

Supporting Information for

Regioselective synthesis of arylsulfonyl heterocycles from bromoallyl sulfones via intramolecular Heck coupling reaction

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General Information

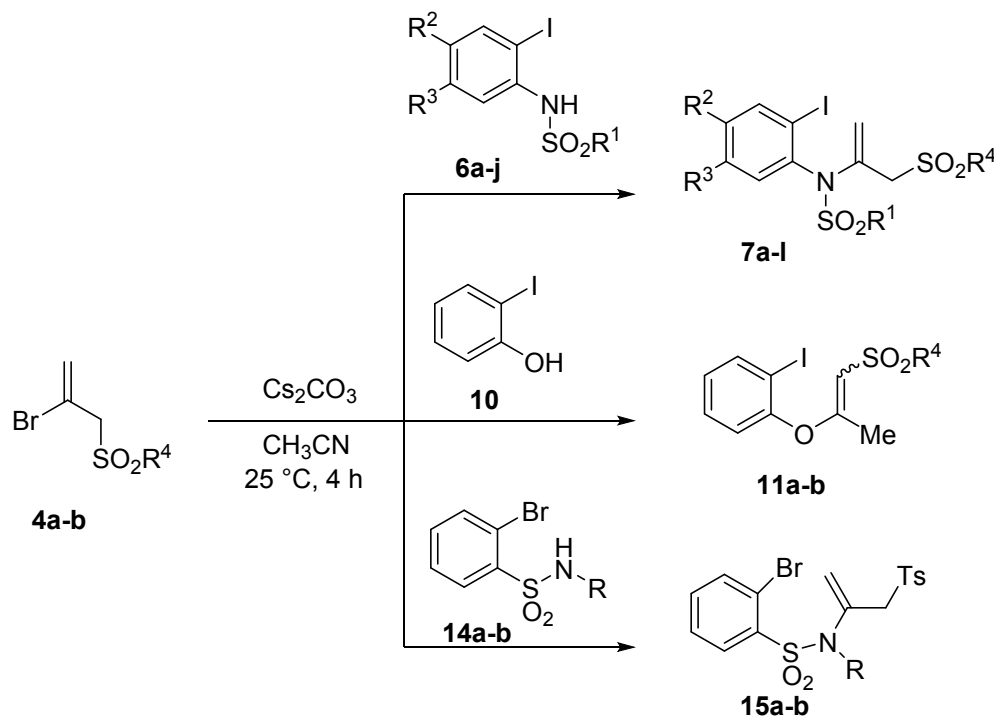
Solvents and reagents: All the reagents were used without further purification unless specified otherwise. Technical grade ethyl acetate and petroleum ether used for column chromatography were distilled prior to use. All reactions were performed in oven-dried glassware with magnetic stirring. HPLC grade acetonitrile and DMF were used as purchased.

Purification and chromatography: TLC analysis was performed on commercially prepared 60 F₂₅₄ silica gel plates. Visualization of spots on TLC plate was accomplished with UV light (254 nm) and staining by KMnO₄ solution. Column chromatography was carried out using silica gel (60-120 mesh and 100- 200 mesh) packed in glass columns using distilled ethyl acetate and petroleum ether.

Characterisation: All ¹H NMR (400 MHz) and ¹³C NMR (100 MHz) spectra were recorded in CDCl₃ solvent at ambient temperature, chemical shift δ are given in ppm on a scale downfield from TMS, and the coupling constant *J* are in Hz. The signal patterns are indicated as follows: s, Singlet; d, doublet; t, triplet; dd, doublet of doublet; m, multiplet; brs = broad, AB q, AB quartet). IR spectra were recorded on a Bruker Alfa FTIR spectrometer by dispersing samples in KBr pellets. Melting points were recorded on an electrothermal apparatus and are uncorrected.

The 2-bromoallylsulfones **4a-b**,¹ sulfonamides **6a-j**² and **14a-b**³ were prepared as described previously.

General procedure A: Preparation of N-vinyl-o-halo sulfonamides 7a-j, enol ethers 11a-b and N-vinyl sulfonamides 15a-b



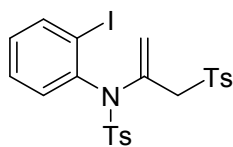
To a solution of the nucleophile (1.0 mmol) (N-sulfonyl-o-iodoaniline **6** or 2-iodophenol **10** or 2-bromobenzenesulfonamides **14**) and 2-bromoallyl sulfone **4** (1.5 mmol) in acetonitrile (10 mL), cesium carbonate (815 mg, 2.5 mmol) was added at room temperature and stirred the mixture for 4 hours. After completion of reaction, solvent was removed on a rotavapor and deionized water (20 mL) was added. The solution was extracted with ethyl acetate (3 X 15 mL). The combined extracts was washed with brine, dried over anhydrous sodium sulfate and concentrated on a rotavapor. Column chromatography of the residue on silica gel using petroleum ether-ethyl acetate as eluent afforded analytically pure products.

Spectroscopic data for N-vinyl-o-iodo sulfonamides 7a-j

¹ S. Undeela, S. Thadkapally, J. B. Nanubolu, K. K. Singarapu and R. S. Menon, *Chem. Commun.*, 2015, **51**, 13748-13751.

² C. Rossy, E. Fouquet and F.-X. Felpin, *Beilstein J. Org. Chem.*, 2013, **9**, 1426-1431.

³ S. Debnath and S. Mondal, *J. Org. Chem.*, 2015, **80**, 3940-3948.



N-(2-iodophenyl)-4-methyl-*N*-(3-tosylprop-1-en-2-yl)benzenesulfonamide (**7a**)

White solid, 448 mg, 79%

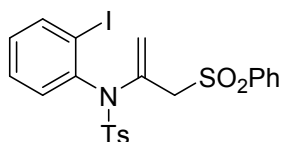
Melting point: 131-133 °C

IR (KBr) ν_{max} : 2922, 1620, 1595, 1460, 1346, 1311, 1157, 655, 586 cm^{-1}

^1H NMR (400 MHz, CDCl_3) δ 7.83 (d, $J = 8.0, 1.2$ Hz, 1H), 7.72 (d, $J = 8.4$ Hz, 2H), 7.56 (d, $J = 8.4$ Hz, 2H), 7.34-7.21 (m, 4H), 7.22 (d, $J = 8.0$ Hz, 2H), 7.05 (ddd, $J = 8.0, 6.9, 2.2$ Hz, 1H), 5.53 (d, $J = 1.2$ Hz, 1H), 5.29 (d, $J = 1.2$ Hz, 1H), 3.84 (AB q, $J = 15.2$ Hz, 2H), 2.45 (s, 3H), 2.42 (s, 3H).

^{13}C NMR (100 MHz, CDCl_3) δ 144.8, 144.5, 140.9, 140.0, 136.1, 135.1, 133.5, 132.5, 130.5, 129.7, 129.6, 129.2, 128.9, 128.7, 118.9, 102.3, 59.7, 21.7

HRMS calcd for $\text{C}_{23}\text{H}_{22}\text{INO}_4\text{S}_2$ (M+H) 568.0113 ; found 568.0116.



N-(2-iodophenyl)-4-methyl-*N*-(3-(phenylsulfonyl)prop-1-en-2-yl)benzenesulfonamide (**7b**)

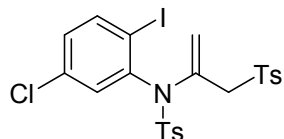
Colorless oil, 448 mg, 81%

IR (KBr) ν_{max} : 3062, 2924, 1591, 1496, 1315, 1153, 526 cm^{-1}

^1H NMR (400 MHz, CDCl_3) δ 7.84 (dd, $J = 8.0, 1.2$ Hz, 1H), 7.72-7.69 (m, 4H), 7.62-7.58 (m, 1H), 7.46 (t, $J = 7.8$ Hz, 2H), 7.36-7.29 (m, 4H), 7.05 (ddd, $J = 8.0, 6.8, 2.0$ Hz, 1H), 5.53 (d, $J = 1.2$ Hz, 1H), 5.28 (d, $J = 1.2$ Hz, 1H), 3.86 (AB q, $J = 15.6$ Hz, 2H), 2.45 (s, 3H)

^{13}C NMR (100 MHz, CDCl_3) δ 144.5, 141.0, 139.9, 138.1, 136.1, 133.9, 133.3, 132.5, 130.6, 129.6, 129.2, 129.1, 128.9, 128.7, 118.8, 102.2, 59.7, 21.7

HRMS calcd for $\text{C}_{22}\text{H}_{20}\text{INO}_4\text{S}_2$ (M+H) 553.9957 ; found 553.9977



N-(5-chloro-2-iodophenyl)-4-methyl-*N*-(3-tosylprop-1-en-2-yl)benzenesulfonamide (**7c**)

White solid, 499 mg, 83%

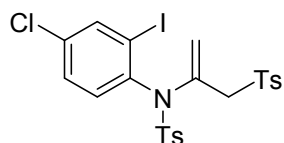
Melting point: 123-125 °C

IR (KBr) ν_{\max} : 3244, 2924, 1620, 1595, 1448, 1309, 1157, 586, 516

¹H NMR (400 MHz, CDCl₃) δ 7.73 (t, J = 8.4 Hz, 3H), 7.57 (d, J = 8.4 Hz, 2H), 7.33 (d, J = 8.0 Hz, 2H), 7.24 (d, J = 8.0 Hz, 2H), 7.14 (d, J = 2.4 Hz, 1H), 7.04 (dd, J = 8.4, 2.4 Hz, 1H), 5.55 (d, J = 1.2 Hz, 1H), 5.43 (d, J = 1.2 Hz, 1H), 3.85 (AB q, J = 15.6 Hz, 2H), 2.46 (s, 3H), 2.42 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 145.0, 144.8, 141.3, 141.2, 135.7, 135.2, 134.9, 133.4, 132.2, 130.7, 129.8, 129.7, 128.9, 128.6, 119.7, 99.9, 59.9, 21.8, 21.7

HRMS calcd for C₂₃H₂₁ClINO₄S₂ (M+H) 601.9723; found 601.9737.



N-(4-chloro-2-iodophenyl)-4-methyl-*N*-(3-tosylprop-1-en-2-yl)benzenesulfonamide (**7d**)

White solid, 469 mg, 78%

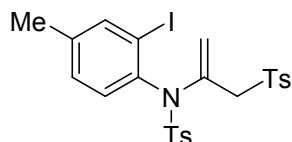
Melting point: 119-120 °C

IR (KBr) ν_{\max} : 3091, 1597, 1577, 1463, 1334, 1163, 578

¹H NMR (400 MHz, CDCl₃) δ 7.77 (d, J = 2.4 Hz, 1H), 7.71 (d, J = 8.4 Hz, 2H), 7.54 (d, J = 8.4 Hz, 2H), 7.33-7.28 (m, 3H), 7.23-7.19 (m, 3H), 5.55 (d, J = 1.2 Hz, 1H), 5.37 (d, J = 1.2 Hz, 1H), 3.81 (s, 2H), 2.46 (s, 3H), 2.43 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 145.0, 144.7, 140.2, 138.6, 135.9, 135.6, 134.9, 133.2, 132.7, 129.7, 129.6, 129.3, 128.9, 128.7, 120.0, 102.7, 59.6, 21.7

HRMS calcd for C₂₃H₂₁ClINO₄S₂ (M+H) 601.9723 ; found 601.9748.



N-(2-iodo-4-methylphenyl)-4-methyl-*N*-(3-tosylprop-1-en-2-yl)benzenesulfonamide (**7e**)

White solid, 442 mg, 76%

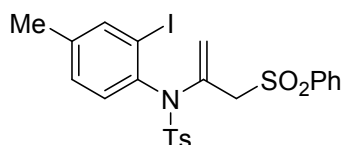
Melting point: 116-117 °C

IR (KBr) ν_{max} : 3041, 2924, 1624, 1595, 1477, 1319, 1159, 509 cm^{-1}

¹H NMR (400 MHz, CDCl_3) δ 7.71 (d, $J = 8.4$ Hz, 2H), 7.64 (s, 1H), 7.55 (d, $J = 8.0$ Hz, 2H), 7.31 (d, $J = 8.0$ Hz, 2H), 7.22 (d, $J = 8.4$ Hz, 2H), 7.16-7.10 (m, 2H), 5.52 (s, 1H), 5.25 (s, 1H), 3.82 (s, 2H), 2.45 (s, 3H), 2.42 (s, 3H), 2.31 (s, 3H)

¹³C NMR (100 MHz, CDCl_3) δ 144.8, 144.4, 141.3, 141.1, 137.2, 136.2, 135.1, 133.5, 131.9, 130.0, 129.6, 129.5, 128.9, 128.7, 118.6, 102.0, 59.6, 21.7, 20.7

HRMS calcd for $\text{C}_{24}\text{H}_{24}\text{INO}_4\text{S}_2$ (M+H) 582.0270 ; found 582.0284.



N-(2-iodo-4-methylphenyl)-4-methyl-*N*-(3-(phenylsulfonyl)prop-1-en-2-yl)benzenesulfonamide (**7f**)

White solid, 419 mg, 74%

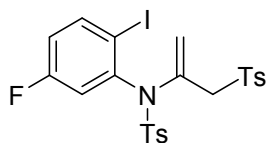
Melting point: 119-121 °C

IR (KBr) ν_{max} : 3040, 2922, 1620, 1585, 1440, 1307, 1153, 547 cm^{-1}

¹H NMR (400 MHz, CDCl_3) δ 7.72-7.69 (m, 4H), 7.65 (d, $J = 1.2$ Hz, 1H), 7.60 (t, $J = 7.6$ Hz, 1H), 7.45 (t, $J = 7.6$ Hz, 2H), 7.31 (d, $J = 8.0$ Hz, 2H), 7.16 (d, $J = 8.0$ Hz, 1H), 7.12 (d, $J = 8.0$, 1.6 Hz, 1H), 5.52 (d, $J = 1.2$ Hz, 1H), 5.24 (d, $J = 1.2$ Hz, 1H), 3.85 (AB q, $J = 15.2$ Hz, 2H), 2.45 (s, 3H), 2.31 (s, 3H)

¹³C NMR (100 MHz, CDCl_3) δ 144.4, 141.4, 141.1, 138.1, 137.1, 136.2, 133.8, 133.4, 131.9, 130.0, 129.5, 129.0, 128.9, 128.8, 118.4, 101.9, 59.7, 21.7, 20.6

HRMS calcd for $\text{C}_{23}\text{H}_{22}\text{INO}_4\text{S}_2$ (M+H) 568.0114 ; found 568.0131.



N-(5-fluoro-2-iodophenyl)-4-methyl-*N*-(3-tosylprop-1-en-2-yl)benzenesulfonamide (**7g**)

White solid, 416 mg, 71%

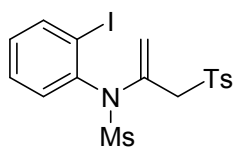
Melting point: 114-115 °C

IR (KBr) ν_{\max} : 3099, 1589, 1460, 1354, 1292, 1159, 815, 580, 518 cm^{-1}

^1H NMR (400 MHz, CDCl_3) δ 7.78 (dd, $J = 8.8, 6.0$ Hz, 1H), 7.73 (d, $J = 8.4$ Hz, 2H), 7.57 (d, $J = 8.4$ Hz, 2H), 7.33 (d, $J = 8.0$ Hz, 2H), 7.24 (d, $J = 8.0$ Hz, 2H), 6.99 (dd, $J = 8.8, 3.2$ Hz, 1H), 6.85 (ddd, $J = 8.8, 7.6, 3.2$ Hz, 1H), 5.53 (s, $J = 1.6$ Hz, 1H), 5.35 (s, $J = 1.6$ Hz, 1H), 3.84 (AB q, $J = 15.6$ Hz, 2H), 2.46 (s, 3H), 2.42 (s, 3H)

^{13}C NMR (100 MHz, CDCl_3) δ 162.7 (d, $J = 251.2$ Hz), 144.9 (d, $J = 20.9$ Hz), 141.4, 141.3 (d, $J = 8.3$ Hz), 135.8, 135.1, 133.4, 129.8, 129.7, 128.9, 128.7, 119.8 (d, $J = 22.8$ Hz), 119.3, 118.2 (d, $J = 21.6$ Hz), 95.7 (d, $J = 3.9$ Hz), 59.9, 21.8, 21.7.

HRMS calcd for $\text{C}_{23}\text{H}_{21}\text{FINO}_4\text{S}_2$ (M+H) 586.0019 ; found 586.0026,



N-(2-iodophenyl)-*N*-(3-tosylprop-1-en-2-yl)methanesulfonamide (**7h**) [Spectroscopic data is in agreement with the previous report]⁴

White solid, 354 mg, 72%

Melting point: 133-135 °C (Lit. 134-136 °C)^{10b}

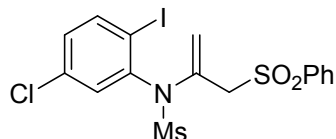
IR (KBr) ν_{\max} : 2922, 1629, 1595, 1462, 1334, 1309, 1286, 1147, 765, 516 cm^{-1}

^1H NMR (400 MHz, CDCl_3) δ 7.91 (d, $J = 8.0$ Hz, 1H), 7.76 (d, $J = 8.0$ Hz, 2H), 7.61 (d, $J = 8.0$ Hz, 1H), 7.44 (t, $J = 8.0$ Hz, 1H), 7.34 (d, $J = 8.4$ Hz, 2H), 7.09 (t, $J = 7.6$ Hz, 1H), 5.83 (s, 1H), 5.11 (s, 1H), 3.66 (AB q, $J = 15.2$ Hz, 2H), 3.38 (s, 1H), 2.44 (s, 3H)

^{13}C NMR (100 MHz, CDCl_3) δ 145.3, 141.0, 139.6, 135.4, 132.7, 132.5, 130.8, 130.0, 129.6, 128.5, 116.9, 102.3, 59.7, 41.2, 21.7.

HRMS calcd for $\text{C}_{17}\text{H}_{18}\text{INO}_4\text{S}_2$ (M+H) 491.9800; found 491.9811.

⁴ S. Undeela, G. Ravikumar, J. B. Nanubolu, K. K. Singarapu and R. S. Menon, *Chem. Commun.*, 2016, **52**, 4824-4827.



N-(5-chloro-2-iodophenyl)-*N*-(3-(phenylsulfonyl)prop-1-en-2-yl)methanesulfonamide (**7i**)

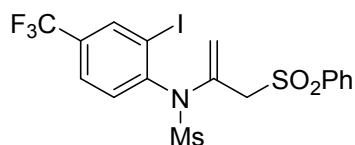
Pale yellow oil, 399 mg, 78%

IR (KBr) ν_{\max} : 2931, 1579, 1469, 1315, 1149, 746, 518 cm^{-1}

^1H NMR (400 MHz, CDCl_3) δ 7.88-7.86 (m, 3H), 7.67 (t, $J = 7.6$ Hz, 1H), 7.58-7.51 (m, 3H), 7.42-7.39 (m, 1H), 5.84 (s, 1H), 5.16 (s, 1H), 3.68 (AB q, $J = 15.2$ Hz, 2H), 3.37 (s, 3H)

^{13}C NMR (100 MHz, CDCl_3) δ 140.3, 138.4, 138.3, 136.0, 134.3, 132.9, 132.4, 129.9, 129.5, 128.5, 117.5, 102.5, 59.6, 41.3.

HRMS calcd for $\text{C}_{16}\text{H}_{15}\text{ClINO}_4\text{S}_2$ (M+H) 511.9254; found 511.9250.



N-(2-iodo-4-(trifluoromethyl)phenyl)-*N*-(3-(phenylsulfonyl)prop-1-en-2-yl)methanesulfonamide (**7j**)

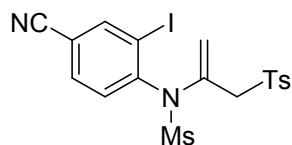
Brown viscous oil, 371 mg, 68%

Melting point: **IR (KBr)** ν_{\max} : 2933, 1600, 1446, 1315, 1126, 524 cm^{-1}

^1H NMR (400 MHz, CDCl_3) δ 8.13 (s, 1H), 7.87 (d, $J = 7.6$ Hz, 2H), 7.73-7.64 (m, 3H), 7.56 (t, $J = 7.6$ Hz, 2H), 5.88 (s, 1H), 5.21 (s, 1H), 3.67 (AB q, $J = 15.2$ Hz, 2H), 3.40 (s, 3H)

^{13}C NMR (100 MHz, CDCl_3) δ 143.1, 138.3, 137.9 (q, $J = 3.7$ Hz), 134.4, 132.7, 132.5 (q, $J = 33.2$ Hz), 132.2, 129.5, 128.4, 126.6, (q, $J = 3.3$ Hz), 123.7, 121.0, 118.0, 102.3, 59.7, 41.5.

HRMS calcd for $\text{C}_{17}\text{H}_{15}\text{F}_3\text{INO}_4\text{S}_2$ (M+H) 545.9518; found 545.9517.



N-(4-cyano-2-iodophenyl)-*N*-(3-tosylprop-1-en-2-yl)methanesulfonamide (**7k**)

Yellow solid, 325 mg, 63%

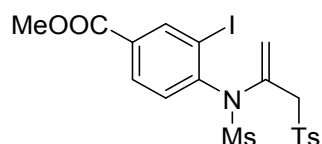
Melting point: 116-117 $^{\circ}\text{C}$

IR (KBr) ν_{\max} : 2924, 2233, 1629, 1595, 1469, 1315, 1149, 513 cm^{-1}

^1H NMR (400 MHz, CDCl_3) δ 8.16 (s, 1H), 7.73-7.71 (m, 4H), 7.34 (d, $J = 8.4$ Hz, 2H), 5.88 (s, 1H), 5.20 (s, 1H), 3.61 (AB q, $J = 15.6$ Hz, 2H), 3.40 (s, 3H), 2.44 (s, 3H)

^{13}C NMR (100 MHz, CDCl_3) δ 145.6, 144.2, 144.0, 135.3, 133.0, 132.9, 132.1, 130.1, 128.4, 118.1, 116.2, 114.6, 102.6, 59.8, 41.5, 21.8.

HRMS calcd for $\text{C}_{18}\text{H}_{17}\text{IN}_2\text{O}_4\text{S}_2$ (M+H) 516.9753; found 516.9764.



Methyl-3-iodo-4-(N-(3-tosylprop-1-en-2-yl)methylsulfonamido)benzoate (7I)

Pale yellow solid, 379 mg, 69%

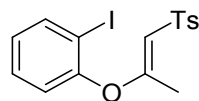
Melting point: 132-134 $^{\circ}\text{C}$

IR (KBr) ν_{\max} : 2927, 1639, 1593, 1429, 1340, 1149, 509 cm^{-1}

^1H NMR (400 MHz, CDCl_3) δ 8.55 (s, 1H), 8.08 (dt, $J = 8.4, 1.6$ Hz, 1H), 7.74 (d, $J = 8.0$ Hz, 2H), 7.66 (dd, $J = 8.4, 1.6$ Hz, 1H), 7.34 (d, $J = 8.0$ Hz, 2H), 5.88 (s, 1H), 5.20 (s, 1H), 3.94 (s, 3H), 3.65 (AB q, $J = 15.6$ Hz, 2H), 3.41 (s, 3H), 2.44 (s, 3H).

^{13}C NMR (100 MHz, CDCl_3) δ 164.7, 145.4, 143.7, 142.0, 135.4, 132.3, 132.2, 132.1, 130.6, 130.0, 128.4, 117.6, 101.9, 59.7, 52.8, 21.7.

HRMS calcd for $\text{C}_{19}\text{H}_{20}\text{INO}_6\text{S}_2$ (M+H) 549.9856; found 549.9858.



1-iodo-2-((1-tosylprop-1-en-2-yl)oxy)benzene (11a)

White solid, 265 mg, 64%

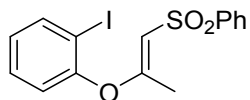
Melting point: 136-137 $^{\circ}\text{C}$

IR (KBr) ν_{\max} : 3068, 1627, 1462, 1284, 1130, 757 cm^{-1}

^1H NMR (400 MHz, CDCl_3) δ 7.91 (d, $J = 8.4$ Hz, 2H), 7.76 (dd, $J = 8.0, 1.6$ Hz, 1H), 7.30-7.25 (m, 3H), 6.92-6.88 (m, 1H), 6.85 (dd, $J = 8.0, 1.2$ Hz, 1H), 5.95 (d, $J = 0.8$ Hz, 1H), 2.39 (s, 3H), 1.75 (d, $J = 0.8$ Hz, 3H).

^{13}C NMR (100 MHz, CDCl_3) δ 161.7, 153.5, 143.8, 139.8, 139.5, 129.8, 129.4, 128.3, 127.1, 121.0, 113.7, 89.4, 21.6, 19.1.

HRMS calcd for $\text{C}_{16}\text{H}_{15}\text{IO}_3\text{S}$ (M+H) 414.9865; found 414.9887.



1-iodo-2-((1-(phenylsulfonyl)prop-1-en-2-yl)oxy)benzene (11b)

White solid, 268 mg, 67%

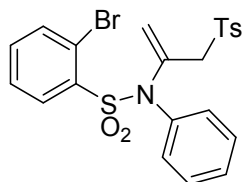
Melting point: 122-123 °C

IR (KBr) ν_{max} : 3070, 2924, 1627, 1458, 1436, 1286, 1126, 752, 567 cm^{-1}

^1H NMR (400 MHz, CDCl_3) δ 8.03 (d, $J = 7.6$ Hz, 2H), 7.76 (d, $J = 8.0$ Hz, 1H), 7.57-7.54 (m, 1H), 7.48 (t, $J = 7.2$ Hz, 2H), 7.29 (t, $J = 7.6$ Hz, 1H), 6.92 (t, $J = 7.6$ Hz, 1H), 6.84 (d, $J = 8.0$ Hz, 1H), 5.96 (s, 1H), 1.77 (s, 3H)

^{13}C NMR (100 MHz, CDCl_3) δ 162.2, 153.4, 142.4, 139.8, 132.9, 129.8, 128.8, 128.3, 127.3, 121.2, 113.0, 89.5, 19.2

HRMS calcd for $\text{C}_{15}\text{H}_{13}\text{IO}_3\text{S}$ (M+H) 400.9708; found 400.9711.



2-bromo-N-phenyl-N-(3-tosylprop-1-en-2-yl)benzenesulfonamide (15a)

White solid, 349 mg, 69%

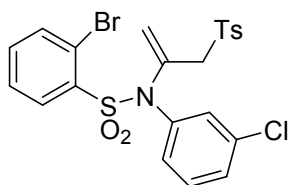
Melting point: 144-145 °C

IR (KBr) ν_{max} : 3062, 2924, 1593, 1489, 1448, 1317, 1149, 689, 513 cm^{-1}

^1H NMR (400 MHz, CDCl_3) δ 7.93 (dd, $J = 7.2, 2.4$ Hz, 1H), 7.70 (dd, $J = 7.6, 1.6$ Hz, 1H), 7.58 (d, $J = 8.4$ Hz, 2H), 7.37-7.33 (m, 2H), 7.23-7.19 (m, 7H), 5.38 (s, 1H), 5.37 (s, 1H), 4.06 (s, 2H), 2.41 (s, 3H).

^{13}C NMR (101 MHz,) δ 144.8, 137.8 (2), 135.7, 135.3, 135.1, 134.2, 133.3, 129.7, 129.5, 129.2, 128.5, 128.4, 127.4, 120.9, 119.9, 60.4, 21.6.

HRMS calcd for $\text{C}_{22}\text{H}_{20}\text{BrNO}_4\text{S}_2$ (M+H) 506.0095; found 506.0093.



2-bromo-N-(3-chlorophenyl)-N-(3-tosylprop-1-en-2-yl)benzenesulfonamide (15b)

White solid, 384 mg, 71%

Melting point: 151-152 °C

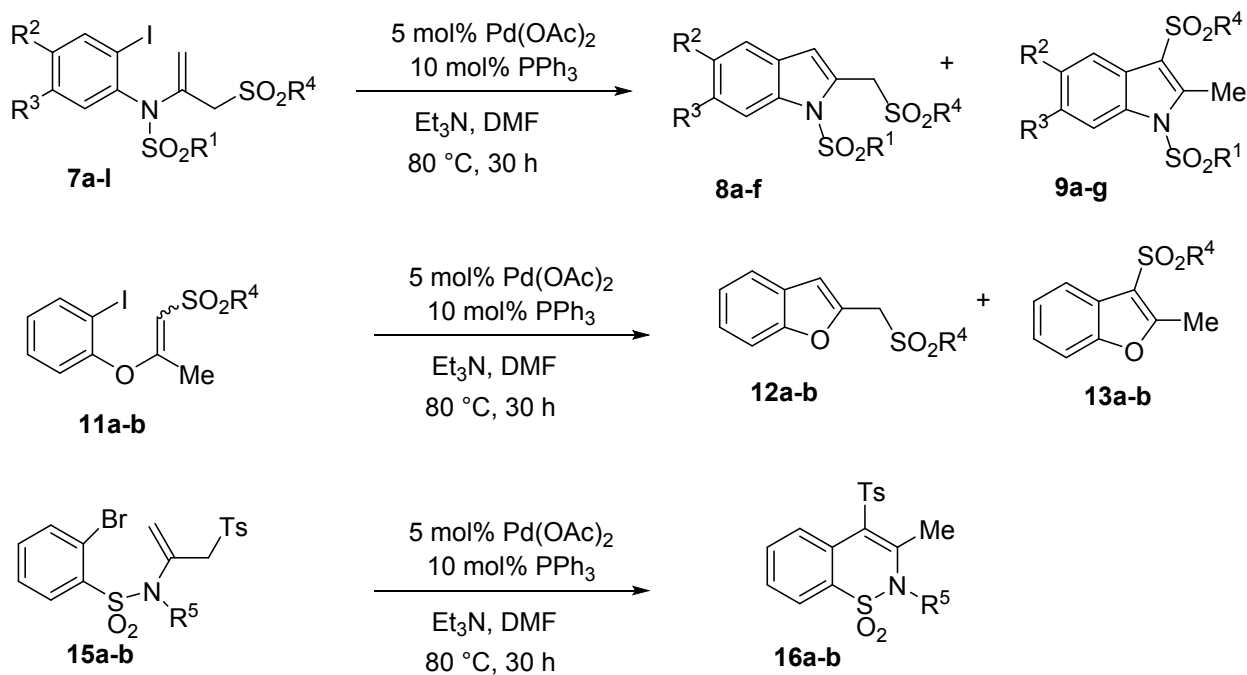
IR (KBr) ν_{max} : 3089, 2924, 1585, 1471, 1317, 1083, 684, 514 cm^{-1}

^1H NMR (400 MHz, CDCl_3) δ 7.97 (dd, $J = 6.8, 2.4$ Hz, 1H), 7.73 (d, $J = 6.8$ Hz, 1H), 7.58 (d, $J = 8.0$ Hz, 2H), 7.40 (t, $J = 4.4$ Hz, 2H), 7.26-7.23 (m, 3H), 7.17-7.13 (m, 3H), 5.50 (s, 1H), 5.35 (s, 1H), 4.08 (s, 2H), 2.43 (s, 3H)

^{13}C NMR (100 MHz, CDCl_3) δ 145.0, 139.0, 137.5, 135.8, 135.1, 134.9, 134.5 (2), 133.3, 129.9, 129.7, 129.3, 128.5, 128.4, 127.5 (2), 121.5, 120.8, 60.4, 21.7.

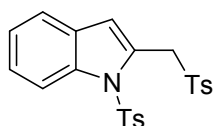
HRMS calcd for $\text{C}_{22}\text{H}_{19}\text{BrClNO}_4\text{S}_2$ (M+H) 539.9706; found 539.9700.

General procedure B: Intramolecular Heck coupling reaction of 7, 11 and 15



The halo alkenes (**7**, **11** or **15**) (0.4 mmol), $\text{Pd}(\text{OAc})_2$ (5 mg, 5 mol%), PPh_3 (11 mg, 10 mol%) and triethylamine (0.17 ml, 1.2 mmol) were suspended in DMF (4 ml) in a reaction tube. The

mixture was heated at 80 °C in an oil bath for 30 h with stirring. Upon completion of reaction, the reaction mixture was diluted with saturated NH₄Cl (20 ml) and product was extracted with ethyl acetate (3×15 ml). The combined organic layer was washed with brine, dried over sodium sulfate and concentrated at rotavapor under reduced pressure. The residue was subjected to column chromatography on silica gel using petroleum ether-ethyl acetate as eluent to afford analytically pure sample of the products.



1-tosyl-2-(tosylmethyl)-1H-indole (8a)

White solid, 28 mg, 16%

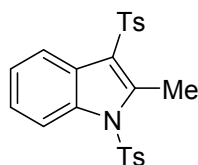
Melting point: 139-140 °C

IR (KBr) ν_{\max} : 2935, 1593, 1490, 1446, 1367, 1309, 1147, 813, 651 cm⁻¹

¹H NMR (400 MHz, CDCl₃) δ 7.94 (d, *J* = 8.4 Hz, 1H), 7.66 (d, *J* = 8.0 Hz, 2H), 7.55 (d, *J* = 8.0 Hz, 2H), 7.48 (d, *J* = 7.6 Hz, 1H), 7.30-7.20 (m, 4H), 7.14 (d, *J* = 8.4 Hz, 2H), 6.89 (s, 1H), 5.03 (s, 2H), 2.42 (s, 3H), 2.29 (s, 3H)

¹³C NMR (100 MHz, CDCl₃) δ 145.2, 145.1, 137.3, 135.4, 135.1, 129.9, 129.7, 129.2, 128.8, 127.6, 126.5, 125.4, 124.1, 121.3, 116.1, 115.2, 55.1, 21.8, 21.6

HRMS calcd for C₂₃H₂₁NO₄S₂ (M+H) 440.0990; found 440.0990.



2-methyl-1,3-ditosyl-1H-indole (9a)

White solid, 113 mg, 64%

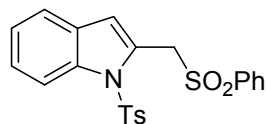
Melting point: 176-178 °C

IR (KBr) ν_{\max} : 2922, 1593, 1543, 1442, 1371, 1153, 715, 534 cm⁻¹

¹H NMR (400 MHz, CDCl₃) δ 8.22-8.19 (m, 1H), 8.11-8.09 (m, 1H), 7.80 (d, *J* = 8.0 Hz, 2H), 7.69 (d, *J* = 8.4 Hz, 2H), 7.34-7.31 (m, 2H), 7.25 (d, *J* = 8.0 Hz, 4H), 2.97 (s, 3H), 2.37 (s, 3H), 2.36 (s, 3H)

^{13}C NMR (100 MHz, CDCl_3) δ 146.1, 144.2, 142.3, 139.8, 135.6, 135.4, 130.3, 129.9, 126.7, 126.5, 125.5, 125.4, 124.8, 120.4, 119.9, 114.4, 21.7, 21.6, 13.1

HRMS calcd for $\text{C}_{23}\text{H}_{21}\text{NO}_4\text{S}_2$ (M+H) 440.0990 ; found 440.1000.



2-((phenylsulfonyl)methyl)-1-tosyl-1H-indole (8b)

White solid, 27 mg, 16%

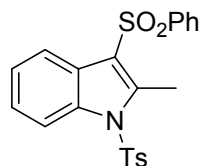
Melting point: 118-119 °C

IR (KBr) ν_{max} : 3014, 2947, 1565, 1448, 1361, 1300, 1145, 736, 538 cm^{-1}

^1H NMR (400 MHz, CDCl_3) δ 7.93 (d, $J = 8.4$ Hz, 1H), 7.78 (d, $J = 8.0$ Hz, 2H), 7.64 (t, $J = 7.6$ Hz, 1H), 7.54 (d, $J = 8.4$ Hz, 2H), 7.49-7.45 (m, 3H), 7.30-7.22 (m, 2H), 7.13 (d, $J = 8.4$ Hz, 2H), 6.90 (s, 1H), 5.05 (s, 2H), 2.29 (s, 3H)

^{13}C NMR (100 MHz, CDCl_3) δ 145.2, 138.3, 137.3, 135.0, 134.1, 129.9, 129.2, 129.1, 128.8, 127.4, 126.5, 125.5, 124.1, 121.3, 116.3, 115.2, 55.2, 21.6.

HRMS calcd for $\text{C}_{22}\text{H}_{19}\text{NO}_4\text{S}_2$ (M+H) 426.0834 ; found 426.0838



2-methyl-3-(phenylsulfonyl)-1-tosyl-1H-indole (9b)

White solid, 106 mg, 62%

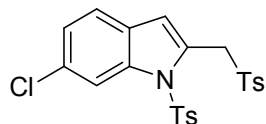
Melting point: 164-165 °C

IR (KBr) ν_{max} : 3057, 1544, 1442, 1373, 1313, 1182, 700, 542 cm^{-1}

^1H NMR (400 MHz, CDCl_3) δ 8.23-8.21 (m, 1H), 8.12-8.10 (m, 1H), 7.92 (d, $J = 8.2$ Hz, 2H), 7.69 (d, $J = 8.2$ Hz, 2H), 7.56-7.52 (m, 1H), 7.48-7.45 (m, 2H), 7.36-7.33 (m, 2H), 7.26 (d, $J = 8.1$ Hz, 2H), 2.98 (s, 3H), 2.38 (s, 3H).

^{13}C NMR (100 MHz, CDCl_3) δ 146.1, 142.7, 142.6, 135.6, 135.4, 133.2, 130.4, 129.3, 126.7, 126.4, 125.6, 125.4, 124.9, 120.4, 119.5, 114.5, 21.7, 13.1

HRMS calcd for $\text{C}_{22}\text{H}_{19}\text{NO}_4\text{S}_2$ (M+H) 426.0834; found 426.0838



6-chloro-1-tosyl-2-(tosylmethyl)-1H-indole (8c)

White solid, 27mg, 14%

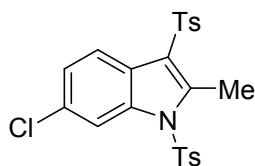
Melting point: 127-129 °C

IR (KBr) ν_{\max} : 3107, 2924, 1563, 1452, 1369, 1317, 1153, 536 cm^{-1}

^1H NMR (400 MHz, CDCl_3) δ 7.99 (d, $J = 1.6$ Hz, 1H), 7.65 (d, $J = 8.4$ Hz, 2H), 7.56 (d, $J = 8.4$ Hz, 2H), 7.40 (d, $J = 8.4$ Hz, 1H), 7.28 (d, $J = 8.0$ Hz, 2H), 7.22 (dd, $J = 8.4, 2.0$ Hz, 1H), 7.18 (d, $J = 8.0$ Hz, 2H), 6.88 (s, 1H), 4.99 (s, 2H), 2.44 (s, 3H), 2.32 (s, 3H)

^{13}C NMR (100 MHz, CDCl_3) δ 145.6, 145.3, 137.6, 135.3, 134.9, 131.5, 130.0, 129.8, 128.7, 128.3, 127.6, 126.5, 124.8, 122.0, 115.4, 115.3, 55.0, 21.8, 21.6

HRMS calcd for $\text{C}_{23}\text{H}_{20}\text{ClNO}_4\text{S}_2$ (M+H) 474.0601; found 474.0610.



6-chloro-2-methyl-1,3-ditosyl-1H-indole (9c)

White solid, 131 mg, 69%

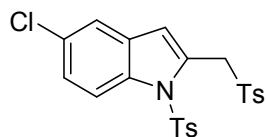
Melting point: 194-196 °C

IR (KBr) ν_{\max} : 2922, 1544, 1417, 1373, 1311, 1151, 761, 535 cm^{-1}

^1H NMR (400 MHz, CDCl_3) δ 8.25 (d, $J = 1.6$ Hz, 1H), 8.02 (d, $J = 8.8$ Hz, 1H), 7.77 (d, $J = 8.4$ Hz, 2H), 7.68 (d, $J = 8.4$ Hz, 2H), 7.31-7.24 (m, 5H), 2.92 (s, 3H), 2.39 (s, 3H), 2.36 (s, 3H).

^{13}C NMR (100 MHz, CDCl_3) δ 146.4, 144.4, 142.8, 139.5, 135.9, 135.1, 131.7, 130.5, 130.0, 126.7, 126.5, 125.5, 124.0, 121.2, 119.8, 114.6, 21.8, 21.6, 13.1.

HRMS calcd for $\text{C}_{23}\text{H}_{20}\text{ClNO}_4\text{S}_2$ (M+H) 474.0601; found 474.0608.



5-chloro-1-tosyl-2-(tosylmethyl)-1H-indole (8d)

White solid, 25 mg, 13%

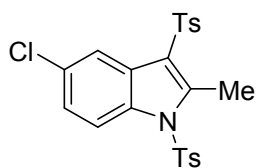
Melting point: 135-136 °C

IR (KBr) ν_{\max} : 2922, 1595, 1442, 1371, 1317, 1155, 715, 536 cm^{-1}

^1H NMR (400 MHz, CDCl_3) δ 7.87 (d, $J = 8.8$ Hz, 1H), 7.65 (d, $J = 8.4$ Hz, 2H), 7.53 (d, $J = 8.0$ Hz, 2H), 7.44 (d, $J = 2.0$ Hz, 1H), 7.27 (d, $J = 8.0$ Hz, 2H), 7.23 (dd, $J = 8.8, 2.0$ Hz, 1H), 7.15 (d, $J = 8.4$ Hz, 2H), 6.81 (s, 1H), 5.00 (s, 2H), 2.42 (s, 3H), 2.30 (s, 3H)

^{13}C NMR (100 MHz, CDCl_3) δ 145.5, 145.3, 135.6, 135.3, 134.9, 130.3, 130.0, 129.9, 129.8, 129.2, 128.8, 126.5, 125.7, 120.8, 116.2, 115.1, 55.0, 21.8, 21.6.

HRMS calcd for $\text{C}_{23}\text{H}_{20}\text{ClNO}_4\text{S}_2$ (M+H) 474.0601; found 474.0616.



5-chloro-2-methyl-1,3-ditosyl-1H-indole (9d)

White solid, 129 mg, 68%

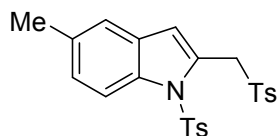
Melting point: 188-189 °C

IR (KBr) ν_{\max} : 2924, 1541, 1436, 1373, 1315, 1149, 759, 532 cm^{-1}

^1H NMR (400 MHz, CDCl_3) δ 8.13 (d, $J = 8.8$ Hz, 1H), 8.11 (d, $J = 2.0$ Hz, 1H), 7.78 (d, $J = 8.4$ Hz, 2H), 7.66 (d, $J = 8.4$ Hz, 2H), 7.31-7.25 (m, 5H), 2.93 (s, 3H), 2.38 (s, 3H), 2.37 (s, 3H).

^{13}C NMR (100 MHz, CDCl_3) δ 146.4, 144.5, 143.5, 139.5, 135.1, 134.0, 130.8, 130.4, 130.0, 126.7, 126.5, 125.8, 120.0, 119.5, 115.5, 21.7, 21.6, 13.2

HRMS calcd for $\text{C}_{23}\text{H}_{20}\text{ClNO}_4\text{S}_2$ (M+H) 474.0601; found 474.0617.



5-methyl-1-tosyl-2-(tosylmethyl)-1H-indole (8e)

White solid, 24 mg, 13%

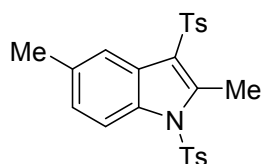
Melting point: 120-122 °C

IR (KBr) ν_{\max} : 3035, 2922, 1581, 1435, 1365, 1292, 1130, 661 cm^{-1}

¹H NMR (400 MHz, CDCl₃) δ 7.82 (d, *J* = 8.6 Hz, 1H), 7.65 (d, *J* = 8.0 Hz, 2H), 7.52 (d, *J* = 8.1 Hz, 2H), 7.27- 7.25 (m, 3H), 7.13-7.08 (m, 3H), 6.82 (s, 1H), 5.01 (s, 2H), 2.42 (s, 3H), 2.38 (s, 3H), 2.29 (s, 2H).

¹³C NMR (100 MHz, CDCl₃) δ 145.0, 135.6, 135.4, 135.1, 133.8, 129.8, 129.7, 129.4, 128.8, 127.6, 126.9, 126.5, 121.1, 116.0, 114.9, 55.2, 21.8, 21.6, 21.2

HRMS calcd for C₂₄H₂₃NO₄S₂ (M+H) 454.1147 ; found 454.1149.



2,5-dimethyl-1,3-ditosyl-1H-indole (9e)

White solid, 131 mg, 72%

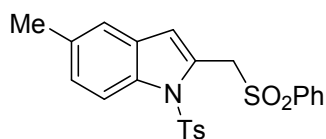
Melting point: 191-193 °C

IR (KBr) ν_{\max} : 2924, 1591, 1544, 1456, 1369, 1315, 1145, 677, 534 cm⁻¹

¹H NMR (400 MHz, CDCl₃) δ 8.07 (d, *J* = 8.8 Hz, 1H), 7.89 (d, *J* = 1.6 Hz, 1H), 7.79 (d, *J* = 8.4 Hz, 2H), 7.66 (d, *J* = 8.4 Hz, 2H), 7.25-7.22 (m, 4H), 7.15 (dd, *J* = 8.8, 1.6 Hz, 1H), 2.94 (s, 3H), 2.43 (s, 3H), 2.36 (s, 6H).

¹³C NMR (100 MHz, CDCl₃) δ 146.0, 144.1, 142.3, 139.8, 135.4, 134.6, 133.8, 130.3, 129.9, 126.9, 126.6, 126.4, 125.6, 120.1, 119.6, 114.1, 21.7, 21.6, 21.5, 13.1.

HRMS calcd for C₂₄H₂₃NO₄S₂ (M+H) 454.1147; found 454.1147.



5-methyl-2-((phenylsulfonyl)methyl)-1-tosyl-1H-indole (8f)

White solid, 26 mg, 15%

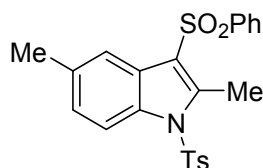
Melting point: 117-118 °C

IR (KBr) ν_{\max} : 3010, 2941, 1585, 1450, 1359, 1298, 1170, 738, 578 cm⁻¹

¹H NMR (400 MHz, CDCl₃) δ 7.81 (d, *J* = 8.8 Hz, 1H), 7.77 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.66-7.11 (m, 1H), 7.52-7.45 (m, 4H), 7.25 (s, 1H), 7.13-7.09 (m, 3H), 6.83 (s, 1H), 5.03 (s, 2H), 2.38 (s, 3H), 2.29 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 145.1, 138.2, 135.6, 135.0, 134.0, 133.8, 129.8, 129.4, 129.0, 128.9, 127.4, 127.0, 126.4, 121.1, 116.2, 114.9, 55.2, 21.6, 21.1.

HRMS calcd for C₂₃H₂₁NO₄S₂ (M+H) 440.0990; found 440.1004.



2,5-dimethyl-3-(phenylsulfonyl)-1-tosyl-1H-indole (9f)

White solid, 121 mg, 69%

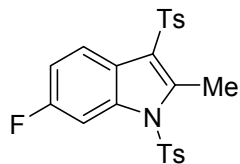
Melting point: 172-173 °C

IR (KBr) ν_{\max} : 2924, 1593, 1544, 1444, 1373, 1313, 1147, 678, 538 cm⁻¹

¹H NMR (400 MHz, CDCl₃) δ 8.07 (d, *J* = 8.4 Hz, 1H), 7.92-7.89 (m, 3H), 7.67 (d, *J* = 8.4 Hz, 2H), 7.55-7.51 (m, 1H), 7.48-7.44 (m, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 7.16 (dd, *J* = 8.8, 1.6 Hz, 1H), 2.94 (s, 3H), 2.43 (s, 3H), 2.37 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 146.0, 142.7, 142.6, 135.4, 134.7, 133.8, 133.2, 130.3, 129.2, 127.0, 126.6, 126.4, 125.6, 120.1, 119.2, 114.1, 21.7, 21.5, 13.1.

HRMS calcd for C₂₃H₂₁NO₄S₂ (M+H) 440.0990; found 440.1005.



6-fluoro-2-methyl-1,3-ditosyl-1H-indole (9g)

White solid, 111 mg, 61%

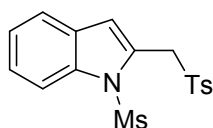
Melting point: 187-188 °C

IR (KBr) ν_{\max} : 2922, 1591, 1546, 1483, 1373, 1317, 1149, 806, 532 cm⁻¹

¹H NMR (400 MHz, CDCl₃) δ 8.05 (dd, *J* = 8.8, 5.6 Hz, 1H), 7.96 (dd, *J* = 10.4, 2.0 Hz, 1H), 7.78 (d, *J* = 8.0 Hz, 2H), 7.69 (d, *J* = 8.0 Hz, 2H), 7.27 (t, *J* = 8.4 Hz, 4H), 7.09 (td, *J* = 8.8, 2.0 Hz, 1H), 2.93 (s, 3H), 2.39 (s, 3H), 2.36 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 161.1 (d, *J* = 243 Hz), 146.4, 144.4, 142.6 (d, *J* = 4.2 Hz), 139.6, 135.8 (d, *J* = 12.5 Hz), 135.1, 130.5, 130.0, 126.7, 126.5, 121.7, 121.4 (d, *J* = 2.5 Hz), 119.7, 113.2 (d, *J* = 24.0 Hz), 102.0 (d, *J* = 30.0 Hz), 21.7, 21.6, 13.1

HRMS calcd for C₂₃H₂₀FNO₄S₂ (M+H) 458.0896; found 458.0921.



1-(methylsulfonyl)-2-(tosylmethyl)-1H-indole (8g)

White solid, 108 mg, 74%

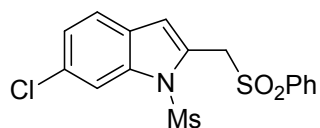
Melting point: 146-147 °C

IR (KBr) ν_{\max} : 3014, 2926, 1565, 1446, 1355, 1309, 1151, 536 cm⁻¹

¹H NMR (400 MHz, CDCl₃) δ 7.94 (d, *J* = 8.4 Hz, 1H), 7.79 (d, *J* = 8.0 Hz, 2H), 7.56 (d, *J* = 7.6 Hz, 1H), 7.37-7.34 (m, 3H), 7.30 (d, *J* = 7.6 Hz, 1H), 6.65 (s, 1H), 4.97 (s, 2H), 3.42 (s, 3H), 2.46 (s, 3H)

¹³C NMR (100 MHz, CDCl₃) δ 145.3, 147.0, 135.9, 130.0, 128.5, 126.7, 125.6, 123.8, 121.5, 114.4, 114.0, 54.8, 41.2, 21.8.

HRMS calcd for C₁₇H₁₇NO₄S₂ (M+H) 364.0677; found 364.0681.



6-chloro-1-(methylsulfonyl)-2-((phenylsulfonyl)methyl)-1H-indole (8h)

White solid, 112 mg, 73%

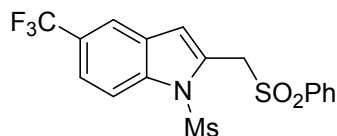
Melting point: 186-187 °C

IR (KBr) ν_{\max} : 2953, 1583, 1444, 1361, 1309, 1161, 543 cm⁻¹

¹H NMR (400 MHz, CDCl₃) δ 7.92 (d, *J* = 7.6 Hz, 2H), 7.87 (d, *J* = 8.8 Hz, 1H), 7.70 (t, *J* = 7.6 Hz, 1H), 7.59 (t, *J* = 7.6 Hz, 2H), 7.53 (s, 1H), 7.34 (dd, *J* = 7.2, 1.6 Hz, 1H), 6.58 (s, 1H), 4.98 (s, 2H), 3.43 (s, 3H).

^{13}C NMR (100 MHz, CDCl_3) δ 138.6, 135.3, 134.4, 129.7, 129.6, 129.5, 128.5, 127.9, 125.9, 121.0, 115.1, 113.7, 54.6, 41.5.

HRMS calcd for $\text{C}_{16}\text{H}_{14}\text{ClNO}_4\text{S}_2$ (M+H) 384.0131; found 384.0149.



1-(methylsulfonyl)-2-((phenylsulfonyl)methyl)-5-(trifluoromethyl)-1H-indole (8i)

White solid, 102 mg, 61%

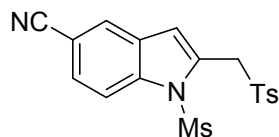
Melting point: 204-205 °C

IR (KBr) ν_{max} : 3008, 2953, 1620, 1448, 1356, 1313, 1159, 542 cm^{-1}

^1H NMR (400 MHz, CDCl_3) δ 8.06 (d, J = 8.8 Hz, 1H), 7.93 (d, J = 8.4 Hz, 2H), 7.86 (d, J = 0.8 Hz, 1H), 7.73-7.69 (m, 1H), 7.63-7.58 (m, 3H), 6.71 (s, 1H), 5.02 (s, 2H), 3.49 (s, 3H).

^{13}C NMR (100 MHz, CDCl_3) δ 138.6, 138.4, 134.4, 129.5, 128.6, 128.5, 128.1, 126.4 (q, J = 32.5 Hz), 125.7, 123.0, 122.3 (q, J = 3.1 Hz), 119.0 (q, J = 4.1 Hz), 114.5, 114.2, 54.6, 41.8

HRMS calcd for $\text{C}_{17}\text{H}_{14}\text{F}_3\text{NO}_4\text{S}_2$ (M+H) 418.0395; found 418.0415.



1-(methylsulfonyl)-2-(tosylmethyl)-1H-indole-5-carbonitrile (8j)

White solid, 90 mg, 58%

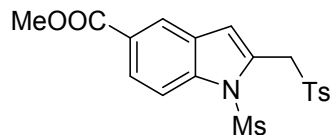
Melting point: 180-181 °C

IR (KBr) ν_{max} : 3020, 2926, 2223, 1595, 1456, 1363, 1303, 1138, 509 cm^{-1}

^1H NMR (400 MHz, CDCl_3) δ 8.05 (d, J = 8.4 Hz, 1H), 7.91 (d, J = 1.6 Hz, 1H), 7.80 (d, J = 8.0 Hz, 2H), 7.63 (dd, J = 8.4, 1.6 Hz, 1H), 7.39 (d, J = 8.0 Hz, 2H), 6.69 (s, 1H), 4.98 (s, 2H), 3.53 (s, 3H), 2.48 (s, 3H).

^{13}C NMR (100 MHz, CDCl_3) δ 145.7, 138.6, 135.5, 130.2, 129.4, 128.5, 128.4, 128.3, 126.3, 119.0, 115.0, 113.5, 107.6, 54.6, 42.0, 21.8.

HRMS calcd for $\text{C}_{18}\text{H}_{16}\text{N}_2\text{O}_4\text{S}_2$ (M+H) 389.0630; found 389.0631.



Methyl-1-(methylsulfonyl)-2-(tosylmethyl)-1H-indole-5-carboxylate (8k)

White solid, 106 mg, 63%

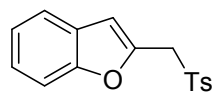
Melting point: 178-179 °C

IR (KBr) ν_{max} : 3014, 2958, 1716, 1606, 1438, 1354, 1136, 538 cm^{-1}

¹H NMR (400 MHz, CDCl₃) δ 8.29 (s, 1H), 8.08 (d, $J = 8.8$ Hz, 1H), 7.99 (d, $J = 8.8$ Hz, 1H), 7.80 (d, $J = 7.6$ Hz, 2H), 7.39 (d, $J = 7.6$ Hz, 2H), 6.68 (s, 1H), 4.99 (s, 2H), 3.95 (s, 3H), 3.51 (s, 3H), 2.48 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 167.0, 145.5, 139.4, 135.6, 130.1, 128.5, 128.3, 128.2, 126.6, 125.9, 123.7, 114.5, 113.8, 54.7, 52.3, 41.7, 21.8.

HRMS calcd for C₁₉H₁₉NO₆S₂ (M+H) 422.0732; found 422.0749.



2-(tosylmethyl)benzofuran (12a)

White solid, 72 mg, 63%

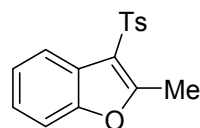
Melting point: 196-197 °C

IR (KBr) ν_{max} : 2987, 1591, 1448, 1303, 1286, 1145, 719, 520 cm^{-1}

¹H NMR (400 MHz, CDCl₃) δ 7.64 (d, $J = 8.4$ Hz, 2H), 7.53-7.51 (m, 1H), 7.37-7.35 (m, 1H), 7.29-7.27 (m, 3H), 7.22 (td, $J = 7.6, 1.2$ Hz, 1H), 6.67 (d, $J = 0.8$ Hz, 1H), 4.53 (s, 2H), 2.43 (s, 3H)

¹³C NMR (100 MHz, CDCl₃) δ 155.3, 145.3, 145.2, 135.3, 129.8, 128.6, 128.0, 125.0, 123.1, 121.3, 111.3, 108.9, 56.5, 21.7

HRMS calcd for C₁₆H₁₄O₃S (M+H) 287.0742; found 287.0746.



2-methyl-3-tosylbenzofuran (13a)

White solid, 18 mg, 16%

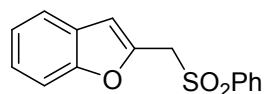
Melting point: 122-123 °C

IR (KBr) ν_{\max} : 2922, 1583, 1446, 1296, 1143, 758, 580 cm^{-1}

^1H NMR (400 MHz, CDCl_3) δ 7.90-7.85 (m, 3H), 7.42-7.39 (m, 1H), 7.31-7.28 (m, 4H), 2.80 (s, 3H), 2.38 (s, 3H).

^{13}C NMR (100 MHz, CDCl_3) δ 160.6, 153.2, 144.3, 139.7, 129.9, 126.7, 125.2, 124.4, 124.3, 120.3, 118.2, 111.2, 21.6, 13.6.

HRMS calcd for $\text{C}_{16}\text{H}_{14}\text{O}_3\text{S}$ (M+H) 287.0742; found 287.0740.



2-((phenylsulfonyl)methyl)benzofuran (12b)

White solid, 70 mg, 64%

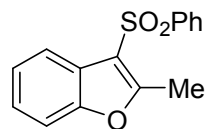
Melting point: 162-163 °C

IR (KBr) ν_{\max} : 2880, 1581, 1448, 1305, 1141, 735, 569 cm^{-1}

^1H NMR (400 MHz, CDCl_3) δ 7.76 (d, $J = 8.0\text{Hz}$, 2H), 7.63 (t, $J = 7.6\text{Hz}$, 1H), 7.52-7.45 (m, 3H), 7.33 (d, $J = 8.0\text{Hz}$, 1H), 7.24-7.19 (m, 2H), 6.63 (s, 1H), 4.54 (s, 2H).

^{13}C NMR (100 MHz, CDCl_3) δ 155.3, 145.1, 138.2, 134.1, 129.2, 128.6, 127.9, 125.0, 123.2, 121.3, 111.3, 109.0, 56.5

HRMS calcd for $\text{C}_{15}\text{H}_{12}\text{O}_3\text{S}$ (M+H) 273.0585; found 273.0589.



2-methyl-3-(phenylsulfonyl)benzofuran (13b)

White solid, 17 mg, 16%

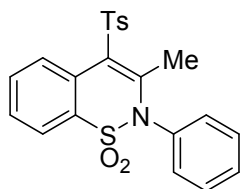
Melting point: 106-107 °C

IR (KBr) ν_{\max} : 3064, 2920, 1577, 1444, 1309, 1149, 750, 545 cm^{-1}

^1H NMR (400 MHz, CDCl_3) δ 8.00 (d, $J = 8.4\text{ Hz}$, 2H), 7.88-7.86 (m, 1H), 7.56 (t, $J = 7.8\text{ Hz}$, 1H), 7.50 (t, $J = 7.6\text{ HZ}$, 2H), 7.42-7.39 (m, 1H), 7.31-7.28 (m, 2H), 2.80 (s, 3H).

^{13}C NMR (100 MHz, CDCl_3) δ 160.9, 153.3, 142.5, 133.3, 129.3, 126.7, 125.3, 124.5, 124.4, 120.3, 117.9, 111.3, 13.7

HRMS calcd for $\text{C}_{15}\text{H}_{12}\text{O}_3\text{S}$ (M+H) 273.0585; found 273.0589.



3-methyl-2-phenyl-4-tosyl-2H-benzo[e][1,2]thiazine 1,1-dioxide (16a)

White solid, 97 mg, 57%

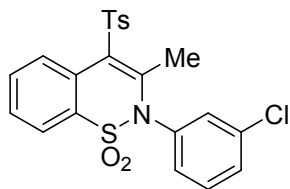
Melting point: 168-169 °C

IR (KBr) ν_{max} : 3064, 2924, 1570, 1541, 1492, 1346, 1282, 1139, 1083, 665, 565 cm^{-1}

^1H NMR (400 MHz, CDCl_3) δ 8.42 (d, $J = 8.4\text{Hz}$, 1H), 7.74 (d, $J = 8.0\text{Hz}$, 3H), 7.59 (t, $J = 4.0\text{Hz}$, 1H), 7.47 (d, $J = 7.6\text{Hz}$, 1H), 7.44-7.39 (m, 3H), 7.24 (d, $J = 8.0\text{Hz}$, 2H), 7.14-7.12 (m, 2H), 2.41 (s, 3H), 2.35 (s, 3H)

^{13}C NMR (100 MHz, CDCl_3) δ 149.7, 144.2, 139.0, 134.9, 132.3, 132.2, 129.8, 129.7, 129.6, 128.8, 128.3, 127.6, 126.9, 123.1, 122.0, 21.6, 20.7

HRMS calcd for $\text{C}_{22}\text{H}_{19}\text{NO}_4\text{S}_2$ (M+H) 426.0834; found 426.0833.



2-(3-chlorophenyl)-3-methyl-4-tosyl-2H-benzo[e][1,2]thiazine 1,1-dioxide (16b)

White solid, 109 mg, 59%

Melting point: 184-185 °C

IR (KBr) ν_{max} : 2960, 1571, 1546, 1469, 1357, 1284, 1143, 1083, 671, 565 cm^{-1}

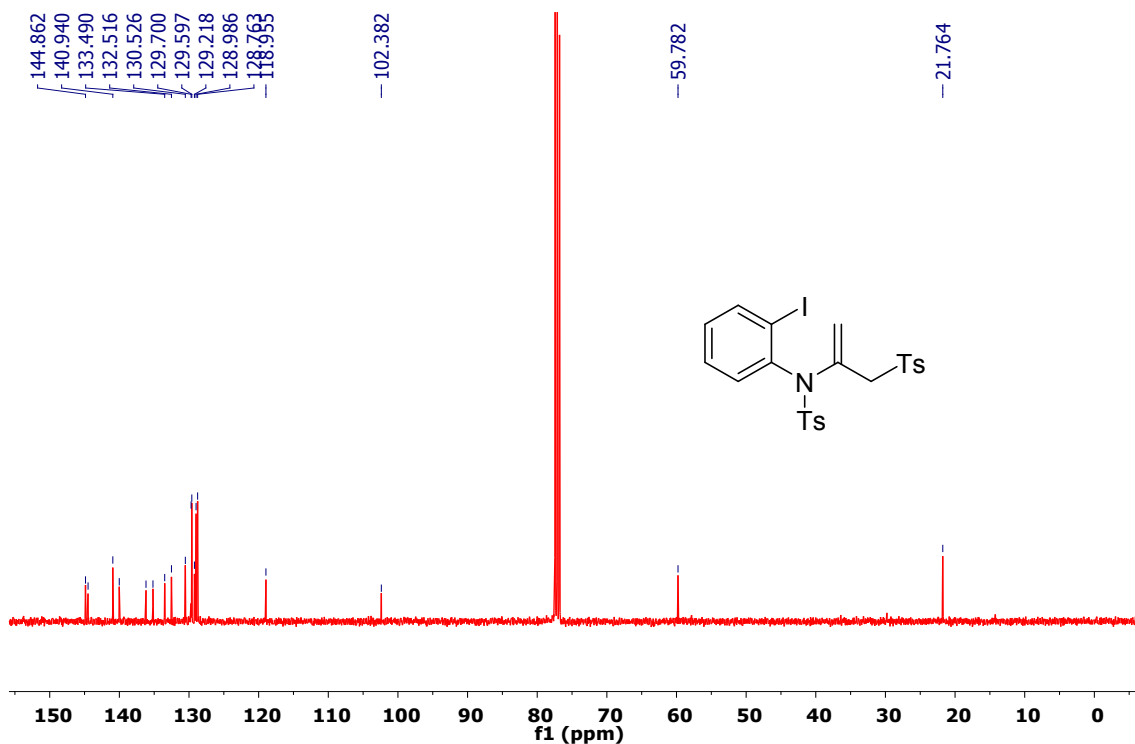
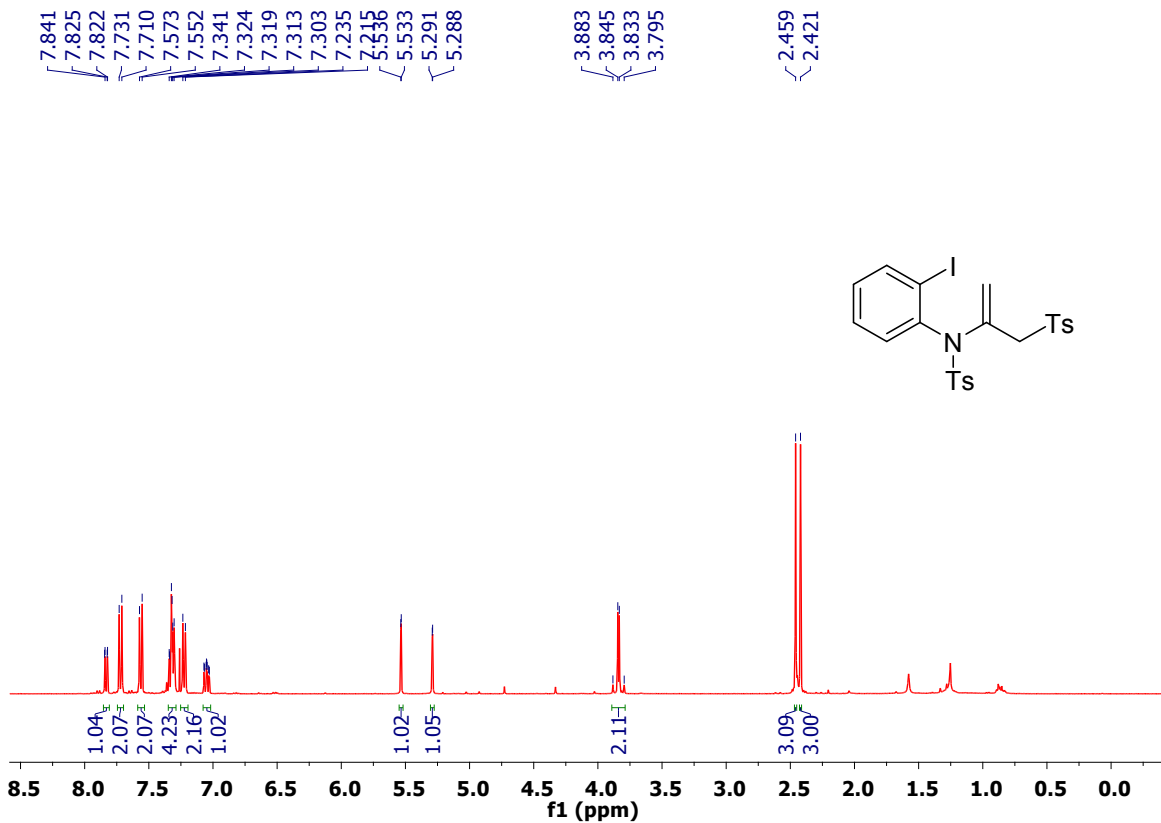
^1H NMR (400 MHz, CDCl_3) δ 8.41 (d, $J = 8.4\text{ Hz}$, 1H), 7.72 (d, $J = 8.4\text{ Hz}$, 3H), 7.61-7.57 (m, 1H), 7.46 (td, $J = 8.0, 0.8\text{ Hz}$, 1H), 7.38 (dt, $J = 8.0, 1.6\text{ Hz}$, 1H), 7.32 (t, $J = 8.0\text{ Hz}$, 1H), 7.23 (d, $J = 8.0\text{ Hz}$, 2H), 7.11 (t, $J = 2.0\text{ Hz}$, 1H), 7.05-7.02 (m, 1H), 2.41 (s, 3H), 2.34 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 149.0, 144.3, 138.7, 135.9, 135.3, 132.4, 130.5, 129.8, 129.7, 129.4, 128.8, 128.6, 127.8, 127.0, 124.0, 122.1, 21.6, 20.7.

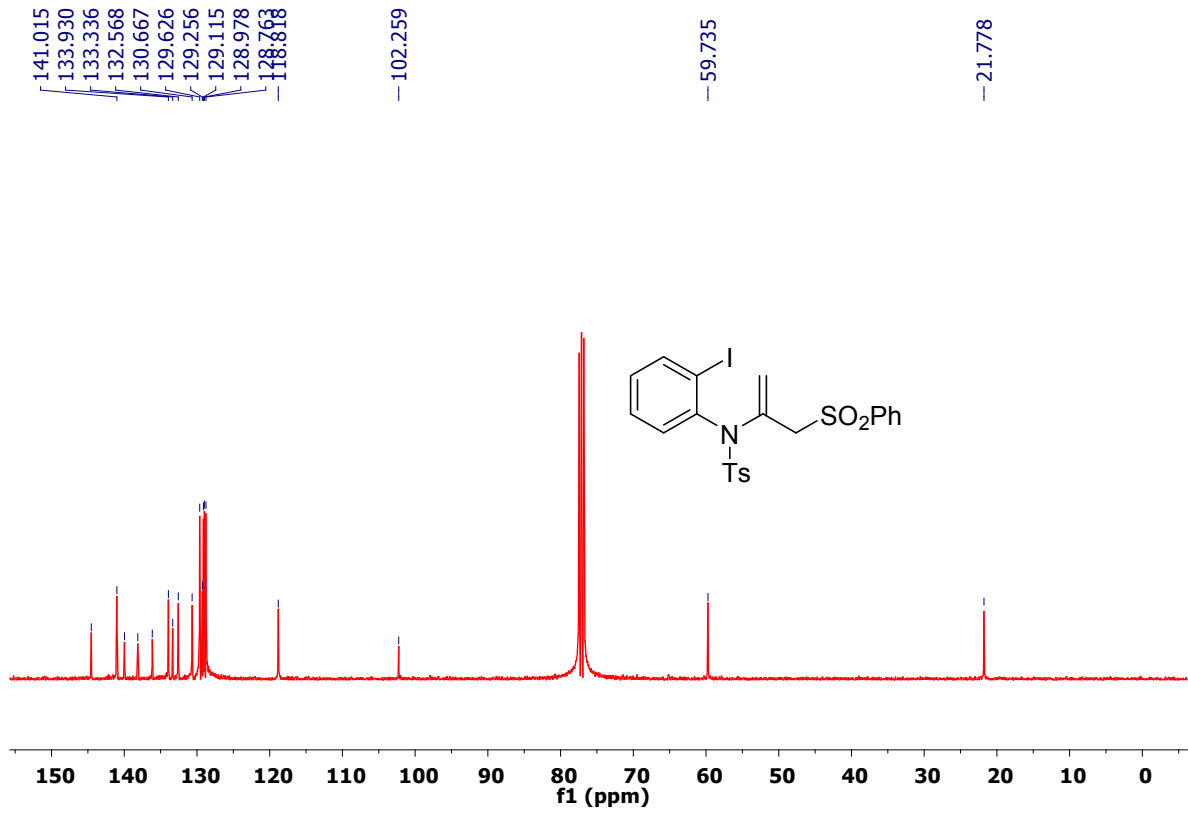
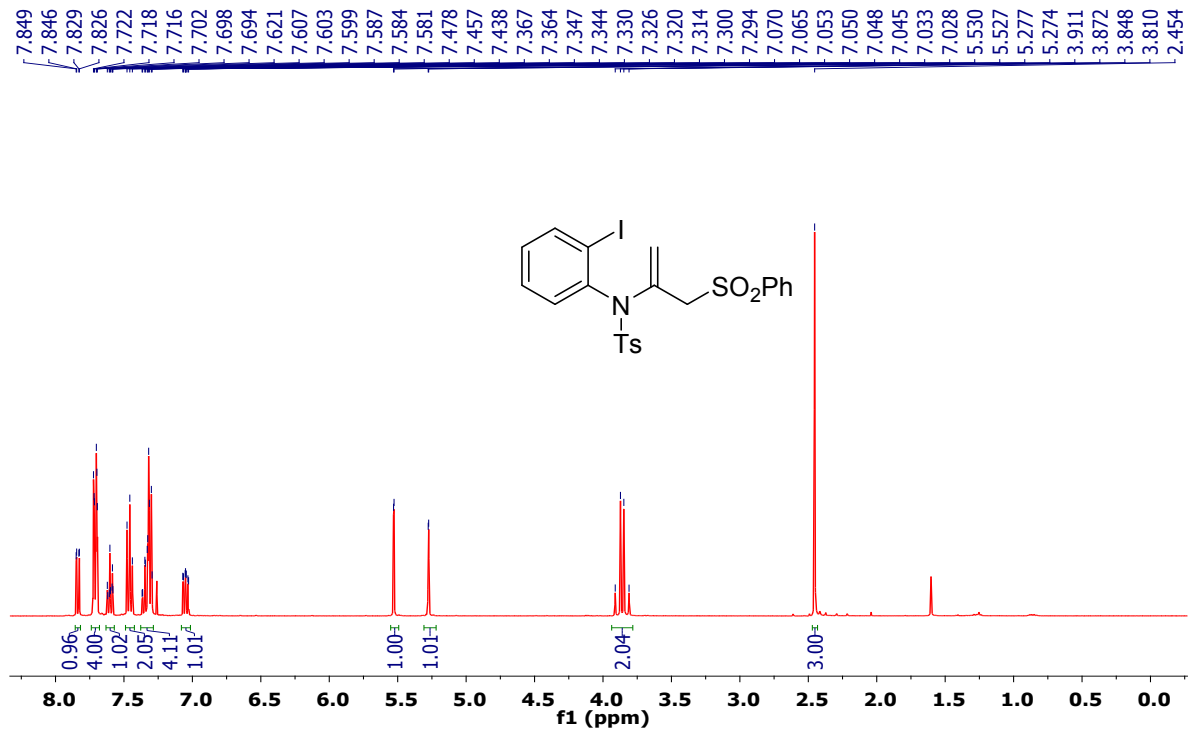
HRMS calcd for C₂₂H₁₈ClNO₄S₂ (M+H) 460.0444; found 460.0436.

NMR spectra of new compounds

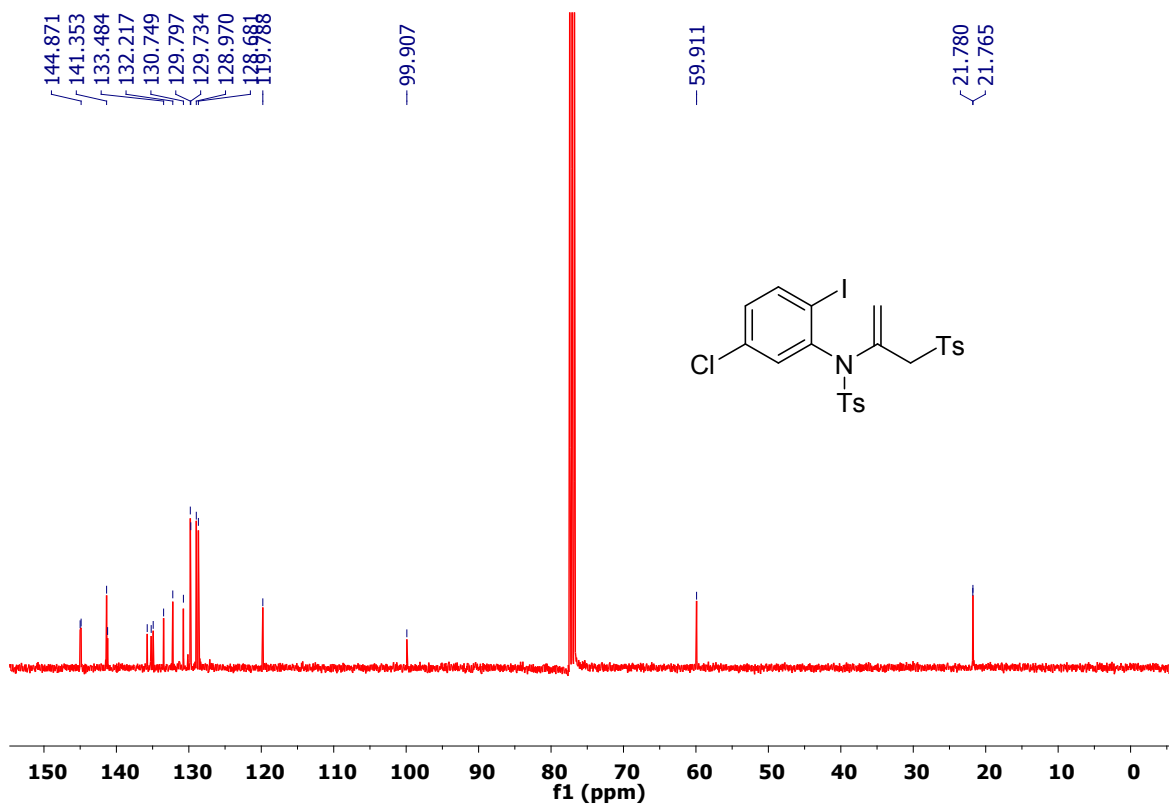
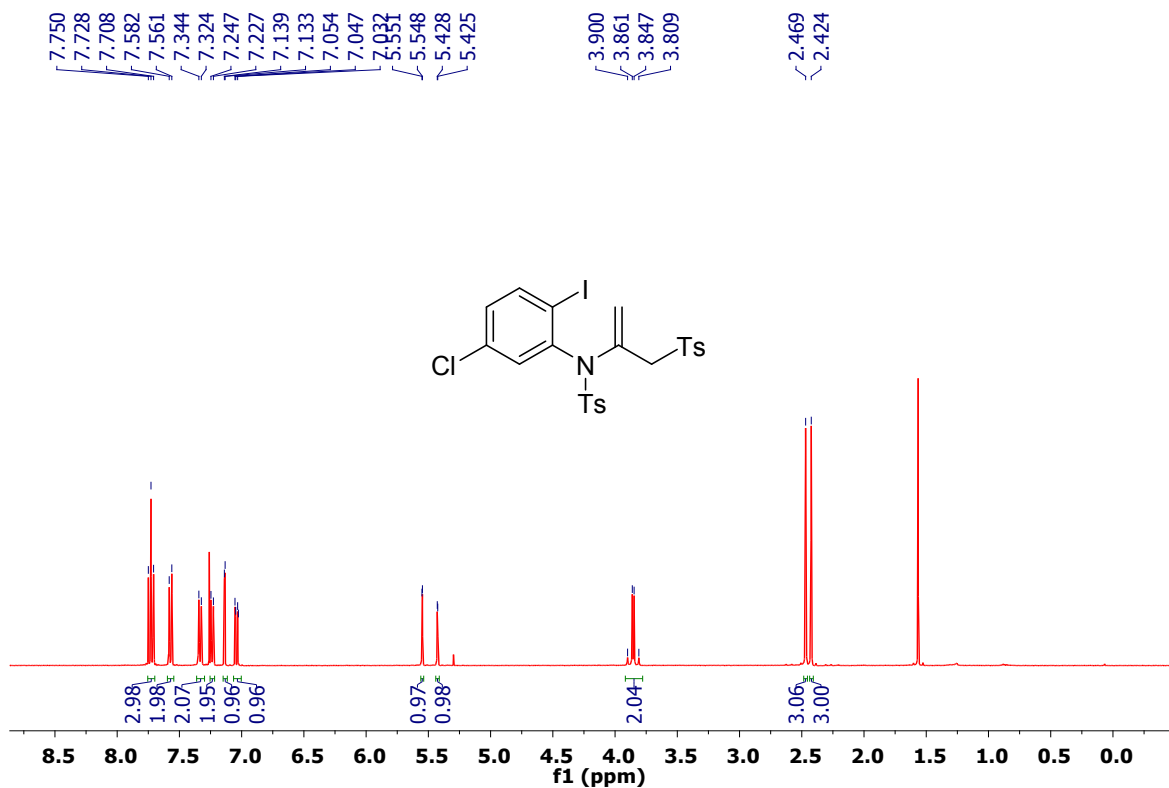
7a, CDCl₃



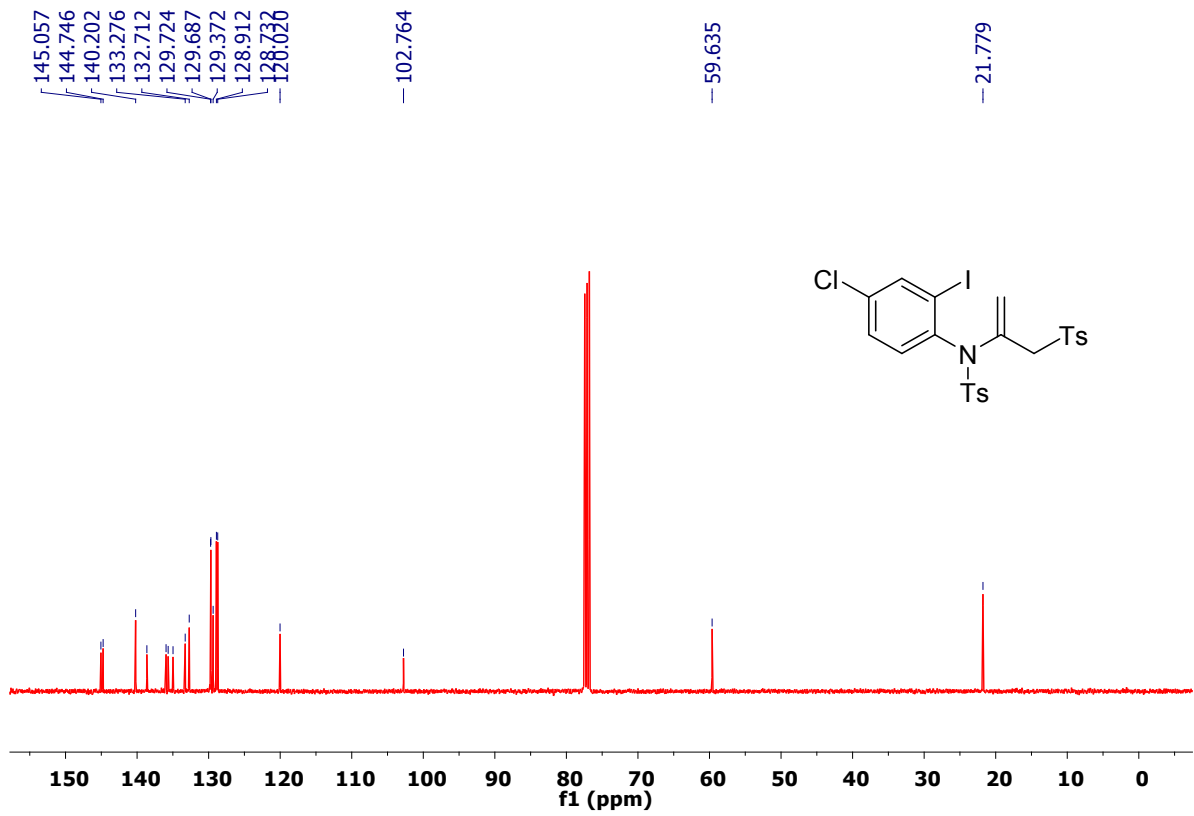
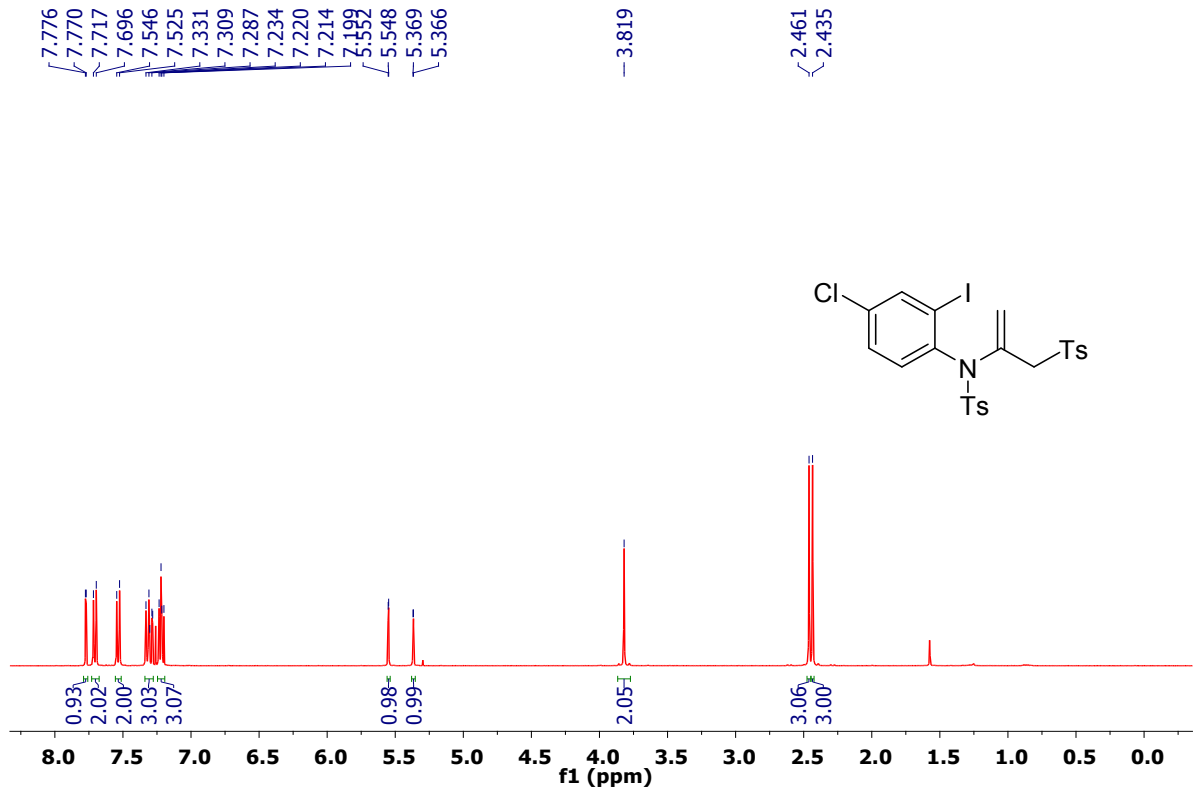
7b, CDCl₃



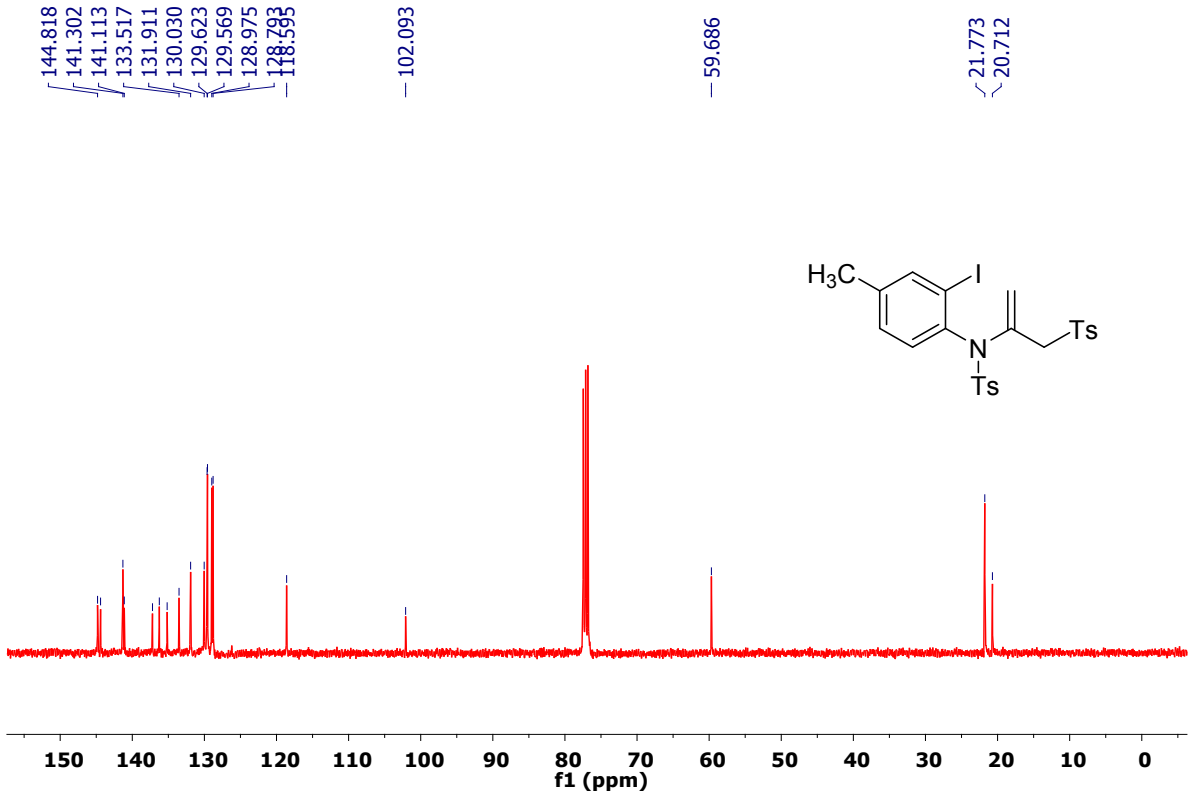
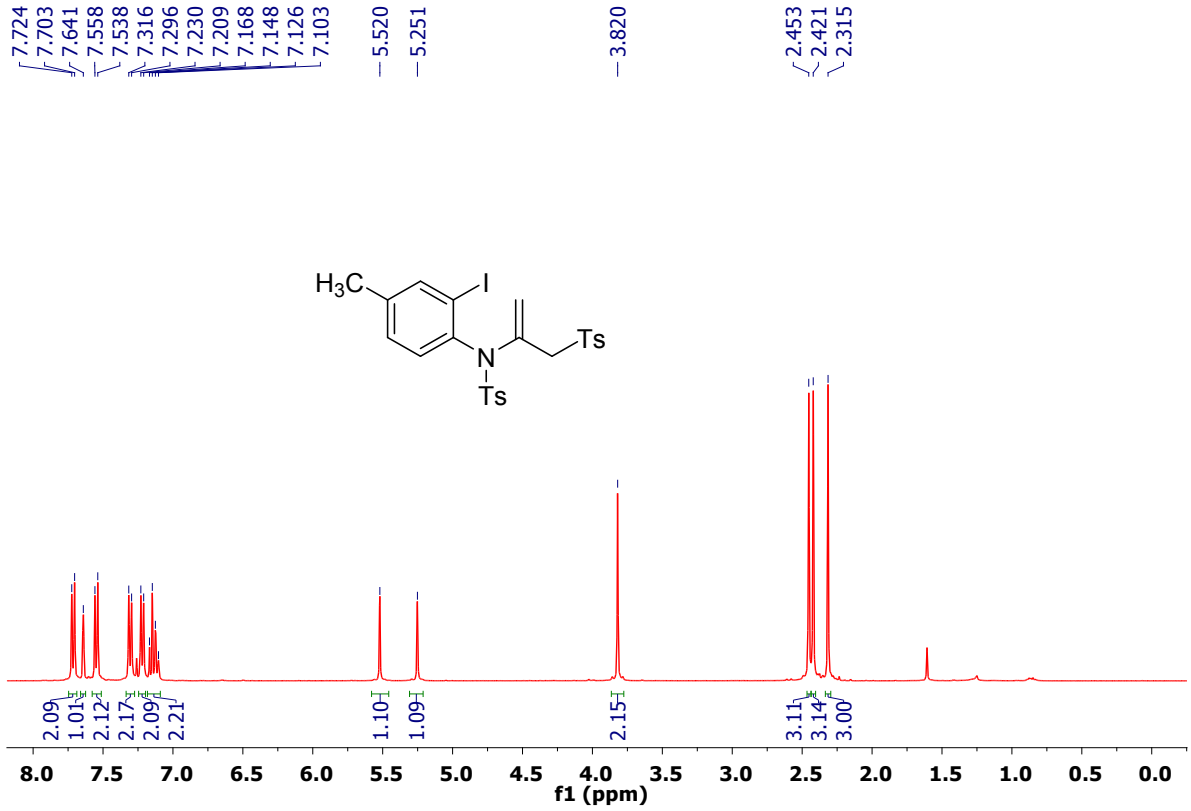
7c, CDCl₃



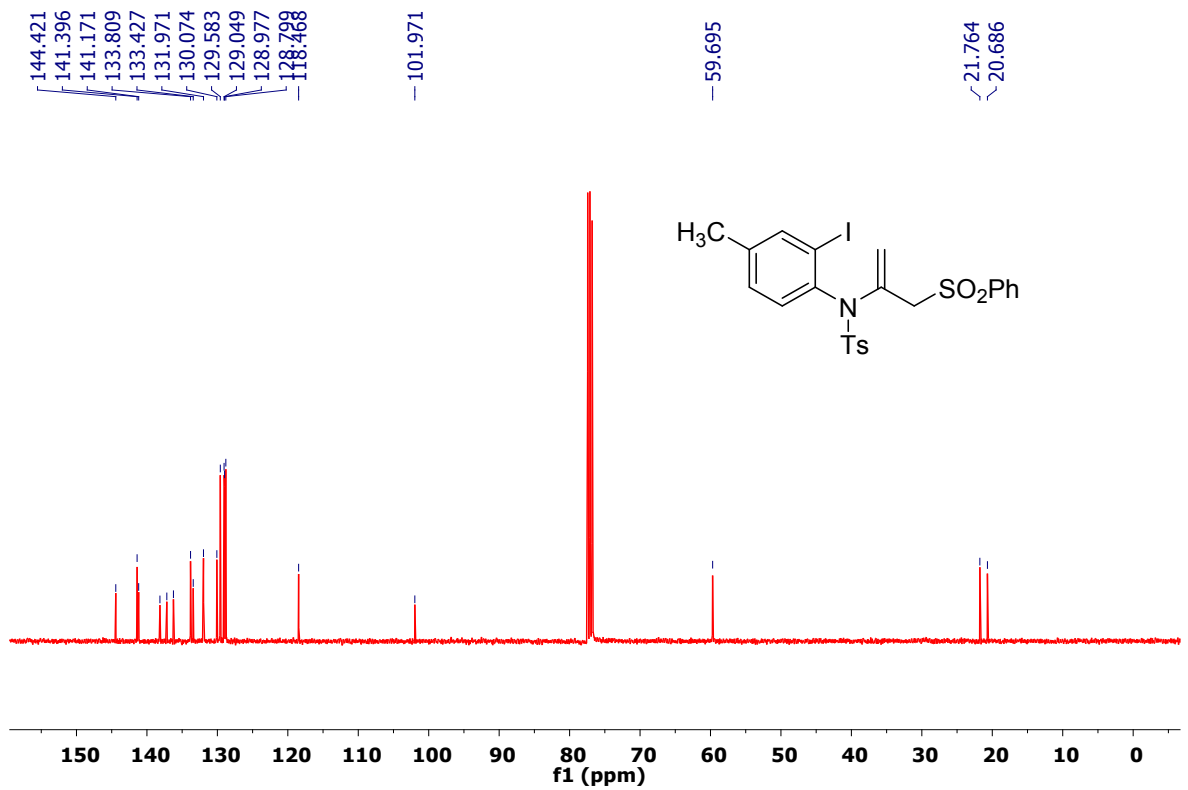
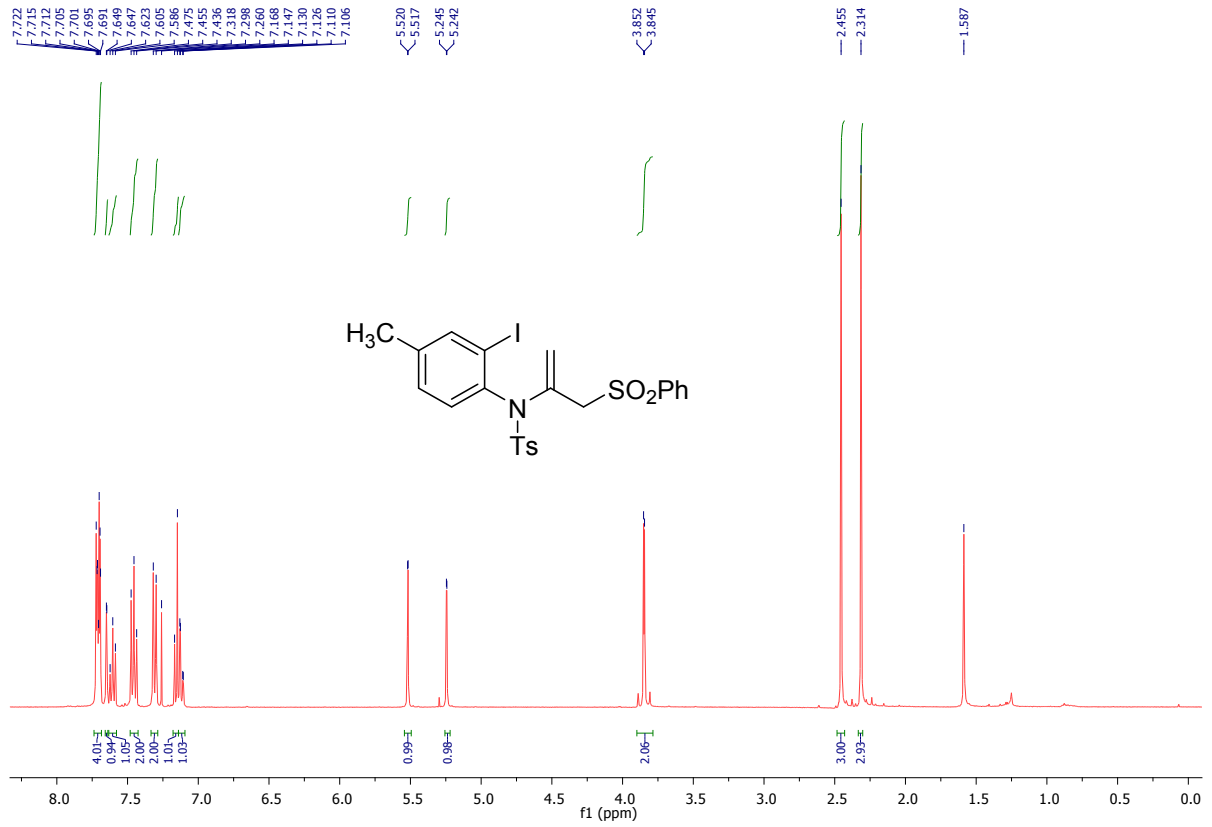
7d, CDCl₃



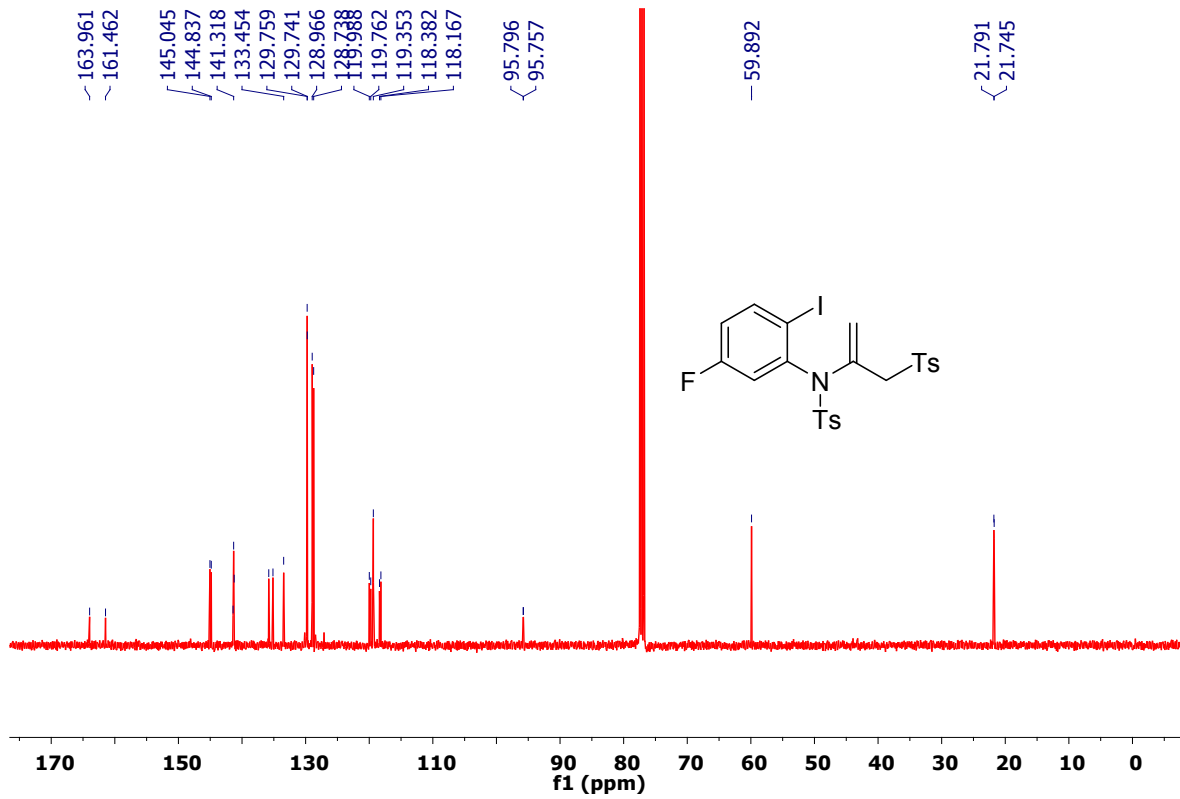
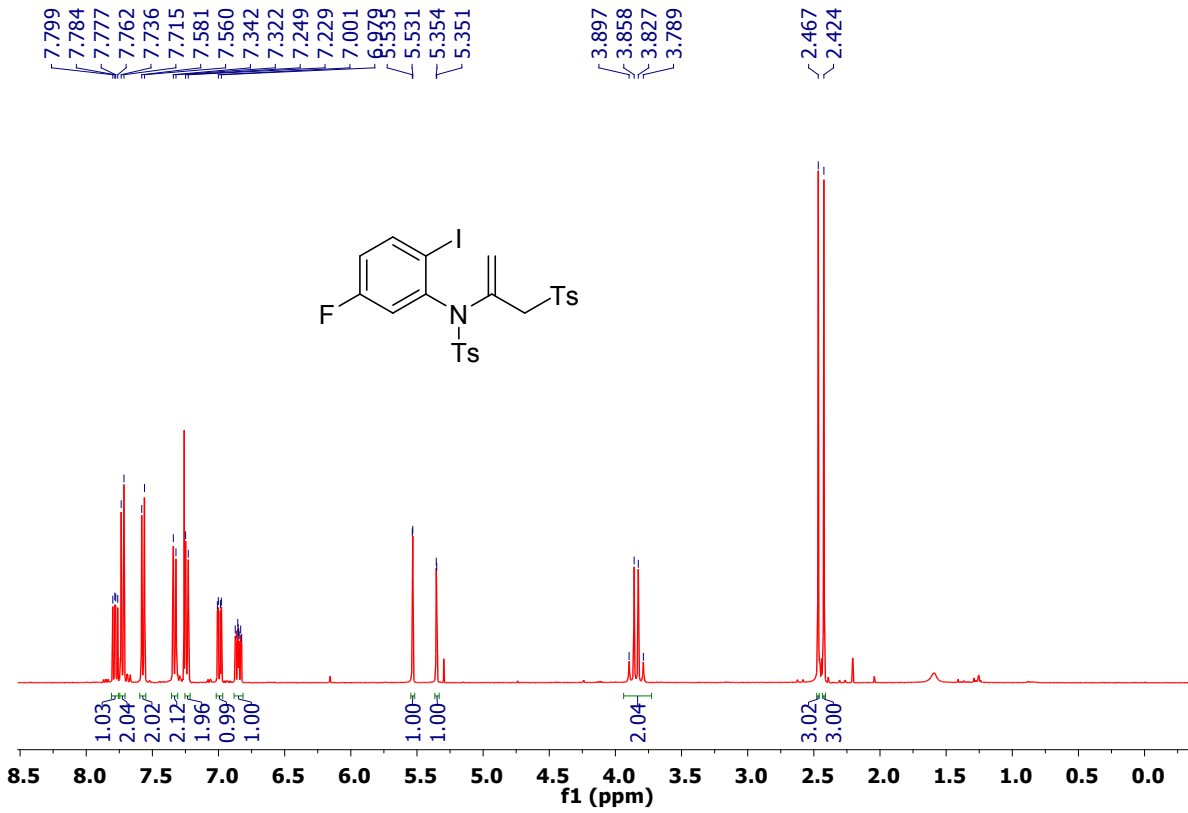
7e, CDCl₃



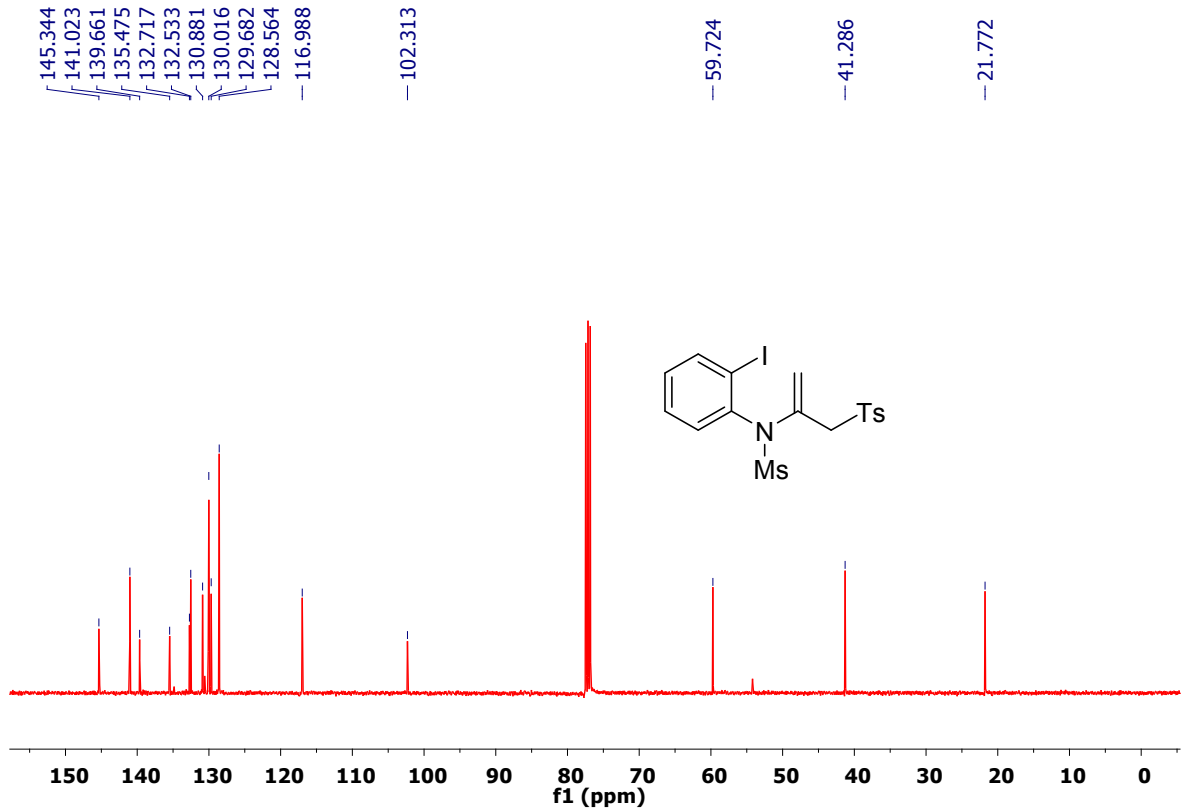
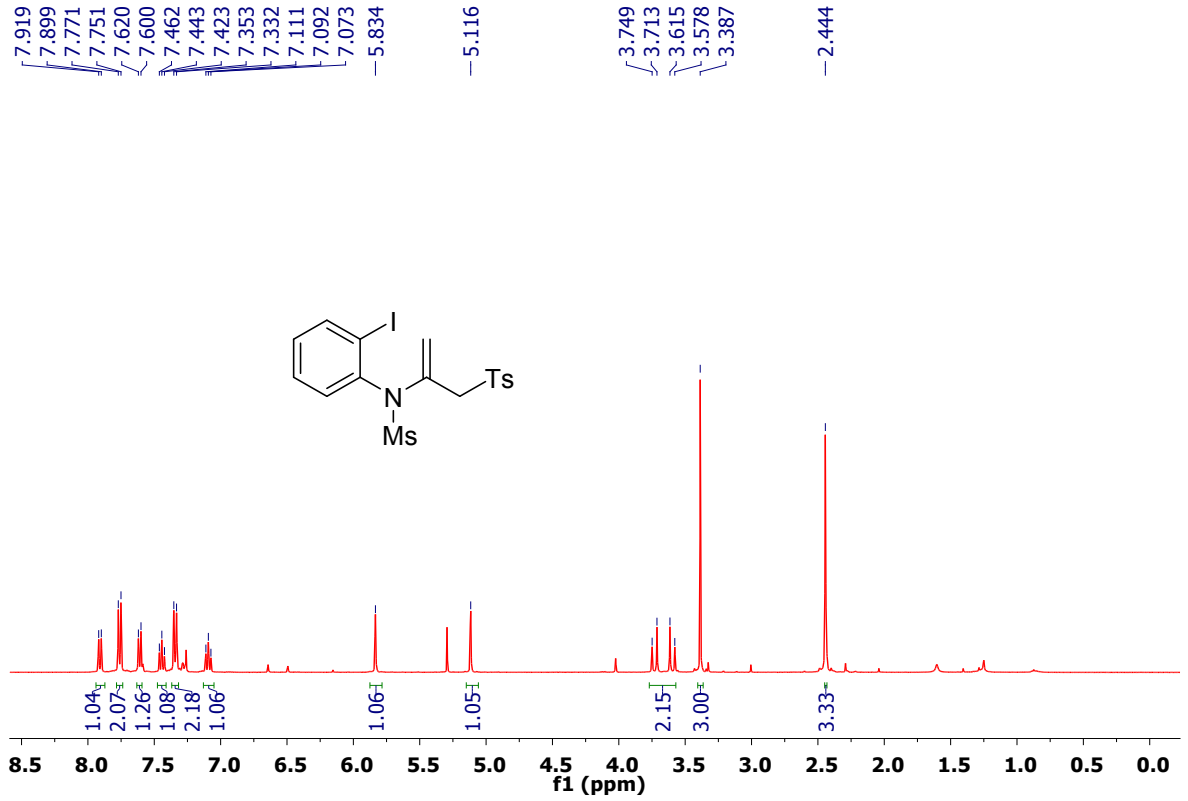
7f, CDCl₃



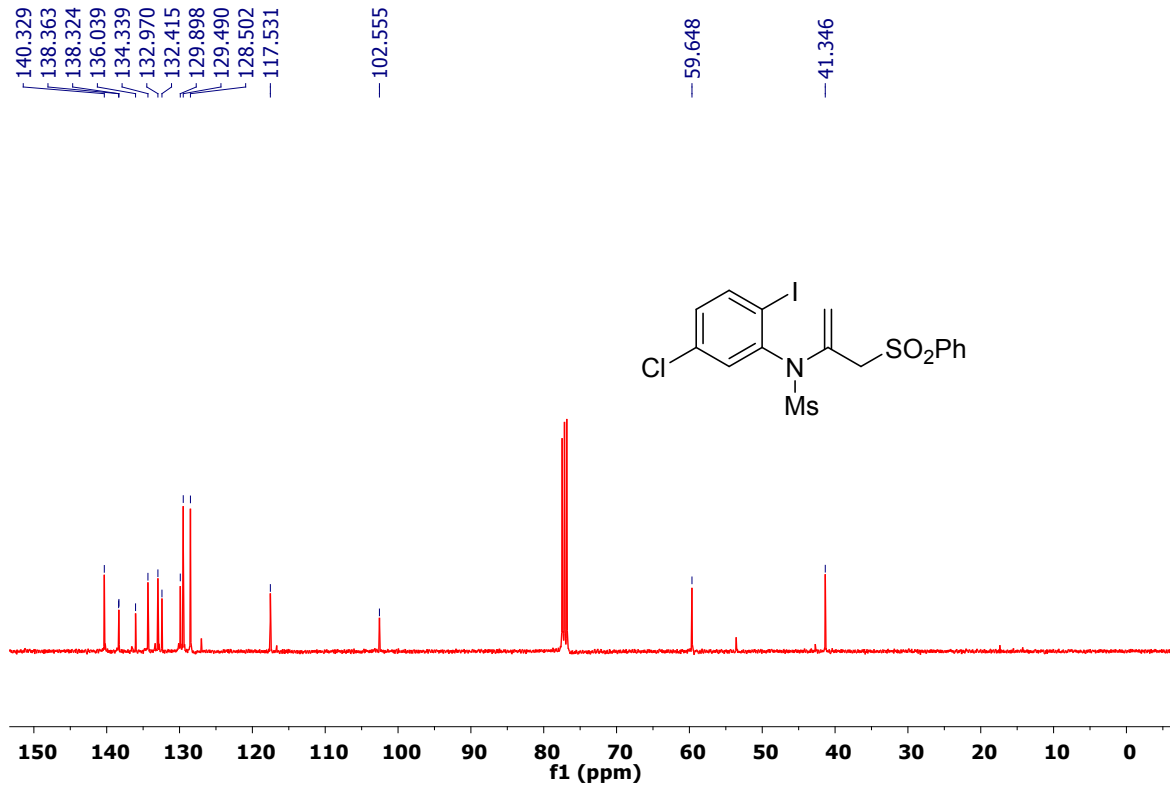
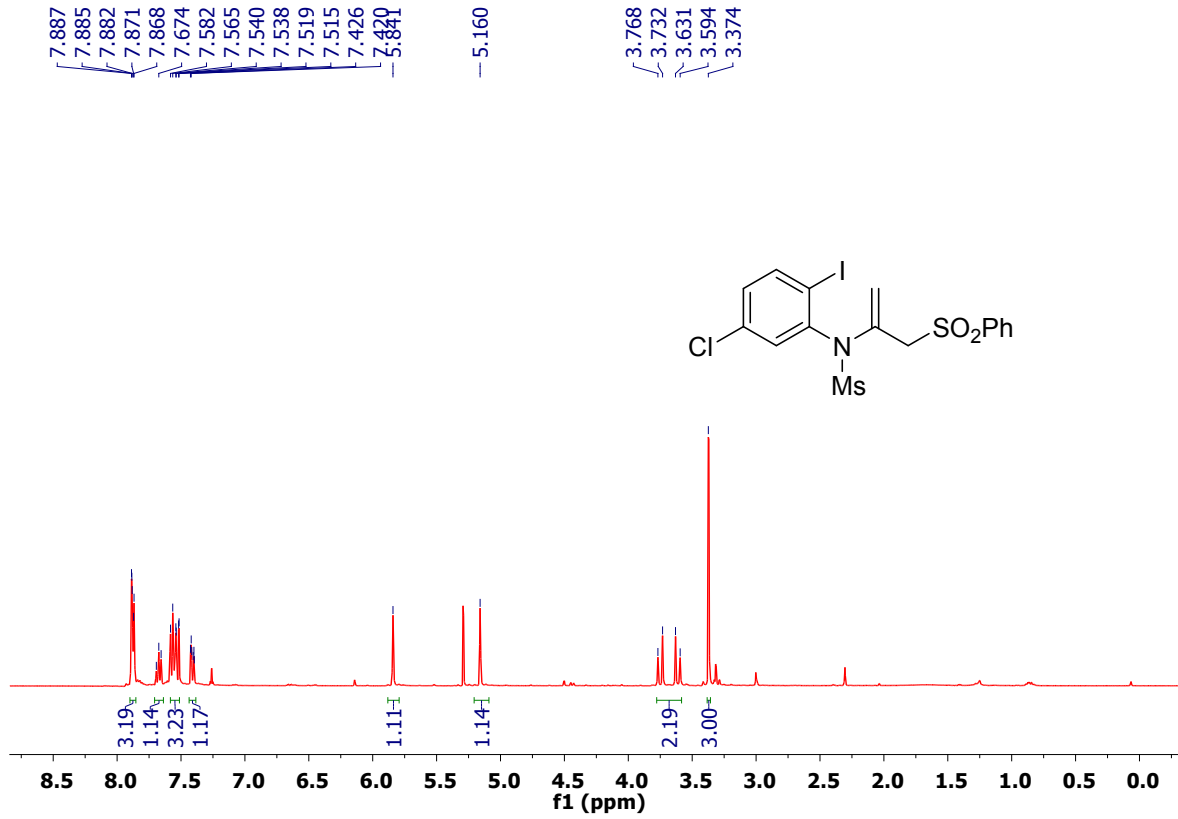
7g, CDCl₃



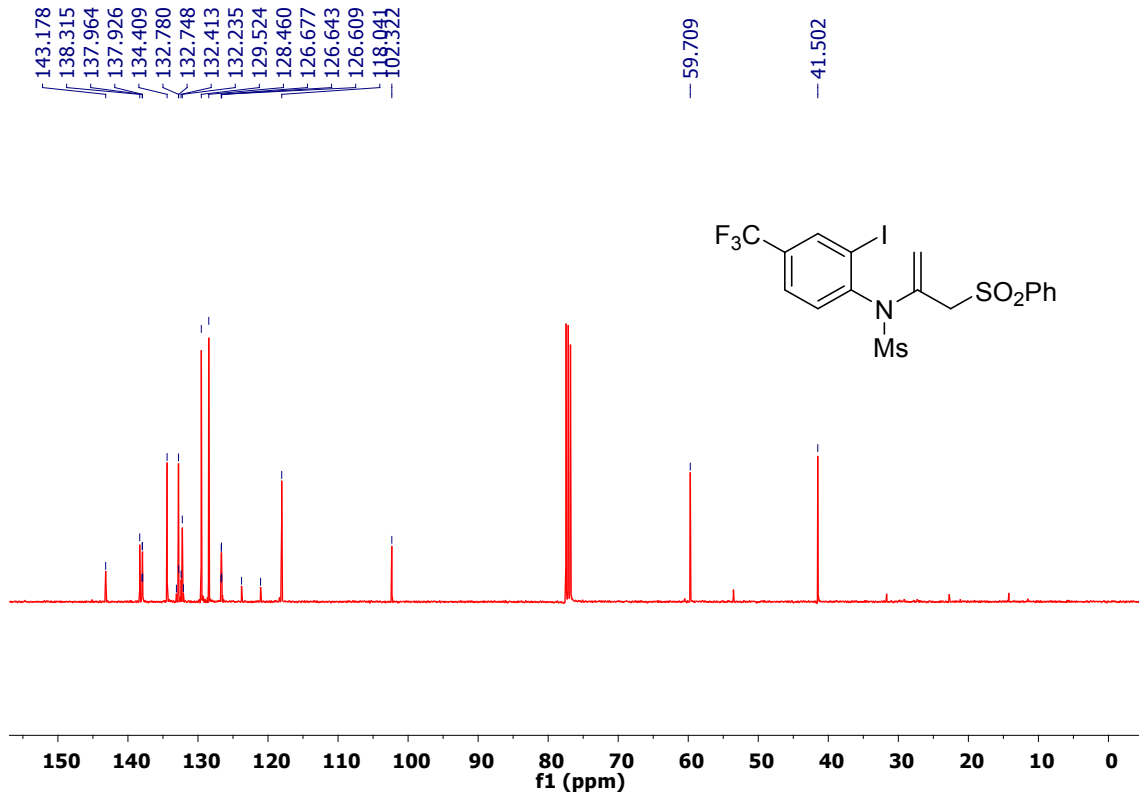
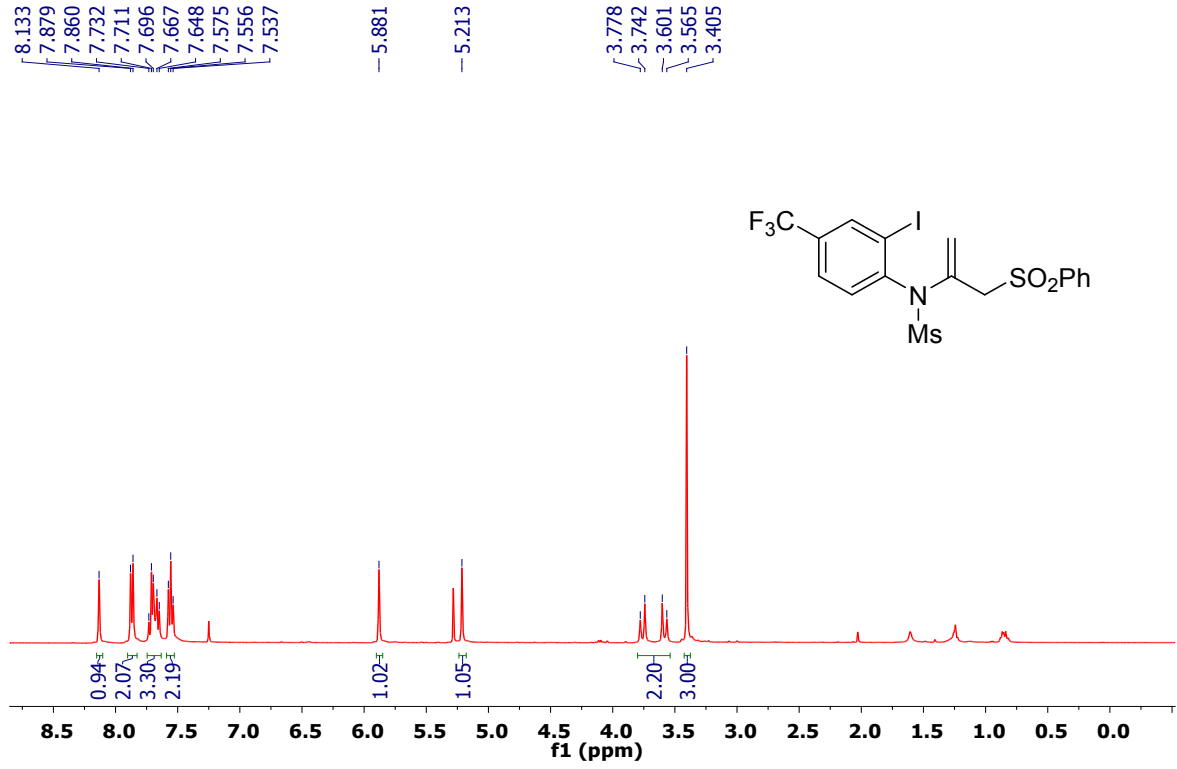
7h, CDCl₃



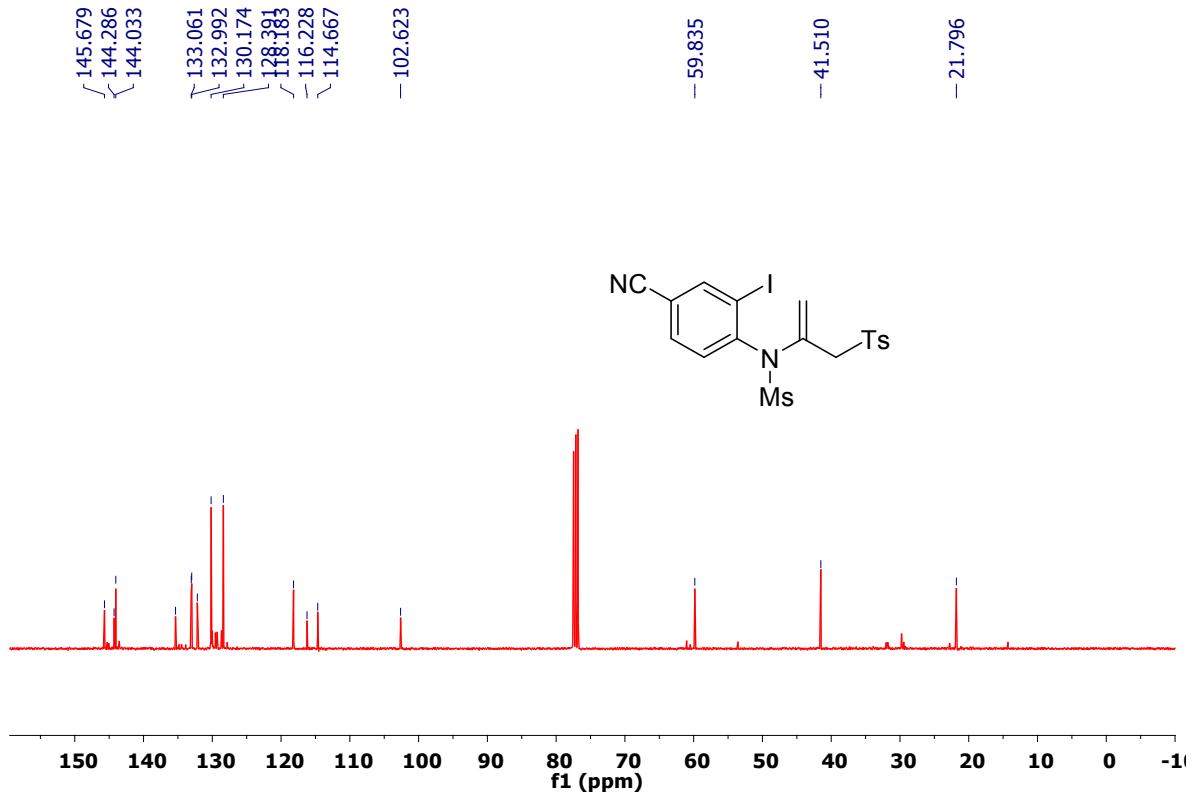
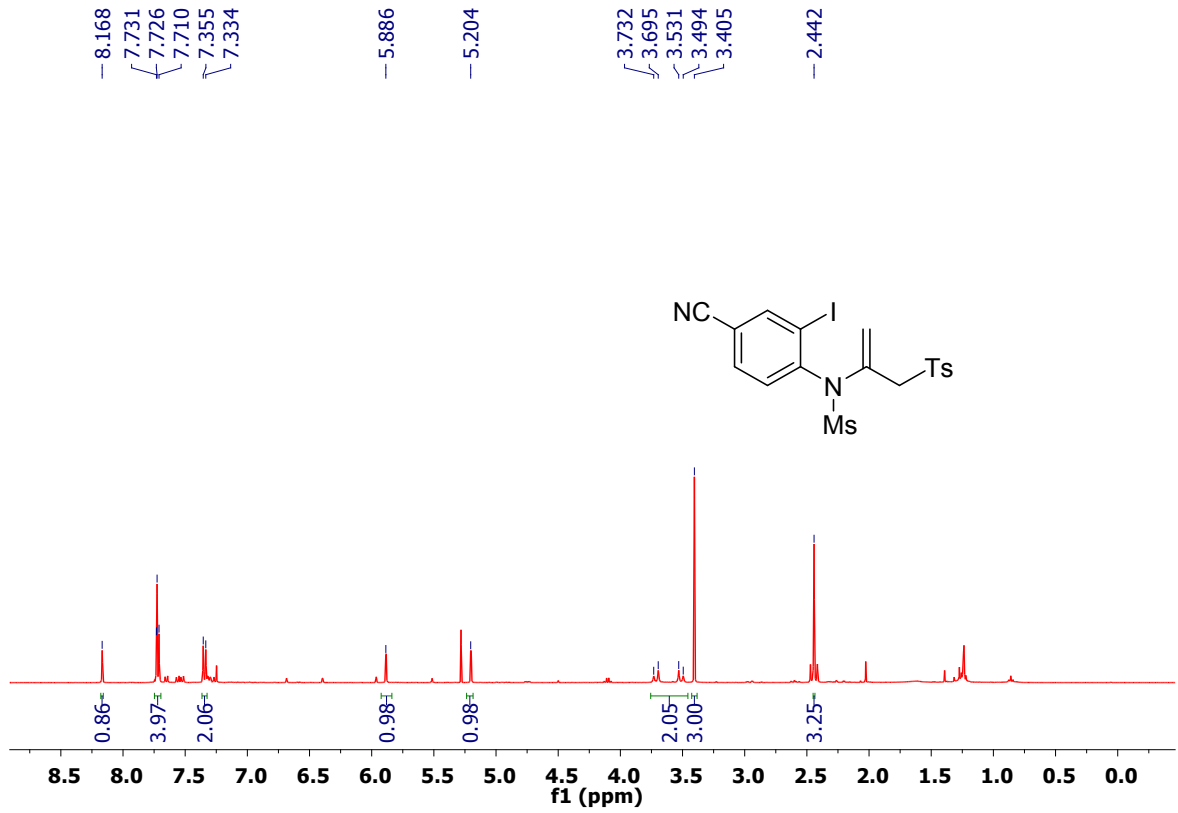
7i, CDCl₃



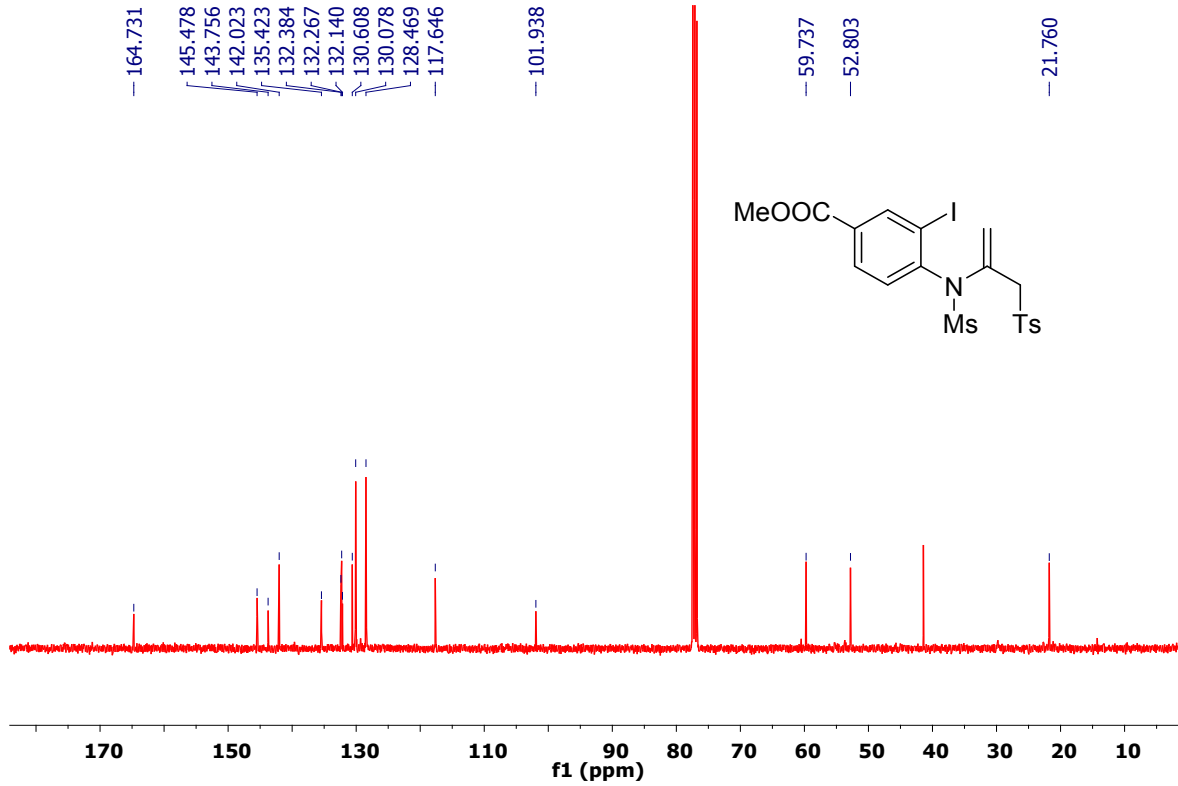
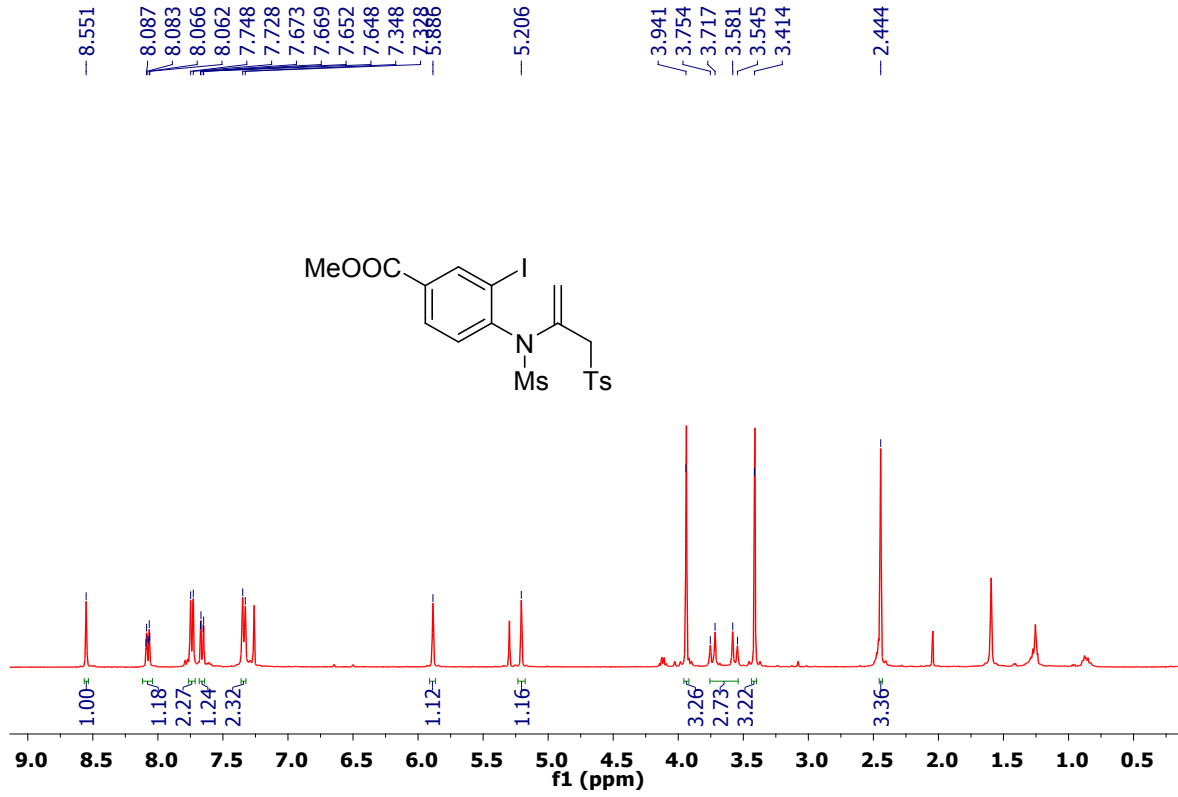
7j, CDCl₃



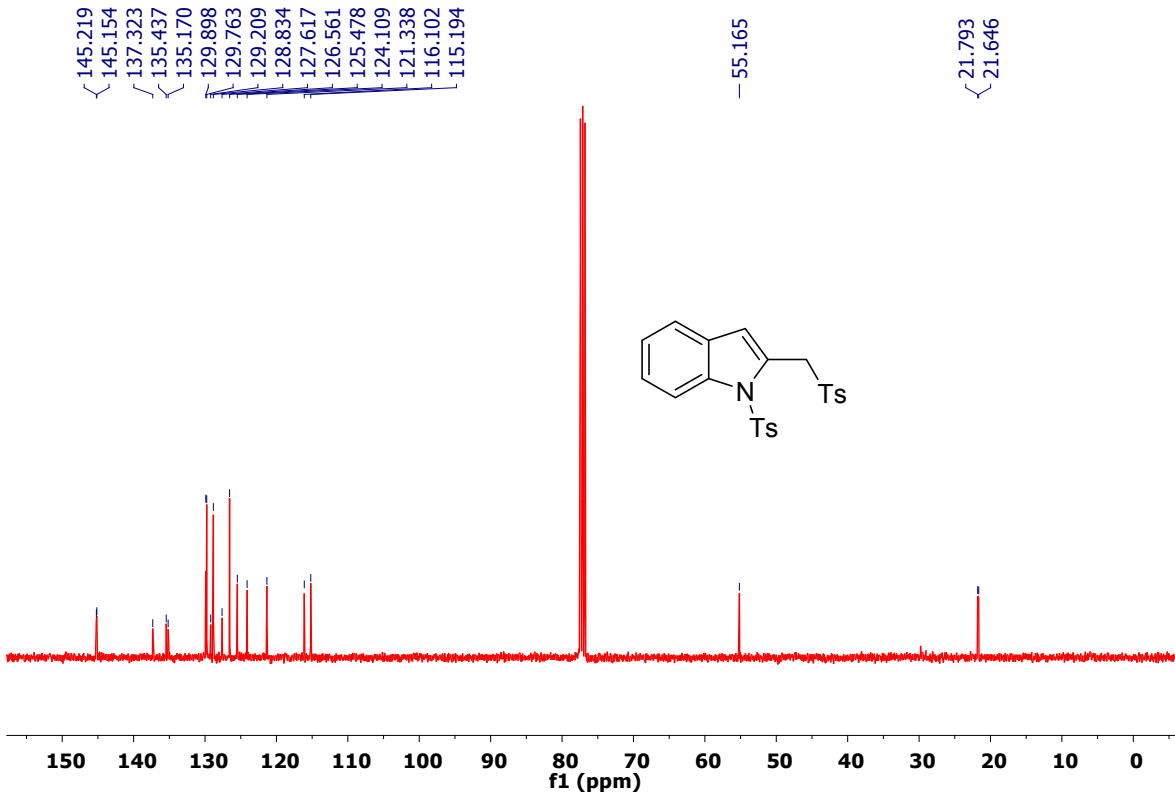
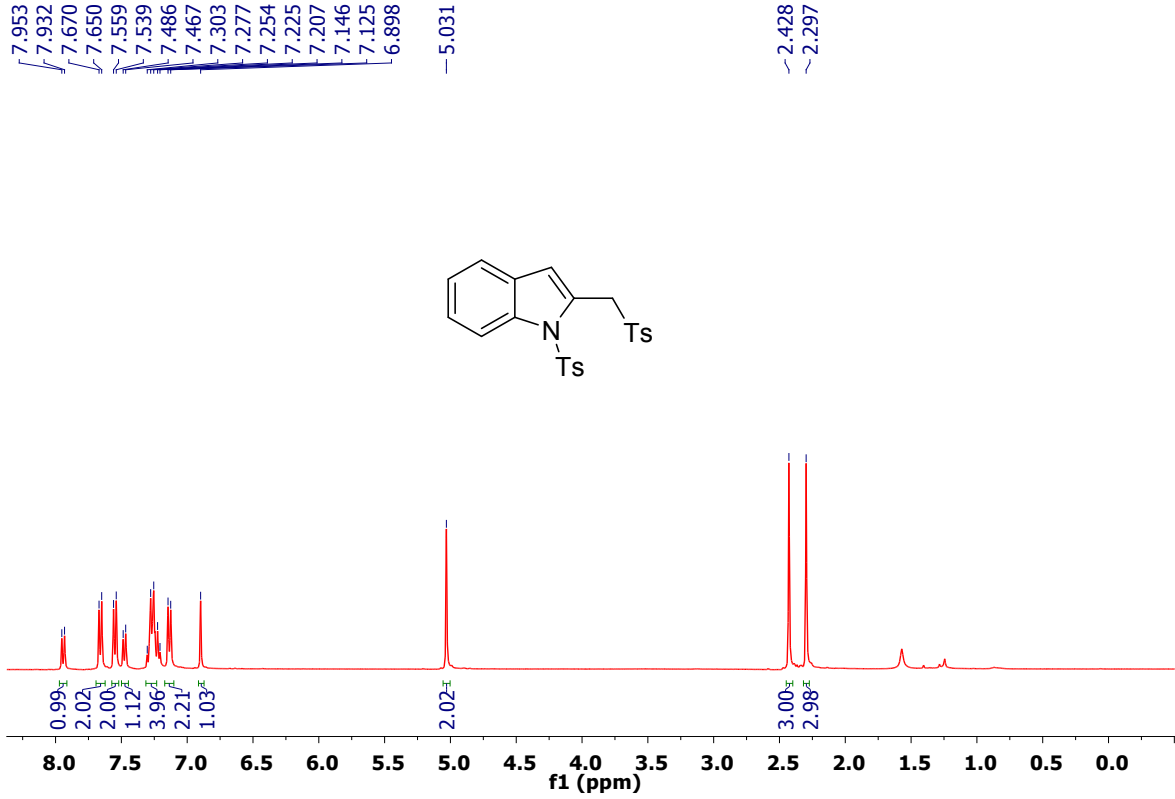
7k, CDCl₃



7l, CDCl₃



8a, CDCl₃

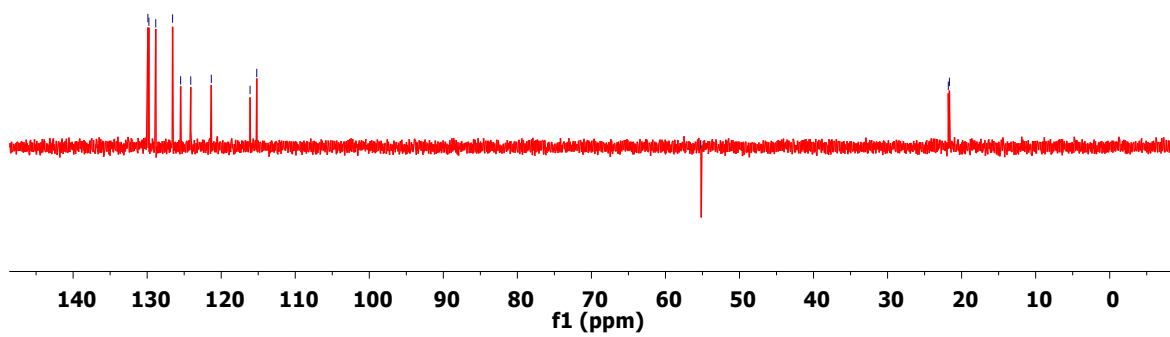
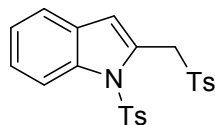


8a, CDCl₃, DEPT-135

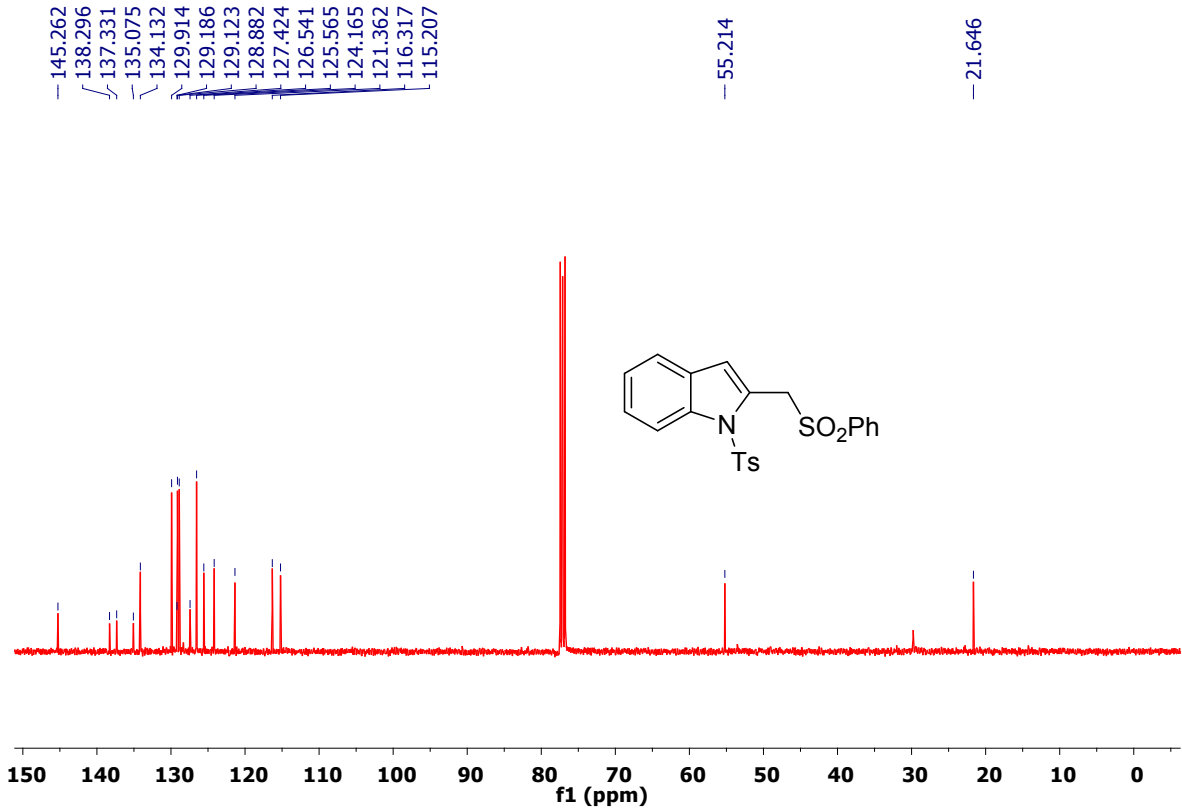
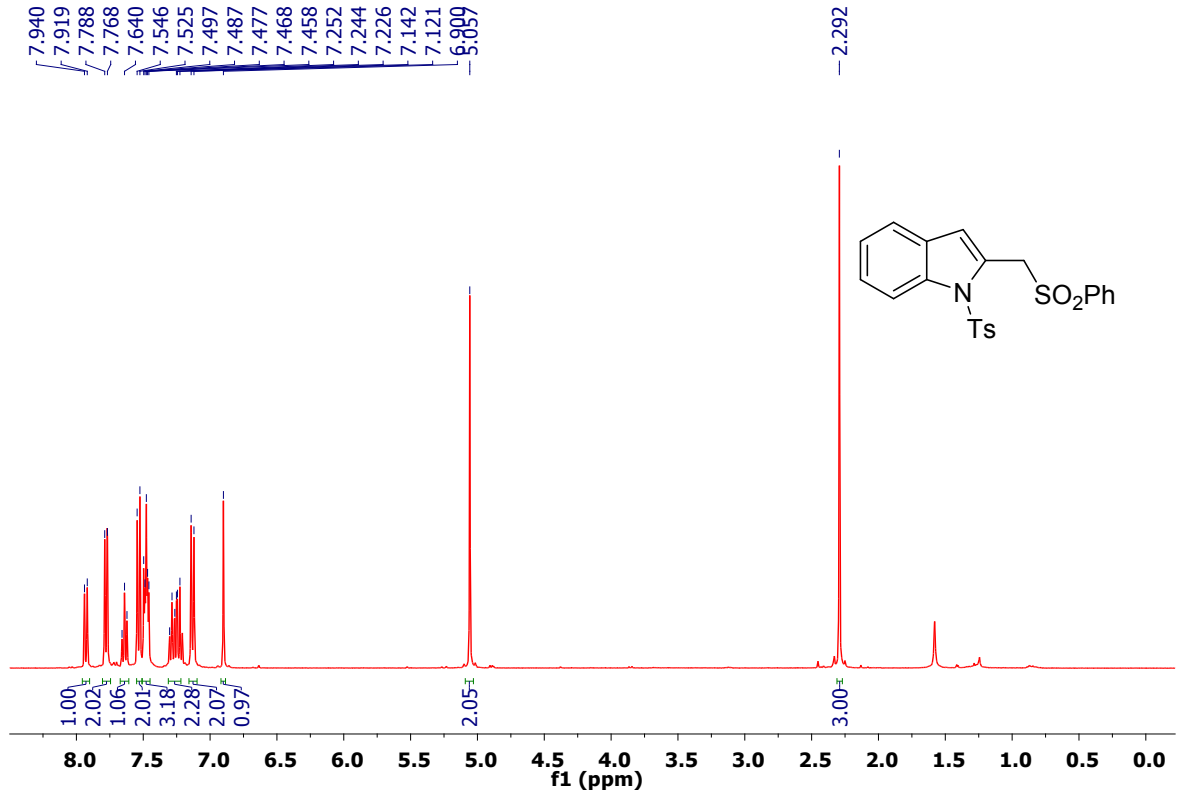
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128.839
126.565
125.480
124.111
121.339
116.101
115.197

-55.234

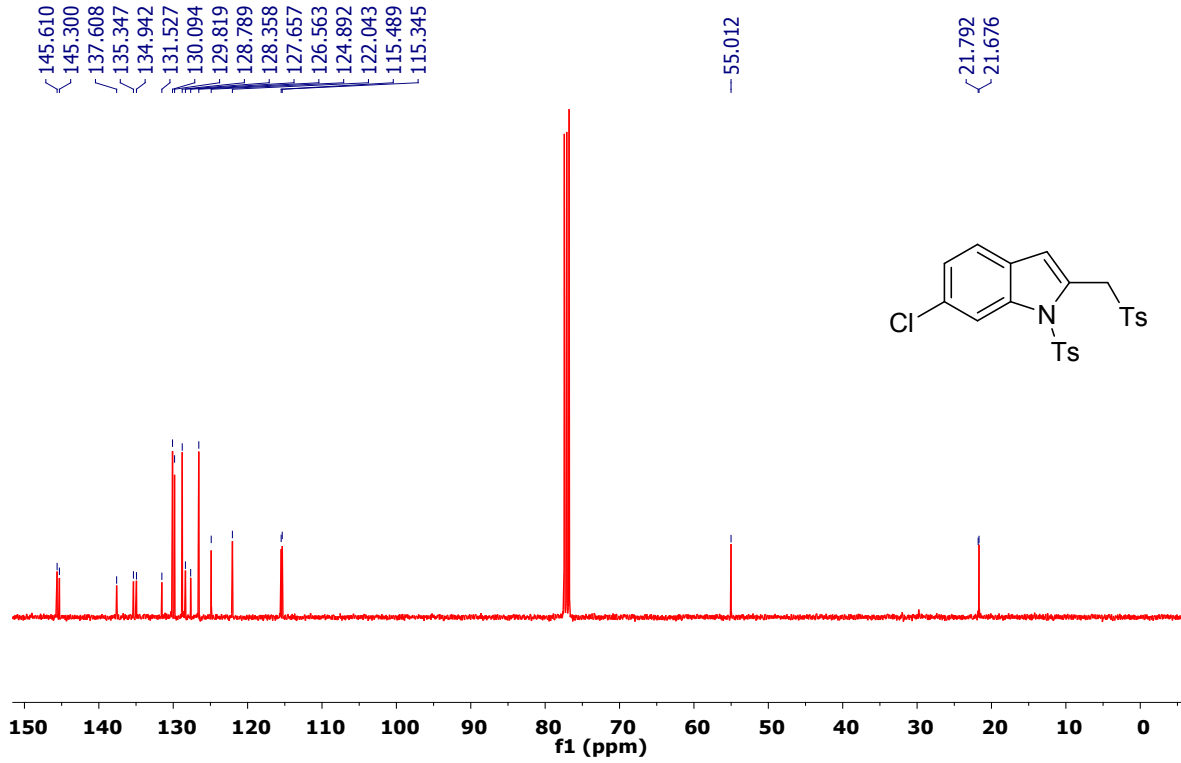
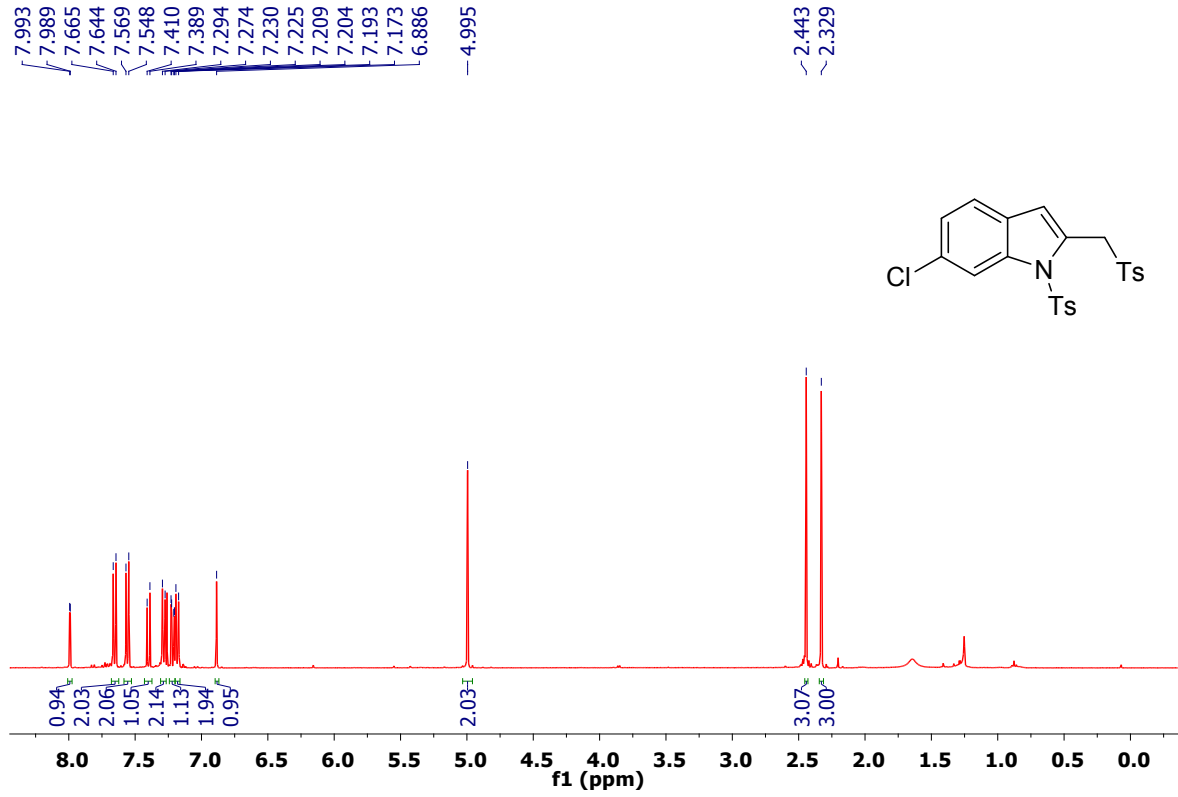
21.798
21.649



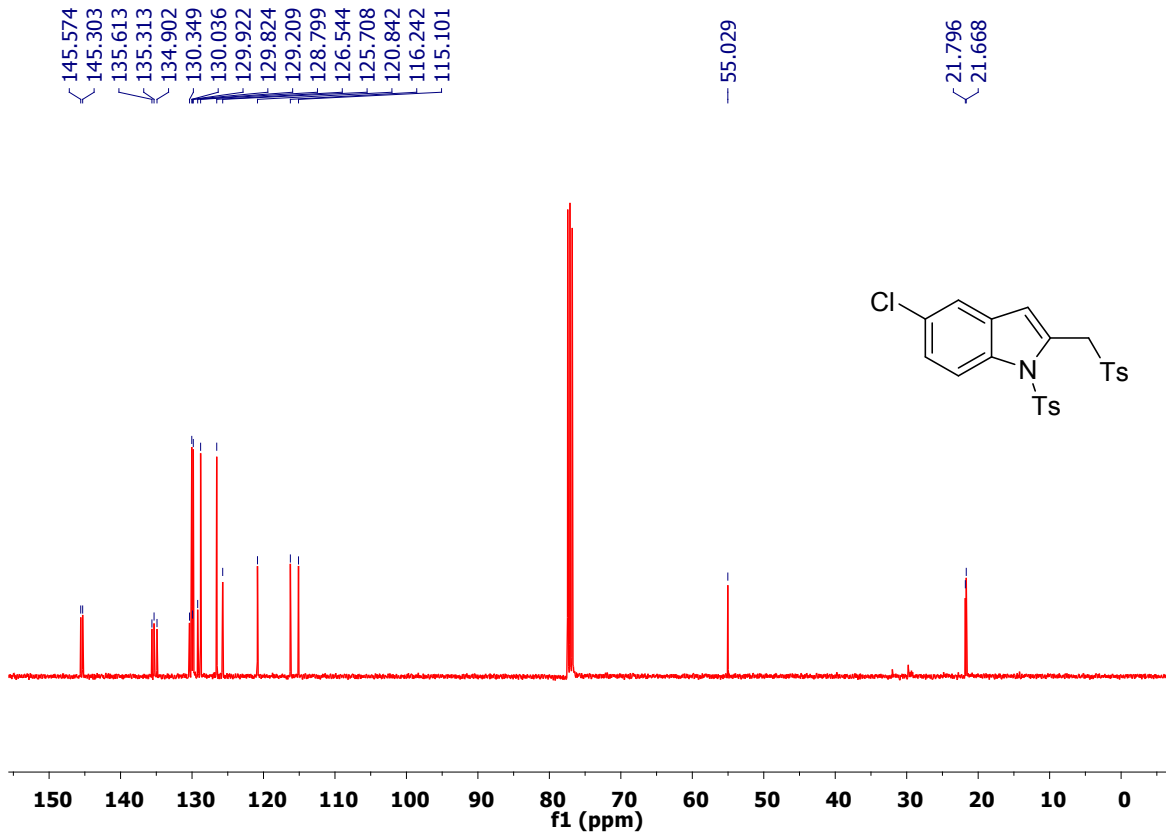
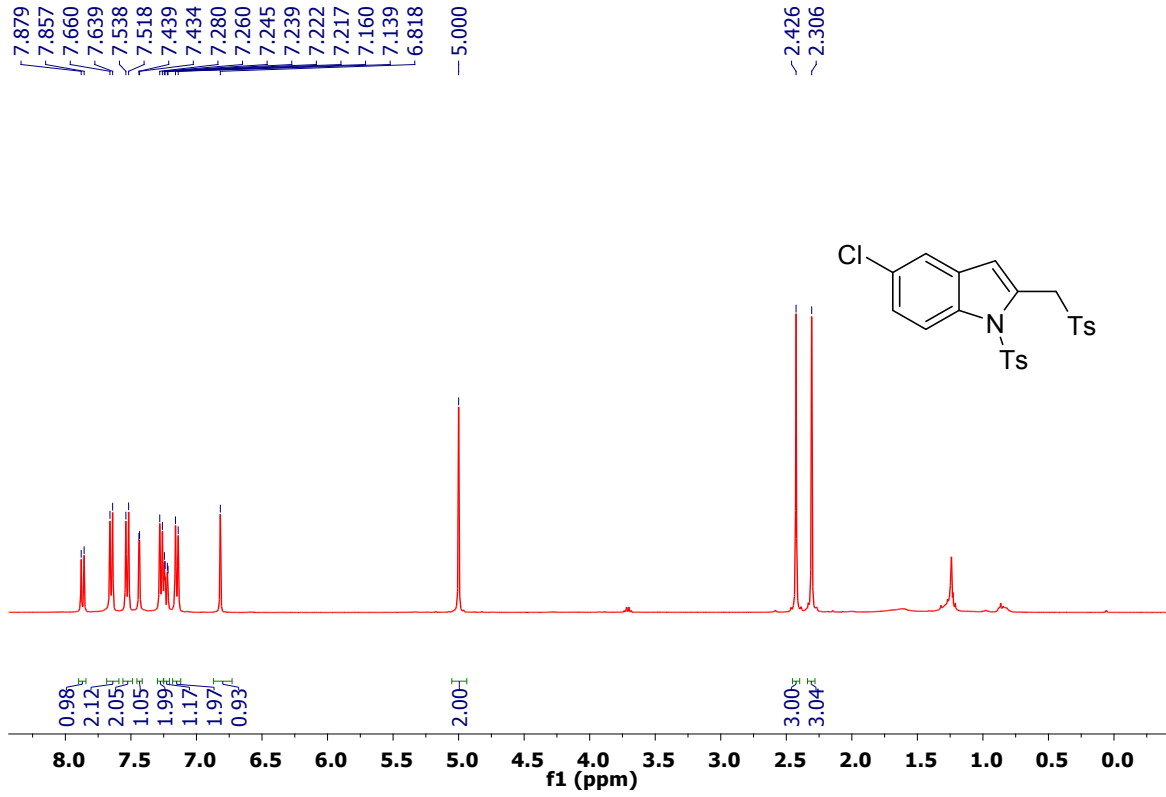
8b, CDCl₃



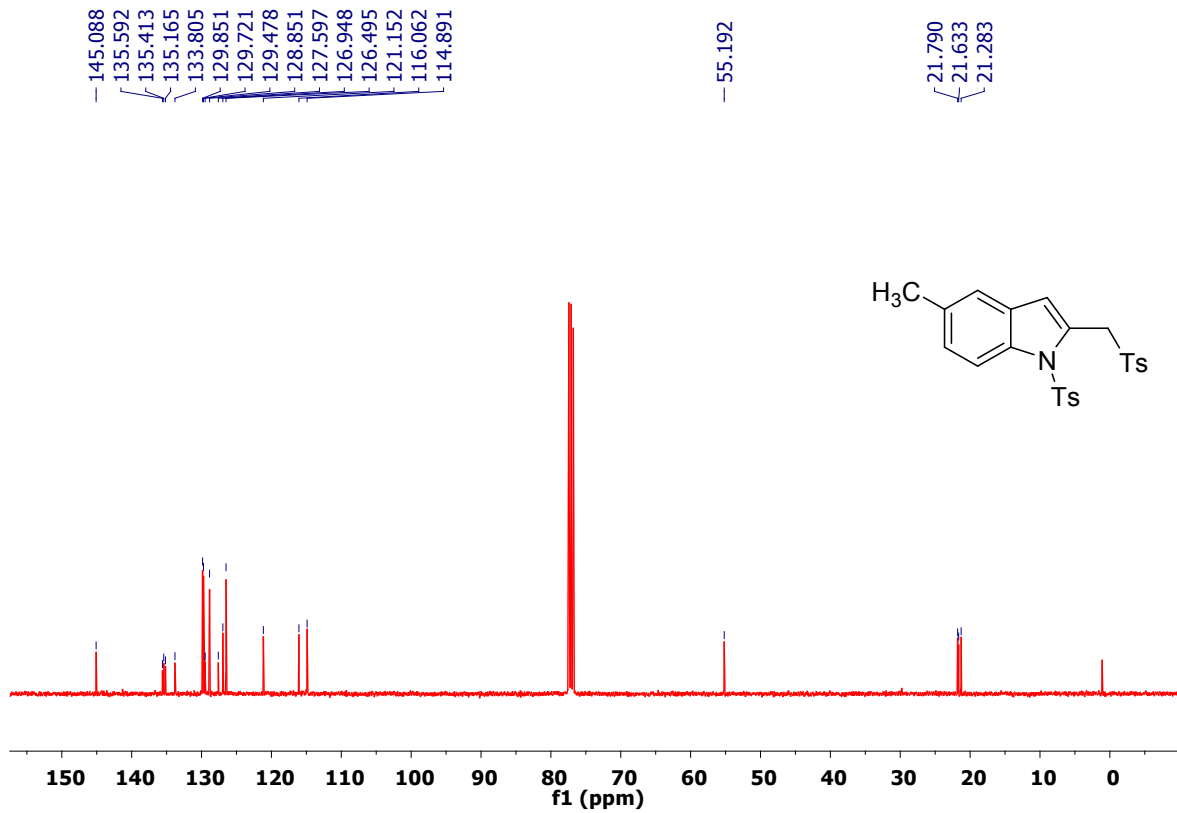
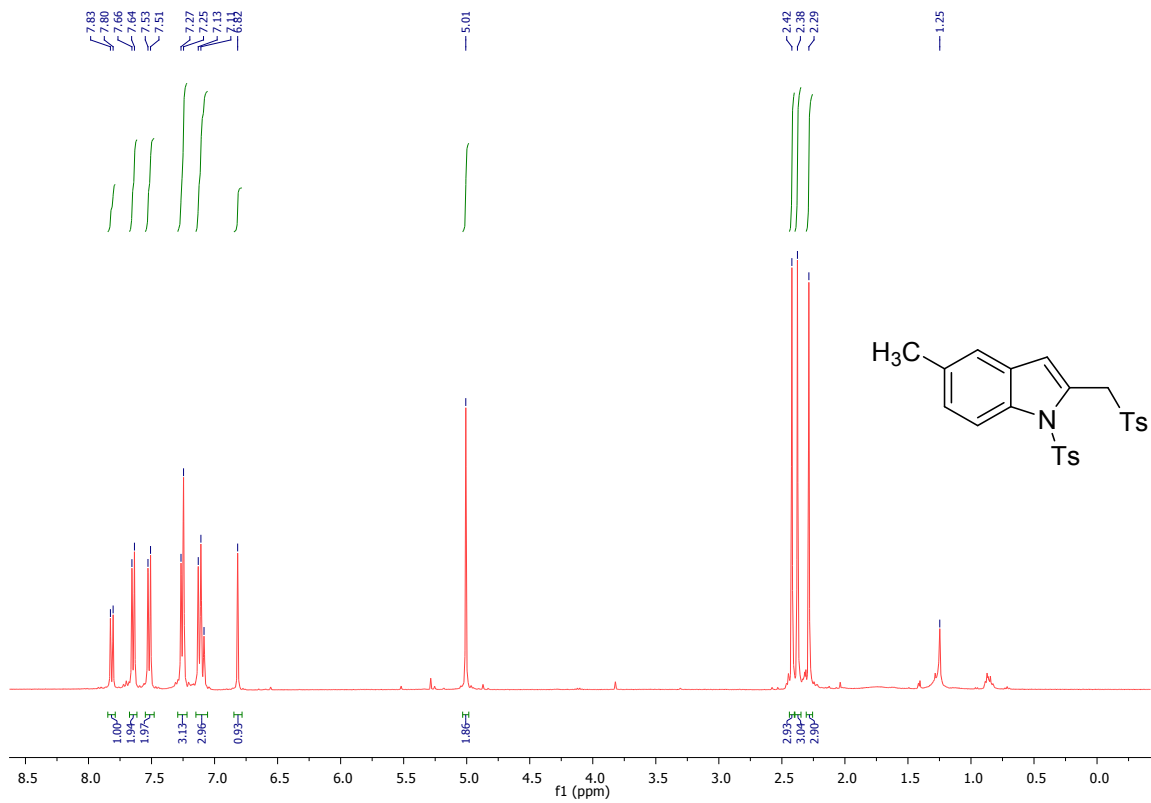
8c, CDCl₃



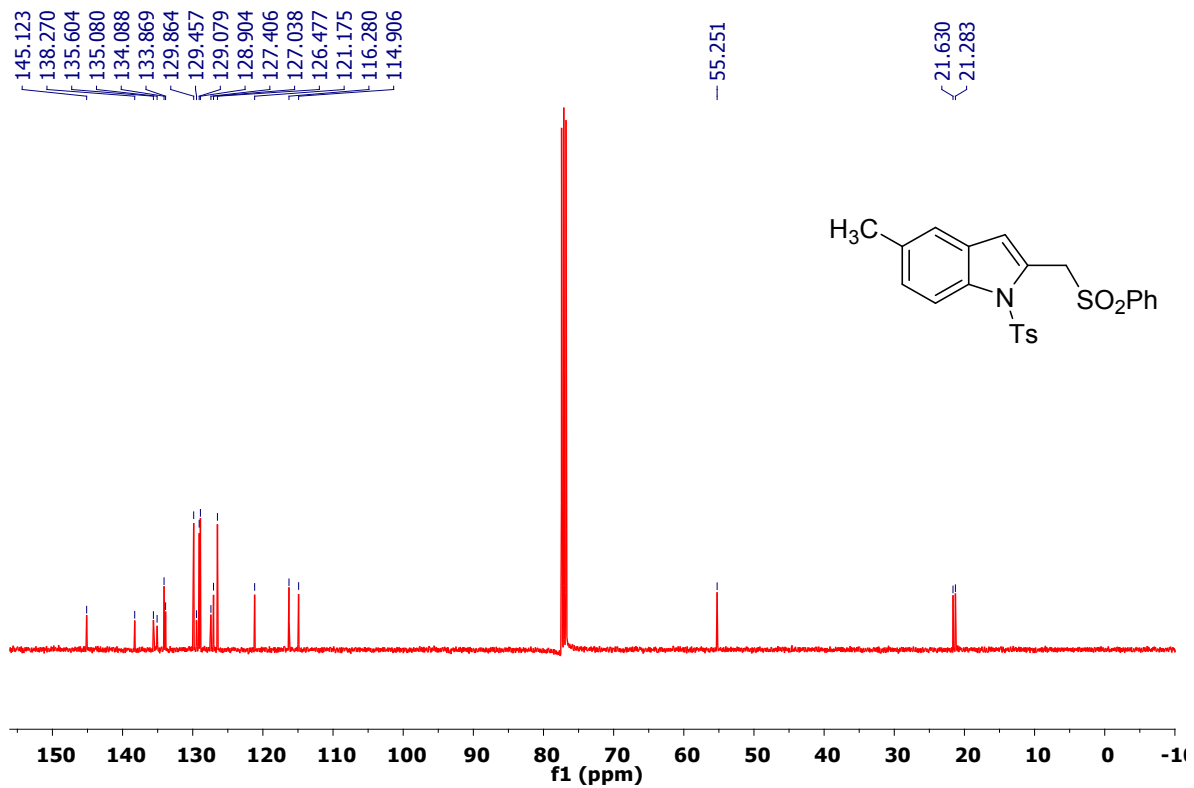
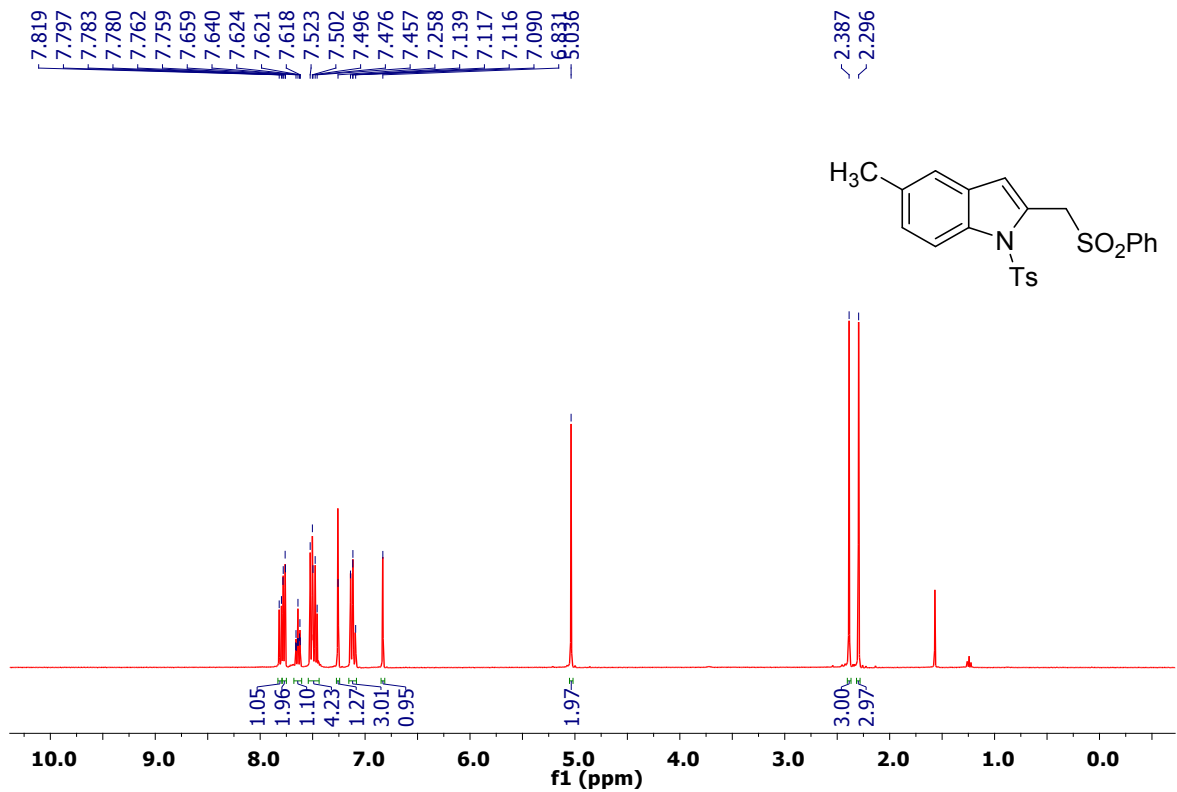
8d, CDCl₃



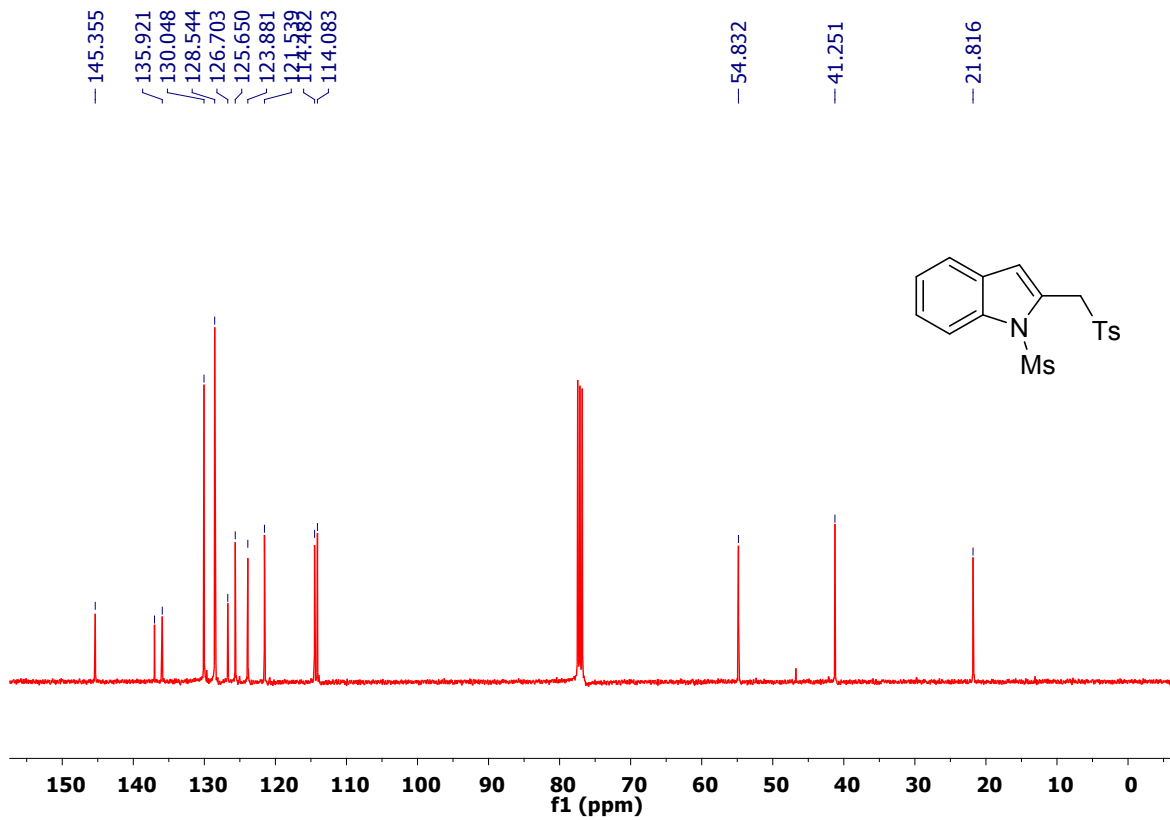
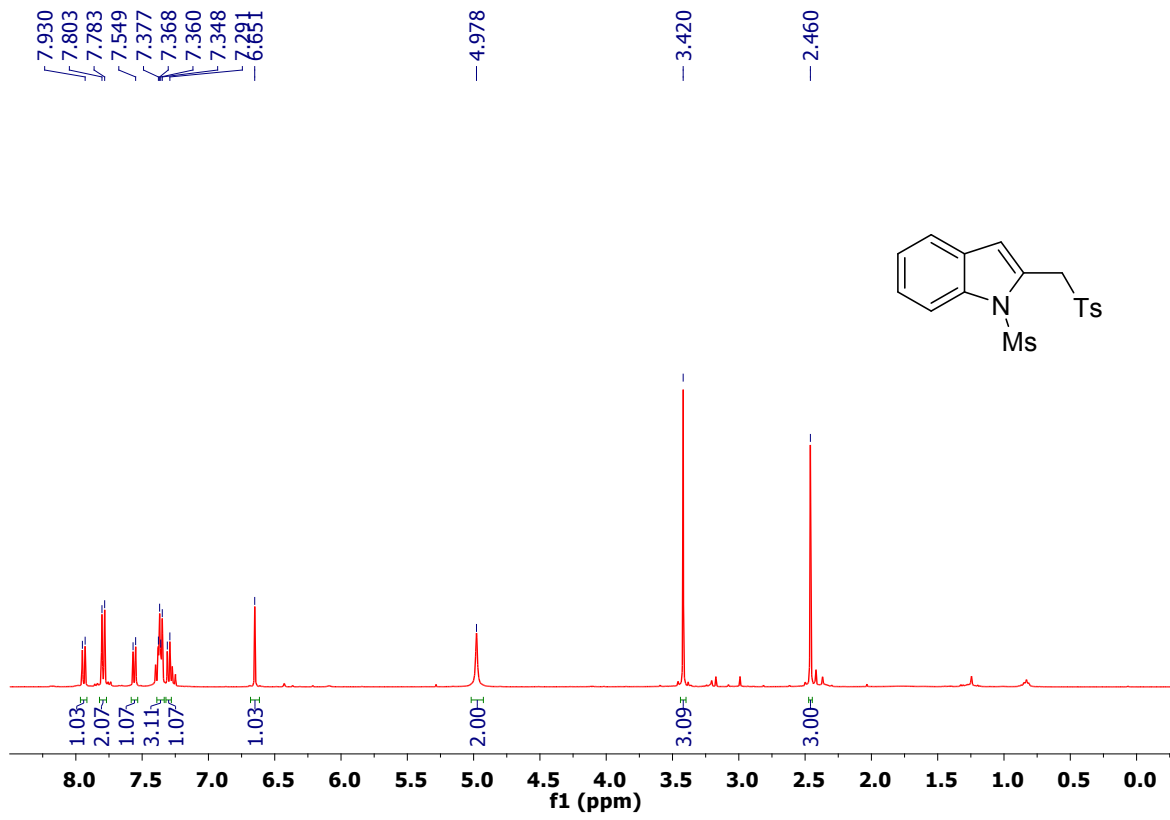
8e, CDCl₃



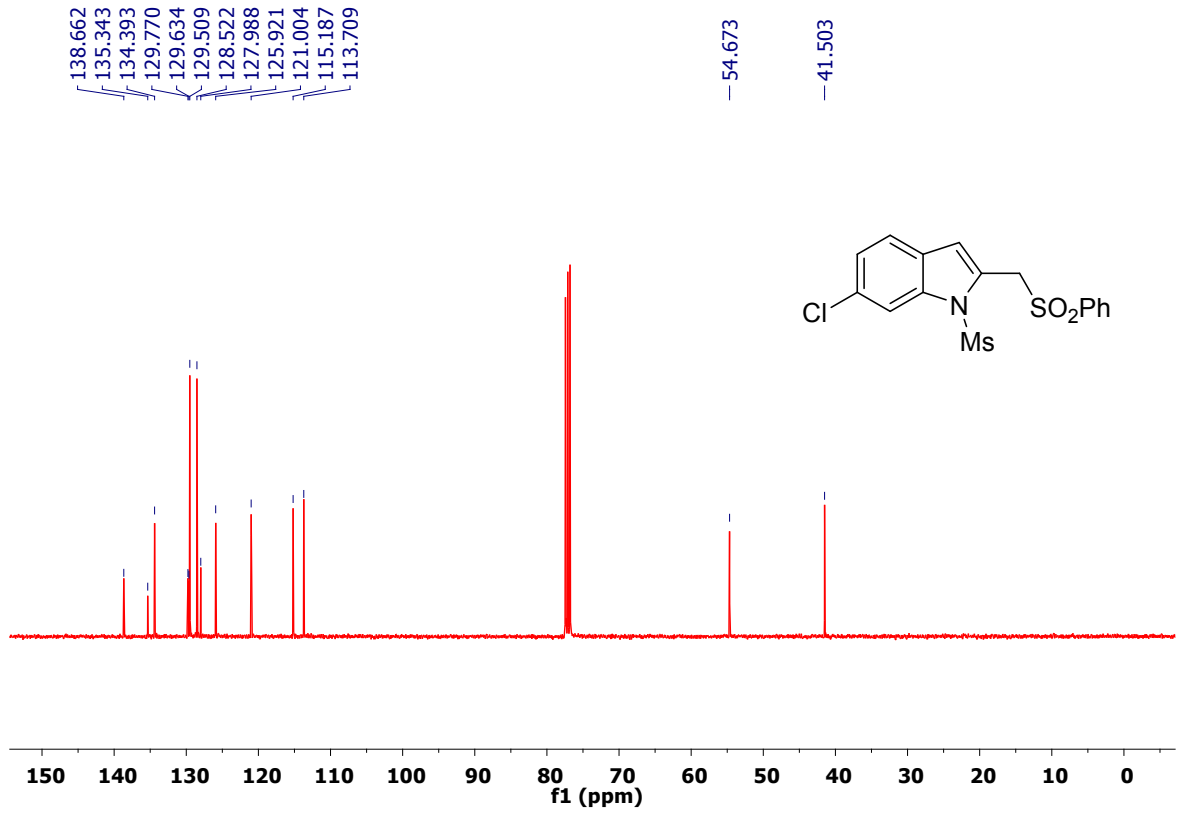
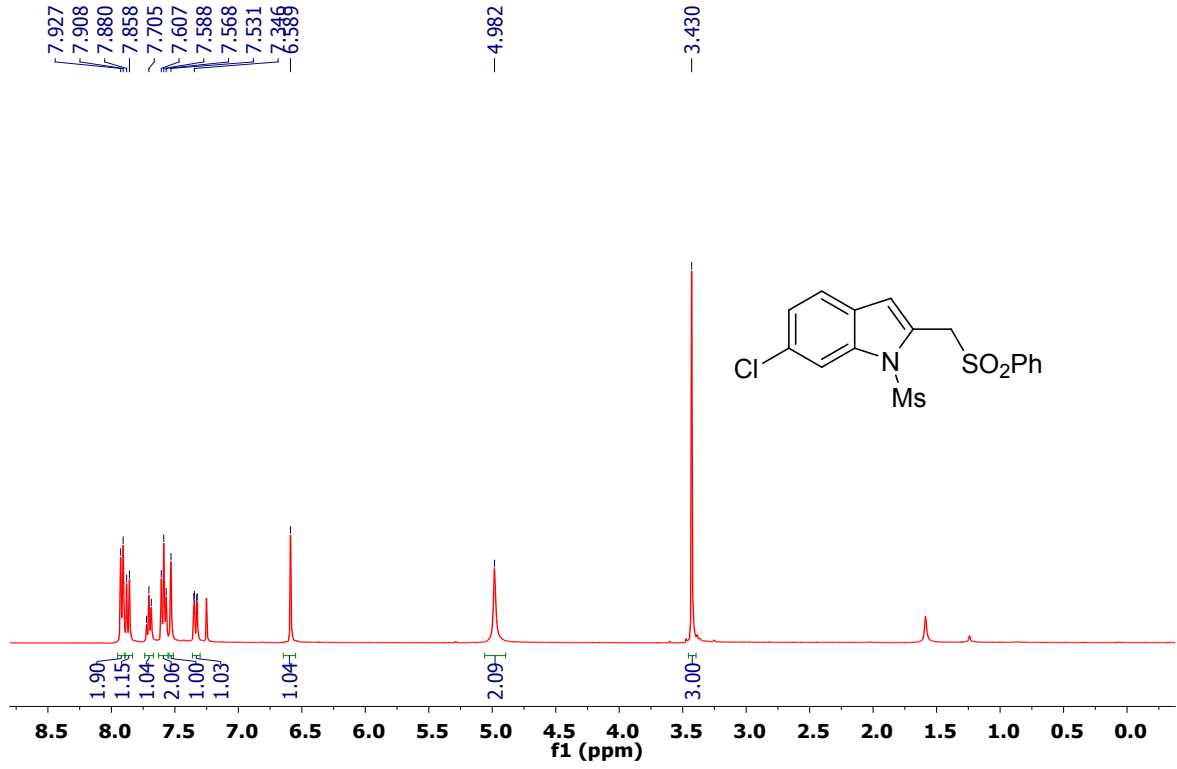
8f, CDCl₃



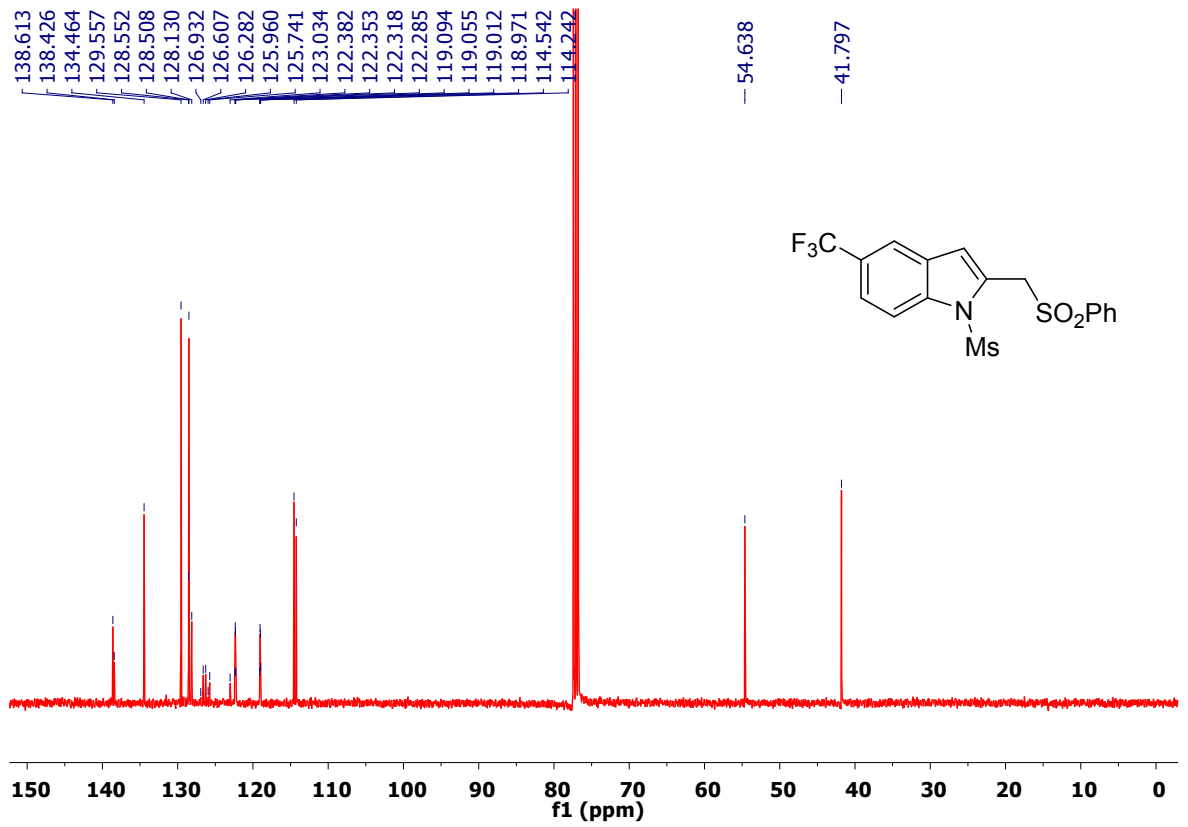
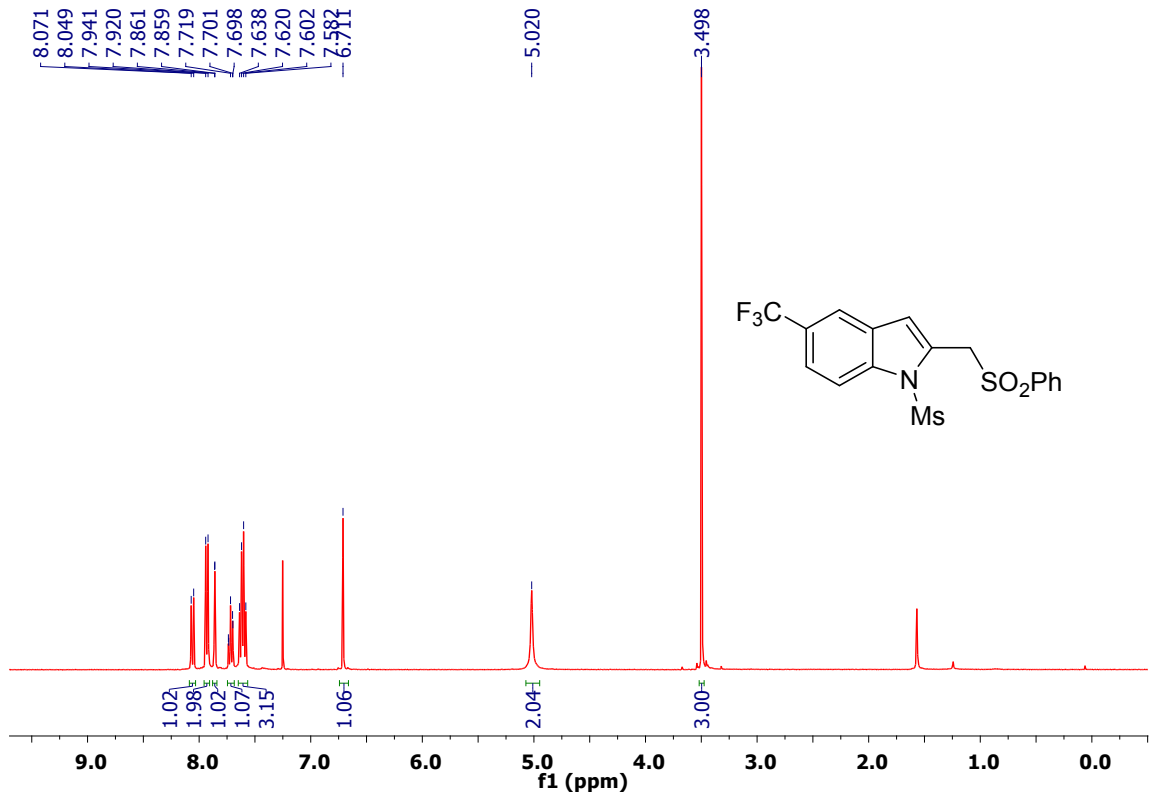
8g, CDCl₃



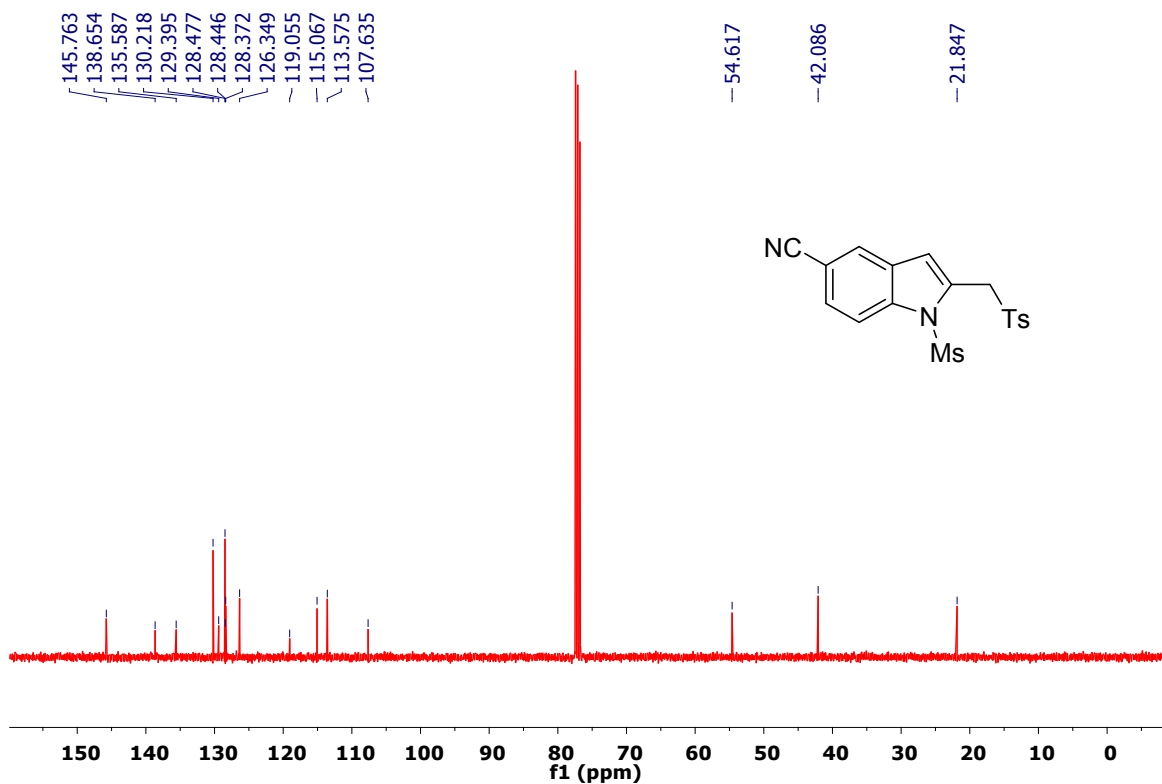
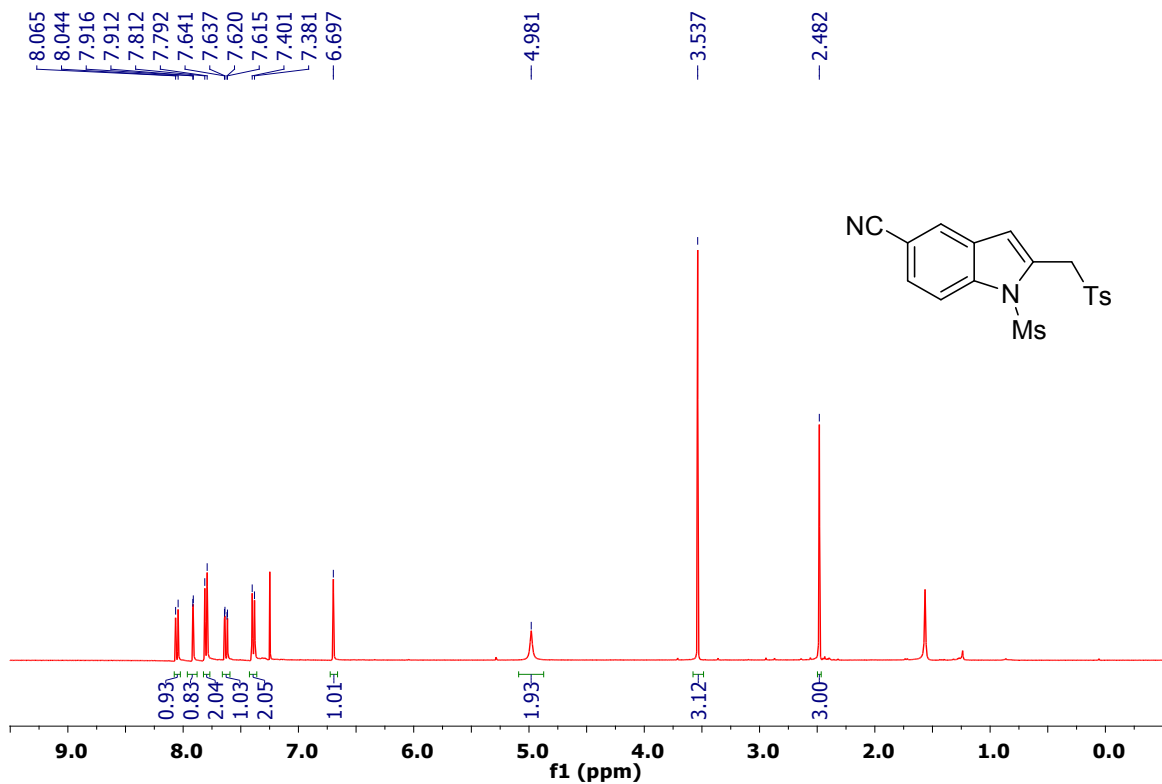
8h, CDCl₃



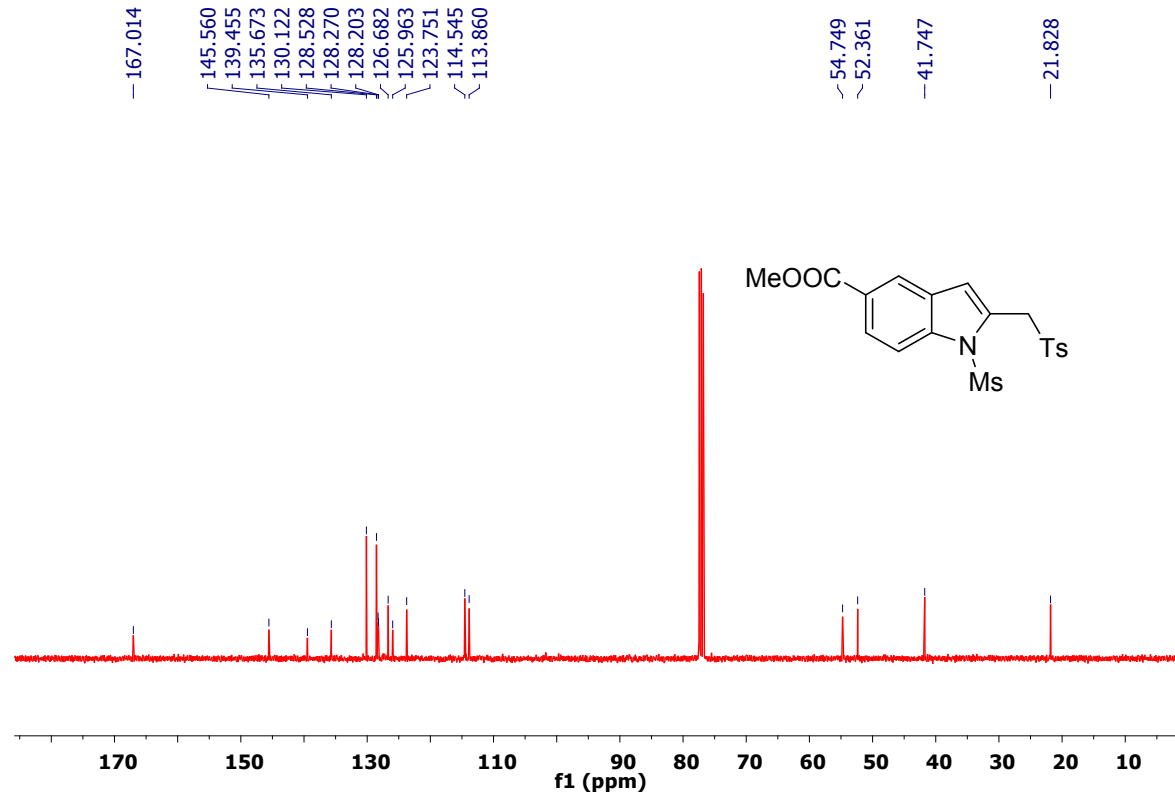
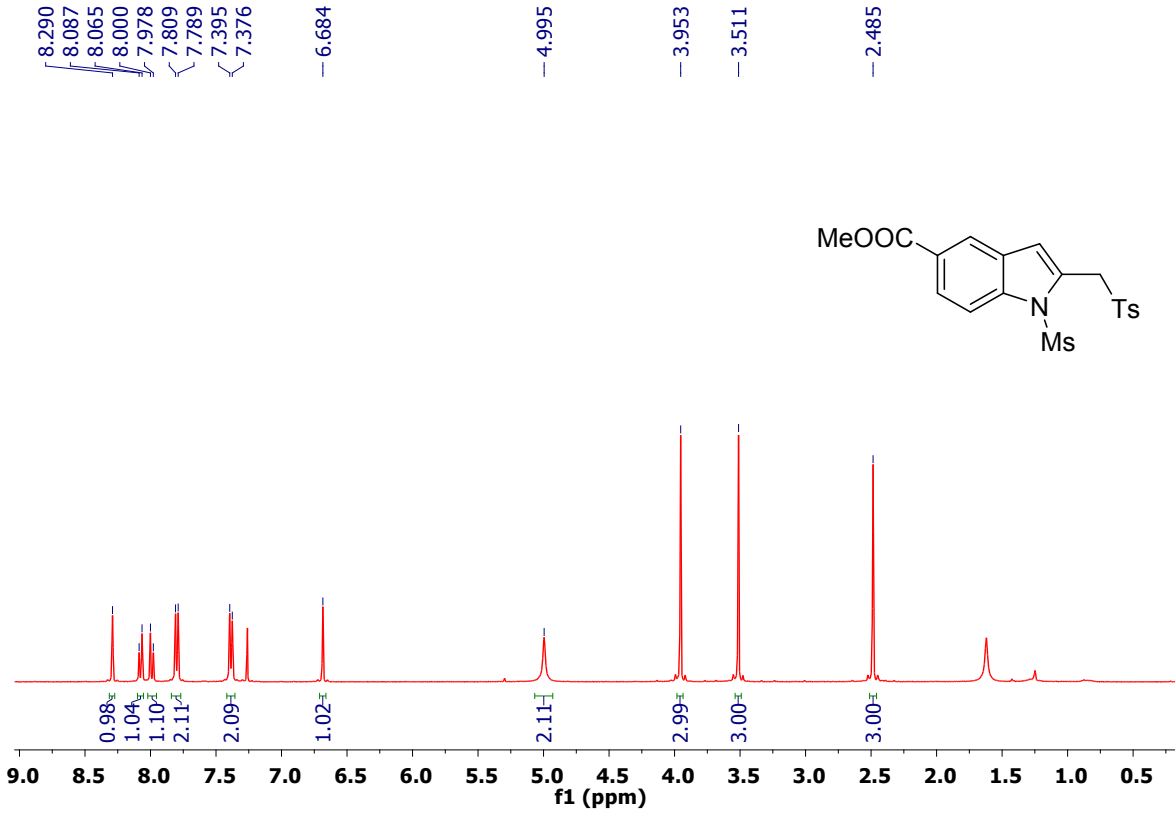
8i, CDCl₃



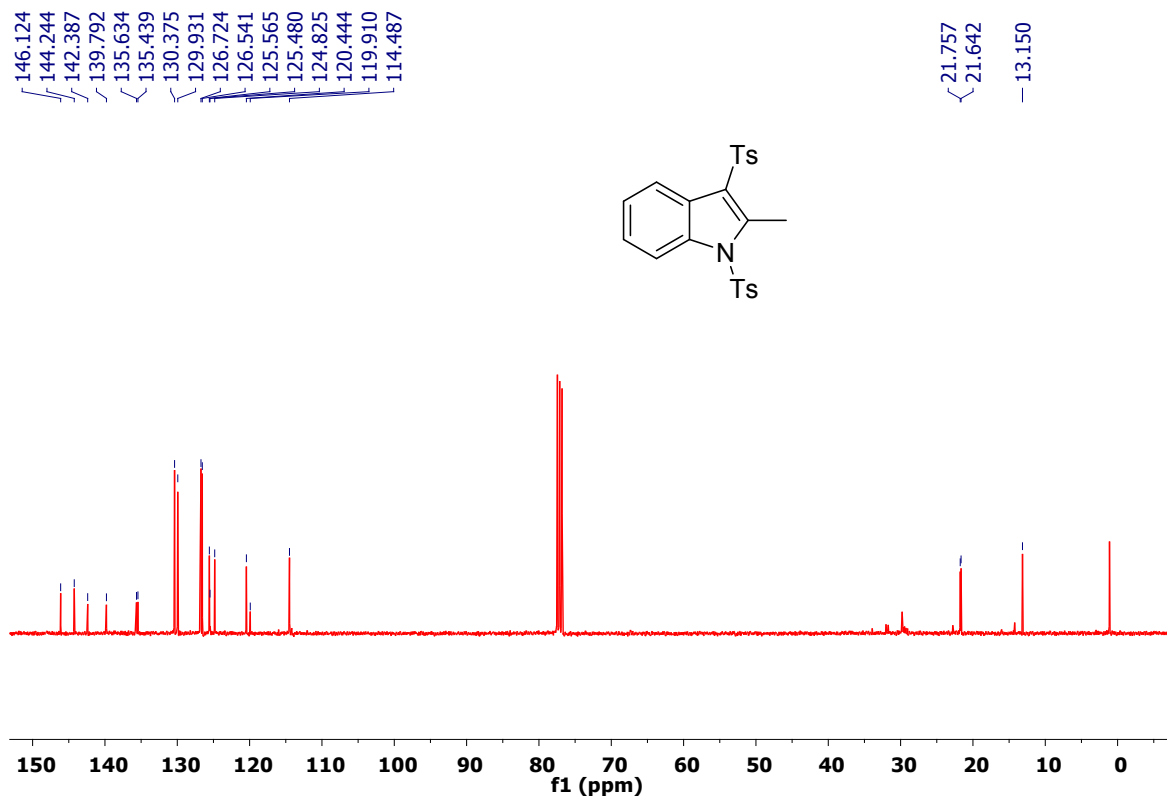
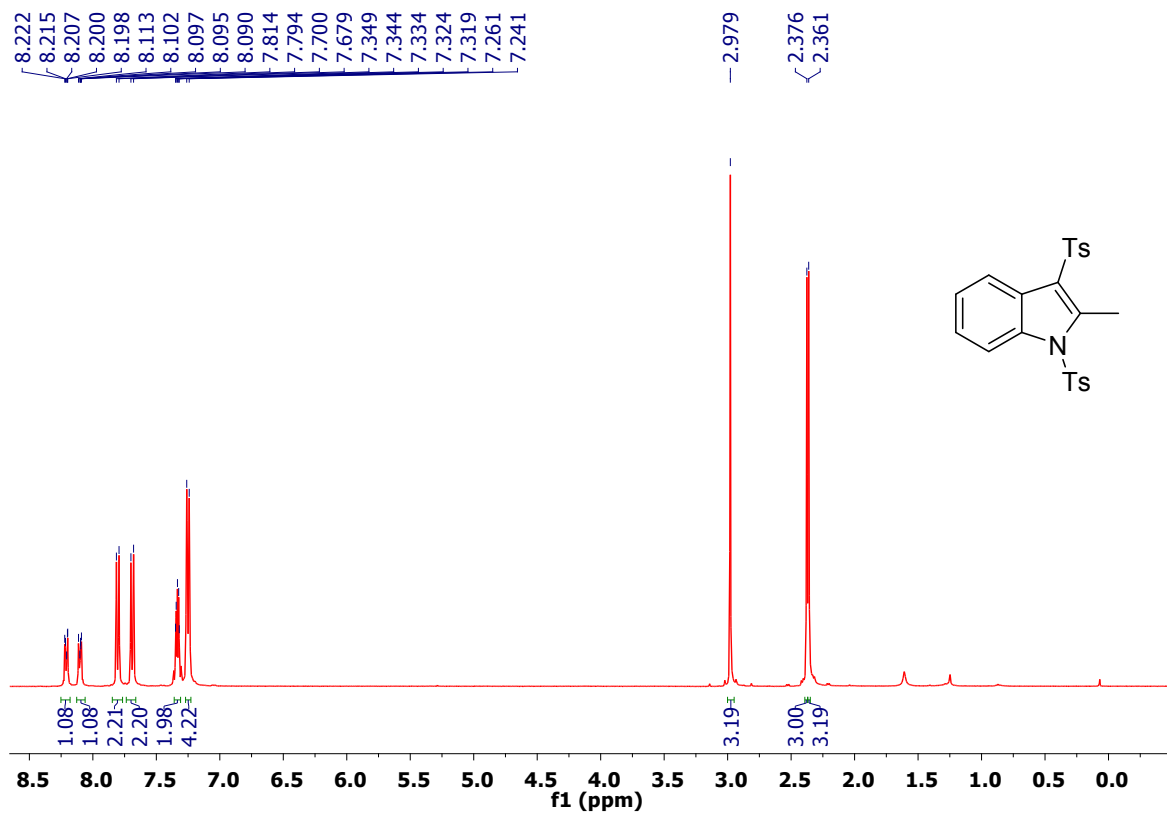
8j, CDCl₃



8k, CDCl₃



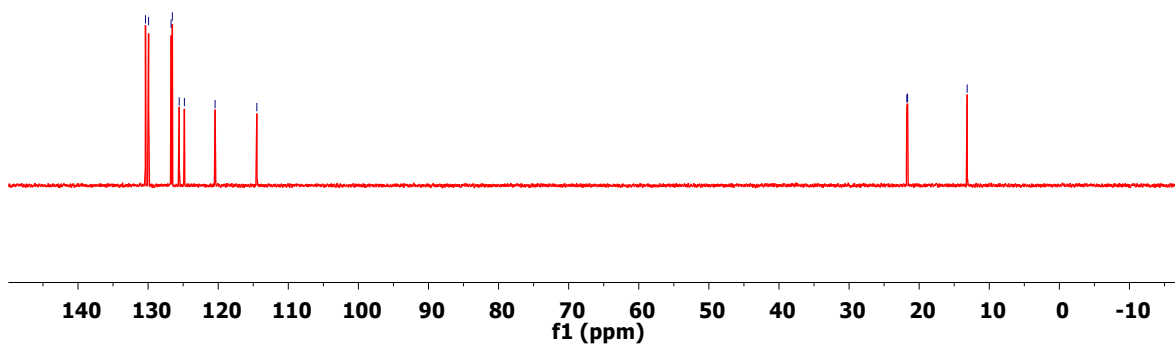
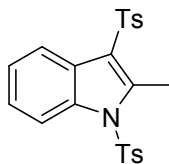
9a, CDCl₃



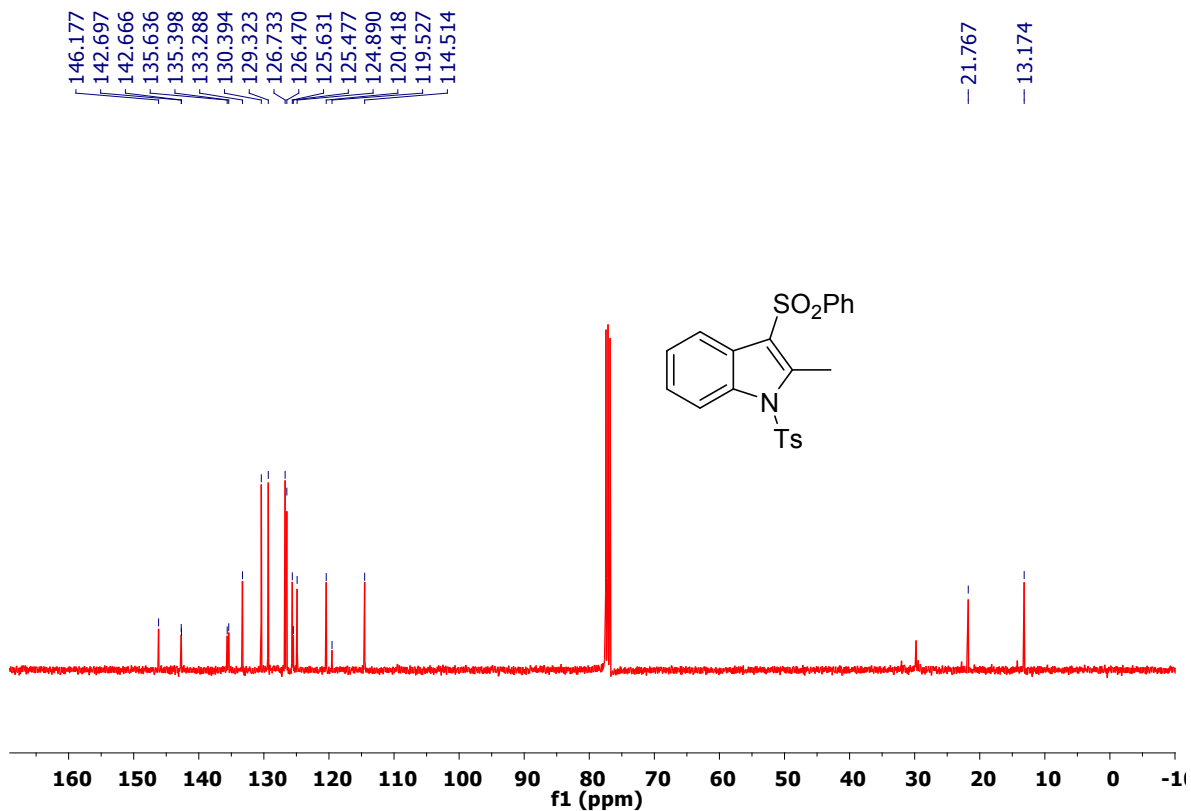
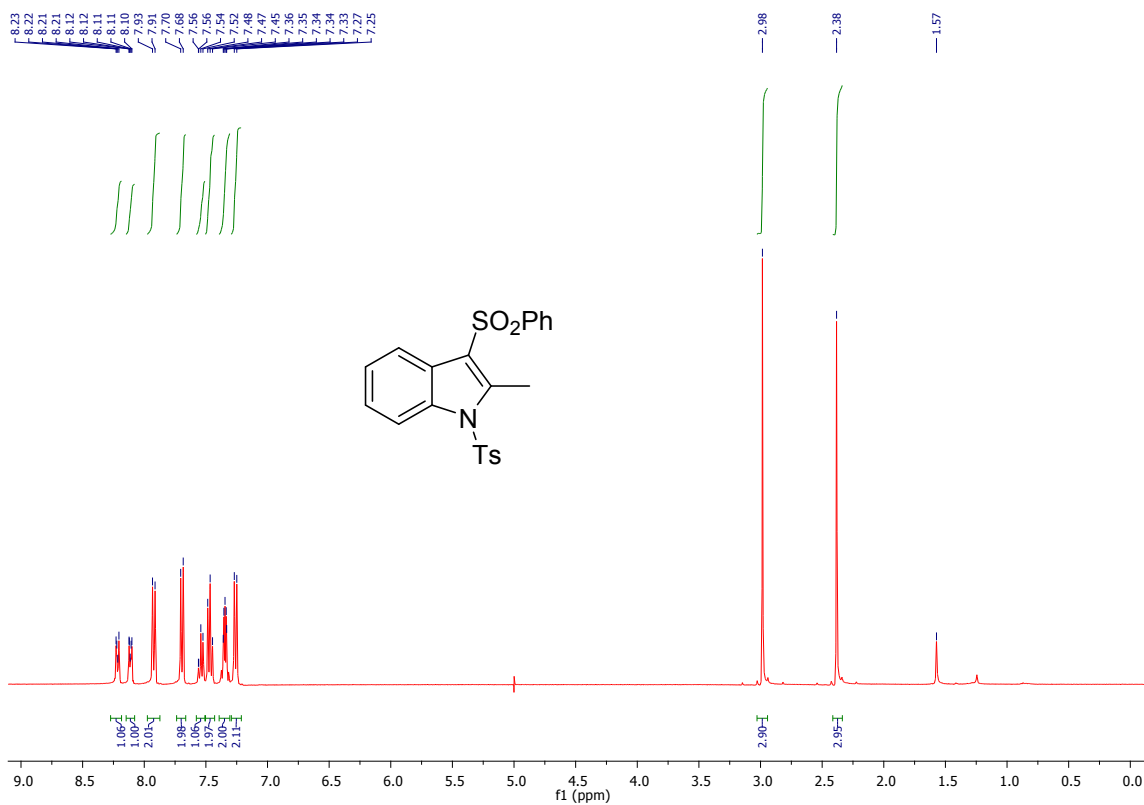
9a, CDCl₃, DEPT-135

130.373
129.929
126.723
126.540
125.562
124.823
120.444
114.487

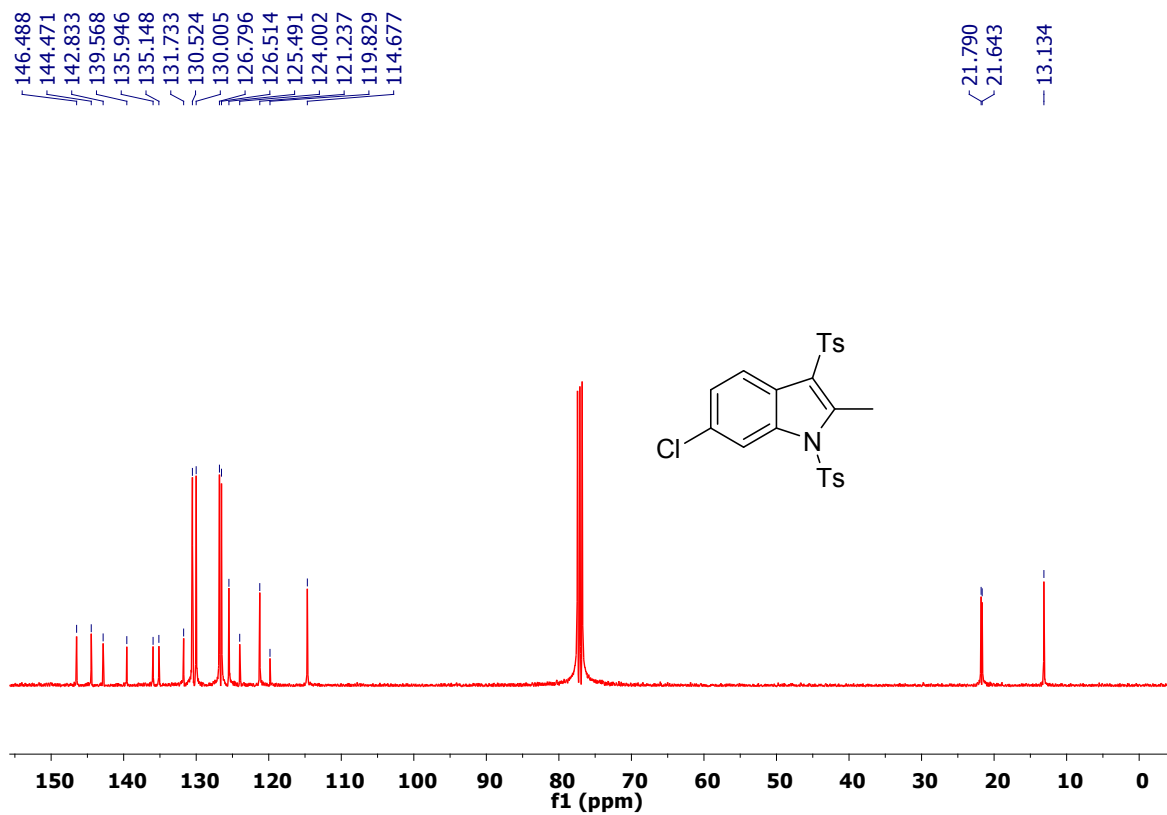
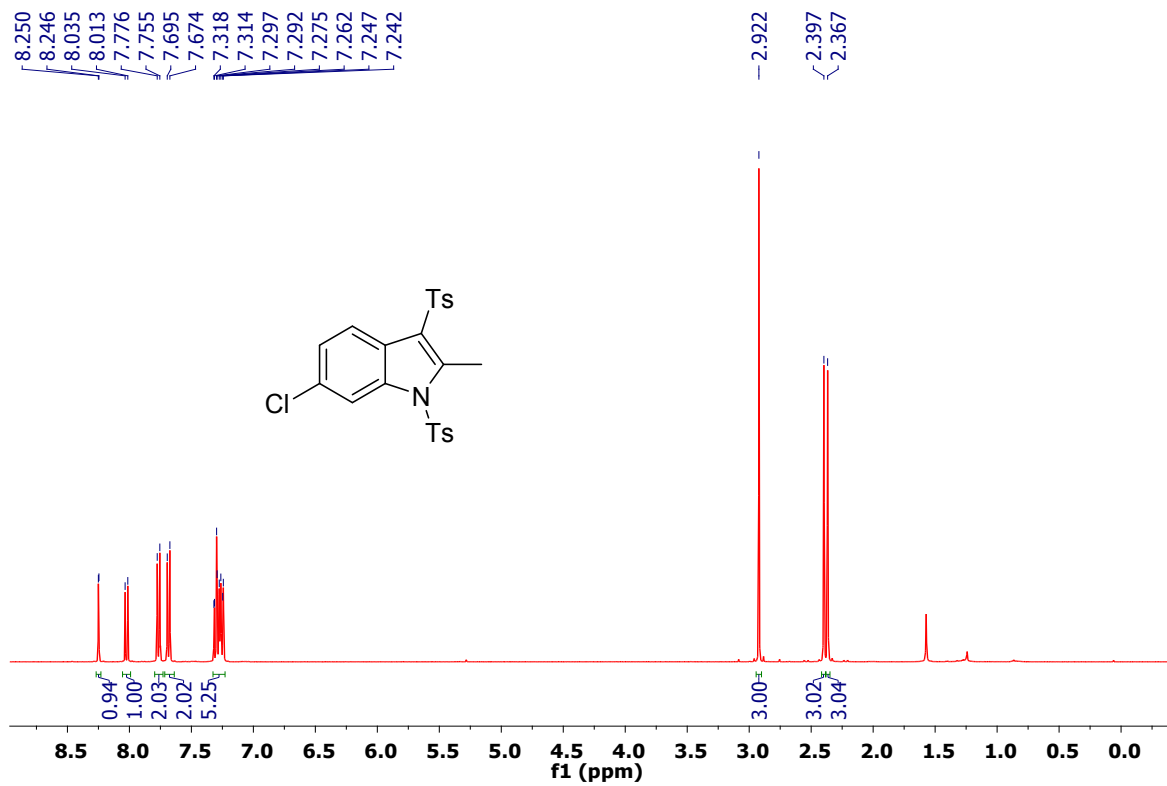
21.763
21.647
13.152



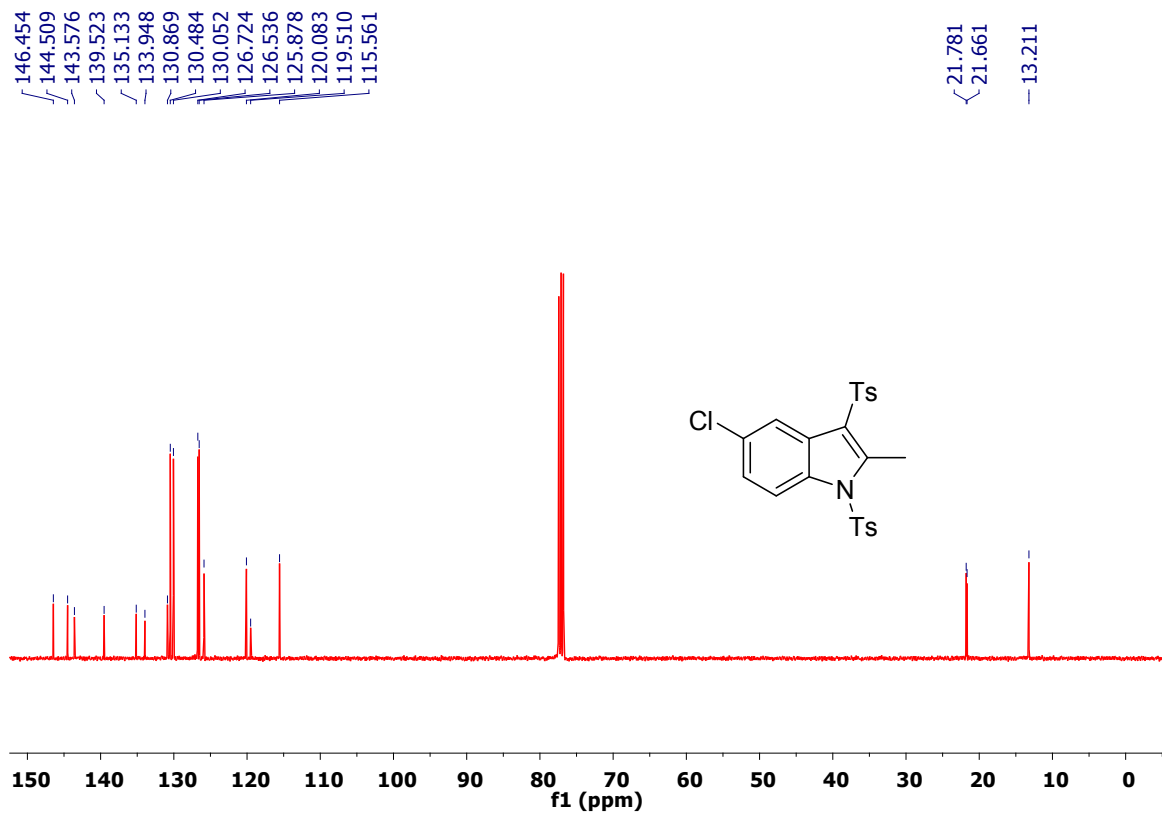
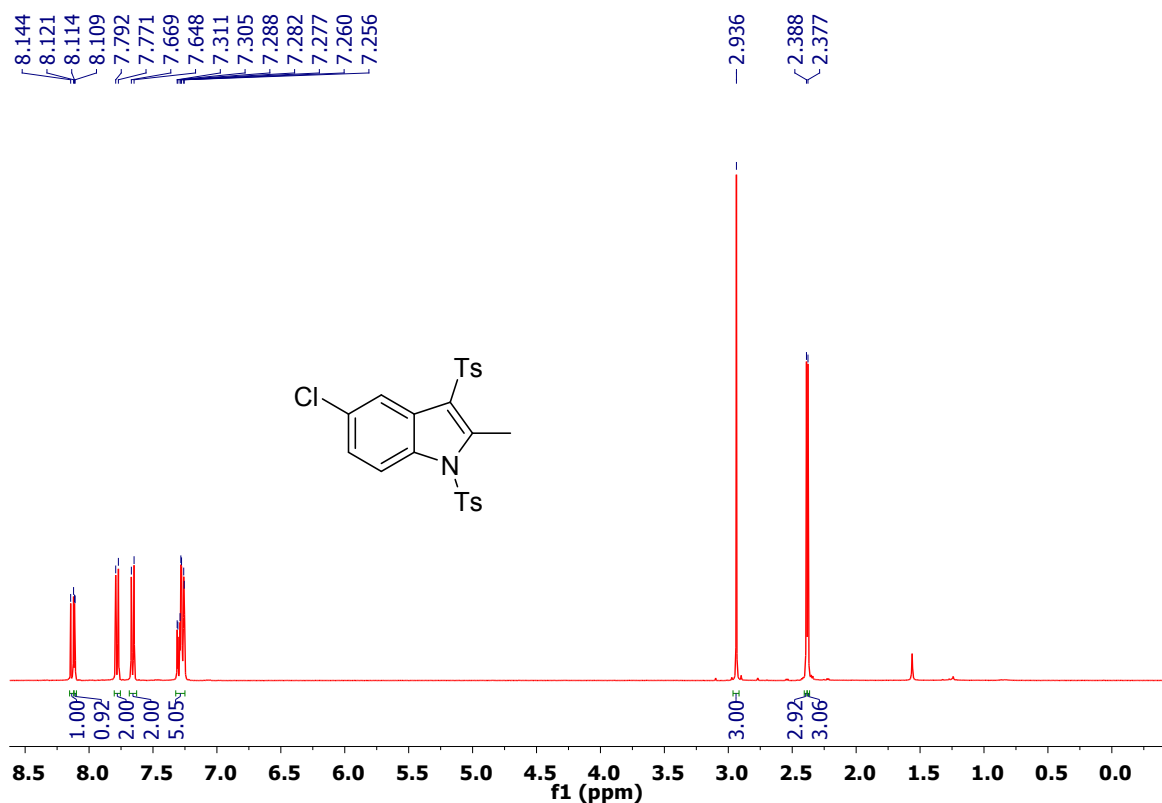
9b, CDCl₃



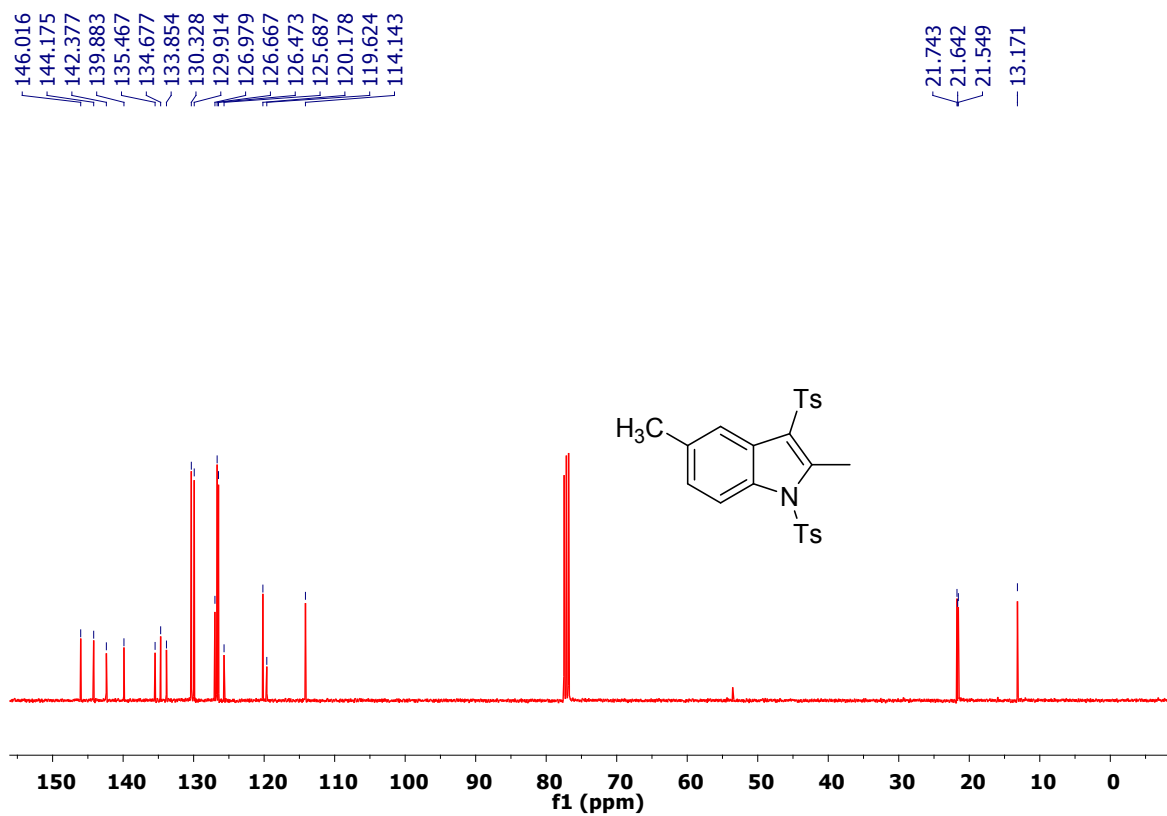
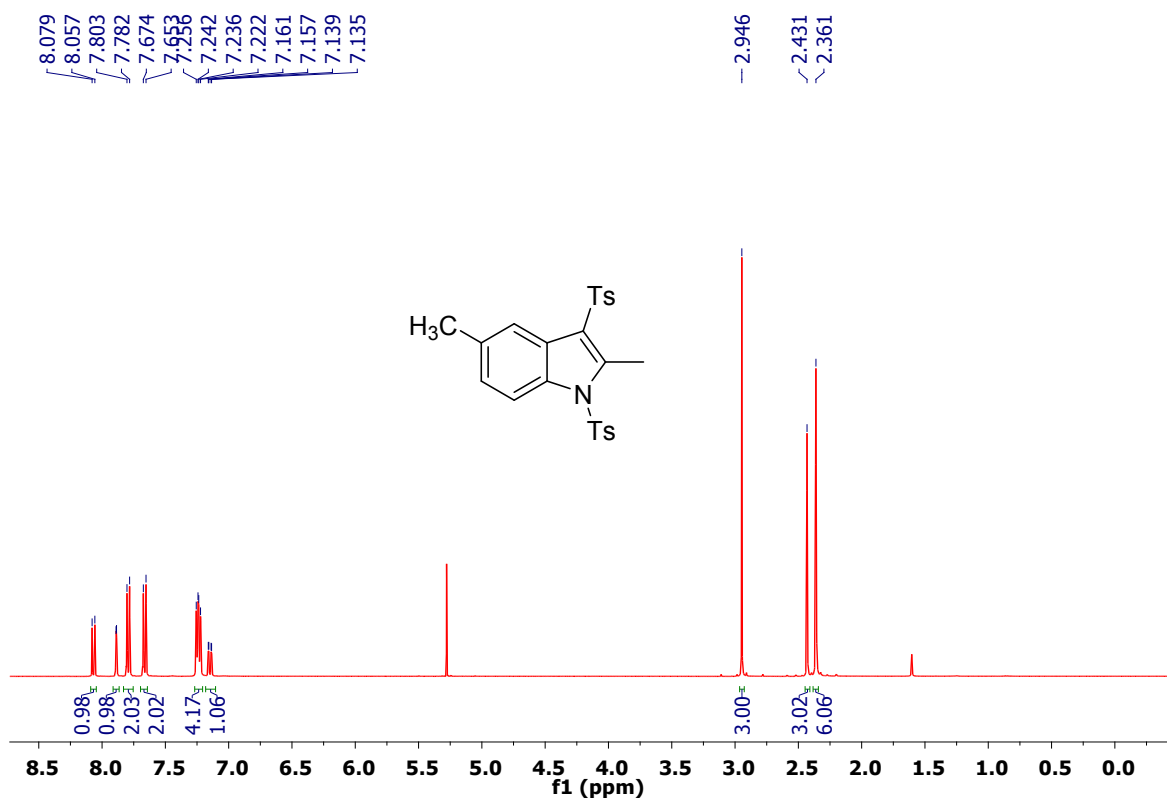
9c, CDCl₃



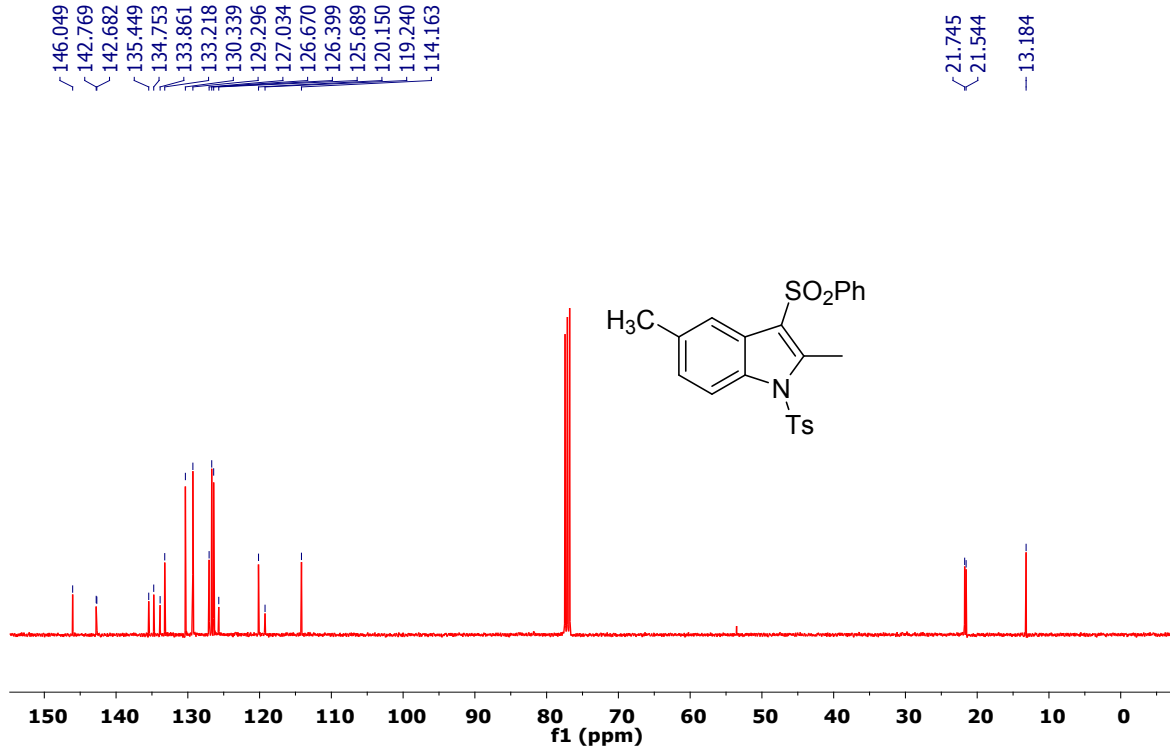
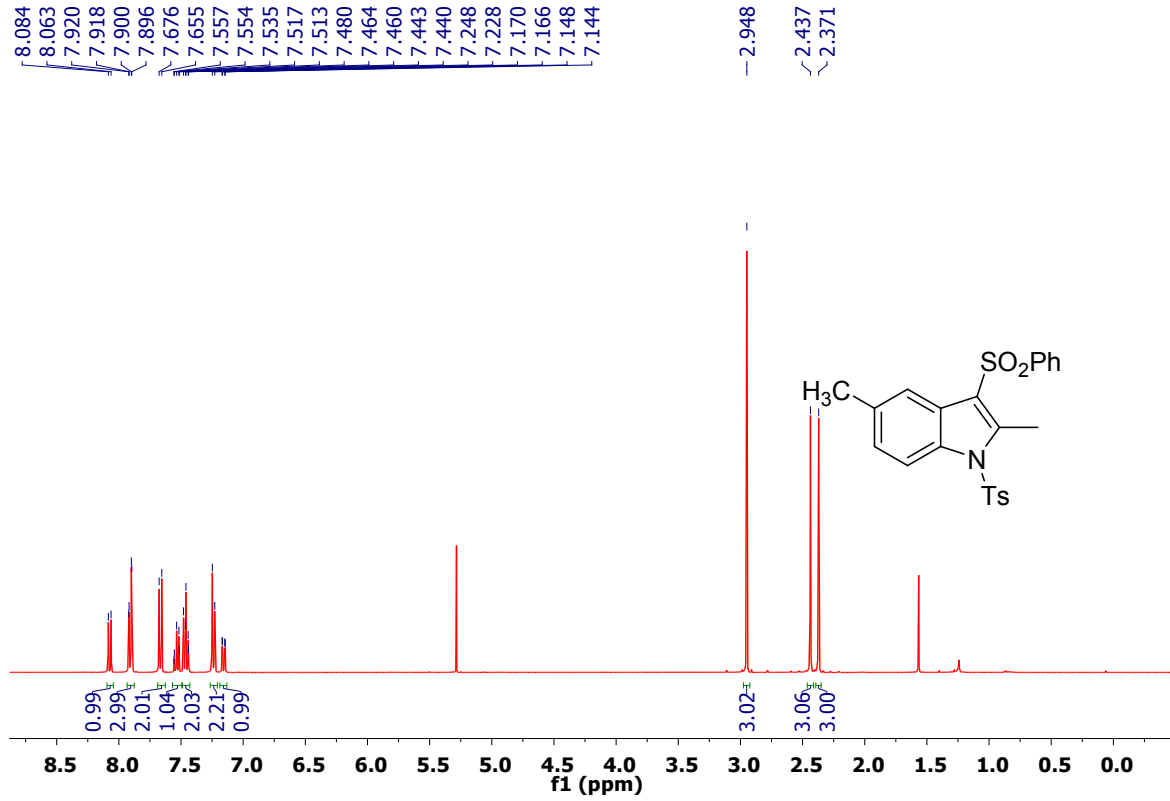
9d, CDCl₃



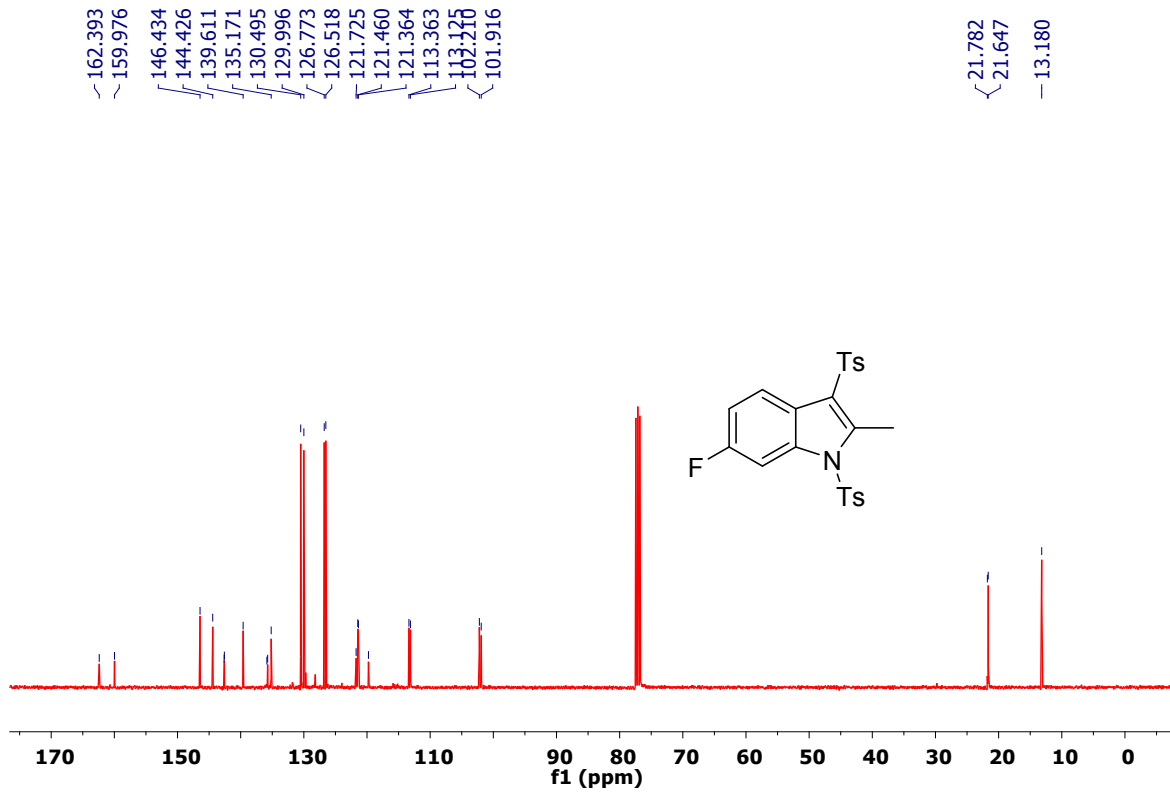
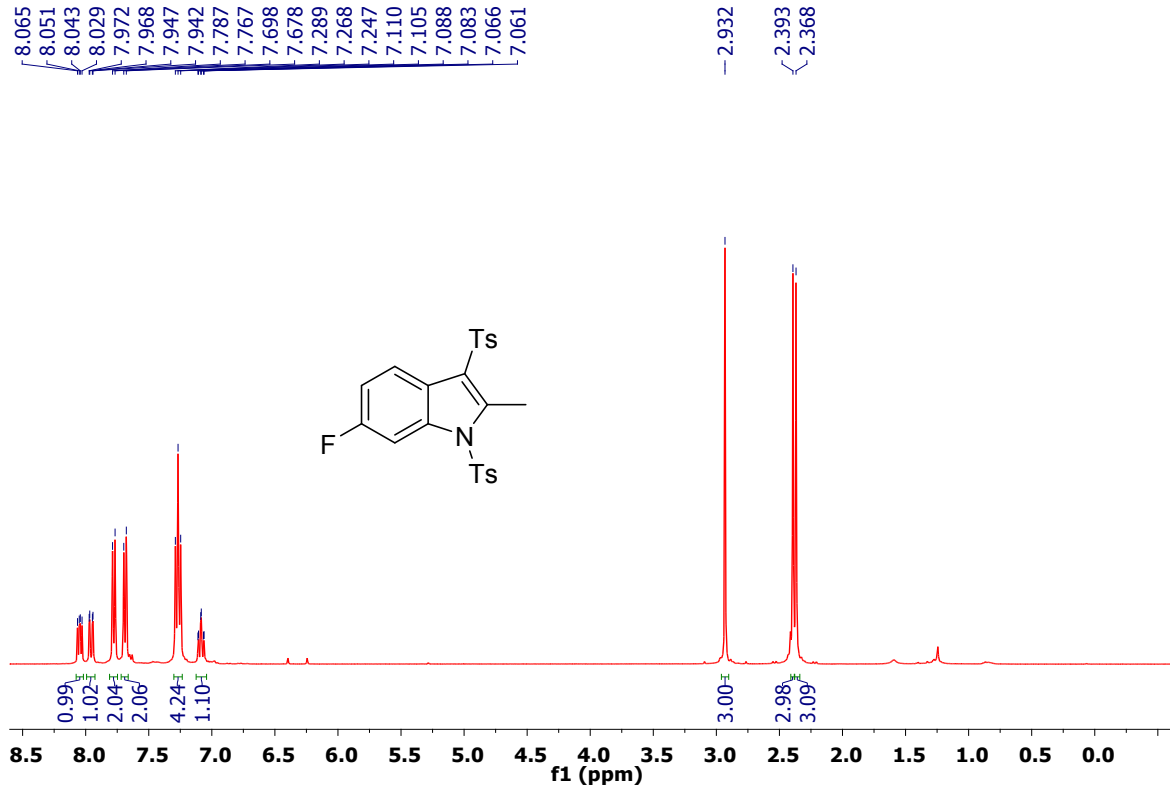
9f, CDCl₃



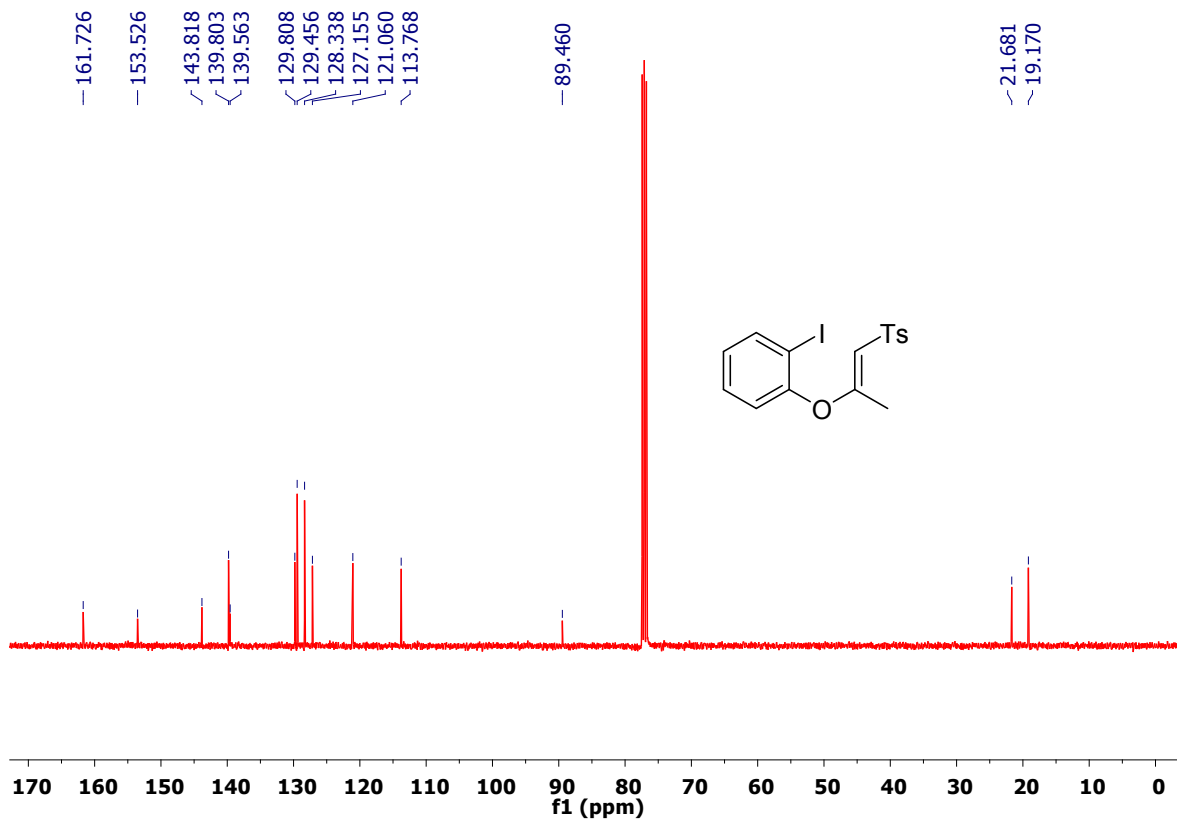
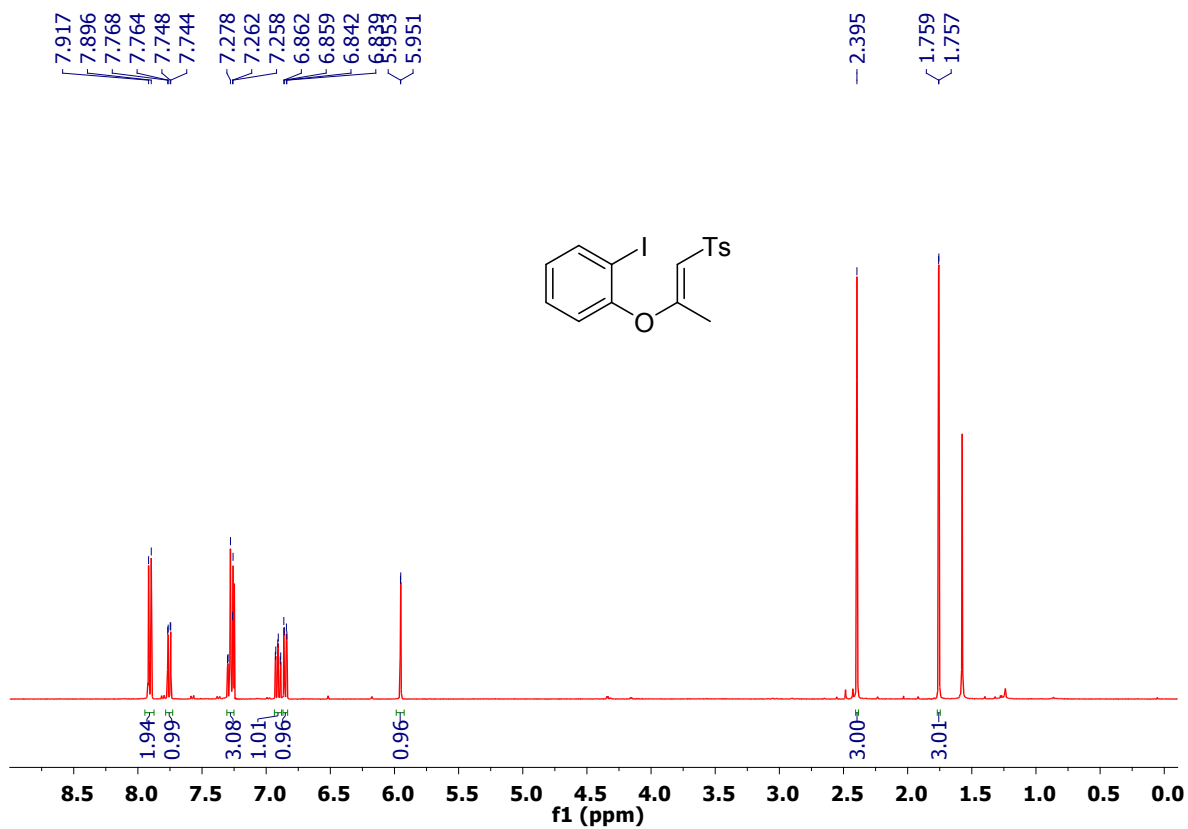
9g, CDCl₃



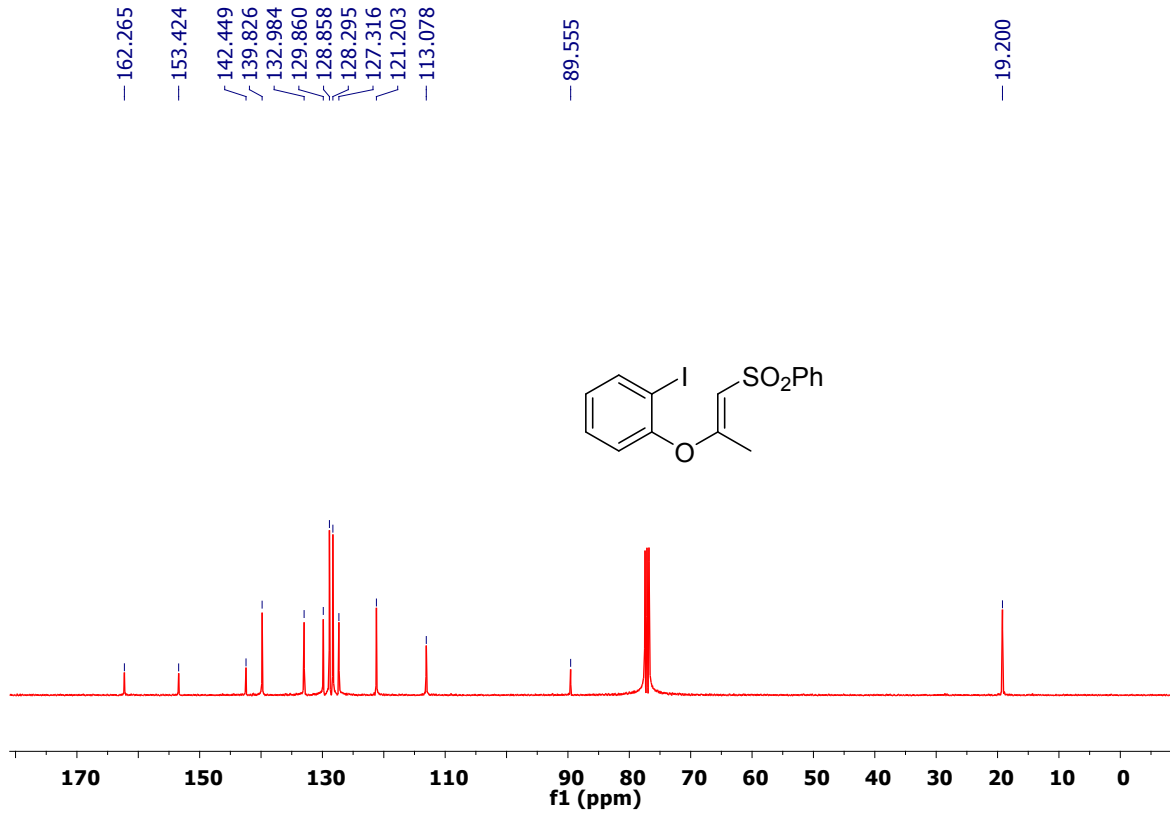
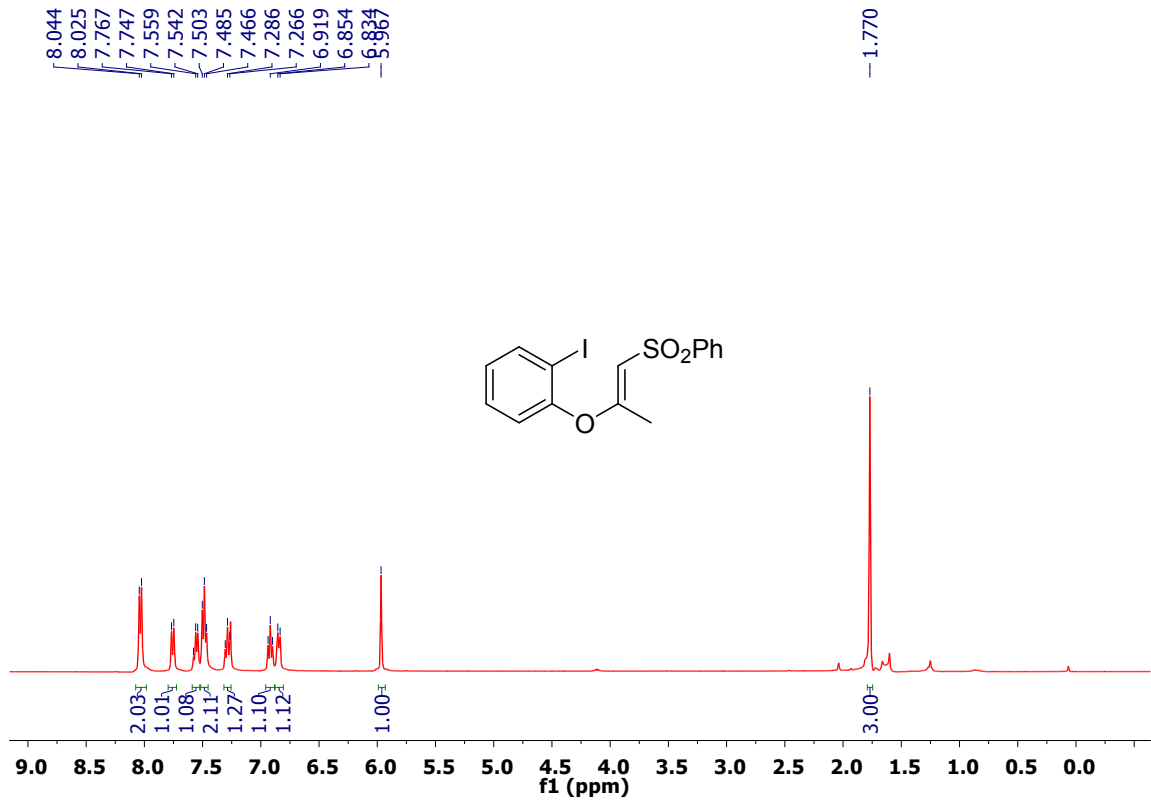
9h, CDCl₃



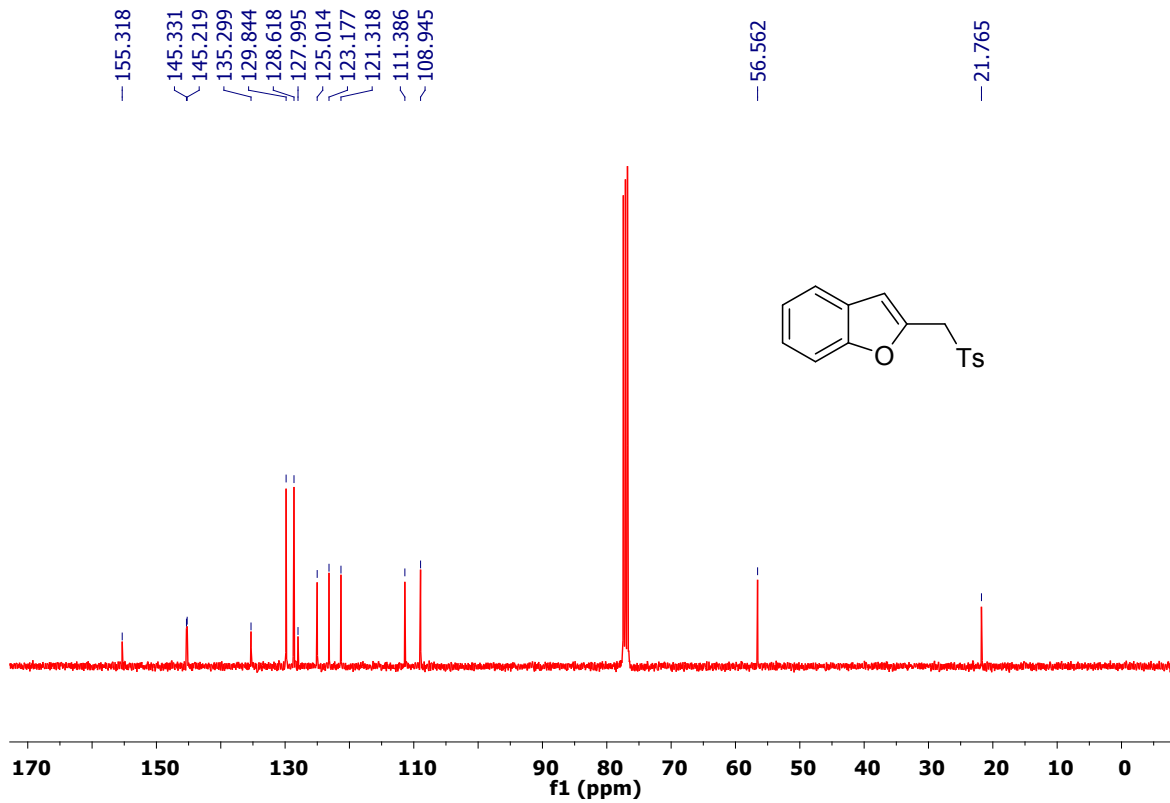
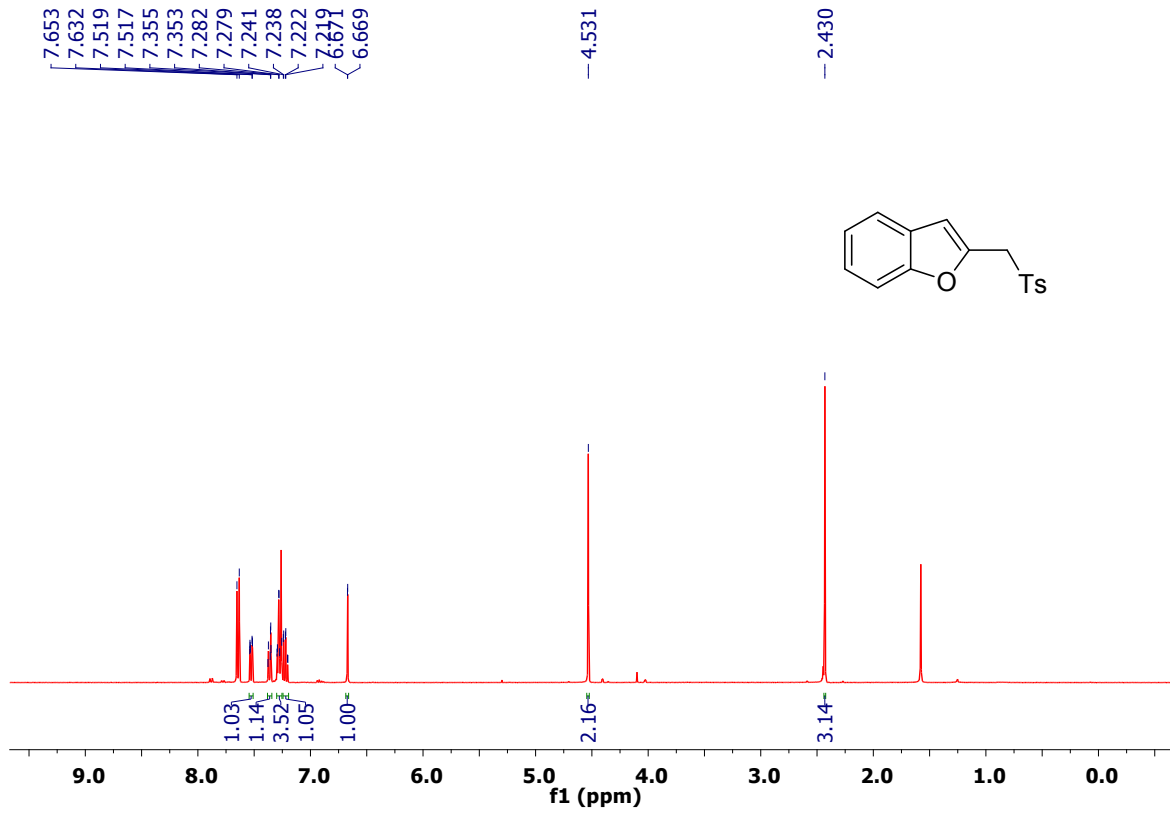
11a, CDCl₃



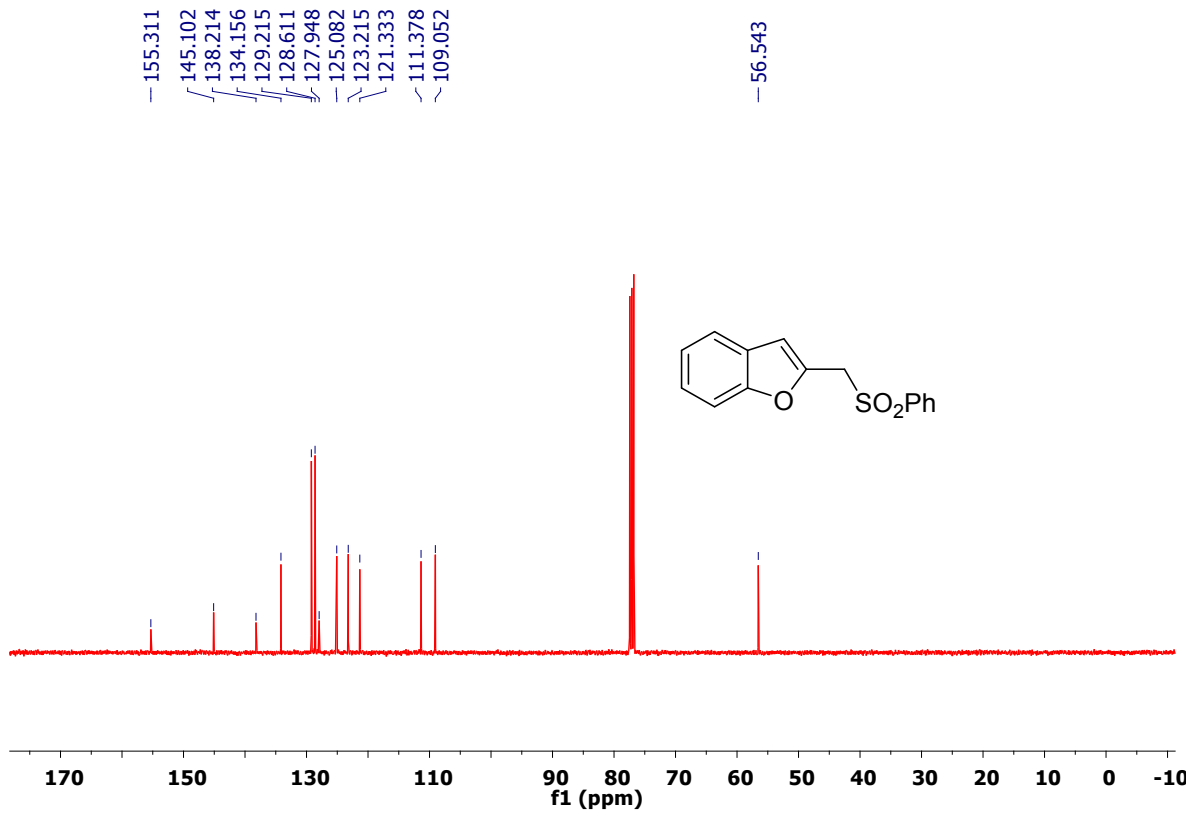
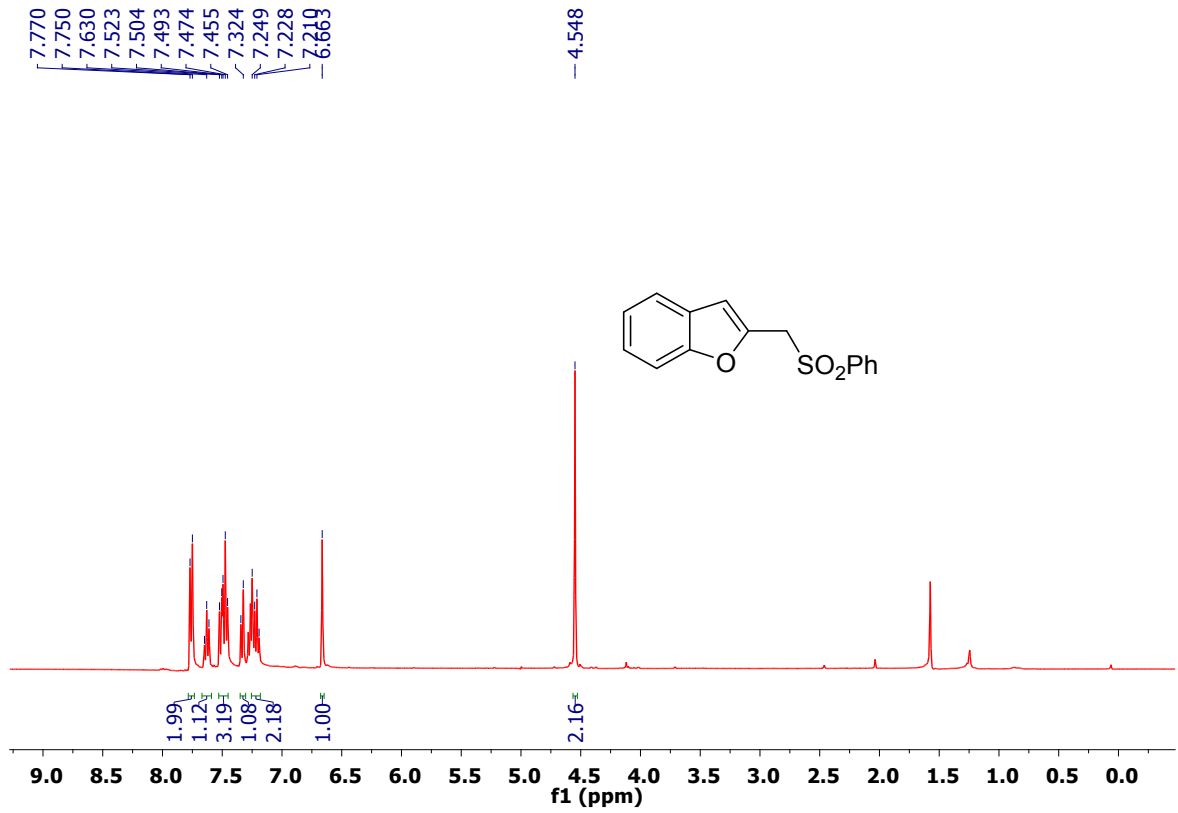
11b, CDCl₃



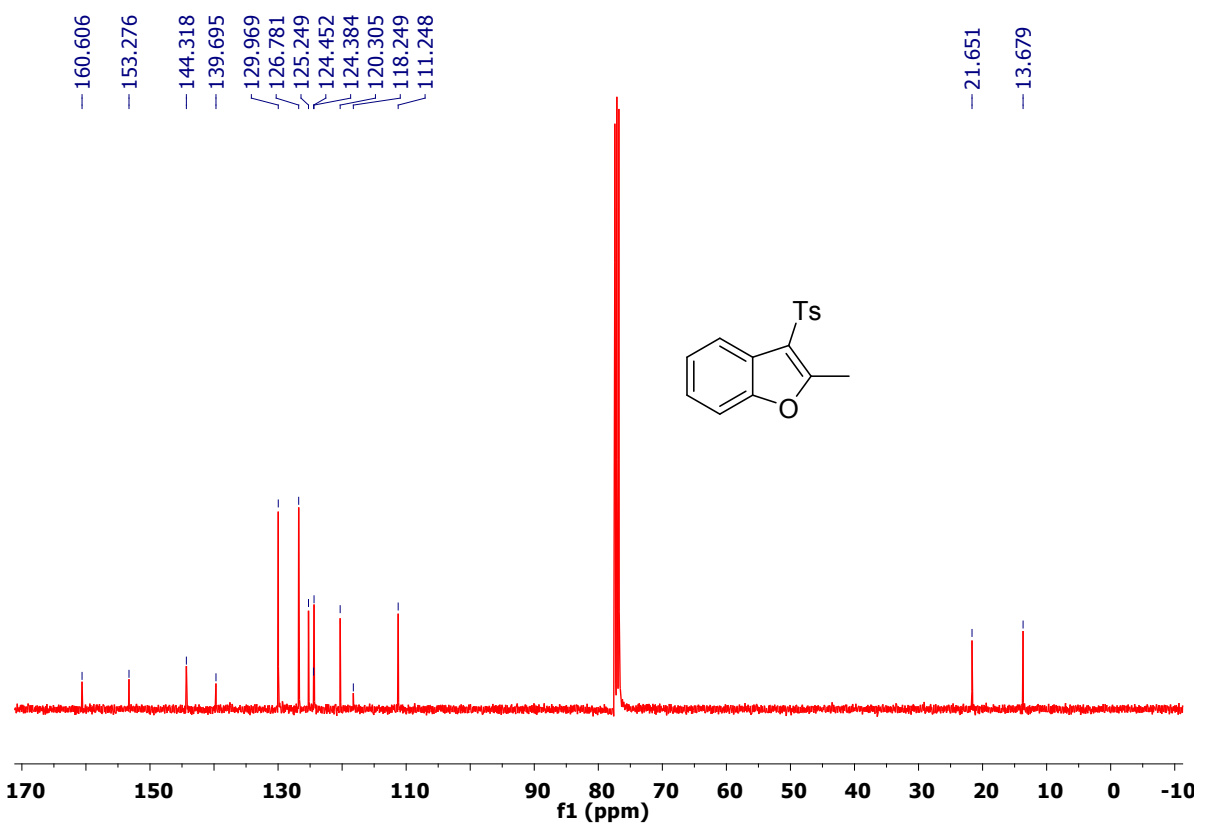
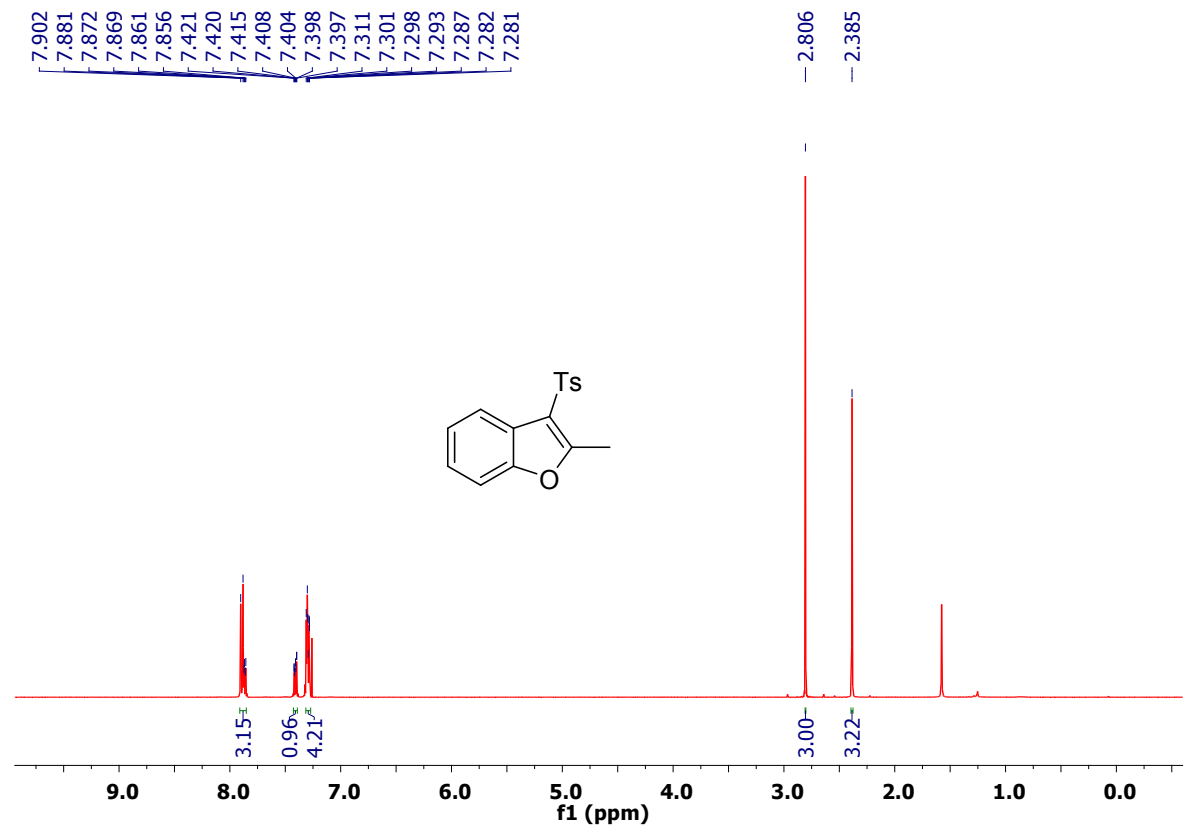
12a, CDCl₃



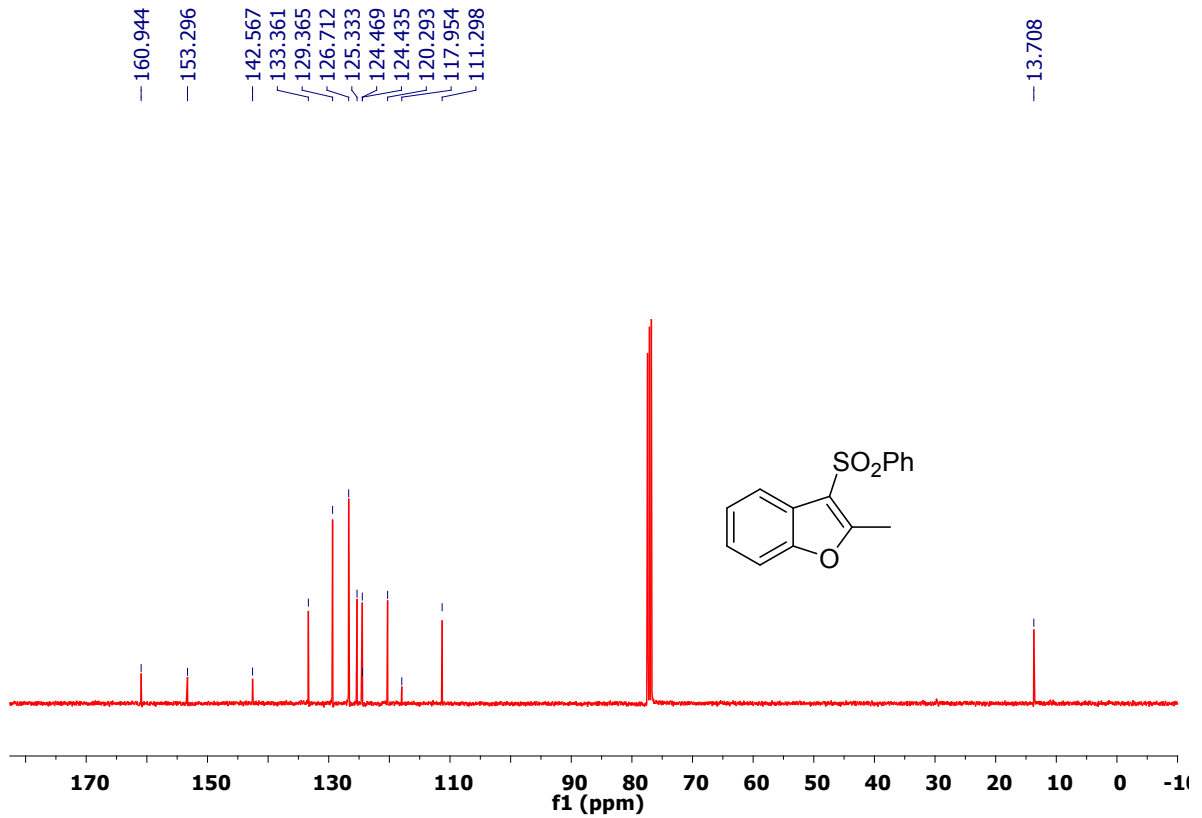
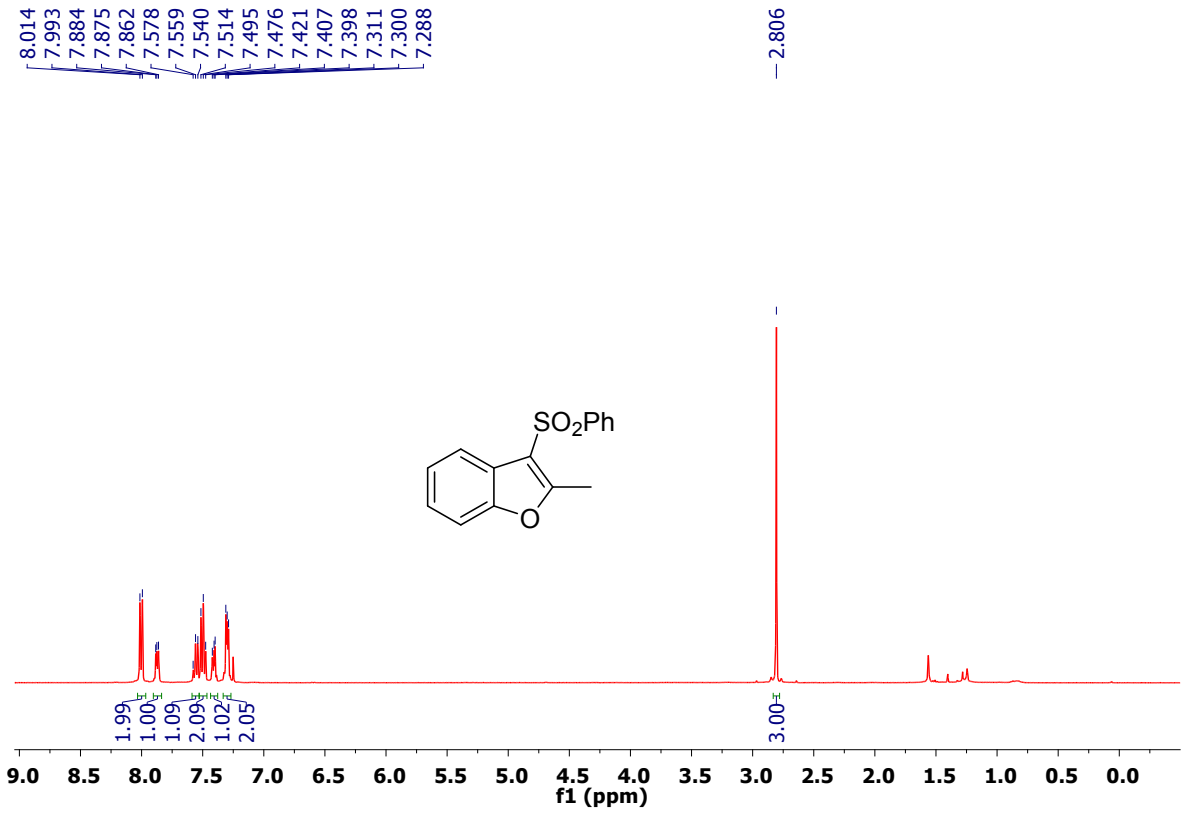
12b, CDCl₃



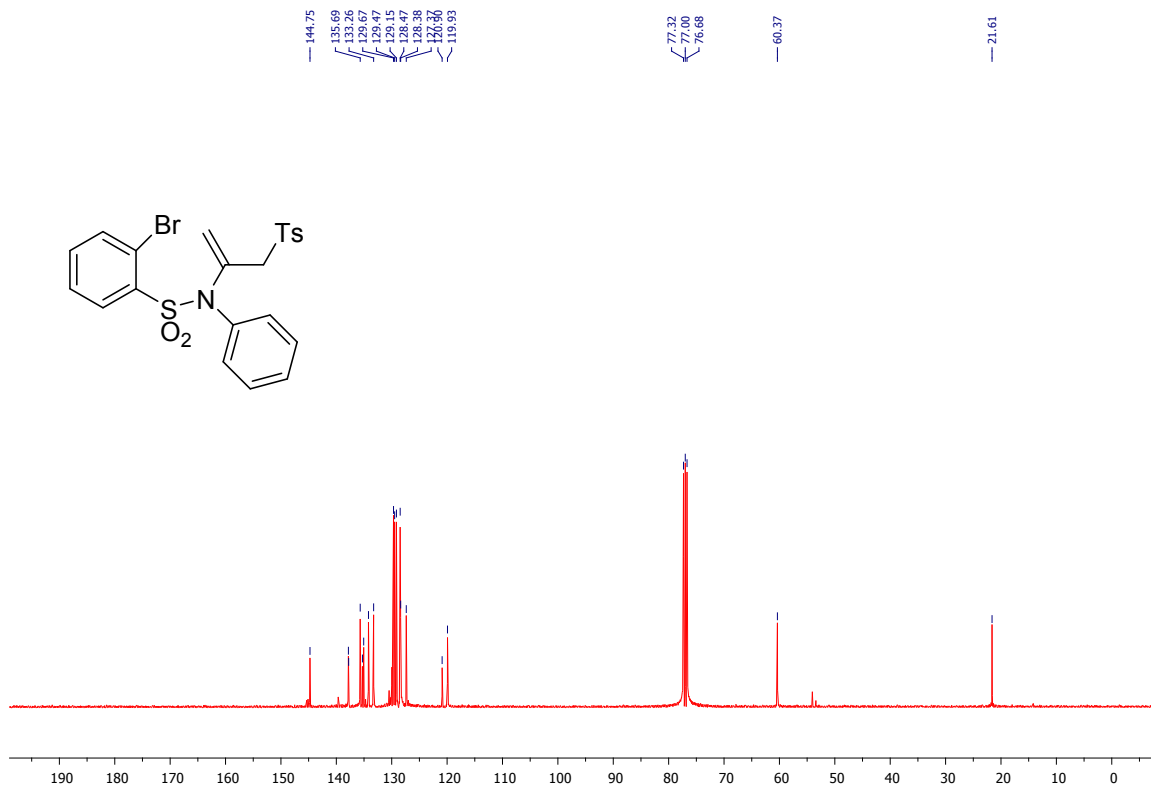
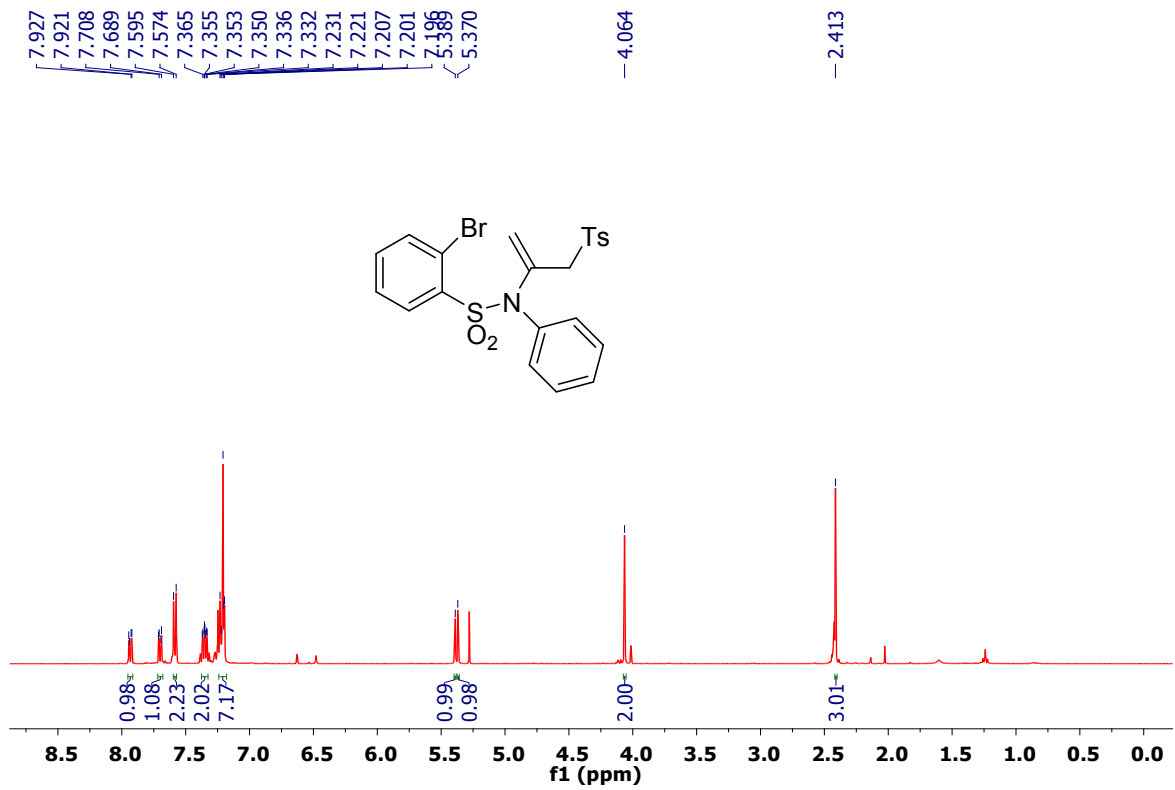
13a, CDCl₃



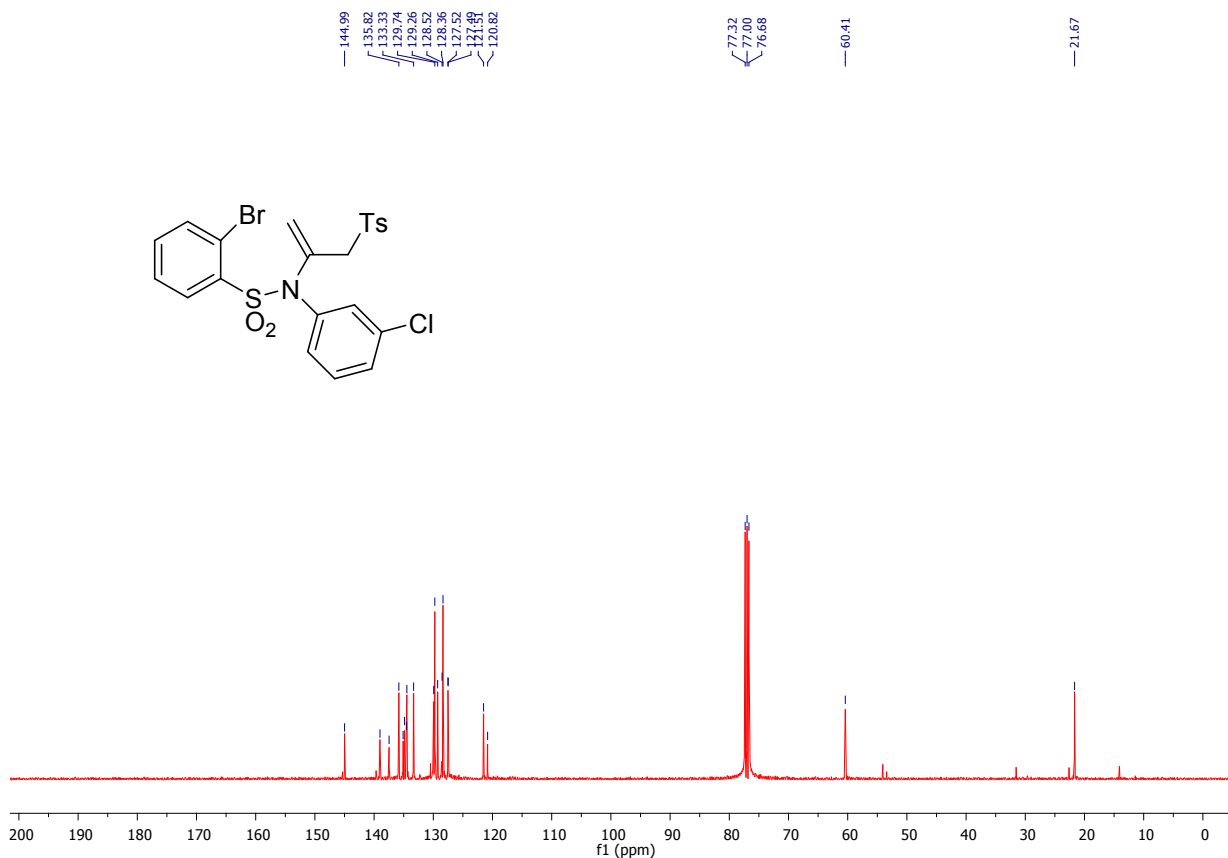
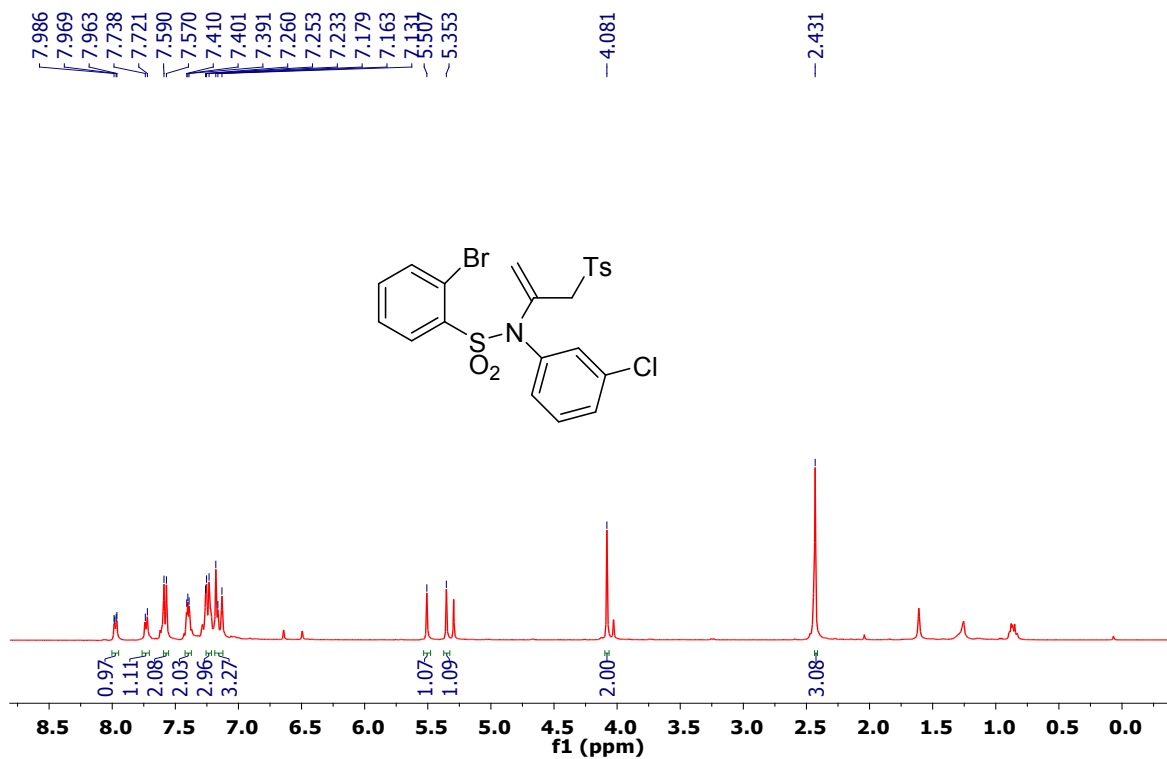
13b, CDCl₃



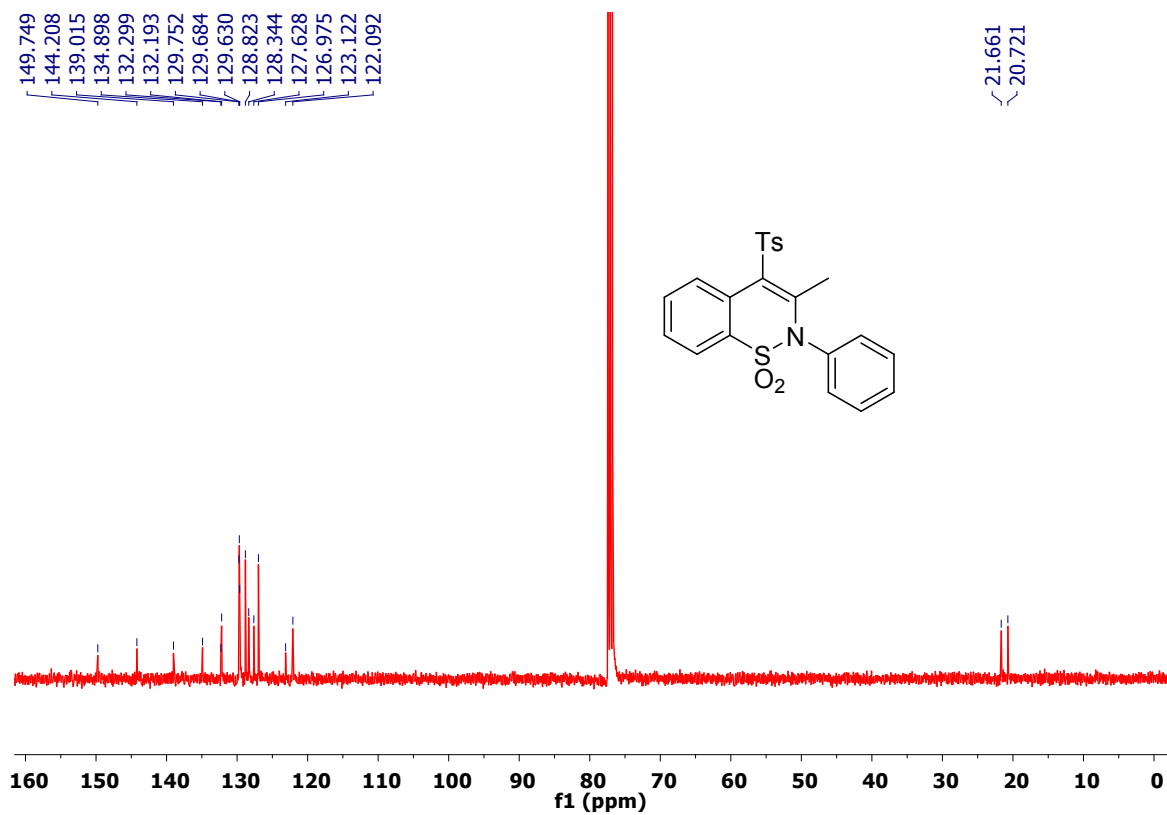
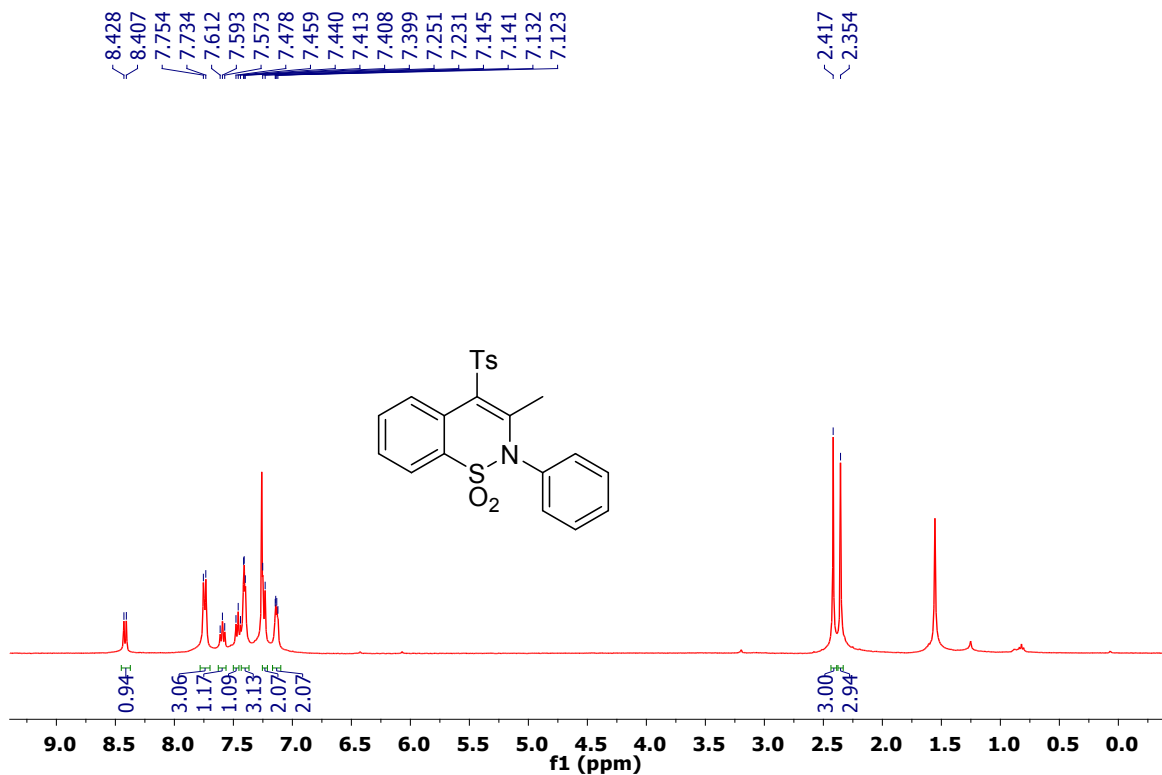
15a, CDCl₃



15b, CDCl₃



16a, CDCl₃



16b, CDCl₃

