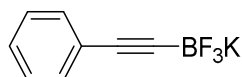


Supplementary Materials: Brønsted Acid-Catalyzed Direct Substitution of 2-Ethoxytetrahydrofuran with Trifluoroborate Salts

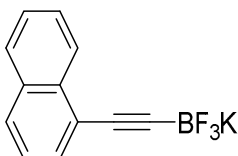
Kayla M. Fisher and Yuri Bolshan

1. Trifluoroborate Salts:



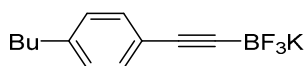
Potassium trifluoro(phenylethynyl)borate (S1)

The title compound was derived from phenylacetylene (2.45 g, 24.0 mmol, 1.0 equiv), *n*-BuLi (1.54 g, 24.0 mmol, 1.0 equiv), B(OMe)₃ (3.75 g, 36.1 mmol, 1.5 equiv), and aqueous KHF₂ (11.26 g, 144.2 mmol, 6.0 equiv) in 50 mL of THF. **S1** was obtained as a white crystalline solid (1.190 g, 24% yield). ¹H-NMR (DMSO) δ 7.27–7.29 (m, 4H), 7.21–7.26 (m, 1H); ¹³C {¹H} NMR (DMSO) δ 130.9, 128.2, 126.7, 125.5; ¹⁹F NMR (DMSO) δ −131.71 (broad s, 3F); ¹¹B {¹H} NMR (DMSO) δ −1.55 (s, 1B); HRMS (ESI/M-) calcd. for C₈H₅BF₃ 169.0442, found 169.0438. These data are consistent with reported literature values [1–4].



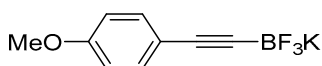
Potassium trifluoro(naphthalen-1-ylethynyl)borate (S2)

The title compound was derived from 1-ethynynaphthalene (0.854 g, 5.44 mmol, 1.0 equiv), *n*-BuLi (0.349 g, 5.44 mmol, 1.0 equiv), B(OMe)₃ (0.85 g, 8.16 mmol, 1.5 equiv), and aqueous KHF₂ (2.55 g, 32.7 mmol, 6.0 equiv) in 17.0 mL of THF. **S2** was obtained as a slightly pink crystalline solid (0.876 g, 62% yield). ¹H-NMR (DMSO) δ 8.33 (d, *J* = 8.2 Hz, 1H), 7.91 (d, *J* = 8.6 Hz, 1H), 7.82 (d, *J* = 8.2 Hz, 1H), 7.51–7.61 (m, 3H), 7.42–7.45 (m, 1H); ¹³C {¹H} NMR (DMSO) δ 132.9, 132.8, 128.9, 128.1, 126.9, 126.3, 126.2, 126.1, 125.5, 123.1; ¹⁹F NMR (DMSO) δ −131.46 (broad s, 3F); ¹¹B {¹H} NMR (DMSO) δ −1.61 (s, 1B); HRMS (ESI/M-) calcd. for C₁₂H₇BF₃ 219.0598, found 219.0601. These data are consistent with reported literature values [3,4].



Potassium ((4-butylphenyl)ethynyl)trifluoroborate (S3)

The title compound was derived from 1-butyl-4-ethynylbenzene (3.00 g, 18.0 mmol, 1.0 equiv.), *n*-BuLi (1.15 g, 18.0 mmol, 1.0 equiv.), B(OMe)₃ (2.81 g, 27.0 mmol, 1.5 equiv.), and aqueous KHF₂ (8.463 g, 108 mmol, 6.0 equiv.) in 50 mL THF. **S3** was obtained as a white crystalline solid (2.609 g, 55% yield). ¹H-NMR (DMSO) δ 7.17–7.20 (m 2H), 7.08–7.10 (m, 2H), 2.54 (t, *J* = 7.4 Hz 2H), 1.49–1.56 (m, 2H), 1.24–1.33 (m, 2H), 0.88 (t, *J* = 7.4 Hz, 3H); ¹³C {¹H} NMR (DMSO) δ 140.9, 130.8, 128.2, 122.8, 34.6, 32.9, 21.7, 13.8; ¹⁹F NMR (DMSO) δ −131.60 (broad s, 3F); ¹¹B {¹H} NMR (DMSO) δ −1.67 (s, 1B); HRMS (ESI/M-) calcd. for C₁₂H₁₃BF₃ 225.1068, found 225.1065. These data are consistent with reported literature values [2,3].



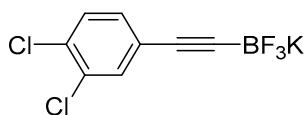
Potassium trifluoro((4-methoxyphenyl)ethynyl)borate (S4)

The title compound was derived from 4-ethynylanisole (1.00 g, 7.34 mmol, 1.0 equiv.), *n*-BuLi (0.470 g, 7.34 mmol, 1.0 equiv.), B(OMe)₃ (1.14 g, 11.0 mmol, 1.5 equiv.), and aqueous KHF₂ (3.462 g, 44.3 mmol, 6.0 equiv.) in 25 mL THF. **S4** was obtained as a white crystalline solid (2.609 g, 55% yield). ¹H-NMR (DMSO) δ 7.20–7.22

(m, 2H), 6.83–6.85 (m, 2H), 3.73 (s, 3H); ^{13}C { ^1H } NMR (DMSO) δ 158.0, 132.2, 117.8, 113.8, 55.0; ^{19}F NMR (DMSO) δ –131.50 (broad s, 3F); ^{11}B { ^1H } NMR (DMSO) δ –1.67 (s, 1B); HRMS (ESI/M-) calcd. for $\text{C}_9\text{H}_7\text{OBF}_3$ 199.0548, found 199.0543. These data are consistent with reported literature values [2].

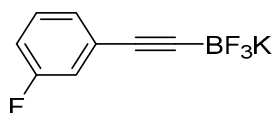
Potassium trifluoro((3,4-dichlorophenyl)ethynyl)borate (S5)

The title compound was derived from 3,4-dichloro-1-ethynylbenzene (0.894 g, 5.22 mmol, 1.0 equiv), *n*-BuLi (0.335 g, 5.22 mmol, 1.0 equiv), $\text{B}(\text{OMe})_3$ (0.81 g, 7.84 mmol, 1.5 equiv), and aqueous KHF_2 (2.45 g, 31.3 mmol, 6.0 equiv) in 17.5 mL of THF. **S5** was obtained as an off-white crystalline solid (0.618 g, 43% yield). ^1H -NMR (DMSO) δ 7.51–7.54 (m, 2H), 7.26 (dd, J = 2.0, 8.2 Hz, 1H); ^{13}C { ^1H } NMR (DMSO) δ 132.8, 131.7, 131.4, 130.9, 130.0, 126.4, 109.9; ^{19}F NMR (DMSO) δ –132.12 (broad s, 3F); ^{11}B { ^1H } NMR (DMSO) δ –1.70 (s, 1B); HRMS (ESI/M-) calcd. For $\text{C}_8\text{H}_3\text{BCl}_2\text{F}_3$: calculated: 236.9662, found 236.9664. These data are consistent with reported literature values [4].



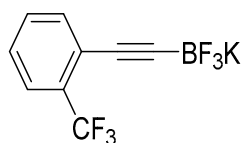
Potassium trifluoro((3-fluorophenyl)ethynyl)borate (S6)

The title compound was derived from 1-ethynyl-3-fluorobenzene (0.67 g, 5.44 mmol, 1.0 equiv), *n*-BuLi (0.349 g, 5.44 mmol, 1.0 equiv), $\text{B}(\text{OMe})_3$ (0.85 g, 8.16 mmol, 1.5 equiv), and aqueous KHF_2 (2.55 g, 32.7 mmol, 6.0 equiv) in 17.0 mL of THF. **S6** was obtained as a white crystalline solid (1.038 g, 84% yield). ^1H -NMR (DMSO) δ 7.30–7.35 (m, 1H), 7.07–7.14 (m, 3H); ^{13}C { ^1H } NMR (DMSO) δ 161.8 (d, J = 243.1 Hz), 130.3 (d, J = 9.2 Hz), 127.5 (d, J = 9.2 Hz), 127.3 (d, J = 3.1 Hz), 117.3 (d, J = 22.2 Hz), 114.0 (d, J = 21.5 Hz); ^{19}F NMR (DMSO) δ –113.49 (q, J = 6.64 Hz, 1F), –131.97 (broad s, 3F); ^{11}B { ^1H } NMR (DMSO) δ –1.56 (s, 1B); HRMS (ESI/M-) calcd. For $\text{C}_8\text{H}_4\text{BF}_4$ 187.0348, found 187.0348. These data are consistent with reported literature values [3,4].



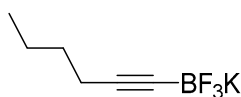
Potassium trifluoro((2-(trifluoromethyl)phenyl)ethynyl) borate (S7)

The title compound was derived from 1-ethynyl-2-trifluoromethylbenzene (1.00 g, 5.70 mmol, 1.0 equiv), *n*-BuLi (0.365 g, 5.70 mmol, 1.0 equiv), $\text{B}(\text{OMe})_3$ (0.89 g, 8.55 mmol, 1.5 equiv), and aqueous KHF_2 (2.67 g, 34.2 mmol, 6.0 equiv) in 17.0 mL of THF. **S7** was obtained as a white crystalline solid (0.879 g, 56% yield). ^1H -NMR (DMSO) δ 7.65 (d, J = 7.4 Hz, 1H), 7.51–7.58 (m, 2H), 7.39–7.44 (m, 1H); ^{13}C { ^1H } NMR (DMSO) δ 134.1, 132.0, 129.4 (q, J = 29.1 Hz), 126.9, 125.5 (q, J = 5.4 Hz), 123.7 (q, J = 273.0 Hz), 123.6; ^{19}F NMR (DMSO) δ –60.85 (s, 3F), –132.09 (broad s, 3F); ^{11}B { ^1H } NMR (DMSO) δ –1.61 (s, 1B); HRMS (ESI/M-) calcd. For $\text{C}_9\text{H}_4\text{BF}_6$ 237.0316, found 237.0318. These data are consistent with reported literature values [3,4].

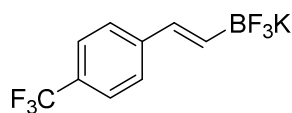


Potassium trifluoro(hex-1-yn-1-yl)borate (S8)

The title compound was derived from 1-hexyne (2.0 g, 23.6 mmol, 1.0 equiv), *n*-BuLi (1.51 g, 23.6 mmol, 1.0 equiv), $\text{B}(\text{OMe})_3$ (3.68 g, 35.4 mmol, 1.5 equiv), and aqueous KHF_2 (11.06 g, 142 mmol, 6.0 equiv) in 25 mL of THF. **S8** was obtained as a white crystalline solid (1.659 g, 36% yield). ^1H -NMR (DMSO) δ 1.98 (m, 2H), 1.33 (m, 4H), 0.85 (m, 3H); ^{13}C { ^1H } NMR (DMSO) δ 31.1, 21.4, 18.5, 13.5; ^{19}F NMR (DMSO) δ –131.01 (broad s, 3F); ^{11}B { ^1H } NMR (DMSO) δ –1.30 (s, 1B); HRMS

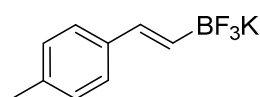


(ESI/M-) calcd. for $C_6H_5BF_3$ 149.0755, found 149.0749. These data are consistent with reported literature values [2,4].



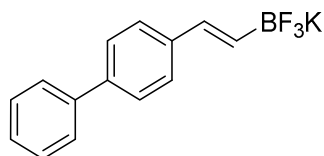
Potassium (E)-trifluoro(4-(trifluoromethyl)styryl)borate (S9)

The title compound was derived from *trans*-2-[4-(trifluoromethyl)phenyl]vinylboronic acid (0.65 g, 3 mmol, 1.0 equiv.) and aqueous KHF_2 (0.66 g, 8.4 mmol, 2.8 equiv.) in 6 mL Et₂O. **S9** was obtained as a white crystalline solid (0.694 g, 83% yield). 1H -NMR (DMSO) δ 7.58–7.60 (m, 2H), 7.51–7.53 (m, 2H), 6.56 (d, J = 18.0 Hz, 1H), 6.39 (dq, J = 3.5, 18.0 Hz, 1H); ^{13}C { 1H } NMR (DMSO) δ 144.3, 131.8 (q, J = 4.6 Hz), 125.9, 125.2 (q, J = 3.8 Hz), 124.7 (q, J = 300.6 Hz); ^{19}F NMR (DMSO) δ -60.60 (s, 3F), -138.31 (broad s, 3F). These data are consistent with reported literature values [5].



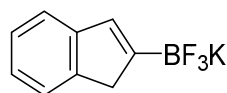
Potassium (E)-trifluoro(4-methylstyryl)borate (S10)

The title compound was derived from *trans*-2-(4-methylphenyl)vinylboronic acid (0.49 g, 3 mmol, 1.0 equiv.) and aqueous KHF_2 (0.66 g, 8.4 mmol, 2.8 equiv.) in 6 mL Et₂O. **S10** was obtained as a white crystalline solid (0.562 g, 84% yield). 1H -NMR (DMSO) δ 7.19 (d, J = 8.2 Hz, 2H), 7.05 (d, J = 7.8 Hz, 2H), 6.42 (d, J = 18.0 Hz, 1H), 6.10 (dq, J = 3.5, 18.0 Hz, 1H), 2.25 (s, 3H); ^{13}C { 1H } NMR (DMSO) δ 137.6, 134.7, 132.8, 128.8, 125.3, 20.7; ^{19}F NMR (DMSO) δ -137.73 (broad s, 3F). These data are consistent with reported literature values [6].



Potassium (E)-2-([1,1'-biphenyl]-4-yl)vinyltrifluoroborate (S11)

The title compound was derived from *trans*-2-(4-biphenyl)vinylboronic acid (0.67 g, 3 mmol, 1.0 equiv.) and aqueous KHF_2 (0.66 g, 8.4 mmol, 2.8 equiv.) in 6 mL Et₂O. **S11** was obtained as a white crystalline solid (0.108 g, 13% yield). 1H -NMR (DMSO) δ 7.63–7.66 (m, 2H), 7.55–7.58 (m, 2H), 7.39–7.46 (m, 4H), 7.30–7.35 (m, 1H), 6.52 (d, J = 18.0 Hz, 1H), 6.25 (dq, J = 3.5, 18.0 Hz, 1H); ^{13}C { 1H } NMR (DMSO) δ 140.1, 139.5, 137.5, 132.5, 128.9, 127.0, 126.6, 126.3, 125.9; ^{19}F NMR (DMSO) δ -137.85 (broad s, 3F). These data are consistent with reported literature values [7].

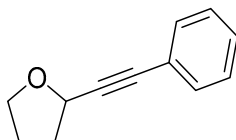


Potassium trifluoro(1H-inden-2-yl)borate (S12)

The title compound was derived from 1H-indene-2-boronic acid (0.48 g, 3 mmol, 1.0 equiv.) and aqueous KHF_2 (0.66 g, 8.4 mmol, 2.8 equiv.) in 6 mL Et₂O. **S12** was obtained as an off-white crystalline solid (0.537 g, 81% yield). 1H -NMR (DMSO) δ 7.33–7.35 (m, 1H), 7.19–7.20 (m, 1H), 7.08–7.12 (m, 1H), 6.94–6.98 (m, 1H), 6.55 (s, 1H), 3.16 (s, 1H); ^{13}C { 1H } NMR (DMSO) δ 147.5, 145.7, 129.8, 125.4, 123.1, 122.2, 119.0, 41.7; ^{19}F NMR (DMSO) δ -137.30 (broad s, 3F); HRMS (ESI/M-) calcd. for $C_9H_7BF_3$ 183.0598, found 183.0609.

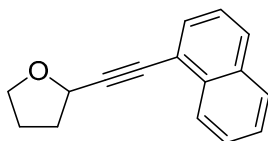
2. Tetrahydrofurans:

2-(phenylethynyl)tetrahydrofuran (1a)



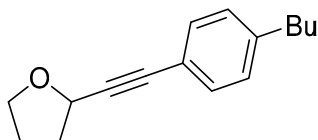
The title compound was derived from 2-ethoxytetrahydrofuran (20.2 mg, 0.174 mmol, 1.0 equiv.), potassium trifluoro(phenylethynyl)borate (54.4 mg, 0.261 mmol, 1.5 equiv.) and $\text{HBF}_4 \cdot \text{OEt}_2$ (35.6 μL , 0.261 mmol, 1.5 equiv.) in 1.74 mL of CH_3CN ($C = 0.1 \text{ M}$). Purification by automated flash column chromatography on silica gel using hexanes/ethyl acetate (gradient: 50:1 $\rightarrow$ 17:1) and subsequent CH_3CN /hexanes extraction afforded product **1a** (27.5 mg, 92% yield) as a yellow oil. ^1H -NMR (CDCl_3) δ 7.42–7.44 (m, 2H), 7.28–7.30 (m, 3H), 4.79–4.83 (m, 1H), 3.98–4.04 (m, 1H), 3.83–3.88 (m, 1H), 2.20–2.26 (m, 1H), 2.04–2.12 (m, 2H), 1.90–1.98 (m, 1H); ^{13}C $\{^1\text{H}\}$ NMR (CDCl_3) δ 131.7, 128.19, 128.16, 122.78, 89.0, 84.4, 68.6, 67.9, 33.4, 25.5; IR (Diamond-ATR) ν 2979, 2950, 2870, 1489, 1333, 1047, 914, 754, 689 cm^{-1} . These data are consistent with reported literature values [8].

2-(naphthalene-1-ylethynyl)tetrahydrofuran (1b)

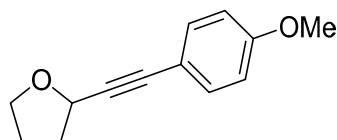


The title compound was derived from 2-ethoxytetrahydrofuran (15.7 mg, 0.135 mmol, 1.0 equiv.), potassium trifluoro(naphthalene-1-ylethynyl)borate (52.2 mg, 0.202 mmol, 1.5 equiv.) and $\text{HBF}_4 \cdot \text{OEt}_2$ (27.5 μL , 0.202 mmol, 1.5 equiv.) in 1.35 mL of CH_3CN ($C = 0.1 \text{ M}$). Purification by automated flash column chromatography on silica gel using hexanes/ethyl acetate (100:1) and subsequent CH_3CN /hexanes extraction afforded product **1b** (29.7 mg, 99% yield) as a yellow oil. ^1H -NMR (CDCl_3) δ 8.30 (d, $J = 8.2 \text{ Hz}$, 1H), 7.81 (t, $J = 9.0 \text{ Hz}$, 2H), 7.66 (d, $J = 7.0 \text{ Hz}$, 1H), 7.48–7.57 (m, 2H), 7.40 (t, $J = 7.4 \text{ Hz}$, 1H), 4.95–4.98 (m, 1H), 4.05–4.11 (m, 1H), 3.89–3.94 (m, 1H), 2.25–2.35 (m, 1H), 2.11–2.23 (m, 2H), 1.93–2.04 (m, 1H); ^{13}C $\{^1\text{H}\}$ NMR (CDCl_3) δ 133.3, 133.1, 130.5, 128.7, 128.2, 126.7, 126.3, 126.1, 125.1, 120.4, 94.1, 82.5, 68.8, 67.9, 33.6, 25.5; IR (Diamond-ATR) ν 2978, 2948, 2868, 1394, 1331, 1045, 912, 798, 770, 567 cm^{-1} . These data are consistent with reported literature values [9].

2-((4-butylphenyl)ethynyl)tetrahydrofuran (1c)

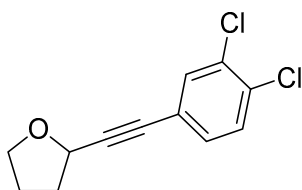


The title compound was derived from 2-ethoxytetrahydrofuran (15.3 mg, 0.131 mmol, 1.0 equiv.), potassium ((4-butylphenyl)ethynyl) trifluoroborate (52.1 mg, 0.197 mmol, 1.5 equiv.) and $\text{HBF}_4 \cdot \text{OEt}_2$ (26.8 μL , 0.197 mmol, 1.5 equiv.) in 1.31 mL of CH_3CN ($C = 0.1 \text{ M}$). Purification by automated flash column chromatography on silica gel using hexanes/ethyl acetate (gradient: 99:1 $\rightarrow$ 16:1) afforded product **1c** (28.0 mg, 93% yield) as a yellow oil. ^1H -NMR (CDCl_3) δ 7.32–7.35 (m, 2H), 7.09–7.11 (m, 2H), 4.79–4.82 (m, 1H), 3.98–4.03 (m, 1H), 3.82–3.87 (m, 1H), 2.58 (t, $J = 7.8 \text{ Hz}$, 2H), 2.18–2.27 (m, 1H), 2.02–2.14 (m, 2H), 1.88–1.98 (m, 1H), 1.53–1.61 (m, 2H), 1.28–1.38 (m, 2H), 0.91 (t, $J = 7.4 \text{ Hz}$, 3H); ^{13}C $\{^1\text{H}\}$ NMR (CDCl_3) δ 143.3, 131.6, 128.3, 119.9, 88.3, 84.6, 68.6, 67.8, 35.5, 33.4, 33.3, 25.5, 22.3, 13.9; IR (Diamond-ATR) ν 2955, 2928, 2858, 1508, 1458, 1333, 1049, 914, 831, 561 cm^{-1} ; HRMS (DART-TOF+) m/z $[M + H]$ calcd for $\text{C}_{16}\text{H}_{21}\text{O}$ 229.1592, found 229.1589.



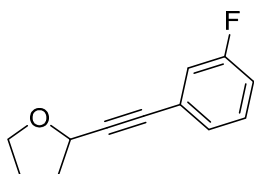
2-((4-methoxyphenyl)ethynyl)tetrahydrofuran (1d)

The title compound was derived from 2-ethoxytetrahydrofuran (17.2 mg, 0.148 mmol, 1.0 equiv.), potassium trifluoro((4-methoxyphenyl)ethynyl)borate (53.0 mg, 0.223 mmol, 1.5 equiv.) and $\text{HBF}_4 \cdot \text{OEt}_2$ (30.3 μL , 0.223 mmol, 1.5 equiv.) in 1.48 mL of CH_3CN ($C = 0.1 \text{ M}$). Purification by automated flash column chromatography on silica gel using hexanes/ethyl acetate (gradient: 99:1 $\rightarrow$ 12:1) afforded product **1d** (23.3 mg, 78% yield) as a yellow oil. ^1H -NMR (CDCl_3) δ 7.35–7.38 (m, 2H), 6.80–6.83 (m, 2H), 4.78–4.81 (m, 1H), 3.98–4.03 (m, 1H), 3.82–3.87 (m, 1H), 3.79 (s, 3H), 2.18–2.25 (m, 1H), 2.02–2.14 (m, 2H), 1.89–1.98 (m, 1H); ^{13}C [^1H] NMR (CDCl_3) δ 159.5, 133.1, 114.9, 113.8, 87.6, 84.3, 68.7, 67.8, 55.2, 33.4, 25.5; IR (Diamond-ATR) ν 2952, 2870, 2837, 1605, 1507, 1288, 1244, 1171, 1046, 1028, 830 cm^{-1} . These data are consistent with reported literature values [8].



2-((3,4-dichlorophenyl)ethynyl)tetrahydrofuran (1e)

The title compound was derived from 2-ethoxytetrahydrofuran (14.5 mg, 0.124 mmol, 1.0 equiv.), potassium trifluoro((3,4-dichlorophenyl)-ethynyl)borate (51.7 mg, 0.187 mmol, 1.5 equiv.) and $\text{HBF}_4 \cdot \text{OEt}_2$ (25.4 μL , 0.187 mmol, 1.5 equiv.) in 1.24 mL of CH_3CN ($C = 0.1 \text{ M}$). Purification by automated flash column chromatography on silica gel using hexanes/ethyl acetate (99:1) and subsequent CH_3CN /hexanes extraction afforded product **1e** (19.3 mg, 64% yield) as a yellow oil. ^1H -NMR (CDCl_3) δ 7.51–7.52 (m, 1H), 7.35–7.37 (m, 1H), 7.23–7.26 (m, 1H), 4.77–4.80 (m, 1H), 3.96–4.02 (m, 1H), 3.83–3.88 (m, 1H), 2.19–2.28 (m, 1H), 2.02–2.14 (m, 2H), 1.90–1.99 (m, 1H); ^{13}C [^1H] NMR (CDCl_3) δ 133.3, 132.7, 132.4, 130.8, 130.3, 122.8, 91.2, 82.2, 68.4, 68.1, 33.3, 25.5; IR (Diamond-ATR) ν 2979, 2951, 2870, 1462, 1130, 1048, 1029, 878, 818, 682 cm^{-1} ; HRMS (DART-TOF+) m/z [$\text{M} + \text{NH}_4^+$] calcd for $\text{C}_{12}\text{H}_{14}\text{Cl}_2\text{NO}$ 258.0452, found 258.0444.

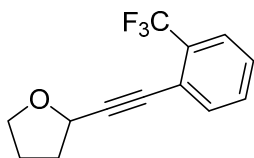


2-((3-fluorophenyl)ethynyl)tetrahydrofuran (1f)

The title compound was derived from 2-ethoxytetrahydrofuran (18.3 mg, 0.158 mmol, 1.0 equiv.), potassium trifluoro((3-fluorophenyl)ethynyl) borate (53.5 mg, 0.237 mmol, 1.5 equiv.) and $\text{HBF}_4 \cdot \text{OEt}_2$ (32.2 μL , 0.237 mmol, 1.5 equiv.) in 1.58 mL of CH_3CN ($C = 0.1 \text{ M}$). Purification by automated flash column chromatography on silica gel using hexanes/ethyl acetate (50:1) and subsequent CH_3CN /hexanes extraction afforded product **1f** (18.4 mg, 61% yield) as a yellow oil. ^1H -NMR (CDCl_3) δ 7.19–7.28 (m, 2H), 7.11–7.14 (m, 1H), 6.98–7.03 (m, 1H), 4.79–4.82 (m, 1H), 3.98–4.03 (m, 1H), 3.84–3.89 (m, 1H), 2.20–2.29 (m, 1H), 2.03–2.13 (m, 2H), 1.90–1.99 (m, 1H); ^{13}C [^1H] NMR (CDCl_3) δ 162.3 (d, $J = 246.1 \text{ Hz}$), 129.8 (d, $J = 9.2 \text{ Hz}$), 127.5 (d, $J = 3.8 \text{ Hz}$), 124.6 (d, $J = 9.2 \text{ Hz}$), 118.5 (d, $J = 22.2 \text{ Hz}$), 115.6 (d, $J = 21.5 \text{ Hz}$), 90.1, 83.2 (d, $J = 3.8 \text{ Hz}$), 68.5, 68.0, 33.3, 25.5; ^{19}F NMR (CDCl_3) δ -113.14 (q, $J = 5.92 \text{ Hz}$, 1F); IR (Diamond-ATR) ν 2980, 2952, 2872, 1579, 1485, 1173, 1149, 1048, 869, 782, 681 cm^{-1} . These data are consistent with reported literature values [10].

2-((2-(trifluoromethyl)phenyl)ethynyl)tetrahydrofuran (1g)

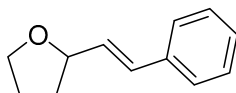
The title compound was derived from 2-ethoxytetrahydrofuran (14.5 mg, 0.123 mmol, 1.0 equiv.), potassium trifluoro((2-(trifluoromethyl)phenyl)ethynyl)borate (51.7 mg, 0.187 mmol, 1.5 equiv.) and $\text{HBF}_4 \cdot \text{OEt}_2$ (25.5 μL , 0.187 mmol, 1.5 equiv.) in 1.25 mL of CH_3CN ($C = 0.1 \text{ M}$). Purification by automated flash column chromatography on silica gel using hexanes/ethyl acetate (gradient: 99:1 $\rightarrow$ 16:1) and subsequent CH_3CN /hexanes extraction afforded product **1g** (24.7 mg, 82% yield) as a yellow oil. $^1\text{H-NMR}$ (CDCl_3) δ 7.62–7.64 (m, 1H), 7.56–7.58 (m, 1H), 7.45–7.48 (m, 1H), 7.37–7.40 (m, 1H), 4.85–4.87 (m, 1H), 3.98–4.04 (m, 1H), 3.85–3.91 (m, 1H), 2.18–2.26 (m, 1H), 2.06–2.17 (m, 2H), 1.90–1.99 (m, 1H); ^{13}C $\{^1\text{H}\}$ NMR (CDCl_3) δ = 133.9, 131.8, 131.3, 128.0, 125.7 (q, $J = 5.4 \text{ Hz}$), 123.5 (q, $J = 273.8 \text{ Hz}$), 121.1 (q, $J = 2.3 \text{ Hz}$), 95.0, 80.3, 68.5, 67.9, 33.1, 25.1; ^{19}F NMR (CDCl_3) δ -62.48 (s, 3F); IR (Diamond-ATR) ν 2981, 2874, 1315, 1166, 1128, 1109, 1049, 1032, 764 cm^{-1} ; HRMS (DART-TOF+) m/z $[M + \text{NH}_4^+]$ calcd for $\text{C}_{13}\text{H}_{15}\text{F}_3\text{NO}$ 258.1106, found 258.1102.

**2-(hex-1-yn-1-yl)tetrahydrofuran (1h)**

The title compound was derived from 2-ethoxytetrahydrofuran (22.9 mg, 0.197 mmol, 1.0 equiv.), potassium trifluoro(hex-1-yn-1-yl)borate (55.6 mg, 0.296 mmol, 1.5 equiv.) and $\text{HBF}_4 \cdot \text{OEt}_2$ (40.2 μL , 0.296 mmol, 1.5 equiv.) in 1.97 mL of CH_3CN ($C = 0.1 \text{ M}$). Aqueous workup afforded product **1h** (19.3 mg, 64% yield) as a yellow oil. A pure sample was obtained after the work-up. Attempts to run the crude product through a pad of silica gel resulted in the decomposition of **1h**. $^1\text{H-NMR}$ (CDCl_3) δ 4.53–4.57 (m, 1H), 3.91–3.97 (m, 1H), 3.75–3.80 (m, 1H), 2.20 (td, $J = 2.0, 7.0 \text{ Hz}$, 2H), 2.08–2.16 (m, 1H), 1.97–2.07 (m, 1H), 1.82–1.95 (m, 2H), 1.44–1.52 (m, 2H), 1.35–1.42 (m, 2H), 0.90 (t, $J = 7.4 \text{ Hz}$, 3H); ^{13}C $\{^1\text{H}\}$ NMR (CDCl_3) δ 85.2, 79.9, 68.4, 67.6, 33.5, 30.7, 25.4, 21.9, 18.4, 13.6; IR (Diamond-ATR) ν 2956, 2931, 2871, 1458, 1355, 1332, 1051, 907 cm^{-1} .

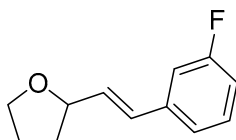
**(E)-2-styryltetrahydrofuran (2a)**

The title compound was derived from 2-ethoxytetrahydrofuran (20.0 mg, 0.172 mmol, 1.0 equiv.), potassium *trans*-styryltrifluoroborate (54.2 mg, 0.258 mmol, 1.5 equiv.) and $\text{HBF}_4 \cdot \text{OEt}_2$ (35.1 μL , 0.258 mmol, 1.5 equiv.) in 1.72 mL of CH_3CN ($C = 0.1 \text{ M}$). Purification by automated flash column chromatography on silica gel using hexanes/ethyl acetate (gradient: 99:1 $\rightarrow$ 19:1) and subsequent CH_3CN /hexanes extraction afforded product **2a** (22.3 mg, 74% yield) as a yellow oil. $^1\text{H-NMR}$ (CDCl_3) δ 7.37–7.39 (m, 2H), 7.28–7.32 (m, 2H), 7.20–7.25 (m, 1H), 6.58 (d, $J = 16.0 \text{ Hz}$, 1H), 6.20 (dd, $J = 6.3, 15.6 \text{ Hz}$, 1H), 4.44–4.50 (m, 1H), 3.94–4.00 (m, 1H), 3.81–3.86 (m, 1H), 2.08–2.16 (m, 1H), 1.88–2.04 (m, 2H), 1.67–1.75 (m, 1H); ^{13}C $\{^1\text{H}\}$ NMR (CDCl_3) δ 136.8, 130.5, 130.4, 128.5, 127.4, 126.4, 79.6, 68.1, 32.4, 25.9; IR (Diamond-ATR) ν 2971, 2867, 1493, 1448, 1049, 963, 745, 691 cm^{-1} . These data are consistent with reported literature values [8].

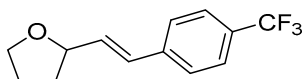


(E)-2-(3-fluorostyryl)tetrahydrofuran (2b)

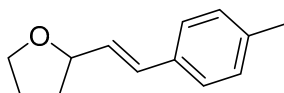
The title compound was derived from 2-ethoxytetrahydrofuran (18.1 mg, 0.156 mmol, 1.0 equiv.), potassium 2-(3-fluorophenyl)vinyltrifluoroborate (53.4 mg, 0.234 mmol, 1.5 equiv.) and $\text{HBF}_4 \cdot \text{OEt}_2$ (31.9 μL , 0.234 mmol, 1.5 equiv.) in 1.56 mL of CH_3CN ($C = 0.1 \text{ M}$). Purification by automated flash column chromatography on silica gel using hexanes/ethyl acetate (gradient: 99:1 $\rightarrow$ 19:1) and subsequent CH_3CN /hexanes extraction afforded product **2b** (23.4 mg, 78% yield) as a yellow oil. ^1H -NMR (CDCl_3) δ 7.23–7.28 (m, 1H), 7.06–7.14 (m, 2H), 6.89–6.94 (m, 1H), 6.55 (d, $J = 15.6 \text{ Hz}$, 1H), 6.22 (dd, $J = 6.3, 16.0 \text{ Hz}$, 1H), 4.45–4.50 (m, 1H), 3.94–4.00 (m, 1H), 3.82–3.87 (m, 1H), 2.09–2.17 (m, 1H), 1.89–2.04 (m, 2H), 1.65–1.75 (m, 1H); ^{13}C $\{^1\text{H}\}$ NMR (CDCl_3) δ 163.0 (d, $J = 245.4 \text{ Hz}$), 139.2 (d, $J = 7.7 \text{ Hz}$), 132.0, 129.9 (d, $J = 8.4 \text{ Hz}$), 129.1 (d, $J = 3.1 \text{ Hz}$), 122.3 (d, $J = 3.1 \text{ Hz}$), 114.2 (d, $J = 21.5 \text{ Hz}$), 112.8 (d, $J = 21.5 \text{ Hz}$), 79.3, 68.2, 32.3, 25.9; ^{19}F NMR (CDCl_3) δ –113.71 (q, $J = 6.25 \text{ Hz}$, 1F); IR (Diamond-ATR) ν 2972, 2869, 1582, 1487, 1445, 1264, 1142, 1050, 962, 870, 776, 682 cm^{-1} . These data are consistent with reported literature values [11].

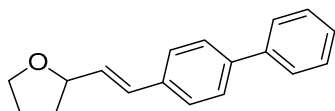
**(E)-2-(4-(trifluoromethyl)styryl)tetrahydrofuran (2c)**

The title compound was derived from 2-ethoxytetrahydrofuran (14.4 mg, 0.124 mmol, 1.0 equiv.), potassium (*E*)-trifluoro(4-(trifluoromethyl)-styryl)borate (51.7 mg, 0.186 mmol, 1.5 equiv.) and $\text{HBF}_4 \cdot \text{OEt}_2$ (25.3 μL , 0.186 mmol, 1.5 equiv.) in 1.24 mL of CH_3CN ($C = 0.1 \text{ M}$). Purification by automated flash column chromatography on silica gel using hexanes/ethyl acetate (gradient: 99:1 $\rightarrow$ 16:1) and subsequent CH_3CN /hexanes extraction afforded product **2c** (23.5 mg, 78% yield) as a yellow oil. ^1H -NMR (CDCl_3) δ 7.55 (d, $J = 8.2 \text{ Hz}$, 2H), 7.45 (d, $J = 8.2 \text{ Hz}$, 2H), 6.62 (d, $J = 16.0 \text{ Hz}$, 1H), 6.31 (dd, $J = 6.6, 16.0 \text{ Hz}$, 1H), 4.50 (q, $J = 6.6 \text{ Hz}$, 1H), 3.96–4.01 (m, 1H), 3.83–3.89 (m, 1H), 2.11–2.19 (m, 1H), 1.92–2.04 (m, 2H), 1.68–1.77 (m, 1H); ^{13}C $\{^1\text{H}\}$ NMR (CDCl_3) δ 140.3 (q, $J = 1.5 \text{ Hz}$), 133.3, 129.4, 129.1, 128.8, 126.5, 125.4 (q, $J = 3.8 \text{ Hz}$), 79.2, 68.3, 32.3, 25.9; ^{19}F NMR (CDCl_3) δ –62.50 (s, 1F); IR (Diamond-ATR) ν 2977, 2869, 1612, 1322, 1162, 1103, 1066, 1047, 860, 813 cm^{-1} . These data are consistent with reported literature values [12].

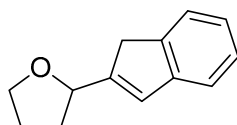
**(E)-2-(4-methylstyryl)tetrahydrofuran (2d)**

The title compound was derived from 2-ethoxytetrahydrofuran (18.5 mg, 0.159 mmol, 1.0 equiv.), potassium (*E*)-trifluoro(4-methylstyryl)borate (53.6 mg, 0.239 mmol, 1.5 equiv.) and $\text{HBF}_4 \cdot \text{OEt}_2$ (32.5 μL , 0.239 mmol, 1.5 equiv.) in 1.59 mL of CH_3CN ($C = 0.1 \text{ M}$). Purification by automated flash column chromatography on silica gel using hexanes/ethyl acetate (gradient: 99:1 $\rightarrow$ 16:1) afforded product **2d** (16.1 mg, 54% yield) as a yellow oil. ^1H -NMR (CDCl_3) δ 7.26–7.28 (m, 2H), 7.10–7.11 (m, 2H), 6.55 (d, $J = 16.0 \text{ Hz}$, 1H), 6.15 (dd, $J = 6.6, 15.6 \text{ Hz}$, 1H), 4.45 (q, $J = 6.7 \text{ Hz}$, 1H), 3.94–3.99 (m, 1H), 3.80–3.86 (m, 1H), 2.32 (s, 3H), 2.07–2.15 (m, 1H), 1.88–2.01 (m, 2H), 1.66–1.75 (m, 1H); ^{13}C $\{^1\text{H}\}$ NMR (CDCl_3) δ 137.3, 134.1, 130.4, 129.4, 129.2, 126.3, 79.77, 68.1, 32.4, 25.9, 21.2; IR (Diamond-ATR) ν 2970, 2922, 2864, 1513, 1050, 964, 795, 513 cm^{-1} . These data are consistent with reported literature values [13].



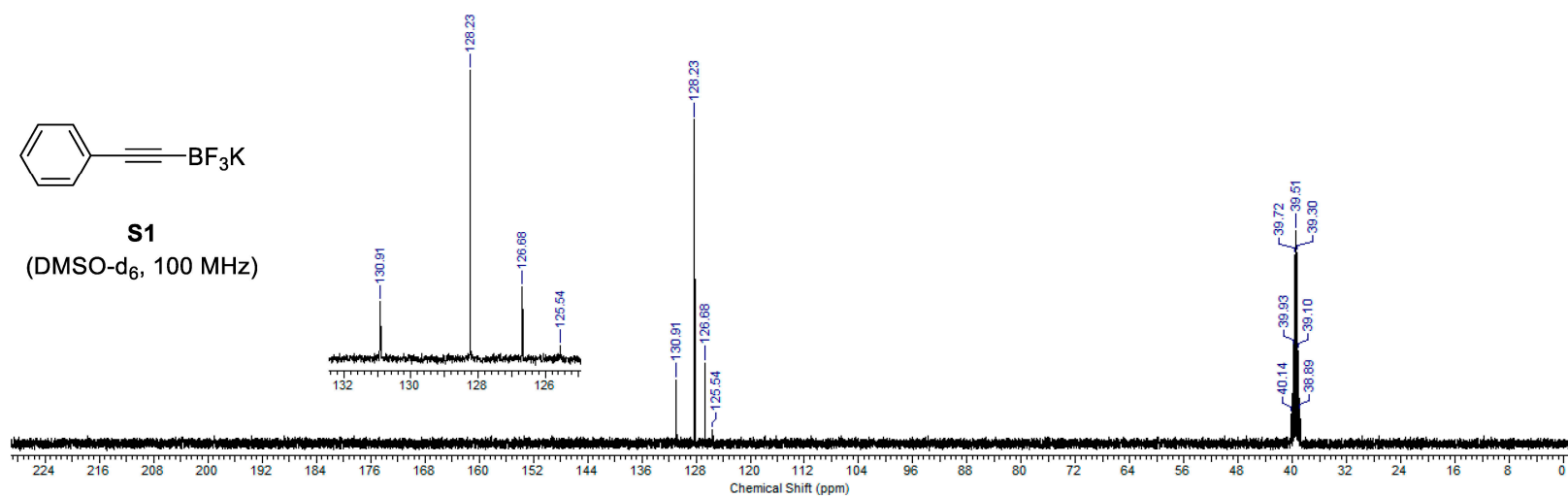
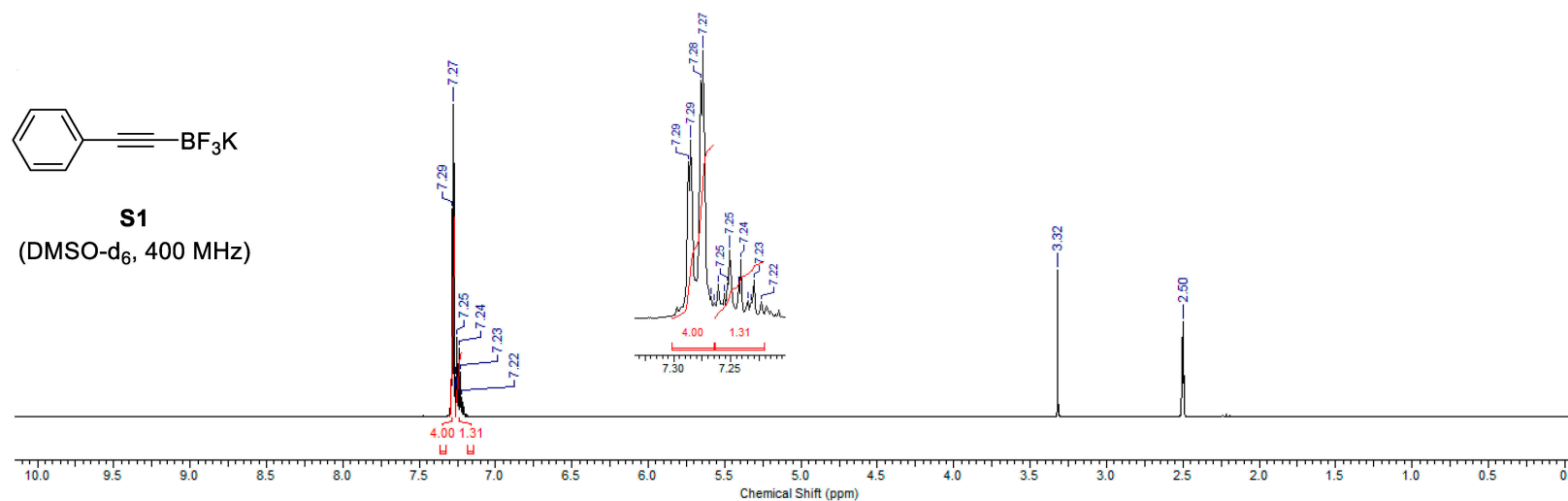
(E)-2-(2-([1,1'-biphenyl]-4-yl)vinyl)tetrahydrofuran (2e)

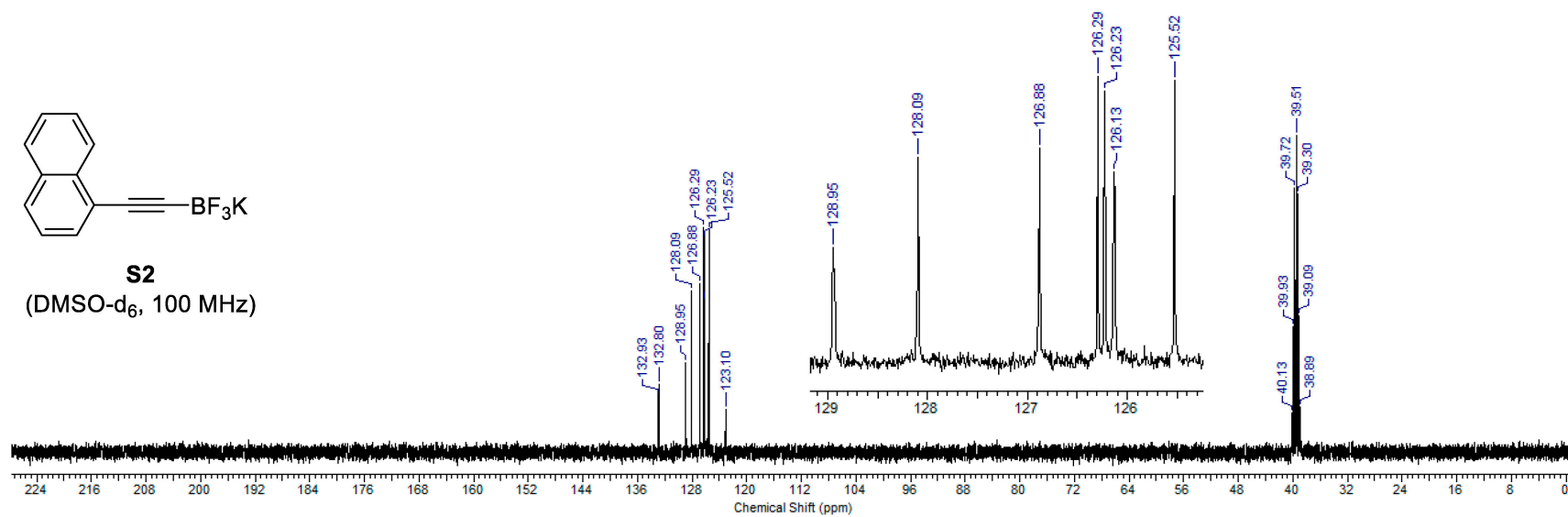
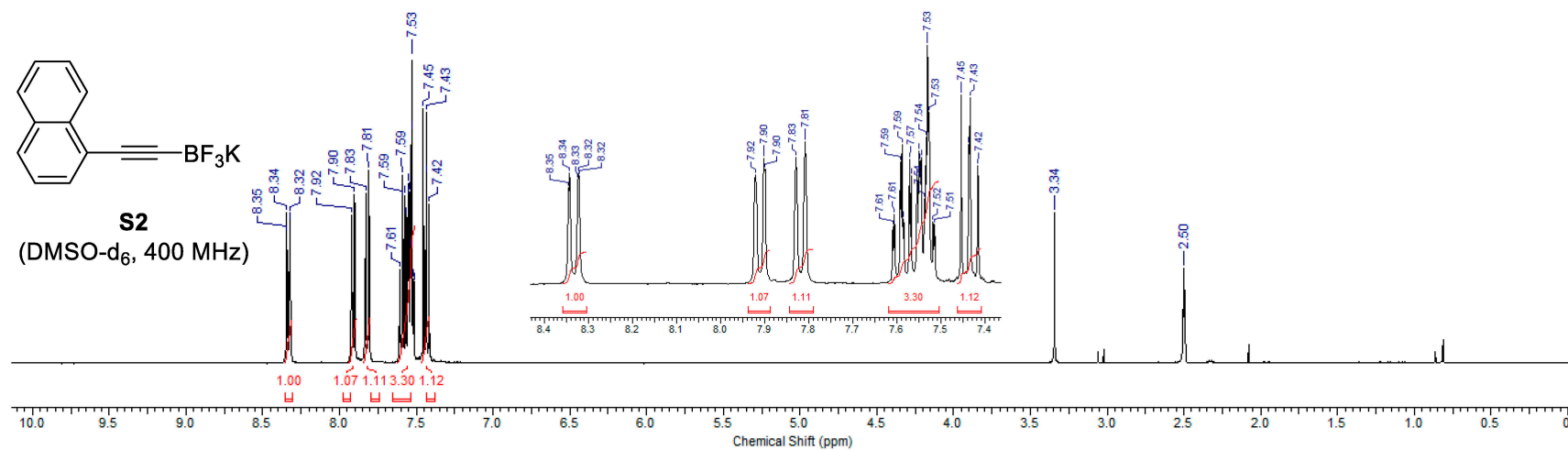
The title compound was derived from 2-ethoxytetrahydrofuran (13.9 mg, 0.120 mmol, 1.0 equiv.), potassium (E)-2-([1,1'-biphenyl]-4-yl)vinyltrifluoroborate (51.4 mg, 0.180 mmol, 1.5 equiv.), and $\text{HBF}_4 \cdot \text{OEt}_2$ (24.5 μL , 0.180 mmol, 1.5 equiv.) in 1.20 mL of CH_3CN ($C = 0.1 \text{ M}$). Purification by automated flash column chromatography on silica gel using hexanes/ethyl acetate (gradient: 99:1 $\rightarrow$ 13:1) and subsequent CH_3CN /hexanes extraction afforded product **2e** (21.6 mg, 72% yield) as a white solid. $^1\text{H-NMR}$ (CDCl_3) δ 7.53–7.60 (m, 4H), 7.40–7.46 (m, 4H), 7.31–7.35 (m, 1H), 6.62 (d, $J = 15.6 \text{ Hz}$, 1H), 6.25 (dd, $J = 6.6, 15.6 \text{ Hz}$, 1H), 4.49 (q, $J = 6.6 \text{ Hz}$, 1H), 3.95–4.01 (m, 1H), 3.82–3.86 (m, 1H), 2.10–2.18 (m, 1H), 1.89–2.02 (m, 2H), 1.68–1.77 (m, 1H); $^{13}\text{C} \{^1\text{H}\}$ NMR (CDCl_3) δ 140.7, 140.2, 135.9, 130.6, 129.9, 128.7, 127.2, 127.1, 126.9, 126.8, 79.7, 68.2, 32.4, 25.9; IR (Diamond-ATR) ν 2928, 2852, 1486, 1048, 971, 854, 758, 687, 489 cm^{-1} ; HRMS (DART-TOF+) m/z $[\text{M} + \text{H}]$ calcd for $\text{C}_{18}\text{H}_{19}\text{O}$ 251.1436, found 251.1437.

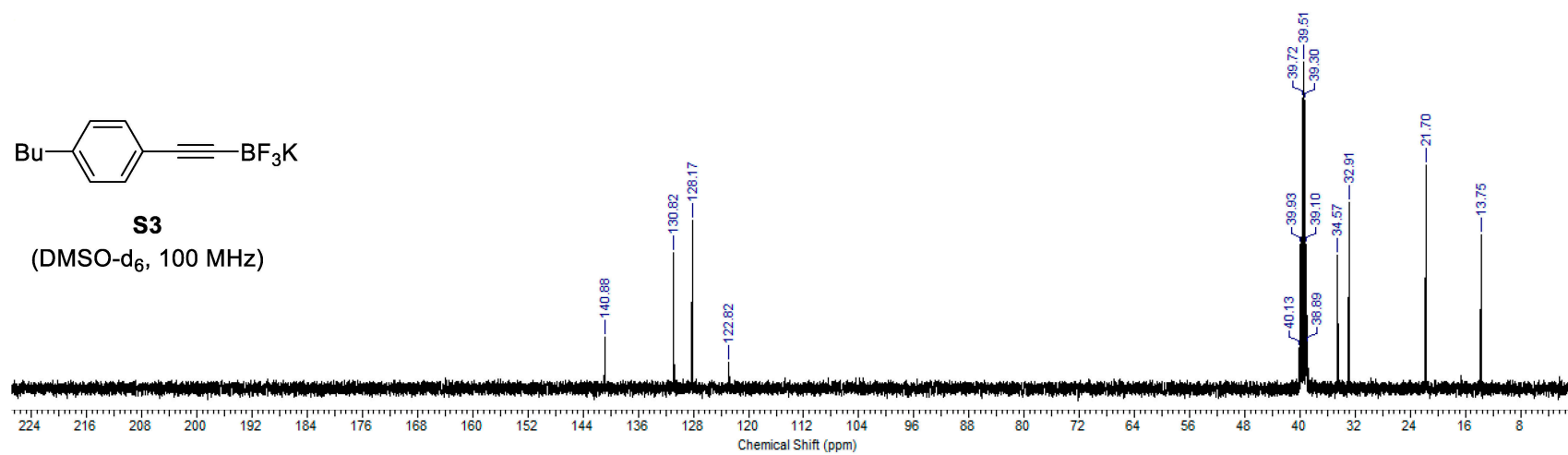
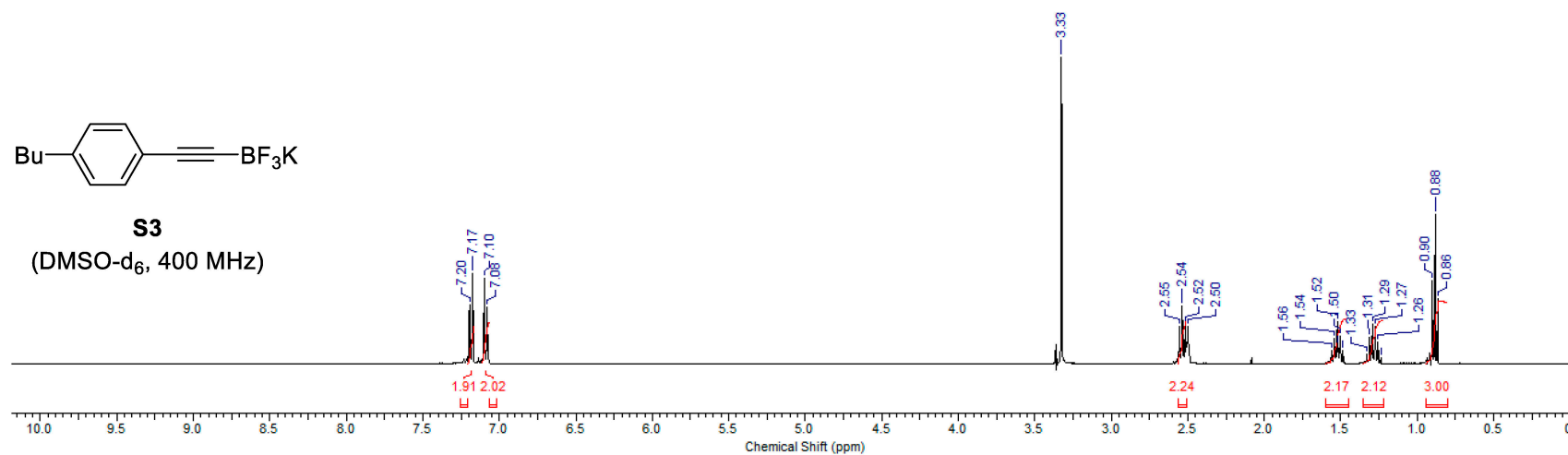
2-(1H-inden-2-yl)tetrahydrofuran (2f)

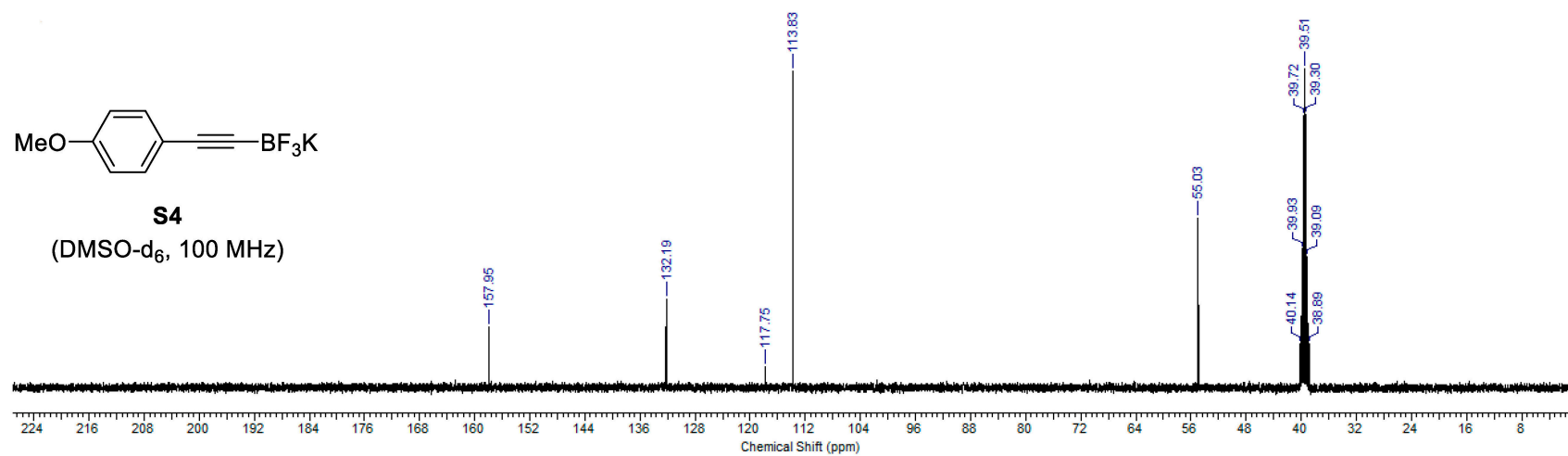
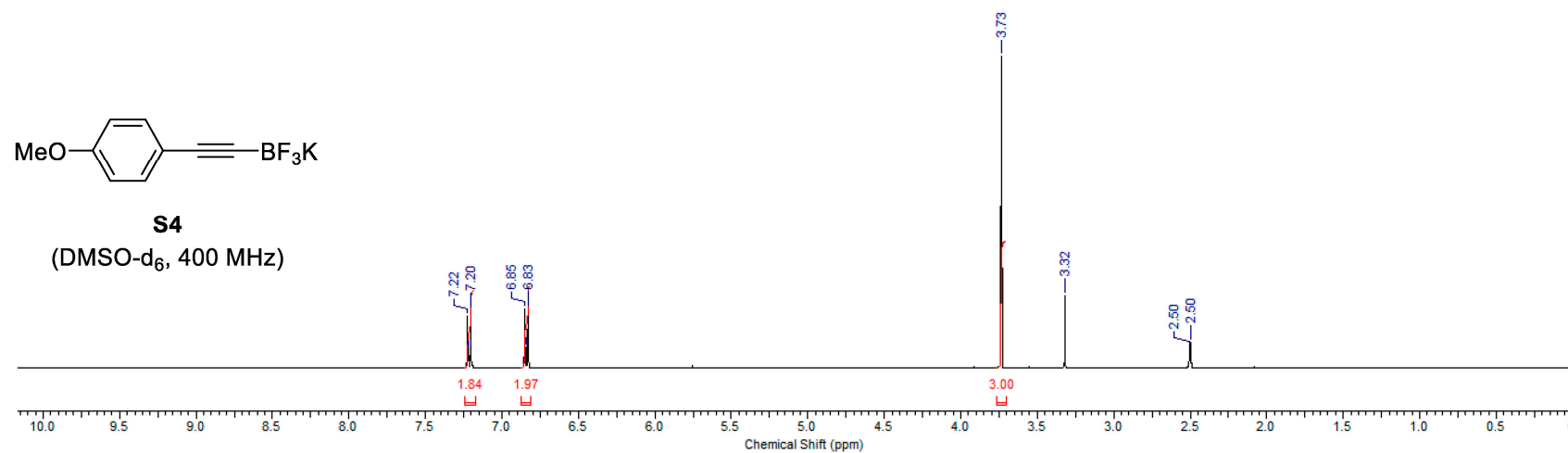
The title compound was derived from 2-ethoxytetrahydrofuran (18.7 mg, 0.161 mmol, 1.0 equiv.), potassium trifluoro(1H-inden-2-yl)borate (53.6 mg, 0.242 mmol, 1.5 equiv.) and $\text{HBF}_4 \cdot \text{OEt}_2$ (32.9 μL , 0.242 mmol, 1.5 equiv.) in 1.61 mL of CH_3CN ($C = 0.1 \text{ M}$). Purification by automated flash column chromatography on silica gel using hexanes/ethyl acetate (gradient: 99:1 $\rightarrow$ 13:1) and subsequent CH_3CN /hexanes extraction afforded product **2f** (23.6 mg, 79% yield) as a yellow oil. $^1\text{H-NMR}$ (CDCl_3) δ 7.40–7.42 (m, 1H), 7.30–7.32 (m, 1H), 7.21–7.25 (m, 1H), 7.11–7.15 (m, 1H), 6.71 (s, 1H), 4.82 (t, $J = 7.0 \text{ Hz}$, 1H), 3.97–4.02 (m, 1H), 3.84–3.90 (m, 1H), 3.39 (s, 2H), 2.15–2.23 (m, 1H), 1.95–2.03 (m, 2H), 1.81–1.89 (m, 1H); $^{13}\text{C} \{^1\text{H}\}$ NMR (CDCl_3) δ 150.4, 144.7, 143.2, 126.6, 126.3, 124.2, 123.6, 120.6, 77.7, 68.2, 38.1, 32.1, 26.0; IR (Diamond-ATR) ν 2971, 2868, 1459, 1390, 1050, 916, 850, 751, 716, 555 cm^{-1} . These data are consistent with reported literature values [13].

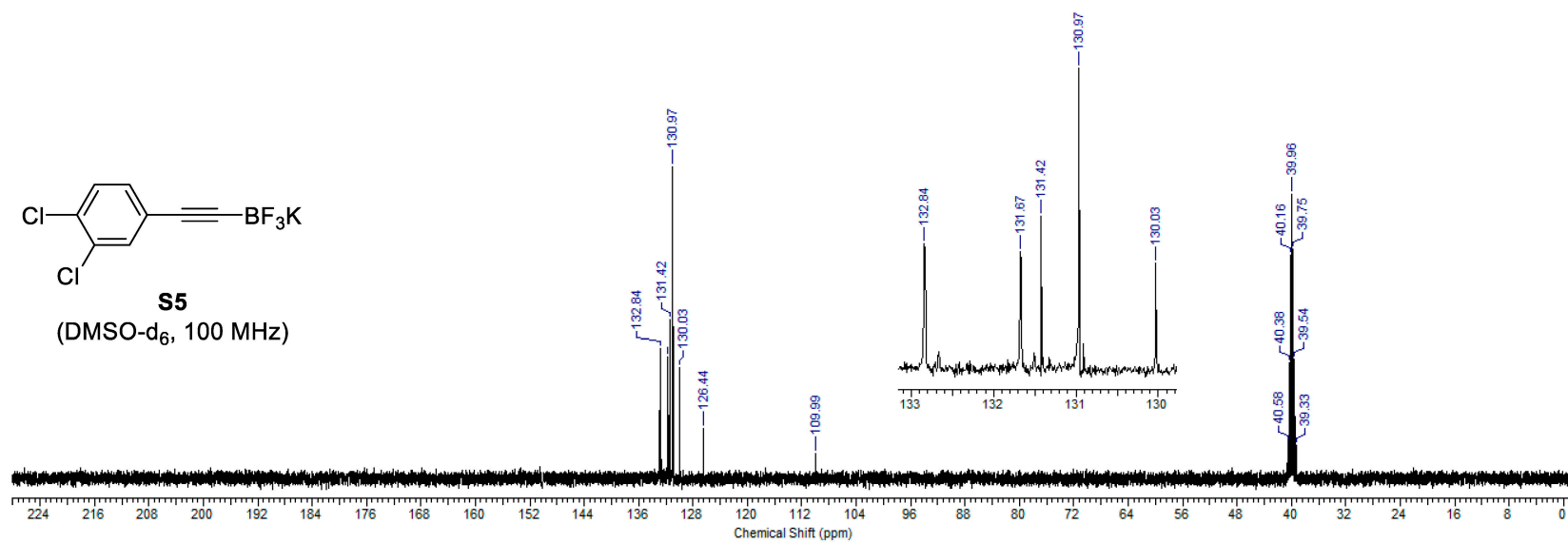
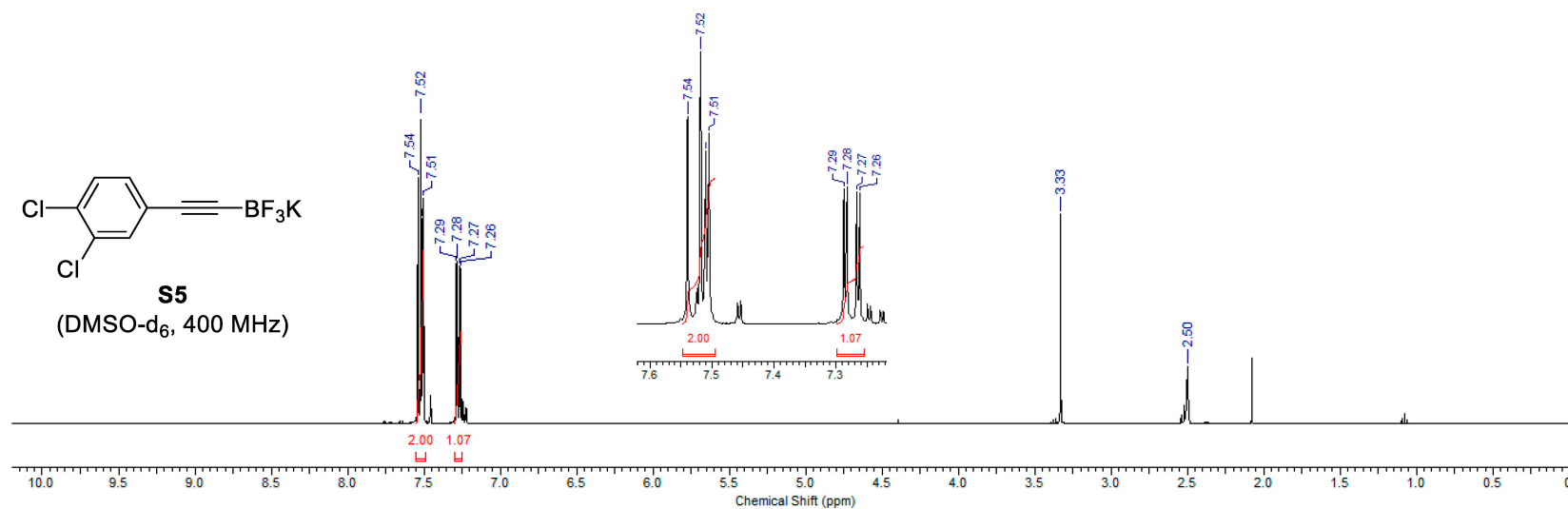
3. Spectral Data:

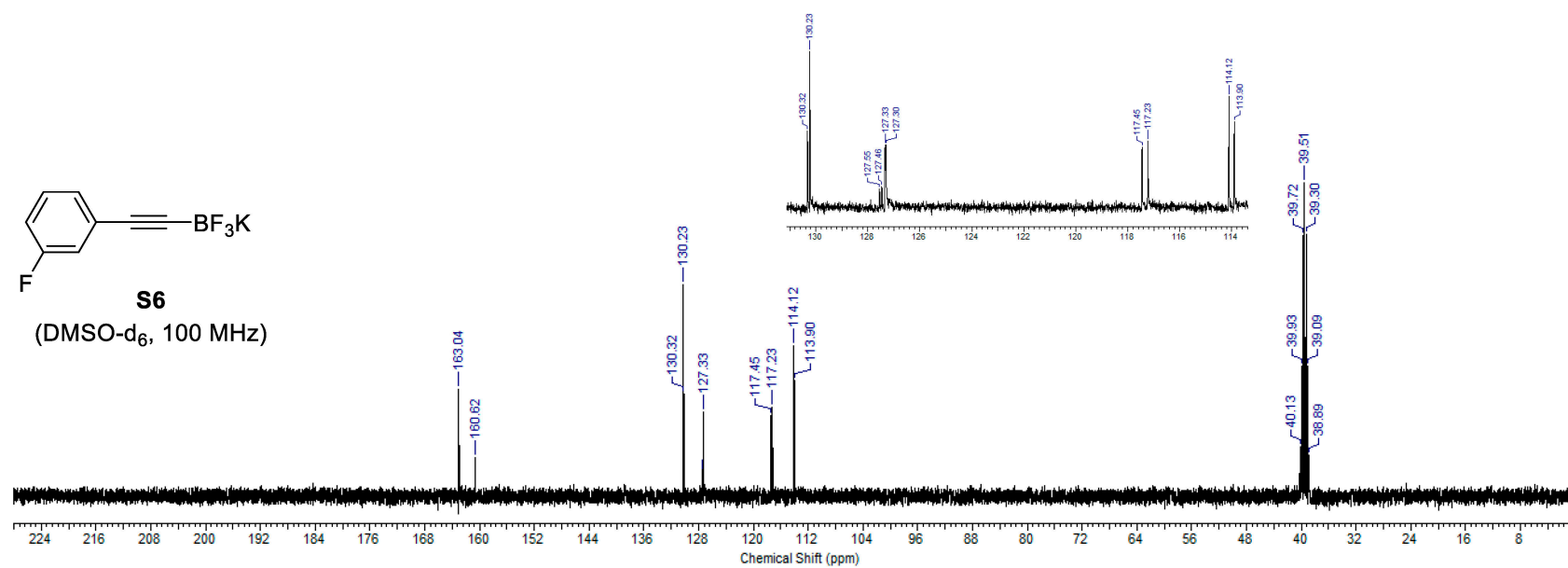
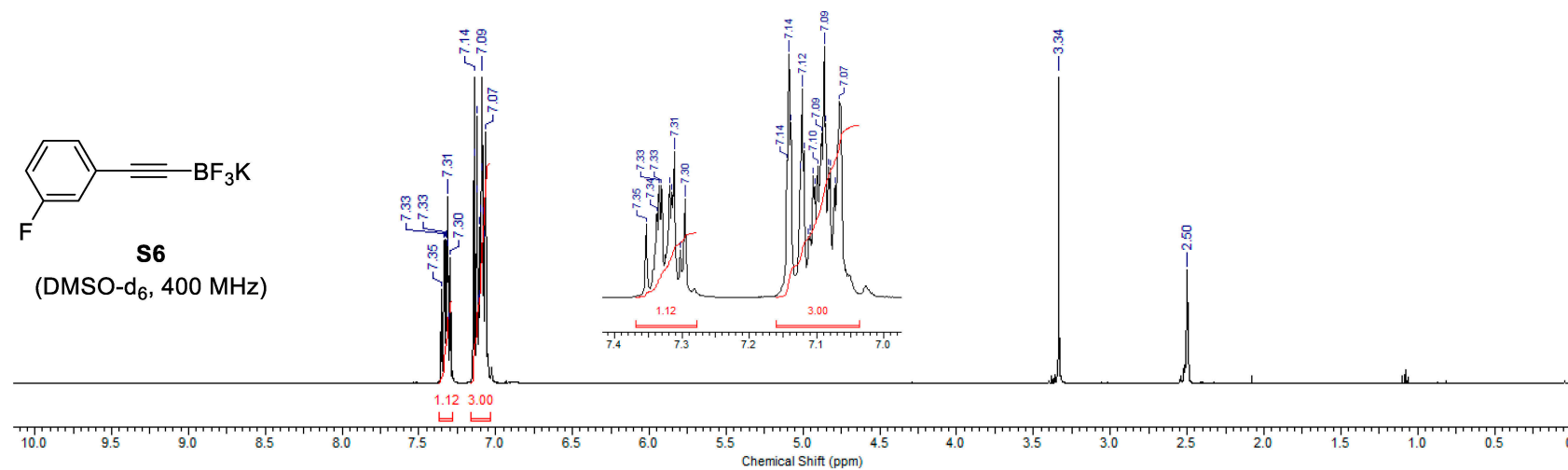


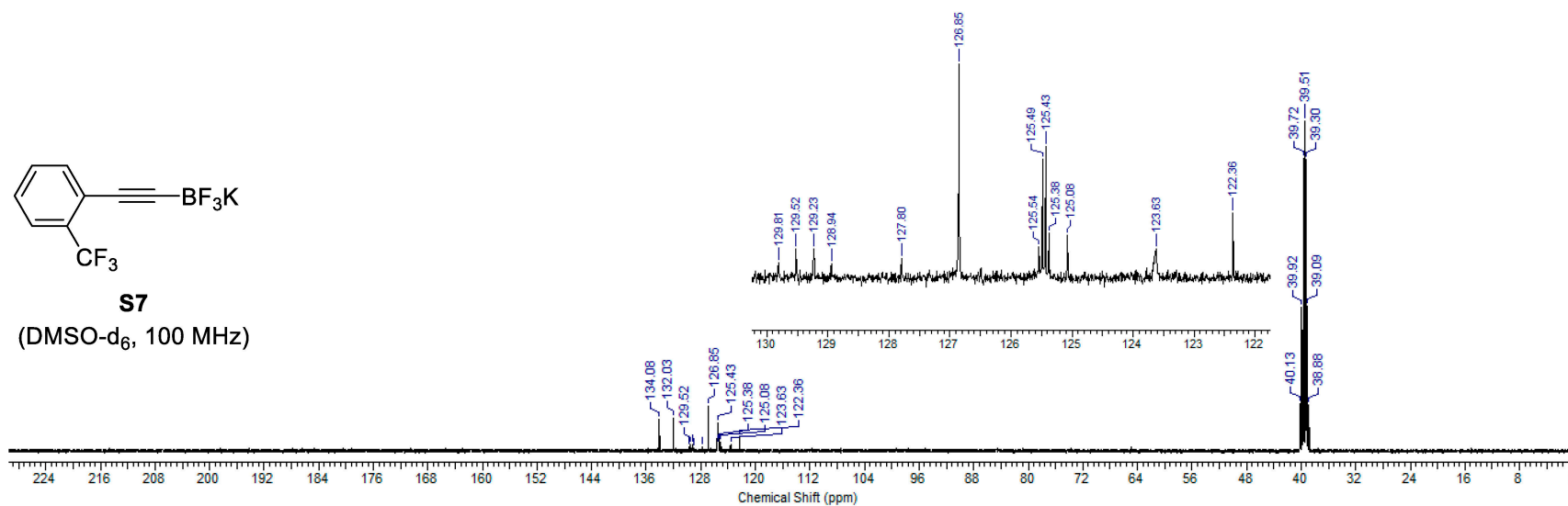
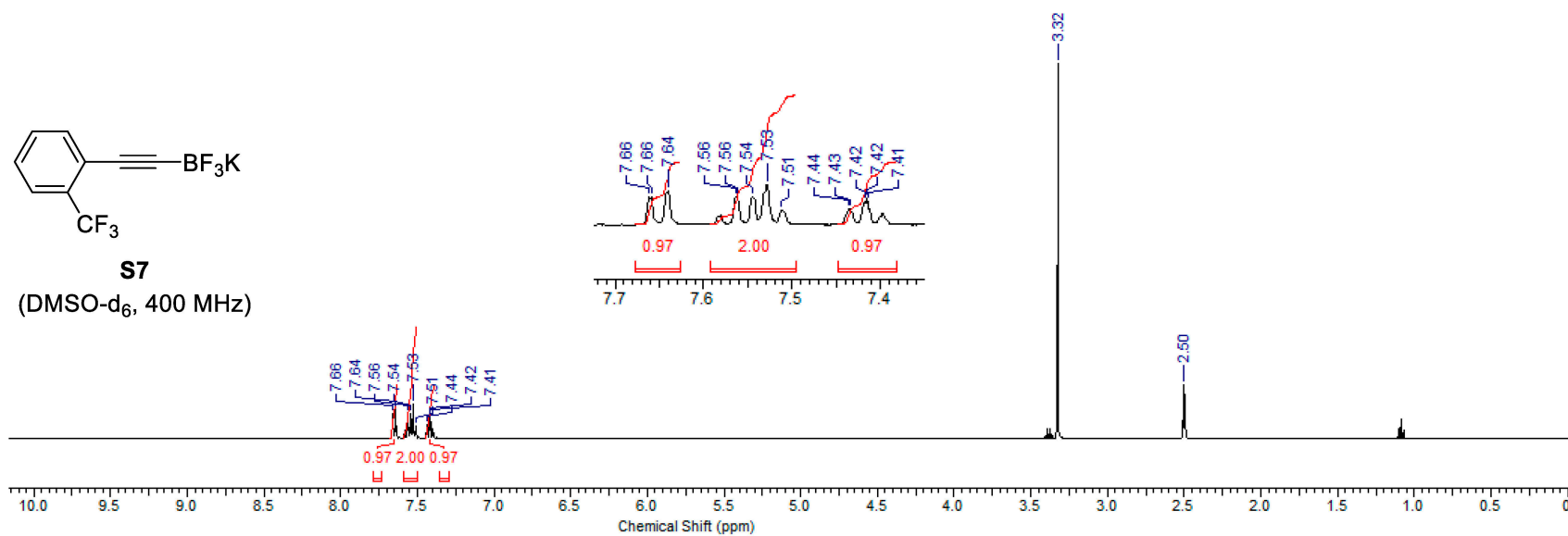


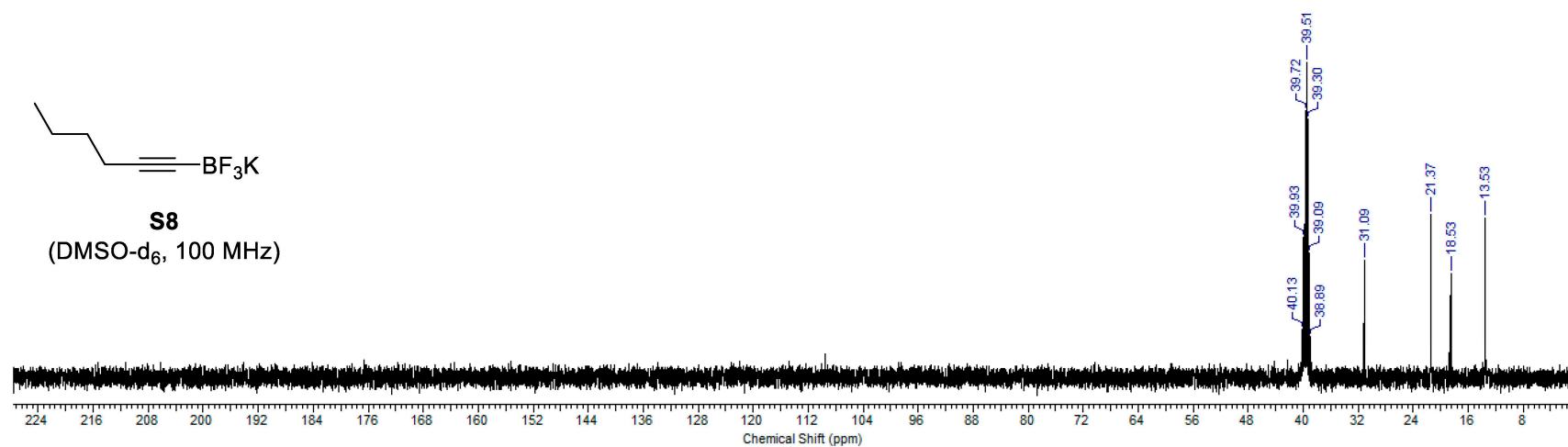
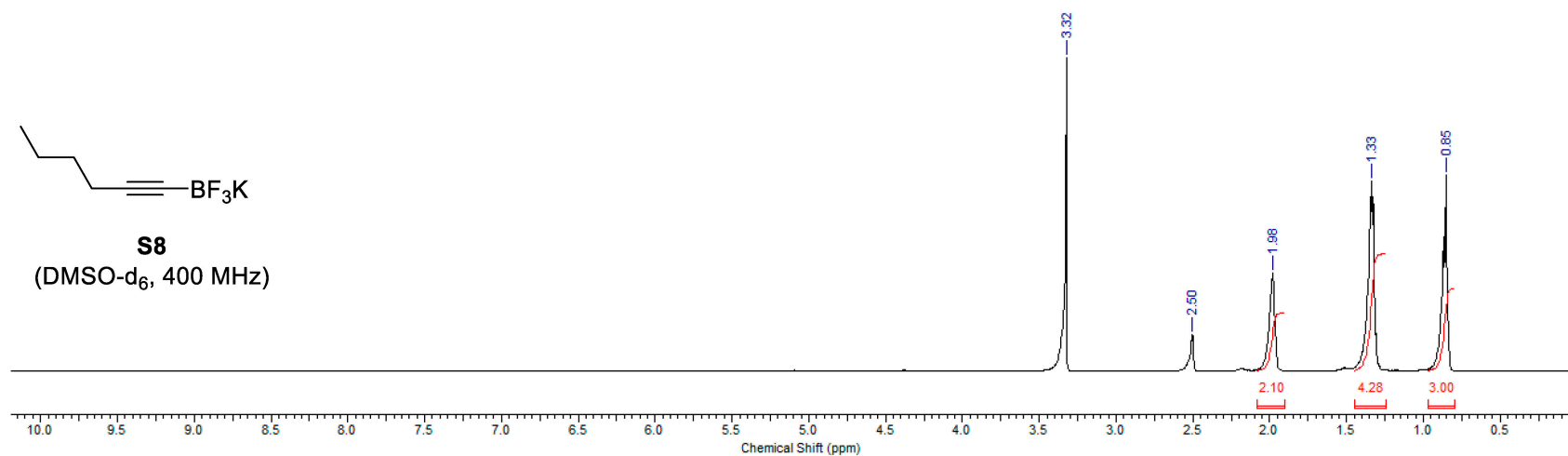


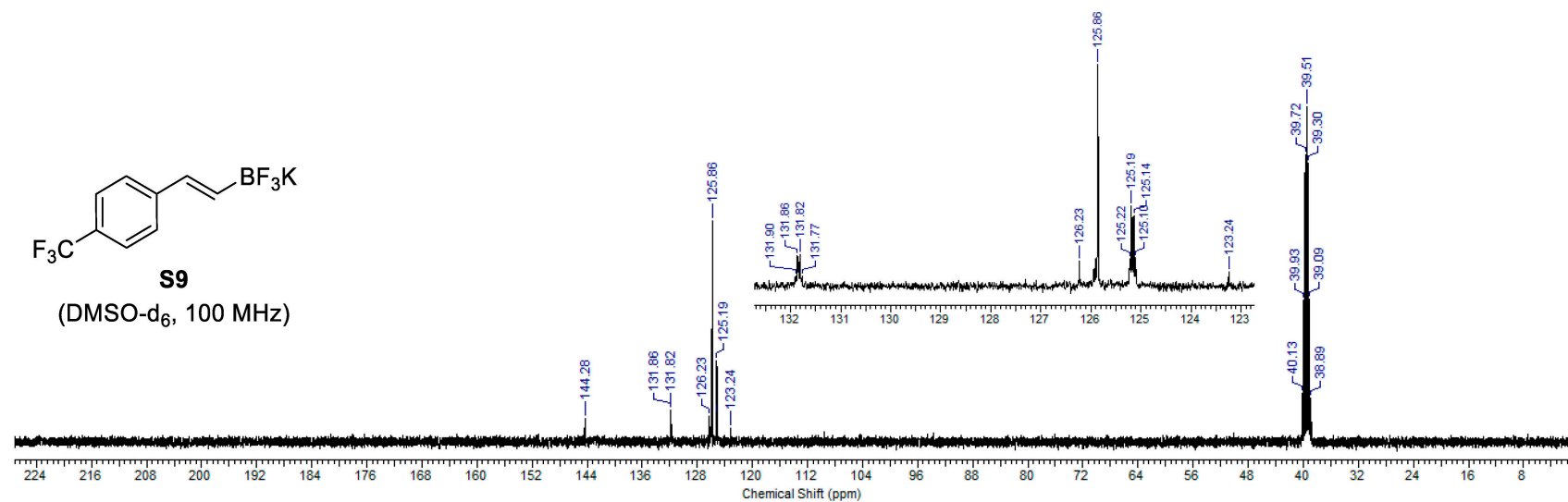
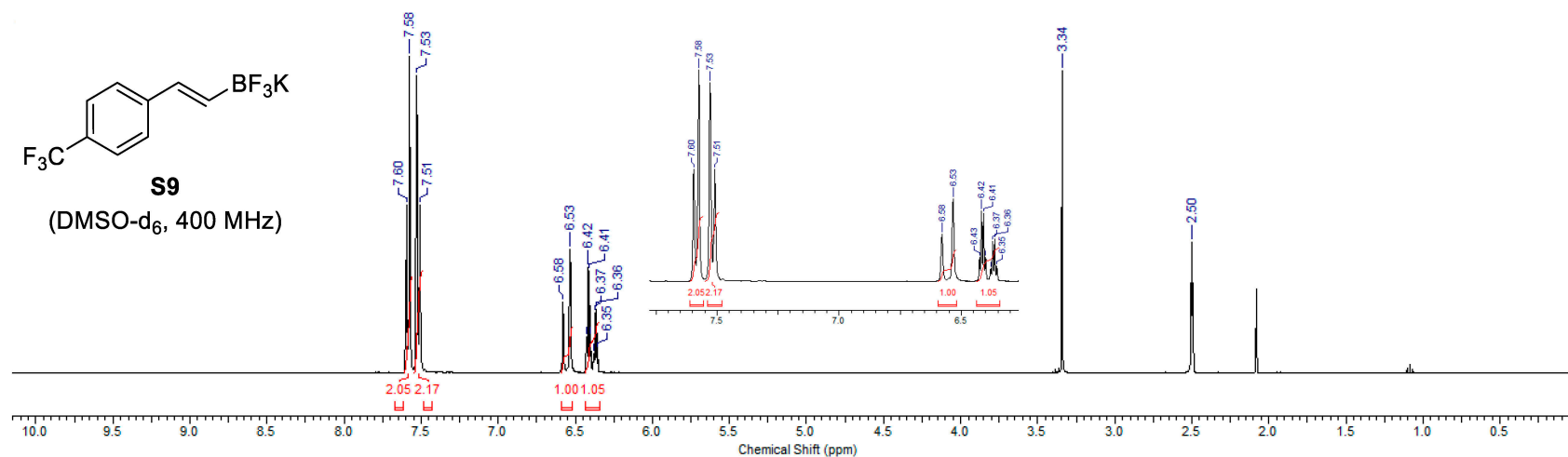


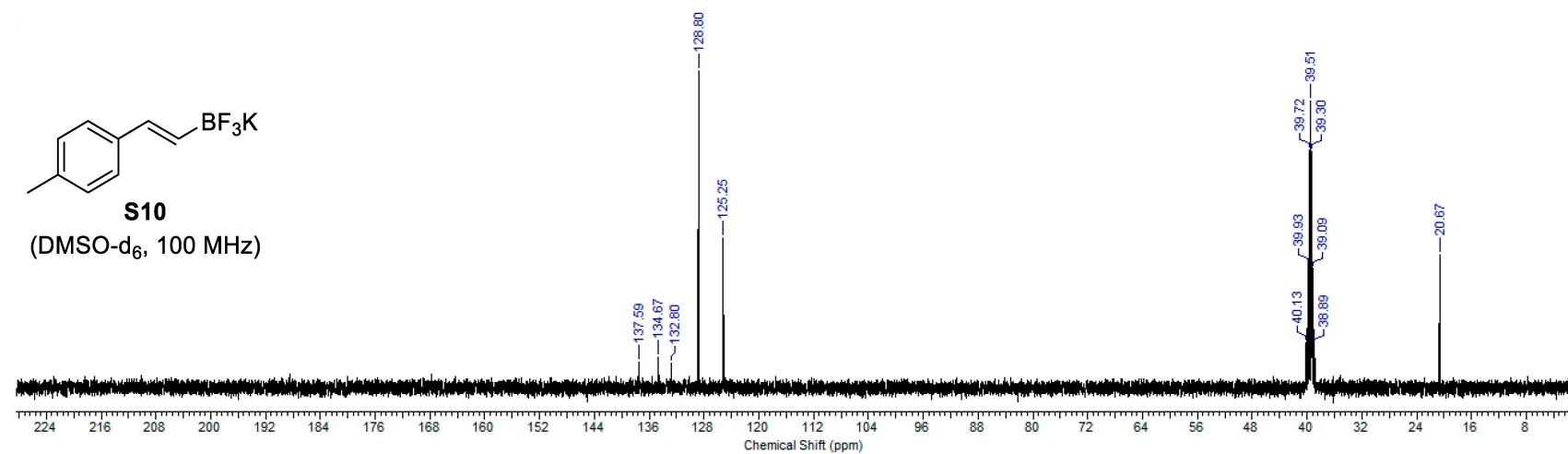
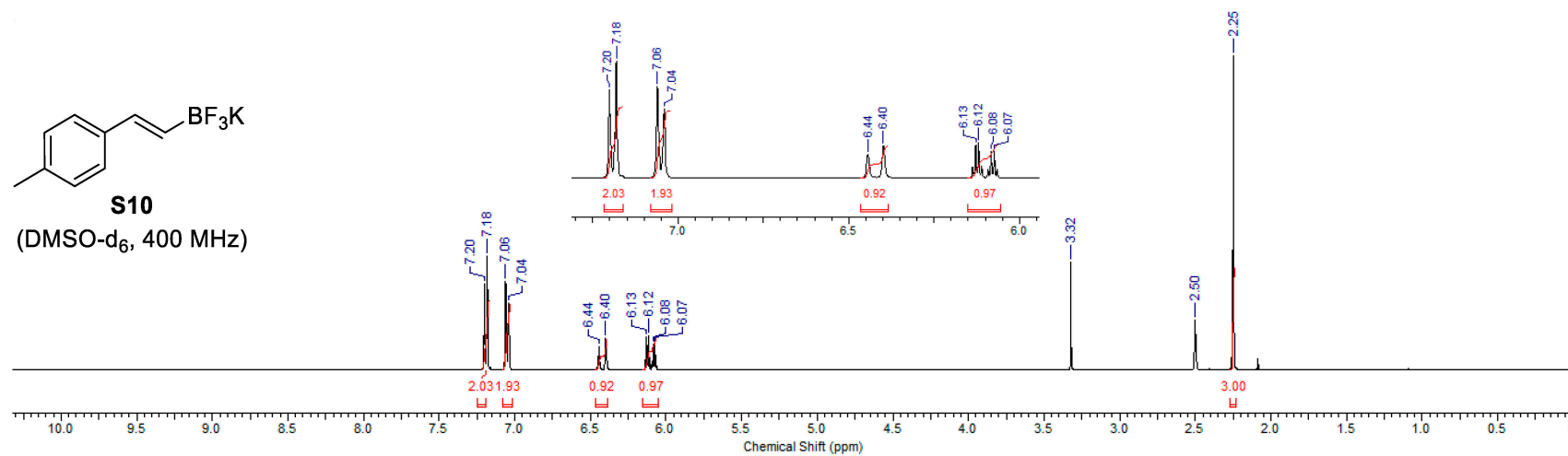


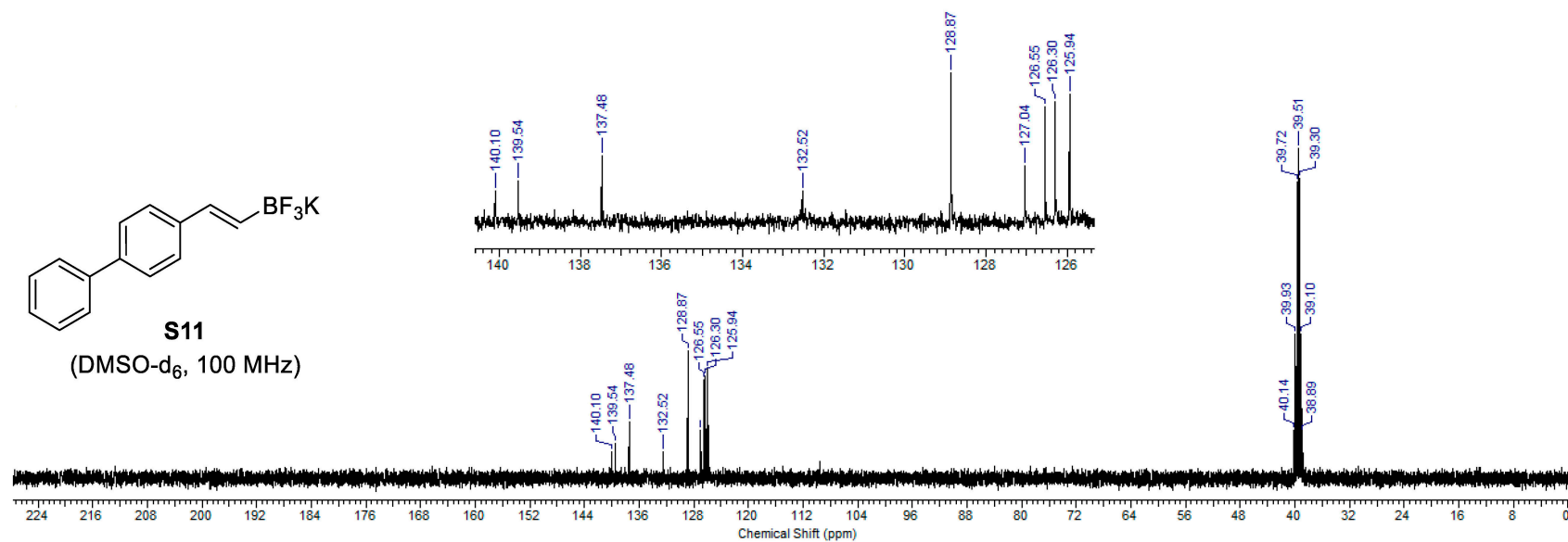
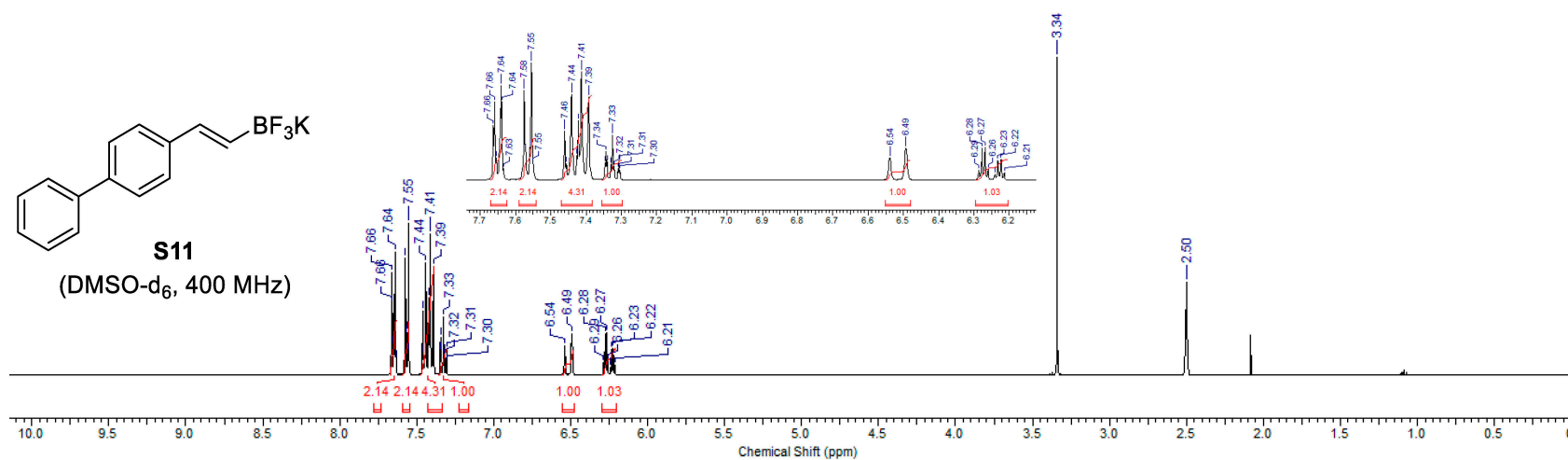


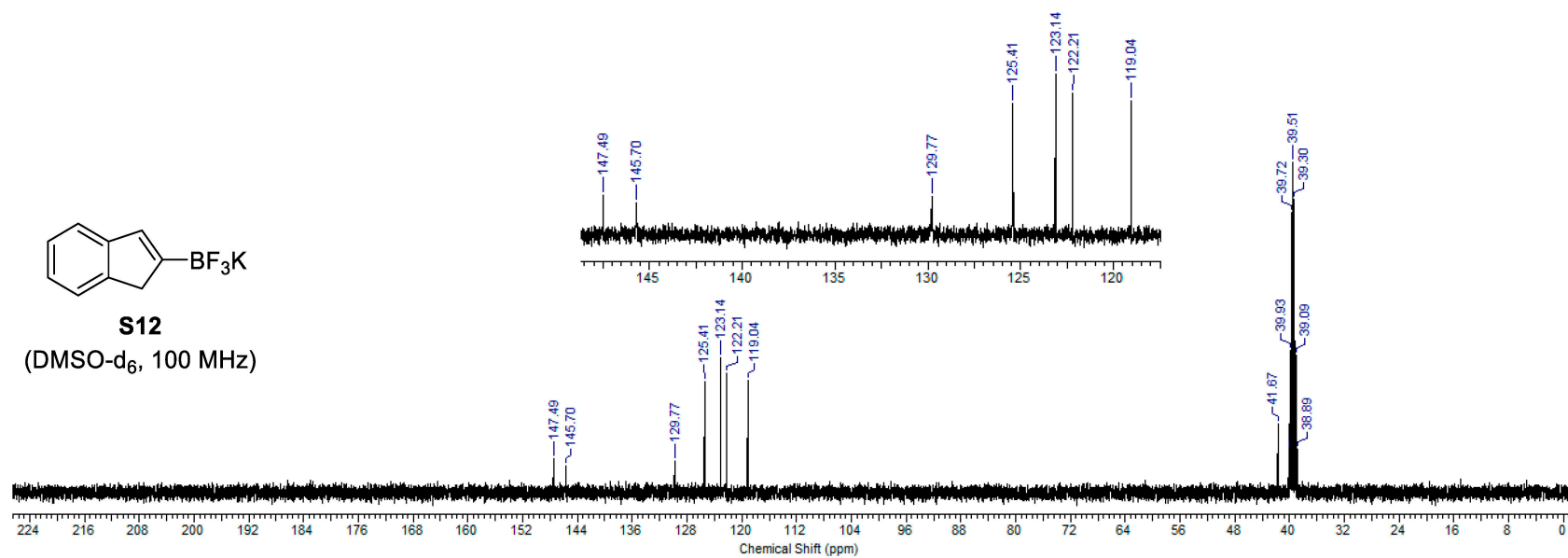
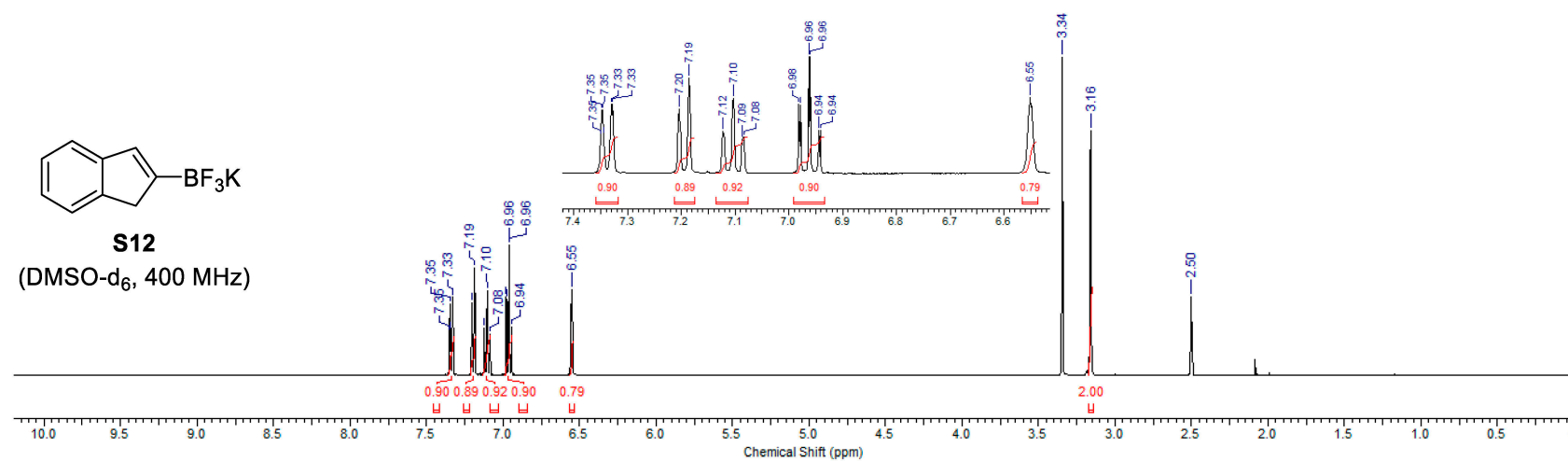


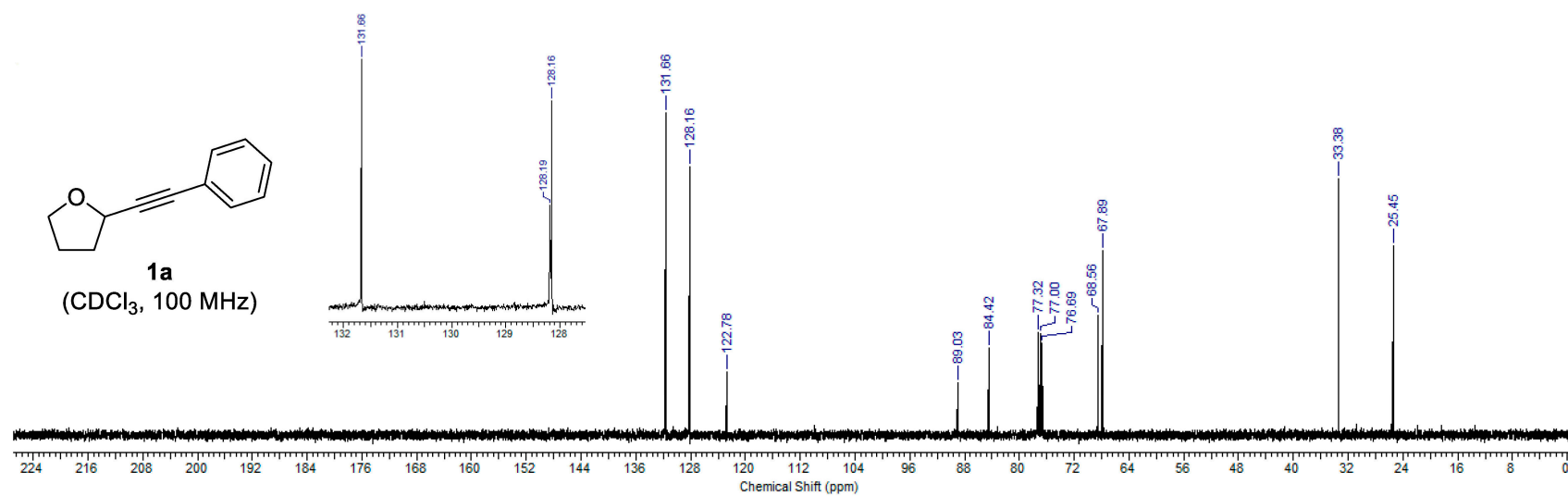
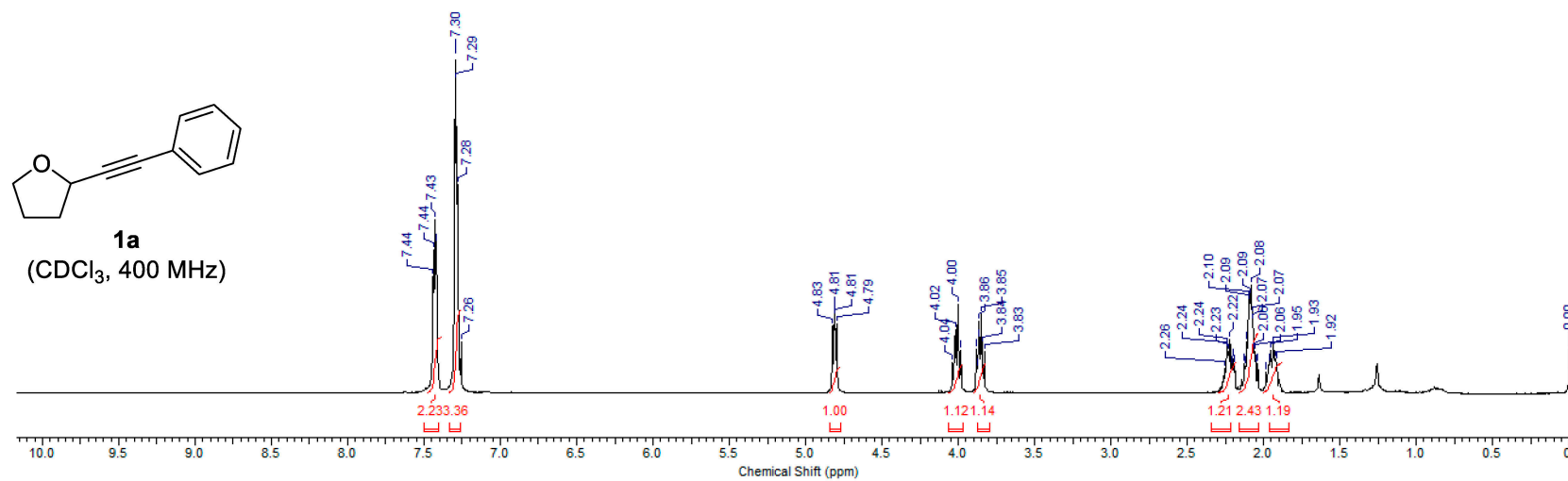


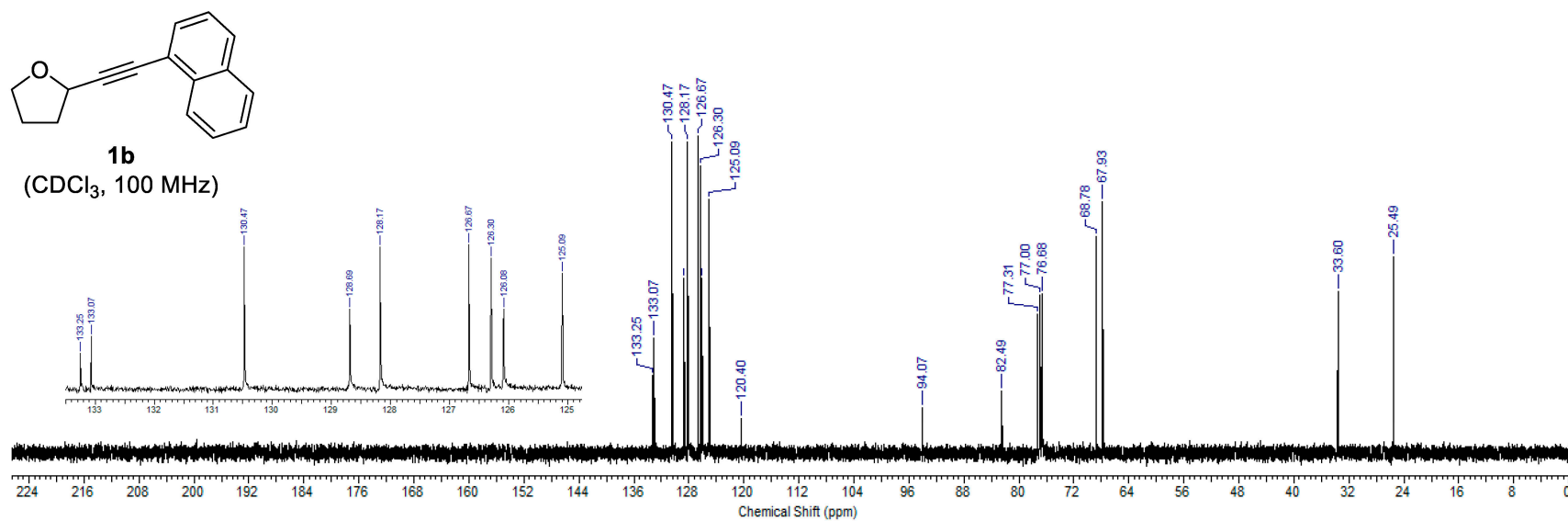
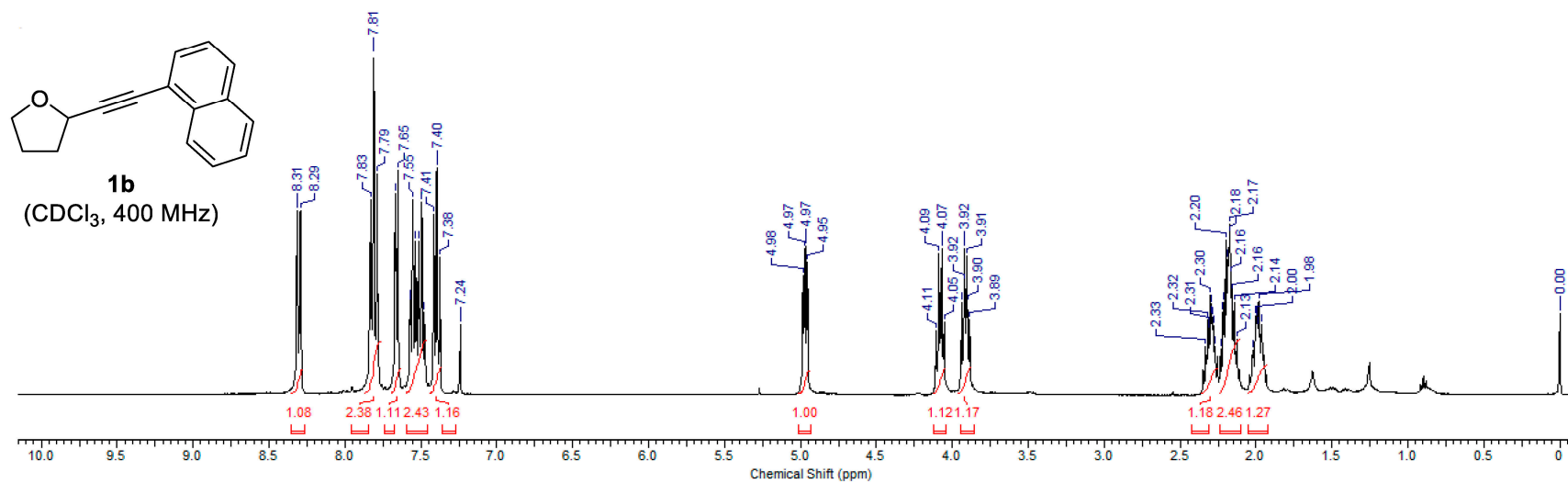


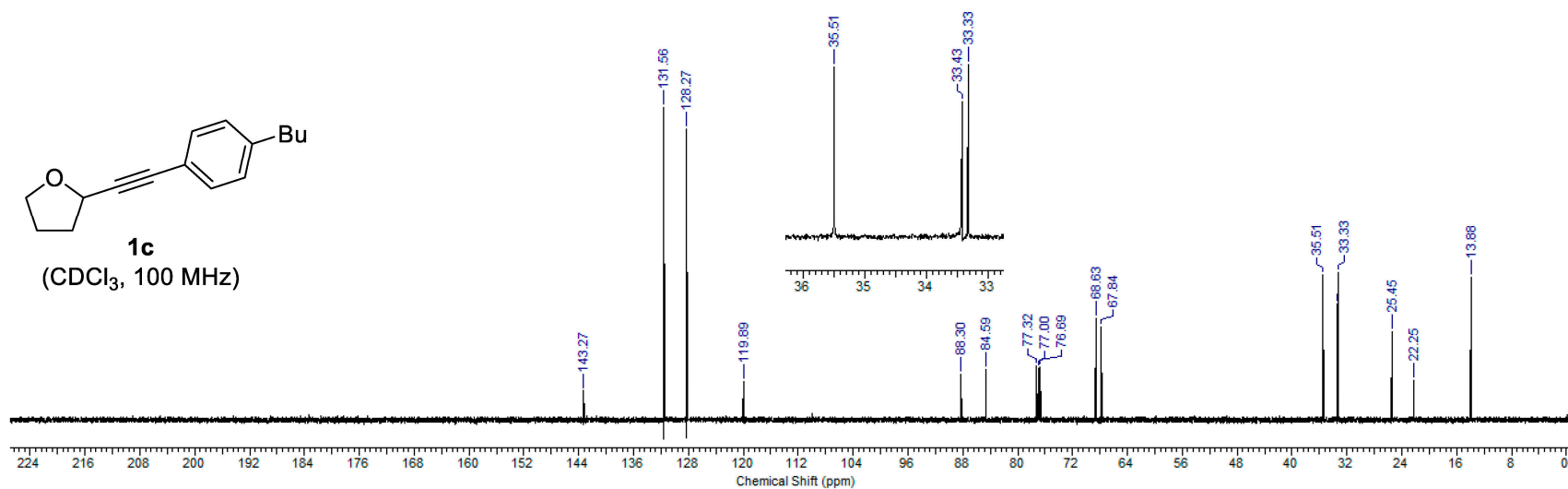
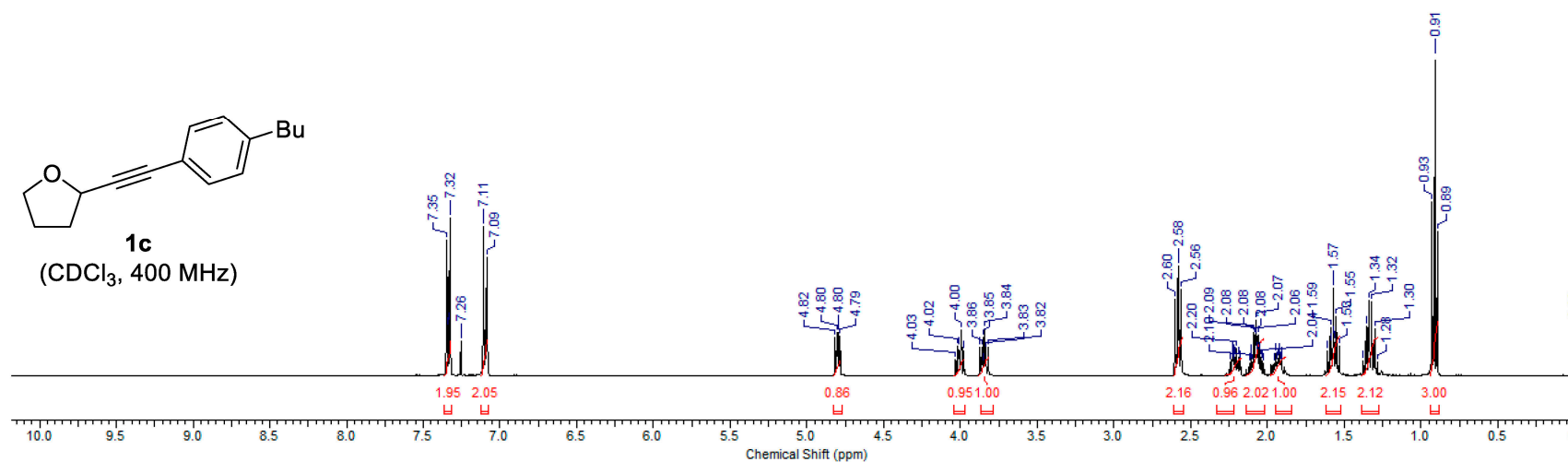


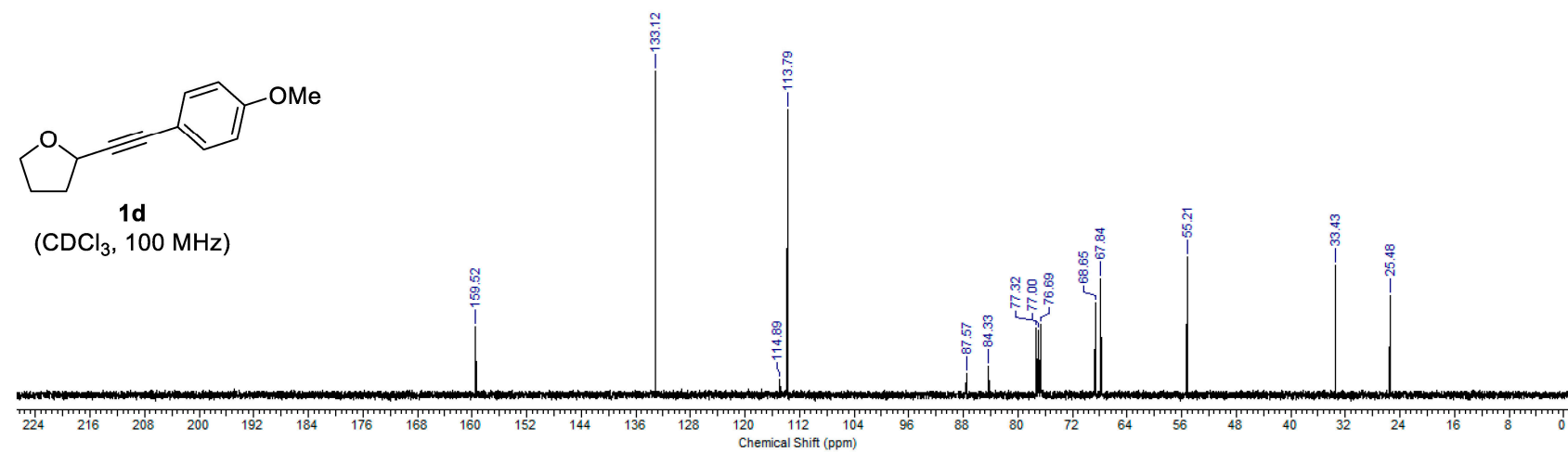
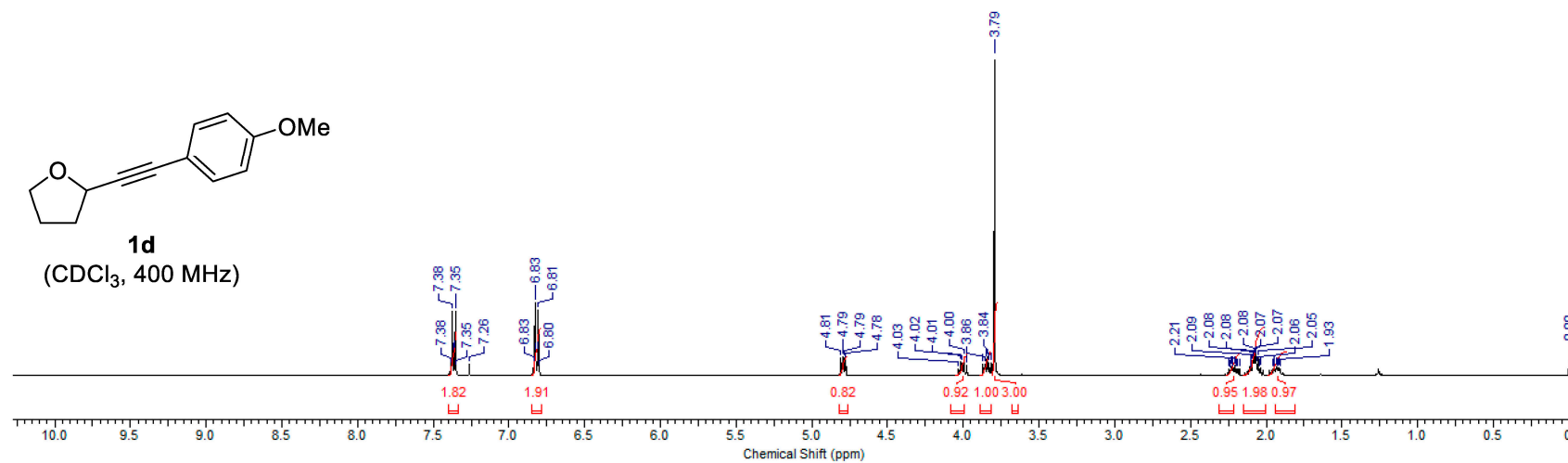


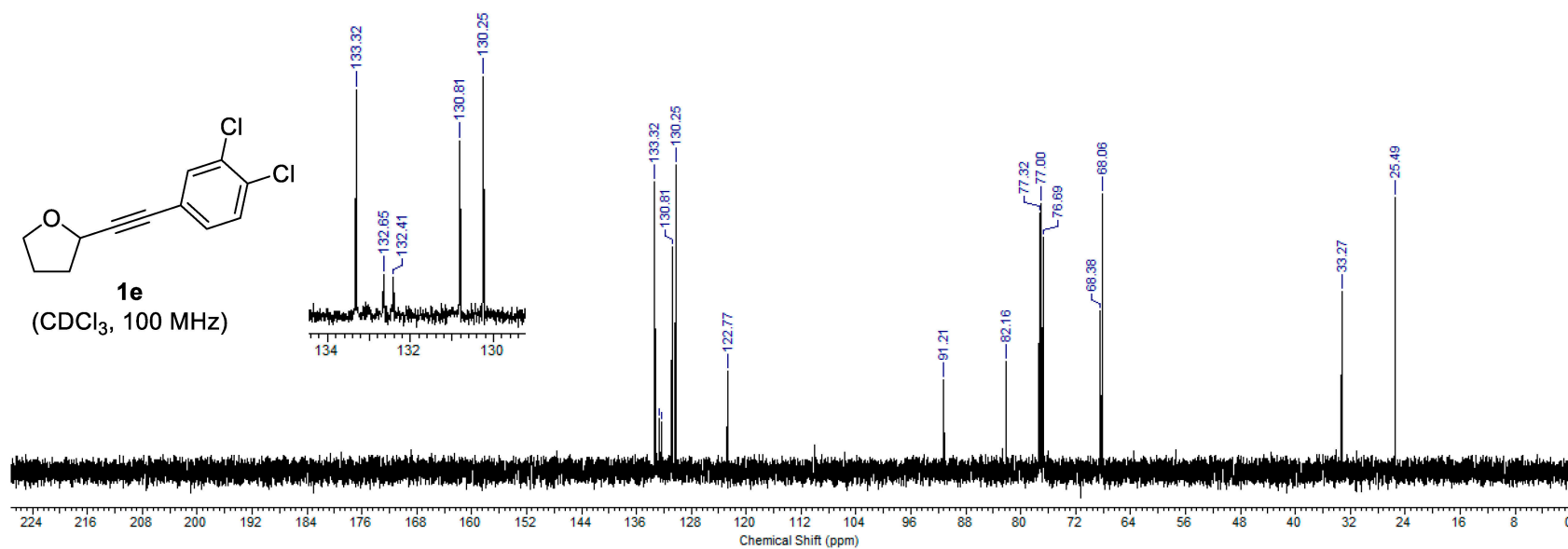
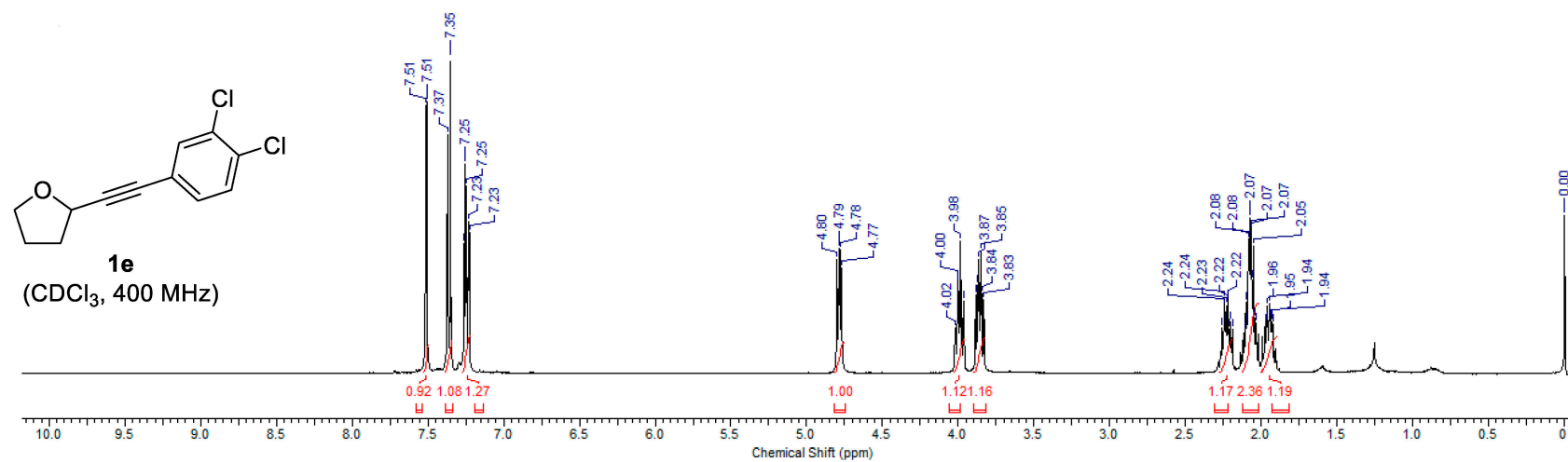


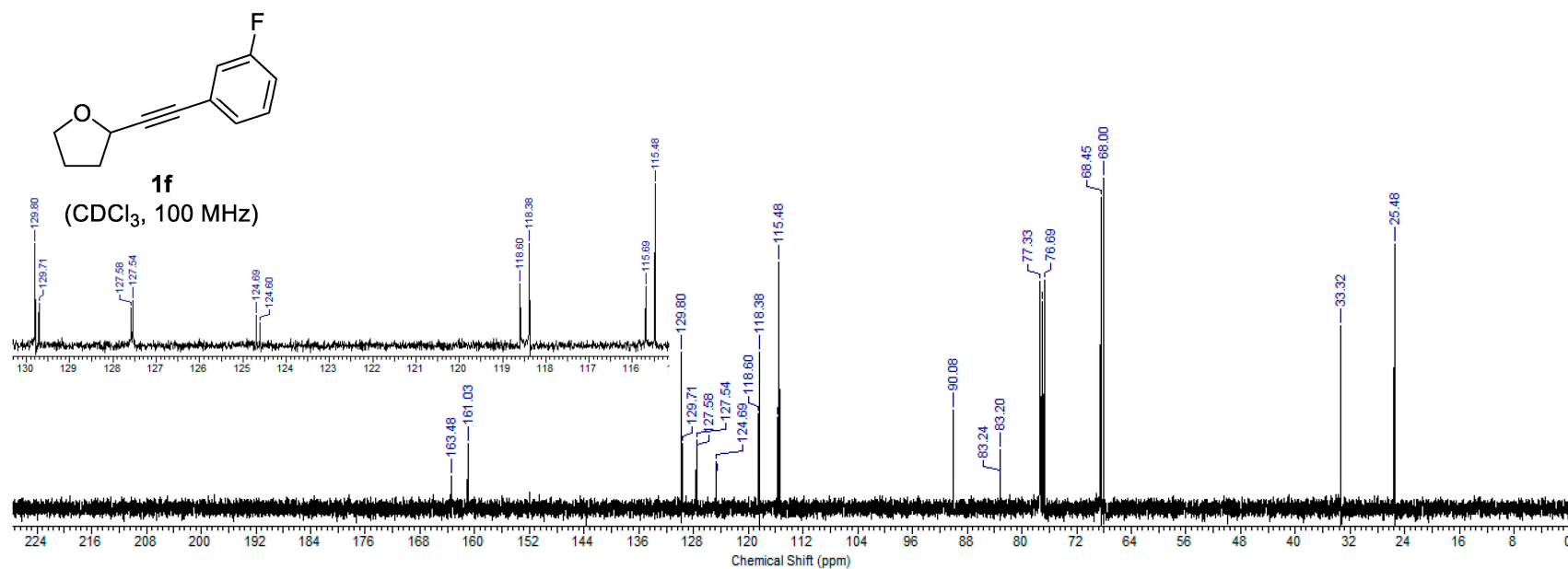
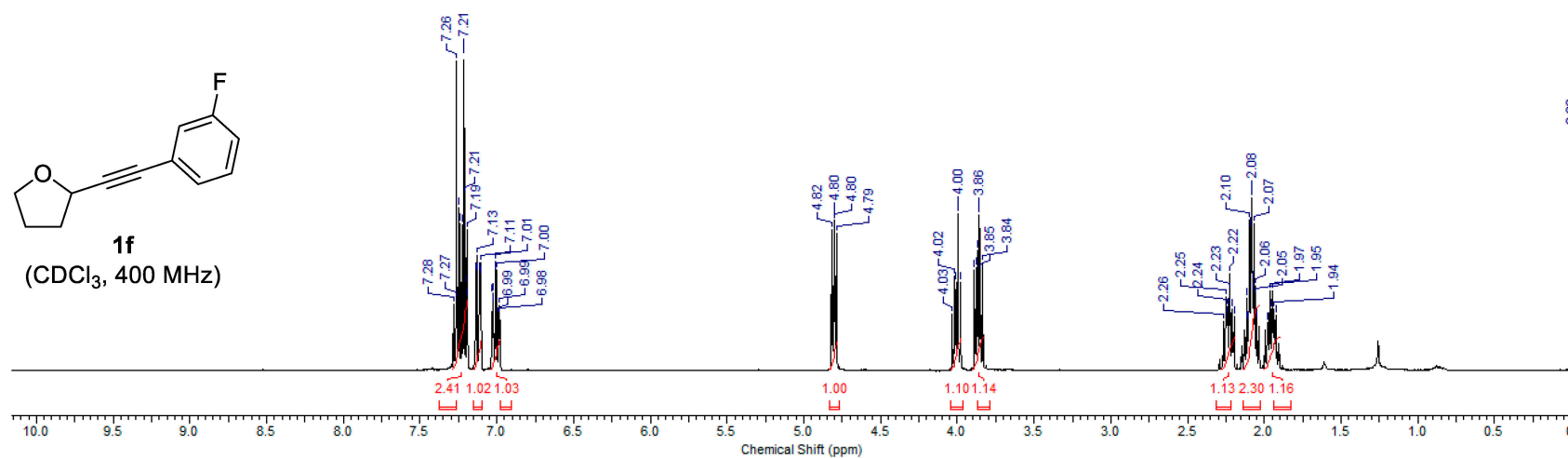


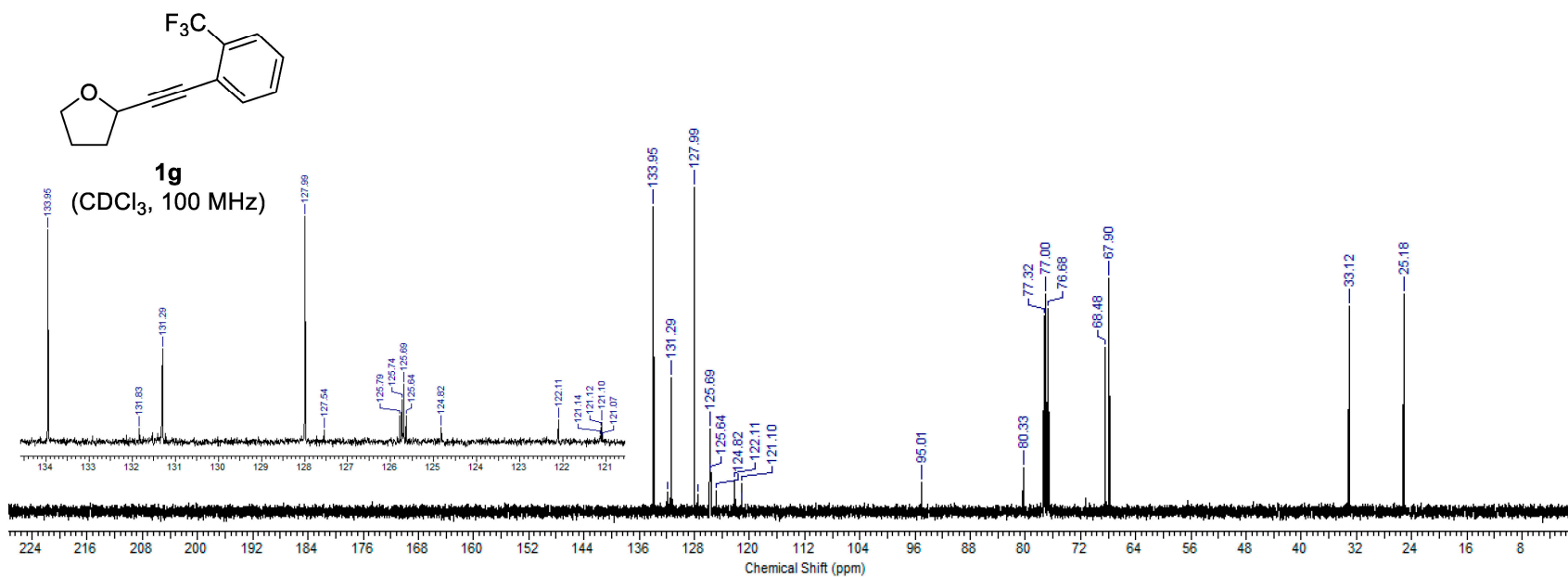
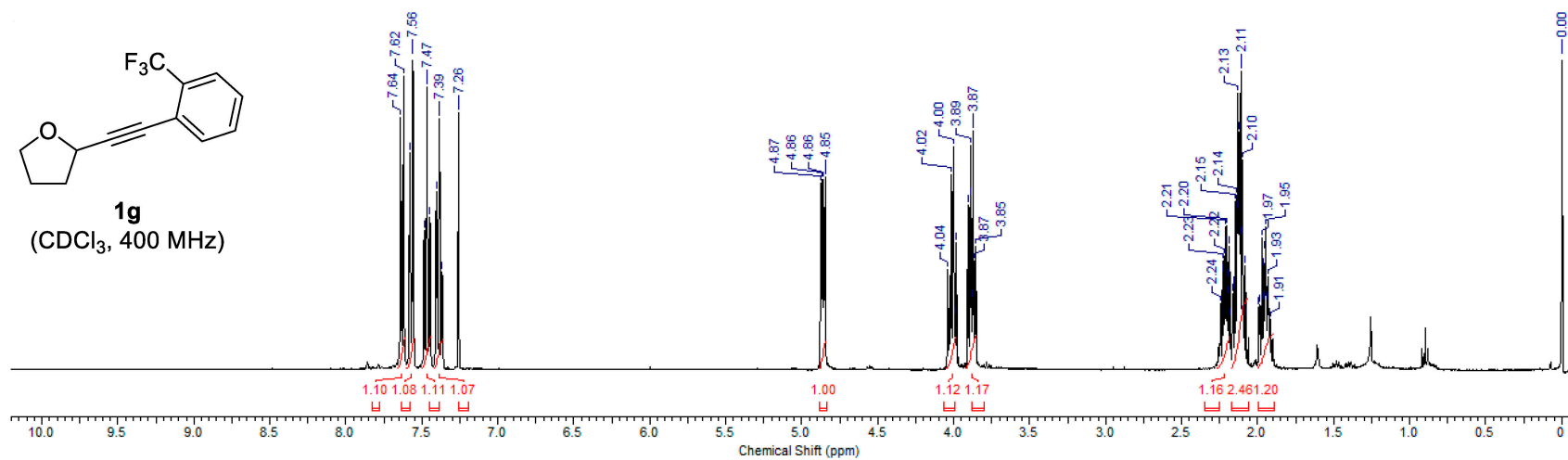


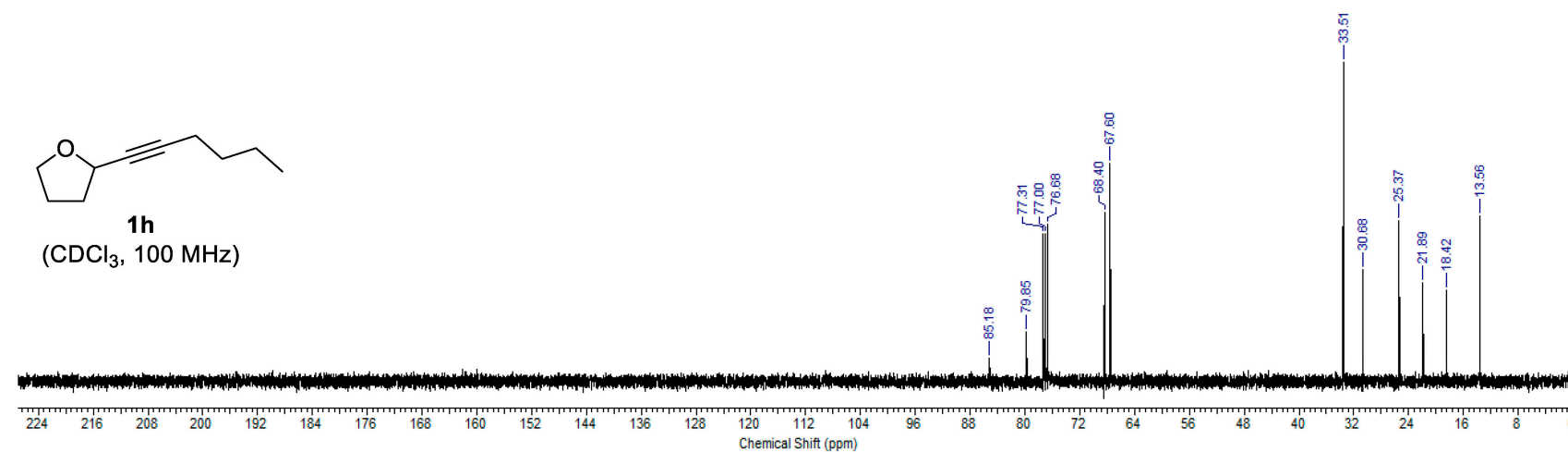
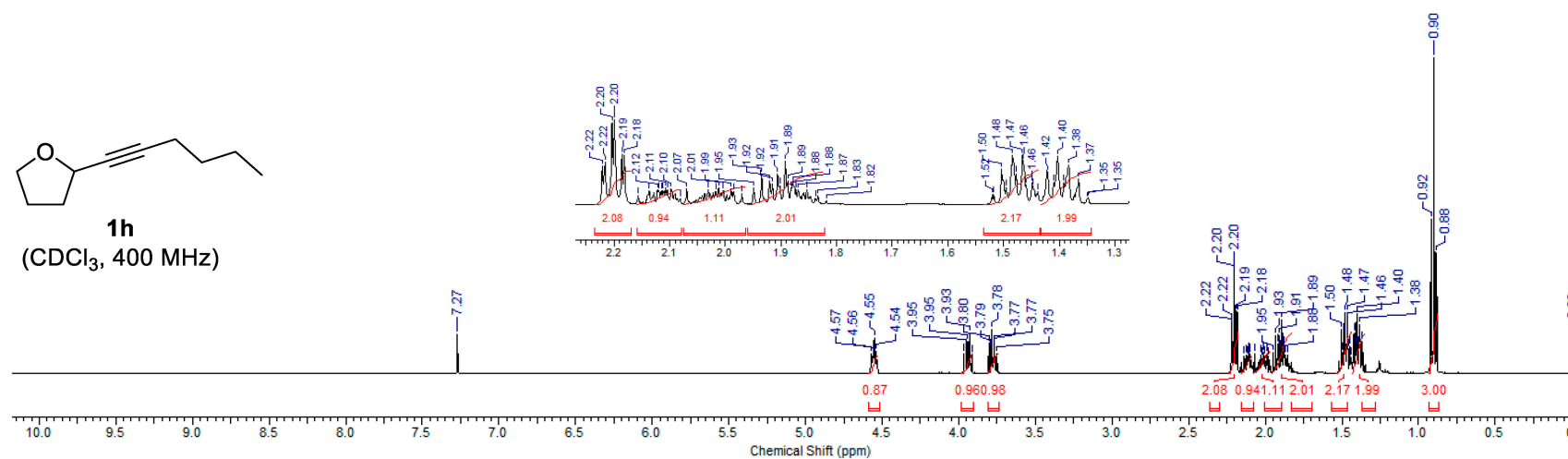


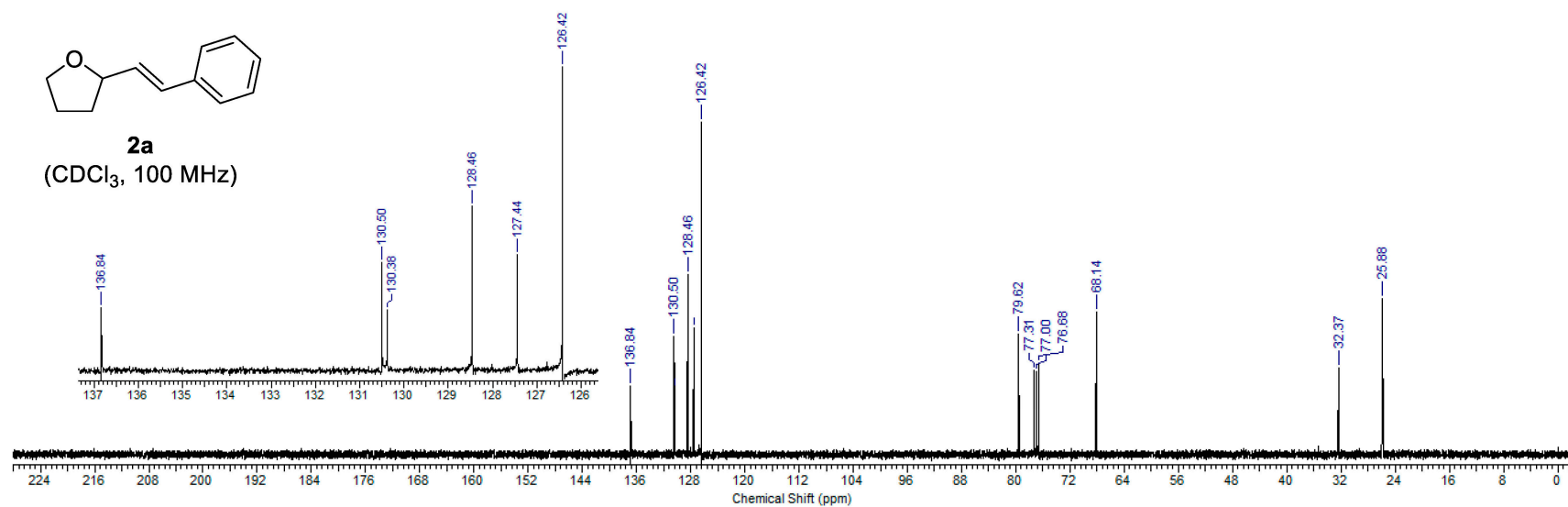
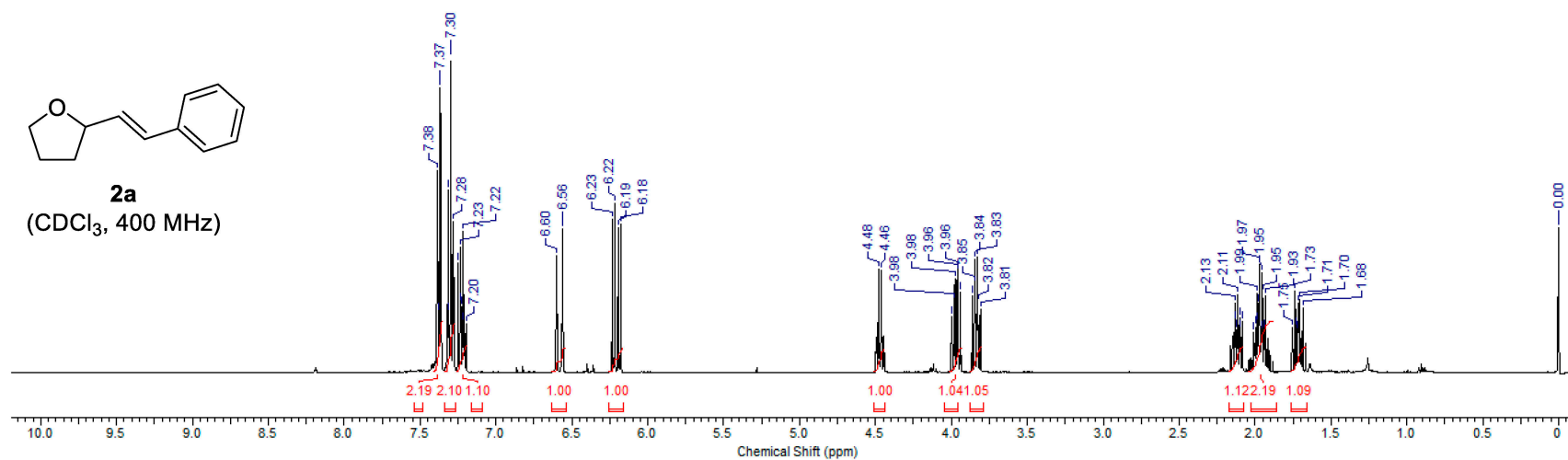


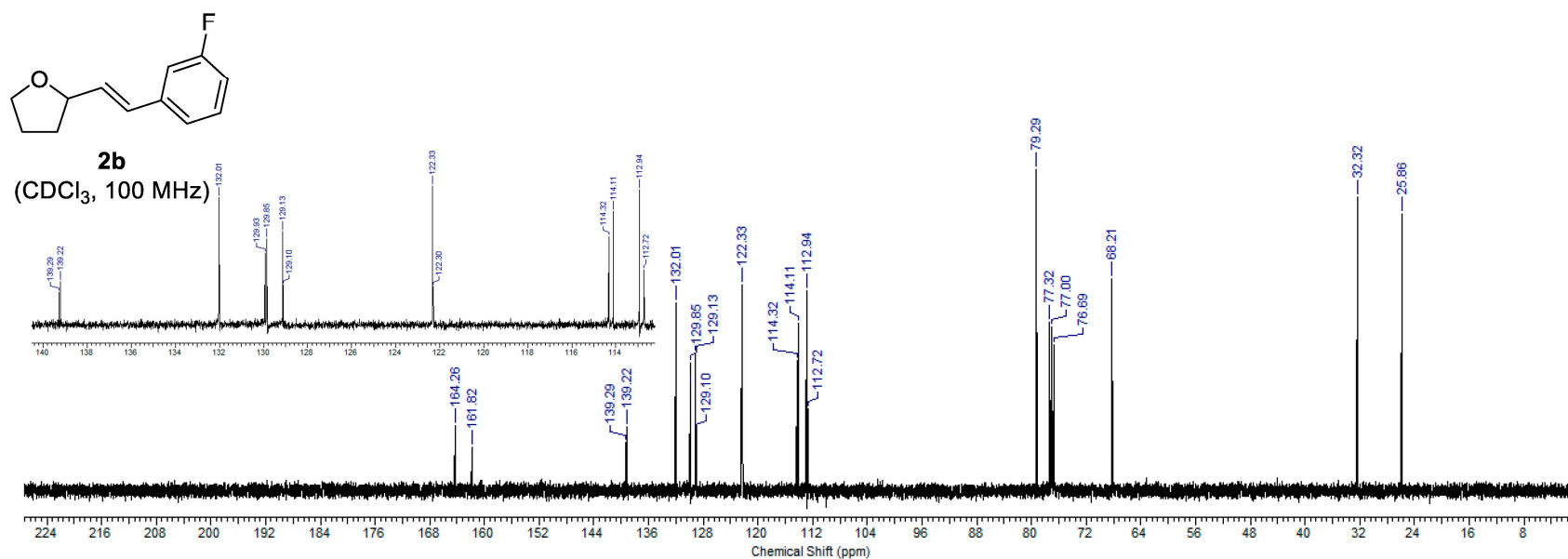
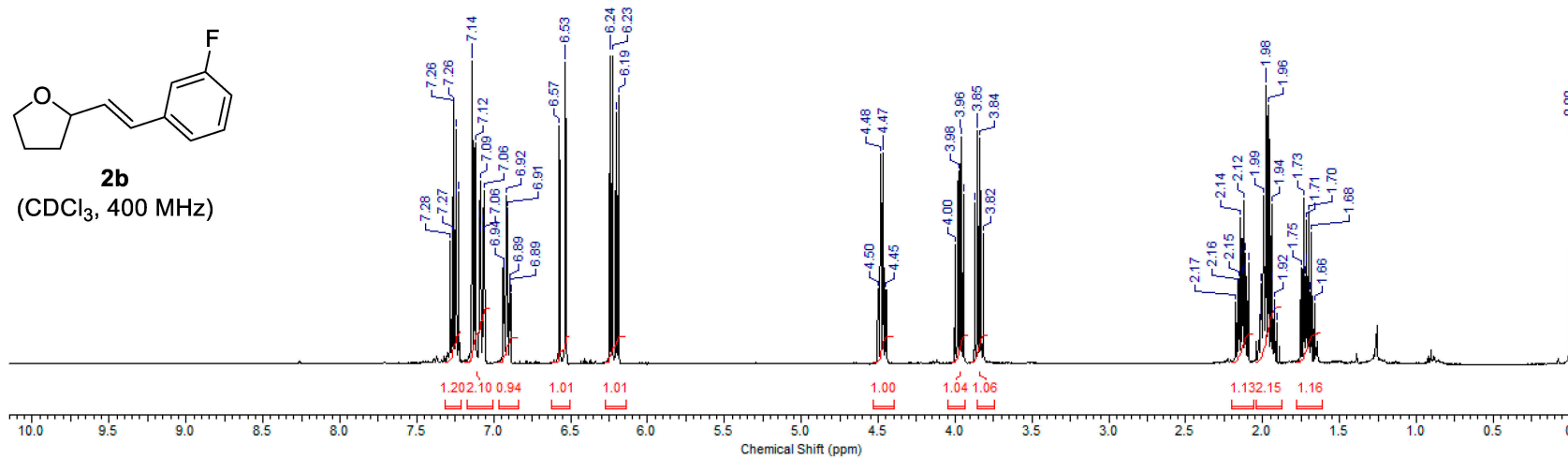


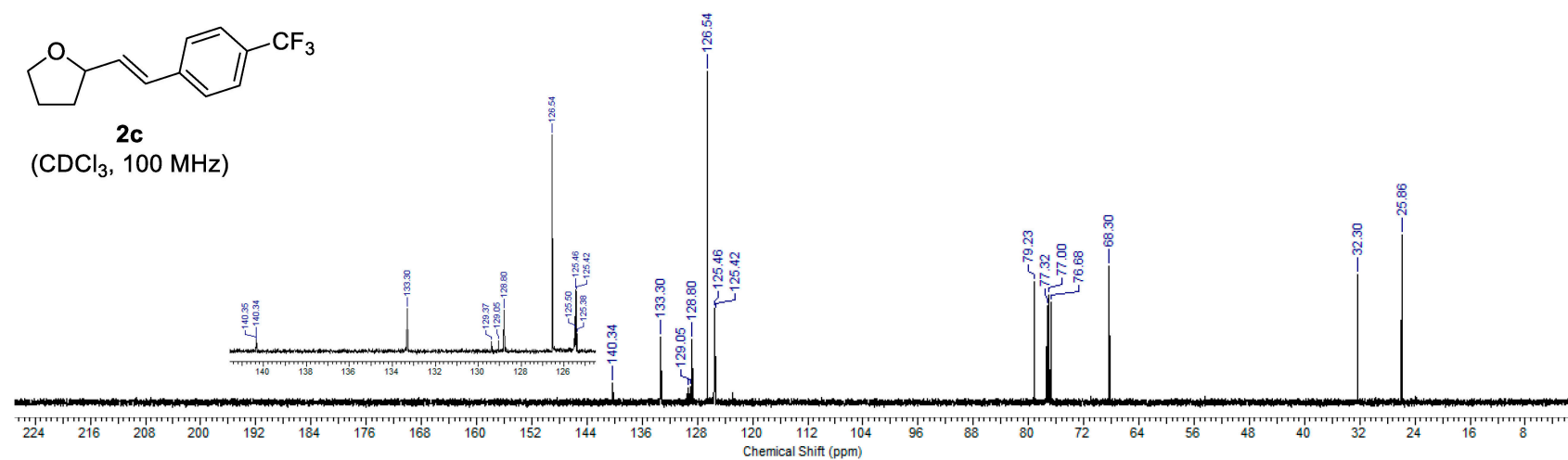
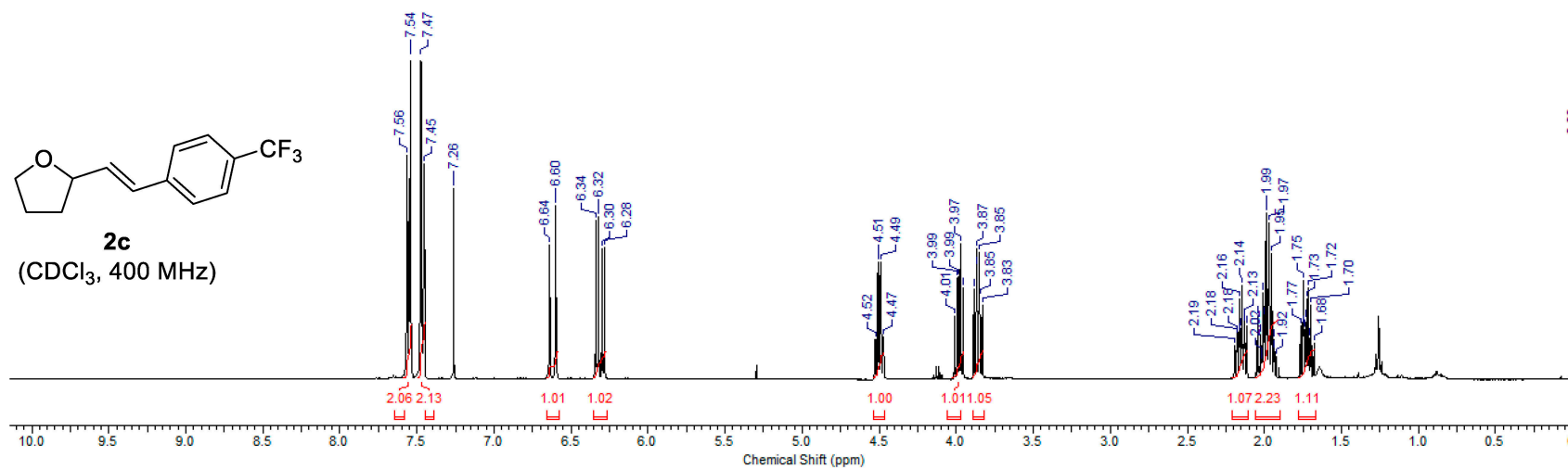


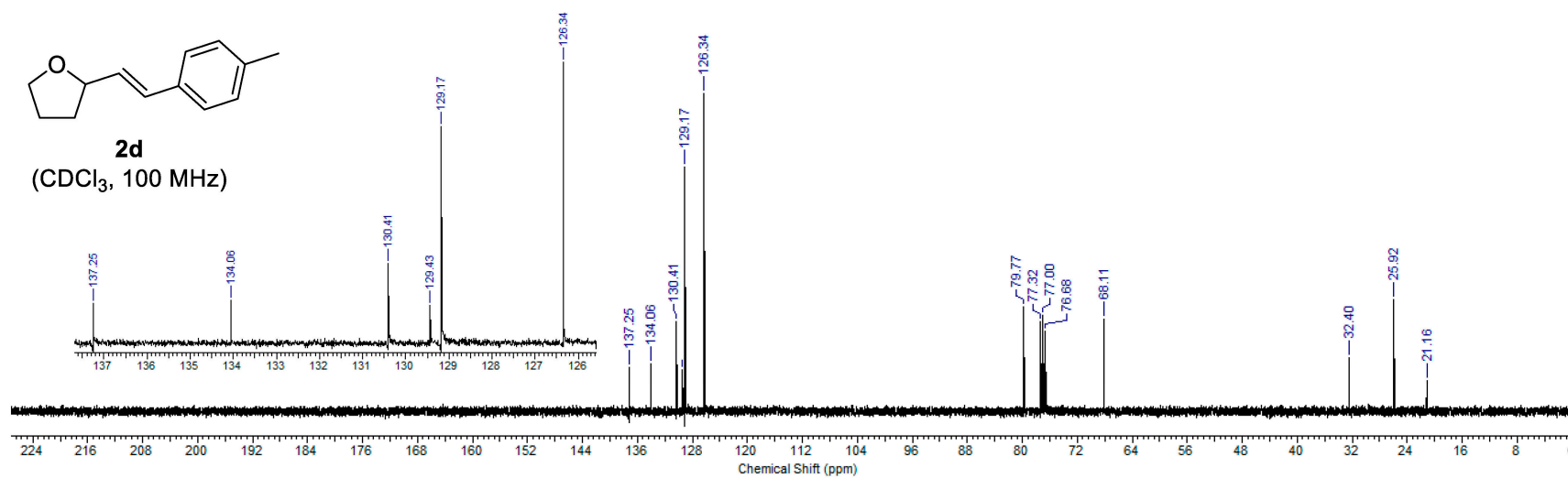
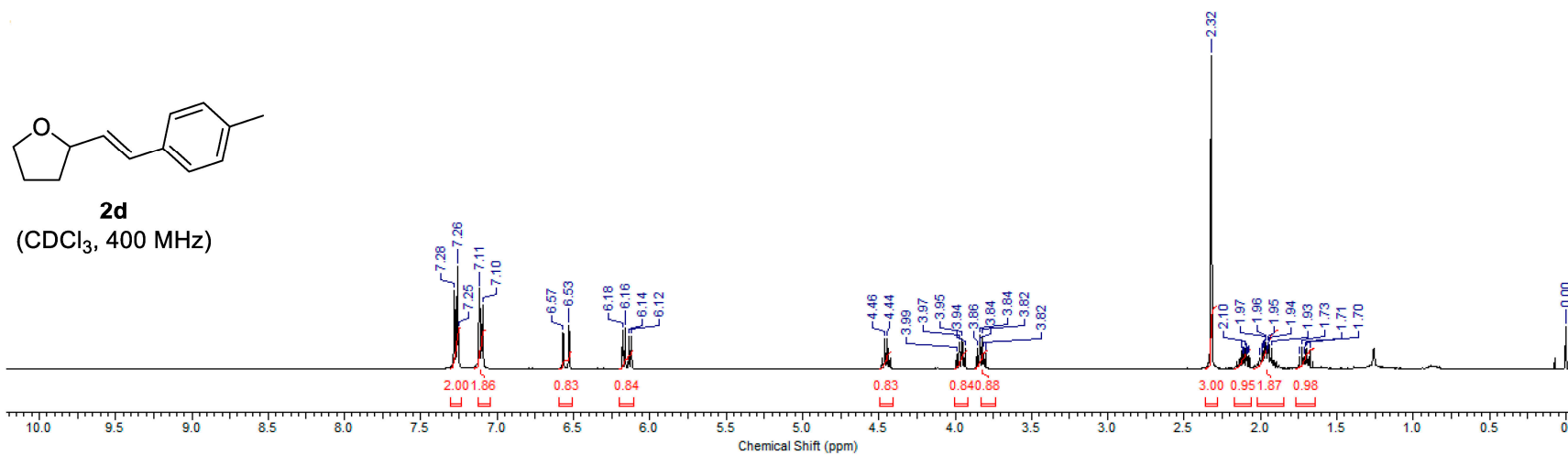


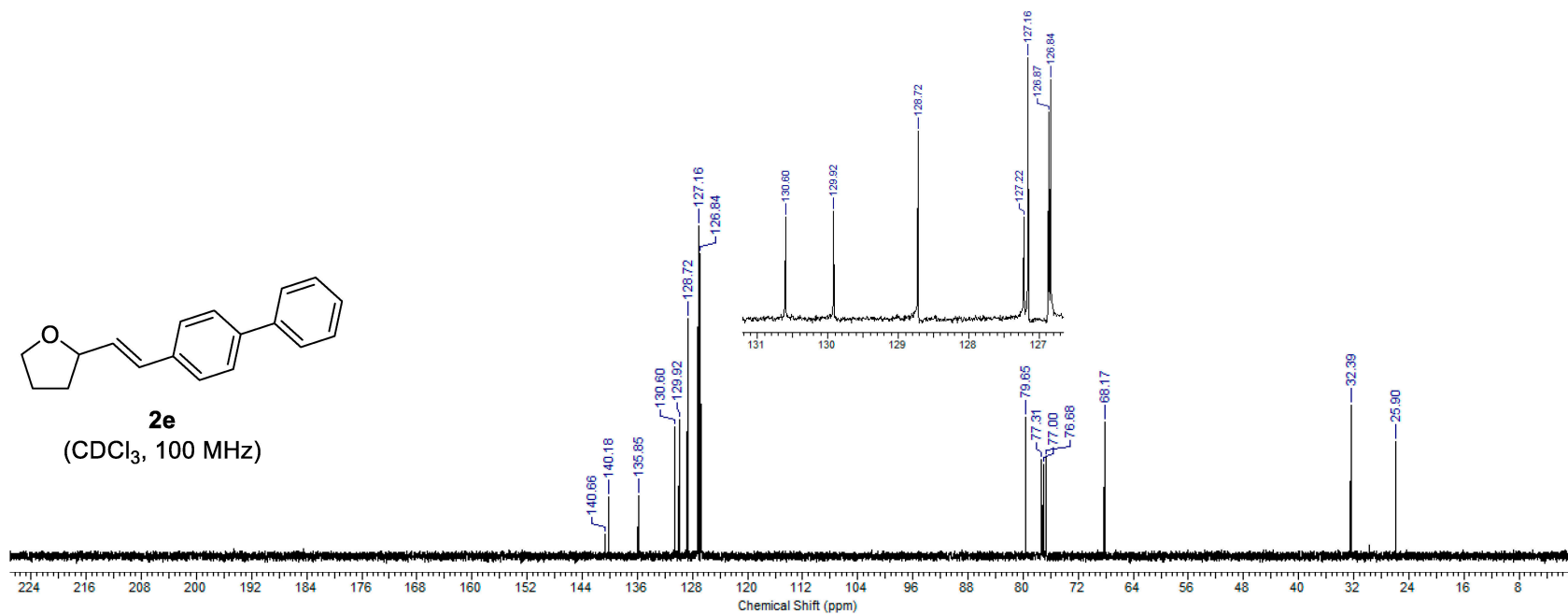
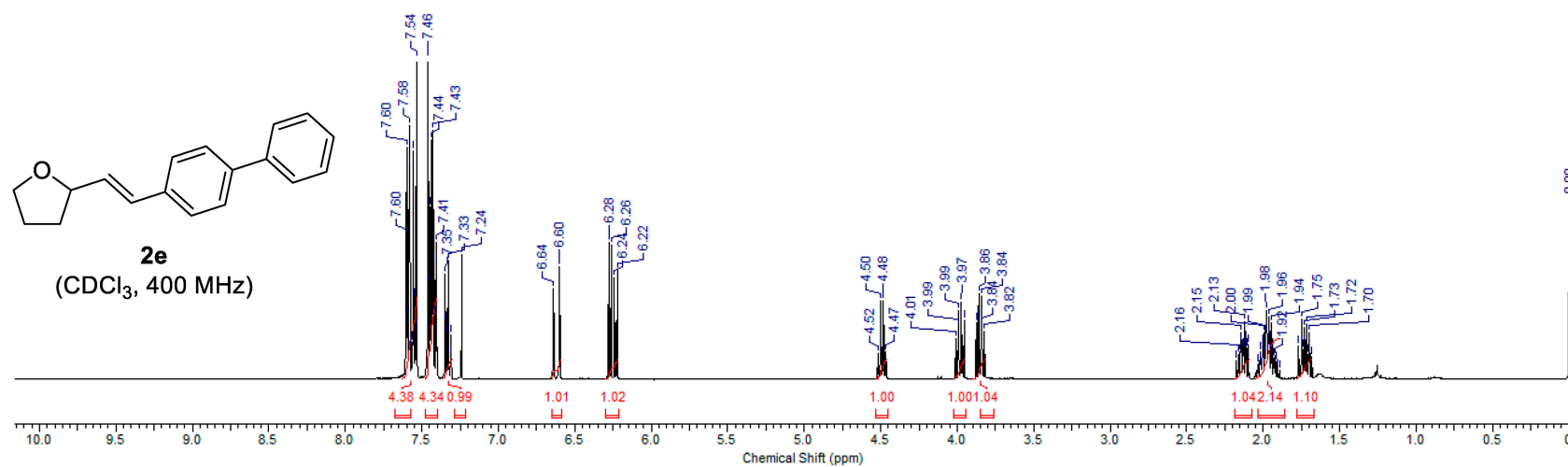


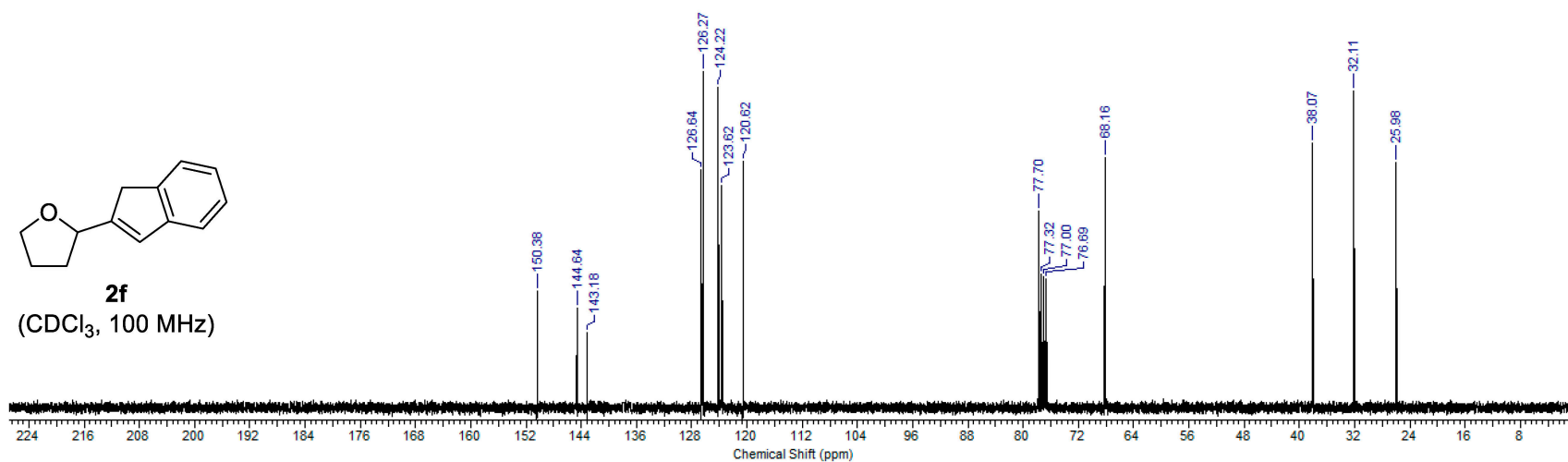
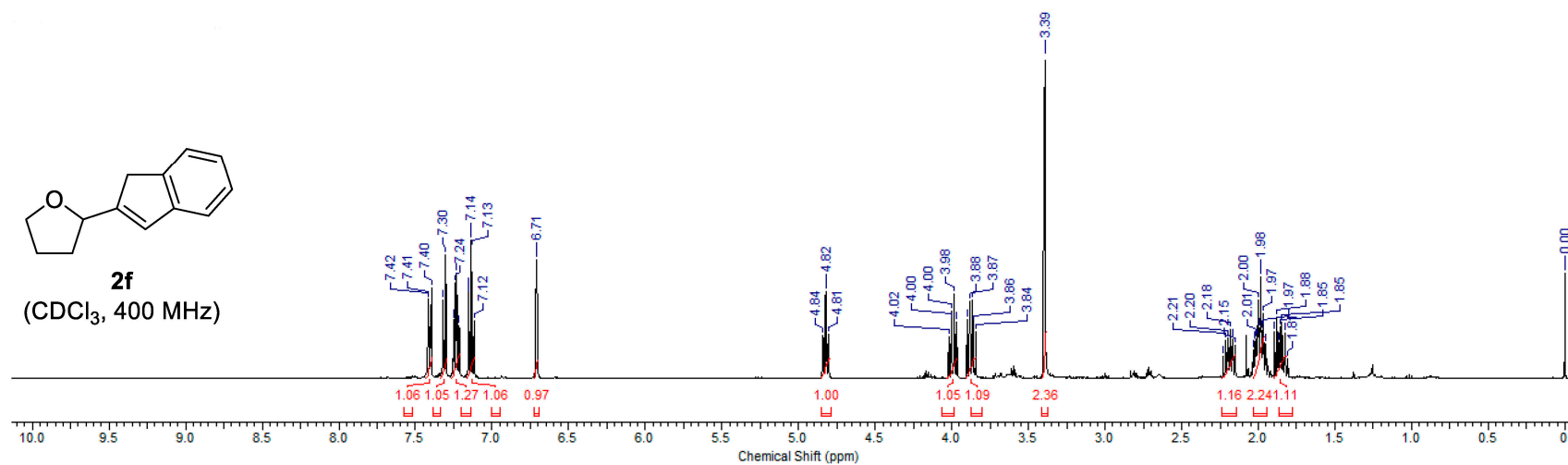












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