Supporting Information

An Unprecedented Ring-Opening Reaction of *N*-(Aziridin-2-ylmethylene)hydrazines to Facile Synthesis of Functionalized Enamines Catalysed by Lewis Acid

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Content

1. General Information

Melting points were obtained with a Yanagimoto micro melting point apparatus and are uncorrected. ^{1}H NMR spectra were recorded on a Bruker AM-300 or AM-400 spectrometer for solution in $CDCl_3$ with tetramethylsilane (TMS) as internal standard; *J*-values are in Hz. Mass spectra were recorded with a HP-5989 instrument. All of the compounds reported in this paper gave satisfactory HRMS analytic data. Commercially obtained reagents were used without further purification. Dichloromethane was distilled from calcium hydride under argon. All reactions were monitored by TLC with Huanghai GF_{254} silica gel coated plates. Flash column chromatography was carried out using 300–400 mesh silica gel at increased pressure.

2. General Procedure for the Preparation of Compound 1

N-Sulfonylhydrazone was synthesized from various aldehydes and sulfonohydrazides by the known procedure.[1-3] Substituted *N*-sulfonylhydrazone **S1** was produced according to the typical Mitsunobu reaction procedure.[4]

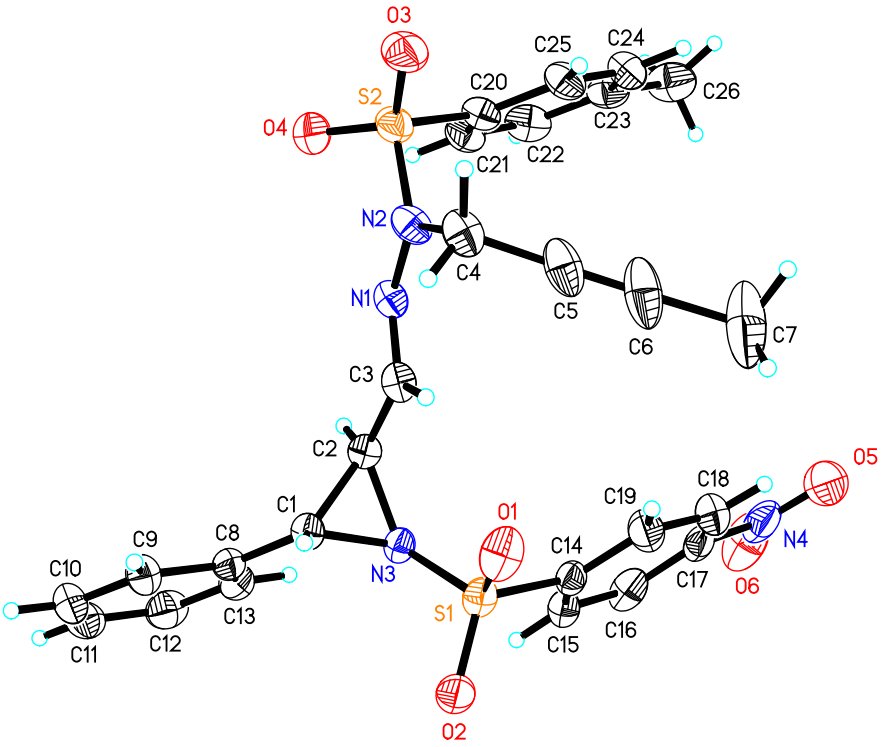
N-(Aziridin-2-ylmethylene)hydrazine **1** was obtained by copper-catalyzed olefin aziridination according to the reported procedure.[5] CuCl (10 mol %) was added to a suspension of the *N*-sulfonylhydrazone **S1** (2.0 equiv) and PhI=NNs (1.0 equiv) in MeCN at room temperature.[6] When all of the PhI=NNs was consumed (< 5 h), the solvent was removed under reduced pressure and the residue was purified by silica gel flash chromatography (eluent: petroleum ether/ethyl acetate = 4/1) to afford **1**.

3. General Procedure for the Preparation of Compound 2

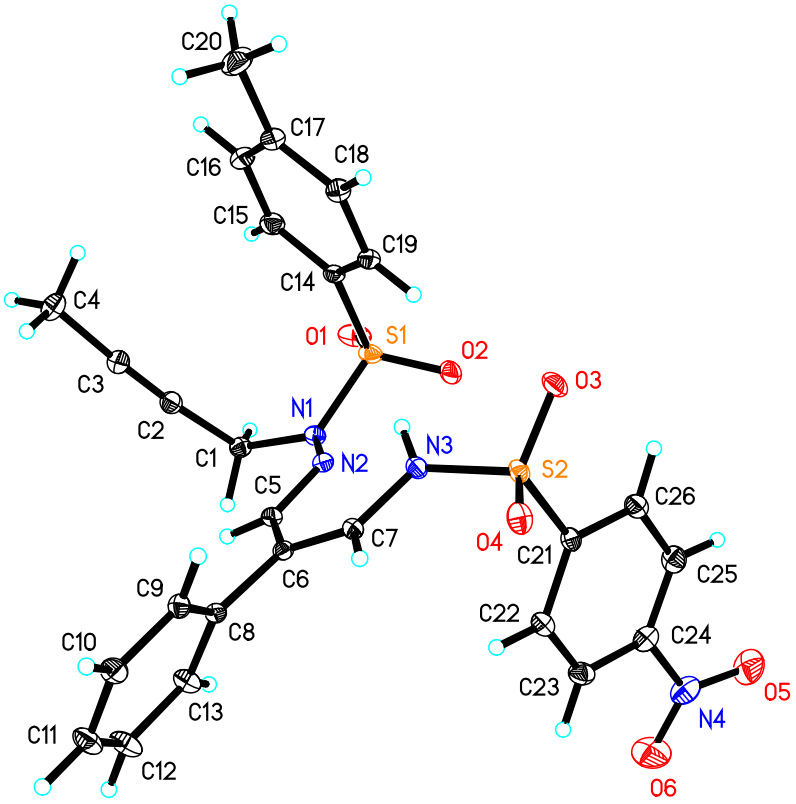
To a solution of substrate **1** (0.2 mmol) in dry dichloromethane (1.0 mL) was added $BF_3{\cdot}Et_2O$

(0.02 mmol) dropwise at room temperature then the reaction was stirred for 5 min. When the reaction completed, the yellow mixture was evaporated under reduced pressure and the residue was purified by silica gel flash column chromatography eluting with petroleum and ethyl acetate (v/v, 3/1). Compound **2** could be afforded as a yellow solid or oil.

4. X-ray Data of 1i and 2i



The crystal data of **1i** have been deposited in CCDC with number 848929. Empirical Formula: $C_{26}H_{24}N_4O_6S_2$; Formula Weight: 552.61; Crystal Color, Habit: colorless; Crystal Dimensions: 0.276 x 0.165 x 0.137 mm; Crystal System: Triclinic; Lattice Parameters: a = 9.682(2)Å, alpha = 107.220(4) deg.; b = 10.655(2)Å, beta = 96.011(4) deg.; c = 15.011(3)Å, gamma = 110.395(3) deg.; V = 1348.5(5) $Å^3$; Space group: P-1; Z = 2; D_{calc} = 1.361 g/cm^3; F_{000} = 576; Diffractometer: Rigaku AFC7R; Residuals: R; R_w: 0.0563, 0.1491.



The crystal data of **2i** have been deposited in CCDC with number 845691. Empirical Formula: $C_{26}H_{24}N_4O_6S_2$; Formula Weight: 552.61; Crystal Color, Habit: colorless; Crystal Dimensions: 0.25 x 0.18 x 0.15 mm; Crystal System: Triclinic; Lattice Parameters: a = 9.0221(10) Å, alpha = 69.652(2) deg.; b = 12.4227(14) Å, beta = 74.456(2) deg.; c = 12.8373(14) Å, gamma = 87.696(2) deg.; V = 1297.4(2) $Å^3$; Space group: P-1; Z = 2; D_{calc} = 1.415 g/cm^3; F_{000} = 576; Diffractometer: Rigaku AFC7R; Residuals: R; R_w: 0.0473, 0.1271.

5. References

[1] L. Nagarapu, N. Ravirala, D. Akkewar, *Synth. Commun.* **2002**, *32*, 2195–2202.

[2] V. K. Aggarwal, E. Alonso, I. Bae, G. Hynd, K. M. Lydon, M. J. Palmer, M. Patel, M. Porcelloni, J. Richardson, R. A. Stenson, J. R. Studley, J.-L. Vasse, C. L. Winn, *J. Am. Chem. Soc.* **2003**, *125*, 10926–10940.

[3] Z. Zhang, M. Shi, *Chem. Eur. J.* **2012**, *18*, 3654–3658.

[4] J. M. Keith, L. Gomez, *J. Org. Chem.* **2006**, *71*, 7113–7116.

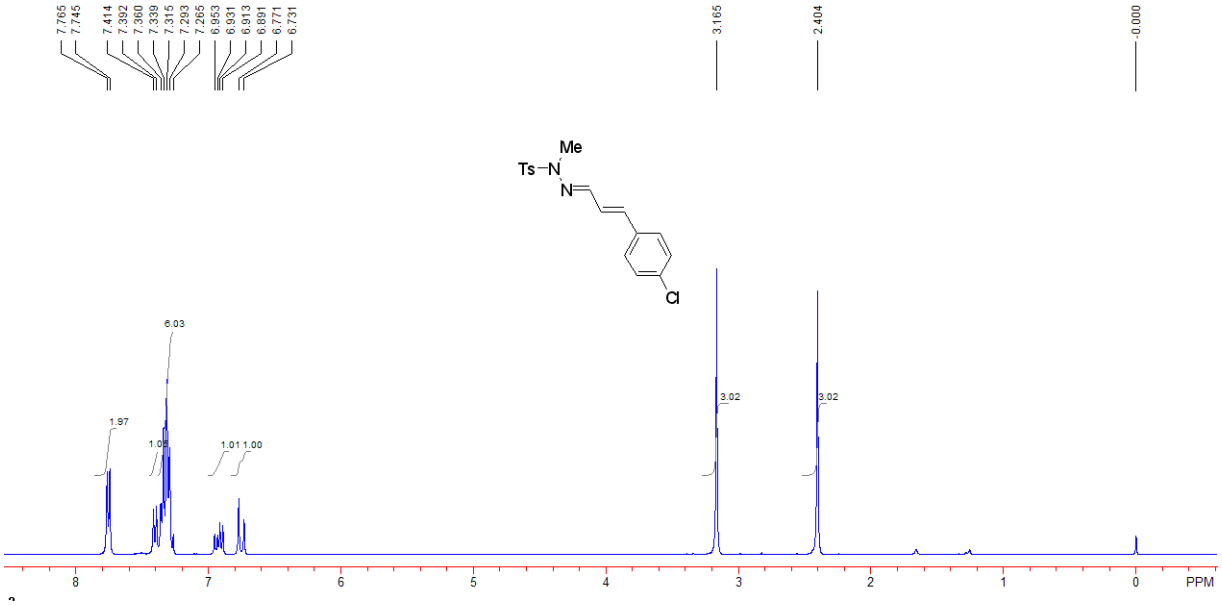
[5] D. A. Evans, M. M. Faul, M. T. Bilodeau, *J. Am. Chem. Soc.* **1994**, *116*, 2742–2753.

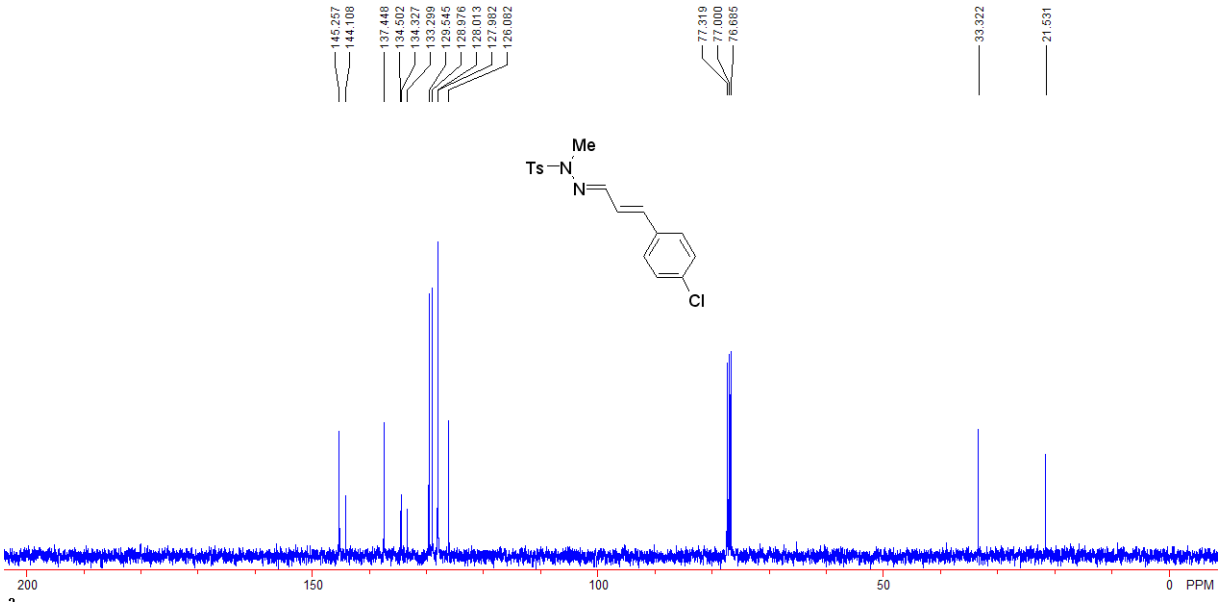
[6] J. Gullick, D. Ryan, P. McMorn, D. Bethell, F. King, F. Hancock, G. Hutching, *New J.*

Chem. **2004**, *28*, 1470–1478.

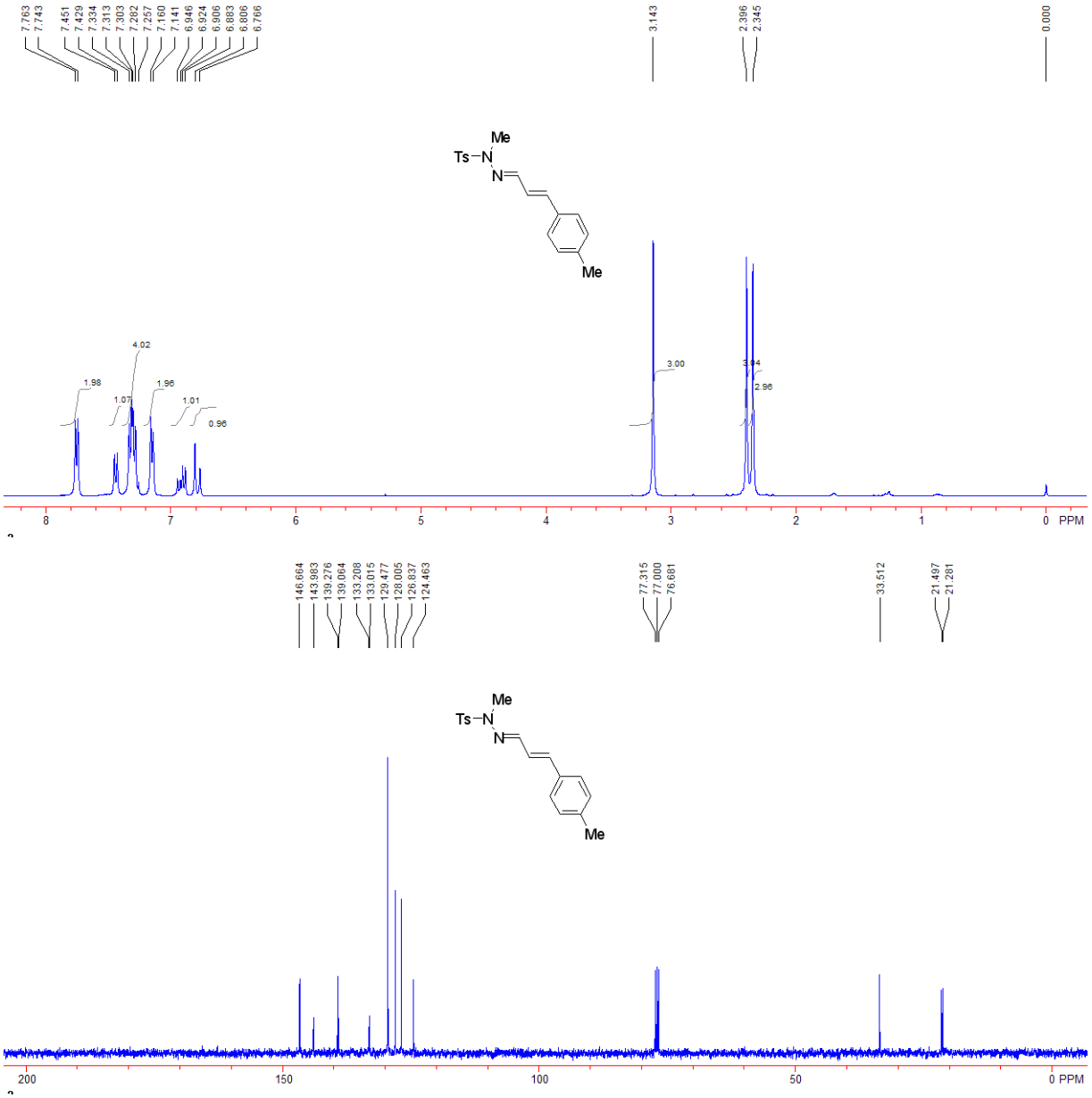
6. Spectroscopic Data of the Synthesized Compounds

Compound **S1b**: a white solid; mp. 185–187 ^{o}C; IR (neat) ν 2951, 2924, 1623, 1596, 1491, 1463, 1353, 1167, 1090, 1012, 973 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.40 (3H, s), 3.17 (3H, s), 6.75 (1H, d, *J* = 16.0 Hz), 6.92 (1H, dd, *J* = 8.8, 16.0 Hz), 7.29–7.36 (6H, m), 7.40 (1H, d, *J* = 8.8 Hz), 7.76 (2H, d, *J* = 8.0 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.5, 33.3, 126.1, 127.98, 128.01, 129.0, 129.5, 133.3, 134.3, 134.5, 137.4, 144.1, 145.3; MS (ESI) *m/z* 349.0 (M^++H); HRMS (ESI) calcd. for $C_{17}H_{18}N_2O_2SCl^{+1}$: 349.0772, Found: 349.0770.



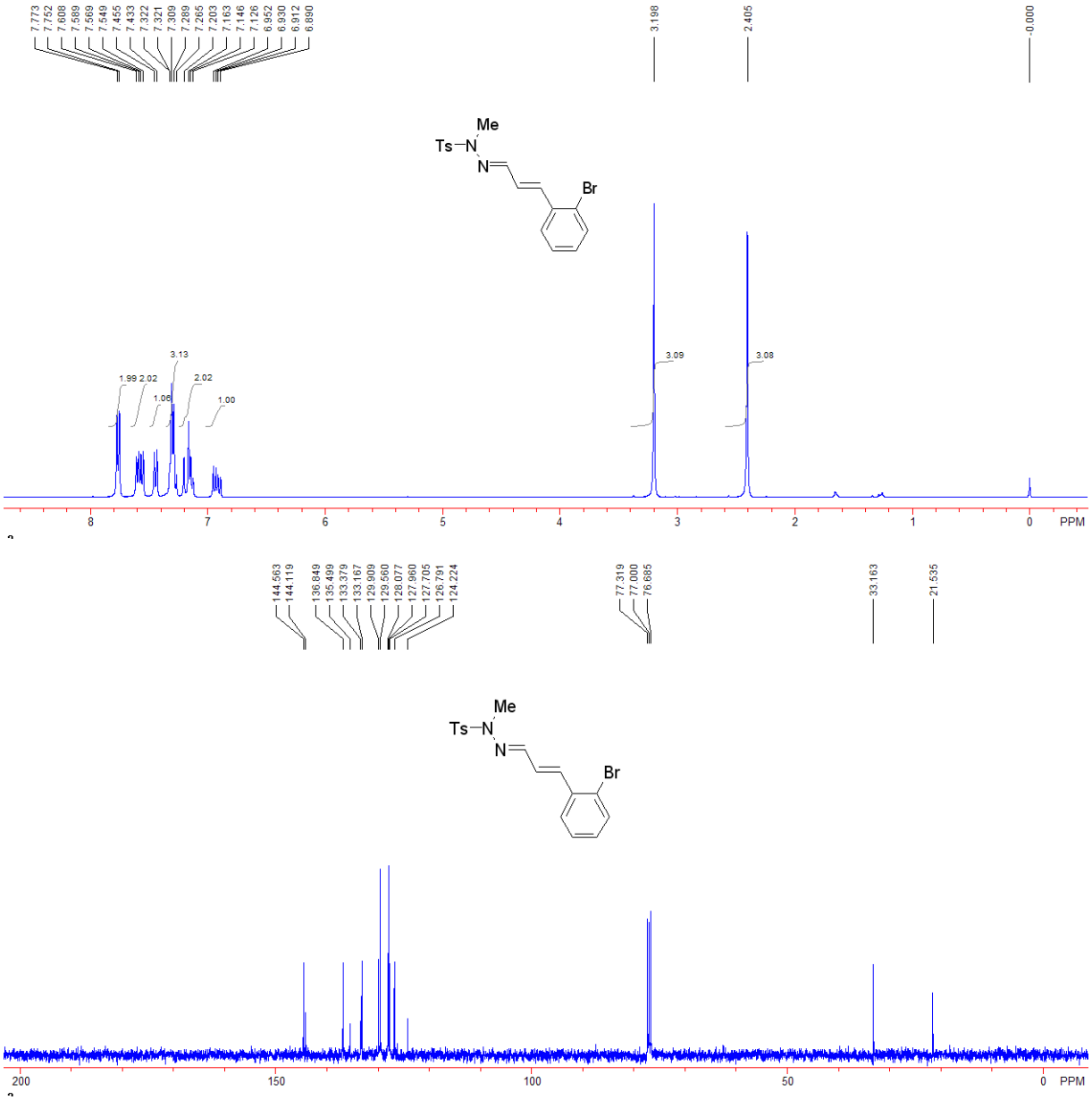


Compound **S1c**: a white solid; mp. 125–127 ^{o}C; IR (neat) ν 2923, 2868, 1629, 1597, 1511, 1461, 1352, 1206, 1166, 1087, 975 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.35 (3H, s), 2.40 (3H, s), 3.14 (3H, s), 6.79 (1H, d, *J* = 16.0 Hz), 6.91 (1H, dd, *J* = 8.8, 16.0 Hz), 7.15 (2H, d, *J* = 7.6 Hz), 7.26–7.33 (4H, m), 7.44 (1H, d, *J* = 8.8 Hz), 7.75 (2H, d, *J* = 8.0 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.3, 21.5, 33.5, 124.5, 126.8, 128.0, 129.5, 133.0, 133.2, 139.1, 139.3, 144.0, 146.7; MS (ESI) *m/z* 329.1 (M^++H); HRMS (ESI) calcd. for $C_{18}H_{21}N_2O_2S^{+1}$: 329.1318, Found: 329.1311.



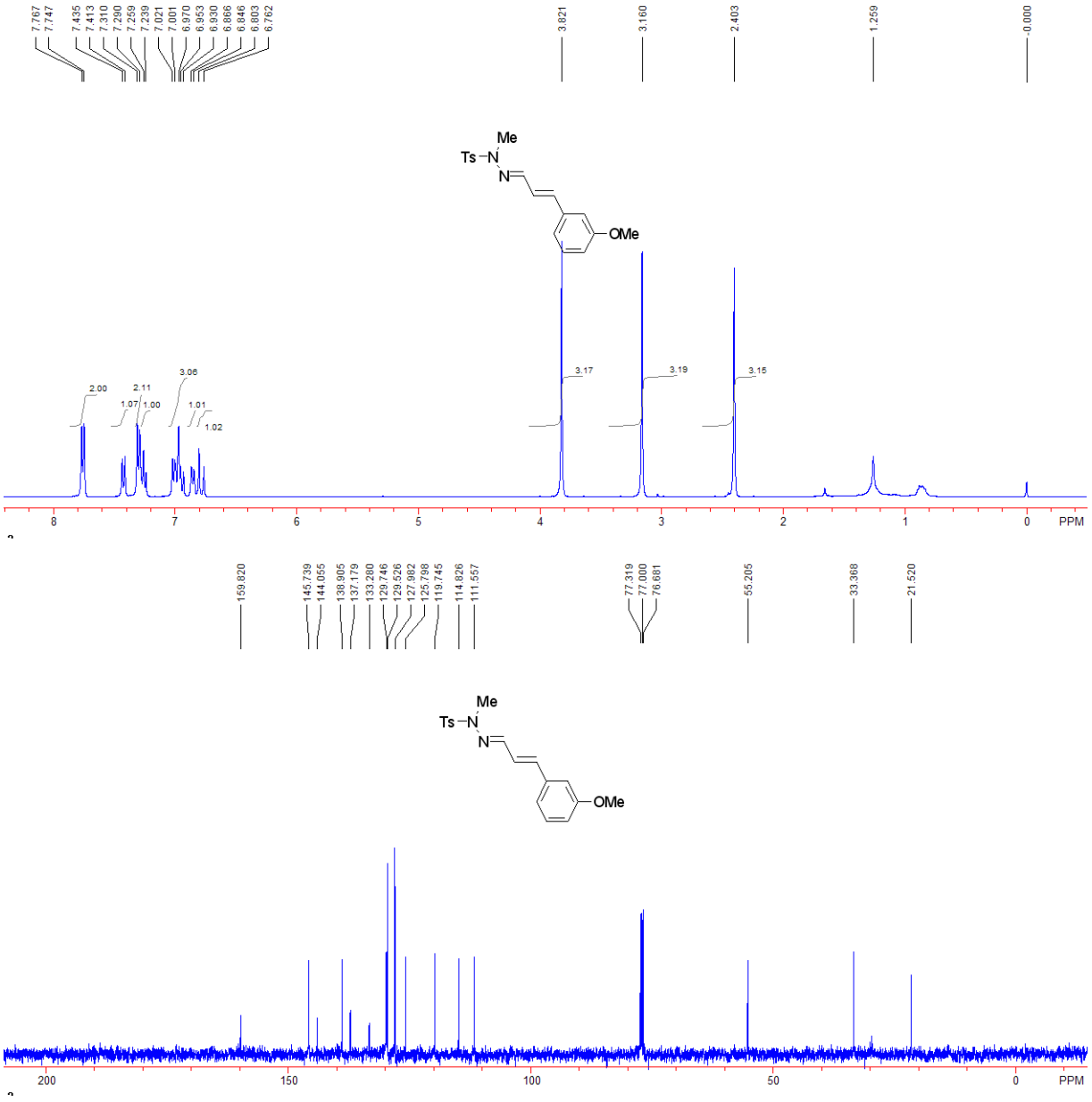
Compound **S1d**: a white solid; mp. 137–139 ^{o}C; IR (neat) ν 2954, 1596, 1465, 1354, 1206, 1168, 1089, 1023, 971 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.41 (3H, s), 3.20 (3H, s), 6.92 (1H, dd, *J* = 8.8, 16.0 Hz), 7.14 (1H, d, *J* = 8.0 Hz), 7.18 (1H, d, *J* = 16.0 Hz), 7.29–7.32 (3H, m), 7.44 (1H, d, *J* = 8.8 Hz), 7.58 (2H, dd, *J* = 8.0, 16.0 Hz), 7.76 (2H, d, *J* = 8.4 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.5, 33.2, 124.2, 126.8, 127.7, 128.0, 128.1, 129.6,

129.9, 133.2, 133.4, 135.5, 136.8, 144.1, 144.6; MS (ESI) *m/z* 395.0 (M^++H); HRMS (ESI) calcd. for $C_{17}H_{18}N_2O_2SBr^{+1}$: 393.0267, Found: 393.0250.

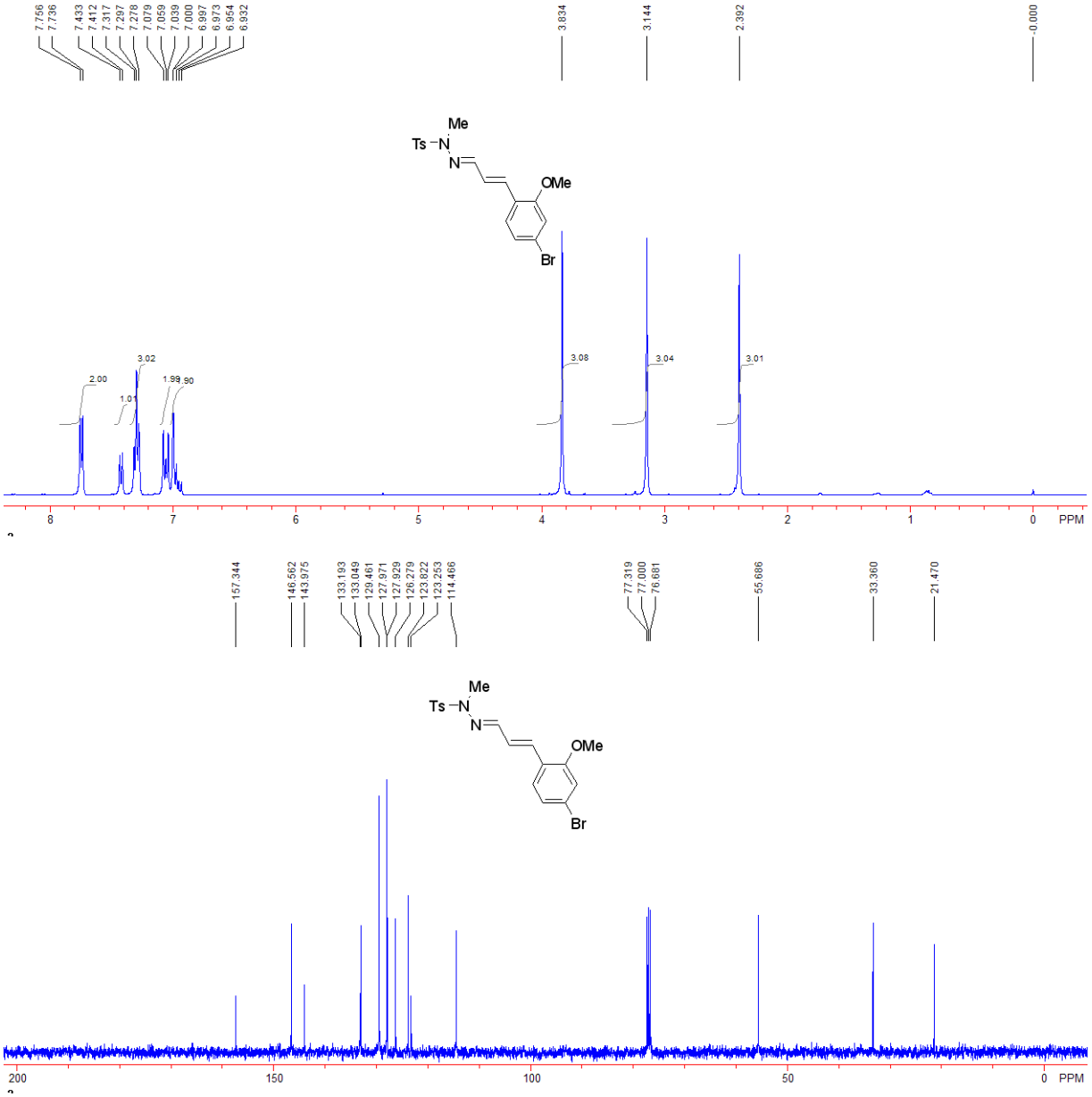


Compound **S1e**: a white solid; mp. 121–123 ^oC; IR (neat) ν 2956, 1628, 1597, 1489, 1464, 1352, 1291, 1273, 1159, 1089, 1043, 975 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.40 (3H, s), 3.16 (3H, s), 3.82 (3H, s), 6.78 (1H, d, *J* = 16.0 Hz), 6.86 (1H, d, *J* = 8.0 Hz),

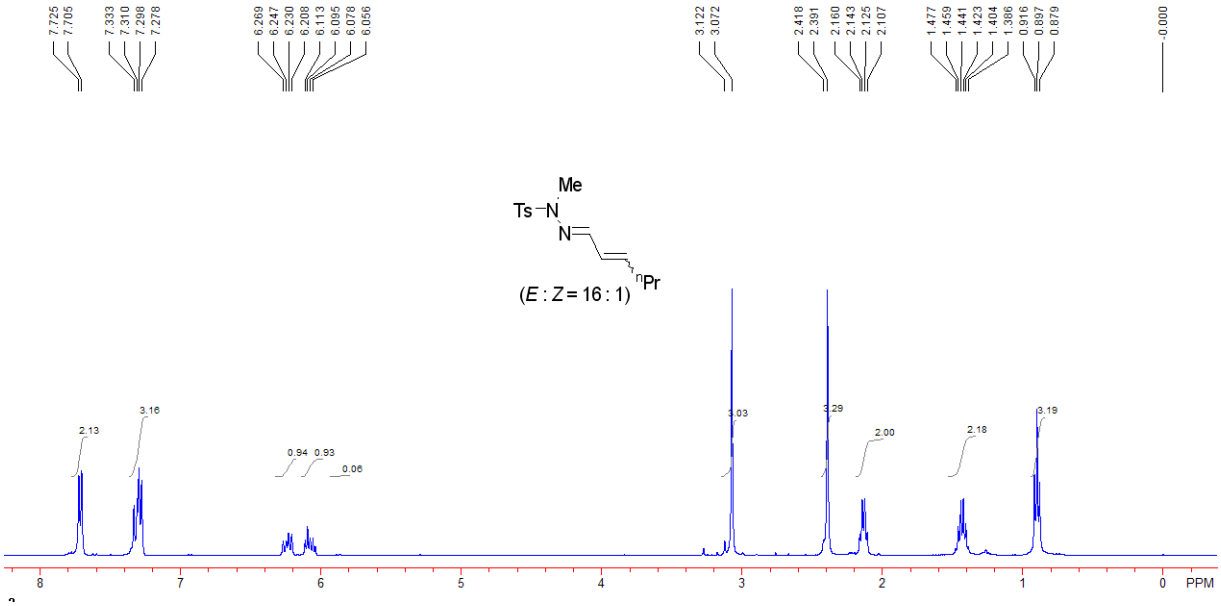
6.93–7.02 (3H, m), 7.25 (1H, d, *J* = 8.0 Hz), 7.30 (2H, d, *J* = 8.0 Hz), 7.42 (1H, d, *J* = 8.8 Hz), 7.76 (2H, d, *J* = 8.0 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.5, 33.4, 55.2, 111.6, 114.8, 119.7, 125.8, 128.0, 129.5, 129.7, 133.3, 137.2, 138.9, 144.1, 145.7, 159.8; MS (ESI) *m/z* 345.1 (M^++H); HRMS (ESI) calcd. for $C_{18}H_{21}N_2O_3S^{+1}$: 345.1267, Found: 345.1275.

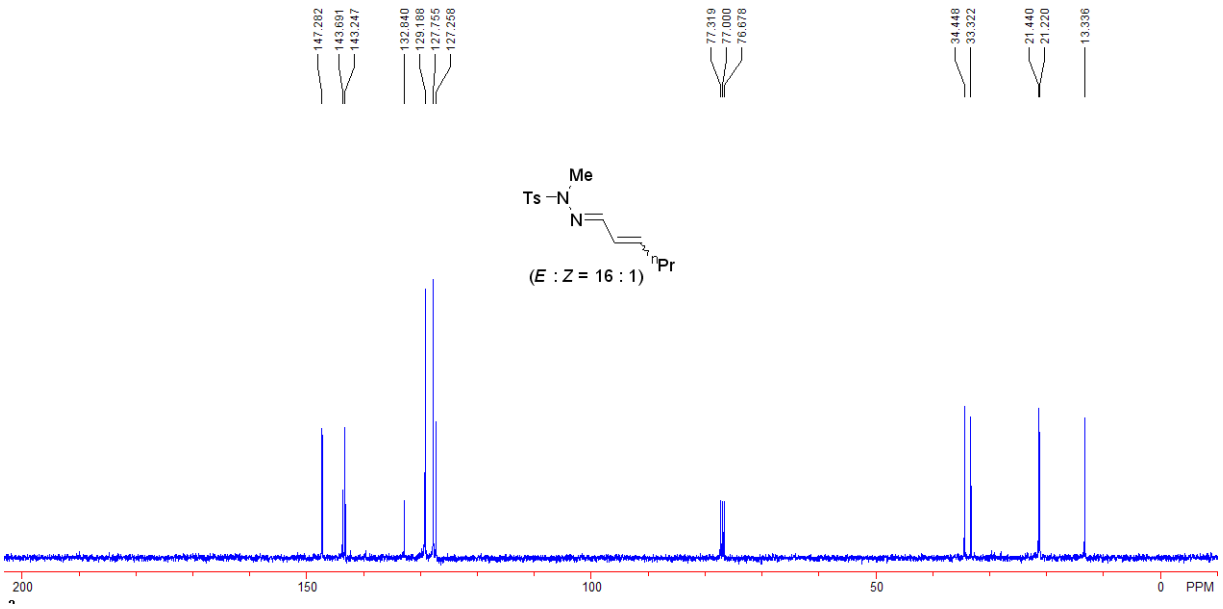


Compound **S1f**: a white solid; mp. 173–175 ^{o}C; IR (neat) ν 2924, 1587, 1485, 1462, 1400, 1353, 1246, 1167, 1088, 1027, 977 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.39 (3H, s), 3.14 (3H, s), 3.83 (3H, s), 6.96 (1H, dd, *J* = 8.0, 16.0 Hz), 7.00 (1H, s), 7.05 (1H, d, *J* = 8.0 Hz), 7.07 (1H, d, *J* = 8.0 Hz), 7.29 (2H, d, *J* = 8.0 Hz), 7.30 (1H, d, *J* = 8.0 Hz), 7.42 (1H, d, *J* = 8.4 Hz), 7.75 (2H, d, *J* = 8.0 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.5, 33.4, 55.7, 114.5, 123.3, 123.8, 126.3, 127.9, 128.0, 129.5, 133.0, 133.2, 144.0, 146.6, 157.3; MS (ESI) *m/z* 425.0 (M^{+}+H); HRMS (ESI) calcd. for $C_{18}H_{20}N_2O_3SBr^{+1}$: 423.0373, Found: 423.0360.

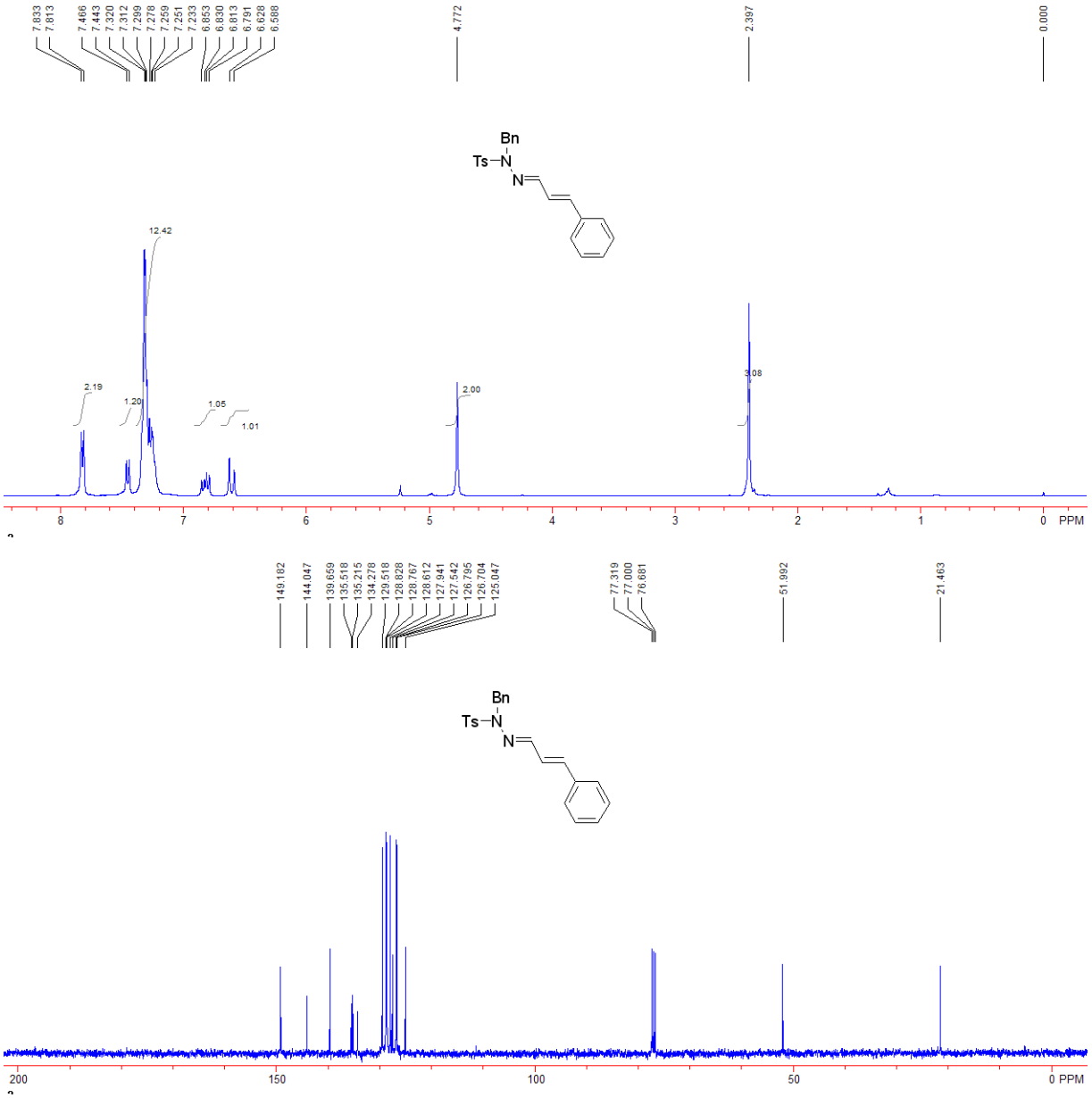


Compound **S1g**: a yellow oil; IR (neat) ν 2960, 1647, 1597, 1462, 1352, 1223, 1166, 1088, 977 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) (*E*-isomer) δ 0.90 (3H, t, *J* = 7.2 Hz), 1.39–1.48 (2H, m), 2.11–2.16 (2H, m), 2.39 (3H, s), 3.07 (3H, s), 6.06–6.11 (1H, m), 6.21–6.27 (1H, m), 7.28-7.33 (3H, m), 7.72 (2H, d, *J* = 8.0 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) (*E*-isomer) δ 13.3, 21.2, 21.4, 33.3, 34.4, 127.3, 127.8, 129.2, 132.8, 143.2, 143.7, 147.3; MS (EI) *m/z* 280 (M^+, 2.68), 155 (4.03), 125 (100.00), 83 (58.19), 81 (15.09); HRMS (EI) calcd. for $C_{14}H_{20}N_2O_2S^{+1}$: 280.1245, Found: 280.1244.



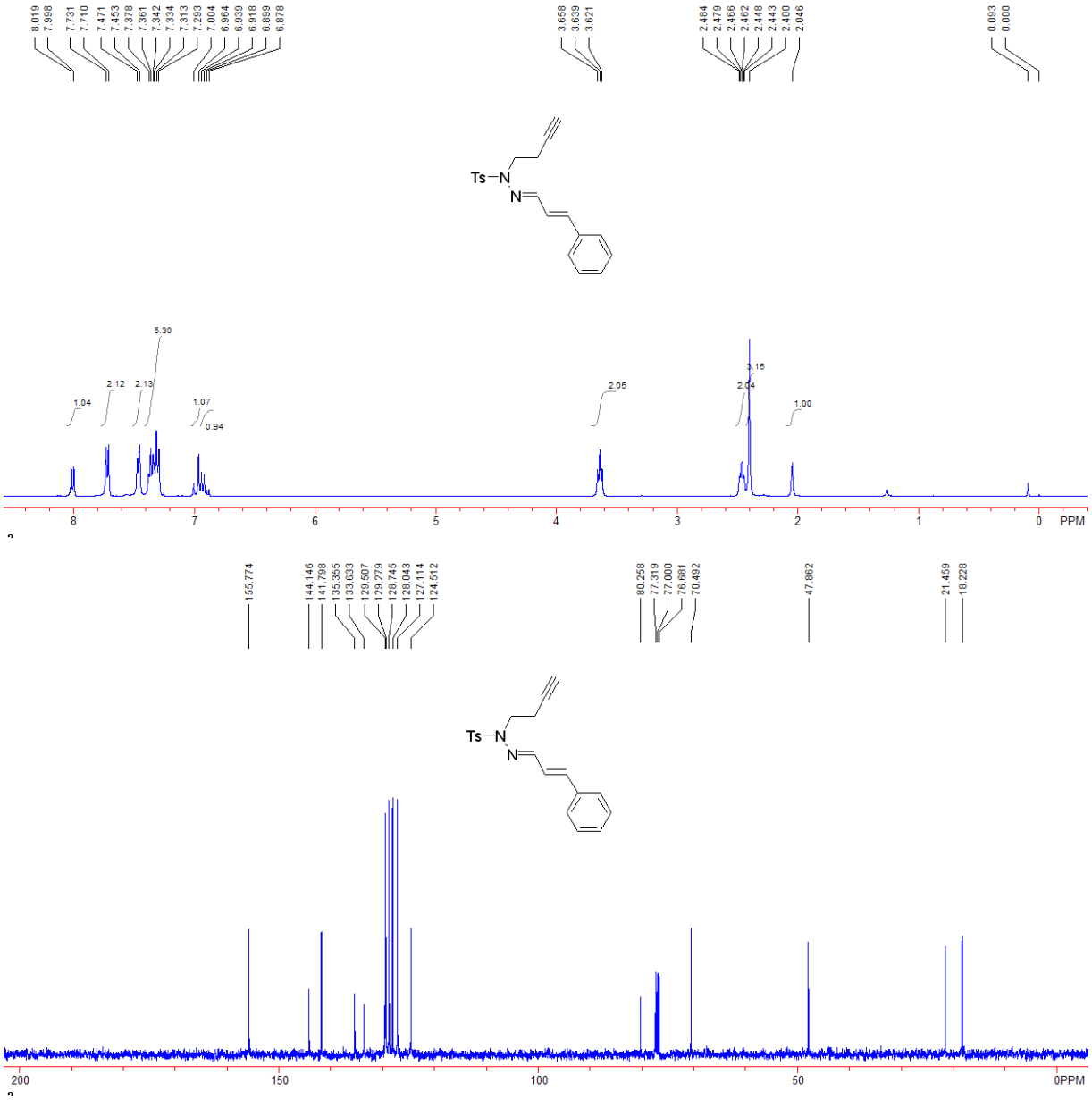


Compound **S1h**: a white solid; mp. 157–159 ^{o}C; IR (neat) ν 2957, 1598, 1494, 1452, 1354, 1166, 1089, 1046, 973 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.40 (3H, s), 4.77 (2H, s), 6.61 (1H, d, *J* = 16.0 Hz), 6.82 (1H, dd, *J* = 8.8, 16.0 Hz), 7.23–7.32 (12H, m), 7.45 (1H, d, *J* = 8.8 Hz), 7.82 (2H, d, *J* = 8.0 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.5, 52.0, 125.0, 126.7, 126.8, 127.5, 127.9, 128.6, 128.77, 128.83, 129.5, 134.3, 135.2, 135.5, 139.7, 144.0, 149.2; MS (ESI) *m/z* 391.0 (M^{+}+H); HRMS (ESI) calcd. for $C_{23}H_{23}N_2O_2S^{+1}$: 391.1475, Found: 394.1476.



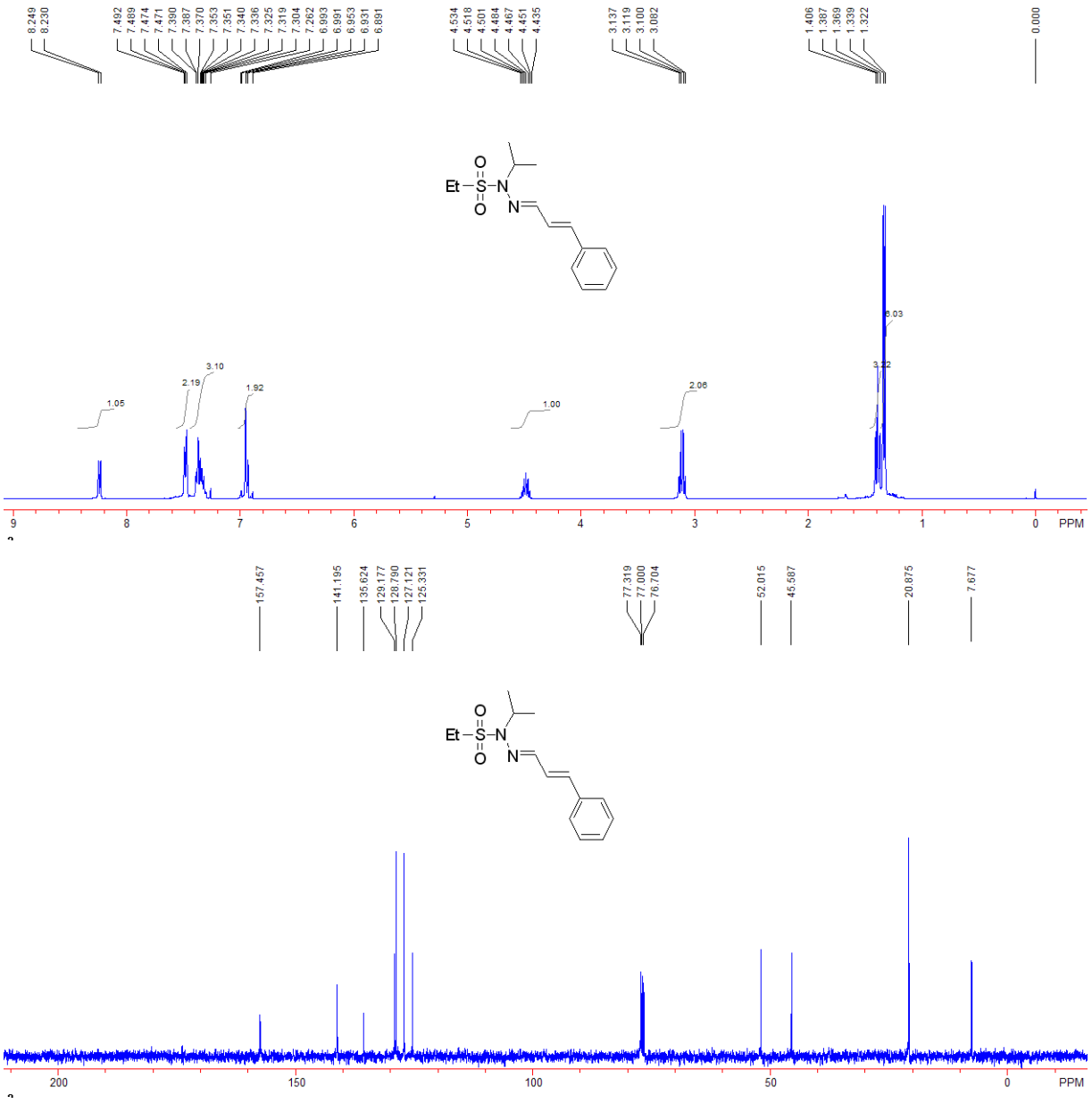
Compound **S1j**: a yellow oil; IR (neat) ν 3291, 2924, 1628, 1597, 1493, 1449, 1351, 1164, 1089, 973 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.05 (1H, t, *J* = 2.0 Hz), 2.40 (3H, s), 2.46 (2H, td, *J* = 2.0, 7.6 Hz), 3.64 (2H, t, *J* = 7.6 Hz), 6.91 (1H, dd, *J* = 8.4, 16.0 Hz), 6.98 (1H, d, *J* = 16.0 Hz), 7.29–7.38 (5H, m), 7.46 (2H, d, *J* = 7.2 Hz), 7.72 (2H, d, *J* = 8.4 Hz),

8.01 (1H, d, *J* = 8.4 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 18.2, 21.5, 47.9, 70.5, 80.3, 124.5, 127.1, 128.0, 128.7, 129.3, 129.5, 133.6, 135.4, 141.8, 144.1, 155.8; MS (ESI) *m/z* 353.1 (M^++H); HRMS (ESI) calcd. for $C_{20}H_{21}N_2O_2S^{+1}$:353.1318, Found: 353.1318.



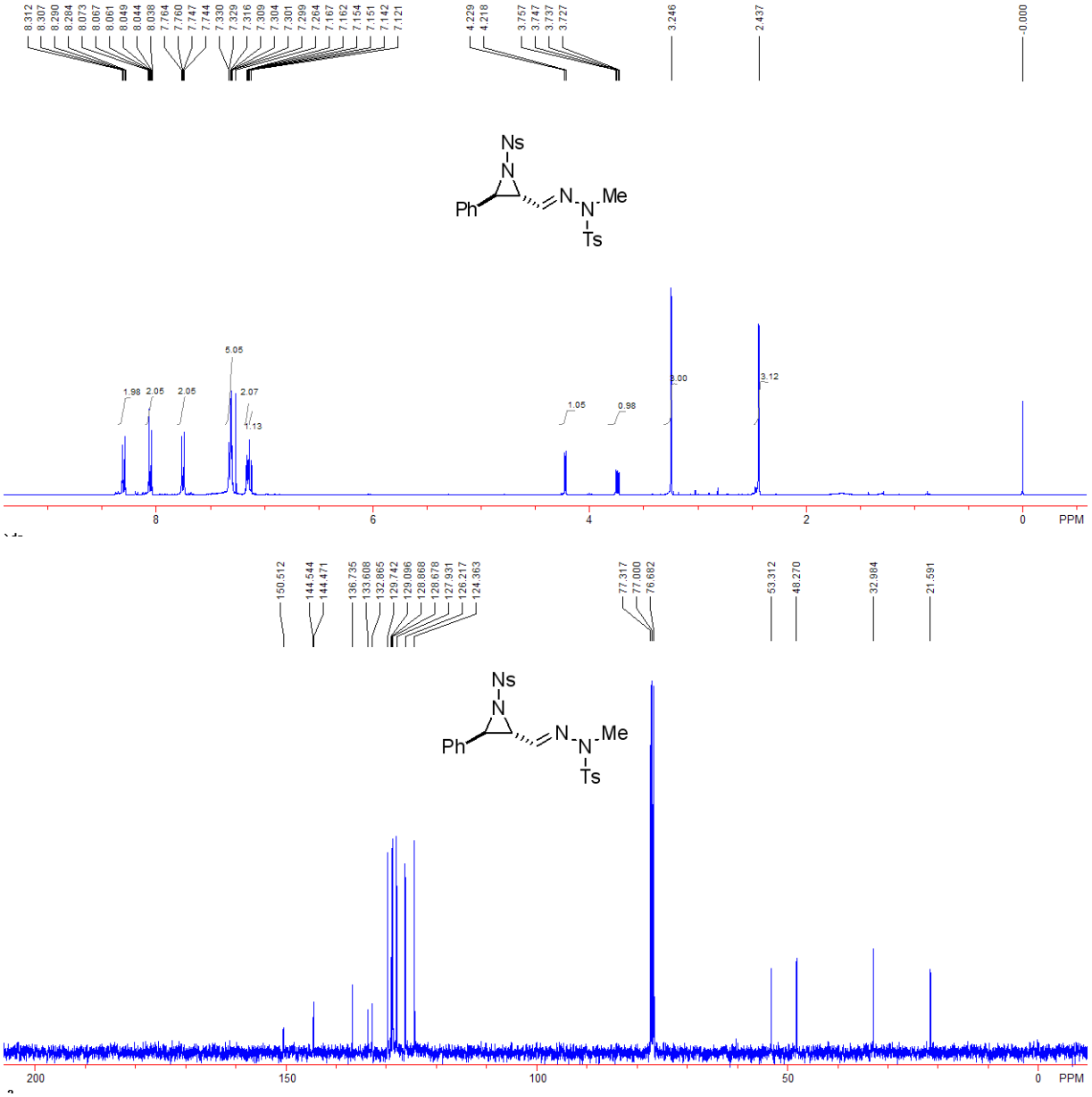
Compound **S1k**: a colorless oil; IR (neat) ν 2977, 2938, 1677, 1627, 1582, 1493, 1450, 1332, 1149, 1131, 1032 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.33 (6H, d, *J* = 6.8 Hz), 1.39

(3H, t, *J* = 7.6 Hz), 3.11 (2H, q, *J* = 7.6 Hz), 4.44–4.53 (1H, m), 6.89–6.99 (2H, m), 7.30–7.39 (3H, m), 7.47–7.49 (2H, m), 8.24 (1H, d, *J* = 7.6 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 7.7, 20.9, 45.6, 52.0, 125.3, 127.1, 128.8, 129.2, 135.6, 141.2, 157.5; MS (ESI) *m/z* 281.1 (M^++H); HRMS (ESI) calcd. for $C_{14}H_{20}N_2O_2S^{+1}$:280.1245, Found: 280.1236.



Compound **1a**: Prepared according to the general method (2.0 mmol PhI=NNs) and the title compound was isolated as a white solid (603 mg, 59% yield); a white solid; mp. 163–165 ^{o}C;

IR (neat) ν 2925, 1533, 1458, 1351, 1309, 1167, 1089, 939 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.44 (3H, s), 3.25 (3H, s), 3.74 (1H, dd, *J* = 4.0, 8.0 Hz), 4.22 (1H, d, *J* = 4.0 Hz), 7.13 (1H, d, *J* = 8.0 Hz), 7.15–7.17 (2H, m), 7.30–7.33 (5H, m), 7.74–7.46 (2H, m), 8.04–8.07 (2H, m), 8.28–8.31(2H, m); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.6, 33.0, 48.3, 53.3, 124.4, 126.2, 127.9, 128.7, 128.9, 129.1, 129.7, 132.9, 133.6, 136.7, 144.47, 144.54, 150.5; MS (ESI) *m/z* 515.1 (M^{+}+H); HRMS (ESI) calcd. for $C_{23}H_{23}N_4O_6S_2^{+1}$: 515.1054, Found: 515.1053.

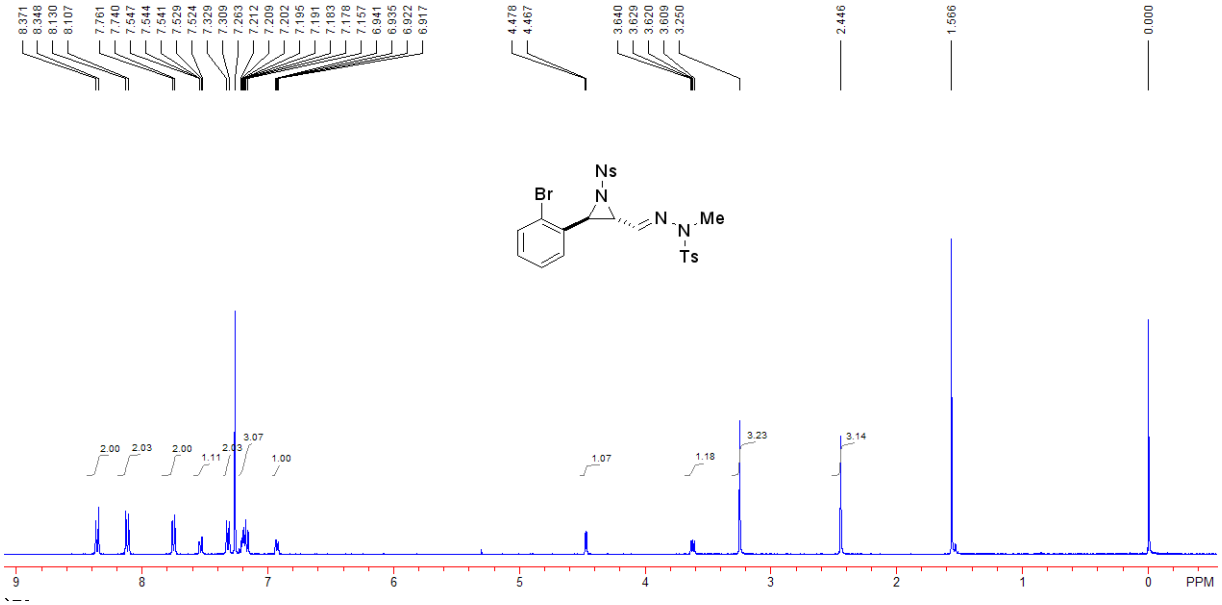


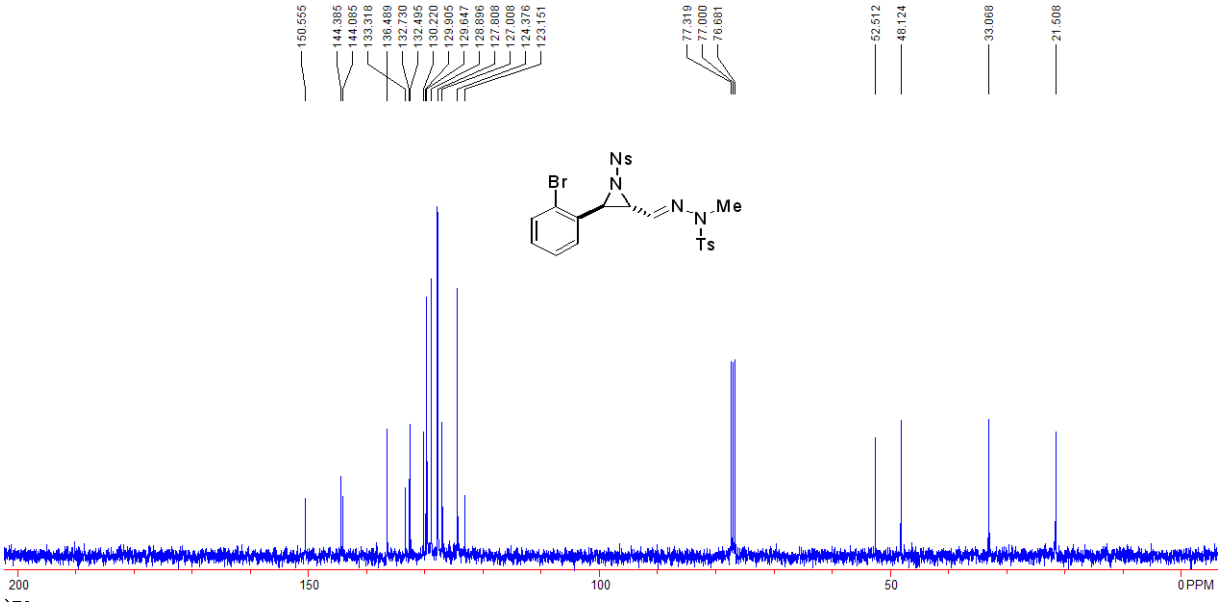
Compound **1b** (insoluble in various solvents, such as $CHCl_3$, CH_2Cl_2, acetone, methanol, and DMSO): Prepared according to the general method (1.5 mmol PhI=NNs) and the title compound was isolated as a white solid (250 mg, 30% yield); mp. 168–170 ^oC; IR (neat) ν 2925, 1598, 1532, 1494, 1350, 1310, 1166, 1089, 1015, 924 cm^{-1}; MS (ESI) *m/z* 570.8 (M^++Na); HRMS (ESI) calcd. for $C_{23}H_{21}N_4O_6S_2ClNa^{+1}$: 571.0483, Found: 571.0503.

Compound **1c** (insoluble in various solvents, such as $CHCl_3$, CH_2Cl_2, acetone, methanol, and DMSO): Prepared according to the general method (1.5 mmol PhI=NNs) and the title compound was isolated as a white solid (303 mg, 38% yield); mp. 170–172 ^oC; IR (neat) ν 2956, 1598, 1531, 1349, 1309, 1164, 1088, 921 cm^{-1}; MS (ESI) *m/z* 551.0 (M^++Na); HRMS (ESI) calcd. for $C_{24}H_{24}N_4O_6S_2Na^{+1}$: 551.1030, Found: 551.1040.

Compound **1d**: Prepared according to the general method (1.5 mmol PhI=NNs) and the title compound was isolated as a white solid (304 mg, 34% yield); mp. 192–194 ^oC; IR (neat) ν 2924, 2852, 1607, 1598, 1532, 1464, 1350, 1310, 1167, 1089, 934 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.45 (3H, s), 3.25 (3H, s), 3.62 (1H, dd, *J* = 4.4, 8.0 Hz), 4.47 (1H, d, *J* = 4.4 Hz), 6.93 (1H, dd, *J* = 3.0, 7.2 Hz), 7.16–7.21 (3H, m), 7.32 (2H, d, *J* = 8.0 Hz), 7.52–7.55 (1H, m), 7.75 (2H, d, *J* = 8.0 Hz), 8.12 (2H, d, *J* = 9.2 Hz), 8.36 (2H, d, *J* = 9.2 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.5, 33.1, 48.1, 52.5, 123.2, 124.4, 127.0, 127.8, 128.9, 129.6, 129.9, 130.2, 132.5, 132.7, 133.3, 136.5, 144.1, 144.4, 150.6; MS (ESI) *m/z* 614.8 (M^++Na);

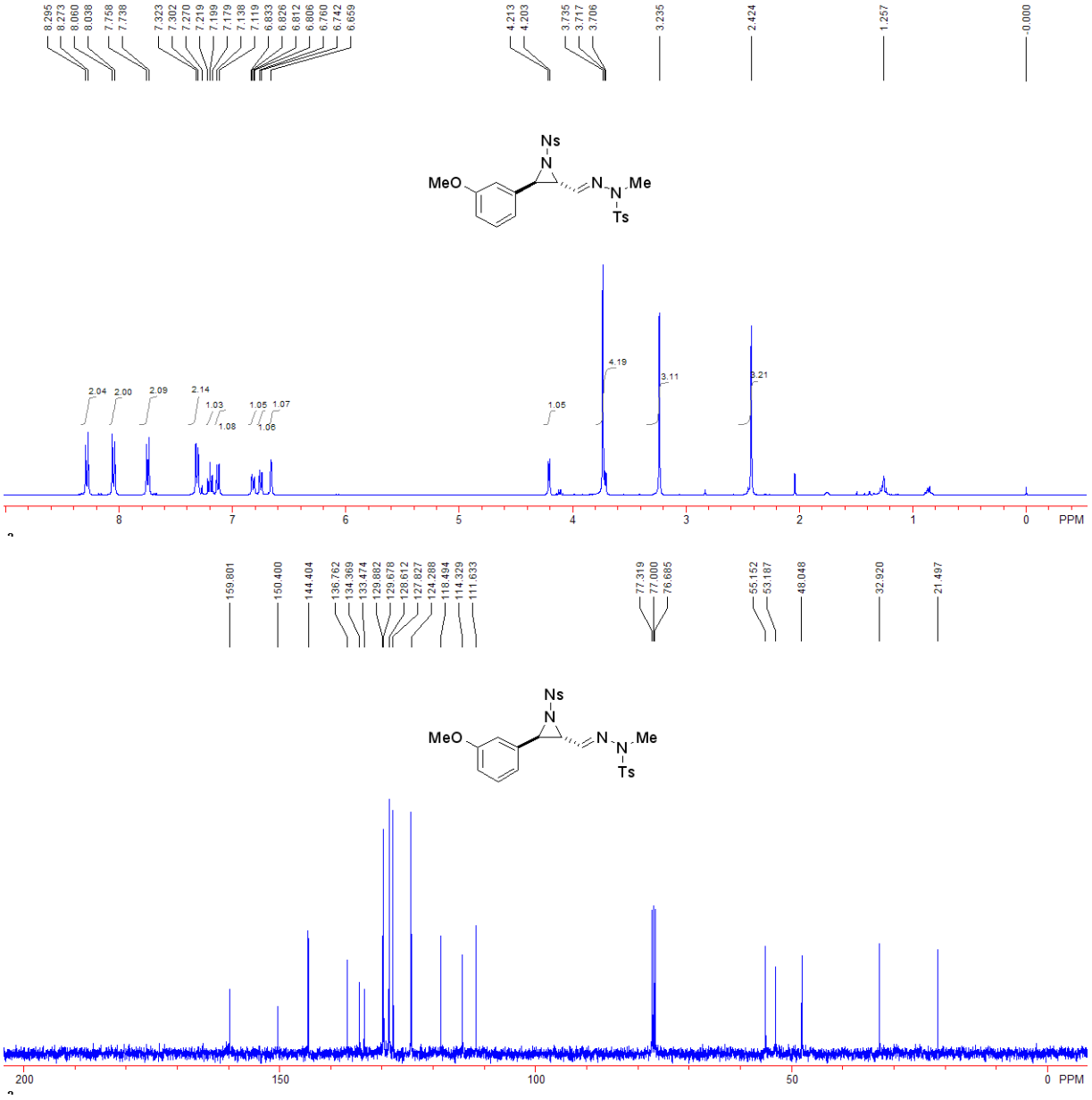
HRMS (ESI) calcd. for $C_{23}H_{21}N_4O_6S_2BrNa^{+1}$: 614.9978, Found: 614.9990.



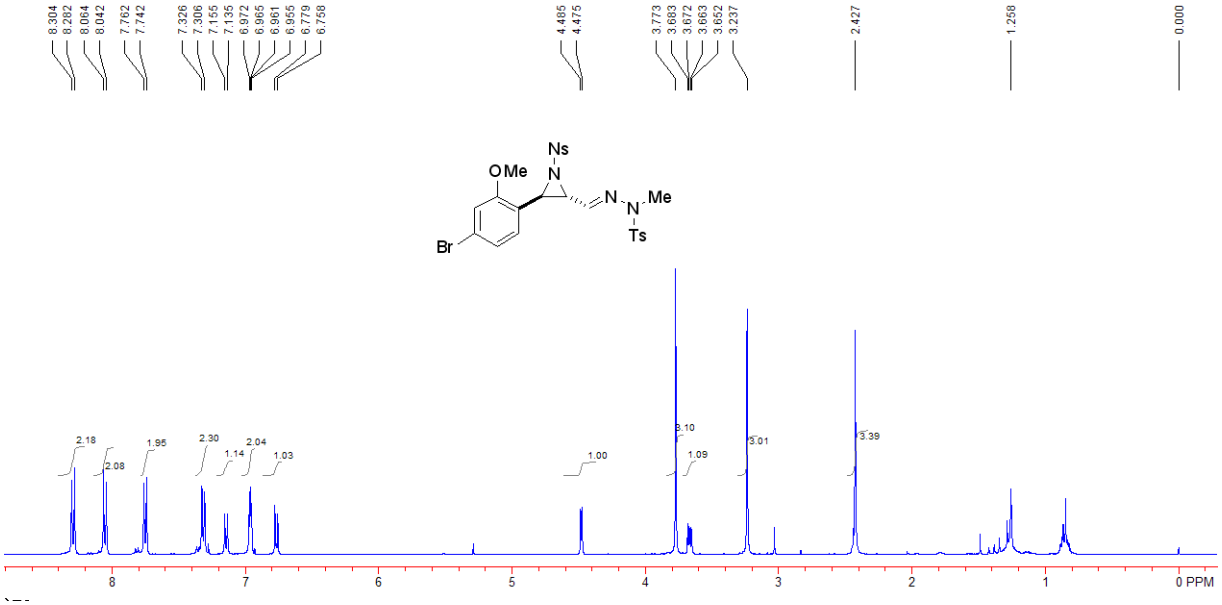


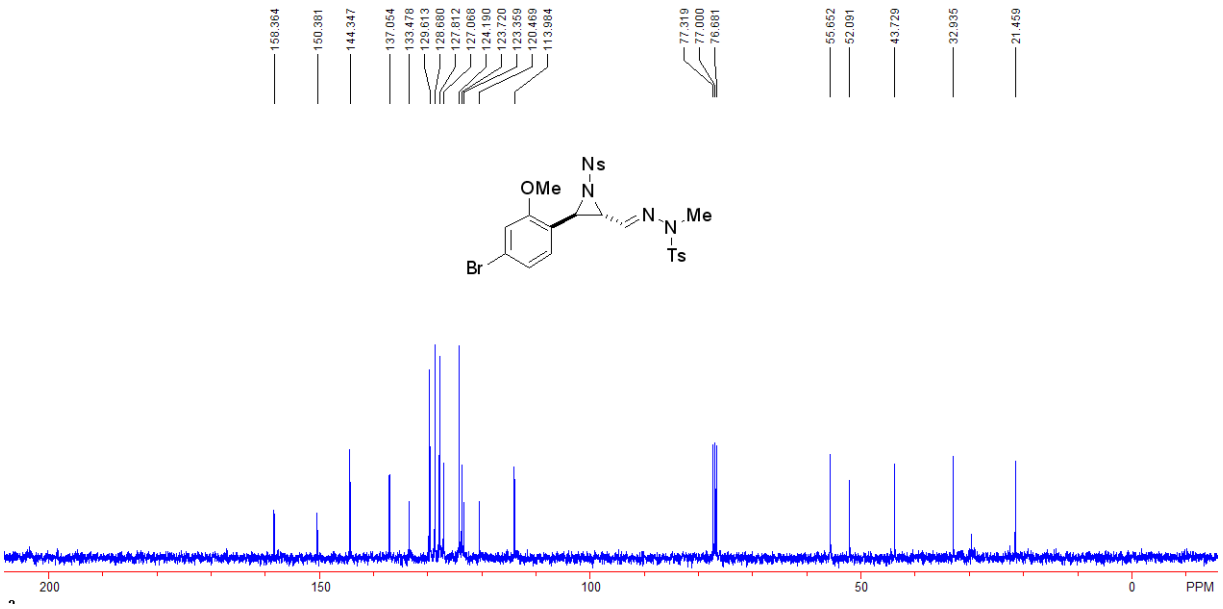
Compound **1e**: Prepared according to the general method (1.5 mmol PhI=NNs) and the title compound was isolated as a white solid (281 mg, 34% yield); mp. 144–146 ^{o}C; IR (neat) ν 2926, 1604, 1532, 1494, 1465, 1350, 1310, 1166, 1089, 1044, 920 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.42 (3H, s), 3.24 (3H, s), 3.72 (1H, dd, *J* = 4.0, 8.0 Hz), 3.74 (3H, s), 4.21

(1H, d, *J* = 4.0 Hz), 6.66 (1H, s), 6.75 (1H, d, *J* = 7.2 Hz), 6.82 (1H, dd, *J* = 2.4, 8.0 Hz), 7.13 (1H, d, *J* = 7.6 Hz), 7.20 (1H, t, *J* = 8.0 Hz), 7.31 (2H, d, *J* = 8.0 Hz), 7.75 (2H, d, *J* = 8.0 Hz), 8.05 (2H, d, *J* = 8.8 Hz), 8.28 (2H, d, *J* = 8.8 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.5, 32.9, 48.0, 53.2, 55.2, 111.6, 114.3, 118.5, 124.3, 127.8, 128.6, 129.7, 129.9, 133.5, 134.4, 136.8, 144.4, 150.4, 159.8; MS (ESI) *m/z* 567.0 (M^++Na); HRMS (ESI) calcd. for $C_{24}H_{24}N_4O_7S_2Na^{+1}$: 567.0979, Found: 567.0967.

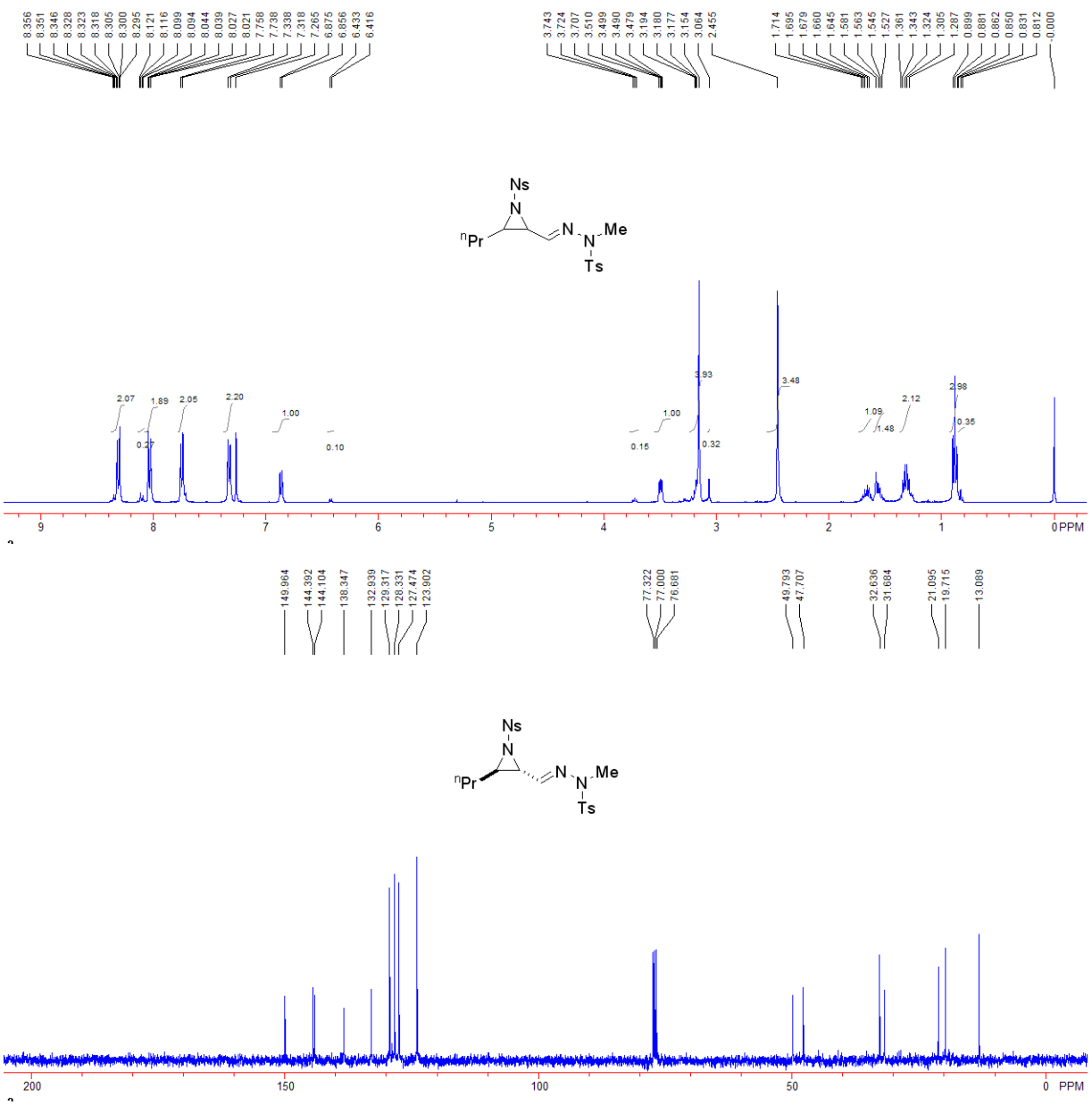


Compound **1f**: Prepared according to the general method (1.0 mmol PhI=NNs) and the title compound was isolated as a yellow oil (186 mg, 30% yield); IR (neat) ν 2954, 2923, 2852, 1733, 1595, 1531, 1491, 1462, 1400, 1349, 1308, 1251, 1164, 1088, 1024 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.43 (3H, s), 3.24 (3H, s), 3.67 (1H, dd, *J* = 4.0, 8.0 Hz), 3.77 (3H, s), 4.48 (1H, d, *J* = 4.0 Hz), 6.77 (1H, d, *J* = 8.4 Hz), 6.96–6.97 (2H, m), 7.15 (1H, d, *J* = 8.0 Hz), 7.32 (2H, d, *J* = 8.0 Hz), 7.75 (2H, d, *J* = 8.0 Hz), 8.05 (2H, d, *J* = 8.8 Hz), 8.29 (2H, d, *J* = 8.8 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.5, 32.9, 43.7, 52.1, 55.7, 114.0, 120.5, 123.4, 123.7, 124.2, 127.1, 127.8, 128.7, 129.6, 133.5, 137.1, 144.3, 150.4, 158.4; MS (ESI) *m/z* 644.9 (M^{+}+Na); HRMS (ESI) calcd. for $C_{24}H_{23}N_4O_7S_2BrNa^{+1}$: 645.0084, Found: 645.0101.



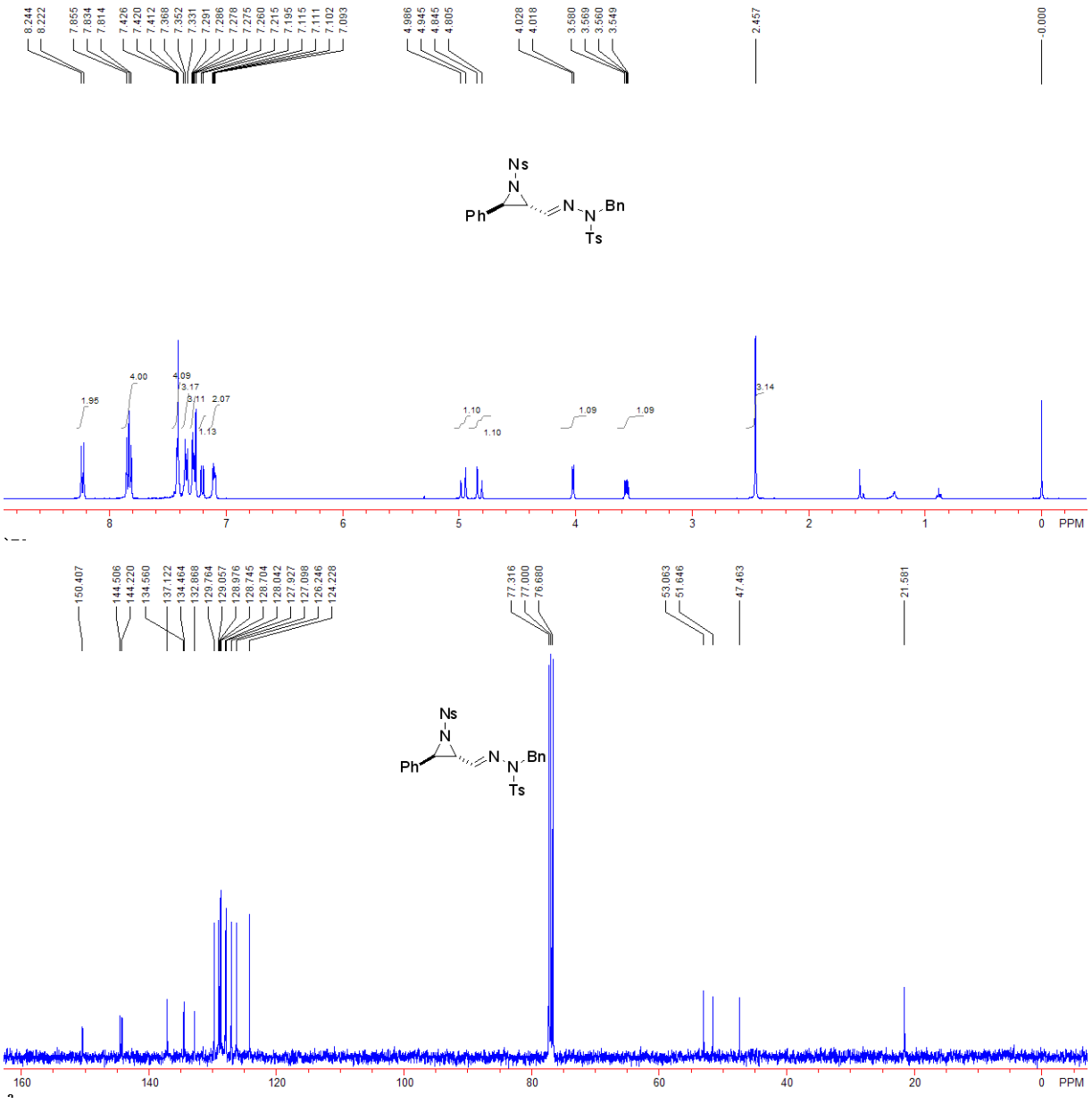


Compound **1g** (*trans*/*cis*-isomer = 10/1): Prepared according to the general method (2.0 mmol PhI=NNs) and the title compound was isolated as a yellow oil (447 mg, 47% yield); IR (neat) ν 2960, 2927, 1597, 1530, 1463, 1349, 1306, 1267, 1219, 1162, 1088, 1013 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) (*trans*-isomer) δ 0.88 (3H, t, *J* = 7.2 Hz), 1.29–1.36 (2H, m), 1.53–1.58 (1H, m), 1.65–1.71 (1H, m), 2.46 (3H, s), 3.15 (3H, s), 3.15–3.19 (1H, m), 3.49 (1H, dd, *J* = 4.4, 8.0 Hz), 6.87 (1H, d, *J* = 7.6 Hz), 7.33 (2H, d, *J* = 8.0 Hz), 7.75 (2H, d, *J* = 8.0), 8.02–8.04 (2H, m), 8.30–8.33 (2H, m); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 13.1, 19.7, 21.1, 31.7, 32.6, 47.7, 49.8, 123.9, 127.5, 128.3, 129.3, 132.9, 138.3, 144.1, 144.4, 150.0; MS (ESI) *m/z* 481.0 (M^{+}+H); HRMS (ESI) calcd. for $C_{20}H_{24}N_4O_6S_2Na^{+1}$: 503.1030, Found: 503.1044.



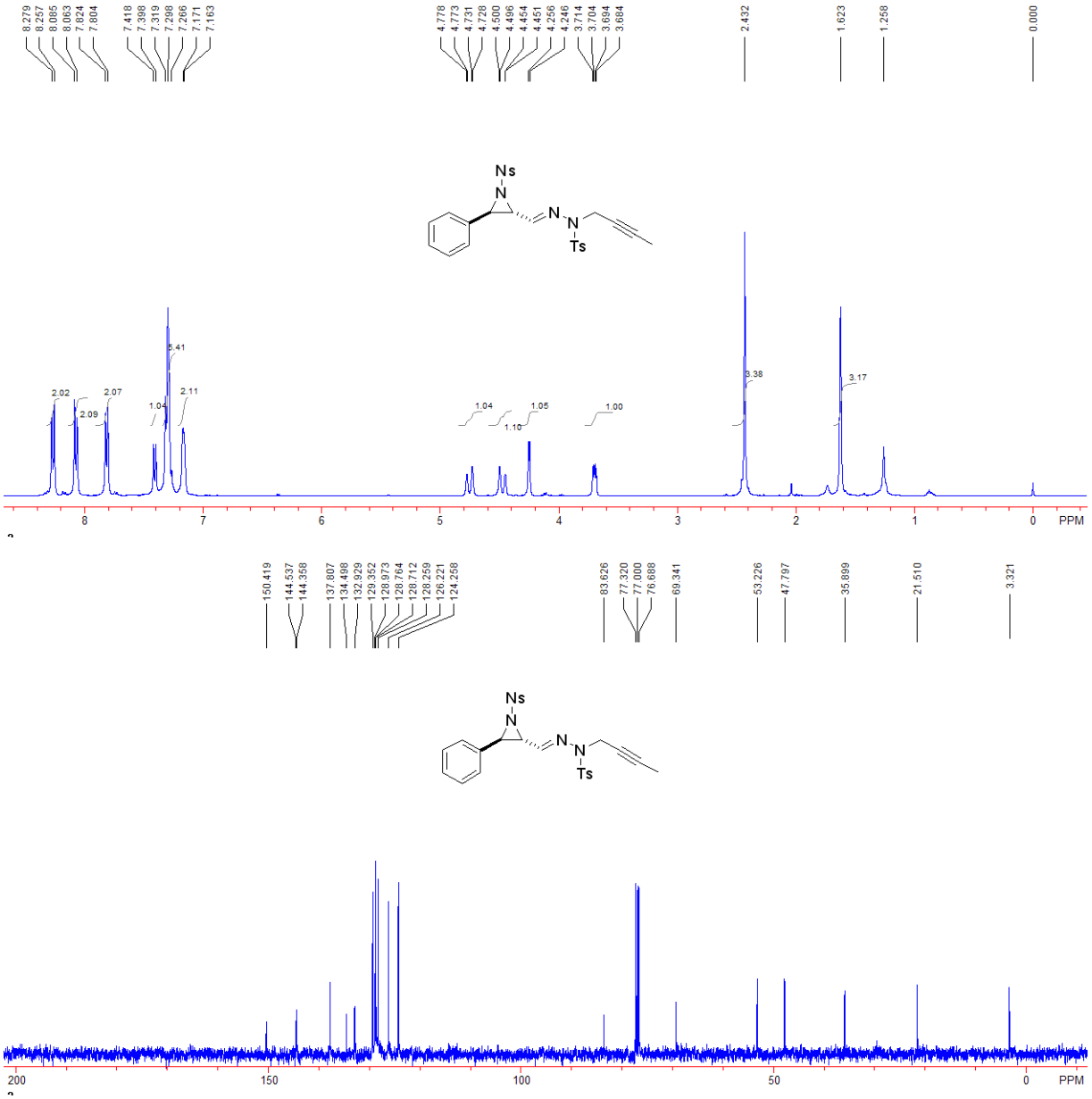
Compound **1h**: Prepared according to the general method (1.5 mmol PhI=NNs) and the title compound was isolated as a white solid (331 mg, 37% yield); mp. 72–75 ^{o}C; IR (neat): 2959, 2924, 2853, 1607, 1530, 1495, 1455, 1349, 1308, 1261, 1163, 1089, 1026, 1015 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.46 (3H, s), 3.56 (1H, dd, *J* = 4.0, 8.0 Hz), 4.02 (1H, d, *J* = 4.0 Hz), 4.83 (1H, d, *J* = 16.4 Hz), 4.97 (1H, d, *J* = 16.4 Hz), 7.09–7.12 (2H, m), 7.21 (1H, d, *J* = 8.0 Hz), 7.28–7.29 (3H, m), 7.33–7.37 (3H, m), 7.41–7.43 (4H, m), 7.81–7.86 (4H, m),

8.23 (2H, d, *J* = 8.8 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.6, 47.5, 51.6, 53.1, 124.2, 126.2, 127.1, 127.9, 128.0, 128.70, 128.74, 129.0, 129.8, 132.9, 134.5, 134.6, 137.1, 144.2, 144.5, 150.4; MS (ESI) m/z 613.0 (M^++Na); HRMS (ESI) calcd. for $C_{29}H_{27}N_4O_6S_2^{+1}$: 591.1367, Found: 591.1367.

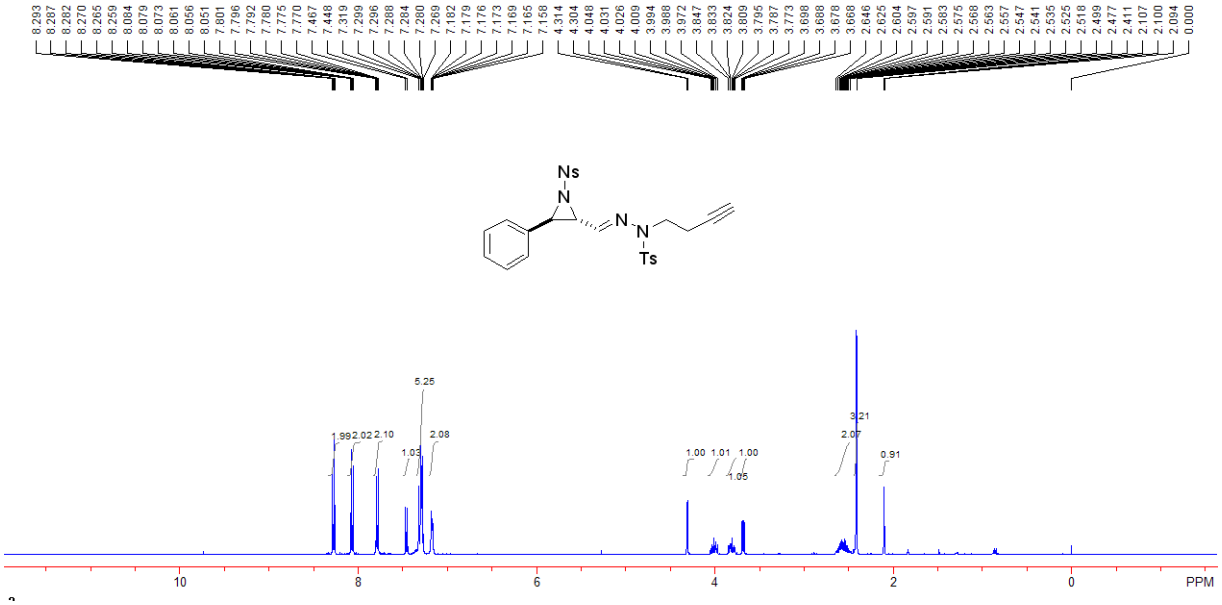


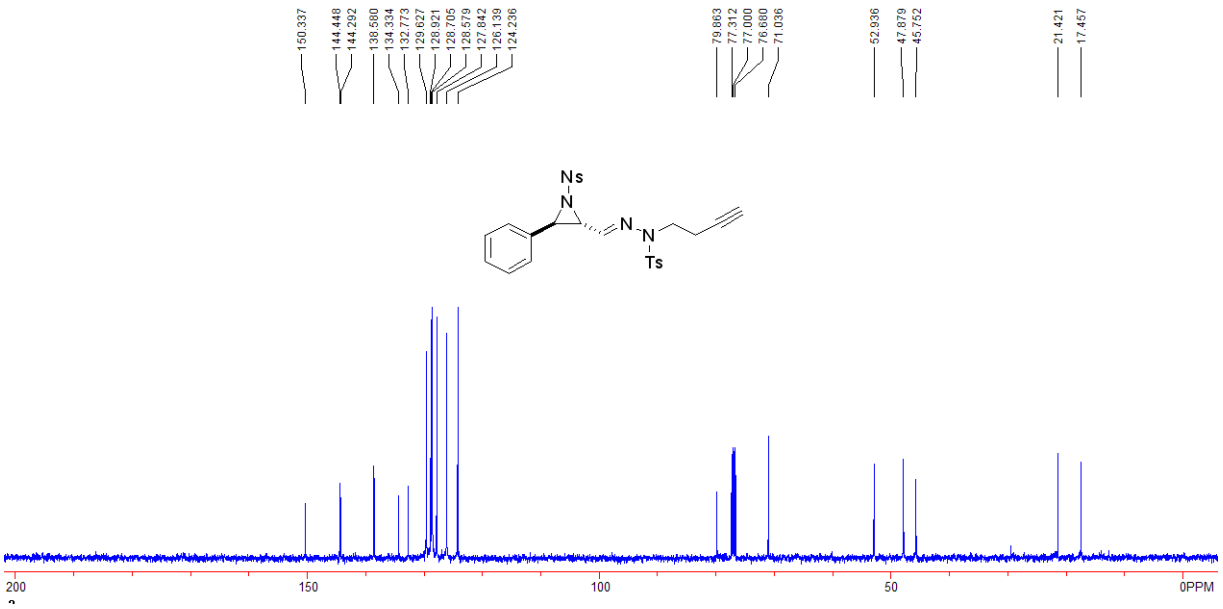
Compound **1i**: Prepared according to the general method (1.0 mmol PhI=NNs) and the title

compound was isolated as a white solid (221 mg, 40% yield); mp. 177–179 ^{o}C; IR (neat) ν 2924, 1598, 1532, 1350, 1309, 1166, 1090, 1042, 903 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.62 (3H, s), 2.43 (3H, s), 3.70 (1H, dd, *J* = 4.0, 8.0 Hz), 4.26 (1H, d, *J* = 4.0 Hz), 4.47 (1H, dd, *J* = 2.0, 18.4 Hz), 4.75 (1H, dd, *J* = 2.0, 18.4 Hz), 7.16–7.17 (2H, m), 7.27–7.32 (5H, m), 7.41 (1H, d, *J* = 8.0 Hz), 7.81 (2H, d, *J* = 8.0 Hz), 8.07 (2H, d, *J* = 8.8 Hz), 8.27 (2H, d, *J* = 8.8 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 3.32, 21.5, 35.9, 47.8, 53.2, 69.3, 83.6, 124.3, 126.2, 128.3, 128.7, 128.8, 129.0, 129.4, 132.9, 134.5, 137.8, 144.4, 144.5, 150.4; MS (ESI) *m/z* 553.1 (M^{+}+H); HRMS (ESI) calcd. for $C_{26}H_{25}N_4O_6S_2^{+1}$: 553.1210, Found: 553.1225.

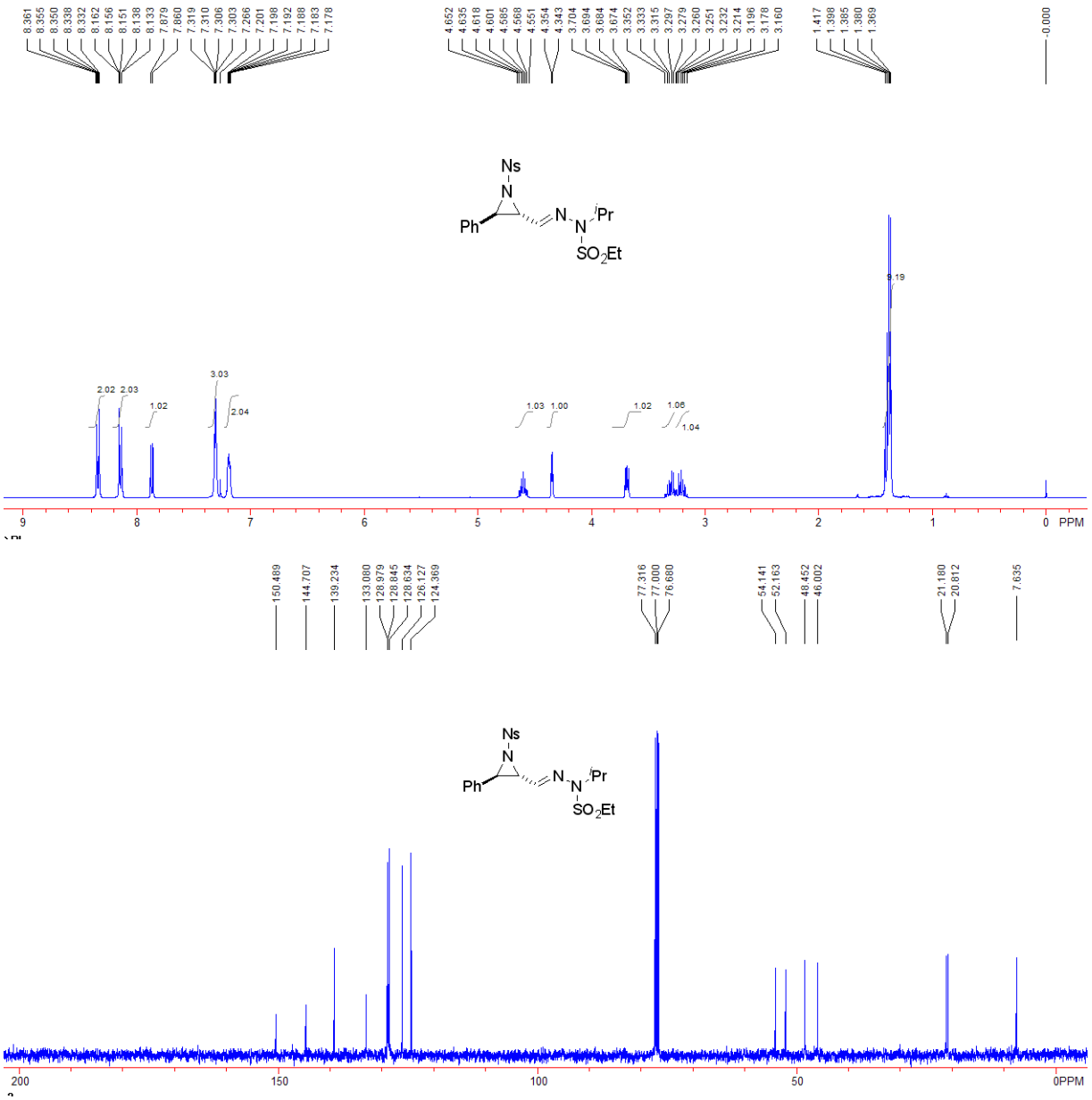


Compound **1j**: Prepared according to the general method (1.3 mmol PhI=NNs) and the title compound was isolated as a yellow oil (355 mg, 49% yield); IR (neat) ν 3291, 2925, 1606, 1598, 1532, 1456, 1350, 1310, 1165, 1091, 930 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.10 (1H, t, *J* = 2.4 Hz), 2.41 (3H, s), 2.48–2.65 (2H, m), 3.68 (1H, dd, *J* = 4.0, 8.0 Hz), 3.77–3.85 (1H, m), 3.97–4.05 (1H, m), 4.31 (1H, d, *J* = 8.0 Hz), 7.16–7.18 (2H, m), 7.27–7.32 (5H, m), 7.46 (1H, d, *J* = 7.6 Hz), 7.77–7.80 (2H, m), 8.05–8.08 (2H, m), 8.26–8.29 (2H, m); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 17.5, 21.4, 45.8, 47.9, 52.9, 71.0, 79.9, 124.2, 126.1, 127.8, 128.6, 128.7, 128.9, 129.6, 132.8, 134.3, 138.6, 144.3, 144.4, 150.3; MS (ESI) *m/z* 553.0 (M^{+}+H); HRMS (ESI) calcd. for $C_{26}H_{25}N_4O_6S_2^{+1}$: 553.1210, Found: 553.1226.



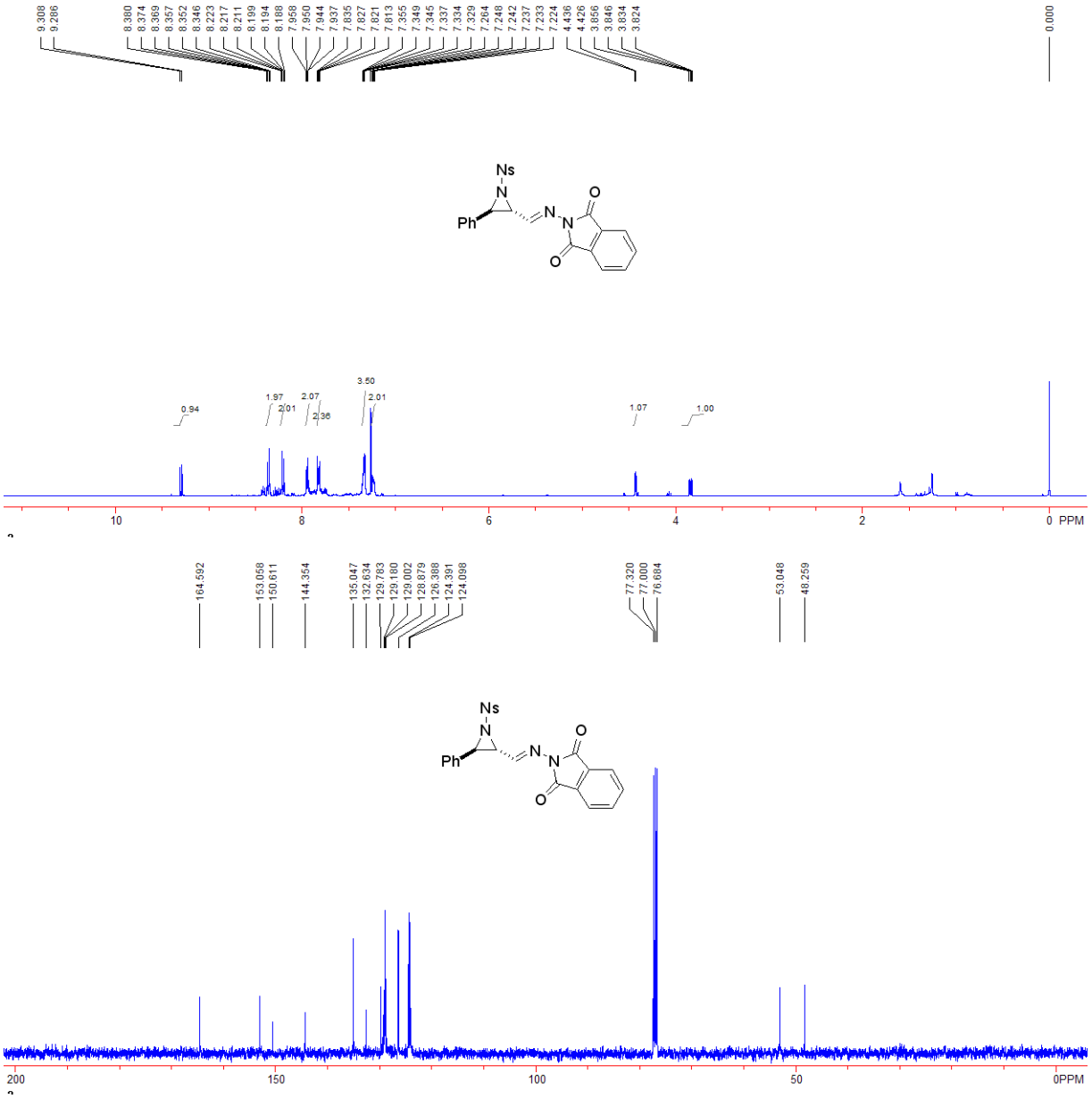


Compound **1k**: Prepared according to the general method (1.5 mmol PhI=NNs) and the title compound was isolated as a colorless oil (260 mg, 36% yield); IR (neat) ν 2960, 2926, 1688, 1607, 1529, 1496, 1456, 1348, 1311, 1163, 1090 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.38 (6H, d, *J* = 6.4 Hz), 1.40 (3H, t, *J* = 7.2 Hz), 3.16–3.25 (1H, m), 3.26–3.35 (1H, m), 3.69 (1H, dd, *J* = 4.0, 8.0 Hz), 4.35 (1H, d, *J* = 4.0 Hz), 4.55–4.65 (1H, m), 7.18–7.20 (2H, m), 7.30–7.32 (3H, m), 7.87 (1H, d, *J* = 8.0 Hz), 8.13–8.16 (2H, m), 8.33–8.36 (2H, m); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 7.6, 20.8, 21.2, 46.0, 48.5, 52.2, 54.1, 124.4, 126.1, 128.6, 128.8, 129.0, 133.1, 139.2, 144.7, 150.5; MS (ESI) *m/z* 481.0 (M^++H); HRMS (ESI) calcd. for $C_{20}H_{25}N_4O_6S_2^{+1}$: 481.1210, Found: 481.1226.



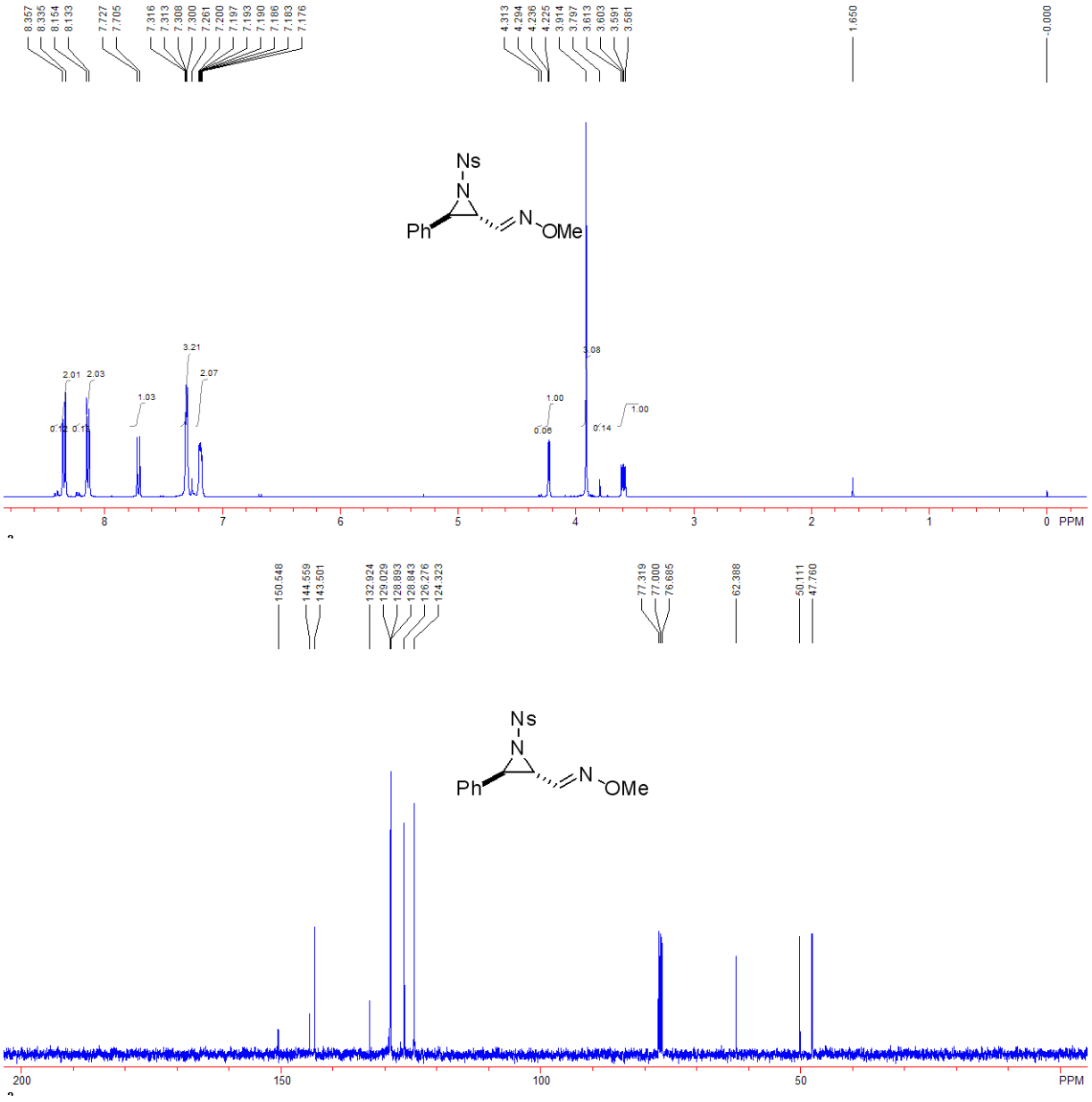
Compound **1l**: Prepared according to the general method (1.5 mmol PhI=NNs) and the title compound was isolated as a white solid (105 mg, 15% yield); mp. 181–183 ^{o}C; IR (neat) ν 2924, 2854, 1726, 1629, 1606, 1530, 1346, 1304, 1165, 1107, 1086 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 3.84 (1H, dd, *J* = 4.0, 8.8 Hz), 4.43 (1H, d, *J* = 4.0 Hz), 7.22–7.25 (2H, m), 7.33–7.36 (3H, m), 7.81–7.84 (2H, m), 7.94–7.96 (2H, m), 8.19–8.22 (2H, m), 8.35–8.38

(2H, m), 9.30 (1H, d, J = 8.8 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 48.3, 53.0, 124.1, 124.4, 126.4, 128.9, 129.0, 129.2, 129.8, 132.6, 135.0, 144.4, 150.6, 153.1, 164.6; MS (ESI) *m/z* 499.1 (M^++Na); HRMS (ESI) calcd. for $C_{23}H_{16}N_4O_6S_2^{+1}$: 476.0791, Found: 476.0787.



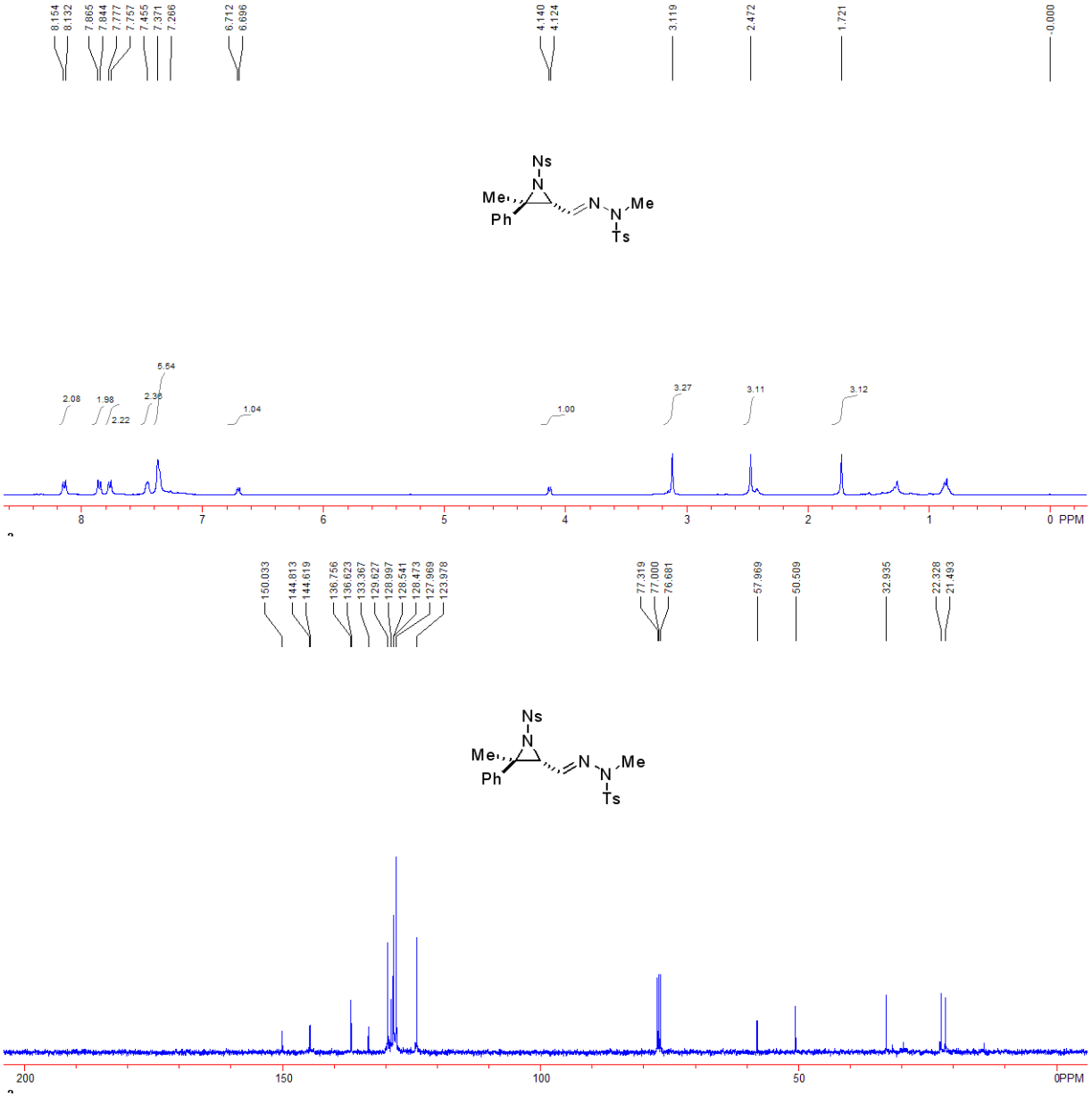
Compound **1m**: Prepared according to the general method (1.5 mmol PhI=NNs) and the title compound was isolated as a white solid (160 mg, 30% yield); mp. 170–172 ^{o}C; IR (neat) ν 2928, 1606, 1531, 1458, 1402, 1349, 1309, 1165, 1085, 1037 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 3.60 (1H, dd, J = 4.0, 8.8 Hz), 3.91 (3H, s), 4.23 (1H, d, J = 4.0 Hz), 7.18–7.20

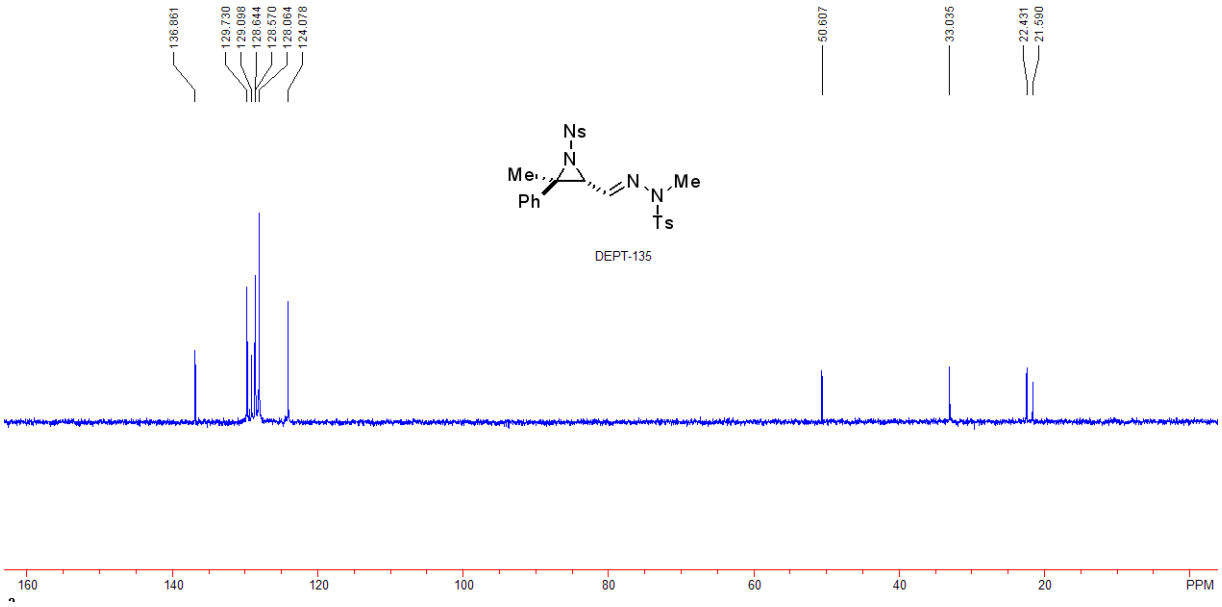
(2H, m), 7.30–7.32 (3H, m), 7.72 (1H, d, J = 8.8 Hz), 8.14 (2H, d, J = 8.4 Hz), 8.35 (2H, d, J = 8.4 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 47.8, 50.1, 62.4, 124.3, 126.3, 128.8, 128.9, 129.0, 132.9, 143.5, 144.6, 150.5; MS (ESI) *m/z* 362.1 (M^++H); HRMS (ESI) calcd. for $C_{16}H_{16}N_3O_5S^{+1}$: 361.0728, Found: 361.0732.



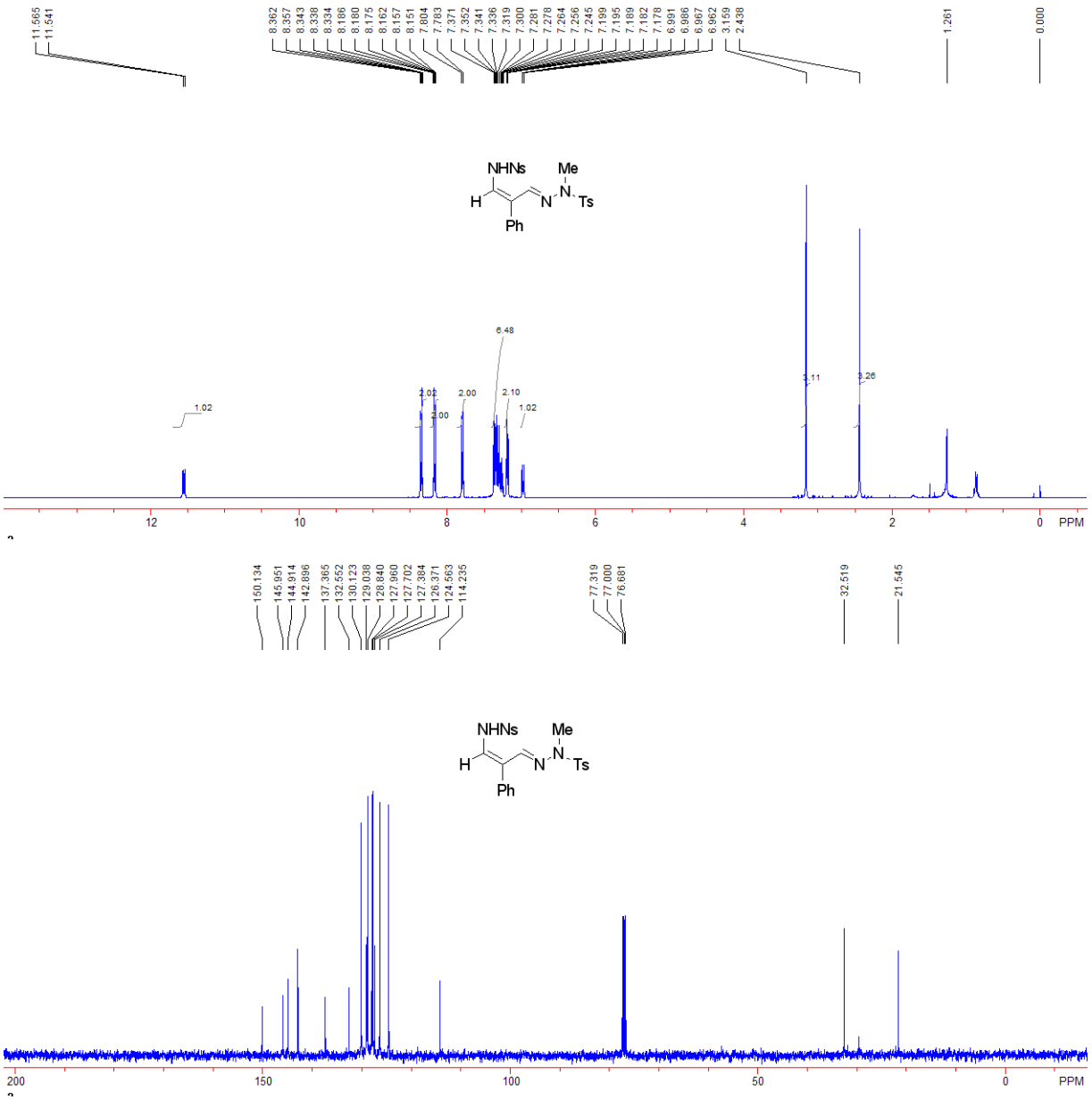
Compound **1n**: Prepared according to the general method (2.0 mmol PhI=NNs) and the title compound was isolated as a white solid (91mg, 9% yield); mp. 67–70 ^{o}C; IR (neat) ν 2958,

2925, 2854, 1597, 1531, 1448, 1350, 1309, 1260, 1166, 1088, 1012 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.72 (3H, s), 2.47 (3H, s), 3.12 (3H, s), 4.13 (1H, d, *J* = 6.4 Hz), 6.70 (1H, d, *J* = 6.4 Hz), 7.33–7.39 (5H, m), 7.43–7.48 (2H, m), 7.77 (2H, d, *J* = 8.0 Hz), 7.85 (2H, d, *J* = 8.4 Hz), 8.14 (2H, d, *J* = 8.4 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.5, 22.3, 32.9, 50.5, 58.0, 124.0, 128.0, 128.5, 129.0, 129.6, 133.4, 136.6, 136.8, 144.6, 144.8, 150.0; MS (ESI) *m/z* 551.0 (M^{+}+Na); HRMS (ESI) calcd. for $C_{24}H_{24}N_4O_6S_2Na^{+1}$: 551.1030, Found: 551.1033.



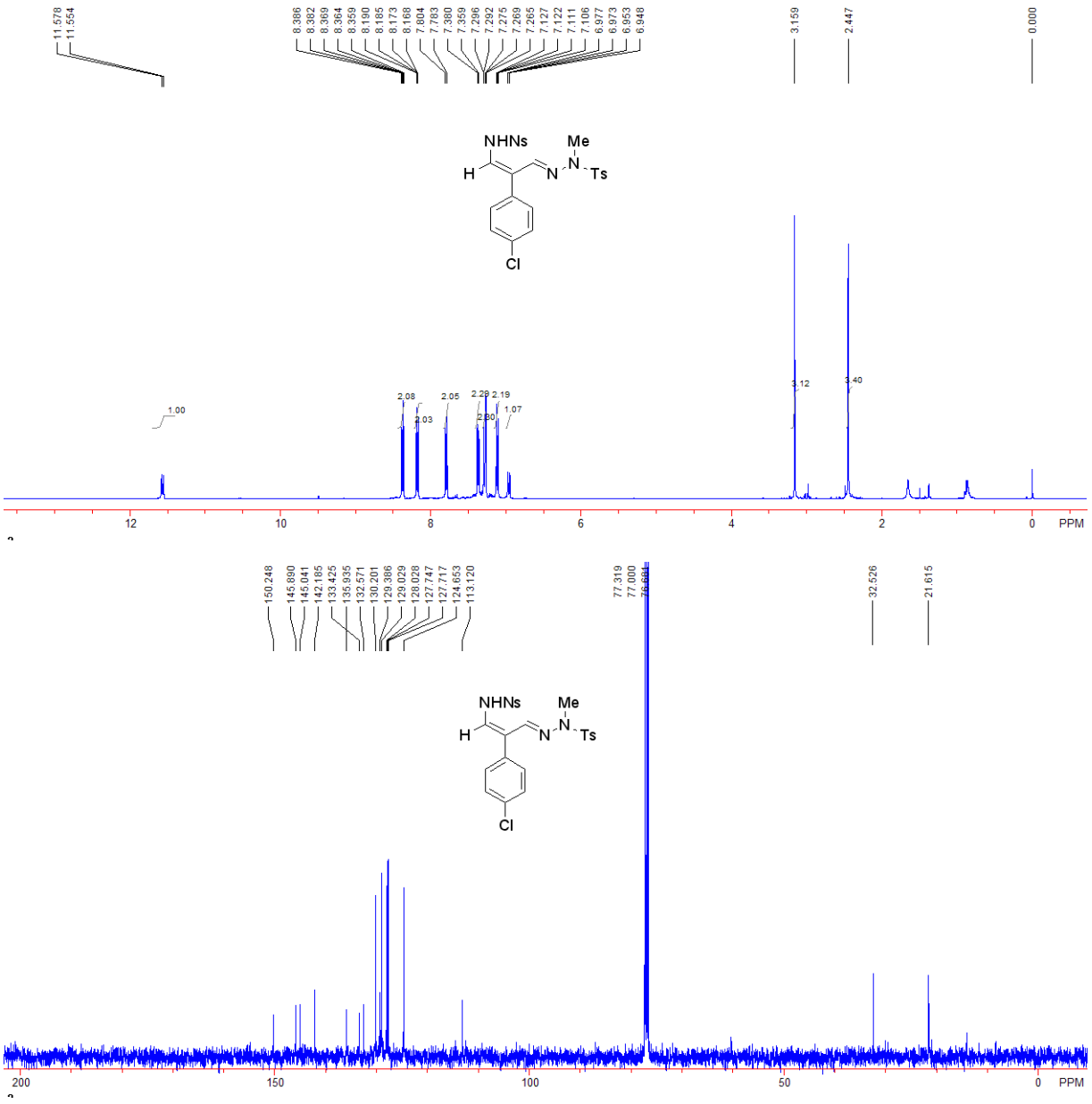


Compound **2a**: General procedure was followed (**1a**: 31 mg, 0.06 mmol) and flash column chromatography gave the title compound as a yellow solid (31 mg, 99%); mp. 78–80 ^{o}C; IR (neat) ν 2925, 1628, 1598, 1530, 1449, 1350, 1309, 1224, 1164, 1089, 1015, 935 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.44 (3H, s), 3.16 (3H, s), 6.98 (1H, dd, *J* = 2.0, 9.6 Hz), 7.18–7.20 (2H, m), 7.25–7.37 (6H, m), 7.79 (2H, d, *J* = 8.4 Hz), 8.15–8.19 (2H, m), 8.33–8.36 (2H, m), 11.55 (1H, d, *J* = 9.6 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.5, 32.5, 114.2, 124.6, 126.4, 127.4, 127.7, 128.0, 128.8, 129.0, 130.1, 132.6, 137.4, 142.9, 144.9, 146.0, 150.1; MS (ESI) *m/z* 515.0 (M^{+}+H); HRMS (ESI) calcd. for $C_{23}H_{23}N_4O_6S_2^{+1}$: 515.1054, Found: 515.1069.



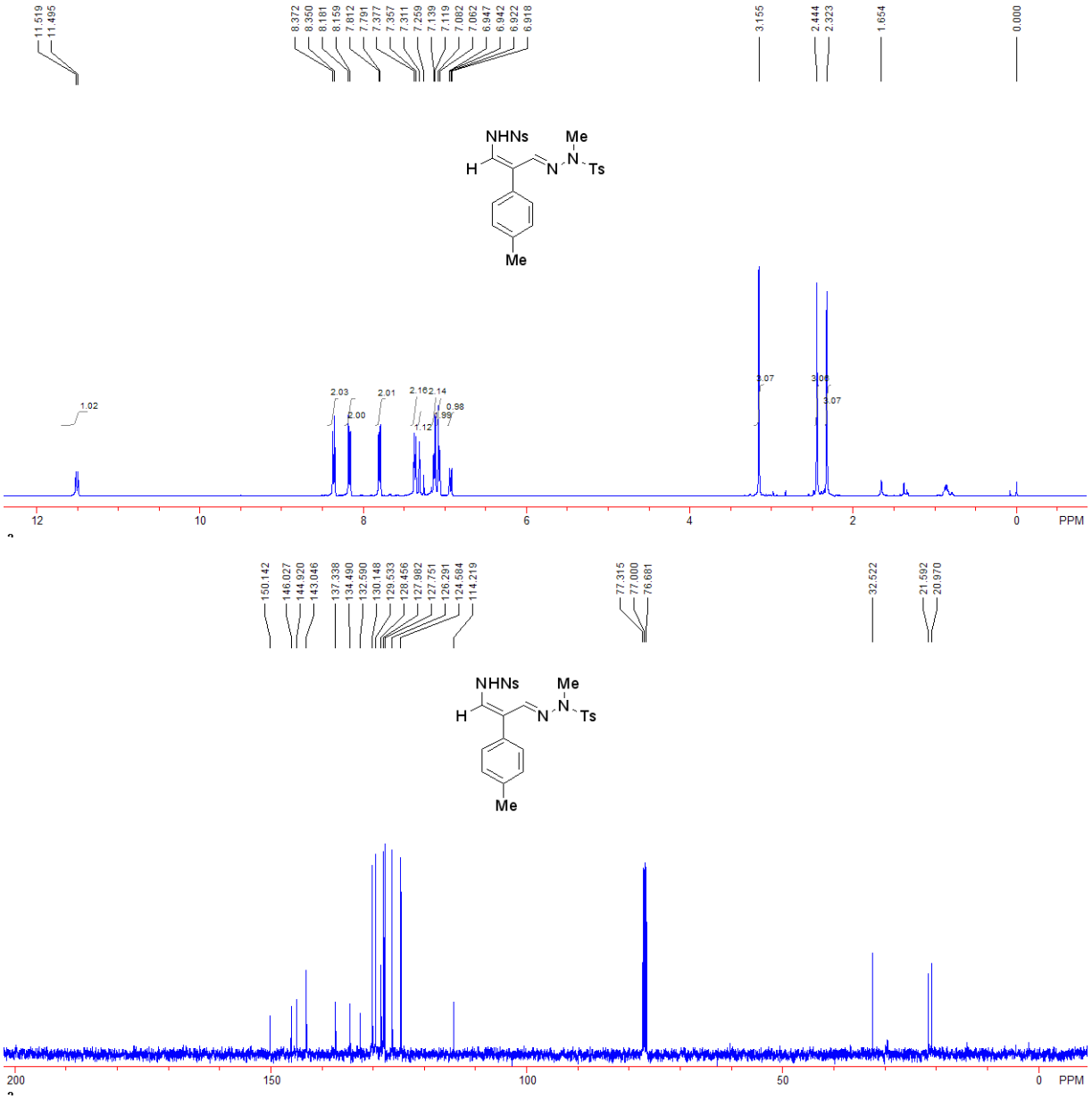
Compound **2b**: General procedure was followed (**1b**: 39 mg, 0.07 mmol) and flash column chromatography gave the title compound as a yellow solid (32 mg, 82%); mp. 102–105 ^{o}C; IR (neat) ν 2926, 1629, 1531, 1309, 1224, 1164, 1090, 1013, 934 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.45 (3H, s), 3.16 (3H, s), 6.96 (1H, dd, *J* = 2.0, 9.6 Hz), 7.11–7.13 (2H, m), 7.27–7.30 (2H, m), 7.37 (2H, d, *J* = 8.4 Hz), 7.79 (2H, d, *J* = 8.4 Hz), 8.17–8.19 (2H, m),

8.36–8.39 (2H, m), 11.57 (1H, d, J = 9.6 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.6, 32.5, 113.1, 124.6, 127.71, 127.75, 128.0, 129.0, 129.4, 130.2, 132.6, 133.4, 135.9, 142.2, 145.0, 145.9, 150.2; MS (ESI) *m/z* 548.9 (M^++H); HRMS (ESI) calcd. for $C_{23}H_{21}N_4O_6S_2ClNa^{+1}$: 571.0483, Found: 571.0509.

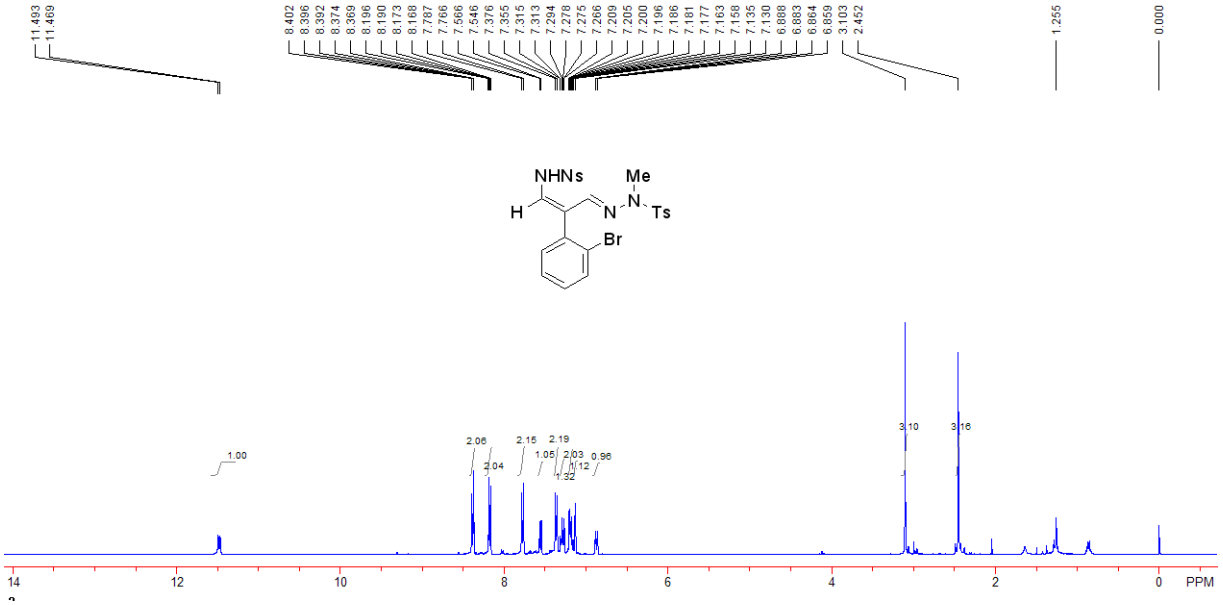


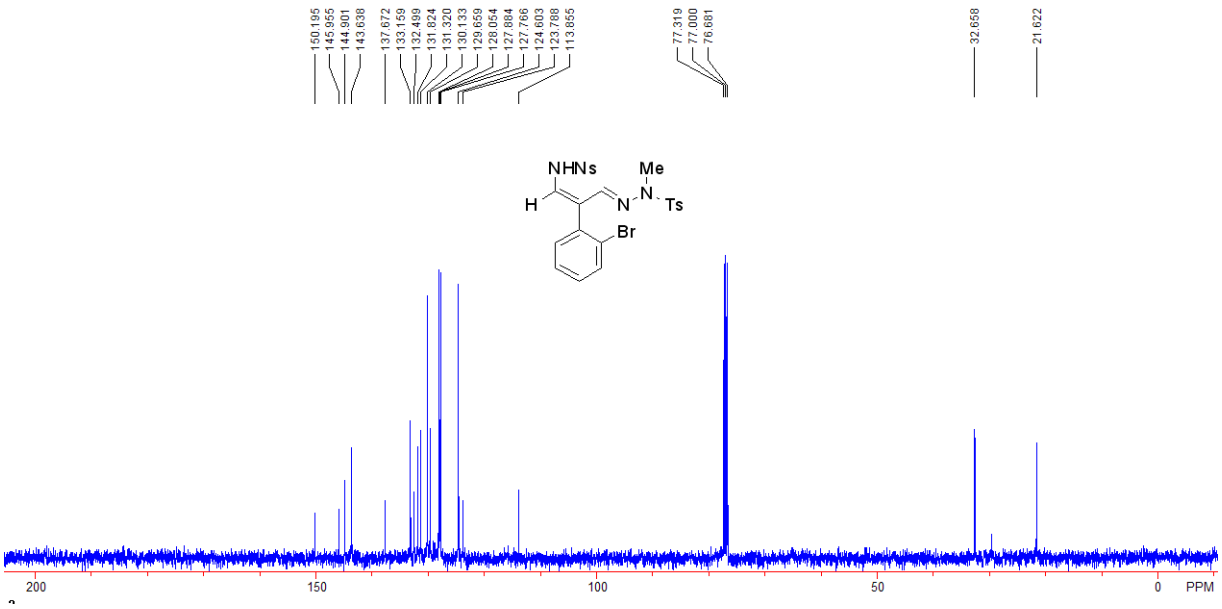
Compound **2c**: General procedure was followed (**1c**: 53 mg, 0.10 mmol) and flash column

chromatography gave the title compound as a yellow solid (49 mg, 92%); mp. 70–72 ^{o}C; IR (neat) ν 2925, 1628, 1531, 1309, 1224, 1164, 1089, 1014, 934 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.32 (3H, s), 2.44 (3H, s), 3.16 (3H, s), 6.93 (1H, dd, *J* = 2.0, 9.6 Hz), 7.07 (2H, d, *J* = 8.0 Hz), 7.13 (2H, d, *J* = 8.0 Hz), 7.31 (1H, s), 7.37 (2H, d, *J* = 8.0 Hz), 7.80 (2H, d, *J* = 8.0 Hz), 8.17 (2H, d, *J* = 8.8 Hz), 8.36 (2H, d, *J* = 8.8 Hz), 11.51 (1H, d, *J* = 9.6 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.0, 21.6, 32.5, 114.2, 124.6, 126.3, 127.8, 128.0, 128.5, 129.5, 130.1, 132.6, 134.5, 137.3, 143.0, 144.9, 146.0, 150.1; MS (ESI) *m/z* 529.0 (M^{+}+H); HRMS (ESI) calcd. for $C_{24}H_{24}N_4O_6S_2Na^{+1}$: 551.1030, Found: 551.1045.

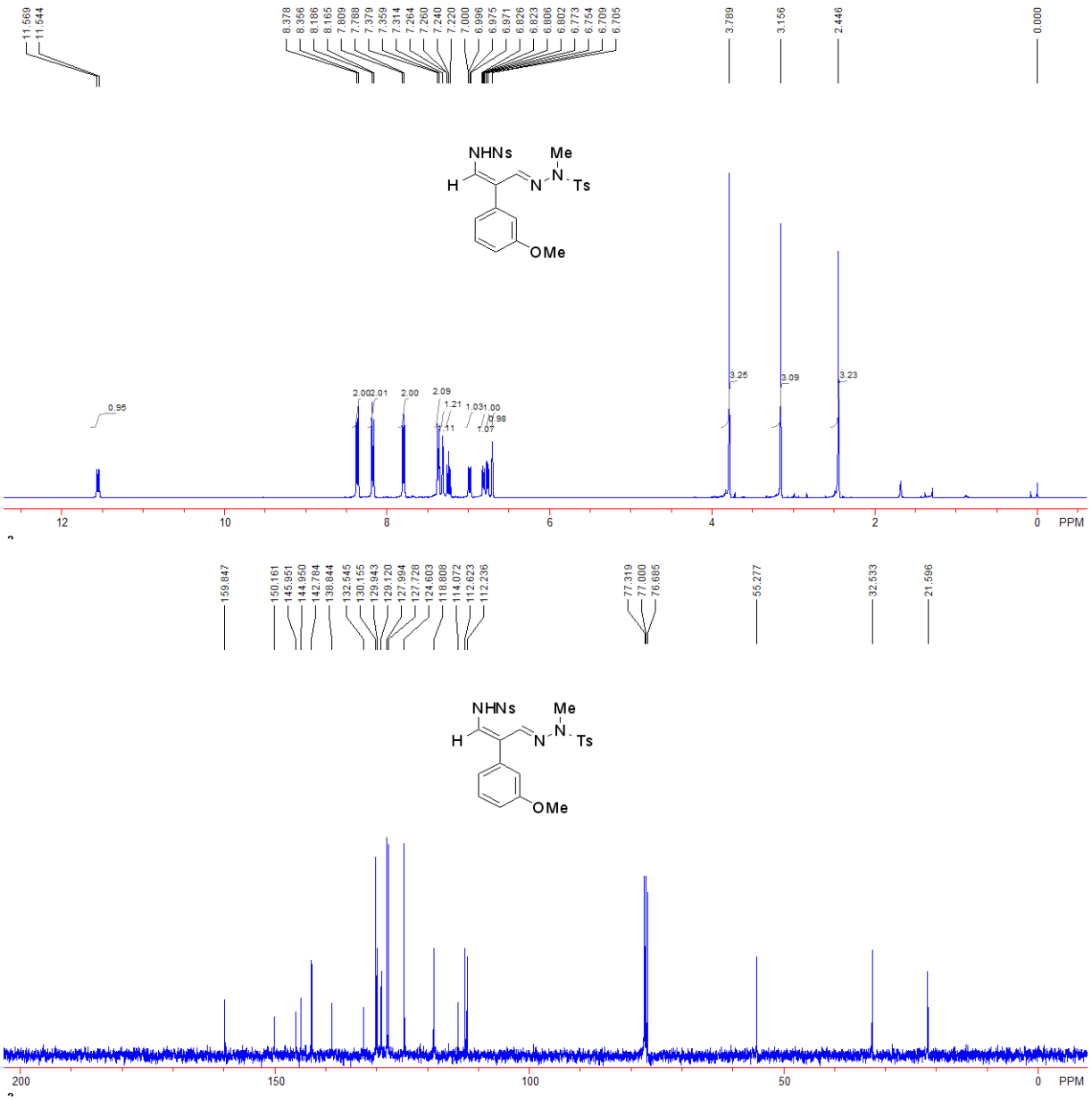


Compound **2d**: General procedure was followed (**1d**: 52 mg, 0.09 mmol) and flash column chromatography gave the title compound as a yellow solid (34 mg, 65%); mp. 88–90 ^{o}C; IR (neat) ν 2926, 1632, 1531, 1350, 1308, 1261, 1165, 1088, 1016, 934 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.45 (3H, s), 3.10 (3H, s), 6.87 (1H, dd, *J* = 2.0, 9.6 Hz), 7.13 (1H, d, *J* = 2.0 Hz), 7.18–7.21 (2H, m), 7.28–7.32 (1H, m), 7.37 (1H, d, *J* = 8.4 Hz), 7.56 (1H, d, *J* = 8.0 Hz), 7.78 (2H, d, *J* = 8.4 Hz), 8.17–8.20 (2H, m), 8.37–8.40 (2H, m), 11.48 (1H, d, *J* = 9.6 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.6, 32.7, 113.9, 123.8, 124.6, 127.8, 127.9, 128.1, 129.7, 130.1, 131.3, 131.8, 132.5, 133.2, 137.7, 143.6, 144.9, 146.0, 150.2; MS (ESI) *m/z* 592.9 (M^{+}+H); HRMS (ESI) calcd. for $C_{23}H_{21}N_4O_6S_2BrNa^{+1}$: 614.9978, Found: 614.9977.



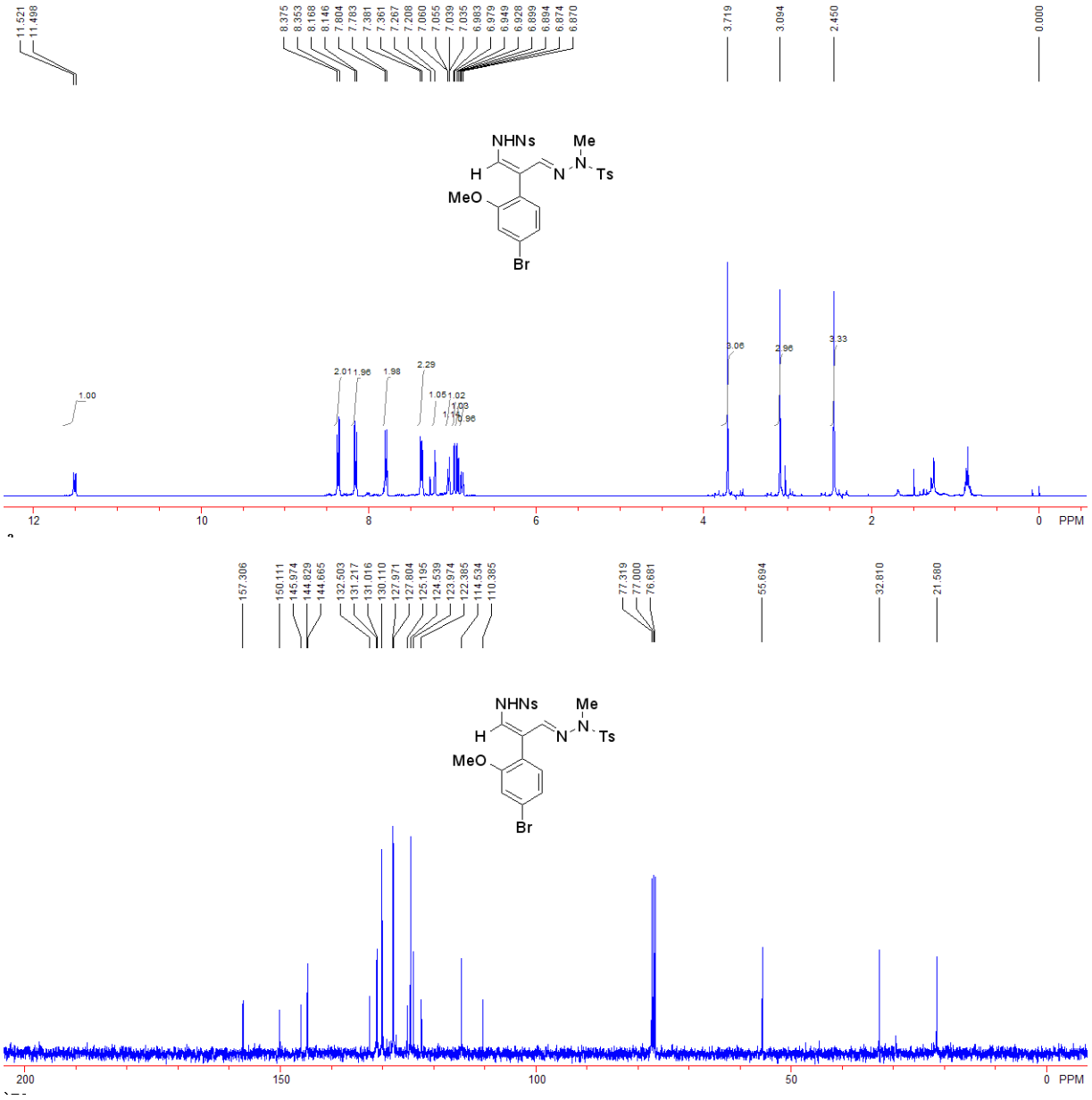


Compound **2e**: General procedure was followed (**1e**: 54 mg, 0.10 mmol) and flash column chromatography gave the title compound as a yellow solid (43 mg, 80%); mp. 76–78 ^{o}C; IR (neat) ν 2925, 1628, 1605, 1530, 1350, 1310, 1227, 1164, 1089, 1021, 941 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.45 (3H, s), 3.16 (3H, s), 3.79 (3H, s), 6.71 (1H, d, *J* = 1.6 Hz), 6.76 (1H, d, *J* = 8.0 Hz), 6.82 (1H, dd, *J* = 1.6, 8.0 Hz), 6.99 (1H, dd, *J* = 1.6, 10.0 Hz), 7.24 (1H, t, *J* = 8.0 Hz), 7.31 (1H, s), 7.37 (2H, d, *J* = 8.0 Hz), 7.80 (2H, d, *J* = 8.0 Hz), 8.18 (2H, d, *J* = 8.4 Hz), 8.37 (2H, d, *J* = 8.4 Hz), 11.56 (1H, d, *J* = 10.0 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.6, 32.5, 55.3, 112.2, 112.6, 114.1, 118.8, 124.6, 127.7, 128.0, 129.1, 129.9, 130.2, 132.5, 138.8, 142.8, 145.0, 146.0, 150.2, 159.8; MS (ESI) *m/z* 545.0 (M^++H); HRMS (ESI) calcd. for $C_{24}H_{24}N_4O_7S_2Na^{+1}$: 567.0979, Found: 567.0981.



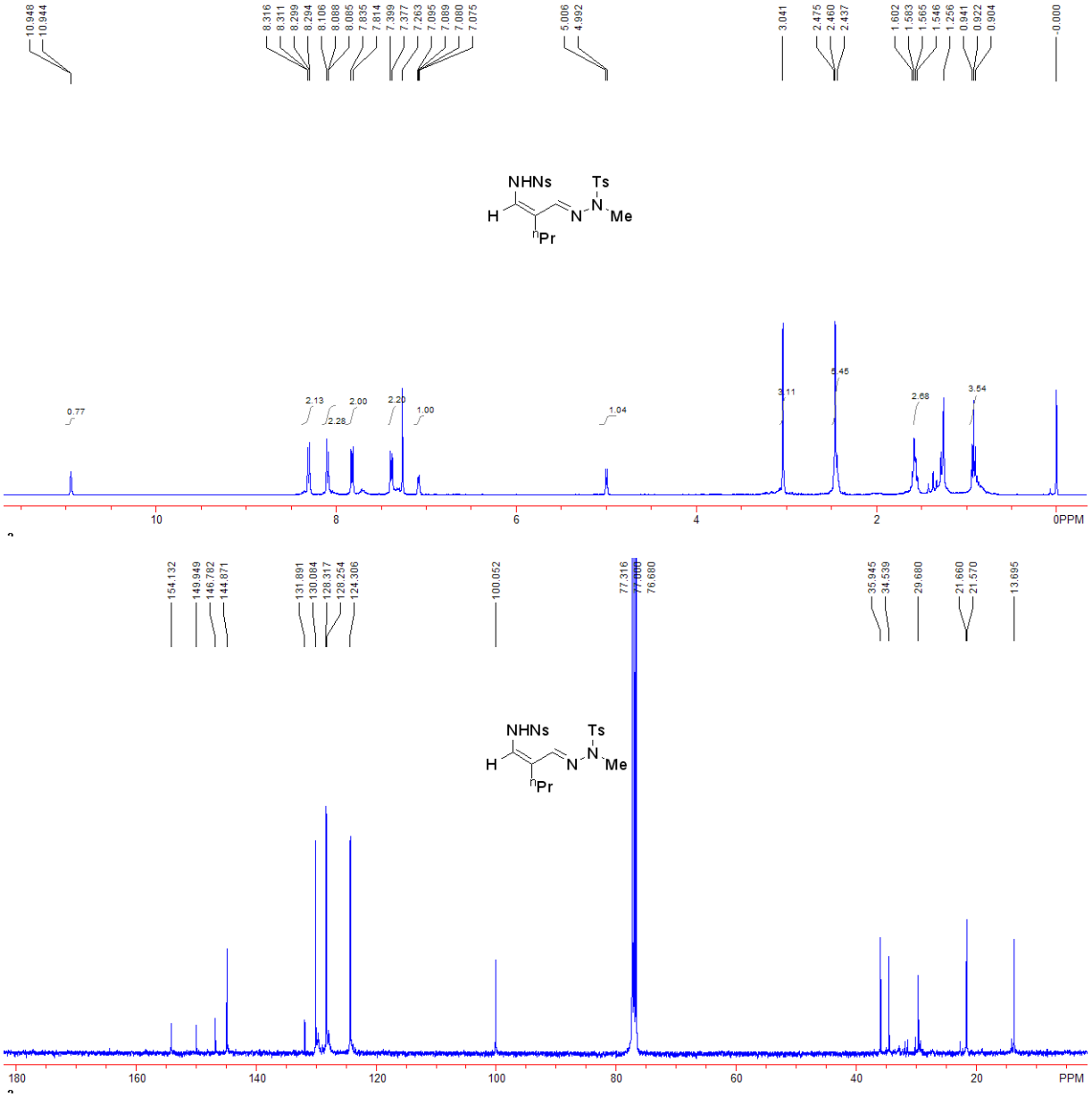
Compound **2f**: General procedure was followed (**1f**: 62 mg, 0.10 mmol) and flash column chromatography gave the title compound as a yellow solid (53 mg, 85%); mp. 178–180 ^{o}C; IR (neat) ν 2954, 2923, 2852, 1735, 1632, 1588, 1530, 1489, 1462, 1378, 1348, 1248, 1227, 1164, 1087 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.45 (3H, s), 3.09 (3H, s), 3.72 (3H, s), 6.88 (1H, dd, *J* = 2.0, 9.6 Hz), 6.94 (1H, d, *J* = 8.4 Hz), 6.98 (1H, d, *J* = 2.0 Hz), 7.05 (1H, dd, *J* =

2.0, 8.0 Hz), 7.21 (1H, s), 7.37 (2H, d, *J* = 8.0 Hz), 7.79 (2H, d, *J* = 8.0 Hz), 8.16 (2H, d, *J* = 8.8 Hz), 8.36 (2H, d, *J* = 8.8 Hz), 11.51 (1H, d, *J* = 9.6 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.6, 32.8, 55.7, 110.4, 114.5, 122.4, 124.0, 124.5, 125.2, 127.8, 128.0, 130.1, 131.0, 131.2, 132.5, 144.7, 144.8, 146.0, 150.1, 157.3; MS (ESI) *m/z* 622.9 (M^++H); HRMS (ESI) calcd. for $C_{24}H_{23}N_4O_7S_2BrNa^{+1}$: 645.0084, Found: 645.0086.

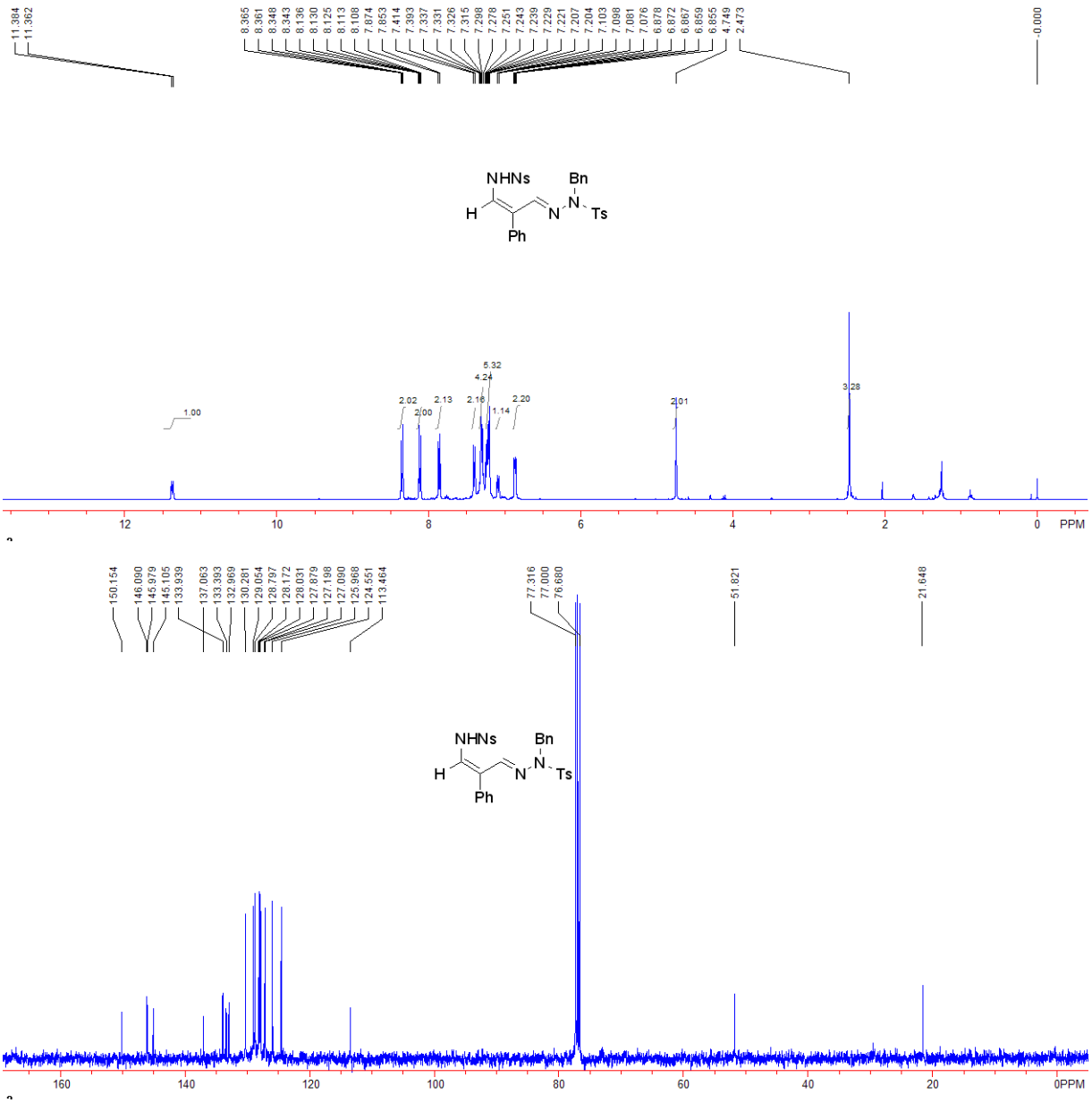


Compound **2g**: TfOH (10 mol%) was used (**1g**: 48 mg, 0.10 mmol) and flash column chromatography gave the title compound as a yellow solid (15 mg, 30%); mp. 125–127 ^{o}C; IR

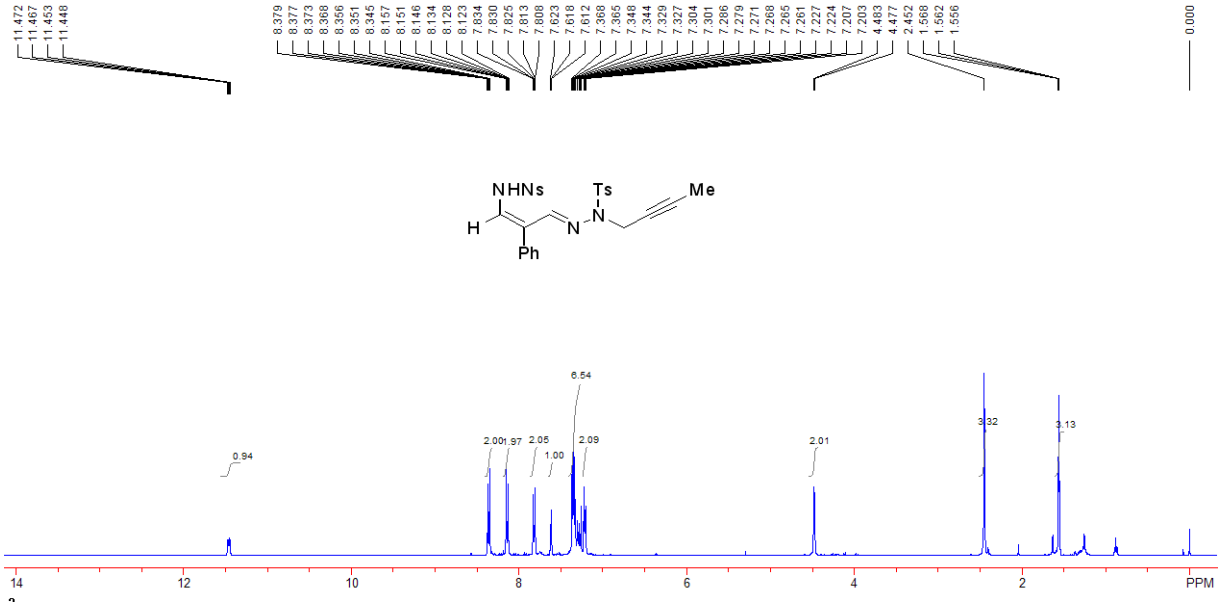
(neat) ν 3267, 2960, 2924, 2871, 1632, 1530, 1456, 1401, 1347, 1307, 1212, 1162, 1107, 1087 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 0.92 (3H, t, *J* = 7.6 Hz), 1.55–1.60 (2H, m), 2.44–2.48 (2H, m), 2.46 (3H, s), 3.04 (3H, s), 5.00 (1H, d, *J* = 5.6 Hz), 7.08 (1H, dd, *J* = 1.6, 5.6 Hz), 7.39 (2H, d, *J* = 8.4 Hz), 7.82 (2H, d, *J* = 8.4 Hz), 8.09–8.11 (2H, m), 8.29–8.32 (2H, m), 10.95 (1H, d, *J* = 1.6 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 13.7, 21.6, 21.7, 34.5, 35.9, 100.1, 124.3, 128.25, 128.32, 130.1, 131.9, 144.9, 146.8, 149.9, 154.1; MS (ESI) *m/z* 481.0 (M^{+}+H); HRMS (ESI) calcd. for $C_{20}H_{24}N_4O_6S_2Na^{+1}$: 503.1030, Found: 503.1036.

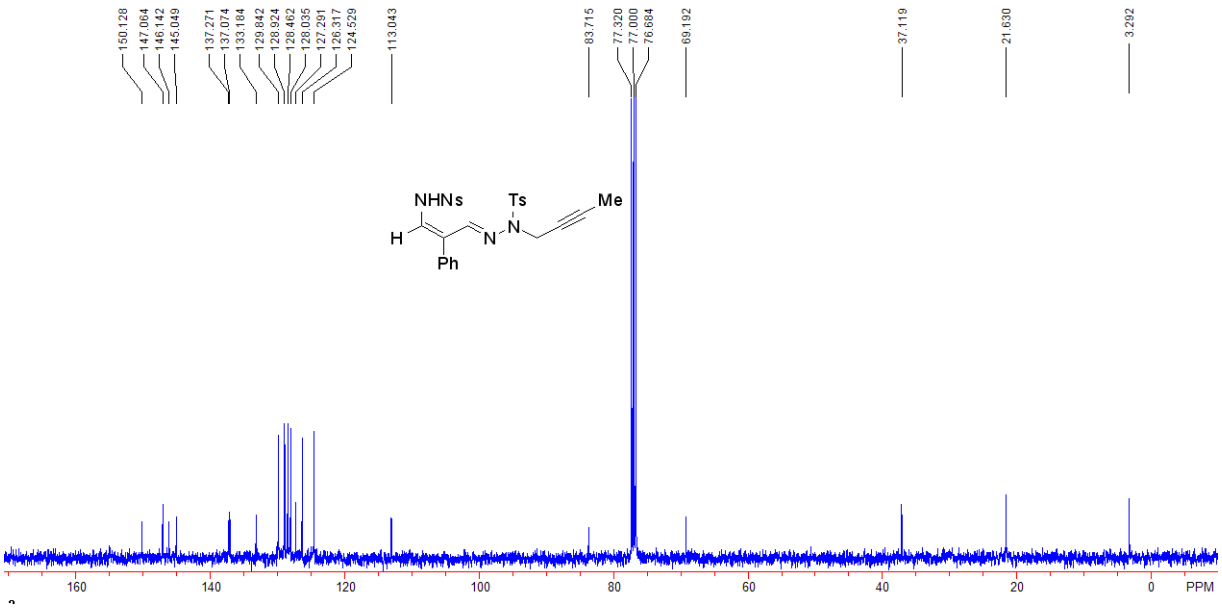


Compound **2h**: General procedure was followed (**1h**: 59 mg, 0.10 mmol) and flash column chromatography gave the title compound as a yellow solid (51 mg, 86%); mp. 168–170 ^{o}C; IR (neat) ν 2957, 2923, 2853, 1685, 1628, 1605, 1531, 1496, 1454, 1349, 1260, 1167, 1089, 1018 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.47 (3H, s), 4.75 (2H, s), 6.86–6.88 (2H, m), 7.08–7.10 (1H, m), 7.20–7.25 (5H, m), 7.28–7.34 (4H, m), 7.40 (2H, d, *J* = 8.4 Hz), 7.86 (2H, d, *J* = 8.4 Hz), 8.11–8.14 (2H, m), 8.34–8.37 (2H, m), 11.37 (1H, d, *J* = 8.8 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.6, 51.8, 113.5, 124.6, 126.0, 127.1, 127.2, 127.9, 128.0, 128.2, 128.8, 129.1, 130.3, 133.0, 133.4, 133.9, 137.1, 145.1, 146.0, 146.1, 150.2; MS (ESI) *m/z* 591.0 (M^{+}+H); HRMS (ESI) calcd. for $C_{29}H_{27}N_4O_6S_2^{+1}$: 591.1367, Found: 591.1360.

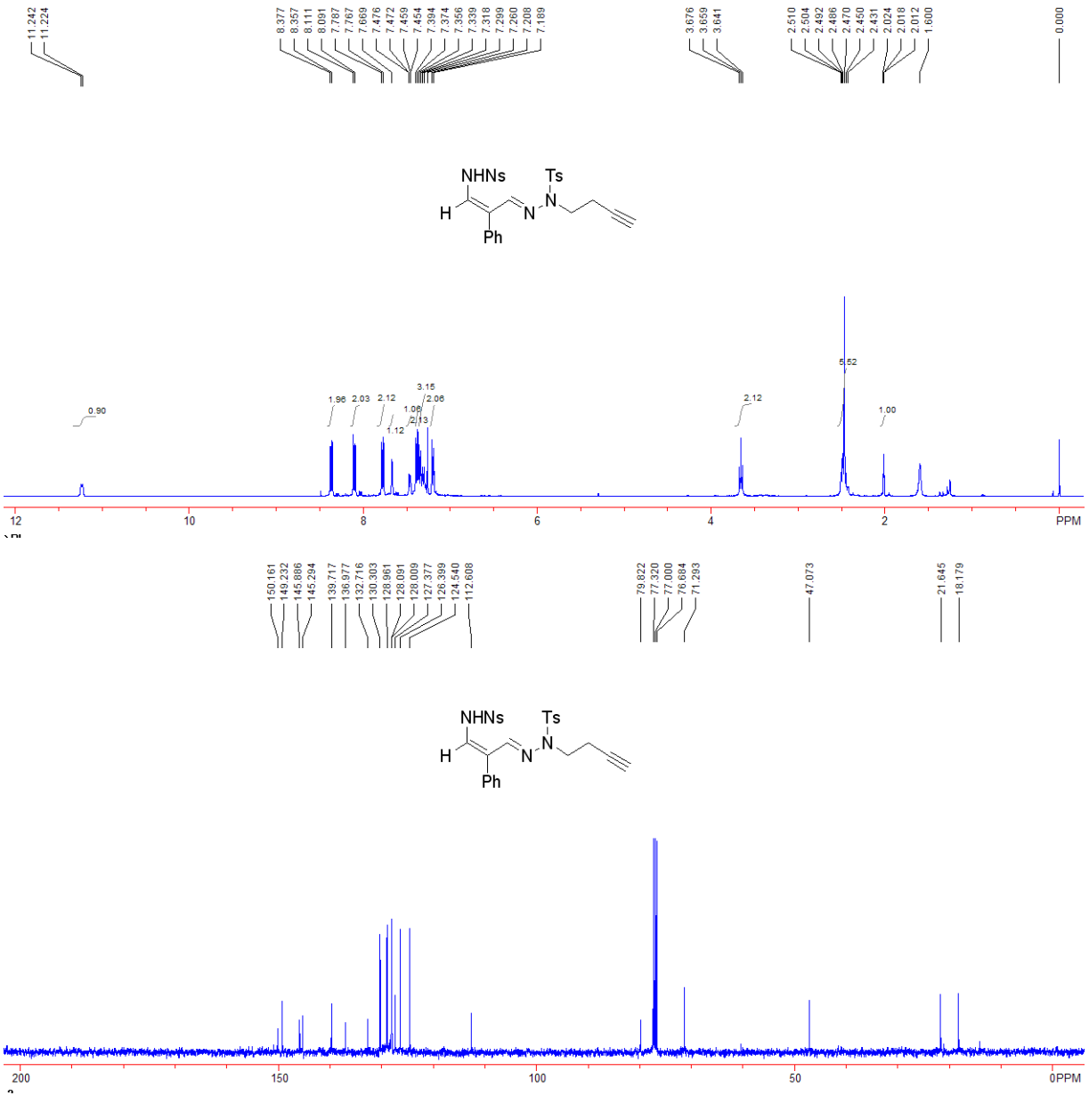


Compound **2i**: General procedure was followed (**1i**: 55 mg, 0.10 mmol) and flash column chromatography gave the title compound as a yellow solid (48 mg, 87%); mp. 177–179 ^{o}C; IR (neat) ν 2926, 1598, 1532, 1309, 1168, 1089, 899 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.56 (3H, t, *J* = 2.4 Hz), 2.45 (3H, s), 4.48 (2H, d, *J* = 2.4 Hz), 7.20–7.23 (2H, m), 7.27–7.37 (6H, m), 7.62 (1H, t, *J* = 2.0 Hz), 7.81–7.83 (2H, m), 8.12–8.16 (2H, m), 8.35–8.38 (2H, m), 11.46 (1H, dd, *J* = 2.0, 7.6 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 3.3, 21.6, 37.1, 69.2, 83.7, 113.0, 124.5, 126.3, 127.3, 128.0, 128.5, 128.9, 129.8, 133.2, 137.1, 137.3, 145.0, 146.1, 147.1, 150.1; MS (ESI) *m/z* 553.1 (M^{+}+H); HRMS (ESI) calcd. for $C_{26}H_{25}N_4O_6S_2^{+1}$: 553.1210, Found: 553.1226.



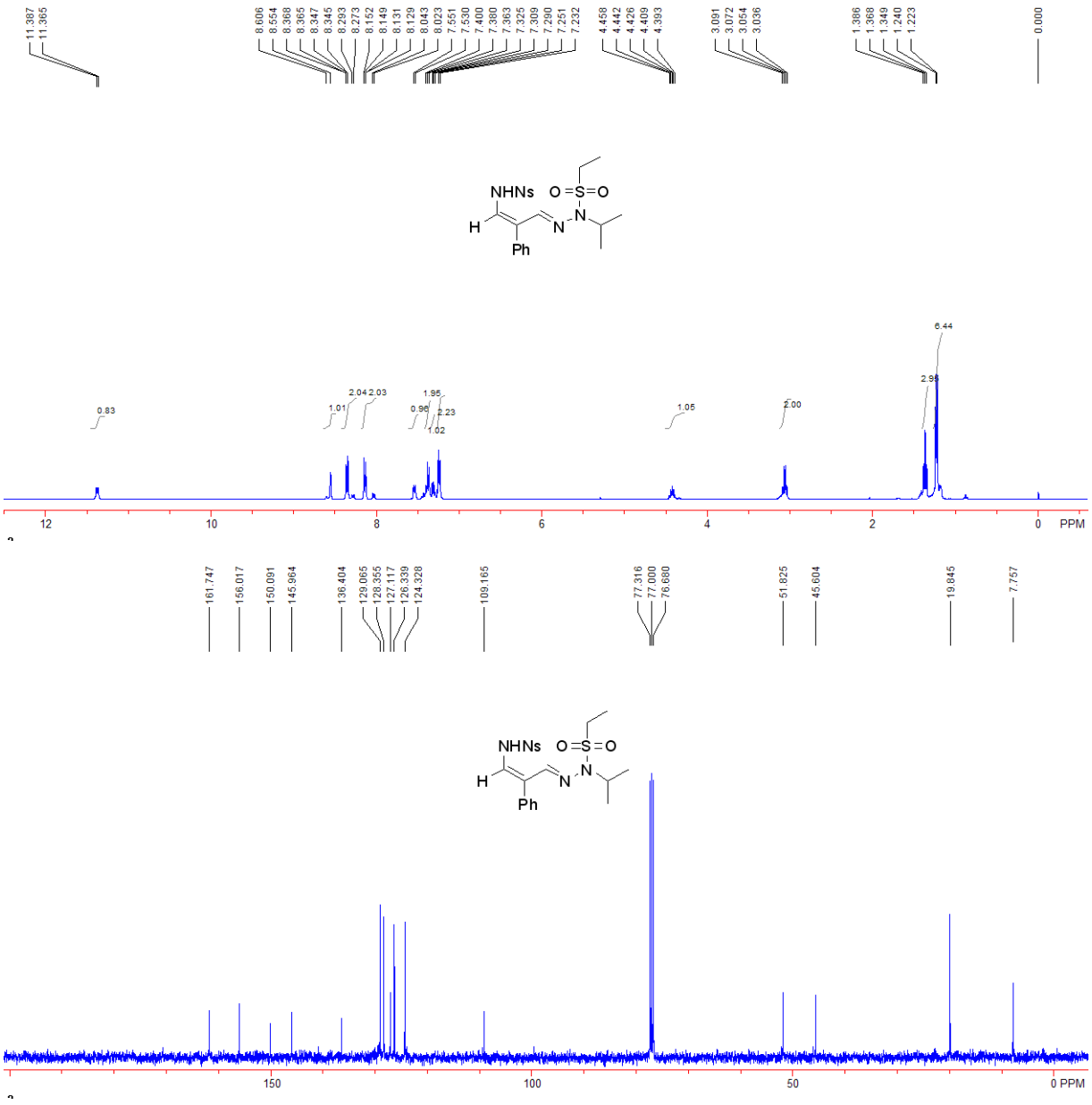


Compound **2j**: General procedure was followed (**1j**: 55 mg, 0.10 mmol) and flash column chromatography gave the title compound as a yellow solid (49 mg, 89%); mp. 158–160 ^{o}C; IR (neat) ν 3290, 2925, 1627, 1531, 1350, 1308, 1167, 1088, 935 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.02 (1H, t, *J* = 2.4 Hz), 2.43–2.51 (2H, m), 2.47 (3H, s), 3.66 (2H, t, *J* = 7.2 Hz), 7.20 (2H, d, *J* = 7.6 Hz), 7.30–7.36 (3H, m), 7.38 (2H, d, *J* = 8.0 Hz), 7.46 (1H, dd, *J* = 2.0, 7.2 Hz), 7.67 (1H, s), 7.78 (2H, d, *J* = 8.0 Hz), 8.10 (2H, d, *J* = 8.0 Hz), 8.37 (2H, d, *J* = 8.0 Hz), 11.23 (1H, d, *J* = 7.2 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 18.2, 21.6, 47.1, 71.3, 79.8, 112.6, 124.5, 126.4, 127.4, 128.0, 128.1, 129.0, 130.3, 132.7, 137.0, 139.7, 145.3, 145.9, 149.2, 150.2; MS (ESI) *m/z* 553.0 (M^++H); HRMS (ESI) calcd. for $C_{26}H_{25}N_4O_6S_2^{+1}$: 553.1210, Found: 553.1224.



Compound **2f**: General procedure was followed (**1f**: 60 mg, 0.12 mmol) and flash column chromatography gave the title compound as a yellow solid (54 mg, 90%); mp. 178–180 ^{o}C; IR (neat) ν 2954, 2923, 2852, 1735, 1622, 1529, 1459, 1348, 1304, 1253, 1152, 1086 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) 1.23 (6H, d, *J* = 6.8 Hz), 1.37 (3H, t, *J* = 7.6 Hz), 3.06 (2H, q, *J* = 7.6 Hz), 4.39–4.46 (1H, m), 7.24 (2H, d, *J* = 7.6 Hz), 7.32 (1H, d, *J* = 6.4 Hz), 7.36–7.40

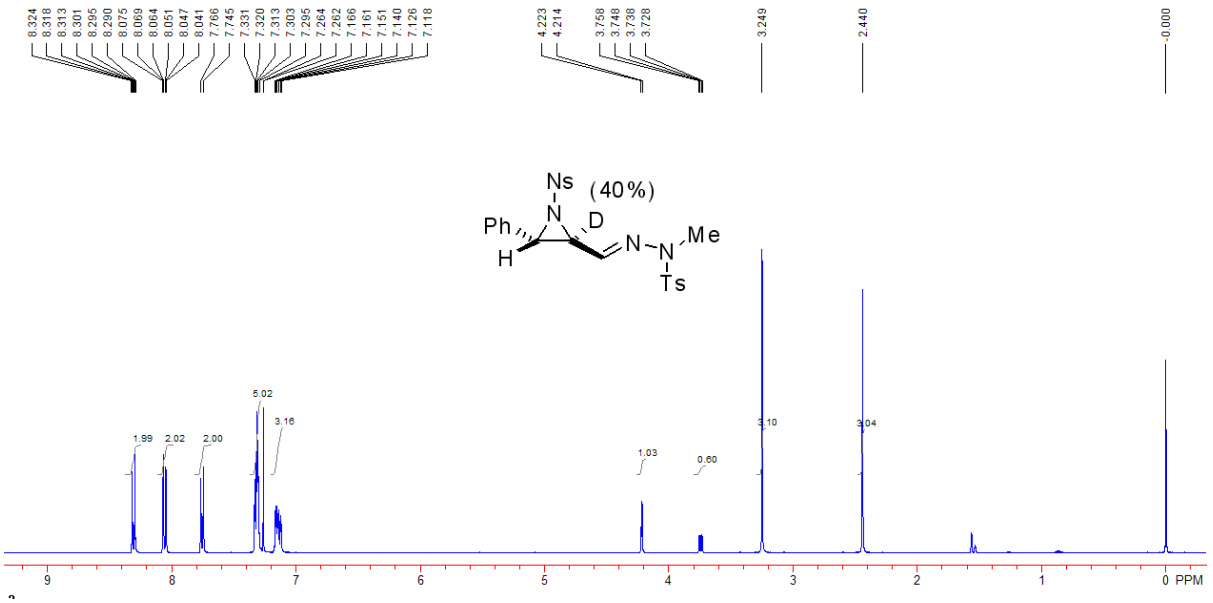
(2H, m), 7.54 (1H, d, *J* = 8.8 Hz), 8.13–8.15 (2H, m), 8.35–8.37 (2H, m), 8.55 (1H, s), 11.38 (1H, d, *J* = 8.8 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) 7.8, 19.8, 45.6, 51.8, 109.2, 124.3, 126.3, 127.1, 128.4, 129.1, 136.4, 146.0, 150.1, 156.0, 161.7; MS (ESI) *m/z* 481.0 (M^++H); HRMS (ESI) calcd. for $C_{20}H_{25}N_4O_6S_2^{+1}$: 481.1210, Found: 481.1214.

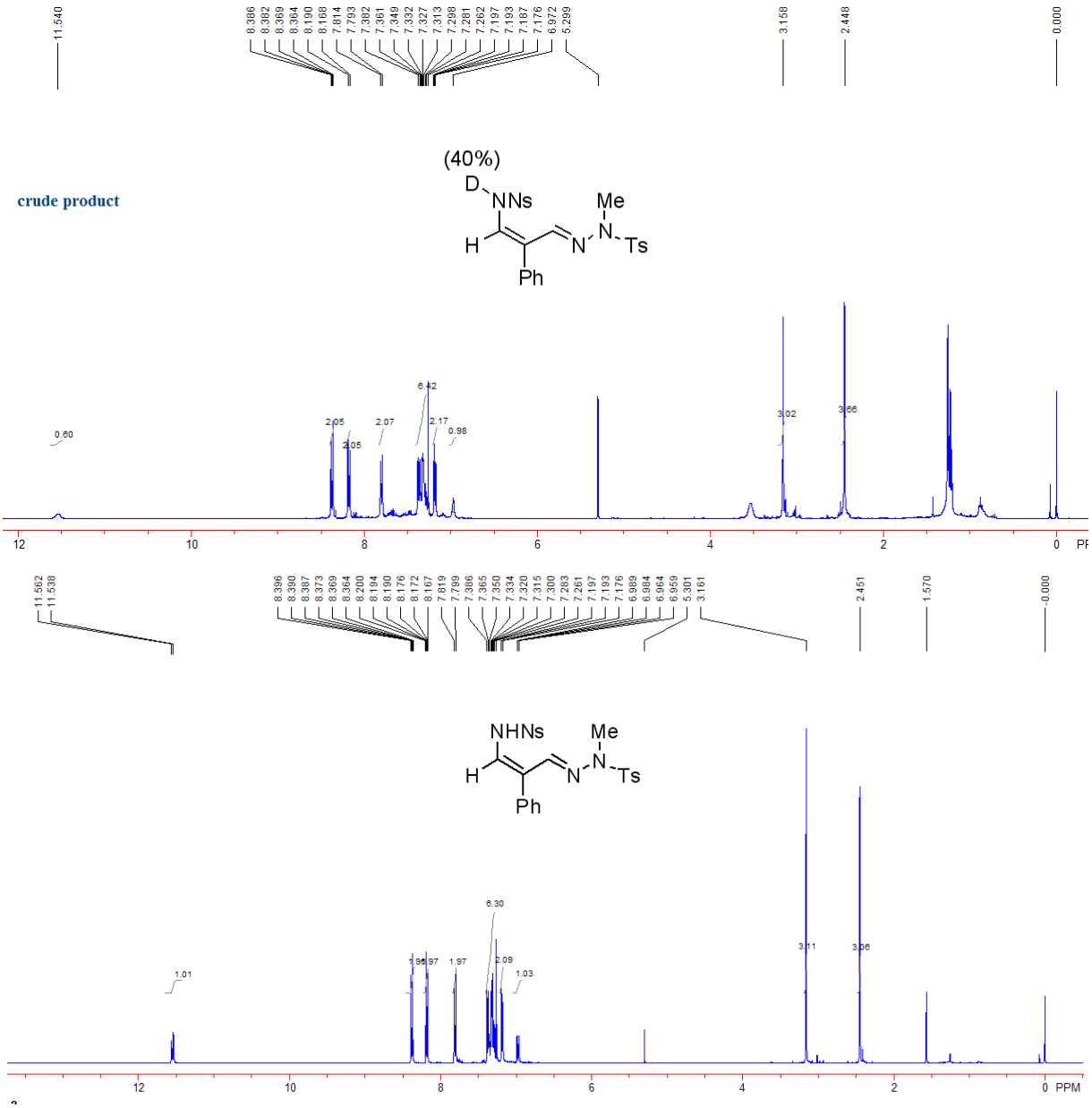


7. Isotope Labeling Experiments

Hydrazonylaziridines **1a**-d_1, **1a**-d_2 and **1a**-d_3 were prepared according to the general procedure by using deuterium labeled cinnamaldehydes as starting materials. Various deuterium labeled cinnamaldehydes were produced by acid hydrolysis of 1-aminopropa-1,2-dienes according the reported reference[J. C. Craig, N. N. Ekwuribe, *Tetrahedron Lett.* **1980**, *21*, 2587–2590].

The general procedure was followed by treating **1a**-*d* with $BF_3{\cdot}Et_2O$. Then the solvent was evaporated under reduced pressure and the crude product was analyzed by ^{1}H NMR to identify the D content at the nitrogen atom which would easily undergo proton transfer with ambient moisture. Pure **2a**-*d* was afforded by a flash column chromatography on a silica gel eluting with petroleum ether and ethyl acetate (v/v, 3:1). According to the ^{1}H NMR spectroscopic analysis, the D content of **2a**-*d* will be clear.

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8.190
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7.814
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7.382
7.361
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7.332
7.327
7.313
7.298
7.281
7.262
7.197
7.193
7.187
7.176
6.972
5.299
3.158
2.448
0.000
(40%)
crude product
D
NNs
Me
H
N
N
Ts
Ph
0.60
2.05
2.05
2.07
6.42
2.17
0.98
3.02
3.06
12
10
8
6
4
2
0
PPM
11.562
11.538
8.396
8.390
8.387
8.373
8.369
8.364
8.200
8.194
8.190
8.176
8.172
8.167
7.819
7.799
7.386
7.365
7.350
7.334
7.320
7.315
7.300
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7.261
7.197
7.193
7.176
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6.984
6.964
6.959
5.301
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0.000
NHNs
Me
H
N
N
Ts
Ph
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1.96
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3.06
12
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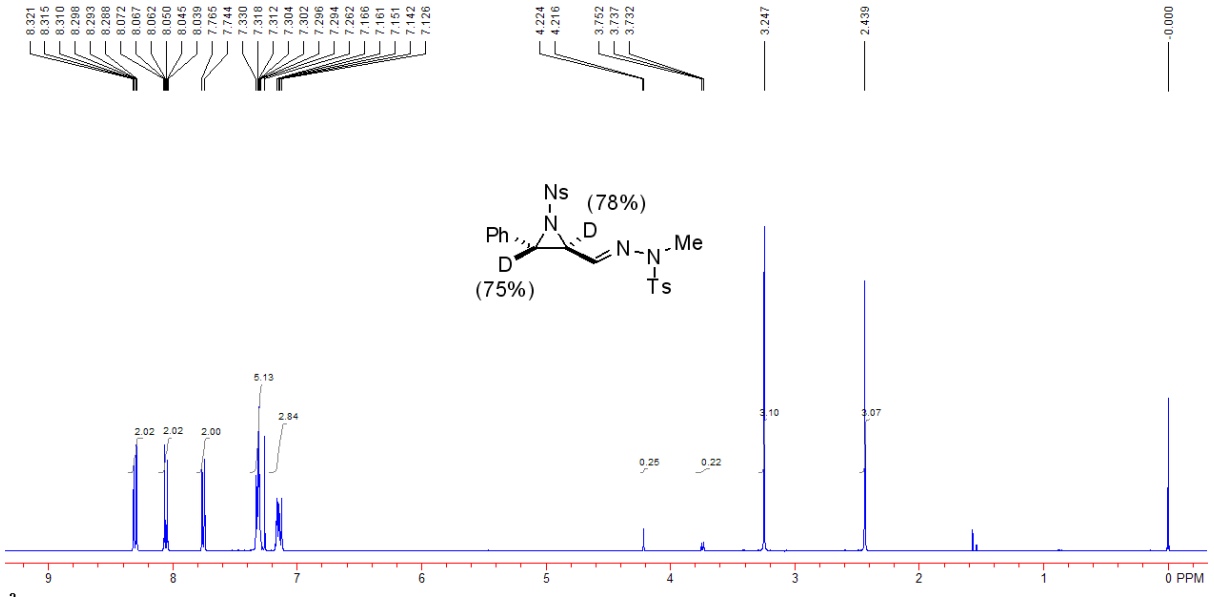
PPM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7.166
7.161
7.151
7.142
7.126
4.224
4.216
3.752
3.737
3.732
3.247
2.439
0.000
Ns
N
(78%)
Ph
D
D
N
N
Me
Ts
(75%)
5.13
2.84
2.02
2.02
2.00
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0.22
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3.07
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7
6
5
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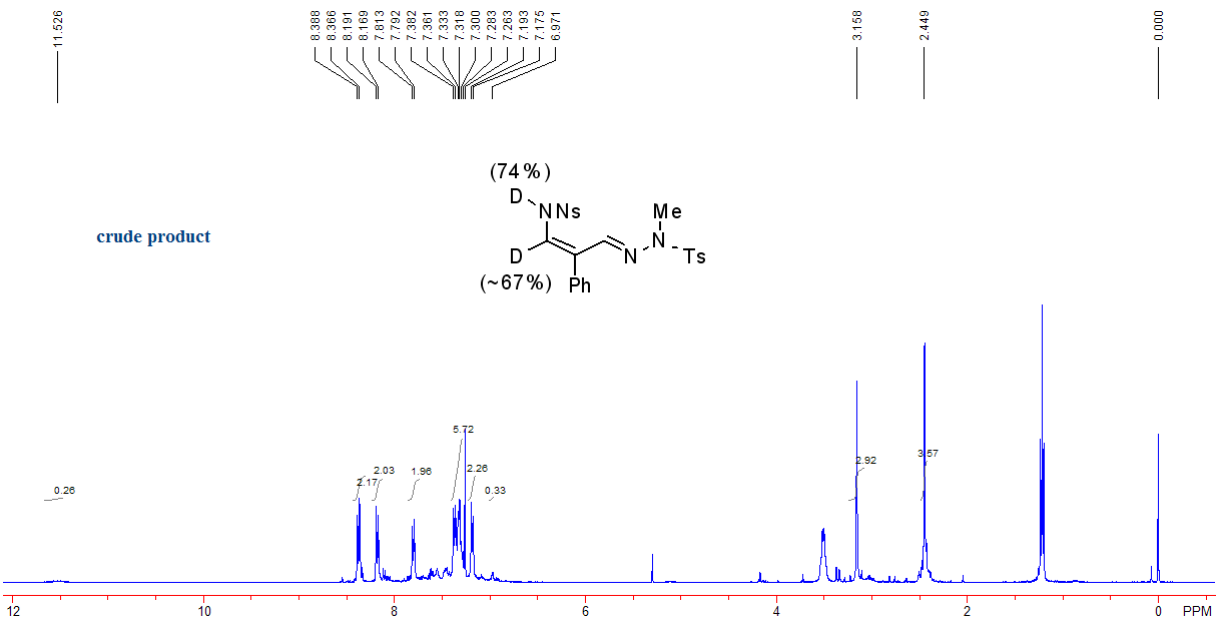
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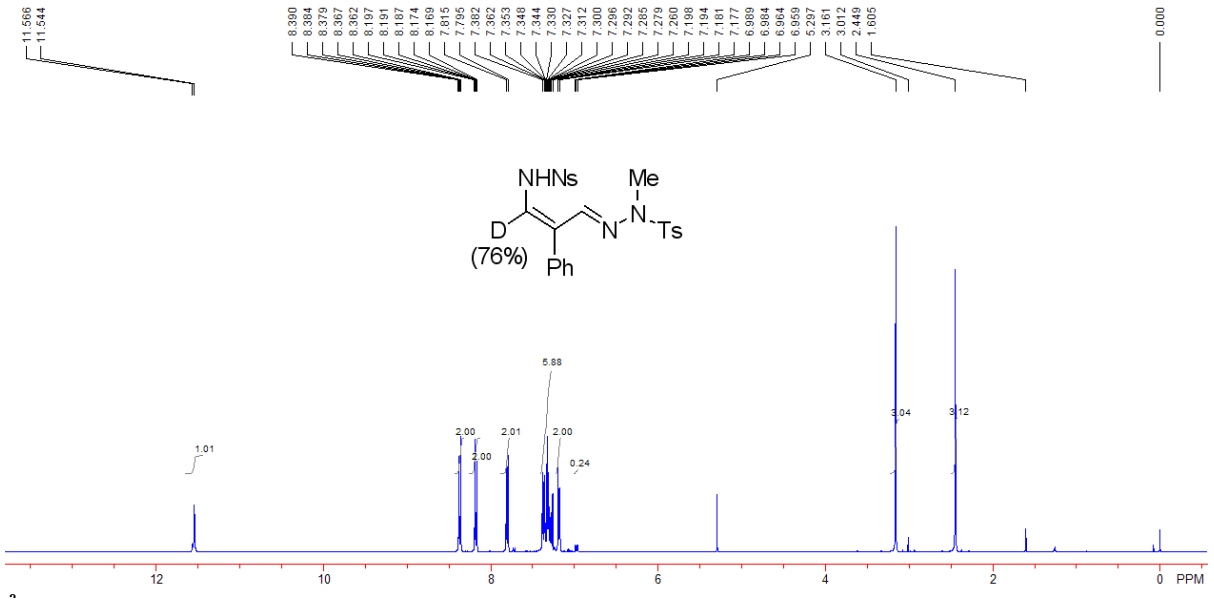
8.191
8.169
7.813
7.792
7.382
7.361
7.333
7.318
7.300
7.283
7.263
7.193
7.175
6.971
3.158
2.449
0.000
(74%)
D
NNs
Me
D
N
N
Ts
(~67%)
Ph
crude product
5.72
2.03
2.17
1.96
2.26
0.33
0.26
2.92
3.57
12
10
8
6
4
2
0 PPM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7.382
7.362
7.353
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7.344
7.330
7.327
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7.300
7.296
7.292
7.285
7.279
7.260
7.198
7.194
7.181
7.177
6.989
6.984
6.964
6.959
5.297
3.161
3.012
2.449
1.605
0.000
NHNs
Me
D
N
N
Ts
(76%)
Ph
5.88
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3.12
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2.01
2.00
2.00
1.01
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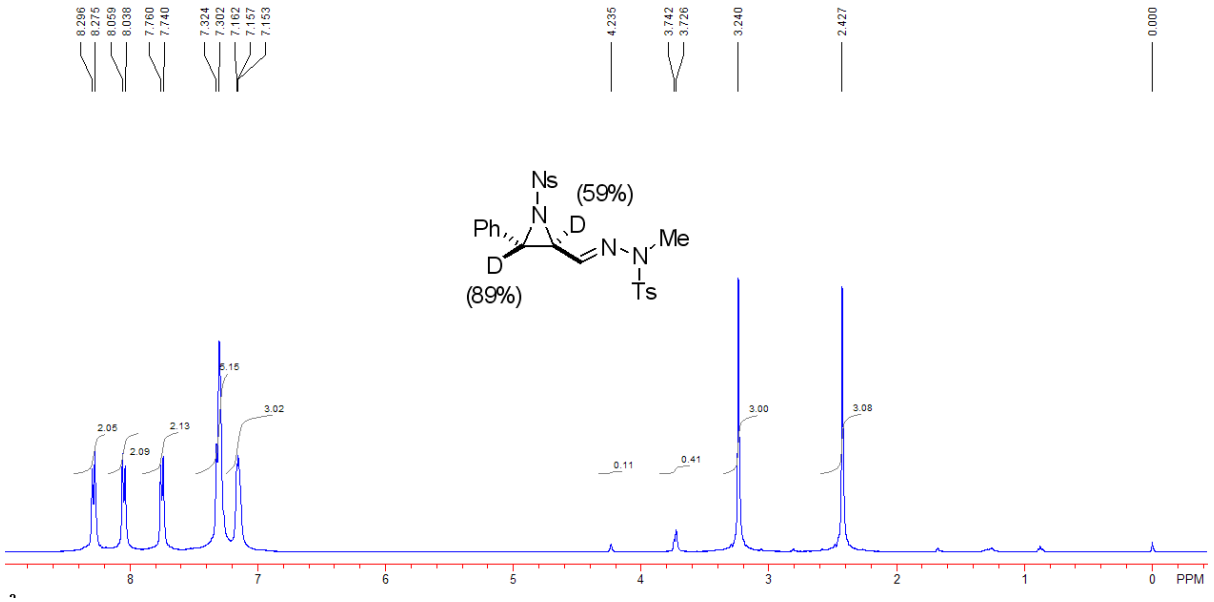
12
10
8
6
4
2
0 PPM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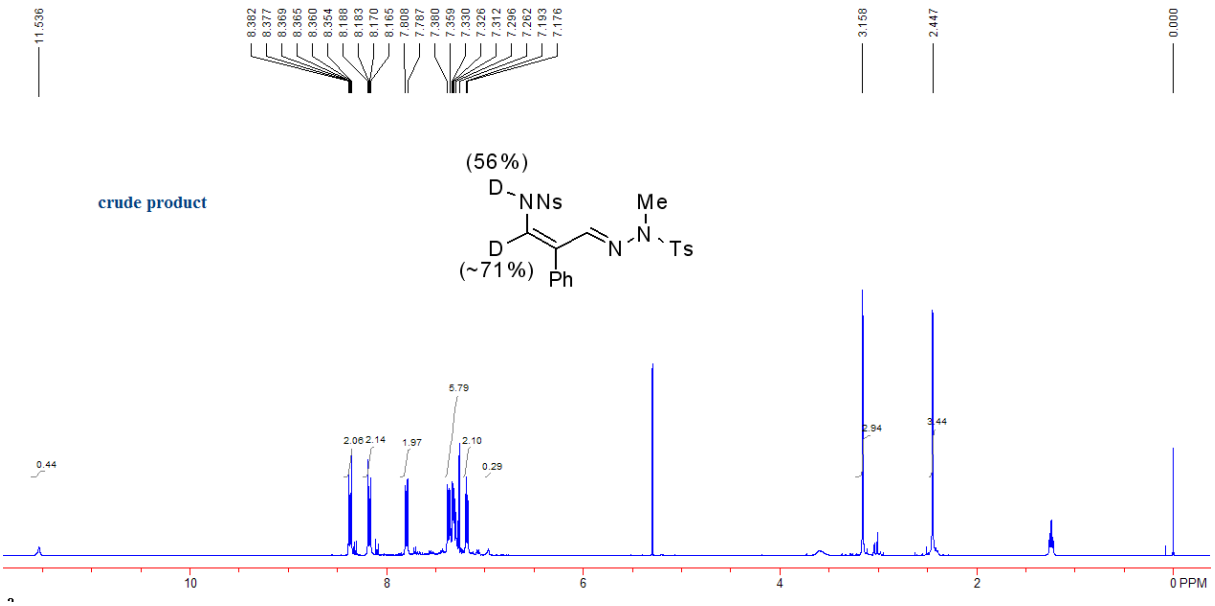
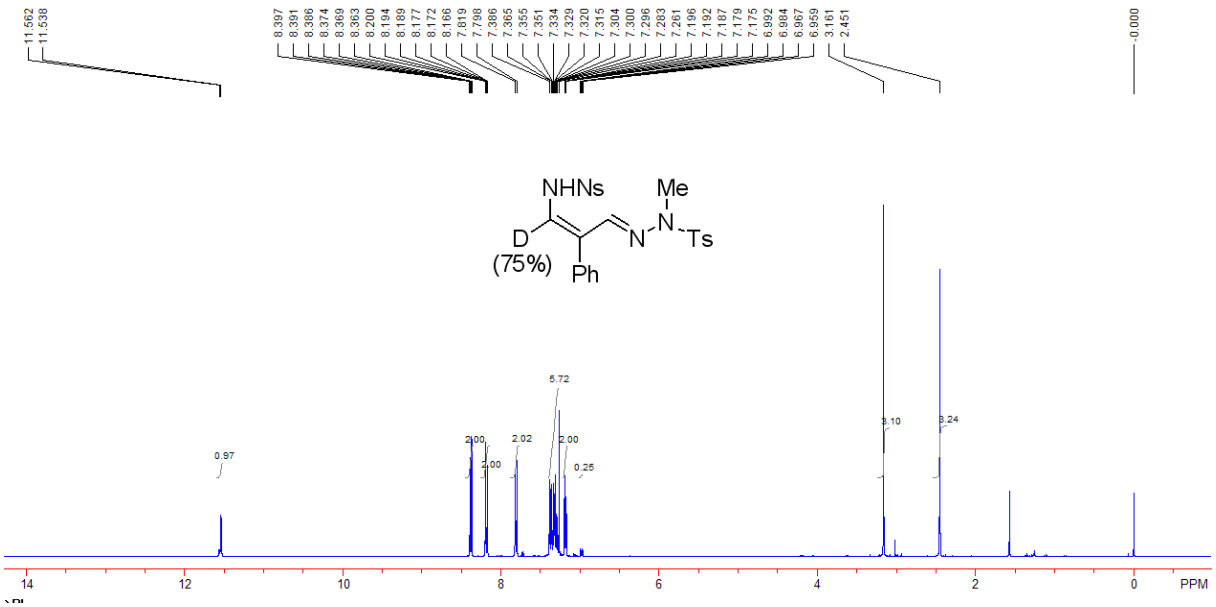
3.726
3.240
2.427
0.000
Ns
(59%)
N
D
Ph
N
N
Me
D
Ts
(89%)
6.15
3.02
2.05
2.09
2.13
0.11
0.41
3.00
3.08
8
7
6
5
4
3
2
1
0
PPM


11.536
8.382
8.377
8.369
8.365
8.360
8.354
8.188
8.183
8.170
8.165
7.808
7.787
7.380
7.359
7.330
7.326
7.312
7.296
7.262
7.193
7.176
3.158
2.447
0.000
crude product
(56%)
D
NNs
Me
N
N
Ts
D
(~71%)
Ph
5.79
2.06
2.14
1.97
2.10
0.29
0.44
2.94
3.44
10
8
6
4
2
0
PPM


11.562
11.538
8.397
8.391
8.386
8.374
8.369
8.363
8.200
8.194
8.189
8.177
8.172
8.166
7.819
7.798
7.386
7.365
7.355
7.351
7.334
7.329
7.320
7.315
7.304
7.300
7.296
7.283
7.261
7.196
7.192
7.187
7.179
7.175
6.992
6.984
6.967
6.959
3.161
2.451
0.000
NHNs
Me
N
N
Ts
D
(75%)
Ph
0.97
2.00
2.00
2.02
5.72
2.00
0.25
3.10
3.24
14
12
10
8
6
4
2
0
PPM