

Supporting Information for

Iodine-mediated regioselective synthesis of vinyl triflones from styrenes with CF₃SO₂Na

Li-Na Hua,^a Huan Li,^a Feng-LingQing,^{a,b} Yangen Huang,^{a*} and Xiu-Hua Xu^{b*}

^a College of Chemistry, Chemical Engineering and Biotechnology,
DonghuaUniversity, 2999 North Renmin Lu, Shanghai 201620, China

^b Key Laboratory of Organofluorine Chemistry, Shanghai Institute of
OrganicChemistry, Chinese Academy of Sciences, 345 Lingling Lu, Shanghai
200032, China

E-mail: hyg@dhu.edu.cn or xuxiuhua@sioc.ac.cn

Table of Contents

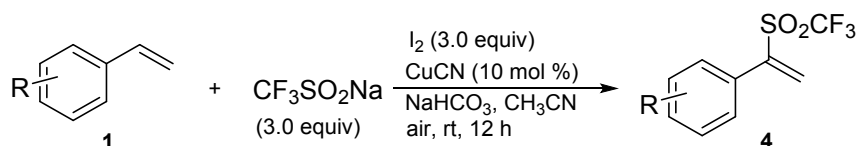
1) General information.....	S2
2) Synthesis of vinyl triflones.....	S2
3) Michael addition of vinyl triflones.....	S8
4) Gram-scale preparation of 10	S11
5) Copies of ¹ H, ¹³ C and ¹⁹ F NMR spectra for the products.....	S12
6) Copies of DEPT135 and HMQC NMR spectra for 4h	S35

1. General information.

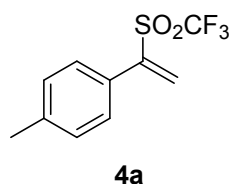
^{19}F (using trifluoromethylbenzene as an internal standard), ^1H , ^{13}C NMR spectra were recorded on a Bruker AM 400 spectrometer. Chemical shifts (δ) were reported in ppm, and coupling constants (J) were in Hertz (Hz). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. The NMR yield was determined by ^{19}F NMR using trifluoromethylbenzene as an internal standard before working up the reaction. High-resolution mass spectra (HRMS) were recorded as electron ionization (EI/HRMS) utilizing a GC/MS TOF high-resolution mass spectrometer equipped with a liquid chromatography system or as electron spray ionization (ESI/HRMS) using a Thermo Fischer Scientific LTQ FT Ultra instrument in DART-positive mode.

Materials: Unless otherwise noted, all reagents were obtained commercially and used without further purification. CH_3CN and CH_2Cl_2 was distilled from CaH_2 and stored with 4 Å molecular sieves. Reactions were performed using glassware that was flame-dried under vacuum.

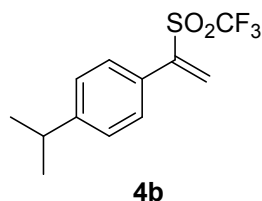
2. Synthesis of vinyl triflones



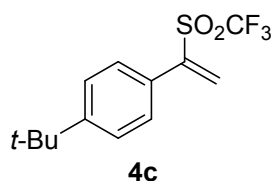
A 15 mL glass tube equipped with a magnetic stirring bar was charged with alkenes (0.5 mmol), $\text{CF}_3\text{SO}_2\text{Na}$ (0.234 mg, 1.5 mmol), I_2 (0.380 mg, 1.5 mmol), NaHCO_3 (0.084 mg, 1.0 mmol), CuCN (0.004 mg, 0.05 mmol) and CH_3CN (2 mL). After stirring at rt for 12 hours, saturated aqueous $\text{Na}_2\text{S}_2\text{O}_3$ solution was added. Then, the reaction mixture was extracted with ethyl acetate. The organic phase was washed with H_2O and brine, dried by Na_2SO_4 , concentrated in vacuo. The residue was purified by silica gel column chromatography to afford the corresponding vinyl triflones **4**.



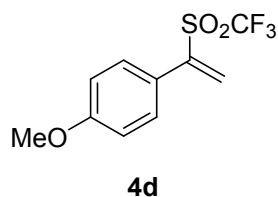
Methyl-4-(1-((trifluoromethyl)sulfonyl)vinyl)benzene (**4a**) (72.1 mg, 54%): yellow liquid. ^1H NMR (400 MHz, CDCl_3) δ 7.46 (d, J = 7.8 Hz, 2H), 7.27 (d, J = 7.7 Hz, 2H), 6.82 (s, 1H), 6.46 (s, 1H), 2.42 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 144.1, 141.0, 135.0, 129.5, 128.9, 127.6, 119.8 (q, J = 330.3 Hz), 21.6. ^{19}F NMR (377 MHz, CDCl_3) δ -75.9 (s, 3F). IR (thin film) ν 2255, 1606, 1573, 1510, 1462, 1298, 904, 725 cm^{-1} . MS (ESI): m/z (%) 289 $[\text{M}+\text{K}]^+$. HRMS (ESI-TOF) m/z : $[\text{M}+\text{NH}_4]^+$ Calcd for $\text{C}_{10}\text{H}_{13}\text{F}_3\text{NO}_2\text{S}$: 268.0614; Found: 268.0612.



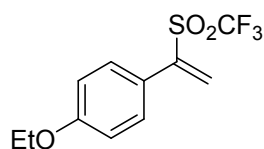
Isopropyl-4-(1-((trifluoromethyl)sulfonyl)vinyl)benzene (**4b**) (70.9 mg, 51%): yellow liquid. ^1H NMR (400 MHz, CDCl_3) δ 7.51 (d, $J = 7.5$ Hz, 2H), 7.33 (d, $J = 7.6$ Hz, 2H), 6.82 (s, 1H), 6.47 (s, 1H), 3.05–2.94 (m, 1H), 1.31 (d, $J = 6.8$ Hz, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 151.5, 144.1, 135.1, 129.1, 127.9, 126.9, 119.8 (q, $J = 329.3$ Hz), 33.9, 23.7. ^{19}F NMR (377 MHz, CDCl_3) δ -76.1 (s, 3F). IR (thin film) ν 2965, 2349, 1610, 1508, 1411, 1208, 1019, 905, 726 cm^{-1} . MS (EI): m/z (%) 278 (M^+). HRMS (EI-TOF) m/z : (M^+) Calcd for $\text{C}_{12}\text{H}_{13}\text{F}_3\text{O}_2\text{S}$: 278.0588; Found: 278.0585.



1-(*Tert*-butyl)-4-(1-((trifluoromethyl)sulfonyl)vinyl)benzene (**4c**) (83.5 mg, 57%): yellow liquid. ^1H NMR (400 MHz, CDCl_3) δ 7.49–7.47 (m, 4H), 6.82 (s, 1H), 6.48 (s, 1H), 1.37 (s, 9H). ^{13}C NMR (101 MHz, CDCl_3) δ 153.7, 144.1, 135.1, 128.8, 127.6, 125.7, 119.8 (q, $J = 329.2$ Hz), 34.8, 31.1. ^{19}F NMR (377 MHz, CDCl_3) δ -75.9 (s, 3F). IR (thin film) ν 2255, 1711, 1606, 1485, 1509, 1361, 1209, 904, 840, 725 cm^{-1} . MS (EI): m/z (%) 292 (M^+). HRMS (EI-TOF) m/z : (M^+) Calcd for $\text{C}_{13}\text{H}_{15}\text{F}_3\text{O}_2\text{S}$: 292.0745; Found: 292.0753.

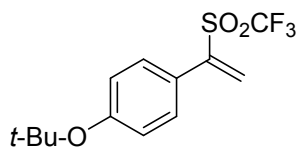


1-Methoxy-4-(1-((trifluoromethyl)sulfonyl)vinyl)benzene (**4d**) (59.8 mg, 45%): brown liquid. ^1H NMR (400 MHz, CDCl_3) δ 7.51 (d, $J = 8.2$ Hz, 2H), 6.96 (d, $J = 8.2$ Hz, 2H), 6.77 (s, 1H), 6.42 (s, 1H), 3.87 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 161.2, 143.7, 134.1, 130.6, 122.6, 119.8 (q, $J = 328.9$ Hz), 114.2, 55.3. ^{19}F NMR (377 MHz, CDCl_3) δ -75.9 (s, 3F). IR (thin film) ν 2255, 1510, 1462, 1510, 1443, 1359, 837, 650 cm^{-1} . MS (ESI): m/z (%) 284 [$\text{M}+\text{NH}_4$] $^+$. HRMS (ESI-TOF) m/z : [$\text{M}+\text{NH}_4$] $^+$ Calcd for $\text{C}_{10}\text{H}_{13}\text{F}_3\text{NO}_2\text{S}$: 284.0563; Found: 284.0561.



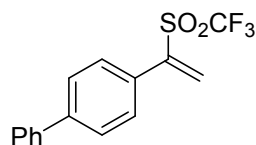
4e

1-Ethoxy-4-(1-((trifluoromethyl)sulfonyl)vinyl)benzene (**4e**) (63.2 mg, 45%): brown liquid. ^1H NMR (400 MHz, CDCl_3) δ 7.50 (d, $J = 7.7$ Hz, 2H), 6.94 (d, $J = 7.8$ Hz, 2H), 6.74 (s, 1H), 6.40 (s, 1H), 4.07 (q, $J = 6.7$ Hz, 2H), 1.44 (t, $J = 6.4$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 160.7, 143.7, 134.1, 130.5, 122.4, 119.5 (q, $J = 329.3$ Hz), 114.6, 63.6, 14.5. ^{19}F NMR (377 MHz, CDCl_3) δ -76.1 (s, 3F). IR (thin film) ν 2984, 1606, 1509, 1359, 1204, 1117, 907, 730 cm^{-1} . MS (ESI): m/z (%) 298 [$\text{M}+\text{NH}_4$] $^+$. HRMS (ESI-TOF) m/z : [$\text{M}+\text{NH}_4$] $^+$ Calcd for $\text{C}_{11}\text{H}_{15}\text{F}_3\text{NO}_3\text{S}$: 298.0719; Found: 298.0716.



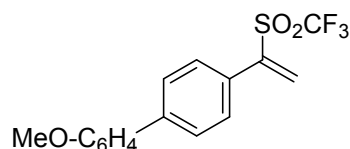
4f

1-(*Tert*-butoxy)-4-(1-((trifluoromethyl)sulfonyl)vinyl)benzene (**4f**) (84.7 mg, 55%): yellow liquid. ^1H NMR (400 MHz, CDCl_3) δ 7.48 (d, $J = 7.7$ Hz, 2H), 7.05 (d, $J = 7.8$ Hz, 2H), 6.78 (s, 1H), 6.44 (s, 1H), 1.41 (s, 9H). ^{13}C NMR (101 MHz, CDCl_3) δ 157.8, 143.8, 134.5, 129.9, 124.7, 123.4, 119.8 (q, $J = 328.9$ Hz), 29.7, 28.8. ^{19}F NMR (377 MHz, CDCl_3) δ -76.0 (s, 3F). IR (thin film) ν 2980, 2930, 2254, 1602, 1462, 1361, 1237, 904, 726 cm^{-1} . MS (EI): m/z (%) 308 (M^+). HRMS (EI-TOF) m/z : (M^+) Calcd for $\text{C}_{13}\text{H}_{15}\text{F}_3\text{O}_3\text{S}$: 308.0694; Found: 308.0690.



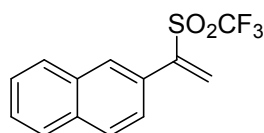
4g

4-(1-((Trifluoromethyl)sulfonyl)vinyl)-1,1'-biphenyl (**4g**) (77.8 mg, 50%): white solid, m.p. 62–64 $^{\circ}\text{C}$. ^1H NMR (400 MHz, CDCl_3) δ 7.30–7.67 (m, 6H), 7.53 (t, $J = 6.9$ Hz, 2H), 7.47 (d, $J = 6.5$ Hz, 1H), 6.91 (s, 1H), 6.56 (s, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 143.8, 143.2, 139.7, 135.6, 129.5, 129.4, 129.1, 128.1, 127.4, 127.1, 119.9 (q, $J = 328.9$ Hz). ^{19}F NMR (377 MHz, CDCl_3) δ -75.8 (s, 3F). IR (thin film) ν 2254, 1599, 1486, 1361, 1209, 1118, 904, 846 cm^{-1} . MS (EI): m/z (%) 312 (M^+). HRMS (EI-TOF) m/z : (M^+) Calcd for $\text{C}_{15}\text{H}_{11}\text{F}_3\text{O}_2\text{S}$: 312.0432; Found: 312.0439.



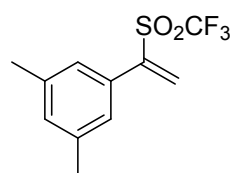
4h

4-Methoxy-4'-((trifluoromethyl)sulfonyl)vinyl-1,1'-biphenyl (**4h**) (111.1 mg, 65%): white solid, m.p. 84–86 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.64 (s, 4H), 7.59 (d, $J = 8.2$ Hz, 2H), 7.03 (d, $J = 8.0$ Hz, 2H), 6.86 (s, 1H), 6.53 (s, 1H), 3.89 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 159.7, 143.9, 142.8, 135.2, 132.1, 129.4, 128.6, 128.3, 126.8, 119.8 (q, $J = 328.9$ Hz), 114.5, 55.0. ^{19}F NMR (377 MHz, CDCl_3) δ -76.3 (s, 3F). IR (thin film) ν 2923, 1607, 1497, 1359, 1249, 1195, 1117, 1038, 822 cm^{-1} . MS (EI): m/z (%) 342 (M^+). HRMS (EI-TOF) m/z : (M^+) Calcd for $\text{C}_{16}\text{H}_{13}\text{F}_3\text{O}_3\text{S}$: 342.0538; Found: 342.0532.



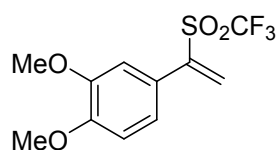
4i

2-((Trifluoromethyl)sulfonyl)vinyl)naphthalene (**4i**) (60.1 mg, 42%): white solid, m.p. 58–60 °C. ^1H NMR (400 MHz, CDCl_3) δ 8.12 (s, 1H), 7.95–7.91 (m, 3H), 7.65 (d, $J = 2.1$ Hz, 1H), 7.61–7.60 (m, 2H), 6.95 (s, 1H), 6.60 (s, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 144.1, 135.9, 133.7, 132.7, 129.3, 128.7, 128.6, 127.8, 127.7, 127.6, 127.0, 125.6, 119.8 (q, $J = 329.3$ Hz). ^{19}F NMR (377 MHz, CDCl_3) δ -75.7 (s, 3F). IR (thin film) ν 2255, 1711, 1606, 1509, 1465, 1361, 1209, 904, 726 cm^{-1} . MS (EI): m/z (%) 286 (M^+). HRMS (EI-TOF) m/z : (M^+) Calcd for $\text{C}_{13}\text{H}_9\text{F}_3\text{O}_2\text{S}$: 286.0275; Found: 286.0270.



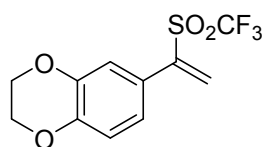
4j

1,3-Dimethyl-5-((trifluoromethyl)sulfonyl)vinylbenzene (**4j**) (59.4 mg, 45%): yellow liquid. ^1H NMR (400 MHz, CDCl_3) δ 7.20 (s, 2H), 7.15 (s, 1H), 6.83 (s, 1H), 6.46 (s, 1H), 2.39 (s, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 144.4, 138.4, 135.2, 132.1, 130.4, 126.8, 119.9 (q, $J = 328.9$ Hz), 29.7, 21.1. ^{19}F NMR (377 MHz, CDCl_3) δ -75.8 (s, 3F). IR (thin film) ν 2925, 1599, 1360, 1217, 1197, 1236, 908, 728 cm^{-1} . MS (EI): m/z (%) 264 (M^+). HRMS (EI-TOF) m/z : (M^+) Calcd for $\text{C}_{11}\text{H}_{11}\text{F}_3\text{O}_2\text{S}$: 264.0432; Found: 264.0435.



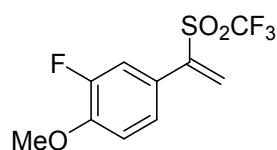
4k

1,2-Dimethoxy-4-((trifluoromethyl)sulfonyl)vinylbenzene (**4k**) (59.2 mg, 40%): yellow liquid. ^1H NMR (400 MHz, CDCl_3) δ 7.09 (s, 2H), 6.90 (d, $J = 8.4$ Hz, 1H), 6.75 (s, 1H), 6.43 (s, 1H), 3.91 (s, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 150.8, 148.7, 143.6, 134.3, 122.8, 122.3, 119.8 (q, $J = 329.2$ Hz), 111.7, 110.9, 55.9, 55.8. ^{19}F NMR (377 MHz, CDCl_3) δ -75.9 (s, 3F). IR (thin film) ν 2932, 2254, 1596, 1508, 1482, 1246, 1025, 908, 728 cm^{-1} . MS (EI): m/z (%) 296 (M^+). HRMS (EI-TOF) m/z : (M^+) Calcd for $\text{C}_{11}\text{H}_{11}\text{F}_3\text{O}_4\text{S}$: 296.0330; Found: 296.0328.



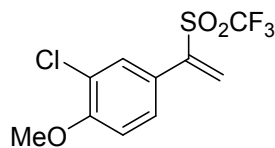
4l

6-((Trifluoromethyl)sulfonyl)vinyl-2,3-dihydrobenzo[b][1,4]dioxine (**4l**) (91.1 mg, 62%): brown liquid. ^1H NMR (400 MHz, CDCl_3) δ 7.10 (s, 1H), 7.02 (d, $J = 8.3$ Hz, 1H), 6.89 (d, $J = 8.3$ Hz, 1H), 6.73 (s, 1H), 6.41 (s, 1H), 4.26 (s, 4H). ^{13}C NMR (101 MHz, CDCl_3) δ 145.6, 143.5, 143.3, 134.8, 123.3, 122.4, 118.1, 117.6, 119.8 (q, $J = 329.2$ Hz), 64.4, 64.1. ^{19}F NMR (377 MHz, CDCl_3) δ -76.2 (s, 3F). IR (thin film) ν 2933, 2877, 1579, 1503, 1305, 1287, 1245, 903, 725 cm^{-1} . MS (EI): m/z (%) 294 (M^+). HRMS (EI-TOF) m/z : (M^+) Calcd for $\text{C}_{11}\text{H}_9\text{F}_3\text{O}_4\text{S}$: 294.0174; Found: 294.0175.



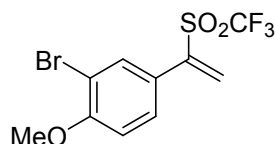
4m

2-Fluoro-1-methoxy-4-((trifluoromethyl)sulfonyl)vinylbenzene (**4m**) (106.5 mg, 75%): yellow liquid. ^1H NMR (400 MHz, CDCl_3) δ 7.32 (t, $J = 10.7$ Hz, 2H), 7.02 (t, $J = 8.3$ Hz, 1H), 6.79 (s, 1H), 6.47 (s, 1H), 3.93 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 151.7 (d, $J = 248.4$ Hz), 149.6 (d, $J = 10.1$ Hz), 142.6, 135.3, 125.6 (d, $J = 4.0$ Hz), 122.8 (d, $J = 7.1$ Hz), 119.7 (q, $J = 329.3$ Hz), 116.8 (d, $J = 20.3$ Hz), 113.1 (d, $J = 3.0$ Hz), 56.1. ^{19}F NMR (377 MHz, CDCl_3) δ -75.9 (s, 3F), -133.69 (t, $J = 9.4$ Hz, 1F). IR (thin film) ν 2843, 1603, 1514, 1473, 1302, 1264, 905, 725, 649 cm^{-1} . MS (EI): m/z (%) 284 (M^+). HRMS (EI-TOF) m/z : (M^+) Calcd for $\text{C}_{10}\text{H}_8\text{F}_4\text{O}_3\text{S}$: 284.0130; Found: 284.0135.



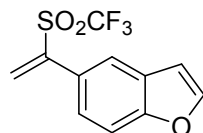
4n

2-Chloro-1-methoxy-4-((trifluoromethyl)sulfonyl)vinylbenzene (**4n**) (120.1 mg, 80%): colourless liquid. ^1H NMR (400 MHz, CDCl_3) δ 7.57 (s, 1H), 7.45 (d, J = 8.6 Hz, 1H), 6.98 (d, J = 8.6 Hz, 1H), 6.77 (s, 1H), 6.46 (s, 1H), 3.92 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 156.7, 142.4, 135.4, 130.6, 128.9, 123.3, 122.8, 119.7 (q, J = 329.2 Hz), 111.9, 56.1. ^{19}F NMR (377 MHz, CDCl_3) δ -76.1 (s, 3F). IR (thin film) ν 2933, 2255, 1597, 1502, 1361, 1206, 1196, 905, 727 cm^{-1} . MS (ESI): m/z (%) 339 $[\text{M}+\text{K}]^+$. HRMS (ESI-TOF) m/z : $[\text{M}+\text{NH}_4]^+$ Calcd for $\text{C}_{10}\text{H}_{12}\text{ClF}_3\text{NO}_3\text{S}$: 318.0173; Found: 318.0173.



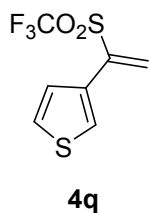
4o

2-Bromo-1-methoxy-4-((trifluoromethyl)sulfonyl)vinylbenzene (**4o**) (117.3 mg, 68%), yellow liquid. ^1H NMR (400 MHz, CDCl_3) δ 7.72 (s, 1H), 7.50 (d, J = 8.5 Hz, 1H), 6.94 (d, J = 8.6 Hz, 1H), 6.76 (s, 1H), 6.46 (s, 1H), 3.90 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 157.5, 142.2, 135.5, 133.6, 129.6, 123.7, 119.7 (q, J = 329.2 Hz), 111.8, 111.7, 56.3. ^{19}F NMR (377 MHz, CDCl_3) δ -76.1 (s, 3F). IR (thin film) ν 2931, 2845, 1596, 1496, 1454, 1341, 1185, 1116, 1009, 736 cm^{-1} . MS (EI): m/z (%) 343 (M^+). HRMS (EI-TOF) m/z : (M^+) Calcd for $\text{C}_{10}\text{H}_8\text{BrF}_3\text{O}_3\text{S}$: 343.9330; Found: 343.9339.



4p

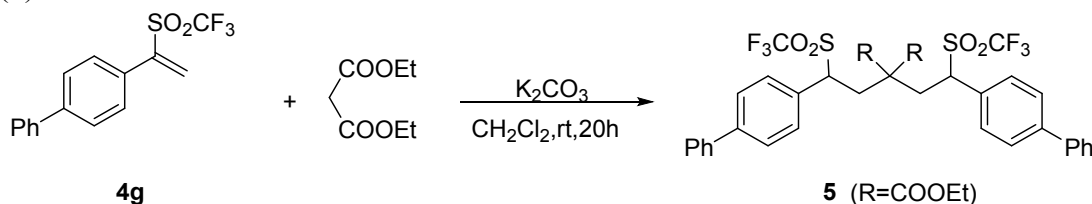
5-(1-((Trifluoromethyl)sulfonyl)vinyl)benzofuran (**4p**) (71.7 mg, 52%): colourless liquid, ^1H NMR (400 MHz, CDCl_3) δ 7.86 (s, 1H), 7.69 (s, 1H), 7.55 (d, J = 8.4 Hz, 1H), 7.48 (d, J = 8.5 Hz, 1H), 6.87 (s, 1H), 6.81 (s, 1H), 6.48 (s, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 155.7, 146.4, 144.2, 135.6, 127.9, 125.4, 125.3, 122.6, 119.9 (q, J = 329.3 Hz), 111.7, 106.7. ^{19}F NMR (377 MHz, CDCl_3) δ -75.9 (s, 3F). IR (thin film) ν 2929, 1360, 1222, 1207, 1110, 904, 726, 688, 649 cm^{-1} . MS (EI): m/z (%) 276 (M^+). HRMS (EI-TOF) m/z : (M^+) Calcd for $\text{C}_{11}\text{H}_7\text{F}_3\text{O}_3\text{S}$: 276.0068; Found: 276.0063.



3-(1-((Trifluoromethyl)sulfonyl)vinyl)thiophene (**4q**) (60.1 mg, 50%): yellow liquid. ^1H NMR (400 MHz, CDCl_3) δ 7.80 (s, 1H), 7.41 (s, 1H), 7.33 (s, 1H), 6.73 (s, 1H), 6.56 (s, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 138.9, 133.2, 130.1, 127.2, 127.1, 126.8, 119.7 (q, $J = 328.5$ Hz). ^{19}F NMR (377 MHz, CDCl_3) δ -76.4 (s, 3F). IR (thin film) ν 2928, 2253, 1459, 1339, 1204, 903, 723, 660 cm^{-1} . MS (EI): m/z (%) 241 (M^+). HRMS (EI-TOF) m/z : (M^+) Calcd for $\text{C}_7\text{H}_5\text{F}_3\text{O}_2\text{S}_2$: 241.9683; Found: 241.9684.

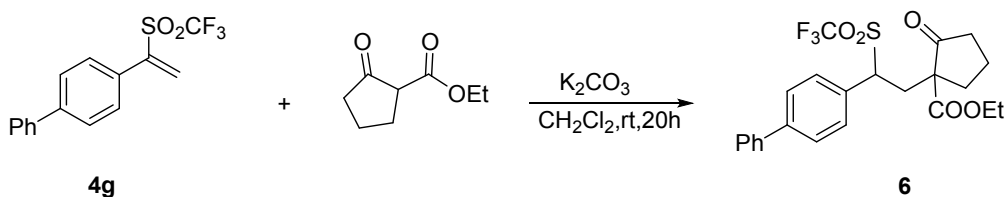
3. Michael addition of vinyl triflones

Diethyl 2,2-bis(2-([1,1'-biphenyl]-4-yl)-2-((trifluoromethyl)sulfonyl)ethyl)malonate (**5**)



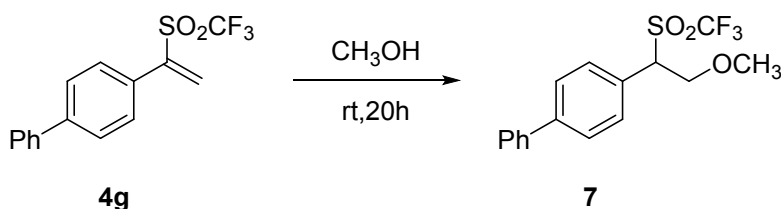
A 15mL glass tube equipped with a magnetic stirring bar was charged with diethyl malonate (16.0 mg, 0.1 mmol) and K_2CO_3 (13.8 mg, 0.1 mmol) in dry CH_2Cl_2 (1 mL) and allowed to stirred at room temperature for 20 minutes. Then **4g** (31.2 mg, 0.1 mmol) in dry CH_2Cl_2 (1 mL) was slowly added by a syringe. After stirring at rt for 20 hours, the reaction mixture was directly purified by flash chromatography on silica gel to give desired product as a white solid (35.3 mg, 90%). m.p. 180–182 $^\circ\text{C}$. ^1H NMR (400 MHz, CDCl_3) δ 7.67 (d, $J = 7.5$ Hz, 4H), 7.61 (d, $J = 7.2$ Hz, 4H), 7.57–7.45 (m, 8H), 7.43 (d, $J = 6.9$ Hz, 2H), 4.71 (d, $J = 11.4$ Hz, 2H), 3.69–3.53 (m, 2H), 3.33–3.14 (m, 4H), 3.04–2.90 (m, 2H), 0.97 (s, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 168.1, 143.3, 139.5, 129.0, 128.1, 127.5, 127.0, 126.3, 119.7 (q, $J = 330.9$ Hz), 62.4, 62.1, 53.3, 29.2, 13.4. ^{19}F NMR (377 MHz, CDCl_3) δ -72.4 (s, 6F). IR (thin film) ν 2254, 1731, 1487, 1359, 1212, 1114, 903, 723, 649 cm^{-1} . MS (ESI): m/z (%) 807 [$\text{M} + \text{Na}$] $^+$.

Ethyl 1-(2-([1,1'-biphenyl]-4-yl)-2-((trifluoromethyl)sulfonyl)ethyl)-2-oxocyclopentane-1-carboxylate (**6**)



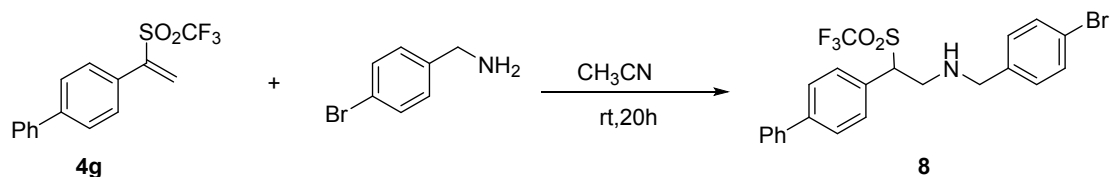
A 15 mL glass tube equipped with a magnetic stirring bar was charged with ethyl 2-oxocyclopentane-1-carboxylate (15.6 mg, 0.1 mmol) and K_2CO_3 (13.2 mg, 0.1 mmol) in dry CH_2Cl_2 (1 mL) and allowed to stirred at room temperature for 20 minutes. Then **4g** (31.2 mg, 0.1 mmol) in dry CH_2Cl_2 (1 mL) was slowly added by a syringe. After stirring at rt for 20 hours, The reaction mixture was directly purified by flash chromatography on silica gel to give desired product as a white solid (39.7 mg, 85%); m.p. 86–88 °C. 1H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, J = 6.7 Hz, 2H), 7.61 (d, J = 7.5 Hz, 2H), 7.52–7.46 (m, 4H), 7.42 (d, J = 7.0 Hz, 1H), 5.21 (d, J = 10.9 Hz, 0.3H), 4.60 (d, J = 10.1 Hz, 0.7H), 4.02–3.90 (m, 0.5H), 3.90–3.76 (m, 1H), 3.61–3.50 (m, 0.5H), 3.06 (d, J = 9.1 Hz, 0.5H), 3.02 (s, 0.5H), 2.76–2.71 (m, 0.5H), 2.67 (d, J = 15.0 Hz, 1H), 2.56 (d, J = 12.6 Hz, 0.5H), 2.39 (d, J = 19.3 Hz, 0.5H), 2.22 (d, J = 9.1 Hz, 0.5H), 2.20–2.12 (m, 0.5H), 1.99 (d, J = 7.1 Hz, 1.5H), 1.91–1.81 (m, 1.5H), 1.52 (dd, J = 21.4, 9.2 Hz, 0.5H), 1.18 (t, J = 6.9 Hz, 1H), 1.05 (t, J = 6.9 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 213.1, 212.0, 169.9, 168.6, 143.0, 142.9, 131.0, 128.9, 128.0, 128.0, 127.6, 127.5, 127.4, 127.3, 127.0, 119.9 (q, J = 330.3 Hz), 119.8 (q, J = 330.9 Hz), 64.4, 63.4, 62.0, 61.9, 59.1, 58.1, 37.0, 37.0, 35.0, 32.6, 32.5, 32.4, 19.4, 19.1, 13.8, 13.6. ^{19}F NMR (377 MHz, $CDCl_3$) δ -72.62 (s, 2F), -73.10 (s, 1F). IR (thin film) ν 2254, 1724, 1363, 1210, 1115, 903, 724, 649 cm^{-1} . MS (ESI): m/z (%) 491 $[M+Na]^+$.

4-(2-Methoxy-1-((trifluoromethyl)sulfonyl)ethyl)-1,1'-biphenyl (**7**)



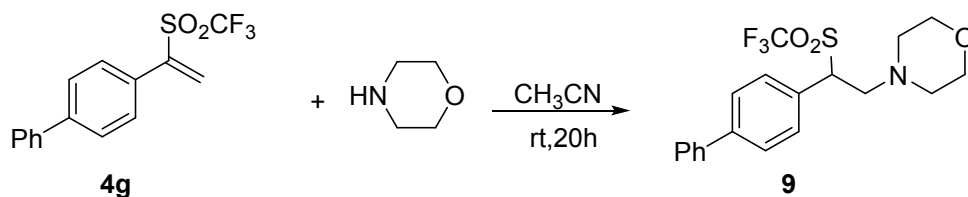
A 15 mL glass tube equipped with a magnetic stirring bar was charged with **4g** (31.2 mg, 0.1 mmol) and in dry CH_3OH (2 mL) and allowed to stirred at room temperature for 20 h under N_2 atmosphere. The reaction mixture was directly purified by flash chromatography on silica gel to give desired product as a white solid (30.9 mg, 90%). m.p. 132–134 °C. 1H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, J = 7.2 Hz, 2H), 7.62 (d, J = 6.6 Hz, 2H), 7.53 (d, J = 8.5 Hz, 2H), 7.48 (d, J = 6.9 Hz, 2H), 7.42 (d, J = 6.5 Hz, 1H), 4.76 (s, 1H), 4.31 (t, J = 8.3 Hz, 1H), 4.11 (d, J = 5.1 Hz, 1H), 3.46 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.1, 139.9, 130.4, 128.9, 127.9, 127.8, 127.1, 126.1, 119.6 (q, J = 329.5 Hz), 70.1, 67.4, 59.3. ^{19}F NMR (377 MHz, $CDCl_3$) δ -74.3 (s, 3F). IR (thin film) ν 2973, 1460, 1380, 1087, 1045, 903, 880, 723 cm^{-1} . MS (ESI): m/z (%) 367 $[M+Na]^+$.

2-([1,1'-Biphenyl]-4-yl)-N-(4-bromobenzyl)-2-((trifluoromethyl)sulfonyl)ethan-1-amine (**8**)



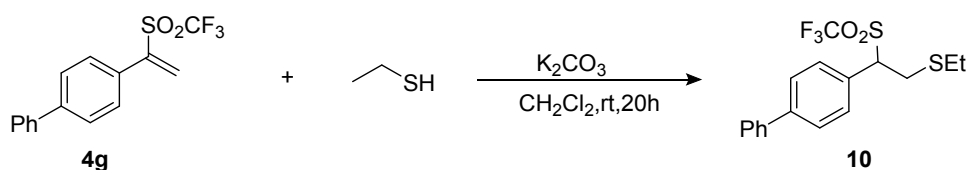
A 15 mL glass tube equipped with a magnetic stirring bar was charged with **4g** (31.2 mg, 0.1 mmol) and (4-bromophenyl)methanamine (37.2 mg, 0.2 mmol) in dry CH_3CN (2 mL) and allowed to stirred at room temperature for 20 h under N_2 atmosphere. The reaction mixture was directly purified by flash chromatography on silica gel to give desired product as a white solid (44.7 mg, 90%). m.p. 84–86 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.68 (d, J = 7.1 Hz, 2H), 7.62 (d, J = 7.0 Hz, 2H), 7.53–7.39 (m, 7H), 7.15 (d, J = 7.3 Hz, 2H), 4.71 (s, 1H), 3.84–3.75 (m, 2H), 3.74–3.64 (m, 1H), 3.50–3.41 (m, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 143.1, 139.7, 138.0, 131.6, 130.2, 129.7, 128.9, 128.1, 128.2, 127.1, 126.8, 121.2, 119.7 (q, J = 328.9 Hz), 66.6, 52.5, 47.2. ^{19}F NMR (377 MHz, CDCl_3) δ -73.96 (s, 3F). IR (thin film) ν 2254, 1381, 1212, 1114, 1072, 903, 723, 649 cm^{-1} . MS (ESI): m/z (%) 498 $[\text{M}+\text{H}]^+$.

4-(2-([1,1'-Biphenyl]-4-yl)-2-((trifluoromethyl)sulfonyl)ethyl)morpholine (**9**)



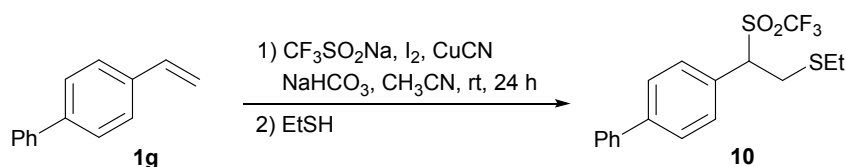
A 15 mL glass tube equipped with a magnetic stirring bar was charged with **4g** (31.2 mg, 0.1 mmol) and morpholine (17.4 mg, 0.2 mmol) in dry CH_3CN (2 mL) and allowed to stirred at room temperature for 20 h under N_2 atmosphere. The reaction mixture was directly purified by flash chromatography on silica gel to give desired product as a white solid (35.9 mg, 90%). m.p. 136–138 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.68 (d, J = 7.1 Hz, 2H), 7.63 (d, J = 6.9 Hz, 2H), 7.50 (d, J = 7.9 Hz, 4H), 7.42 (d, J = 6.6 Hz, 1H), 4.71 (d, J = 5.3 Hz, 1H), 3.68 (s, 4H), 3.57 (dd, J = 13.1 Hz, 6.9 Hz, 1H), 3.11 (dd, J = 13.7 Hz, 4.8 Hz, 1H), 2.56 (s, 4H). ^{13}C NMR (101 MHz, CDCl_3) δ 142.9, 139.8, 130.4, 128.9, 127.9, 127.8, 127.4, 127.1, 119.9 (q, J = 328.5 Hz), 66.6, 65.9, 57.8, 53.5. ^{19}F NMR (377 MHz, CDCl_3) δ -73.3 (s, 3F). IR (thin film) ν 2918, 2864, 1486, 1454, 1341, 1185, 1116, 1009, 736 cm^{-1} . MS (ESI): m/z (%) 400 $[\text{M}+\text{H}]^+$.

2-([1,1'-Biphenyl]-4-yl)-2-((trifluoromethyl)sulfonyl)ethyl(ethyl)sulfane (**10**)



A 15 mL glass tube equipped with a magnetic stirring bar was charged with ethanethiol (6.2 mg, 0.1 mmol) and K_2CO_3 (13.6 mg, 0.1 mmol) in dry CH_2Cl_2 (1 mL) and allowed to stirred at room temperature for 20 minutes. Then **4g** (31.2 mg, 0.1 mmol) in dry CH_2Cl_2 (1 mL) was slowly added by a syringe. After stirring at rt for 20 hours, the reaction mixture was directly purified by flash chromatography on silica gel to give desired product as white solid (32.1 mg, 86%). m.p. 90–92 °C. 1H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, J = 7.5 Hz, 2H), 7.64 (d, J = 7.3 Hz, 2H), 7.56–7.45 (m, 4H), 7.45–7.38 (m, 1H), 4.62 (d, J = 11.6 Hz, 1H), 3.53 (d, J = 13.5 Hz, 1H), 3.37 (t, J = 12.6 Hz, 1H), 2.48 (q, J = 7.0 Hz, 2H), 1.24 (t, J = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.2, 139.7, 130.5, 128.9, 127.9, 127.8, 127.2, 126.7, 119.9 (q, J = 332.3 Hz), 67.5, 29.7, 26.9, 14.4. ^{19}F NMR (377 MHz, $CDCl_3$) δ -73.1 (s, 3F). IR (thin film) ν 2254, 1559, 1487, 1362, 1213, 1114, 903, 723 cm^{-1} . MS (ESI): m/z (%) 392 $[M+NH_4]^+$.

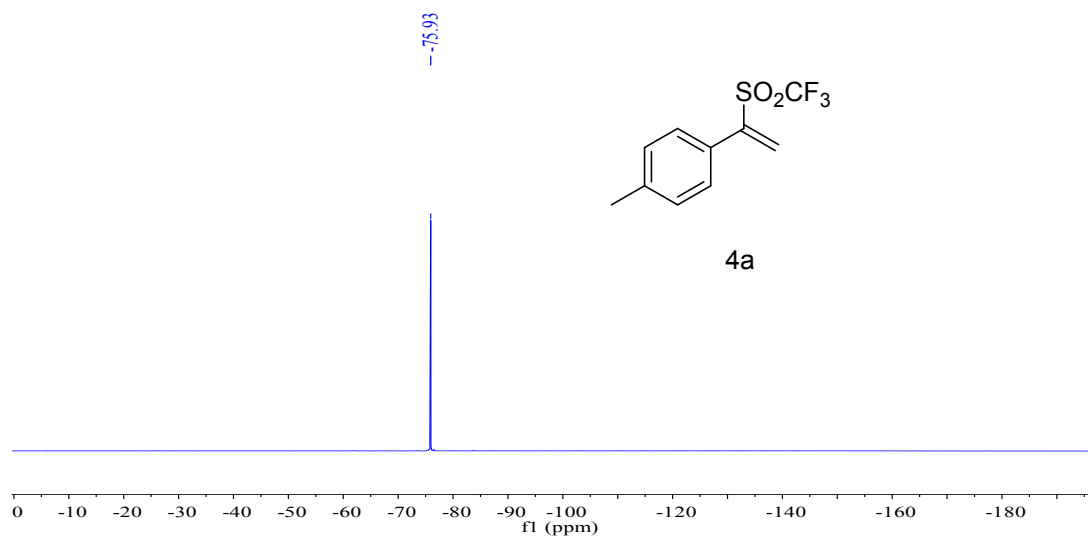
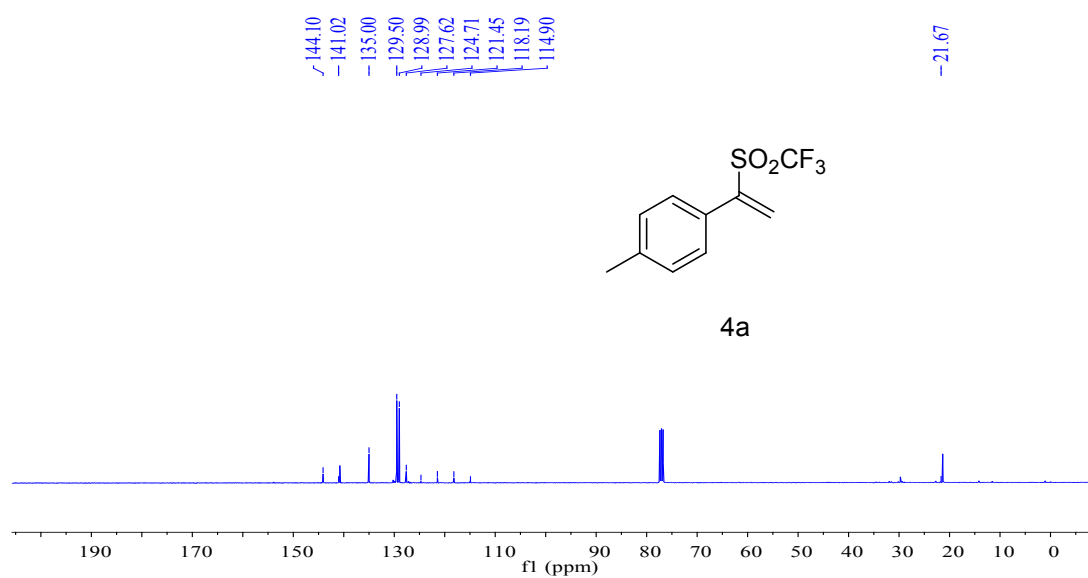
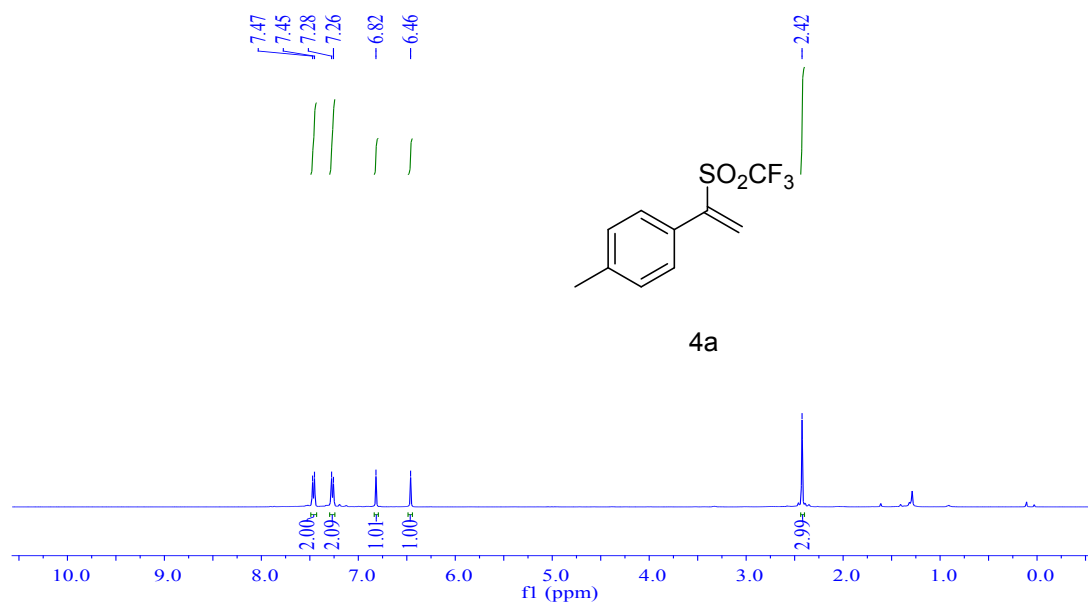
4. Gram-scale preparation of **10**

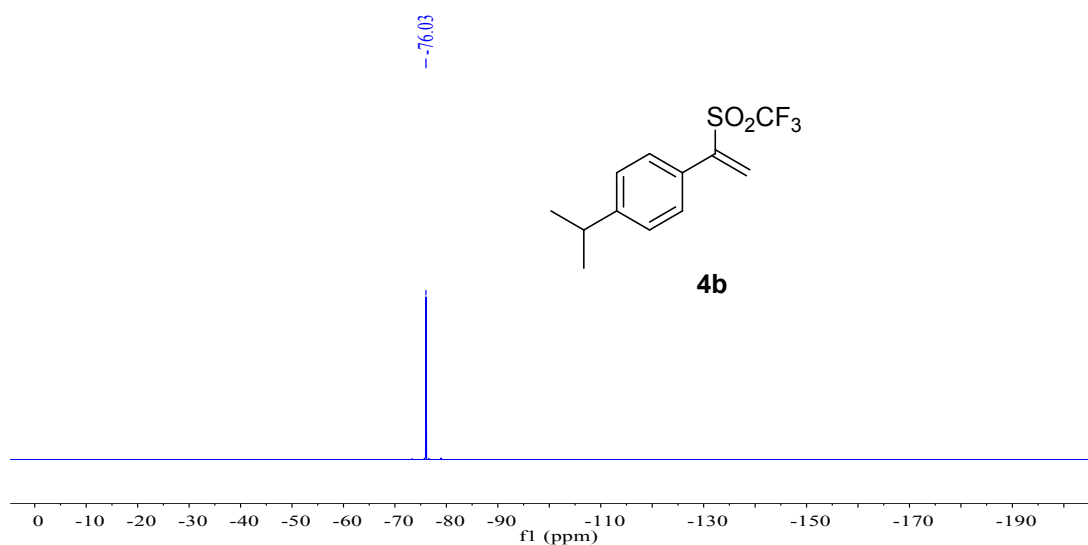
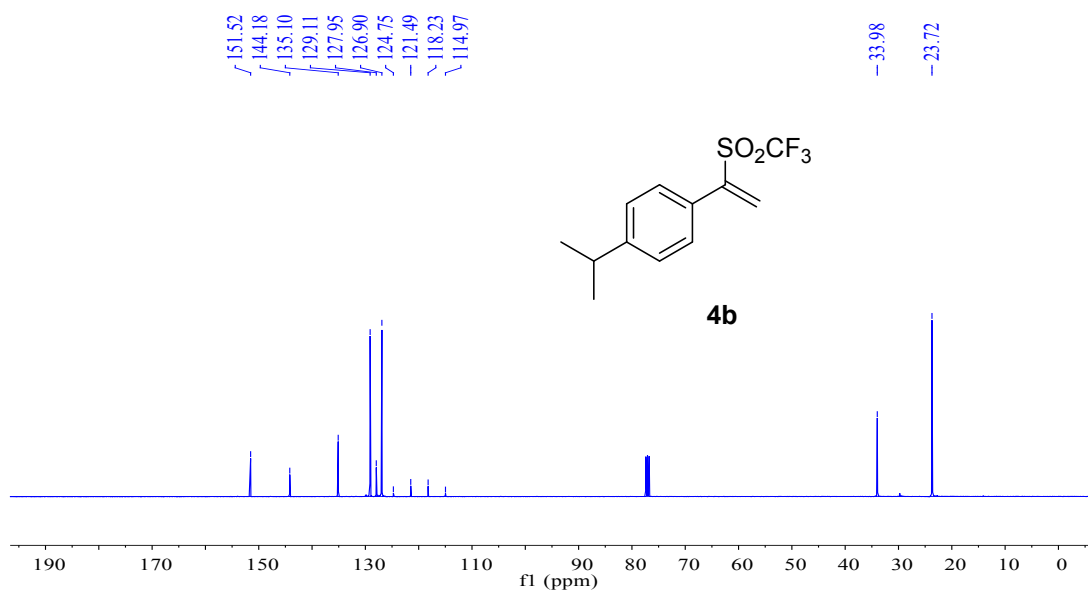
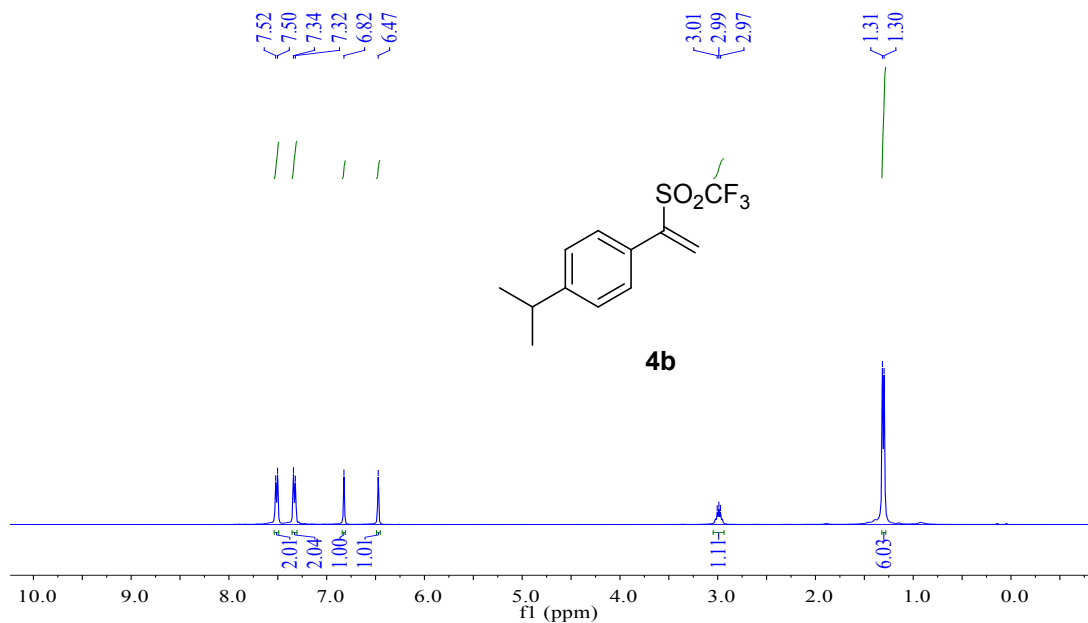


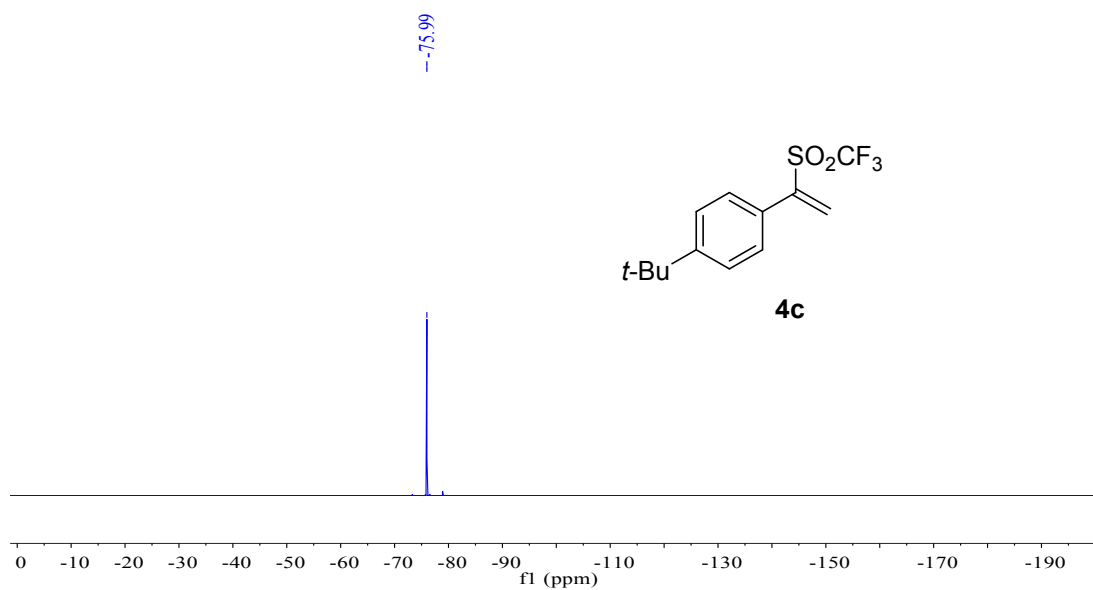
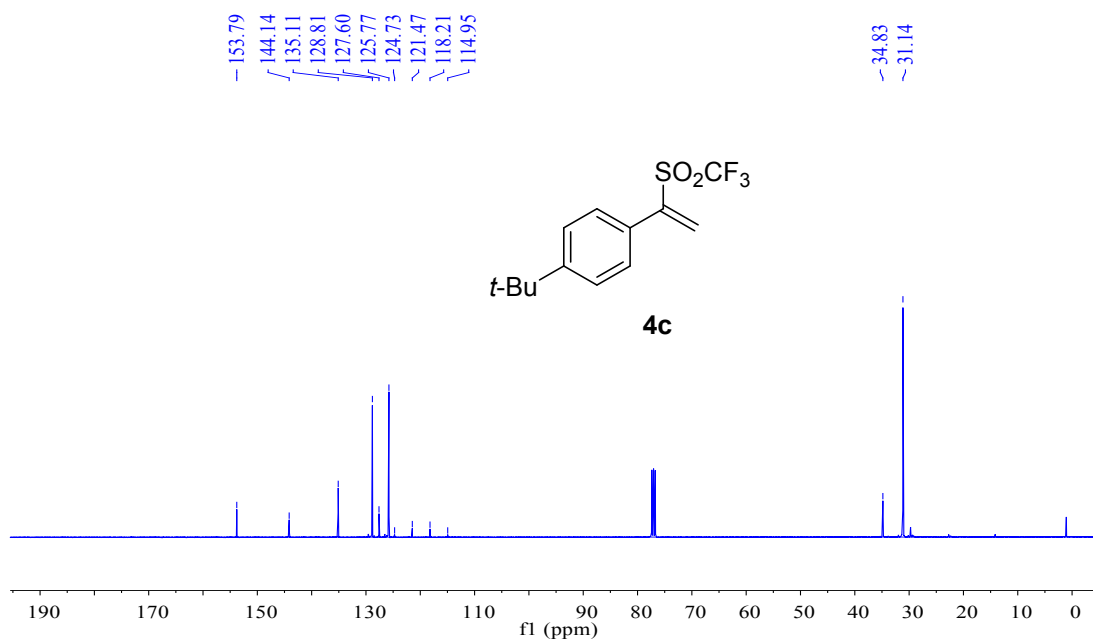
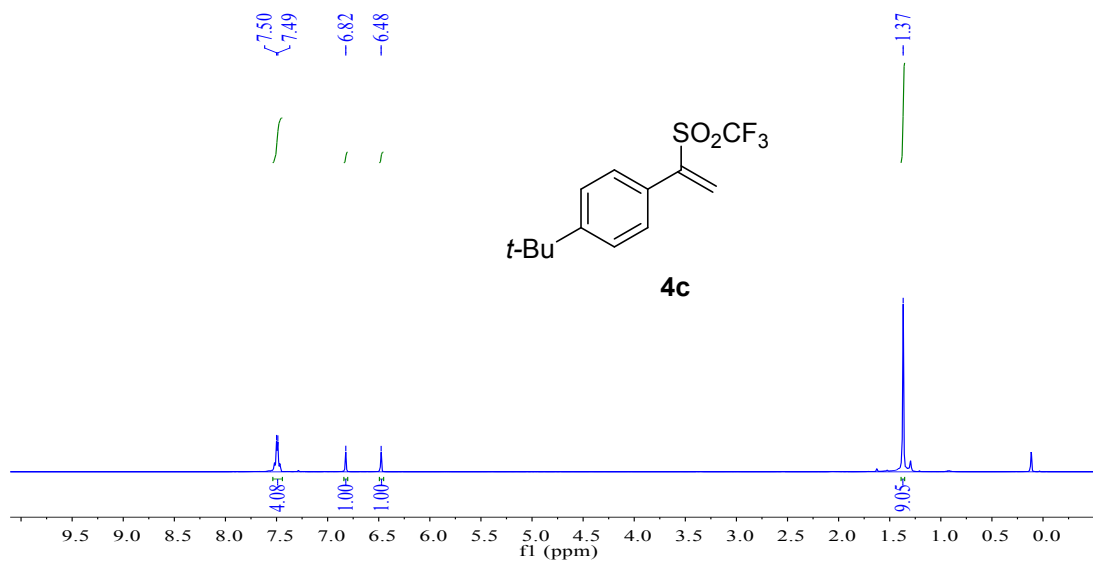
A 100 mL three neck flask equipped with a magnetic stirring bar was charged with **1g** (1.8 g, 10.0 mmol), CF_3SO_2Na (4.68 g, 30.0 mmol), I_2 (7.6 g, 30.0 mmol), $NaHCO_3$ (1.68 g, 20.0 mmol), $CuCN$ (88.9 mg, 1.0 mmol) and CH_3CN (38.0 mL). After stirring at rt for 12 hours, saturated aqueous $Na_2S_2O_3$ solution was added. Then, the reaction mixture was extracted with ethyl acetate. The organic phase was washed with H_2O and brine, dried by Na_2SO_4 , concentrated in vacuo to give the crude product.

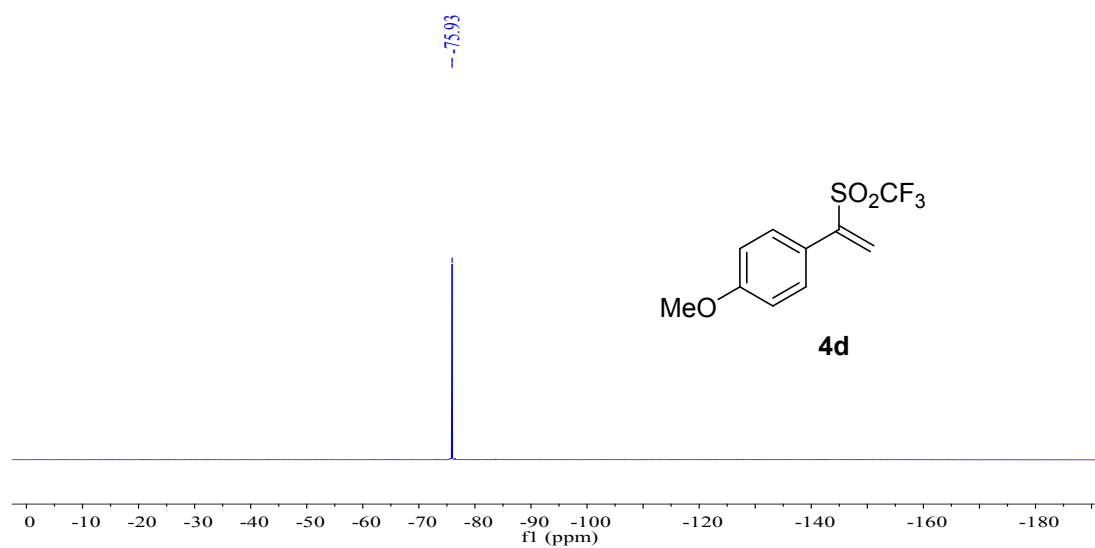
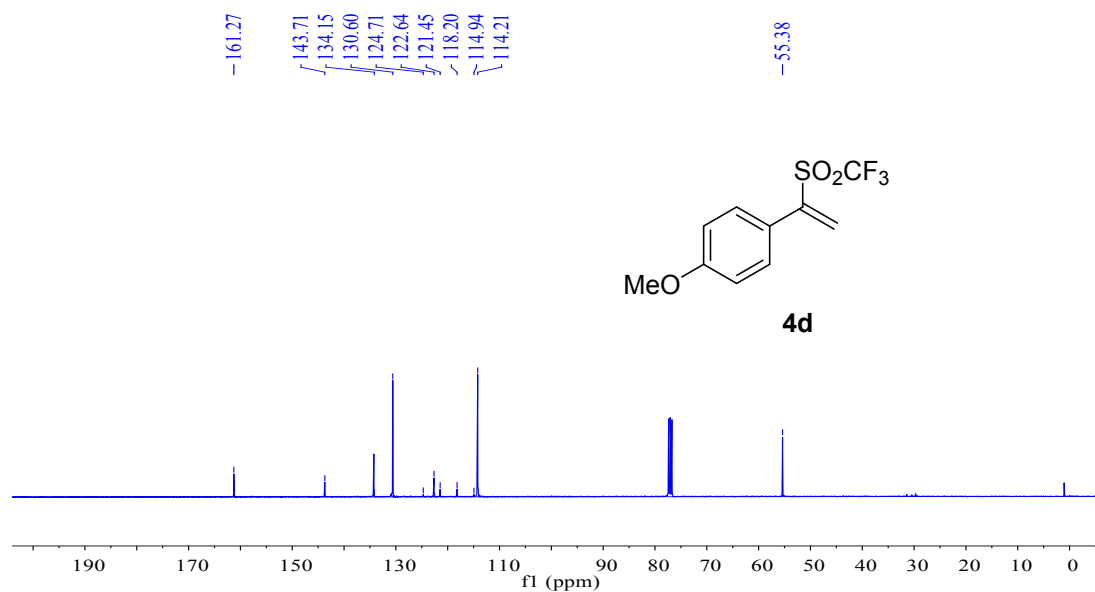
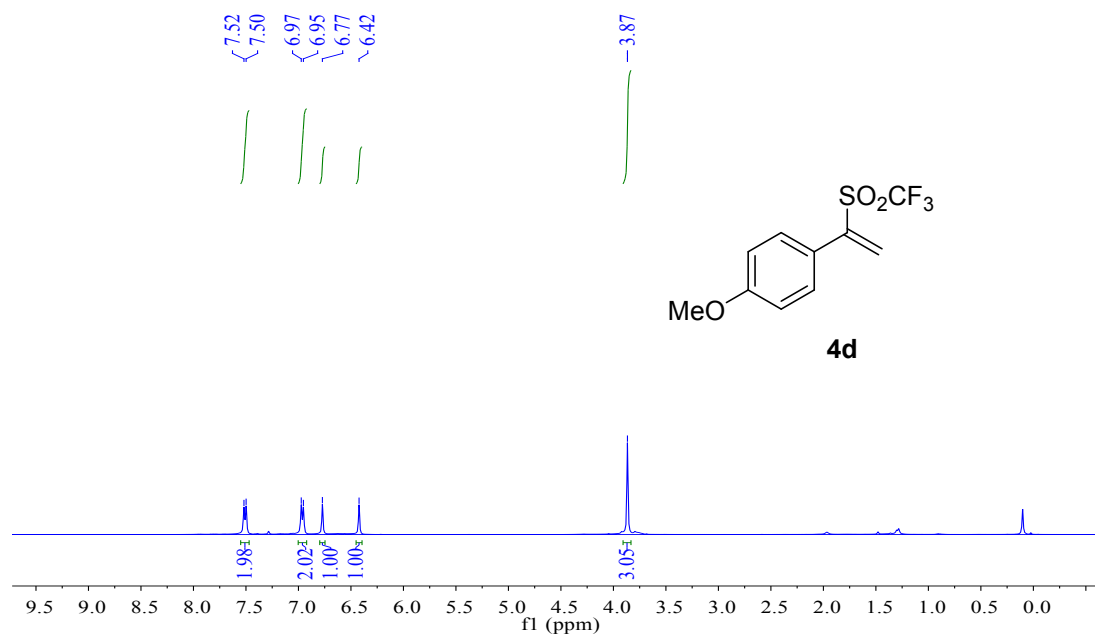
A 100 mL three neck flask equipped with a magnetic stirring bar was charged with ethanethiol (372.6 mg, 6.0 mmol) and K_2CO_3 (829.2 mg, 6.0 mmol) in dry CH_2Cl_2 (60 mL) and allowed to stirred at room temperature for 20 minutes. And then the crude product in dry CH_2Cl_2 (60 mL) was slowly added by a stringe. After stirring at rt for 20 hours, the reaction mixture was directly purified by flash chromatography on silica gel to give desired product **10** in as white solid (1.71 g, 46%).

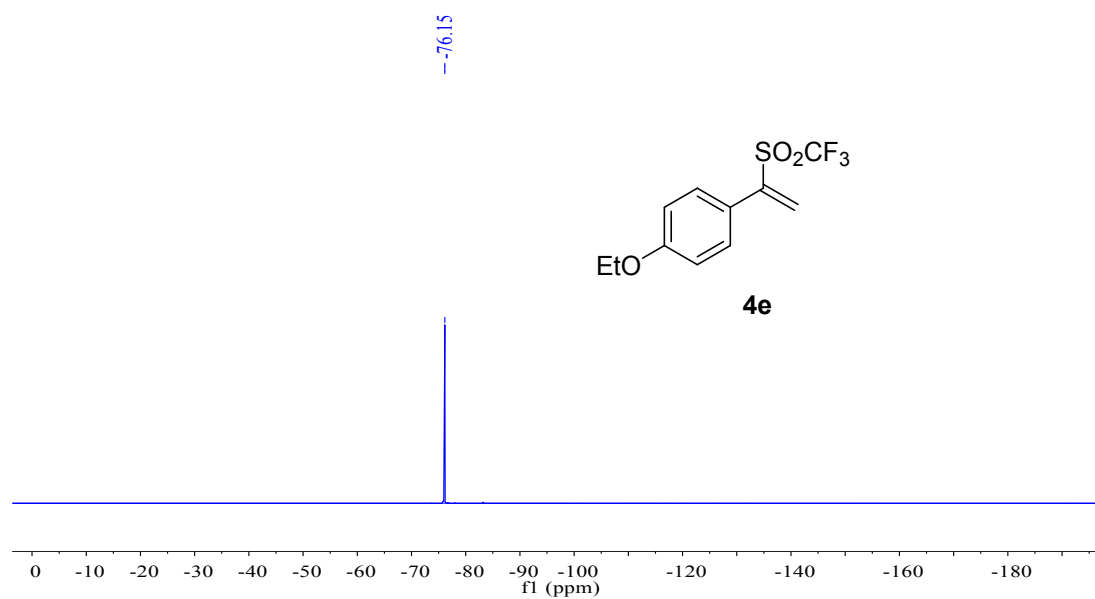
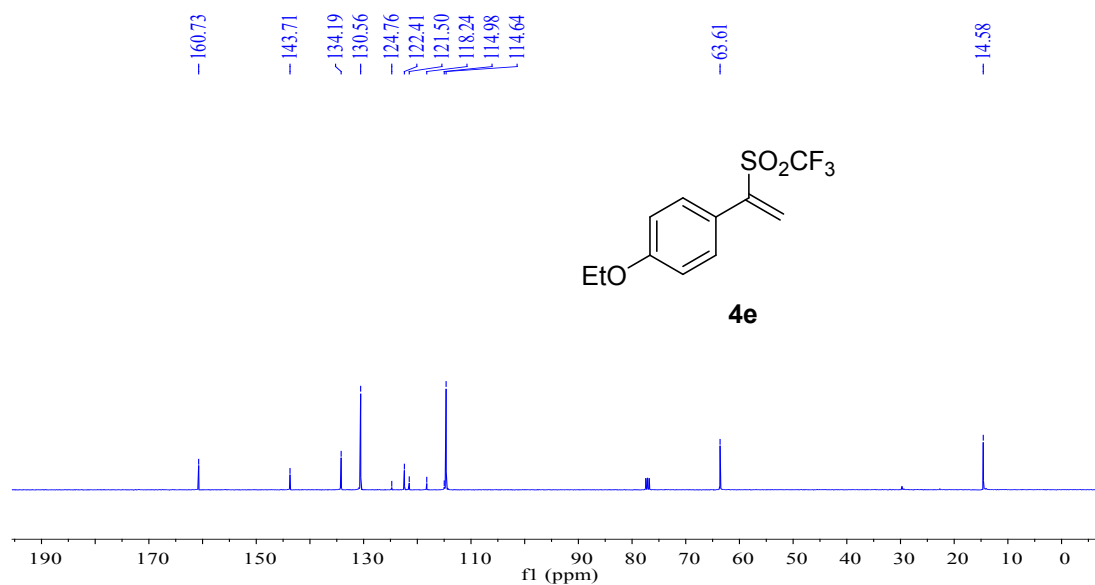
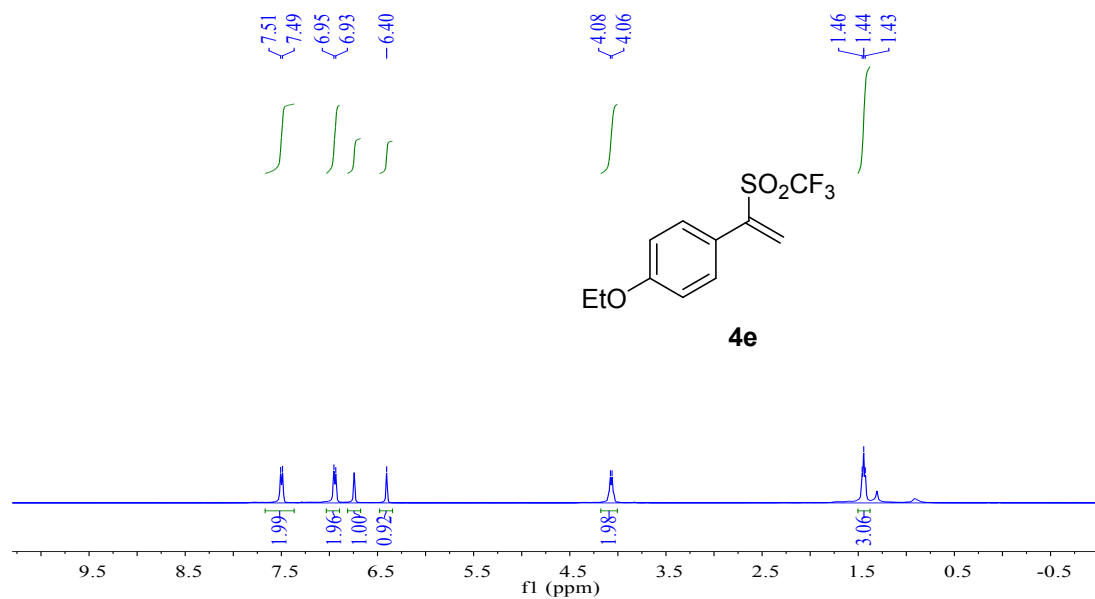
5. Copies of ^1H , ^{19}F and ^{13}C NMR spectra for the products.

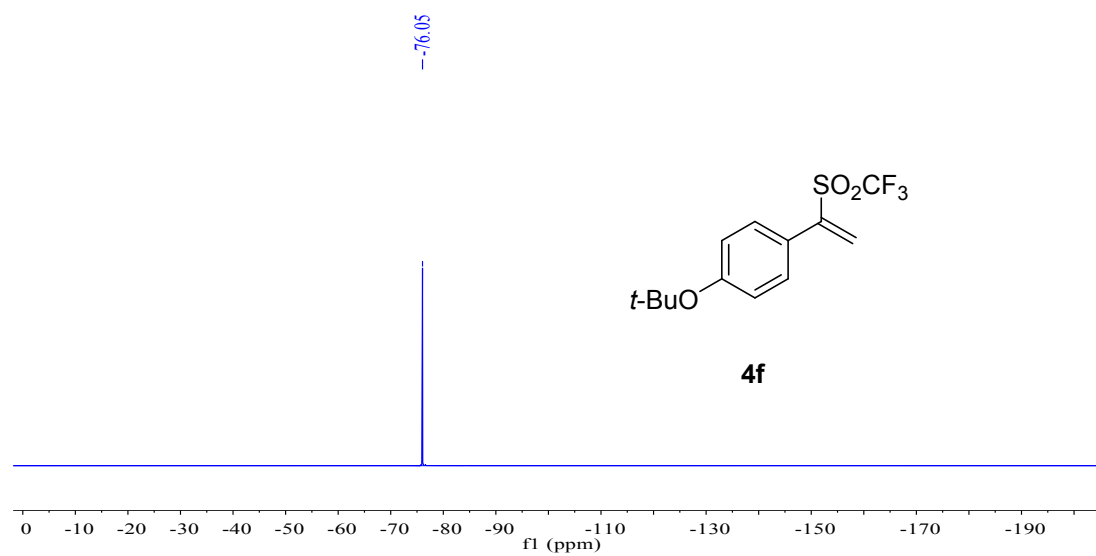
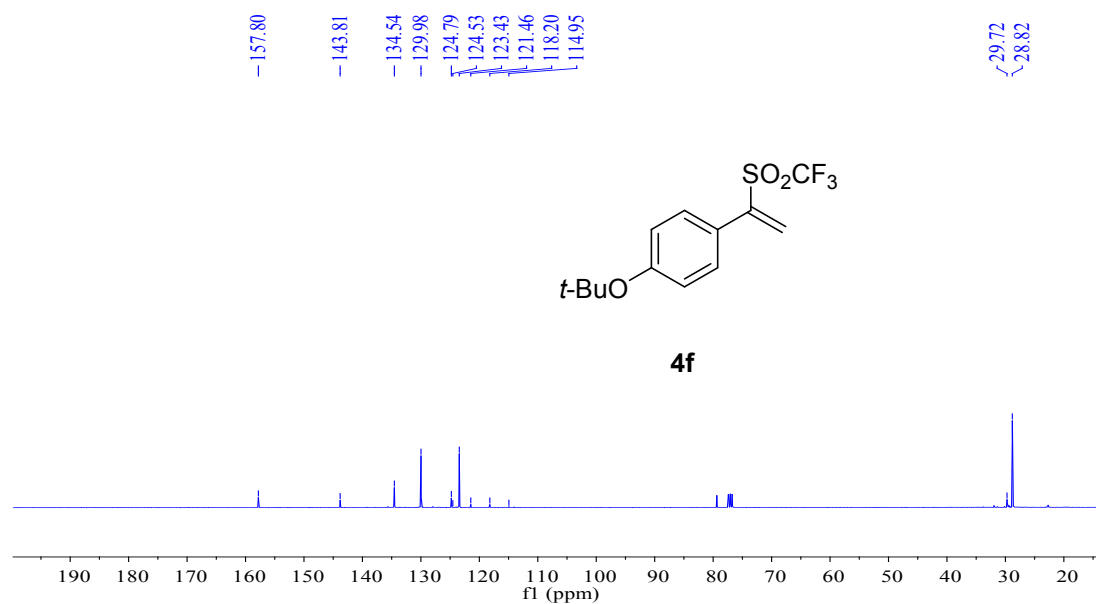
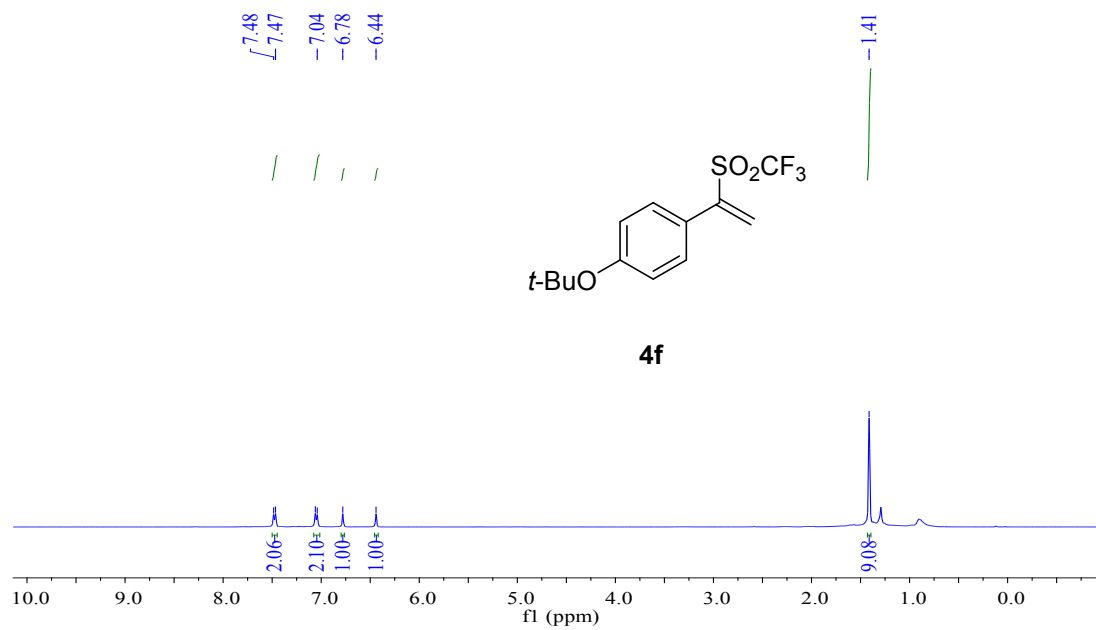


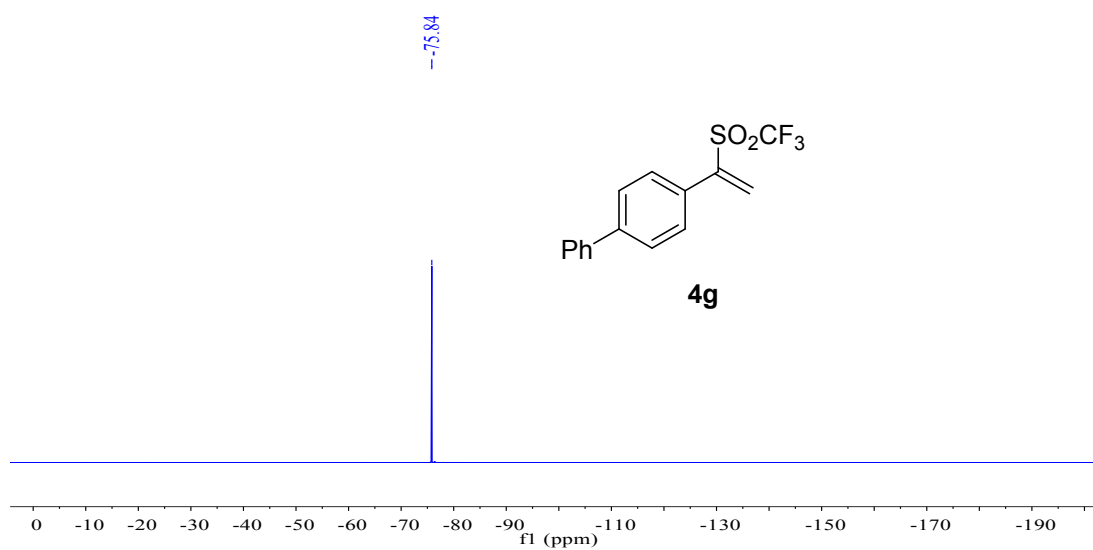
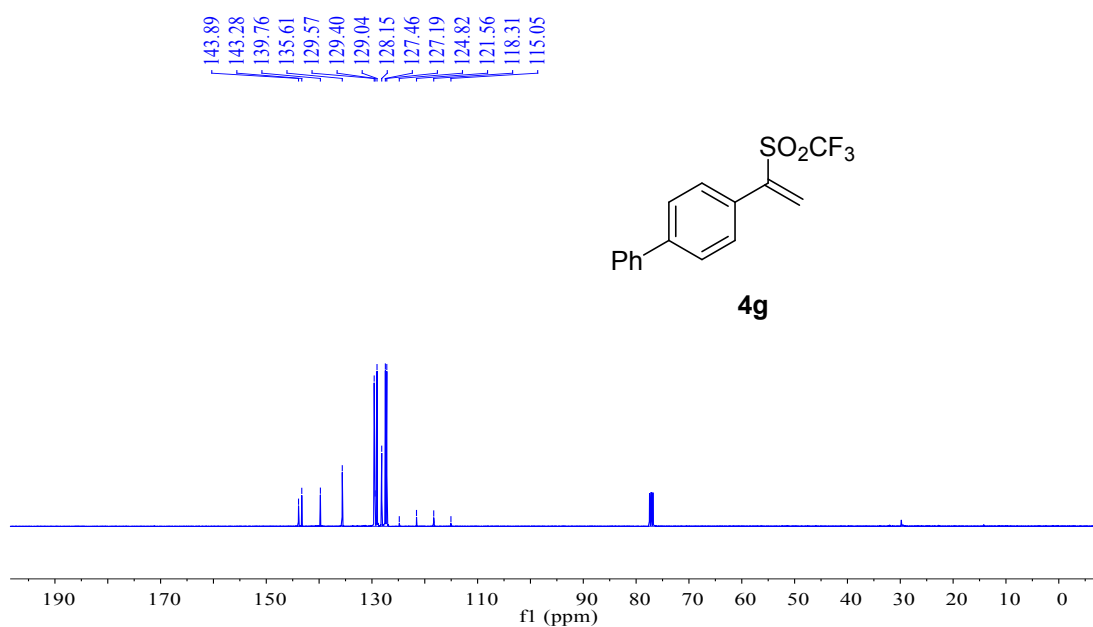
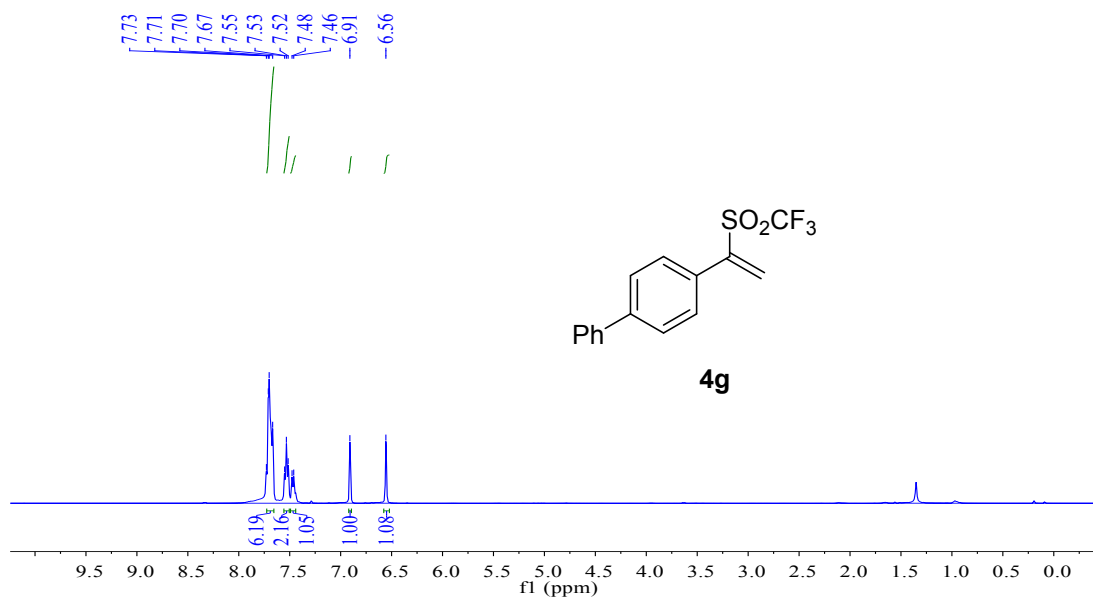


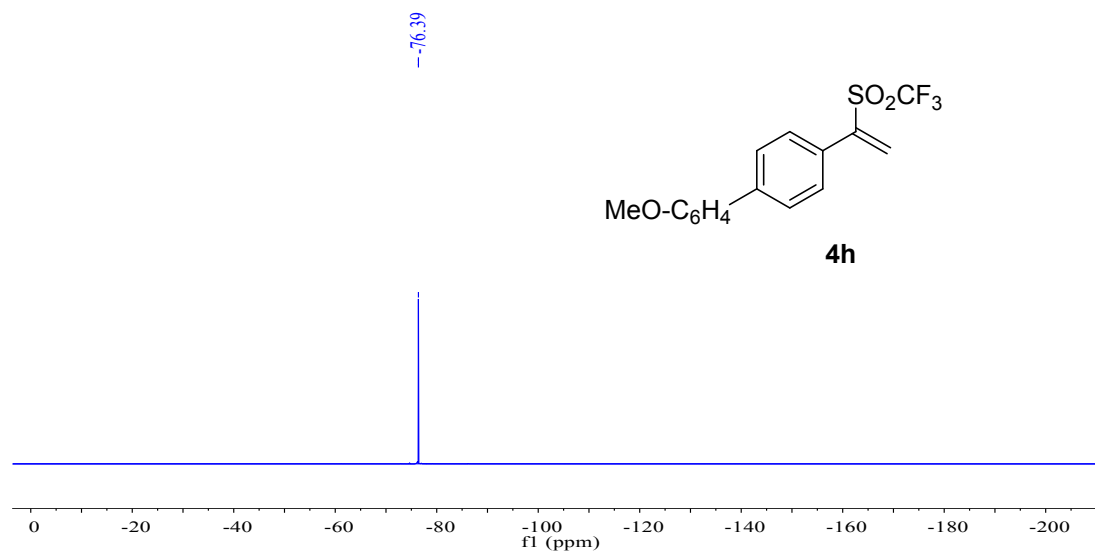
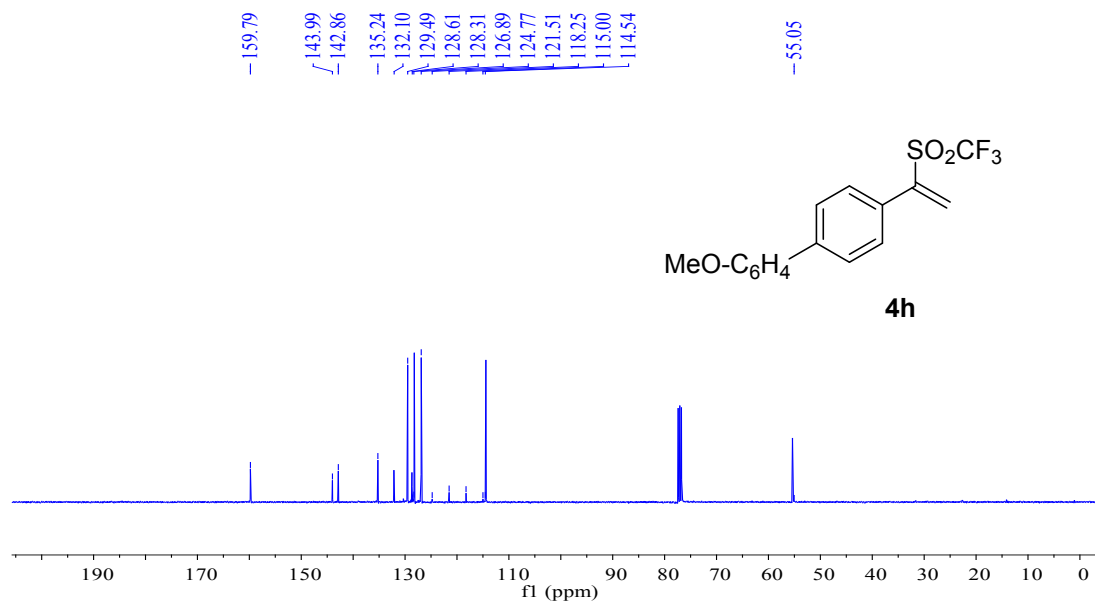
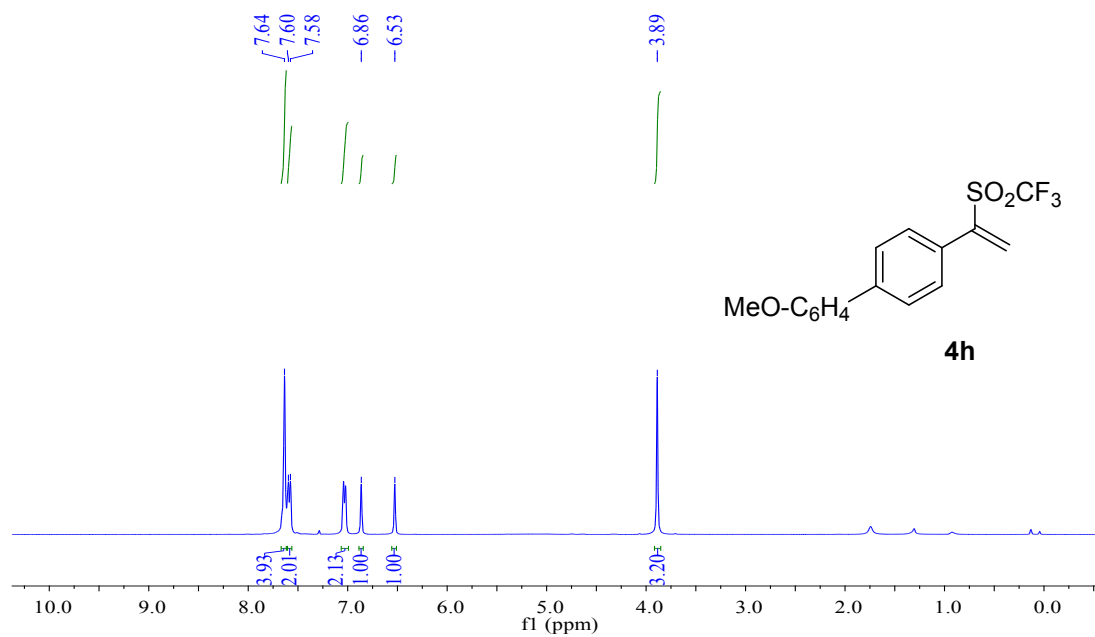


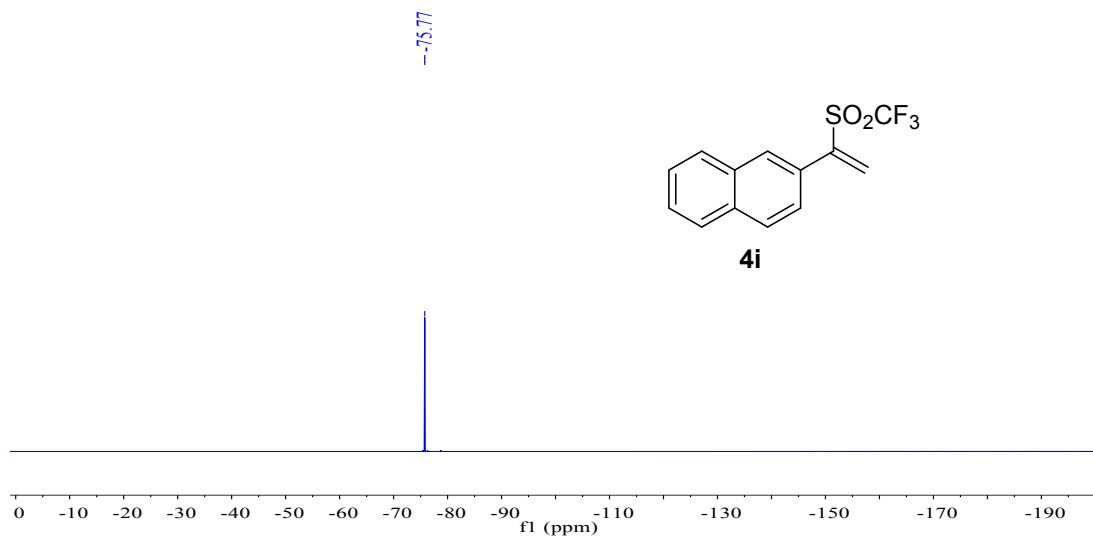
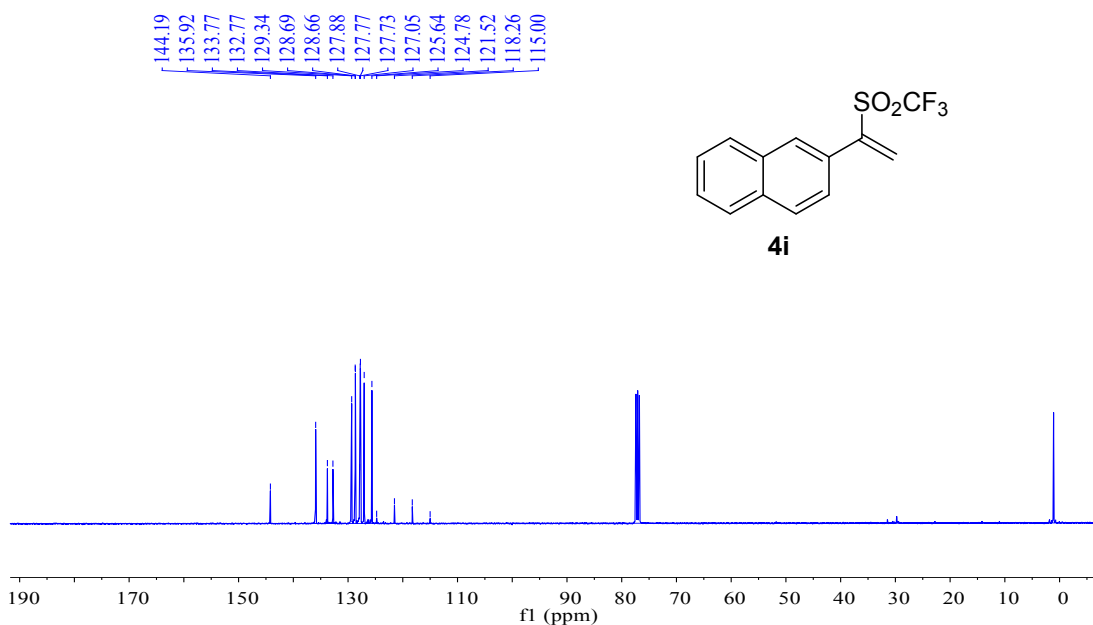
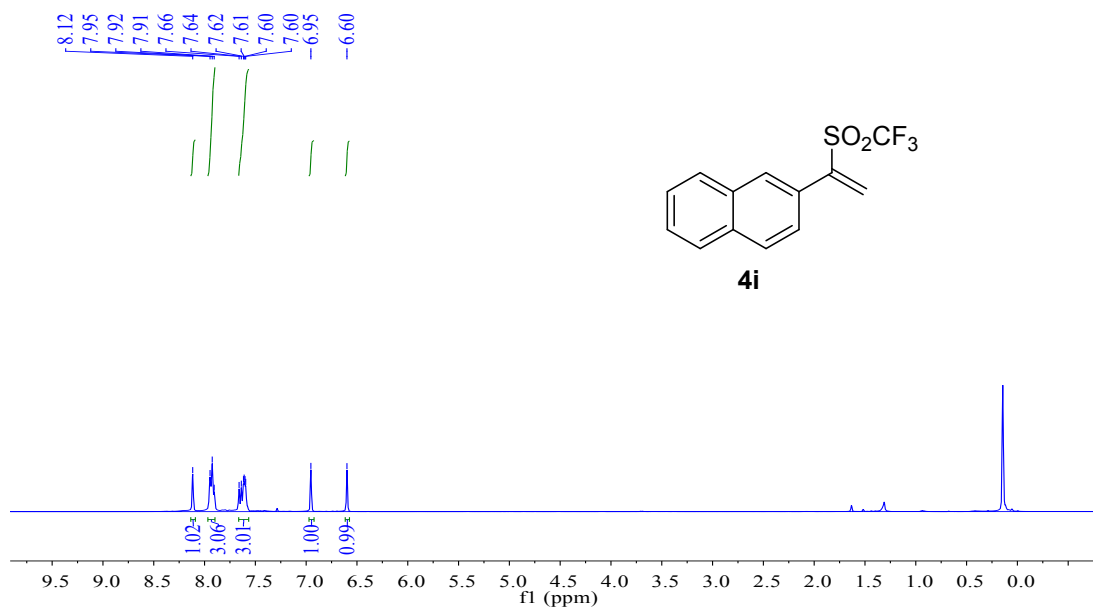


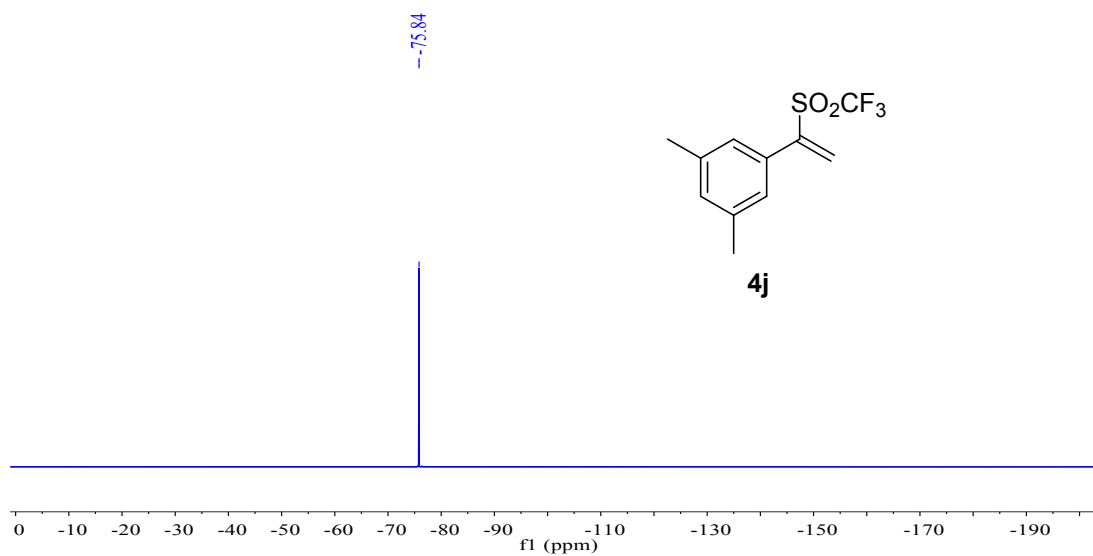
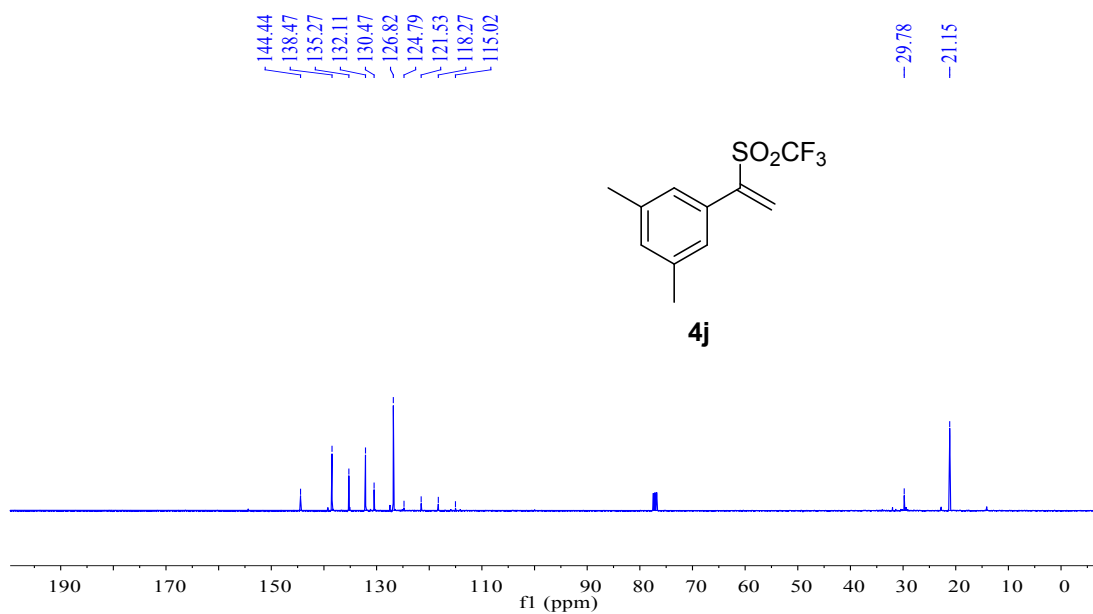
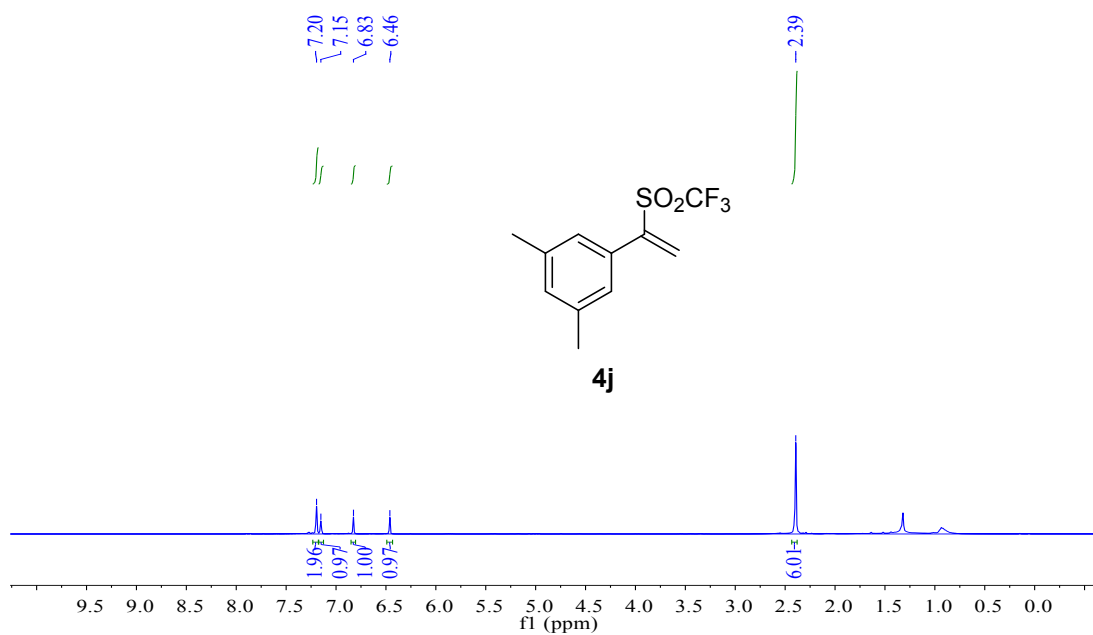


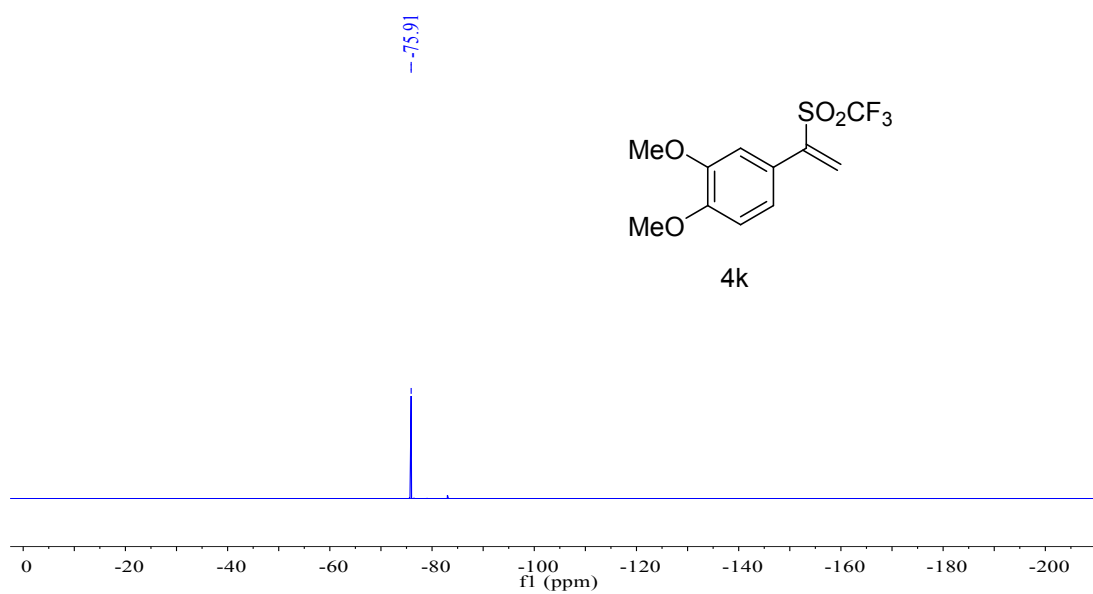
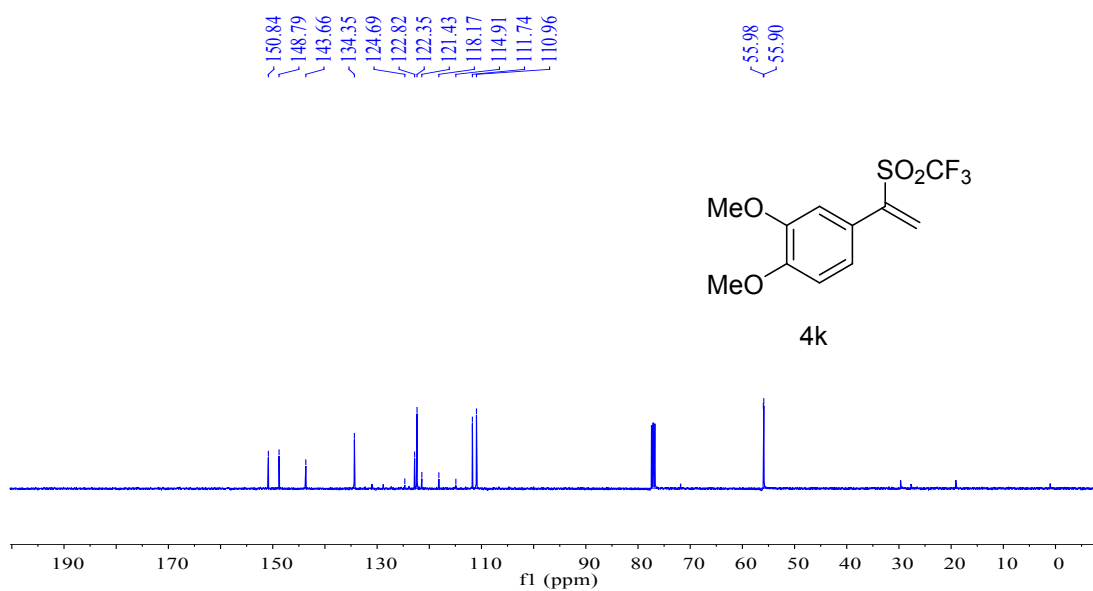
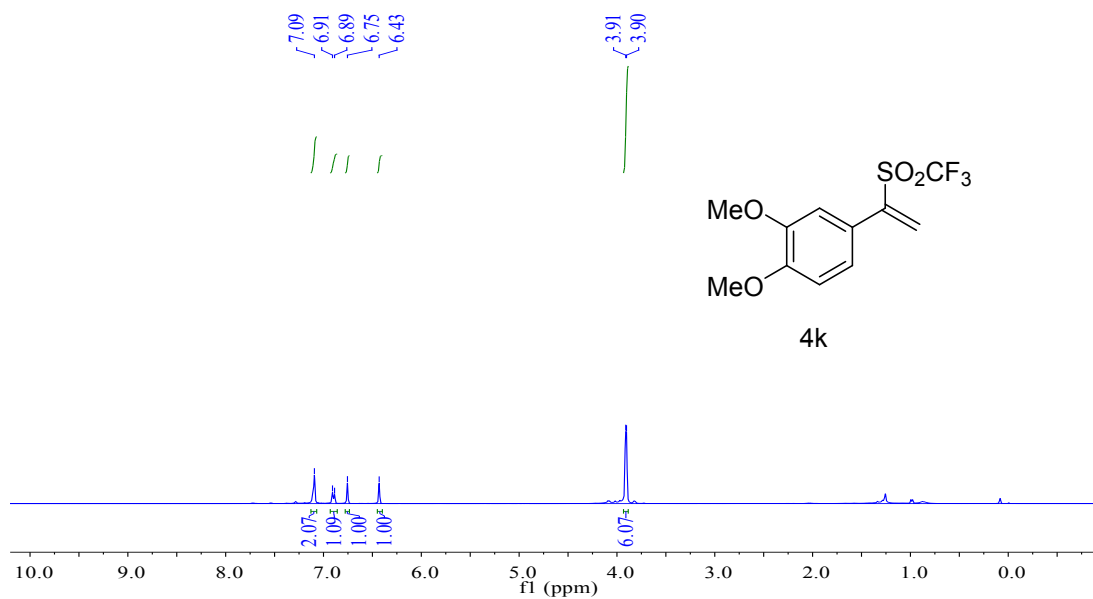


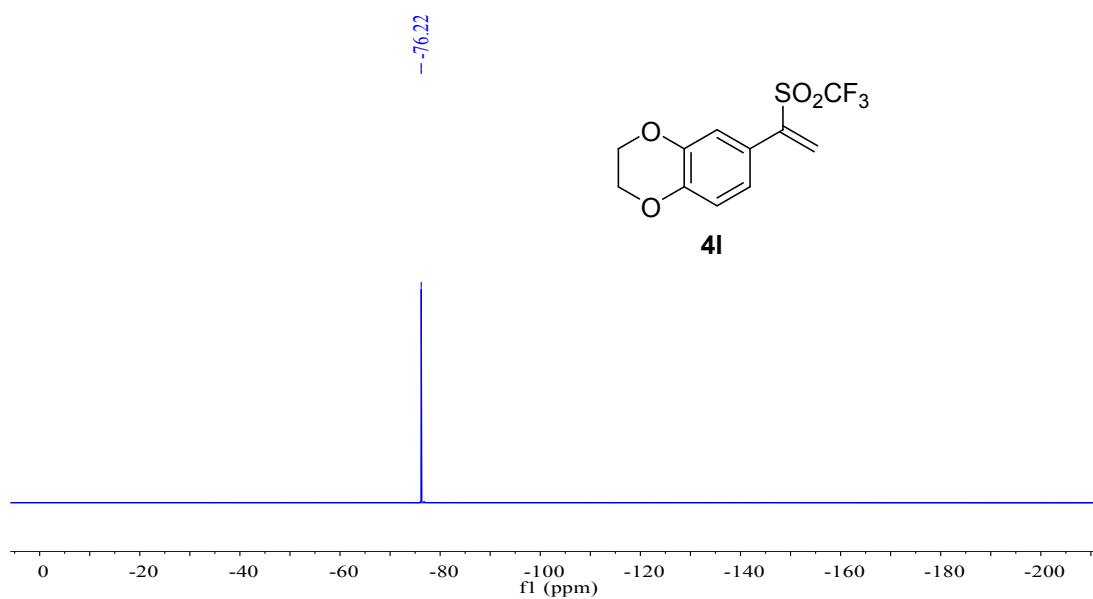
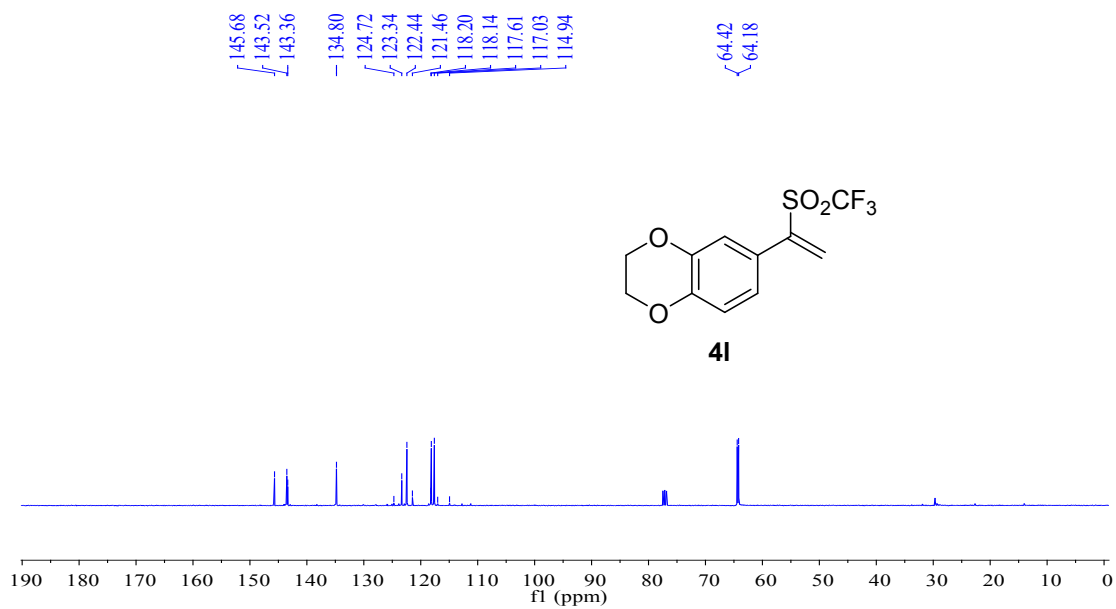
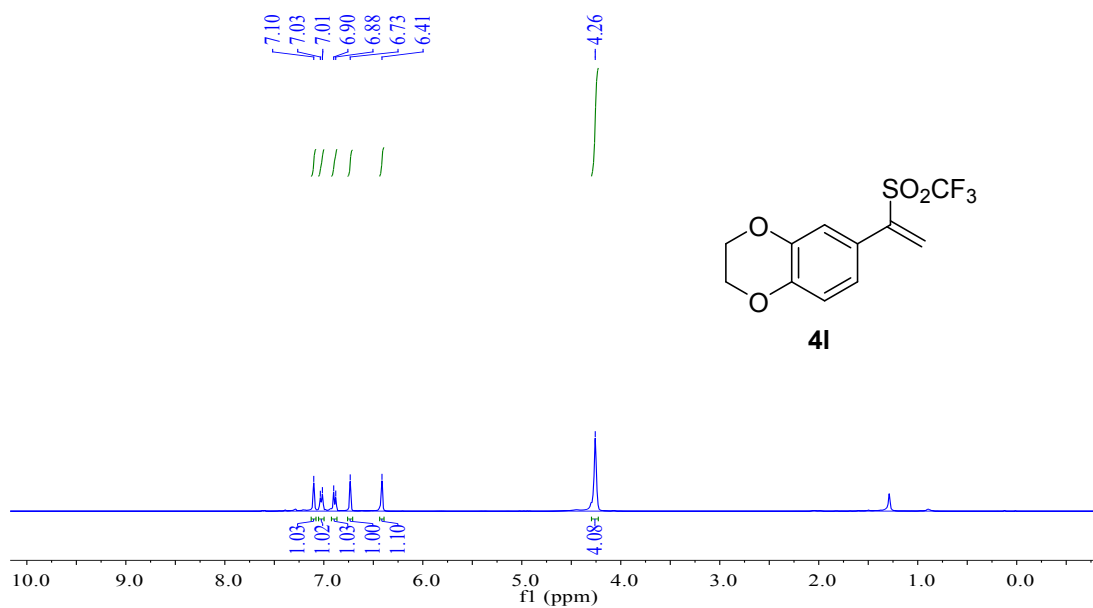


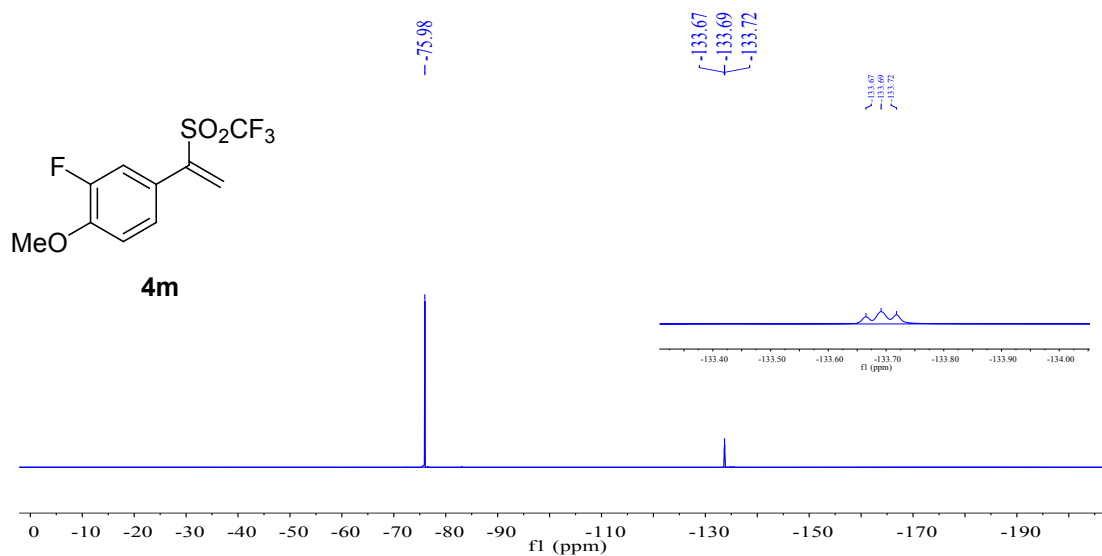
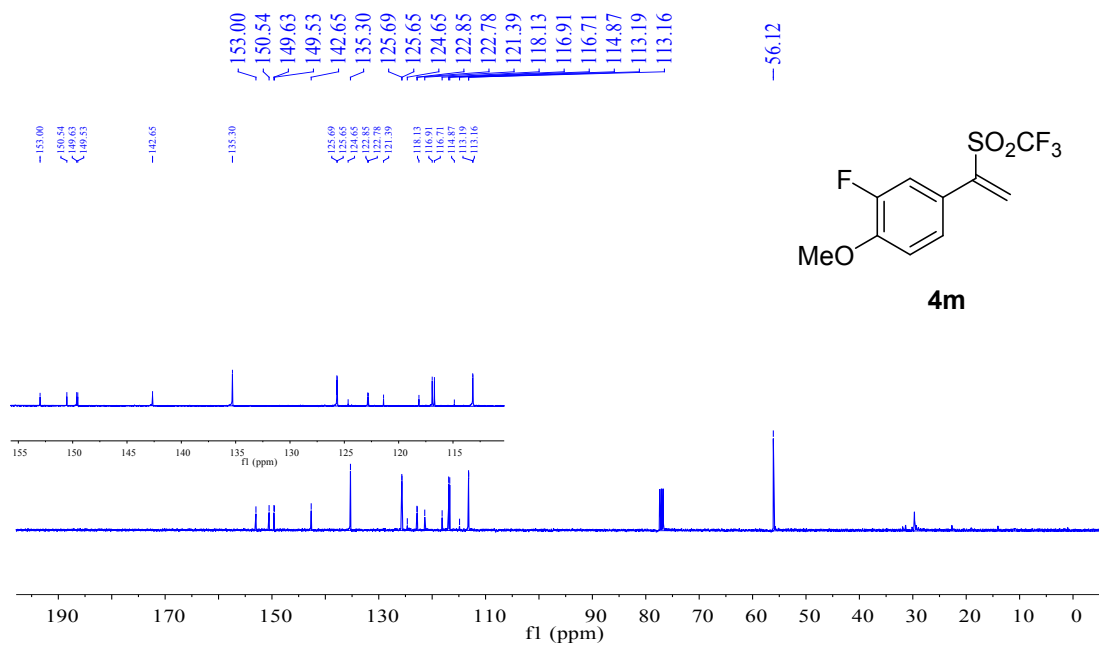
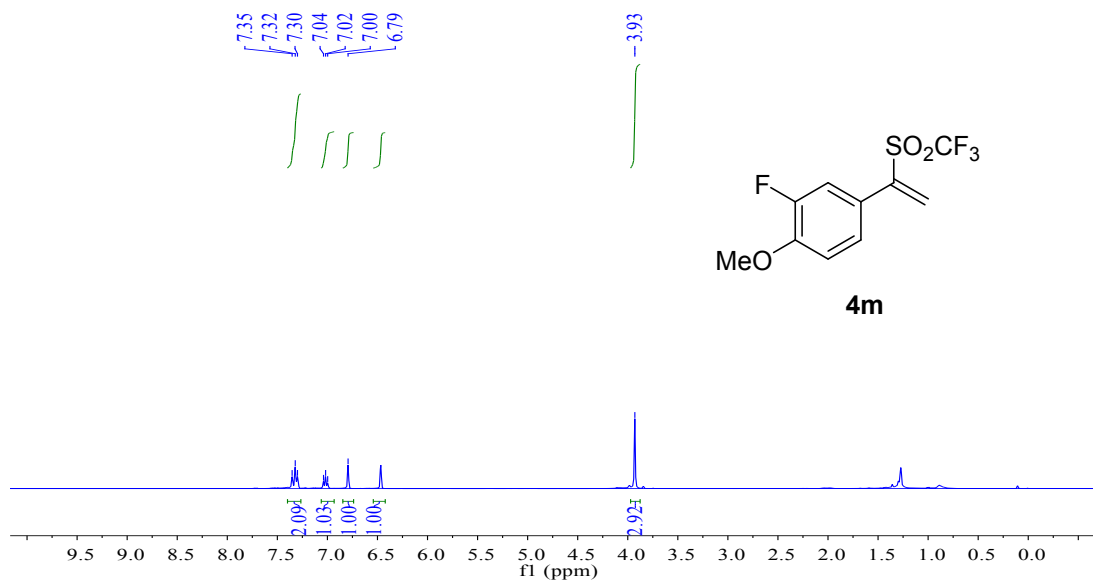


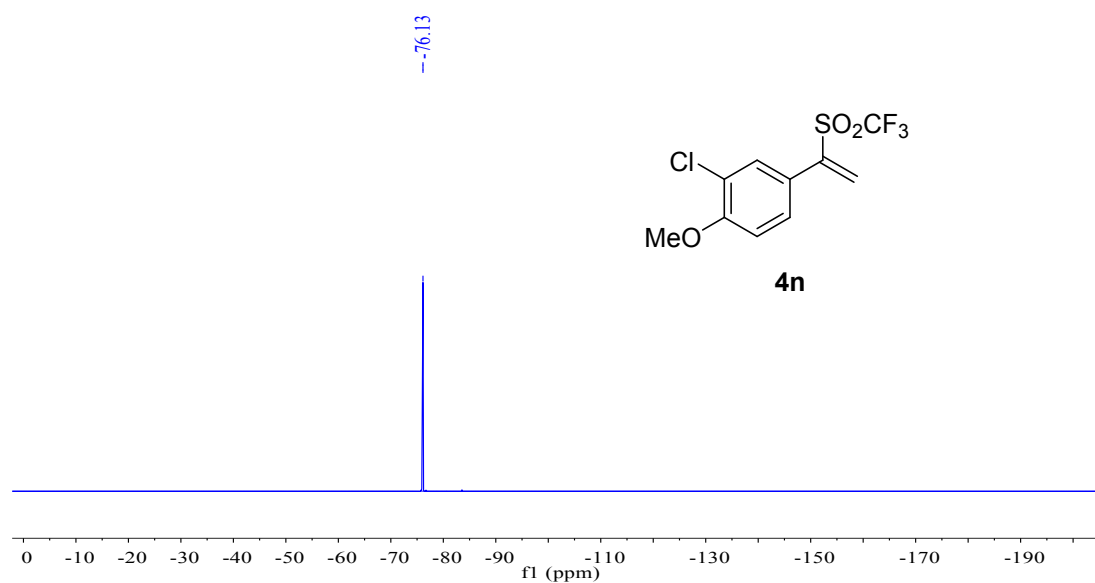
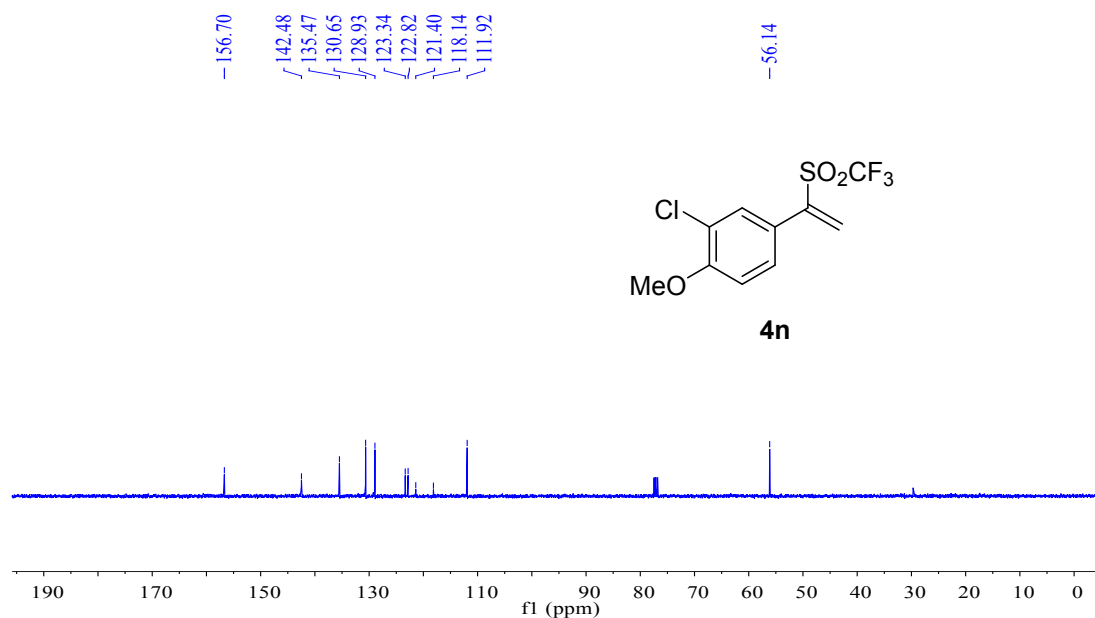
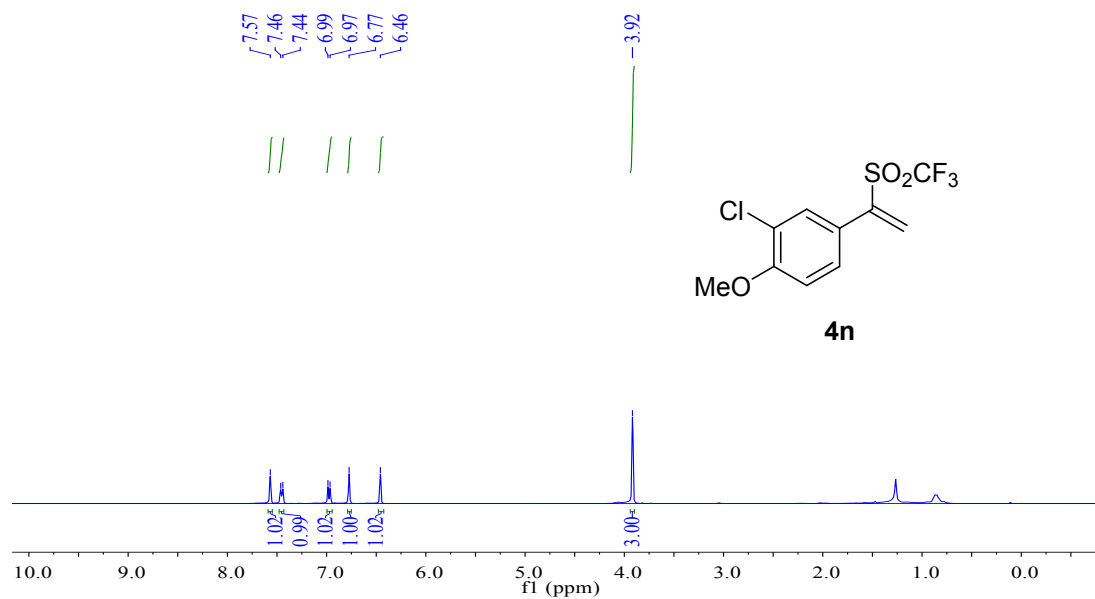


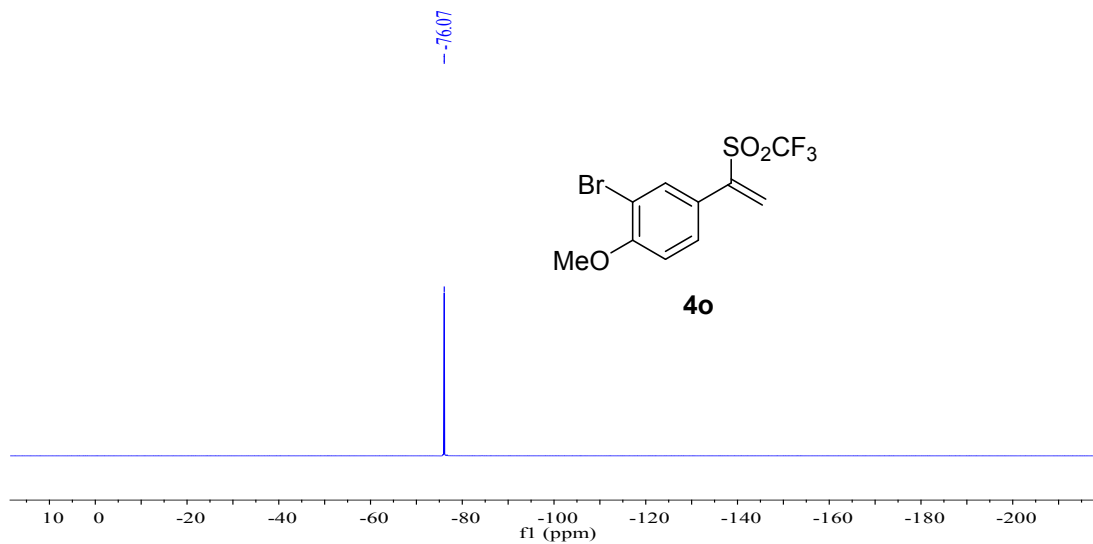
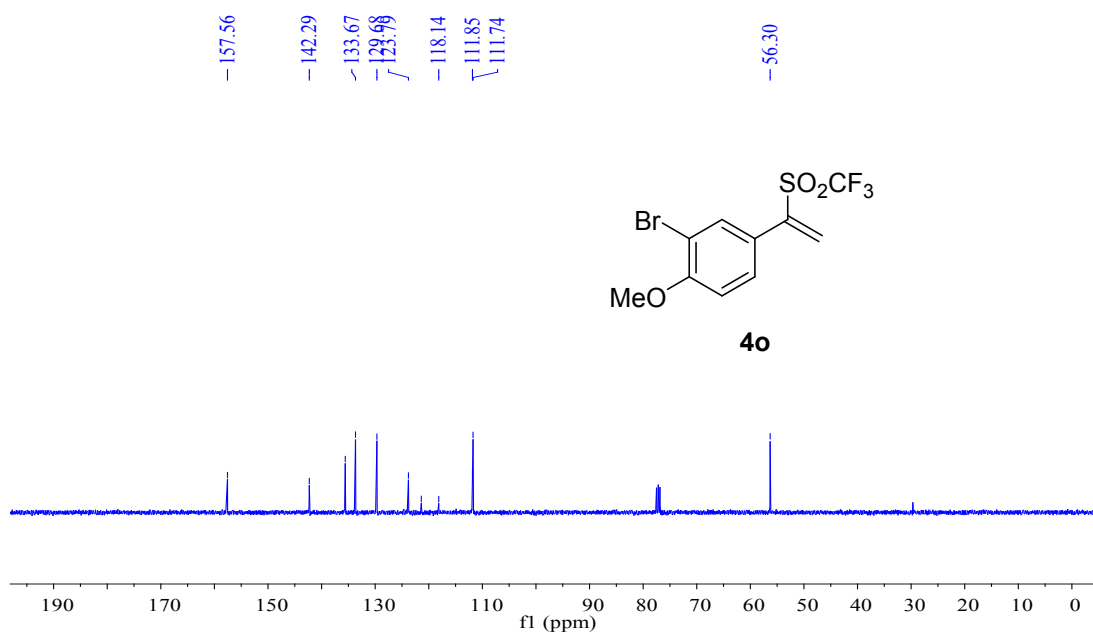
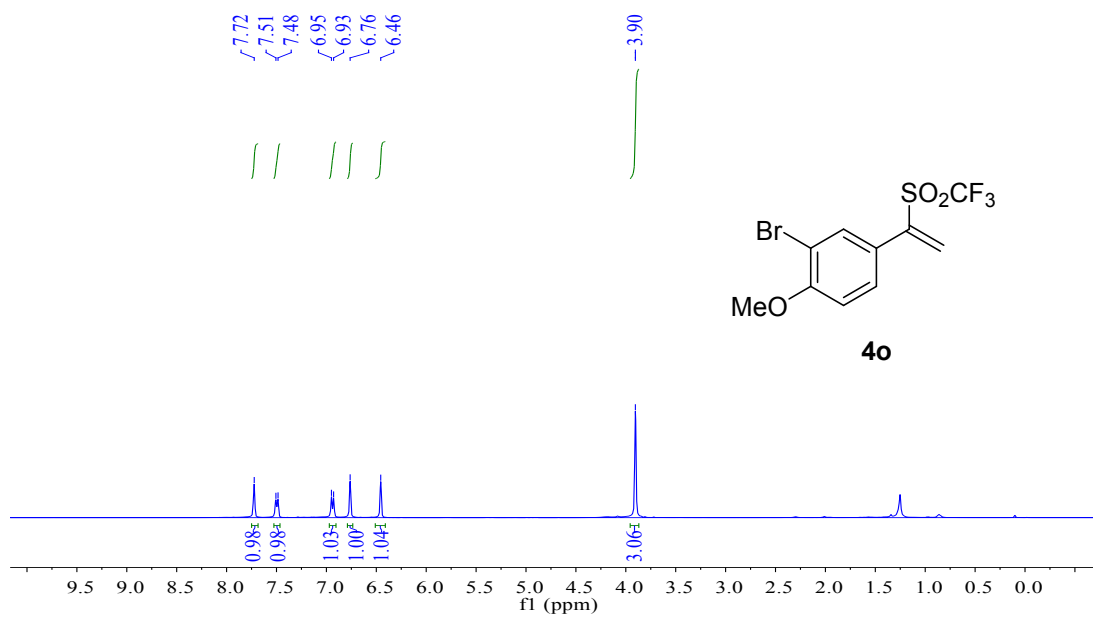


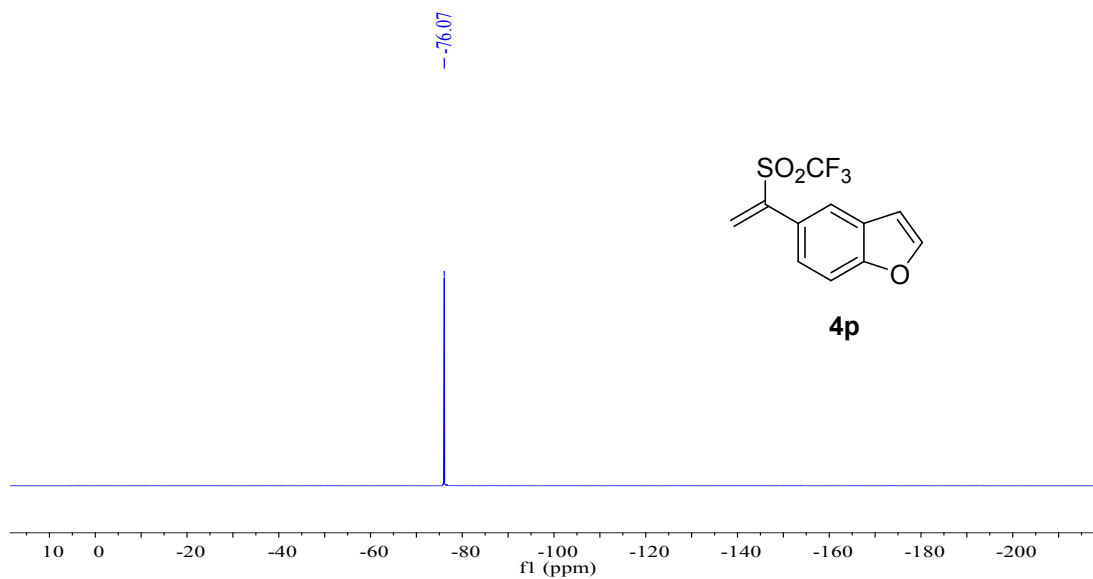
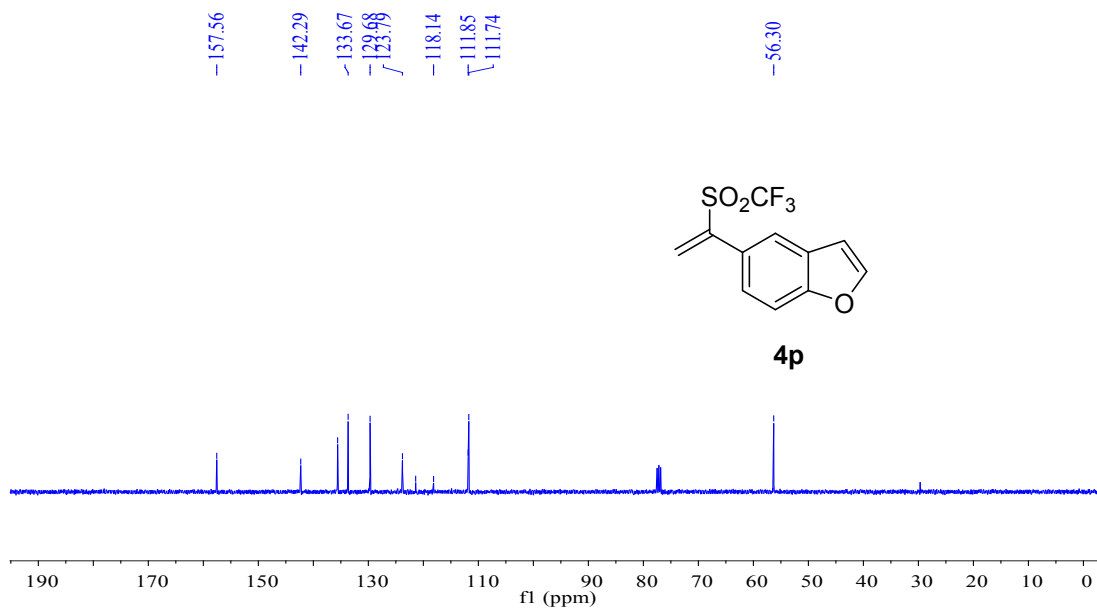
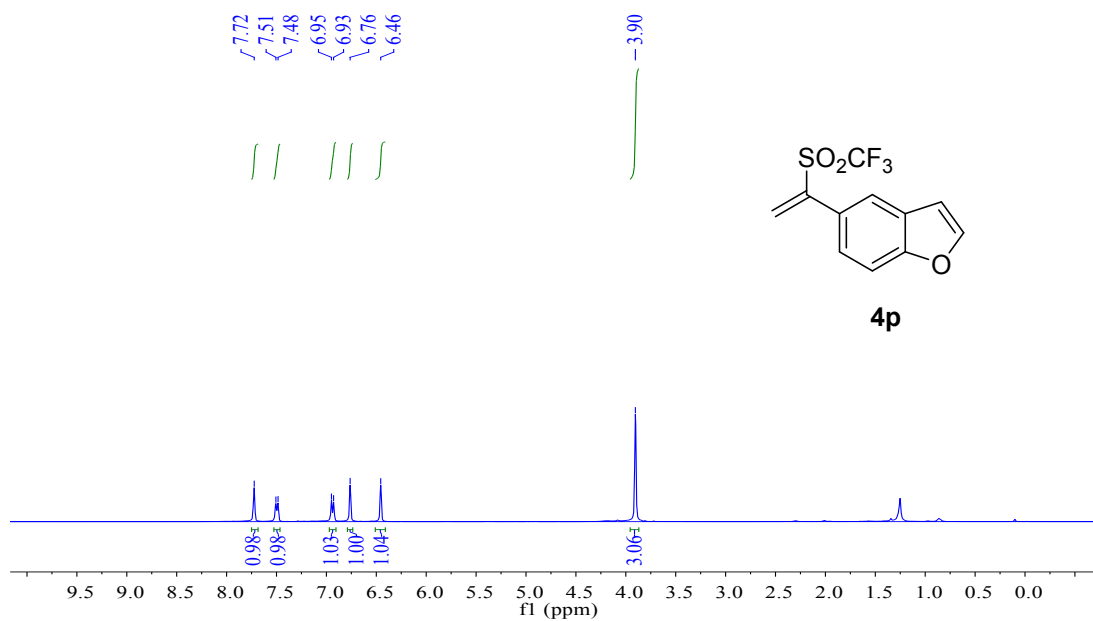


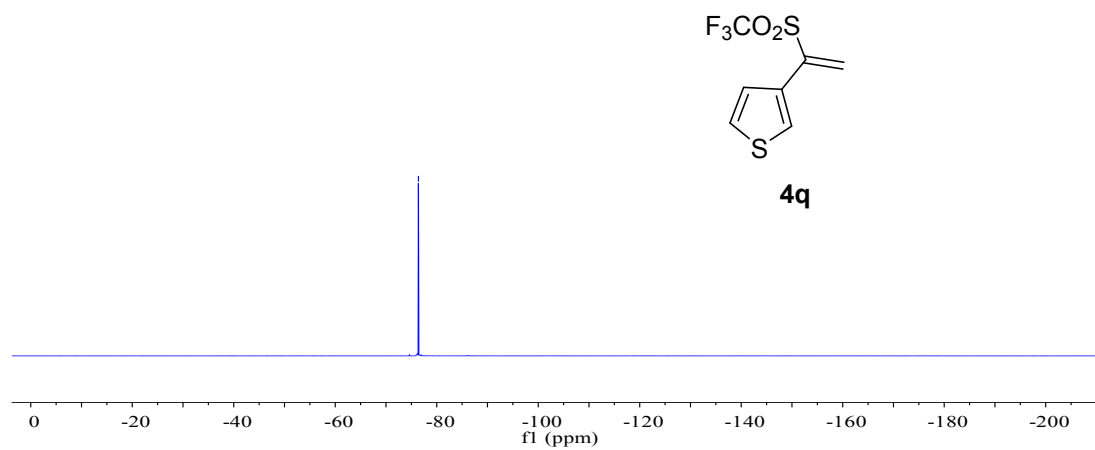
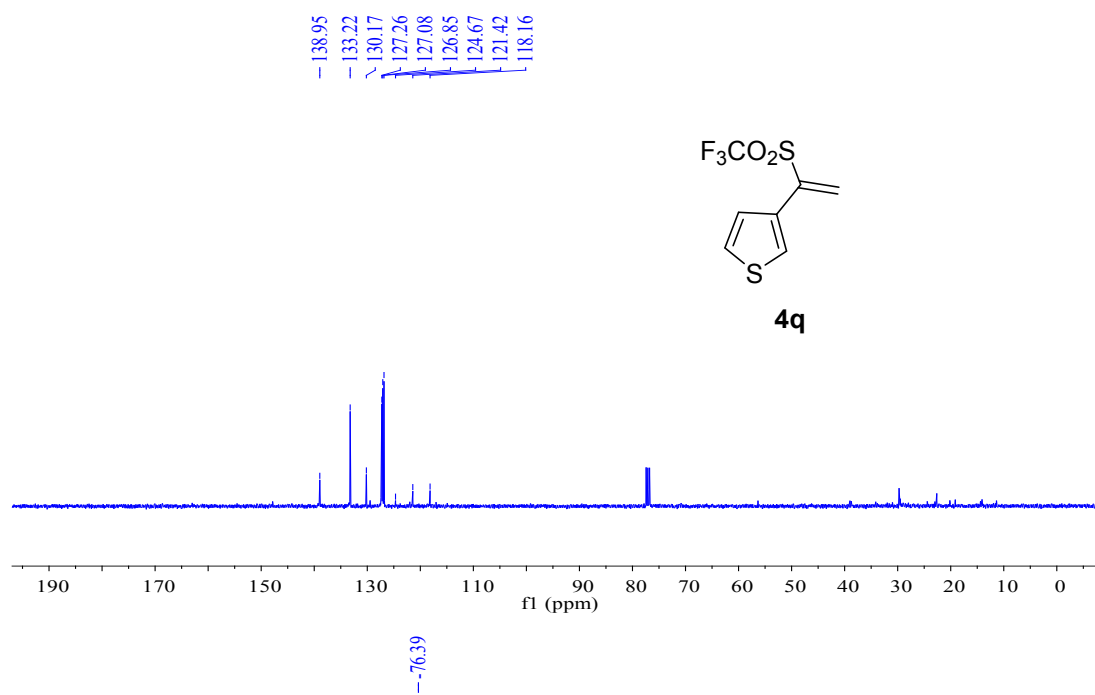
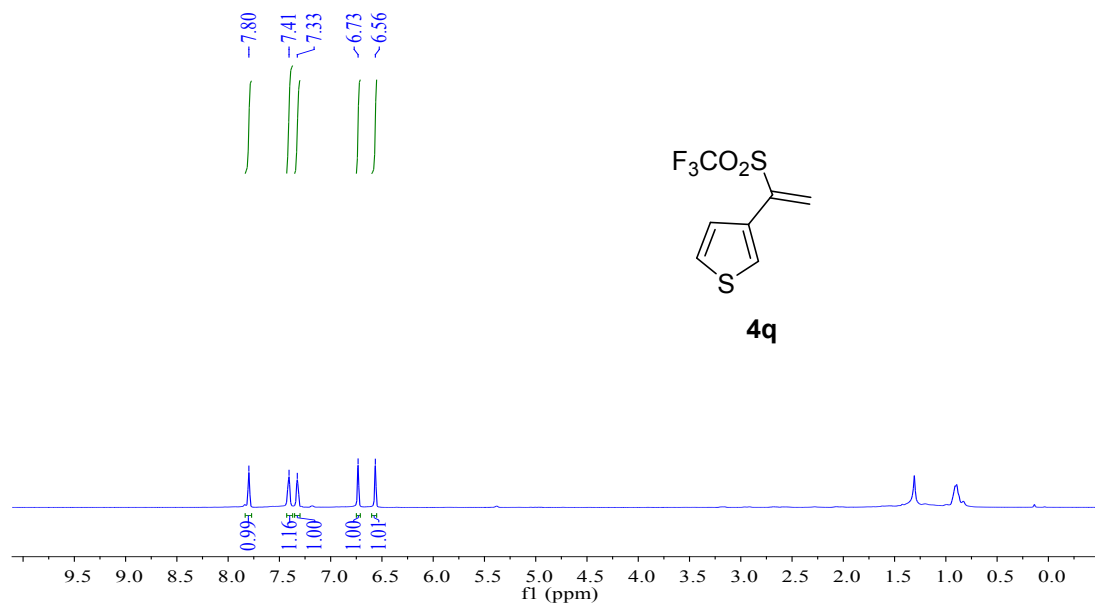


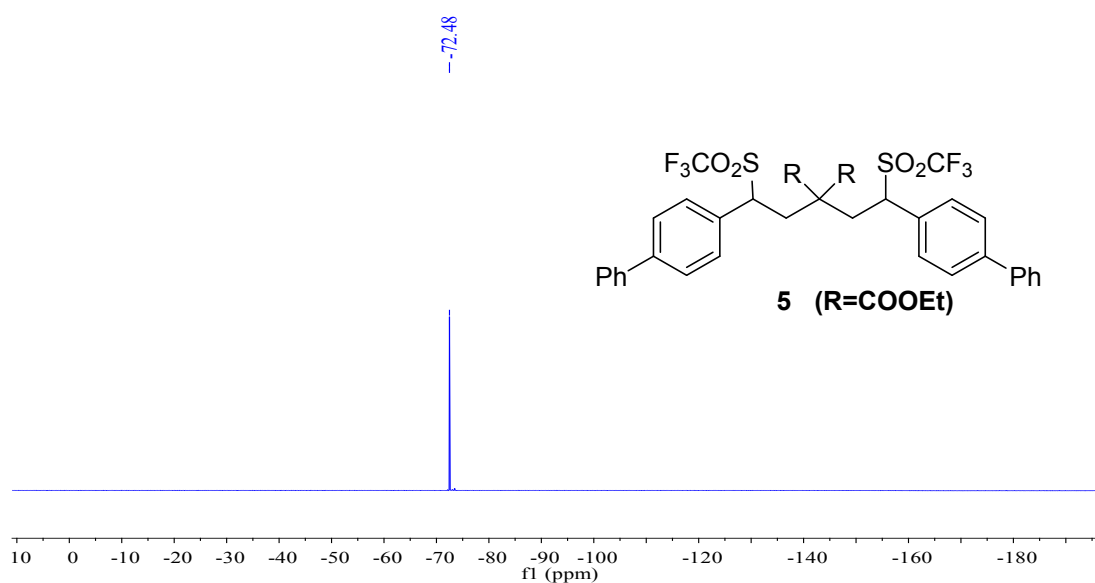
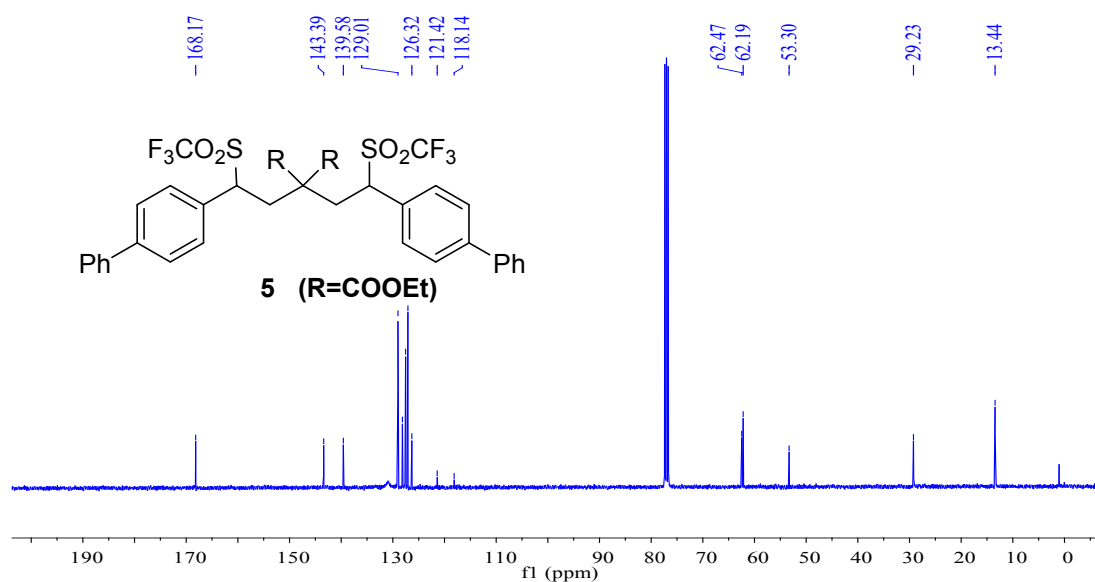
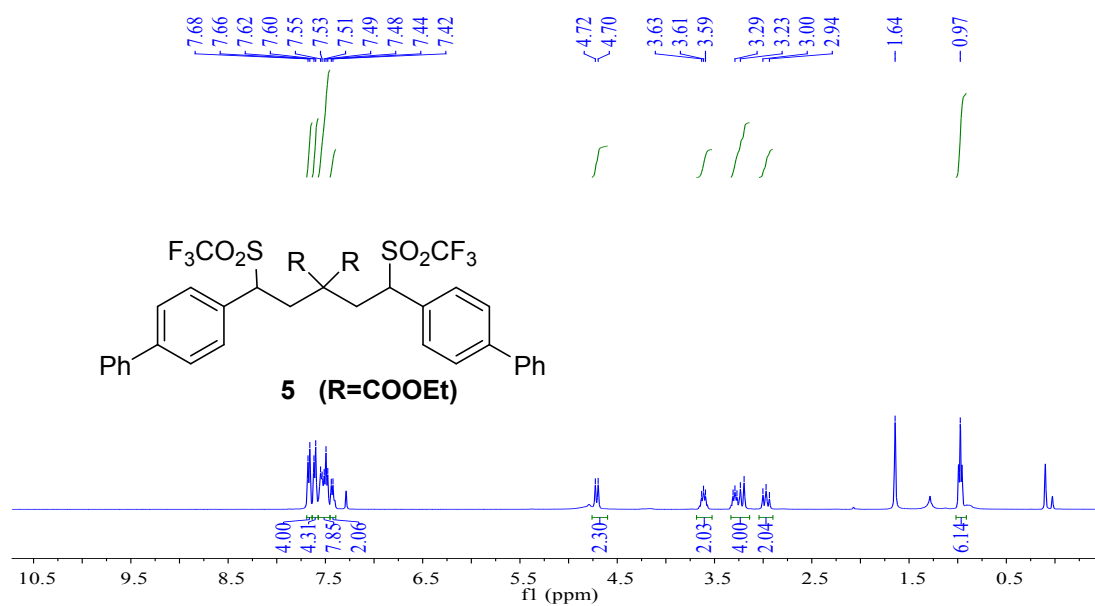


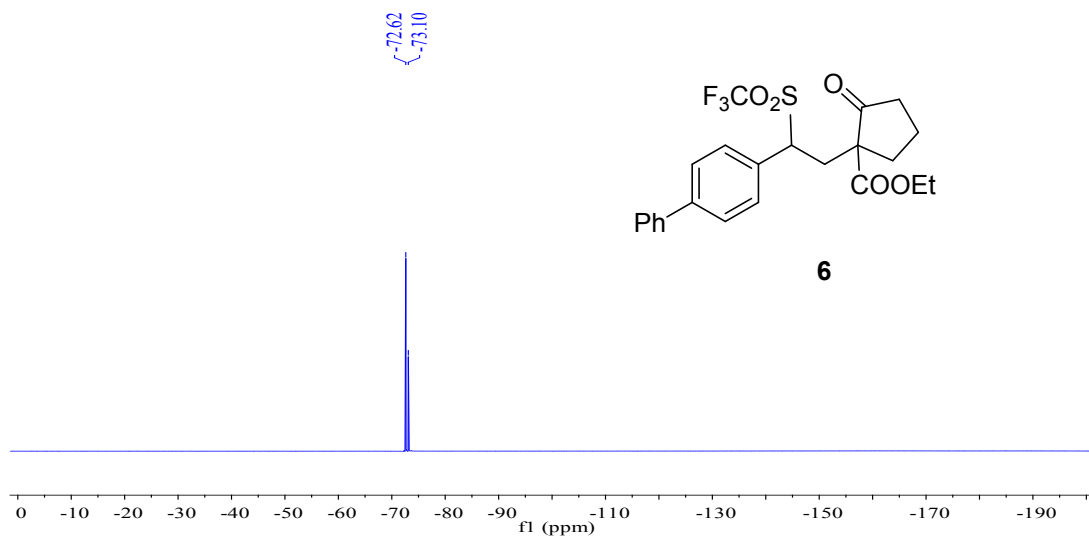
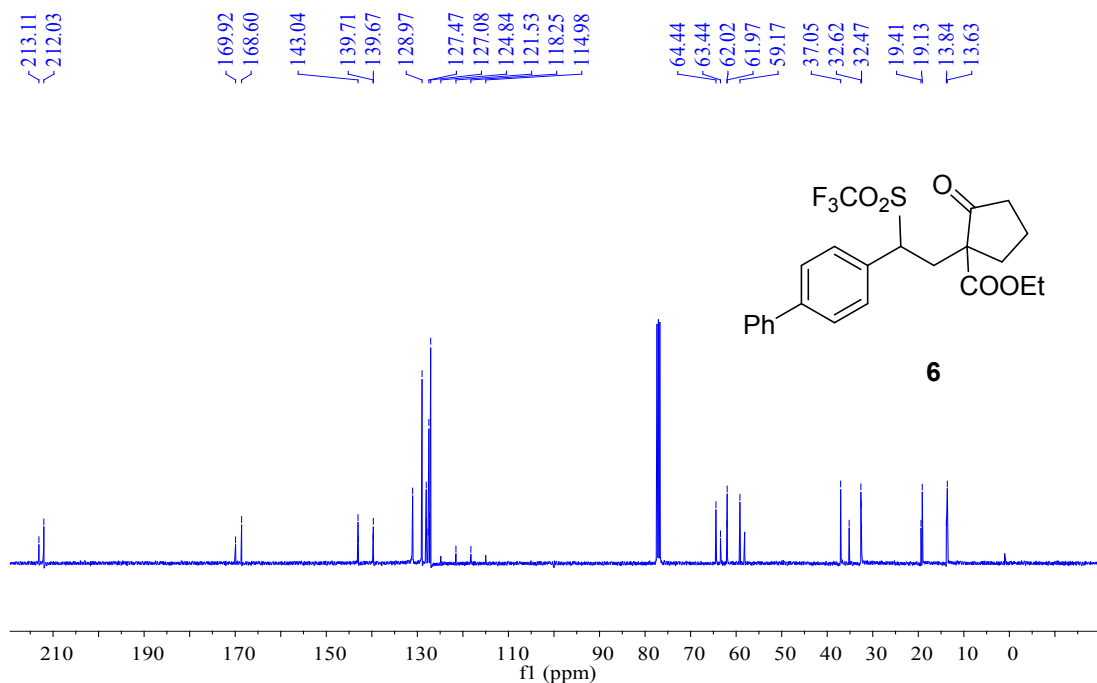
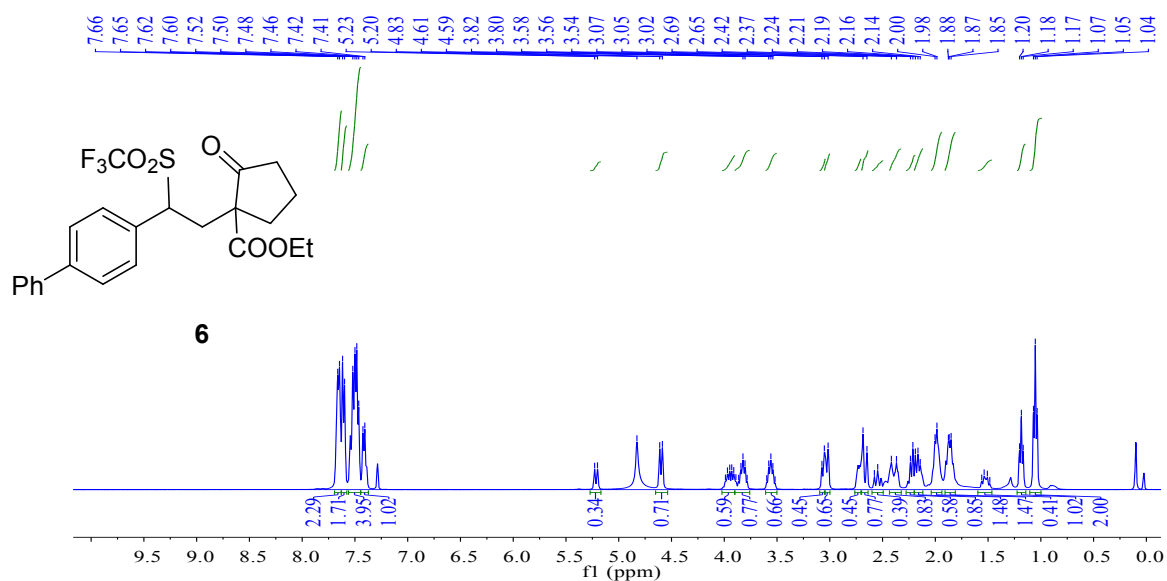


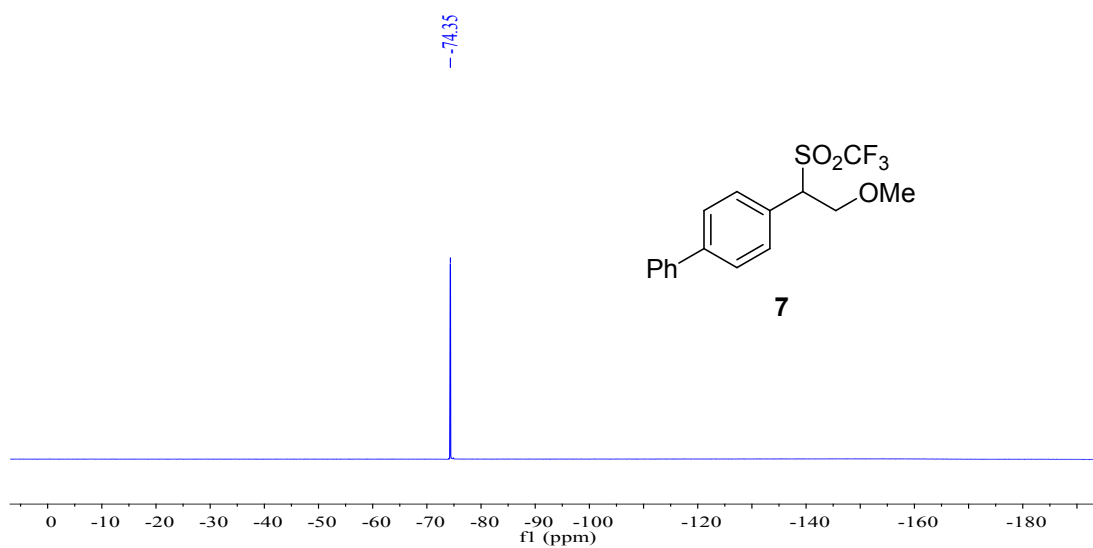
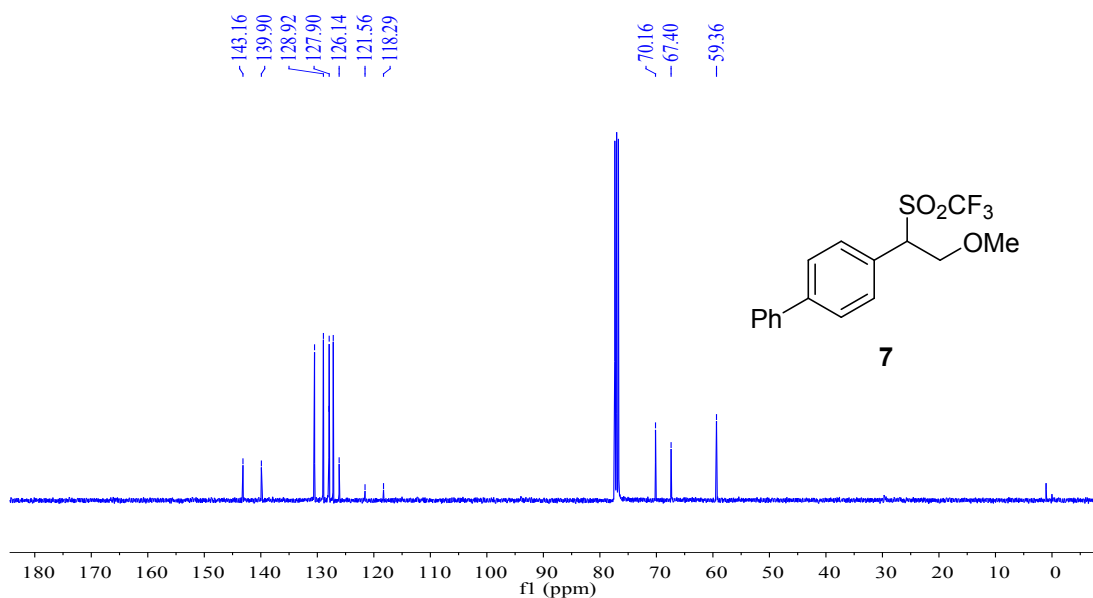
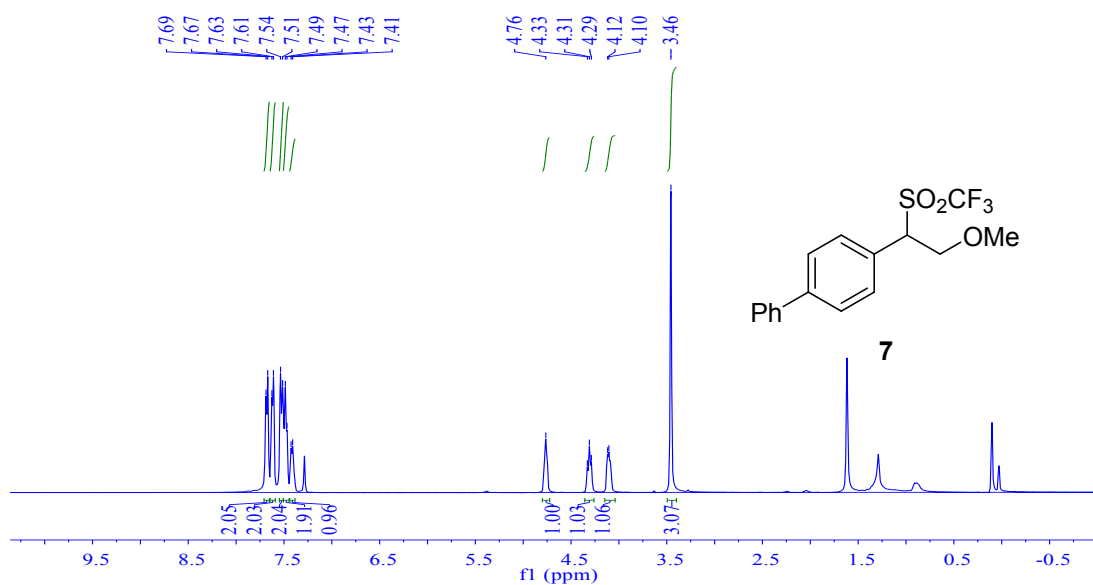


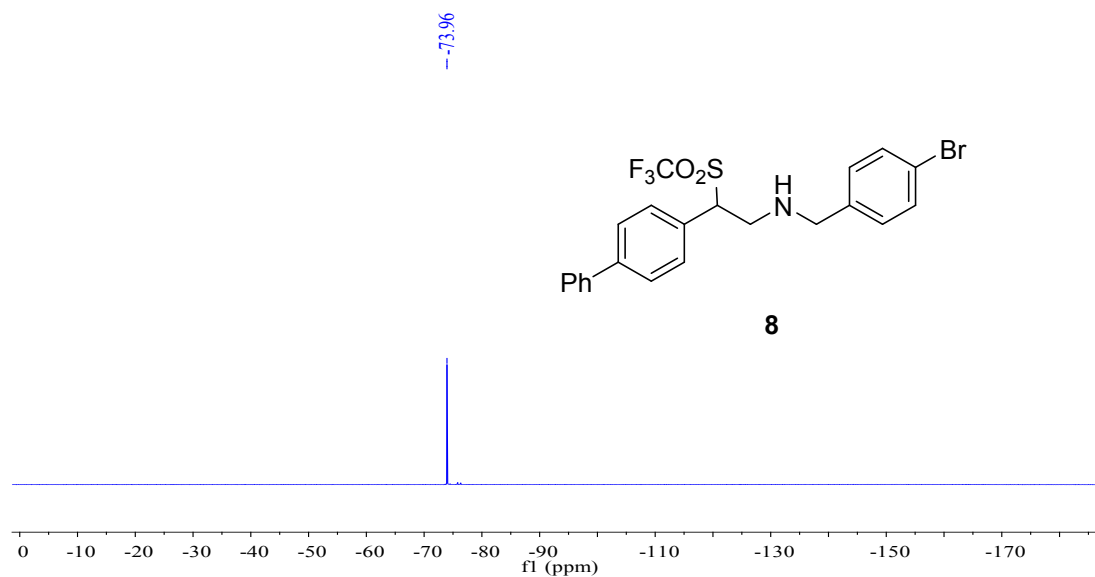
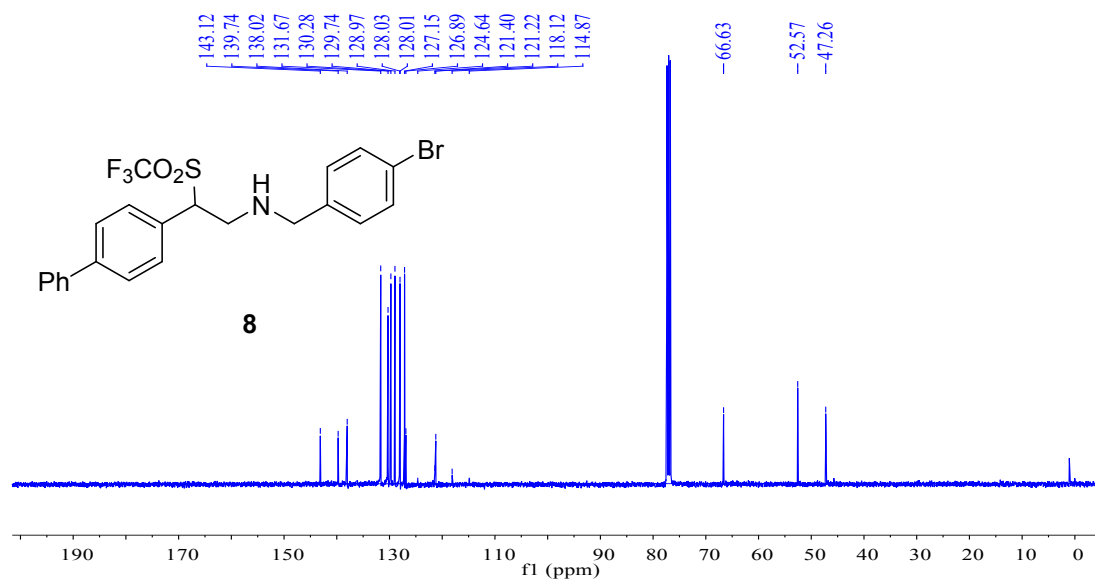
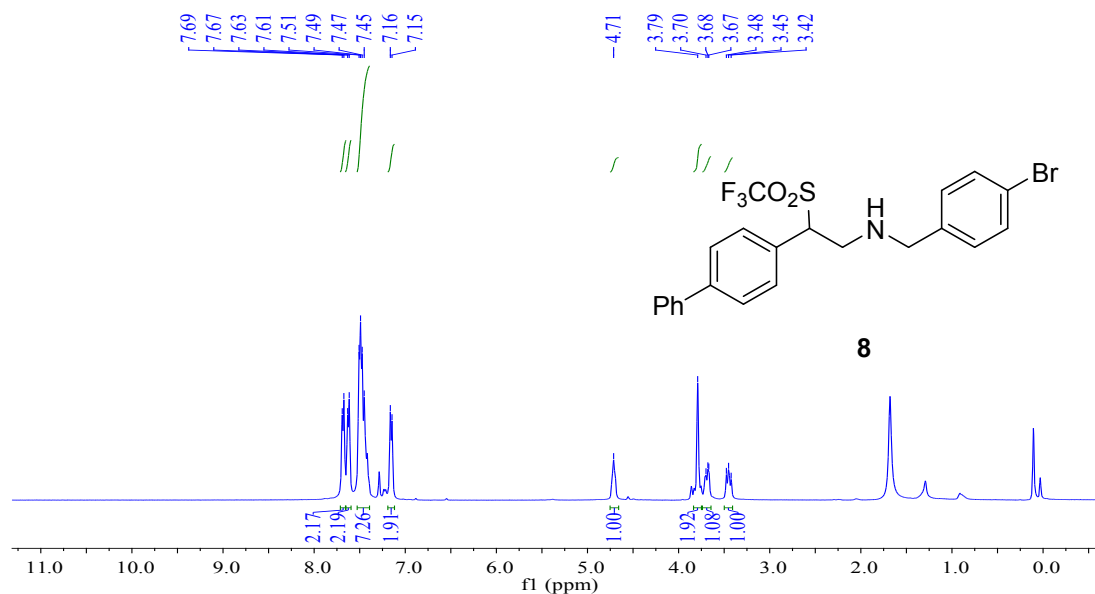


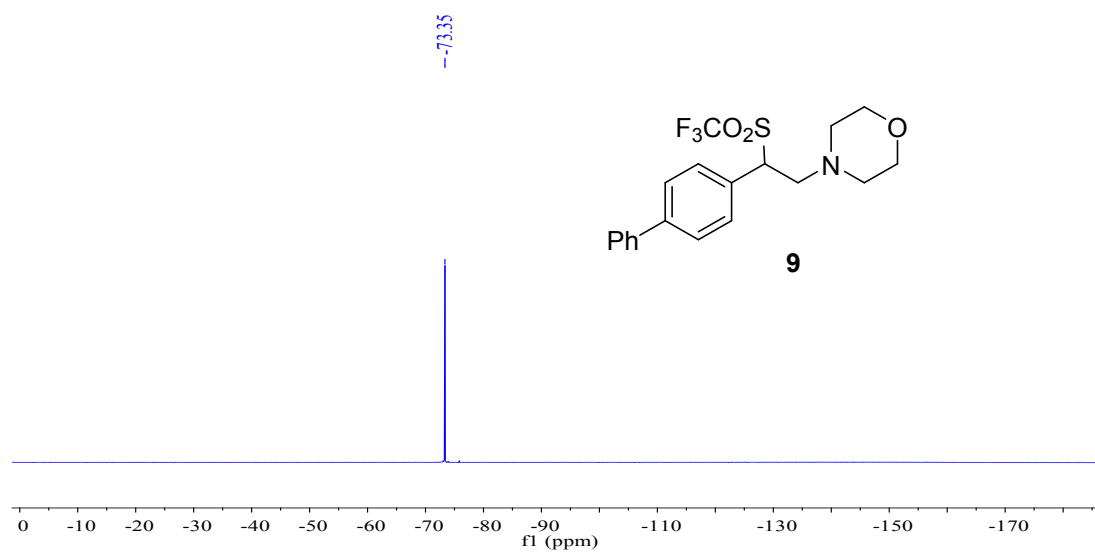
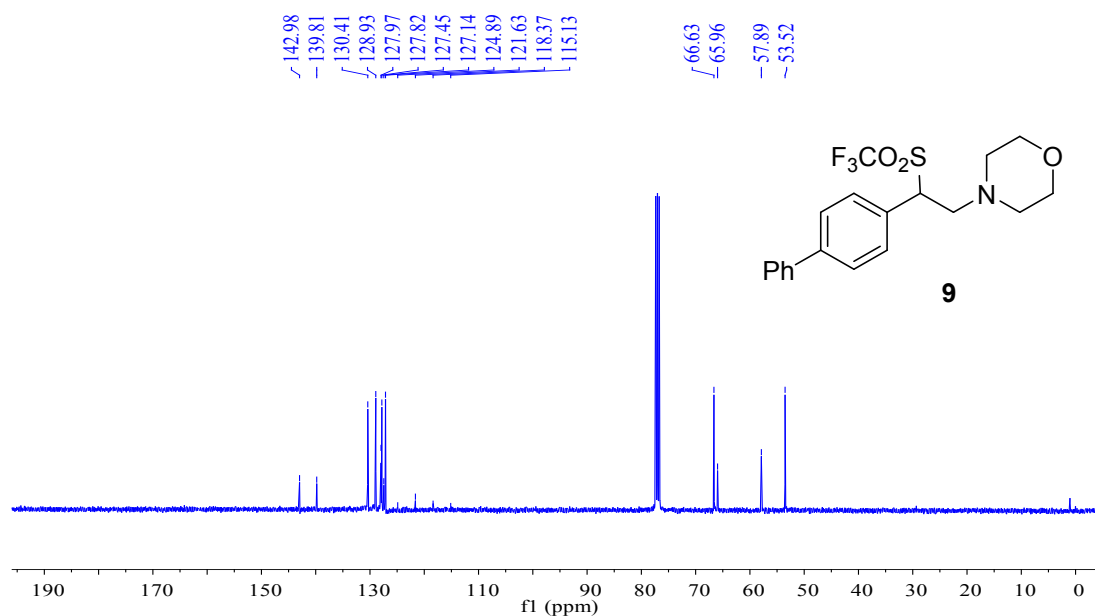
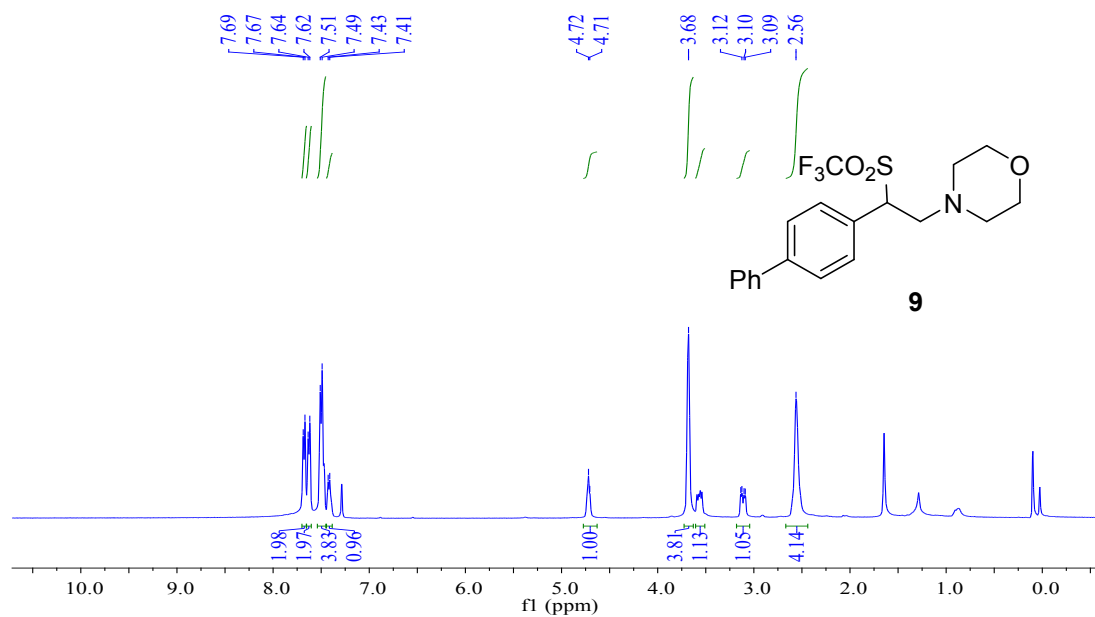


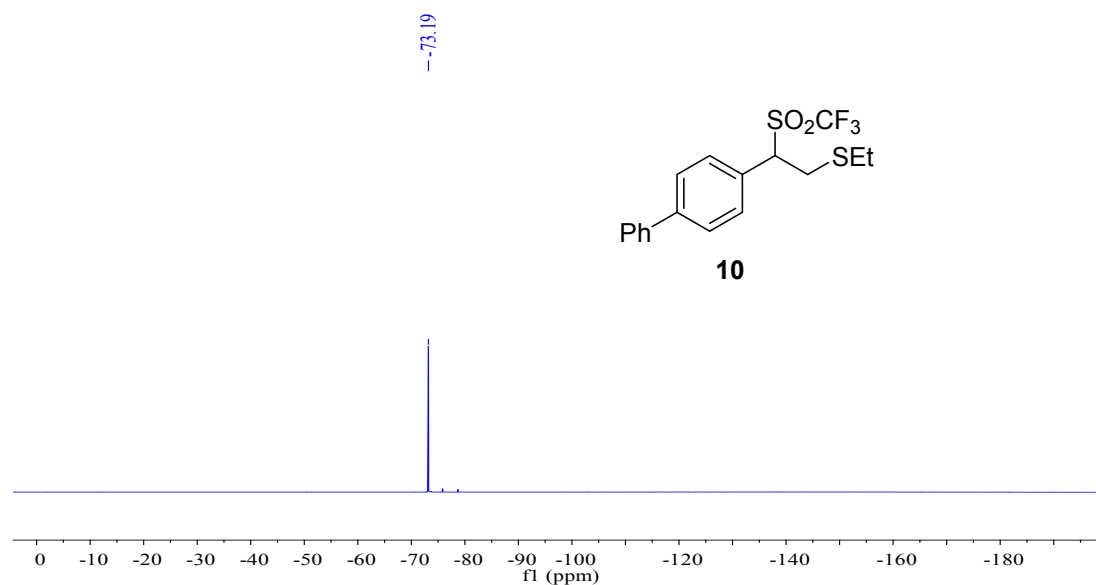
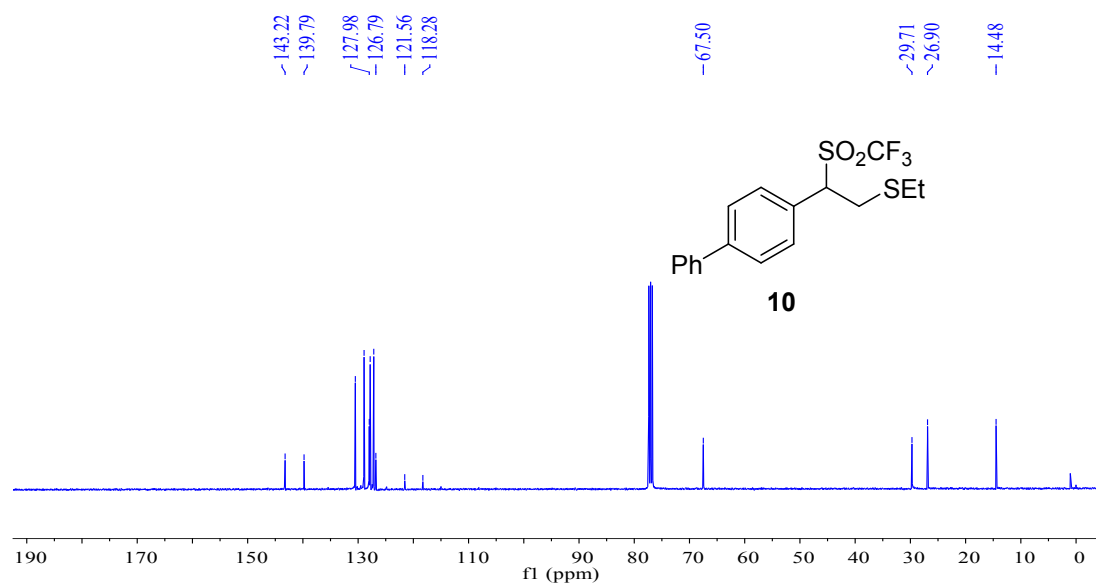
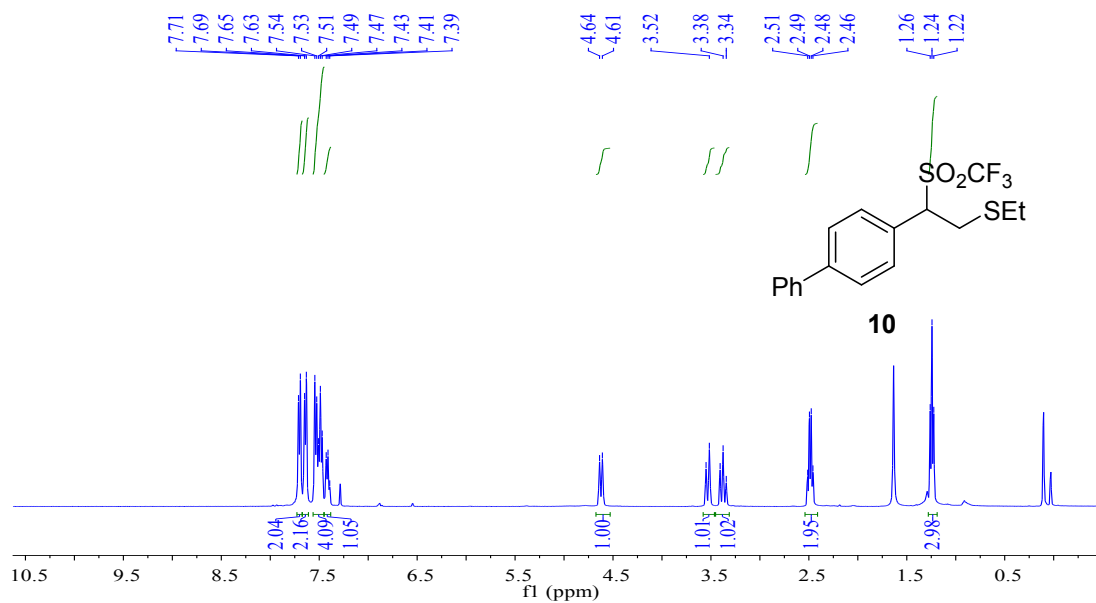












6. Copies of DEPT135 and HMQC NMR spectra for product 4h.

