Supporting Information

Stereoselective synthesis of C-sulfonylated aziridines from halomethyl phenyl sulfone and N-tert-butanesulfinyl imines

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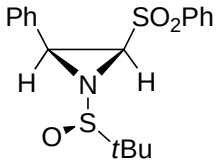
General:

Unless otherwise mentioned, solvents and reagent were purchased from commercial sources and used as received. THF was freshly distilled over sodium. Chloromethyl phenyl sulfone and bromomethyl phenyl sulfone were prepared using known procedures. ^{1}H NMR spectra were recorded on 400 MHz spectrometers with Me_4Si as internal standard. ^{13}C NMR spectra were recorded on 100 MHz spectrometers. High-resolution mass data were recorded on a high-resolution mass spectrometer in the ESI mode.

Typical procedure for the Synthesis of 2-Sulfonylated Aziridine 4a from Bromomethyl Phenyl Sulfone and (R)-N-tert-Butanesulfinyl imine 2a:

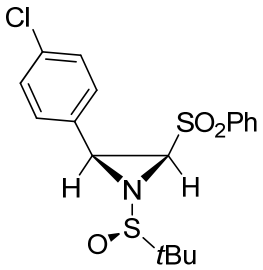
NaHMDS (1.2 equiv, 1.2 mmol, 1.0 mol/L in THF) was added to a mixture of the imine **2a** (1.0 mmol) and bromomethyl phenyl sulfone (1.2 equiv, 1.2 mmol) in THF (3.0 mL) at –70 ^{o}C. Reaction mixture was stirred over 0.5 h. Then half saturated NH_4Cl-H_2O (10 mL) was added at –70 ^{o}C and the quenched reaction mixture was extracted three times with ethyl acetate. The combined organic layers were dried over anhydrous $MgSO_4$. Evaporation of the solvent afforded the crude product, which was subject to flash chromatography to give pure aziridine **4a** (302 mg, 83 %).

(Rs,2S,3R)-1-(tert-butylsulfinyl)-2-phenyl-3-(phenylsulfonyl)aziridine (**4a**)



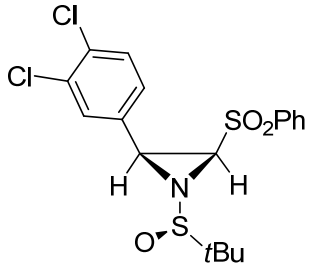
White solid, mp 122.7–128.6 ^{o}C; $[\alpha]_D^{25}$ – 7.0 (c = 1.06, $CHCl_3$); IR (film) 1448, 1333, 1157, 1081, 741, 690 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.64 – 7.56 (m, 1H), 7.54 – 7.49 (m, 2H), 7.46 – 7.38 (m, 4H), 7.37 – 7.30 (m, 3H), 4.00 (d, J = 6.5 Hz, 1H), 3.64 (d, J = 6.5 Hz, 1H), 1.26 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 138.4, 134.0, 129.4, 129.0, 128.9, 128.6, 128.2, 128.1, 57.8, 54.5, 38.4, 22.4; ESI (m/z) 364.1 (M^+ + 1), 386.1 (M^+ + 23); HRMS (ESI) calcd. For $C_{18}H_{21}NO_3S_2Na$ (M^+ + Na): 386.0855, Found 386.0855.

(Rs,2S,3R)-1-(tert-butylsulfinyl)-2-(4-chlorophenyl)-3-(phenylsulfonyl)aziridine (**4b**)



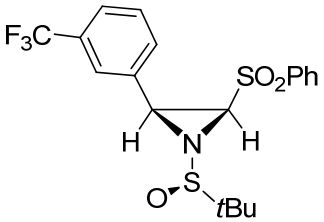
Sticky oil; $[\alpha]_D^{25}$ + 9.7 (c = 0.73, $CHCl_3$); IR (film) 1143, 1059, 1013, 880, 839, 737 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.63 (dd, J = 11.7, 4.3 Hz, 1H), 7.61 – 7.55 (m, 2H), 7.47 (t, J = 7.8 Hz, 2H), 7.38 (d, J = 8.5 Hz, 2H), 7.34 – 7.29 (m, 2H), 3.95 (d, J = 6.5 Hz, 1H), 3.62 (d, J = 6.5 Hz, 1H), 1.24 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 138.4, 134.7, 134.1, 130.3, 129.1, 128.9, 128.3, 128.1, 57.8, 54.5, 37.9, 22.4; ESI (m/z) 398.1 (M^+ + 1), 420.1 (M^+ + 23); HRMS (ESI) calcd. For $C_{18}H_{20}ClNO_3S_2Na$ (M^+ + Na): 420.0465, Found 420.0467.

(Rs,2S,3R)-1-(tert-butylsulfinyl)-2-(3,4-dichlorophenyl)-3-(phenylsulfonyl)aziridine (**4c**)



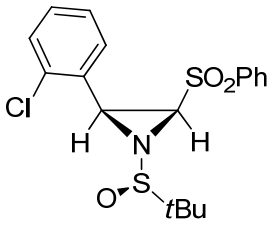
White solid, mp.50.2-52.2 °C; $[\alpha]^{25}$ – 35.9 (c = 1.11, $CHCl_3$); IR (film) 1474, 1334, 1155, 1083, 874, 729 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.69 – 7.58 (m, 3H), 7.49 (t, J = 7.8 Hz, 2H), 7.45 – 7.41 (m, 2H), 7.33 (dd, J = 8.4, 1.9 Hz, 1H), 3.92 (d, J = 6.5 Hz, 1H), 3.62 (d, J = 6.5 Hz, 1H), 1.24 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 138.2, 134.3, 133.0, 132.4, 130.9, 130.1, 130.0, 129.2, 128.23, 128.20; ESI (m/z) 432.1 (M^+ + 1), 454.1 (M^+ + 23); HRMS (ESI) calcd. For $C_{18}H_{19}Cl_2NO_3S_2Na$ (M^+ + Na): 454.0076, Found 454.0075.

(Rs,2R,3S)-1-(tert-butylsulfinyl)-2-(phenylsulfonyl)-3-(3-(trifluoromethyl)phenyl)aziridine (**4d**)



Oil; $[\alpha]^{25}$ + 3.7 (c = 0.97, $CHCl_3$); IR (film) 1471, 1069, 867, 809, 769, 746 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.71 (d, *J* = 7.7 Hz, 1H), 7.63 (t, *J* = 7.3 Hz, 2H), 7.58 (s, 1H), 7.55 – 7.50 (m, 3H), 7.46 (q, *J* = 7.7 Hz, 2H), 4.02 (d, *J* = 6.5 Hz, 1H), 3.67 (d, *J* = 6.5 Hz, 1H), 1.26 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 138.1, 134.2, 132.2, 130.6, 130.4 (q, J = 32.0 Hz), 129.1, 128.6, 128.0, 125.6 (dd, *J* = 43.0, 3.8 Hz), 125.1, 122.40, 57.8, 54.4, 37.7, 22.3; ESI (m/z) 432.1 (M^+ + 1), 454.1 (M^+ + 23); HRMS (ESI) calcd. For $C_{19}H_{20}F_3NO_3S_2Na$ (M^+ + Na): 454.0729, Found 454.0730.

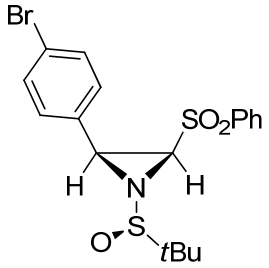
(Rs,2S,3R)-1-(tert-butylsulfinyl)-2-(2-chlorophenyl)-3-(phenylsulfonyl)aziridine (**4e**)



Sticky oil; $[\alpha]^{25}$ – 251.1 (c = 0.54, $CHCl_3$); IR (film) 1447, 1324, 1153, 1085, 925, 750 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.05 – 7.99 (m, 2H), 7.72 (t, *J* = 7.5 Hz, 1H), 7.62 (t, *J* = 7.7 Hz, 2H), 7.41 (dd, *J* = 8.0, 0.9 Hz, 1H), 7.32 (td, *J* = 7.8, 1.3 Hz, 1H), 7.20 (td, *J* = 7.6, 0.9 Hz, 1H), 7.08 (dd, *J* = 7.7, 1.2 Hz, 1H), 4.54 (s, 1H), 4.22 (d, *J* = 3.8 Hz, 1H), 1.14 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 137.4, 136.6, 134.5, 131.0, 130.1, 129.6,

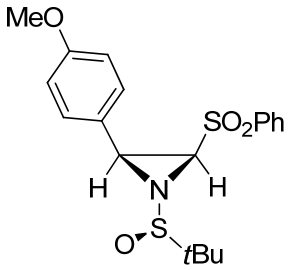
129.5, 128.8, 128.0, 126.9, 57.4, 50.7, 44.5, 21.9; ESI (m/z) 398.1 (M^+ + 1), 420.1 (M^+ + 23); HRMS (ESI) calcd. For $C_{18}H_{20}ClNO_3S_2Na$ (M^+ + Na): 420.0465, Found 420.0468.

(Rs,2R,3S)-1-(tert-butylsulfinyl)-(4-bromophenyl)-3-(phenylsulfonyl)aziridine (**4f**)



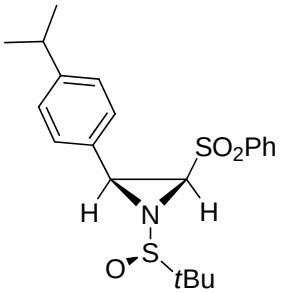
Sticky oil; $[\alpha]^{25}$ + 13.8 (c = 1.23, $CHCl_3$); IR (film) 1489, 1447, 1333, 1155, 1083, 728 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.63 (t, J = 7.4 Hz, 1H), 7.59 – 7.53 (m, 2H), 7.47 (dd, J = 7.9, 5.3 Hz, 4H), 7.30 (d, J = 8.4 Hz, 2H), 3.93 (d, J = 6.5 Hz, 1H), 3.61 (d, J = 6.5 Hz, 1H), 1.23 (s, 9H); ^{13}C NMR ($CDCl_3$) δ138.3, 134.1, 131.3, 130.5, 129.1, 128.6, 128.1, 122.8, 57.8, 54.4, 37.9, 22.4; ESI (m/z) 443 (M^+ + 1); HRMS (ESI) calcd. For $C_{18}H_{20}BrNO_3S_2Na$ (M^+ + Na): 463.9960, Found 463.9979.

(Rs,2R,3S)-1-(tert-butylsulfinyl)-(4-methoxyphenyl)-3-(phenylsulfonyl)aziridine (**4g**)



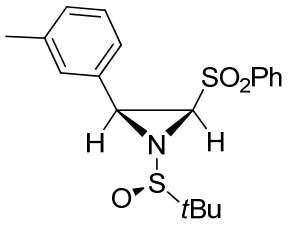
Sticky oil; $[\alpha]^{25}$ + 1.2 (c = 0.47, $CHCl_3$); IR (film) 1515, 1332, 1253, 1155, 1082, 824, 730 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.64 – 7.58 (m, 1H), 7.55 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.44 (dd, *J* = 8.1, 7.5 Hz, 2H), 7.34 (t, *J* = 5.8 Hz, 2H), 6.90 – 6.84 (m, 2H), 3.94 (d, *J* = 6.4 Hz, 1H), 3.83 (s, 3H), 3.58 (d, *J* = 6.4 Hz, 1H), 1.25 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 159.9, 138.6, 133.9, 130.2, 129.0, 128.2, 121.3, 113.5, 57.7, 55.2, 54.5, 38.3, 22.4; ESI (m/z) 394.1 (M^+ + 1), 416.1 (M^+ + 23); HRMS (ESI) calcd. For $C_{19}H_{23}NO_4S_2Na$ (M^+ + Na): 416.0961, Found 416.0963.

(Rs,2S,3R)-1-(tert-butylsulfinyl)-2-(4-isopropylphenyl)-3-(phenylsulfonyl)aziridine (**4h**)



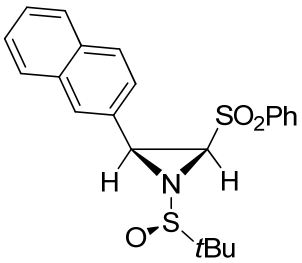
Sticky oil; $[\alpha]^{25}$ – 6.1 (c = 0.70, $CHCl_3$); IR (film) 1081, 1030, 964, 908, 783, 746 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.61 – 7.55 (m, 1H), 7.50 – 7.45 (m, 2H), 7.42 – 7.36 (m, 2H), 7.29 (d, J = 8.2 Hz, 2H), 7.16 (d, J = 8.2 Hz, 2H), 3.96 (d, J = 6.5 Hz, 1H), 3.63 (d, J = 6.5 Hz, 1H), 2.92 (dt, J = 13.8, 6.9 Hz, 1H), 1.28 (d, J = 1.2 Hz, 3H), 1.26 (s, 12H); ^{13}C NMR ($CDCl_3$) δ 149.3, 138.5, 133.8, 128.9, 128.8, 128.2, 126.6, 126.1, 57.7, 54.6, 38.4, 33.8, 23.98, 23.90, 22.5; ESI (m/z) 406.2 (M^+ + 1), 428.2 (M^+ + 23); HRMS (ESI) calcd. For $C_{21}H_{27}NO_3S_2Na$ (M^+ + Na): 428.1325, Found 428.1331.

(Rs,2R,3S)-1-(tert-butylsulfinyl)-2-(phenylsulfonyl)-3-m-tolylaziridine (**4i**)



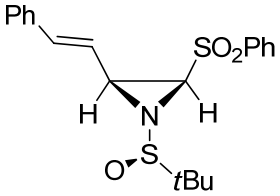
Oil; $[\alpha]^{25}$ + 4.0 (c = 0.85, $CHCl_3$); IR (film) 1333, 1156, 1076, 755, 728, 685 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.63 – 7.56 (m, 1H), 7.51 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.41 (t, *J* = 7.8 Hz, 2H), 7.25 – 7.20 (m, 2H), 7.16 – 7.09 (m, 2H), 3.96 (d, *J* = 6.6 Hz, 1H), 3.63 (d, *J* = 6.6 Hz, 1H), 2.32 (s, 3H), 1.26 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 138.3, 137.6, 133.8, 129.6, 129.3, 129.2, 128.9, 128.2, 127.9, 125.9, 57.7, 54.4, 38.3, 22.4, 21.3; ESI (m/z) 378.1 (M^+ + 1), 400.1 (M^+ + 23); HRMS (ESI) calcd. For $C_{19}H_{23}NO_3S_2Na$ (M^+ + Na): 400.1012, Found 400.1009.

(Rs,2S,3R)-1-(tert-butylsulfinyl)-2-(naphthalen-1-yl)-3-(phenylsulfonyl)aziridine (**4j**)



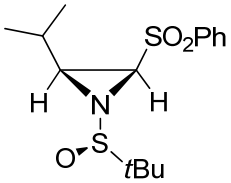
White solid, mp. 54.8-56.2 °C; $[\alpha]^{25}$ + 30.8 (c = 0.66, $CHCl_3$); IR (film) 1456, 1108, 1058, 873, 810, 770 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.88 – 7.74 (m, 4H), 7.58 – 7.45 (m, 6H), 7.32 (t, *J* = 7.8 Hz, 2H), 4.16 (d, *J* = 6.5 Hz, 1H), 3.72 (d, *J* = 6.5 Hz, 1H), 1.28 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 138.4, 134.0, 133.3, 132.7, 128.9, 128.7, 128.2, 128.0, 127.7, 127.0, 126.5, 126.4, 126.0, 57.8, 54.7, 38.6, 22.5; ESI (m/z) 414.2 (M^+ + 1), 436.1 (M^+ + 23); HRMS (ESI) calcd. For $C_{22}H_{23}NO_3S_2Na$ (M^+ + Na): 436.1012, Found 436.1002.

(Rs,2R,3S)-1-(tert-butylsulfinyl)-2-(phenylsulfonyl)-3-styrylaziridine (**4k**)



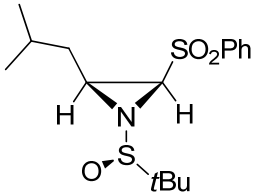
White solid, mp.106.9-108.0 °C; $[\alpha]^{25}$ + 43.7 (c = 1.00, $CHCl_3$); IR (film) 1332, 1159, 1079, 966, 742, 686 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.94 (d, *J* = 7.3 Hz, 2H), 7.69 (t, *J* = 7.5 Hz, 1H), 7.58 (t, *J* = 7.7 Hz, 2H), 7.46 (d, *J* = 7.1 Hz, 2H), 7.42 – 7.29 (m, 3H), 6.84 (d, *J* = 16.1 Hz, 1H), 6.70 (dd, *J* = 16.0, 9.2 Hz, 1H), 3.66 (dd, *J* = 9.2, 6.3 Hz, 1H), 3.54 (d, *J* = 6.3 Hz, 1H), 1.22 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 138.4, 135.7, 134.3, 129.3, 128.7, 128.6, 128.4, 126.8, 120.2, 57.8, 53.9, 40.1, 22.6; ESI (m/z) 390.2 (M^+ + 1), 412.1 (M^+ + 23); HRMS (ESI) calcd. For $C_{20}H_{23}NO_3S_2Na$ (M^+ + Na): 412.1012, Found 412.1011.

(Rs,2S,3R)-1-(tert-butylsulfinyl)-2-isopropyl-3-(phenylsulfonyl)aziridine (**4l**)



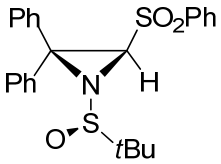
White solid, mp. 89.1-91.6 °C; $[\alpha]^{25}$ – 110.5 (c = 0.56, $CHCl_3$); IR (film) 1334, 1304, 1152, 1084, 854, 688 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.97 – 7.90 (m, 2H), 7.68 (d, *J* = 7.5 Hz, 1H), 7.59 (t, *J* = 7.6 Hz, 2H), 3.29 (d, *J* = 6.6 Hz, 1H), 2.83 (dd, *J* = 9.8, 6.6 Hz, 1H), 2.57 (ddt, *J* = 13.5, 9.8, 6.7 Hz, 1H), 1.21 (s, 9H), 1.20 (d, *J* = 6.7 Hz, 3H), 1.14 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 139.0, 134.1, 129.2, 128.3, 57.0, 54.6, 47.7, 26.3, 22.3, 21.39, 21.37; ESI (m/z) 330.1 (M^+ + 1), 352.1 (M^+ + 23); HRMS (ESI) calcd. For $C_{15}H_{23}NO_3S_2Na$ (M^+ + Na): 352.1012, Found 352.1004.

(Rs,2S,3R)-1-(tert-butylsulfinyl)-2-isobutyl-3-(phenylsulfonyl)aziridine (**4m**)



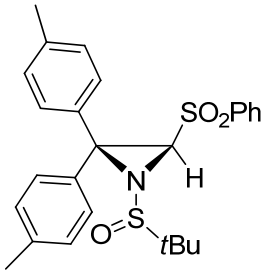
Oil; $[\alpha]^{25}$ – 82.9 (c = 0.49, $CHCl_3$); IR (film) 1366, 1020, 898, 837, 757; ^1H NMR ($CDCl_3$) δ 7.96 – 7.88 (m, 2H), 7.69 (t, *J* = 7.4 Hz, 1H), 7.58 (t, *J* = 7.7 Hz, 2H), 3.25 (d, *J* = 6.4 Hz, 1H), 3.10 (ddd, *J* = 10.2, 6.3, 4.1 Hz, 1H), 2.24 (ddd, *J* = 13.9, 10.0, 6.0 Hz, 1H), 1.94 (tt, *J* = 13.2, 6.4 Hz, 1H), 1.70 (ddd, *J* = 13.7, 8.2, 4.1 Hz, 1H), 1.20 (s, 9H), 1.04 (d, *J* = 6.6 Hz, 6H); ^{13}C NMR ($CDCl_3$) δ 138.9, 134.1, 129.2, 128.3, 57.0, 52.7, 38.9, 34.8, 27.2, 22.9, 22.3, 22.2; ESI (m/z) 344.1 (M^+ + 1), 366.2 (M^+ + 23); HRMS (ESI) calcd. For $C_{16}H_{25}NO_3S_2Na$ (M^+ + Na): 366.1168, Found 366.1168.

(Rs,3R)-1-(tert-butylsulfinyl)-2,2-diphenyl-3-(phenylsulfonyl)aziridine (**5a**)



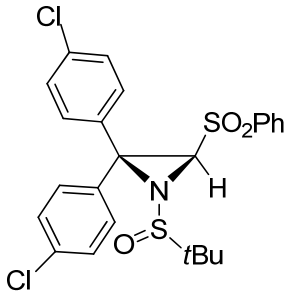
White solid, mp. 139.5 – 141.2 ^{o}C; $[\alpha]^{25}$ – 54.7 (c = 1.0, $CHCl_3$); IR (film) 1493, 1445, 1316, 1147, 1087, 756 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.59 – 7.50 (m, 1H), 7.41 – 7.30 (m, 9H), 7.26 – 7.17 (m, 1H), 7.16 – 7.05 (m, 4H), 4.75 (s, 1H), 1.47 (s, 9H); ^{13}C NMR ($CDCl_3$) δ137.25, 135.4, 135.3, 133.7, 130.7, 129.2, 129.1, 128.7, 128.5, 128.3, 127.9, 127.7, 63.2, 58.1, 29.6, 22.4; ESI (m/z) 440.1 (M^+ + 1), 462.1 (M^+ + 23); HRMS (ESI) calcd. For $C_{24}H_{26}NO_3S_2Na$ (M^+ + Na): 440.1349, Found 440.1345.

(Rs,3R)- 1-(tert-butylsulfinyl)-3-(phenylsulfonyl)-2,2-dip-tolylaziridine (**5b**)



White solid, mp. 128.6 – 129.2 ^{o}C; $[\alpha]^{25}$ + 155.9 (c = 0.95, $CHCl_3$); IR (film) 1473, 1338, 1153, 1088, 810, 730 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.55 (dd, J = 10.3, 4.3 Hz, 1H), 7.41 – 7.35 (m, 2H), 7.32 (t, J = 7.8 Hz, 2H), 7.22 (d, J = 8.2 Hz, 2H), 7.13 (d, J = 8.0 Hz, 2H), 7.00 (d, J = 7.2 Hz, 2H), 6.90 (d, J = 8.2 Hz, 2H), 4.72 (s, 1H), 2.32 (d, J = 4.2 Hz, 6H), 1.45 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 139.2, 137.6, 137.3, 133.6, 132.6, 132.5, 130.5, 129.0, 128.9, 128.6, 128.5, 128.3, 63.4, 58.0, 22.4, 21.2, 21.1; ESI (m/z) 490.1 (M^+ + 23); HRMS (ESI) calcd. For $C_{26}H_{29}NNaO_3S_2$ (M^+ + Na): 490.1481, Found 490.1487.

(Rs,3R)- 1-(tert-butylsulfinyl)-2,2-bis(4-chlorophenyl)-3-(phenylsulfonyl)aziridine (**5c**)

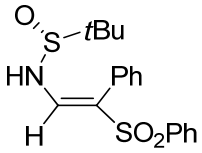


White solid, mp. 102.1 – 103.8 ^{o}C; $[\alpha]^{25}$ + 96.0 (c = 1.14, $CHCl_3$); IR (film) 2926, 1490, 1322, 1152, 1088, 814 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.55 – 7.59 (m, 1H), 7.33 – 7.39 (m, 4H), 7.23 – 7.28 (m, 4H), 7.01 – 7.07 (m, 4H), 4.66 (s, 1H), 1.42 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 136.9, 135.7, 134.3, 134.0, 133.7, 133.3, 132.0, 130.3, 128.8, 128.7, 128.5, 128.0, 63.2, 58.3, 56.9, 22.3; ESI (m/z) 530.0 (M^+ + 23); HRMS (ESI) calcd. For $C_{24}H_{23}Cl_2NO_3S_2Na$ (M^+ + Na): 530.0389, Found 530.0385.

Procedure for synthesis of chiral enamine 6:

$BF_3 \cdot OEt_2$ (71 mg, 0.5 mmol) was added to a mixture of compound **4a** (182 mg, 0.5mmol) and dichloromethane (2 mL) at 0 ^oC. The reaction mixture was stirred at 0 ^oC for 12 h and was then subject to flash chromatography to give the corresponding enamine **6** (110 mg, 61 %).

(Rs)-(E)-2-methyl-N-(2-phenyl-2-(phenylsulfonyl)vinyl)propane-2-sulfinamide (6)

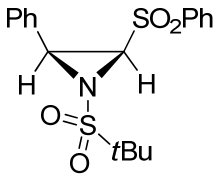


White solid, mp. 202.5 – 203.4; $[\alpha]^{25}$ + 22.7 (c = 0.54, $CHCl_3$); IR (film) 1620, 1446, 1241, 1140, 1070, 690 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.88 (d, J = 13.2 Hz, 1H), 7.68 – 7.61 (m, 2H), 7.54 (dd, J = 10.6, 4.3 Hz, 1H), 7.48 – 7.31 (m, 5H), 7.15 – 7.05 (m, 2H), 5.72 (d, J = 13.4 Hz, 1H), 1.17 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 140.1, 138.5, 132.7, 130.8, 129.5, 129.4, 128.7, 128.3, 127.7, 119.3, 57.8, 22.0; ESI (m/z) 364 (M^+ + 1), 386 (M^+ + 23); HRMS (ESI) calcd. For $C_{18}H_{21}NO_3S_2Na$ (M^+ + Na): 386.0855, Found 386.0864.

Typical procedure for oxidation of compound 4a to N-sulfonylated product 7:

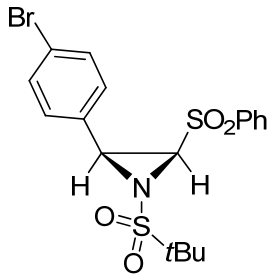
Compound **4a** (364 mg, 1 mmol) was dissolved in 5 mL dichloromethane, then 1.2 mmol MCPBA was added at 0 ^{o}C. The reaction mixture was stirred at 0 ^{o}C for 4 h and was then 2N Na_2CO_3 (4 mL) was added. The reaction mixture was extracted three times with ethyl acetate (20 mL x 3). The combined organic layers were dried over anhydrous $MgSO_4$. Evaporation of the solvent afforded the crude product, which was subject to flash chromatography to give the corresponding aziridine **7a** (330 mg, 87 %).

*(2S,3R)-1-(tert-butylsulfonyl)-2-phenyl-3-(phenylsulfonyl)aziridine (**7a**)*



White solid, mp 136.8-138.1; $[\alpha]^{25}$ + 47.7 (c = 0.66, $CHCl_3$); IR (film) 1449, 1324, 1160, 1128, 765, 713 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.65 – 7.57 (m, 1H), 7.54 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.42 (t, *J* = 7.9 Hz, 2H), 7.40 – 7.29 (m, 5H), 4.19 (d, *J* = 6.7 Hz, 1H), 4.10 (d, *J* = 6.7 Hz, 1H), 1.60 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 137.7, 134.2, 129.0, 128.8, 128.7, 128.5, 128.2, 128.1, 60.9, 57.8, 45.8, 24.0; ESI (m/z) 402.1 (M^+ + 23); HRMS (ESI) calcd. For $C_{18}H_{21}NO_4S_2Na$ (M^+ + Na):402.0804, Found 402.0802.

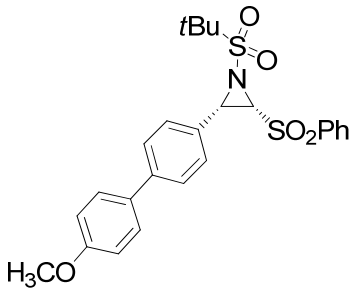
*(2S,3R)-1-(tert-butylsulfonyl)-2-phenyl-3-(phenylsulfonyl)aziridine (**7b**)*



White solid, mp 156.5 - 157.2; $[\alpha]^{25}$ + 30.3 (c = 1.11, $CHCl_3$); IR (film) 1448, 1318, 1158, 1124, 893, 720 cm^{-1}; ^{1}H NMR ($CDCl_3$) δδ 7.62 (d, J = 7.4 Hz, 1H), 7.61 – 7.53 (m, 2H), 7.46 (dd, J = 7.9, 6.0 Hz, 4H), 7.29 – 7.19 (m, 2H), 4.18 (d, J = 6.7 Hz, 1H), 4.03 (d, J = 6.7 Hz, 1H), 1.58 (s, 9H).; ^{13}C NMR ($CDCl_3$) δ 137.7, 134.4, 131.4, 129.7, 129.1, 128.4, 128.0, 123.1, 61.0, 57.8, 45.2, 24.0; ESI (m/z) 480.0 (M + Na^+); HRMS (ESI) calcd. For $C_{18}H_{20}BrNO_4S_2Na$ (M + Na^+): 479.9909, Found 479.9903.

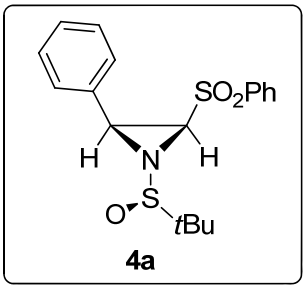
Procedure for synthesis of Suzuki-coupling product 8:

A mixture of **7b** (137 mg, 0.3 mmol), 4-methoxyphenylboronic acid (55 mg, 0.36 mmol), $PdCl_2(PPh_3)_2$ (10 mg, 0.015 mmol), Ag_2O (21 mg, 0.09 mmol) and K_2CO_3 (41 mg, 0.3 mmol) was stirred in THF at 65 ^oC under N_2 atmosphere for 8 h. The mixture was filtered and the filtrate was concentrated under reduced pressure. The residue was purified by flash column chromatography with ethyl acetate/petroleum ether (1 : 5) to afford **8** (91 mg, 63 %).

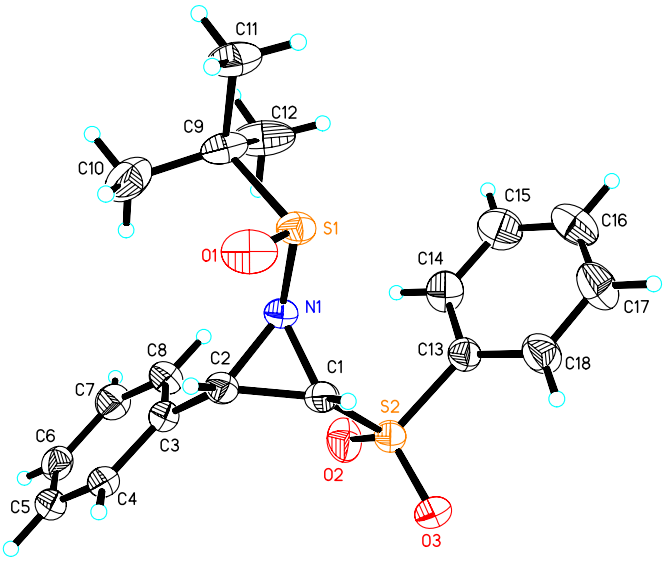


Sticky oil; $[\alpha]^{25}$ + 26.9 (c = 0.87, $CHCl_3$); IR (film) 2920, 1448, 1303, 1140, 1070, 690 cm^{-1}; ^1H NMR ($CDCl_3$) δδ 7.51 – 7.63 (m, 7H), 7.40 (dd, J = 12.1, 8.3 Hz, 4H), 6.99 (d, J = 8.7 Hz, 2H), 4.21 (d, J = 6.7 Hz, 1H), 4.12 (d, J = 6.7 Hz, 1H), 3.86 (s, 3H), 1.61 (s, 9H); ^{13}C NMR ($CDCl_3$) δ159.4, 141.3, 137.8, 134.2, 132.8, 129.0, 128.57, 128.50, 128.0, 127.0, 126.4, 114.2, 60.9, 57.8, 55.3, 45.8, 24.1; ESI (m/z) 508.1 (M^+ + 23); HRMS (ESI) calcd. For $C_{25}H_{27}NO_5S_2Na$ (M^+ + Na): 508.1223, Found 508.1208.

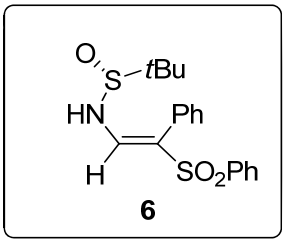
Determination of the absolute configuration of **4a** (from ethyl acetate/hexane) by X-ray analysis



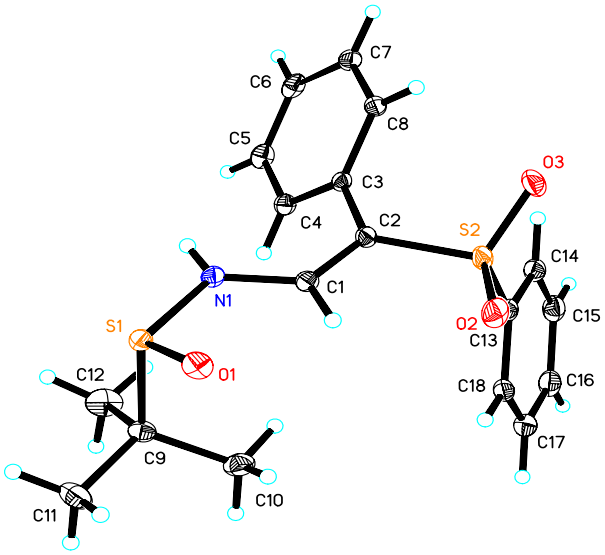
4a



Determination of the absolute configuration of **6** (from DCM/hexane) by X-ray analysis



6



Examples for determination of diastereomer ratio of 4a by LC-MS.

LC-MS spectroscopy for the crude mixture of entry 2 (Table 1): chloromethyl phenyl sulfone, imine 2a and LiHMDS in DMF

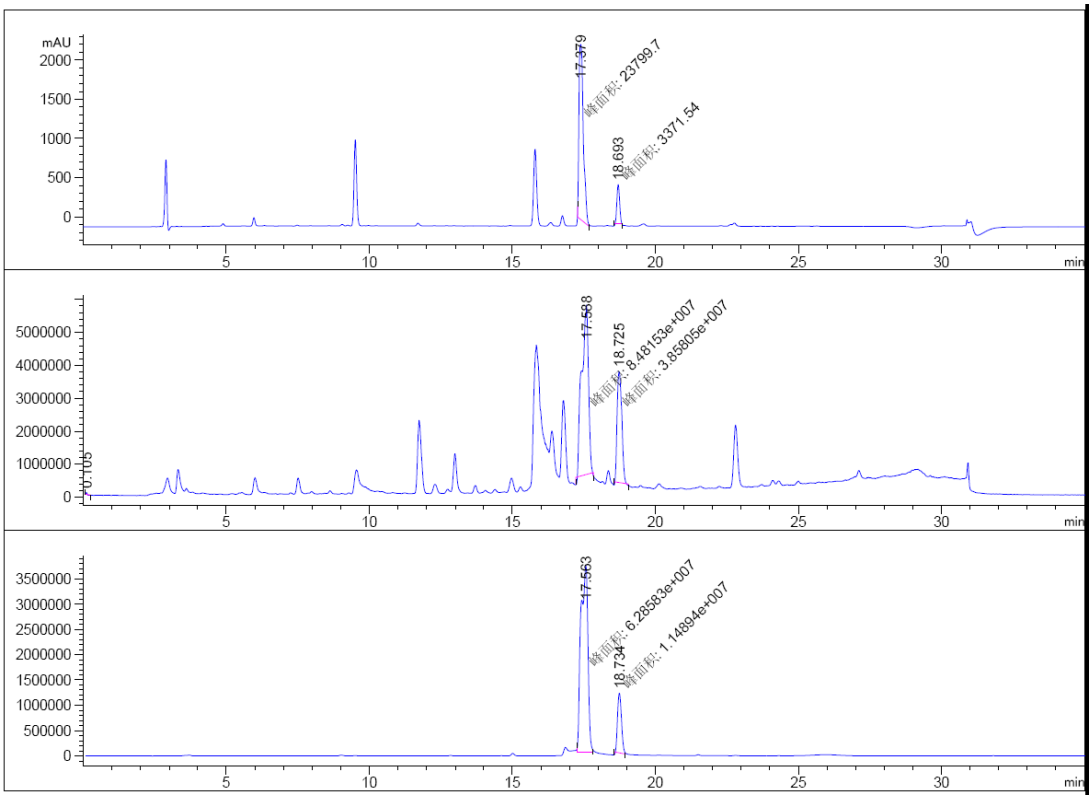
4a/other diastereomers = 7 : 1

4a, rt = 17.3 min; the other diastereomer, rt = 18.6 min
dr = 23799 : 3371 = 7 : 1

1a) HPLC spectroscopy

1b) Total ion current chromatogram

1c) Selected ion



LC-MS spectroscopy for the crude mixture of entry 4 (Table 1): bromomethyl phenyl sulfone, imine 2a and LiHMDS in THF

4a, rt = 16.1 min;

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Acq. Instrument  : Instrument 1                   Location : P1-B-02
Injection Date   : 5/23/2013 3:38:51 PM              Inj :   1
                                                Inj Volume : 3.000 µl

Acq. Method      : D:\DATA\CHEMDATA\AT20130523\DEF_LC 2013-05-23 14-54-35\ANAL_LC.M
Last changed     : 5/23/2013 4:12:27 PM by SMSC, SIOC
                   (modified after loading)
Analysis Method  : C:\CHEM32\1\METHODS\ANAL2_LC.M
Last changed     : 5/31/2013 9:25:07 AM by SMSC, SIOC
                   (modified after loading)
Additional Info  : Peak(s) manually integrated
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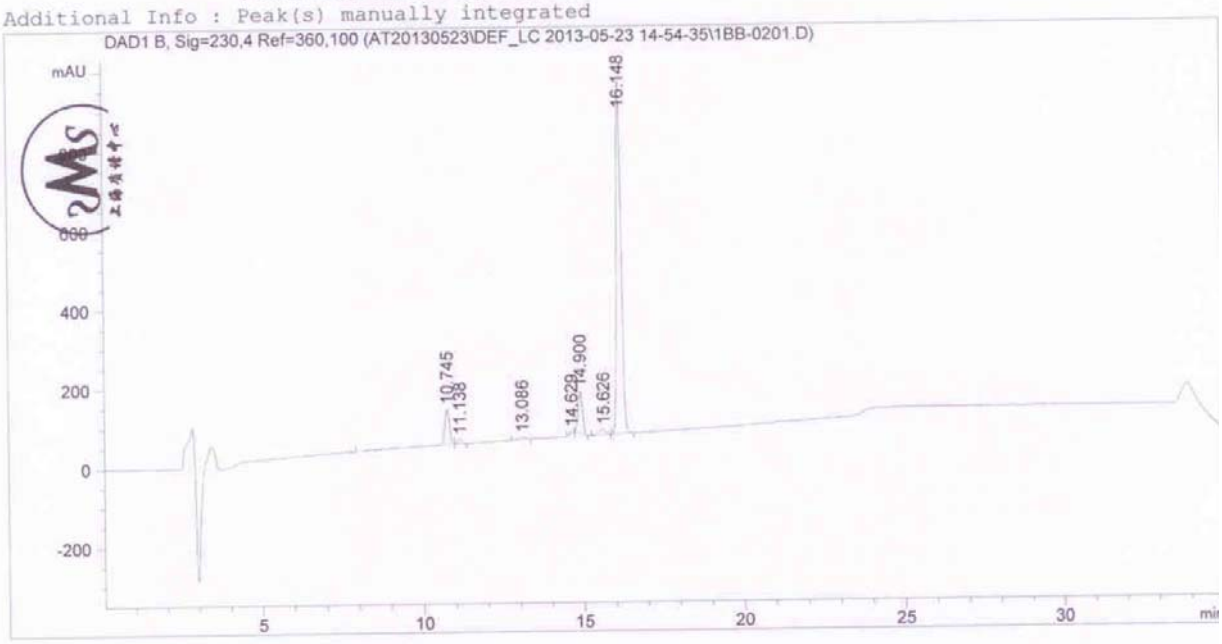


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                        Area Percent Report

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 B, Sig=230,4 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  10.745 BB    0.1689  975.35931   89.66570   8.3299
   2  11.138 BB    0.1511  103.43333   11.05737   0.8834
   3  13.086 BB    0.2255   92.79410    6.31342   0.7925
   4  14.629 BB    0.1327   52.63054    6.48494   0.4495
   5  14.900 BB    0.1595 1050.48169  106.07941   8.9715
   6  15.626 BB    0.2206  199.46008   13.32716   1.7035
   7  16.148 BB    0.1649 9234.96387  891.31616  78.8698

Instrument 1 5/31/2013 9:54:46 AM SMSC, SIOC                    Page   1 of 2
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LC-MS spectroscopy for the crude mixture of entry 6 (Table 1): bromomethyl phenyl sulfone, imine 2a and NaHMDS in THF

4a, rt = 16.2 min;

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Acq. Instrument  : Instrument 1                   Location : P1-B-01
Injection Date   : 5/23/2013 2:55:44 PM              Inj :   1
                                                 Inj Volume : 3.000 µl

Acq. Method      : D:\DATA\CHEMDATA\AT20130523\DEF_LC 2013-05-23 14-54-35\ANAL_LC.M
Last changed     : 5/23/2013 2:54:35 PM by SMSC, SIOC
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Last changed     : 5/31/2013 9:25:07 AM by SMSC, SIOC
                   (modified after loading)
Additional Info  : Peak(s) manually integrated
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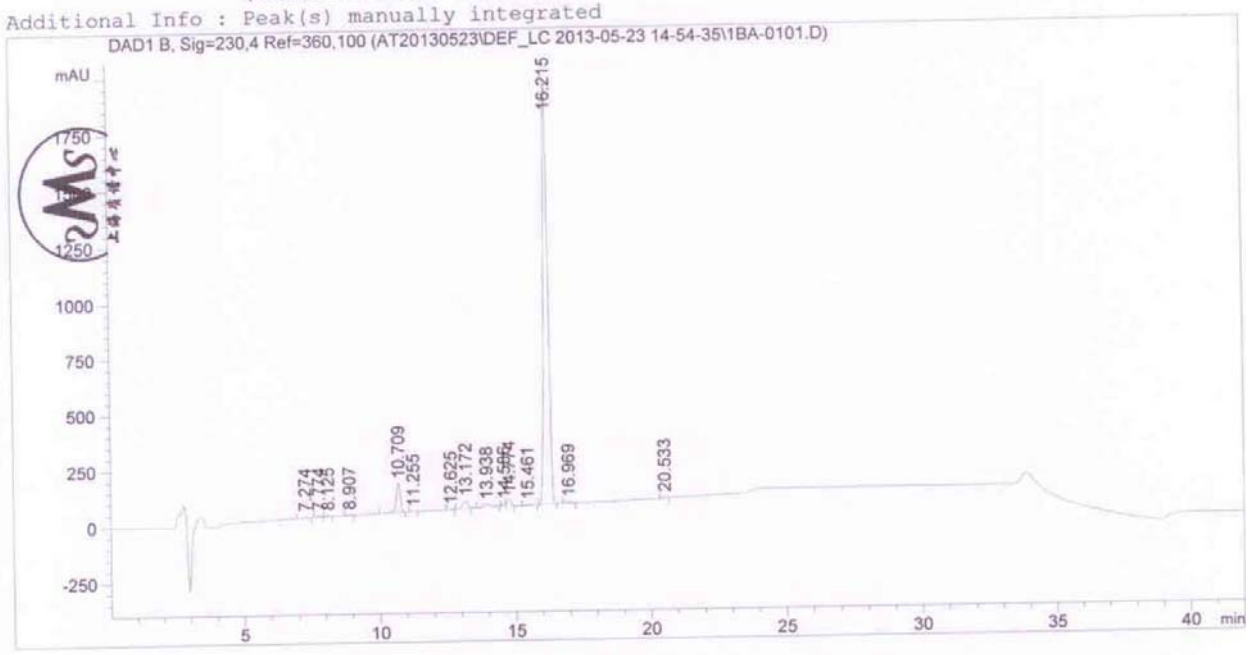


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                        Area Percent Report

Sorted By             :      Signal
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Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 B, Sig=230,4 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
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----|-------|----|-------|----------|----------|--------|
   1   7.274 BB    0.1700   88.83517    8.09746   0.3469
   2   7.774 BB    0.1452   65.12118    7.22048   0.2543
   3   8.125 BB    0.1498   39.15896    4.23814   0.1529
   4   8.907 BB    0.1453   28.99157    3.21292   0.1132
   5  10.709 BB    0.1671 1387.73975  129.43439   5.4190
   6  11.255 BB    0.1599   12.46509    1.27695   0.0487
   7  12.625 BB    0.1453   24.93269    2.81647   0.0974
   8  13.172 BB    0.1954  418.02344   33.55160   1.6323

Instrument 1 5/31/2013 9:53:34 AM SMSC, SIOC                Page   1 of 2
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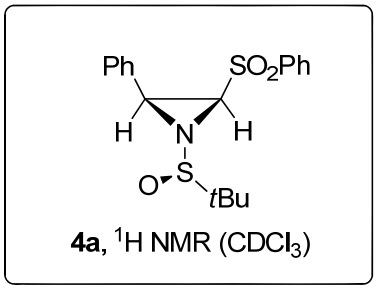
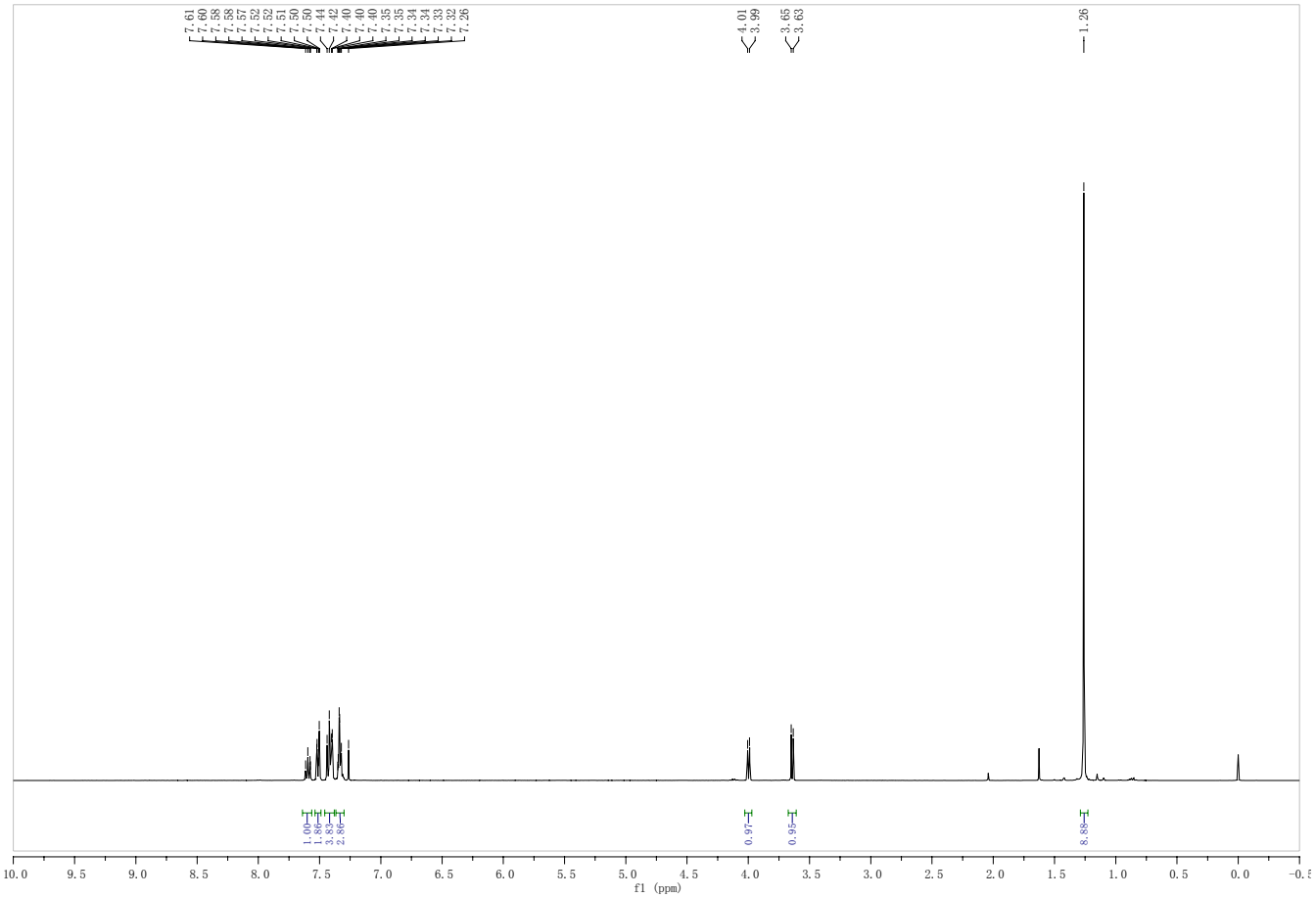
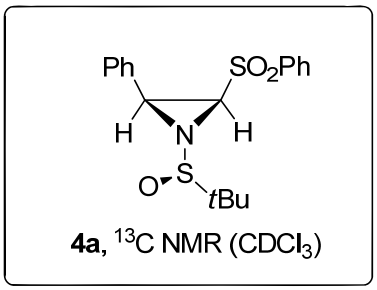
NMR Spectra for All New Compounds

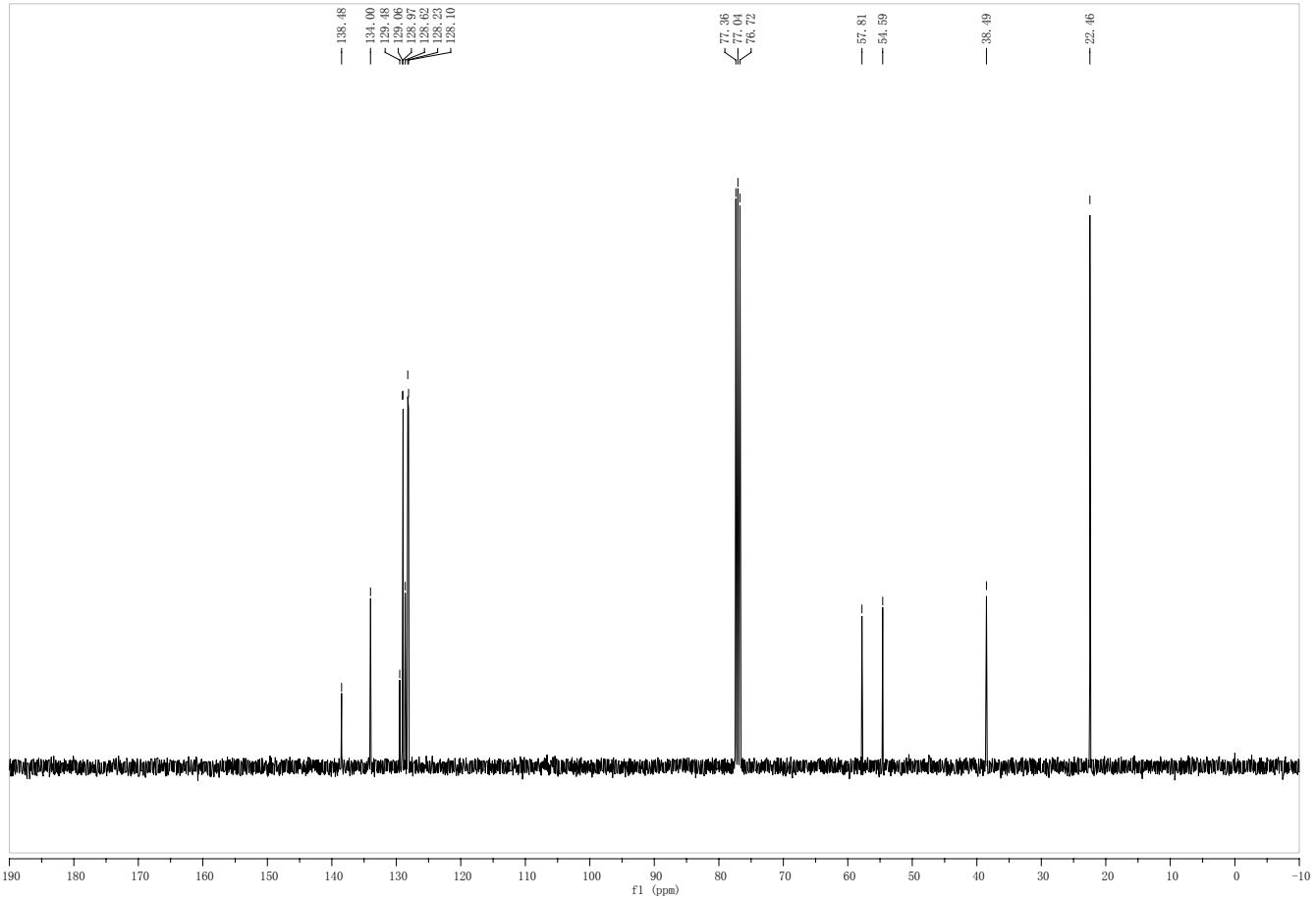


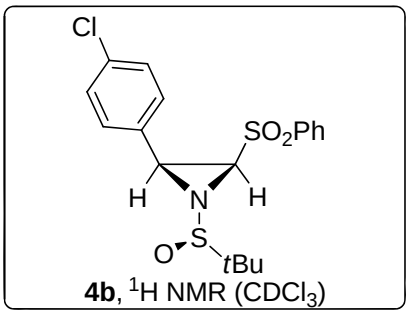
4a, ^{1}H NMR ($CDCl_3$)



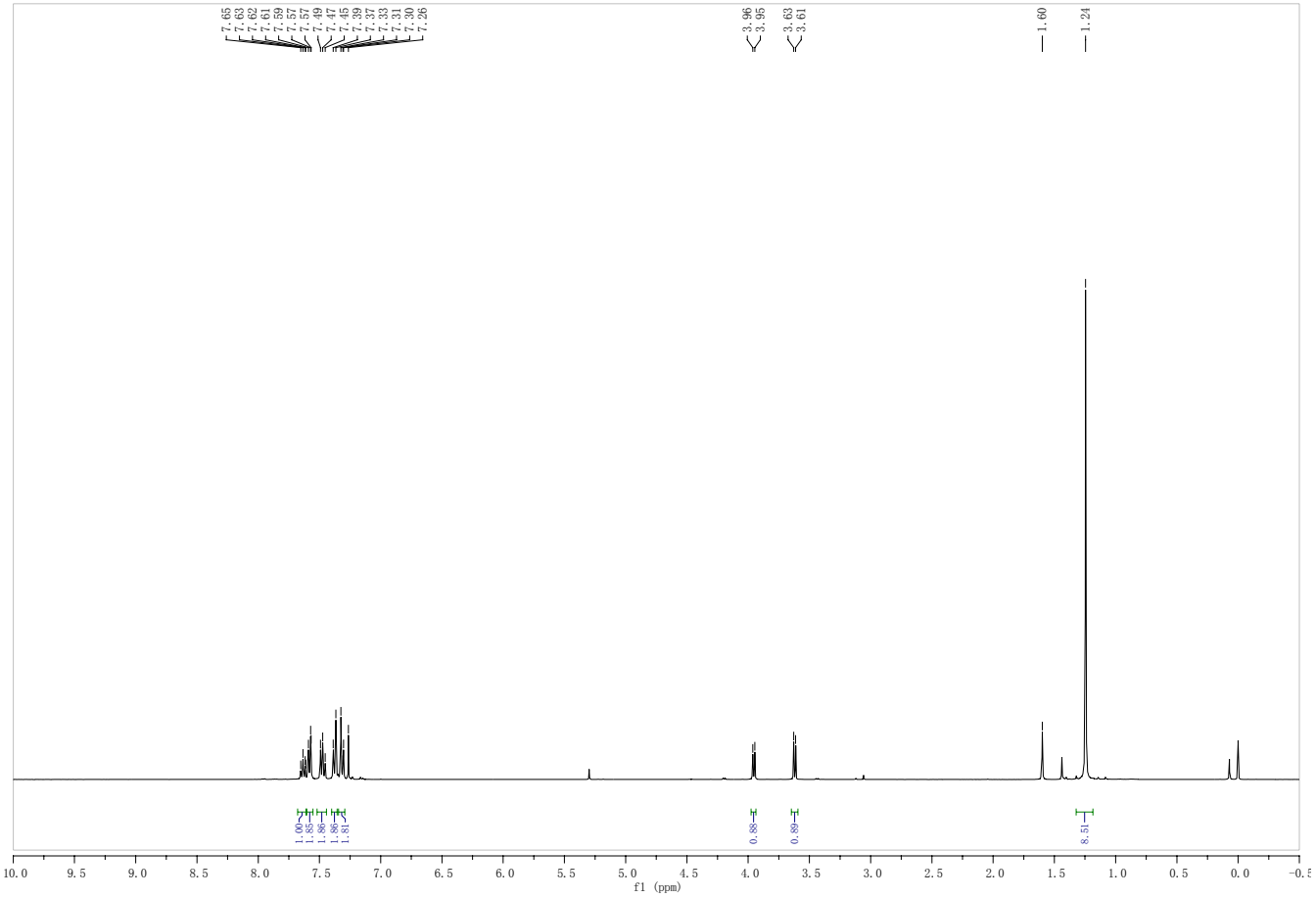


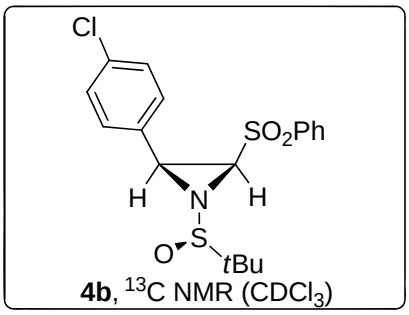
4a, ^{13}C NMR ($CDCl_3$)



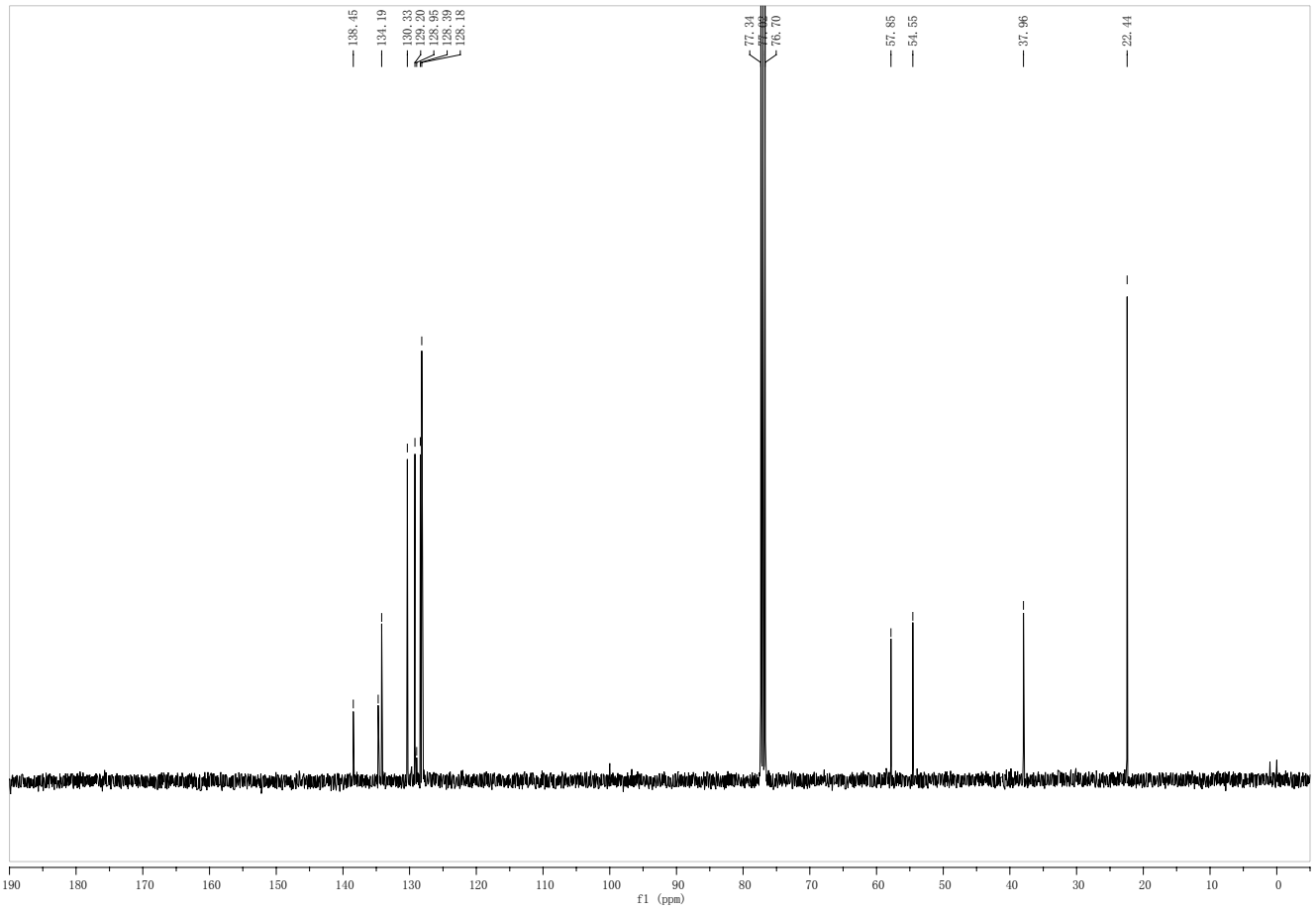


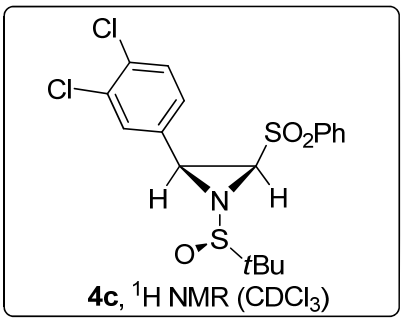
4b, ^{1}H NMR ($CDCl_3$)



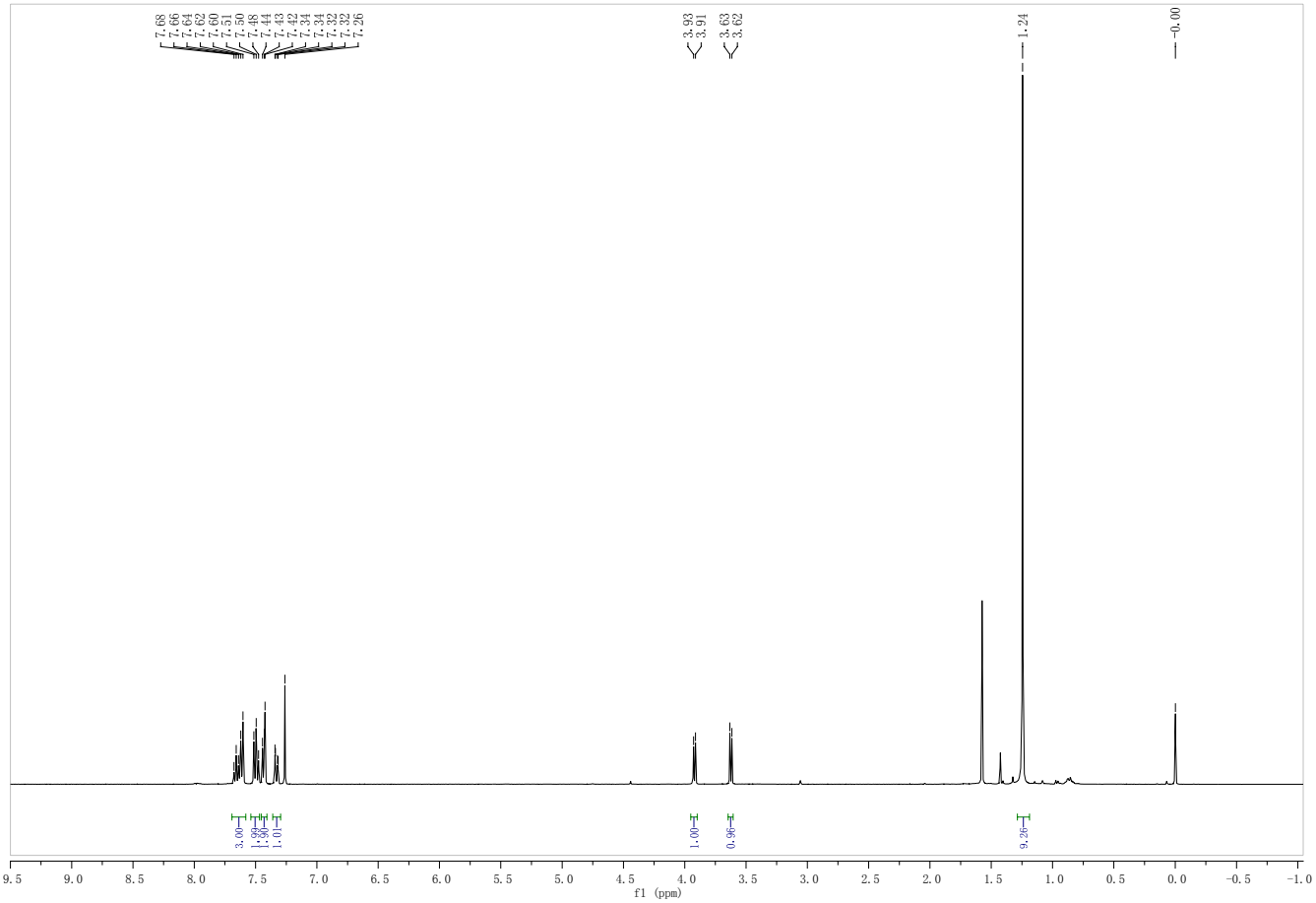


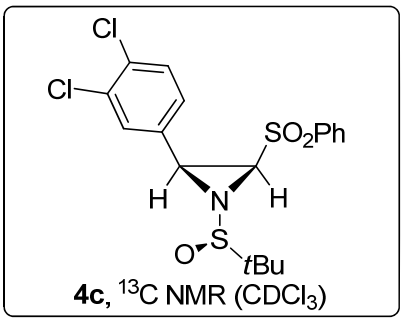
4b, ^{13}C NMR ($CDCl_3$)



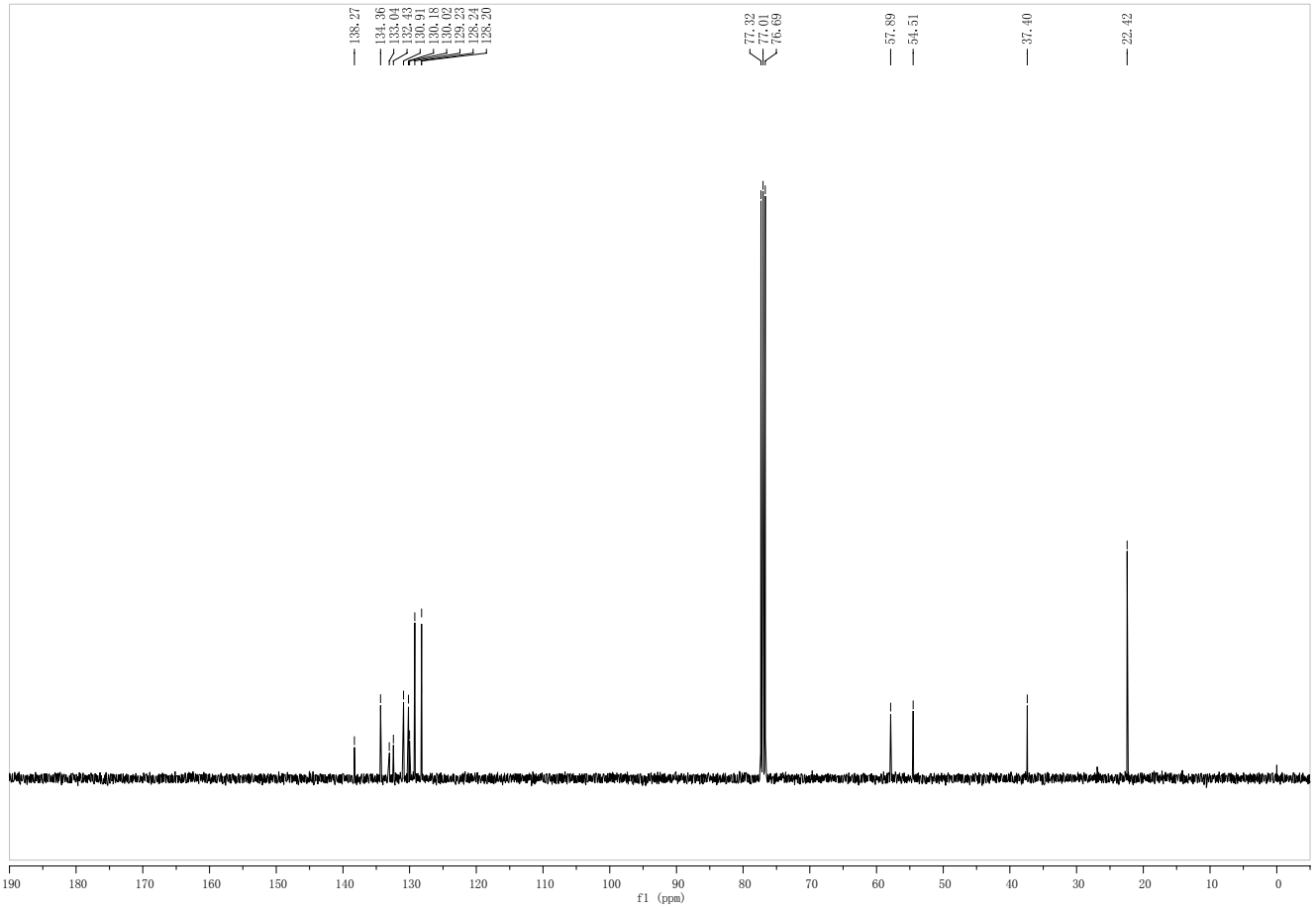


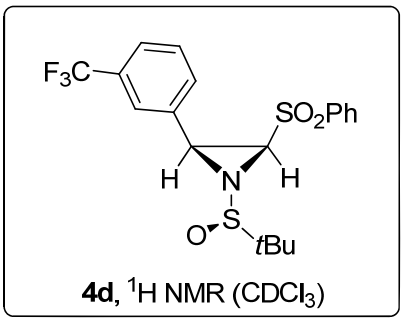
4c, ^{1}H NMR ($CDCl_3$)



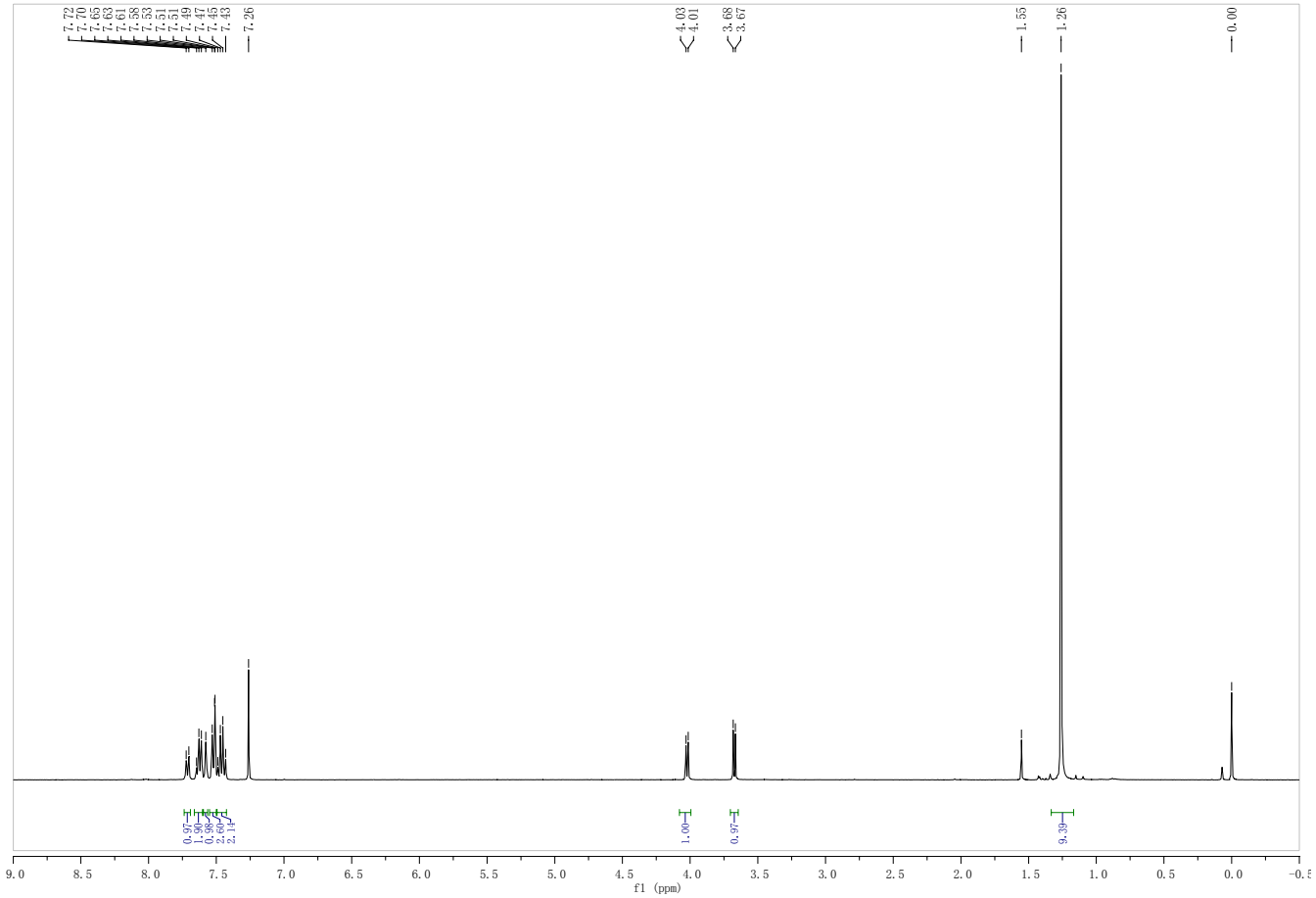


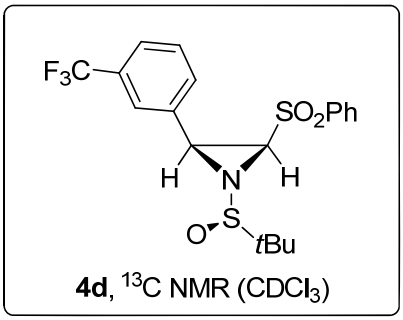
4c, ^{13}C NMR ($CDCl_3$)



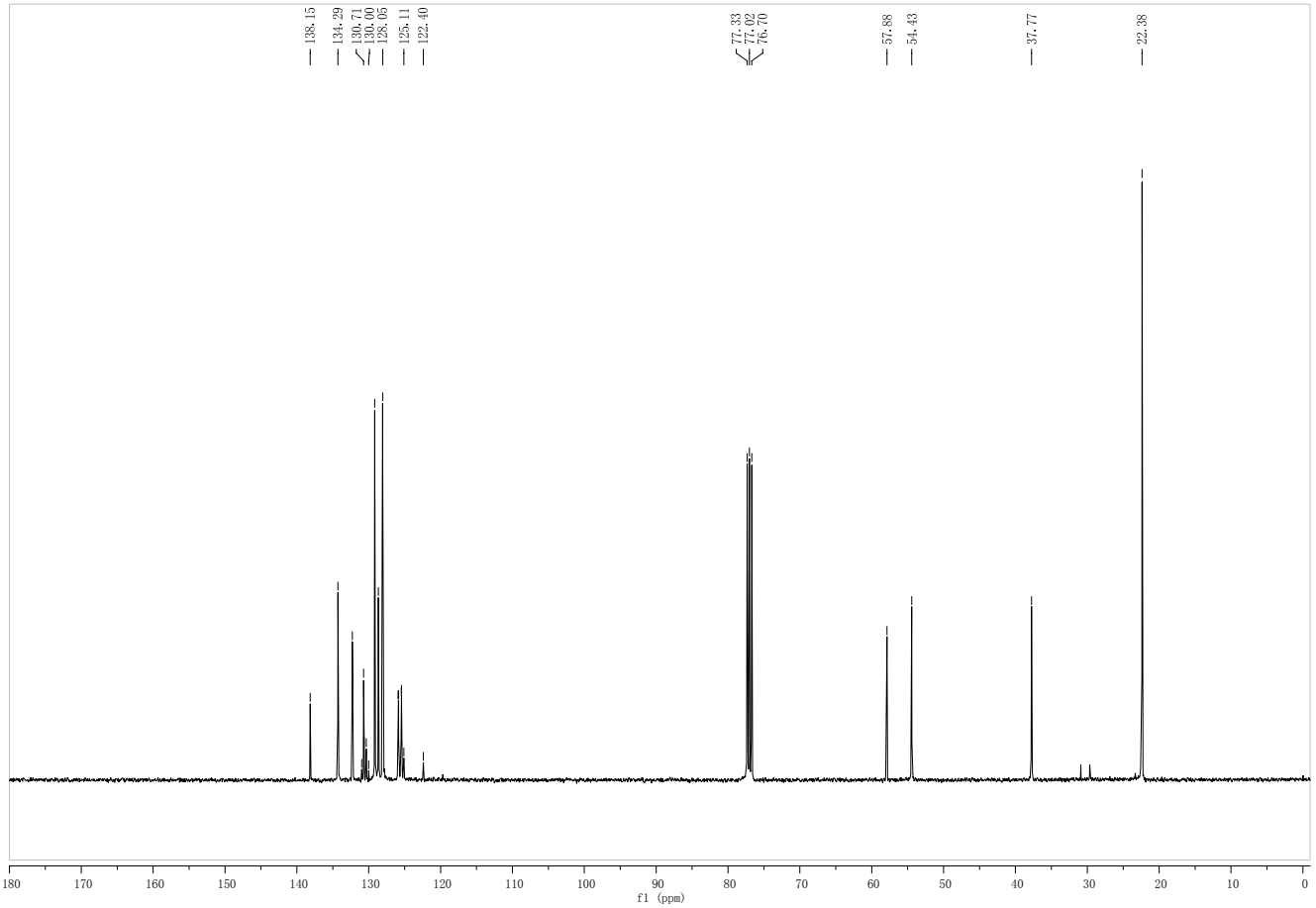


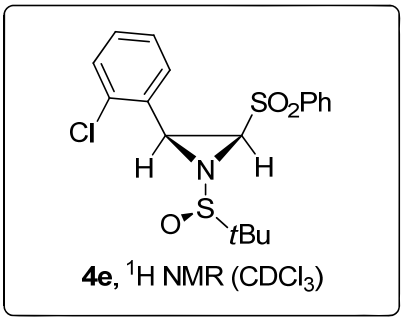
4d, ^{1}H NMR ($CDCl_3$)



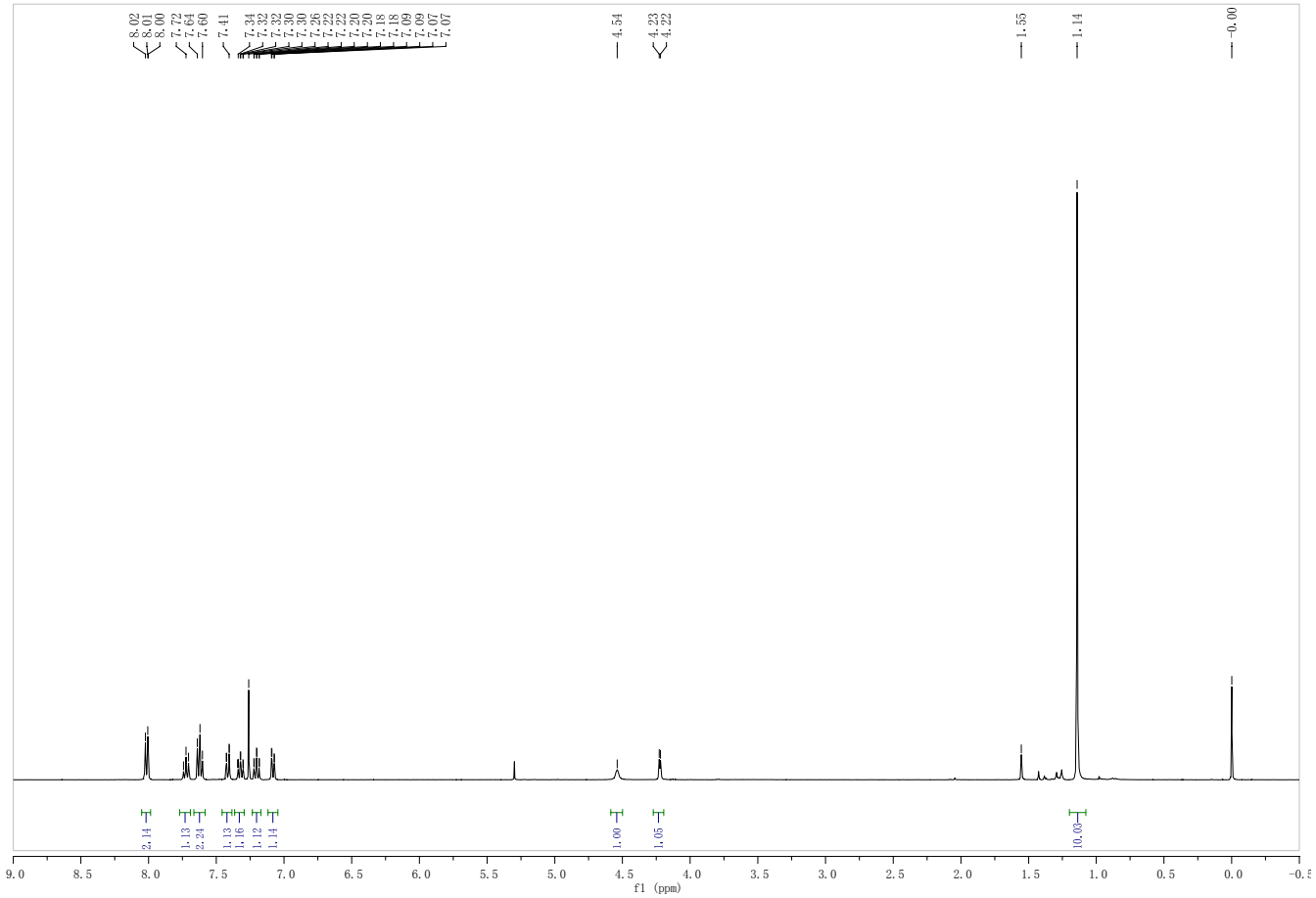


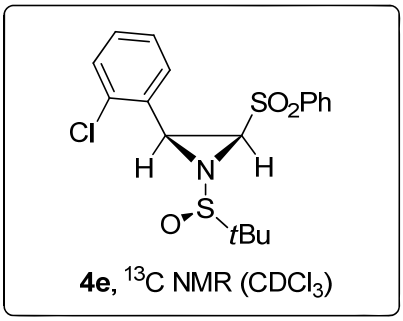
4d, ^{13}C NMR ($CDCl_3$)



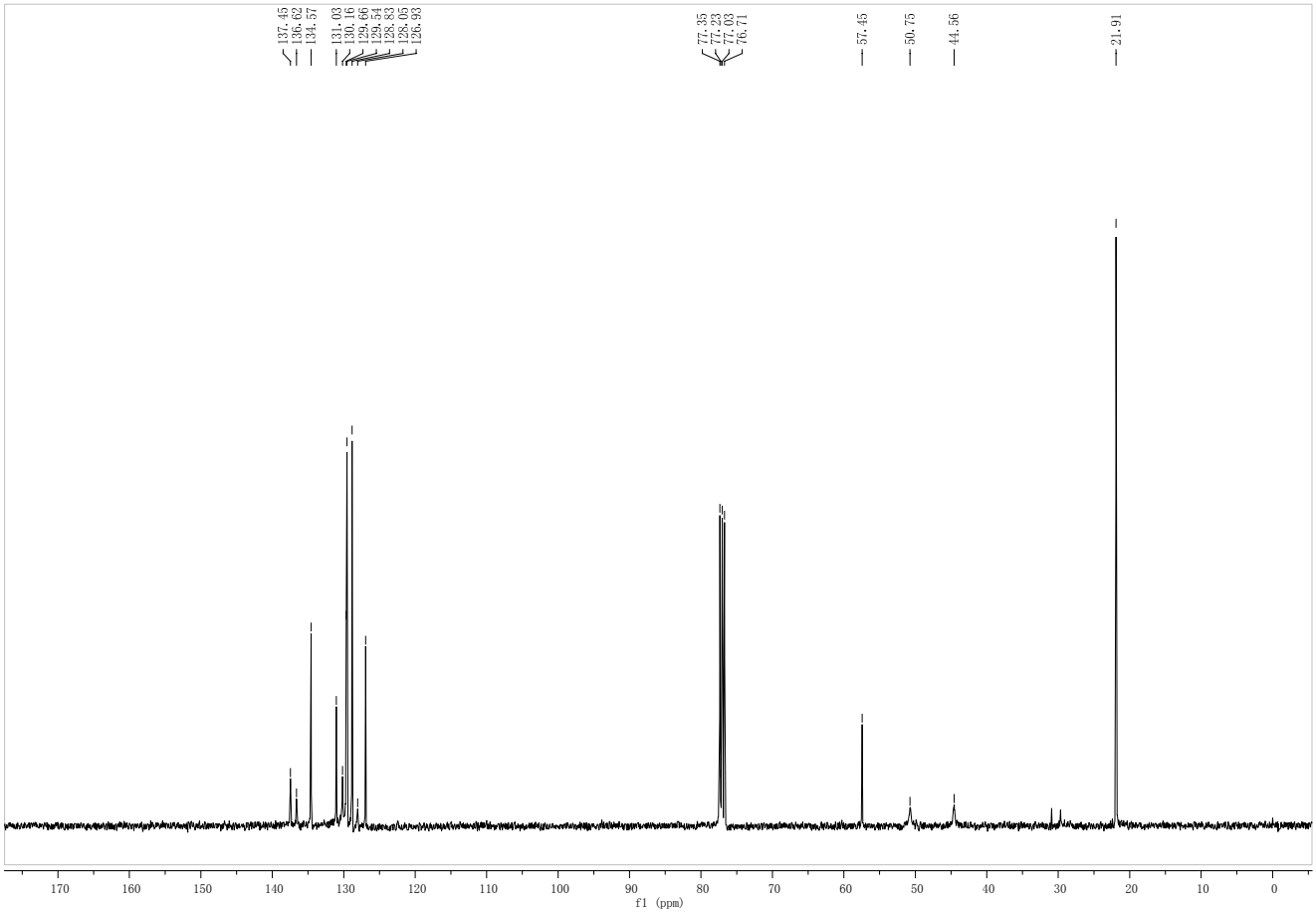


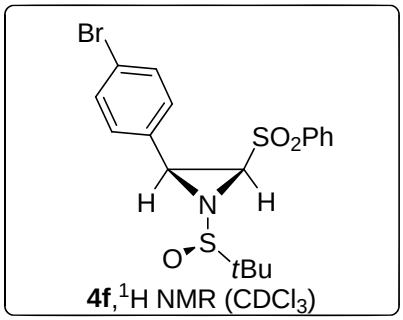
4e, ^{1}H NMR ($CDCl_3$)



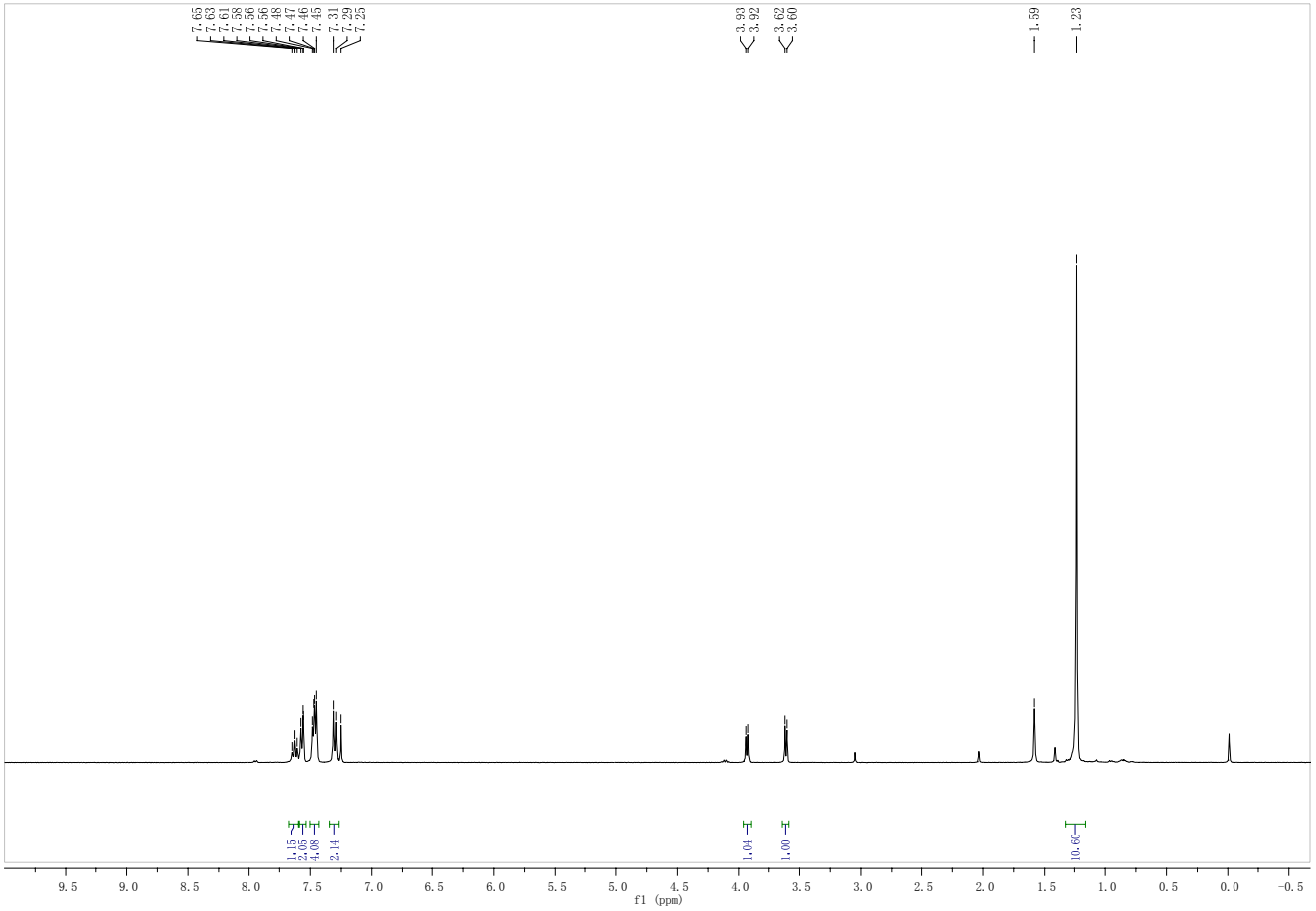


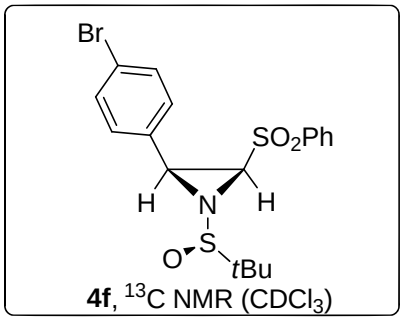
4e, ^{13}C NMR ($CDCl_3$)



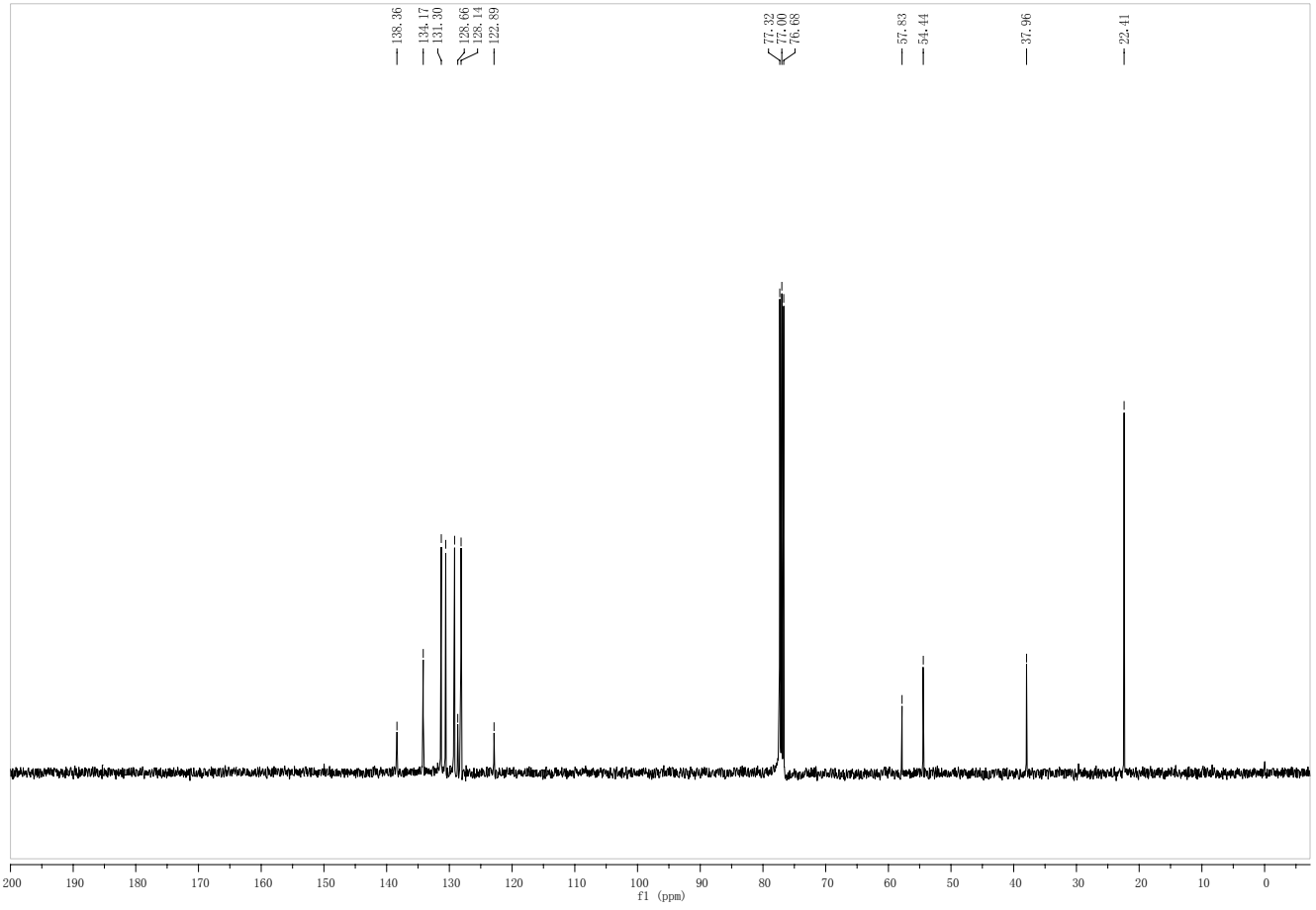


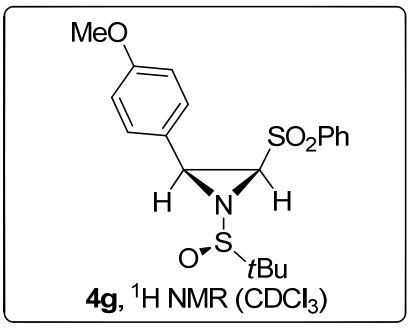
4f,^{1}H NMR ($CDCl_3$)



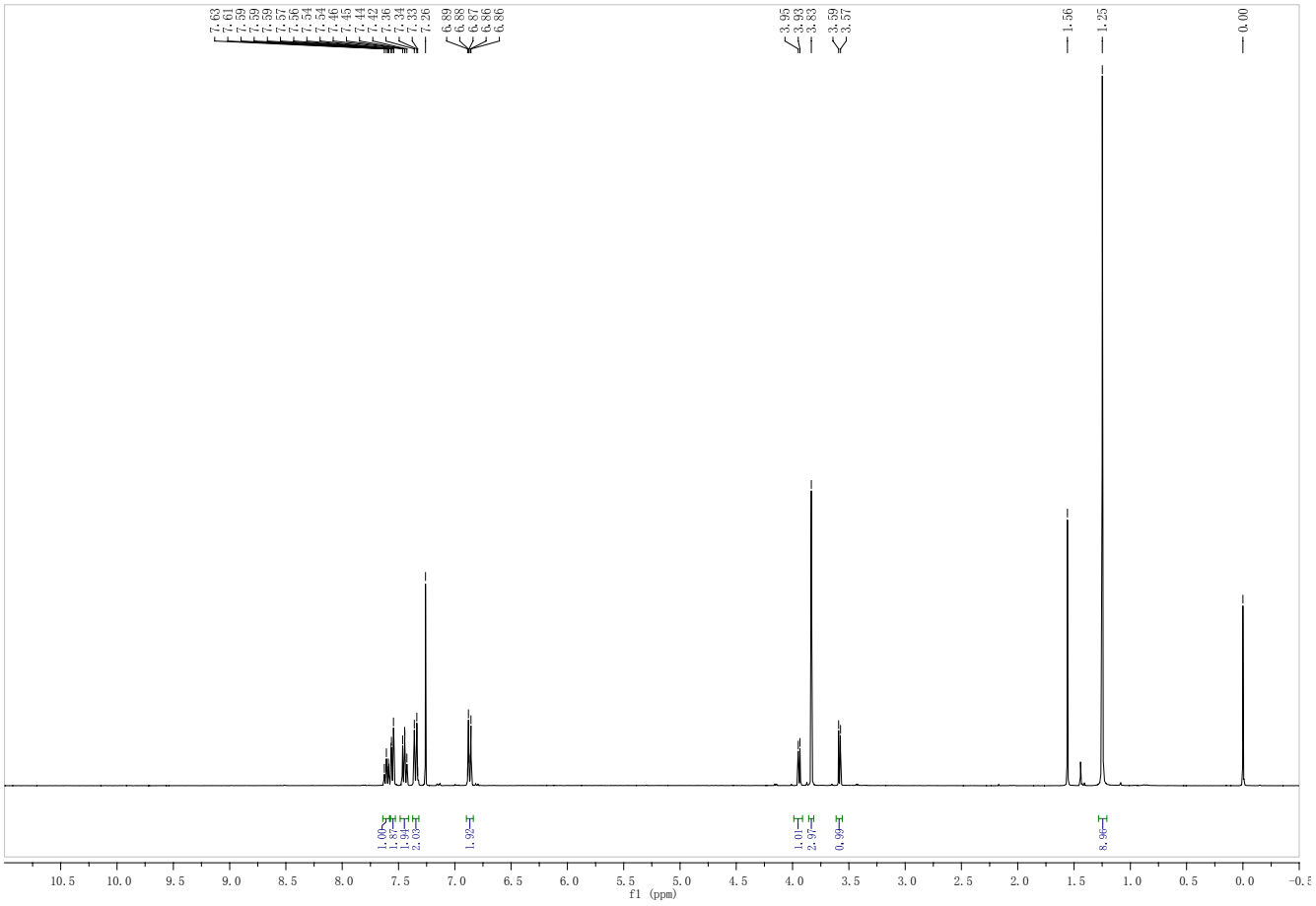


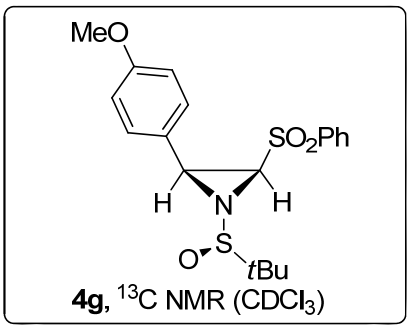
4f, ^{13}C NMR ($CDCl_3$)



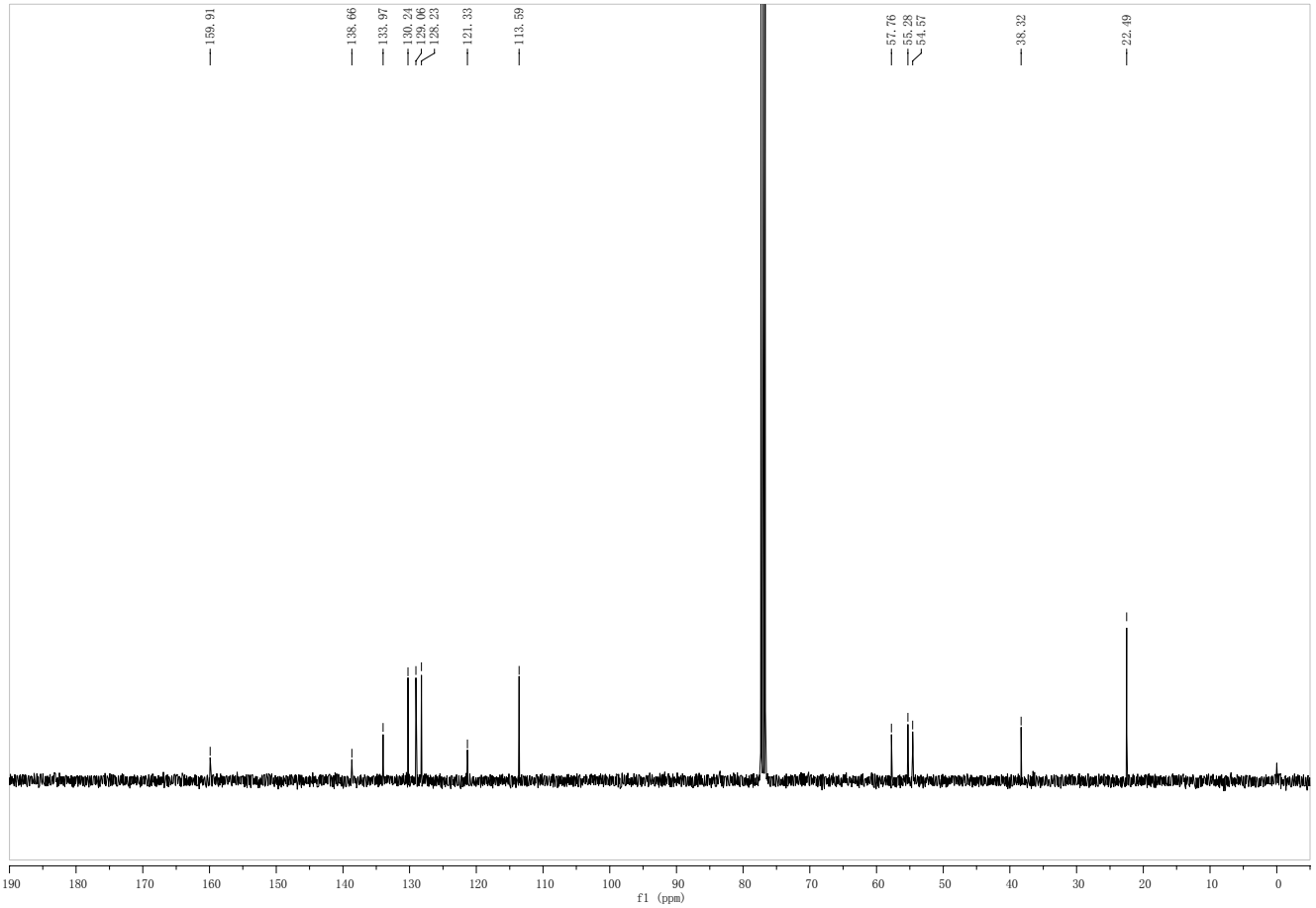


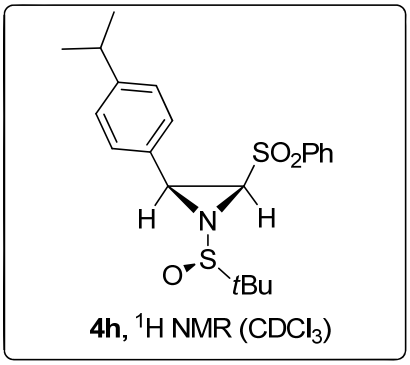
4g, ^{1}H NMR ($CDCl_3$)



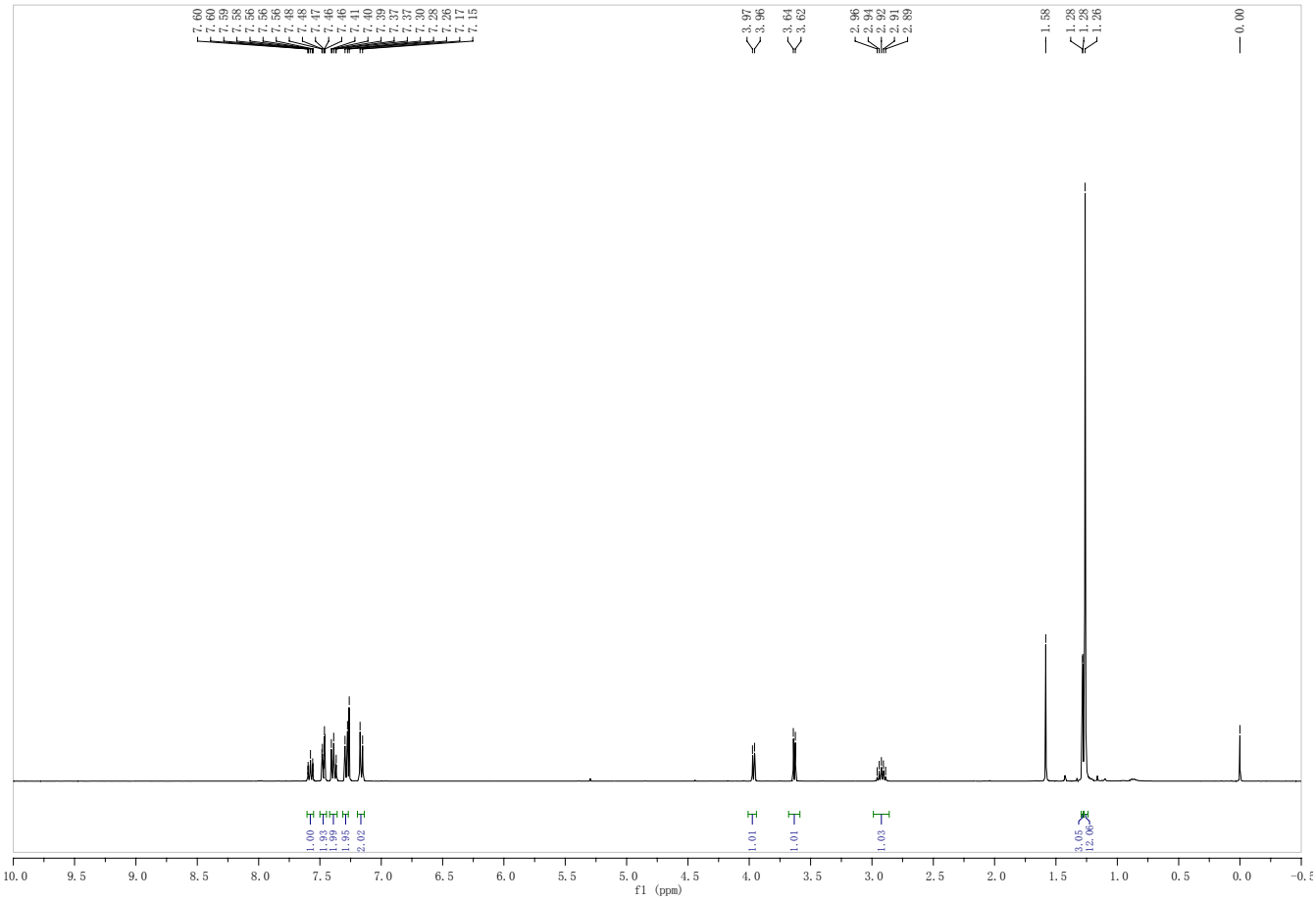


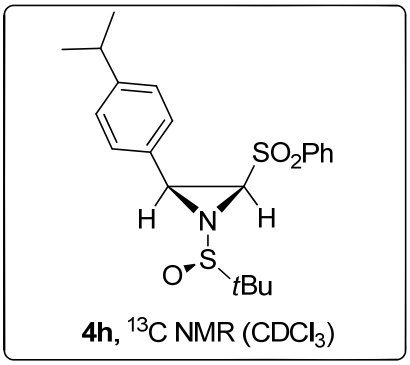
4g, ^{13}C NMR ($CDCl_3$)



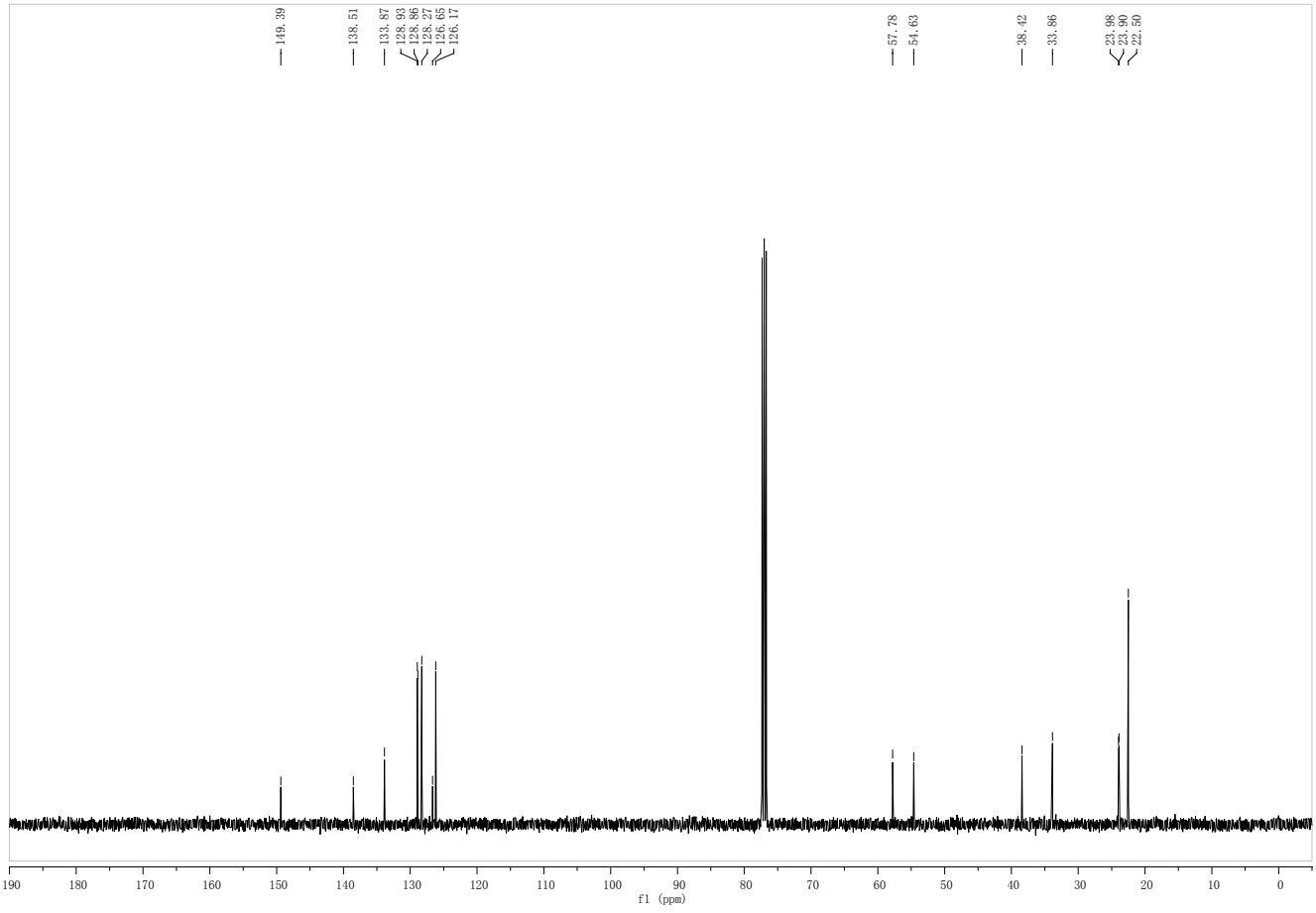


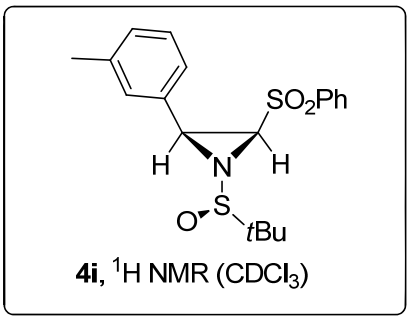
4h, ^{1}H NMR ($CDCl_3$)



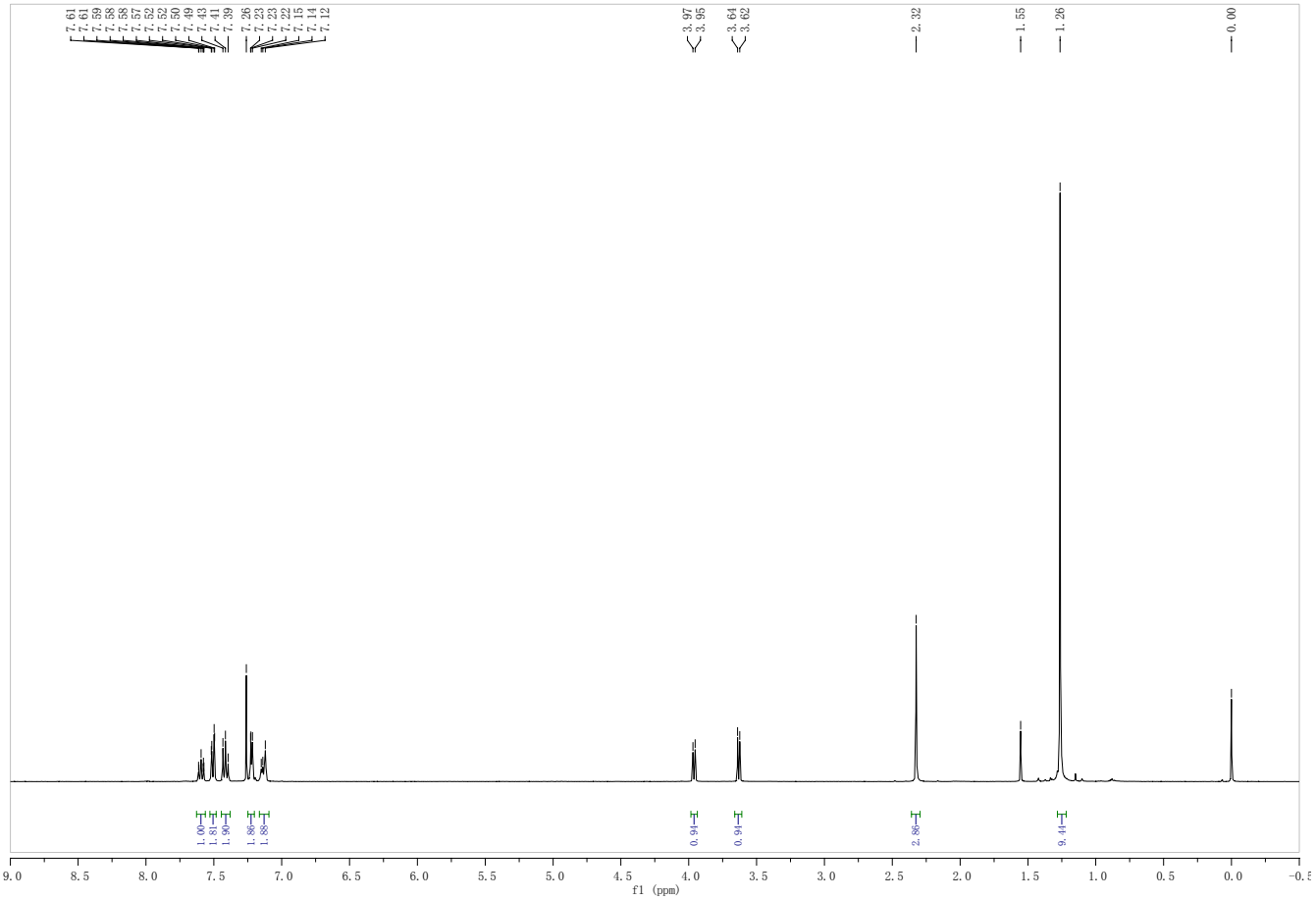


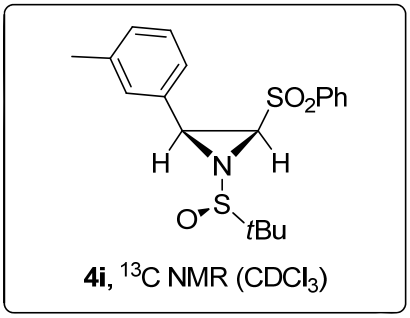
4h, ^{13}C NMR ($CDCl_3$)



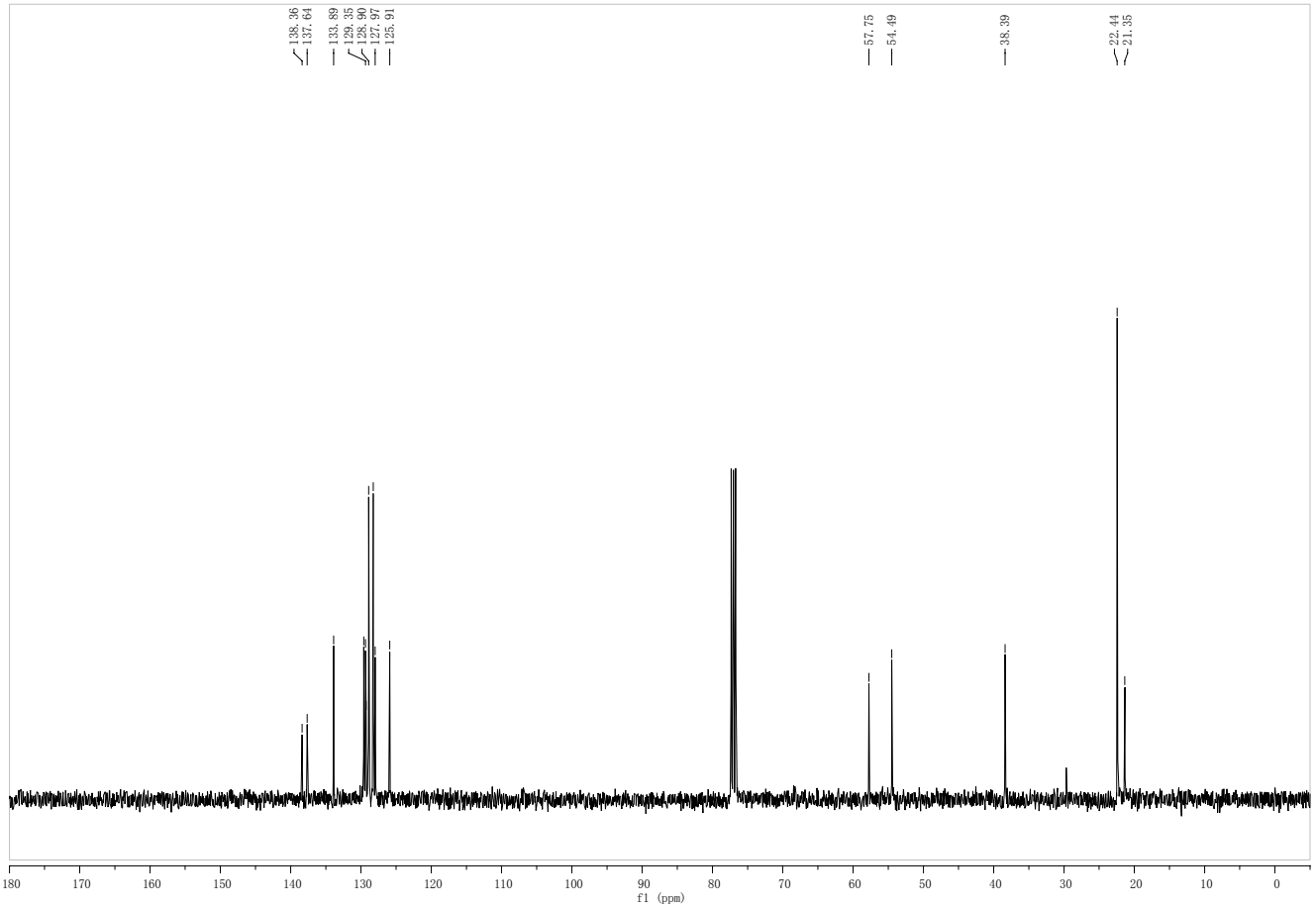


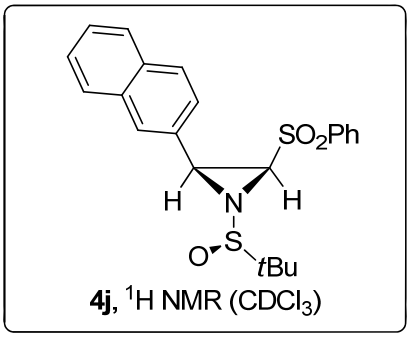
4i, ^{1}H NMR ($CDCl_3$)



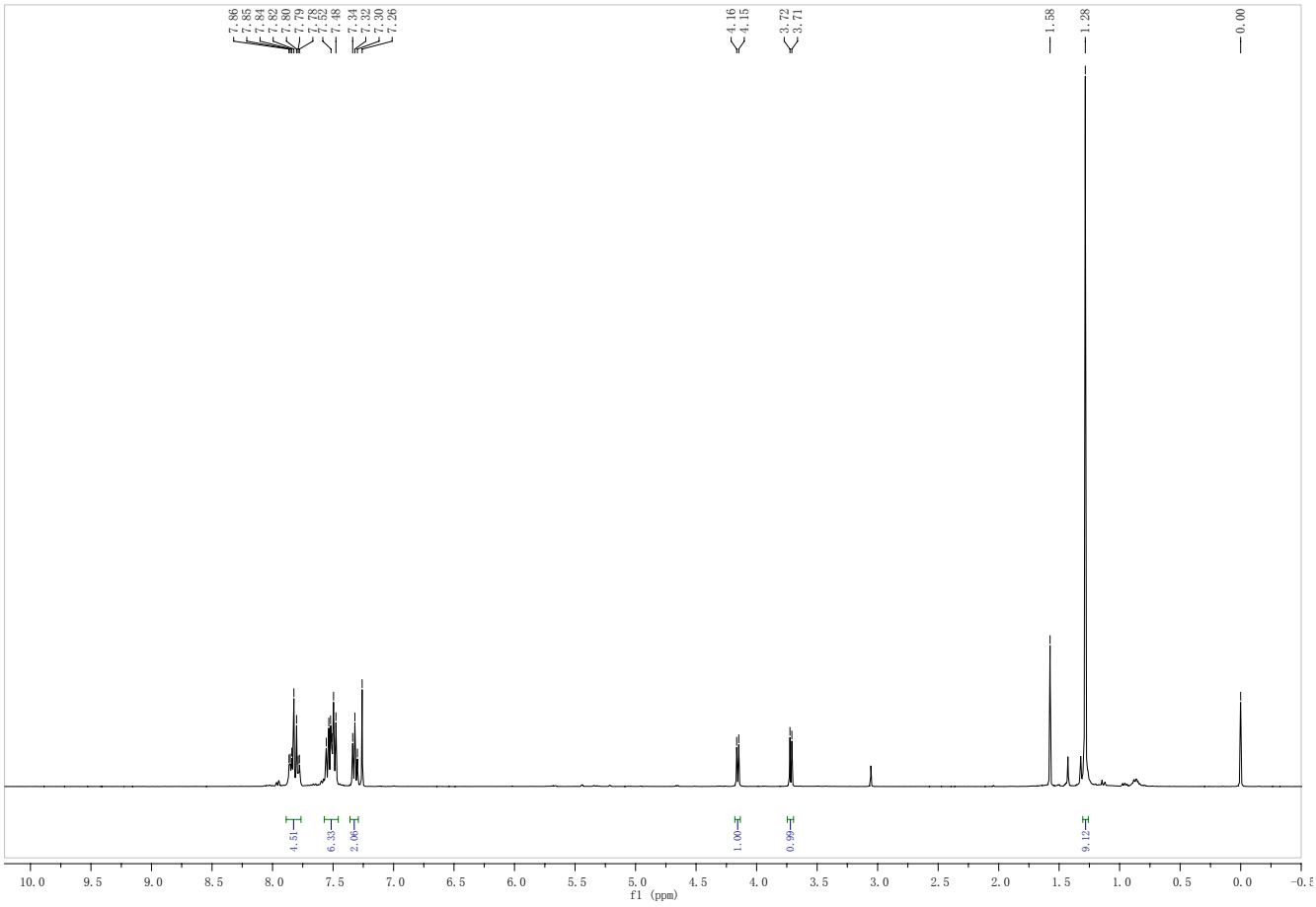


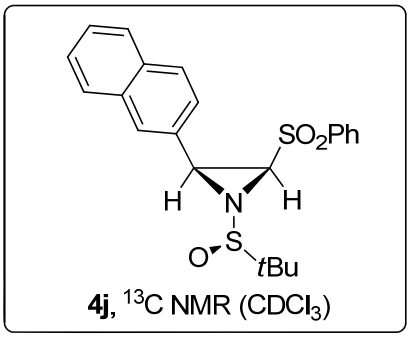
4i, ^{13}C NMR ($CDCl_3$)



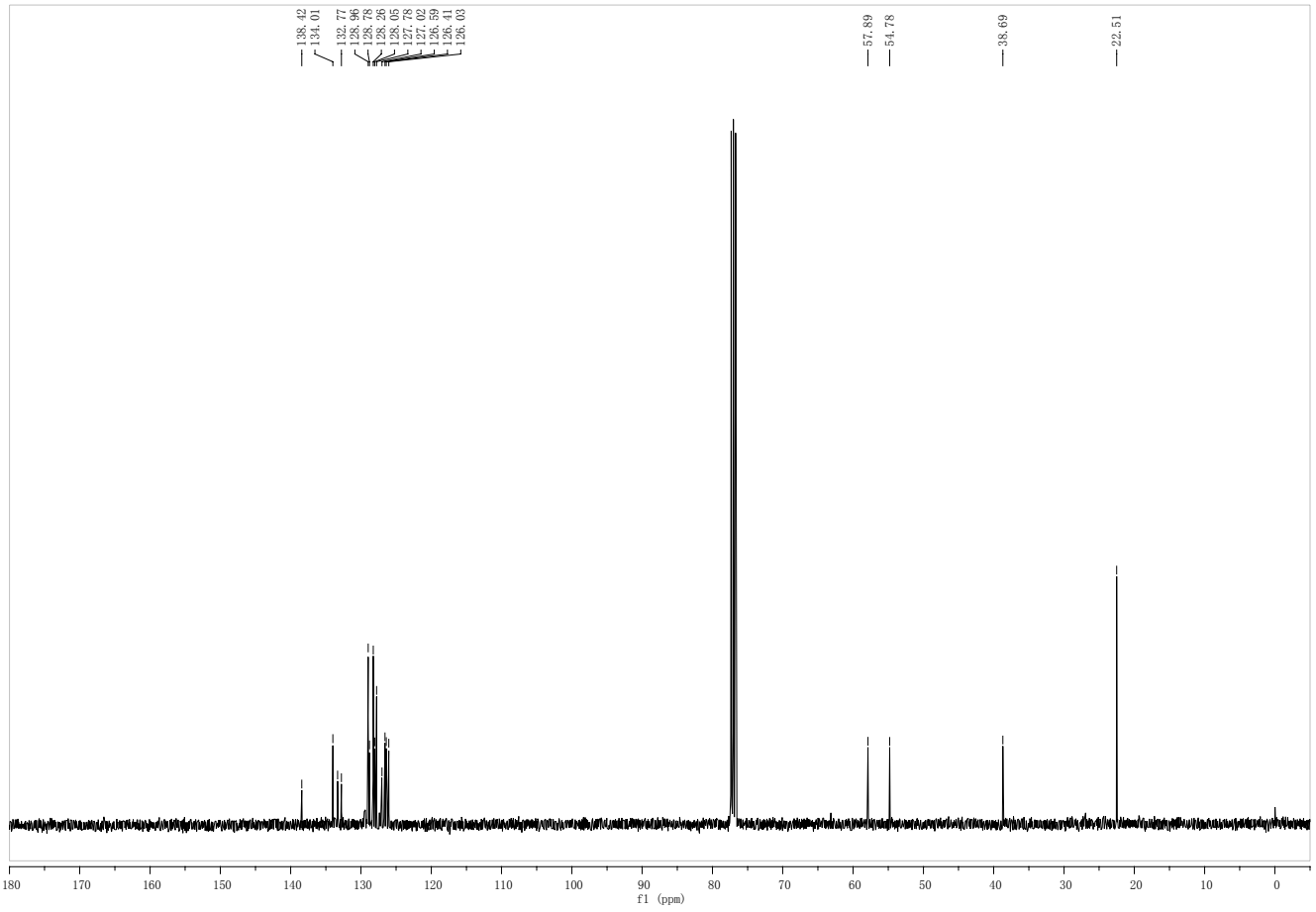


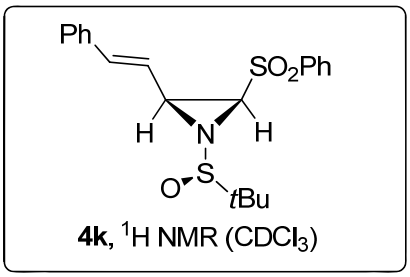
4j, ^{1}H NMR ($CDCl_3$)



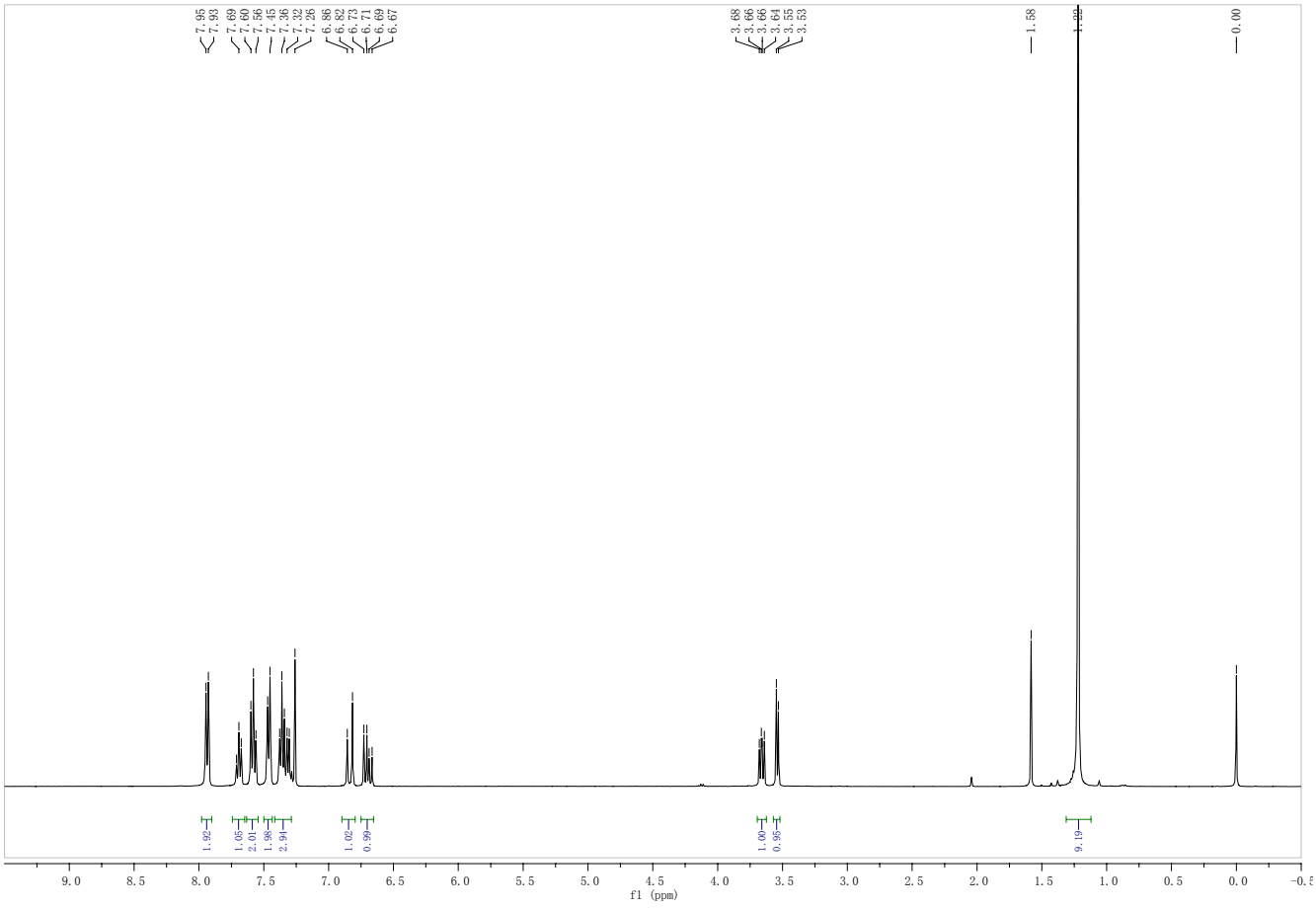


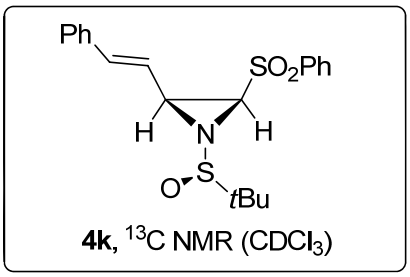
4j, ^{13}C NMR ($CDCl_3$)



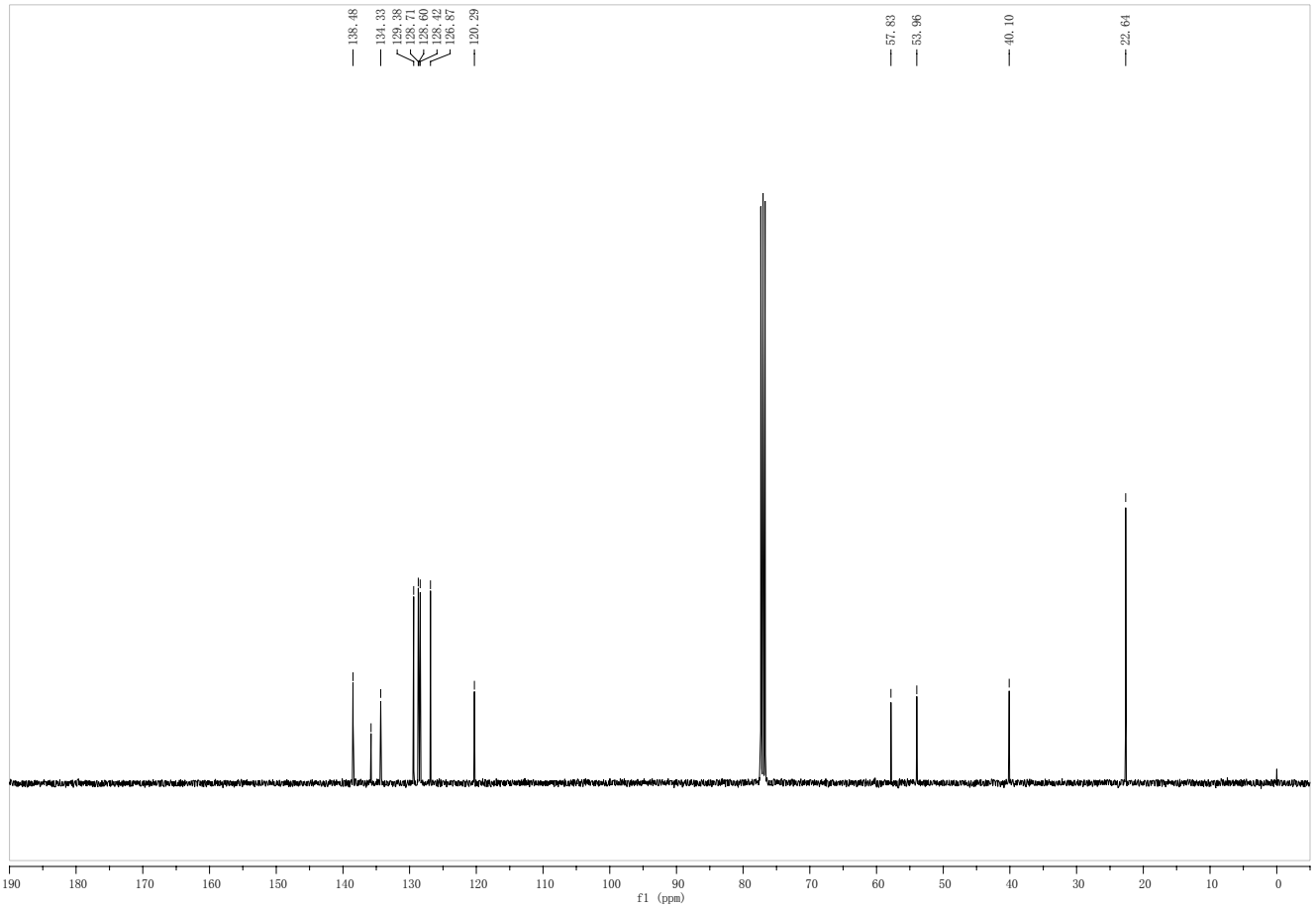


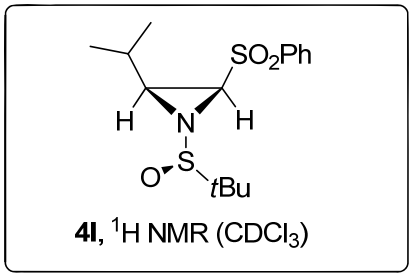
4k, ^{1}H NMR ($CDCl_3$)



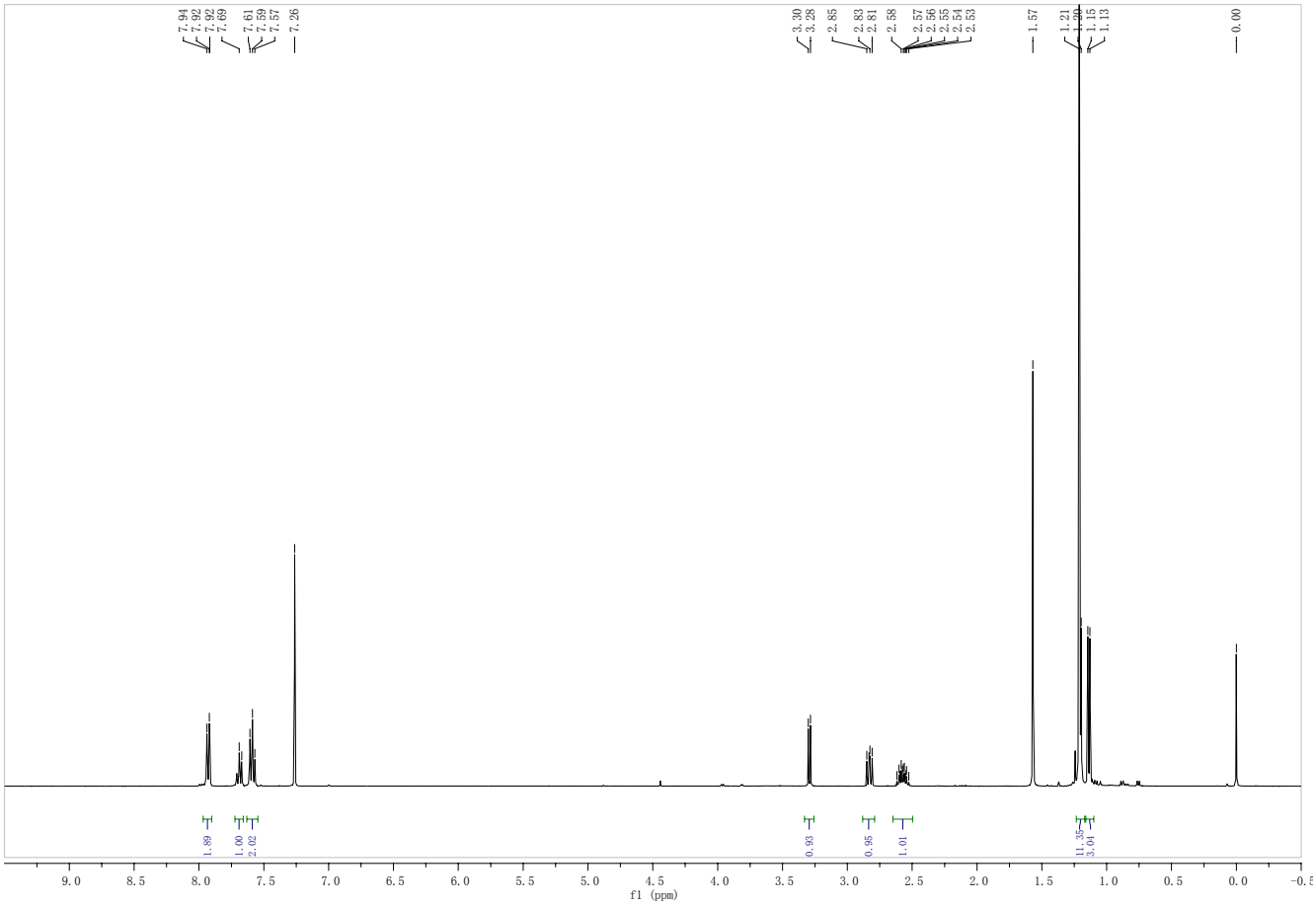


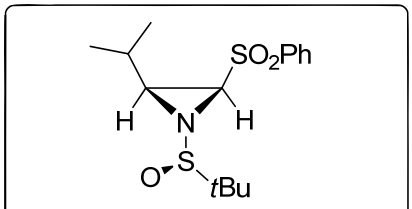
4k, ^{13}C NMR ($CDCl_3$)



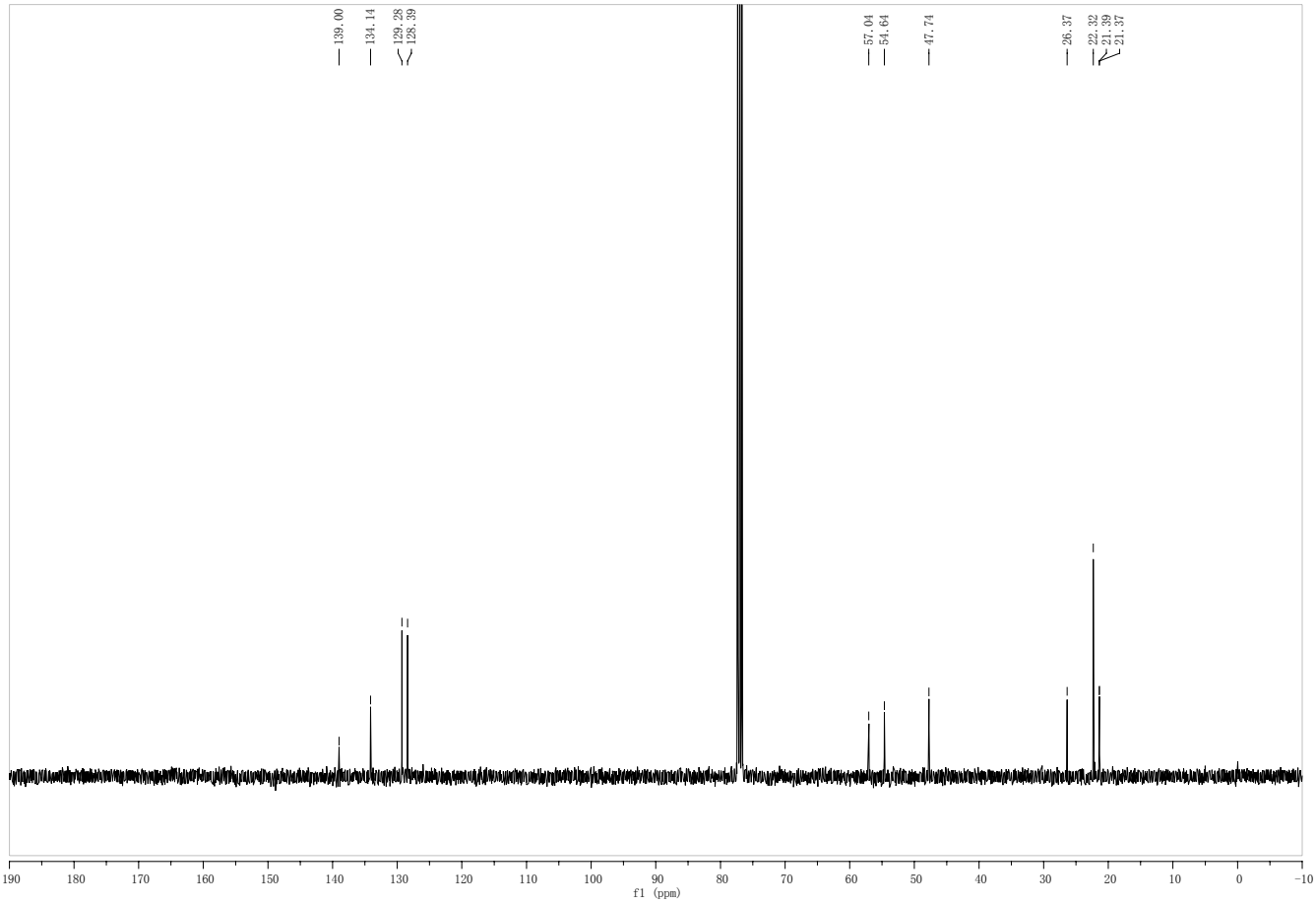


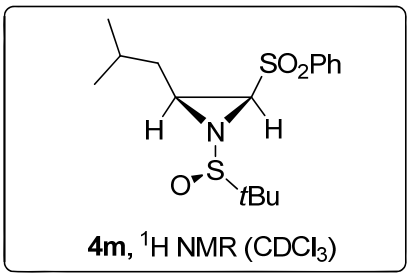
4l, ^{1}H NMR ($CDCl_3$)



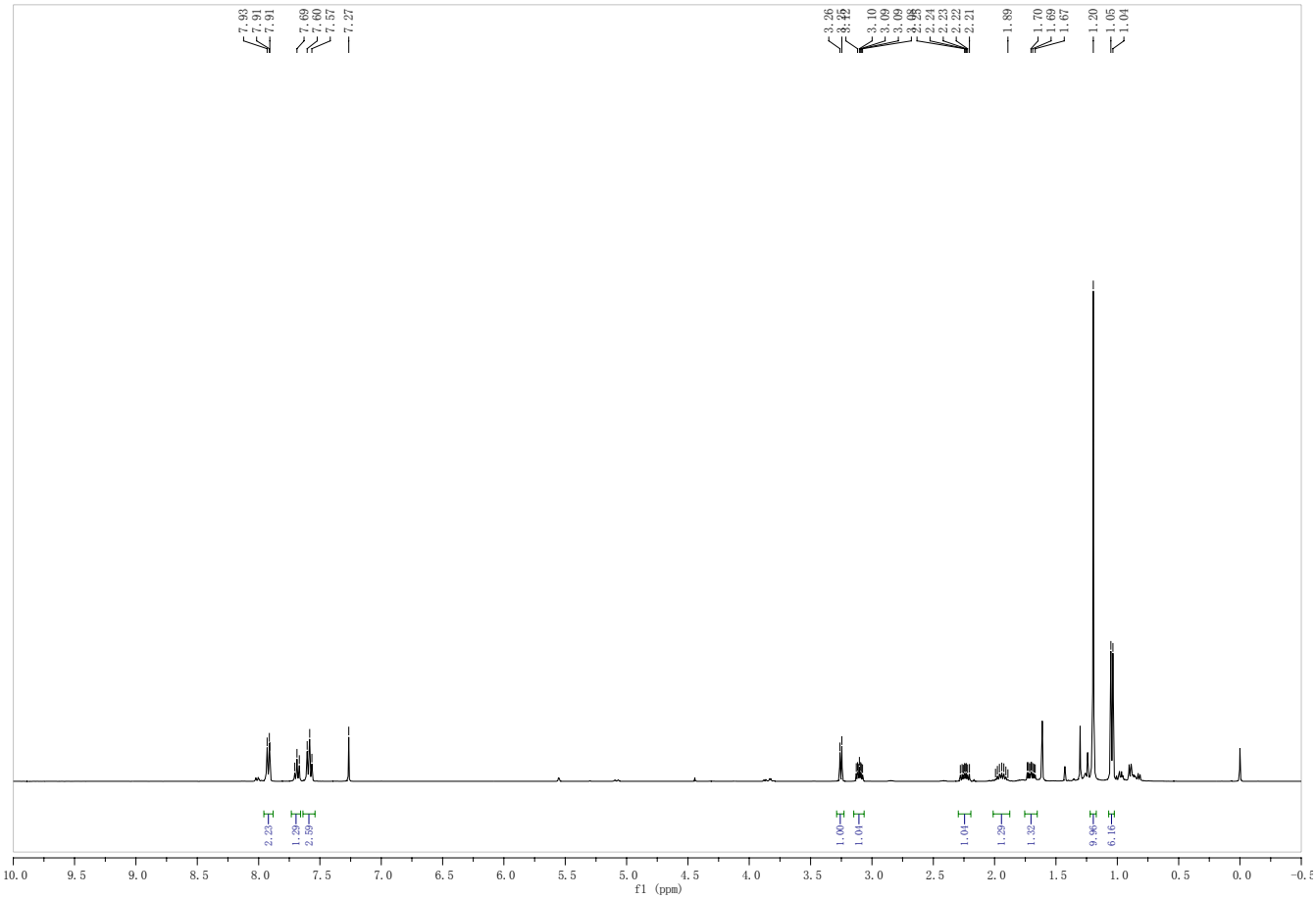


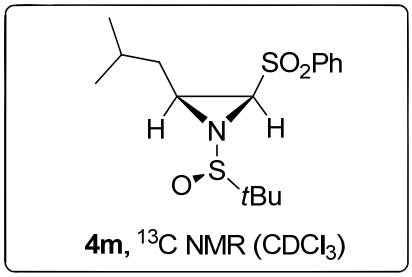
4l, ^{13}C NMR ($CDCl_3$)



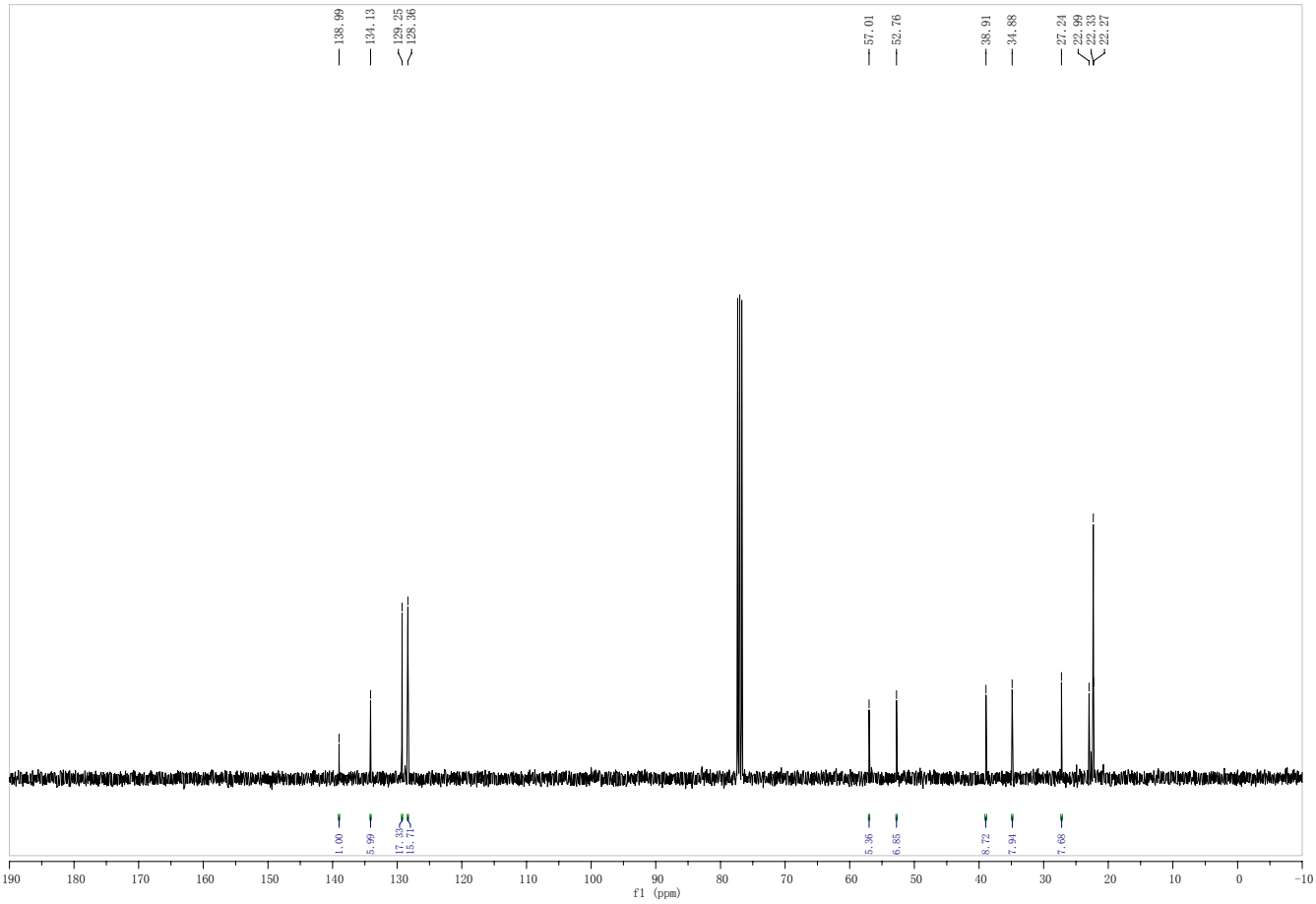


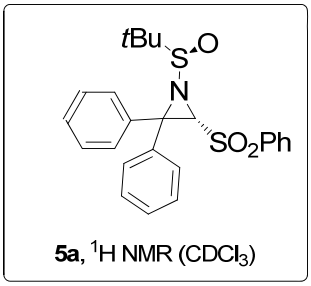
4m, ^{1}H NMR ($CDCl_3$)



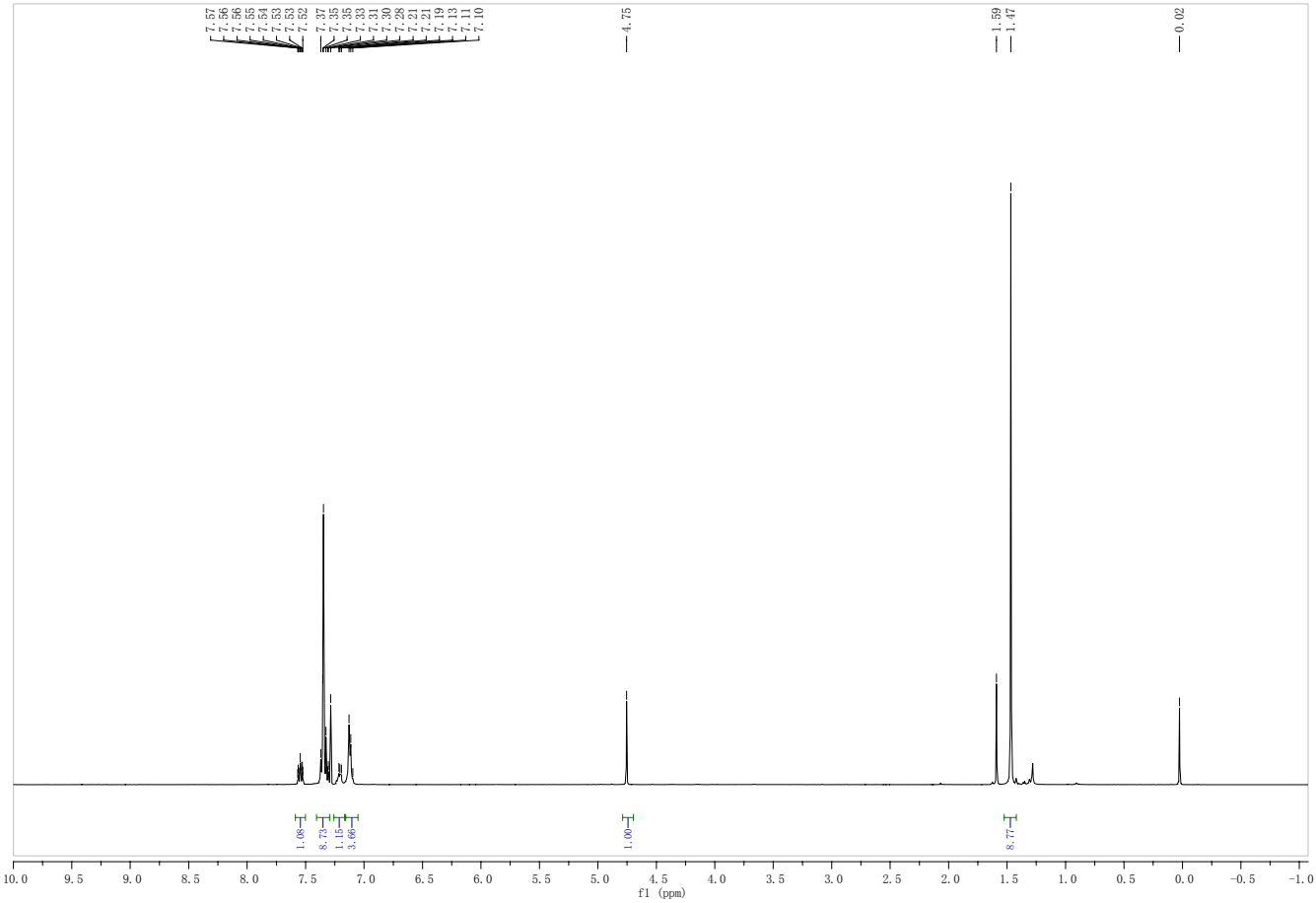


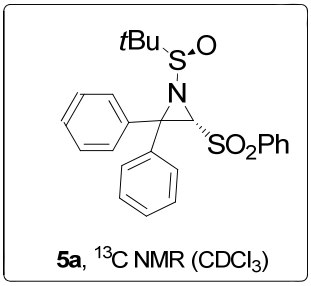
4m, ^{13}C NMR ($CDCl_3$)



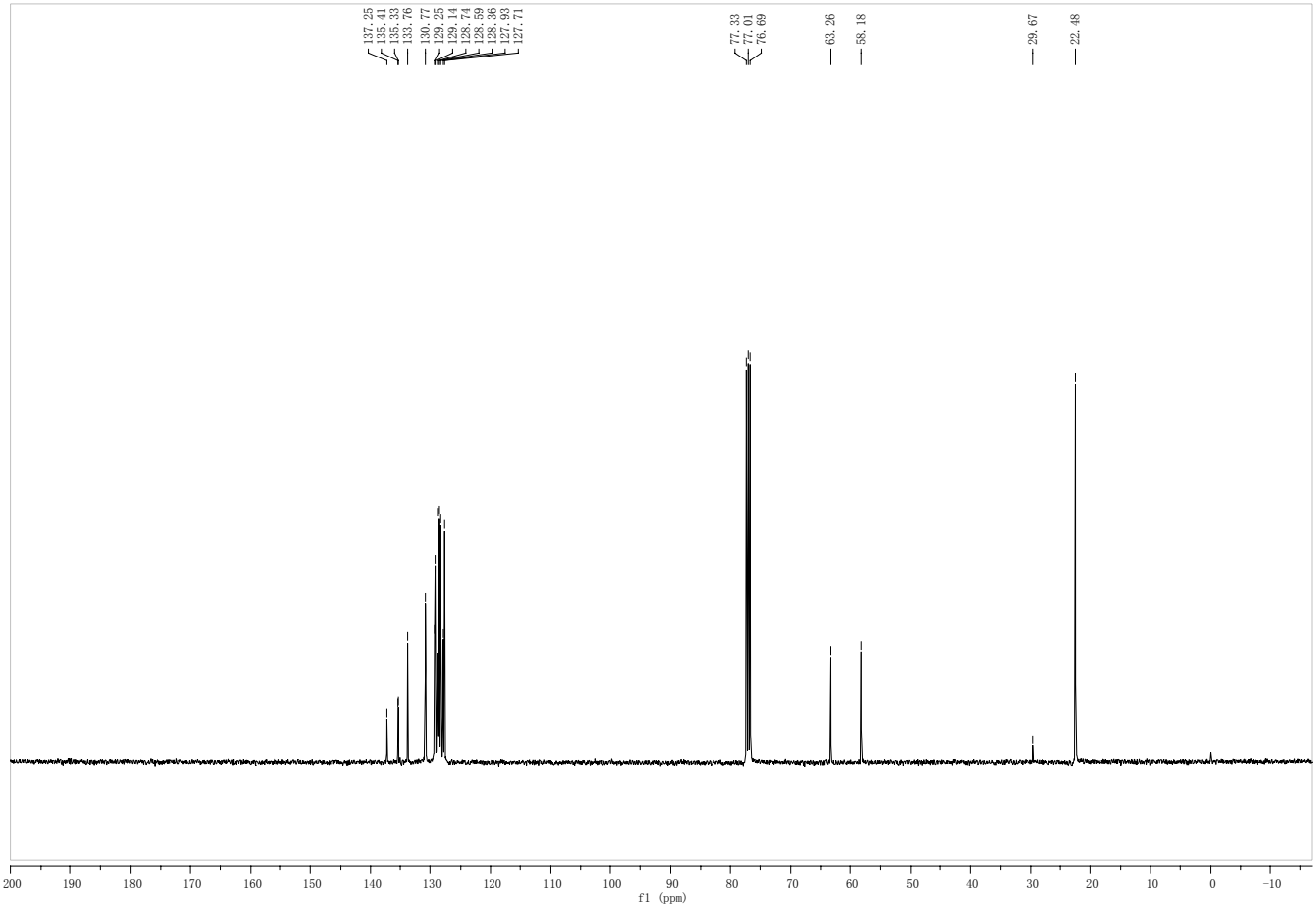


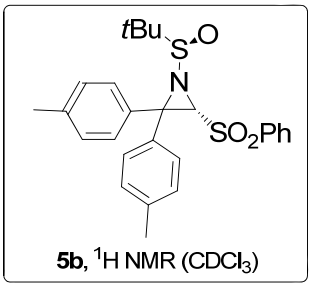
5a, ^{1}H NMR ($CDCl_3$)



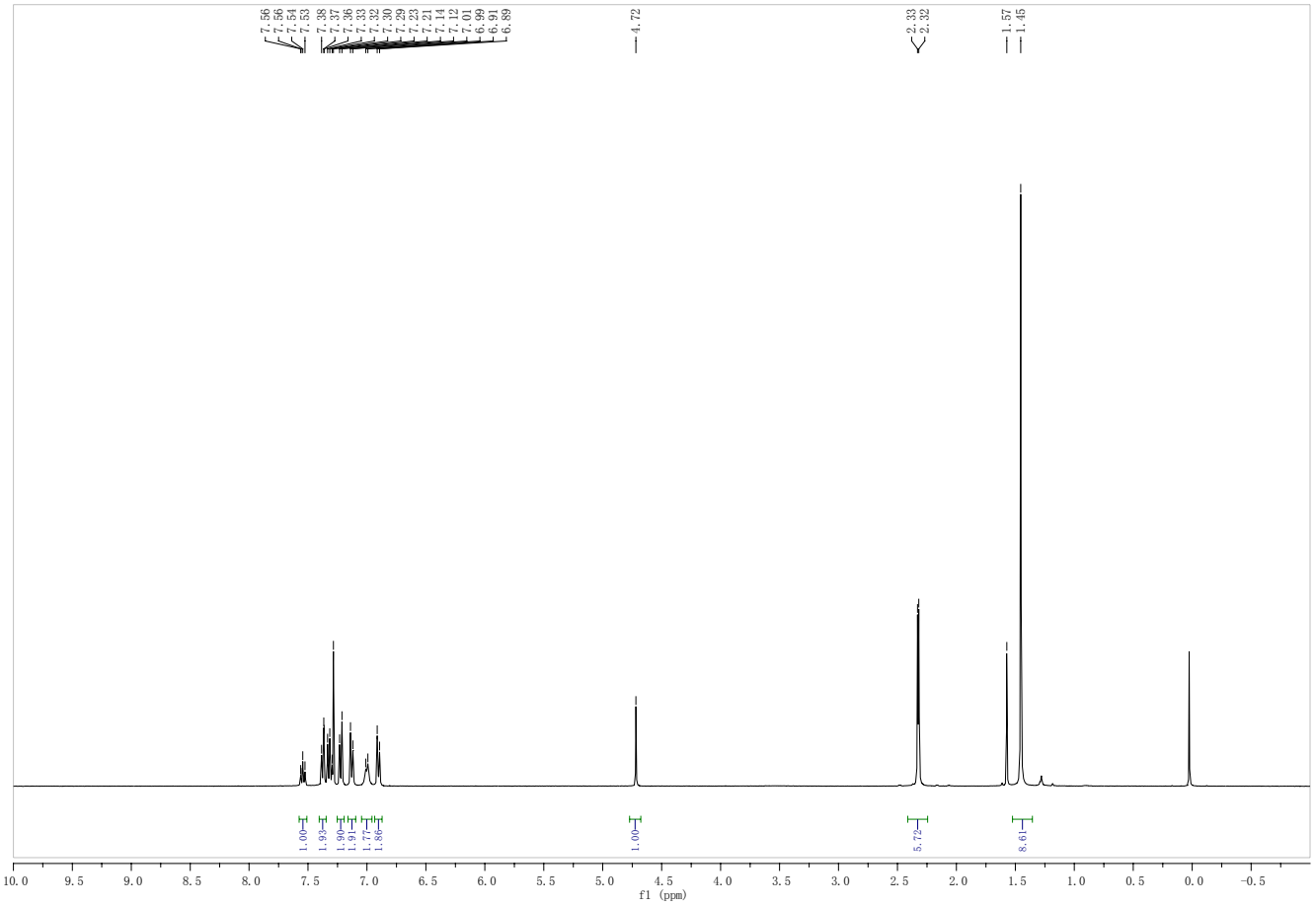


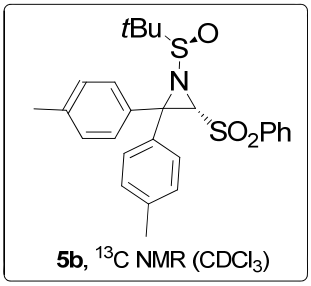
5a, ^{13}C NMR ($CDCl_3$)



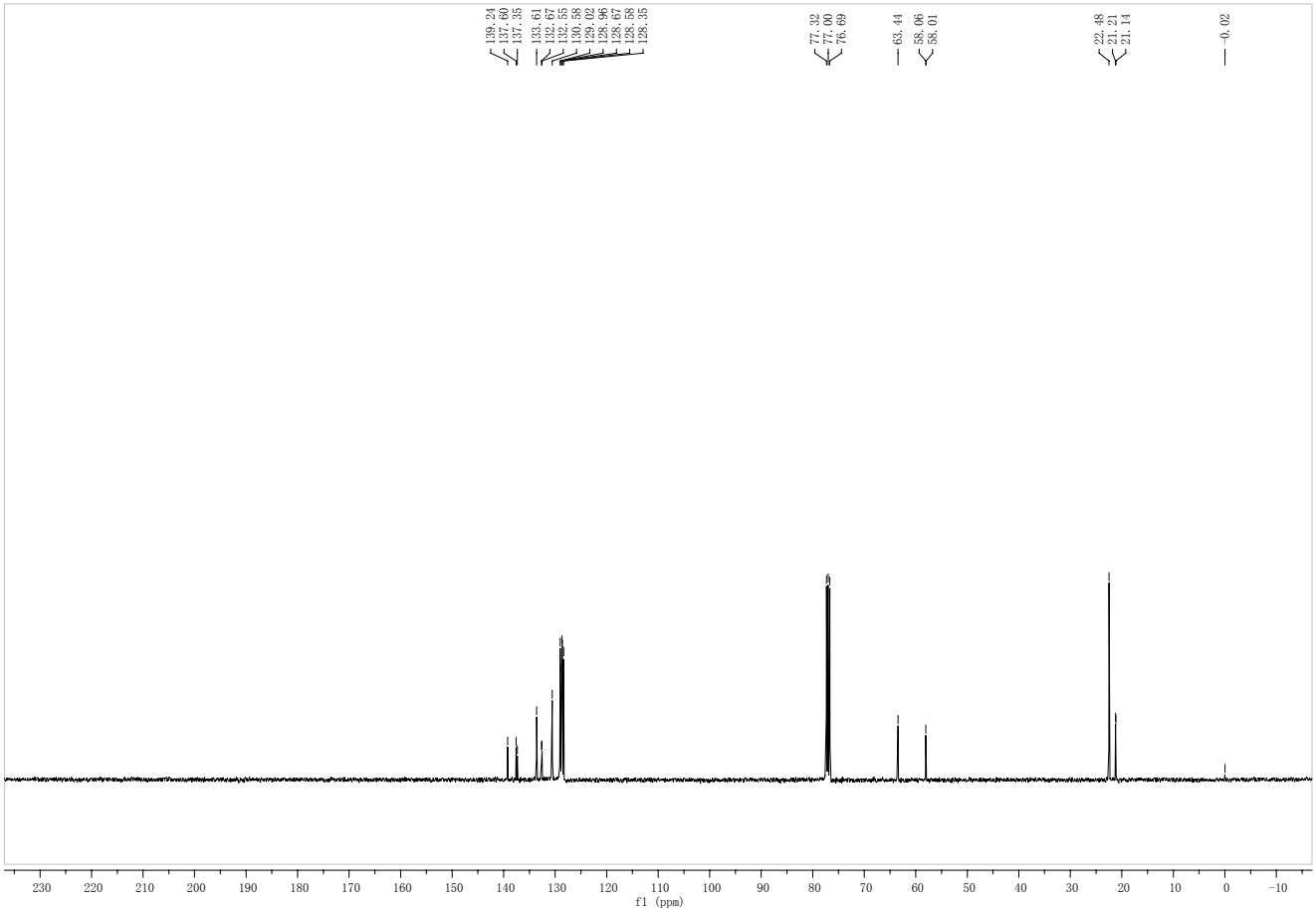


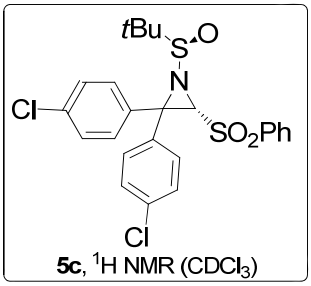
5b, ^{1}H NMR ($CDCl_3$)



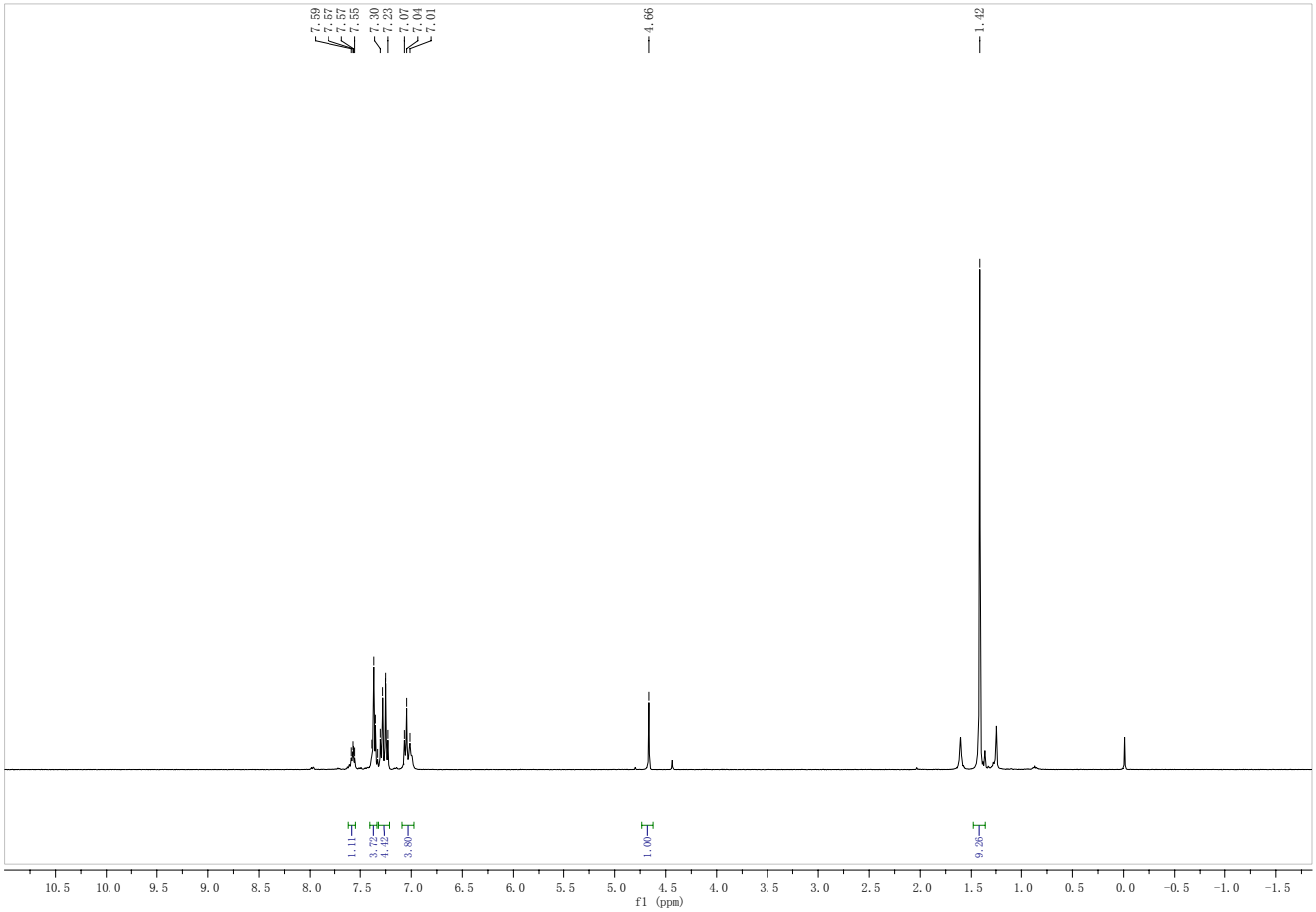


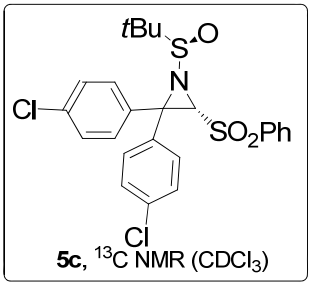
5b, ^{13}C NMR ($CDCl_3$)



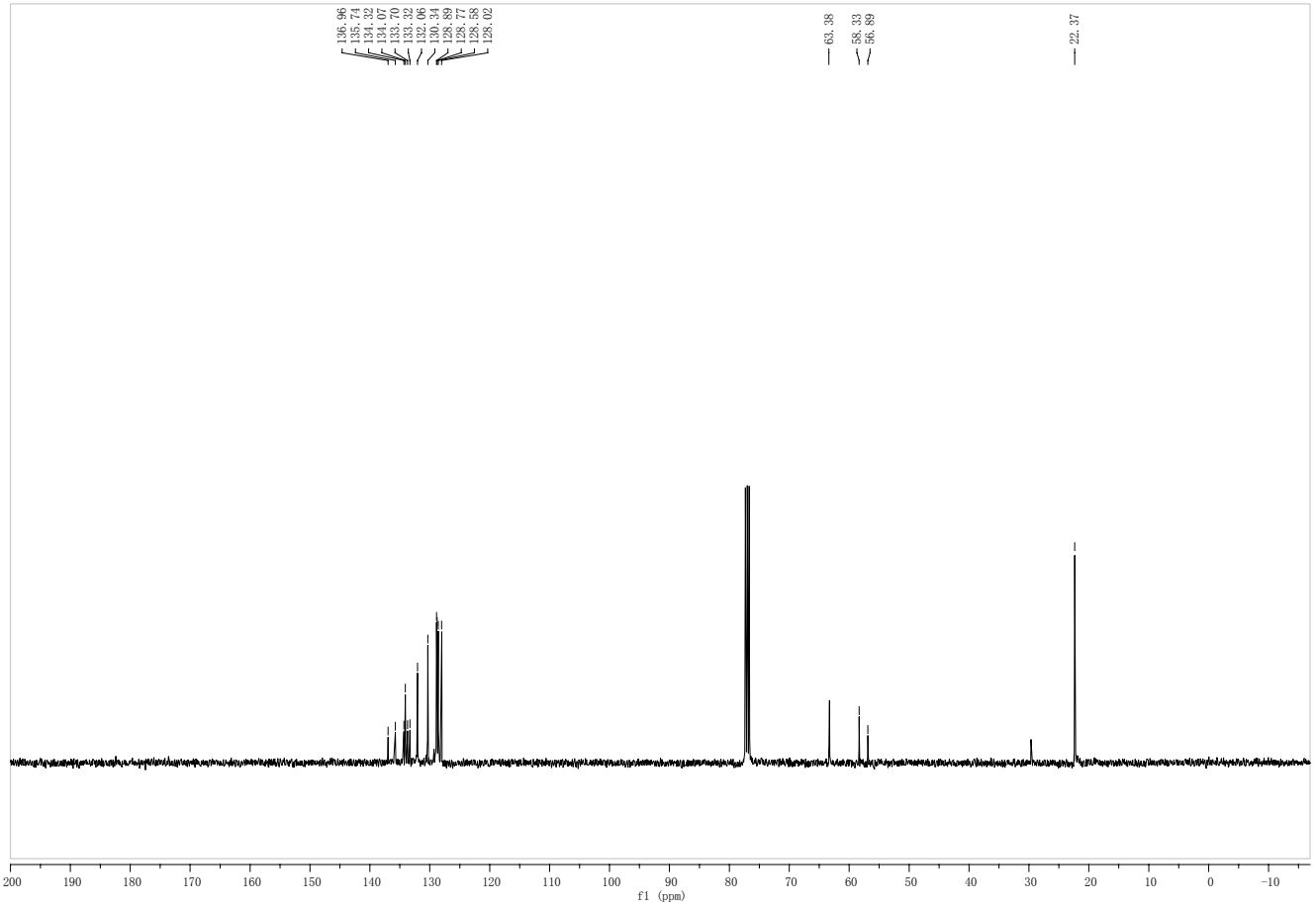


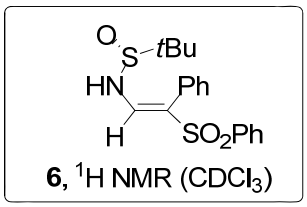
5c, ^{1}H NMR ($CDCl_3$)



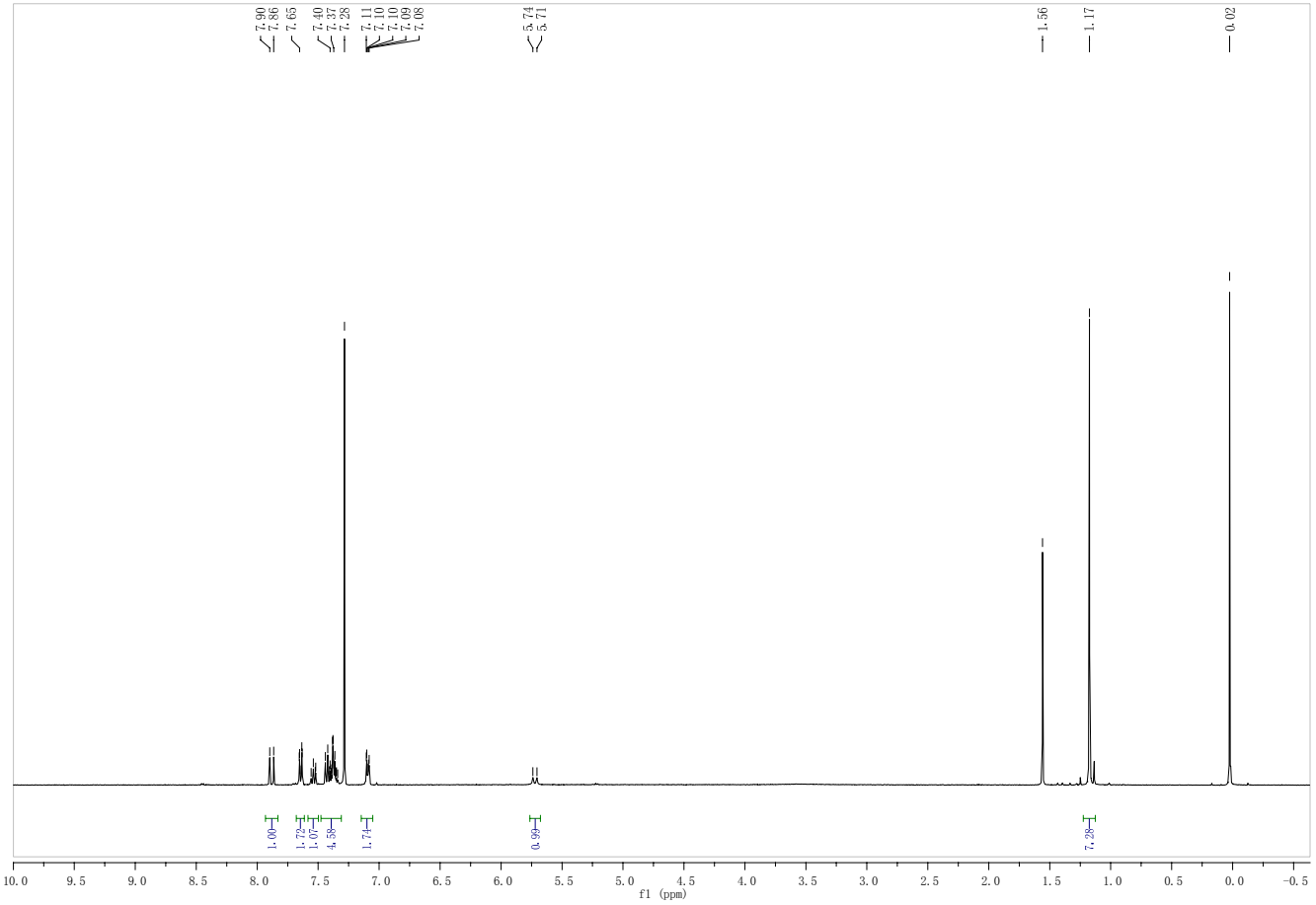


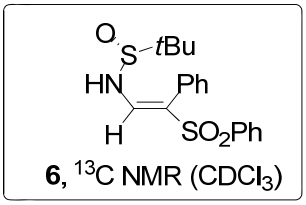
5c, ^{13}C NMR ($CDCl_3$)



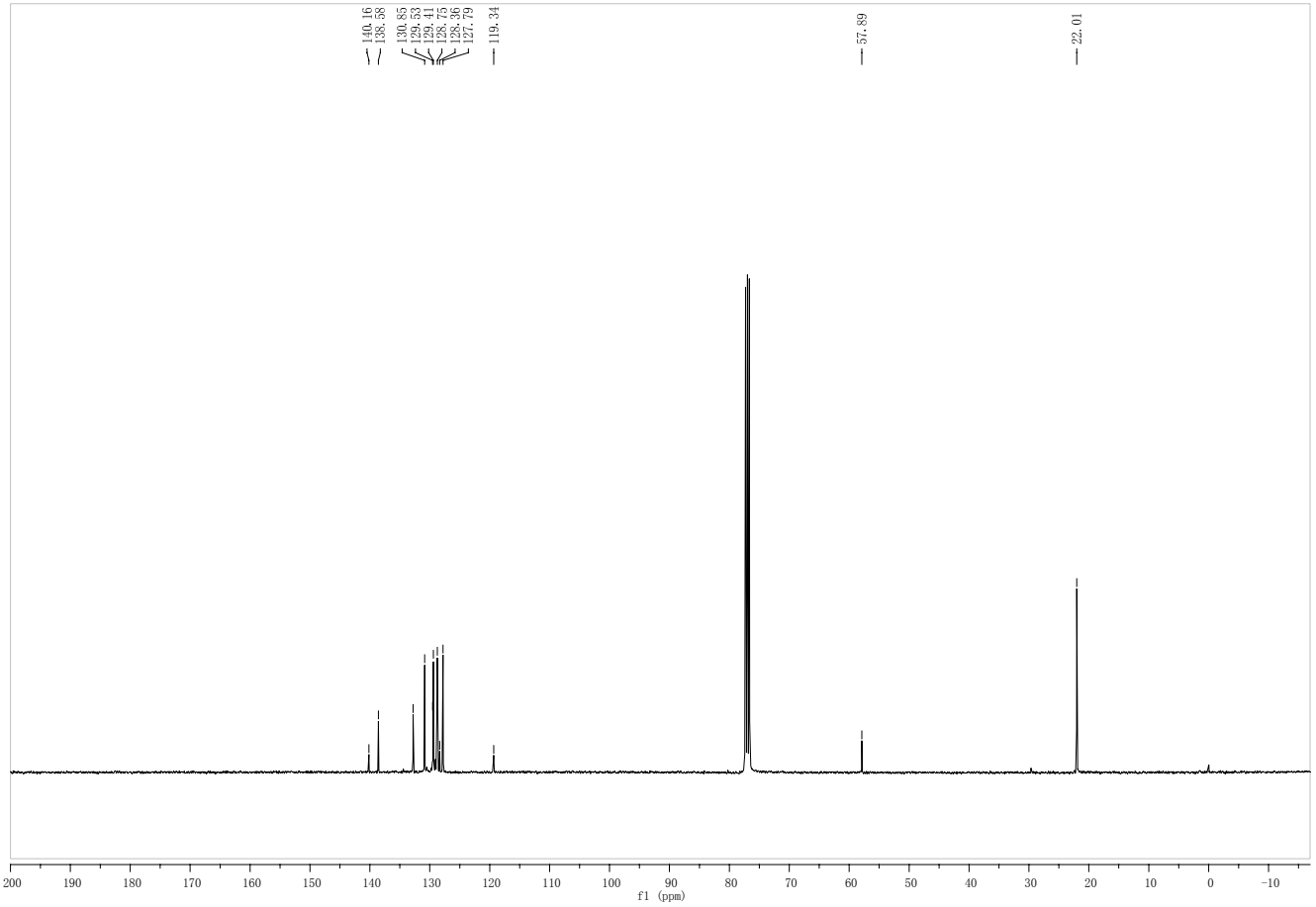


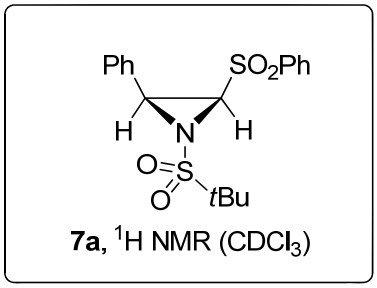
6, ^{1}H NMR ($CDCl_3$)



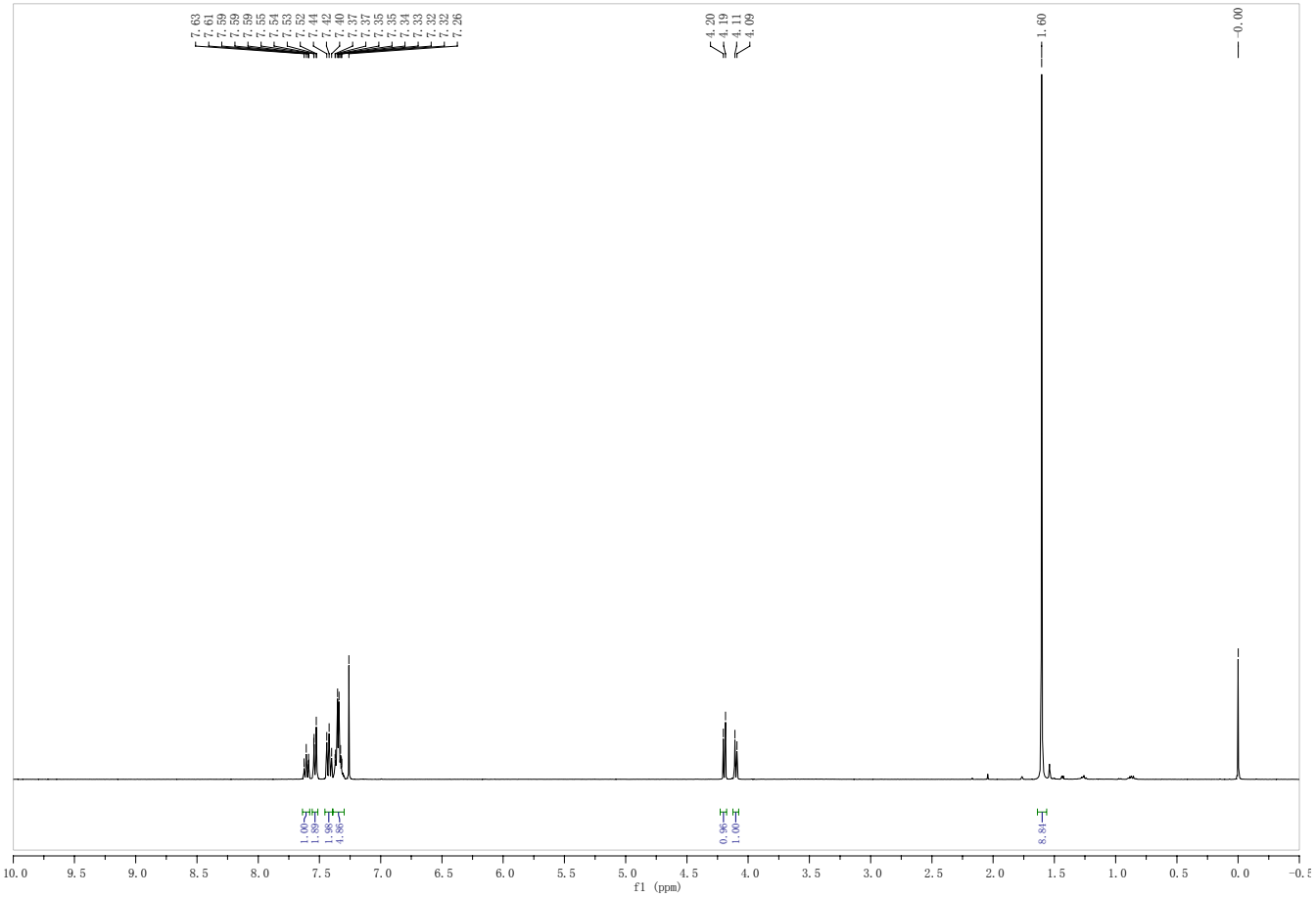


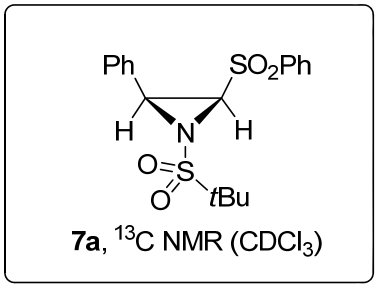
6, ^{13}C NMR ($CDCl_3$)



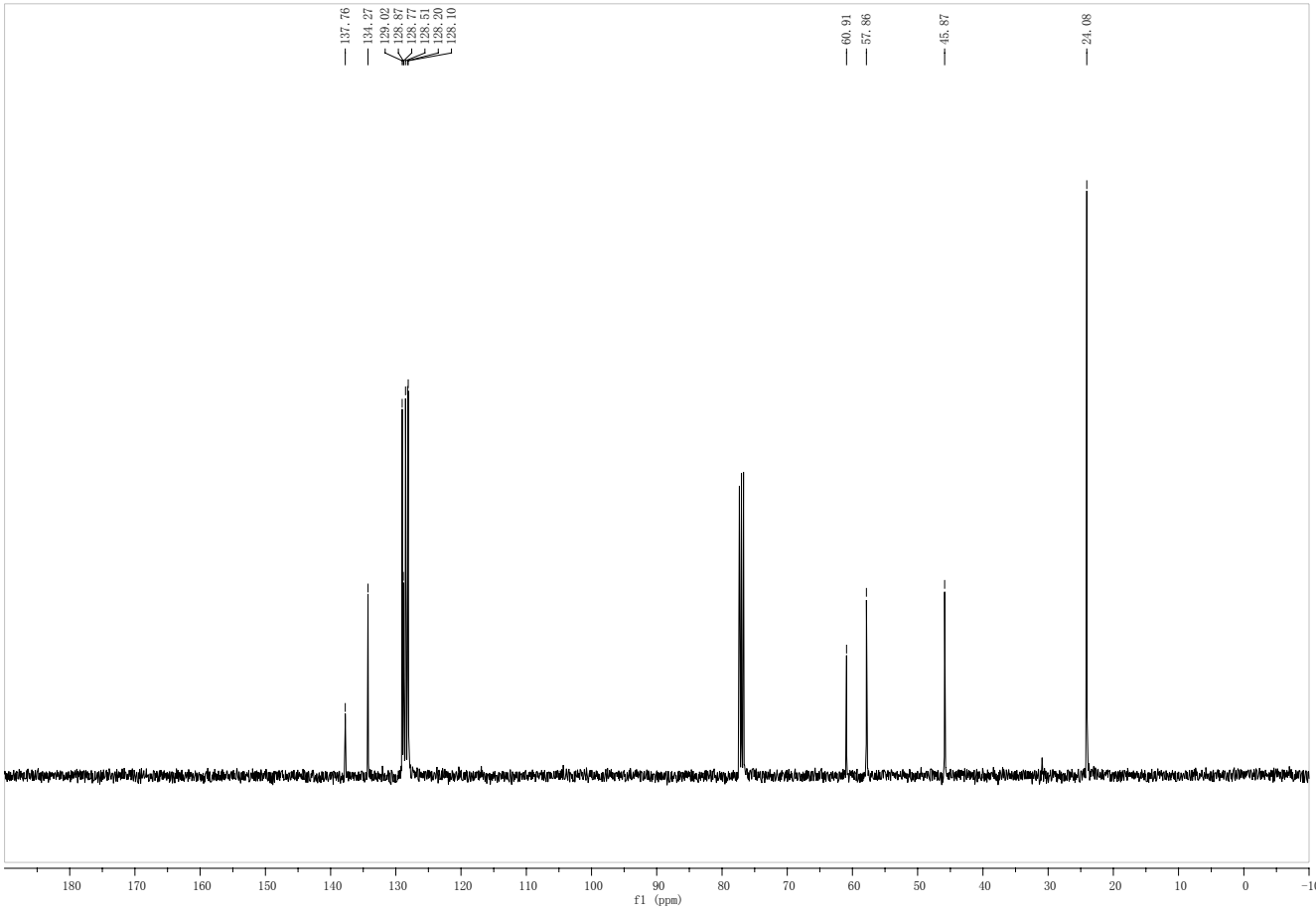


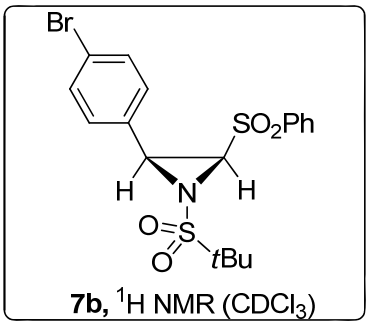
7a, ^{1}H NMR ($CDCl_3$)



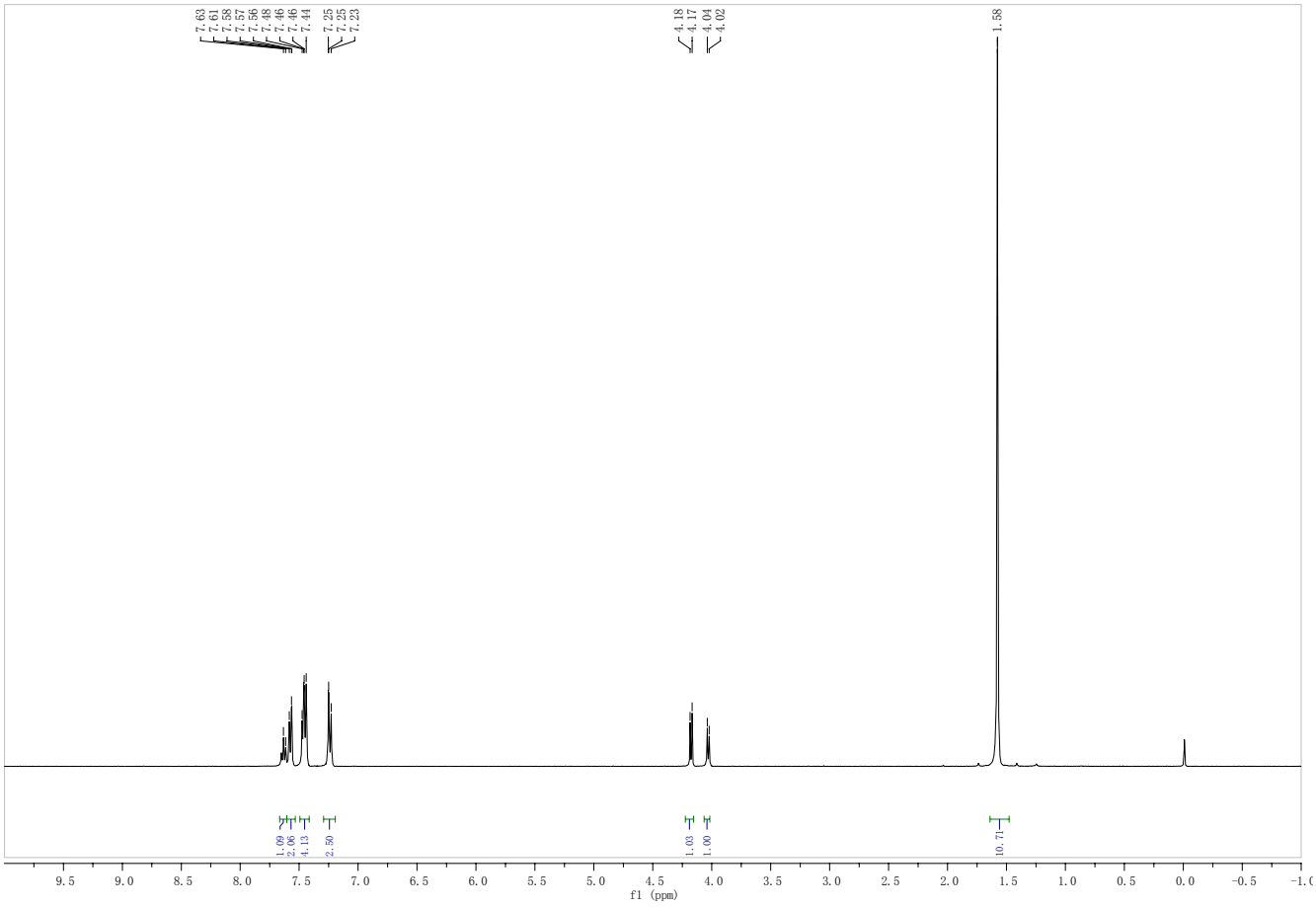


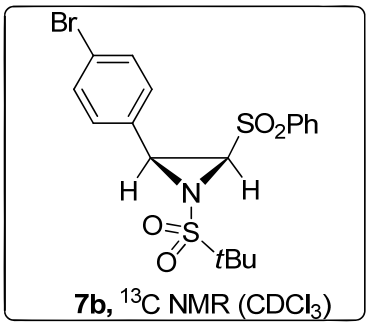
7a, ^{13}C NMR ($CDCl_3$)



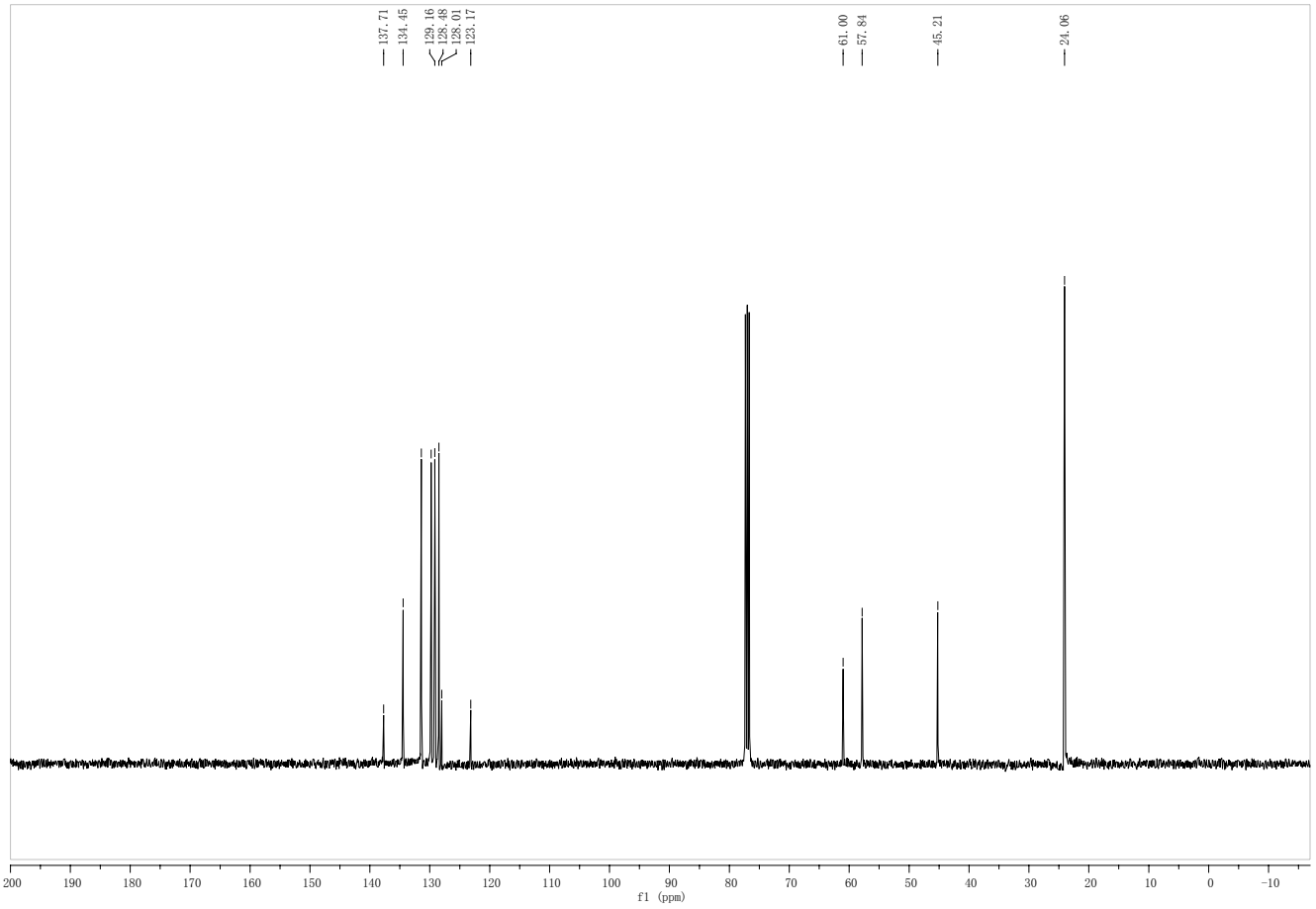


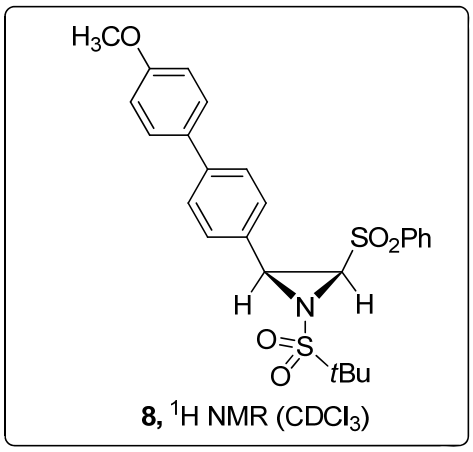
7b, ^{1}H NMR ($CDCl_3$)



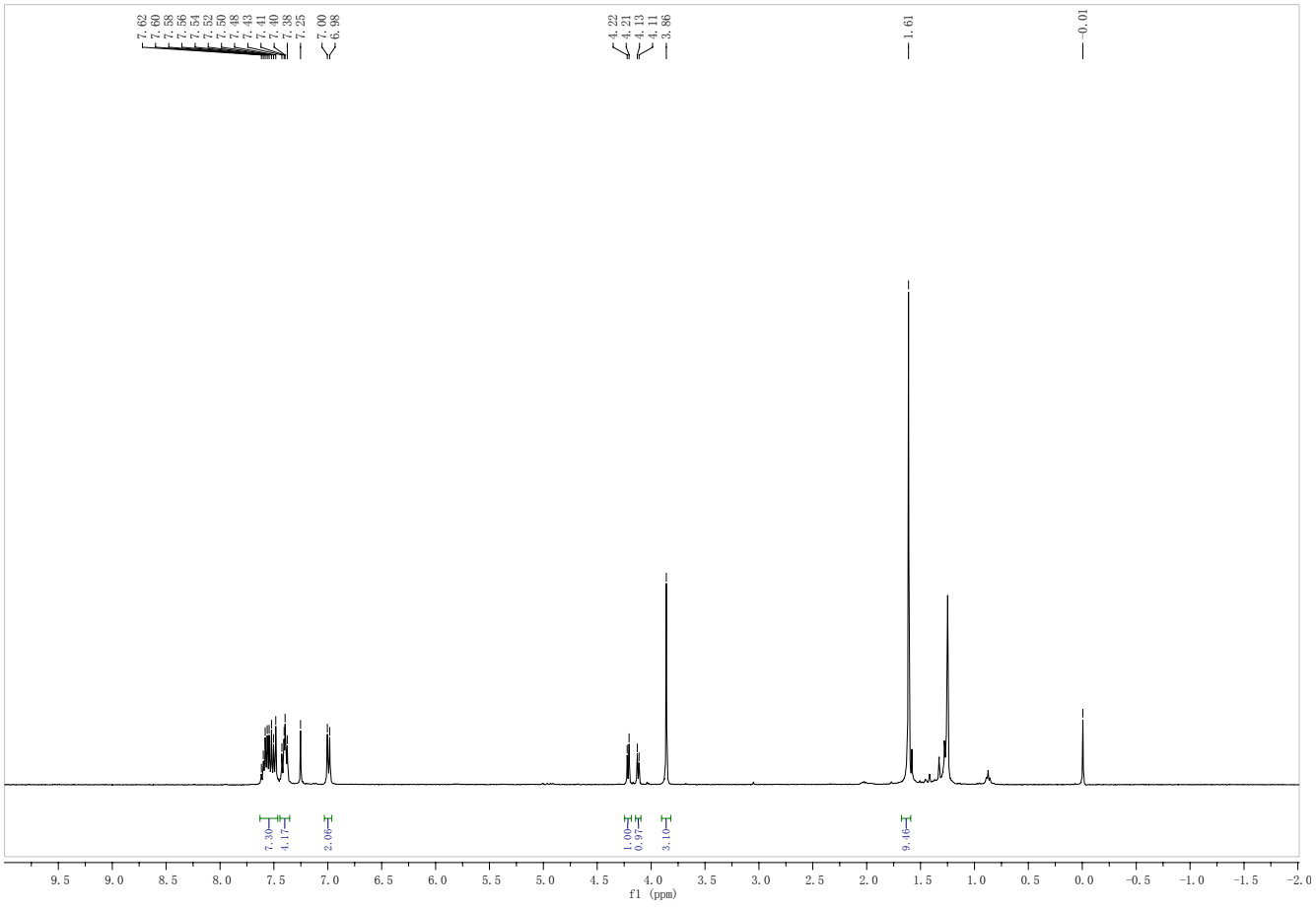


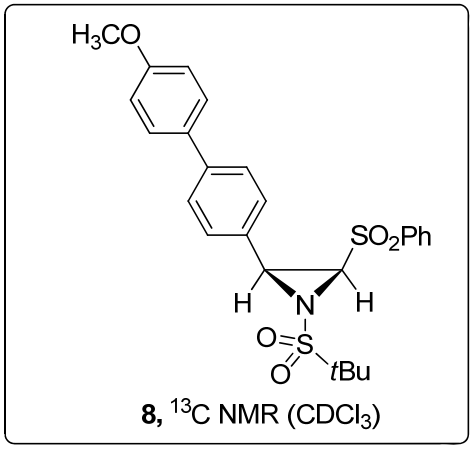
7b, ^{13}C NMR ($CDCl_3$)





8, ^{1}H NMR ($CDCl_3$)





8, ^{13}C NMR ($CDCl_3$)