Electronic Supplementary Information (ESI)

Improved Synthesis and Coordination Behaviour of 1*H*-1,2,3-Triazole-4,5-dithiolates ($tazdt^{2-}$) with Ni^{II}, Pd^{II}, Pt^{II} and Co^{III}

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1. Crystallographic details

Single crystals suitable for X-ray diffraction analysis were selected in Fomblin YR-1800 perfluoropolyether oil (Alfa Aesar) at ambient temperature and mounted on a glass fiber. During the measurement, the samples were cooled to 123(2) K. Diffraction data were collected on a Bruker D8 QUEST diffractometer and a Bruker Kappa Apex II diffractometer using graphite monochromated Mo-Kα radiation. Structure solutions were found by direct methods (SHELXS-97 or SHELXS-2013) and were refined by full-matrix least-squares procedures on F 2 (SHELXL-2013). [48–50] All non-hydrogen atoms were anisotropically refined unless stated otherwise. Hydrogen atoms were included at calculated positions with fixed thermal parameters unless stated otherwise. The unit cell of **2a** contains two compounds.

1.1 Tables with crystallographic details

Table S1. Crystallographic details for **1d**, **1g** and **2a**.

	1d	**1g**	**2a**
empirical formula	$C_{17}H_{17}N_3S$	$C_{15}H_{14}N_4S$	$C_{24}H_{23}N_3OS_2$
M_W / g·mol^{-1}	295.39	282.36	433.57
colour, habit	colourless, block	colourless, needle	colourless, block
crystal system	monoclinic	triclinic	triclinic
space group	$P2_1/n$	P-1	P-1
a / Å	8.6188(6)	5.4374(2)	9.2078(14)
b / Å	13.9311(9)	7.9201(3)	15.456(2)
c / Å	12.5260(8)	16.6052(7)	16.206(3)
α / °	90	100.0720(10)	105.442(5)
β / °	93.247(2)	94.982(2)	91.649(5)
γ / °	90	100.5940(10)	100.910(5)
V / Å^3	1501.57(17)	686.83(5)	2175.3(6)
Z	4	2	4
$\rho_{calcd.}$ / g·cm^{-1}	1.307	1.365	1.324
μ / mm^{-1}	0.212	0.231	0.266
$\lambda_{MoK\alpha}$ / Å	0.71073	0.71073	0.71073
T / K	123(2)	123(2)	123(2)
collected refl.	23731	37434	8857
unique refl.	3995	5598	8857
refl. $I > 2\sigma(I)$	3554	4461	7231
R_{int}	0.0458	0.0551	0.0828
parameters/restraints	192/0	185/84	543/0
R_1 [$I > 2\sigma$(I)]	0.0347	0.0431	0.0455
wR_2 (all data)	0.0976	0.1142	0.1486
GooF	1.024	1.034	1.148
resid. density [eÅ^{-3}]	0.404/-0.240	0.743/–0.351	0.369/-0.459
CCDC	2254519	2254521	2254518

Table S2. Crystallographic details for **6**, **7** and **8**.

	6	**7**	**8**
empirical formula	$C_{37}H_{35}N_3NiO_2P_2S_2$	$C_{37}H_{35}N_3O_2P_2PdS_2$, 2 ($CH_2Cl_2$)	$C_{37}H_{35}N_3O_2P_2PtS_2$ 2 (CH_2Cl_2)
M_W / g·mol^{-1}	738.45	955.66	1044.68
colour, habit	green, block	pink, needle	colourless, needle
crystal system	orthorhombic	triclinic	triclinic
space group	*P*na2$_1$	*P*-1	*P*-1
a / Å	30.228(2)	10.9325(12)	10.9254(9)
b / Å	10.7866(6)	12.2470(13)	12.2865(10)
c / Å	20.9818(14)	17.1602(19)	17.2093(14)
α / °	90	69.284(4)	69.349(3)
β / °	90	86.515(4)	86.005(3)
γ / °	90	69.487(4)	69.187(3)
V / Å^3	6841.3(7)	2007.5(4)	2016.5(3)
Z	8	2	2
$\rho_{calcd.}$ / g·cm^{-1}	1.434	1.582	1.721
μ / mm^{-1}	0.821	0.952	3.967
$\lambda_{MoK\alpha}$ / Å	0.71073	0.71073	0.71073
T / K	123(2)	123(2)	123(2)
collected refl.	183008	64890	139330
unique refl.	14201	9692	10723
refl. $I > 2\sigma(I)$	11824	6645	8974
R_{int}	0.0911	0.1042	0.0881
parameters/restraints	852/1	523/348	524/404
R_1 [$I > 2\sigma$(I)]	0.0336	0.0567	0.0844
wR_2 (all data)	0.0655	0.1571	0.0908
GooF	1.039	1.018	1.031
resid. density [eÅ^{-3}]	0.332/–0.295	1.146/-1.294	1.906/-1.258
CCDC	2254526	2254523	2254525

Table S3. Crystallographic details for **9a**, **9b** and **12**.

	9a	**12**	**9b**
empirical formula	$C_{46}H_{39}N_3OP_2PtS_2$, CH_2Cl_2	$C_{56}H_{50}N_6O_2P_2PtS_2$	$C_{47}H_{41}N_3O_2P_2PtS_2$, 4.79 ($CH_2Cl_2$)
M_W / g·mol^{-1}	1055.88	1160.17	1407.86
colour, habit	yellow, block	yellow, block	yellow, block
crystal system	orthorhombic	triclinic	monoclinic
space group	*Pna*2$_1$	*P*-1	*P* 2$_1$/*n*
a / Å	17.9918(11)	9.7191(11)	15.3012(15)
b / Å	10.8057(7)	10.1845(12)	24.847(2)
c / Å	22.3396(12)	13.1721(15)	16.9747(17)
α / °	90	83.038(3)	90
β / °	90	72.919(3)	115.5(10)
γ / °	90	87.192(3)	90
V / Å^3	4343.1(5)	1237.0(2)	5827.5(10)
Z	4	1	4
$\rho_{calcd.}$ / g·cm^{-1}	1.615	1.557	1.605
μ / mm^{-1}	3.564	3.035	3.015
$\lambda_{MoK\alpha}$ / Å	0.71073	0.71703	0.71703
T / K	123(2)	123(2)	123(2)
collected refl.	207808	19009	99628
unique refl.	14328	7827	16994
refl. $I > 2\sigma(I)$	13456	7570	14429
R_{int}	0.0488	0.0389	0.0406
parameters/restraints	552/11	335/369	690/165
R_1 [$I > 2\sigma$(I)]	0.0407	0.0354	0.0405
wR_2 (all data)	0.0412	0.0782	0.1052
GooF	1.087	1.037	1.097
resid. density [eÅ^{-3}]	1.744/-0.499	1.662/-0.726	3.341/-1.550
CCDC	2254527	2254520	2254524

Table S4. Crystallographic details for **10** and **11.**

	10	**11**
empirical formula	$C_{24}H_{36}Co_6N_3S_4Si_2$	$C_{60}H_{60}Co_4I_4N_{12}O_4S_4$
M_W / g·mol^{-1}	710.87	1884.76
colour, habit	black, block	blue, block
crystal system	monoclinic	monoclinic
space group	$P2_1/c$	$C2/c$
a / Å	15.2846(15)	12.8062(11)
b / Å	11.3042(11)	25.291(2)
c / Å	9.5102(9)	21.6517(19)
α / °	90	90
β / °	104.713(3)	105.197(2)
γ / °	90	90
V / Å^3	1589.3(3)	6767.4(10)
Z	2	4
$\rho_{calcd.}$ / g·cm^{-1}	1.485	1.850
μ / mm^{-1}	1.407	2.966
$\lambda_{MoK\alpha}$ / Å	0.71073	0.71703
T / K	123(2)	123(2)
collected refl.	13214	66373
unique refl.	2806	11746
refl. $I > 2\sigma(I)$	2024	10144
R_{int}	0.0868	0.0329
parameters/restraints	265/406	399/0
R_1 [$I > 2\sigma$(I)]	0.0527	0.0255
wR_2 (all data)	0.1142	0.0637
GooF	1.084	1.052
resid. density [eÅ^{-3}]	0.482/-0.429	1.139/-0.547
CCDC	2254517	2254522

1.2 Molecular structures of 1d, 1g, 2a, 9a and 9b.

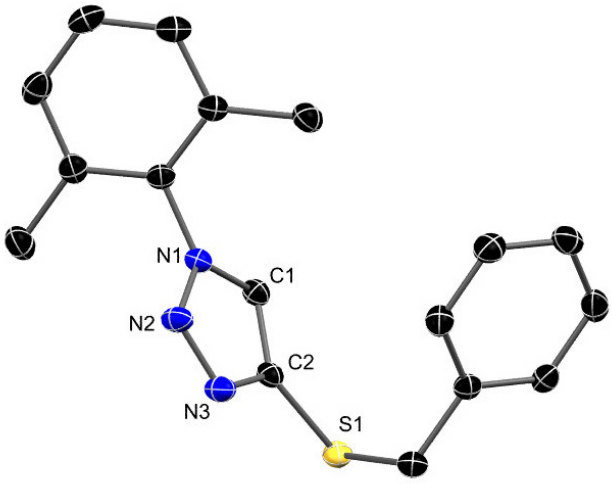


Figure S1. Molecular structure of **1d** in the crystal. Thermal ellipsoids are drawn at 50 % probability. Hydrogen atoms were omitted of clarity. Selected bond lengths [Å], angles [°] and torsion angles [°]: C2-S1 1.751(1), C1-C2 1.377(2), C1-C2-S1 130.42(9).

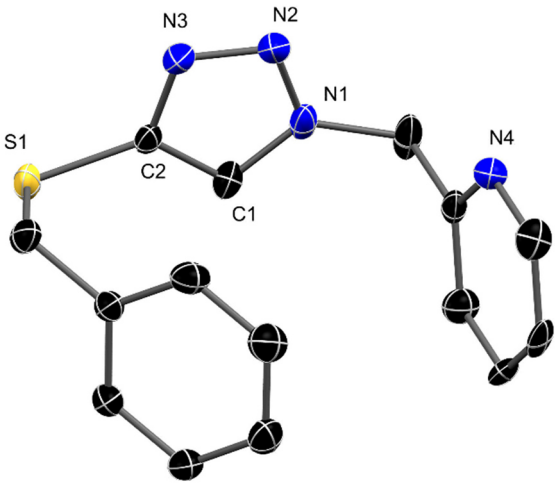


Figure S2. Molecular structure of **1g** in the crystal. Thermal ellipsoids are drawn at 50 % probability. Hydrogen atoms were omitted of clarity. Selected bond lengths [Å], angles [°] and torsion angles [°]: C2-S1 1.745(1), C1-C2 1.370(1), C1-C2-S1 127.78(9).

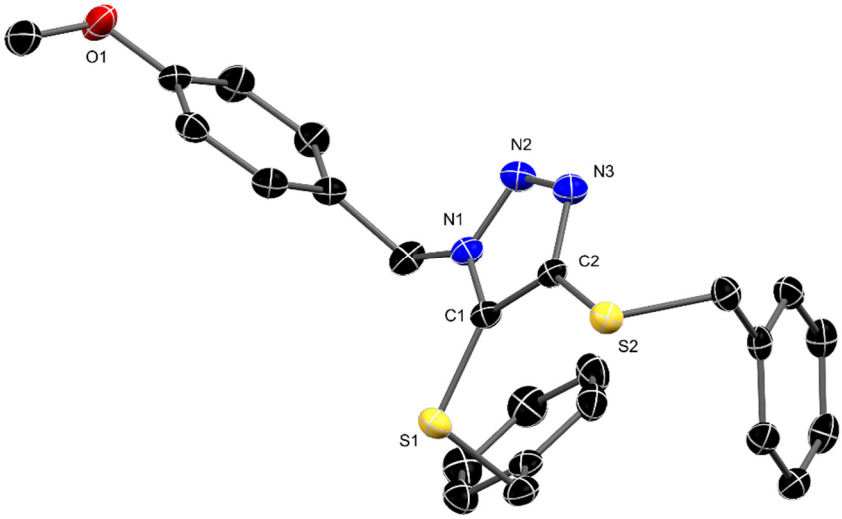


Figure S3. Molecular structure of **2a** in the crystal. Thermal ellipsoids are drawn at 50 % probability. Hydrogen atoms were omitted of clarity. Selected bond lengths [Å], angles [°] and torsion angles [°]: C1-C2 1.375(3), C2-S2 1.746(2), C1-S1 1.743(2), C2-C1-S1 131.1(2), C1-C2-S2 127.5(1), S1-C1-C2-S2 -1.4(3).

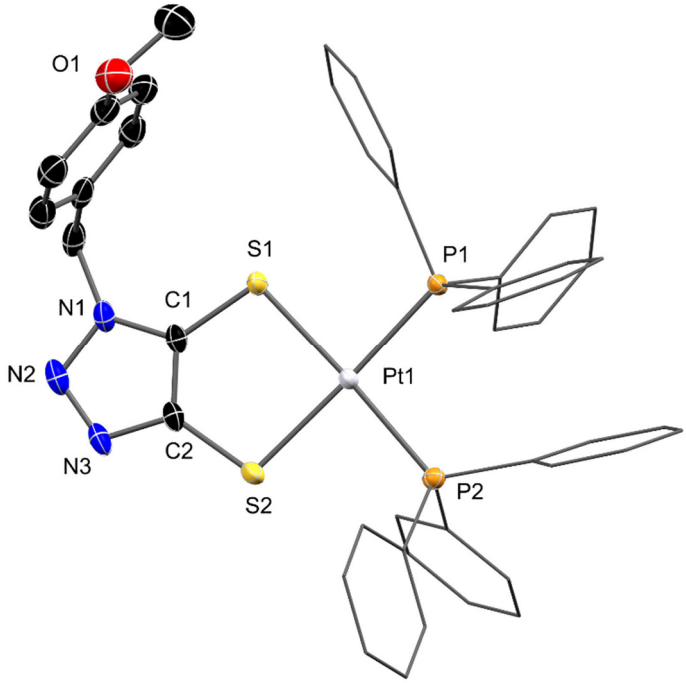


Figure S4. Molecular structure of **9a** in the crystal. Thermal ellipsoids are drawn at 50 % probability. Hydrogen atoms and solvent molecules were omitted of clarity. Phenyl substituents were displayed in wireframe. Selected bond lengths [Å], angles [°] and torsion angles [°]: C1-C2 1.373(3), C2-S2 1.739(3), C1-S1 1.724(3), S1-Pt1 2.3344(7), S2-Pt1 2.3487(7), Pt1-P1 2.853(7), Pt1-P2 2.944(7), S1-C1-C2 126.4(2), S2-C2-C1 122.6(2), S1-Pt1-S2 90.82(2), P1-Pt1-P2 96.19(2), S1-C1-C2-S2 3.1(3).

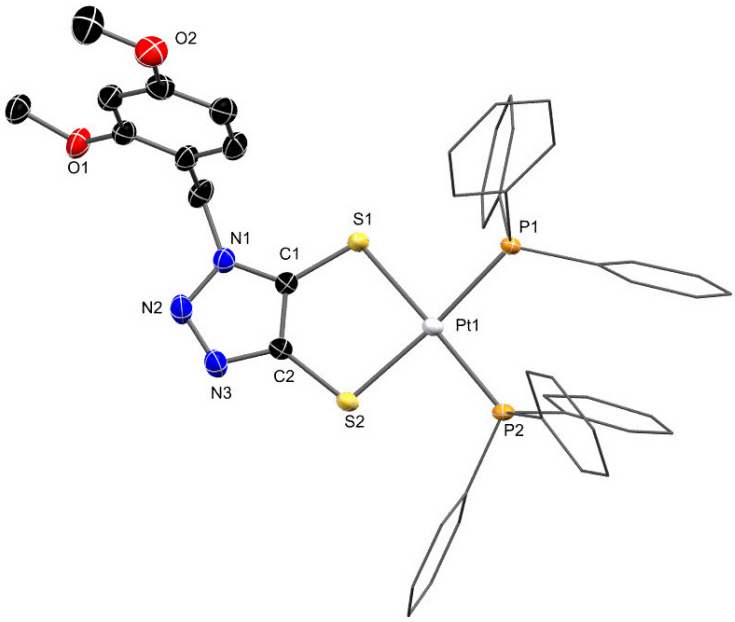


Figure S5. Molecular structure of **9b** in the crystal. Thermal ellipsoids are drawn at 50 % probability. Hydrogen atoms and disordered solvent molecules were omitted of clarity. Phenyl substituents were displayed in wireframe. Selected bond lengths [Å], angles [°] and torsion angles [°]: C1-C2 1.369(6), C2-S2 1.752(3), C1-S1 1.725(5), S2-Pt1 2.336(1), S1-Pt1 2.3536(9), P2-Pt1 2.2771(9), P1-Pt 12.298(1), S2-C2-C1 123.5(3), S1-C1-C2 125.9(3), S1-Pt1-S2 91.08(4), P1-Pt1-P2 96.71(4), S1-C1-C2-S2 2.4(5).

2. Experimental section

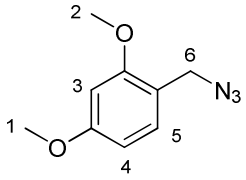
Materials

If not described all operations were carried out in an atmosphere of dry argon using Schlenk and glove box techniques. Solvents were dried and saturated with argon by standard methods and freshly distilled prior to use. 2,4-dimethoxybenzyl chloride, 2-(trimethylsilyl)ethyl bromide, benzylsulfanylacetylene, 4-methoxybenzyl azide, 2,6-dimethylphenyl azide, benzyl azide, 3,4-dimethoxybenzyl azide, 2-methylpyridine azide, 1-(4-methoxybenzyl)-1*H*-1,2,3-triazole, [(dppe)$NiCl_2$], [(dppe)$PdCl_2$], [(dppe)$PtCl_2$], [$(PPh_3)_2PtCl_2$] and [$(\eta^5\text{-}C_5H_5)Co(CO)I_2$] were prepared according to literature methods. [25,51–63] All other chemicals (at least of reaction grade quality) were obtained from commercial source and used as received. Analytical thin layer chromatography was performed on silica gel (TLC Silica gel 60 F_{254}) coated aluminium plates. Column chromatography was performed using silica gel 60 (pore size 0.063 – 0.2 mm) purchased from Merck as the column stationary phase.

Measurements

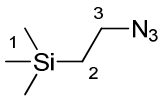
One- and two-dimensional NMR spectra were recorded at 298 K with a BrukerAvance 250, 300 or 500 MHz spectrometer, respectively. In ^1H and $^{13}C\{^1H\}$ NMR the chemical shifts (δ in ppm) were internally referenced to the solvent residual peak (^1H NMR: 7.26 ppm in $CDCl_3$, 5.32 ppm in CD_2Cl_2, 1.72 and 3.58 ppm in THF-D_8, 2.05 ppm in acetone-D_6 and 2.74 ppm in DMF-D_7; ^{13}C NMR: 77.0 ppm in $CDCl_3$, 53.8 ppm in CD_2Cl_2, 25.3 and 67.2 ppm in THF-D_8, 29.8 and 206.3 ppm in acetone-D_6 and 30.1 ppm in DMF-D_7). For the $^{31}P\{^1H\}$ NMR and ^{29}Si NMR respectively were used H_3PO_4 (85 %) and $Si(CH_3)_4$ as external standard (0 ppm). UV/Vis-spectroscopy was carried out with a Agilent technologies Cary 60 UV-Vis spectrometer. Elemental analyses were performed with a Thermo Finnigan Flash EA 1112 Series. Mass spectrometry by Electrospray Ionization was obtained with an Agilent 6210 Time-of-Flight LC/MS or with a Thermo Electron Finnigan MAT 95-XP spectrometer. Cyclic voltammetry was performed using a Princeton Applied Research VersaSTAT 3. A three electrode arrangement with a glassy carbon working electrode, a platinum wire counter electrode and an Ag/AgCl in CH_3CN reference electrode and 0.1 M or 0.3 M *n*-Bu_4NPF_6 as supporting electrolyte was employed. The Fc/Fc+ redox couple was used as internal standard.

Synthesis of 2,4-dimethoxybenzyl azide



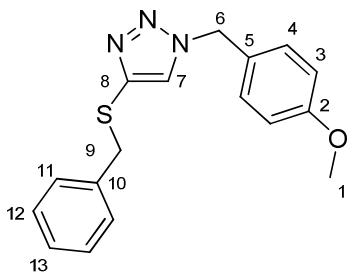
In a 250 ml Schlenk flask 6.085 g (32.487 mmol) 2,4-dimethoxybenzyl chloride are dissolved in 80 ml abs. DMF with 2.534 g (39.116 mmol) sodium azide. After stirring for 2 d at room temperature, the reaction solution is diluted with 70 ml ice water and extracted five times with 50 ml Et_2O. Finally, the organic fractions are washed twice with 50 ml H_2O and once with 50 ml BRINE, dried over Na_2SO_4, filtered, washed with Et_2O and dried in vacuo. Yield, 4.533 g (72 %). ^{1}H NMR ($CDCl_3$, δ, ppm, 300 MHz, 298 K): 7.15 (dd, $^3J_{H,H}$ = 7.93 Hz, $J_{H,H}$ = 0.42 Hz, 1 H, *H*-4), 6.51-6.49 (m, 1 H, *H*-5), 6.48-6.46 (m, 1 H, *H*-3), 4.29 (s, 2 H, *H*-6), 3.84 (s, 3 H, *H*-1), 3.82 (s, 3 H, *H*-2). IR (THF, $\tilde{\nu}$, cm^{-1}): 2996 (s), 2917 (s), 2825 (s), 2097 (s, N_3), 1687 (s), 1613 (s), 1507 (s), 1295 (s), 1212 (s), 1156 (s), 1036 (s), 908 (s), 810 (s).

Synthesis of 2-(trimethylsilyl)ethyl azide



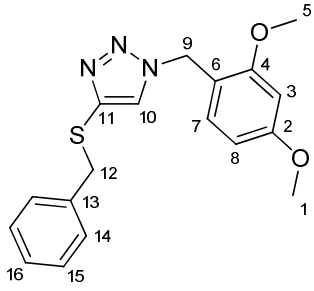
In a 100 ml Schlenk flask 3.593 g (19.834 mmol) 2-(trimethylsilylethyl) bromide are dissolved in 60 ml abs. DMF with 1.934 g (29.752 mmol) NaN_3. The greyish suspension is stirred for 2 d at room temperature. To purify, the reaction solution is diluted with 200 ml H_2O and extracted six times with 50 ml *n*-hexane. The organic phase is washed with 50 ml H_2O and 50 ml BRINE, dried over Na_2SO_4, filtered and washed with *n*-hexane. The solvent is removed in the rotary evaporator; Yield, 1.456 g (50 %). ^{1}H NMR ($CDCl_3$, δ, ppm, 300 MHz, 298 K): 3.32-3.26 (m, 2 H, *H*-3), 0.99-0.93 (m, 2 H, *H*-2), 0.05 (s, 9 H, *H*-1). ^{13}C NMR ($CDCl_3$, δ, ppm, 75 MHz, 298 K): 48.2 (*C*-3), 16.4 (*C*-2), -1.6 (*C*-1). ^{29}Si NMR ($CDCl_3$, δ, ppm, 60 MHz, 298 K): 1.0-0.1 (m, $^3J_{Si,H}$ = 3.4 Hz, *Si*-TMS). IR (Et_2O, $\tilde{\nu}$, cm^{-1}): 2992 (s), 2928 (s), 2842 (s), 2104 (s, N_3), 1502 (m), 1391 (s), 1251 (s), 1088 (s), 835 (m), 660 (m).

*Synthesis of 1-(4-methoxybenzyl)-4-(benzylsulfanyl)-1H-1,2,3-triazole (**1a**)*



1.010 g (6.194 mmol) 4-methoxybenzyl azide, 1.388 g (9.364 mmol) benzylsulfanylacetylene, 0.308 g (1.233 mmol) $CuSO_4 \cdot 5\ H_2O$, 1.287 g (9.312 mmol) K_2CO_3 and 0.491 g (2.478 mmol) sodium ascorbate are solved in 50 ml THF and 5 ml H_2O. The suspension is heated for 1 d at 60 °C. Purification is carried out chromatographically with 4:1 *n*-hexane:EtOAc and later 1:2 *n*-hexane:EtOAc. Crystals suitable for X-ray structural analysis are obtained at -40 °C from a saturated Et_2O solution; Yield, 1.870 g (97 %). Anal. Calcd. for $C_{17}H_{17}N_3SO$: C, 65.67; H, 5.50; N, 13.49; S, 10.30 %. Found: C, 65.94; H, 5.62; N, 13.35; S, 10.67 %. ^{1}H NMR ($CDCl_3$, δ, ppm, 500 MHz, 298 K): 7.18-7.16 (m, 3 H, *H*-12, *H*-13), 7.12-7.10 (m, 4 H, *H*-4, *H*-11), 7.05 (s, 1 H, *H*-7), 6.86 (d, $^3J_{H,H}$ = 8.75 Hz, 2 H, *H*-3), 5.34 (s, 2 H, *H*-6), 4.03 (s, 2 H, *H*-9), 3.79 (s, 3 H, *H*-1). ^{13}C NMR ($CDCl_3$, δ, ppm, 125 MHz, 298 K): 160.0 (*C*-2), 139.2 (*C*-8), 137.7 (*C*-10), 129.6 (*C*-4), 129.0 (*C*-11), 128.4 (*C*-12), 127.2 (*C*-13), 126.3 (*C*-5), 126.1 (*C*-7), 114.5 (*C*-3), 55.4 (*C*-1), 53.8 (*C*-6), 39.7 (*C*-9). MS (ESI-TOF, 9:1 MeOH:H_2O with 0.1 % HCOOH, m/z): 312 (*M*+H$^+$), 334 (*M*+Na$^+$). IR (CH_2Cl_2, $\tilde{\nu}$, cm^{-1}): 3146 (w), 2937 (w), 2839 (w), 1612 (m), 1515 (s), 1453 (m), 1305 (m), 1249 (s), 1177 (m), 1044 (m), 823 (w), 758 (s), 729 (s).

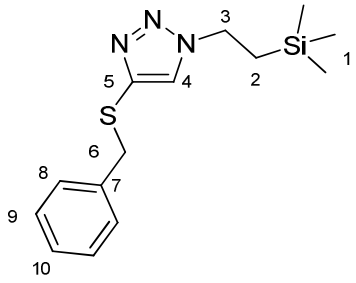
*Synthesis of 1-(2,4-dimethoxybenzyl)-4-(benzylsulfanyl)-1H-1,2,3-triazole (**1b**)*



4.510 g (23.357 mmol) 2,4-dimethoxybenzyl azide, 4.863 g (32.809 mmol) benzylsulfanylacetylene, 1.166 g (4.670 mmol) $CuSO_4 \cdot 5\ H_2O$, 4.522 g (32.719 mmol) K_2CO_3 and 1.847 g (9.323 mmol) sodium ascorbate are solved in 160 ml THF and 32 ml H_2O. The suspension is heated for 4 d at 75 °C. Purification is carried out chromatographically with 4:1 *n*-hexane:EtOAc; Yield, 6.605 g (83 %). Anal. Calcd. for $C_{18}H_{19}N_3SO_2$: C, 63.32; H, 5.61; N, 12.31; S, 9.39 %. Found: C, 62.92; H, 5.63; N, 11.93; S, 9.16 %. ^{1}H NMR (acetone-D_6, δ, ppm, 300 MHz, 298 K): 7.54 (s, 1 H, *H*-10), 7.22-7.18 (m, 5 H, *H*-14, *H*-15, *H*-16), 7.12 (d, $^3J_{H,H}$ = 8.30 Hz, 1 H, *H*-7), 6.60 (d, $J_{H,H}$ = 2.40 Hz, 1 H, *H*-3), 6.52 (dd, $^3J_{H,H}$ = 8.30 Hz, $J_{H,H}$ = 2.40 Hz, 1 H, *H*-8), 5.41 (s, 2 H, *H*-9), 4.07 (s, 2 H, *H*-12), 3.84 (s, 3 H, *H*-1), 3.81 (s, 3 H, *H*-5). ^{13}C NMR ($CDCl_3$, δ, ppm, 150 MHz, 298 K): 161.8 (*C*-2), 158.4 (*C*-4), 138.7 (*C*-11), 137.9 (*C*-13), 131.5 (*C*-7), 129.1 (*C*-16), 128.4 (*C*-14), 127.2 (*C*-15), 126.4 (*C*-10),

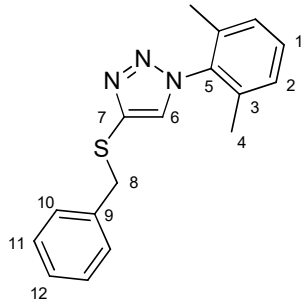
115.2 (*C*-6), 104.6 (*C*-3), 98.8 (*C*-8), 55.6 (*C*-1), 55.6 (*C*-5), 49.1 (*C*-9), 39.9 (*C*-12). MS (ESI-TOF, 9:1 MeOH:H_2O with 0.1 % HCOOH, m/z): 342 (M+H^+), 364 (M+Na^+). IR (CH_2Cl_2, $\tilde{\nu}$, cm^{-1}): 2965 (w), 2838 (w), 1615 (s), 1508 (s), 1466 (m), 1296 (m), 1210 (s), 1159 (s), 1042 (s), 840 (m).

*Synthesis of 1-(2-(trimethylsilyl)ethyl)-4-(methoxybenzyl)-4-(benzylsulfanyl)-1H-1,2,3-triazole (**1c**)*



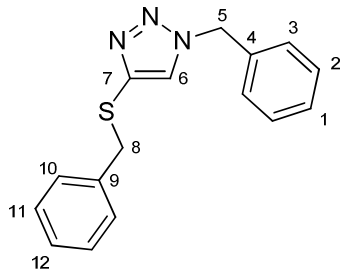
0.540 g (3.774 mmol) 2-(trimethylsilyl)ethyl azide, 0.795 g (5.364 mmol) benzylsulfanylacetylene, 0.195 g (0.781 mmol) $CuSO_4 \cdot 5\ H_2O$, 0.732 g (5.300 mmol) K_2CO_3 and 0.300 g (1.514 mmol) sodium ascorbate are solved in 50 ml THF and 5 ml H_2O. The suspension is heated for 5 d at 75 °C. Purification is carried out chromatographically with 4:1 *n*-hexane:EtOAc; Yield, 1.032 g (93 %). ^{1}H NMR ($CDCl_3$, δ, ppm, 300 MHz, 298 K): 7.28–7.18 (m, 6 H, *H*-10, *H*-9, *H*-8, *H*-4), 4.34-4.28 (m, 2 H, *H*-3), 4.09 (s, 2 H, *H*-6), 1.18-1.12 (m, 2 H, *H*-2), 0.06 (s, 9 H, *H*-1). ^{13}C NMR ($CDCl_3$, δ, ppm, 75 MHz, 298 K): 138.9 (*C*-5), 137.9 (*C*-7), 129.1 (*C*-8), 128.5 (*C*-10), 127.4 (*C*-9), 125.4 (*C*-4), 47.4 (*C*-3), 39.9 (*C*-6), 18.9 (*C*-2), 1.7 (*C*-1). ^{29}Si NMR ($CDCl_3$, δ, ppm, 60 MHz, 298 K): 1.0-0.1 (m, *Si*-TMS).

*Synthesis of 1-(2,6-dimethylphenyl)-4-(benzylsulfanyl)-1H-1,2,3-triazole (**1d**)*



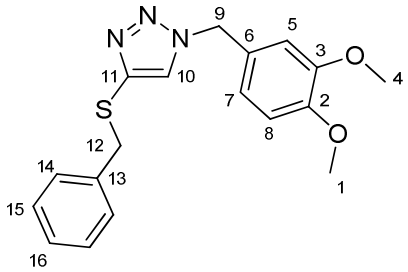
0.995 g (6.760 mmol) 2,6-dimethylphenyl azide, 1.512 g (10.201 mmol) benzylsulfanylacetylene, 0.342 g (1.369 mmol) $CuSO_4 \cdot 5\ H_2O$, 1.409 g (10.195 mmol) K_2CO_3 and 0.539 g (2.721 mmol) sodium ascorbate are solved in 120 ml THF and 26 ml H_2O. The suspension is heated for 4 d at 60 °C. Purification is carried out chromatographically with 4:1 *n*-hexane:EtOAc. Crystals suitable for X-ray structural analysis are obtained at -40 °C from a saturated Et_2O solution; Yield, 0.981 g (49 %). Anal. Calcd. for $C_{17}H_{17}N_3S$: C, 69.12; H, 5.80; N, 14.22; S, 10.85 %. Found: C, 69.08; H, 5.79; N, 14.09; 11.44 %. ^{1}H NMR ($CDCl_3$, δ, ppm, 300 MHz, 298 K): 7.31-7.26 (m, 1 H, *H*-1), 7.24-7.18 (m, 5 H, *H*-Ph), 7.22 (s, 1 H, *H*-6), 7.15-7.13 (m, 2 H, *H*-2), 4.14 (s, 2 H, *H*-8), 1.89 (s, 6 H, *H*-4). ^{13}C NMR ($CDCl_3$, δ, ppm, 75 MHz, 298 K): 138.4 (*C*-7), 137.8 (*C*-9), 135.6 (*C*-5), 135.4 (*C*-3), 130.2 (*C*-1), 129.1 (*C*-10), 128.5 (*C*-11), 128.5 (*C*-2), 128.5 (*C*-6), 127.3 (*C*-12), 39.8 (*C*-8), 17.4 (*C*-4). MS (ESI-TOF, 98:02 MeOH:H_2O with 0.1 % HCOOH, m/z): 296 (M+H^+), 318 (M+Na^+). IR (CH_2Cl_2, $\tilde{\nu}$, cm^{-1}): 3146 (w); 3033 (w), 2928 (w), 1473 (m), 1260 (s), 1035 (m), 778 (m), 754 (s), 719 (s).

*Synthesis of 1-(benzyl)-4-(benzylsulfanyl)-1H-1,2,3-triazole (**1e**)*



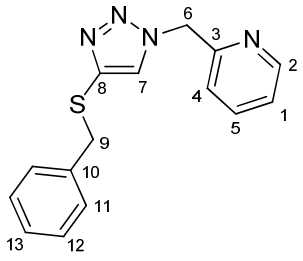
0.800 g (5.991 mmol) benzyl azide, 1.245 g (8.400 mmol) benzylsulfanylacetylene, 0.300 g (1.201 mmol) $CuSO_4 \cdot 5\ H_2O$, 1.063 g (7.691 mmol) K_2CO_3 and 0.477 g (2.408 mmol) sodium ascorbate are solved in 65 ml THF and 15 ml H_2O. The suspension is heated for 30 h at 65 °C. Purification is carried out chromatographically with 3:1 *n*-hexane:EtOAc; Yield, 1.352 g (80 %). ^{1}H NMR ($CDCl_3$, δ, ppm, 500 MHz, 298 K): 7.36-7.35 (m, 3 H, *H*-Ph), 7.18-7.15 (m, 5 H, *H*-Ph), 7.13-7.11 (m, 2 H, *H*-Ph) 7.07 (s, 1 H, *H*-6), 5.43 (s, 2 H, *H*-5), 4.05 (s, 2 H, *H*-8). ^{13}C NMR ($CDCl_3$, δ, ppm, 75 MHz, 298 K): 139.4 (*C*-7), 137.8 (*C*-9), 134.4 (*C*-4), 129.2 (*C*-10), 129.1 (*C*-2), 128.4 (*C*-11), 128.1 (*C*-3), 127.2 (*C*-12), 127.1 (*C*-1), 126.4 (*C*-6), 54.4 (*C*-5), 39.7 (*C*-8). IR (CH_2Cl_2, $\tilde{\nu}$, cm^{-1}): 3146 (w), 3067 (w), 3034 (w), 1496 (m), 1455 (m), 1271 (s), 1042 (m), 758 (s), 739 (s), 708 (s).

*Synthesis of 1-(3,4-dimethoxybenzyl)-4-(benzylsulfanyl)-1H-1,2,3-triazole (**1f**)*



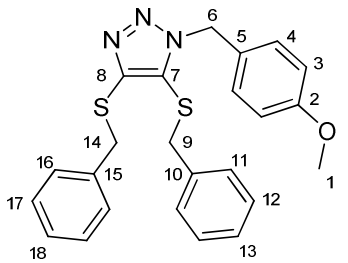
2.049 g (10.612 mmol) 3,4-dimethoxybenzyl azide, 2.364 g (15.949 mmol) benzylsulfanylacetylene, 0.532 g (2.131 mmol) $CuSO_4 \cdot 5\ H_2O$, 2.204 g (15.947 mmol) K_2CO_3 and 0.841 g (4.245 mmol) sodium ascorbate are solved in 100 ml THF and 15 ml H_2O. The suspension is heated for 2 d at 65 °C. Purification is carried out chromatographically with 1:1 *n*-hexane:EtOAc; Yield, 1.643 g (36 %). Anal. Calcd. for $C_{18}H_{19}N_3SO_2$: C, 63.32; H, 5.61; N, 12.31; S, 9.39 %. Found: C, 63.28; H, 5.80; N, 12.08; 9.52 %. ^{1}H NMR (acetone-D_6, δ, ppm, 300 MHz, 298 K): 7.68 (s, 1 H, *H*-10), 7.23-7.16 (m, 5 H, H-Ph), 6.98 (d, $J_{H,H}$ = 2.0 Hz, 1 H, *H*-5), 6.93 (d, $^3J_{H,H}$ = 8.2 Hz, 1 H, *H*-8), 6.84 (dd, $^3J_{H,H}$ = 8.2 Hz, $J_{H,H}$ = 2.0, 1 H, *H*-7), 5.47 (s, 2 H, *H*-9), 4.08 (s, 2 H, *H*-12), 3.81 (s, 3 H, *H*-1), 3.78 (s, 3 H, *H*-4). ^{13}C NMR (acetone-D_6, δ, ppm, 75 MHz, 298 K): 150.6 (*C*-2), 150.6 (*C*-3), 139.7 (*C*-11), 139.0 (*C*-13), 129.7 (*C*-14), 129.1 (*C*-15), 129.0 (*C*-6), 127.9 (*C*-16), 126.9 (*C*-10), 121.6 (*C*-7), 113.0 (*C*-5), 112.8 (*C*-8), 56.2 (*C*-4), 56.2 (*C*-1), 54.3 (*C*-9), 39.8 (*C*-12). MS (ESI-TOF, 9:1 MeOH:H_2O with 0.1 % HCOOH, m/z): 342 (M+H^+), 364 (M+Na^+). IR (CH_2Cl_2, $\tilde{\nu}$, cm^{-1}): 3146 (w), 3011 (w), 2940 (w), 2840 (w), 1594 (w), 1518 (s), 1464 (m), 1266 (s), 1242 (m), 1159 (m), 1027 (m), 758 (s), 711 (s).

*Synthesis of 1-(2-(methylpyridine))-4-(benzylsulfanyl)-1H-1,2,3-triazole (**1g**)*



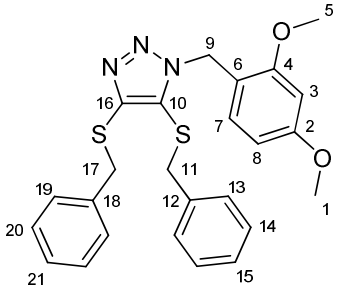
1.007 g (7.512 mmol) 2-methylpyridine azide, 1.664 g (11.227 mmol) benzylsulfanylacetylene, 0.375 g (1.502 mmol) $CuSO_4 \cdot 5\ H_2O$, 1.552 g (11.230 mmol) K_2CO_3 and 0.592 g (2.988 mmol) sodium ascorbate are solved in 40 ml THF and 6 ml H_2O. The suspension is heated for 1 d at 65 °C. Purification is carried out chromatographically with 1:1 *n*-hexane:EtOAc. Crystals suitable for X-ray structural analysis are obtained at -40 °C from a saturated Et_2O solution; Yield, 1.928 g (91 %). ^{1}H NMR ($CDCl_3$, δ, ppm, 300 MHz, 298 K): 8.56 (dd, $^3J_{H,H}$ = 4.88 Hz, $J_{H,H}$ = 1.03 Hz, 1 H, *H*-2), 7.66 (dt, $^3J_{H,H}$ = 7.66 Hz, $J_{H,H}$ = 1.78 Hz, 1 H, *H*-1), 7.34 (s, 1 H, *H*-7), 7.25 (dd, $^3J_{H,H}$ = 4.88 Hz, $J_{H,H}$ = 1.03 Hz, 1 H, *H*-5), 7.18–7.13 (m, 5 H, *H*-Ph), 7.05 (td, $^3J_{H,H}$ = 7.66 Hz, $J_{H,H}$ = 1.01 Hz, 1 H, *H*-4), 5.55 (s, 2 H, *H*-6), 4.07 (s, 2 H, *H*-9). ^{13}C NMR ($CDCl_3$, δ, ppm, 75 MHz, 298 K): 154.3 (*C*-3), 149.9 (*C*-2), 139.6 (*C*-8), 137.7 (*C*-10), 137.4 (*C*-1), 129.1 (*C*-11), 128.4 (*C*-13), 127.2 (*C*-12), 126.8 (*C*-7), 123.5 (*C*-5), 122.3 (*C*-4), 55.8 (*C*-6), 39.7 (*C*-9).

*Synthesis of 1-(4-methoxybenzyl)-4,5-bis(benzylsulfanyl)-1H-1,2,3-triazole (**2a**)*



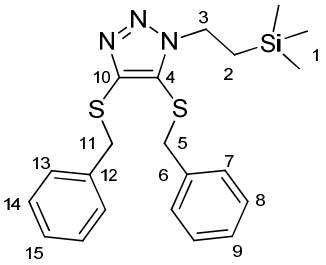
At -78 °C, 0.200 g (0.642 mmol) of **1a** is mixed with 0.34 ml (2.5 M) *n*-BuLi solution, 0.026 g (0.102 mmol) of elemental sulfur and 0.1 ml (0.842 mmol) of benzyl bromide in 40 ml THF. The purification is carried out chromatographically with 3:1 *n*-hexane/EtOAc. Crystals suitable for X-ray structural analysis are obtained at -40 °C from a saturated Et_2O solution; Yield, 0.212 g (76 %). Anal. Calcd. for $C_{24}H_{23}N_3S_2O$: C, 66.48; H, 5.35; N, 9.69; S, 14.79 %. Found: C, 66.91; H, 5.22; N, 9.43; S, 14.63 %. ^{1}H NMR ($CDCl_3$, δ, ppm, 250 MHz, 298 K): 7.28-7.19 (m, 10 H, H-Ph), 7.08 (d, $^3J_{H,H}$ = 8.80 Hz, 2 H, H-4), 6.83 (d, $^3J_{H,H}$ = 8.80 Hz, 2 H, *H*-3), 4.95 (s, 2 H, *H*-6), 4.29 (s, 2 H, *H*-14), 3.77 (s, 3 H, *H*-1), 3.55 (s, 2 H, *H*-9). ^{13}C NMR ($CDCl_3$, δ, ppm, 75 MHz, 298 K): 159.7 (*C*-2), 146.1 (*C*-8), 137.8 (*C*-15), 136.7 (*C*-10), 129.4 (*C*-4), 129.3 (*C*-16), 128.9 (*C*-12), 128.8 (*C*-11), 128.7 (*C*-7), 128.5 (*C*-17), 127.8 (*C*-13), 127.4 (*C*-18), 127.1 (*C*-5), 114.2 (*C*-3), 55.4 (*C*-1), 51.7 (*C*-6), 39.8 (*C*-9), 38.1 (*C*-14). MS (ESI-TOF, 9:1 MeOH:H_2O with 0.1 % HCOOH, m/z): 434 (M+H^+), 456 (M+Na^+). IR (CH_2Cl_2, $\tilde{\nu}$, cm^{-1}): 3049 (w), 2937 (w), 2839 (w), 1612 (m), 1514 (s), 1453 (m), 1249 (s), 1177 (m), 1031 (m), 720 (s).

*Synthesis of 1-(2,4-dimethoxybenzyl)-4,5-bis(benzylsulfanyl)-1H-1,2,3-triazole (**2b**)*

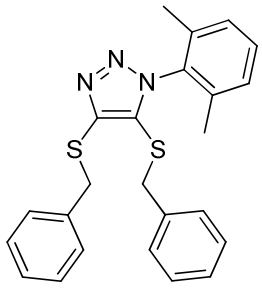


At -78 °C, 3.004 g (8.806 mmol) of **1b** is mixed with 4.6 ml (2.5 M) *n*-BuLi solution, 0.367 g (11.448 mmol) of elemental sulfur and 1.2 ml (10.103 mmol) of benzyl bromide in 80 ml THF. The purification is carried out chromatographically with 2:1 *n*-hexane/EtOAc; Yield, 3.644 g (89 %). Anal. Calcd. for $C_{25}H_{25}N_3S_2O_2$: C, 64.77; H, 5.44; N, 9.06; S, 13.83 %. Found: C, 64.93; H, 5.17; N, 8.70; S, 13.34 %. ^{1}H NMR ($CDCl_3$, δ, ppm, 300 MHz, 298 K): 7.33–7.18 (m, 8 H, *H*-Ph), 6.87–6.84 (m, 2 H, *H*-Ph), 6.73 (d, $^3J_{H,H}$ = 8.21 Hz, 1 H, *H*-7), 6.40 (d, $J_{H,H}$ = 2.31 Hz, 1 H, *H*-8), 6.37 (dd, $^3J_{H,H}$ = 8.21 Hz, $J_{H,H}$ = 2.31 Hz, 1 H, H-3), 5.02 (s, 2 H, H-9), 4.30 (s, 2 H, *H*-17), 3.77 (s, 3 H, *H*-1), 3.76 (s, 3 H, *H*-5), 3.60 (s, 2 H, *H*-11). ^{13}C NMR ($CDCl_3$, δ, ppm, 75 MHz, 298 K): 161.1 (*C*-2), 158.0 (*C*-4), 145.5 (*C*-16), 138.0 (*C*-18), 136.8 (*C*-12), 130.0 (*C*-7), 129.3 (*C*-19), 129.1 (*C*-10), 128.9 (*C*-13), 128.8 (*C*-15), 128.5 (*C*-21), 127.7 (*C*-14), 127.4 (*C*-20), 116.1 (*C*-6), 104.4 (*C*-3), 98.6 (*C*-8), 55.6 (*C*-1), 55.5 (*C*-5), 46.8 (*C*-9), 39.7 (*C*-11), 38.1 (*C*-17). IR (CH_2Cl_2, $\tilde{\nu}$, cm^{-1}): 3049 (w), 2940 (w), 2838 (w), 1616 (m), 1509 (m), 1454 (m), 1254 (s), 1210 (m), 1158 (m), 1035 (m), 742 (s), 701 (s).

*Synthesis of 1-(2-(trimethylsilyl)ethyl)-4,5-bis(benzylsulfanyl)-1H-1,2,3-triazole (**2c**)*



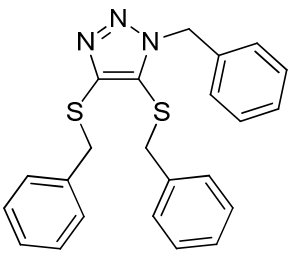
At -78 °C, 0.935 g (3.208 mmol) of **1c** is mixed with 1.70 ml (2.5 M) *n*-BuLi solution, 0.112 g (0.438 mmol) of elemental sulfur and 0.42 ml (3.531 mmol) of benzyl bromide in 60 ml THF. The purification is carried out chromatographically with 4:1 *n*-hexane/EtOAc; Yield, 0.632 g (48 %). ^{1}H NMR ($CDCl_3$, δ, ppm, 300 MHz, 298 K): 7.38-7.16 (m, 8 H, *H*-Ph), 6.79-6.76 (m, 2 H, *H*-Ph), 4.35 (s, 2 H, *H*-11), 3.73-3.67 (m, 2 H, *H*-3), 3.71 (s, 2 H, *H*-5), 0.84-0.78 (m, 2 H, *H*-2), -0.04 (s, 9 H, *H*-1). ^{13}C NMR ($CDCl_3$, δ, ppm, 75 MHz, 298 K): 145.4 (*C*-10), 137.9 (*C*-12), 137.2 (*C*-6), 129.2 (*C*-13), 128.7 (*C*-14), 128.7 (*C*-8), 128.5 (*C*-7), 127.6 (*C*-9), 127.3 (*C*-15), 127.3 (*C*-4), 45.4 (*C*-3), 39.6 (*C*-5), 37.8 (*C*-11), 18.5 (*C*-2), -1.9 (*C*-1). ^{29}Si NMR ($CDCl_3$, δ, ppm, 60 MHz, 298 K): 0.7-0.1 (m, $^2J_{Si,H}$ = 3.4 Hz, *Si*-TMS). IR (CH_2Cl_2, $\tilde{\nu}$, cm^{-1}): 3033 (w), 2957 (m), 1495 (m), 1455 (m), 1260 (m), 1021 (m), 917 (m), 862 (m), 744 (s), 708 (s).



*Synthesis of 1-(2,6-dimethylphenyl)-4,5-bis(benzylsulfanyl)-1H-1,2,3-triazole (**2d**)*

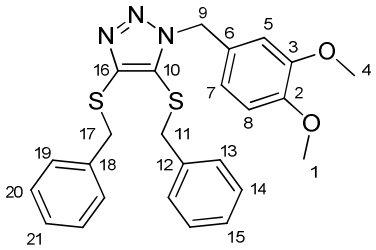
At -78 °C, 0.981 g (3.321 mmol) of **1d** is mixed with 1.73 ml (4.317 mmol, 2.5 M) *n*-BuLi solution, 0.115 g (0.448 mmol) of elemental sulfur and 0.43 ml (3.653 mmol) of benzyl bromide in 60 ml THF. The purification is carried out chromatographically with 4:1 *n*-hexane/EtOAc; Yield, 0.531 g (38 %). ^{1}H NMR ($CDCl_3$, δ, ppm, 300 MHz, 298 K): 7.41-7.20 (m, 11 H, *H*-Ar), 7.08-7.05 (m, 2 H, *H*-Ar), 4.43 (s, 2 H, C*H*$_2$-Bn), 3.79 (s, 2 H, C*H*$_2$-Bn), 1.82 (s, 6 H, C*H*$_3$-Xy). IR (CH_2Cl_2, $\tilde{\nu}$, cm^{-1}): 3031 (w), 1454 (w), 1273-1255 (m), 990 (w), 761 (s), 707 (s).

*Synthesis of 1-(benzyl)-4,5-bis(benzylsulfanyl)-1H-1,2,3-triazole (**2e**)*



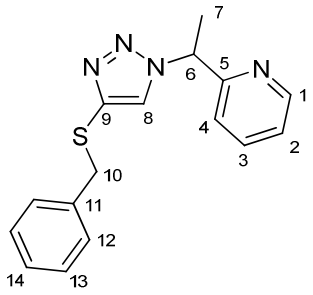
At -78 °C, 1.271 g (4.517 mmol) of **1e** is mixed with 2.40 ml (6.000 mmol, 2.5 M) *n*-BuLi solution, 0.158 g (0.616 mmol) of elemental sulfur and 0.61 ml (5.136 mmol) of benzyl bromide in 60 ml THF. The purification is carried out chromatographically with 4:1 *n*-hexane/EtOAc; Yield, 1.186 g (65 %). ^{1}H NMR (CD_2Cl_2, δ, ppm, 500 MHz, 298 K): 7.33-7.19 (m, 11 H, *H*-Ph), 7.12-7.09 (m, 2 H, *H*-Ph), 6.90-6.86 (m, 2 H, *H*-Ph), 5.08 (s, 2 H, C*H*$_2$-Bn), 4.28 (s, 2 H, C*H*$_2$-Bn), 3.56 (s, 2 H, C*H*$_2$-Bn). IR (CH_2Cl_2, $\tilde{\nu}$, cm^{-1}): 3033 (w), 1496 (m), 1455 (m), 1267 (m) 1030 (w), 743 (s), 723 (s), 710 (s).

*Synthesis of 1-(3,4-dimethoxybenzyl)-4,5-bis(benzylsulfanyl)-1H-1,2,3-triazole (**2f**)*



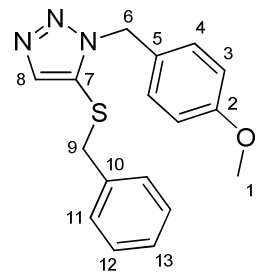
At -78 °C, 0.204 g (0.597 mmol) of **1f** is mixed with 0.31 ml (2.5 M) *n*-BuLi solution, 0.021 g (0.081 mmol) of elemental sulfur and 0.08 ml (0.657 mmol) of benzyl bromide in 30 ml THF. The purification is carried out chromatographically with 2:1 *n*-hexane/EtOAc; Yield, 0.212 g (76 %). ^{1}H NMR ($CDCl_3$, δ, ppm, 500 MHz, 298 K): 7.29-7.16 (m, 8 H, *H*-Ph), 6.83-6.82 (m, 2 H, *H*-Ph), 6.77-6.71 (m, 3 H, *H*-Ph), 4.95 (s, 2 H, *H*-9), 4.29 (s, 2 H, *H*-17), 3.84 (s, 3 H, *H*-1), 3.81 (s, 3 H, *H*-4), 3.57 (s, 2 H, *H*-11). ^{13}C NMR ($CDCl_3$, δ, ppm, 126 MHz, 298 K): 149.2 (*C*-2), 149.1 (*C*-3), 146.1 (*C*-10), 137.7 (*C*-18), 136.6 (*C*-12), 129.2 (*C*-Ph), 128.8 (*C*-Ph), 128.8 (*C*-Ph); 128.7 (*C*-16), 128.5 (*C*-Ph), 127.8 (*C*-Ph), 127.3 (*C*-6), 127.3 (*C*-Ph), 120.7 (*C*-Ph), 111.1 (*C*- Ph), 111.1 (*C*-Ph), 56.0 (*C*-4, *C*-1), 52.0 (*C*-9), 39.7 (*C*-11), 38.0 (*C*-17). IR (CH_2Cl_2, $\tilde{\nu}$, cm^{-1}): 3061 (w), 2936 (w), 1516 (m), 1441 (w), 1267 (s), 1141 (w), 1028 (m), 754 (s), 722 (s).

*Synthesis of 1-(2-pyridylethyl)-4-(benzylsulfanyl)-1H-1,2,3-triazole (**3**)*



In an 80 ml Schlenk tube, 0.196 g (0.695 mmol) **1g** are dissolved in 30 ml THF. To the cold solution (-78 °C) 0.36 ml (2.5 M) *n*-BuLi solution is added, whereupon a dark red colour occurs. After a short time, 0.09 ml (1.390 mmol) of methyl iodide is added. The solution is stirred for 30 min in the cold and 3 d at room temperature. For purification, the reaction solution is dried on silica gel and purified by chromatography with 1:1 *n*-hexane:EtOAc; Yield, 0.202 g (98 %). ^{1}H NMR ($CDCl_3$, δ, ppm, 300 MHz, 298 K): 8.55 (dd, $^{3}J_{H,H}$ = 1.85 Hz, $J_{H,H}$ = 4.88 Hz, 1 H, *H*-1), 7.63 (dd, $^{3}J_{H,H}$ = 1.85 Hz, $J_{H,H}$ = 7.73 Hz, 1 H, *H*-2), 7.38 (s, 1 H, *H*-7), 7.22 (td, $^{3}J_{H,H}$ = 1.13 Hz, $J_{H,H}$ = 4.88 Hz, 1 H, *H*-3), 7.17–7.13 (m, 5 H, *H*-Ph), 7.05 (dt, $^{3}J_{H,H}$ = 1.13 Hz, $J_{H,H}$ = 7.73 Hz, 1 H, *H*-4), 5.85 (q, $^{3}J_{H,H}$ = 7.15 Hz, 1 H, *H*-6), 4.04 (s, 2 H, *H*-10), 1.88 (d, $^{3}J_{H,H}$ = 7.15 Hz, 3 H, *H*-7). ^{13}C NMR ($CDCl_3$, δ, ppm, 75 MHz, 298 K): 158.2 (*C*-5), 149.7 (*C*-1), 138.9 (*C*-9), 137.8 (*C*-11), 137.3 (*C*-2), 129.1 (*C*-12), 128.4 (*C*-14), 127.2 (*C*-13), 125.6 (*C*-8), 123.4 (*C*-3), 121.5 (*C*-4), 61.8 (*C*-6), 39.8 (*C*-10), 20.6 (*C*-7). IR (CH_2Cl_2, $\tilde{\nu}$, cm^{-1}): 3154 (m), 3048 (m), 2938 (m), 1715 (m), 159 (s), 1475 (s), 1436 (s), 1266 (s), 1036 (s), 758 (s), 708 (s), 668 (m).

*Synthesis of 1-(4-methoxybenzyl)-5-(benzylsulfanyl)-1H-1,2,3-triazole (**4**)*



In a 100 ml Schlenk flask, 0.301 g (1.592 mmol) of 1-(4-methoxybenzyl)-1*H*-1,2,3-triazole in 40 are dissolved ml THF. To the cold solution (-78 °C) 0.83 ml of an *n*-BuLi solution (2.5 M) is added, giving a clear red colouration and a colourless precipitate. To the light suspension, 0.056 g (0.219 mmol) of elemental sulfur is suspended. The suspension is stirred for a further 10 min in the cold and then at room temperature, which completely consumes the sulfur. An ice bath is used to cool the orange solution and 0.23 ml (1.910 mmol) of benzyl bromide is added. The solution is stirred overnight at room temperature. For purification, the solution is dried on silica gel and purified by chromatography with 2:1 *n*-hexane:EtOAc; Yield, 0.309 g (62 %). ^{1}H NMR ($CDCl_3$, δ, ppm, 300 MHz, 298 K): 7.48 (s, 1 H, *H*-8), 7.29-7.27 (m, 3 H, *H*-Ph), 7.21 (d, $^{3}J_{H,H}$ = 8.82 Hz, 2 H, *H*-4), 7.03-7.01 (m, 2 H, *H*-Ph), 6.84 (d, $^{3}J_{H,H}$ = 8.82 Hz, 2 H, *H*-3), 5.28 (s, 2 H, *H*-6), 3.77 (s, 3 H, *H*-1), 3.67 (s, 2 H, *H*-8). ^{13}C NMR ($CDCl_3$, δ, ppm, 75 MHz, 298 K): 159.6 (*C*-2), 139.1 (*C*-8), 136.4 (*C*-10) 129.4 (*C*-4), 128.9 (*C*-12), 128.8 (*C*-11), 128.6 (*C*-7), 127.9 (*C*-13), 127.2 (*C*-5), 114.2 (*C*-3), 55.3 (*C*-1), 51.2 (*C*-6), 41.0 (*C*-9). MS (ESI-TOF, 9:1 MeOH:H_2O with 0.1 % HCOOH, m/z): 312 (*M*+H$^+$), 334 (*M*+Na$^+$). IR (CH_2Cl_2, $\tilde{\nu}$, cm^{-1}): 3047 (w), 2838 (w), 1594 (s), 1495 (s), 1249 (m), 1217 (s), 1154 (m), 1033 (m), 808 (m), 759 (s), 723 (s), 686 (m), 499 (m).

2.1 NMR spectroscopy, IR spectroscopy and van't-Hoff-plot

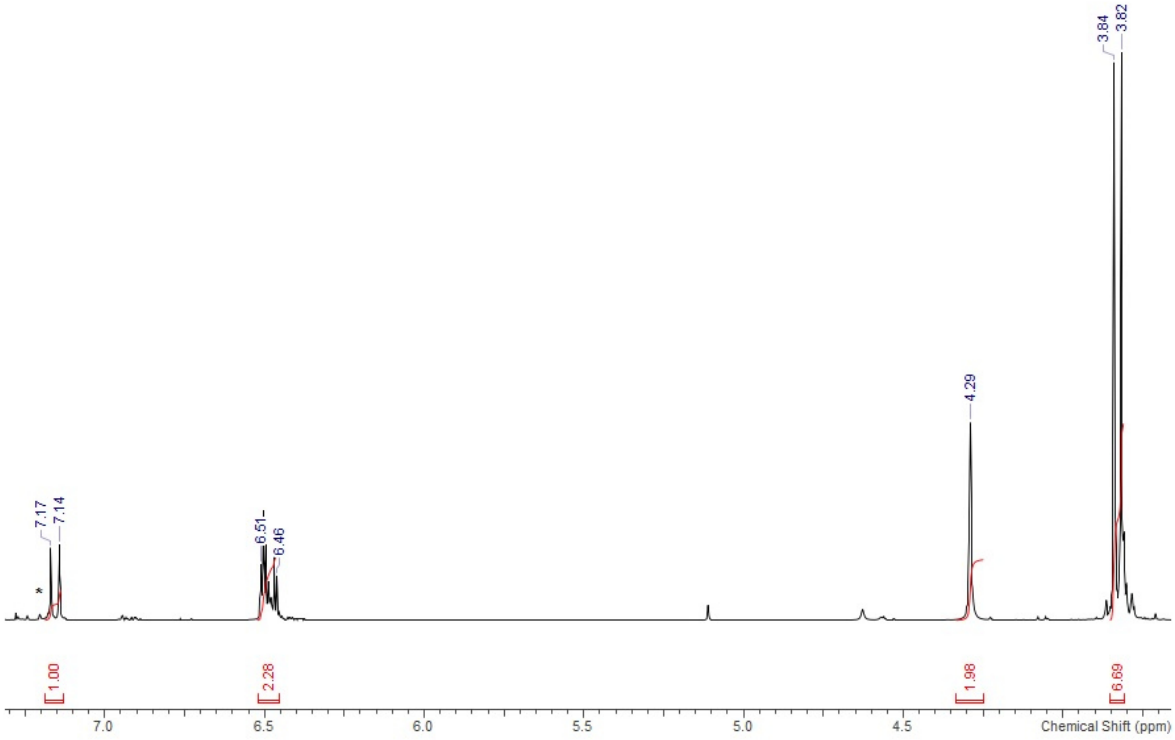


Figure S6. ^{1}H NMR spectrum (300 MHz) of 2,4-dimethoxybenzyl azide in $CDCl_3$ (*) at 298 K.

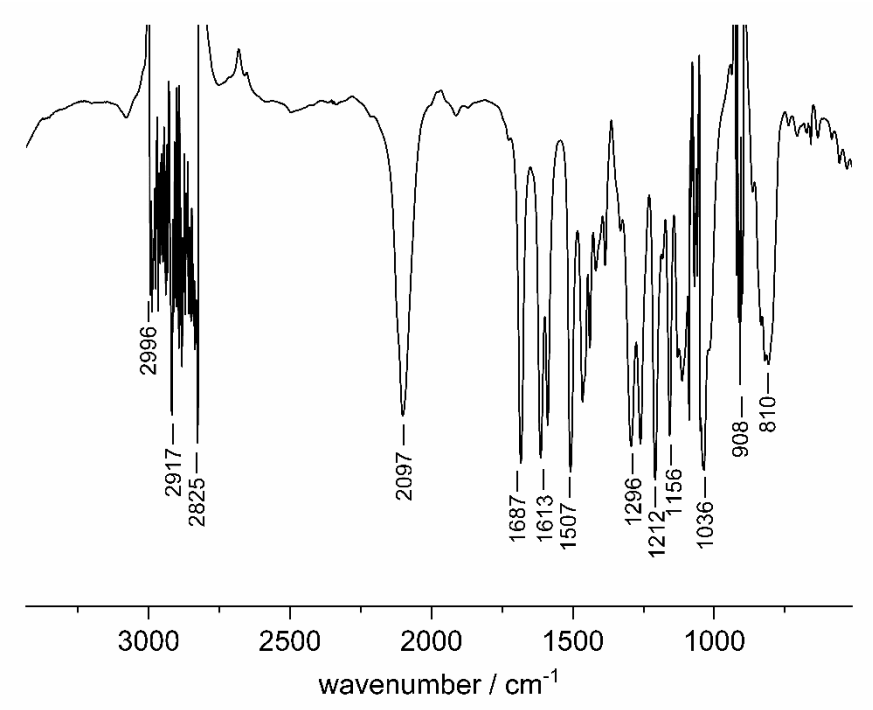


Figure S7. IR spectroscopy of 2,4-dimethoxybenzyl azide in THF.

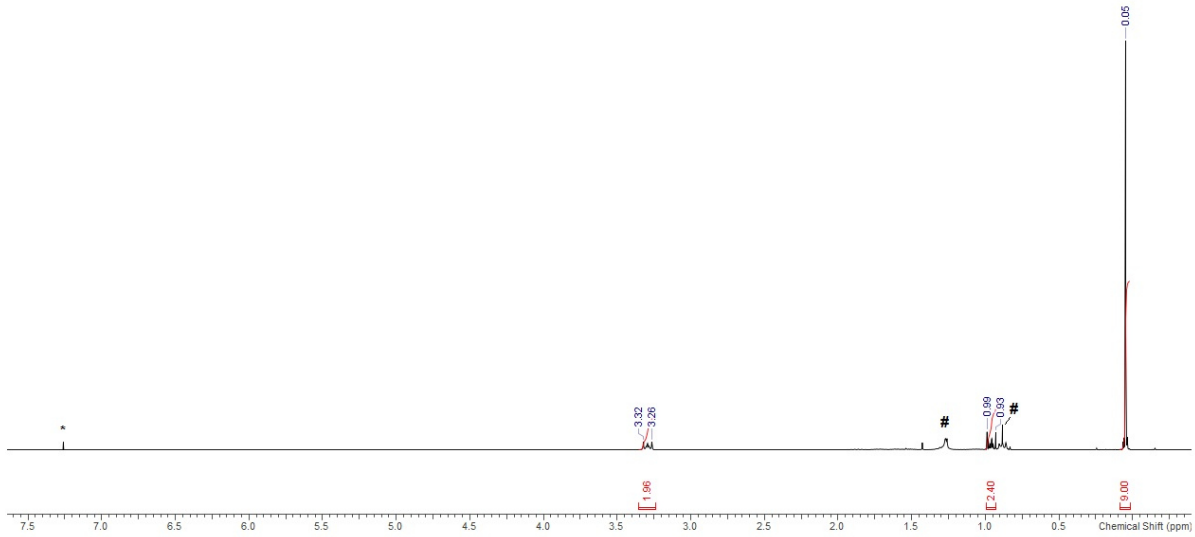


Figure S8. ^{1}H NMR spectrum (300 MHz) of 2-(trimethylsilyl)ethyl azide with traces of *n*-hexane (#) in $CDCl_3$ (*) at 298 K.

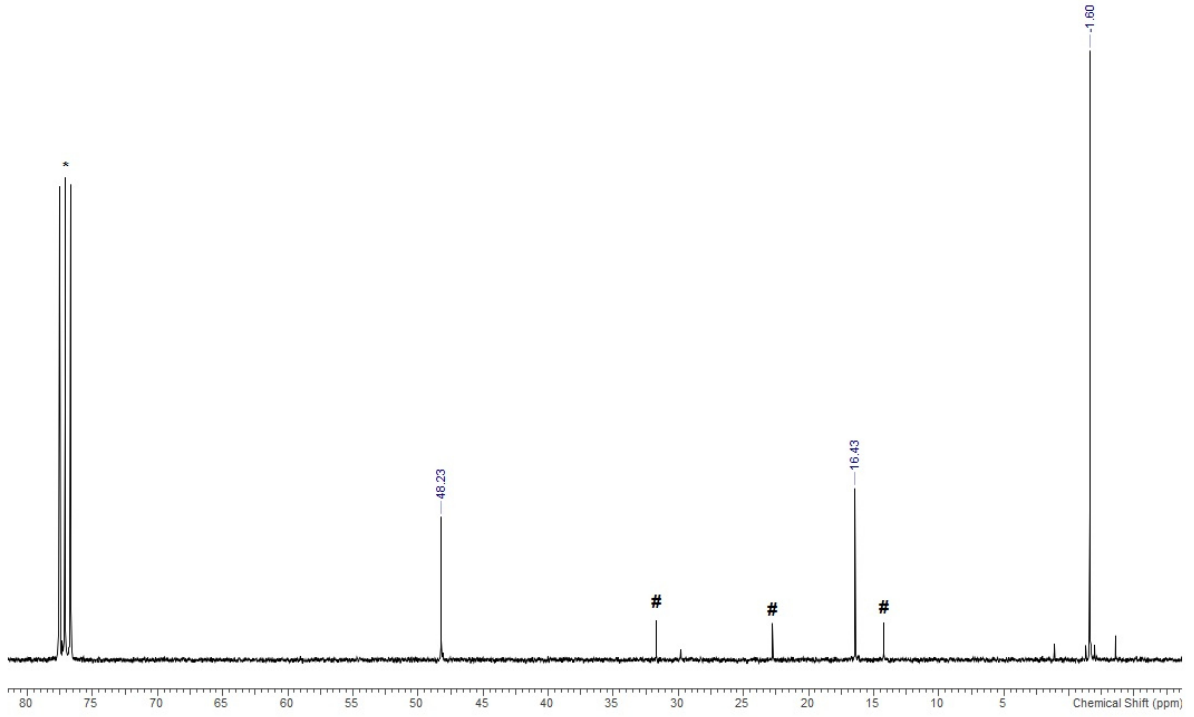


Figure S9. ^{13}C NMR spectrum (75 MHz) of 2-(trimethylsilyl)ethyl azide with traces of *n*-hexane (#) in $CDCl_3$ (*) at 298 K.

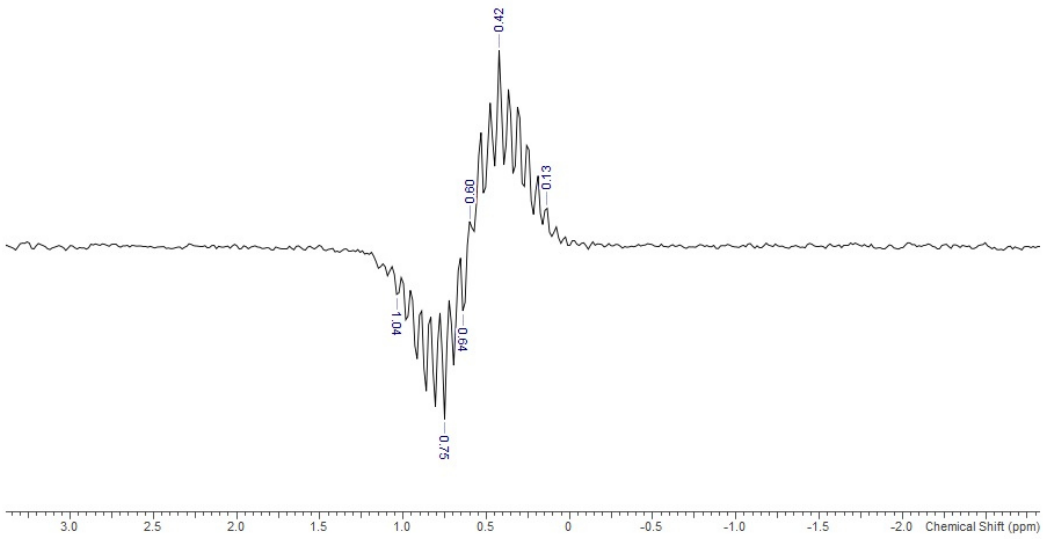


Figure S10. ^{29}Si NMR spectrum (60 MHz) of 2-(trimethylsilyl)ethyl azide in $CDCl_3$ at 298 K.

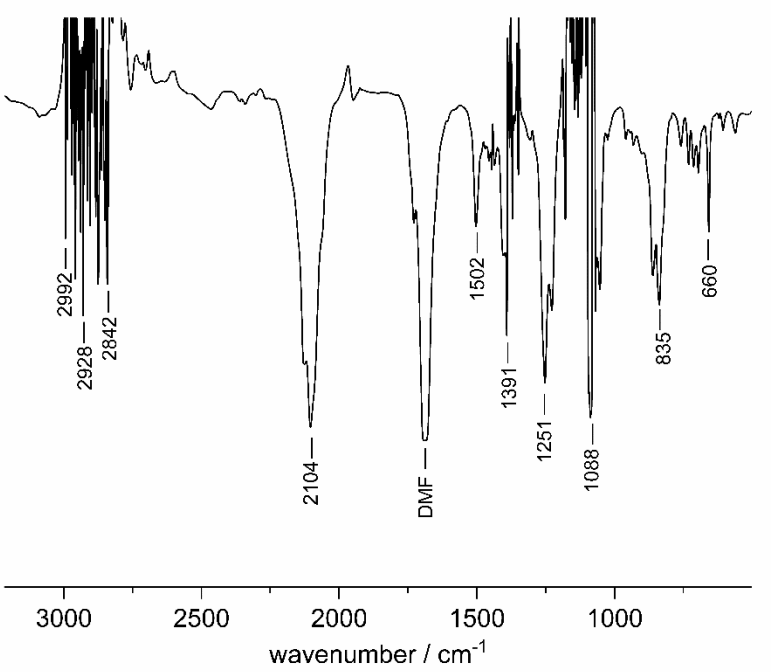


Figure S11. IR spectroscopy of 2-(trimethylsilyl)ethyl azide in Et_2O with traces of DMF.

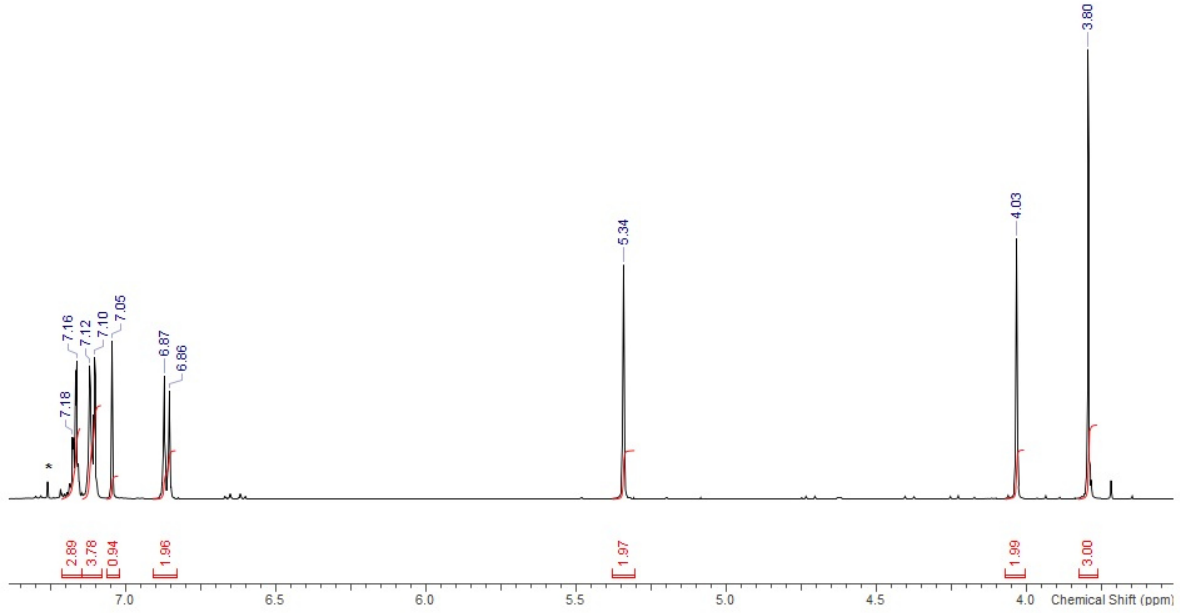


Figure S12. ^{1}H NMR spectrum (500 MHz) of **1a** in $CDCl_3$ (*) at 298 K.

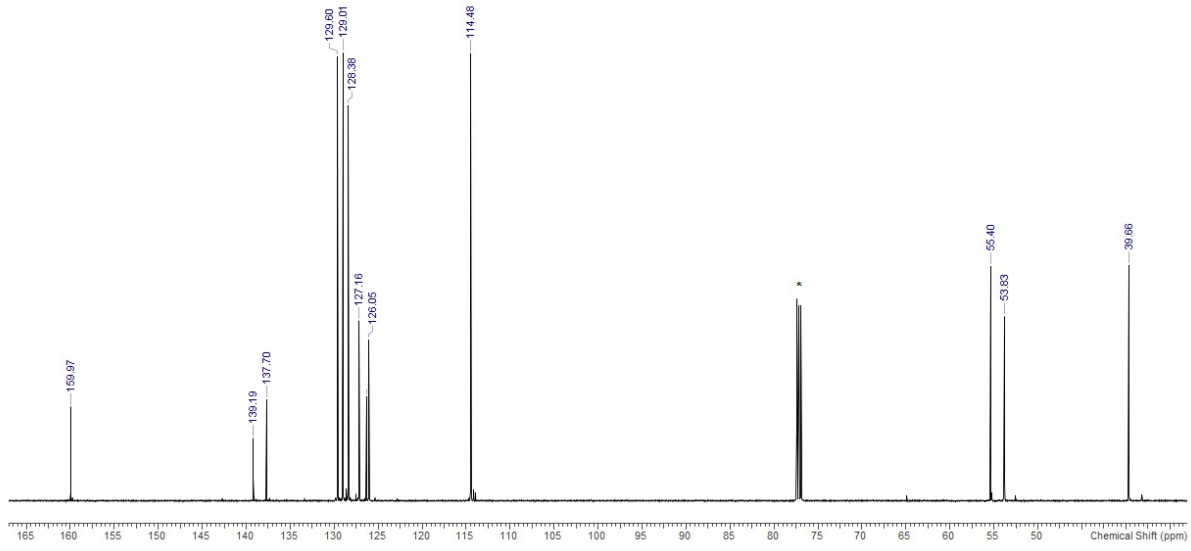


Figure S13. ^{13}C NMR spectrum (125 MHz) of **1a** in $CDCl_3$ (*) at 298 K.

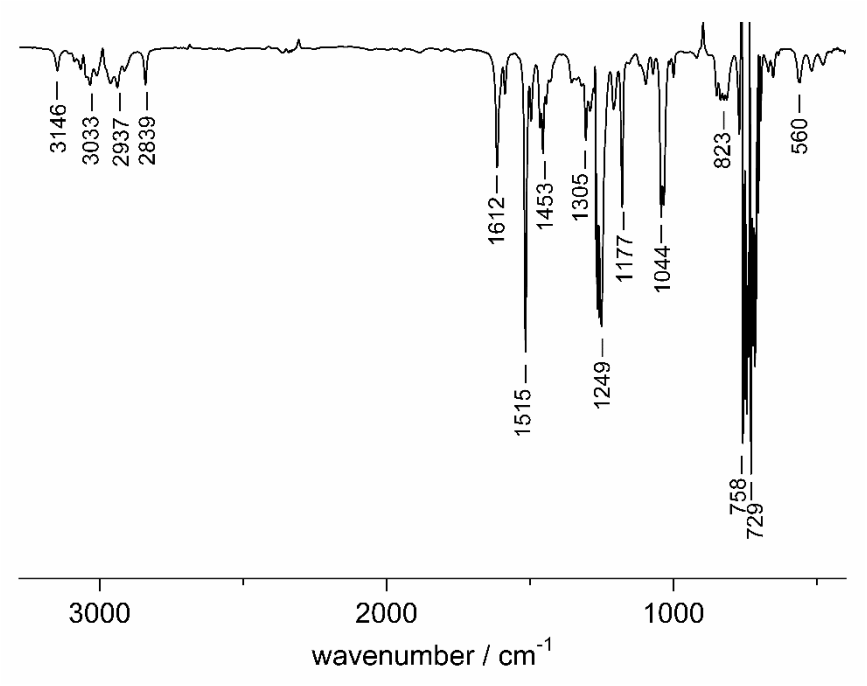


Figure S14. IR spectroscopy of **1a** in CH_2Cl_2.

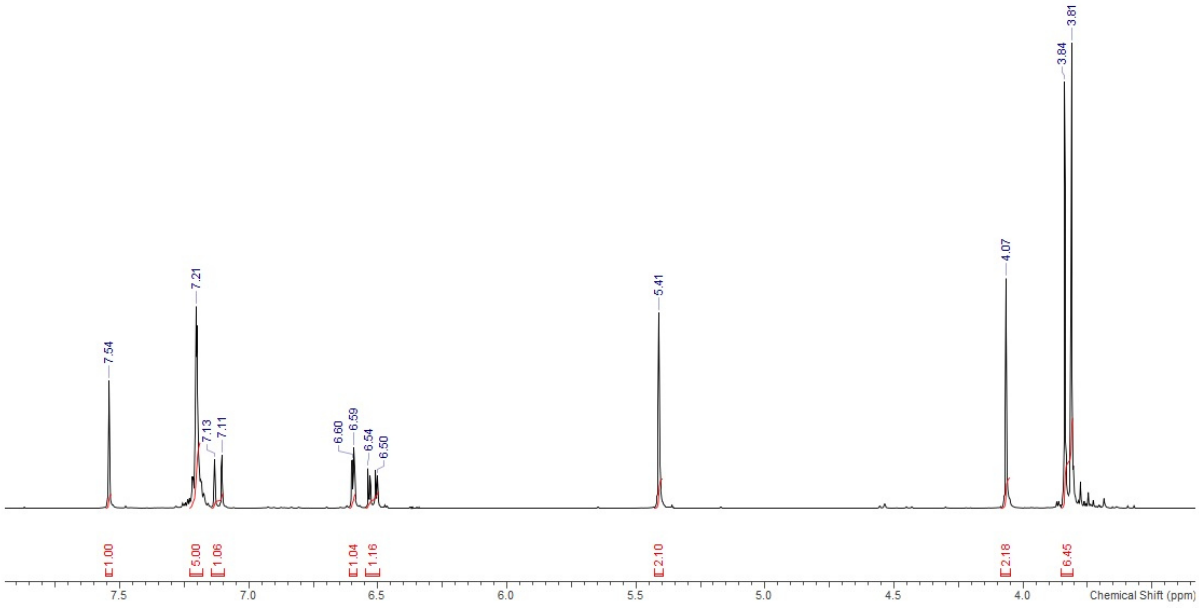


Figure S15. ^1H NMR spectrum (300 MHz) of **1b** in acetone-D_6 at 298 K.

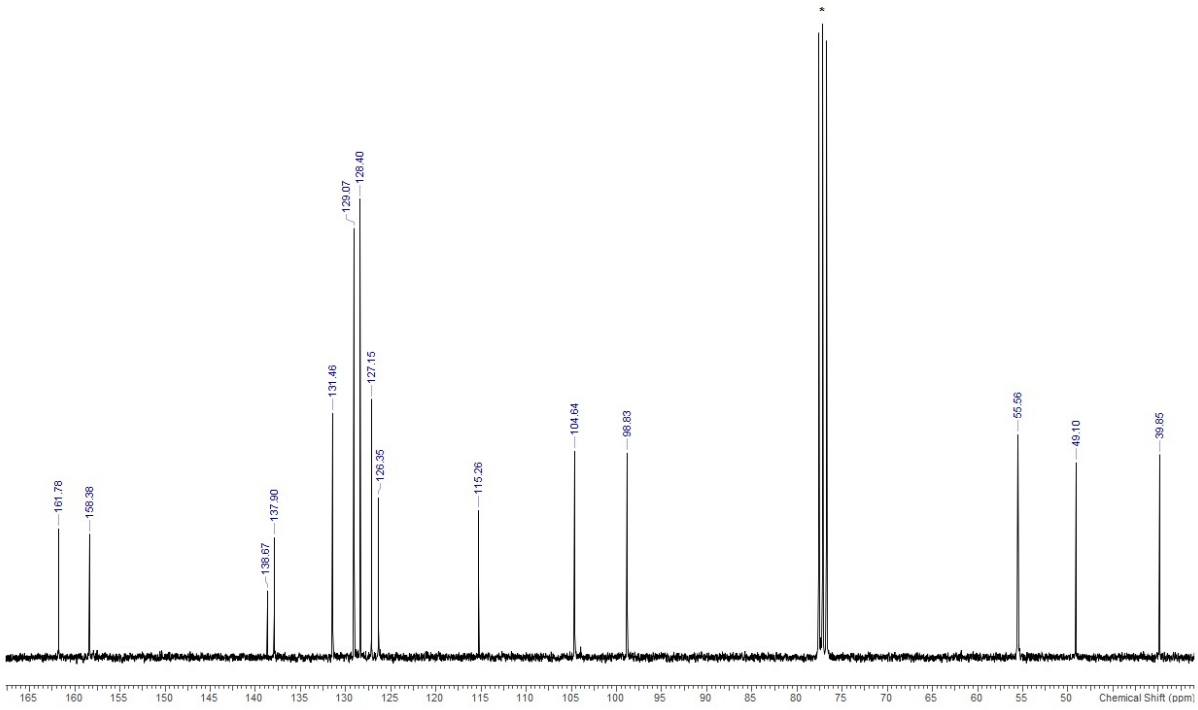


Figure S16. ^{13}C NMR spectrum (75 MHz) of **1b** in $CDCl_3$ (*) at 298 K.

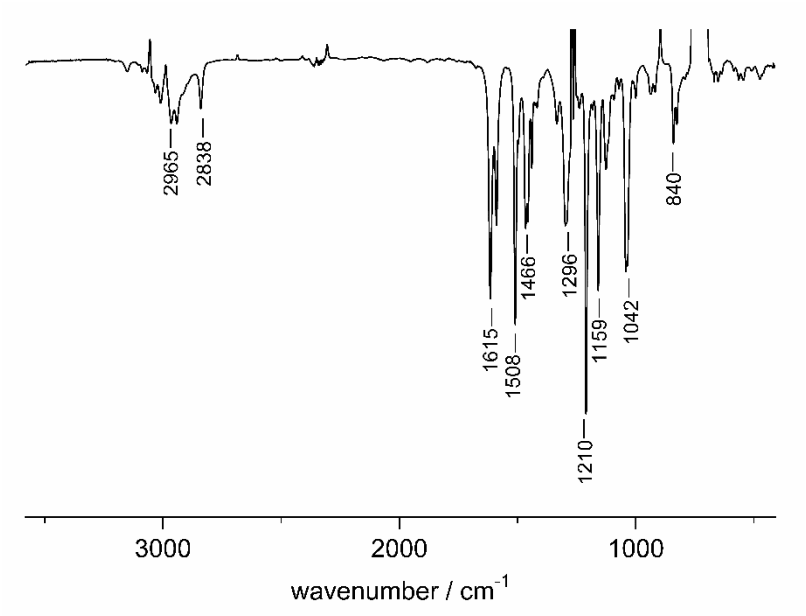


Figure S17. IR spectroscopy of **1b** in CH_2Cl_2.

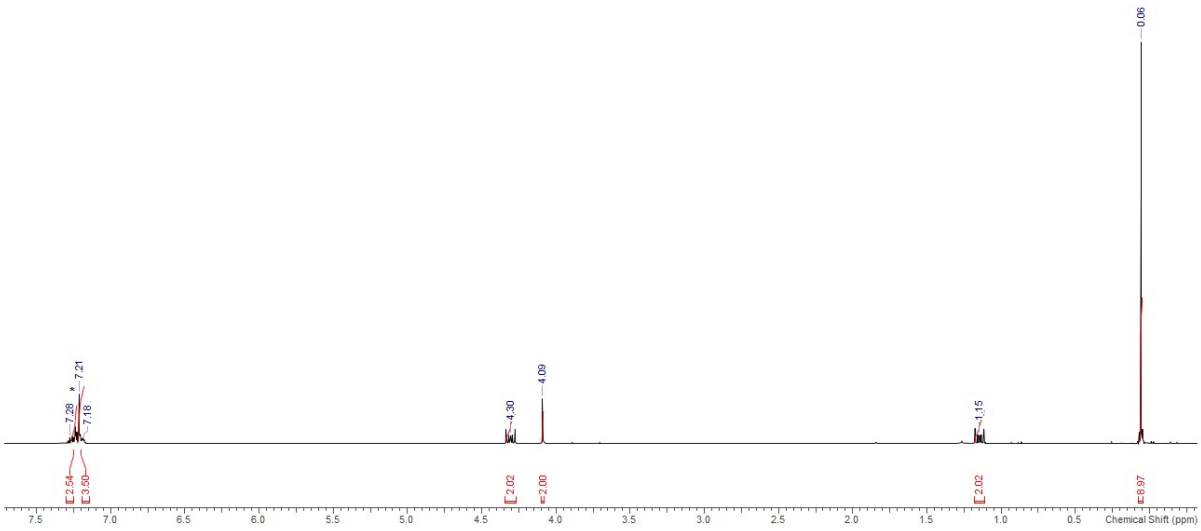


Figure S18. [1]H NMR spectrum (300 MHz) of **1c** in $CDCl_3$ (*) at 298 K.

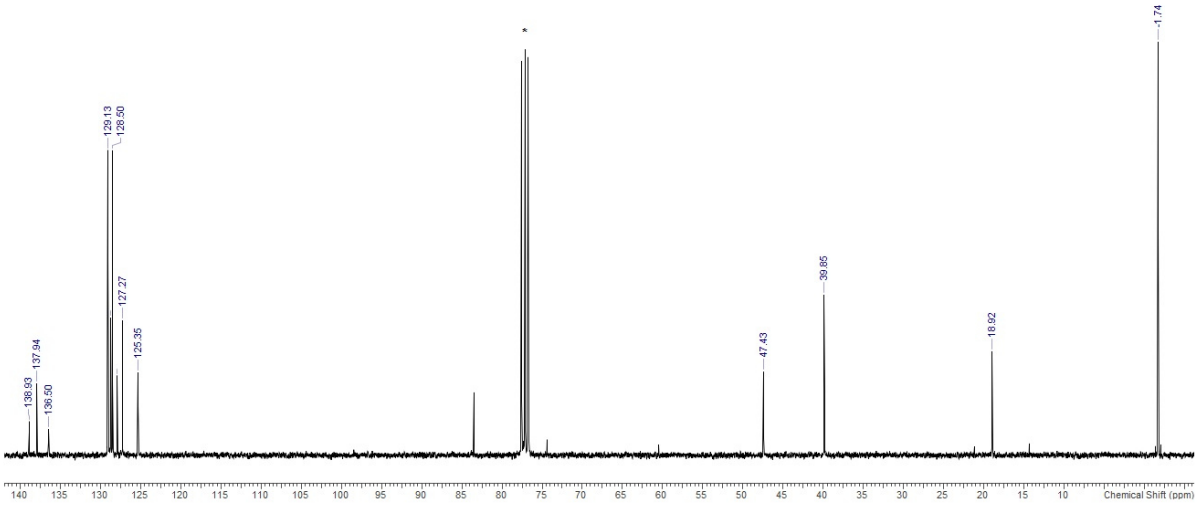


Figure S19. [13]C NMR spectrum (75 MHz) of **1c** in $CDCl_3$ (*) at 298 K.

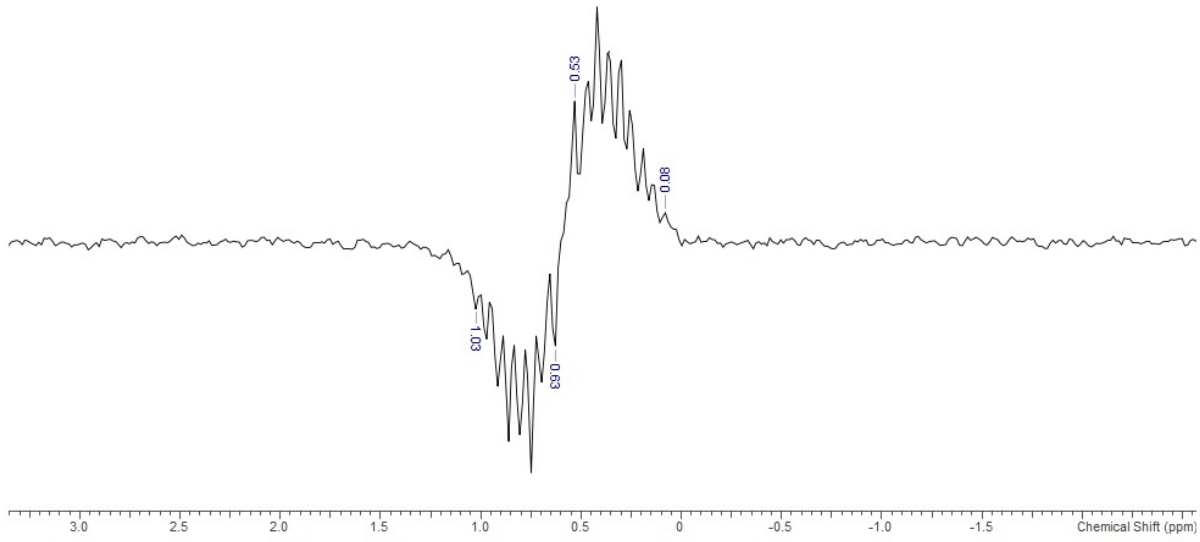


Figure S20. [29]Si NMR spectrum (60 MHz) of **1c** in $CDCl_3$ (*) at 298 K.

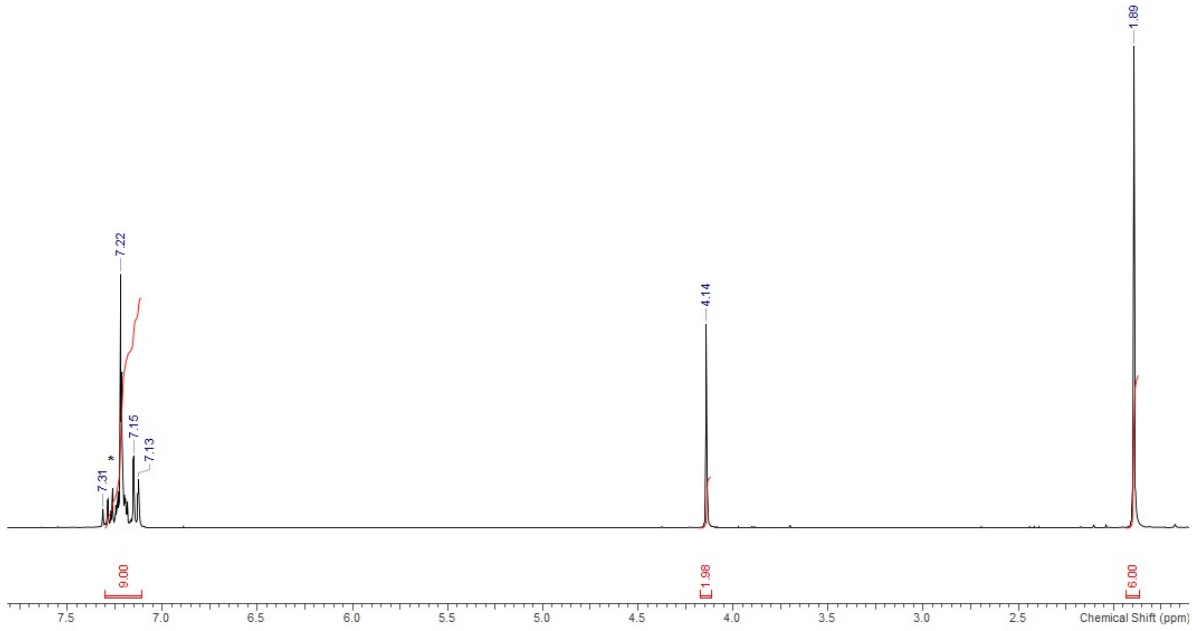


Figure S21. ^{1}H NMR spectrum (300 MHz) of **1d** in $CDCl_3$ (*) at 298 K.

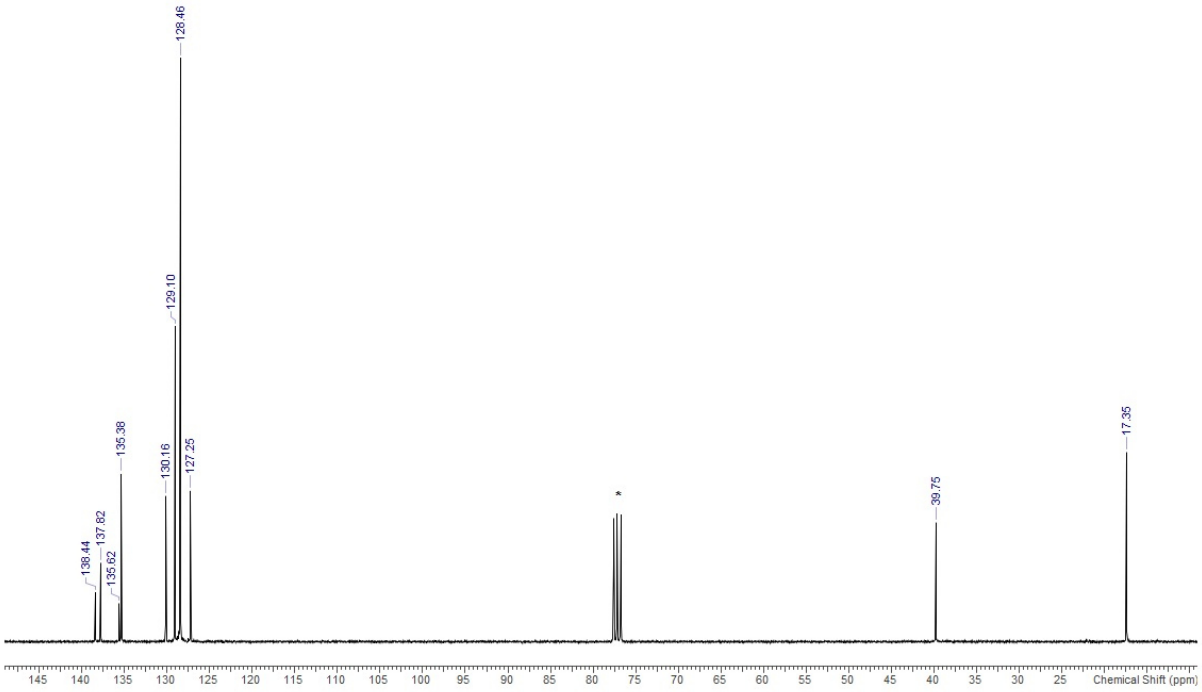


Figure S22. ^{13}C NMR spectrum (75 MHz) of **1d** in $CDCl_3$ (*) at 298 K.

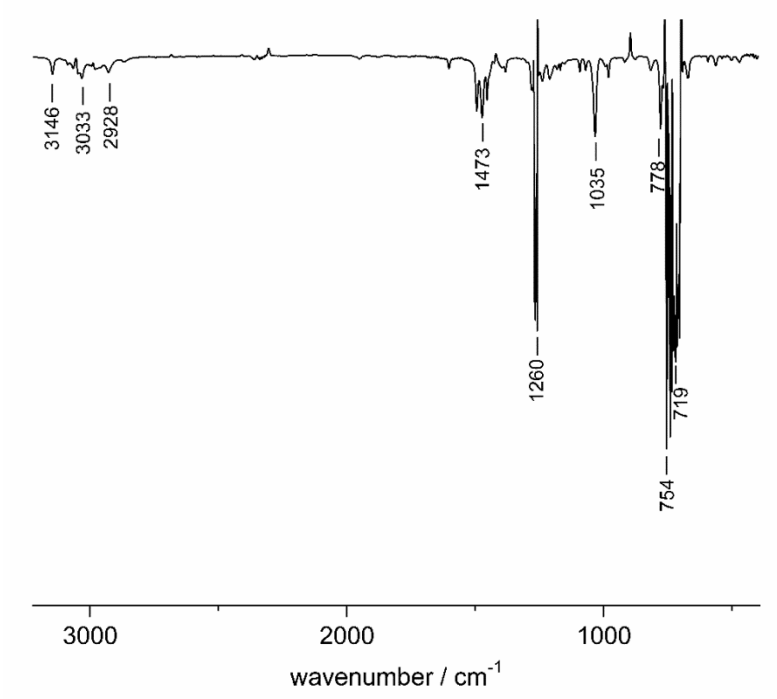


Figure S23. IR spectroscopy of **1d** in CH_2Cl_2.

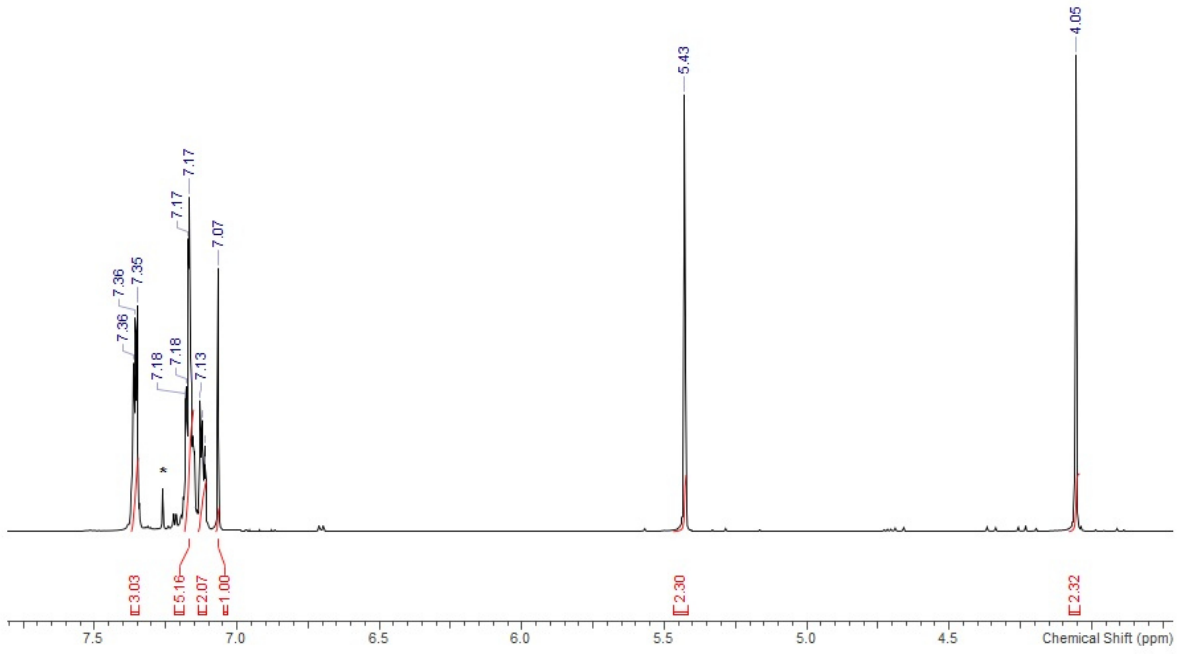


Figure S24. ^{1}H NMR spectrum (500 MHz) of **1e** in $CDCl_3$ (*) at 298 K.

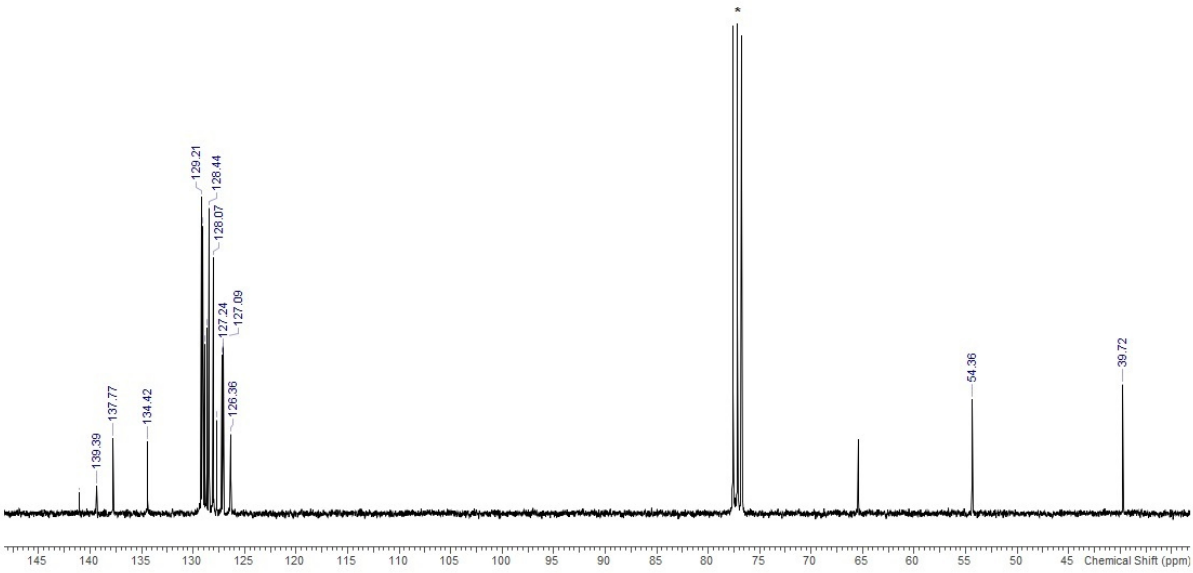


Figure S25. ^{13}C NMR spectrum (75 MHz) of **1e** in $CDCl_3$ (*) at 298 K.

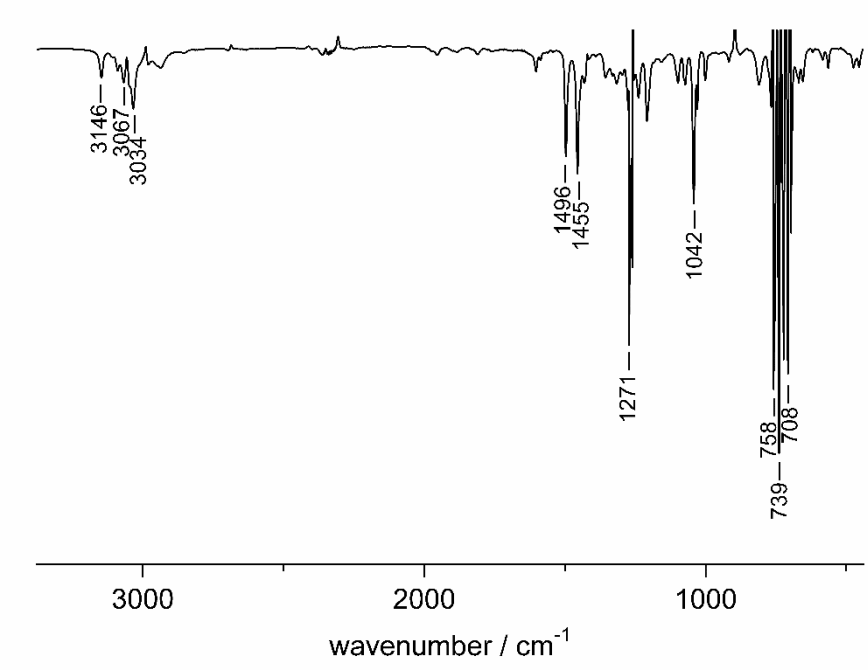


Figure S26. IR spectroscopy of **1e** in CH_2Cl_2.

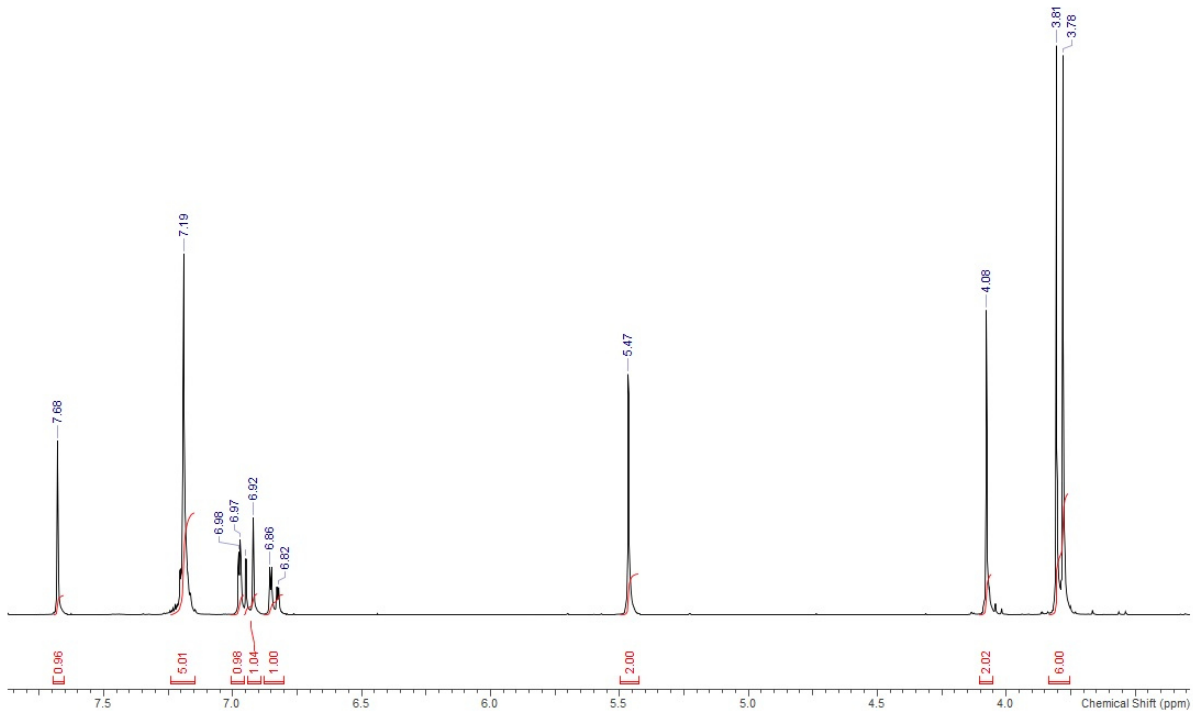


Figure S27. ^{1}H NMR spectrum (300 MHz) of **1f** in acetone-D_6 at 298 K.

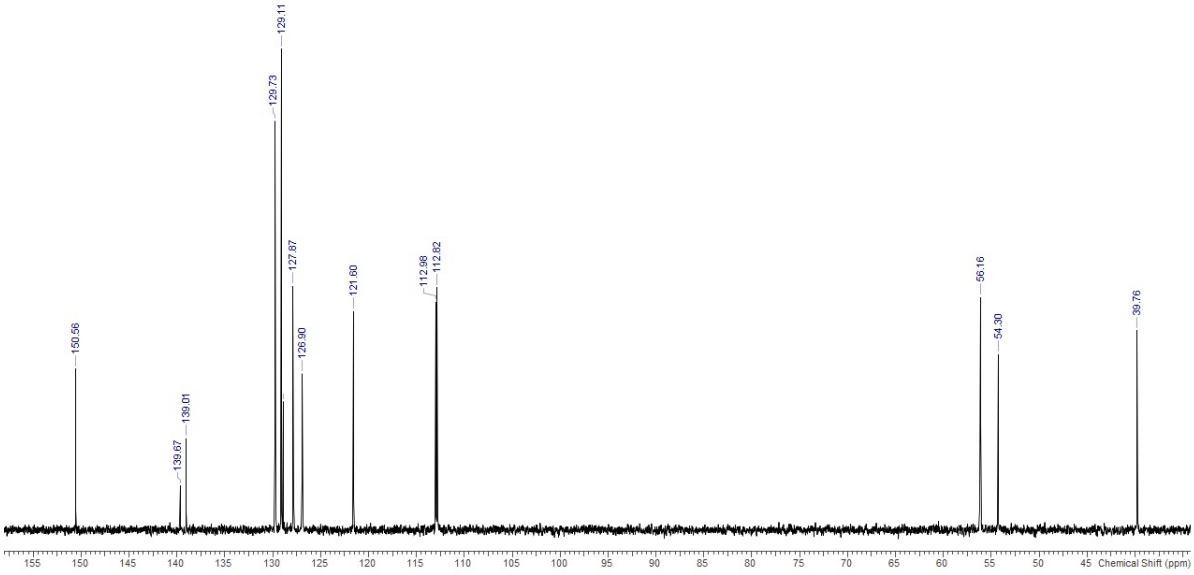


Figure S28. ^{13}C NMR spectrum (75 MHz) of **1f** in acetone-D_6 at 298 K.

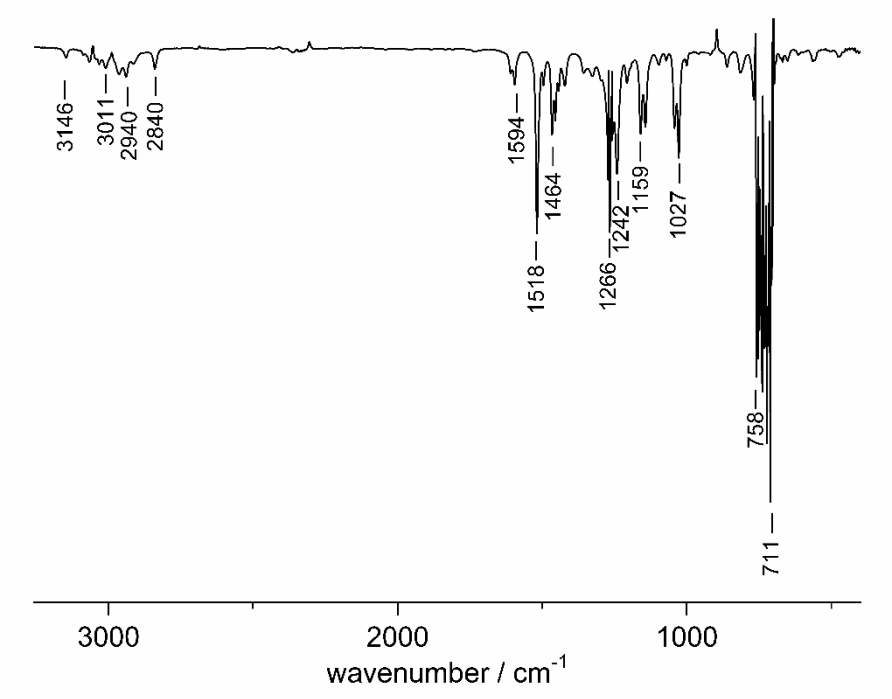


Figure S29. IR spectroscopy of **1f** in CH_2Cl_2.

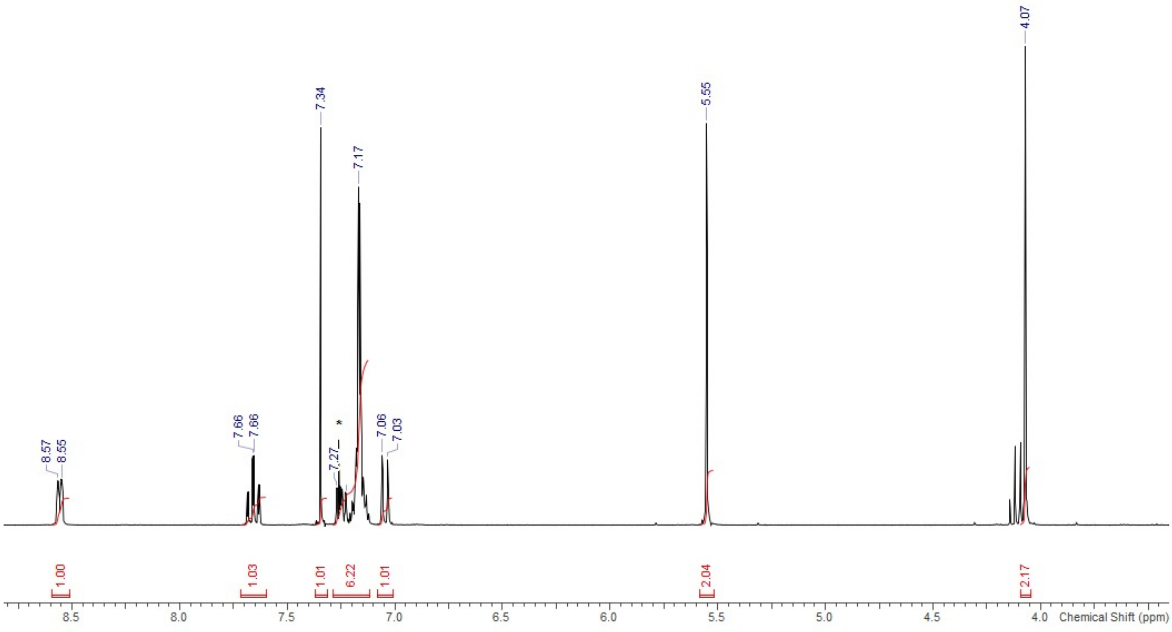


Figure S30. ^{1}H NMR spectrum (300 MHz) of **1g** in $CDCl_3$ (*) at 298 K.

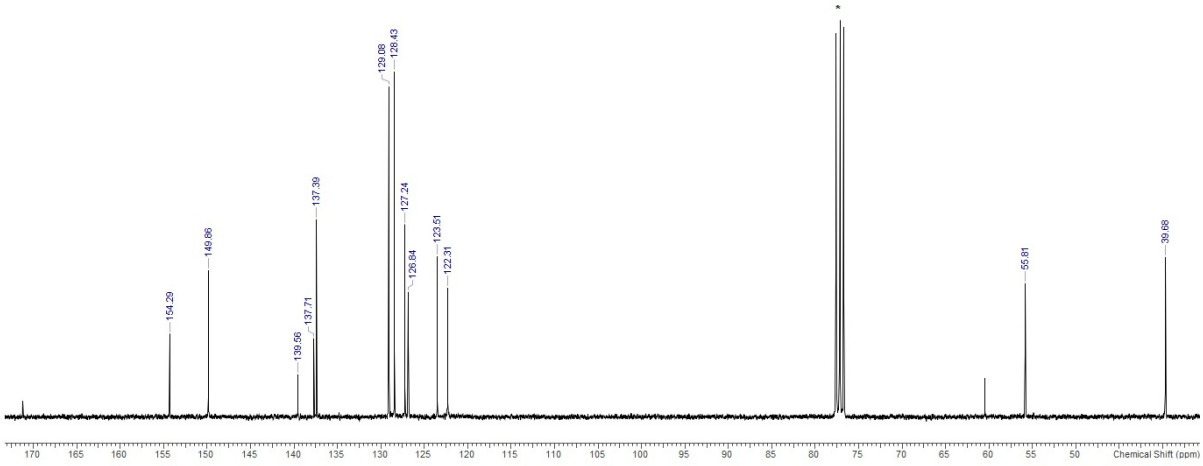


Figure S31. ^{13}C NMR spectrum (75 MHz) of **1g** in $CDCl_3$ (*) at 298 K.

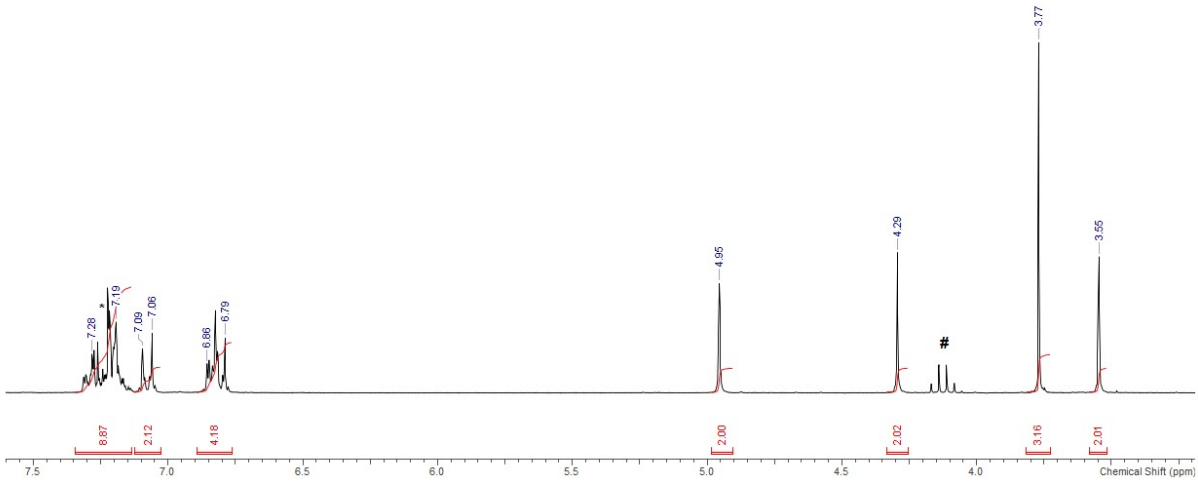


Figure S32. ^{1}H NMR spectrum (250 MHz) of **2a** with traces of EtOAc (#) in $CDCl_3$ (*) at 298 K.

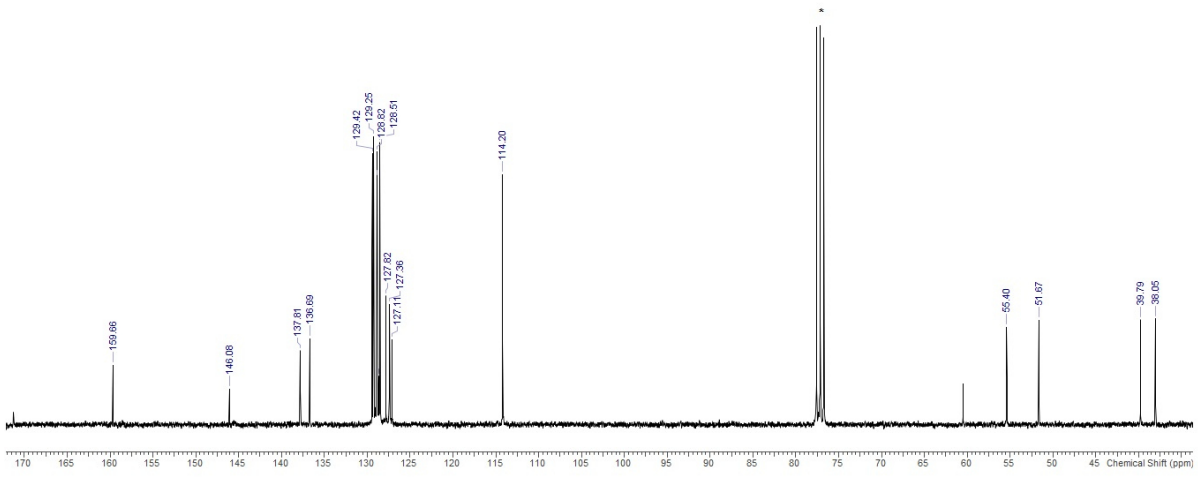


Figure S33. ^{13}C NMR spectrum (75 MHz) of **2a** in $CDCl_3$ (*) at 298 K.

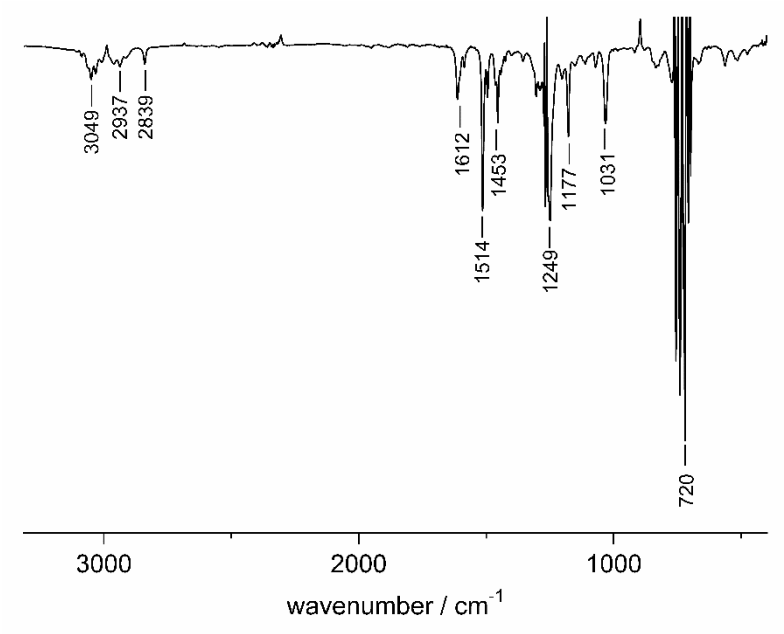


Figure S34. IR spectroscopy of **2a** in CH_2Cl_2.

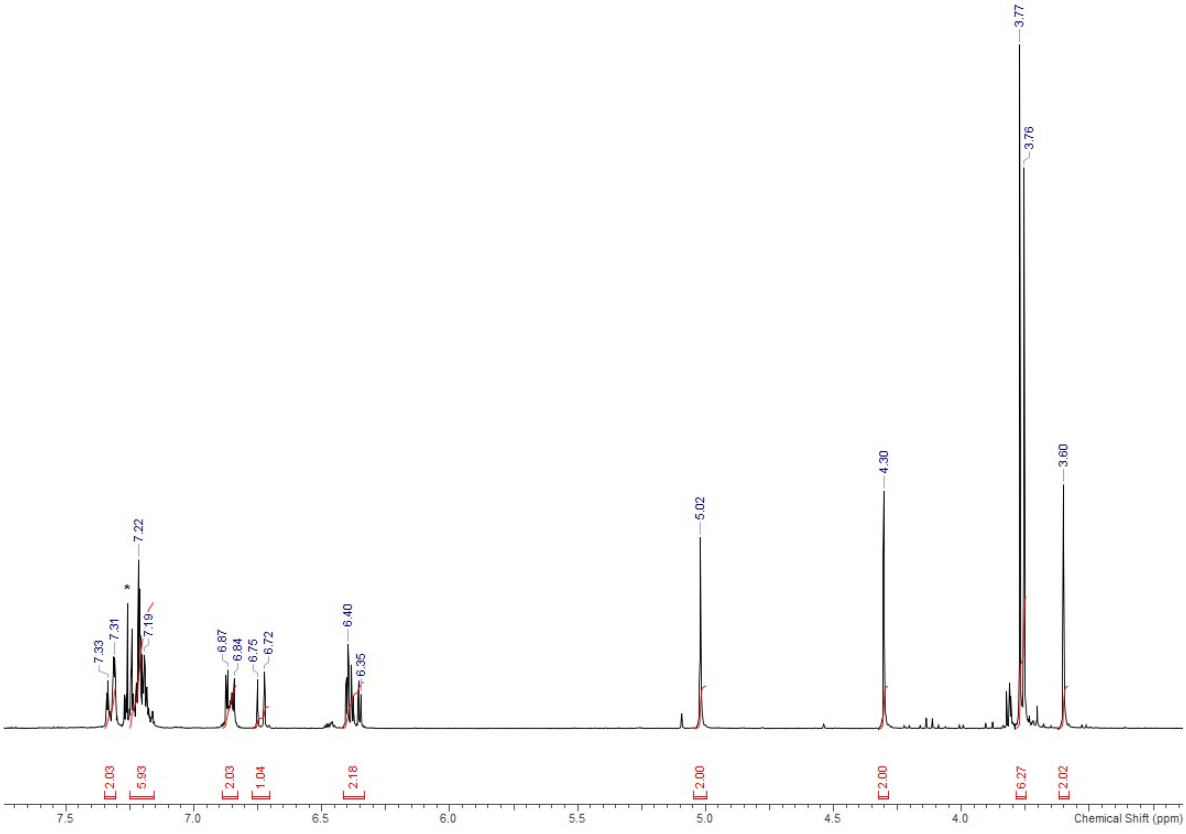


Figure S35. ^1H NMR spectrum (300 MHz) of **2b** in $CDCl_3$ (*) at 298 K.

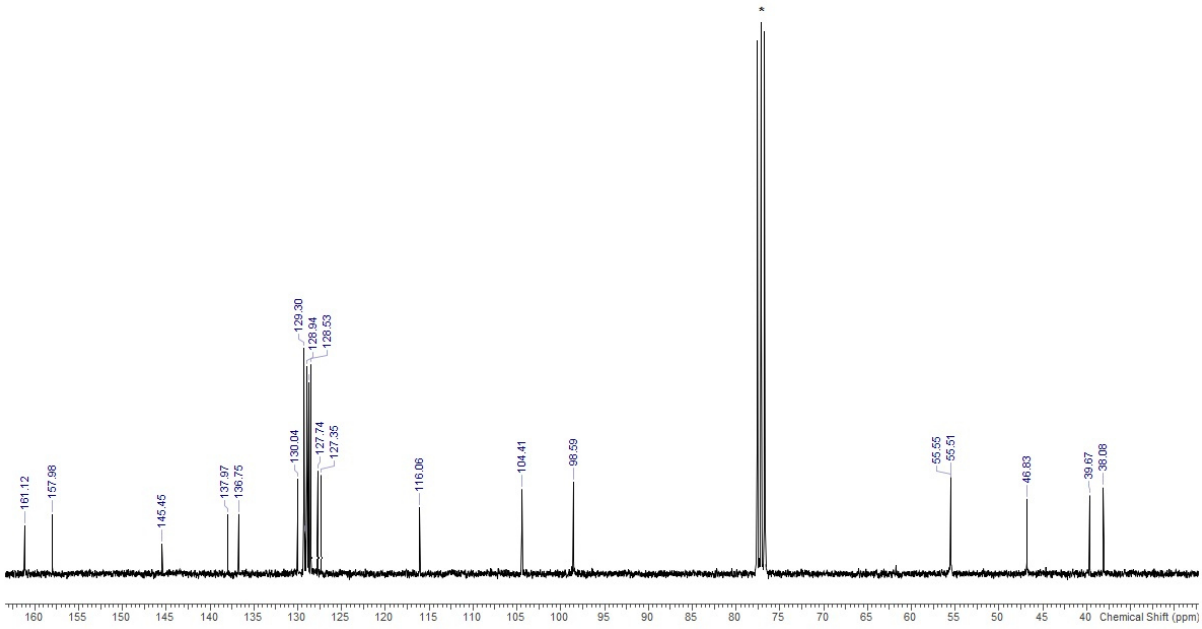


Figure S36. ^{13}C NMR spectrum (75 MHz) of **2b** in $CDCl_3$ (*) at 298 K. 13C von 2b

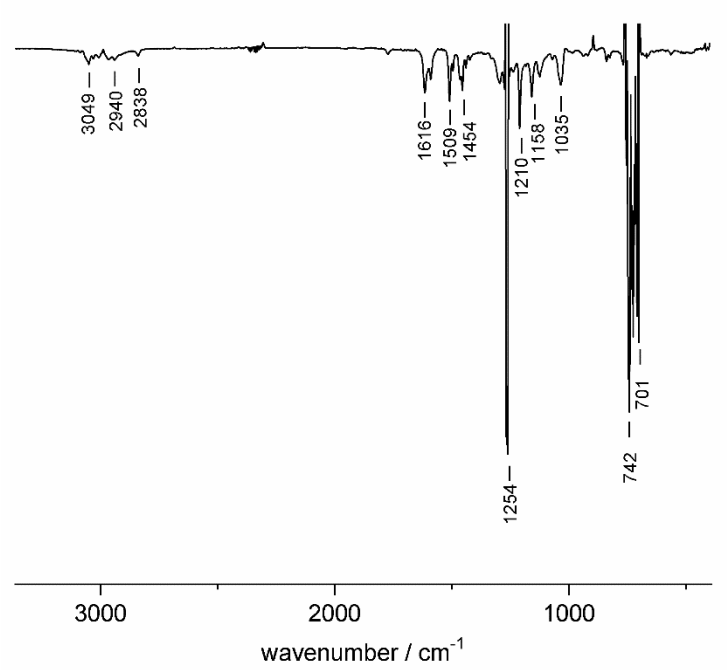


Figure S37. IR spectroscopy of **2b** in CH_2Cl_2.

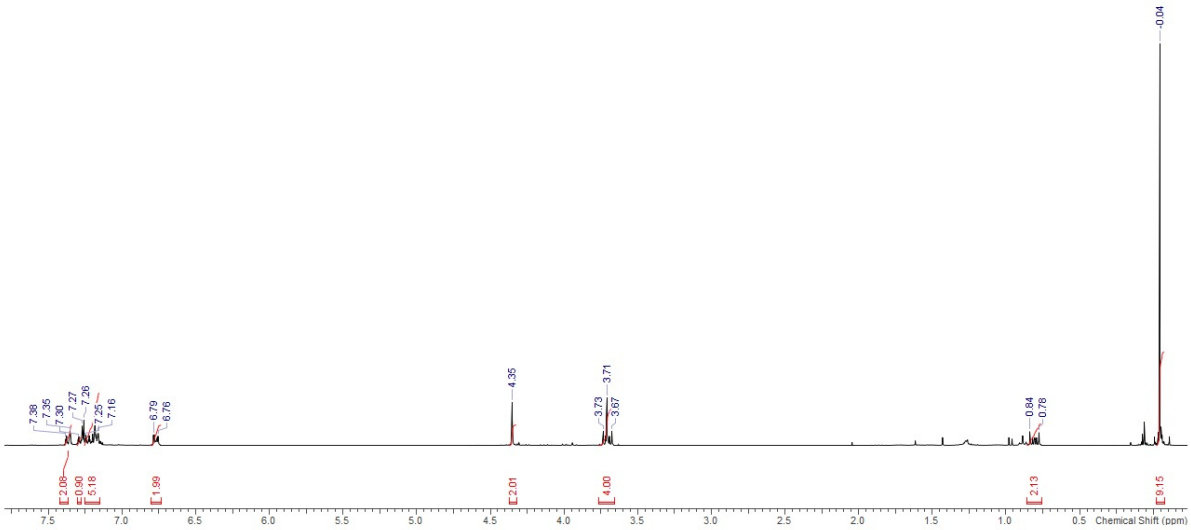


Figure S38. ^{1}H NMR spectrum (300 MHz) of **2c** in $CDCl_3$ (*) at 298 K.

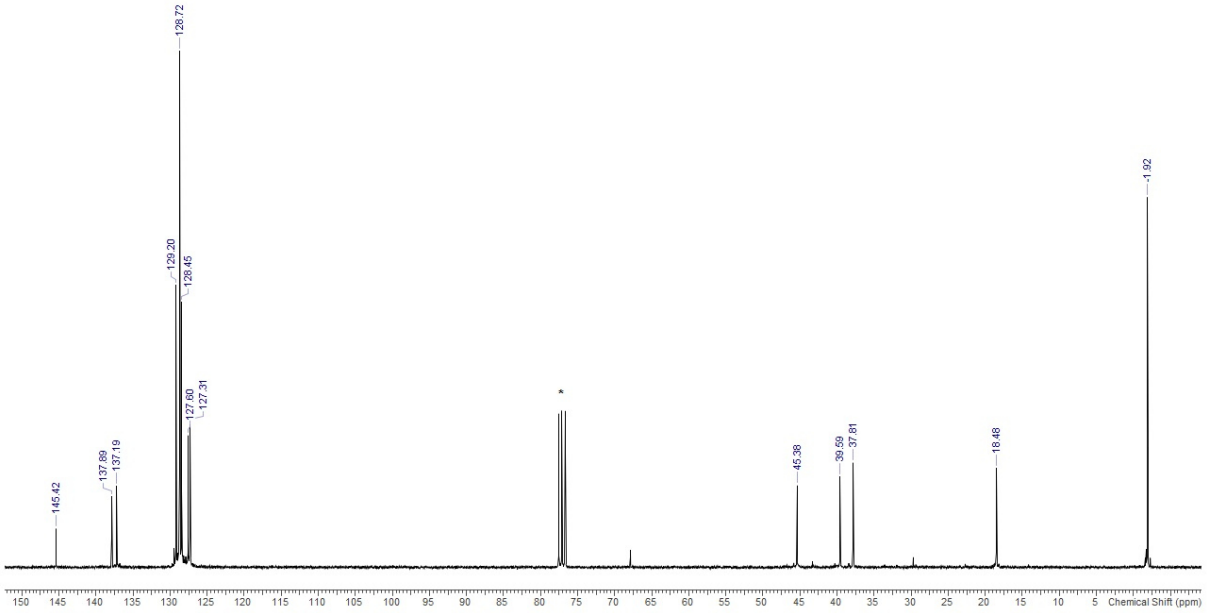


Figure S39. ^{13}C NMR spectrum (75 MHz) of **2c** in $CDCl_3$ (*) at 298 K.

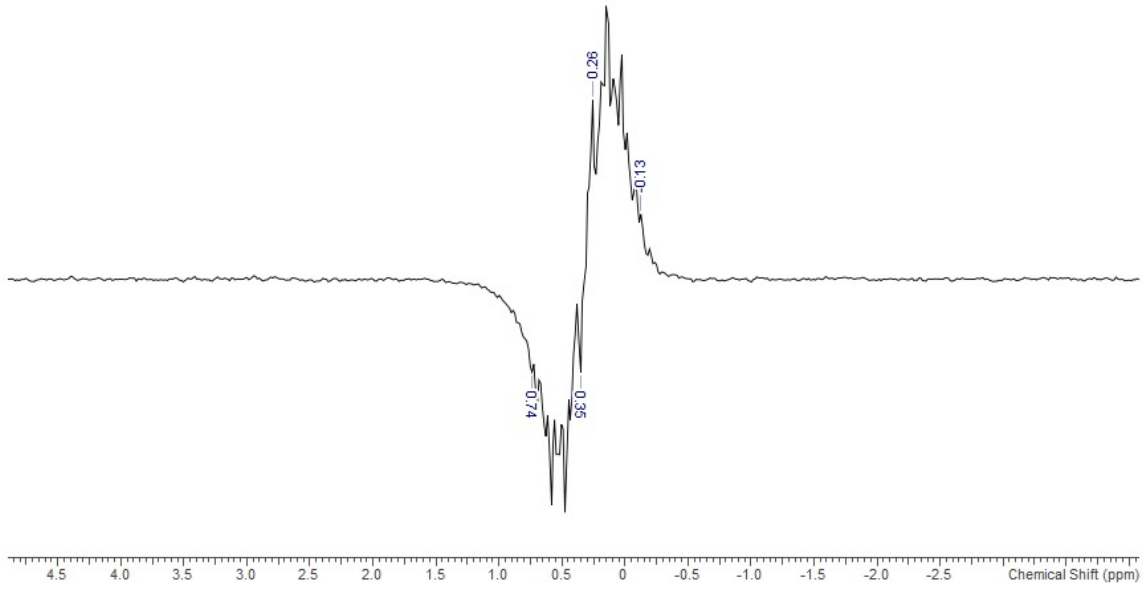


Figure S40. ^{29}Si NMR spectrum (60 MHz) of **2c** in $CDCl_3$ at 298 K.

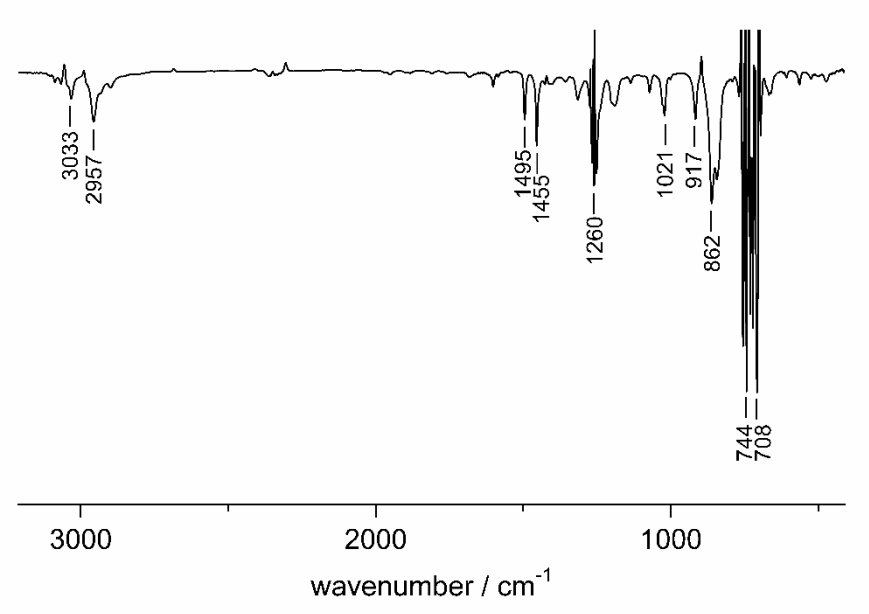


Figure S41. IR spectroscopy of **2c** in CH_2Cl_2.

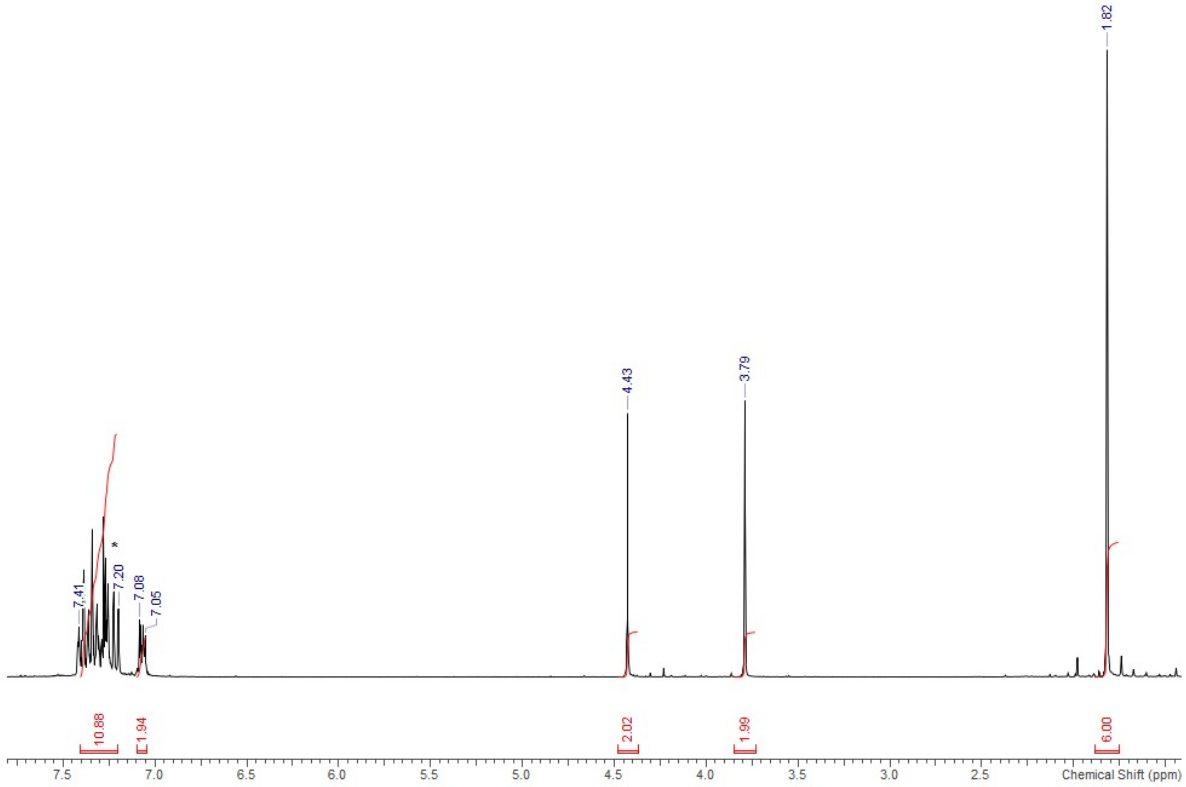


Figure S42. ^{1}H NMR spectrum (300 MHz) of **2d** in $CDCl_3$ (*) at 298 K.

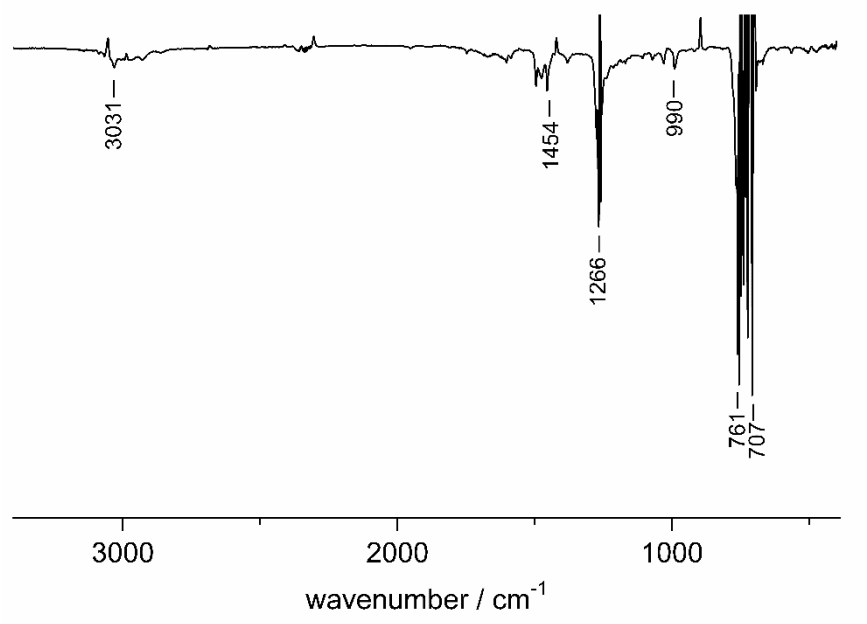


Figure S43. IR spectroscopy of **2d** in CH_2Cl_2.

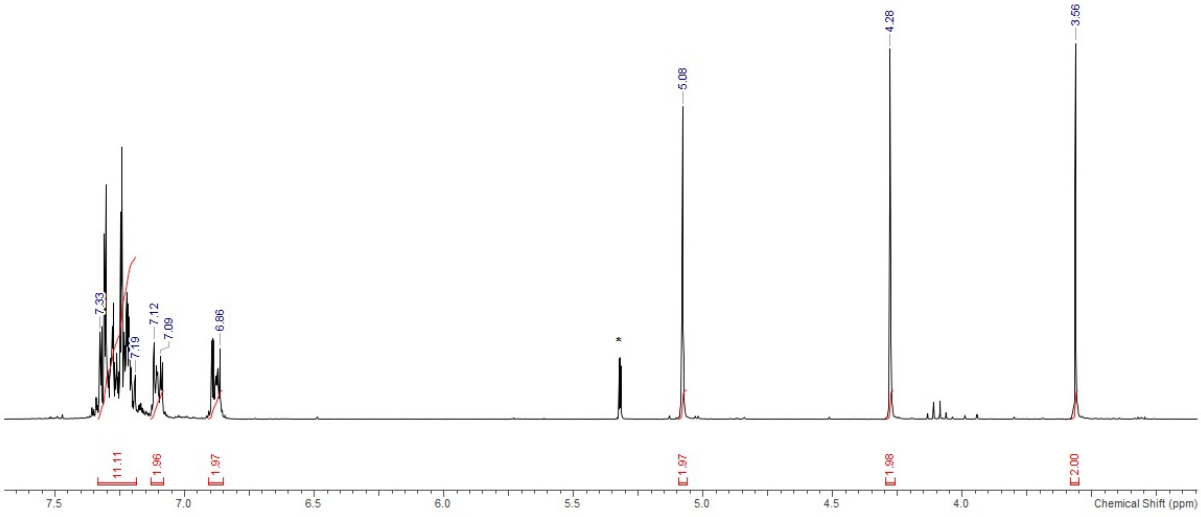


Figure S44. ^{1}H NMR spectrum (500 MHz) of **2e** in CD_2Cl_2 (*) at 298 K.

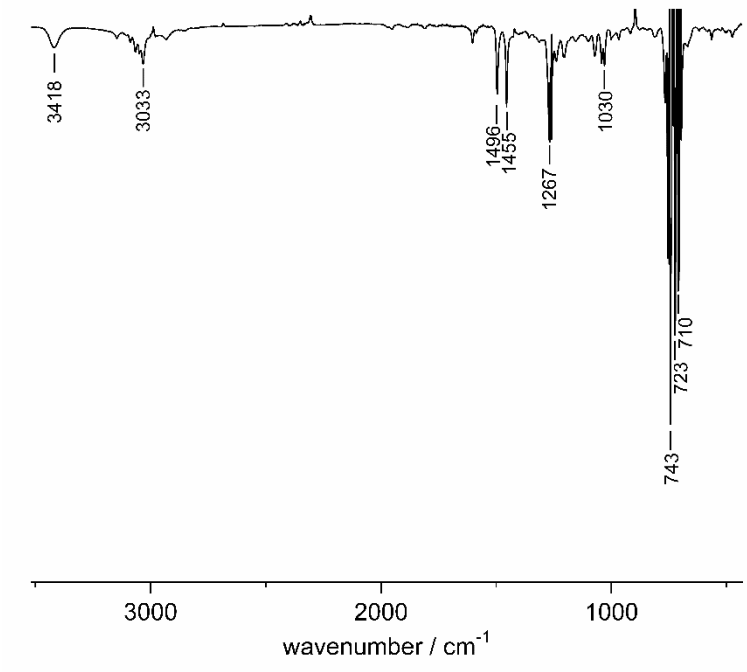


Figure S45. IR spectroscopy of **2e** in CH_2Cl_2.

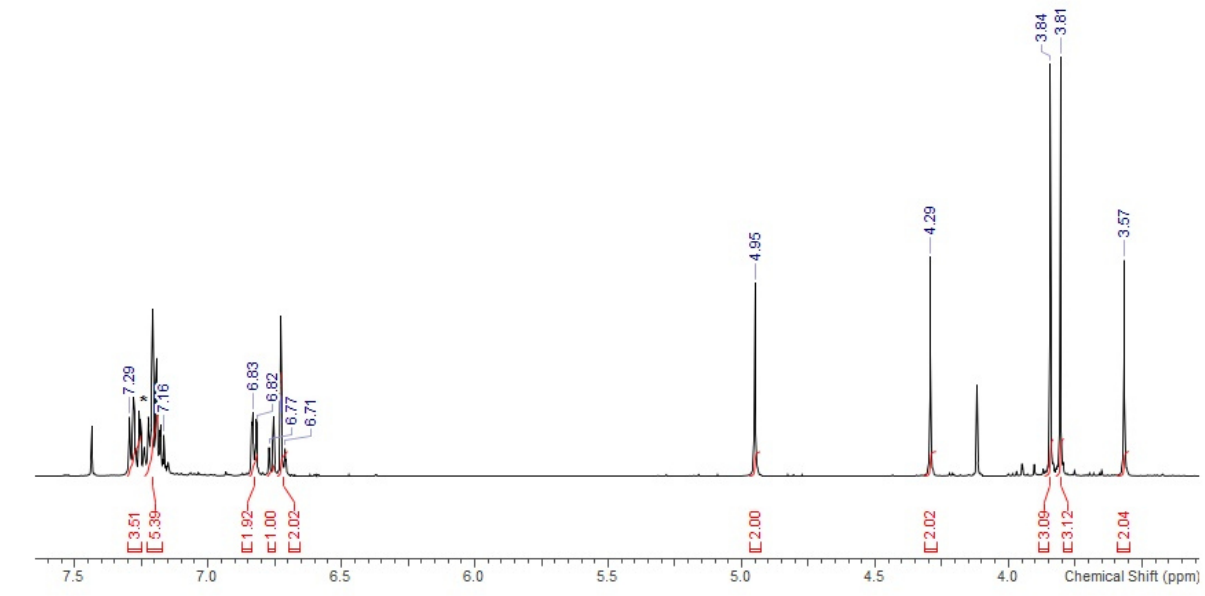


Figure S46. ^{1}H NMR spectrum (500 MHz) of **2f** in $CDCl_3$ (*) at 298 K.

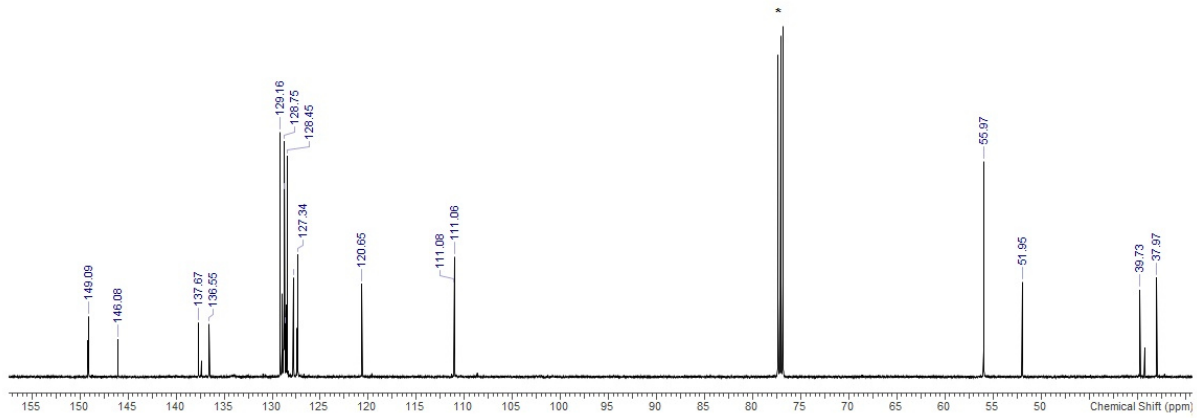


Figure S47. ^{13}C NMR spectrum (126 MHz) of **2f** in $CDCl_3$ (*) at 298 K.

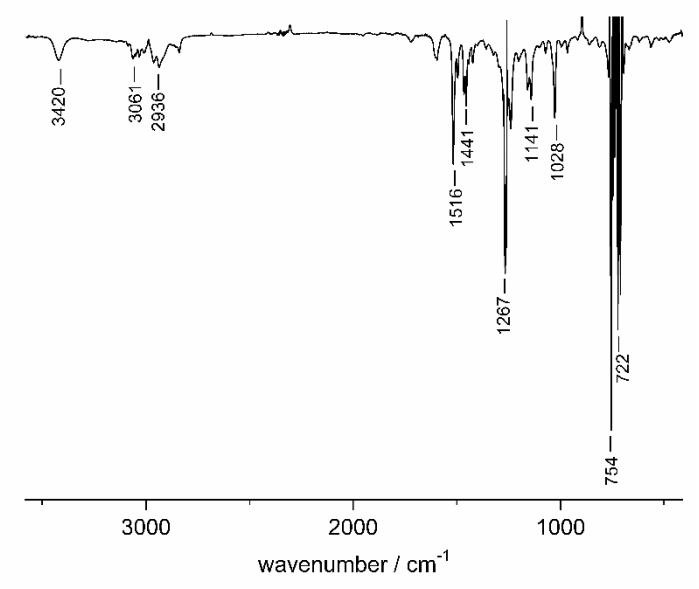


Figure S48. IR spectroscopy of **2f** in CH_2Cl_2.

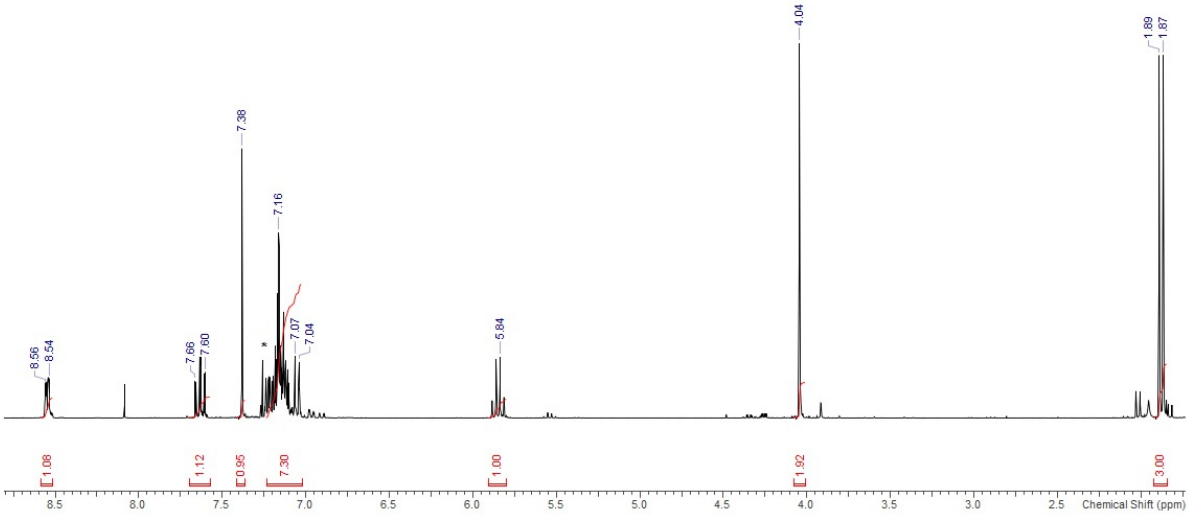


Figure S49. ^{1}H NMR spectrum (300 MHz) of **3** in $CDCl_3$ (*) at 298 K.

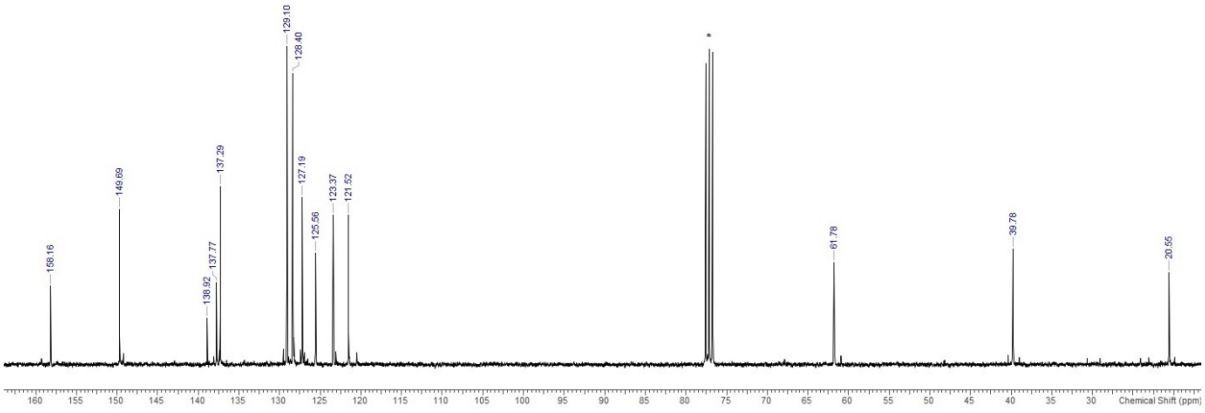


Figure S50. ^{13}C NMR spectrum (75 MHz) of **3** in $CDCl_3$ (*) at 298 K.

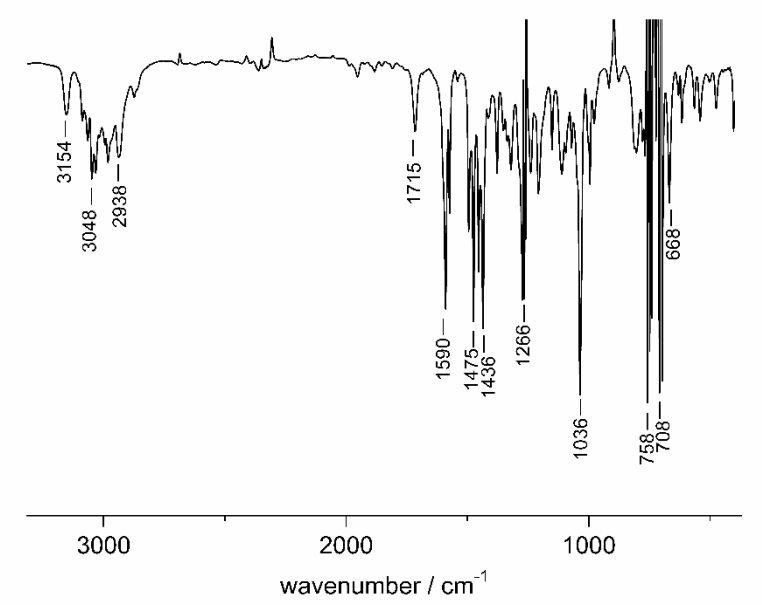


Figure S51. IR spectroscopy of **3** in CH_2Cl_2.

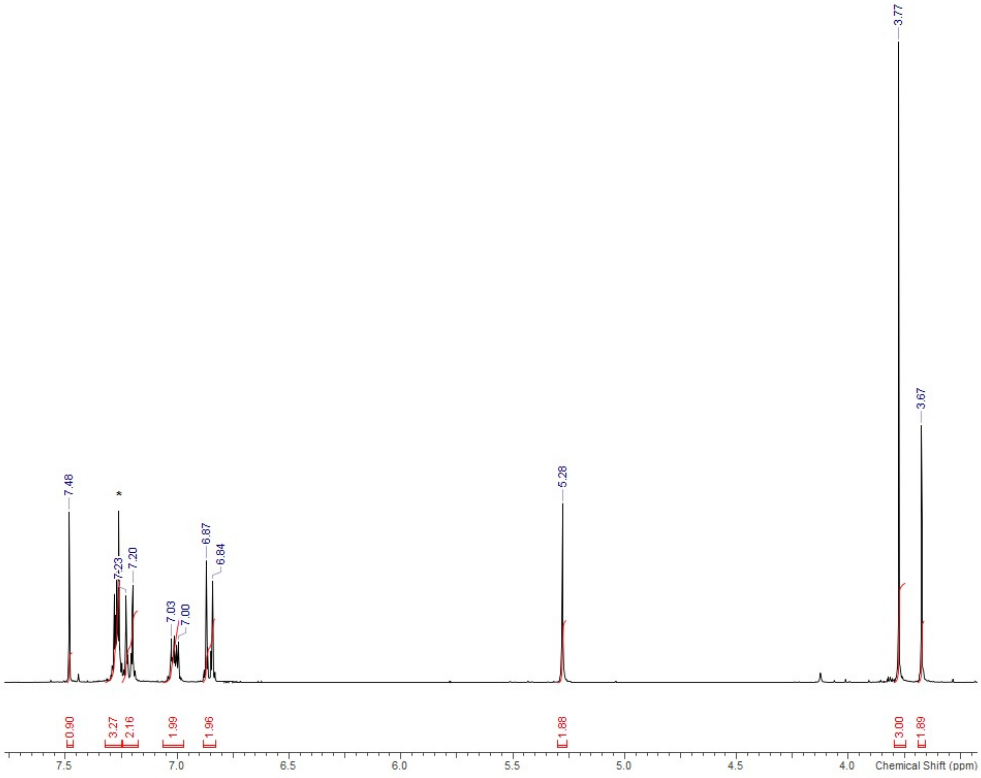


Figure S52. ^1H NMR spectrum (300 MHz) of **4** in $CDCl_3$ (*) at 298 K.

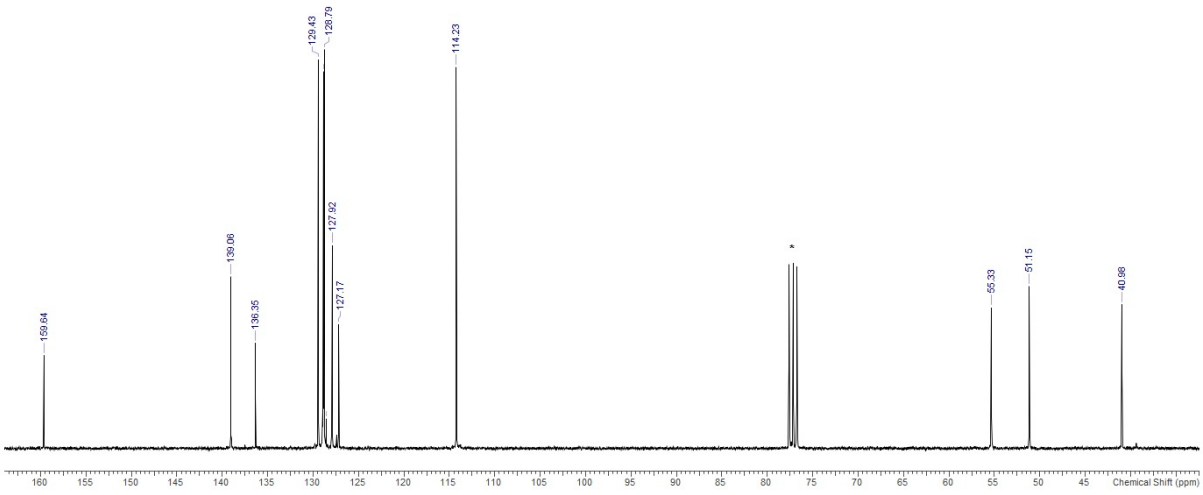


Figure S53. ^{13}C NMR spectrum (75 MHz) of **4** in $CDCl_3$ (*) at 298 K.

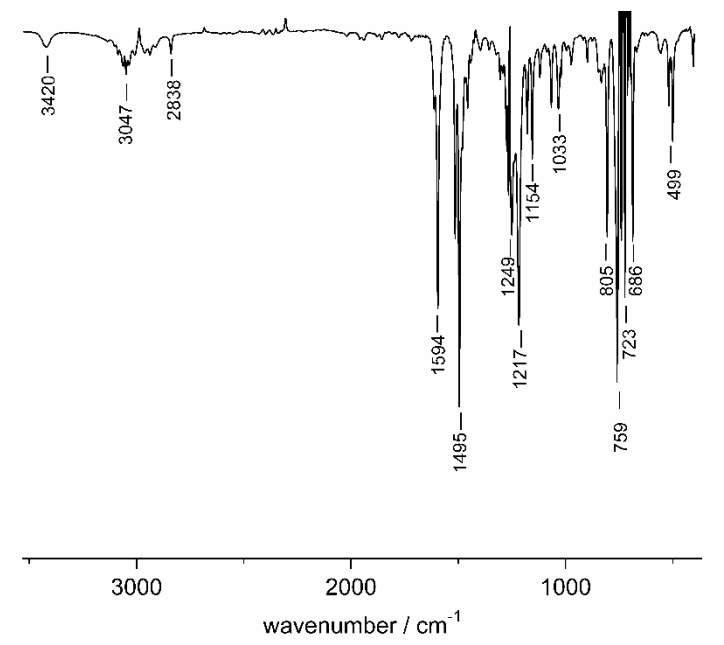


Figure S54. IR spectroscopy of **4** in CH_2Cl_2.

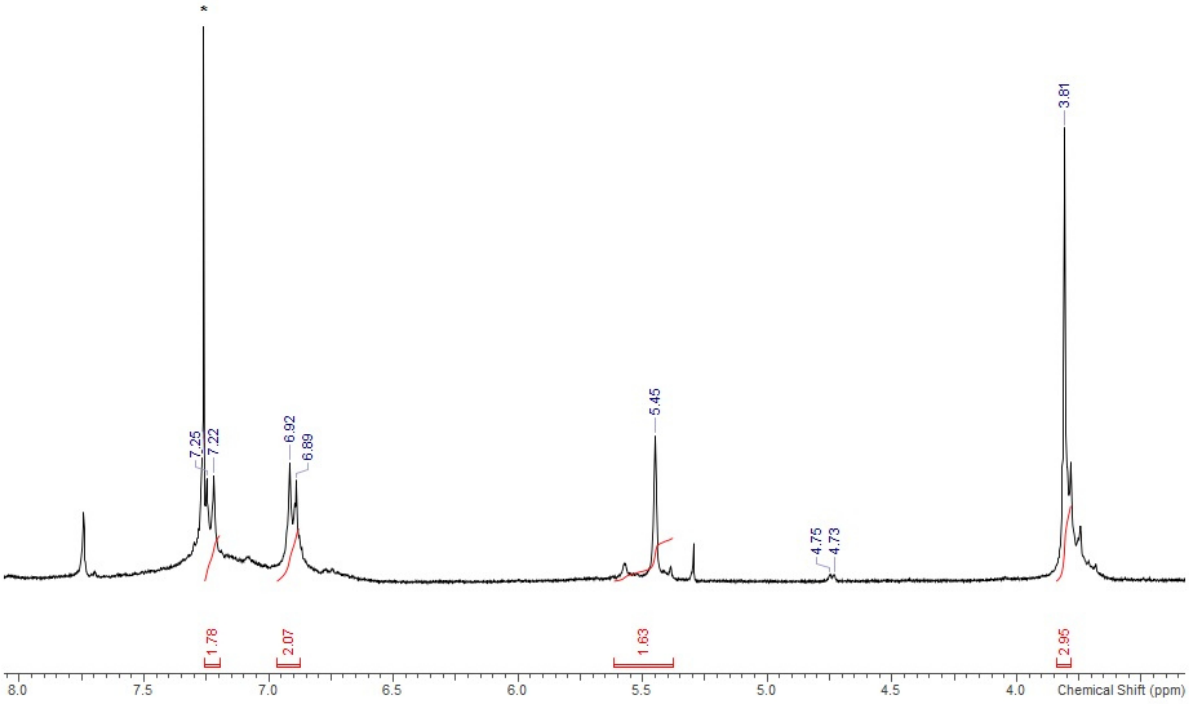


Figure S55. ^{1}H NMR spectrum (300 MHz) of **5a** in $CDCl_3$ (*) at 298 K.

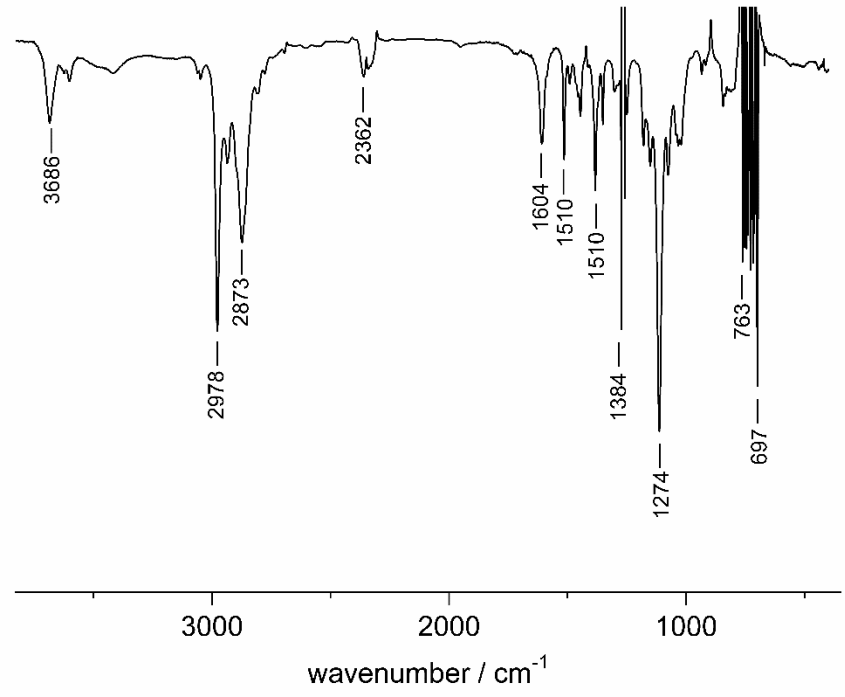


Figure S56. IR spectroscopy of **5a** in CH_2Cl_2.

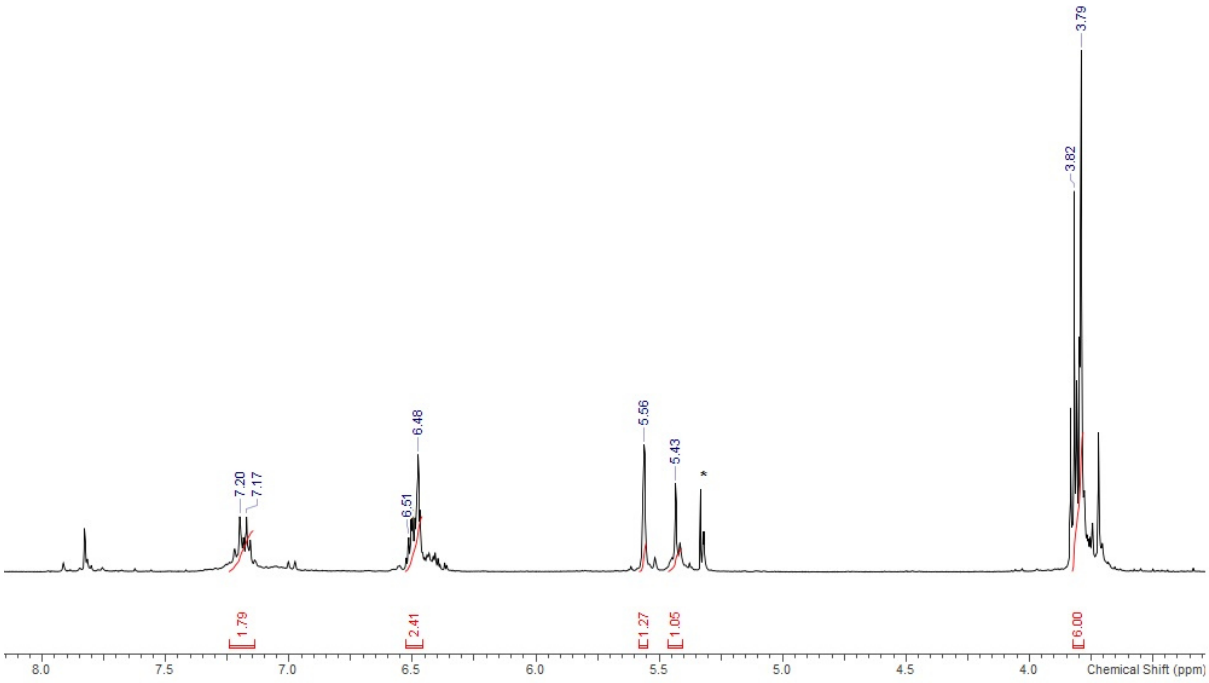


Figure S57. ^{1}H NMR spectrum (300 MHz) of **5b** in CD_2Cl_2 (*) at 298 K.

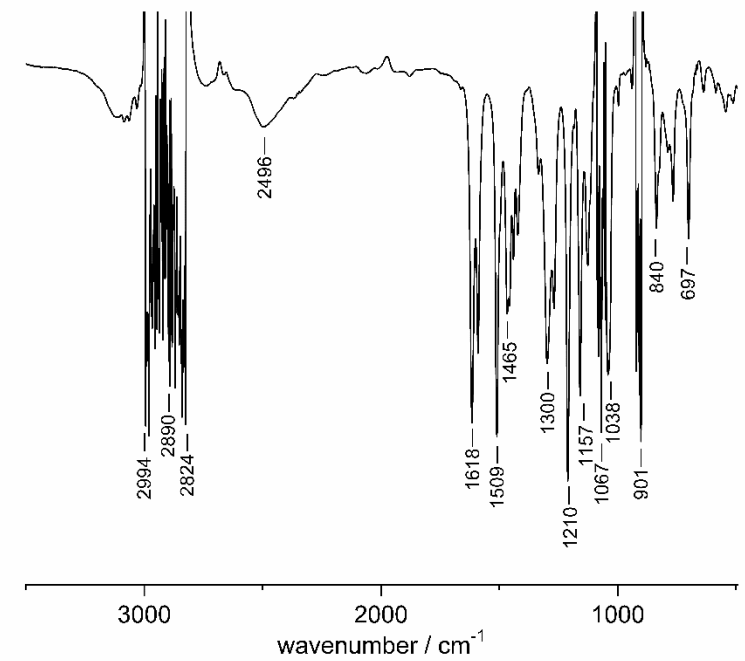


Figure S58. IR spectroscopy of **5b** in CH_2Cl_2.

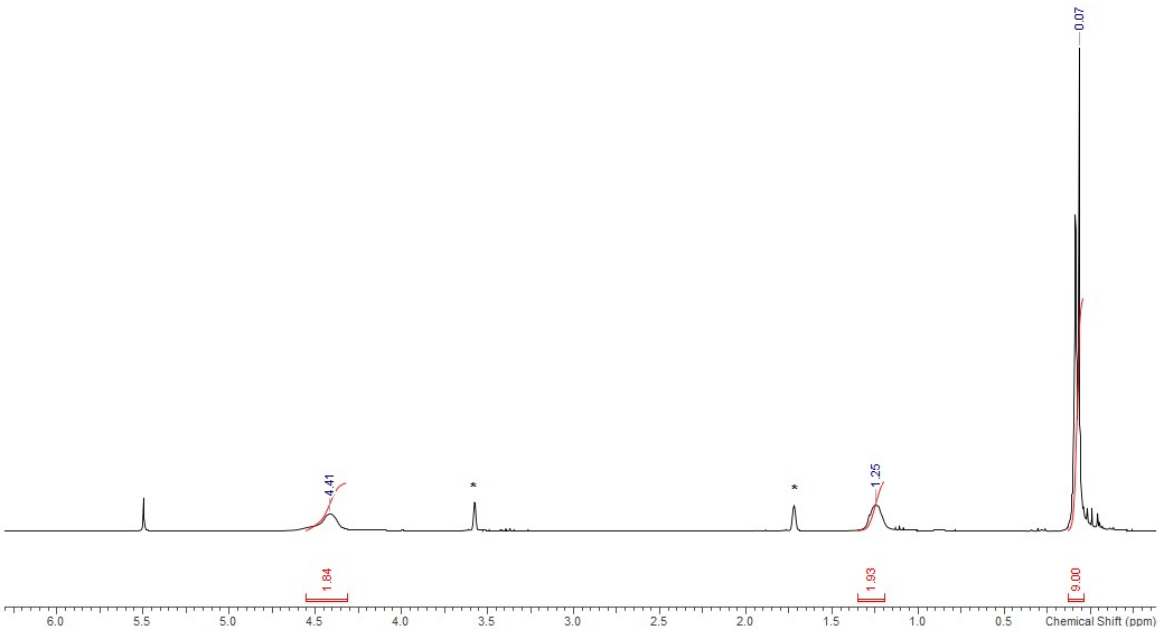


Figure S59. ^{1}H NMR spectrum (300 MHz) of **5c** in THF-D_8 (*) at 298 K.

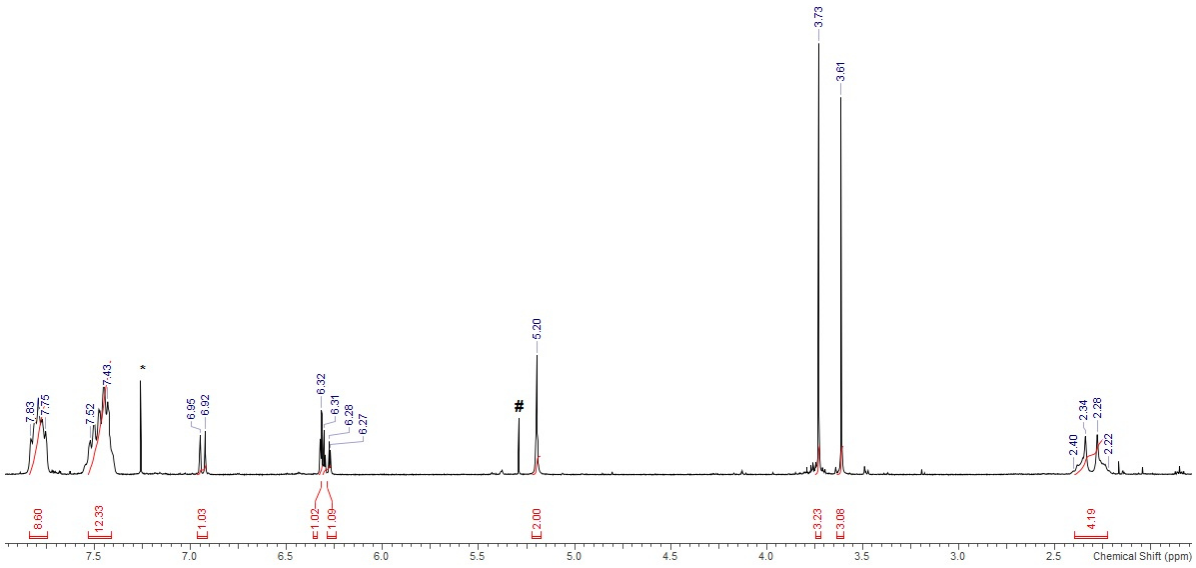


Figure S60. ^{1}H NMR spectrum (300 MHz) of **6** with traces of CH_2Cl_2 (#) in $CDCl_3$ (*) at 298 K.

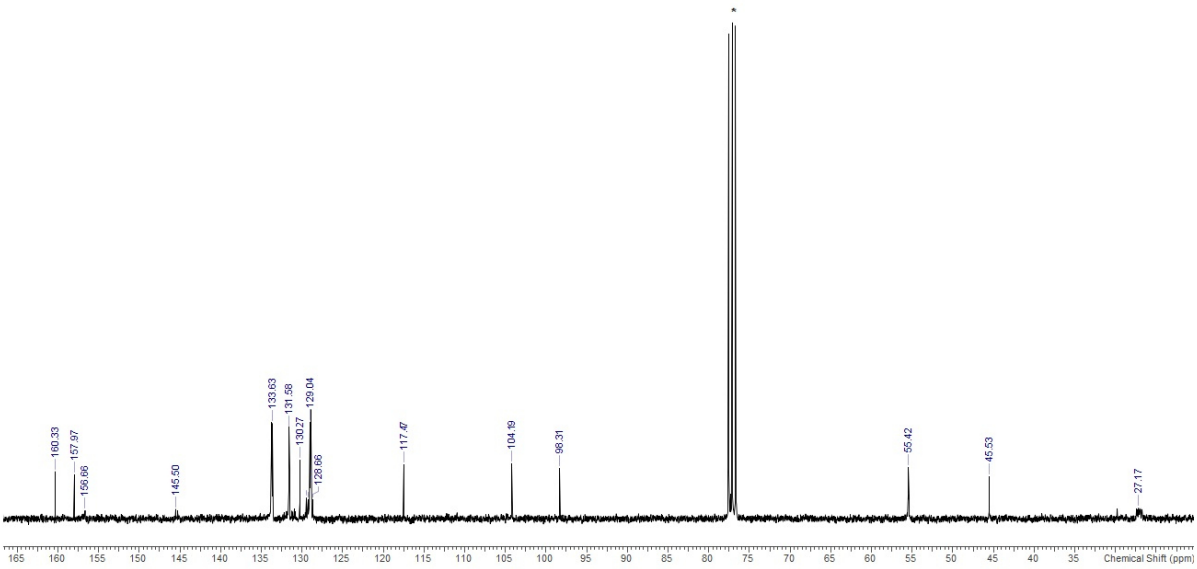


Figure S61. ^{13}C NMR spectrum (75 MHz) of **6** in $CDCl_3$ (*) at 298 K.

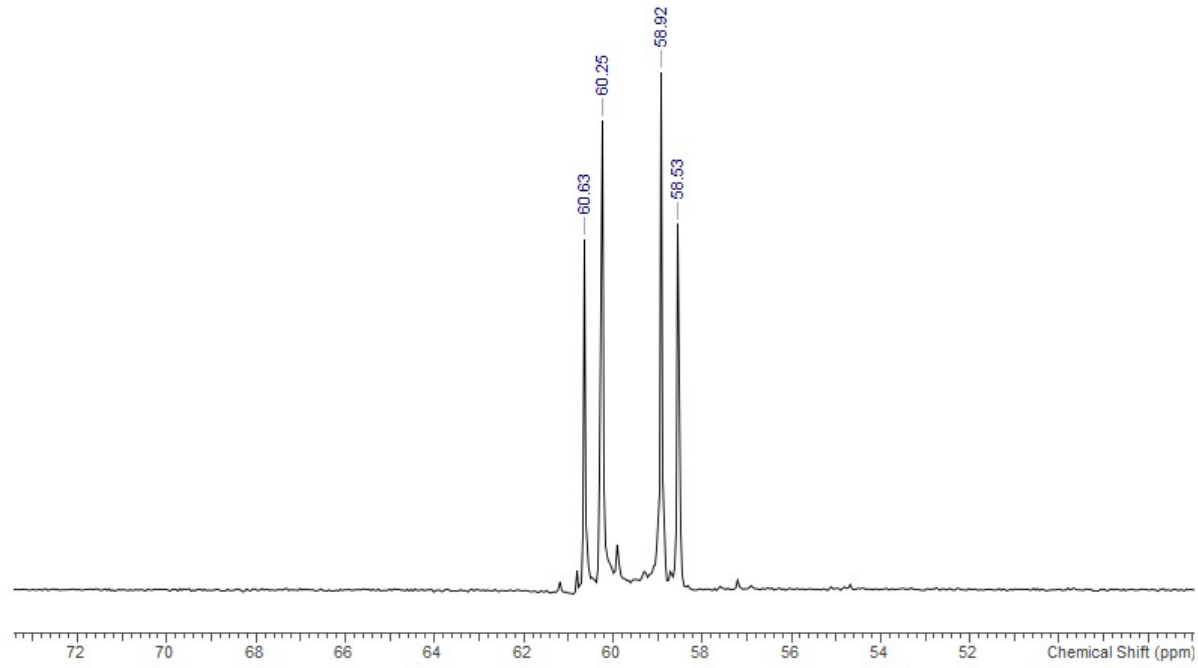


Figure S62. ^{31}P NMR spectrum (122 MHz) of **6** in $CDCl_3$ (*) at 298 K.

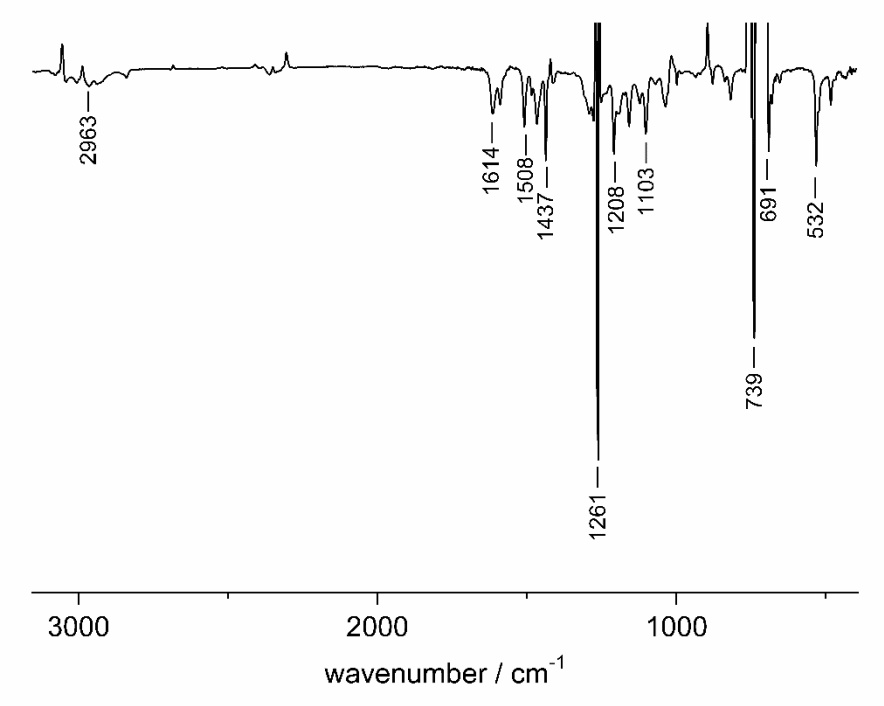


Figure S63. IR spectroscopy of **6** in CH_2Cl_2.

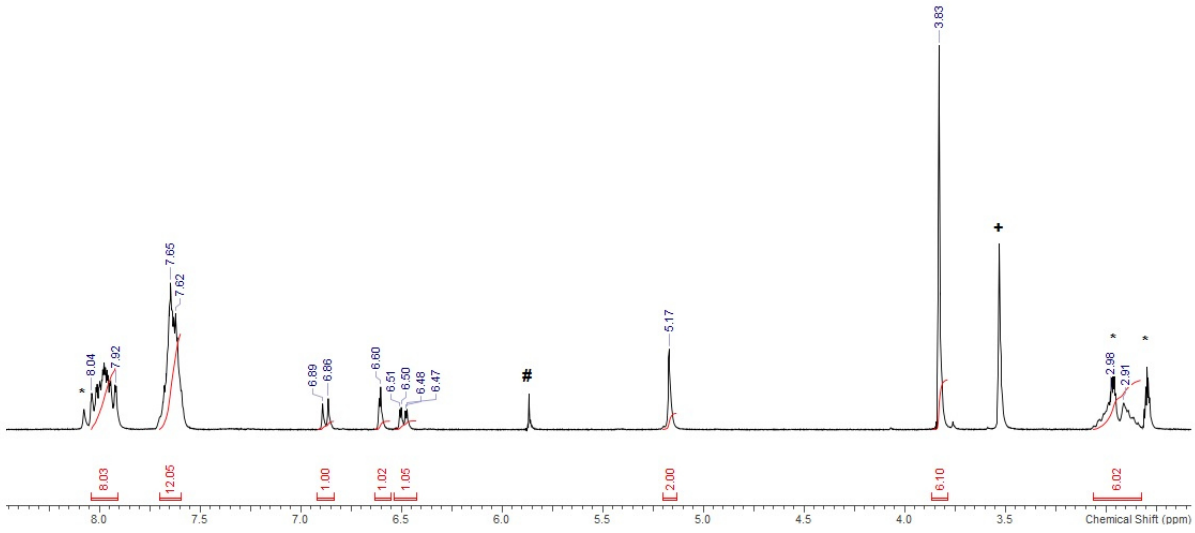


Figure S64. ^1H NMR spectrum (300 MHz) of **7** with traces of CH_2Cl_2 (#) and CH_3OH (+) in DMF-D_7 (*) at 298 K.

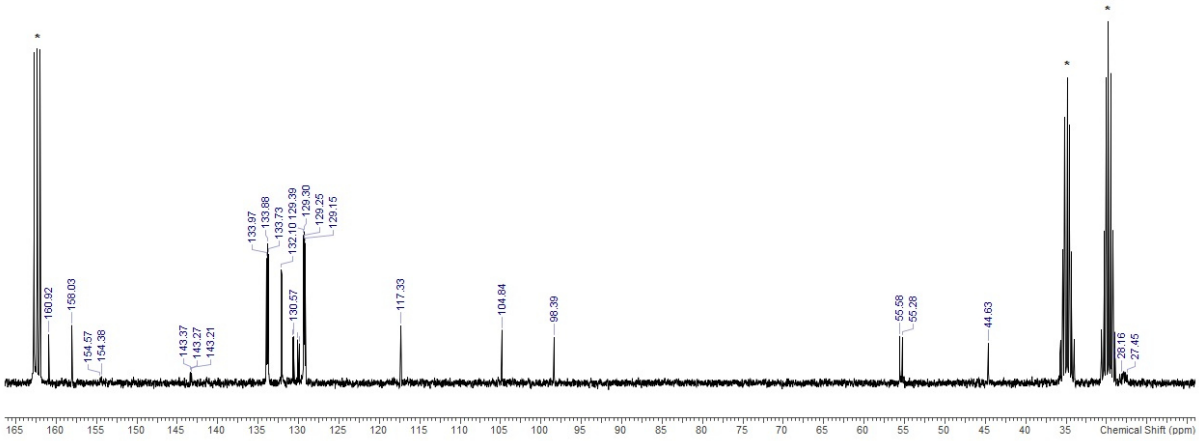


Figure S65. ^{13}C NMR spectrum (75 MHz) of **7** in DMF-D_7 (*) at 298 K.

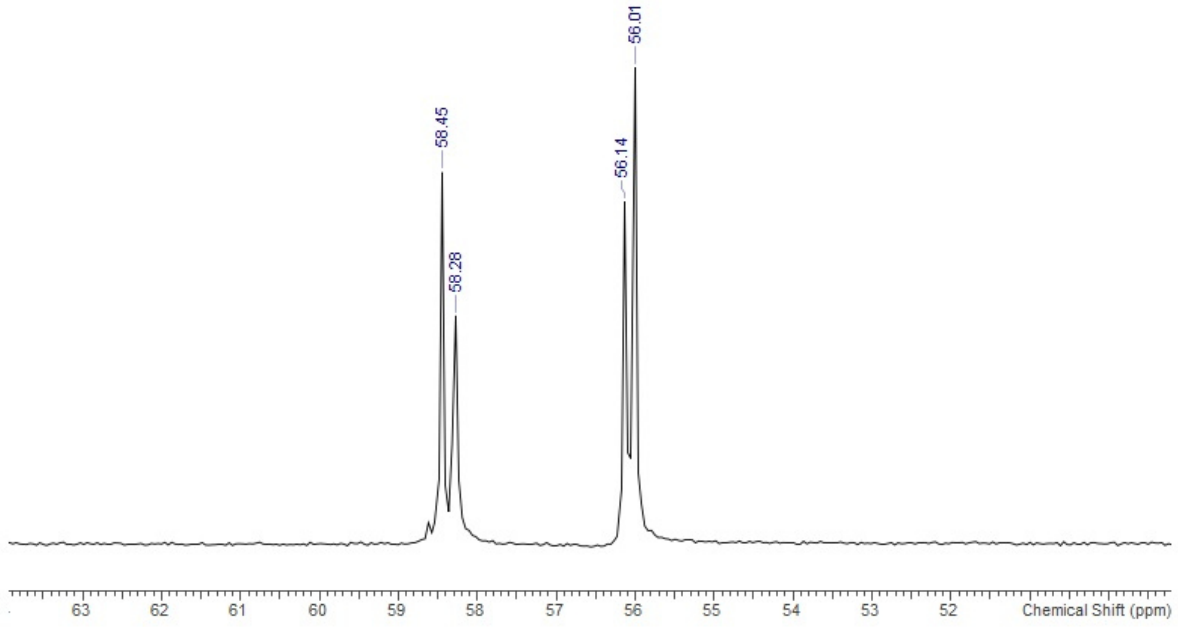


Figure S66. ^{1}H NMR spectrum (122 MHz) of **7** in DMF-D_7 (*) at 298 K.

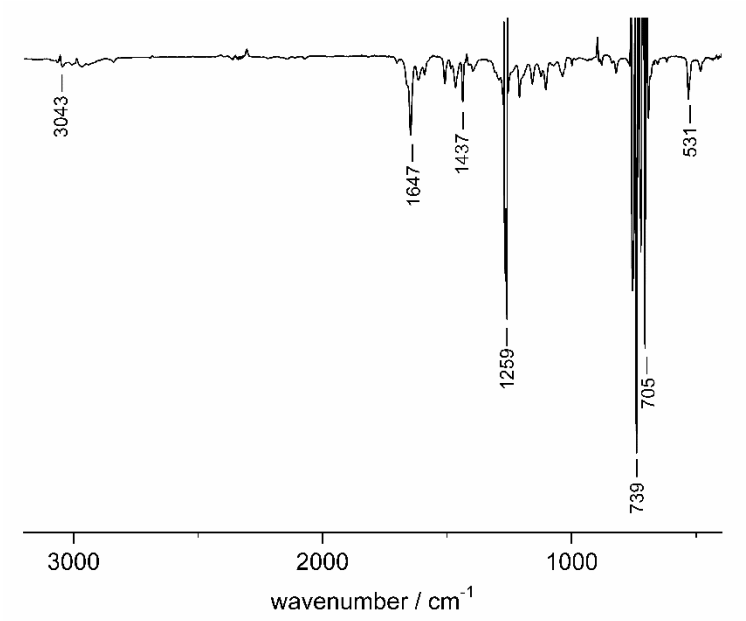


Figure S67. IR spectroscopy of **7** in CH_2Cl_2.

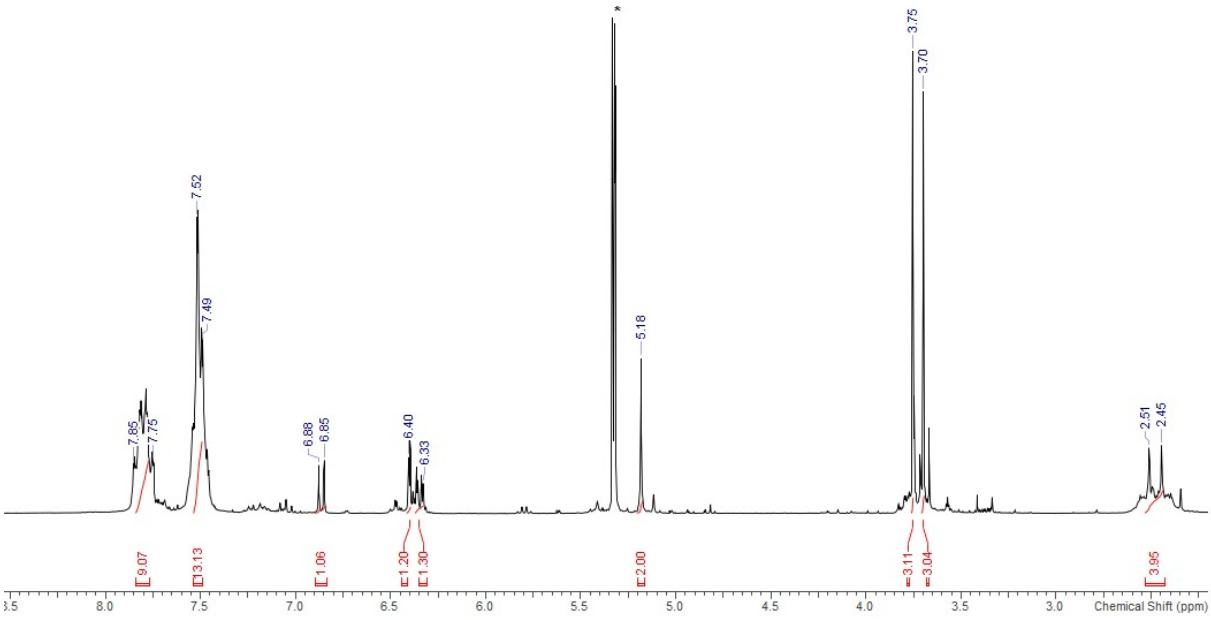


Figure S68. ^1H NMR spectrum (300 MHz) of **8** in CD_2Cl_2 (*) at 298 K.

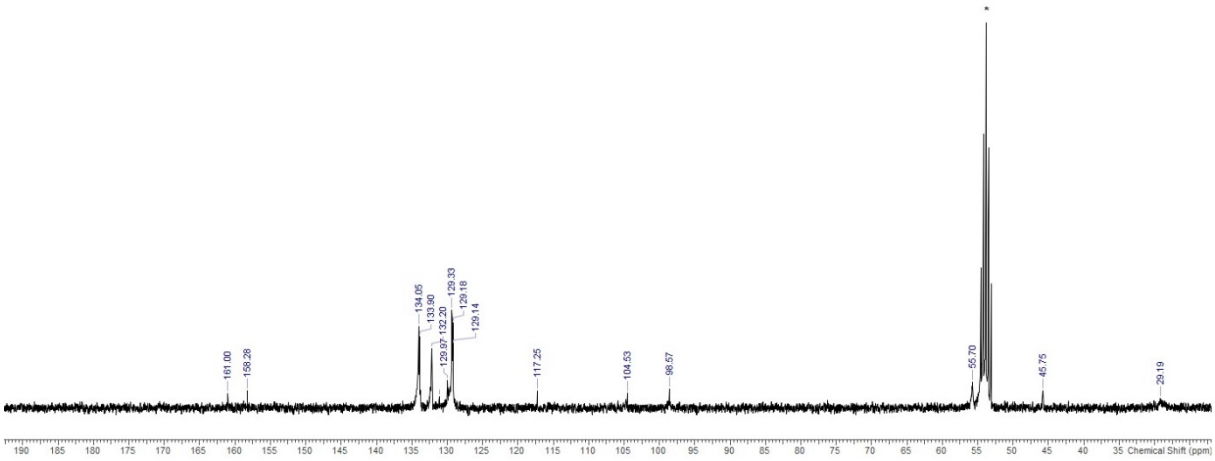


Figure S69. ^{13}C NMR spectrum (75 MHz) of **8** in CD_2Cl_2 (*) at 298 K.

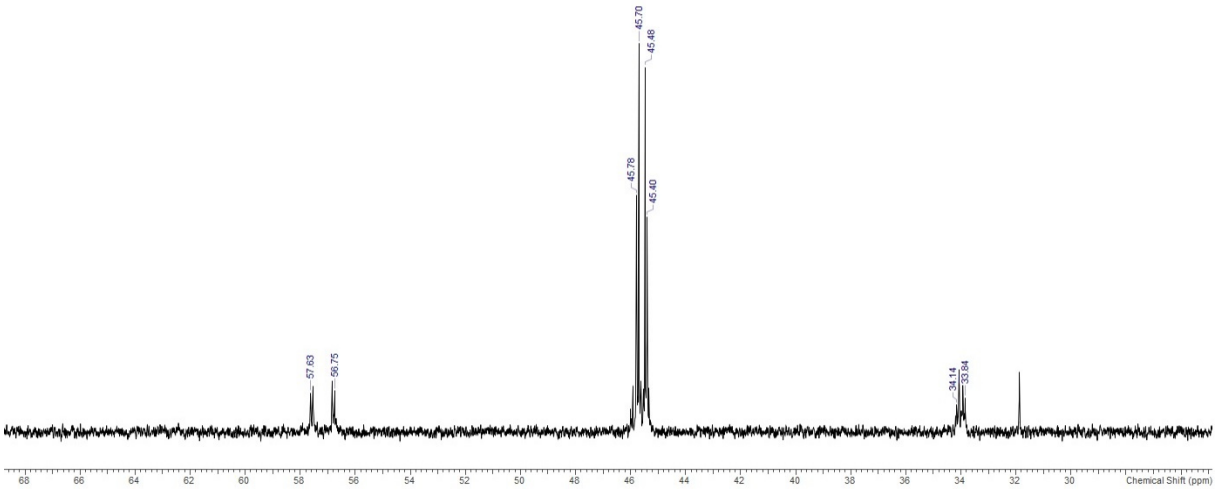


Figure S70. ^{31}P NMR spectrum (122 MHz) of **8** in CD_2Cl_2 (*) at 298 K.

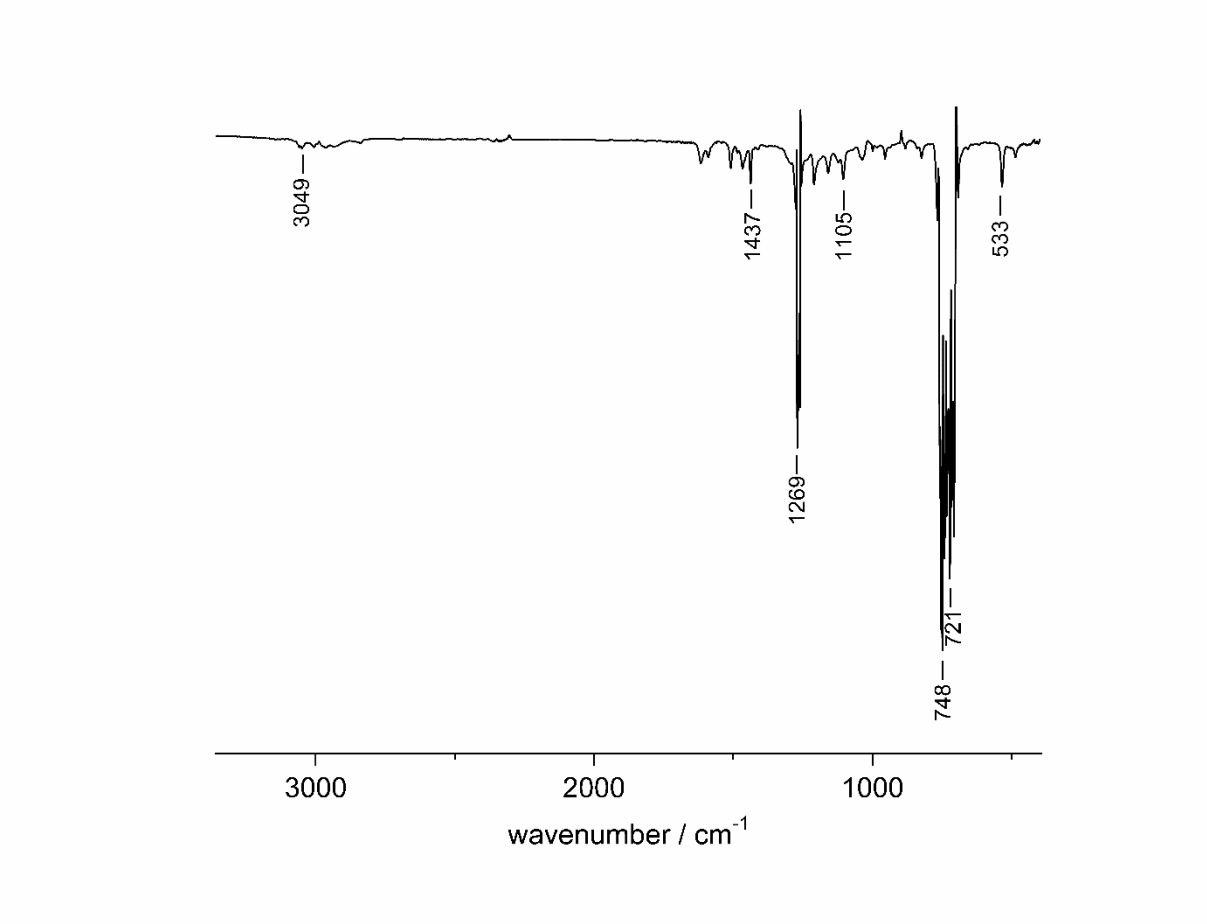


Figure S71. IR spectroscopy of **8** in CH_2Cl_2.

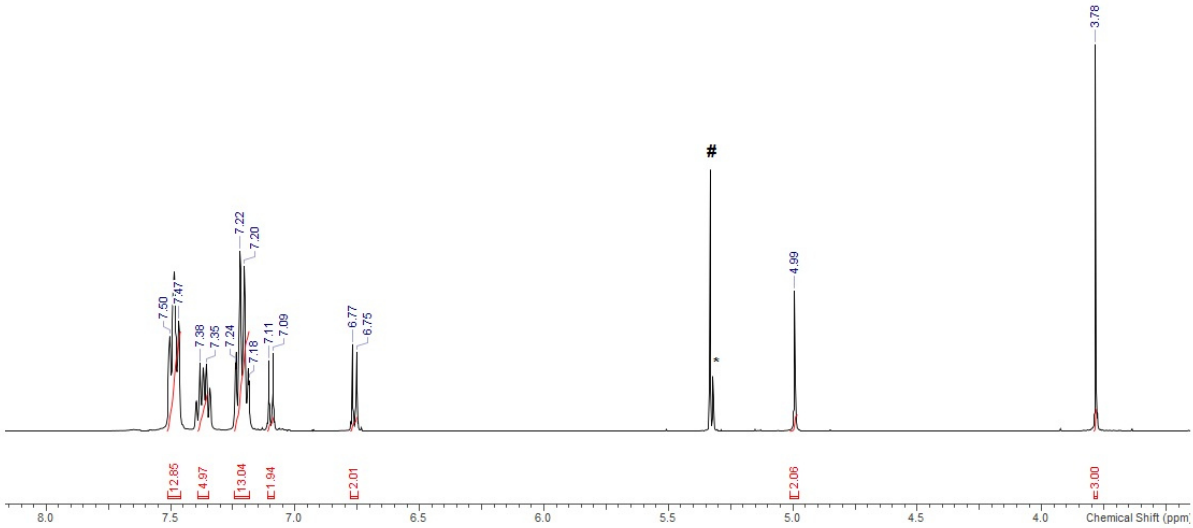


Figure S72. ^1H NMR spectrum (500 MHz) of **9a** with traces of CH_2Cl_2 (#) in CD_2Cl_2 (*) at 298 K.

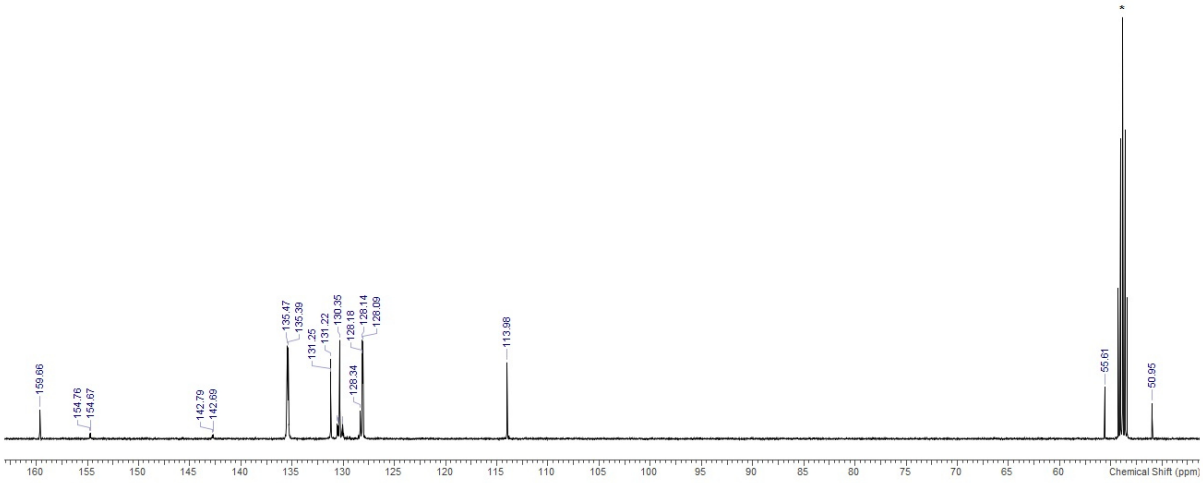


Figure S73. ^{13}C NMR spectrum (125 MHz) of **9a** in CD_2Cl_2 (*) at 298 K.

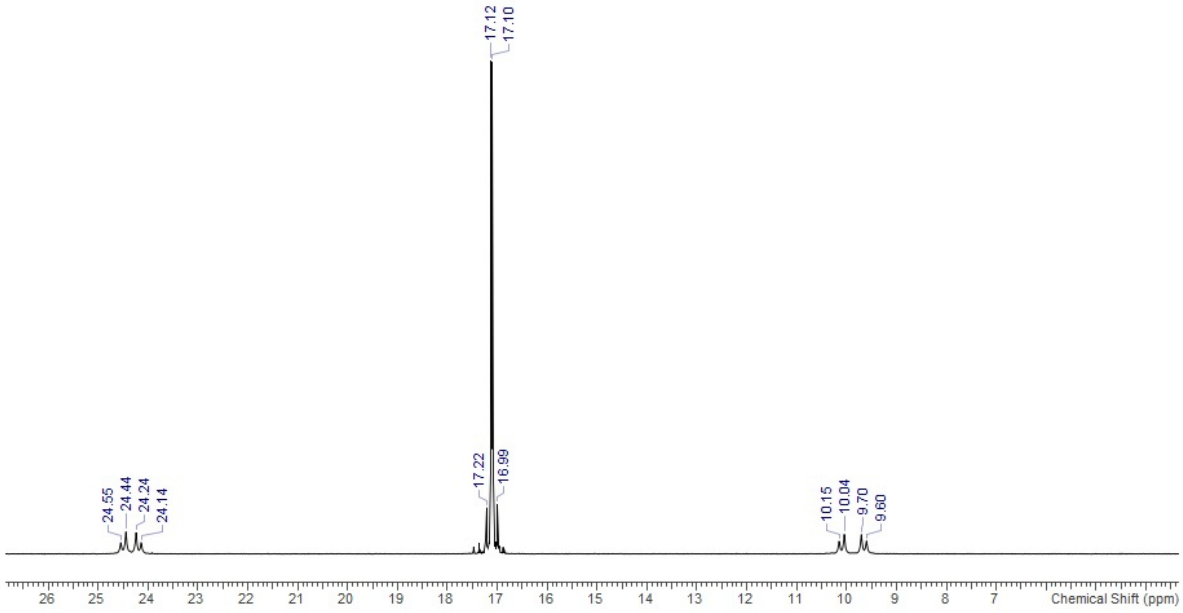


Figure S74. ^{31}P NMR spectrum (202 MHz) of **9a** in CD_2Cl_2 (*) at 298 K.

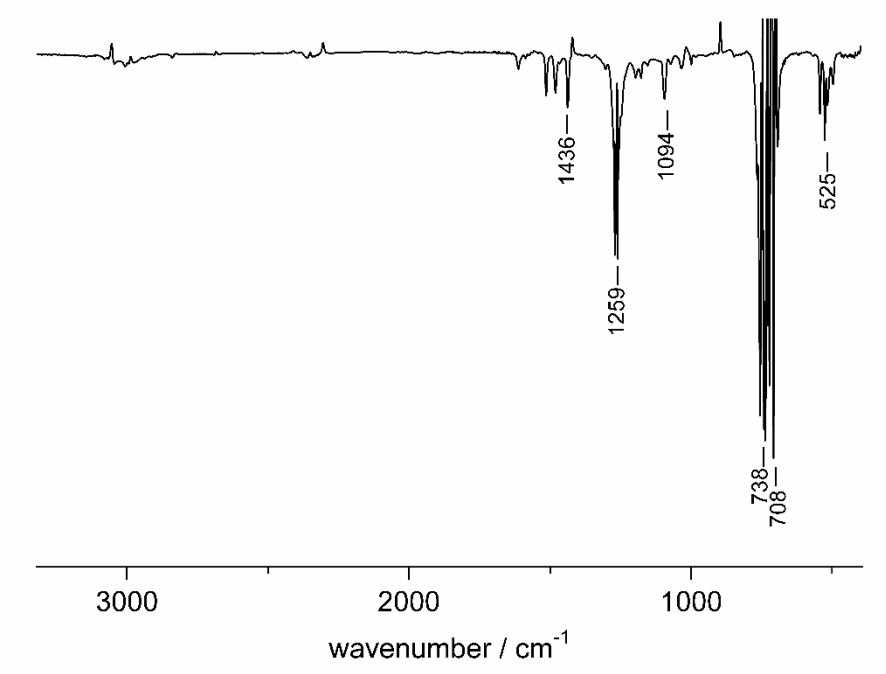


Figure S75. IR spectroscopy of **9a** in CH_2Cl_2.

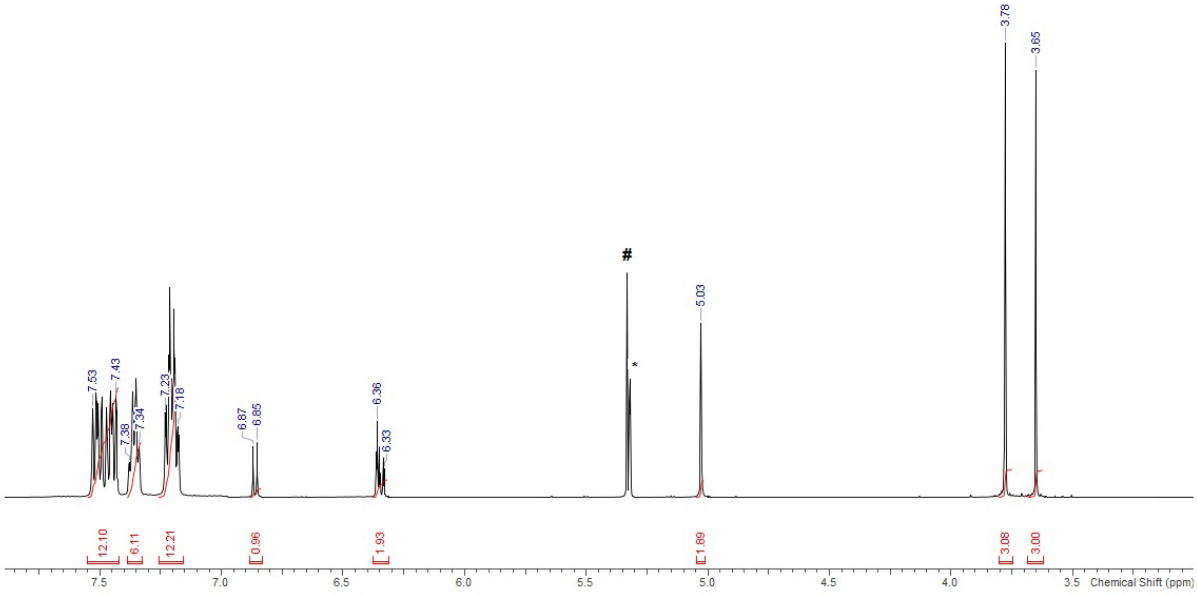


Figure S76. ^{1}H NMR spectrum (500 MHz) of **9b** with traces of CH_2Cl_2 (#) in CD_2Cl_2 (*) at 298 K.

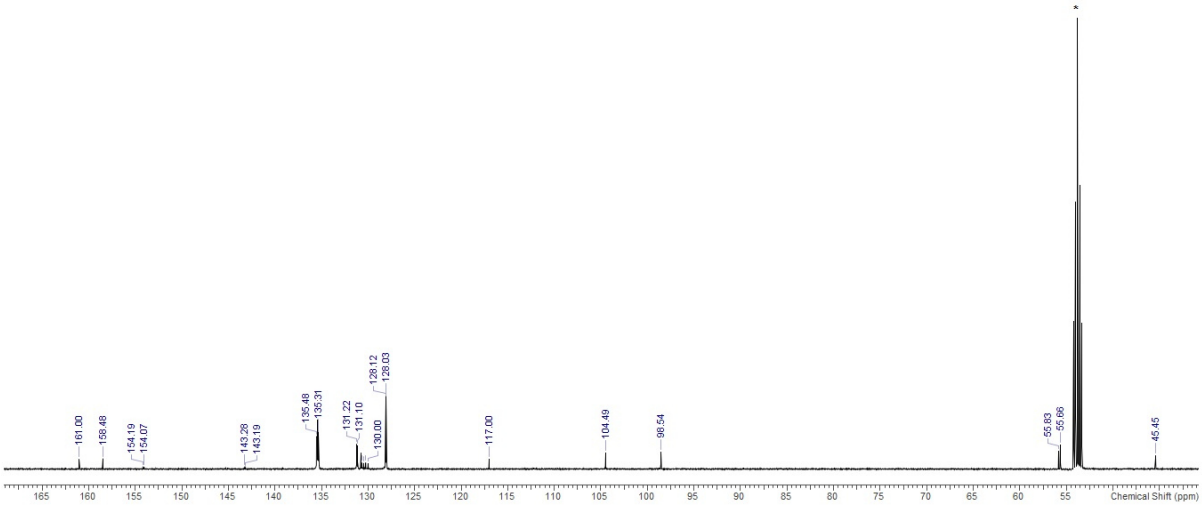


Figure S77. ^{13}C NMR spectrum (125 MHz) of **9b** in CD_2Cl_2 (*) at 298 K.

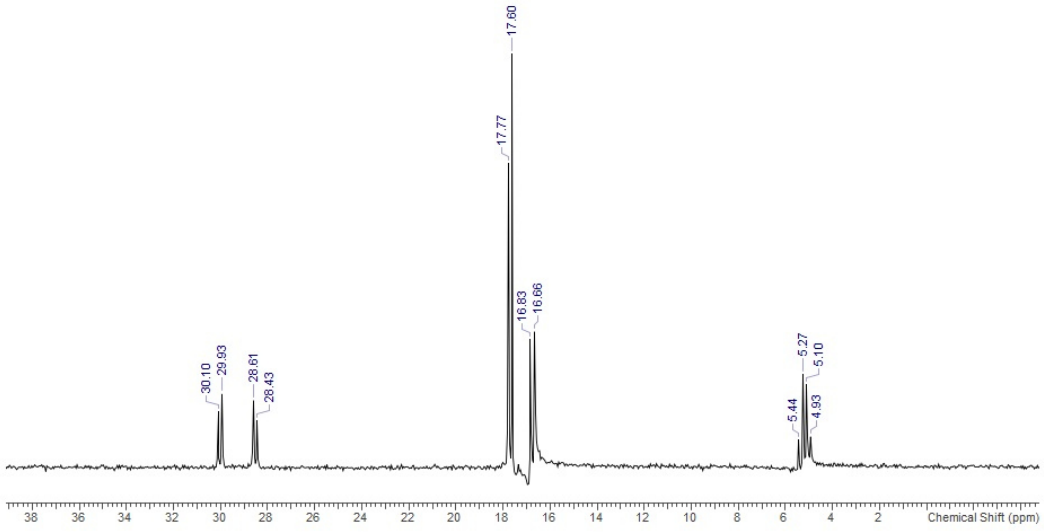


Figure S78. ^{31}P NMR spectrum (202 MHz) of **9b** in CD_2Cl_2 (*) at 298 K.

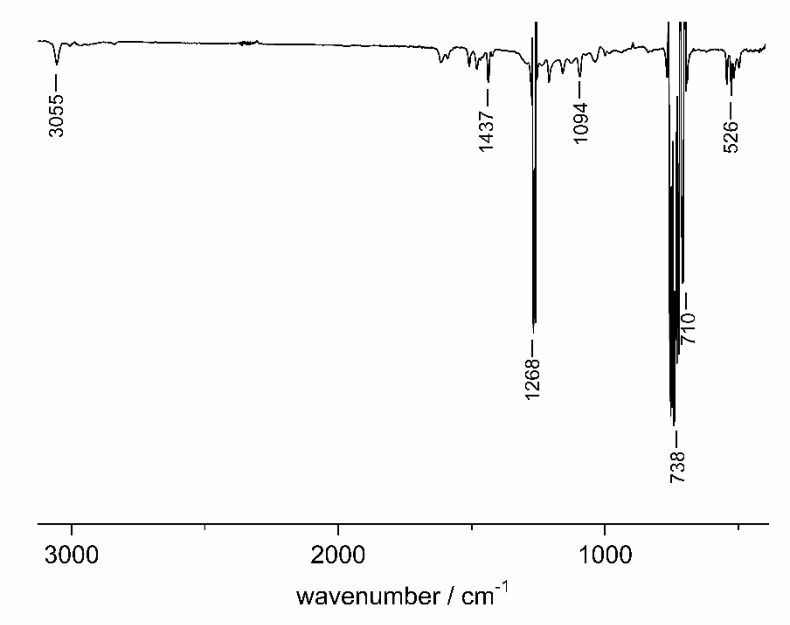


Figure S79. IR spectroscopy of **9b** in CH_2Cl_2.

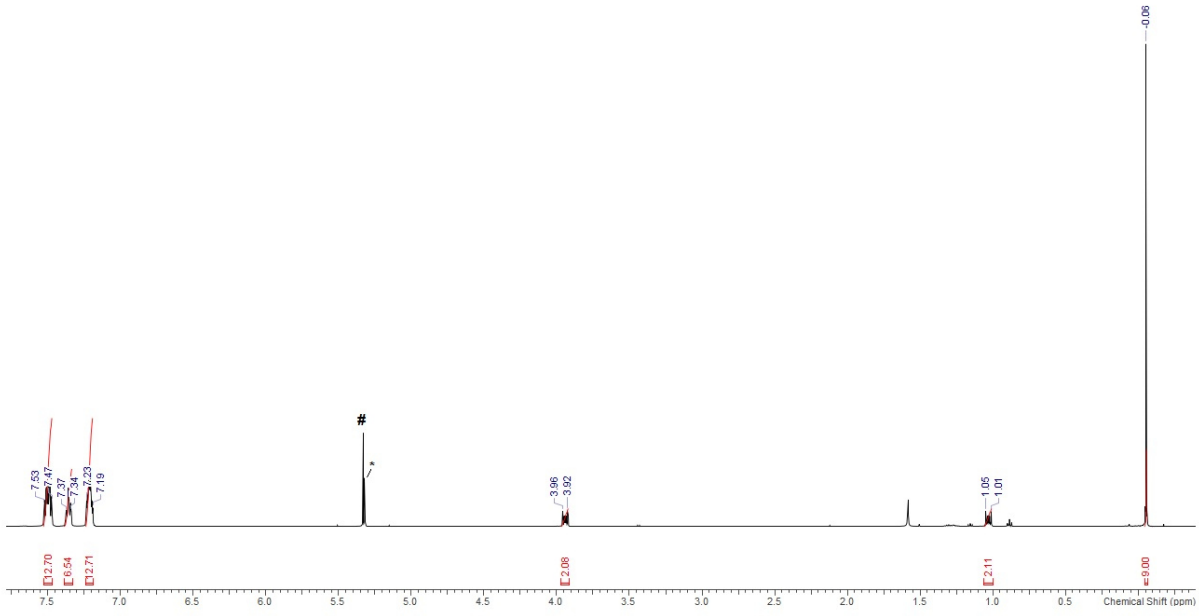


Figure S80. ^{1}H NMR spectrum (500 MHz) of **9c** with traces of CH_2Cl_2 (#) in CD_2Cl_2 (*) at 298 K.

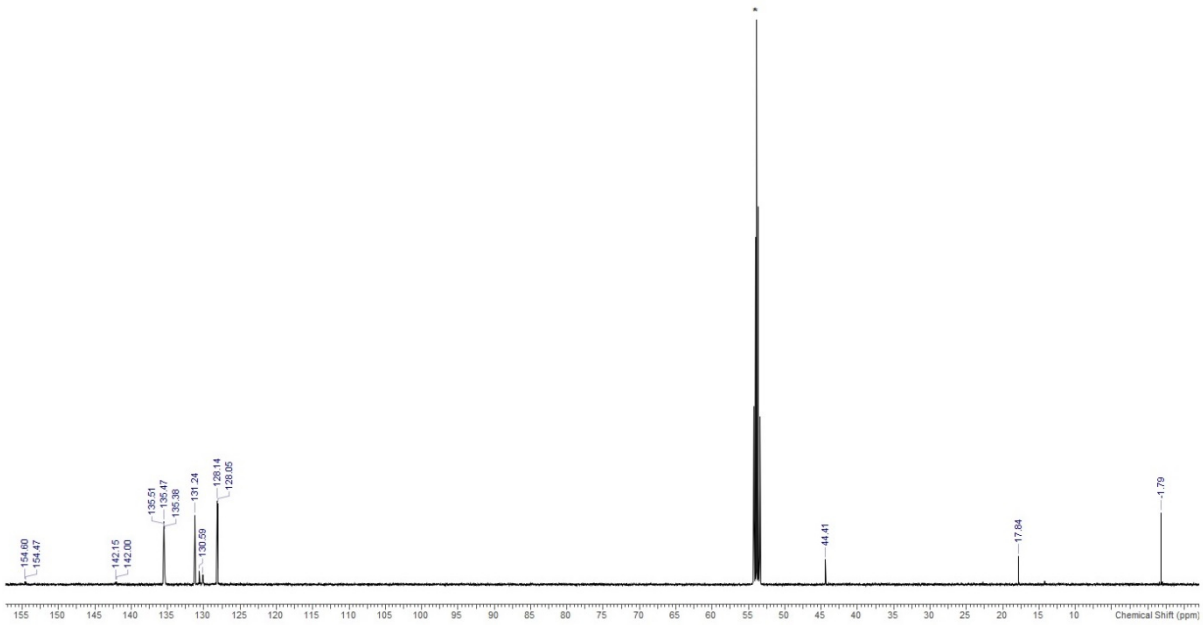


Figure S81. ^{13}C NMR spectrum (125 MHz) of **9c** in CD_2Cl_2 (*) at 298 K.

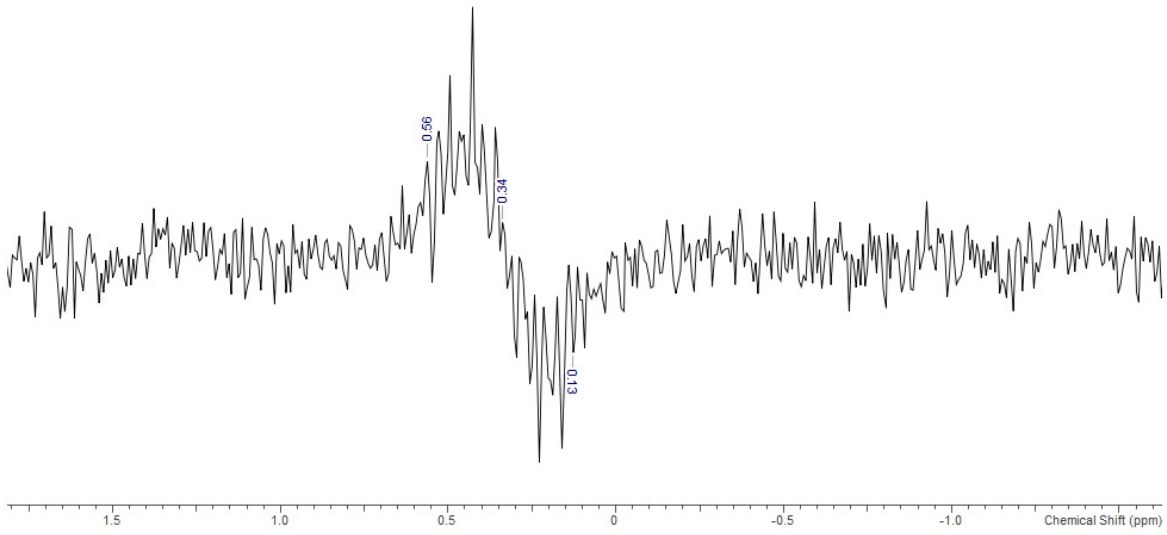


Figure S82. ^{29}Si NMR spectrum (99 MHz) of **9c** in CD_2Cl_2 (*) at 298 K.

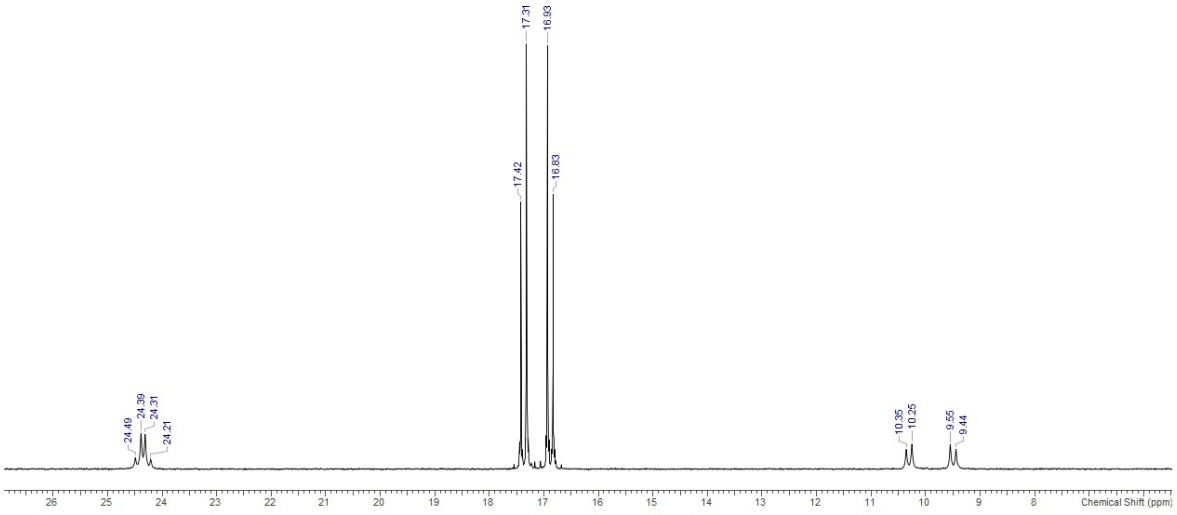


Figure S83. ^{31}P NMR spectrum (202 MHz) of **9c** in CD_2Cl_2 (*) at 298 K.

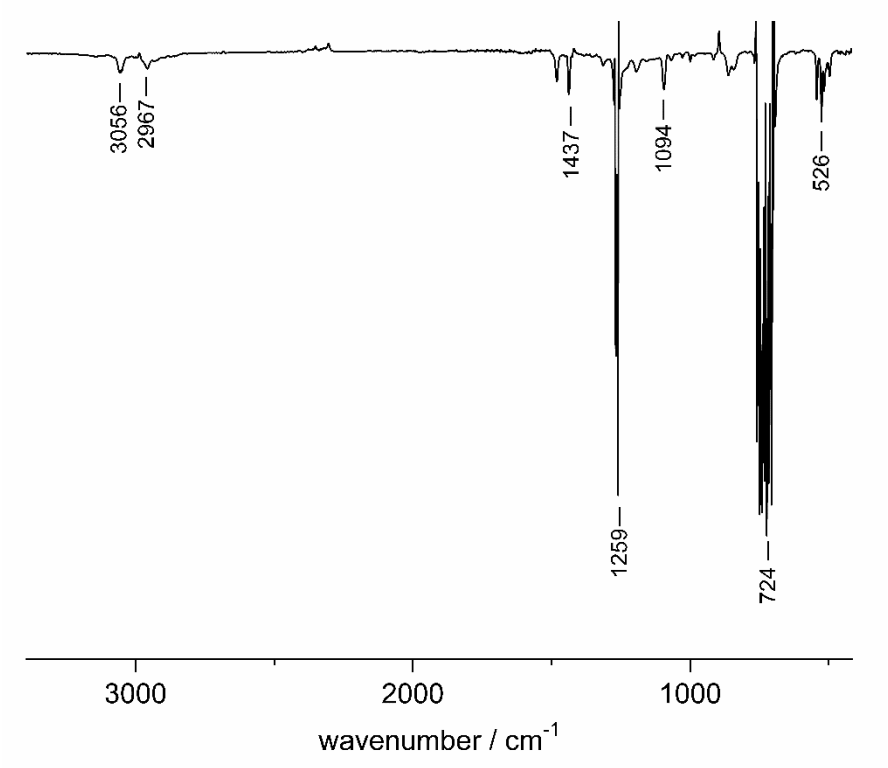


Figure S84. IR spectroscopy of **9c** in CH_2Cl_2.

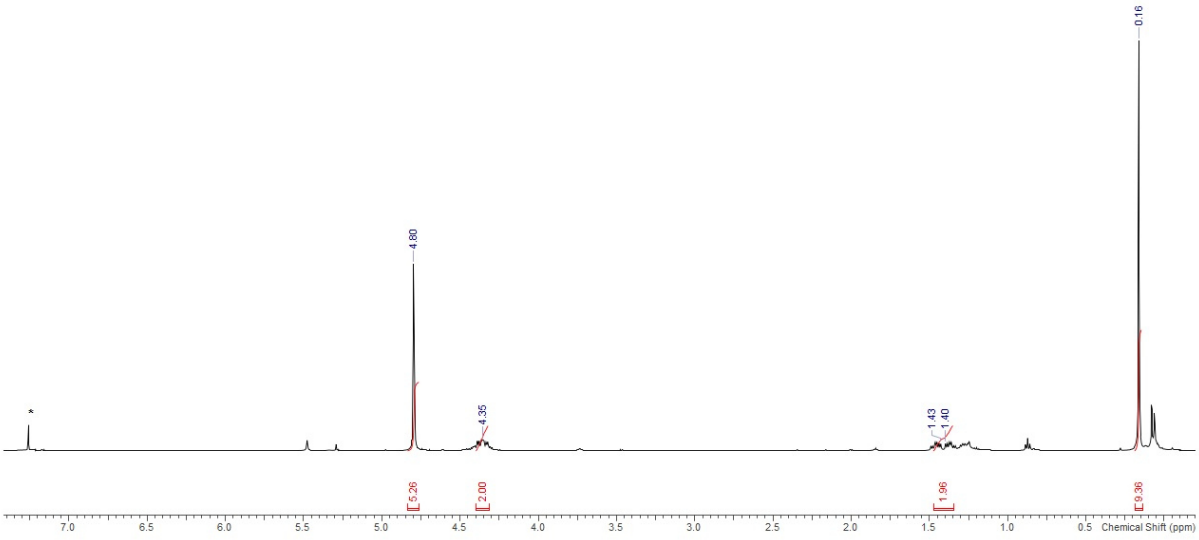


Figure S85. ^{1}H NMR spectrum (500 MHz) of **10** in $CDCl_3$ (*) at 298 K.

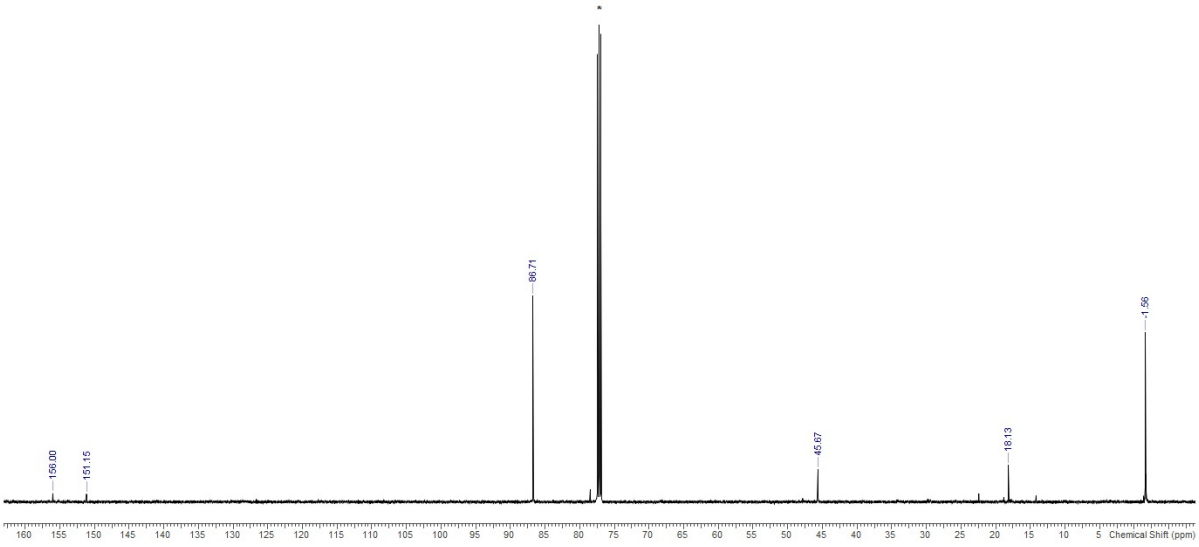


Figure S86. ^{13}C NMR spectrum (125 MHz) of **10** in $CDCl_3$ (*) at 298 K.

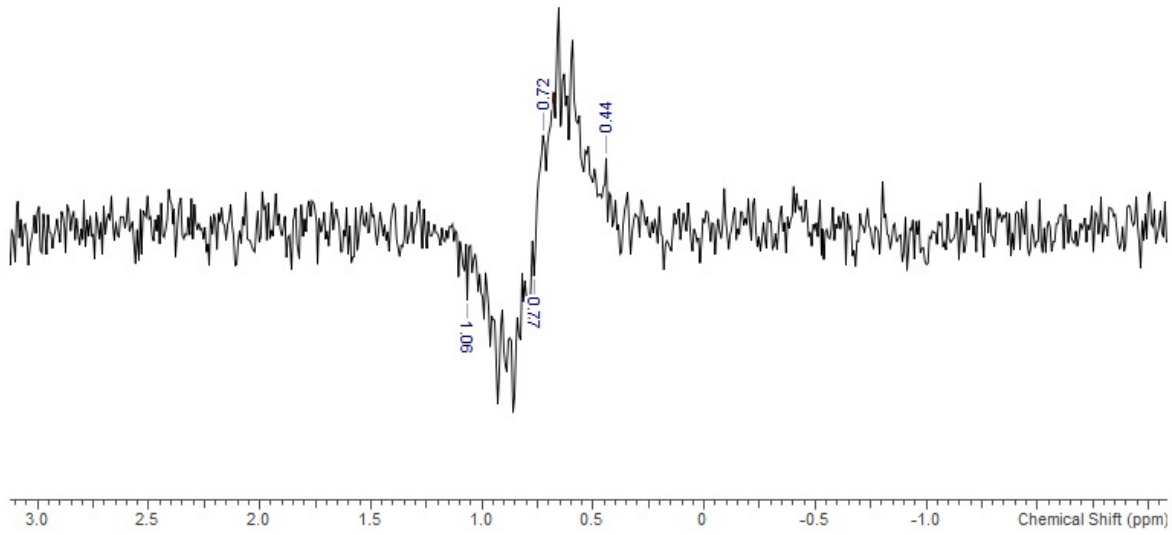


Figure S87. ^{29}Si NMR spectrum (99 MHz) of **10** in $CDCl_3$ (*) at 298 K.

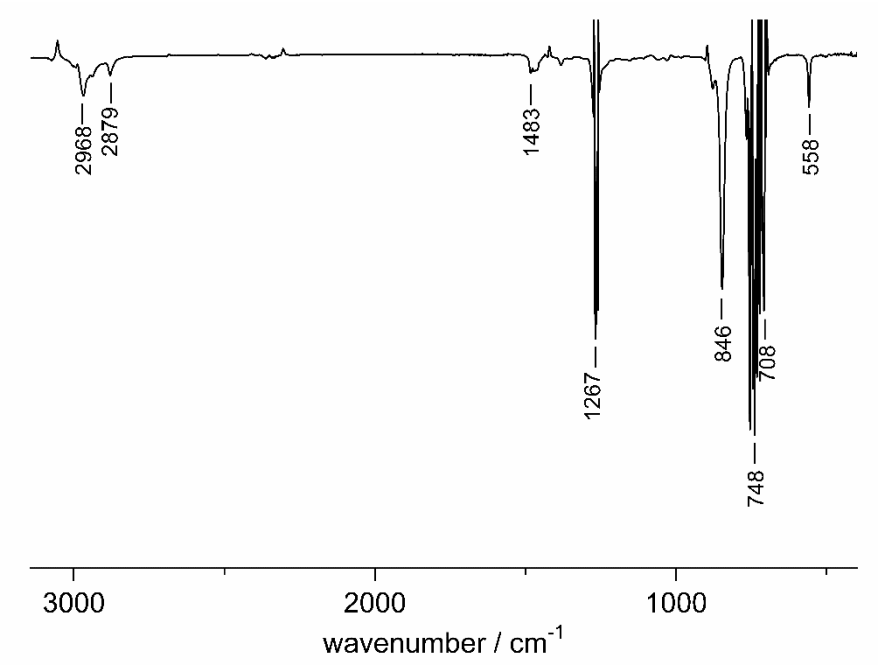


Figure S88. IR spectroscopy of **10** in CH_2Cl_2.

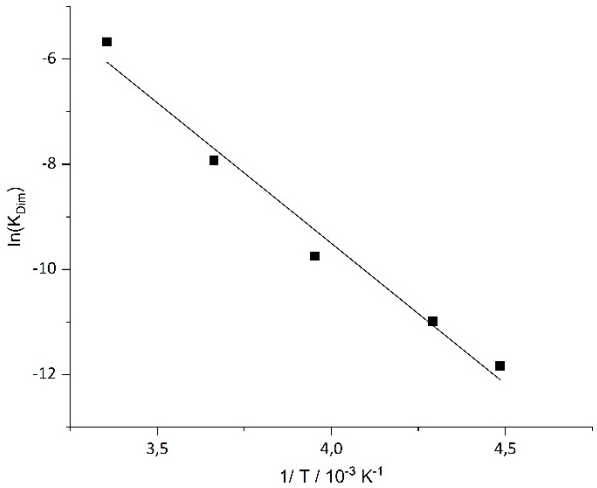


Figure S89. Van't-Hoff-plot of the monomer-dimer equilibrium **10**/(**10**)$_2$.

3. References

25. Seidel, W.W.; Meel, M.J.; Schaffrath, M.; Pape, T. In Pursuit of an Acetylenedithiolate Synthesis. *Eur. J. Org. Chem.* **2007**, *2007*, 3526–3532. https://doi.org/10.1002/ejoc.200601107.
48. Sheldrick, G.M. *SHELXS-2013, Program for Solution of Crystal Structure;* Universität Göttingen: Göttingen, Germany, 2013.
49. Sheldrick, G.M. *SHELXL-2013. Program for Refinement of Crystal Structure*; Universität Göttingen: Göttingen, Germany, 2013.
50. Sheldrick, G.M. SHELXT–Integrated space-group and crystal-structure determination. *Acta Crystallogr. A Found. Adv.* **2015**, *71*, 3–8. https://doi.org/10.1107/S2053273314026370.
51. Kitano, H.; Choi, J.-H.; Ueda, A.; Ito, H.; Hagihara, S.; Kan, T.; Kawagishi, H.; Itami, K. Discovery of Plant Growth Stimulants by C-H Arylation of 2-Azahypoxanthine. *Org. Lett.* **2018**, *20*, 5684–5687. https://doi.org/10.1021/acs.orglett.8b02407.
52. Tran, T.K.; Bricaud, Q.; Ocafrain, M.; Blanchard, P.; Roncali, J.; Lenfant, S.; Godey, S.; Vuillaume, D.; Rondeau, D. Thiolate chemistry: A powerful and versatile synthetic tool for immobilization/functionalization of oligothiophenes on a gold surface. *Chem. Eur. J.* **2011**, *17*, 5628–5640. https://doi.org/10.1002/chem.201003687.
53. Matake, R.; Niwa, Y.; Matsubara, H. Phase-vanishing method with acetylene evolution and its utilization in several organic syntheses. *Org. Lett.* **2015**, *17*, 2354–2357. https://doi.org/10.1021/acs.orglett.5b00827.
54. Spencer, L.P.; Altwer, R.; Wei, P.; Gelmini, L.; Gauld, J.; Stephan, D.W. Pyridine− and Imidazole−Phosphinimine Bidentate Ligand Complexes: Considerations for Ethylene Oligomerization Catalysts. *Organometallics* **2003**, *22*, 3841–3854. https://doi.org/10.1021/om030311t.
56. Zanato, C.; Cascio, M.G.; Lazzari, P.; Pertwee, R.; Testa, A.; Zanda, M. Tricyclic Fused Pyrazoles with a 'Click' 1,2,3-Triazole Substituent in Position 3 Are Nanomolar CB_1 Receptor Ligands. *Synthesis* **2015**, *47*, 817–826. https://doi.org/10.1055/s-0034-1379887.
56. Howell, S.J.; Spencer, N.; Philp, D. Recognition-mediated regiocontrol of a dipolar cycloaddition reaction. *Tetrahedron* **2001**, *57*, 4945–4954. https://doi.org/10.1016/S0040-4020(01)00402-1.
57. Wang, T.; Wang, C.; Zhou, S.; Xu, J.; Jiang, W.; Tan, L.; Fu, J. Nanovalves-Based Bacteria-Triggered, Self-Defensive Antibacterial Coating: Using Combination Therapy, Dual Stimuli-Responsiveness, and Multiple Release Modes for Treatment of Implant-Associated Infections. *Chem. Mater.* **2017**, *29*, 8325–8337. https://doi.org/10.1021/acs.chemmater.7b02678.
58. Kumar, A.S.; Ghule, V.D.; Subrahmanyam, S.; Sahoo, A.K. Synthesis of thermally stable energetic 1,2,3-triazole derivatives. *Chem. Eur. J.* **2013**, *19*, 509–518. https://doi.org/10.1002/chem.201203192.
59. Standley, E.A.; Smith, S.J.; Müller, P.; Jamison, T.F. A Broadly Applicable Strategy for Entry into Homogeneous Nickel(0) Catalysts from Air-Stable Nickel(II) Complexes. *Organometallics* **2014**, *33*, 2012–2018. https://doi.org/10.1021/om500156q.
60. Lobana, T.S.; Bawa, G.; Hundal, G.; Butcher, R.J.; Castineiras, A. The Influence of Substituents at C 2 Carbon of Thiosemicarbazones on the Bonding Pattern of Bis(diphenylphopshano)alkanes in

Palladium(II) Complexes. *Z. Anorg. Allg. Chem.* **2009**, *635*, 1447–1453. https://doi.org/10.1002/zaac.200801307.
61. Li, X.; Zha, M.-Q.; Gao, S.-Y.; Low, P.-J.; Wu, Y.-Z.; Gan, N.; Cao, R. Synthesis, photoluminescence, catalysis and multilayer film assembly of an ethynylpyridine platinum compound. *CrystEngComm* **2011**, *13*, 920–926. https://doi.org/10.1039/C0CE00382D.
62. Ramos-Lima, F.J.; Quiroga, A.G.; Pérez, J.M.; Font-Bardia, M. Synthesis and Characterization of New Transplatinum Complexes Containing Phosphane Groups − Cytotoxic Studies in Cisplatin-Resistant Cells. *Eur. J. Inorg. Chem.* **2003**, *2003*, 1591–1598. https://doi.org/10.1002/ejic.200390209.
63. Shapley, J.R. *Inorganic Syntheses;* Wiley-Interscience: Hoboken, NJ, USA, 2004; Volume 34.