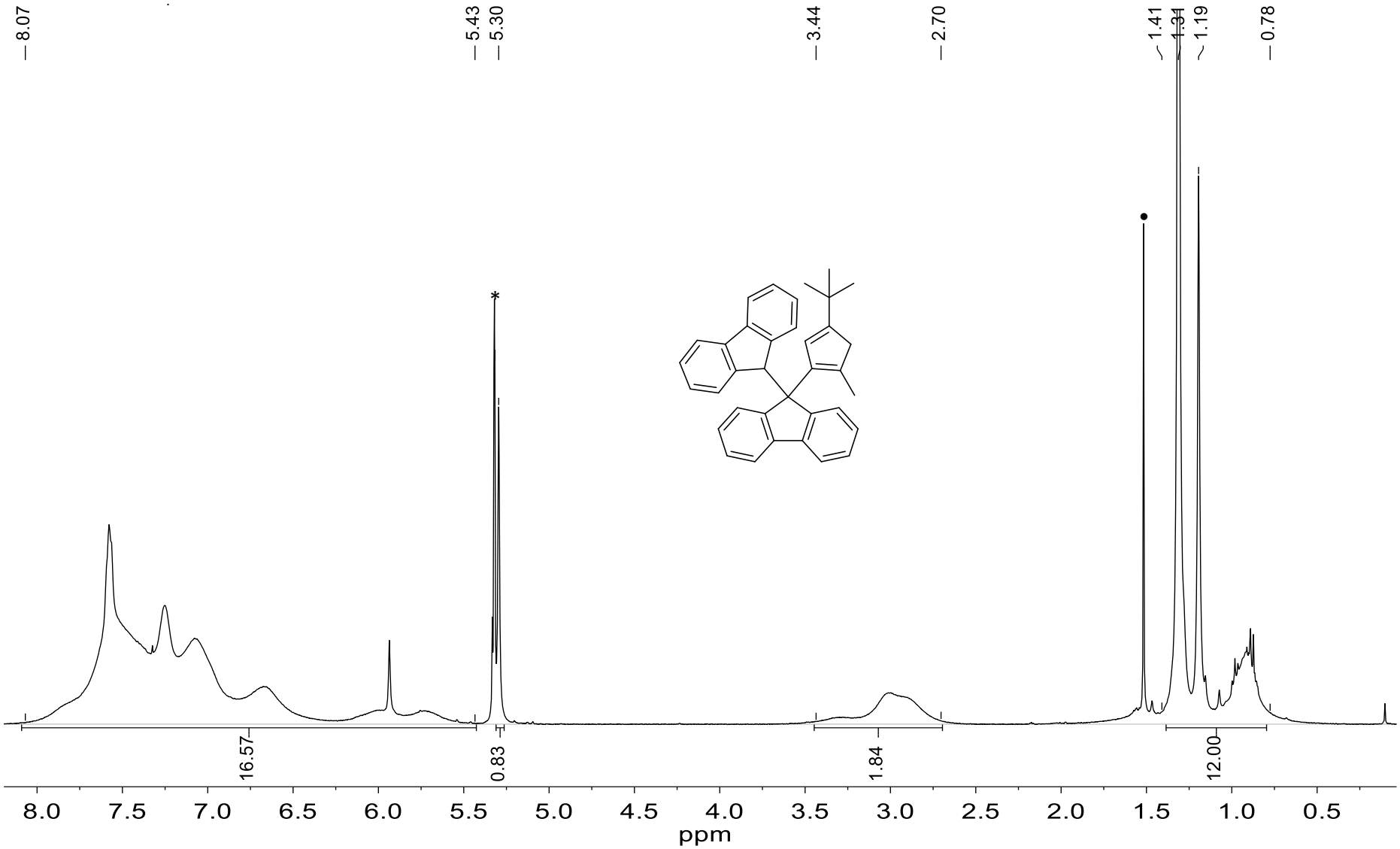

Figure S38. ^{1}H NMR spectrum (CD_2Cl_2, 400 MHz, 25 °C) of **2i**. * stands for residual NMR solvent signal. ● stands NMR solvent for residual water.

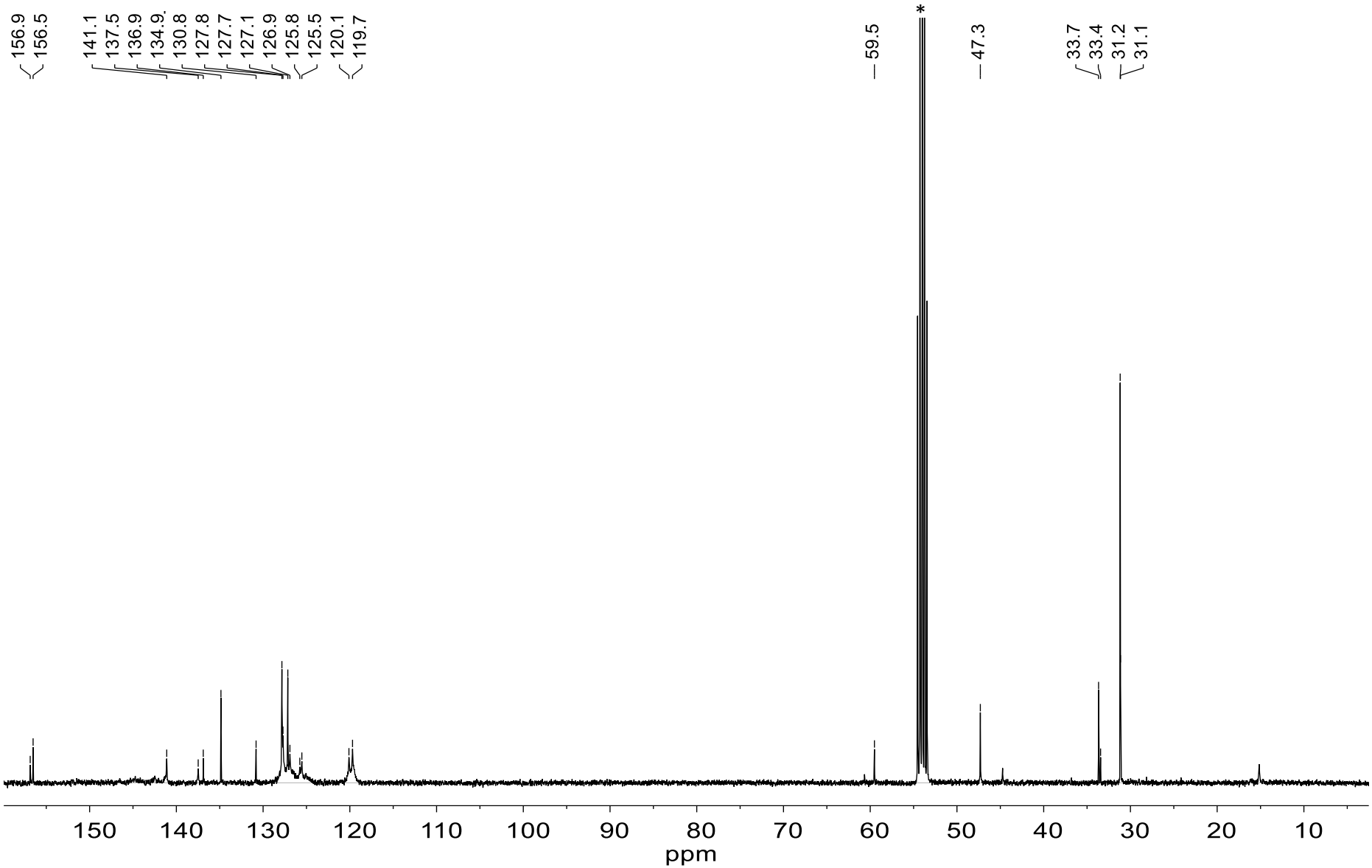

Figure S39. $^{13}C\{^{1}H\}$ NMR spectrum (CD_2Cl_2, 100 MHz, 25 °C) of **2i**. * stands for residual NMR solvent signals.

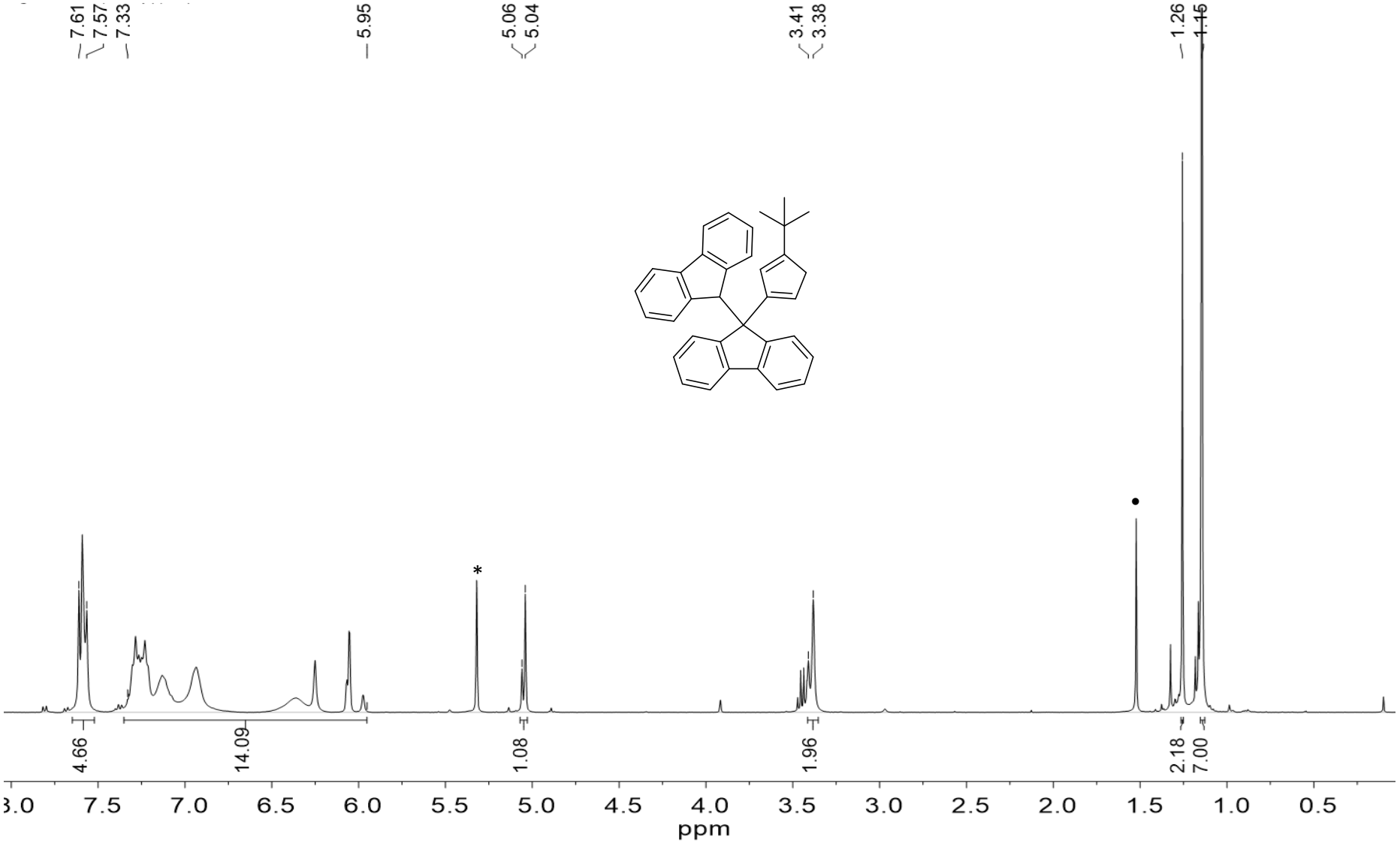

Figure S40. ^{1}H NMR spectrum (CD_2Cl_2, 400 MHz, 25 °C) of **2j**. * stands for residual NMR solvent signal. ● stands for NMR solvent residual water signal.

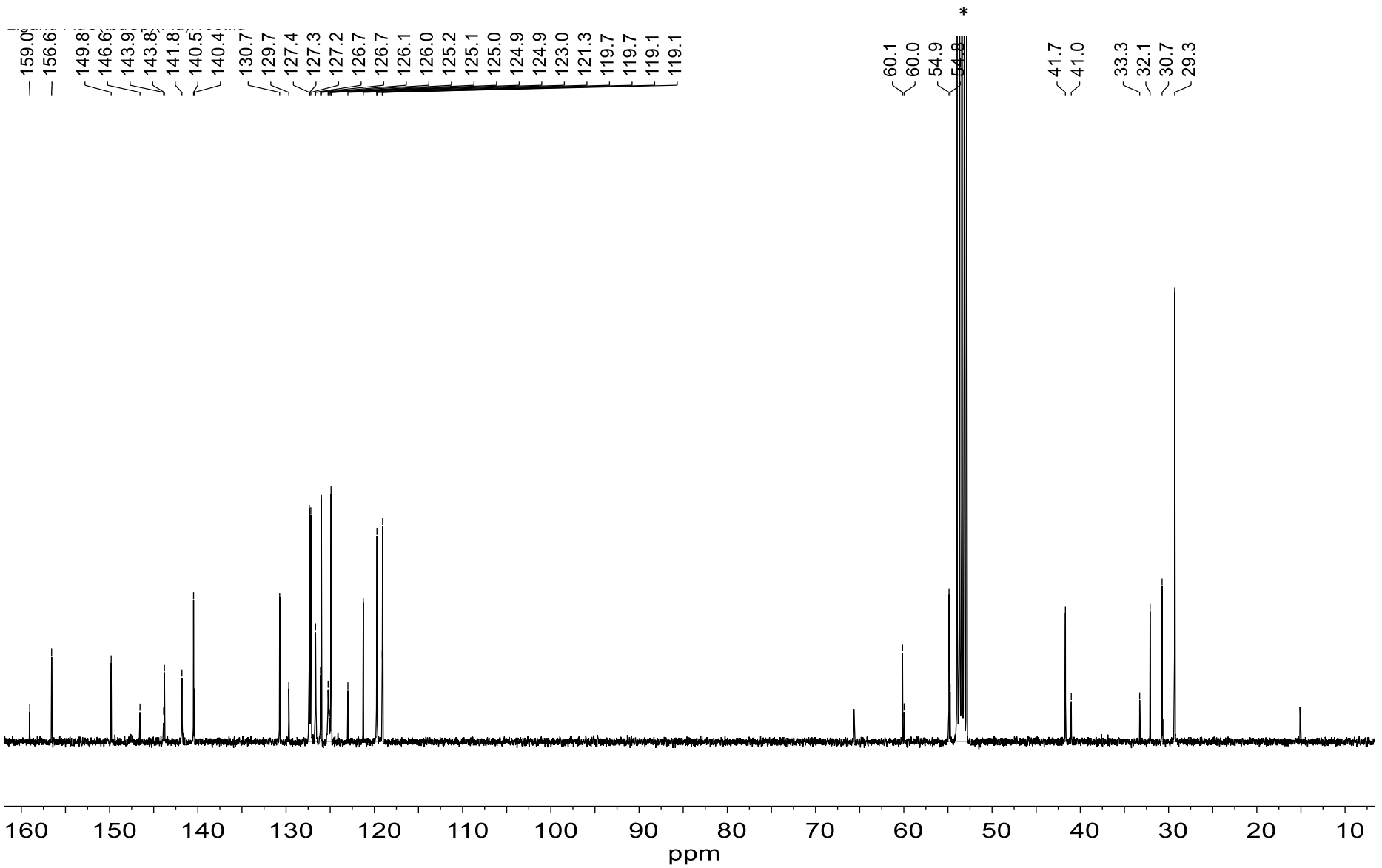

Figure S41. $^{13}C\{^{1}H\}$ NMR spectrum (CD_2Cl_2, 100 MHz, 25 °C) of **2j**. * stands for residual NMR solvent signals.

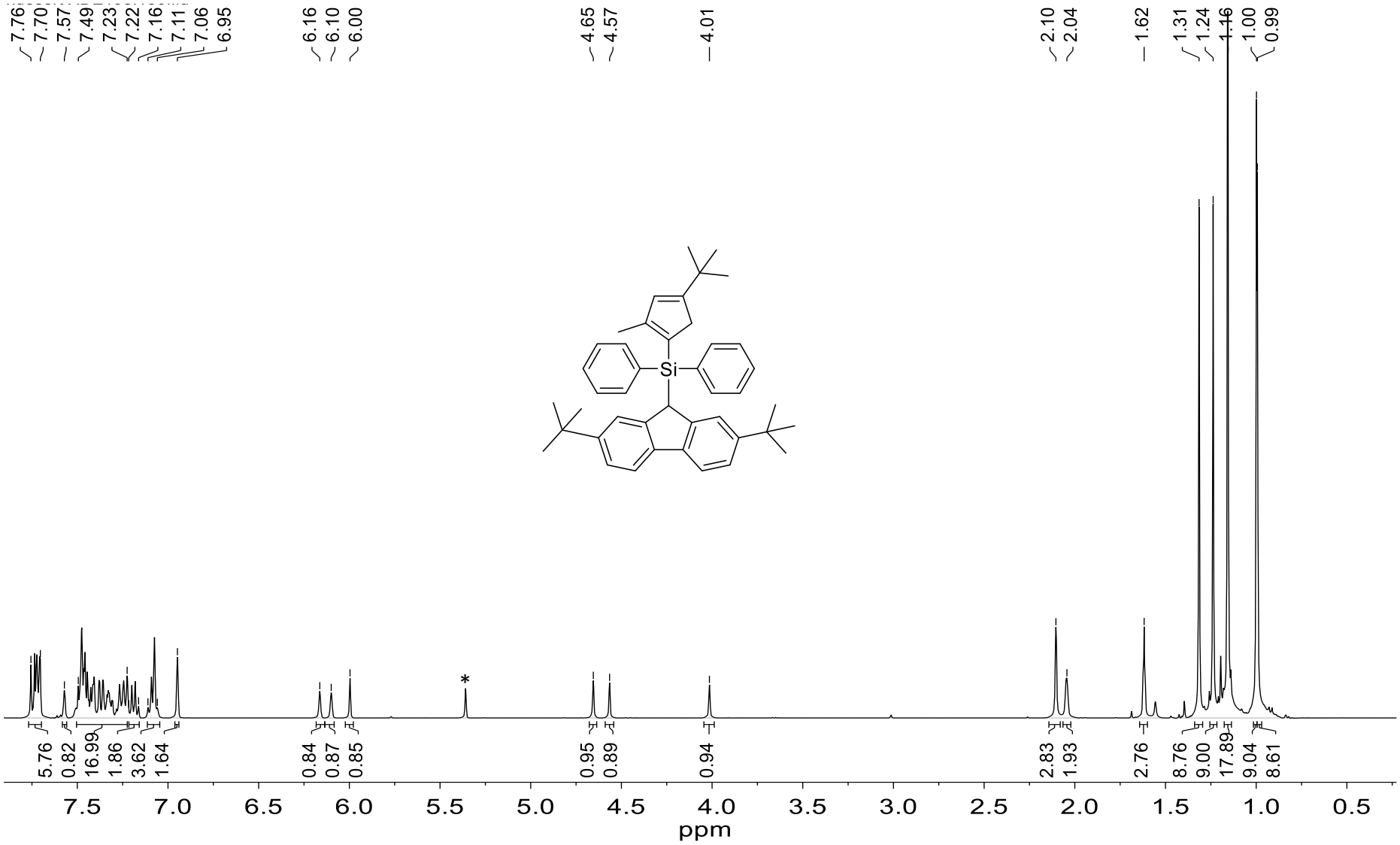

Figure S42. ^{1}H NMR spectrum (CD_2Cl_2, 400 MHz, 25 °C) of **2k**. *stands for residual NMR solvent signal.

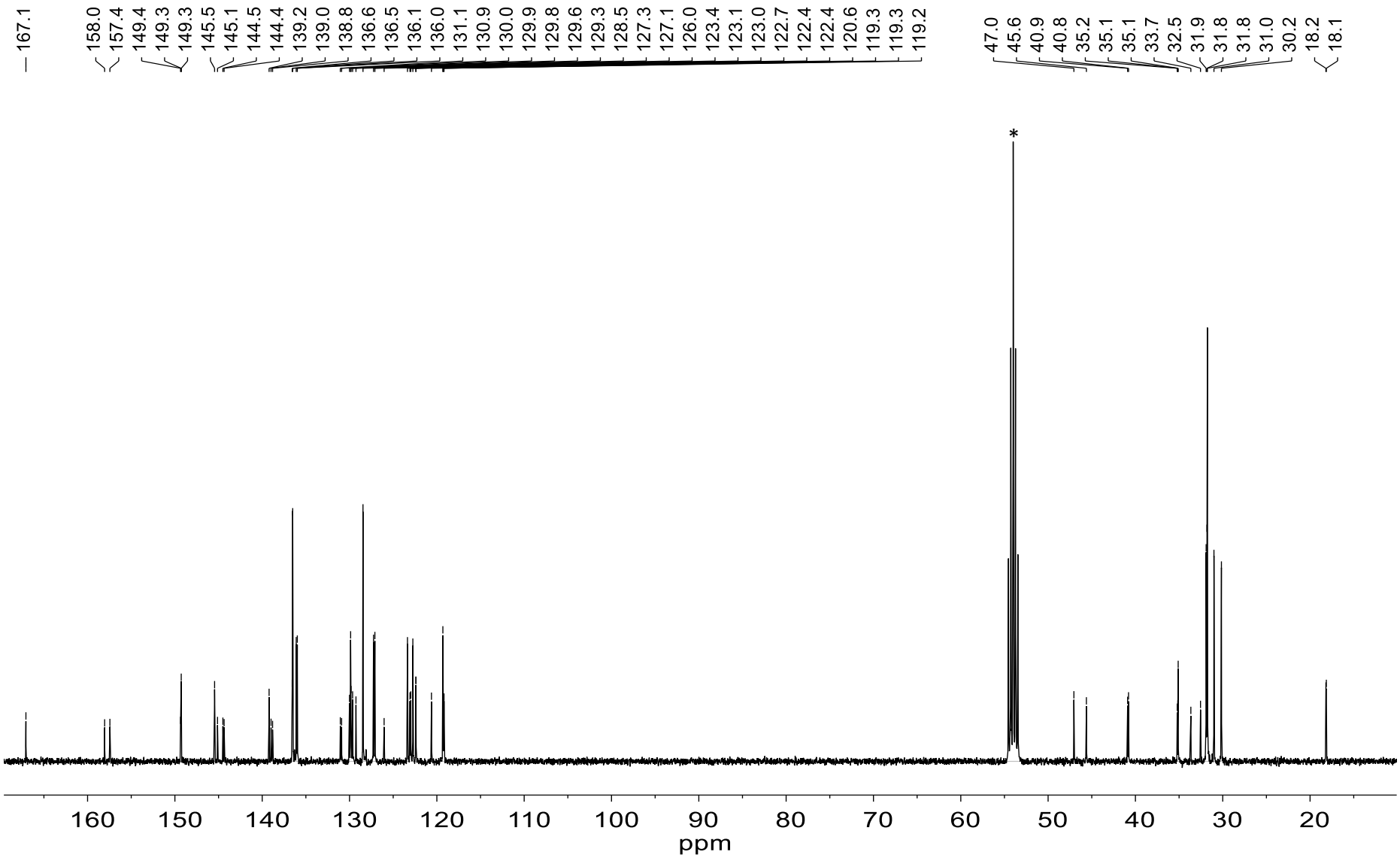

Figure S43. $^{13}C\{^{1}H\}$ NMR spectrum (CD_2Cl_2, 100 MHz, 25 °C) of **2k**. *stands for residual NMR solvent signals.

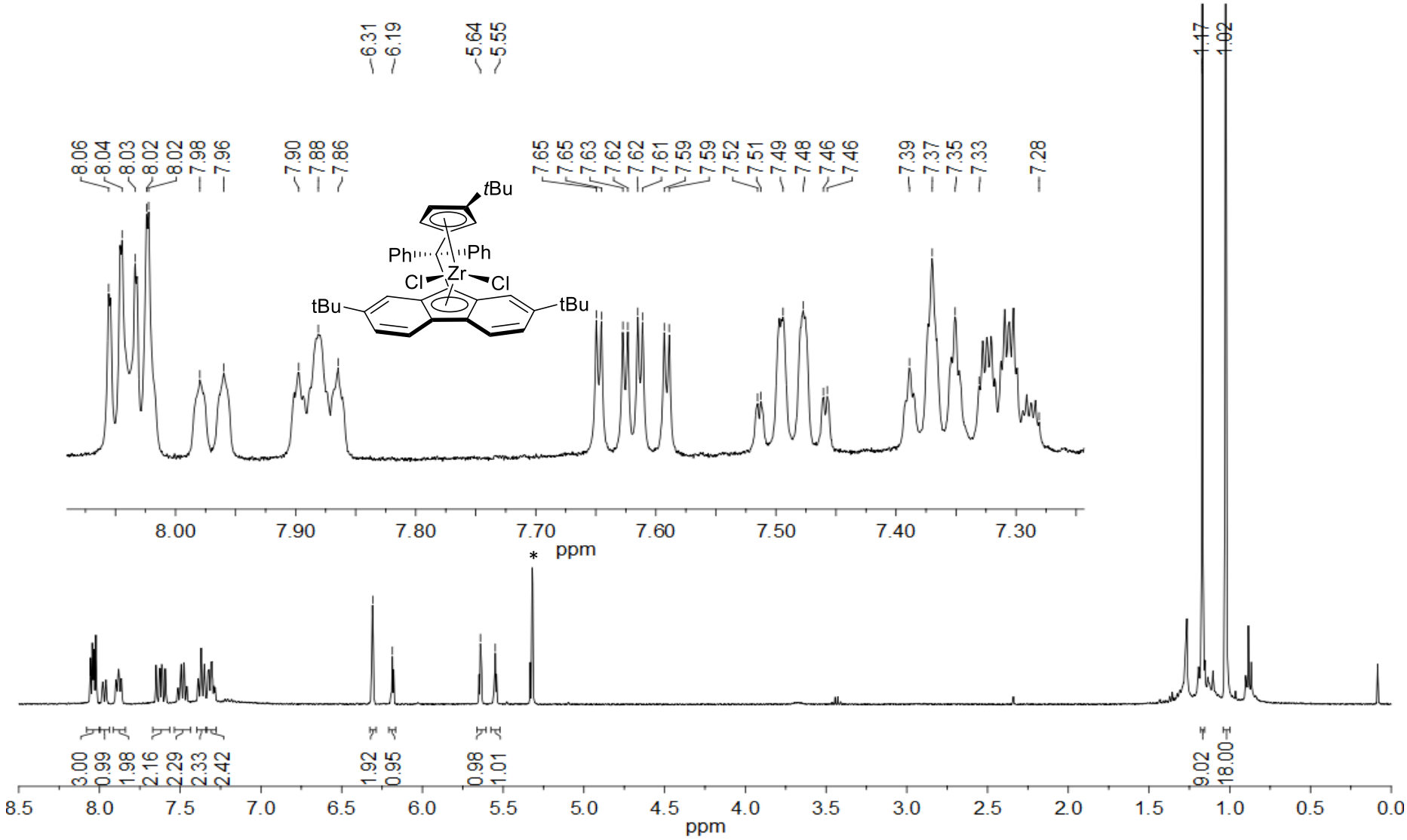

Figure S44. ^{1}H NMR spectrum (CD_2Cl_2, 400 MHz, 25 °C) of **3a**. * stands for residual NMR solvent signal.

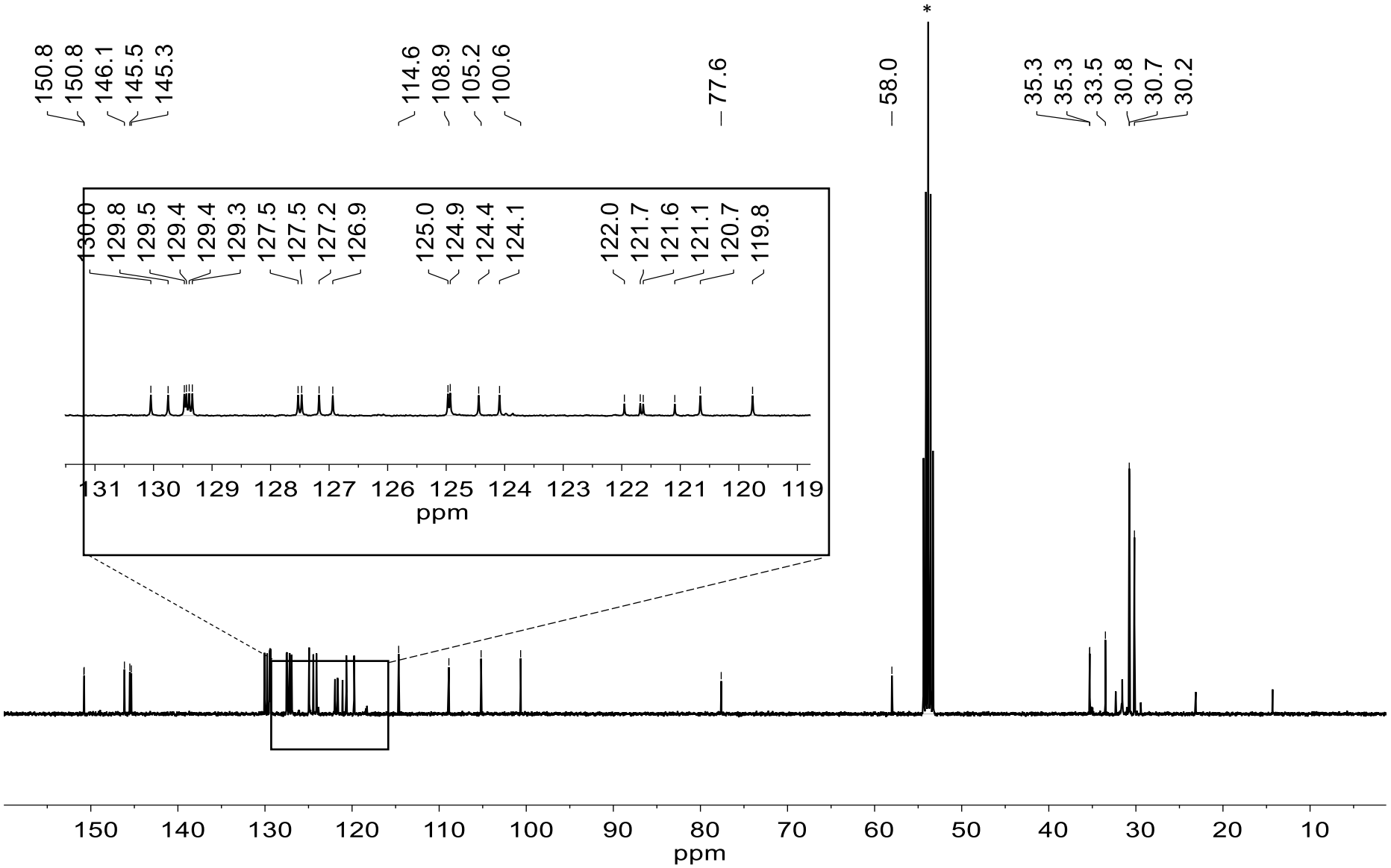

Figure S45. $^{13}C\{^{1}H\}$ NMR spectrum (CD_2Cl_2, 100 MHz, 25 °C) of **3a**. * stands for residual NMR solvent signals.

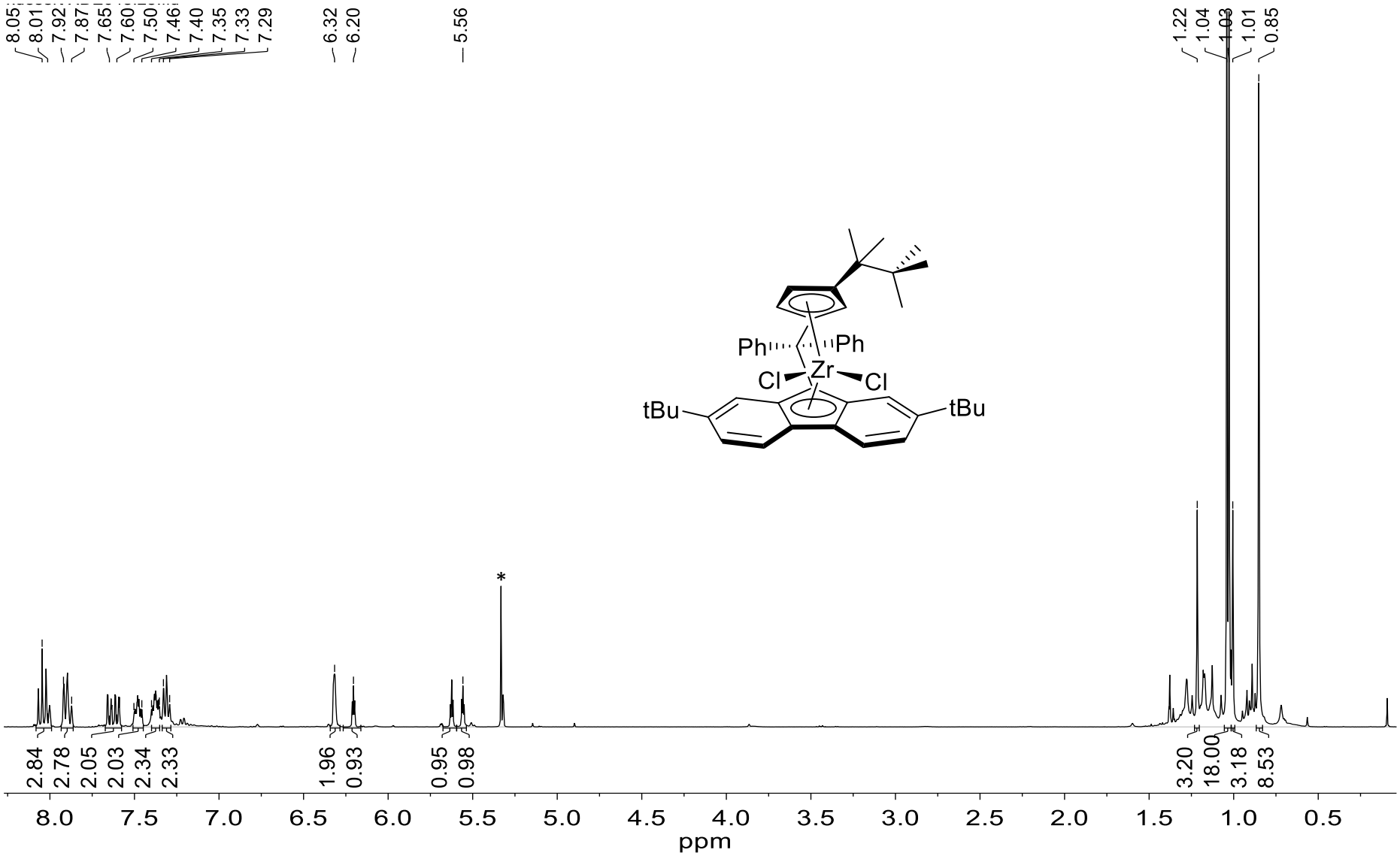

Figure S46. ^{1}H NMR spectrum (CD_2Cl_2, 400 MHz, 25 °C) of **3b**. * stands for residual NMR solvent signal

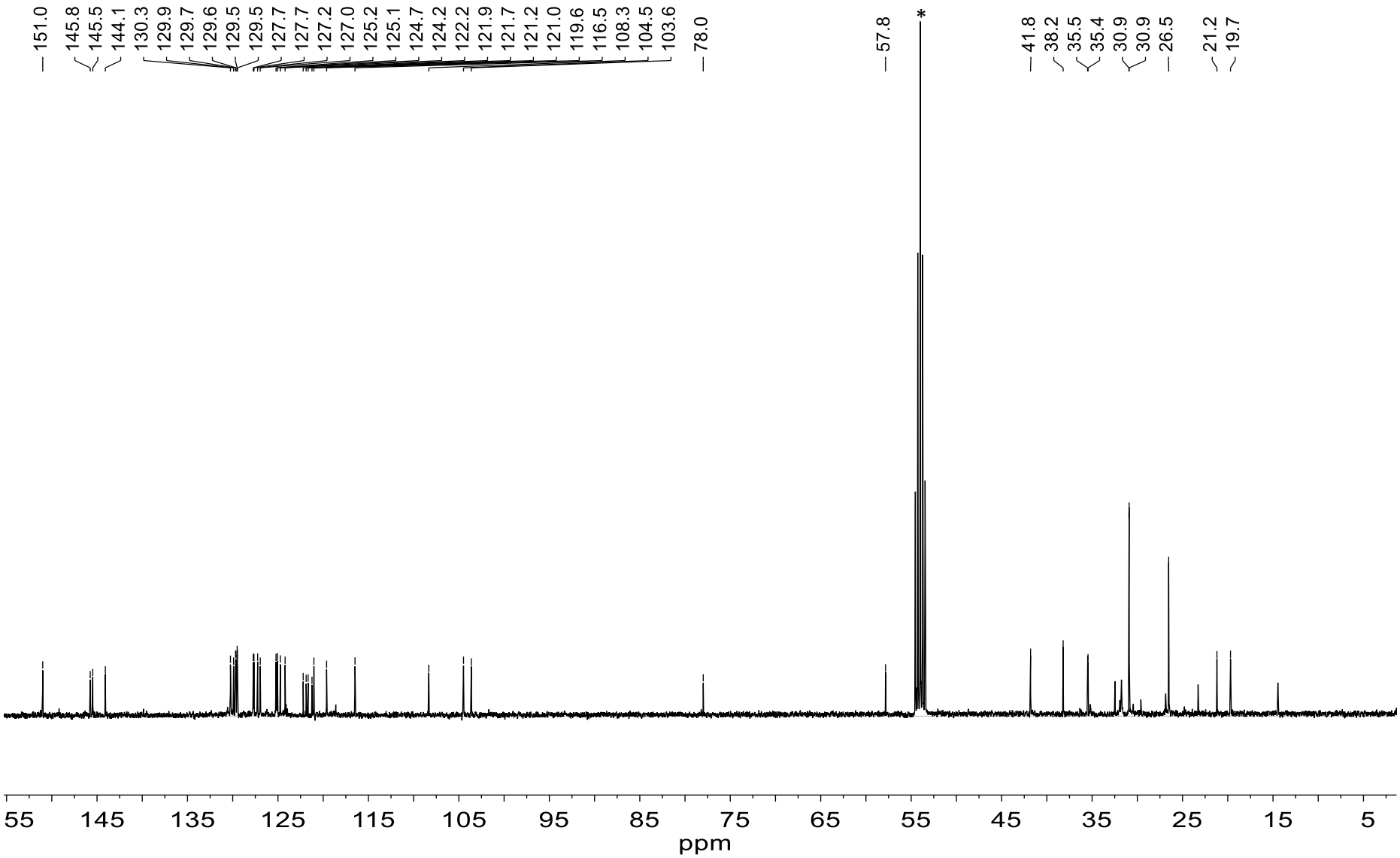

Figure S47. $^{13}C\{^{1}H\}$ NMR spectrum (CD_2Cl_2, 100 MHz, 25 °C) of **3b**. *stands for residual NMR solvent signals.

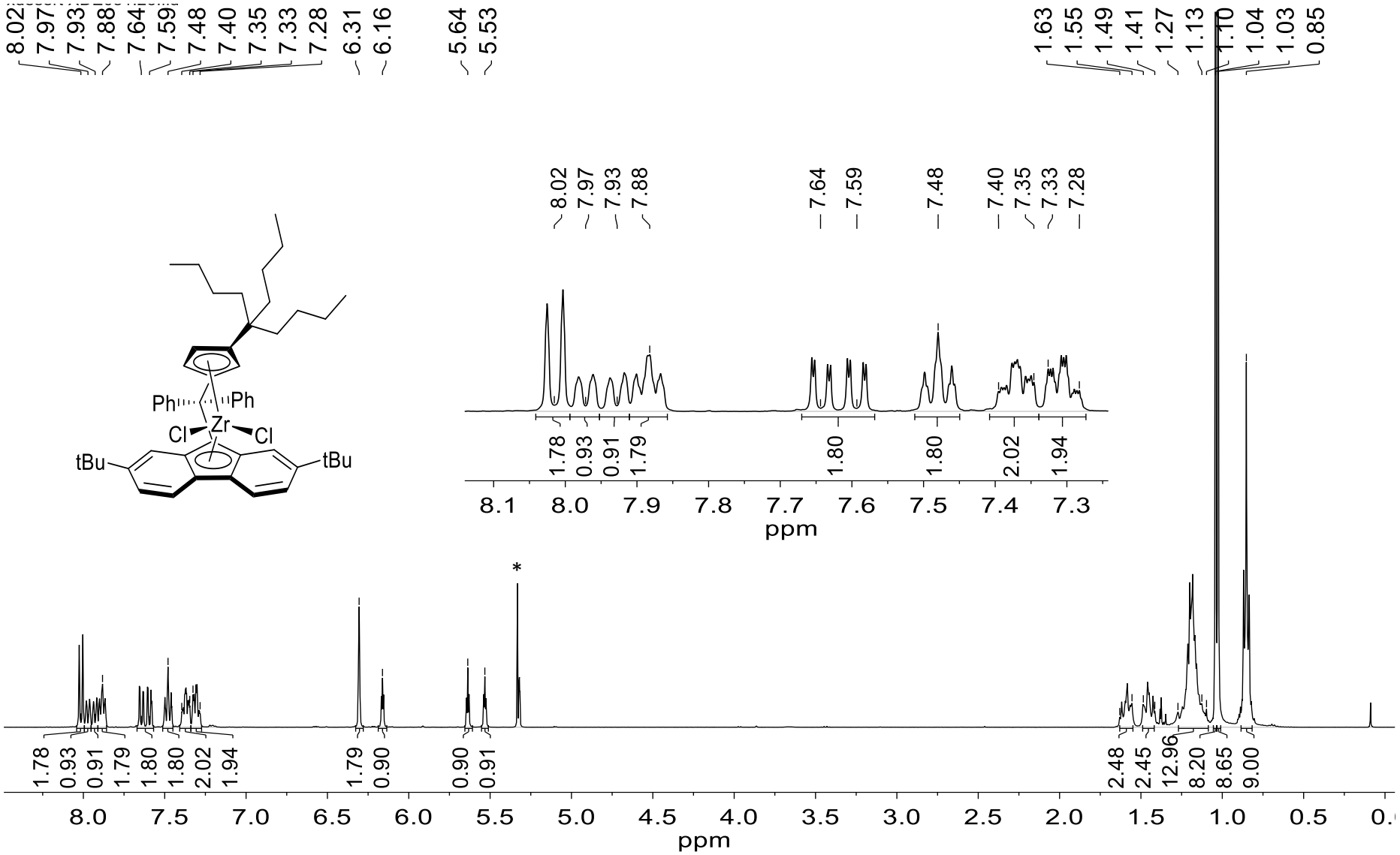

Figure S48. ^{1}H NMR spectrum (CD_2Cl_2, 400 MHz, 25 °C) of **3c**. *stands for residual NMR solvent signal.

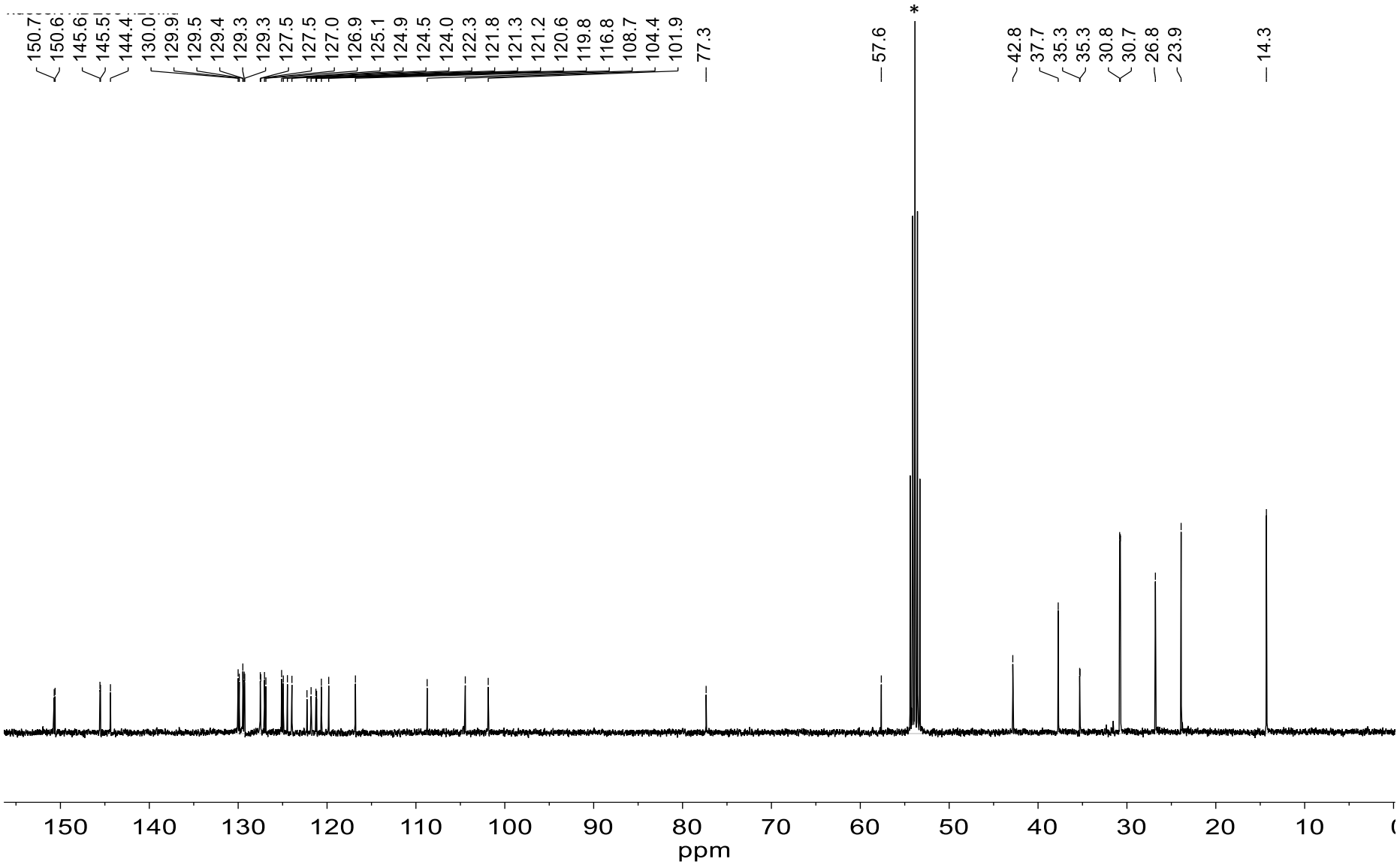

Figure S49. $^{13}C\{^{1}H\}$ NMR spectrum (CD_2Cl_2, 100 MHz, 25 °C) of **3c**. * stands for residual NMR solvent signals.

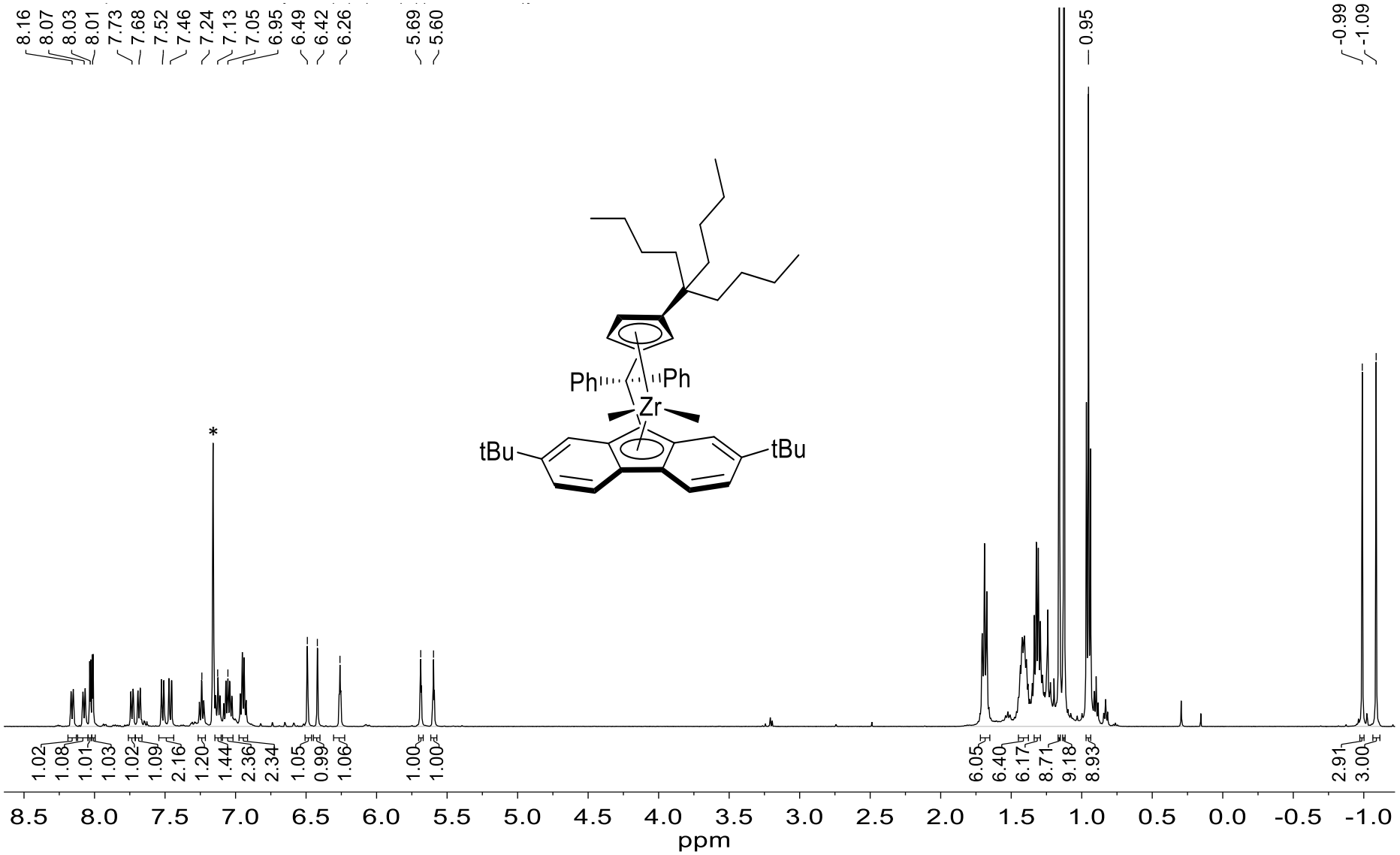

Figure S50. ^{1}H NMR spectrum (C_6D_6, 500 MHz, 25 °C) of **4c**. * stands for residual NMR solvent signal

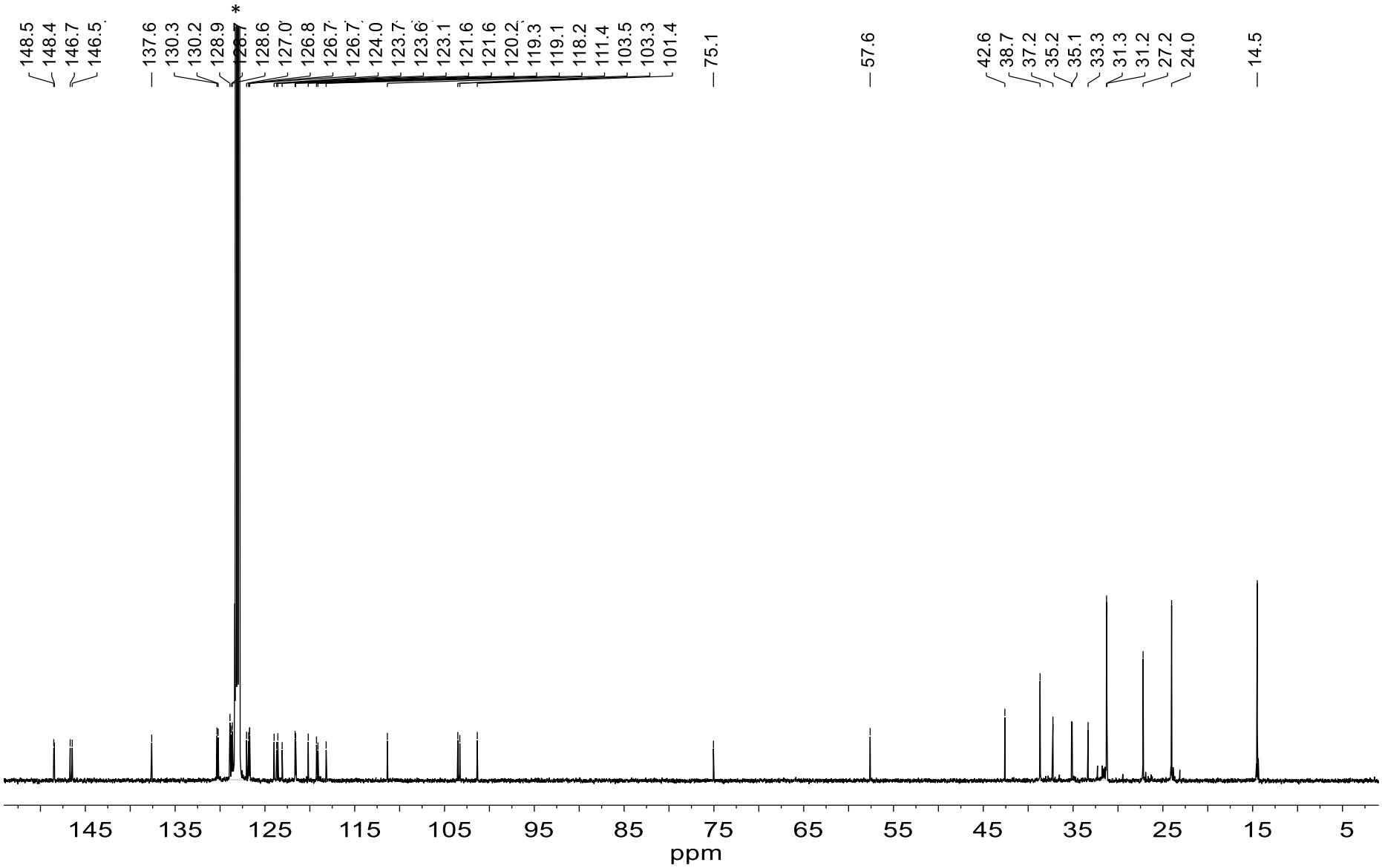

Figure S51. $^{13}C\{^{1}H\}$ NMR spectrum (CD_2Cl_2, 125 MHz, 25 °C) of **4c**. *stands for residual NMR solvent signals.

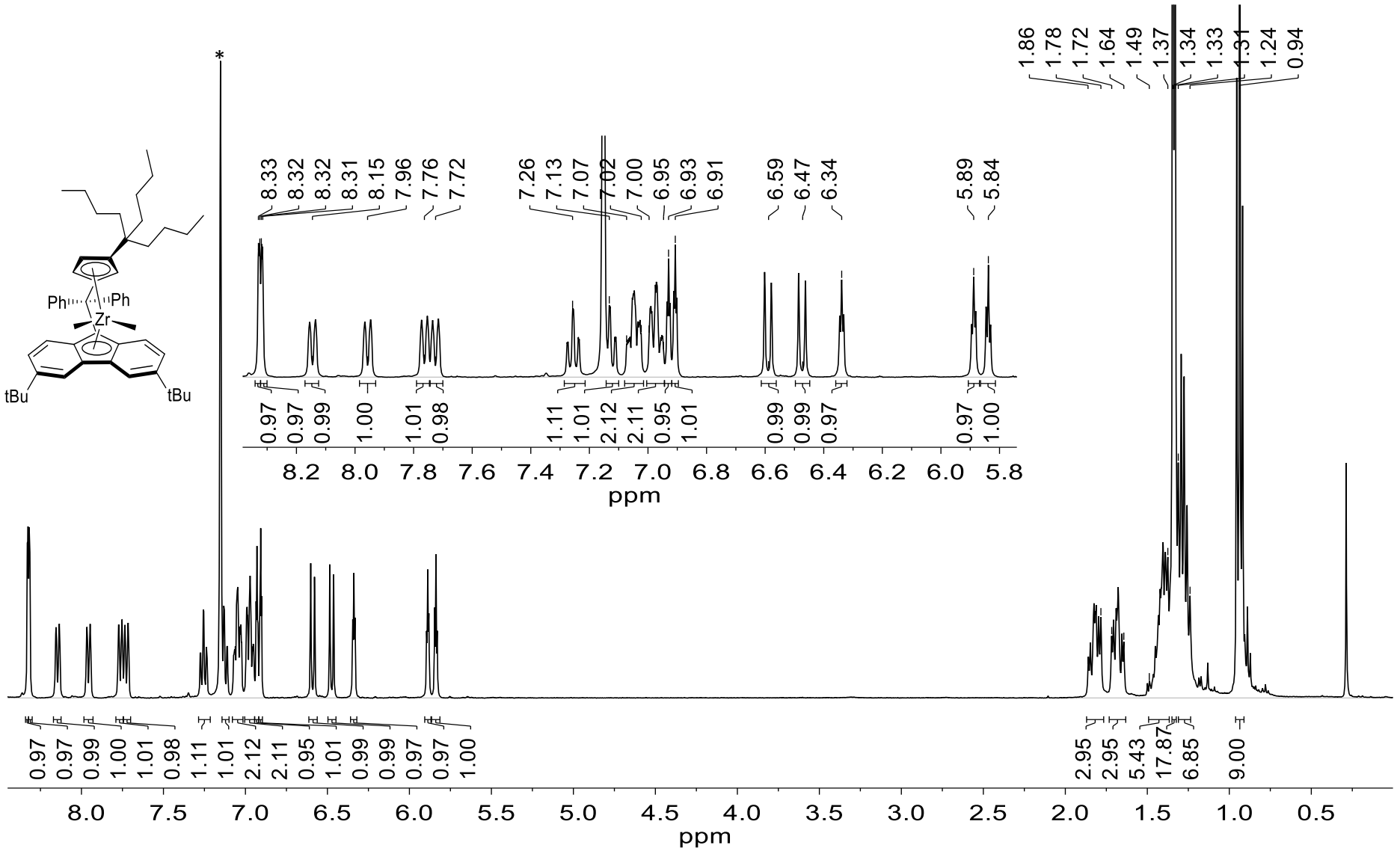

Figure S52. ^{1}H NMR spectrum (C_6D_6, 400 MHz, 25 °C) of **3d**. * stands for residual NMR solvent signal.

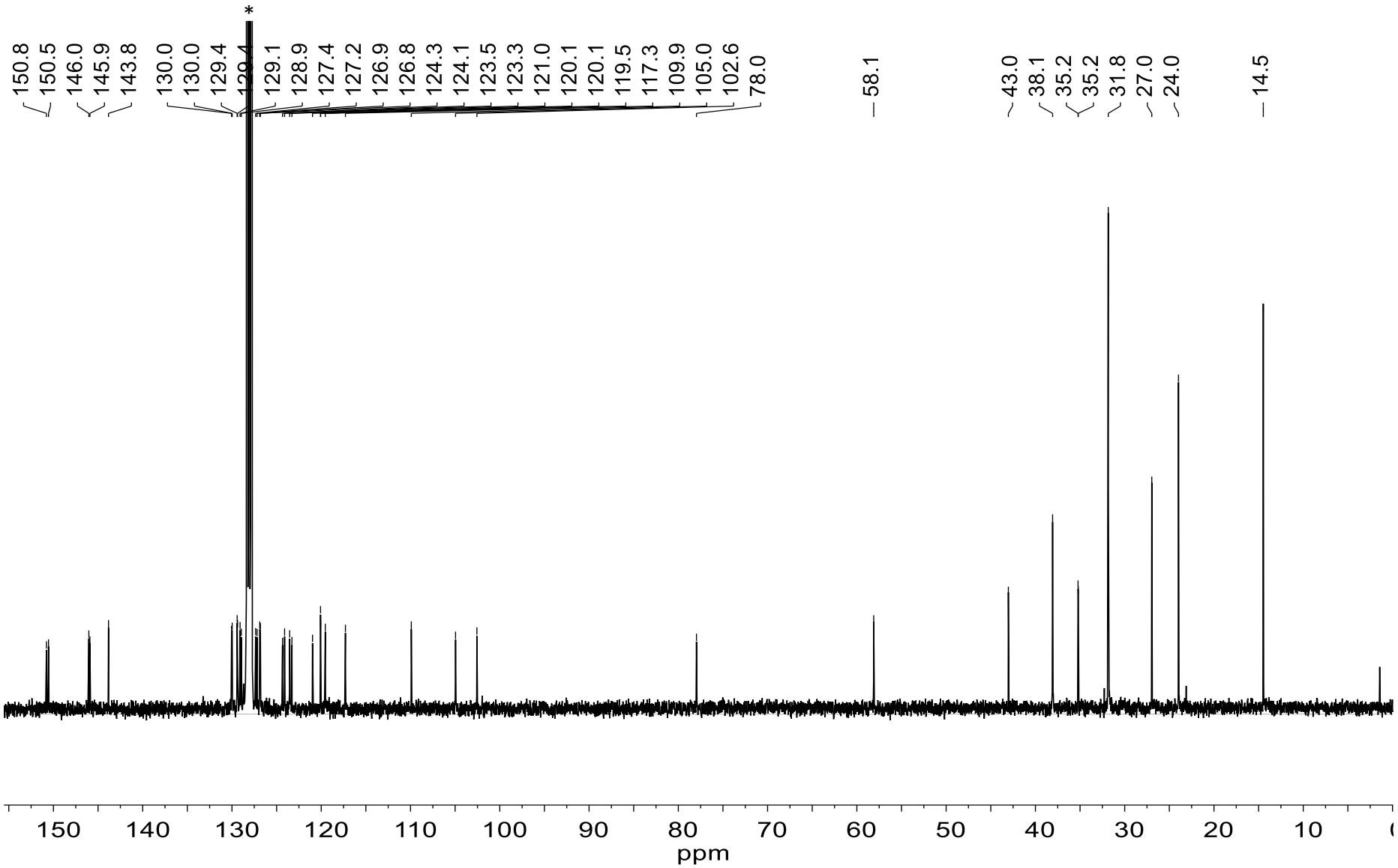

Figure S53. $^{13}C\{^{1}H\}$ NMR spectrum (C_6D_6, 100 MHz, 25 °C) of **3d**. * stands for residual NMR solvent signals.

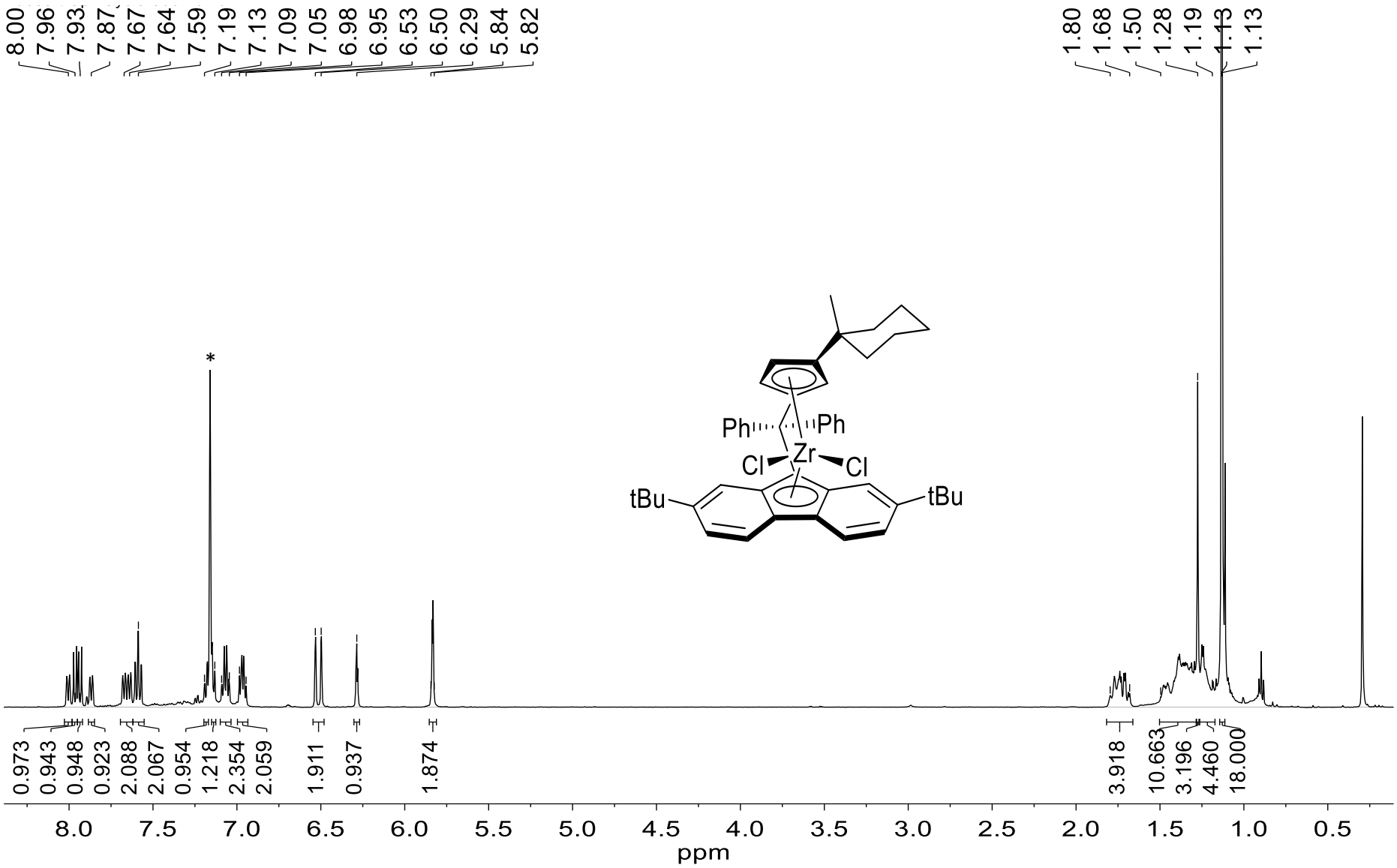

Figure S54. ^{1}H NMR spectrum (C_6D_6, 500 MHz, 25 °C) of **3e**. * stands for residual NMR solvent signal.

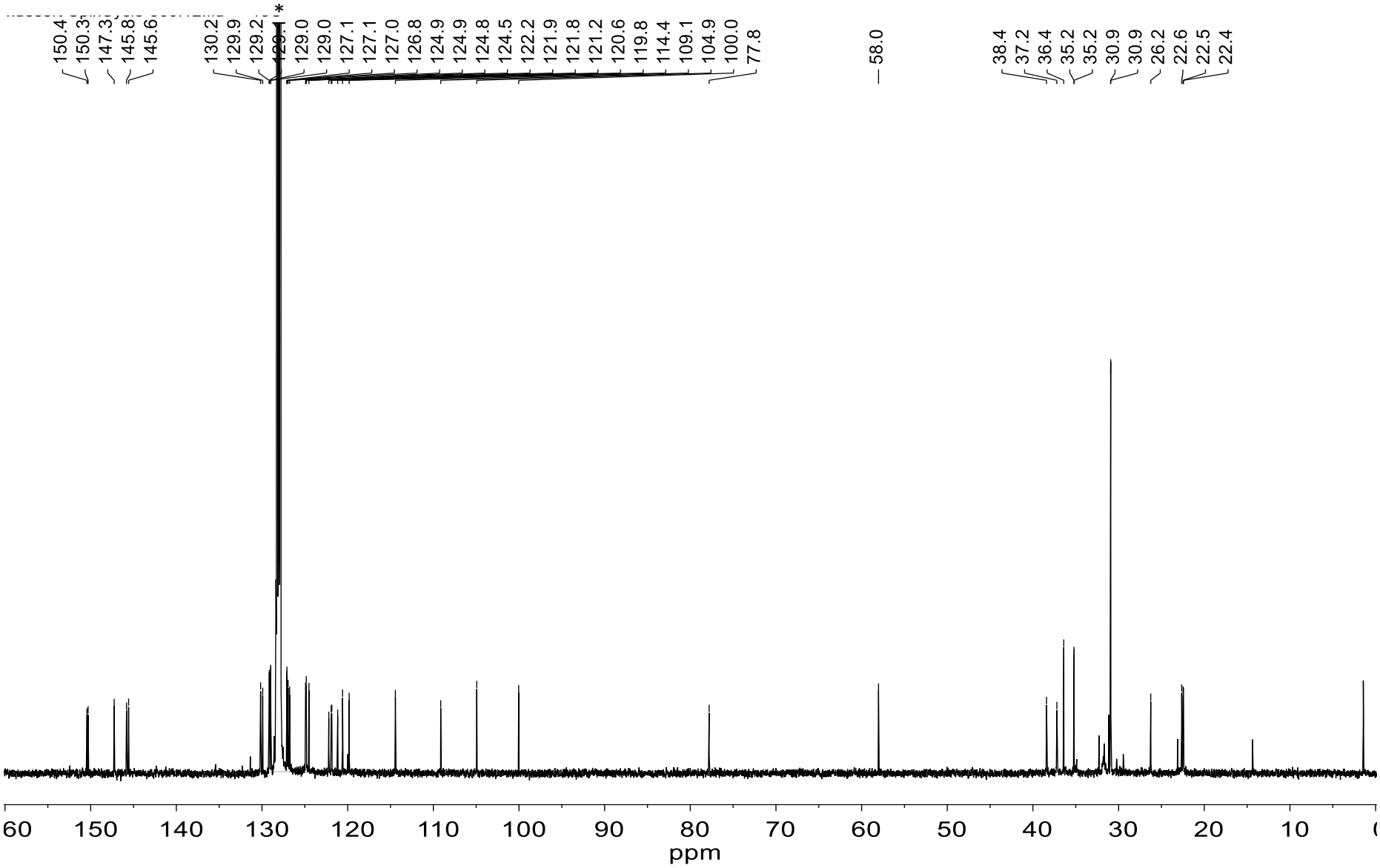

Figure S55. $^{13}C\{^{1}H\}$ NMR spectrum (C_6D_6, 125 MHz, 25 °C) of **3e**. * stands for residual NMR solvent signals.

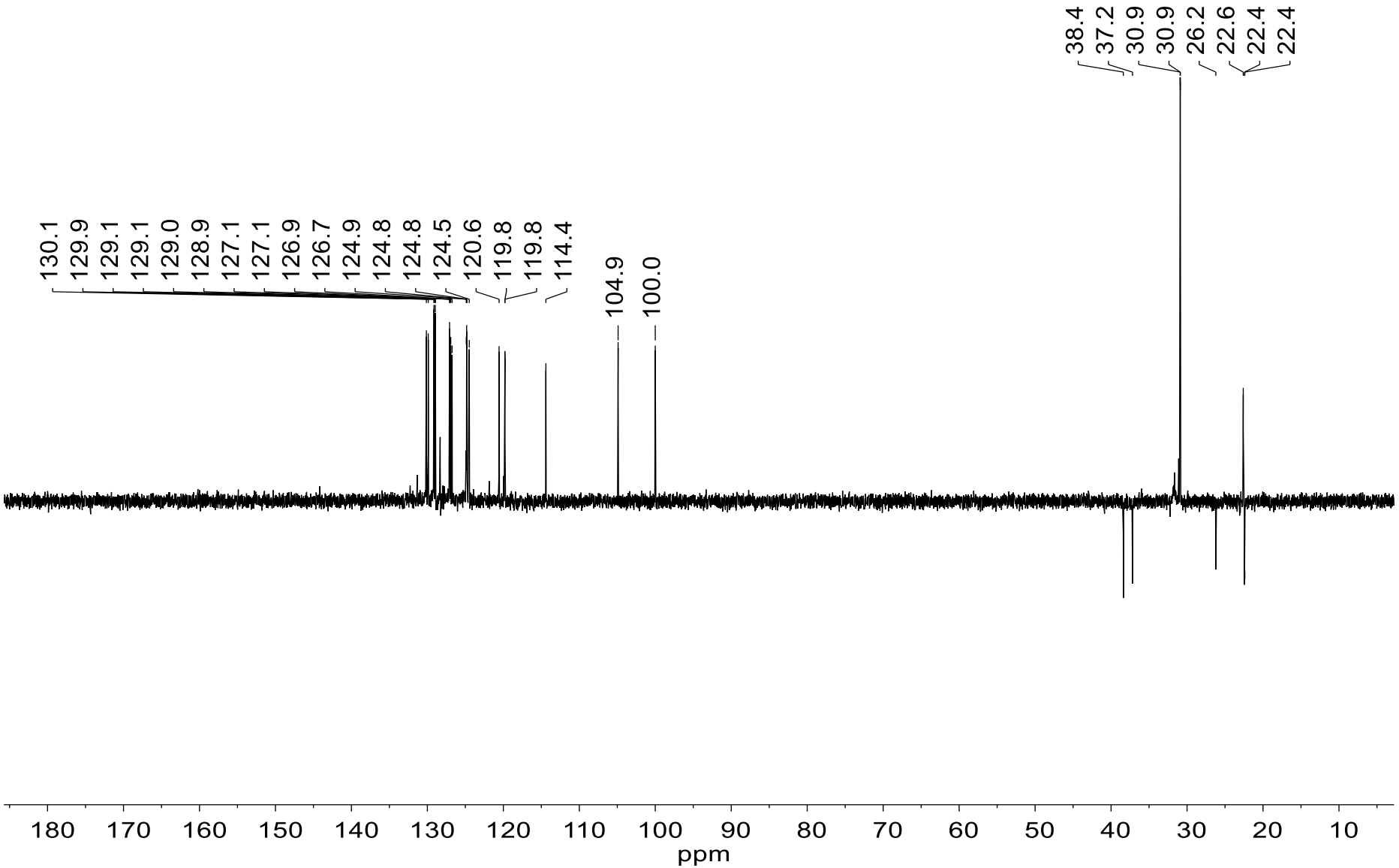

Figure S56. ^{13}C DEPT135 experiment (C_6D_6, 125 MHz, 25 °C) for **3e**.

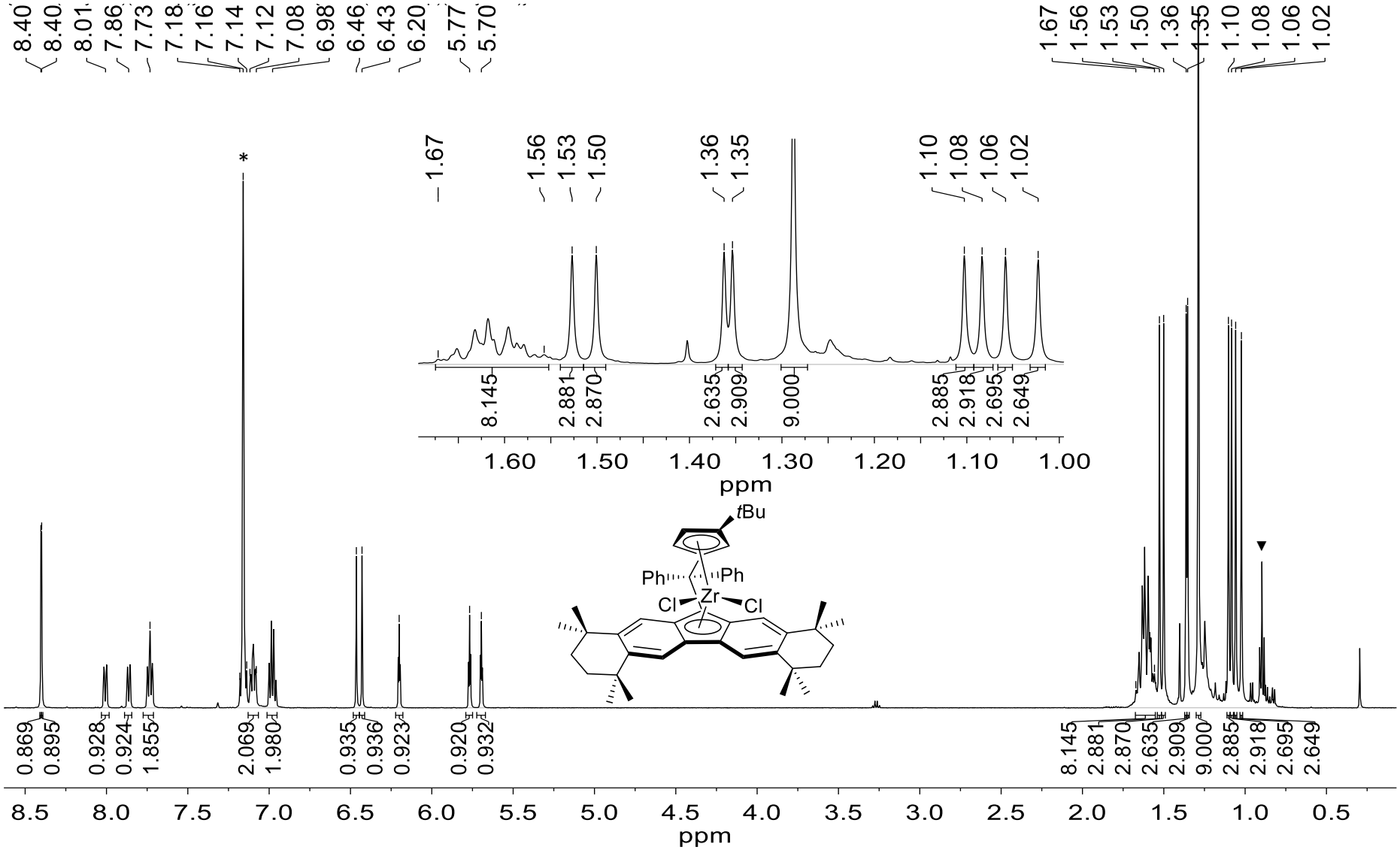

Figure S57. ^{1}H NMR spectrum (C_6D_6, 500 MHz, 25 °C) of **3f**. * stands for residual NMR solvent signal. ▼ stands for residual heptane signal.

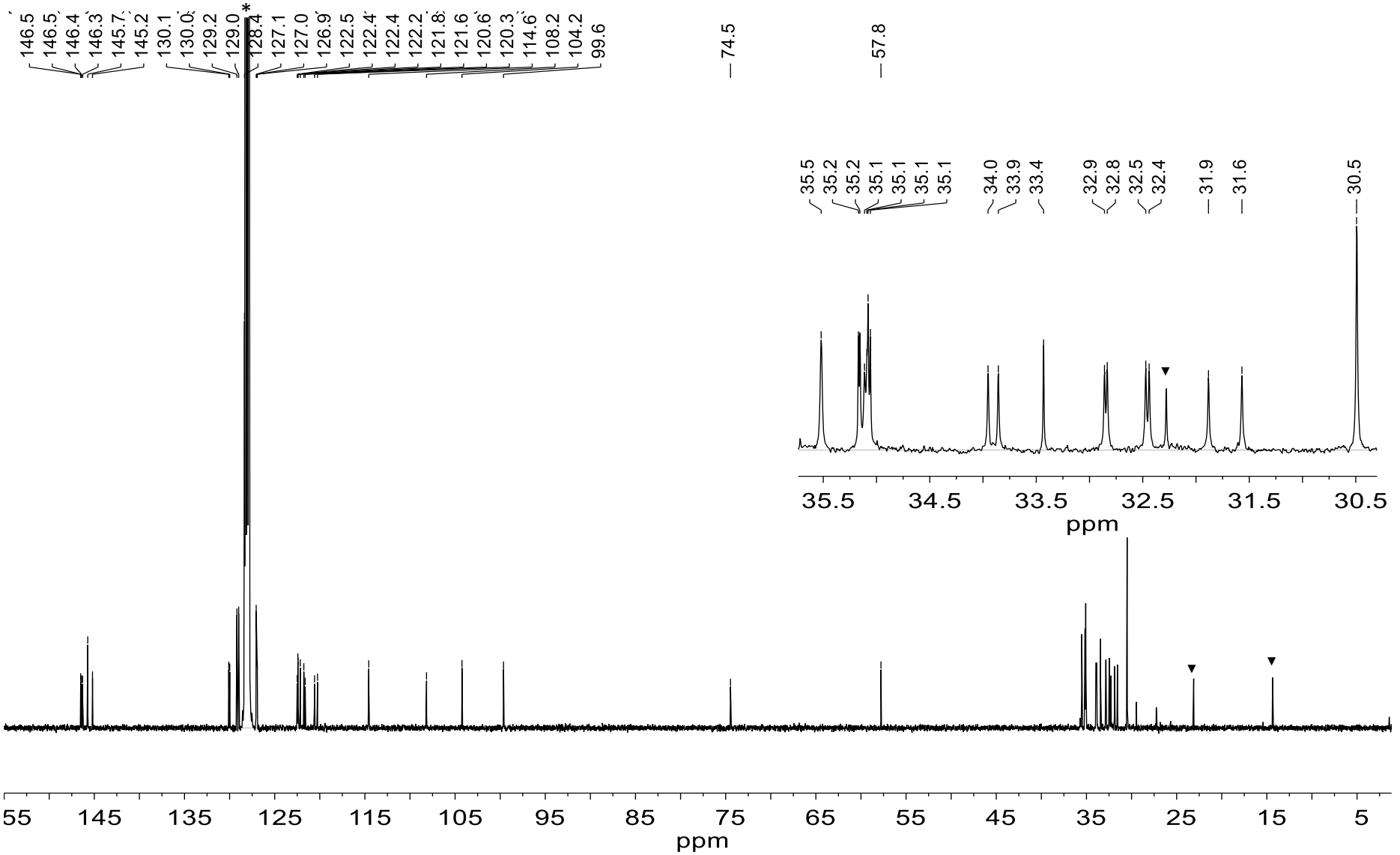

Figure S58. $^{13}C\{^{1}H\}$ NMR spectrum (C_6D_6, 125 MHz, 25 °C) of **3f**. * stands for residual NMR solvent signals. ▼ stands for residual heptane signal.

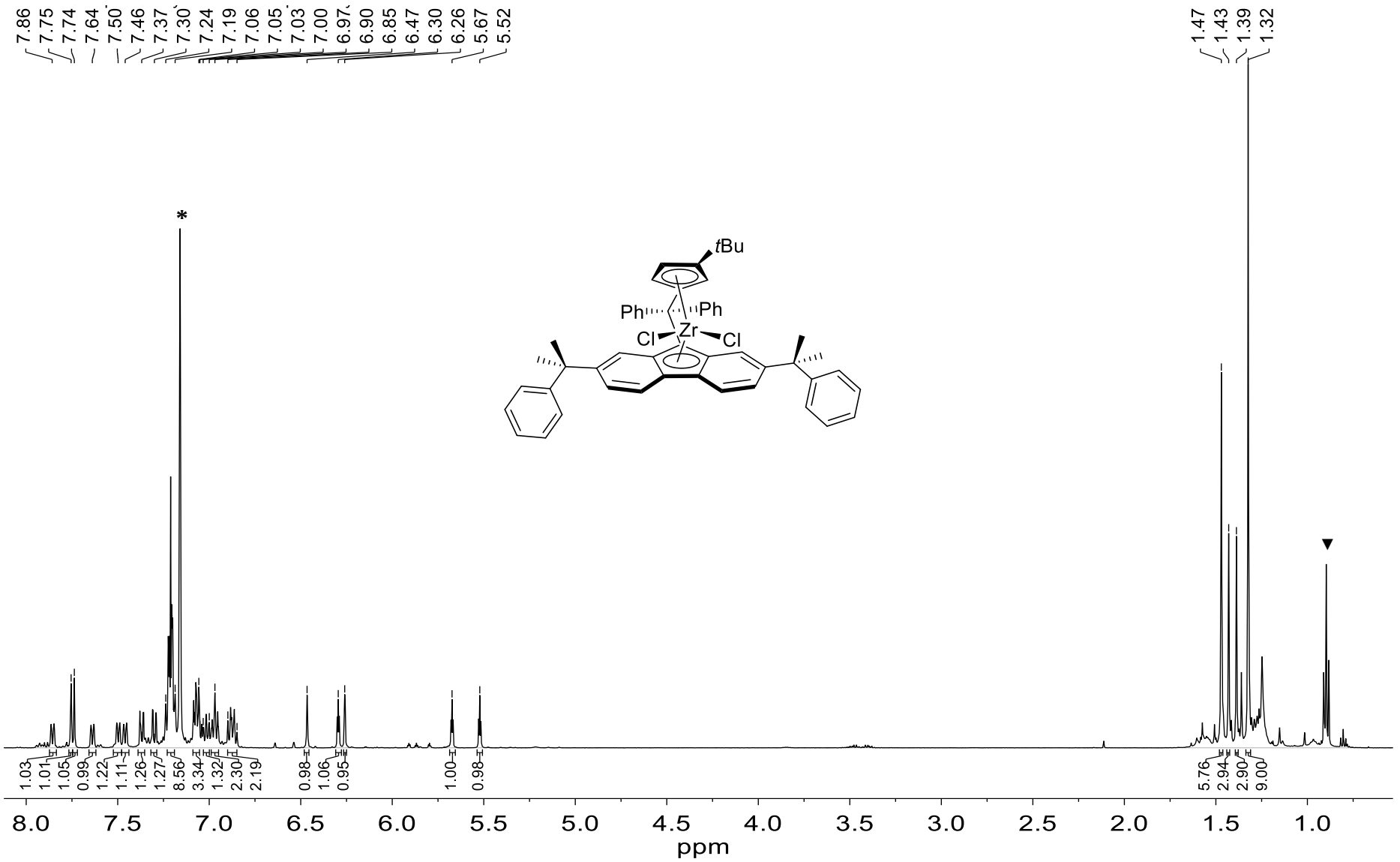

Figure S59. ^{1}H NMR spectrum (C_6D_6, 500 MHz, 25 °C) of **3g**. *stands for residual NMR solvent signal. ▼stands for residual heptane signal.

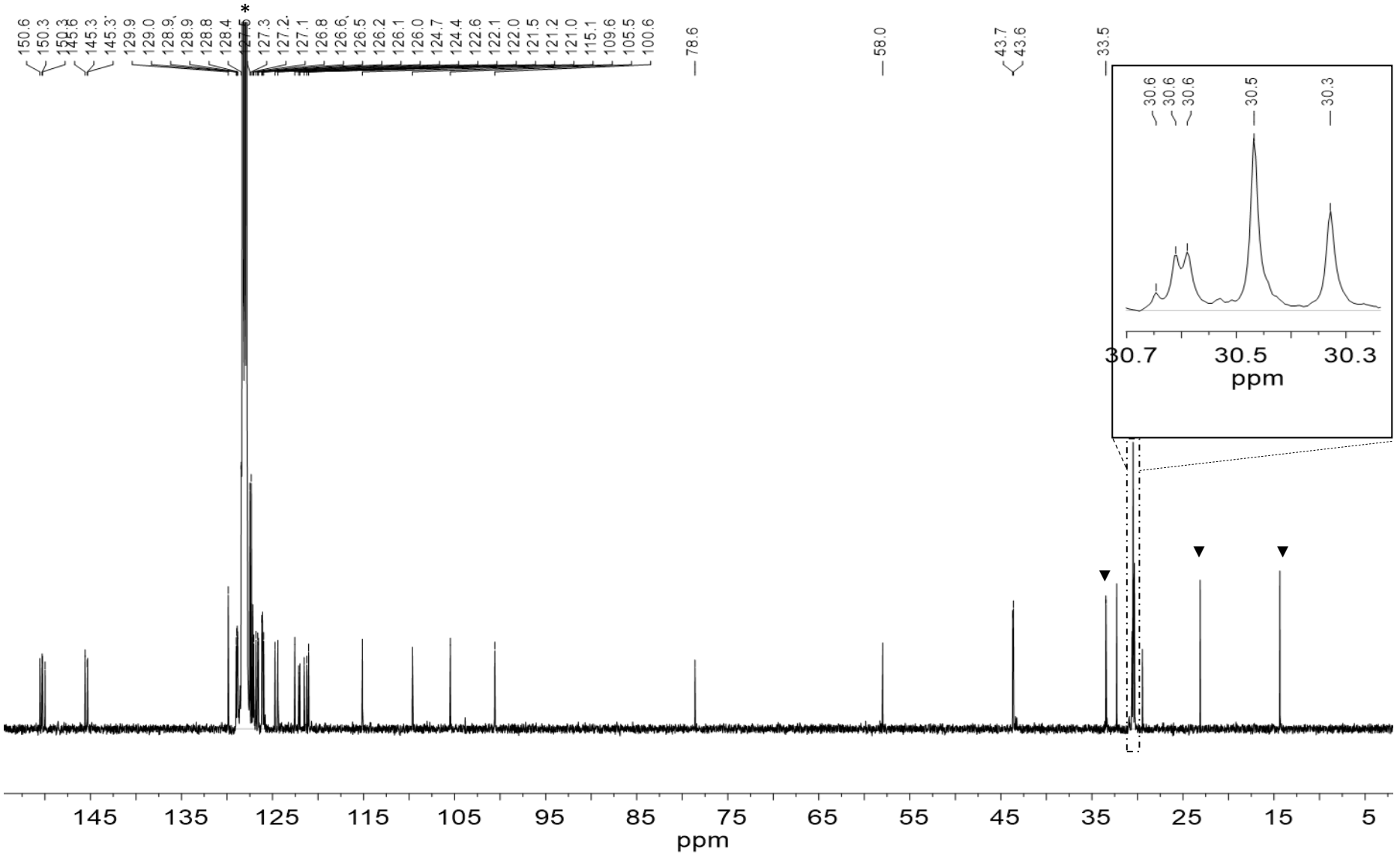

Figure S60. $^{13}C\{^{1}H\}$ NMR spectrum (CD_2Cl_2, 100 MHz, 25 °C) of **3g**. * stands for residual NMR solvent signal. ▼stands for residual heptane signal.

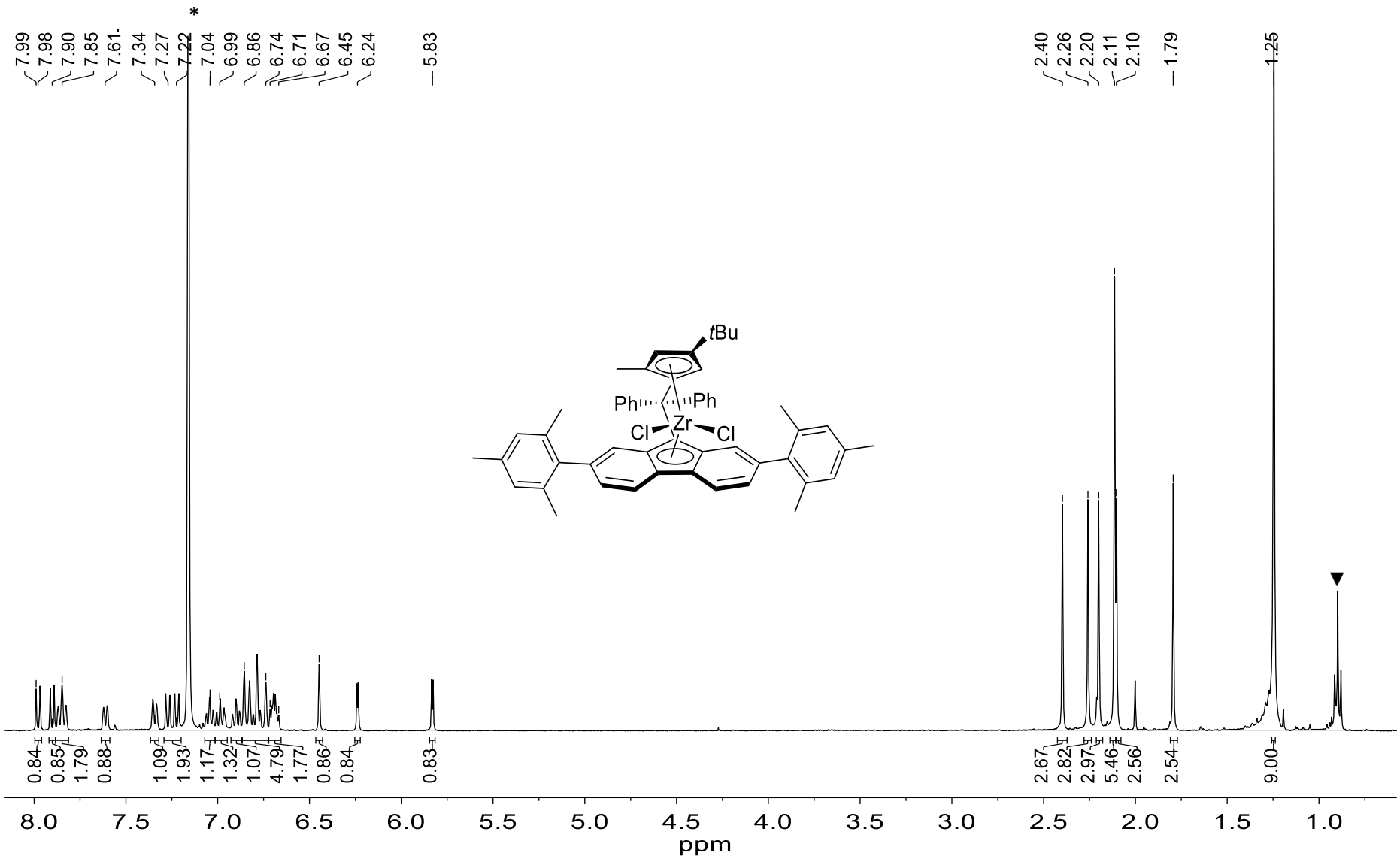

Figure S61. ^{1}H NMR spectrum (C_6D_6, 400 MHz, 25 °C) of **3h. *** stands for residual NMR solvent signal. ▼stands for residual hexane signal

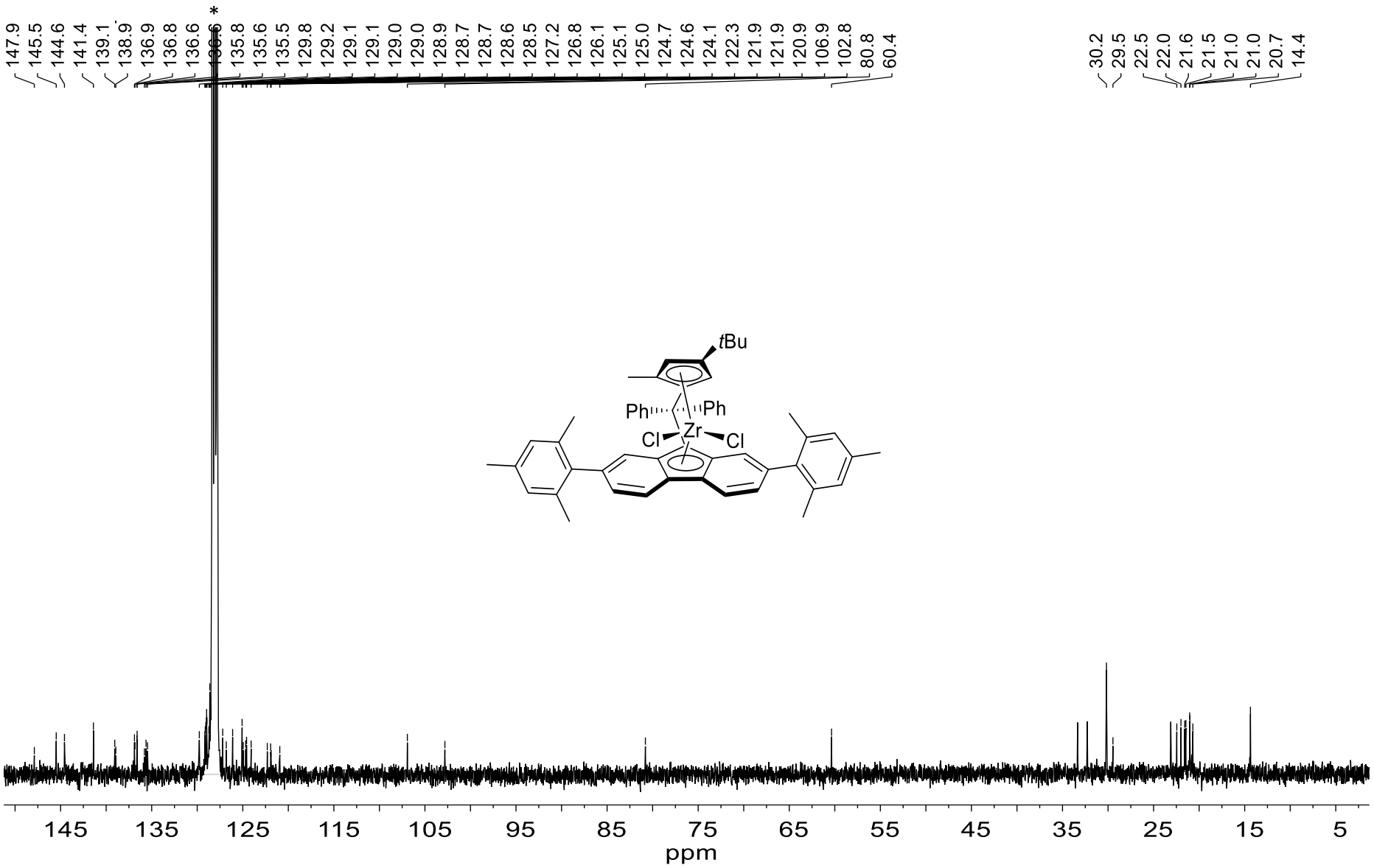

Figure S62. $^{13}C\{^{1}H\}$ NMR spectrum (C_6D_6, 100 MHz, 25 °C) of **3h**. * stands for residual NMR solvent signals.

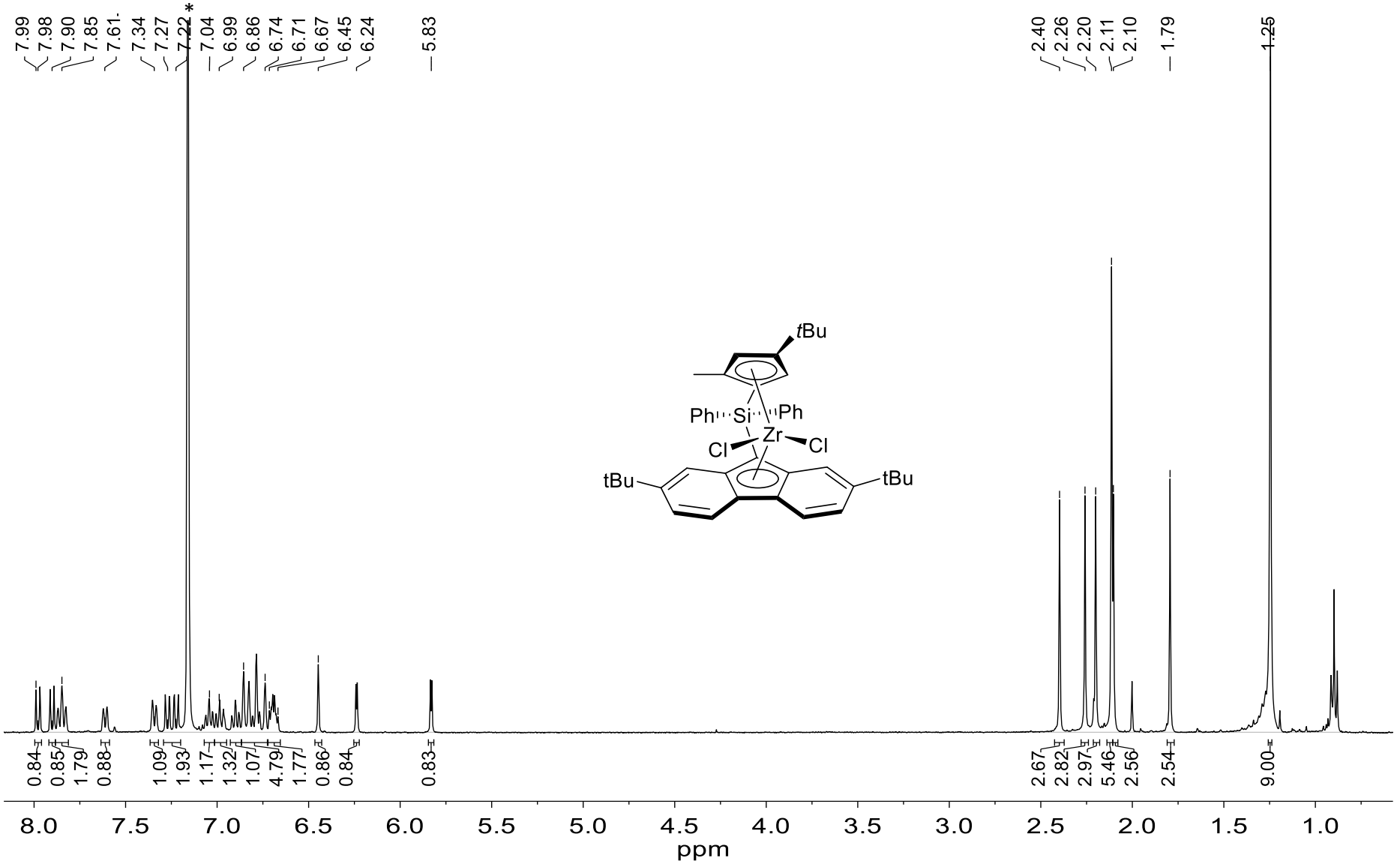

Figure S63. ^{1}H NMR spectrum (C_6D_6, 100 MHz, 25 °C) of **3k.** * stands for residual NMR solvent signal.

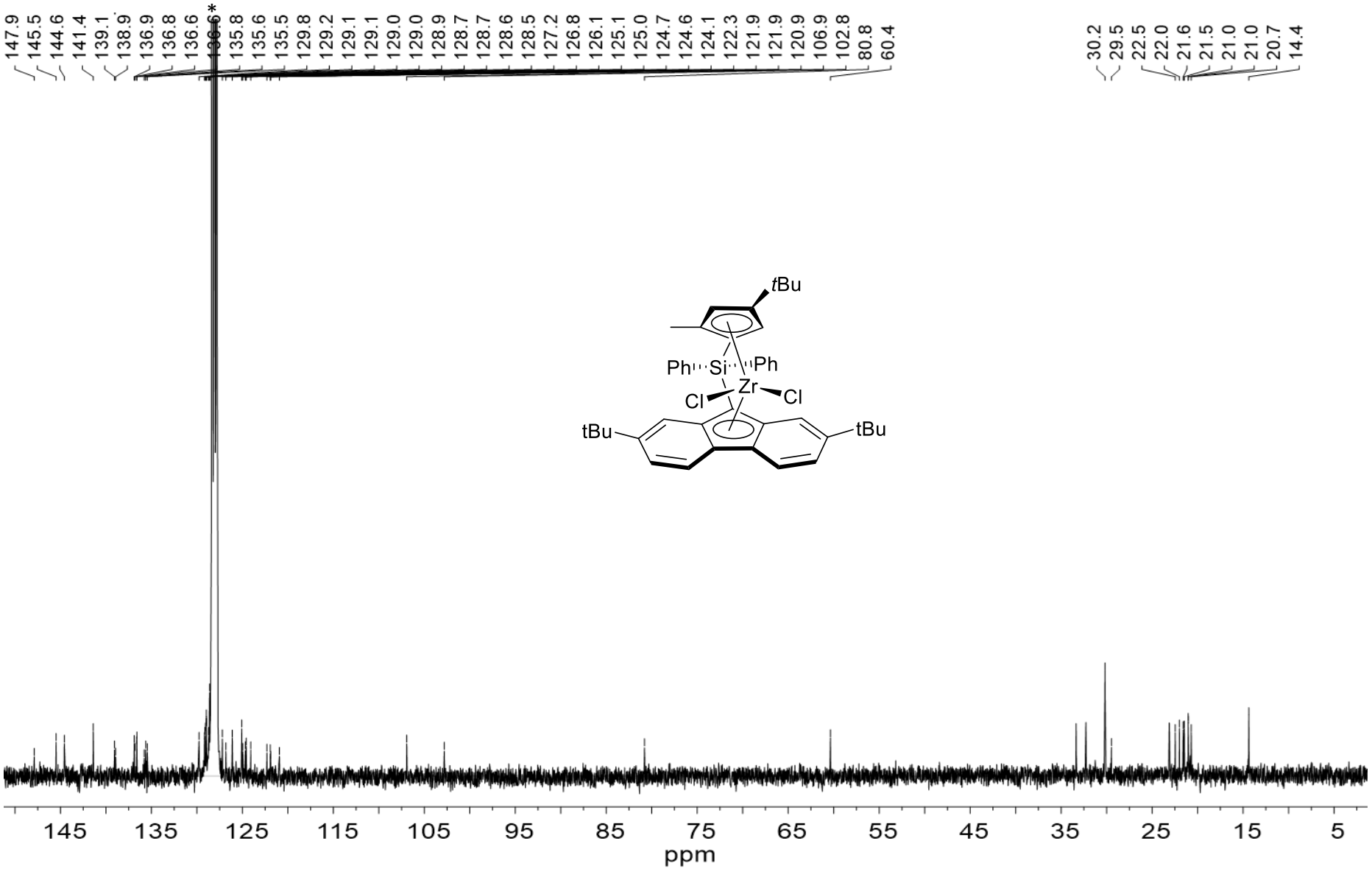

Figure S64. $^{13}C\{^{1}H\}$ NMR spectrum (C_6D_6, 100 MHz, 25 °C) of **3k**. * stands for residual NMR solvent signals.

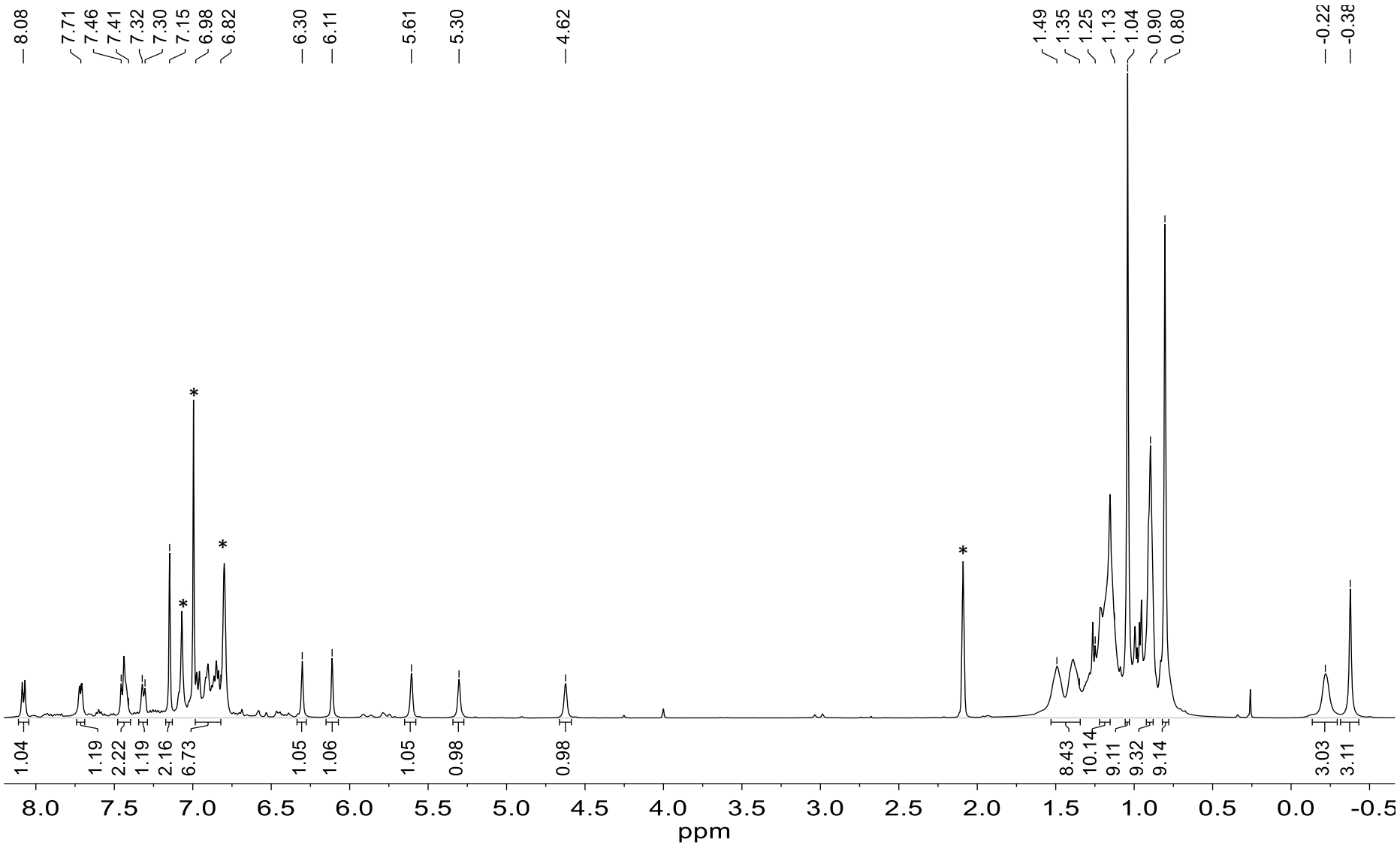

Figure S65. ^{1}H NMR spectrum (tol-d_8, 500 MHz, –50 °C) of the ion-pair **4c**-**MeB(C$_6$F$_5$)$_3$**. * stands for residual NMR solvent signals.

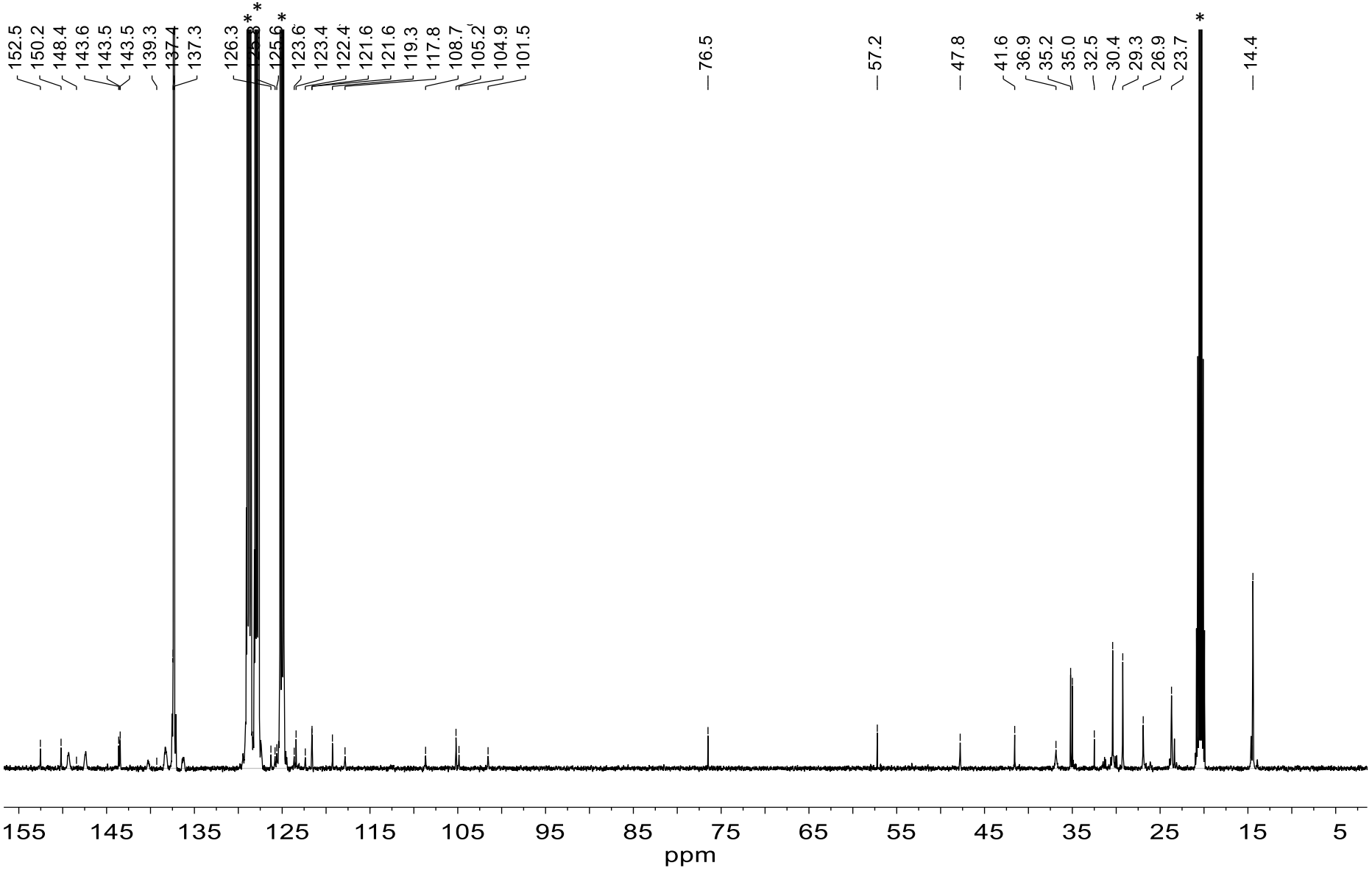

Figure S66. $^{13}C\{^{1}H\}$ NMR spectrum (tol-d_8, 125 MHz, –50 °C) of the ion-pair **4c-MeB(C_6F_5)**.

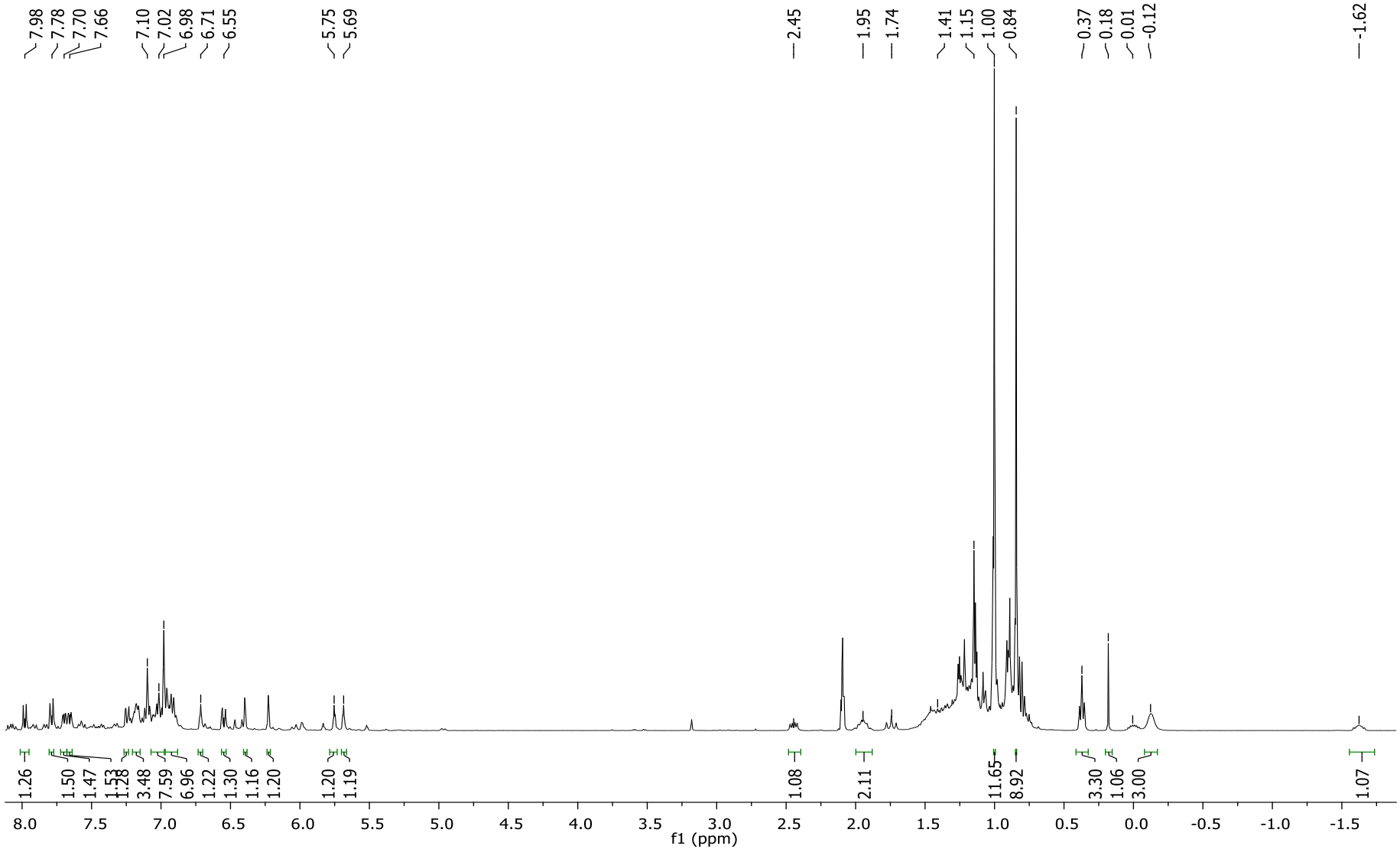

Figure S67. ^{1}H NMR spectrum (tol-d_8, 125 MHz, 25 °C) of **5c-MeB(C_6F_5)$_3$** after 24 h at RT.

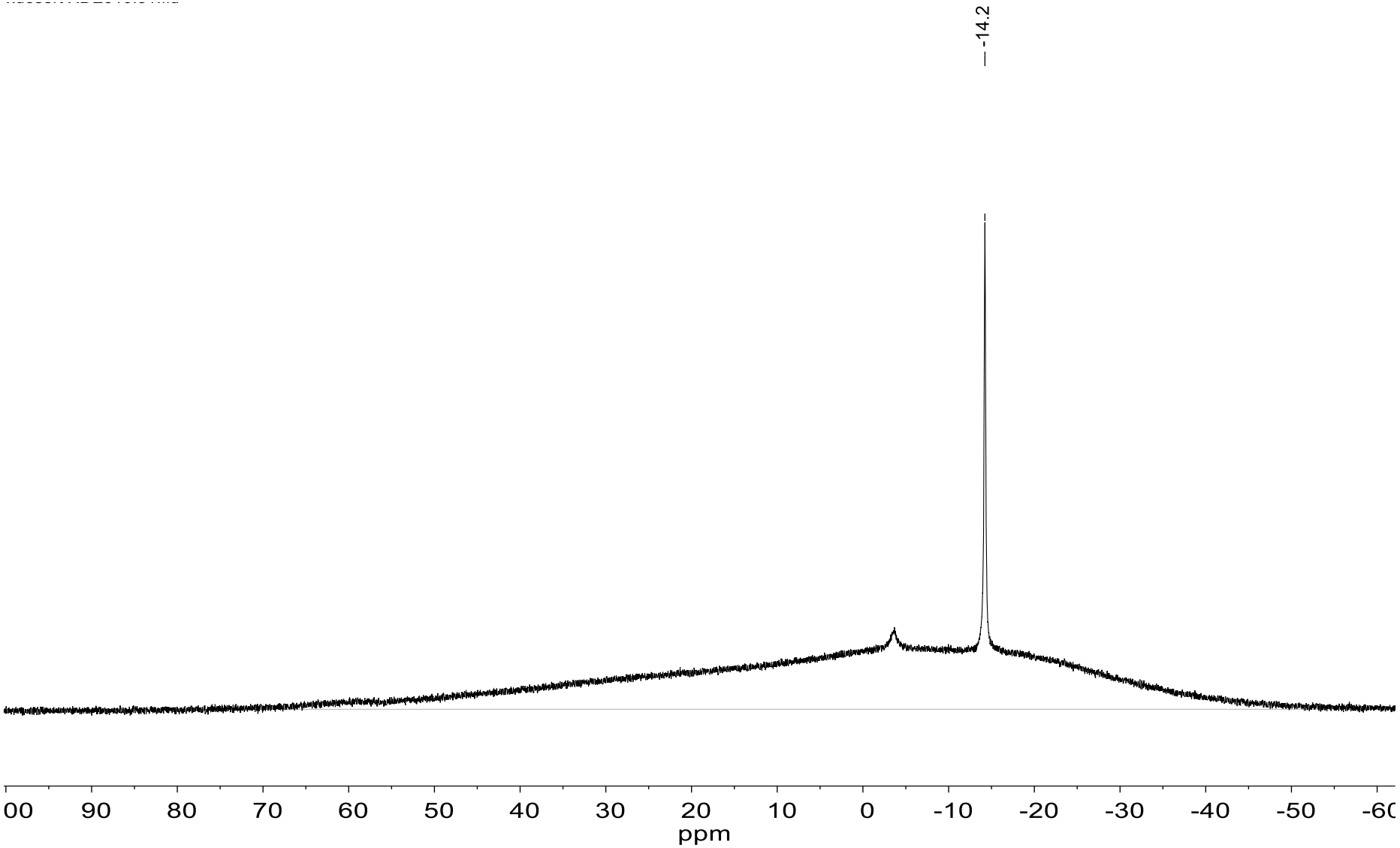

Figure S68. $^{11}B\{^{1}H\}$ NMR spectrum (tol-d_8, 128 MHz, 25 °C) of **5c-MeB(C_6F_5)$_3$** after 24 h at RT.

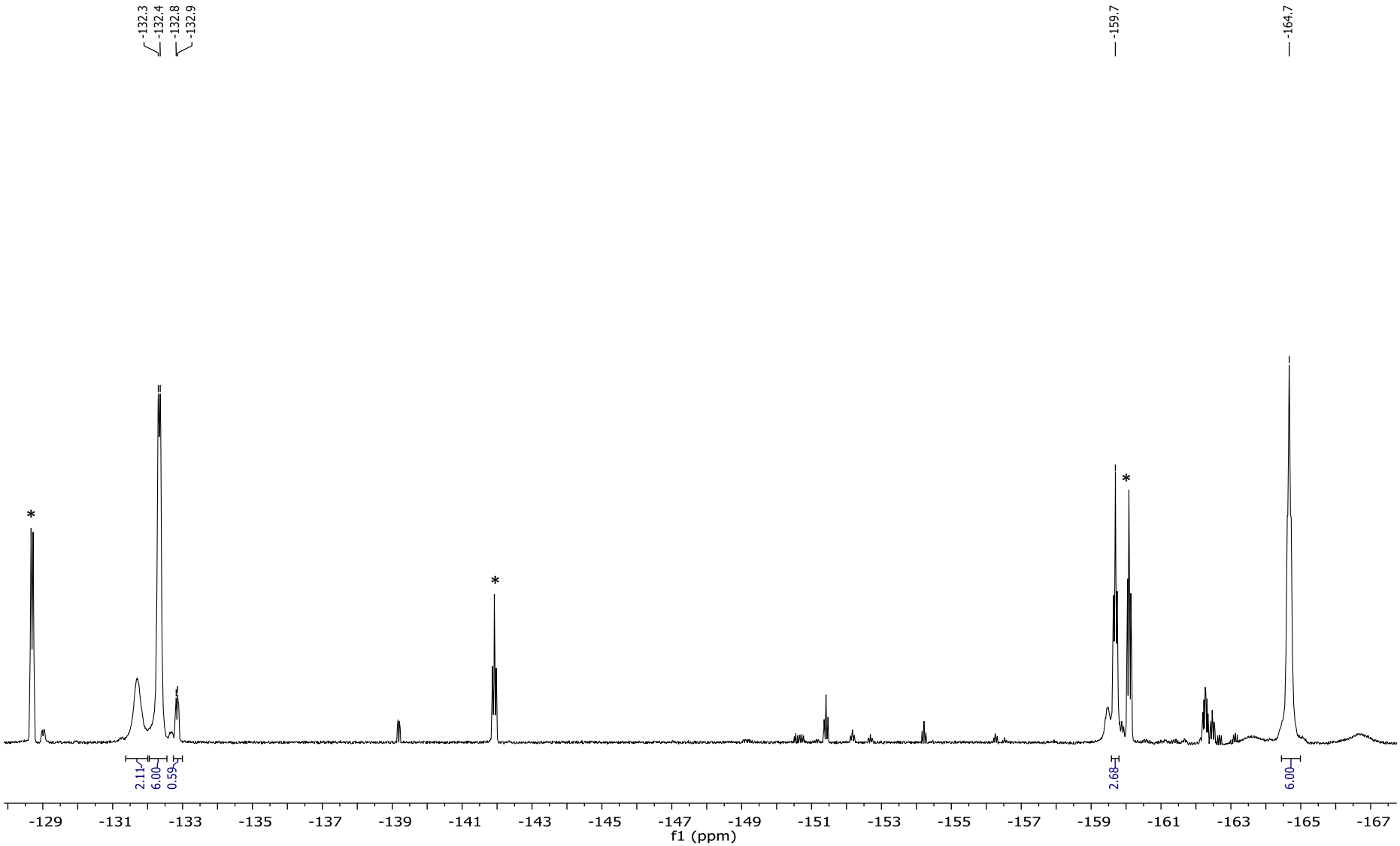

Figure S69. $^{19}F\{^{1}H\}$ NMR Spectrum (tol-d_8, 376 MHz, 25 °C) of **5c-MeB(C_6F_5)$_3$** after 24 h at RT. * stands for signal from excess B(C_6F_5)$_3$.

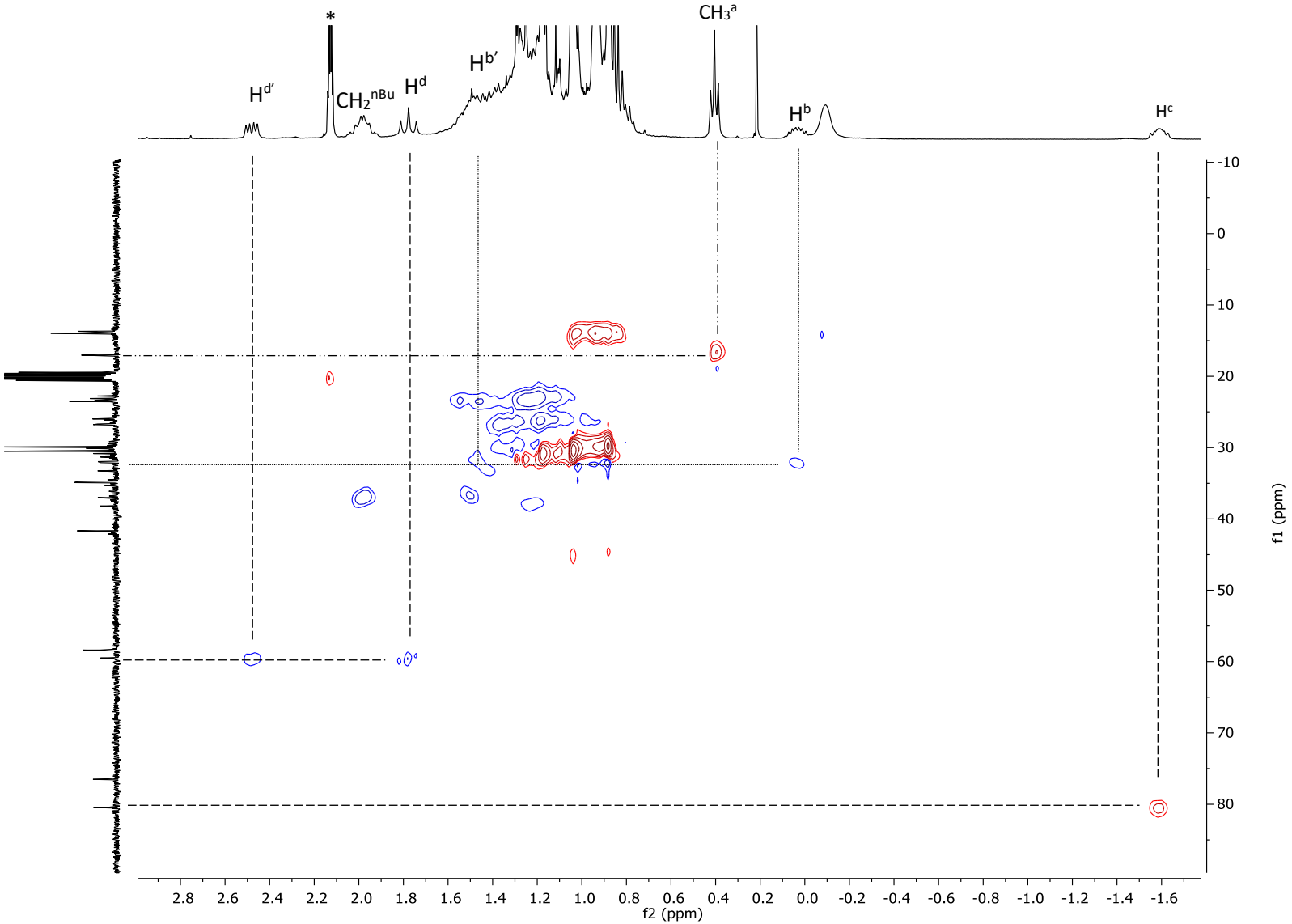

Figure S70. Zoom of the aliphatic region from the 2D HSQC NMR experiment for **5c-MeB(C_6F_5)$_3$** after 24 h at RT. * stands for signal from NMR solvent

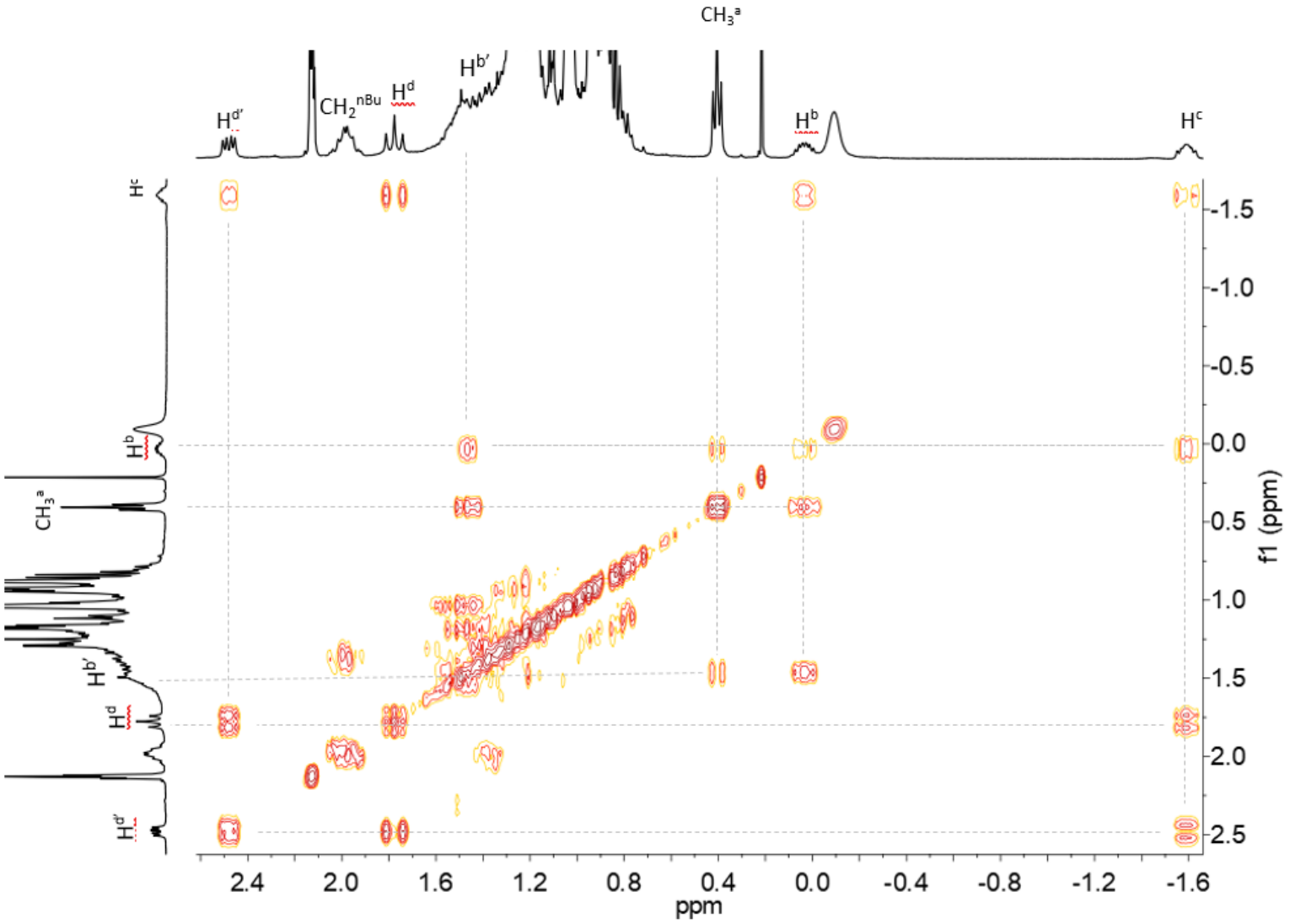

Figure S71. Zoom of the aliphatic area of the 2D COSY-^{1}H spectrum of the **5c-MeB(C$_6$F$_5$)$_3$** after 24 h at RT

iASAP-MS Spectra of complexes:

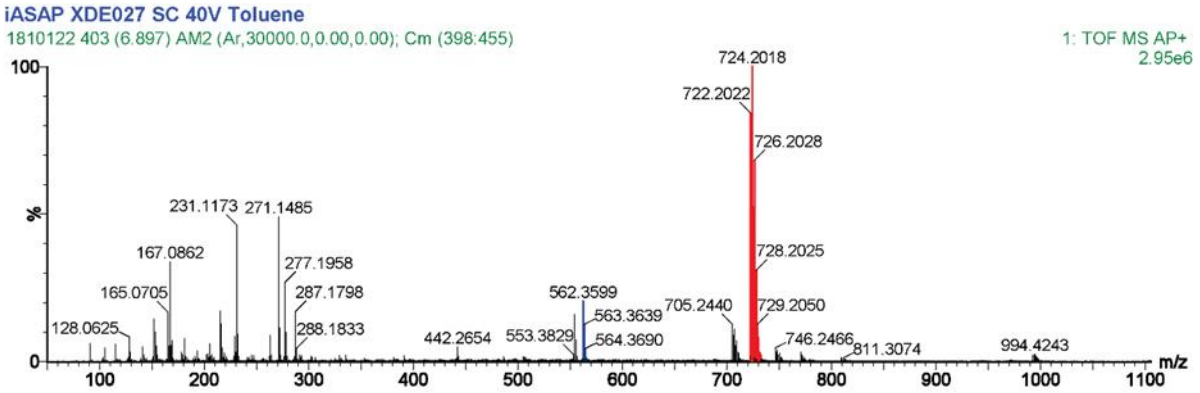

Figure S72. iASAP-MS mass spectrum of **3a** (Sampling cone 40V)

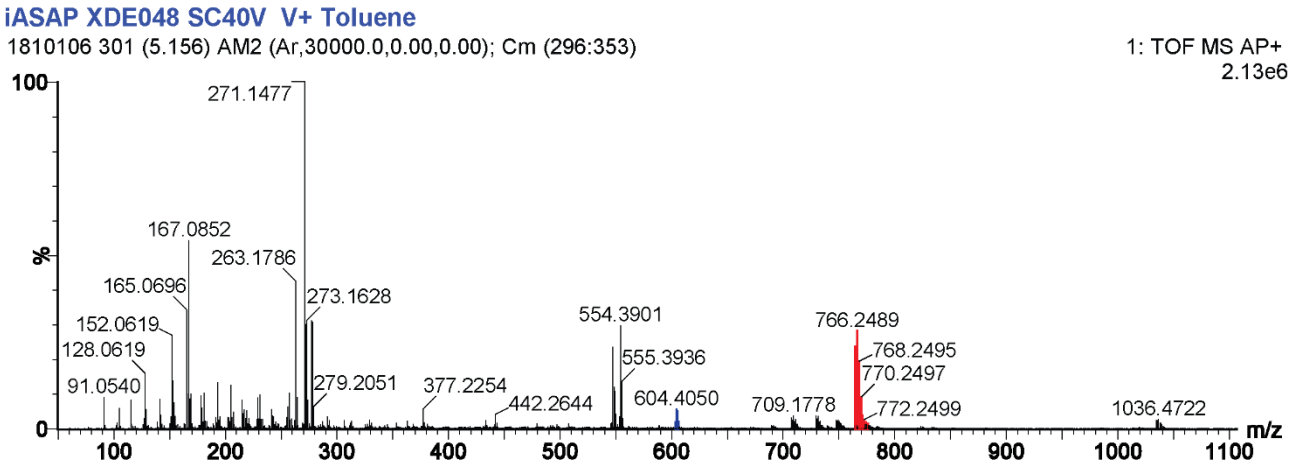

Figure S73. iASAP-MS mass spectrum of **3b** (Sampling cone 40V)

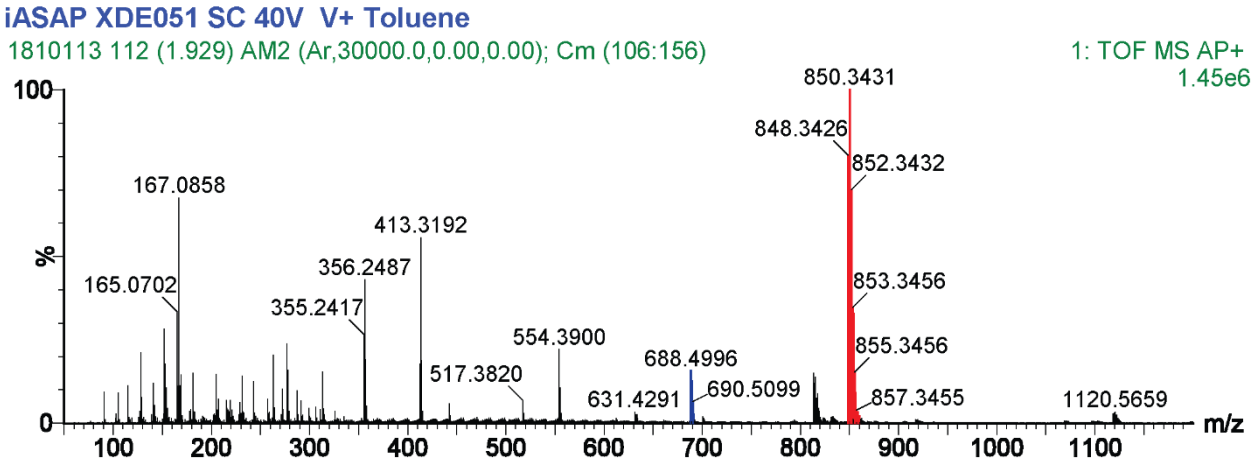

Figure S74. iASAP-MS mass spectrum of **3c** (Sampling cone 40V)

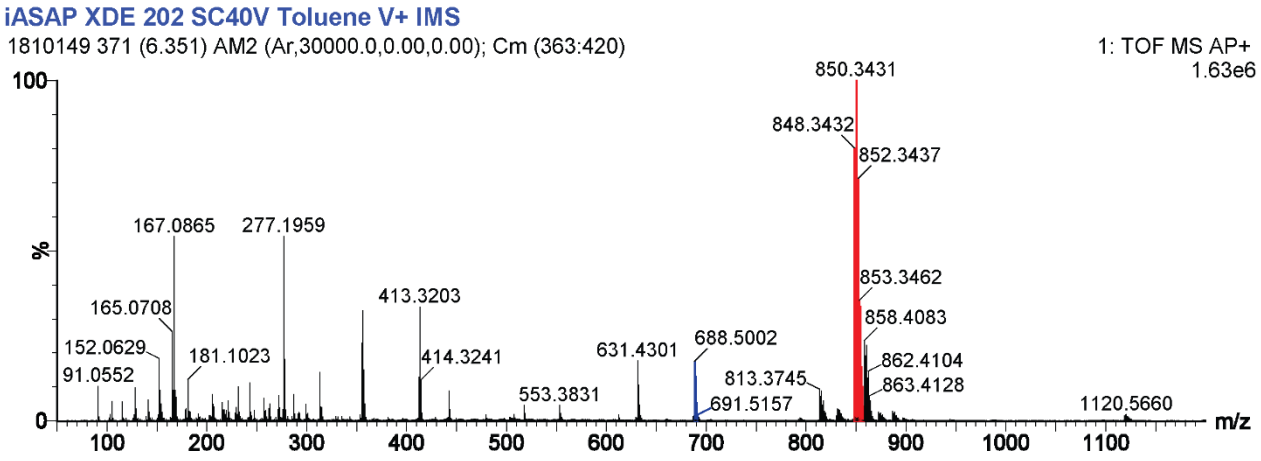

Figure S75. iASAP-MS mass spectrum of **3d** (Sampling cone 40V)

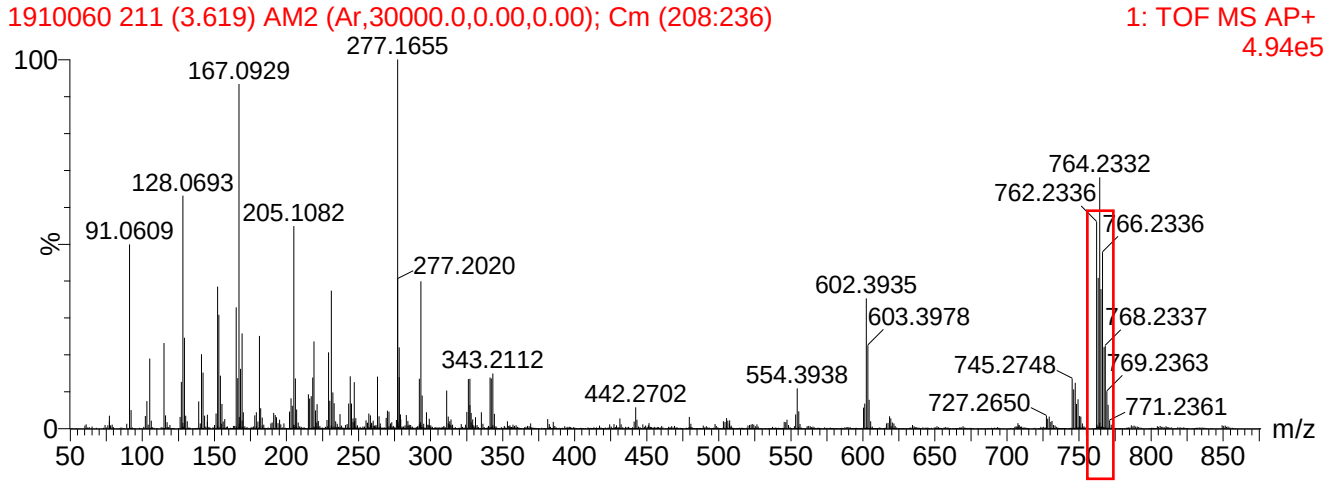

Figure S76. iASAP-MS mass spectrum of **3e** (Sampling cone 40V)

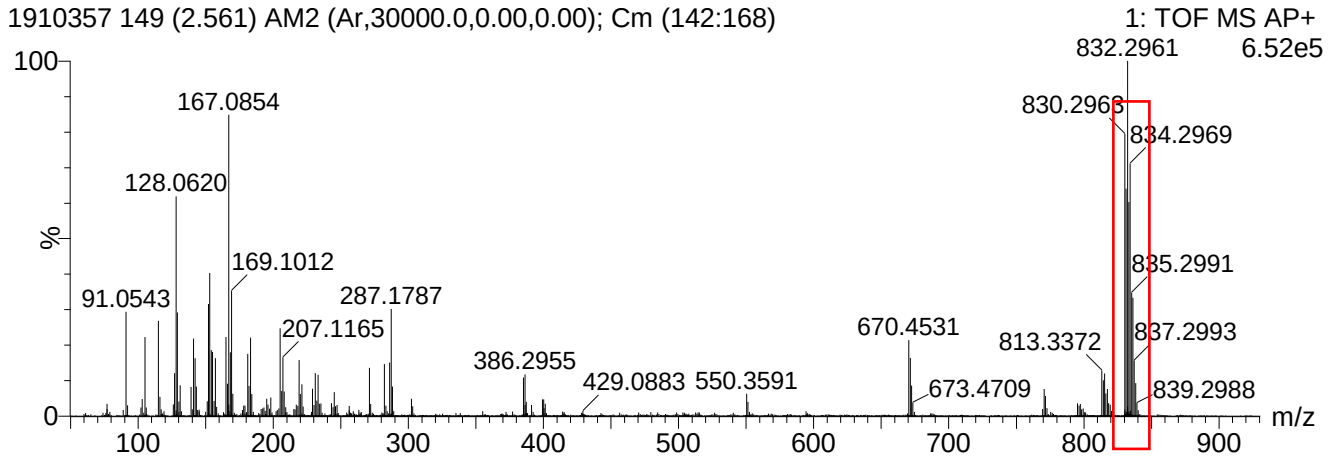

Figure S77. iASAP-MS mass spectrum of **3f** (Sampling cone 20V)

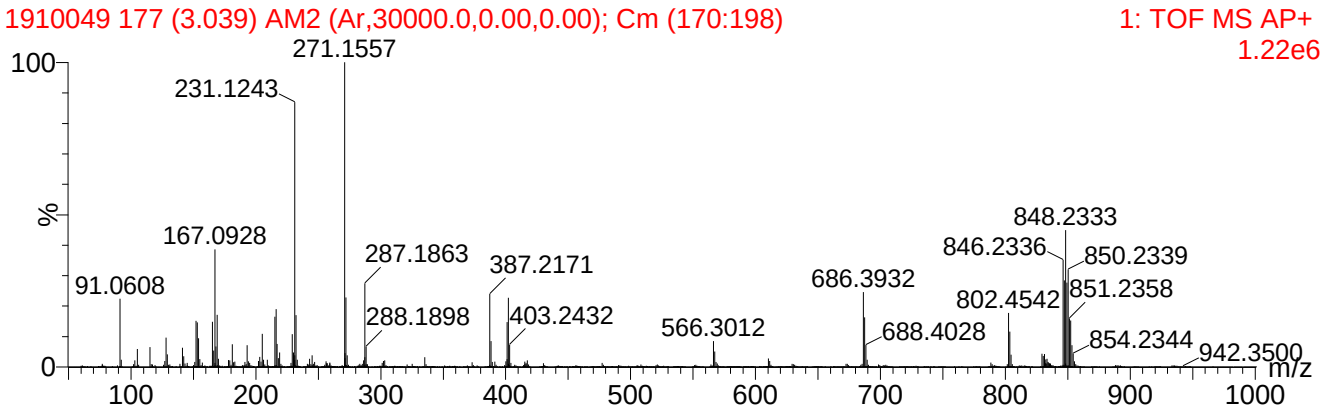

Figure S78. iASAP-MS mass spectrum of **3g** (Sampling cone 40V)

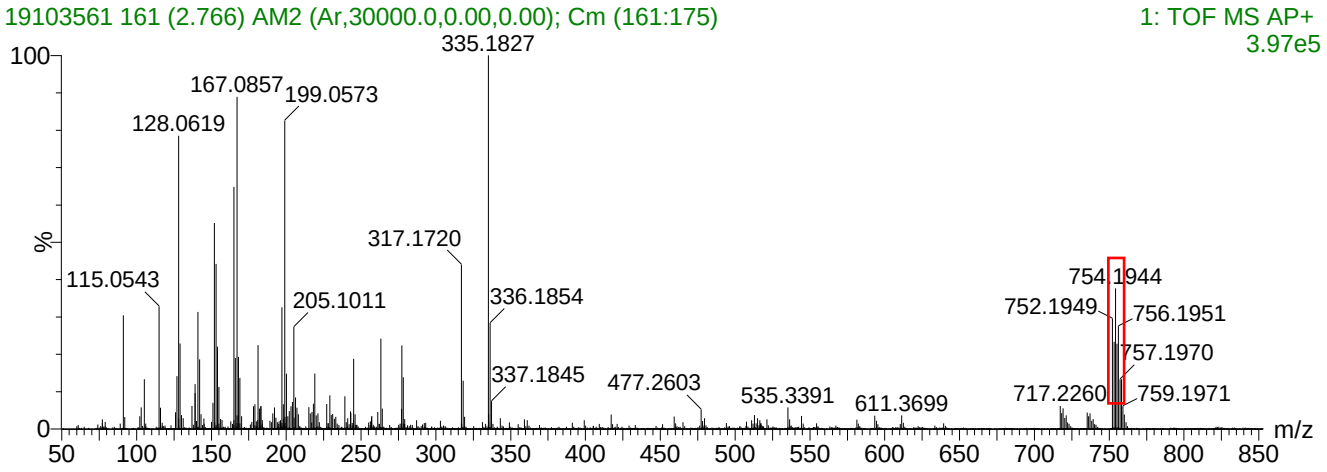

Figure S79. iASAP-MS mass spectrum of **3i** (Sampling cone 40V)

Proligand crystal structures:

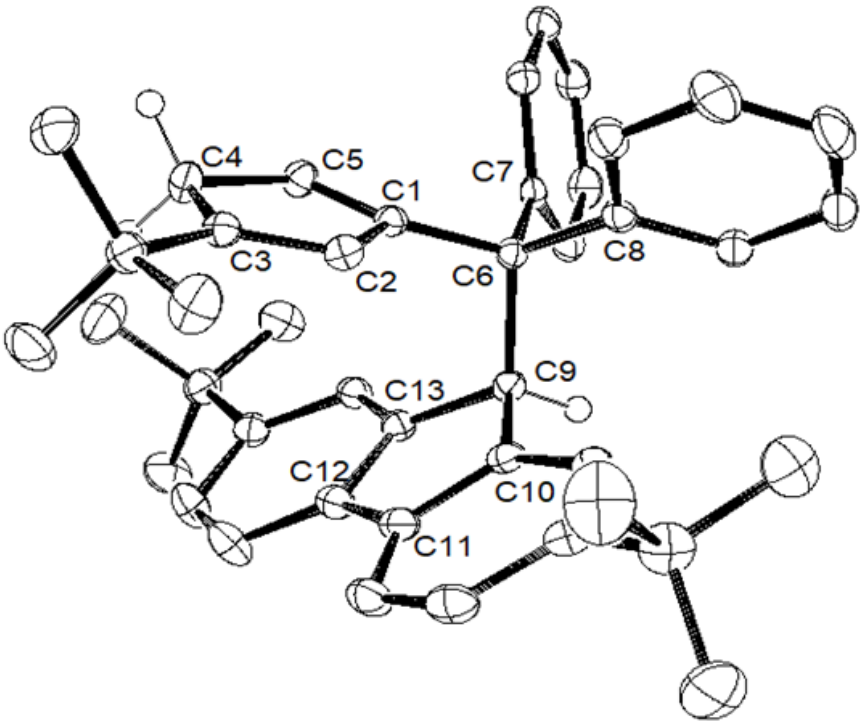

Figure S80. Crystal structure of proligand **2a** (H atoms except those of the five membered rings are omitted for clarity; ellipsoids drawn at the 50% probability level)

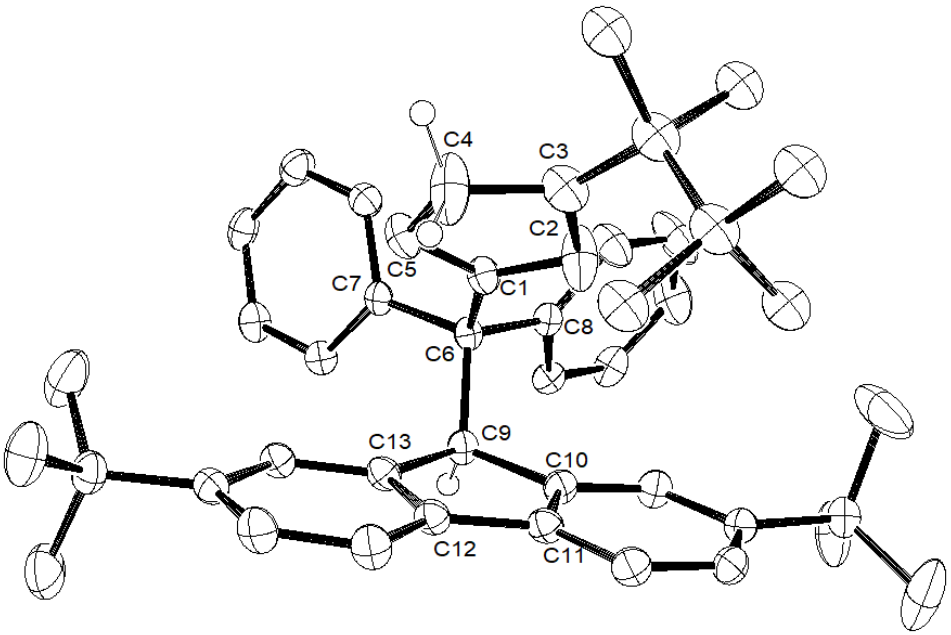

Figure S81. Crystal structure of proligand **2b** (H atoms except those of the five membered rings are omitted for clarity; ellipsoids drawn at the 50% probability level)

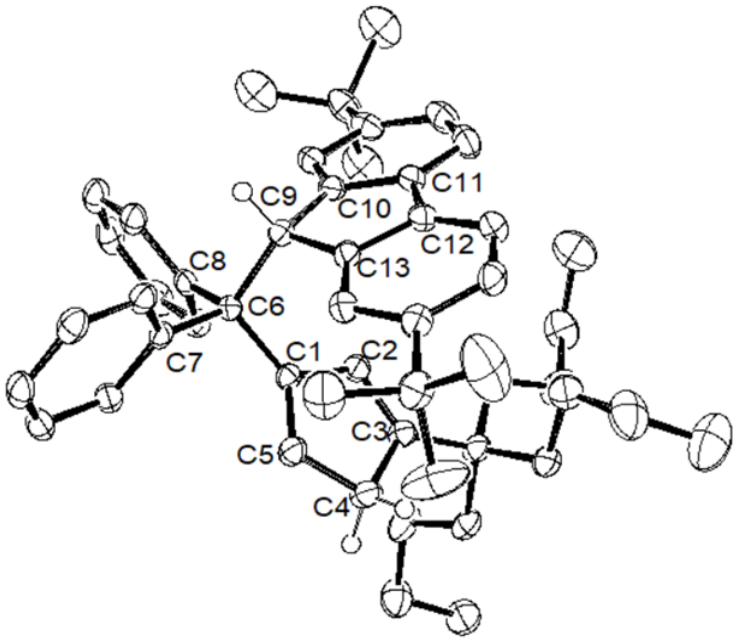

Figure S82. Crystal structure of proligand **2c** (H atoms except those of the five membered rings are omitted for clarity; ellipsoids drawn at the 50% probability level)

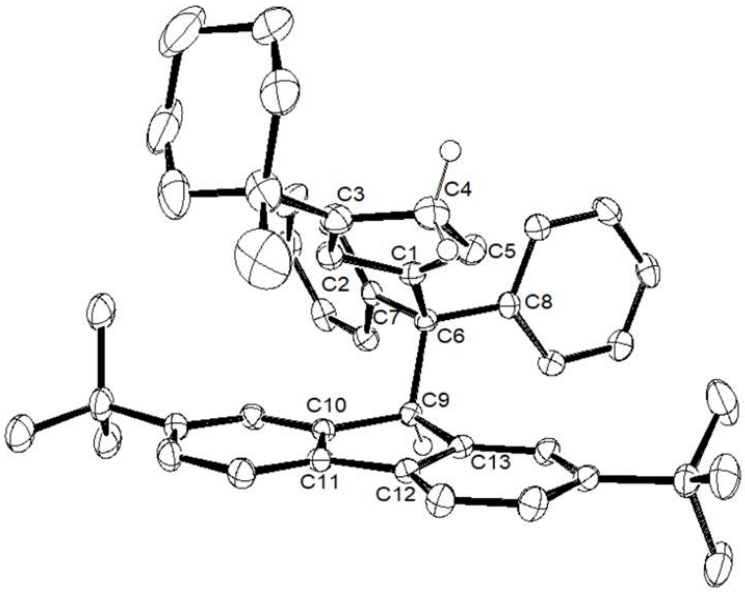

Figure S83. Crystal structure of proligand **2e** (H atoms except those of the five membered rings are omitted for clarity; ellipsoids drawn at the 50% probability level)

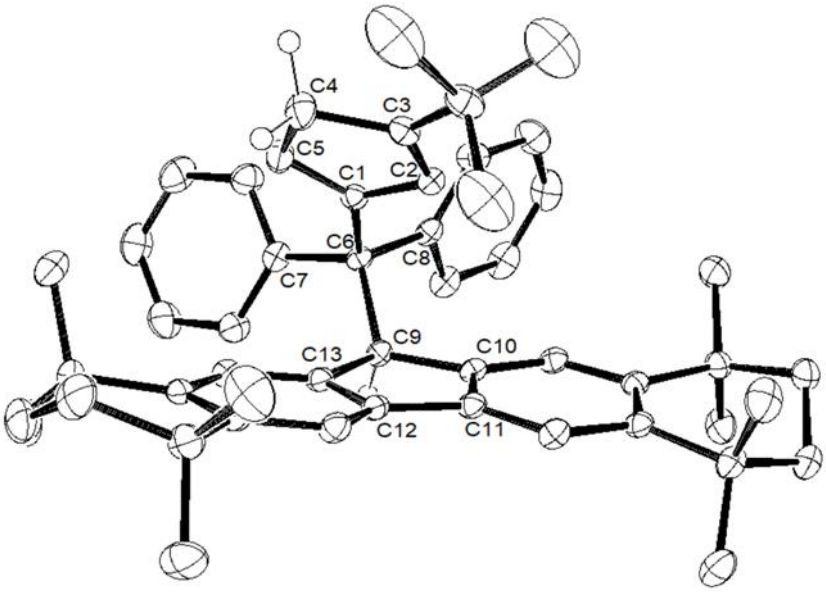

Figure S84. Crystal structure of proligand **2f** (H atoms except those of the five membered rings are omitted for clarity; ellipsoids drawn at the 50% probability level)

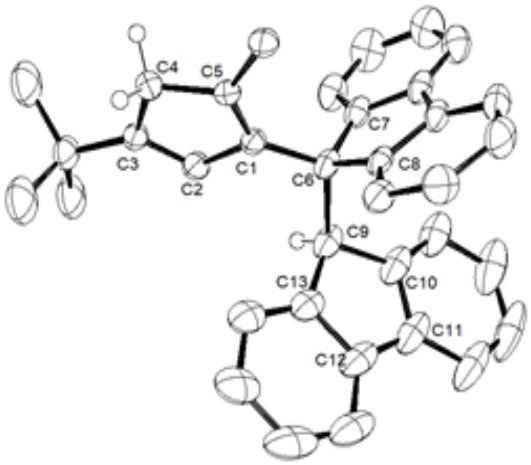

Figure S85. Crystal structure of proligand **2i** (H atoms except those of the five membered rings are omitted for clarity; ellipsoids drawn at the 50% probability level)

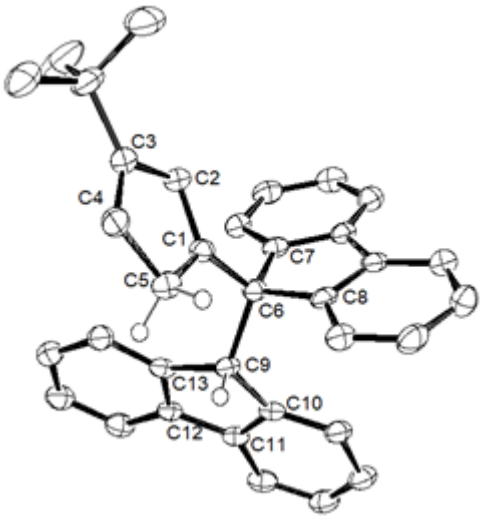

Figure S86. Crystal structure of proligand **2j** (H atoms except those of the five membered rings are omitted for clarity; ellipsoids drawn at the 50% probability level)

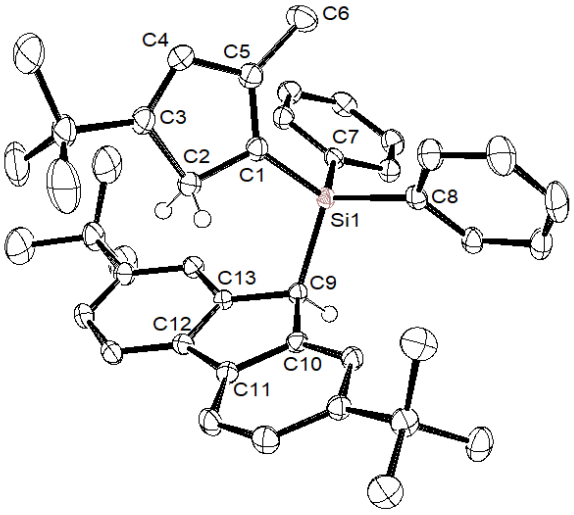

Figure S87. Crystal structure of proligand **2k** (H atoms except those of the five membered rings are omitted for clarity; ellipsoids drawn at the 50% probability level)

Table S1. Summary of crystal refinement data for **2a-c, 2e.**

	2a	**2b**	**2c**	**2e**
Emp. Formula	$C_{43}H_{48}$	$C_{46}H_{54}$	$C_{52}H_{57}$	$C_{46}H_{52}$
Formula wt (g.mol^{-1})	564.81	606.89	681.97	604.87
Temp (K)	150(2)	150	150(2)	150
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
cryst syst	triclinic	monoclinic	triclinic	monoclinic
space group	P $\bar{1}$	P $2_1/n$	P $\bar{1}$	P $2_1/c$
a (Å)	a = 11.4951(9)	15.9925(13)	11.9034(14)	14.2534(18) Å
b (Å)	b = 12.4130(10)	10.2789(8) Å	12.7457(17)	9.9731(11) Å
c (Å)	c = 13.1338(10)	22.0123(14) Å	15.433(2)	25.364(3) Å
α (deg)	α = 103.991(3)	90 °	99.243(5)	90 °
β (deg)	β = 102.779(3)	97.392(3) °	102.407(4)	98.429(5) °
γ (deg)	γ = 104.644(3)	90 °	107.119(4)	90 °
Volume (Å^3)	1677.9(2)	3588.4(5) Å3	2121.7(5)	3566.5(8)
Z	2	4	2	4
Density (calcd, g.cm^{-3})	1.118	1.123	1.067	1.126
Abs coeff (mm^{-1})	0.063	0.063	0.060	0.063
Crystal size	0.560 x 0.480 x 0.410 mm	0.540 x 0.360 x 0.290	0.600 x 0.590 x 0.450	0.550 x 0.270 x 0.160
no. of rflns collected	38100 /	37617	48327	51126
no. of indpt rflns	7582 [R(int)a = 0.0491]	8120 [R(int)a = 0.0472]	9423 [R(int)a = 0.0828]	8190 [R(int)a = 0.0578]
Max. and min. transmission	0.975, 0.892	0.982, 0.809	0.973, 0.737	0.990, 0.901
No. of data/ restraints/ parameters	7582 / 0 / 397	8120 / 0 / 404	9423 / 3 / 473	8190 / 1 / 438
Final R indices [I>2σ]	R1c = 0.0441, wR2d = 0.1051	R1c = 0.0616, wR2d = 0.1481	R1c = 0.0760, wR2d = 0.1930	R1c = 0.0593, wR2d = 0.1324
R indices (all data)	R1c = 0.0608, wR2d = 0.1145	R1c = 0.0786, wR2d = 0.1597	R1c = 0.1132, wR2d = 0.2184	R1c = 0.0743, wR2d = 0.1413
^{b}S (Goodness-of-fit)	1.040	1.008	1.064	1.054
Largest diff. peak and hole (e$^-$.Å^{-3})	0.295 and -0.217	0.385 and -0.476	0.720 and -0.387	0.280 and -0.384

Table S1 (continued). Summary of crystal refinement data for 2f, 2i-k.

	2f	2i	2j	2k
Emp. Formula	$C_{52}H_{62}$	$C_{43}H_{50}Si$	$C_{36}H_{32}$	$C_{35}H_{30}$
Formula wt (g.mol^{-1})	687.01	594.92	464.61	450.59
Temp (K)	150(2)	150(2)	150	150
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
cryst syst	monoclinic	triclinic	monoclinic	monoclinic
space group	P $2_1/n$	P $\bar{1}$	P $2_1/c$	P $2_1/c$
a (Å)	13.8368(9)	10.4218(11)	12.1627(19)	9.798(3)
b (Å)	13.9699(8)	12.5110(12)	22.247(4)	7.244(2)
c (Å)	22.3164(15)	14.8341(16)	9.9020(14)	34.496(14)
α (deg)	90	103.433(4)	90	90
β (deg)	104.210(2)	106.097(4)	102.334(5)	95.352(17)
γ (deg)	90	96.180(4)	90	90
Volume (Å^3)	4181.7(5)	1776.6(3)	2617.4(7)	2437.9(14)
Z	4	2	4	4
Density (calcd, g.cm^{-3})	1.091	1.112	1.179	1.228
Abs coeff (mm^{-1})	0.061	0.094	0.066	0.069
Crystal size	0.600 x 0.280 x 0.190	0.580 x 0.400 x 0.360	0.580 x 0.340 x 0.300	0.300 x 0.160 x 0.050
no. of rflns collected	59362	40641	25603	17226
no. of indpt rflns	9494 [R(int)a = 0.0728]	8066 [R(int)a = 0.0398]	5939 [R(int)a = 0.0529]	5519 [R(int)a = 0.0875]
Max. and min. transmission	0.988, 0.918	0.967, 0.900	0.980, 0.797	0.997, 0.572
No. of data/ restraints/ parameters	9494 / 0 / 482	8066 / 0 / 402	5939 / 0 / 325	5519 / 0 / 319
Final R indices [I>2σ]	R1c = 0.0590, wR2d = 0.1342	R1c = 0.0484, wR2d = 0.1398	R1c = 0.1092, wR2d = 0.2483	R1c = 0.0796, wR2d = 0.1816
R indices (all data)	R1c = 0.0845, wR2d = 0.1500	R1c = 0.0586, wR2d = 0.1519	R1c = 0.1293, wR2d = 0.2592	R1c = 0.1320, wR2d = 0.2105
[b]S (Goodness-of-fit)	1.026	0.939	1.109	1.028
Largest diff. peak and hole (e$^-$.Å^{-3})	0.354 and -0.517	0.562 and -0.629	0.683 and -0.517	0.330 and -0.389

Crystal structures of complexes:

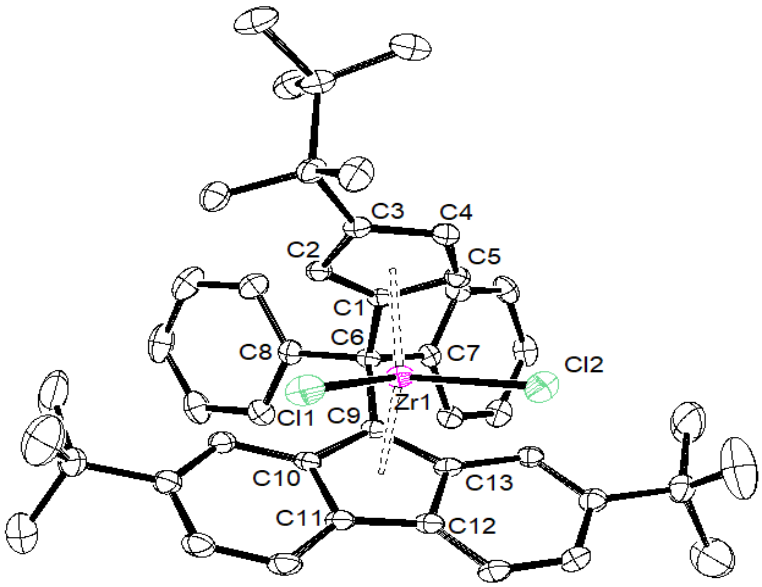

Figure S88. Crystal structure of complex **3b** (H atoms except those of the five membered rings are omitted for clarity; ellipsoids drawn at the 50% probability level)

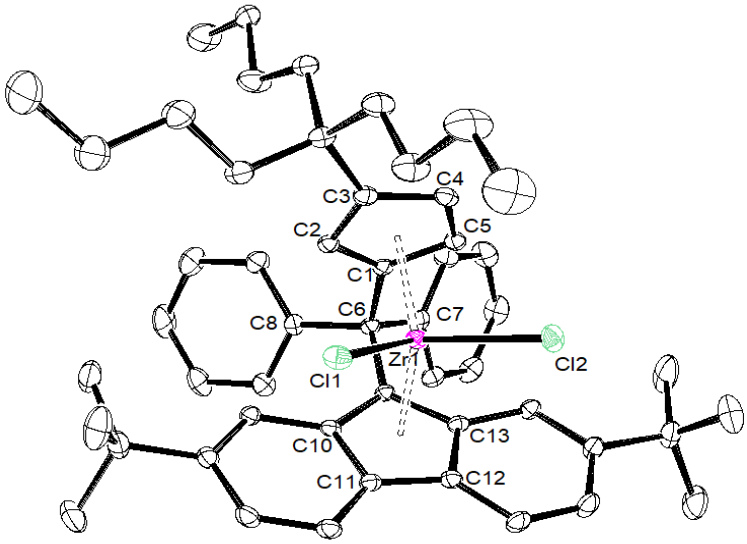

Figure S89. Crystal structure of complex (**3c.CH_2Cl_2**) (H atoms except those of the five membered rings and CH_2Cl_2 are omitted for clarity; ellipsoids drawn at the 50% probability level)

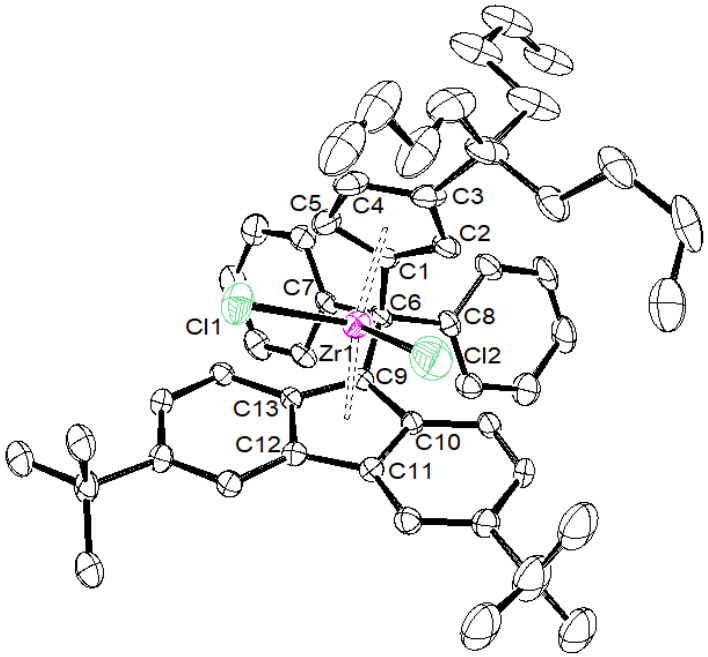

Figure S90. Crystal structure of complex **3d** (H atoms except those of the five membered rings are omitted for clarity; ellipsoids drawn at the 50% probability level)

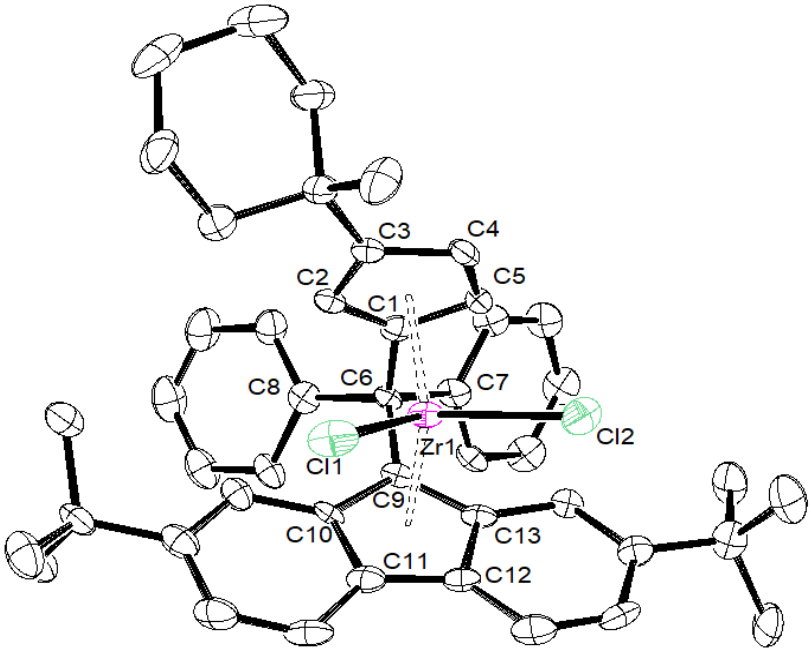

Figure S91. Crystal structure of complex **3e** (H atoms except those of the five membered rings are omitted for clarity; ellipsoids drawn at the 50% probability level)

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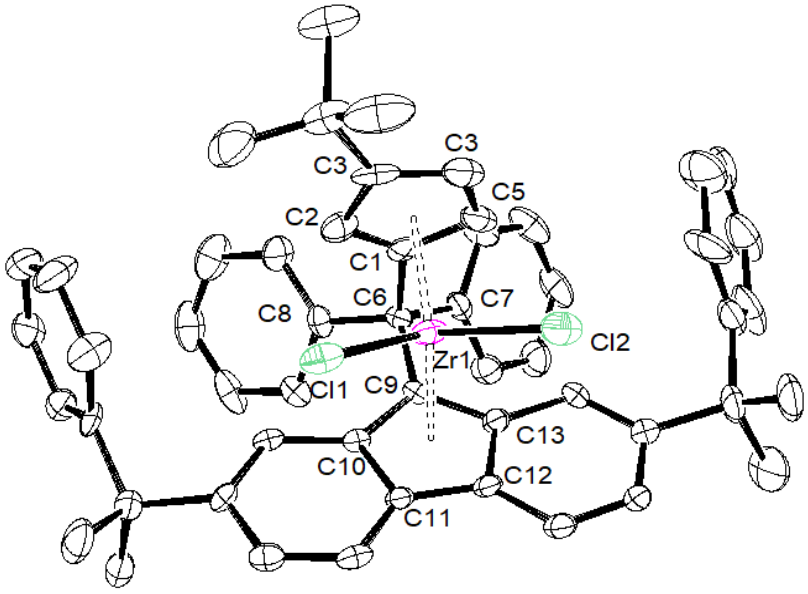

Figure S92. Crystal structure of complex **3g** (H atoms except those of the five membered rings are omitted for clarity; ellipsoids drawn at the 50% probability level**)**

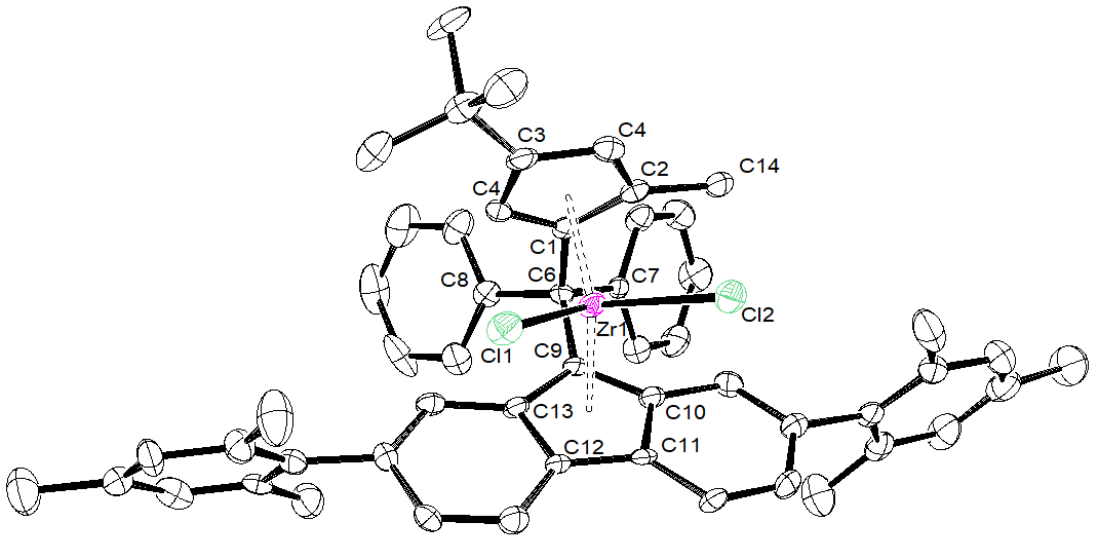

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Figure S93. Crystal structure of complexes **3h.(C_6H_{14})$_{0.5}$** (H atoms except those of the five membered rings and hexane are omitted for clarity; ellipsoids drawn at the 50% probability level)

Table S2. Crystal refinement data for complexes **3b-e, g, h.**

	3b	**3c.CH_2Cl_2**	**3d**	**3e**	**3g**	**3h.$(C_6H_{14})_{0.5}$**
Emp. Formula	$C_{46}H_{52}Cl_2Zr$	$C_{53}H_{66}Cl_4Zr$	$C_{52}H_{64}Cl_2Zr$	$C_{46}H_{50}Cl_2Zr$	$C_{53}H_{50}Cl_2Zr$	$C_{57}H_{59}Cl_2Zr$
Formula wt ($g.mol^{-1}$)	766.99	936.07	851.15	764.98	849.05	906.16
Temp (K)	150(2)	150(2)	150(2)	150	150(2)	150(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
cryst syst	triclinic	triclinic	triclinic	triclinic	monoclinic	monoclinic
space group	P $\bar{1}$	P $\bar{1}$	P $\bar{1}$	P $\bar{1}$	P $2_1/c$	P $2_1/c$
a (Å)	10.3181(7)	11.2674(9)	11.7049(12)	14.403(2)	17.015(2)	15.8497(8)
b (Å)	12.9034(9)	13.9717(12)	14.8848(14)	14.830(2)	13.0978(17)	32.7640(17)
c (Å)	16.0657(13)	17.5036(16)	16.8154(17)	19.387(3)	21.227(2)	20.2613(10)
α (deg)	73.916(3)	90.887(3)	115.290(3)	76.012(5)	90	90
β (deg)	88.413(3)	108.682(3)	96.794(4)	74.990(5)	102.993(5)	113.137(2)
γ (deg)	78.747(3)	108.336(3)	105.509(4)	75.358(6)	90	90
Volume ($Å^3$)	2014.9(3)	2457.0(4)	2459.8(4)	3800.4(10)	4609.6	9675.4(9)
Z	2	2	2	4	4	8
Density (*calcd*, $g.cm^{-3}$)	1.264	1.265	1.149	1.337	1.223	1.244
Abs coeff (mm^{-1})	0.435	0.475	0.363	0.462	0.388	0.374
Crystal size	0.470 x 0.240 x 0.070	0.560 x 0.440 x 0.150	0.240 x 0.150 x 0.070	0.330 x 0.110 x 0.060	0.570 x 0.420 x 0.180	0.310 x 0.140 x 0.060
no. of rflns collected	48218	58491	54855	17364	40845	98593
no. of indpt rflns	9239 [R(int)a = 0.0530]	11273 [R(int)a = 0.0492]	10967 [R(int)a= 0.0970]	17364 [R(int)a = ?]	10047 [R(int)a = 0.1247]	22060 [R(int)a = 0.1425]
Max. and min. transmission	0.970, 0.834	0.931, 0.747	0.975, 0.867	0.973, 0.773	0.933, 0.680	0.978, 0.739
No. of data/ restraints/ parameters	9239 / 0 / 453	11273 / 0 / 532	10967 / 0 / 466	17364 / 60 / 923	10047 / 20 / 518	22060 / 12 / 1073
Final R indices [I>2σ]	R1c = 0.0342 wR2d = 0.0871	R1c = 0.0333 wR2d = 0.0846	R1c = 0.0735 wR2d = 0.1828	R1c = 0.1099 wR2d = 0.2859	R1c = 0.0838 wR2d = 0.1812	R1c = 0.1127 wR2d = 0.2188
R indices (all data)	R1c = 0.0429 wR2d = 0.0931	R1c = 0.0378 wR2d = 0.0888	R1c = 0.1047 wR2d = 0.2033	R1c = 0.1477 wR2d = 0.3111	R1c = 0.1276 wR2d = 0.2041	R1c = 0.1747 wR2d = 0.2436
[b]S (Goodness-of-fit)	1.086	1.095	1.012	1.057	1.023	1.117
Largest diff. peak and hole ($e^-.Å^{-3}$)	1.170 and -0.725	0.861 and -1.018	1.922 and -1.279	3.946 and -2.014	1.764 and -1.632	1.605 and -1.039

POLYMERIZATION DATA

Table S3. Propylene polymerization data for precatalysts **3a-i**. [a]

Entries	Cat	[Zr] (µmol·L^{-1})	T_{Pol} ($T_{pol\ max}$)	Productivity (kgPP·mol·h^{-1})	$\mathbf{T_m}$ [b] (°C)	T_{crys} [b] (°C)	M_n [c] [× 10^3]	M_w/M_n [c]	[*m*]^4 [d]	1,2− insert [d] (% mol)	2,1-insert [d] (% mol)	1,3-insert [d] (% mol)	Term *n*Bu [d] *(%mol)*
1	**3a**	10.0	60	25 500	135.2	101.7	16.2	2.2	86.1	99.3	< 0.1	0.3	0.3
2			60	35 500	135.8	102.6	11.4	2.1	86.5	99.3	< 0.1	0.3	0.2
3	**3b**	10.0	60	4 800	141.0	106.3	-	-	88.6	99.2	0.2	0.3	0.3
4			60	5 300	141.1	106.2	15.4	2.1	88.6	99.2	0.2	0.4	0.3
5	**3c**	10.0	60(63)	29	122.8	101.9	-	-	-	-	-	-	-
6			60(64)	40	134.3	106.0	-	-	-	-	-	-	-
7			60(65)	241	137.1	106.2	-	-	-	-	-	-	-
8	**3d**	10.0	60(64)	-	-	-	-	-	-	-	-	-	-
9			60(64)	-	-	-	-	-	-	-	-	-	-
10	**3k**	10.0	60(64)	1870	131.7	119.8	13.4	2.2	31.9	99.6	< 0.02	< 0.01	< 0.02
11			60(64)	3070	130.3	119.2	12.7	2.1	29.1	99.5	< 0.02	<0.01	< 0.02
12			100(102)	-	-	-	3.4	1.4	-	-	-	-	-
13	**3e**	10.0	60(76)	33 600	132.9	100.3	13.7	2.1	81.6	99.3	< 0.02	0.3	0.04
14			60(76)	34 130	132.8	99.9	13.6	2.1	80.6	99.3	< 0.02	0.3	0.04
15		5.0	60(67)	16 700	139.8	104.5	21.7	2.1	86.2	99.5	<<0.1	0.3	≈ 0.1
16			60(68)	18 000	139.0	103.8	23.9	2.1	85.4	99.4	<<0.1	0.2	0.1
17	**3f**	10.0	60(66)	13 300	148.4	112.6	17.6	2.3	91.7	99.6	< 0.02	0.1	0.1
18			60(67)	13 000	148.7	114.5	17.4	2.3	91.5	99.6	< 0.02	0.1	0.1
19	**3g**	10.0	60(66)	12 700	136.1	102.3	21.0	2.3	82.9	99.4	0.1	0.3	<0.1

20			60(67)	13 300	134.9	101.2	19.6	2.3	82.8	99.3	0.1	0.3	0.1
21	**3h**	10	60(68)	17 200	-	-	24.9	2.1	54.0	99.7	<0.02	0.1<x<0.2	<0.02
22		10	60(67)	15 300	-	-	24.9	2.1	54.8	99.7	<0.02	0.1<x<0.2	<0.02

[a] Polymerization conditions: 300 mL-high pressure glass reactor; solvent: toluene, 150 mL; P (propylene) = 5 bars; T_{pol} = 60 °C, [Al]/[Zr] =5000. [b] Determined by DSC. [c] Determined by GPC. [d] Determined by ^{13}C NMR.

Table S4. Pentad distributions (%) and the corresponding probability parameters[20] determined experimentally, and those simulated using a three-parameter model.[a]

	{Cp/Flu}-2		**3h**		**3k**	
	Exp [b]	Calc	Exp [c]	Calc	Exp [d]	Calc
M_n [$\times 10^3$]	50.8	-	24.9	-	13.4	-
1,2 ins	99.8	-	99.7	-	99.6	-
[*mmmm*]	82.0	81.7	54.0	54.1	31.9	32.7
[*mmmr*]	7.2	6.7	14.5	14.2	16.1	16.6
[*rmmr*]	0.0	0.1	1.6	1.0	3.0	2.6
[*mmrr*]	7.2	6.7	14.4	14.2	18.5	16.6
[*mrmm*] +[*rmrr*]	0.0	0.6	3.5	4.2	8.6	10.3
[*mrmr*]	0.0	0.3	1.4	2.1	3.8	5.1
[*rrrr*]	0.0	0.1	1.2	1.0	3.0	2.6
[*mrrr*]	0.0	0.3	1.8	2.1	5.0	5.1
[*mrrm*]	3.6	3.4	7.6	7.1	9.9	8.3
total	100.0	100.0	100.0	100.0	100.0	100.0
RMS [e]	-	0.35	-	0.45	-	1.15
a		0.9604		0.8842		0.7994
b		0.9606		0.8842		0.7994
k		0.9610		0.9999		0.9746

[a] ***a*** and ***b*** – the probabilities of stereoselective insertion on the open and crowded metallocene faces, respectively; ***k*** – the probability of site epimerization. [b] from Table 2, entry 1. [c] From Table 2, entry 10. [d] From Table 2, entry 11. [e] $RMS = ((\Sigma(I_{obs} - I_{calc})^2/9)^{0.5}$.

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