Supporting Information

Chelation-Assisted Rhodium-Catalyzed Direct Amidation with Amidobenziodoxolones: C(sp^2)−H, C(sp^3)−H and Late-Stage Functionalizations

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General Information

Experiments involving moisture and/or air sensitive components were performed in oven-dried glassware. Commercial solvents and reagents were used without further purification unless otherwise noted.

Analytical thin layer chromatography (TLC) was performed using Merck 60 F254 precoated silica gel plate (0.2 mm thickness). Subsequent to elution, plates were visualized using UV radiation (254 nm) on Spectroline Model ENF-24061/F 254 nm. Further visualization was possible by staining with basic solution of potassium permanganate or acidic solution of ceric molybdate, followed by heating on a hot plate. Flash chromatography was performed using Merck silica gel 60 with distilled solvents. Columns were typically packed as slurry and equilibrated with hexane prior to use.

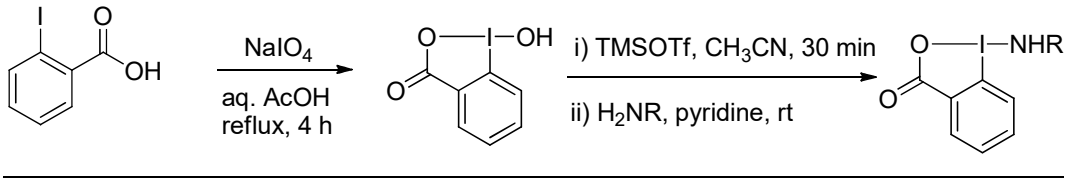
Proton nuclear magnetic resonance (^{1}H NMR) and carbon nuclear magnetic resonance (^{13}C NMR) spectroscopy were performed on Bruker Advance 300, 400 and 500 MHz spectrometers. Chemical shifts ^{1}H NMR spectra are reported as in units of parts per million (ppm) downfield from $SiMe_4$ (δ 0.0) and relative to the signal of chloroform-*d* (*J* = 7.264, singlet). Multiplicities were given as: s (singlet); d (doublet); t (triplet); q (quartet); dd (doublet of doublets); ddd (doublet of doublets of doublets); dddd (doublet of doublets of doublets of doublets); dt (doublet of triplets); m (multiplets) and etc. The number of protons (n) for a given resonance is indicated by nH. Coupling constants are reported as a *J* value in Hz. Carbon nuclear magnetic resonance spectra (^{13}C NMR) are reported as d in units of parts per million (ppm) downfield from $SiMe_4$ (δ 0.0) and relative to the signal of chloroform-*d* (*J* = 77.03, triplet).

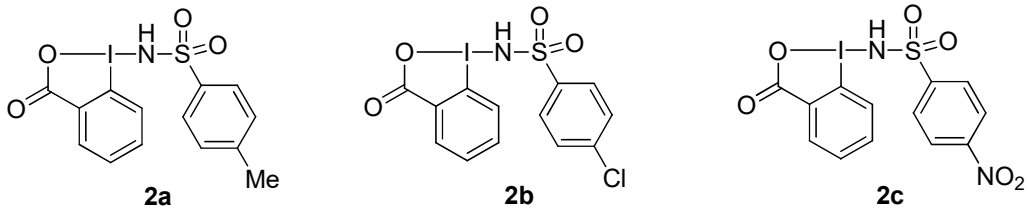
High resolution mass spectral analysis (HRMS) was performed on Water Q-TOF Premier mass spectrometer (Thermo Electron Corporation).

2. Experimental sections

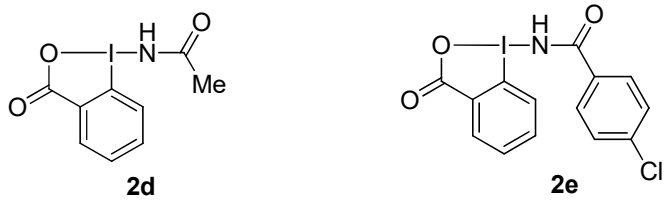
2.1 Procedures for the synthesis of amidobenziodoxolones

(Compounds **2a**−**e** were prepared according to the reported literatures[1,ref. 11a])



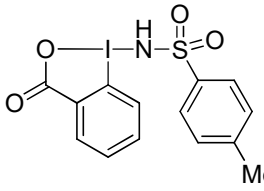


2a **2b** **2c**



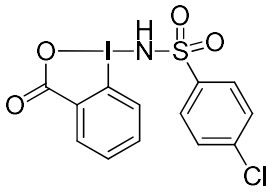
2d **2e**

1-(4-Methylphenylsulfonamido)-1,2-benziodoxol-3(1*H*)-one (2a)[2]



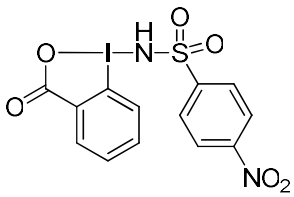
^{1}H NMR (400 MHz, DMSO-d_6): δ 9.61 (s, 1H), 8.06 (dd, J = 7.5, 1.1 Hz, 1H), 7.95 – 7.86 (m, 2H), 7.82 – 7.72 (m, 3H), 7.42 (d, J = 8.1 Hz, 2H), 2.41 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6): δ 167.84, 143.47, 139.73, 135.43, 132.11, 131.65, 131.47, 130.18 × 2, 126.93, 126.77 × 2, 120.57, 21.46. HRMS (ESI): m/z calculated for $C_{14}H_{13}INO_4S$ $[M + H]^+$: 417.9610, found: 417.9616.

1-(4-Chlorophenylsulfonamido)-1,2-benziodoxol-3(1*H*)-one (2b)



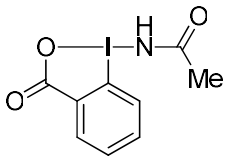
^{1}H NMR (400 MHz, DMSO-d_6): δ 9.71 (s, 1H), 8.05 (dd, J = 7.5, 1.1 Hz, 1H), 7.97 – 7.86 (m, 4H), 7.76 (t, J = 7.1 Hz, 1H), 7.69 – 7.64 (m, 2H). ^{13}C NMR (101 MHz, DMSO-d_6): δ 167.88, 141.42, 137.96, 135.56, 132.19, 131.55, 129.88 × 2, 128.75 × 2, 126.92, 120.55. HRMS (ESI): m/z calculated for $C_{13}H_{10}{}^{35}ClINO_4S$ $[M + H]^+$: 437.9064, found: 437.9062.

1-(4-Nitrophenylsulfonamido)-1,2-benziodoxol-3(1*H*)-one (2c)



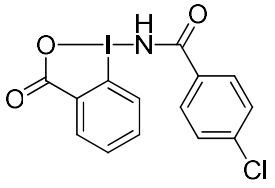
^{1}H NMR (400 MHz, DMSO-d_6): δ 9.92 (s, 1H), 8.44 (d, J = 8.8 Hz, 2H), 8.15 (d, J = 8.8 Hz, 2H), 8.07 (dd, J = 7.5, 1.2 Hz, 1H), 7.97 (t, J = 7.7 Hz, 1H), 7.90 (d, J = 8.2 Hz, 1H), 7.78 (t, J = 7.3 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-d_6): δ 167.92, 150.09, 147.91, 135.73, 132.27, 131.60, 131.40, 128.43 × 2, 126.90, 125.13 × 2, 120.54. HRMS (ESI): m/z calculated for $C_{13}H_{10}IN_2O_6S$ $[M + H]^+$: 448.9304, found: 448.9301.

1-Acetamido-1,2-benziodoxol-3(1*H*)-one (2d)[2]



^{1}H NMR (400 MHz, DMSO-d_6): δ 9.63 (s, 1H), 8.07 (dd, J = 7.5, 1.3 Hz, 1H), 7.91 – 7.83 (m, 1H), 7.73 (t, J = 7.5 Hz, 1H), 7.60 (d, J = 8.1 Hz, 1H), 2.27 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6): δ 173.13, 167.72, 135.10, 132.66, 131.96, 131.15, 126.35, 118.76, 21.87. HRMS (ESI): m/z calculated for $C_9H_9INO_3$ $[M + H]^+$: 305.9627, found: 305.9628.

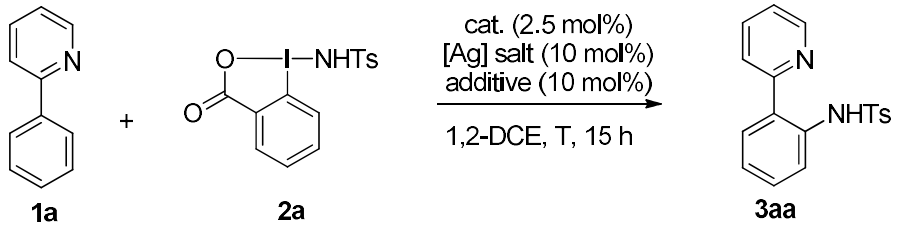
1-(4-Chlorobenzamido)-1,2-benziodoxol-3(1*H*)-one (2e)[2]



^{1}H NMR (400 MHz, DMSO-d_6): δ 10.27 (s, 1H), 8.10 (d, J = 7.2 Hz, 1H), 8.05 (d, J = 8.1 Hz, 2H), 7.87 (d, J = 7.2 Hz, 1H), 7.75 (t, J = 7.2 Hz, 1H), 7.67 (d, J = 8.1 Hz, 2H), 7.61 (d, J = 8.1 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-d_6): δ 168.65, 167.90, 137.82, 135.45, 132.39, 132.12, 131.30, 130.87 × 2, 130.37, 129.34 × 2, 126.41, 118.89. HRMS (ESI): m/z calculated for $C_{14}H_{10}{}^{35}ClINO_3$ $[M + H]^+$: 401.9394, found: 410.9389.

2.2. General procedures for C−H amidation

Table S1. Optimization studies for C−H amidation of (hetero)arenes

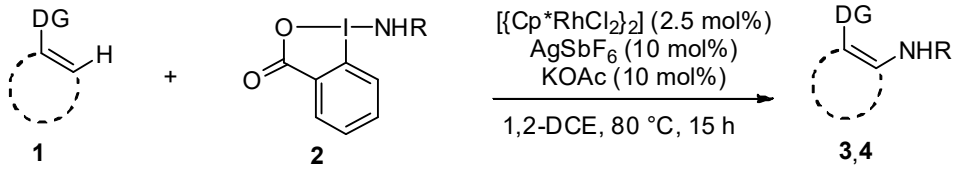


1a 2a 3aa

Entry	cat.	[Ag] salt	additive	T (°C)	yield (%)
1	[{Cp*RhCl$_2$}$_2$]	AgSbF$_6$	-	80	84
2	[{Cp*RhCl$_2$}$_2$]	AgSbF$_6$	KOAc	80	94
3	[{Cp*RhCl$_2$}$_2$]	-	KOAc	80	73
4	[{Cp*RhCl$_2$}$_2$]	AgSbF$_6$	KOAc	60	75
5	-	AgSbF$_6$	KOAc	80	*n.d.*
6	[{Cp*IrCl$_2$}$_2$]	AgNTf$_2$	KOAc	80	29
7	[{Ru(*p*-cymene)Cl$_2$}$_2$]	AgSbF$_6$	KOAc	80	9
8[a]	[Cp*Co(CO)I$_2$]	AgSbF$_6$	KOAc	80	27
9[a]	[Cp*Co(CO)I$_2$]	AgPF$_6$	KOAc	80	31

Reaction conditions: **1a** (31.0 mg, 0.2 mmol, 1.0 equiv), **2a** (100.1 mg, 0.24 mmol, 1.2 equiv), cat. (0.005 mmol, 2.5 mol%), [Ag] salt (0.02 mmol, 10 mol%), KOAc (2.0 mg, 0.02 mmol, 10 mol%), and 1,2-dichloroethane (1.0 mL) at T °C for 15 h. Isolated yields. [a] {Co^{III}} (5.0 mol%) was employed. *n.d.* = not determined.

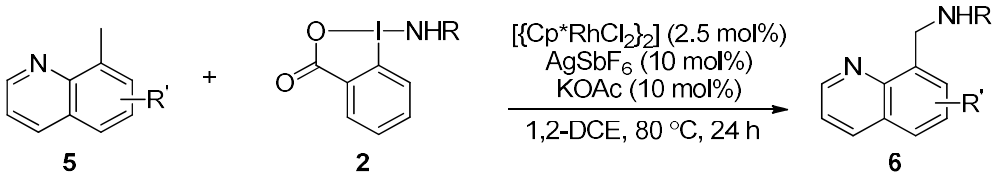
Typical procedure A for C−H amidation of (hetero)arenes and alkenes



1 2 3,4

A 8 mL screw-cap vial was charged with substrate **1** (1.0 equiv, 0.2 mmol), amide **2** (1.2 equiv, 0.24 mmol), [{Cp*RhCl$_2$}$_2$] (3.1 mg, 0.005 mmol, 2.5 mol%), AgSbF$_6$ (6.9 mg, 0.02 mmol, 10 mol%), KOAc (2.0 mg, 0.02 mmol, 10 mol%), and 1,2-dichloroethane (1.0 mL). The vial was carefully blown with nitrogen for 30 seconds and placed into preheated oil bath at 80 °C with stirring for 15 h. After cooling down, the mixture was diluted with CH_2Cl_2 (10 mL) and sequentially washed with sat. aq. $NaHCO_3$ (5 mL). The layer was separated and the aqueous layer was extracted with CH_2Cl_2 (10 mL × 3). The combined organic layers were rinsed with sat. aq. NaCl (10 mL), dried over $MgSO_4$, and concentrated under reduced pressure. The resultant residue was purified by flash chromatography (hexane/EtOAc) on silica gel to afford the amidation product **3** or **4**.

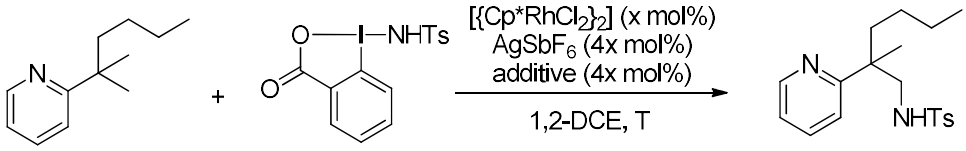
Typical procedure B for C−H amidation of 8-methylquinolines



5 2 6

A 8 mL screw-cap vial was charged with 8-methylquinoline **5** (1.0 equiv, 0.2 mmol), amide **2** (1.2 equiv, 0.24 mmol), [{Cp*RhCl$_2$}$_2$] (3.1 mg, 0.005 mmol, 2.5 mol%), AgSbF$_6$ (6.9 mg, 0.02 mmol, 10 mol%), KOAc (2.0 mg, 0.02 mmol, 10 mol%), and 1,2-dichloroethane (1.0 mL). The vial was carefully blown with nitrogen for 30 seconds and placed into preheated oil bath at 80 °C with stirring for 24 h. After cooling down, the mixture was diluted with CH_2Cl_2 (10 mL) and sequentially washed with sat. aq. $NaHCO_3$ (5 mL). The layer was separated and the aqueous layer was extracted with CH_2Cl_2 (10 mL × 3). The combined organic layers were rinsed with sat. aq. NaCl (10 mL), dried over $MgSO_4$, and concentrated under reduced pressure. The resultant residue was purified by flash chromatography (hexane/EtOAc) on silica gel to afford the amidation product **6**.

Table S2. Optimization studies for C−H amidation of 2-alkylpyridines

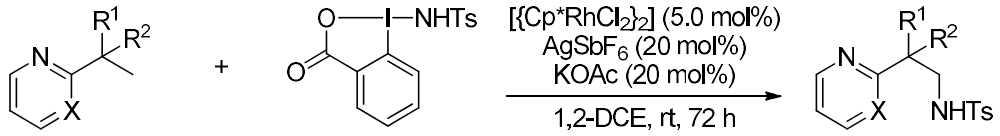


5j **2a** **6ja**

Entry	x	additive	T (°C)	Time (h)	yield (%)
1	2.5	KOAc	80	24	18
2	5.0	KOAc	80	24	33
3	5.0	KOAc	40	24	51
4	7.5	KOAc	rt	24	45
5	5.0	KOAc	rt	48	53
6	5.0	KOAc	rt	72	59
7	5.0	AgOAc	rt	72	52
8	5.0	CsOPiv	rt	72	29
9	5.0	LiOAc	rt	72	50
10	5.0	NaOAc	rt	72	55

Reaction conditions: **5j** (35.5 mg, 0.2 mmol, 1.0 equiv), **2a** (100.1 mg, 0.24 mmol, 1.2 equiv), [{Cp*RhCl$_2$}$_2$] (0.002x mmol, x mol%), AgSbF$_6$ (0.008x mmol, 4x mol%), KOAc (0.008x mmol, 4x mol%), and 1,2-dichloroethane (1.0 mL) at T °C. Isolated yields.

Typical procedure C for C−H amidation of 2-alkylpyridines

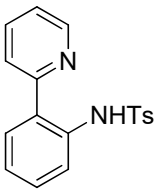


5 **2a** **6**

A 8 mL screw-cap vial was charged with 2-alkylpyridine **5** (1.0 equiv, 0.2 mmol), amide **2a** (100.1 mg, 1.2 equiv, 0.24 mmol), [{Cp*RhCl$_2$}$_2$] (6.2 mg, 0.01 mmol, 5.0 mol%), AgSbF$_6$ (13.7 mg, 0.04 mmol, 20 mol%), KOAc (4.0 mg, 0.04 mmol, 20 mol%), and 1,2-dichloroethane (1.0 mL). The vial was carefully blown with nitrogen for 30 seconds and stirred at room temperature for 72 h. Then the mixture was diluted with CH_2Cl_2 (10 mL) and sequentially washed with sat. aq. $NaHCO_3$ (5 mL). The layer was separated and the aqueous layer was extracted with CH_2Cl_2 (10 mL × 3). The combined organic layers were rinsed with sat. aq. NaCl (10 mL), dried over $MgSO_4$, and concentrated under

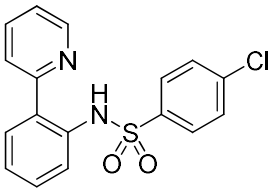
reduced pressure. The resultant residue was purified by flash chromatography (hexane/EtOAc) on silica gel to afford the amidation product **6**.

4-Methyl-*N*-(2-(pyridin-2-yl)phenyl)benzenesulfonamide (3aa)



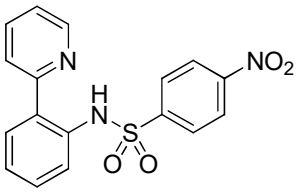
Following typical procedure A, **3aa** was obtained as a white solid (60.8 mg, 0.187 mmol, 94%). mp: 88–90 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 12.15 (s, 1H), 8.71 – 8.52 (m, 1H), 7.77 – 7.62 (m, 2H), 7.53 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.36 (ddd, *J* = 12.8, 11.5, 4.8 Hz, 4H), 7.24 (ddd, *J* = 7.5, 4.9, 1.2 Hz, 1H), 7.19 – 7.12 (m, 1H), 6.96 (d, *J* = 8.0 Hz, 2H), 2.27 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 157.09, 147.36, 142.95, 137.46, 136.83, 136.42, 130.13, 129.13 × 2, 128.51, 127.47, 126.74 × 2, 124.68, 123.41, 122.26, 122.08, 21.40. HRMS (ESI): m/z calculated for $C_{18}H_{17}N_2O_2S$ $[M + H]^+$: 325.1011, found: 325.1017.

4-Chloro-*N*-(2-(pyridin-2-yl)phenyl)benzenesulfonamide (3ab)



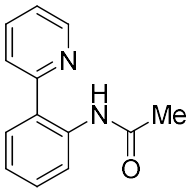
Following typical procedure A, **3ab** was obtained as a white solid (65.2 mg, 0.189 mmol, 95%). mp: 141–143 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 12.12 (s, 1H), 8.62 – 8.56 (m, 1H), 7.72 (ddd, *J* = 15.3, 7.9, 1.5 Hz, 2H), 7.54 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.41 – 7.33 (m, 4H), 7.28 – 7.24 (m, 1H), 7.20 (td, *J* = 7.7, 1.2 Hz, 1H), 7.17 – 7.04 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 156.90, 147.39, 138.70, 137.66, 136.28, 130.27, 128.71 × 2, 128.57, 128.10 × 2, 128.01, 125.33, 124.18, 122.37, 122.25. HRMS (ESI): m/z calculated for $C_{17}H_{14}ClN_2O_2S$ $[M + H]^+$: 345.0465, found: 345.0474.

4-Nitro-*N*-(2-(pyridin-2-yl)phenyl)benzenesulfonamide (3ac)



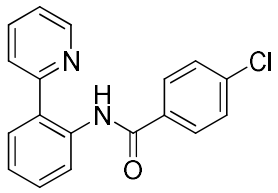
Following a modified procedure A, as the reaction was performed at 100 °C for 24 h, **3ac** was obtained as a yellow solid (60.2 mg, 0.169 mmol, 85%). mp: 132–133 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 12.46 (s, 1H), 8.61 (d, *J* = 4.6 Hz, 1H), 7.97 (d, *J* = 8.7 Hz, 2H), 7.79 – 7.67 (m, 2H), 7.61 (d, *J* = 8.7 Hz, 2H), 7.56 (d, *J* = 7.8 Hz, 1H), 7.40 (dd, *J* = 12.5, 4.6 Hz, 2H), 7.29 (dd, *J* = 7.4, 5.1 Hz, 1H), 7.23 (t, *J* = 7.4 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 156.63, 149.72, 147.38, 144.88, 137.87, 135.82, 130.49, 128.62, 127.92 × 2, 127.65, 125.73, 124.11, 123.64 × 2, 122.47, 122.22. HRMS (ESI): m/z calculated for $C_{17}H_{14}N_3O_4S$ $[M + H]^+$: 356.0705, found: 356.0706.

***N*-(2-(Pyridin-2-yl)phenyl)acetamide (3ad)**



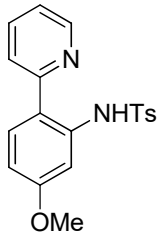
Following a modified procedure A, as the reaction was performed at 100 °C for 24 h, **3ad** was obtained as a yellow oil (21.7 mg, 0.102 mmol, 51%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 12.09 (s, 1H), 8.65 (d, *J* = 4.6 Hz, 1H), 8.53 (d, *J* = 8.2 Hz, 1H), 7.84 (td, *J* = 7.9, 1.8 Hz, 1H), 7.74 (d, *J* = 8.2 Hz, 1H), 7.64 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.46 – 7.36 (m, 1H), 7.31 – 7.27 (m, 1H), 7.16 (t, *J* = 7.6 Hz, 1H), 2.18 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 168.58, 158.38, 147.44, 137.74, 137.56, 130.04, 128.84, 125.61, 123.46, 123.14, 121.95, 121.89, 25.23. HRMS (ESI): m/z calculated for $C_{13}H_{13}N_2O$ $[M + H]^+$: 213.1028, found: 213.1030.

4-Chloro-*N*-(2-(pyridin-2-yl)phenyl)benzamide (3ae)



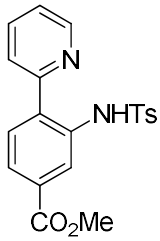
Following a modified procedure A, as the reaction was run for 24 h, **3ae** was obtained as a white solid (32.9 mg, 0.107 mmol, 53%). mp: 159–160 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 13.39 (s, 1H), 8.77 (d, J = 8.3 Hz, 1H), 8.65 (d, J = 4.4 Hz, 1H), 7.98 (d, J = 8.3 Hz, 2H), 7.89 – 7.78 (m, 2H), 7.74 (d, J = 7.8 Hz, 1H), 7.48 (d, J = 8.1 Hz, 3H), 7.34 – 7.27 (m, 1H), 7.21 (t, J = 7.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 164.47, 158.26, 147.20, 138.02, 137.97, 137.74, 134.25, 130.34, 128.87 × 2, 128.80 × 2, 128.75, 125.38, 123.74, 123.01, 122.08, 121.86. HRMS (ESI): m/z calculated for $C_{18}H_{14}{}^{35}ClN_2O$ $[M + H]^+$: 309.0795, found: 309.0793.

***N*-(5-Methoxy-2-(pyridin-2-yl)phenyl)-4-methylbenzenesulfonamide (3ba)**



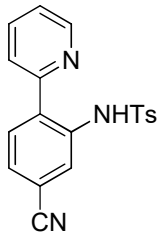
Following typical procedure A, **3ba** was obtained as a white solid (65.4 mg, 0.185 mmol, 92%). mp: 125–126 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 12.76 (s, 1H), 8.60 – 8.52 (m, 1H), 7.68 (td, J = 7.9, 1.9 Hz, 1H), 7.52 – 7.44 (m, 3H), 7.41 (d, J = 8.2 Hz, 1H), 7.24 (d, J = 2.6 Hz, 1H), 7.18 (ddd, J = 7.4, 5.0, 0.9 Hz, 1H), 7.01 (d, J = 8.2 Hz, 2H), 6.65 (dd, J = 8.8, 2.6 Hz, 1H), 3.81 (s, 3H), 2.27 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 160.87, 157.06, 147.03, 143.08, 138.77, 137.42, 136.59, 129.44, 129.21 × 2, 126.88 × 2, 121.29 × 2, 118.97, 110.81, 106.84, 55.45, 21.42. HRMS (ESI): m/z calculated for $C_{19}H_{19}N_2O_3S$ $[M + H]^+$: 355.1116, found: 355.1115.

Methyl 3-(4-methylphenylsulfonamido)-4-(pyridin-2-yl)benzoate (3ca)



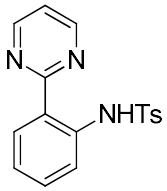
Following typical procedure A, **3ca** was obtained as a pale yellow solid (73.7 mg, 0.193 mmol, 96%). mp: 163–164 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 12.15 (s, 1H), 8.68 – 8.62 (m, 1H), 8.35 (d, J = 1.6 Hz, 1H), 7.82 (dd, J = 8.2, 1.7 Hz, 1H), 7.75 (td, J = 7.9, 1.8 Hz, 1H), 7.61 (d, J = 8.2 Hz, 1H), 7.47 (d, J = 8.1 Hz, 1H), 7.42 (d, J = 8.2 Hz, 2H), 7.35 – 7.27 (m, 1H), 6.99 (d, J = 8.1 Hz, 2H), 3.95 (s, 3H), 2.28 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 166.18, 156.03, 147.57, 143.27, 137.72, 137.01, 136.16, 131.49, 131.03, 129.66, 129.25, 128.58, 126.81, 126.41, 125.47, 124.20, 122.88, 122.76, 52.43, 21.41. HRMS (ESI): m/z calculated for $C_{20}H_{19}N_2O_4S$ $[M + H]^+$: 383.1066, found: 383.1070.

***N*-(5-Cyano-2-(pyridin-2-yl)phenyl)-4-methylbenzenesulfonamide (3da)**



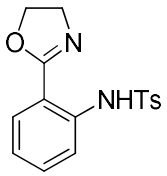
Following a modified procedure A, as $[\{Cp^*RhCl_2\}_2]$ (4.0 mol%), $AgSbF_6$ (16 mol%), and KOAc (16 mol%) were employed, **3da** was obtained as a yellow solid (55.8 mg, 0.160 mmol, 80%). mp: 204–205 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 12.47 (s, 1H), 8.69 (d, J = 4.0 Hz, 1H), 7.97 (s, 1H), 7.83 (t, J = 7.4 Hz, 1H), 7.67 (d, J = 8.2 Hz, 1H), 7.55 (d, J = 8.1 Hz, 1H), 7.49 (d, J = 8.1 Hz, 2H), 7.38 (dd, J = 12.6, 7.6 Hz, 2H), 7.08 (d, J = 7.9 Hz, 2H), 2.32 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 155.43, 147.70, 143.71, 138.02, 136.20, 129.96, 129.54 × 2, 129.14, 127.24, 126.83 × 2, 125.29, 123.34, 122.72, 118.02, 113.61, 21.47. HRMS (ESI): m/z calculated for $C_{19}H_{16}N_3O_2S$ $[M + H]^+$: 350.0963, found: 350.0967.

4-Methyl-*N*-(2-(pyrimidin-2-yl)phenyl)benzenesulfonamide (3ea)



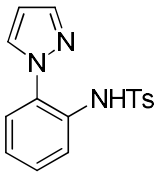
Following a modified procedure A, as the reaction was performed at 100 °C, **3ea** was obtained as a white solid (30.2 mg, 0.093 mmol, 46%). mp: 126–128 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 12.48 (s, 1H), 8.81 (d, *J* = 4.9 Hz, 2H), 8.47 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.69 (d, *J* = 8.3 Hz, 1H), 7.61 (d, *J* = 8.3 Hz, 2H), 7.44 – 7.34 (m, 1H), 7.24 (t, *J* = 4.9 Hz, 1H), 7.17 – 7.12 (m, 1H), 7.10 (d, *J* = 8.2 Hz, 2H), 2.30 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 164.36, 156.41 × 2, 143.40, 138.80, 136.73, 132.10, 130.66, 129.40 × 2, 127.05 × 2, 123.62, 123.57, 120.47, 118.76, 21.44. HRMS (ESI): m/z calculated for $C_{17}H_{16}N_3O_2S$ $[M + H]^+$: 326.0963, found: 326.0967.

_N_-(2-(4,5-Dihydrooxazol-2-yl)phenyl)-4-methylbenzenesulfonamide (3fa)



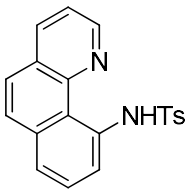
Following typical procedure A, **3fa** was obtained as a white solid (46.2 mg, 0.146 mmol, 73%). mp: 200–201 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 12.34 (s, 1H), 7.74 (t, *J* = 6.7 Hz, 3H), 7.65 (d, *J* = 8.4 Hz, 1H), 7.39 – 7.28 (m, 1H), 7.20 (d, *J* = 8.1 Hz, 2H), 6.99 (t, *J* = 7.6 Hz, 1H), 4.35 (t, *J* = 9.5 Hz, 2H), 4.13 (t, *J* = 9.5 Hz, 2H), 2.35 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 164.51, 143.53, 139.13, 136.97, 132.37, 129.51 × 2, 129.35, 127.22 × 2, 122.29, 117.82, 113.55, 66.45, 54.48, 21.50. HRMS (ESI): m/z calculated for $C_{16}H_{17}N_2O_3S$ $[M + H]^+$: 317.0960, found: 317.0958.

_N_-(2-(1*H*-Pyrazol-1-yl)phenyl)-4-methylbenzenesulfonamide (3ga)



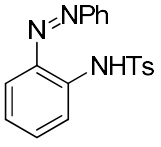
Following typical procedure A, **3ga** was obtained as a white solid (52.8 mg, 0.168 mmol, 84%). mp: 93–95 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.04 (s, 1H), 7.75 (dd, *J* = 9.8, 4.8 Hz, 2H), 7.36 – 7.24 (m, 4H), 7.23 – 7.10 (m, 2H), 7.01 (d, *J* = 8.1 Hz, 2H), 6.36 (t, *J* = 2.1 Hz, 1H), 2.30 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 143.23, 141.13, 136.07, 131.26, 130.18, 129.31, 129.29 × 2, 127.93, 126.60 × 2, 125.85, 125.44, 121.83, 107.21, 21.44. HRMS (ESI): m/z calculated for $C_{16}H_{16}N_3O_2S$ $[M + H]^+$: 314.0963, found: 314.0967.

_N_-(Benzo[*h*]quinolin-10-yl)-4-methylbenzenesulfonamide (3ha)



Following typical procedure A, **3ha** was obtained as a yellow solid (65.4 mg, 0.188 mmol, 94%). mp: 168–170 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 15.28 (s, 1H), 8.95 (dd, *J* = 4.4, 1.5 Hz, 1H), 8.21 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.91 (dd, *J* = 7.5, 1.1 Hz, 1H), 7.80 (d, *J* = 8.2 Hz, 2H), 7.70 (d, *J* = 8.8 Hz, 1H), 7.65 – 7.46 (m, 4H), 7.08 (d, *J* = 8.0 Hz, 2H), 2.24 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 147.39, 145.80, 143.17, 138.60, 137.34, 136.73, 135.17, 129.40 × 2, 129.08, 128.64, 127.30, 127.24 × 2, 125.40, 122.80, 121.20, 117.36, 116.15, 21.39. HRMS (ESI): m/z calculated for $C_{20}H_{17}N_2O_2S$ $[M + H]^+$: 349.1011, found: 349.1009.

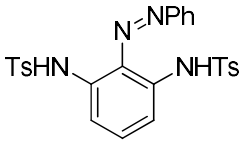
4-Methyl-_N_-(2-(phenyldiazenyl)phenyl)benzenesulfonamide (3ia)



Following typical procedure A, **3ia** was obtained as an orange solid (36.5 mg, 0.104 mmol, 52%). mp: 107–109 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.75 (s, 1H), 7.85 – 7.80 (m, 2H), 7.74 (ddd, *J* = 13.2, 8.2, 1.3 Hz, 2H), 7.68 (d, *J* = 8.2 Hz, 2H), 7.59 – 7.48 (m, 3H), 7.44 – 7.35 (m, 1H), 7.21 – 7.09 (m, 3H), 2.30 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 151.97, 144.00, 140.05, 136.21, 134.50, 132.52, 131.70, 129.65 × 2, 129.30 × 2, 127.15 × 2, 124.28, 122.80 × 2, 122.73, 120.19, 21.49. HRMS (ESI): m/z calculated for $C_{19}H_{18}N_3O_2S$

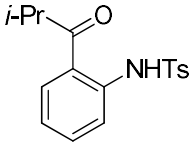
$[M + H]^+$: 352.1120, found: 352.1118.

_N_,_N_'-(2-(Phenyldiazenyl)-1,3-phenylene)bis(4-methylbenzenesulfonamide) (3ia')



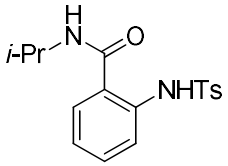
Following typical procedure A, **3ia'** was obtained as a yellow solid (19.9 mg, 0.038 mmol, 19%). mp: 207–209 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.40 (s, 2H), 7.75 (dd, J = 6.5, 3.2 Hz, 2H), 7.68 (d, J = 8.3 Hz, 4H), 7.64 – 7.53 (m, 3H), 7.30 – 7.22 (m, 3H), 7.18 (d, J = 8.2 Hz, 4H), 2.35 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 151.02, 144.32, 136.15, 135.32, 134.33, 132.28, 129.78 × 4, 129.70 × 2, 127.18 × 4, 126.34, 122.51 × 2, 113.12 × 2, 21.54 × 2. HRMS (ESI): m/z calculated for $C_{26}H_{25}N_4O_4S_2$ $[M + H]^+$: 521.1317, found: 521.1319.

_N_-(2-Isobutyrylphenyl)-4-methylbenzenesulfonamide (3ja)



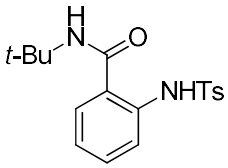
Following typical procedure A, **3ja** was obtained as a white solid (11.4 mg, 0.036 mmol, 18%). mp: 98–99 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 11.39 (s, 1H), 7.85 – 7.77 (m, 1H), 7.71 (t, J = 8.6 Hz, 3H), 7.51 – 7.41 (m, 1H), 7.20 (d, J = 8.2 Hz, 2H), 7.13 – 7.03 (m, 1H), 3.51 (hept, J = 6.7 Hz, 1H), 2.35 (s, 3H), 1.09 (d, J = 6.8 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 208.65, 143.75, 140.41, 136.77, 134.46, 130.71, 129.56 × 2, 127.25 × 2, 122.79, 121.76, 120.20, 36.07, 21.48, 19.21 × 2. HRMS (ESI): m/z calculated for $C_{17}H_{20}NO_3S$ $[M + H]^+$: 318.1164, found: 318.1163.

_N_-Isopropyl-2-(4-methylphenylsulfonamido)benzamide (3la)



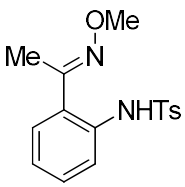
Following a modified procedure A, as the reaction was run for 24 h, **3la** was obtained as a white solid (46.8 mg, 0.141 mmol, 70%). mp: 106–107 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.82 (s, 1H), 7.67 (dd, J = 8.1, 3.9 Hz, 3H), 7.37 (dd, J = 12.1, 4.8 Hz, 1H), 7.33 (d, J = 7.9 Hz, 1H), 7.17 (d, J = 8.1 Hz, 2H), 7.03 (t, J = 7.6 Hz, 1H), 5.90 (d, J = 6.4 Hz, 1H), 4.27 – 4.01 (m, 1H), 2.34 (s, 3H), 1.19 (d, J = 6.6 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 167.55, 143.46, 138.82, 136.76, 132.39, 129.51 × 2, 127.18 × 2, 126.58, 123.47, 121.92, 121.51, 42.06, 22.52 × 2, 21.50. HRMS (ESI): m/z calculated for $C_{17}H_{21}N_2O_3S$ $[M + H]^+$: 333.1273, found: 333.1268.

_N_-(*tert*-Butyl)-2-(4-methylphenylsulfonamido)benzamide (3ma)



Following a modified procedure A, as $[\{Cp^*RhCl_2\}_2]$ (4.0 mol%), $AgSbF_6$ (16 mol%), and KOAc (16 mol%) were employed and the reaction was performed at 100 °C, **3ma** was obtained as a white solid (43.5 mg, 0.126 mmol, 63%). mp: 141–143 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.78 (s, 1H), 7.66 (d, J = 8.2 Hz, 3H), 7.38 – 7.32 (m, 1H), 7.29 (dd, J = 7.8, 1.2 Hz, 1H), 7.18 (d, J = 8.1 Hz, 2H), 7.06 – 6.97 (m, 1H), 5.84 (s, 1H), 2.35 (s, 3H), 1.39 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 168.04, 143.40, 138.69, 136.88, 132.16, 129.54 × 2, 127.16 × 2, 126.64, 123.40, 122.92, 121.52, 52.16, 28.66 × 3, 21.49. HRMS (ESI): m/z calculated for $C_{18}H_{23}N_2O_3S$ $[M + H]^+$: 347.1429, found: 347.1437.

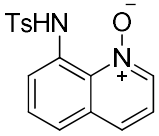
(*E*)-*N*-(2-(1-(Methoxyimino)ethyl)phenyl)-4-methylbenzenesulfonamide (3na)



Following a modified procedure A, as $[\{Cp^*RhCl_2\}_2]$ (4.0 mol%), $AgSbF_6$ (16 mol%), and KOAc (16 mol%) were employed, **3na** was obtained as a white solid

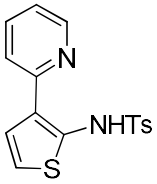
(44.8 mg, 0.141 mmol, 70%). mp: 134–135 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.75 (s, 1H), 7.64 (d, *J* = 8.2 Hz, 1H), 7.58 (d, *J* = 8.2 Hz, 2H), 7.28 (ddd, *J* = 17.0, 8.6, 1.2 Hz, 2H), 7.18 (d, *J* = 8.2 Hz, 2H), 7.09 (dd, *J* = 11.1, 4.2 Hz, 1H), 4.06 (s, 3H), 2.35 (s, 3H), 2.00 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 155.93, 143.45, 136.51, 135.81, 129.69, 129.39 × 2, 128.44, 127.16 × 2, 124.54, 124.12, 121.86, 62.58, 21.47, 13.13. HRMS (ESI): m/z calculated for $C_{16}H_{19}N_2O_3S$ $[M + H]^+$: 319.1116, found: 319.1118.

8-(4-Methylphenylsulfonamido)quinoline 1-oxide (3oa)



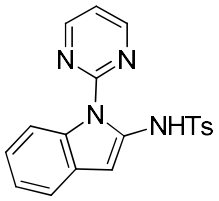
Following typical procedure A, **3oa** was obtained as a yellow solid (51.1 mg, 0.163 mmol, 81%). mp: 164–165 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 14.36 (s, 1H), 8.33 – 8.26 (m, 1H), 7.85 (dd, *J* = 12.6, 4.8 Hz, 3H), 7.70 (d, *J* = 8.4 Hz, 1H), 7.46 (t, *J* = 8.0 Hz, 1H), 7.40 (dd, *J* = 8.2, 1.2 Hz, 1H), 7.23 (dd, *J* = 8.4, 6.2 Hz, 1H), 7.19 (d, *J* = 8.2 Hz, 2H), 2.32 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 143.66, 137.04, 136.70, 133.78, 132.40, 131.10, 129.59 × 2, 129.17, 129.04, 127.37 × 2, 122.30, 120.94, 117.89, 21.48. HRMS (ESI): m/z calculated for $C_{16}H_{15}N_2O_3S$ $[M + H]^+$: 315.0803, found: 315.0805.

4-Methyl-N-(3-(pyridin-2-yl)thiophen-2-yl)benzenesulfonamide (3pa)



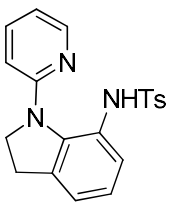
Following a modified procedure A, as MgO (9.7 mg, 0.24 mmol, 1.2 equiv) was added, **3pa** was obtained as a pale brown solid (40.7 mg, 0.123 mmol, 62%). mp: 106–107 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 13.16 (s, 1H), 8.50 (d, *J* = 4.9 Hz, 1H), 7.79 – 7.64 (m, 3H), 7.44 (d, *J* = 8.1 Hz, 1H), 7.14 (t, *J* = 6.8 Hz, 4H), 6.77 (d, *J* = 5.8 Hz, 1H), 2.31 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 153.85, 146.82, 143.53, 142.84, 137.59, 136.53, 129.39 × 2, 127.12 × 2, 123.03, 120.77, 120.61, 120.23, 116.59, 21.47. HRMS (ESI): m/z calculated for $C_{16}H_{15}N_2O_2S_2$ $[M + H]^+$: 331.0575, found: 331.0576.

4-Methyl-*N*-(1-(pyrimidin-2-yl)-1*H*-indol-2-yl)benzenesulfonamide (3qa)



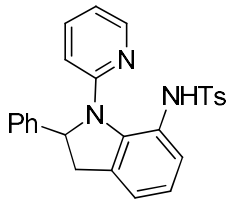
Following a modified procedure A, as MgO (9.7 mg, 0.24 mmol, 1.2 equiv) was added, **3qa** was obtained as a white solid (42.0 mg, 0.115 mmol, 58%). mp: 140–142 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 11.05 (s, 1H), 8.69 (d, *J* = 4.9 Hz, 2H), 8.49 (dd, *J* = 6.0, 3.4 Hz, 1H), 7.61 (d, *J* = 8.3 Hz, 2H), 7.49 (dd, *J* = 6.0, 3.1 Hz, 1H), 7.23 – 7.18 (m, 2H), 7.10 (dd, *J* = 12.6, 6.6 Hz, 3H), 6.64 (s, 1H), 2.29 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 158.05, 157.65 × 2, 143.87, 136.15, 133.59, 133.53, 129.49 × 2, 128.60, 127.08 × 2, 123.07, 122.98, 119.98, 116.37, 115.83, 97.62, 21.44. HRMS (ESI): m/z calculated for $C_{19}H_{17}N_4O_2S$ $[M + H]^+$: 365.1072, found: 365.1074.

4-Methyl-*N*-(1-(pyridin-2-yl)indolin-7-yl)benzenesulfonamide (3ra)



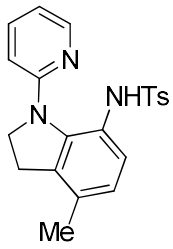
Following typical procedure A, **3ra** was obtained as a white solid (69.7 mg, 0.191 mmol, 95%). mp: 110–112 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.27 (dd, *J* = 4.9, 1.1 Hz, 1H), 7.64 – 7.53 (m, 1H), 7.37 (d, *J* = 7.5 Hz, 1H), 7.10 – 6.90 (m, 6H), 6.80 (dd, *J* = 6.9, 5.3 Hz, 1H), 6.32 (d, *J* = 8.6 Hz, 1H), 3.57 (t, *J* = 8.4 Hz, 2H), 3.00 (t, *J* = 8.4 Hz, 2H), 2.32 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 153.64, 146.27, 142.27, 138.73, 138.08, 137.36, 133.75, 128.72 × 2, 127.48, 126.67 × 2, 123.77, 123.24, 122.78, 114.55, 110.66, 51.86, 28.17, 21.39. HRMS (ESI): m/z calculated for $C_{20}H_{20}N_3O_2S$ $[M + H]^+$: 366.1276, found: 366.1278.

4-Methyl-*N*-(2-phenyl-1-(pyridin-2-yl)indolin-7-yl)benzenesulfonamide (3sa)



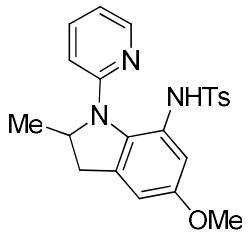
Following typical procedure A, **3sa** was obtained as a pale orange solid (82.6 mg, 0.187 mmol, 94%). mp: 201–202 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 11.57 (s, 1H), 8.36 (dd, *J* = 4.9, 1.4 Hz, 1H), 7.57 – 7.47 (m, 2H), 7.41 (d, *J* = 8.2 Hz, 2H), 7.22 (t, *J* = 7.2 Hz, 1H), 7.14 (t, *J* = 7.4 Hz, 2H), 7.04 (d, *J* = 8.2 Hz, 2H), 6.99 (t, *J* = 7.7 Hz, 1H), 6.91 (d, *J* = 7.2 Hz, 1H), 6.86 (dd, *J* = 7.0, 5.2 Hz, 1H), 6.77 (d, *J* = 7.4 Hz, 2H), 6.47 (d, *J* = 8.6 Hz, 1H), 5.13 (d, *J* = 8.9 Hz, 1H), 3.81 (dd, *J* = 15.8, 10.4 Hz, 1H), 2.81 (d, *J* = 15.8 Hz, 1H), 2.32 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 154.84, 146.21, 142.57, 142.53, 139.04, 138.61, 137.08, 131.83, 129.38 × 2, 129.02 × 2, 127.43, 126.79 × 2, 125.21, 124.79 × 2, 124.14, 123.94, 122.26, 115.32, 110.94, 67.42, 39.02, 21.59. HRMS (ESI): m/z calculated for $C_{26}H_{24}N_3O_2S$ $[M + H]^+$: 442.1589, found: 442.1588.

4-Methyl-*N*-(4-methyl-1-(pyridin-2-yl)indolin-7-yl)benzenesulfonamide (3ta)



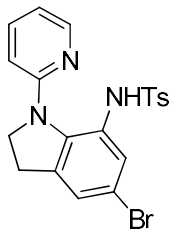
Following typical procedure A, **3ta** was obtained as a white solid (57.4 mg, 0.151 mmol, 76%). mp: 182–184 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.90 (s, 1H), 8.25 (d, *J* = 3.9 Hz, 1H), 7.63 – 7.48 (m, 1H), 7.27 (d, *J* = 8.7 Hz, 1H), 7.04 (d, *J* = 8.1 Hz, 2H), 6.94 (d, *J* = 8.1 Hz, 2H), 6.83 (d, *J* = 8.1 Hz, 1H), 6.78 (dd, *J* = 6.7, 5.5 Hz, 1H), 6.28 (d, *J* = 8.6 Hz, 1H), 3.56 (t, *J* = 8.4 Hz, 2H), 2.89 (t, *J* = 8.4 Hz, 2H), 2.32 (s, 3H), 2.19 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 153.76, 146.31, 142.11, 138.55, 137.80, 137.47, 132.19, 132.01, 128.65 × 2, 127.91, 126.71 × 2, 124.55, 121.31, 114.43, 110.67, 51.75, 27.05, 21.38, 18.48. HRMS (ESI): m/z calculated for $C_{21}H_{22}N_3O_2S$ $[M + H]^+$: 380.1433, found: 380.1429.

***N*-(5-Methoxy-2-methyl-1-(pyridin-2-yl)indolin-7-yl)-4-methylbenzenesulfonamide (3ua)**



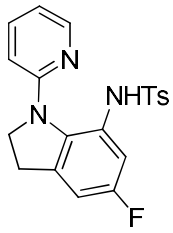
Following typical procedure A, **3ua** was obtained as a white solid (63.7 mg, 0.156 mmol, 78%). mp: 123–124 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 11.44 (s, 1H), 8.24 (d, *J* = 4.0 Hz, 1H), 7.57 (dd, *J* = 11.4, 4.3 Hz, 1H), 7.19 (d, *J* = 8.1 Hz, 2H), 6.97 (d, *J* = 7.2 Hz, 3H), 6.82 – 6.68 (m, 1H), 6.61 (s, 1H), 6.48 (d, *J* = 8.7 Hz, 1H), 4.35 – 3.93 (m, 1H), 3.81 (s, 3H), 3.30 (dd, *J* = 15.4, 8.8 Hz, 1H), 2.34 (d, *J* = 15.4 Hz, 1H), 2.27 (s, 3H), 0.69 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 156.50, 153.79, 146.48, 142.50, 138.84, 137.85, 134.22, 130.09, 129.06 × 2, 126.63 × 2, 125.30, 113.83, 110.49, 108.89, 59.17, 55.80, 36.64, 21.34, 19.39. HRMS (ESI): m/z calculated for $C_{22}H_{24}N_3O_3S$ $[M + H]^+$: 410.1538, found: 410.1533.

***N*-(5-Bromo-1-(pyridin-2-yl)indolin-7-yl)-4-methylbenzenesulfonamide (3va)**



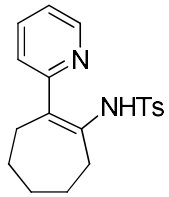
Following typical procedure A, **3va** was obtained as a pale yellow solid (65.4 mg, 0.147 mmol, 74%). mp: 171–172 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 11.46 (s, 1H), 8.25 (dd, *J* = 5.0, 1.2 Hz, 1H), 7.60 (ddd, *J* = 8.9, 7.2, 1.9 Hz, 1H), 7.50 (d, *J* = 1.9 Hz, 1H), 7.10 (dd, *J* = 5.2, 3.1 Hz, 3H), 6.98 (d, *J* = 8.1 Hz, 2H), 6.83 (dd, *J* = 7.2, 5.2 Hz, 1H), 6.35 (d, *J* = 8.6 Hz, 1H), 3.60 (t, *J* = 8.4 Hz, 2H), 2.99 (t, *J* = 8.4 Hz, 2H), 2.32 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 153.36, 146.17, 142.58, 139.01, 137.30, 137.17, 135.66, 129.32, 128.87 × 2, 126.68 × 2, 125.54, 124.87, 114.96, 114.90, 110.75, 51.92, 27.94, 21.42. HRMS (ESI): m/z calculated for $C_{20}H_{19}{}^{79}BrN_3O_2S$ $[M + H]^+$: 444.0381, found: 444.0378.

***N*-(5-Fluoro-1-(pyridin-2-yl)indolin-7-yl)-4-methylbenzenesulfonamide (3wa)**



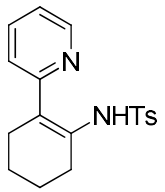
Following typical procedure A, **3wa** was obtained as a yellow solid (67.7 mg, 0.177 mmol, 88%). mp: 146–148 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 11.72 (s, 1H), 8.24 (dd, *J* = 5.0, 1.3 Hz, 1H), 7.65 – 7.55 (m, 1H), 7.16 (d, *J* = 8.2 Hz, 2H), 7.10 (dd, *J* = 10.0, 2.5 Hz, 1H), 7.00 (d, *J* = 8.2 Hz, 2H), 6.80 (dd, *J* = 7.0, 5.0 Hz, 1H), 6.76 – 6.69 (m, 1H), 6.36 (d, *J* = 8.6 Hz, 1H), 3.63 (t, *J* = 8.4 Hz, 2H), 2.99 (t, *J* = 8.4 Hz, 2H), 2.33 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 158.82 (d, *J* = 242.0 Hz), 153.56, 146.06, 142.63, 139.01, 137.26, 135.35 (d, *J* = 9.5 Hz), 133.96 (d, *J* = 2.6 Hz), 128.91 × 2, 126.70 × 2, 124.79 (d, *J* = 11.1 Hz), 114.50, 112.50 (d, *J* = 25.2 Hz), 110.45, 109.86 (d, *J* = 23.9 Hz), 51.98, 28.40, 21.41. ^{19}F NMR (376 MHz, $CDCl_3$): δ -120.05. HRMS (ESI): m/z calculated for $C_{20}H_{19}N_3O_2SF$ $[M + H]^+$: 384.1182, found: 384.1180.

4-Methyl-*N*-(2-(pyridin-2-yl)cyclohept-1-en-1-yl)benzenesulfonamide (4aa)



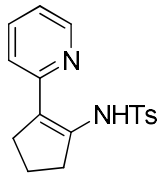
Following a modified procedure A, as the reaction was performed at room temperature, **4aa** was obtained as a yellow solid (42.4 mg, 0.124 mmol, 62%). mp: 120–122 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 13.23 (s, 1H), 8.47 (d, *J* = 4.0 Hz, 1H), 7.60 (td, *J* = 8.1, 1.9 Hz, 1H), 7.53 (d, *J* = 8.3 Hz, 2H), 7.14 – 7.03 (m, 4H), 2.78 – 2.69 (m, 2H), 2.53 – 2.44 (m, 2H), 2.34 (s, 3H), 1.71 (dt, *J* = 11.9, 6.0 Hz, 2H), 1.53 – 1.46 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 158.75, 146.41, 142.96, 142.73, 137.82, 136.88, 129.13 × 2, 126.82 × 2, 121.37, 120.68, 120.21, 31.49, 31.42, 30.11, 26.28, 25.00, 21.44. HRMS (ESI): m/z calculated for $C_{19}H_{23}N_2O_2S$ $[M + H]^+$: 343.1480, found: 343.1475.

4-Methyl-*N*-(2-(pyridin-2-yl)cyclohex-1-en-1-yl)benzenesulfonamide (4ba)



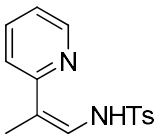
Following a modified procedure A, as the reaction was performed at room temperature, **4ba** was obtained as a yellow solid (46.8 mg, 0.142 mmol, 71%). mp: 121–123 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 14.54 (s, 1H), 8.53 (d, *J* = 4.6 Hz, 1H), 7.75 – 7.62 (m, 3H), 7.23 (d, *J* = 8.3 Hz, 1H), 7.20 (d, *J* = 8.1 Hz, 2H), 7.12 (dd, *J* = 7.3, 5.1 Hz, 1H), 2.52 (t, *J* = 5.1 Hz, 2H), 2.36 (d, *J* = 6.5 Hz, 5H), 1.83 – 1.41 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 158.46, 145.89, 142.86, 139.55, 138.61, 137.15, 129.46 × 2, 126.88 × 2, 120.28, 119.52, 110.75, 27.40, 26.75, 22.41, 21.97, 21.49. HRMS (ESI): m/z calculated for $C_{18}H_{21}N_2O_2S$ $[M + H]^+$: 329.1324, found: 329.1330.

4-Methyl-*N*-(2-(pyridin-2-yl)cyclopent-1-en-1-yl)benzenesulfonamide (4ca)



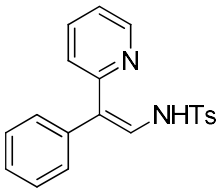
Following typical procedure A, **4ca** was obtained as a yellow solid (40.1 mg, 0.128 mmol, 64%). mp: 114–115 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 12.76 (s, 1H), 8.57 – 8.50 (m, 1H), 7.77 (d, *J* = 8.3 Hz, 2H), 7.65 (td, *J* = 7.8, 1.8 Hz, 1H), 7.25 (d, *J* = 8.3 Hz, 2H), 7.06 (dd, *J* = 7.0, 5.3 Hz, 1H), 6.99 (d, *J* = 8.1 Hz, 1H), 2.80 (t, *J* = 7.6 Hz, 2H), 2.67 – 2.55 (m, 2H), 2.39 (s, 3H), 1.96 – 1.82 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 155.80, 147.26, 143.18, 141.86, 138.65, 136.88, 129.67 × 2, 126.91 × 2, 120.24, 119.80, 113.17, 32.88, 30.26, 21.52, 20.48. HRMS (ESI): m/z calculated for $C_{17}H_{19}N_2O_2S$ $[M + H]^+$: 315.1167, found: 315.1169.

(*Z*)-4-Methyl-*N*-(2-(pyridin-2-yl)prop-1-en-1-yl)benzenesulfonamide (4da)



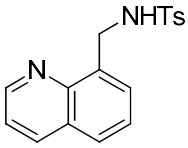
Following typical procedure A, **4da** was obtained as a yellow oil (20.4 mg, 0.071 mmol, 35%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 12.94 (s, 1H), 8.50 (d, *J* = 4.2 Hz, 1H), 7.77 (d, *J* = 8.1 Hz, 2H), 7.69 (t, *J* = 7.8 Hz, 1H), 7.27 (d, *J* = 7.8 Hz, 2H), 7.18 (d, *J* = 8.1 Hz, 1H), 7.17 – 7.00 (m, 1H), 6.69 (s, 1H), 2.39 (s, 3H), 1.98 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 157.89, 146.81, 143.18, 138.53, 137.02, 129.70 × 2, 128.22, 126.47 × 2, 120.49, 120.31, 109.19, 21.50, 18.47. HRMS (ESI): m/z calculated for $C_{15}H_{17}N_2O_2S$ $[M + H]^+$: 289.1011, found: 289.1012.

(*Z*)-4-Methyl-*N*-(2-phenyl-2-(pyridin-2-yl)vinyl)benzenesulfonamide (4ea)



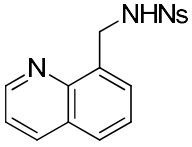
Following typical procedure A, **4ea** was obtained as a yellow solid (44.2 mg, 0.126 mmol, 63%). mp: 151–152 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 13.16 (s, 1H), 8.53 (dd, *J* = 5.0, 0.8 Hz, 1H), 7.81 (d, *J* = 8.1 Hz, 2H), 7.55 (td, *J* = 8.1, 1.8 Hz, 1H), 7.37 (tdd, *J* = 6.7, 4.4, 2.4 Hz, 3H), 7.31 – 7.25 (m, 4H), 7.09 (ddd, *J* = 7.4, 5.0, 0.8 Hz, 1H), 6.98 (d, *J* = 8.2 Hz, 1H), 6.86 (s, 1H), 2.40 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 157.61, 146.60, 143.39, 138.80, 138.41, 136.90, 131.28, 130.10 × 2, 129.79 × 2, 128.61 × 2, 127.40, 126.55 × 2, 122.68, 120.46, 117.46, 21.54. HRMS (ESI): m/z calculated for $C_{20}H_{19}N_2O_2S$ $[M + H]^+$: 351.1167, found: 351.1174.

4-Methyl-*N*-(quinolin-8-ylmethyl)benzenesulfonamide (6aa)



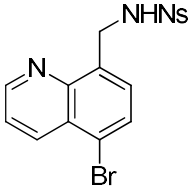
Following typical procedure B, **6aa** was obtained as a white solid (45.4 mg, 0.145 mmol, 73%). mp: 108–109 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.84 – 8.77 (m, 1H), 8.08 (d, *J* = 8.3 Hz, 1H), 7.64 (d, *J* = 8.2 Hz, 1H), 7.53 (d, *J* = 8.2 Hz, 2H), 7.46 (d, *J* = 6.9 Hz, 1H), 7.39 (dd, *J* = 8.3, 4.2 Hz, 1H), 7.33 (t, *J* = 7.6 Hz, 1H), 6.99 (d, *J* = 8.0 Hz, 2H), 6.66 (t, *J* = 6.0 Hz, 1H), 4.66 (d, *J* = 6.0 Hz, 2H), 2.27 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 149.43, 146.41, 142.62, 137.36, 136.53, 133.87, 129.43, 129.00 × 2, 128.34, 127.83, 126.80 × 2, 126.17, 121.26, 46.32, 21.34. HRMS (ESI): m/z calculated for $C_{17}H_{17}N_2O_2S$ $[M + H]^+$: 313.1011, found: 313.1010.

4-Nitro-*N*-(quinolin-8-ylmethyl)benzenesulfonamide (6ba)



Following typical procedure B, **6ba** was obtained as a white solid (53.5 mg, 0.156 mmol, 78%). mp: 154–155 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.87 – 8.78 (m, 1H), 8.04 (d, *J* = 8.3 Hz, 1H), 7.86 (d, *J* = 8.8 Hz, 2H), 7.63 (d, *J* = 8.8 Hz, 3H), 7.47 (d, *J* = 6.9 Hz, 1H), 7.42 (dd, *J* = 8.3, 4.2 Hz, 1H), 7.38 – 7.31 (m, 1H), 6.93 (s, 1H), 4.77 (d, *J* = 6.1 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 149.59, 149.22, 146.29, 146.04, 136.72, 132.95, 129.76, 128.36, 127.65 × 2, 126.07, 123.12 × 2, 121.55, 46.73. HRMS (ESI): m/z calculated for $C_{16}H_{14}N_3O_4S$ $[M + H]^+$: 344.0705, found: 344.0708.

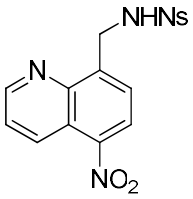
***N*-((5-Bromoquinolin-8-yl)methyl)-4-nitrobenzenesulfonamide (6ca)**



Following typical procedure B, **6ca** was obtained as a white solid (71.2 mg, 0.169 mmol, 84%). mp: 175–176 °C. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 8.89 (d, *J* = 2.8 Hz, 1H), 8.45 (d, *J* = 8.6 Hz, 1H), 7.93 (d, *J* = 8.6 Hz, 2H), 7.69 (d, *J* = 7.6 Hz, 1H), 7.64 (d, *J* = 8.6 Hz, 2H), 7.57 (dd, *J* = 8.6, 4.2 Hz, 1H), 7.42 (d, *J* = 7.6 Hz, 1H), 6.71 (s, 1H), 4.76 (d, *J* = 5.8 Hz, 2H). ^{13}C NMR (101 MHz, CD_2Cl_2): δ 150.38,

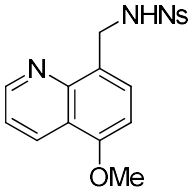
149.21, 146.47, 146.12, 146.07, 136.14, 133.21, 130.11, 129.71, 127.62 × 2, 123.22 × 2, 122.71, 122.27, 46.14. HRMS (ESI): m/z calculated for $C_{16}H_{13}{}^{79}BrN_3O_4S$ $[M + H]^+$: 421.9810, found: 421.9816.

4-Nitro-*N*-((5-nitroquinolin-8-yl)methyl)benzenesulfonamide (6da)



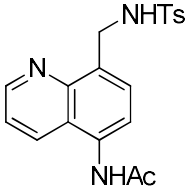
Following typical procedure B, **6da** was obtained as a white solid (46.4 mg, 0.119 mmol, 60%). mp: 138–139 °C. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 8.99 (d, *J* = 4.1 Hz, 1H), 8.87 (d, *J* = 8.7 Hz, 1H), 8.20 (d, *J* = 7.8 Hz, 1H), 8.05 (d, *J* = 8.7 Hz, 2H), 7.79 (d, *J* = 8.7 Hz, 2H), 7.71 (dd, *J* = 8.7, 4.0 Hz, 2H), 6.61 (s, 1H), 4.83 (d, *J* = 5.3 Hz, 2H). ^{13}C NMR (101 MHz, CD_2Cl_2): δ 150.84, 149.65, 146.03, 145.66, 145.62, 140.74, 132.76, 127.96, 127.85 × 2, 124.20, 123.89, 123.65 × 2, 121.02, 45.88. HRMS (ESI): m/z calculated for $C_{16}H_{13}N_4O_6S$ $[M + H]^+$: 389.0556, found: 389.0557.

***N*-((5-Methoxyquinolin-8-yl)methyl)-4-nitrobenzenesulfonamide (6ea)**



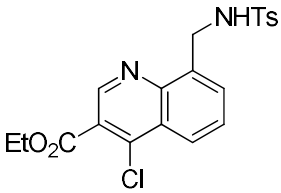
Following typical procedure B, **6ea** was obtained as a white solid (61.6 mg, 0.165 mmol, 82%). mp: 151–152 °C. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 8.82 (d, *J* = 4.1 Hz, 1H), 8.42 (d, *J* = 8.4 Hz, 1H), 7.83 (d, *J* = 8.6 Hz, 2H), 7.57 (d, *J* = 8.6 Hz, 2H), 7.40 (dd, *J* = 8.4, 4.2 Hz, 1H), 7.35 (d, *J* = 7.9 Hz, 1H), 6.84 (s, 1H), 6.63 (d, *J* = 7.9 Hz, 1H), 4.68 (d, *J* = 5.1 Hz, 2H), 3.94 (s, 3H). ^{13}C NMR (101 MHz, CD_2Cl_2): δ 155.62, 149.88, 149.04, 146.26, 131.36, 129.98, 127.58 × 2, 124.68, 122.91 × 2, 120.87, 120.61 × 2, 103.13, 55.81, 46.43. HRMS (ESI): m/z calculated for $C_{17}H_{16}N_3O_5S$ $[M + H]^+$: 374.0811, found: 374.0816.

***N*-(8-((4-Methylphenylsulfonamido)methyl)quinolin-5-yl)acetamide (6fa)**



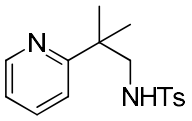
Following typical procedure B, **6fa** was obtained as a white solid (51.8 mg, 0.140 mmol, 70%). mp: 151–152 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.80 (s, 1H), 8.15 (d, *J* = 8.2 Hz, 1H), 7.59 (t, *J* = 9.2 Hz, 4H), 7.41 (s, 2H), 7.11 (d, *J* = 8.2 Hz, 2H), 6.46 (s, 1H), 4.58 (d, *J* = 6.3 Hz, 2H), 2.33 (s, 3H), 2.30 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 169.71, 149.25, 146.24, 143.18, 136.92, 132.72, 131.69, 131.15, 129.39 × 2, 128.72, 126.84 × 2, 123.12, 121.59, 120.87, 45.68, 23.88, 21.41. HRMS (ESI): m/z calculated for $C_{19}H_{20}N_3O_3S$ $[M + H]^+$: 370.1225, found: 370.1226.

Ethyl 4-chloro-8-((4-methylphenylsulfonamido)methyl)quinoline-3-carboxylate (6ga)



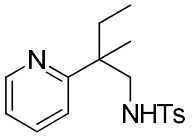
Following a modified procedure B, as the reaction was performed at 60 °C, **6ga** was obtained as a white solid (53.6 mg, 0.128 mmol, 64%). mp: 118–120 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.10 (s, 1H), 8.25 (dd, *J* = 8.6, 1.2 Hz, 1H), 7.65 (d, *J* = 6.9 Hz, 1H), 7.52 (dd, *J* = 8.6, 7.1 Hz, 1H), 7.45 (d, *J* = 8.3 Hz, 2H), 6.98 (d, *J* = 8.1 Hz, 2H), 6.20 (t, *J* = 6.8 Hz, 1H), 4.70 (d, *J* = 6.8 Hz, 2H), 4.52 (q, *J* = 7.1 Hz, 2H), 2.29 (s, 3H), 1.48 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 164.28, 149.20, 147.46, 143.83, 142.84, 137.31, 134.65, 132.03, 128.96 × 2, 127.94, 126.65 × 2, 126.36, 125.41, 123.34, 62.26, 45.94, 21.32, 14.25. HRMS (ESI): m/z calculated for $C_{20}H_{20}ClN_2O_4S$ $[M + H]^+$: 419.0832, found: 419.0829.

4-Methyl-*N*-(2-methyl-2-(pyridin-2-yl)propyl)benzenesulfonamide (6ha)



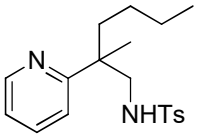
Following typical procedure C, **6ha** was obtained as a white solid (39.4 mg, 0.129 mmol, 65%). mp: 75–76 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.44 (d, J = 4.2 Hz, 1H), 7.73 (d, J = 8.2 Hz, 2H), 7.63 (td, J = 7.9, 1.7 Hz, 1H), 7.28 (d, J = 8.8 Hz, 3H), 7.12 (dd, J = 7.2, 5.1 Hz, 1H), 6.08 (s, 1H), 3.15 (s, 2H), 2.41 (s, 3H), 1.32 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 166.40, 148.22, 142.93, 137.37, 136.96, 129.58 × 2, 126.99 × 2, 121.47, 120.51, 53.04, 40.72, 26.80 × 2, 21.49. HRMS (ESI): m/z calculated for $C_{16}H_{21}N_2O_2S$ [M + H]$^+$: 305.1324, found: 305.1318.

4-Methyl-*N*-(2-methyl-2-(pyridin-2-yl)butyl)benzenesulfonamide (6ia)



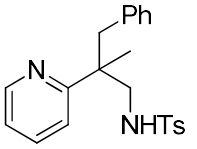
Following typical procedure C, **6ia** was obtained as a white solid (40.5 mg, 0.127 mmol, 64%). mp: 88–89 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.44 (d, J = 4.8 Hz, 1H), 7.72 (d, J = 8.2 Hz, 2H), 7.61 (td, J = 7.8, 1.8 Hz, 1H), 7.27 (d, J = 8.4 Hz, 2H), 7.22 (d, J = 8.2 Hz, 1H), 7.11 (dd, J = 7.4, 4.9 Hz, 1H), 6.08 (t, J = 6.2 Hz, 1H), 3.31 (dd, J = 11.8, 6.4 Hz, 1H), 2.99 (dd, J = 11.8, 6.2 Hz, 1H), 2.40 (s, 3H), 1.78 – 1.62 (m, 2H), 1.30 (s, 3H), 0.71 (t, J = 7.5 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 165.58, 148.33, 142.93, 137.26, 136.77, 129.58 × 2, 127.00 × 2, 121.42, 121.24, 51.23, 43.89, 32.49, 22.75, 21.49, 8.34. HRMS (ESI): m/z calculated for $C_{17}H_{23}N_2O_2S$ [M + H]$^+$: 319.1480, found: 319.1477.

4-Methyl-*N*-(2-methyl-2-(pyridin-2-yl)hexyl)benzenesulfonamide (6ja)



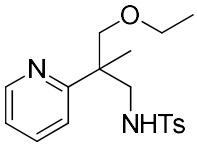
Following typical procedure C, **6ja** was obtained as a colorless oil (40.8 mg, 0.118 mmol, 59%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.48 – 8.41 (m, 1H), 7.73 (d, J = 8.3 Hz, 2H), 7.62 (td, J = 7.8, 1.9 Hz, 1H), 7.28 (d, J = 8.1 Hz, 2H), 7.22 (d, J = 8.1 Hz, 1H), 7.11 (ddd, J = 7.5, 4.9, 0.9 Hz, 1H), 6.09 (t, J = 6.4 Hz, 1H), 3.31 (dd, J = 11.8, 6.4 Hz, 1H), 3.00 (dd, J = 11.8, 6.4 Hz, 1H), 2.41 (s, 3H), 1.73 – 1.51 (m, 2H), 1.32 (s, 3H), 1.23 – 1.13 (m, 2H), 1.08 (ddd, J = 11.7, 10.0, 6.3 Hz, 1H), 1.03 – 0.91 (m, 1H), 0.80 (t, J = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 165.93, 148.32, 142.91, 137.30, 136.68, 129.57 × 2, 127.01 × 2, 121.35, 121.03, 51.50, 43.58, 39.87, 26.04, 23.39, 23.22, 21.49, 13.92. HRMS (ESI): m/z calculated for $C_{19}H_{27}N_2O_2S$ [M + H]$^+$: 347.1793, found: 347.1796.

4-Methyl-*N*-(2-methyl-4-phenyl-2-(pyridin-2-yl)butyl)benzenesulfonamide (6ka)



Following typical procedure C, **6ka** was obtained as a colorless oil (30.9 mg, 0.081 mmol, 41%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.52 (d, J = 4.0 Hz, 1H), 7.72 (d, J = 8.2 Hz, 2H), 7.55 (td, J = 7.8, 1.8 Hz, 1H), 7.28 (d, J = 8.2 Hz, 2H), 7.18 – 7.09 (m, 4H), 6.99 (d, J = 8.0 Hz, 1H), 6.79 (dd, J = 6.8, 2.3 Hz, 2H), 6.29 (s, 1H), 3.38 (dd, J = 11.7, 6.5 Hz, 1H), 3.12 – 2.95 (m, 2H), 2.89 (d, J = 13.2 Hz, 1H), 2.41 (s, 3H), 1.27 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 164.77, 148.33, 143.00, 137.15, 137.11, 136.57, 130.42 × 2, 129.60 × 2, 127.76 × 2, 127.04 × 2, 126.32, 121.76, 121.69, 51.91, 45.77, 44.55, 22.59, 21.50. HRMS (ESI): m/z calculated for $C_{22}H_{25}N_2O_2S$ [M + H]$^+$: 381.1637, found: 381.1630.

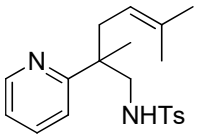
***N*-(3-Ethoxy-2-methyl-2-(pyridin-2-yl)propyl)-4-methylbenzenesulfonamide (6la)**



Following typical procedure C, **6la** was obtained as a colorless oil (41.5 mg, 0.119 mmol, 60%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.50 – 8.41 (m, 1H), 7.73 (d, J = 8.2 Hz, 2H), 7.62 (td, J = 7.8, 1.8 Hz, 1H), 7.29 (dd, J = 12.4, 8.2 Hz, 3H), 7.17 – 7.08 (m, 1H), 6.17 (s, 1H), 3.66 (d, J = 9.3 Hz, 1H), 3.50 (d, J = 9.3 Hz, 1H), 3.43

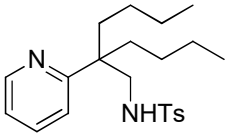
– 3.33 (m, 3H), 3.28 – 3.12 (m, 1H), 2.41 (s, 3H), 1.32 (s, 3H), 1.10 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 163.69, 148.37, 142.90, 137.29, 136.66, 129.56 × 2, 127.03 × 2, 121.72, 121.50, 76.47, 66.94, 49.91, 44.92, 21.90, 21.48, 14.95. HRMS (ESI): m/z calculated for $C_{18}H_{25}N_2O_3S$ $[M + H]^+$: 349.1586, found: 349.1587.

_N_-(2,5-Dimethyl-2-(pyridin-2-yl)hex-4-en-1-yl)-4-methylbenzenesulfonamide (6ma)



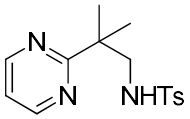
Following typical procedure C, **6ma** was obtained as a pale yellow oil (30.9 mg, 0.086 mmol, 43%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.48 – 8.42 (m, 1H), 7.73 (d, *J* = 8.3 Hz, 2H), 7.61 (td, *J* = 7.8, 1.9 Hz, 1H), 7.28 (d, *J* = 8.1 Hz, 2H), 7.21 (d, *J* = 8.1 Hz, 1H), 7.11 (ddd, *J* = 7.5, 4.9, 0.9 Hz, 1H), 6.15 (t, *J* = 6.3 Hz, 1H), 4.95 – 4.83 (m, 1H), 3.32 (dd, *J* = 11.8, 6.4 Hz, 1H), 3.01 (dd, *J* = 11.8, 6.4 Hz, 1H), 2.41 (s, 3H), 2.32 (ddd, *J* = 21.6, 14.4, 7.1 Hz, 2H), 1.61 (s, 3H), 1.46 (s, 3H), 1.30 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 165.61, 148.28, 142.90, 137.32, 136.59, 134.73, 129.56 × 2, 127.02 × 2, 121.40, 121.20, 119.00, 51.49, 44.37, 38.18, 25.93, 23.06, 21.48, 17.86. HRMS (ESI): m/z calculated for $C_{20}H_{27}N_2O_2S$ $[M + H]^+$: 359.1793, found: 359.1791.

4-Methyl-_N_-(2-propyl-2-(pyridin-2-yl)hexyl)benzenesulfonamide (6na)



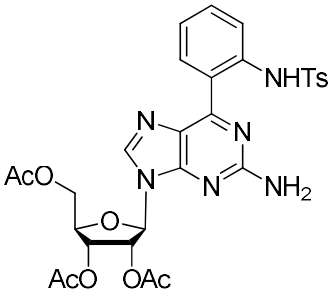
Following typical procedure C, **6na** was obtained as a white solid (20.9 mg, 0.054 mmol, 27%). mp: 98–99 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.45 (d, *J* = 4.0 Hz, 1H), 7.74 (d, *J* = 8.2 Hz, 2H), 7.61 (td, *J* = 7.9, 1.7 Hz, 1H), 7.29 (d, *J* = 8.1 Hz, 2H), 7.20 (d, *J* = 8.1 Hz, 1H), 7.10 (dd, *J* = 7.3, 5.0 Hz, 1H), 6.01 (t, *J* = 6.3 Hz, 1H), 3.21 (d, *J* = 6.4 Hz, 2H), 2.42 (s, 3H), 1.80 – 1.53 (m, 4H), 1.37 – 1.11 (m, 4H), 1.02 (dt, *J* = 14.0, 7.8 Hz, 4H), 0.82 (t, *J* = 7.3 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 165.44, 148.41, 142.91, 137.20, 136.39, 129.57 × 2, 127.06 × 2, 121.31, 121.25, 48.56, 46.38, 36.52 × 2, 25.71 × 2, 23.35 × 2, 21.49, 13.94 × 2. HRMS (ESI): m/z calculated for $C_{22}H_{33}N_2O_2S$ $[M + H]^+$: 389.2263, found: 389.2261.

4-Methyl-_N_-(2-methyl-2-(pyrimidin-2-yl)propyl)benzenesulfonamide (6oa)



Following typical procedure C, **6oa** was obtained as a white solid (38.0 mg, 0.124 mmol, 62%). mp: 78–79 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.63 (d, *J* = 4.9 Hz, 2H), 7.76 (d, *J* = 8.2 Hz, 2H), 7.30 (d, *J* = 8.2 Hz, 2H), 7.11 (t, *J* = 4.9 Hz, 1H), 6.01 (t, *J* = 6.6 Hz, 1H), 3.19 (d, *J* = 6.6 Hz, 2H), 2.41 (s, 3H), 1.35 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 174.86, 156.81 × 2, 143.02, 137.44, 129.62 × 2, 127.03 × 2, 118.75, 52.16, 43.02, 26.08 × 2, 21.50. HRMS (ESI): m/z calculated for $C_{15}H_{20}N_3O_2S$ $[M + H]^+$: 306.1276, found: 306.1280.

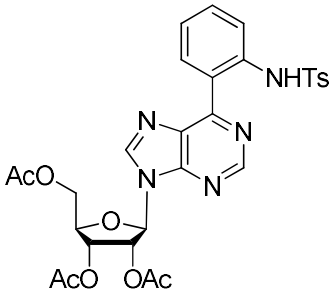
(2*R*,3*R*,4*R*,5*R*)-2-(Acetoxymethyl)-5-(2-amino-6-(2-(4-methylphenylsulfonamido)phenyl)-9*H*-purin-9-yl)tetrahydrofuran-3,4-diyl diacetate (7aa)



Following a modified procedure A (0.1 mmol scale), as $[\{Cp^*RhCl_2\}_2]$ (5.0 mol%), $AgSbF_6$ (20 mol%), and KOAc (20 mol%) were employed and the reaction was run for 48 h, **7aa** was obtained as a white solid (30.7 mg, 0.048 mmol, 48%). mp: 87–89 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 11.96 (s, 1H), 8.59 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.87 (s, 1H), 7.70 (d, *J* = 8.2 Hz, 1H), 7.48 – 7.42 (m, 1H), 7.33 (d, *J*

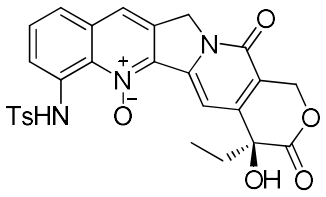
= 8.3 Hz, 2H), 7.30 – 7.24 (m, 1H), 6.91 (d, *J* = 8.2 Hz, 2H), 6.05 (d, *J* = 4.8 Hz, 1H), 6.00 (t, *J* = 5.0 Hz, 1H), 5.80 (t, *J* = 5.0 Hz, 1H), 5.21 (s, 2H), 4.62 – 4.29 (m, 3H), 2.18 (s, 3H), 2.17 (s, 3H), 2.13 (s, 3H), 2.12 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 170.46, 169.64, 169.44, 157.88, 155.94, 153.64, 143.07, 140.11, 137.52, 135.75, 132.60, 131.73, 129.13 × 2, 126.73 × 2, 125.40, 124.95, 124.88, 124.30, 86.47, 79.90, 72.78, 70.52, 63.00, 21.15, 20.74, 20.56, 20.47. HRMS (ESI): m/z calculated for $C_{29}H_{31}N_6O_9S$ $[M + H]^+$: 639.1873, found: 639.1866.

(2*R*,3*R*,4*R*,5*R*)-2-(Acetoxymethyl)-5-(6-(2-(4-methylphenylsulfonamido)phenyl)-9*H*-purin-9-yl)tetrahydrofuran-3,4-diyl diacetate (7ba)



Following a modified procedure A (0.1 mmol scale), as $[\{Cp^*RhCl_2\}_2]$ (5.0 mol%), $AgSbF_6$ (20 mol%), and KOAc (20 mol%) were employed and the reaction was run for 24 h, **7ba** was obtained as a white solid (46.9 mg, 0.075 mmol, 75%). mp: 96–98 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 12.00 (s, 1H), 8.97 (s, 1H), 8.73 (d, *J* = 7.8 Hz, 1H), 8.27 (s, 1H), 7.76 (d, *J* = 8.1 Hz, 1H), 7.49 (t, *J* = 7.8 Hz, 1H), 7.31 (t, *J* = 8.1 Hz, 3H), 6.88 (d, *J* = 8.1 Hz, 2H), 6.28 (d, *J* = 5.2 Hz, 1H), 5.98 (t, *J* = 5.4 Hz, 1H), 5.68 (t, *J* = 5.2 Hz, 1H), 4.59 – 4.37 (m, 3H), 2.19 (s, 3H), 2.16 (s, 6H), 2.12 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 170.25, 169.60, 169.41, 155.28, 151.71, 150.95, 143.03, 142.61, 137.87, 135.93, 132.90, 132.16, 131.14, 129.11 × 2, 126.69 × 2, 124.90, 124.44, 124.09, 86.60, 80.49, 73.12, 70.57, 62.99, 21.13, 20.79, 20.54, 20.41. HRMS (ESI): m/z calculated for $C_{29}H_{30}N_5O_9S$ $[M + H]^+$: 624.1764, found: 624.1754.

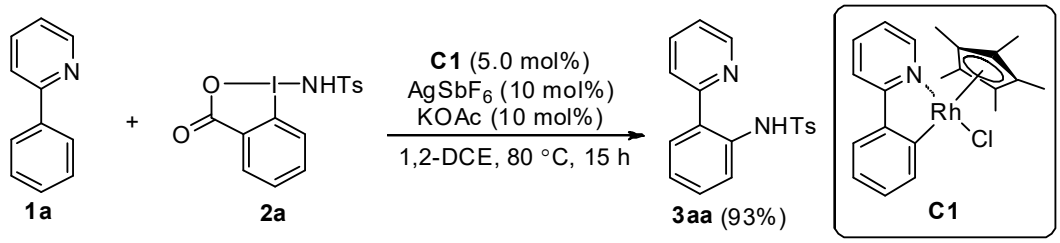
4-Ethyl-4-hydroxy-7-(4-methylphenylsulfonamido)-3,14-dioxo-3,4,12,14-tetrahydro-1*H*-pyrano[3',4':6,7]indolizino[1,2-*b*]quinoline 6-oxide (8)



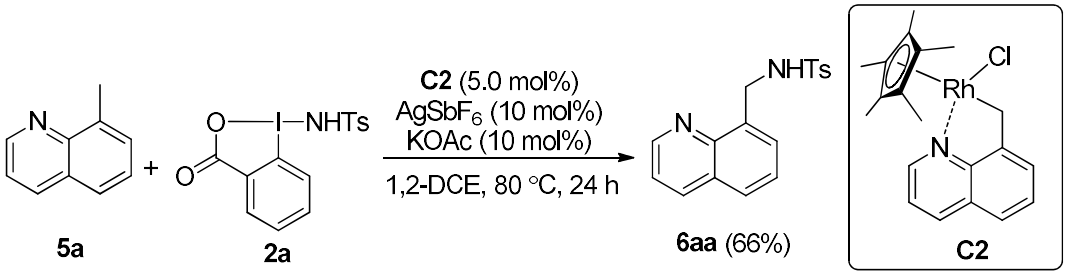
Following typical procedure A (0.1 mmol scale), **8** was obtained as a yellow solid (37.2 mg, 0.070 mmol, 70%). mp: >250 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 14.27 (s, 1H), 8.24 (s, 1H), 8.04 (s, 1H), 7.83 (d, *J* = 8.2 Hz, 2H), 7.76 (d, *J* = 7.5 Hz, 1H), 7.72 (d, *J* = 6.8 Hz, 1H), 7.65 (t, *J* = 7.9 Hz, 1H), 7.33 (d, *J* = 8.2 Hz, 2H), 6.60 (s, 1H), 5.43 (s, 2H), 5.24 (s, 2H), 2.28 (s, 3H), 1.95 – 1.80 (m, 2H), 0.89 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (75 MHz, DMSO-d_6): δ 172.64, 156.70, 150.25, 144.57, 140.19, 139.25, 136.12, 133.37, 132.81, 132.26, 130.45 × 2, 130.38, 130.28, 127.58 × 2, 123.95, 123.76, 121.30, 117.36, 103.63, 72.79, 65.70, 51.10, 31.11, 21.39, 8.26. HRMS (ESI): m/z calculated for $C_{27}H_{24}N_3O_7S$ $[M + H]^+$: 534.1335, found: 534.1333.

2.3 Mechanistic experiments

2.3.1 Cyclometalated rhodium intermediates[3, ref. 18d]

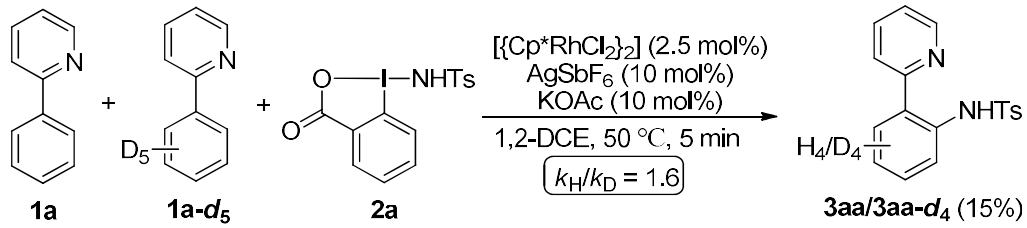


A 8 mL screw-cap vial was charged with 2-phenylpyridine **1a** (31.0 mg, 1.0 equiv, 0.2 mmol), **2a** (100.1 mg, 1.2 equiv, 0.24 mmol), **C1** (4.3 mg, 0.01 mmol, 5.0 mol%), $AgSbF_6$ (6.9 mg, 0.02 mmol, 10 mol%), KOAc (2.0 mg, 0.02 mmol, 10 mol%), and 1,2-dichloroethane (1.0 mL). The vial was carefully blown with nitrogen for 30 seconds and placed into preheated oil bath at 80 °C with stirring for 15 h. After cooling down, the mixture was diluted with CH_2Cl_2 (10 mL) and sequentially washed with sat. aq. $NaHCO_3$ (5 mL). The layer was separated and the aqueous layer was extracted with CH_2Cl_2 (10 mL × 3). The combined organic layers were rinsed with sat. aq. NaCl (10 mL), dried over $MgSO_4$, and concentrated under reduced pressure. The resultant residue was purified by flash chromatography (hexane/EtOAc) on silica gel to afford product **3aa** (60.6 mg, 0.186 mmol, 93%).



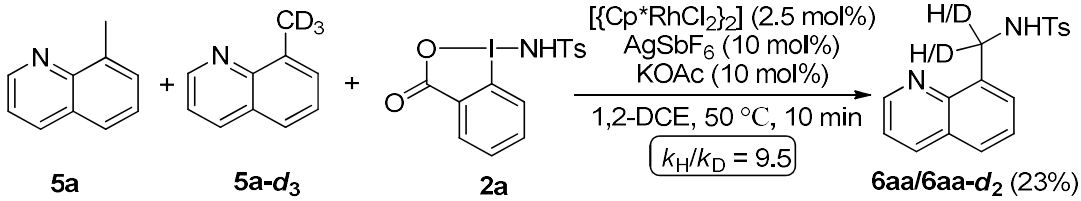
A 8 mL screw-cap vial was charged with 8-methylquinoline **5a** (28.6 mg, 1.0 equiv, 0.2 mmol), amide **2a** (100.1 mg, 1.2 equiv, 0.24 mmol), **C2** (4.2 mg, 0.01 mmol, 5.0 mol%), $AgSbF_6$ (6.9 mg, 0.02 mmol, 10 mol%), KOAc (2.0 mg, 0.02 mmol, 10 mol%), and 1,2-dichloroethane (1.0 mL). The vial was carefully blown with nitrogen for 30 seconds and placed into preheated oil bath at 80 °C with stirring for 24 h. After cooling down, the mixture was diluted with CH_2Cl_2 (10 mL) and sequentially washed with sat. aq. $NaHCO_3$ (5 mL). The layer was separated and the aqueous layer was extracted with CH_2Cl_2 (10 mL × 3). The combined organic layers were rinsed with sat. aq. NaCl (10 mL), dried over $MgSO_4$, and concentrated under reduced pressure. The resultant residue was purified by flash chromatography (hexane/EtOAc) on silica gel to afford the amidation product **6aa** (41.2 mg, 0.132 mmol, 66%).

2.3.2 Intermolecular KIE measurements



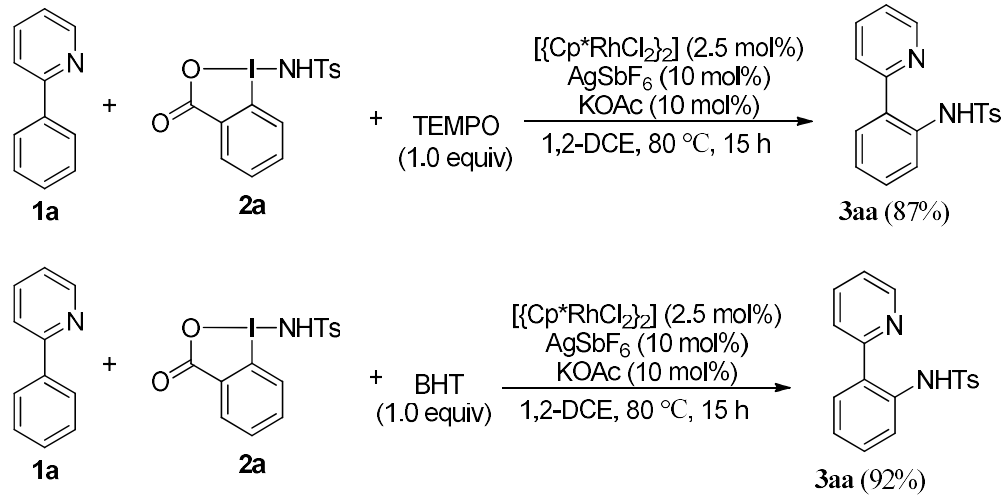
A 8 mL screw-cap vial was charged with **1a** (15.5 mg, 1.0 equiv, 0.1 mmol), **1a-*d*$_5$** (16.0 mg, 1.0 equiv, 0.1 mmol), **2a** (100.1 mg, 1.2 equiv, 0.24 mmol), [{Cp*$RhCl_2$}$_2$] (3.1 mg, 0.005 mmol, 2.5 mol%), $AgSbF_6$ (6.9 mg, 0.02 mmol, 10 mol%), KOAc (2.0 mg, 0.02 mmol, 10 mol%), and 1,2-dichloroethane (1.0 mL). The vial was carefully blown with nitrogen for 30 seconds and placed into preheated oil bath at 50 °C with stirring for 5 min. The reaction mixture was immediately diluted with CH_2Cl_2 (10 mL) and sequentially washed with sat. aq. $NaHCO_3$ (5 mL). The layer was separated and the aqueous layer was extracted with CH_2Cl_2 (10 mL × 3). The combined organic layers were rinsed with sat. aq. NaCl (10 mL), dried over $MgSO_4$, and concentrated under reduced pressure. The resultant residue was purified by flash chromatography (hexane/EtOAc) on silica gel to afford

amidation product **3aa/3aa-*d*$_4$** (9.5 mg, 0.029 mmol, 15%). The ratio of **3aa/3aa-*d*$_4$** was determined by ^{1}H NMR (400 MHz, $CDCl_3$) to be 1.6:1.

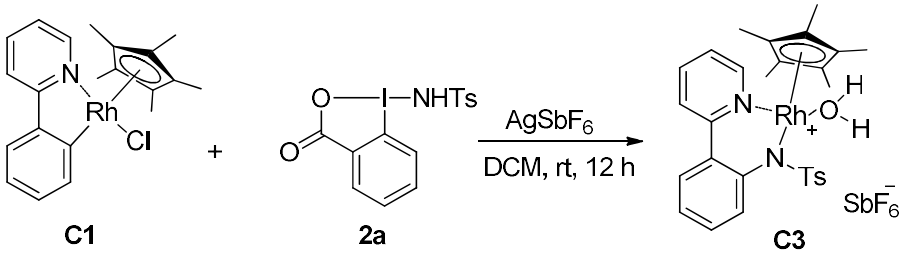


A 8 mL screw-cap vial was charged with **5a** (14.3 mg, 1.0 equiv, 0.1 mmol), **5a-*d*$_3$** (14.6 mg, 1.0 equiv, 0.1 mmol), **2a** (100.1 mg, 1.2 equiv, 0.24 mmol), [{Cp*$RhCl_2$}$_2$] (3.1 mg, 0.005 mmol, 2.5 mol%), $AgSbF_6$ (6.9 mg, 0.02 mmol, 10 mol%), KOAc (2.0 mg, 0.02 mmol, 10 mol%), and 1,2-dichloroethane (1.0 mL). The vial was carefully blown with nitrogen for 30 seconds and placed into preheated oil bath at 50 °C with stirring for 10 min. The reaction mixture was immediately diluted with CH_2Cl_2 (10 mL) and sequentially washed with sat. aq. $NaHCO_3$ (5 mL). The layer was separated and the aqueous layer was extracted with CH_2Cl_2 (10 mL × 3). The combined organic layers were rinsed with sat. aq. NaCl (10 mL), dried over $MgSO_4$, and concentrated under reduced pressure. The resultant residue was purified by flash chromatography (hexane/EtOAc) on silica gel to afford the amidation product **6aa/6aa-*d*$_2$** (14.6 mg, 0.047 mmol, 23%). The ratio of **6aa/6aa-*d*$_2$** was determined by ^{1}H NMR (500 MHz, $CDCl_3$) to be 9.5:1.

2.3.3 Control experiments



2.3.4 Preparation of complex C3



A 8 mL screw-cap vial was charged with complex **C1** (42.8 mg, 1.0 equiv, 0.1 mmol), **2a** (41.7 mg, 1.0 equiv, 0.1 mmol), $AgSbF_6$ (34.4 mg, 1.0 equiv, 0.1 mmol) and DCM (2.0 mL). The vial was sealed under N_2 and stirred at room temperature for overnight. The mixture was filtered through a short pad of celite and concentrated under reduced pressure to afford the mixture of complex **C3** and 2-iodobenzonic acid as an orange solid. The complex **C3** can be recrystallized from chloroform and diethyl ether as a single crystal.

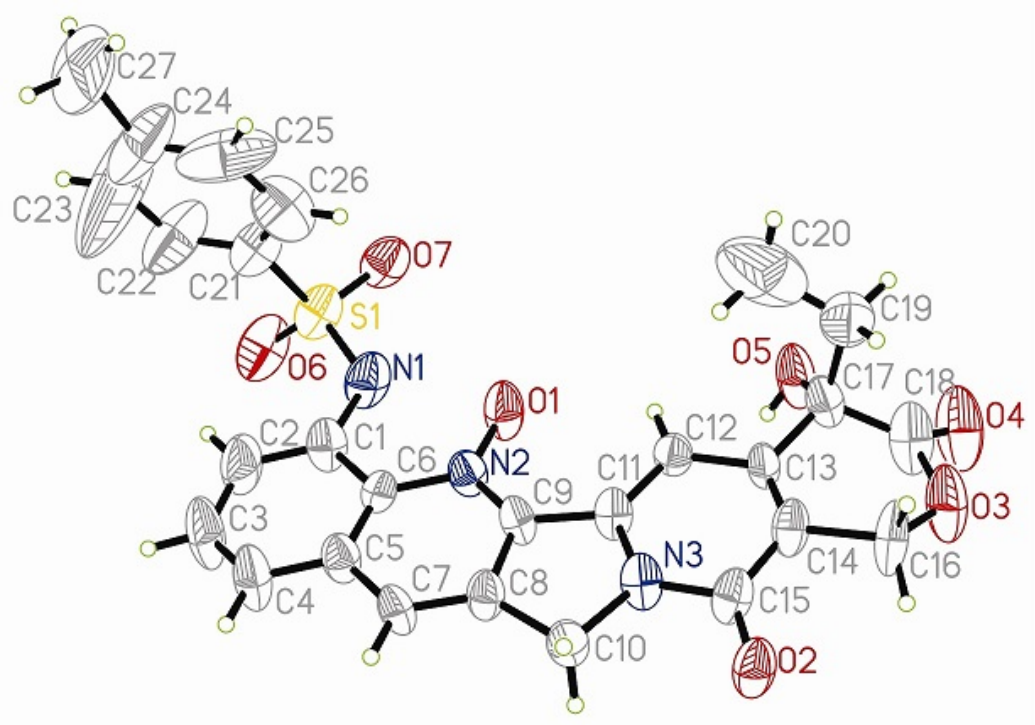
3. References

(1) Brand, J. P.; Chevalley, C.; Scopelliti, R.; Waser, J. *Chem. – Eur. J.* **2012**, *18*, 5655–5666.

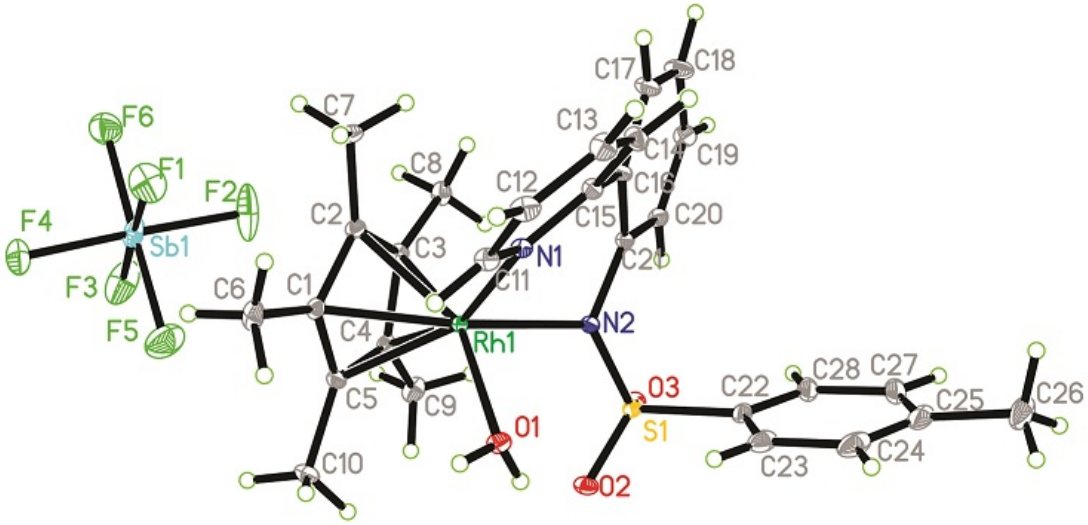
(2) In the original paper, the NMR chemical shifts of amidobenziodoxolones were measured with $CDCl_3$ and CF_3COOH as solvent. Actually, these compounds are insoluble in pure $CDCl_3$ while they displayed satisfactory solubility in dimethyl sulfoxide. It was presumed that the cyclic structures might be destroyed in the presence of trifluoroacetic acid. In addition, compound **2a** in the solution of $CDCl_3/CF_3COOH$ (20:1) was found to partially decompose within 24 h, as determined by ^1H NMR test. Whereas, compound **2a** in the solid state showed reasonable stability even it was stored at room temperature for one month. For a related literature, see: Kitamura, T.; Nagata, K.; Taniguchi, H. *Tetrahedron Lett.* **1995**, *36*, 1081–1084.

(3) Li, L.; Brennessel, W. W.; Jones, W. D. *J. Am. Chem. Soc.* **2008**, *130*, 12414–12419.

4. X-ray structures of compounds 8 and C3

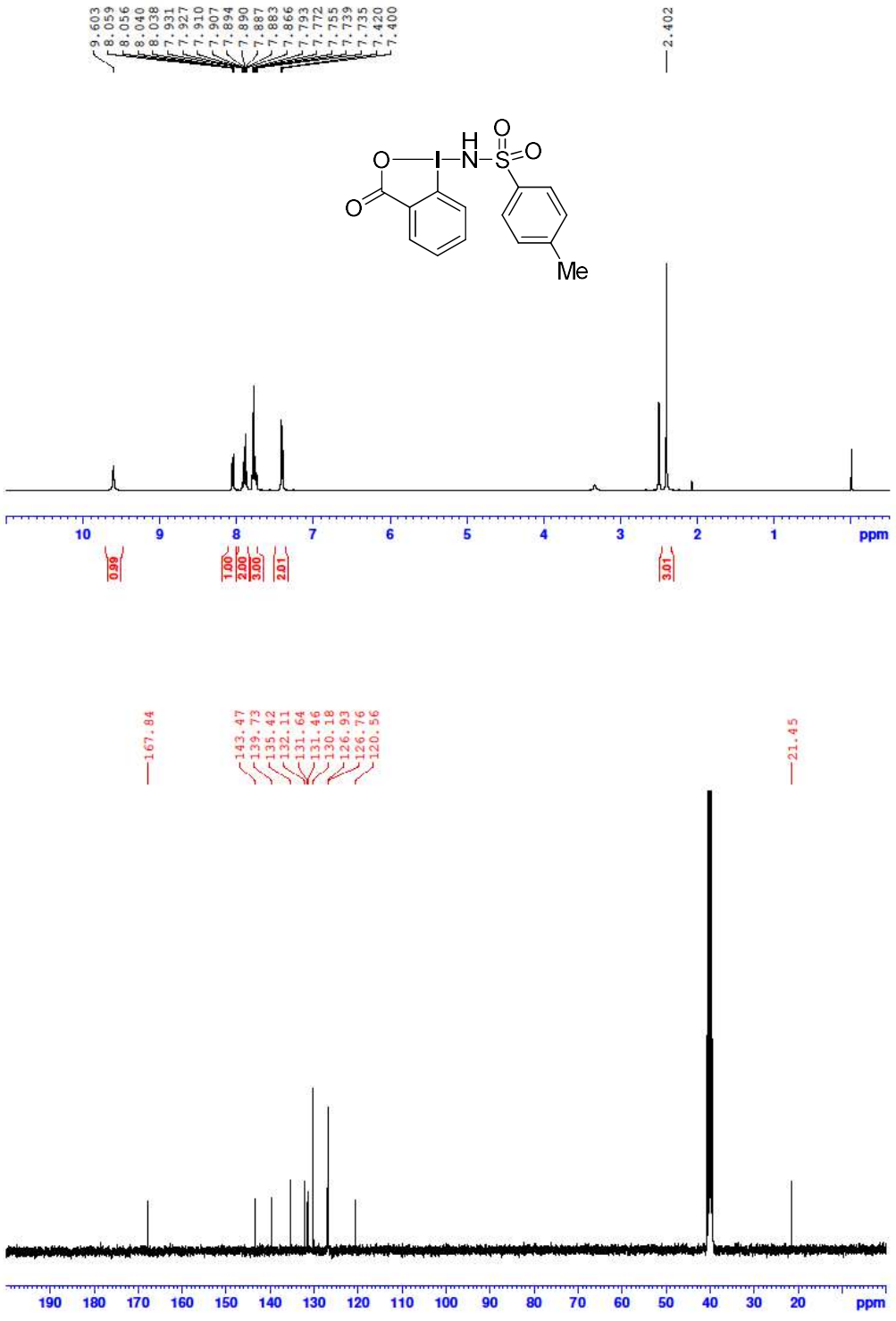


Crystal structure of 8. ORTEP drawing with 50% probability thermal ellipsoids. Cambridge Crystallographic Data Centre Deposition Number: 1471890.

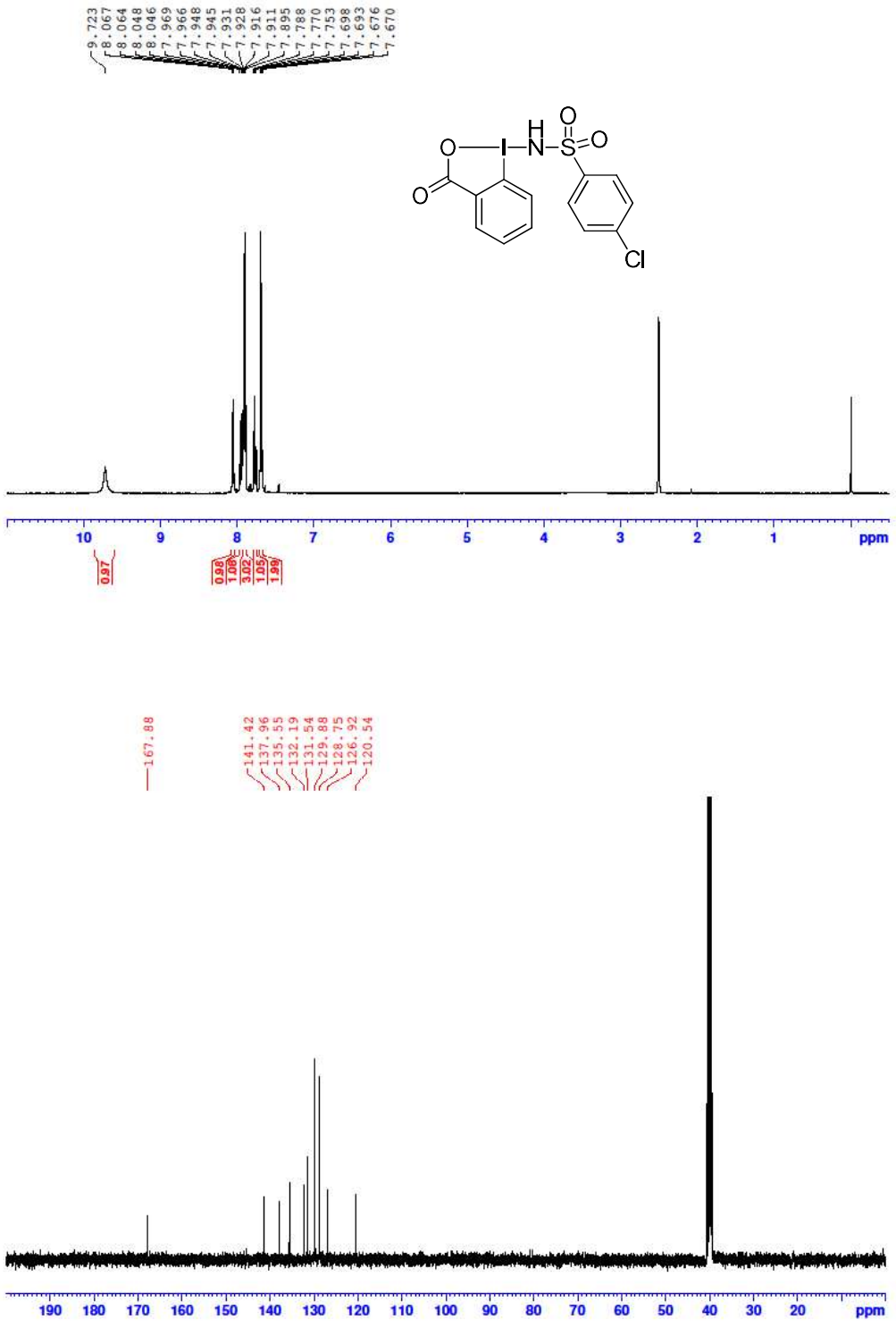


Crystal structure of C3. ORTEP drawing with 50% probability thermal ellipsoids. Cambridge Crystallographic Data Centre Deposition Number: 1477689.

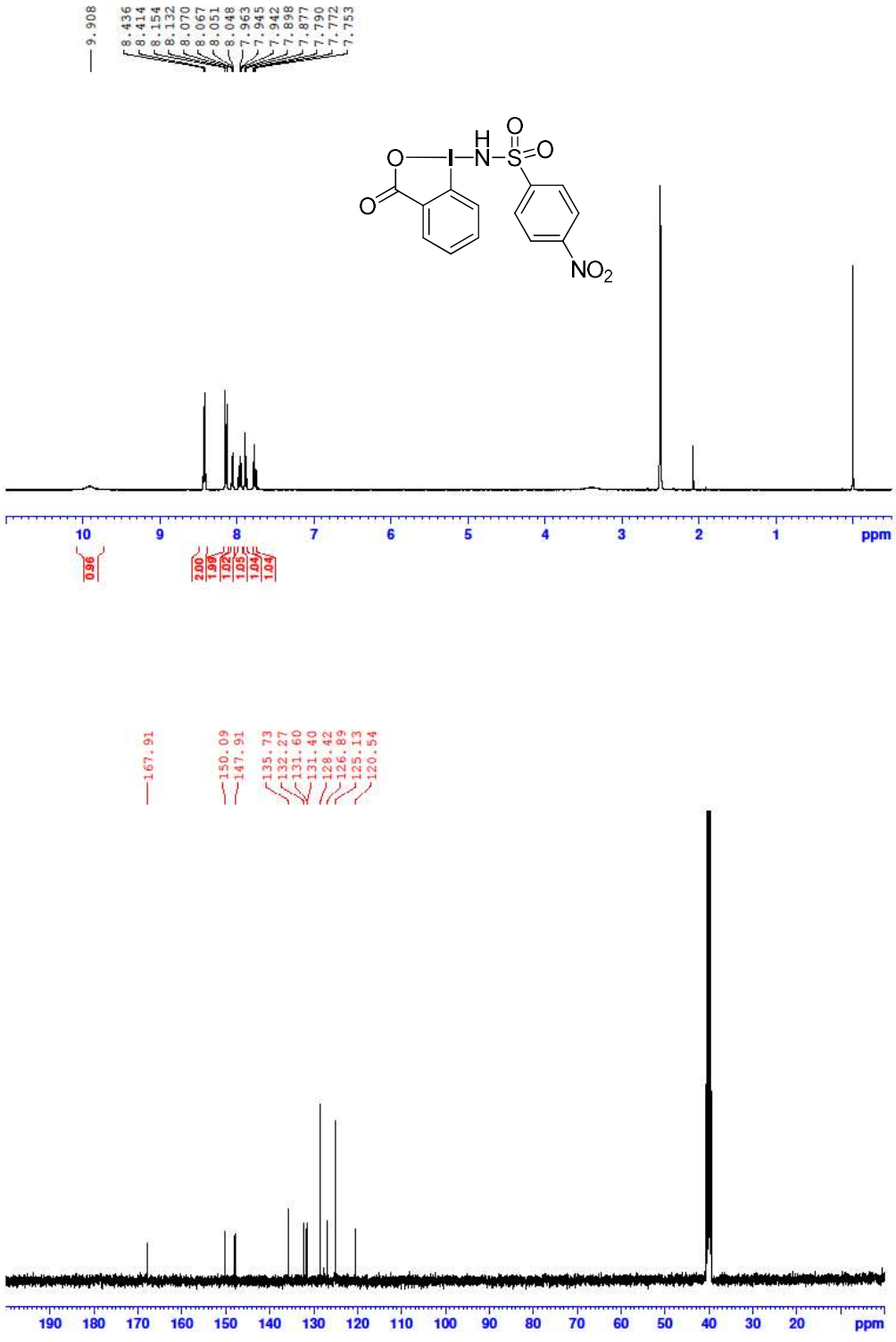
5. NMR spectra of amidobenziodoxolones and the amidation products



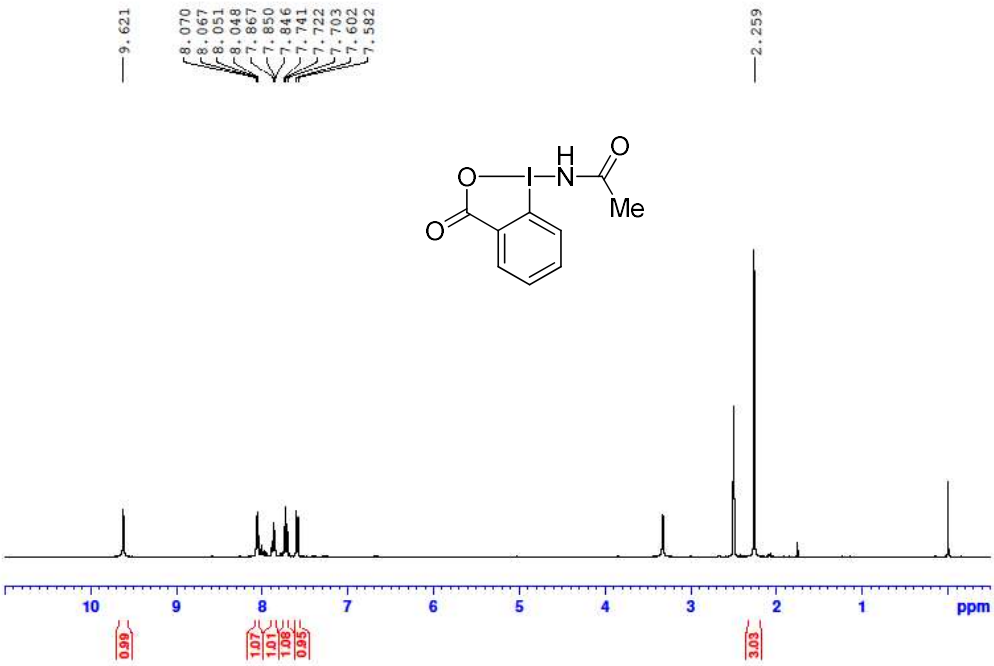
^{1}H and ^{13}C NMR spectra for compound 2a (DMSO-d_6)

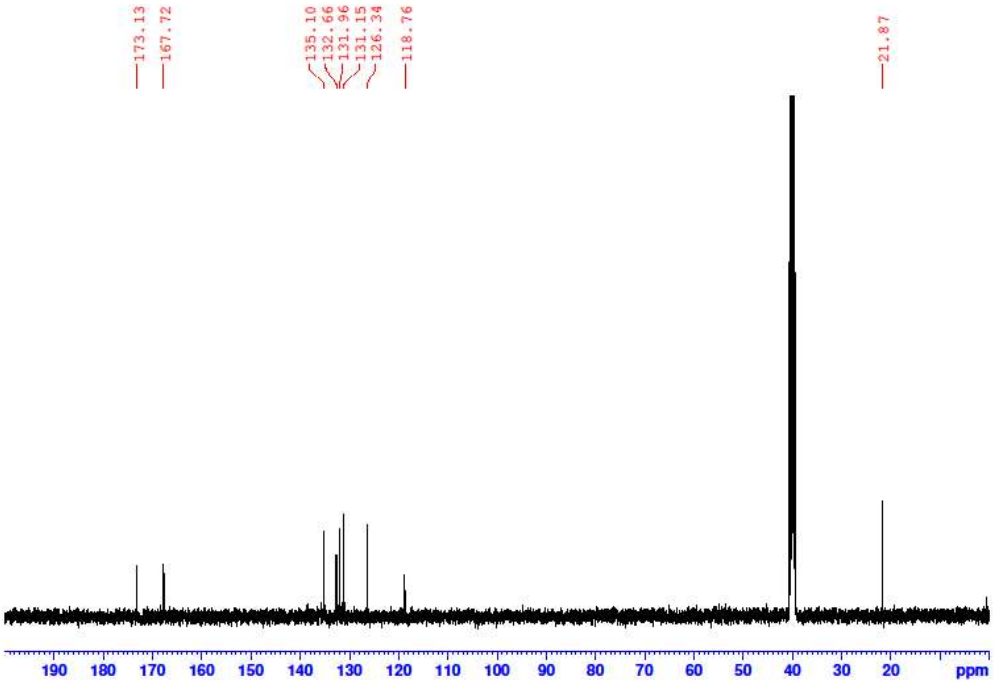


^{1}H and ^{13}C NMR spectra for compound 2b (DMSO-*d*$_6$)

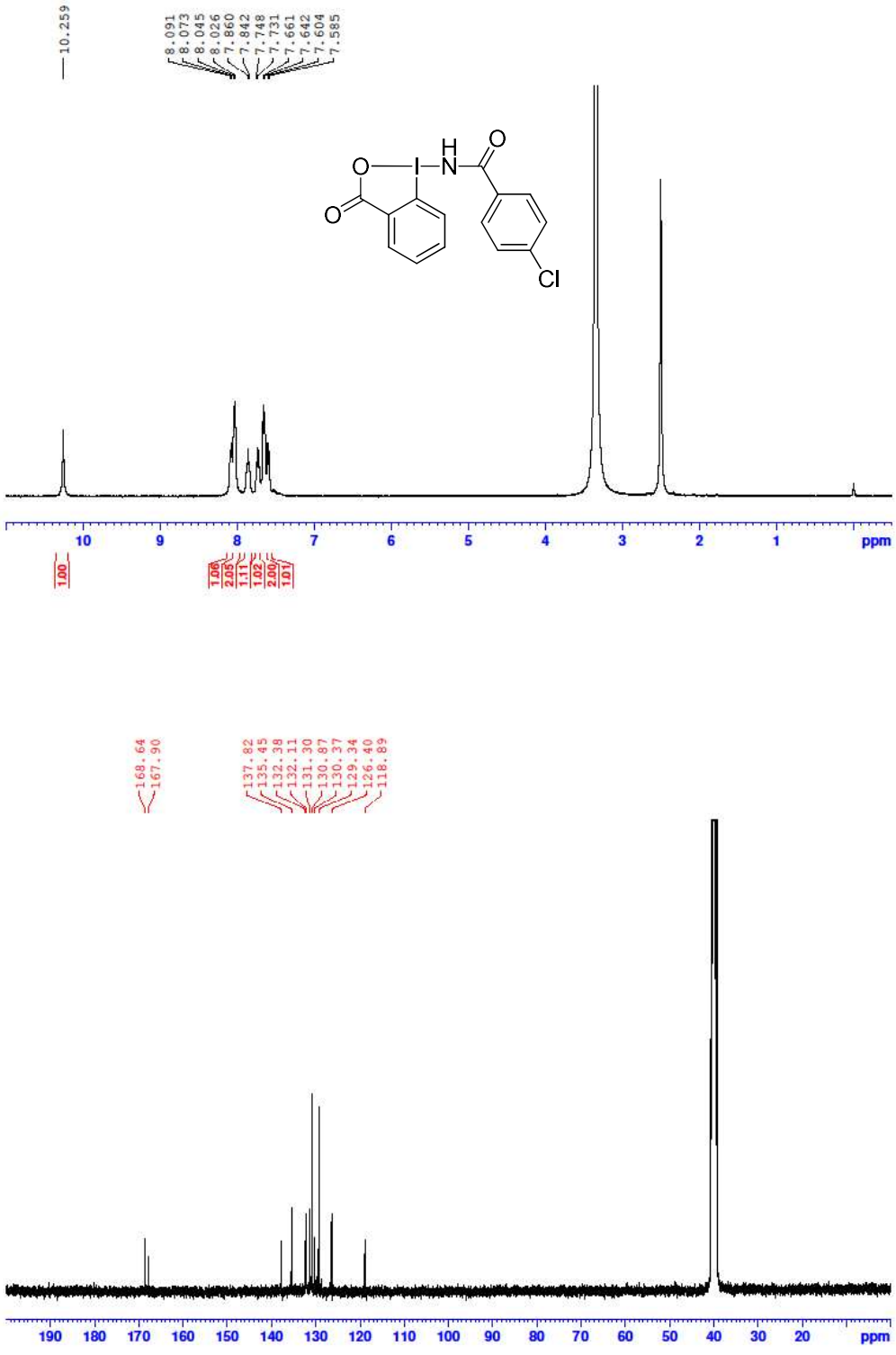


^{1}H and ^{13}C NMR spectra for compound 2c (DMSO-*d*$_6$)

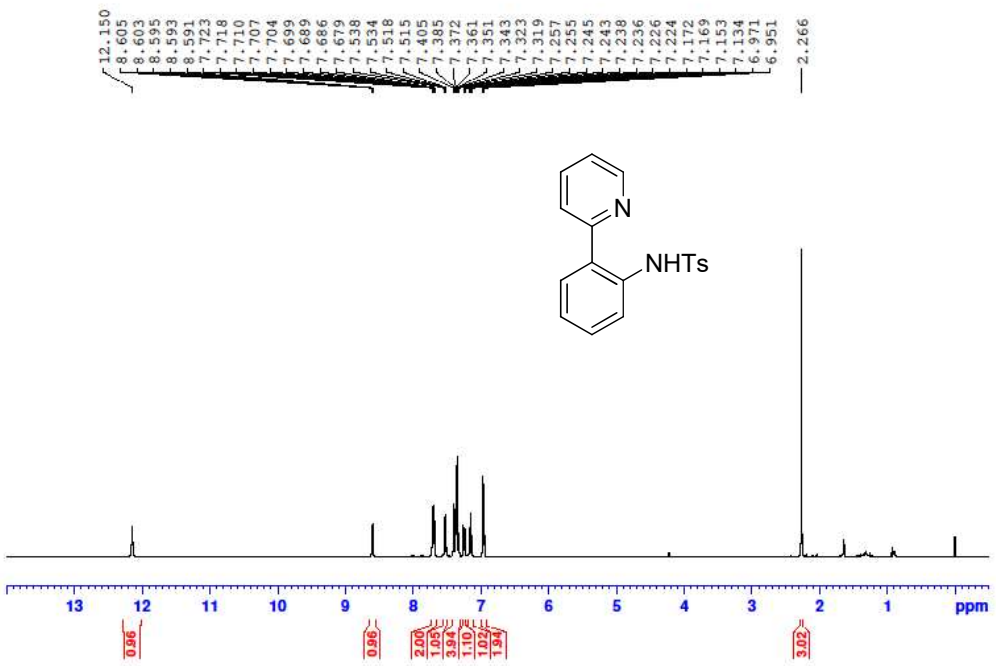


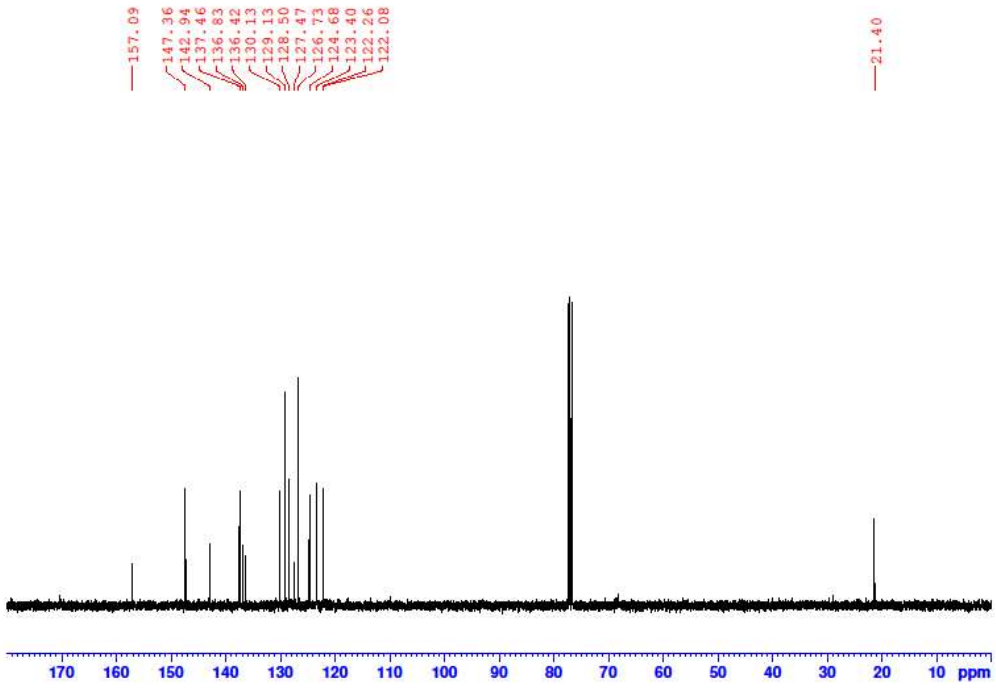


^{1}H and ^{13}C NMR spectra for compound 2d (DMSO-*d*$_6$)

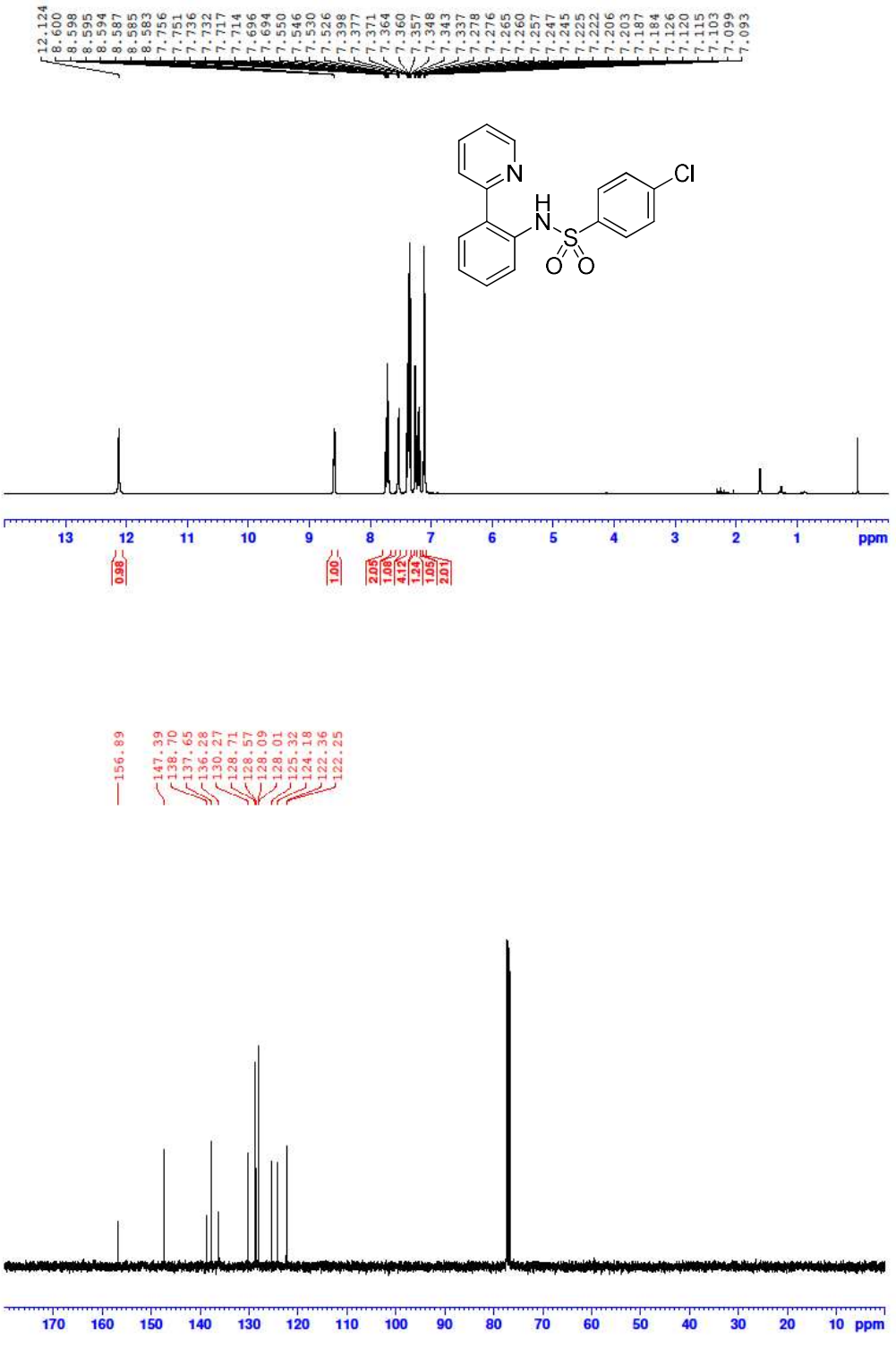


^{1}H and ^{13}C NMR spectra for compound 2e (DMSO-*d*$_6$)

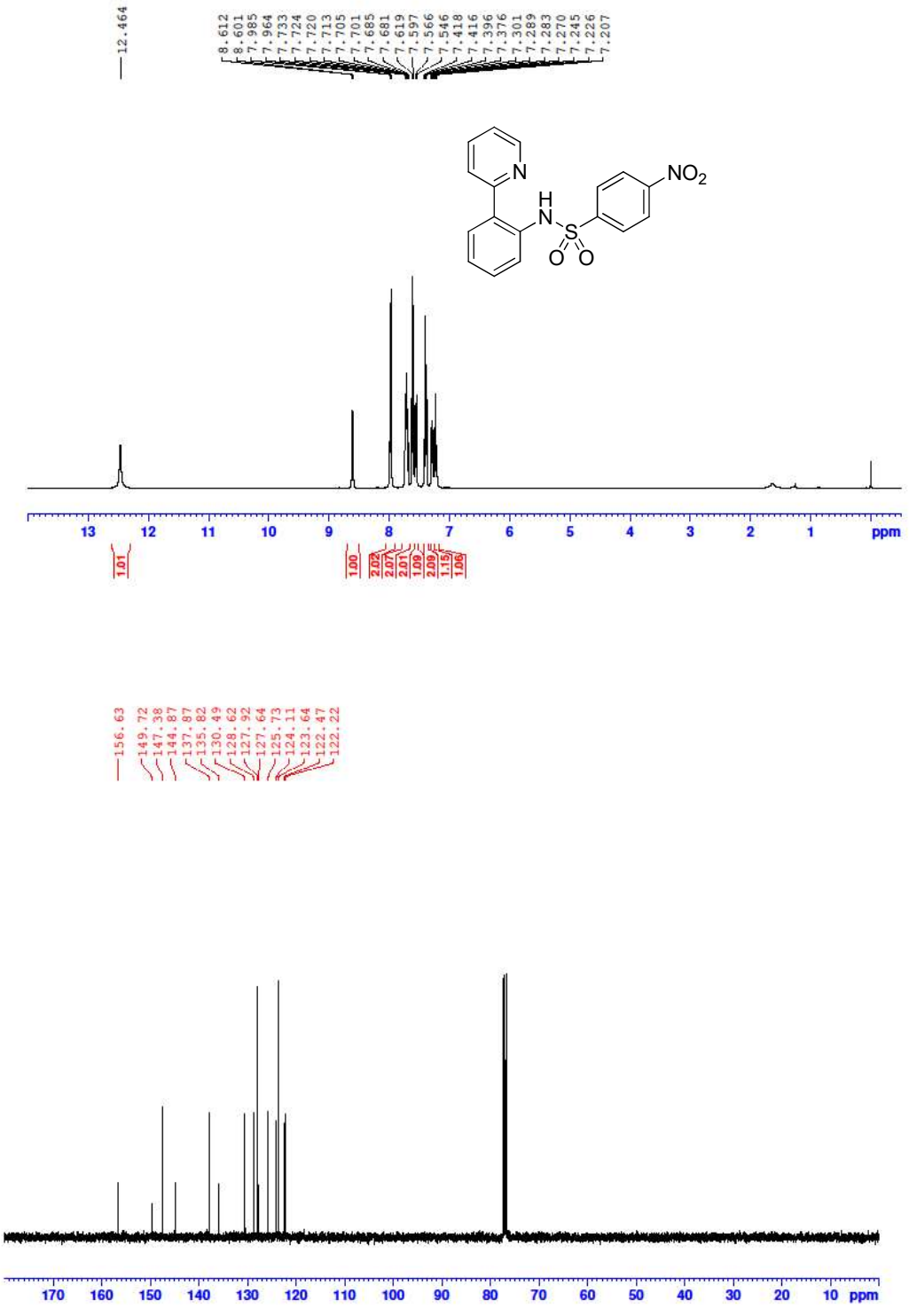




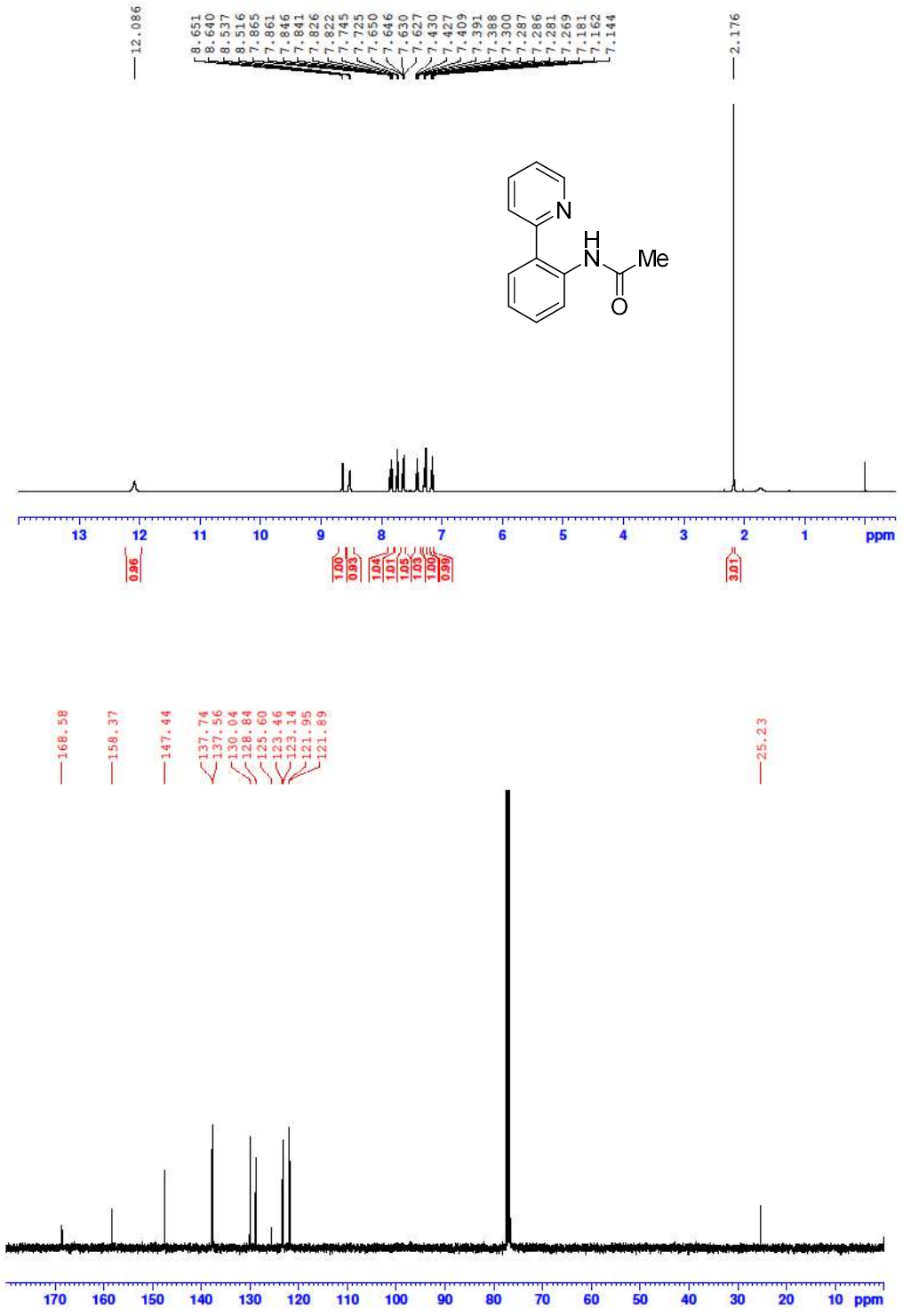
^{1}H and ^{13}C NMR spectra for product 3aa ($CDCl_3$)



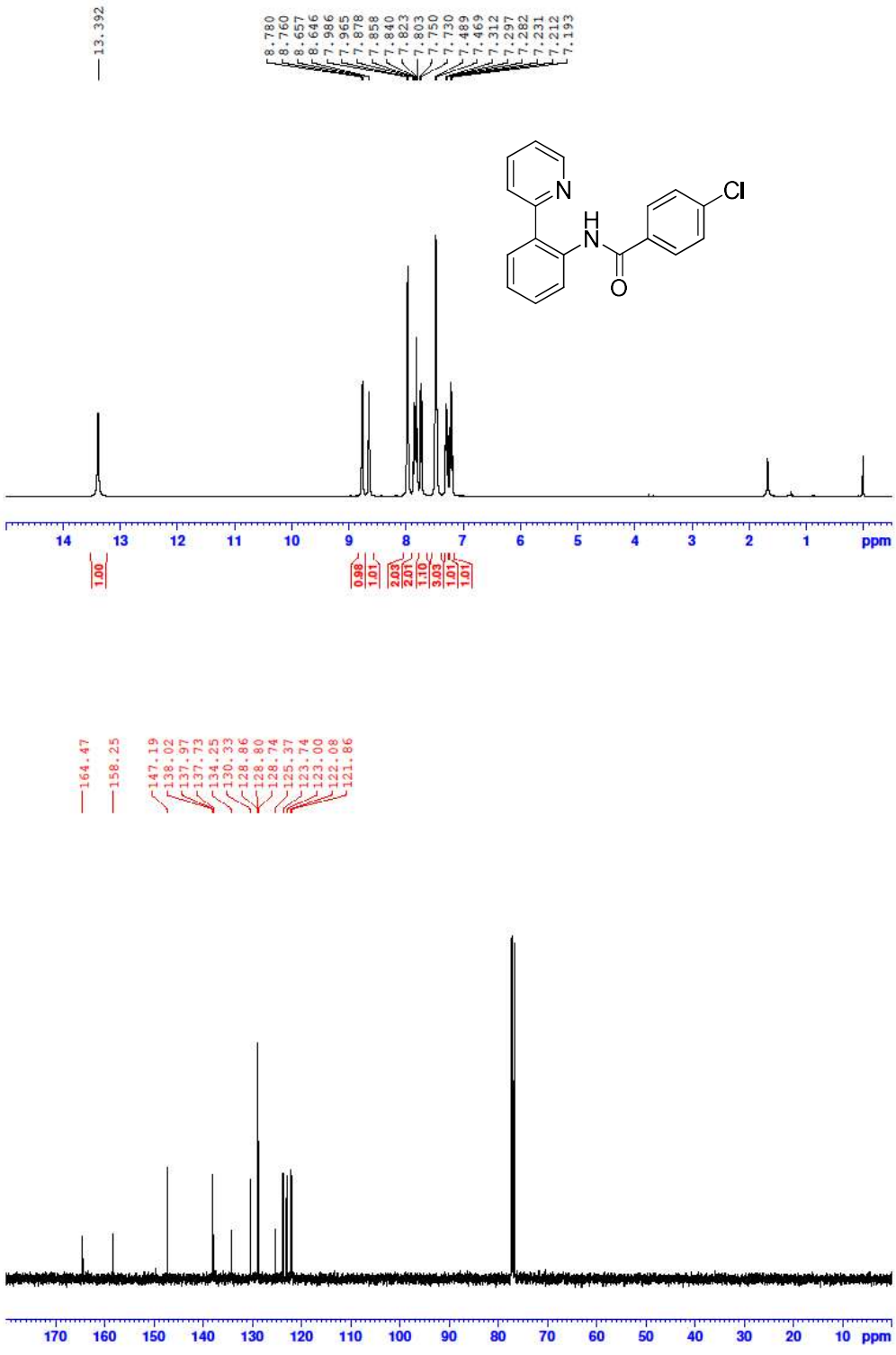
^{1}H and ^{13}C NMR spectra for product 3ab ($CDCl_3$)



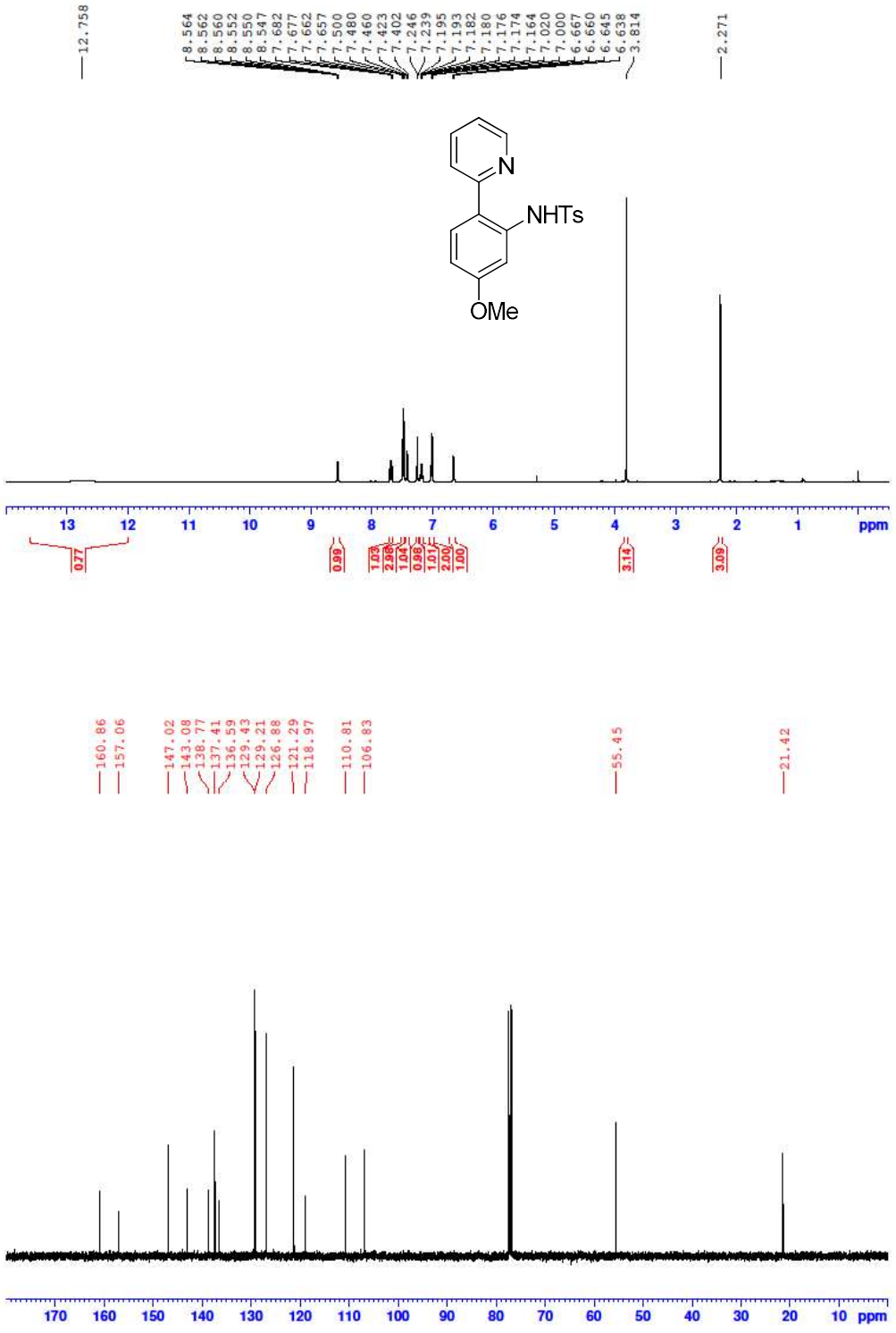
^{1}H and ^{13}C NMR spectra for product 3ac ($CDCl_3$)



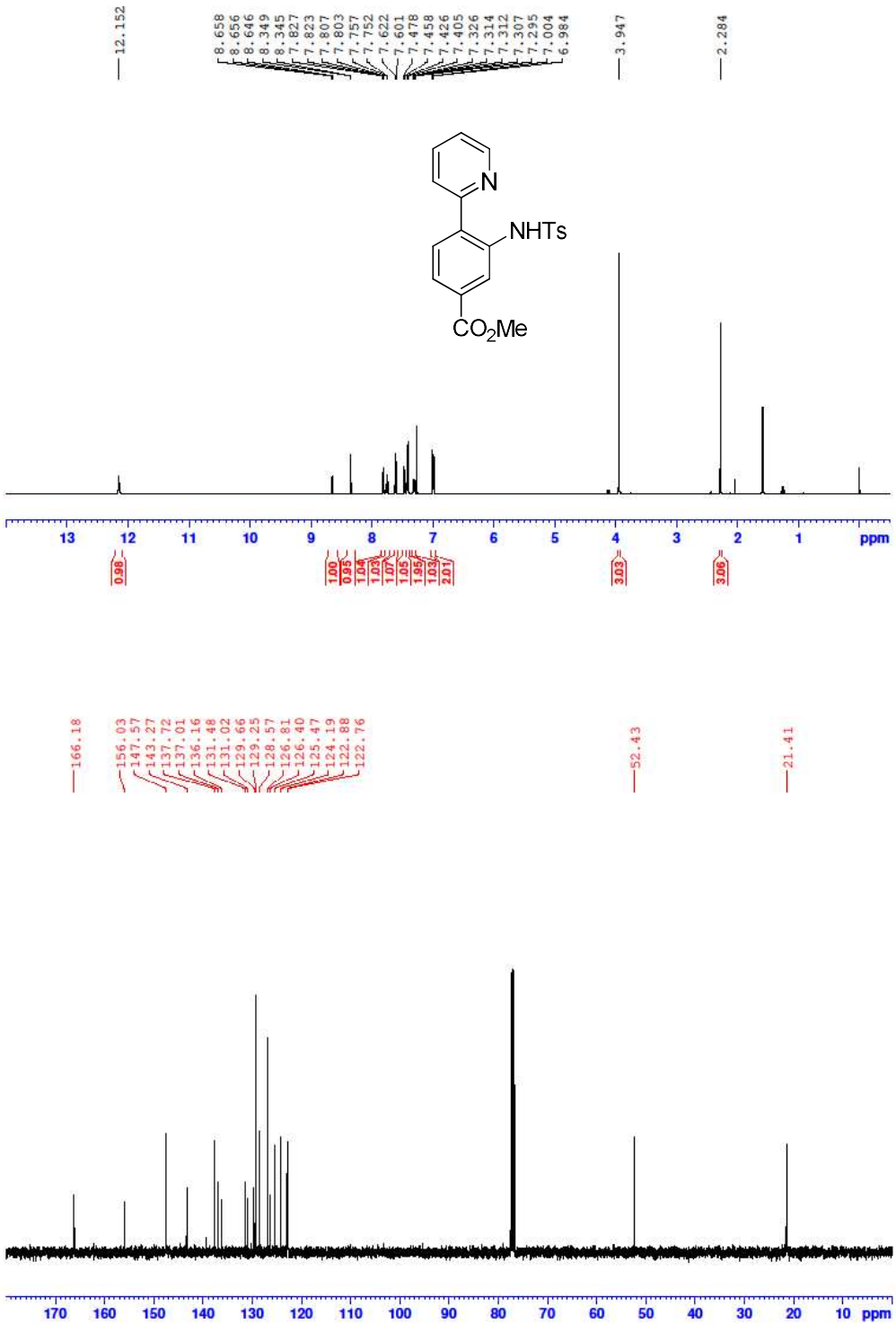
^{1}H and ^{13}C NMR spectra for product 3ad ($CDCl_3$)



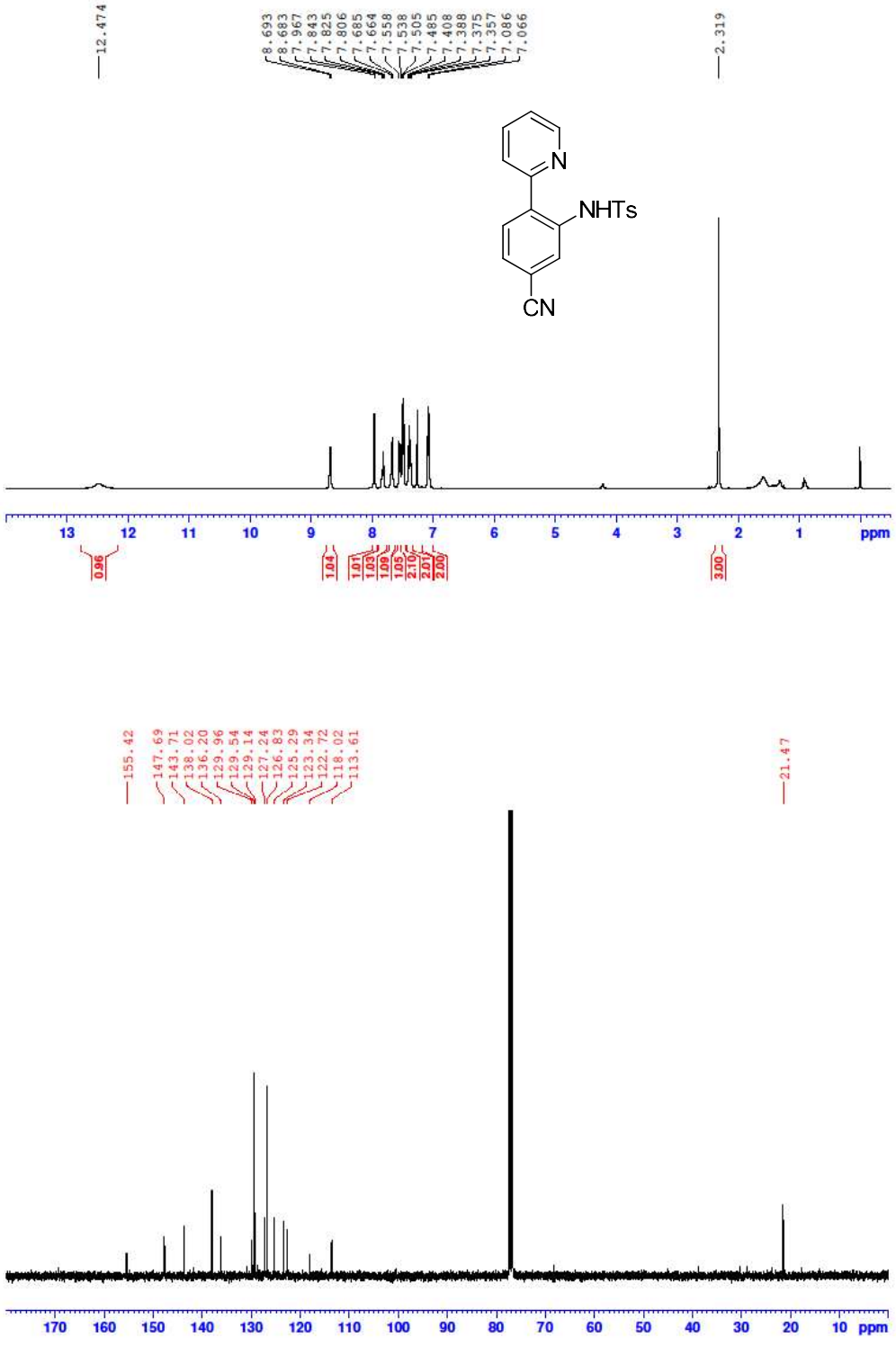
^{1}H and ^{13}C NMR spectra for product 3ae ($CDCl_3$)



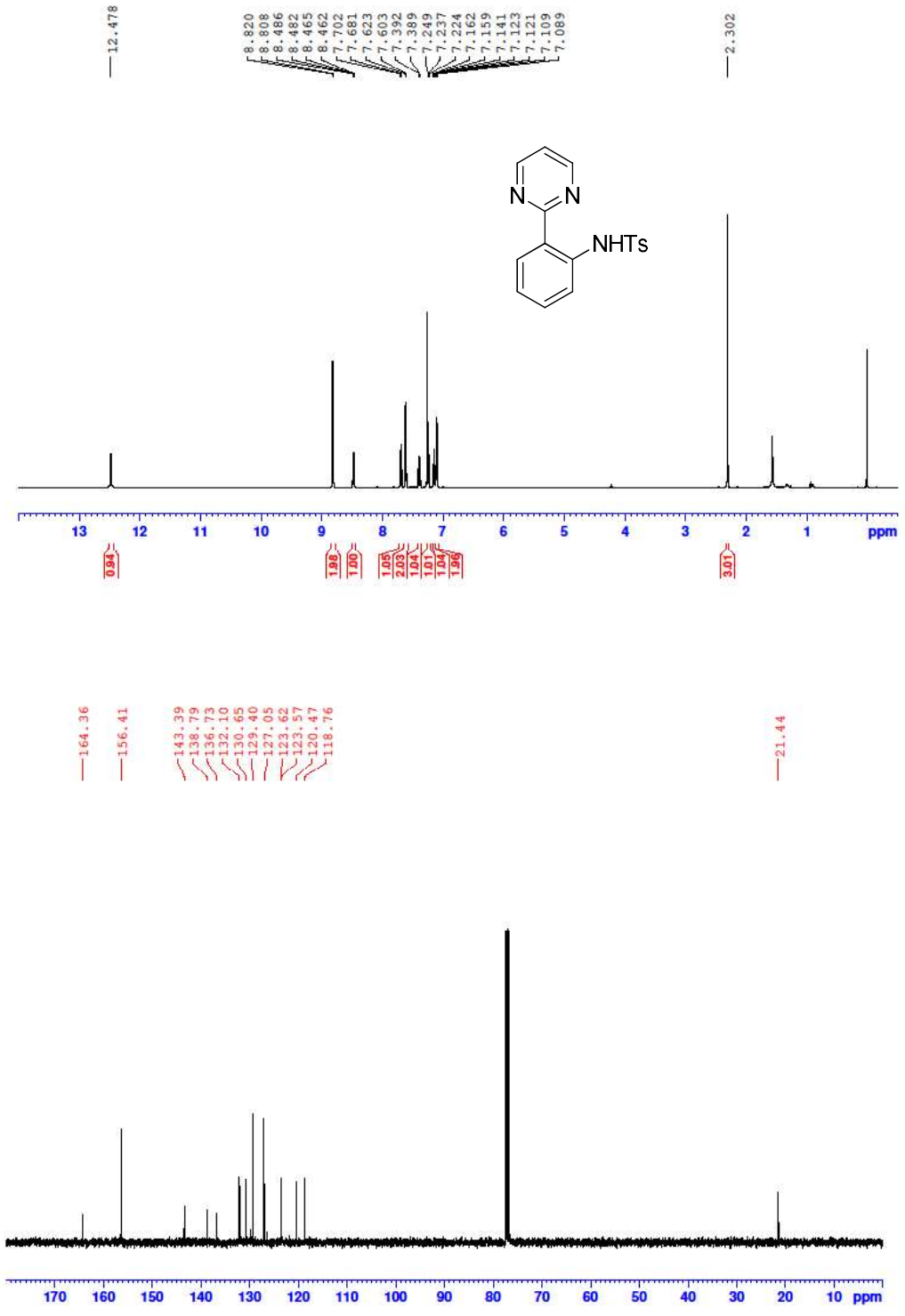
^{1}H and ^{13}C NMR spectra for product 3ba ($CDCl_3$)



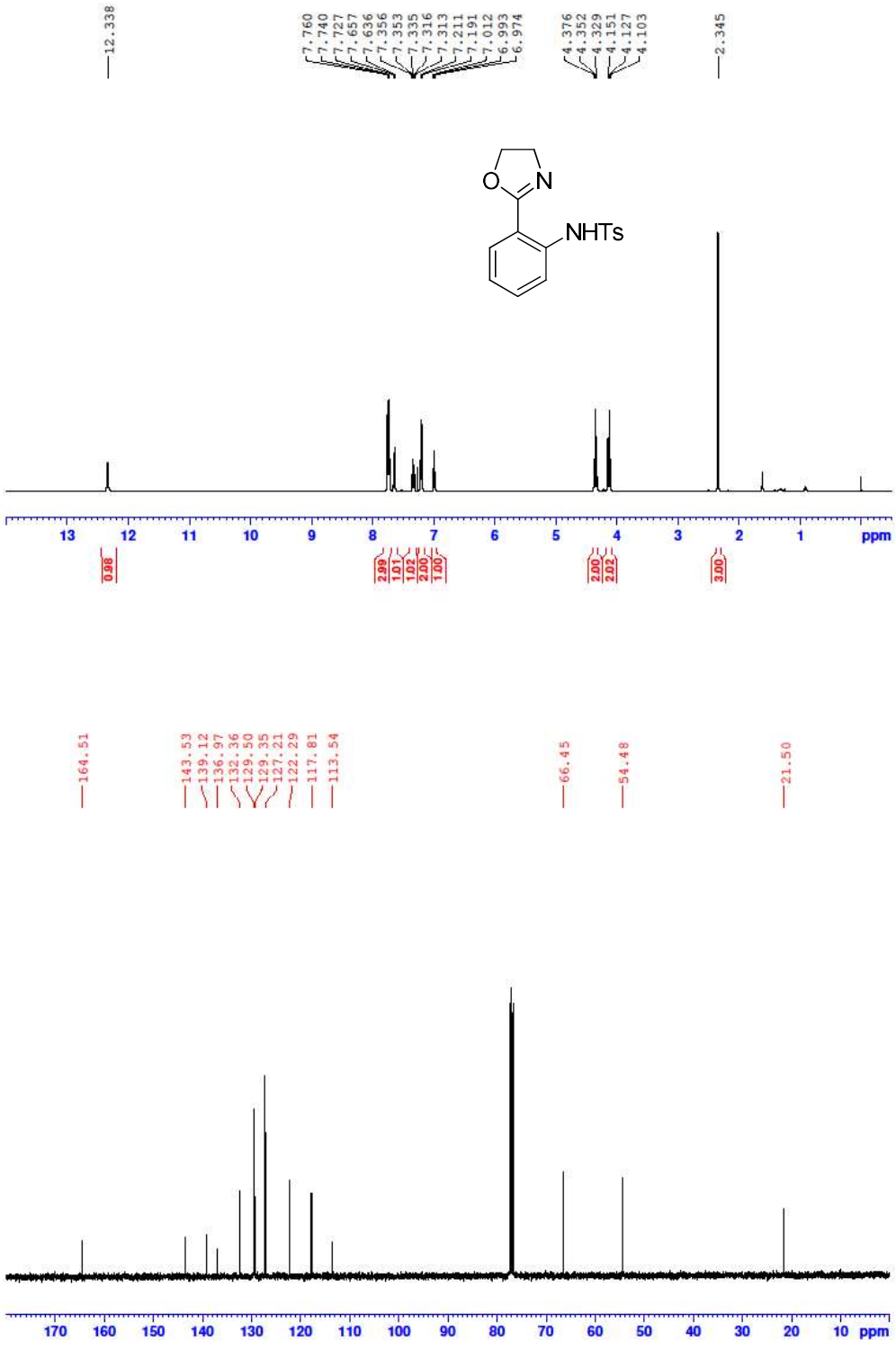
^{1}H and ^{13}C NMR spectra for product 3ca ($CDCl_3$)



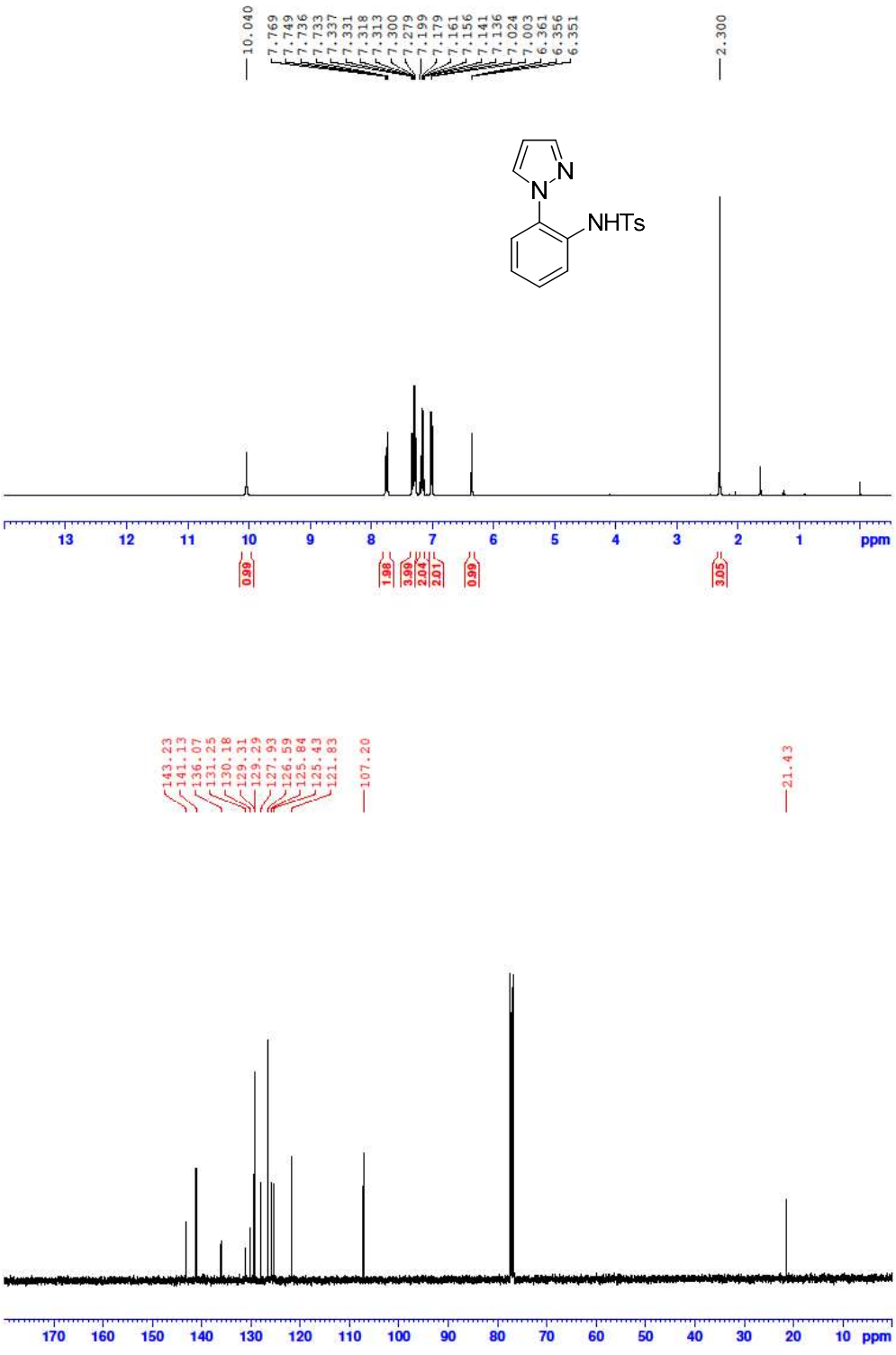
^{1}H and ^{13}C NMR spectra for product 3da ($CDCl_3$)



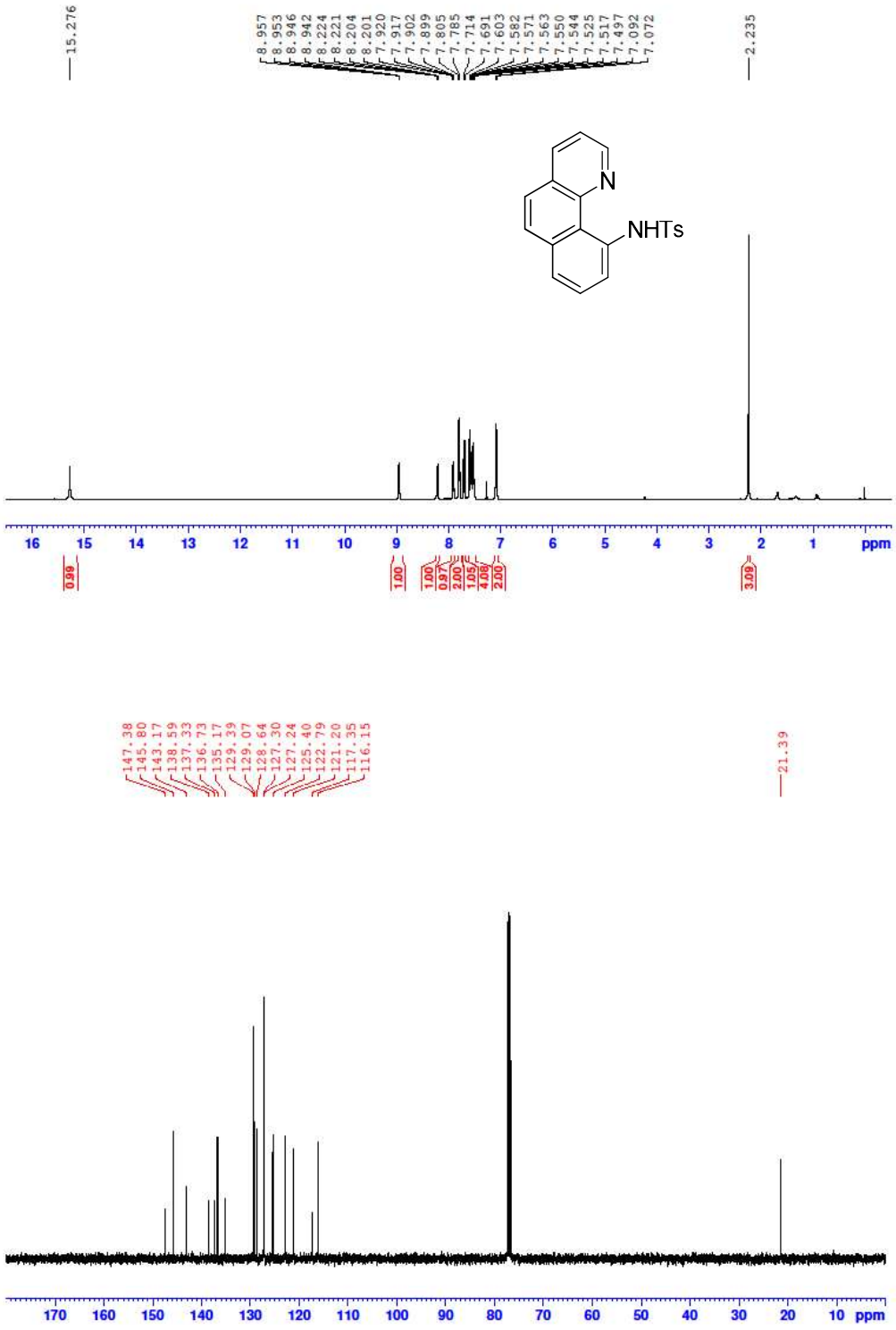
^{1}H and ^{13}C NMR spectra for product 3ea ($CDCl_3$)



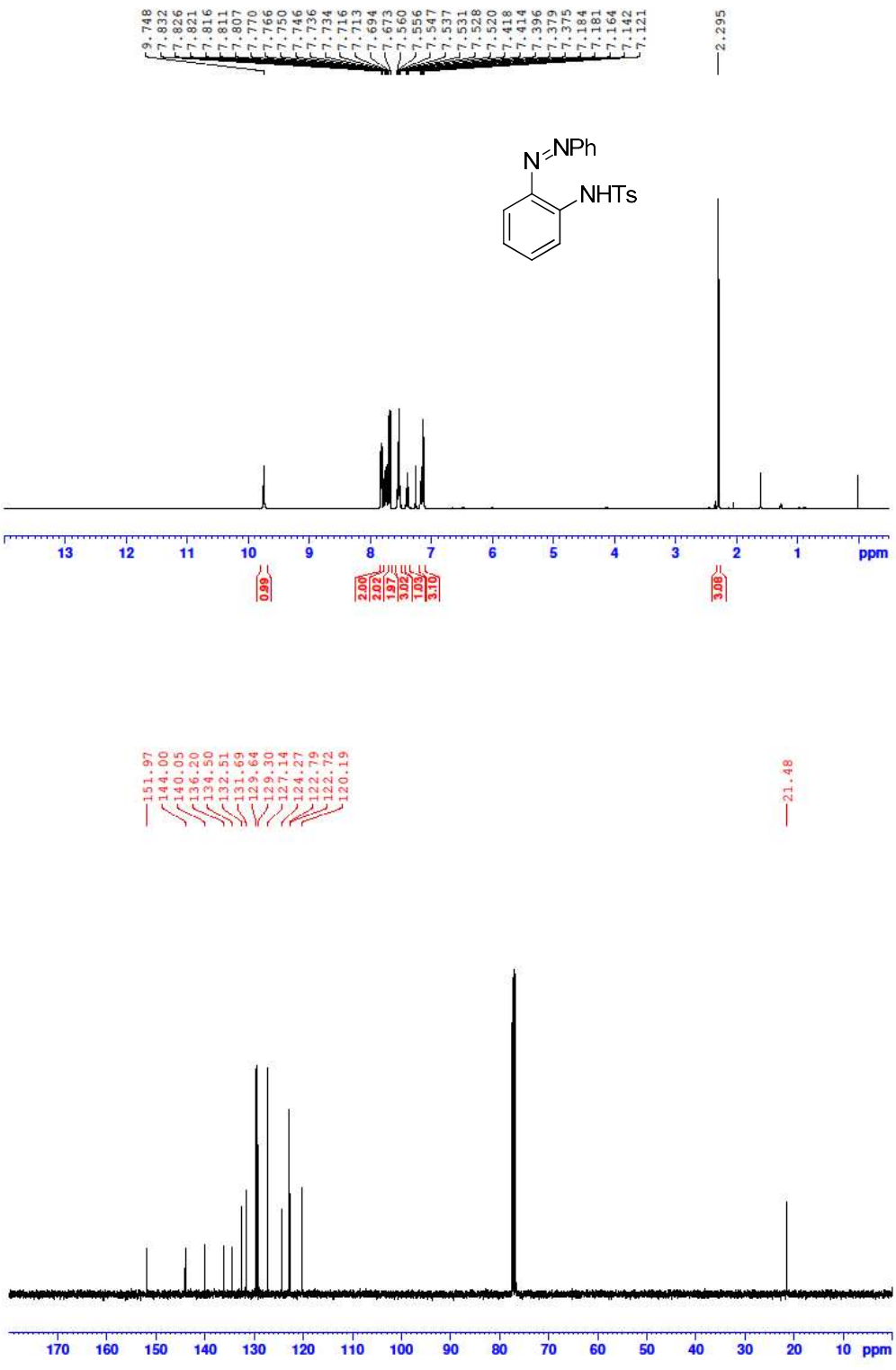
^{1}H and ^{13}C NMR spectra for product 3fa ($CDCl_3$)



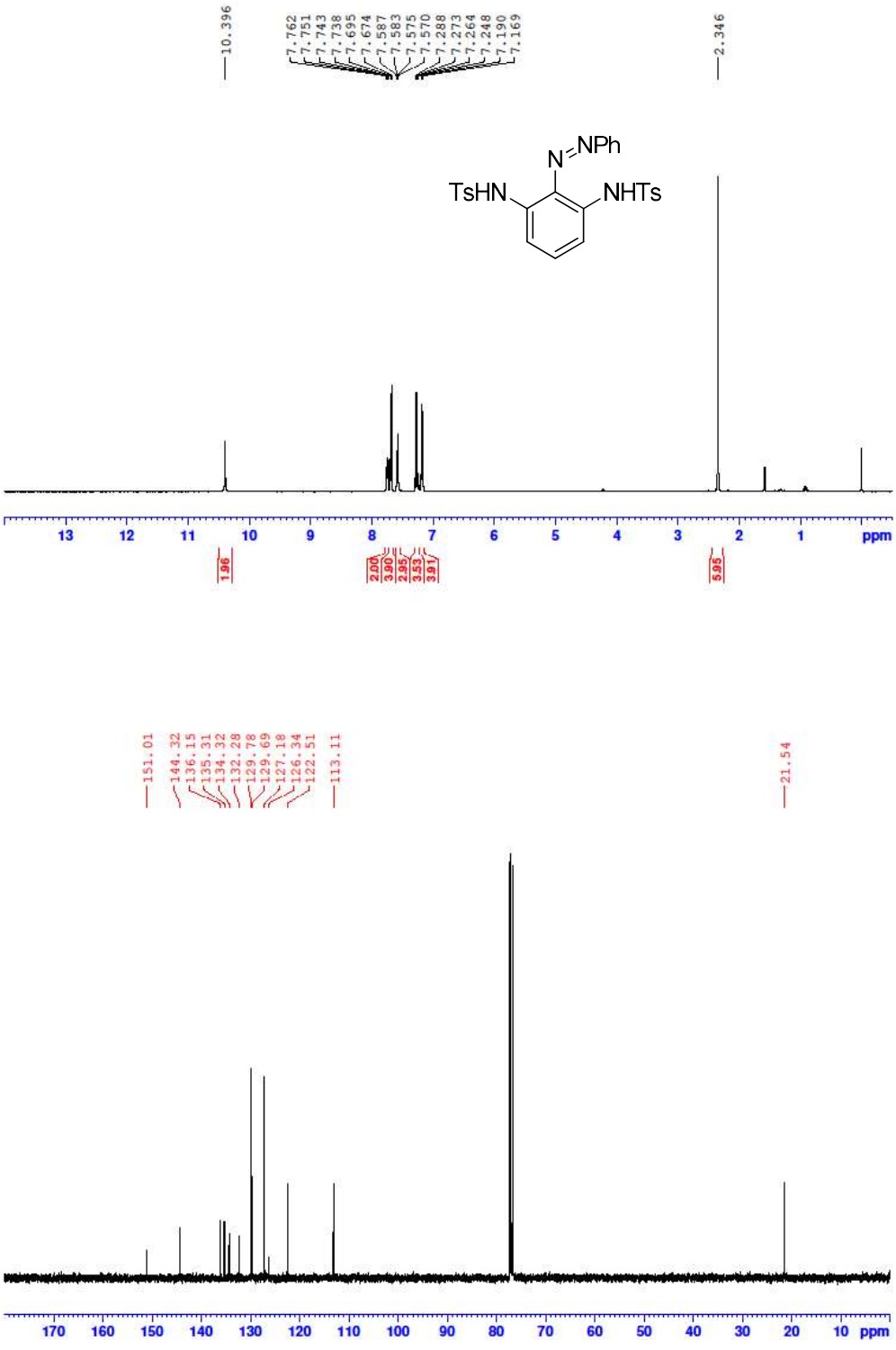
^{1}H and ^{13}C NMR spectra for product 3ga ($CDCl_3$)



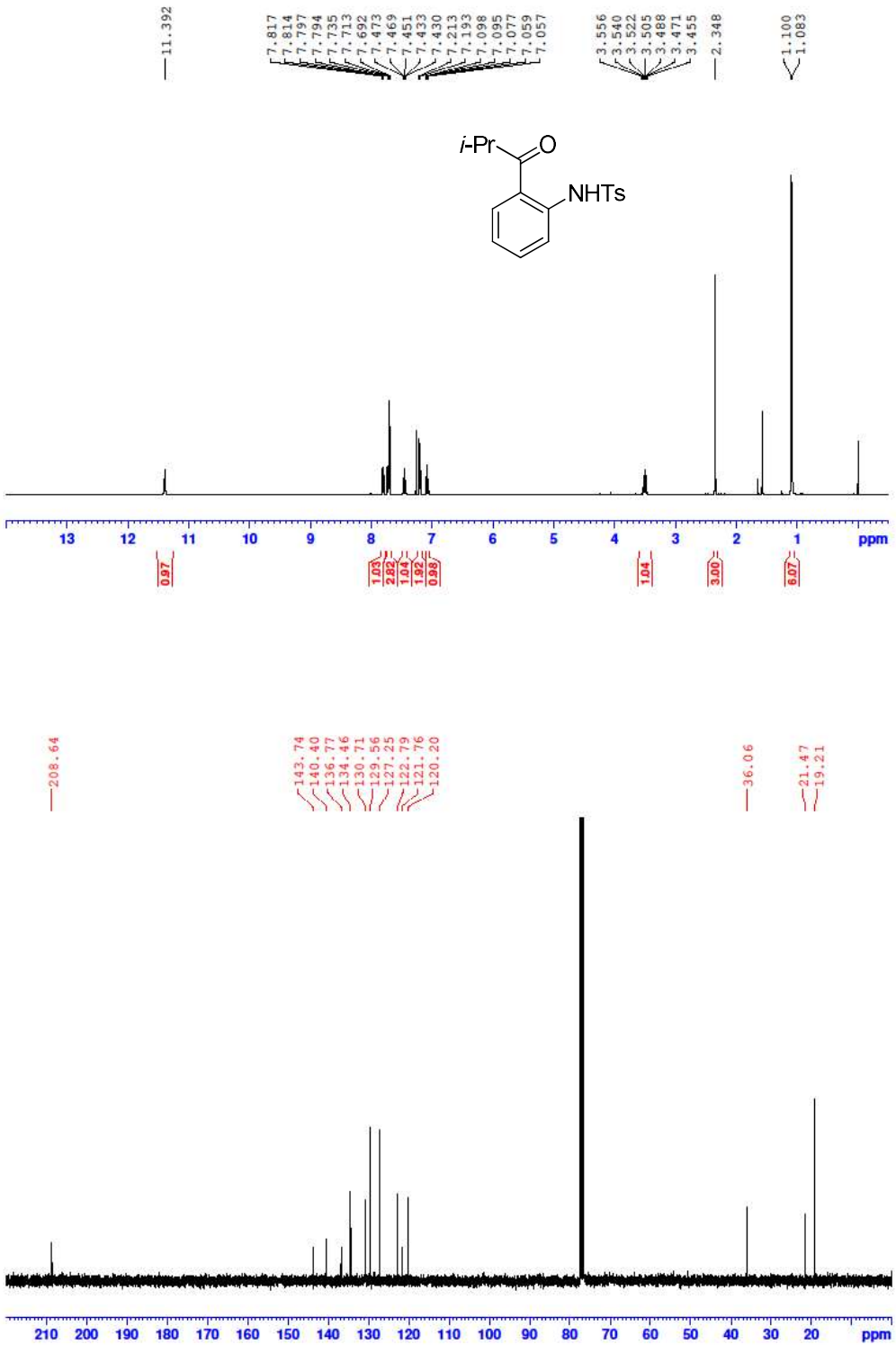
^{1}H and ^{13}C NMR spectra for product 3ha ($CDCl_3$)



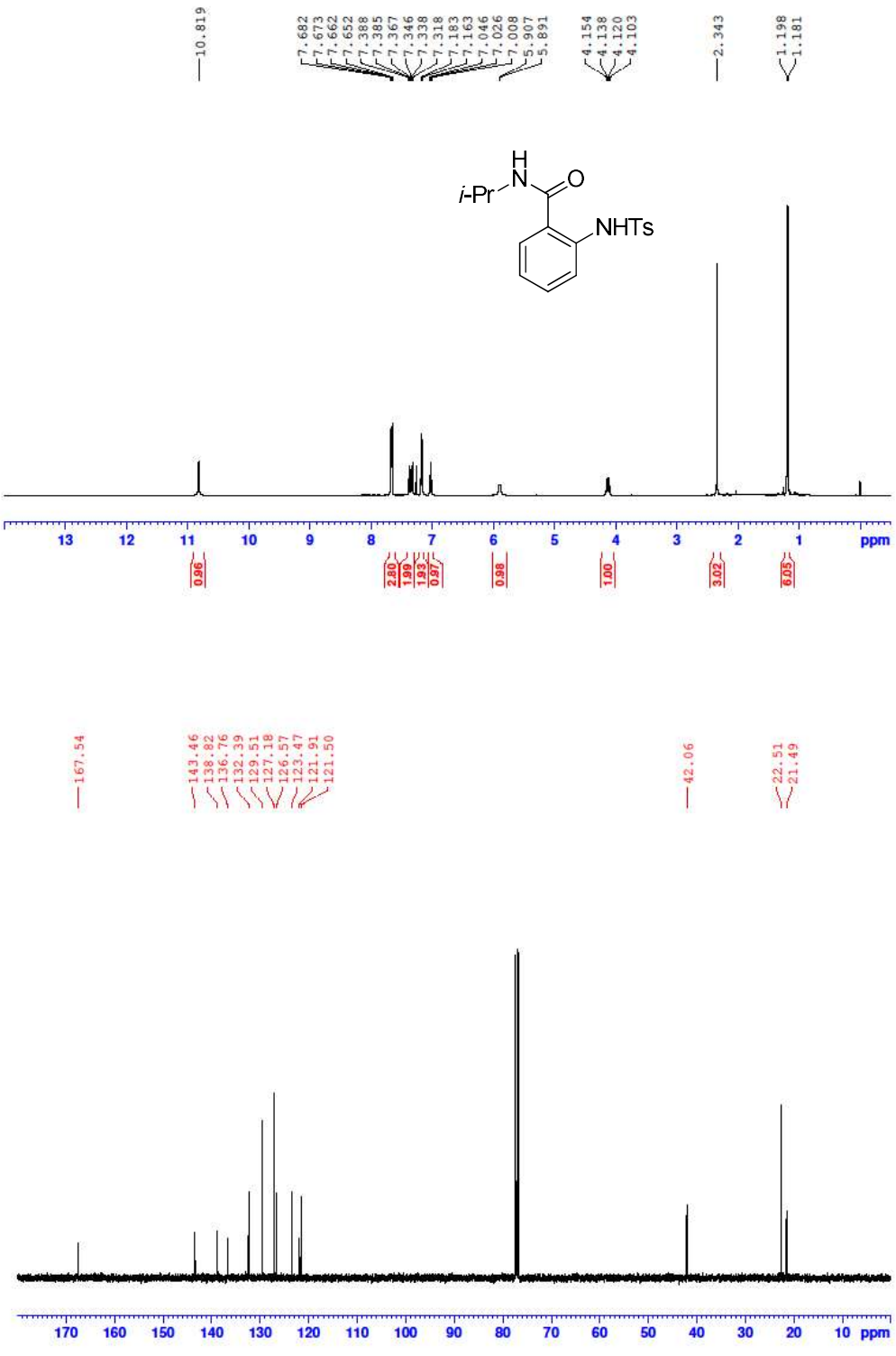
^{1}H and ^{13}C NMR spectra for product 3ia ($CDCl_3$)



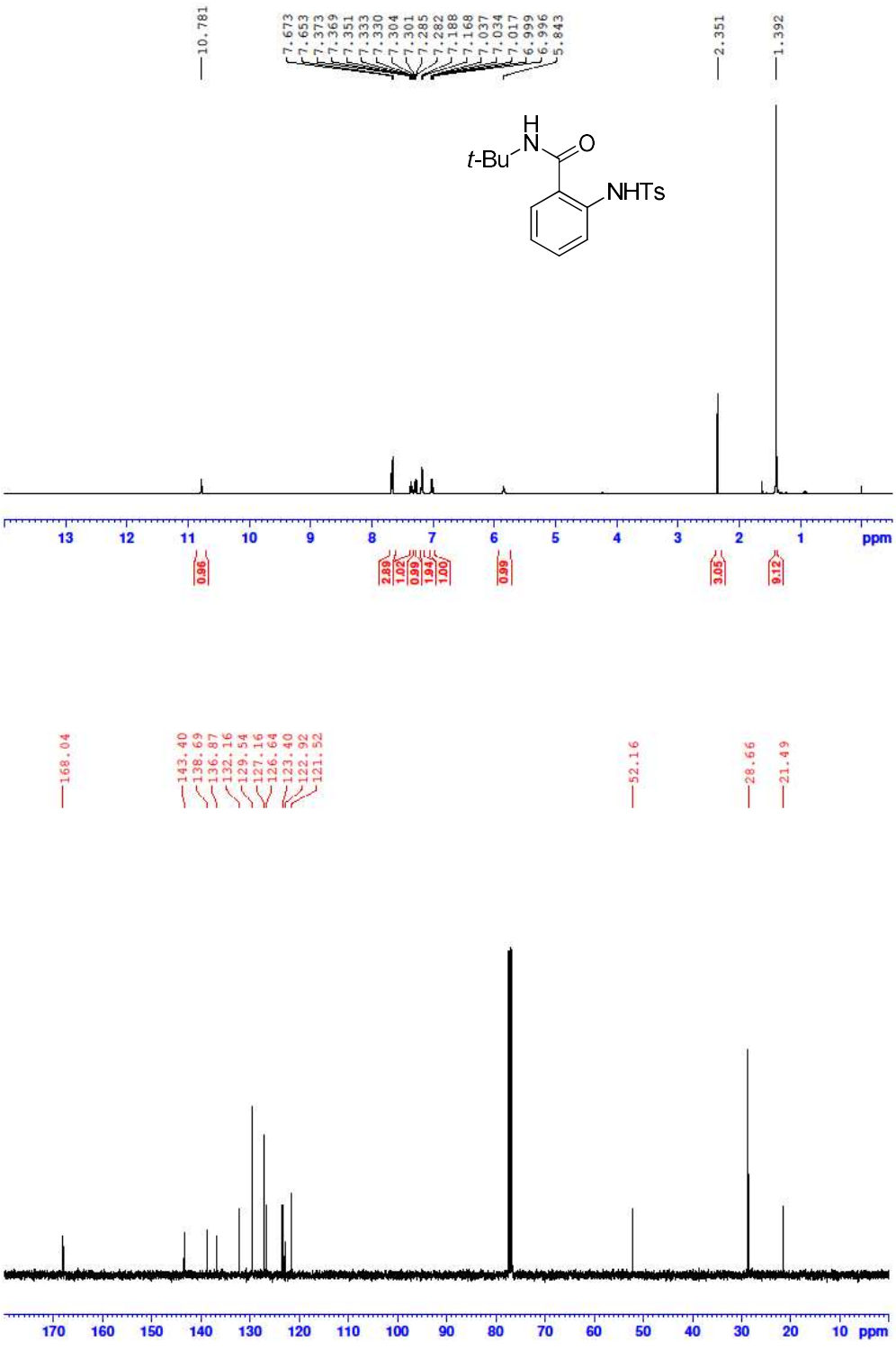
^{1}H and ^{13}C NMR spectra for product 3ia' ($CDCl_3$)



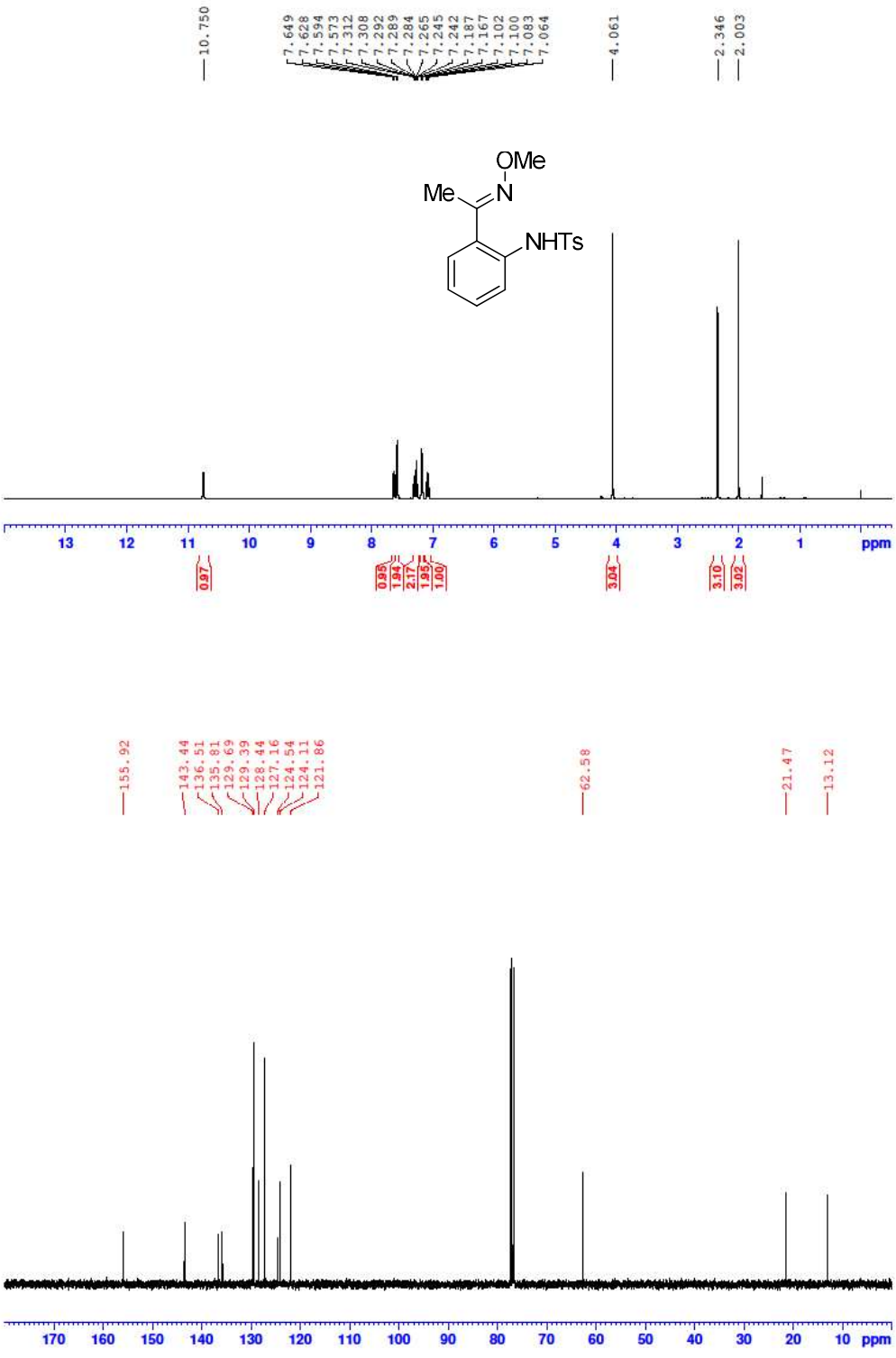
^{1}H and ^{13}C NMR spectra for product 3ja ($CDCl_3$)



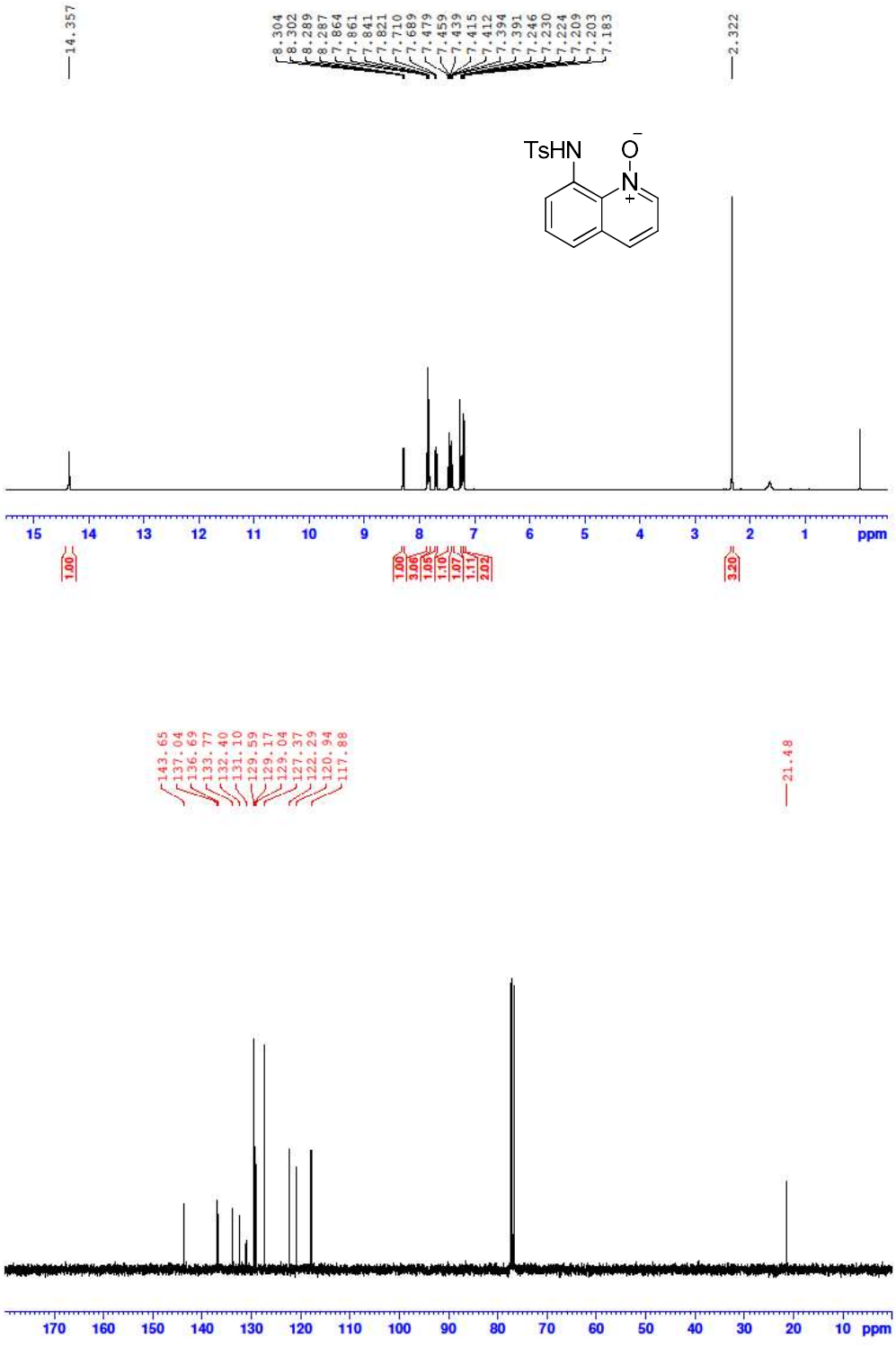
^{1}H and ^{13}C NMR spectra for product 3la ($CDCl_3$)



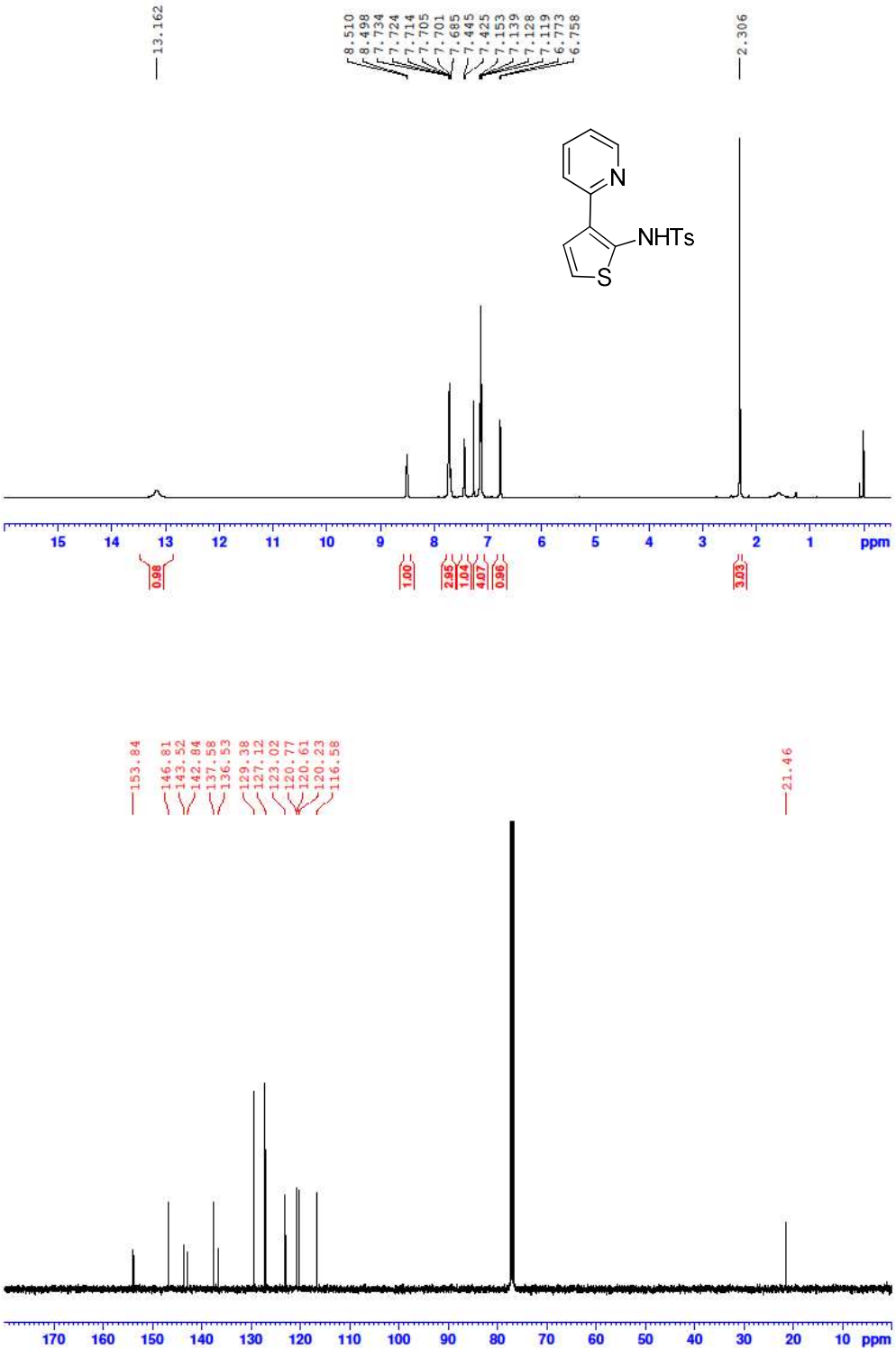
^{1}H and ^{13}C NMR spectra for product 3ma ($CDCl_3$)



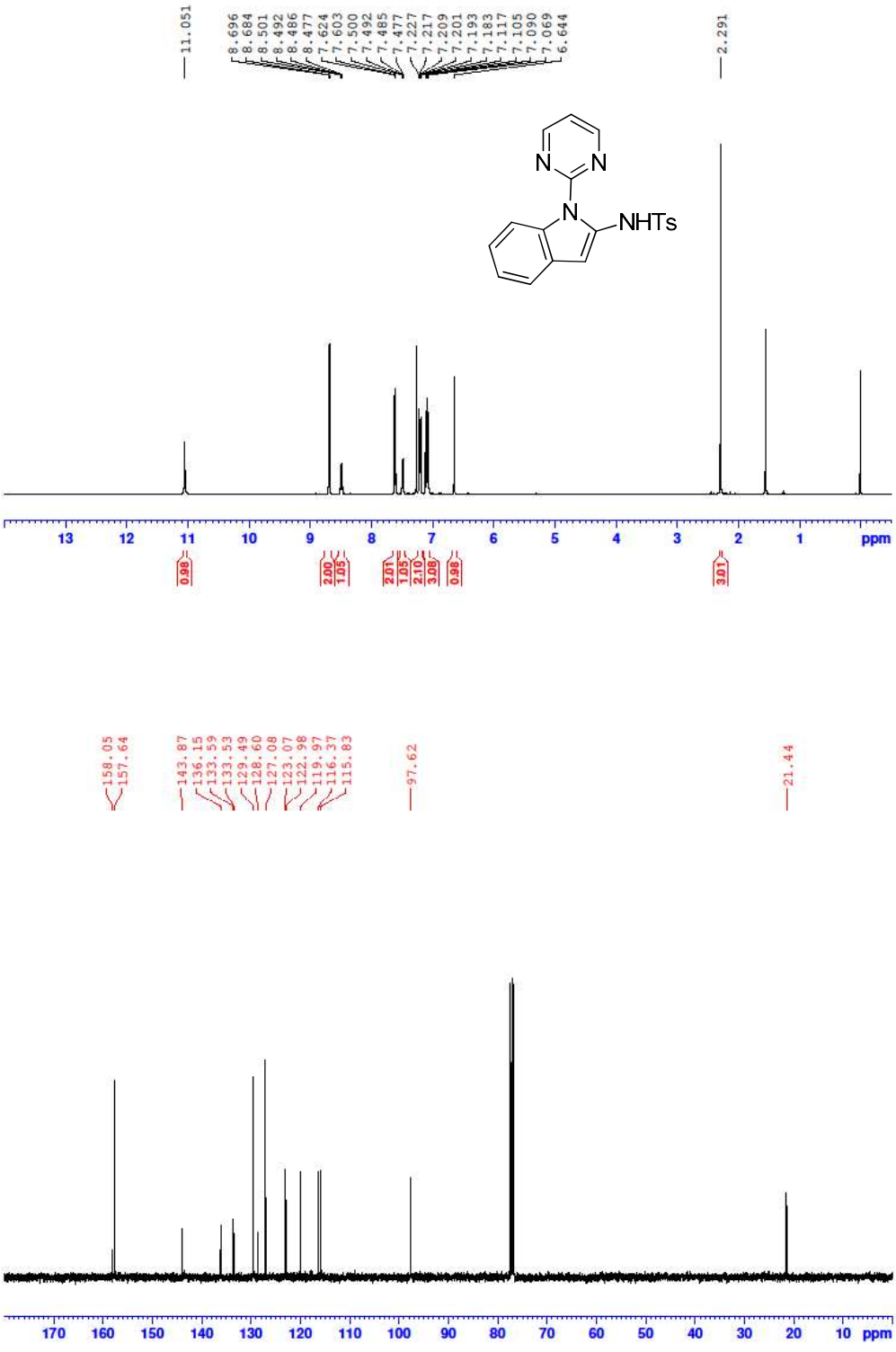
^{1}H and ^{13}C NMR spectra for product 3na ($CDCl_3$)



^{1}H and ^{13}C NMR spectra for product 3oa ($CDCl_3$)



^{1}H and ^{13}C NMR spectra for product 3pa ($CDCl_3$)



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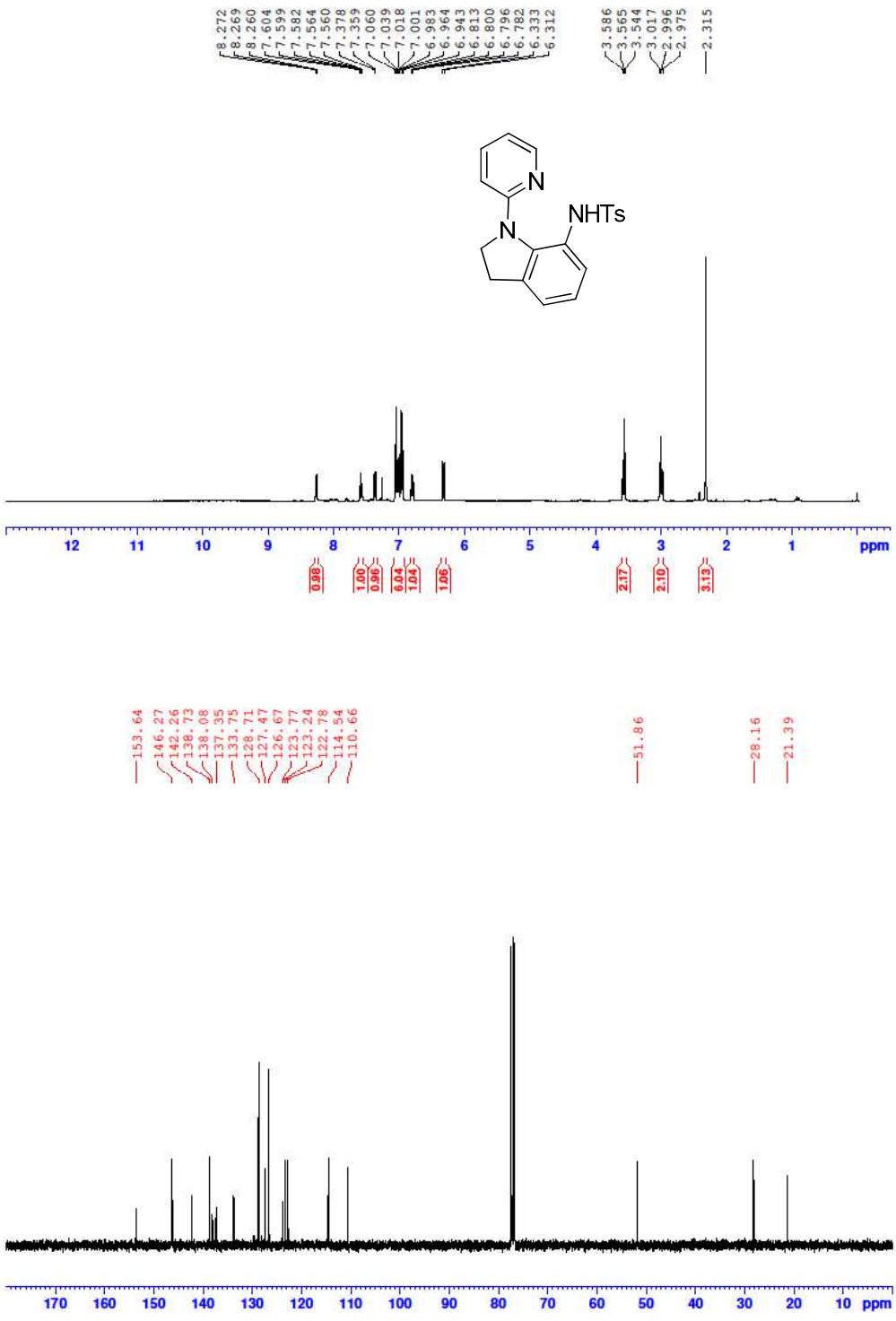
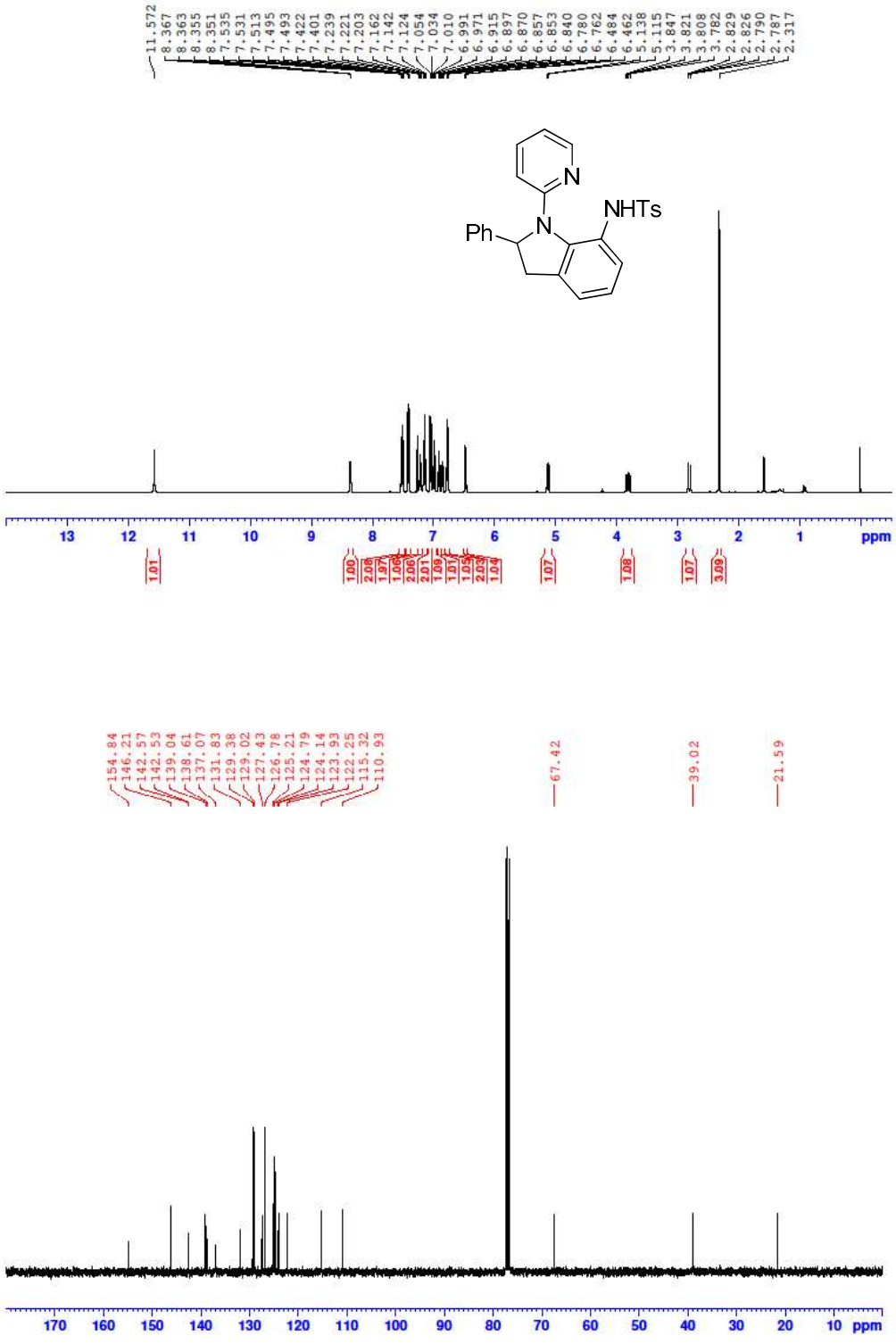
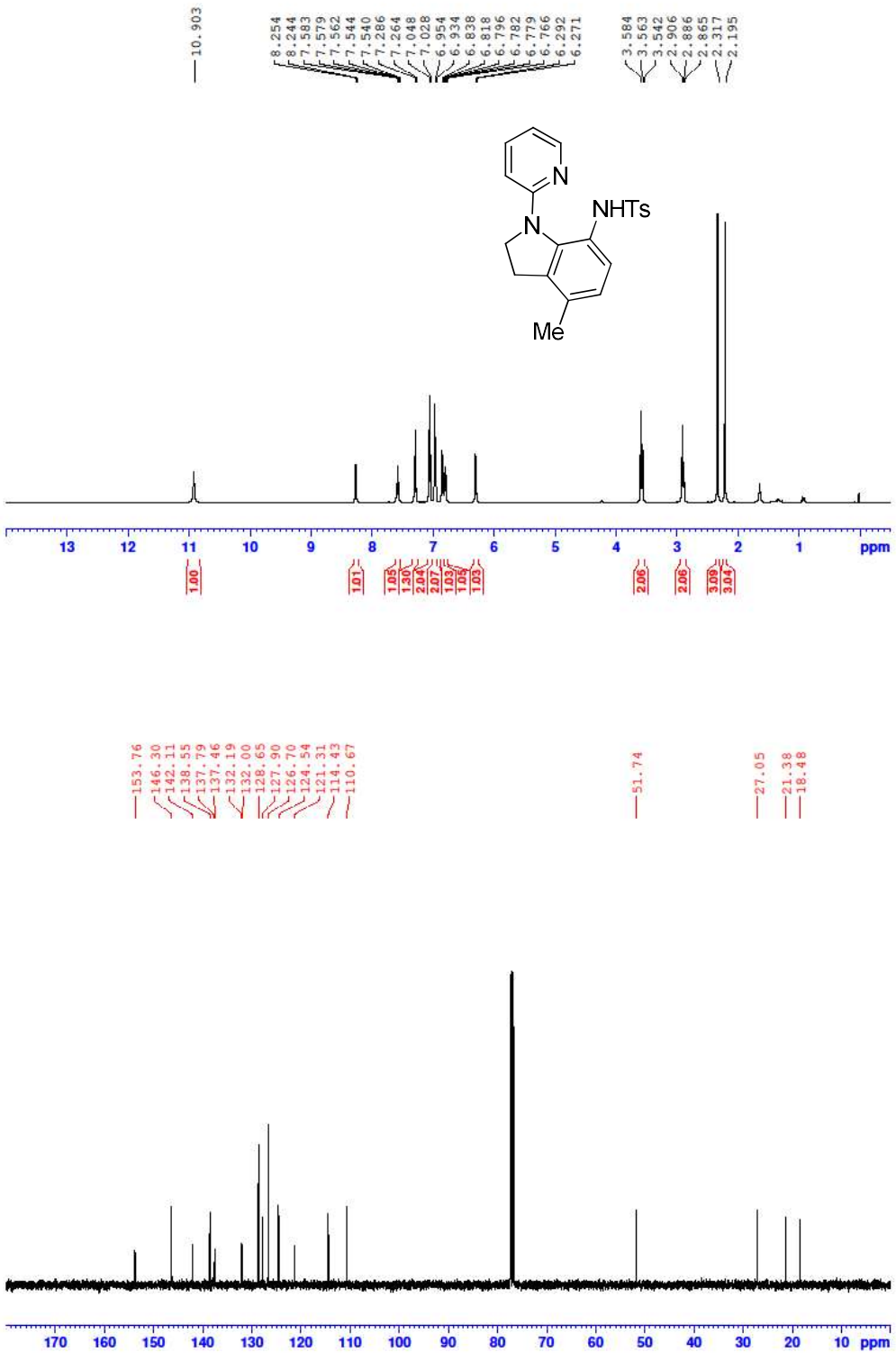


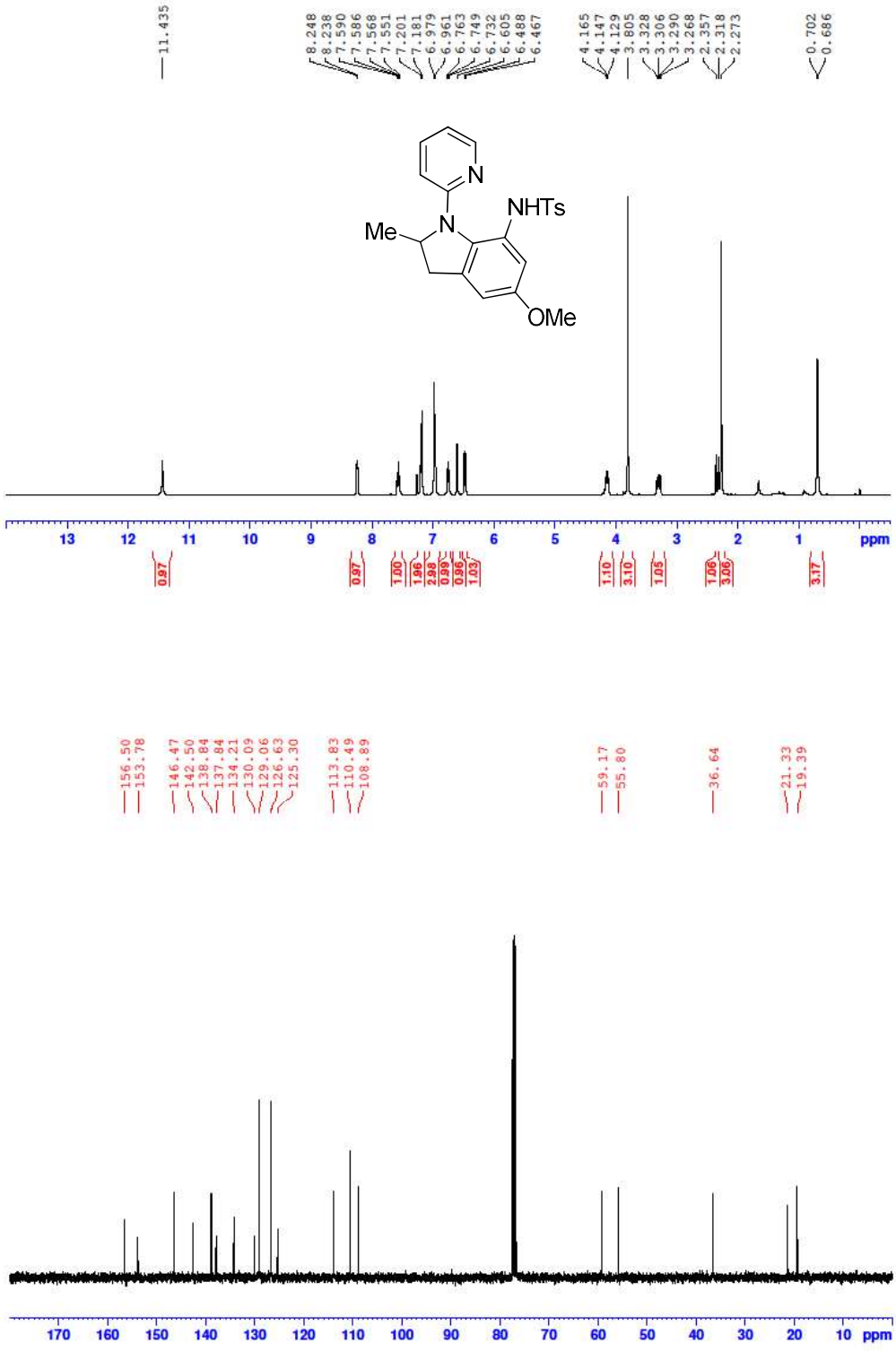
^{1}H and ^{13}C NMR spectra for product 3ra ($CDCl_3$)



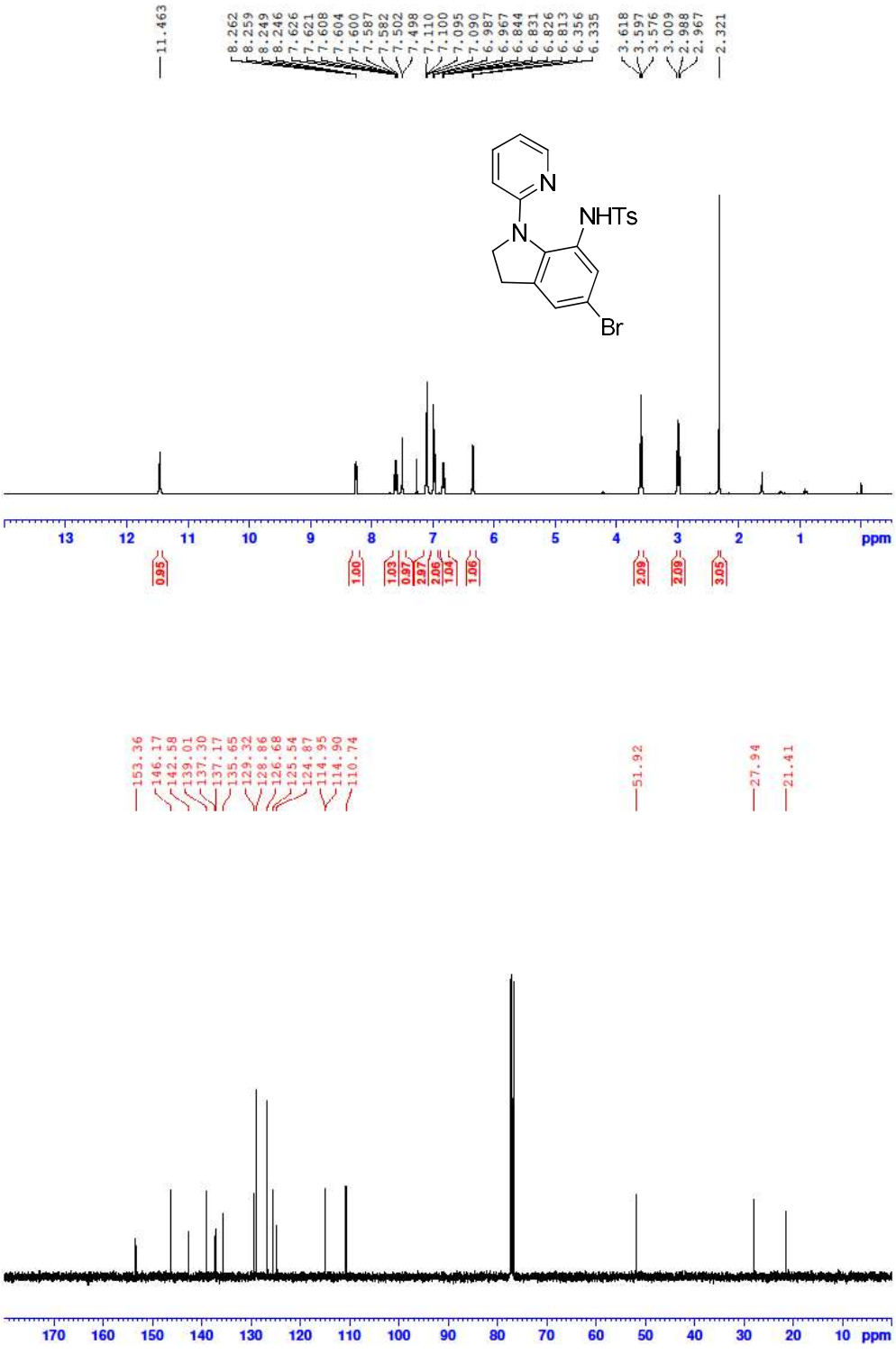
^{1}H and ^{13}C NMR spectra for product 3sa ($CDCl_3$)



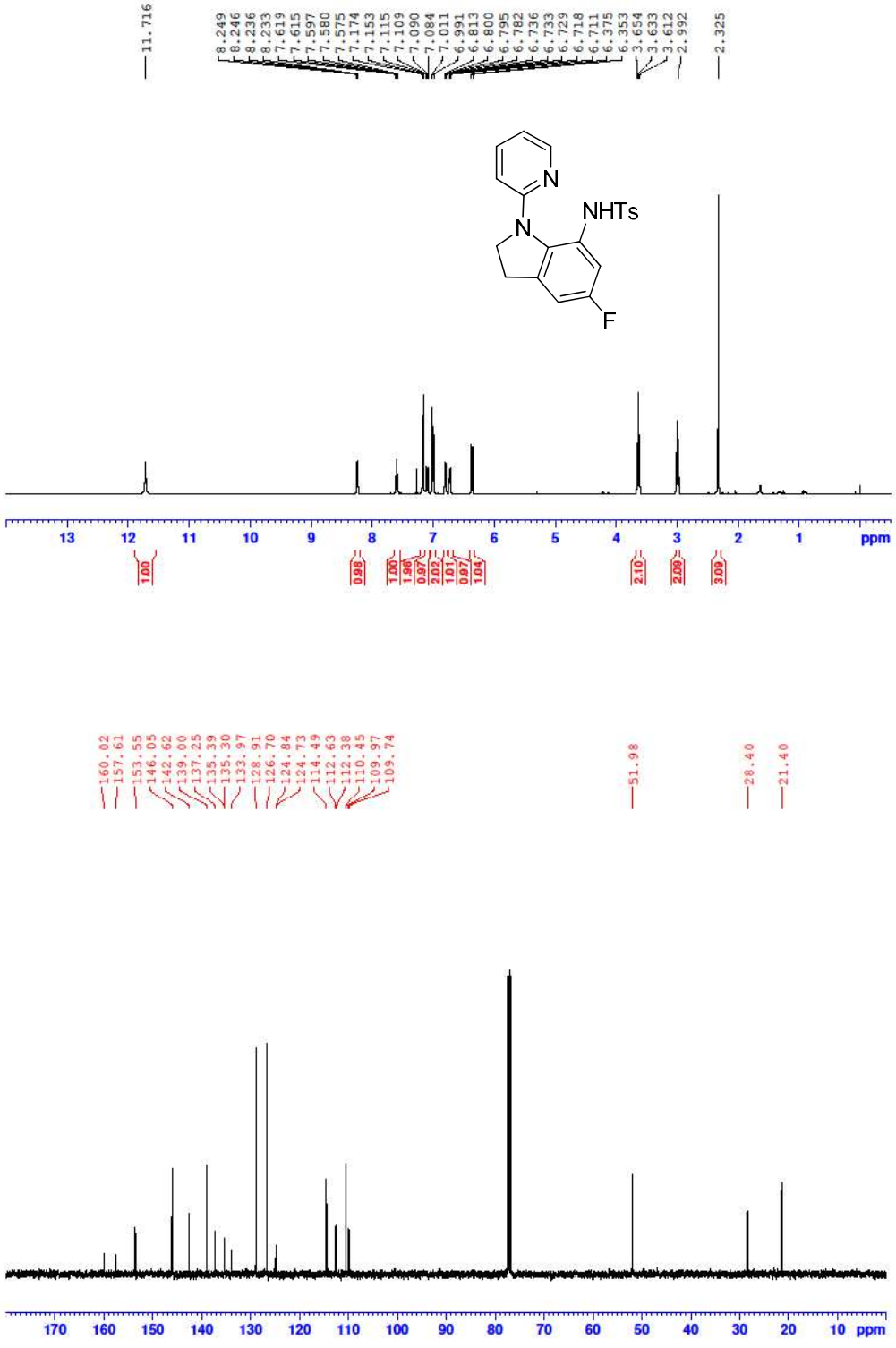
^{1}H and ^{13}C NMR spectra for product 3ta ($CDCl_3$)



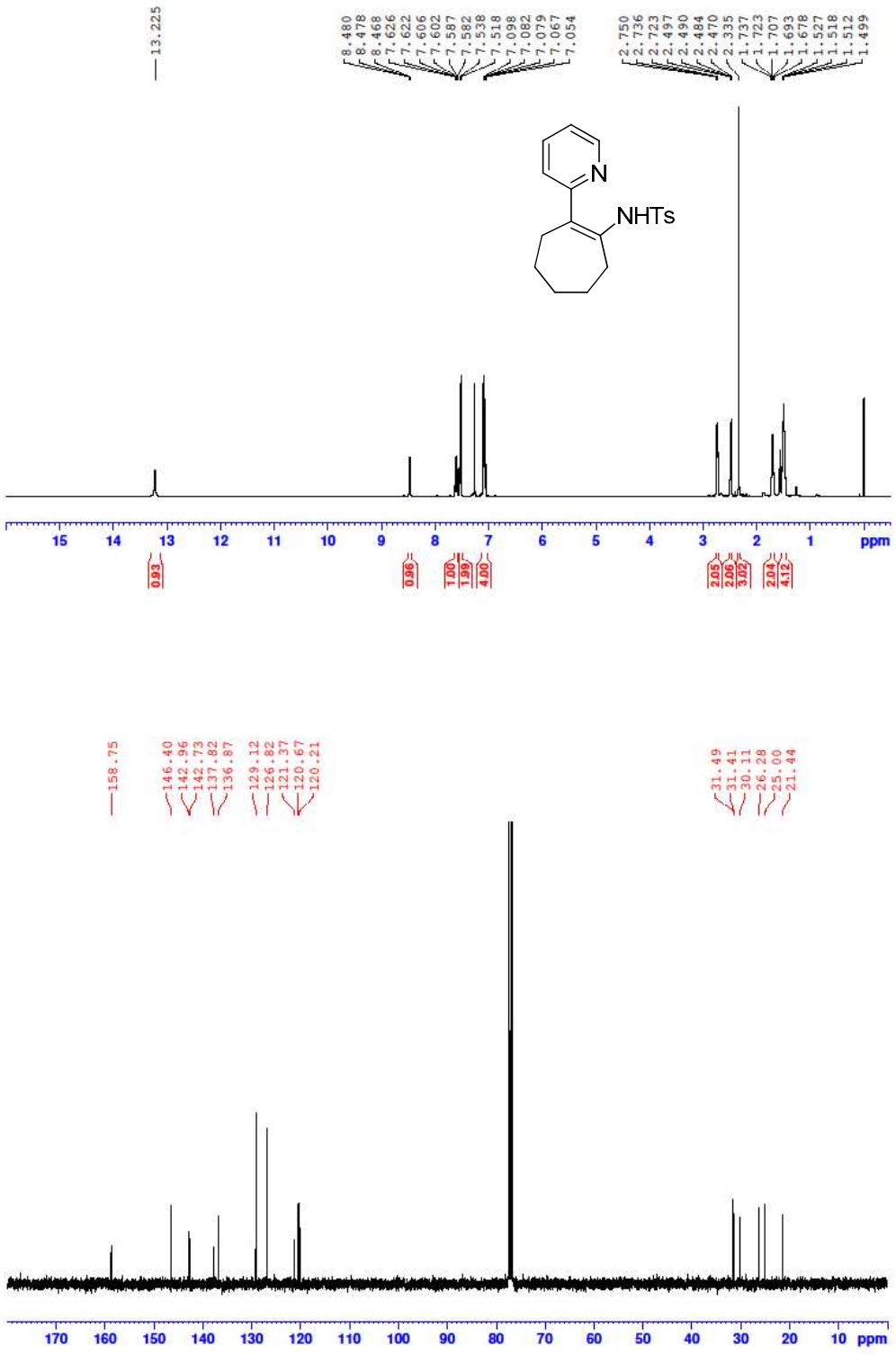
^{1}H and ^{13}C NMR spectra for product 3ua ($CDCl_3$)



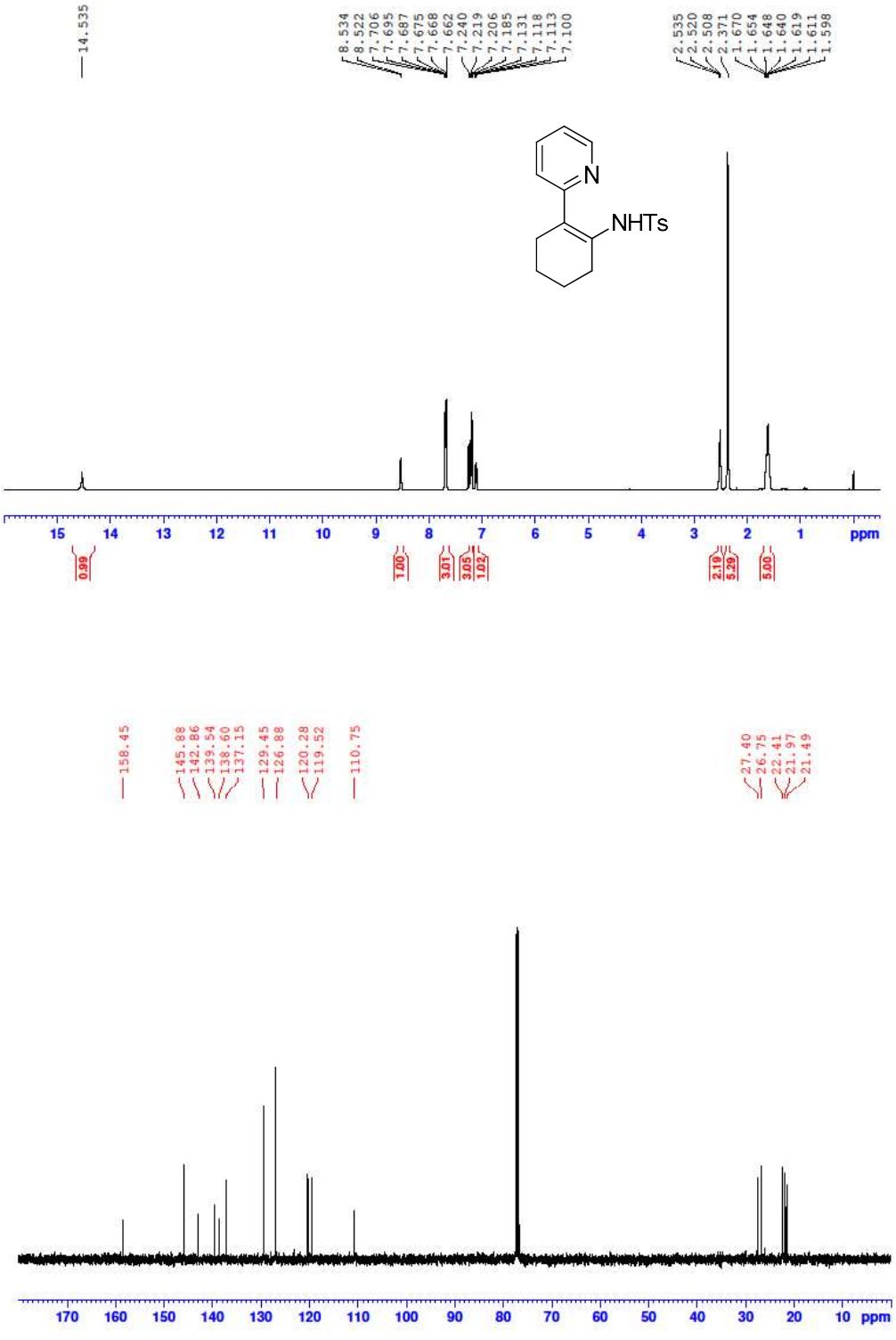
^{1}H and ^{13}C NMR spectra for product 3va ($CDCl_3$)



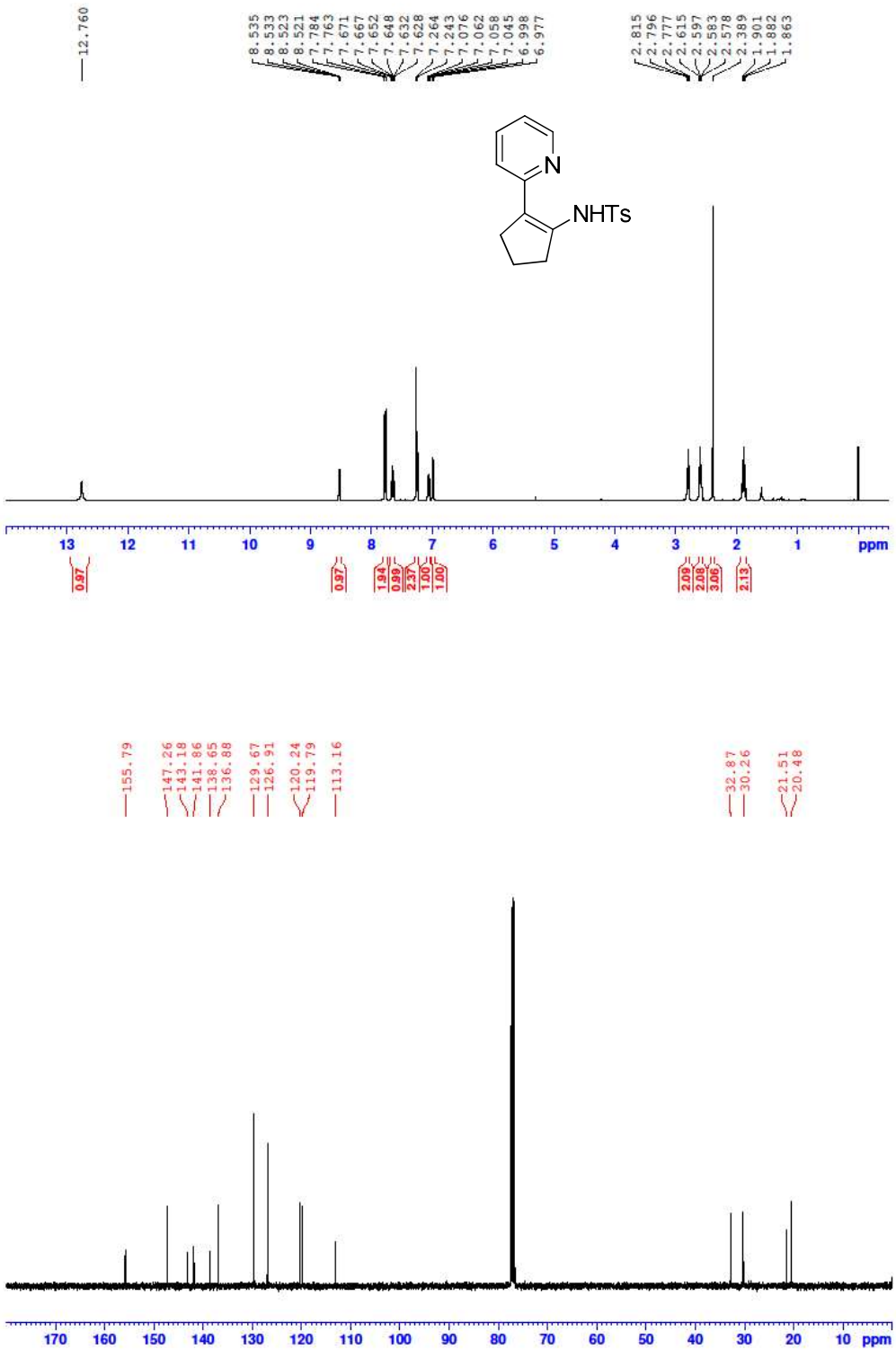
^{1}H and ^{13}C NMR spectra for product 3wa ($CDCl_3$)



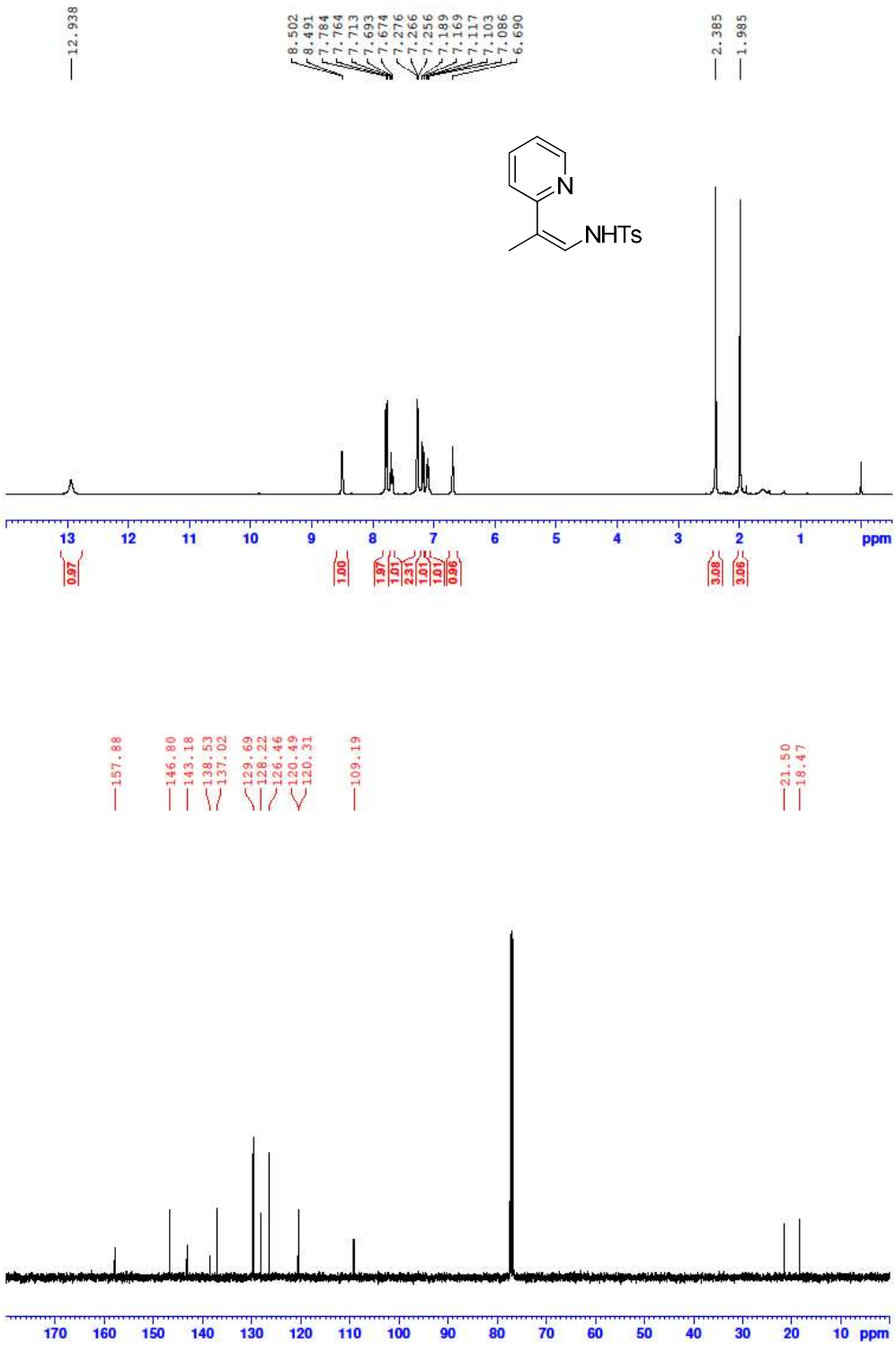
^{1}H and ^{13}C NMR spectra for product 4aa ($CDCl_3$)



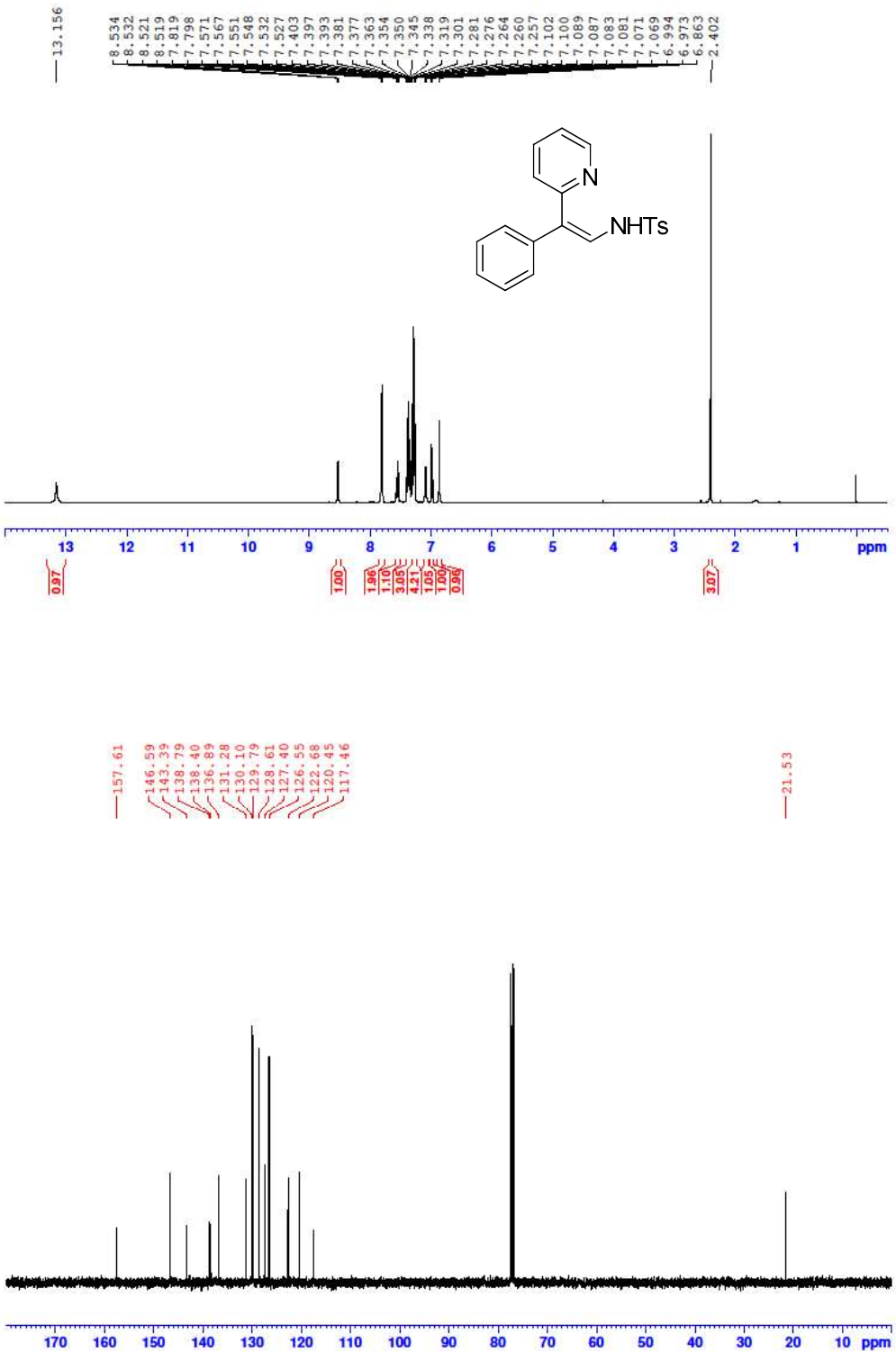
^{1}H and ^{13}C NMR spectra for product 4ba ($CDCl_3$)



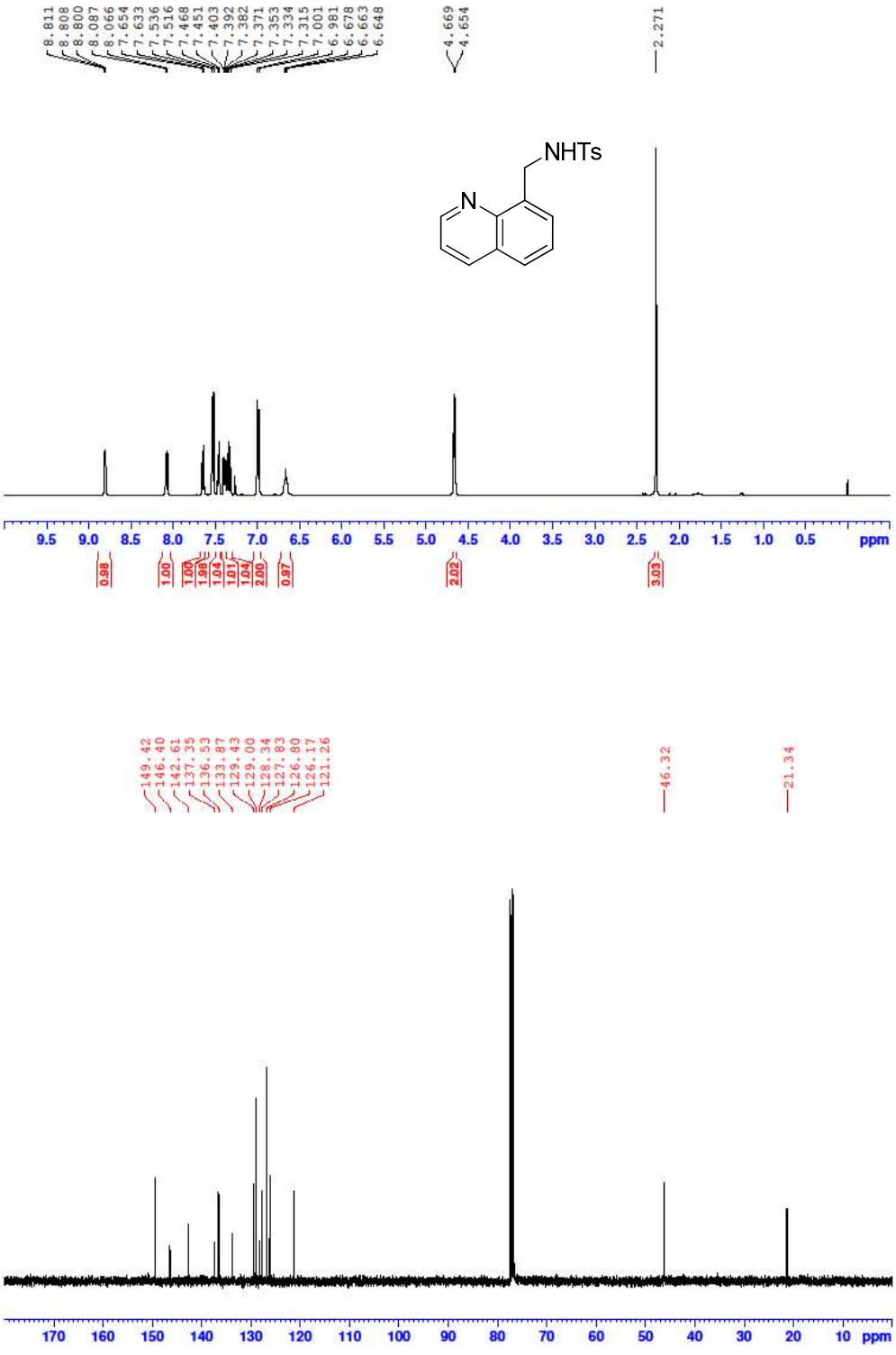
^{1}H and ^{13}C NMR spectra for product 4ca ($CDCl_3$)



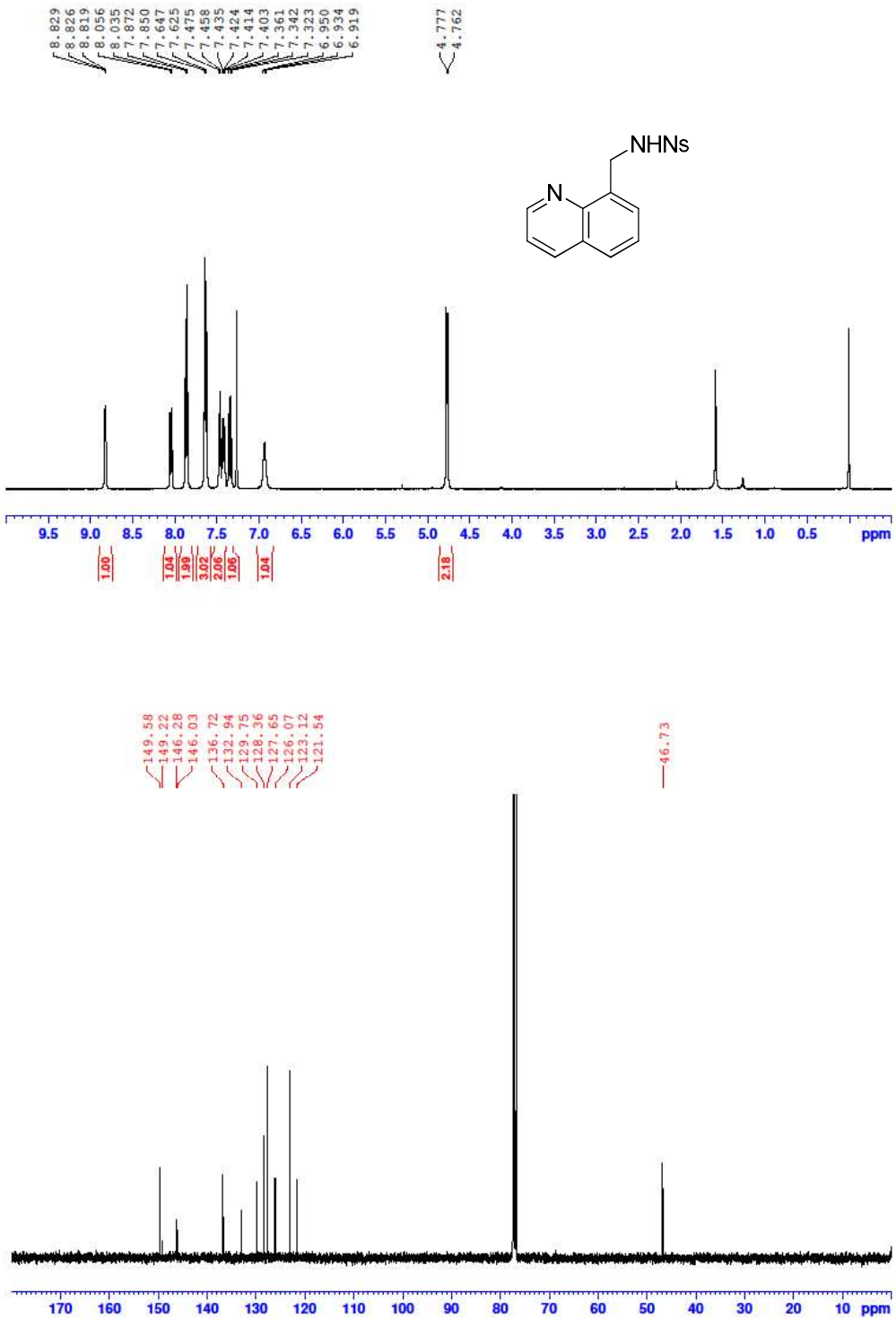
^{1}H and ^{13}C NMR spectra for product 4da ($CDCl_3$)



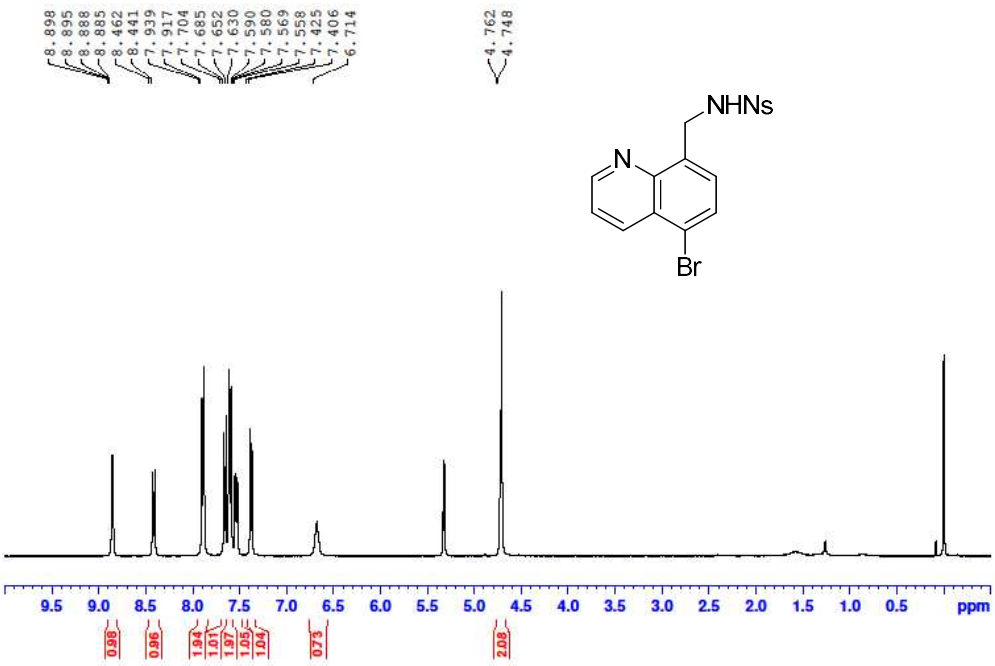
^{1}H and ^{13}C NMR spectra for product 4ea ($CDCl_3$)

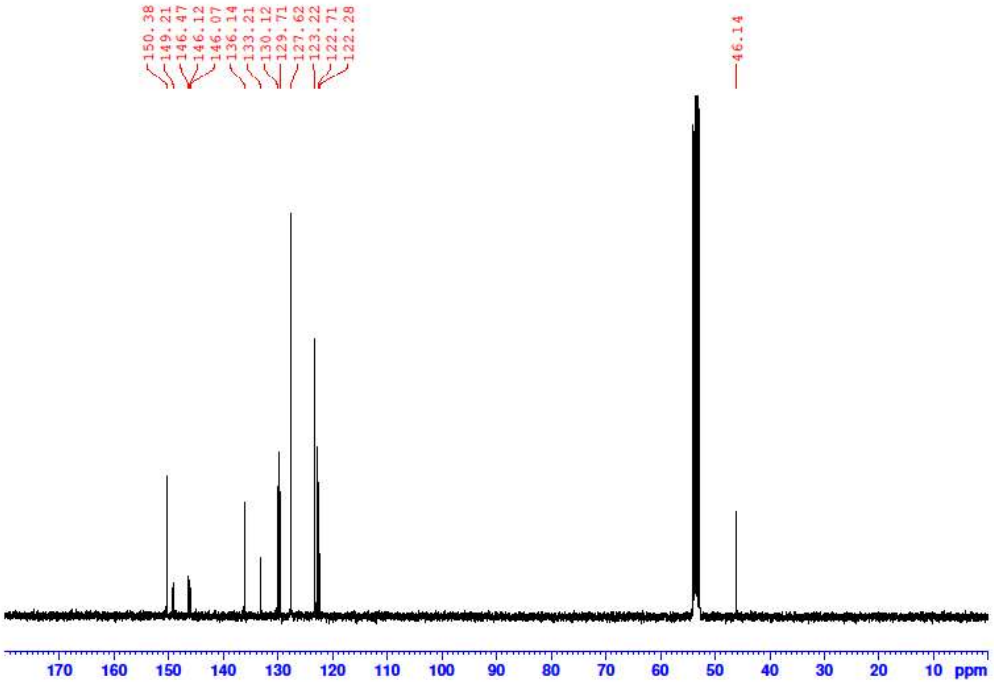


^{1}H and ^{13}C NMR spectra for product 6aa ($CDCl_3$)

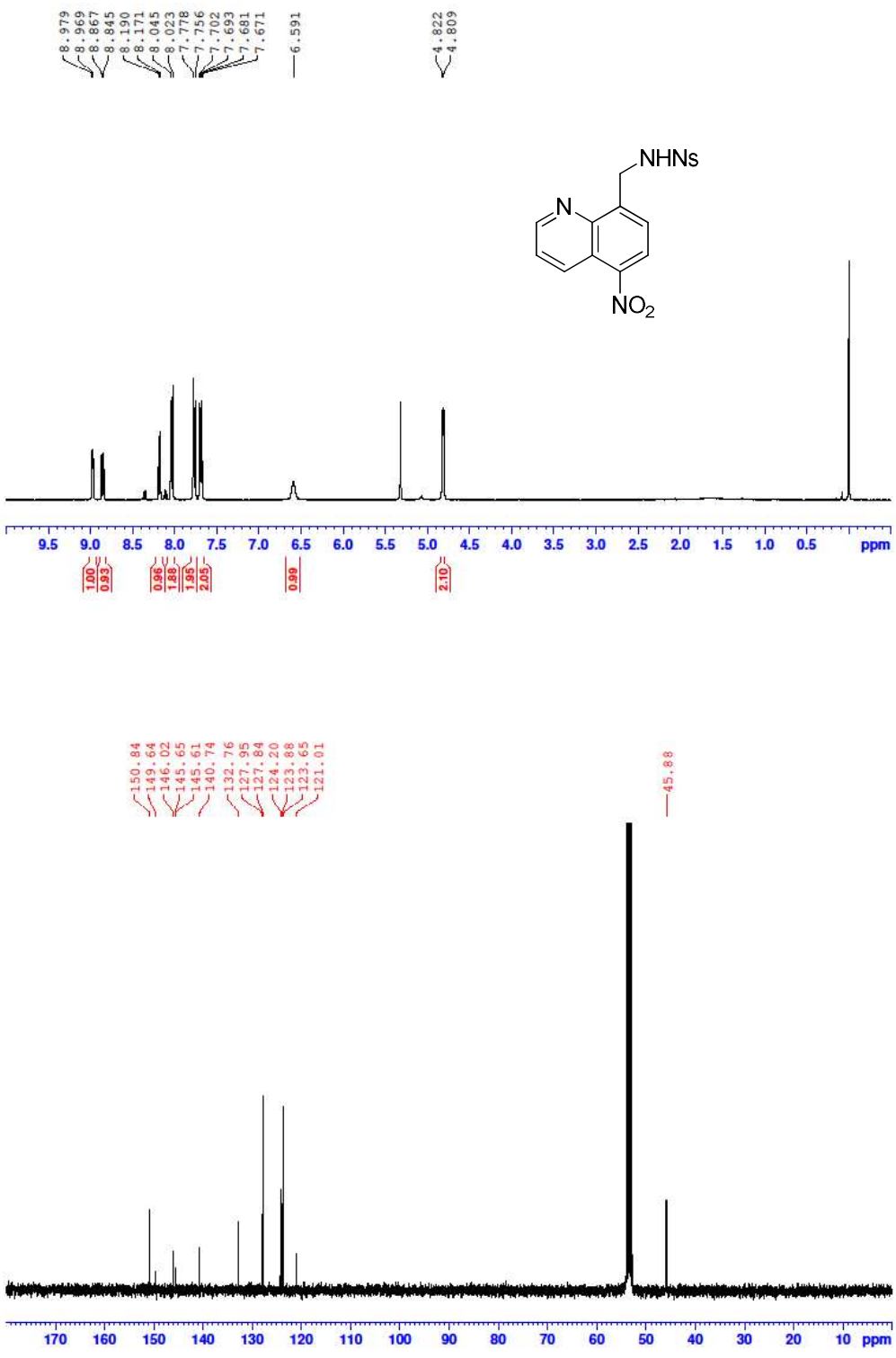


^{1}H and ^{13}C NMR spectra for product 6ba ($CDCl_3$)

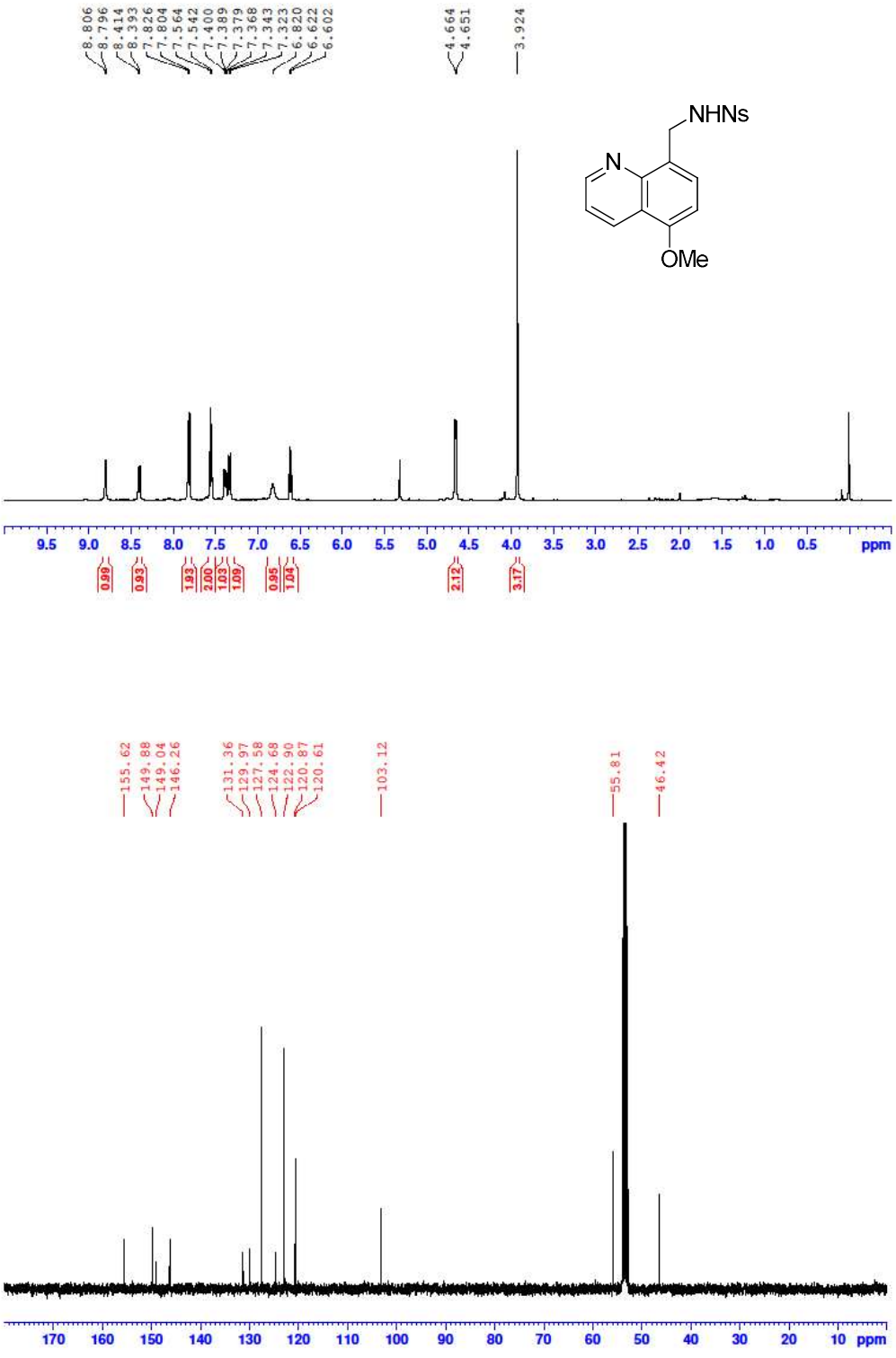




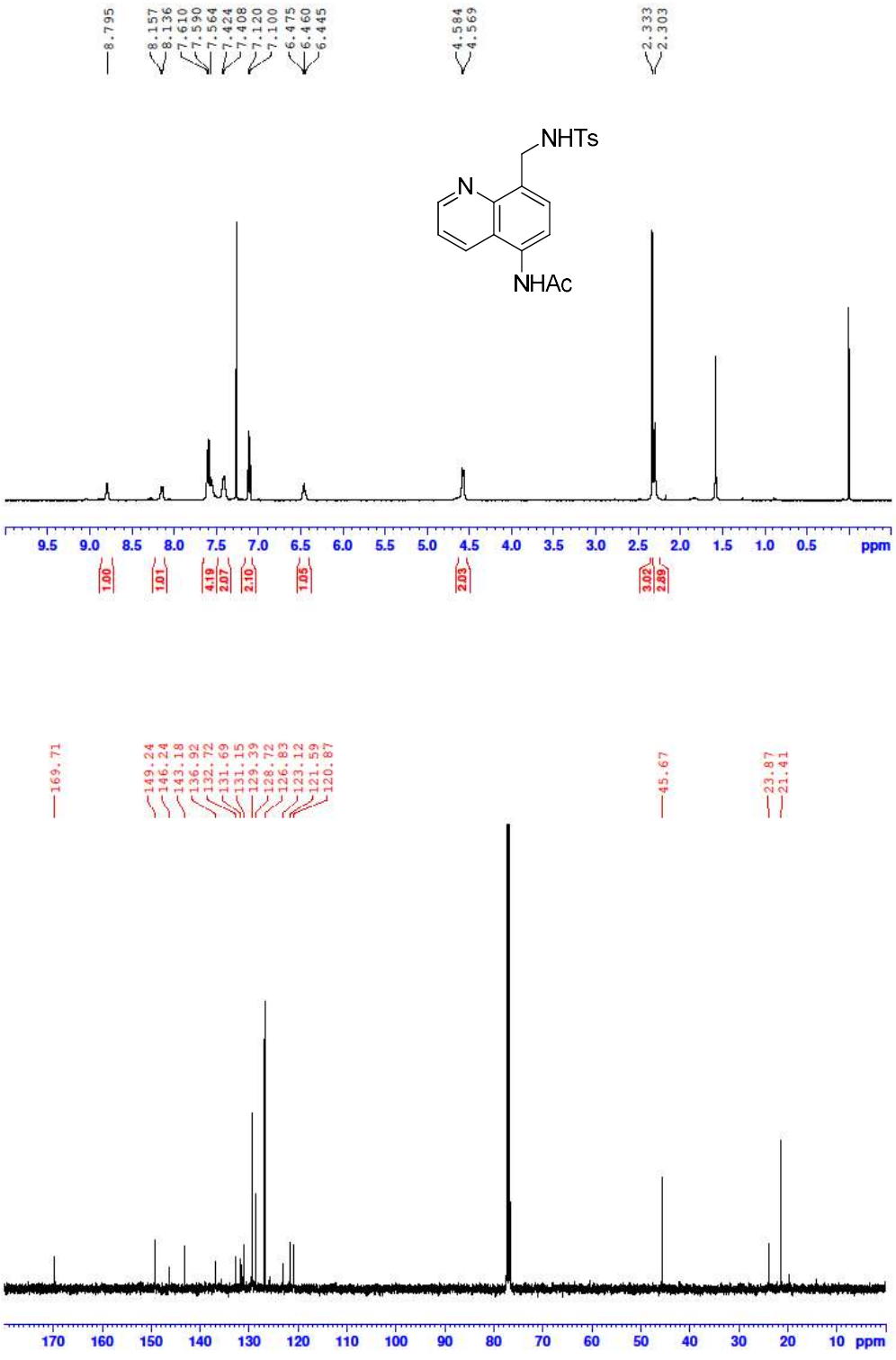
^{1}H and ^{13}C NMR spectra for product 6ca (CD_2Cl_2)



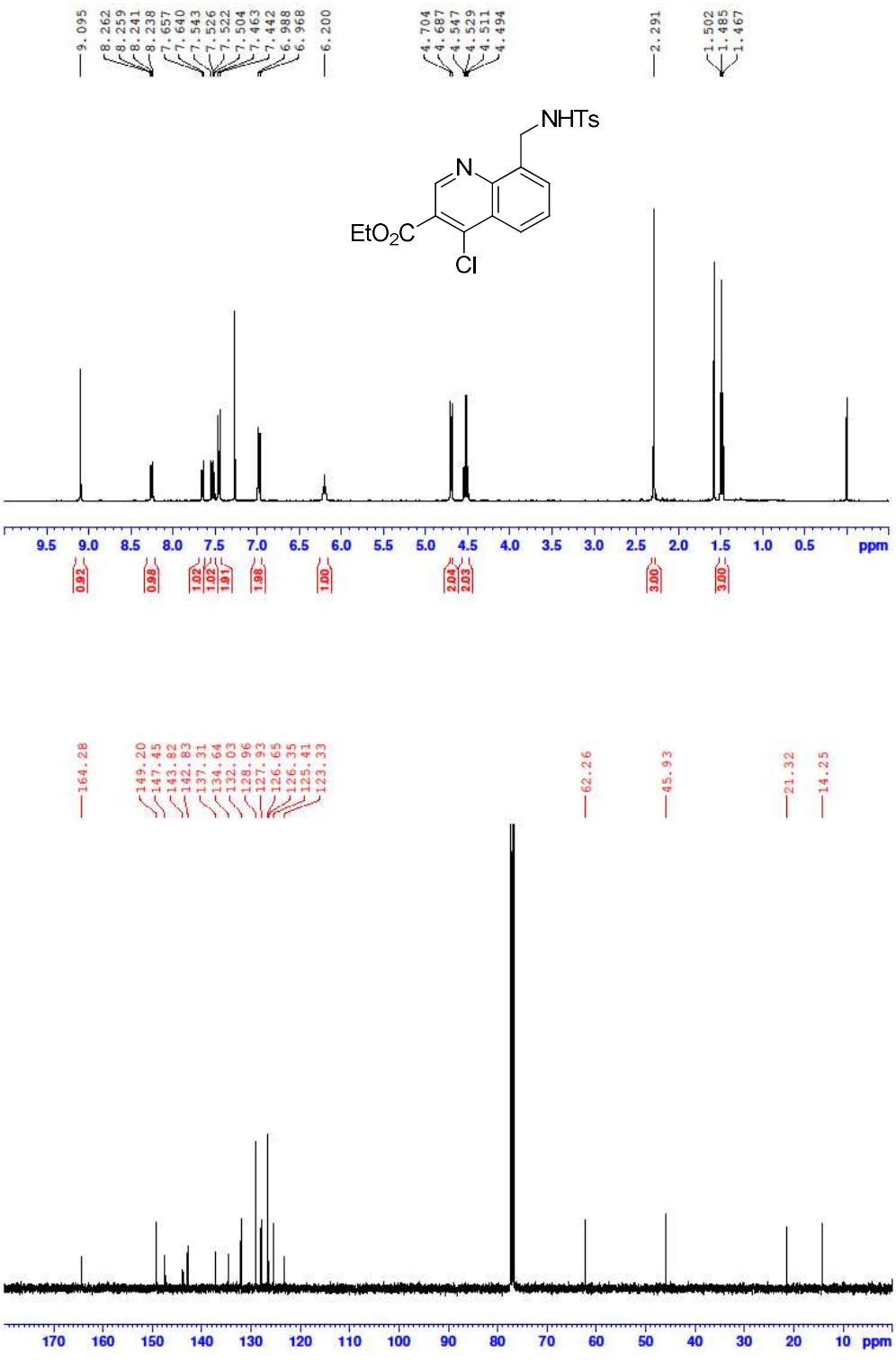
^{1}H and ^{13}C NMR spectra for product 6da (CD_2Cl_2)



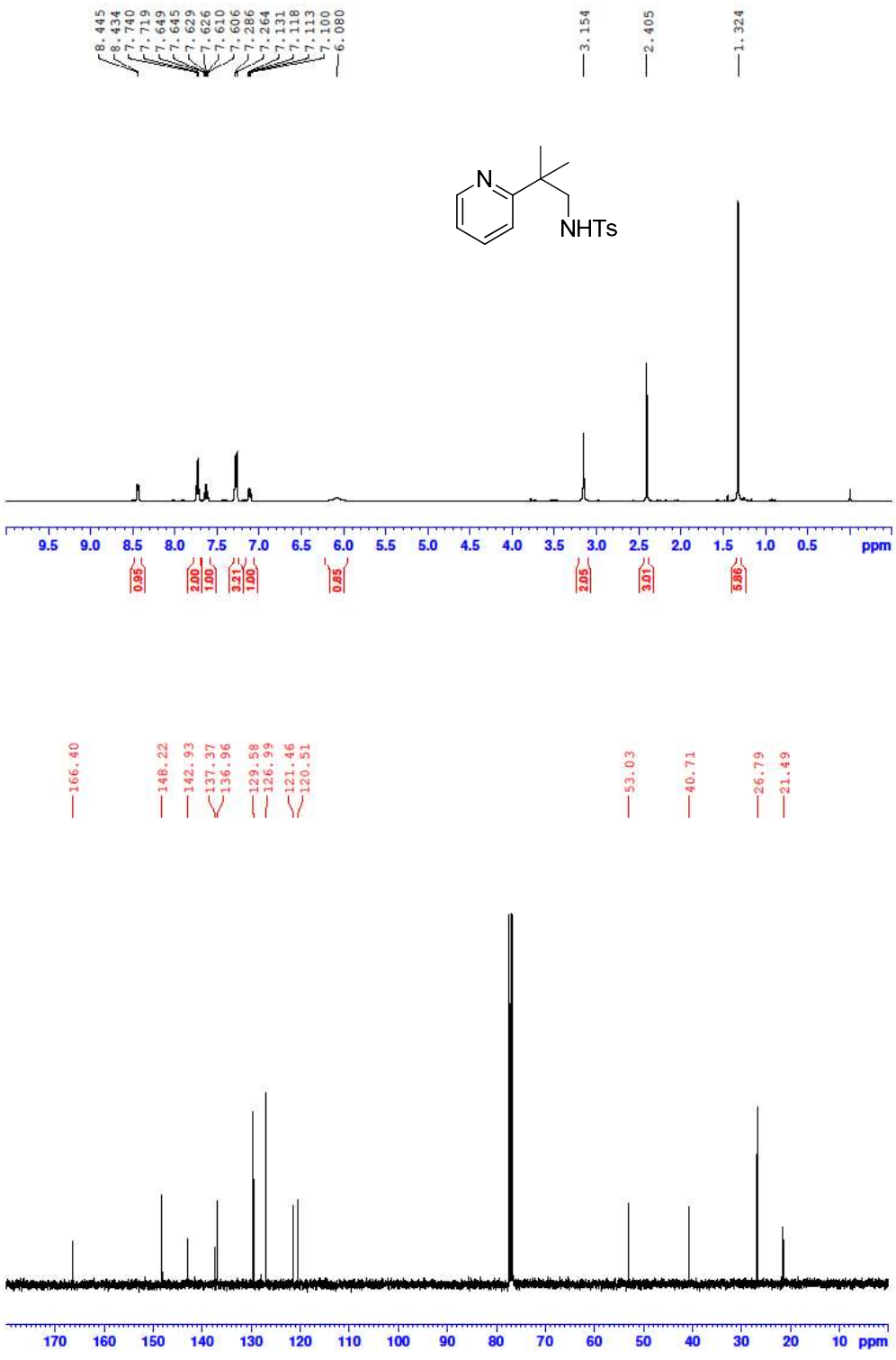
^{1}H and ^{13}C NMR spectra for product 6ea (CD_2Cl_2)



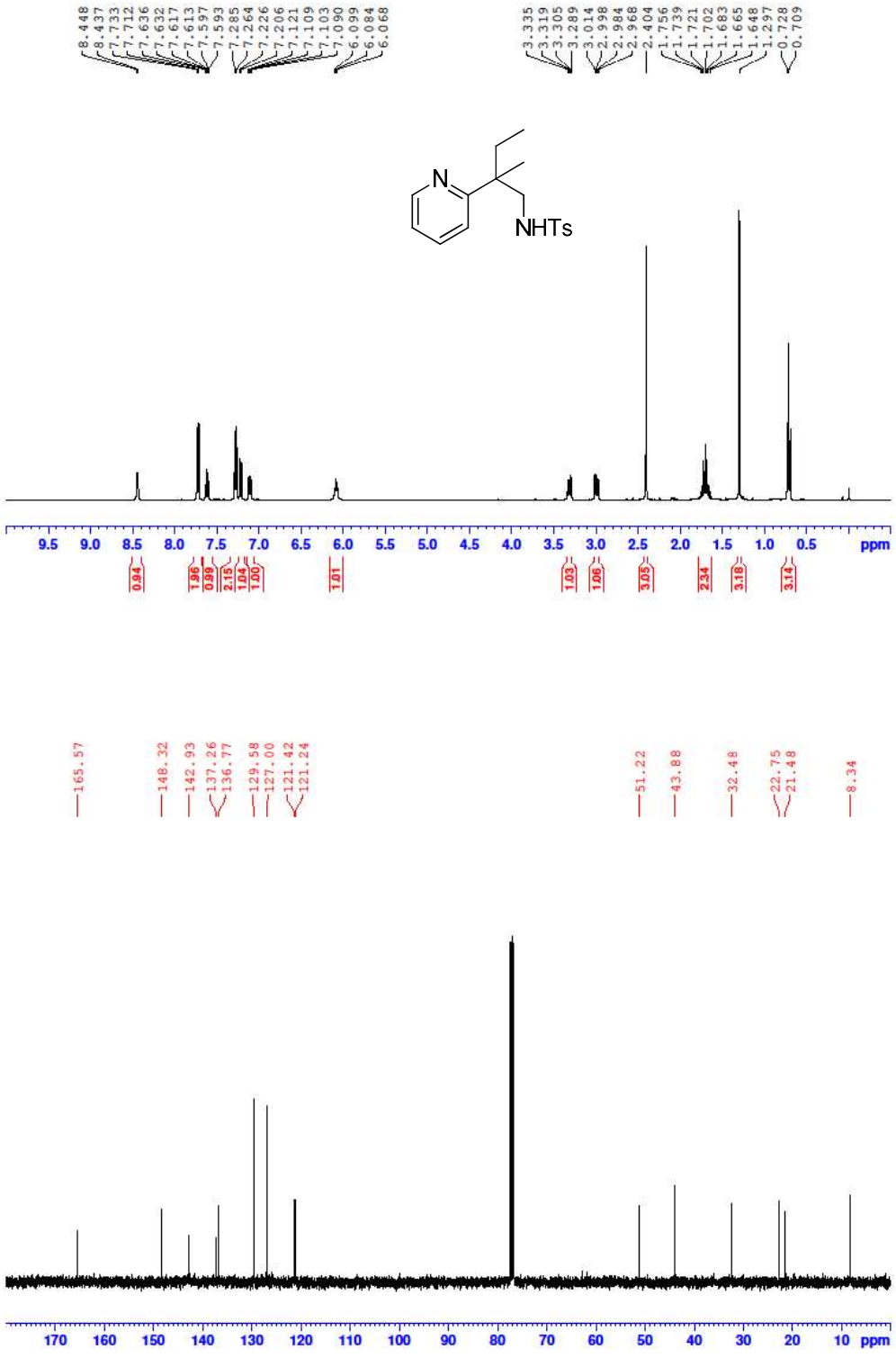
^{1}H and ^{13}C NMR spectra for product 6fa ($CDCl_3$)



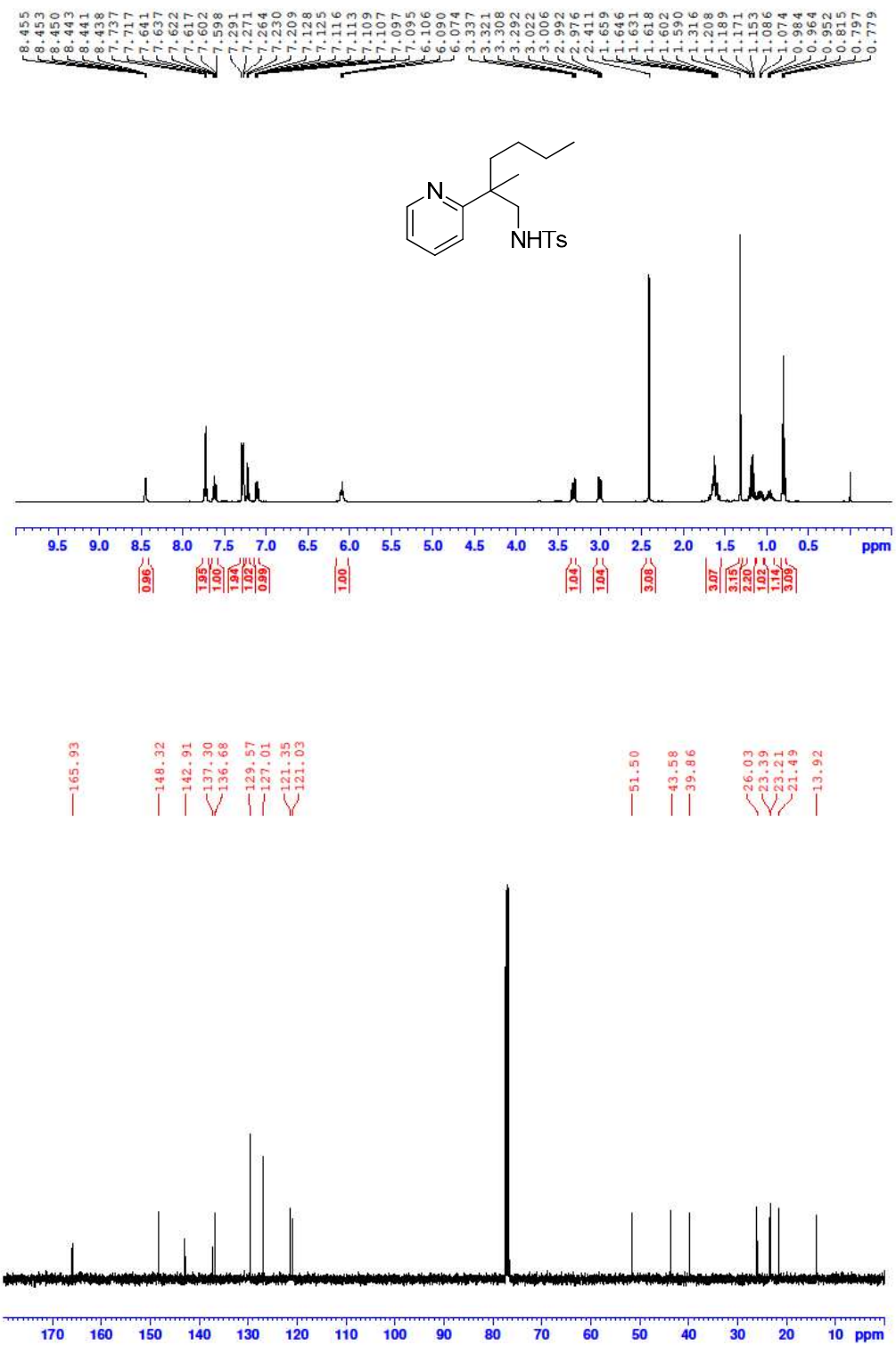
^{1}H and ^{13}C NMR spectra for product 6ga ($CDCl_3$)



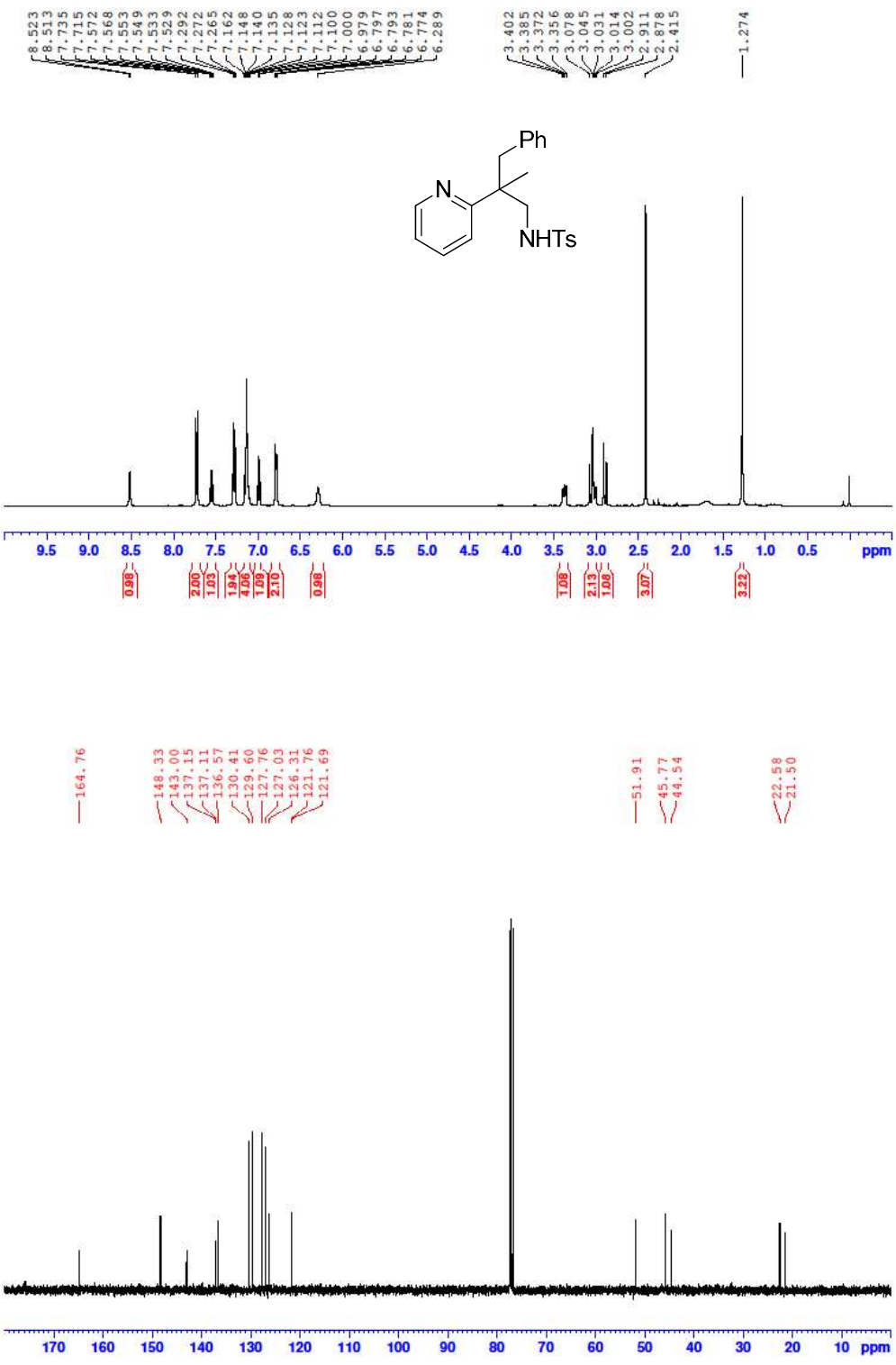
^{1}H and ^{13}C NMR spectra for product 6ha ($CDCl_3$)



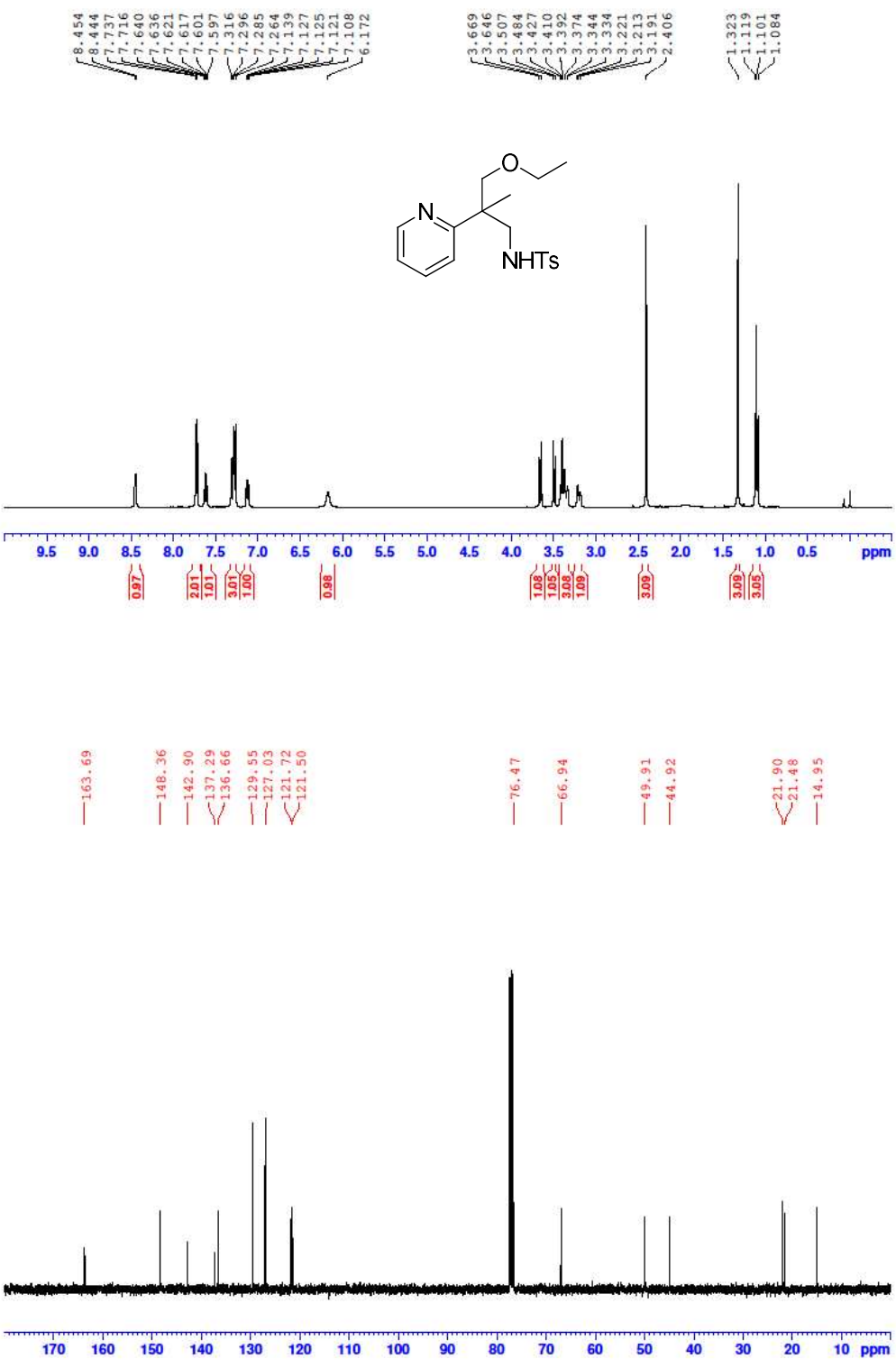
^{1}H and ^{13}C NMR spectra for product 6ia ($CDCl_3$)



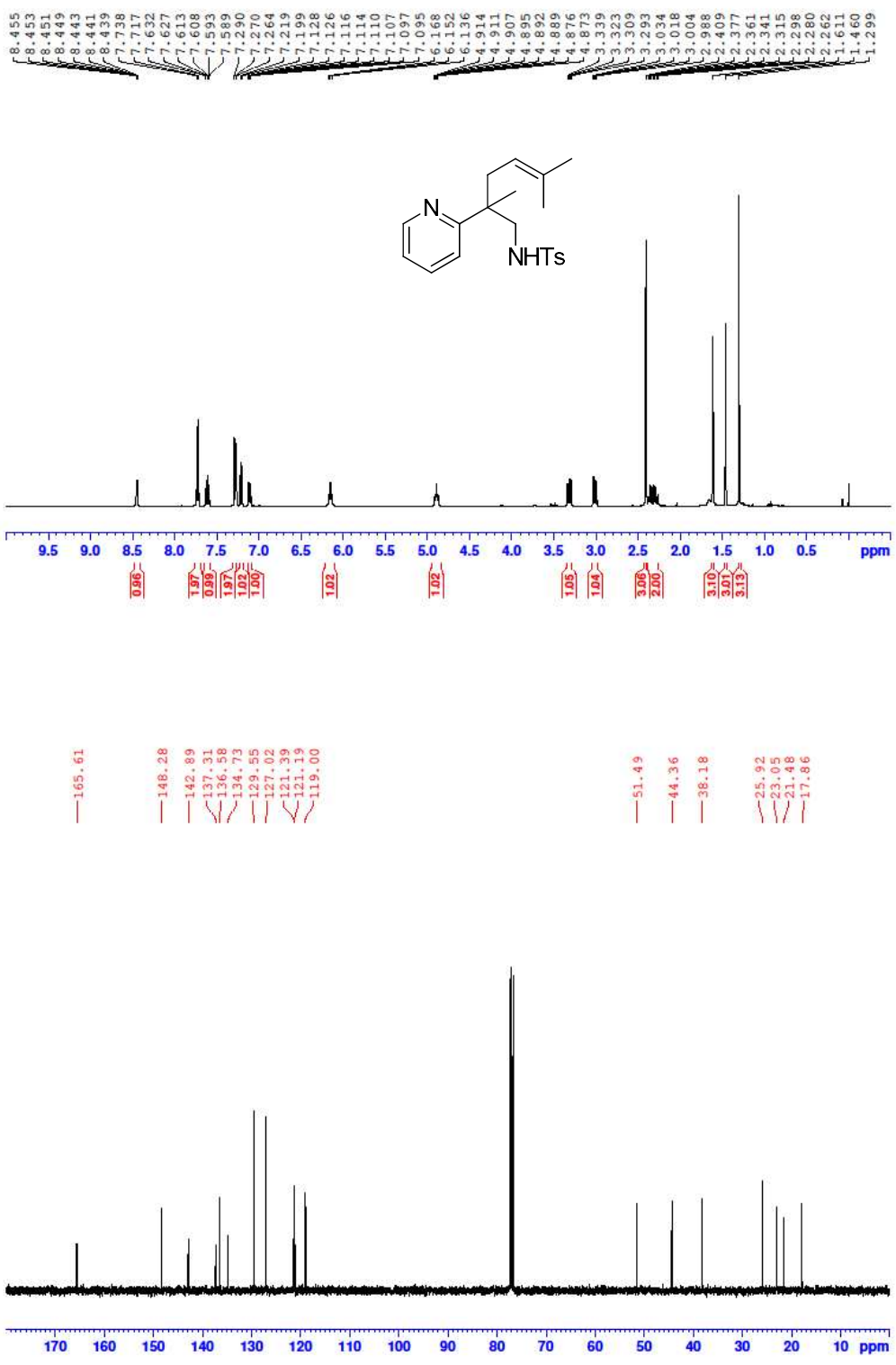
^{1}H and ^{13}C NMR spectra for product 6ja ($CDCl_3$)



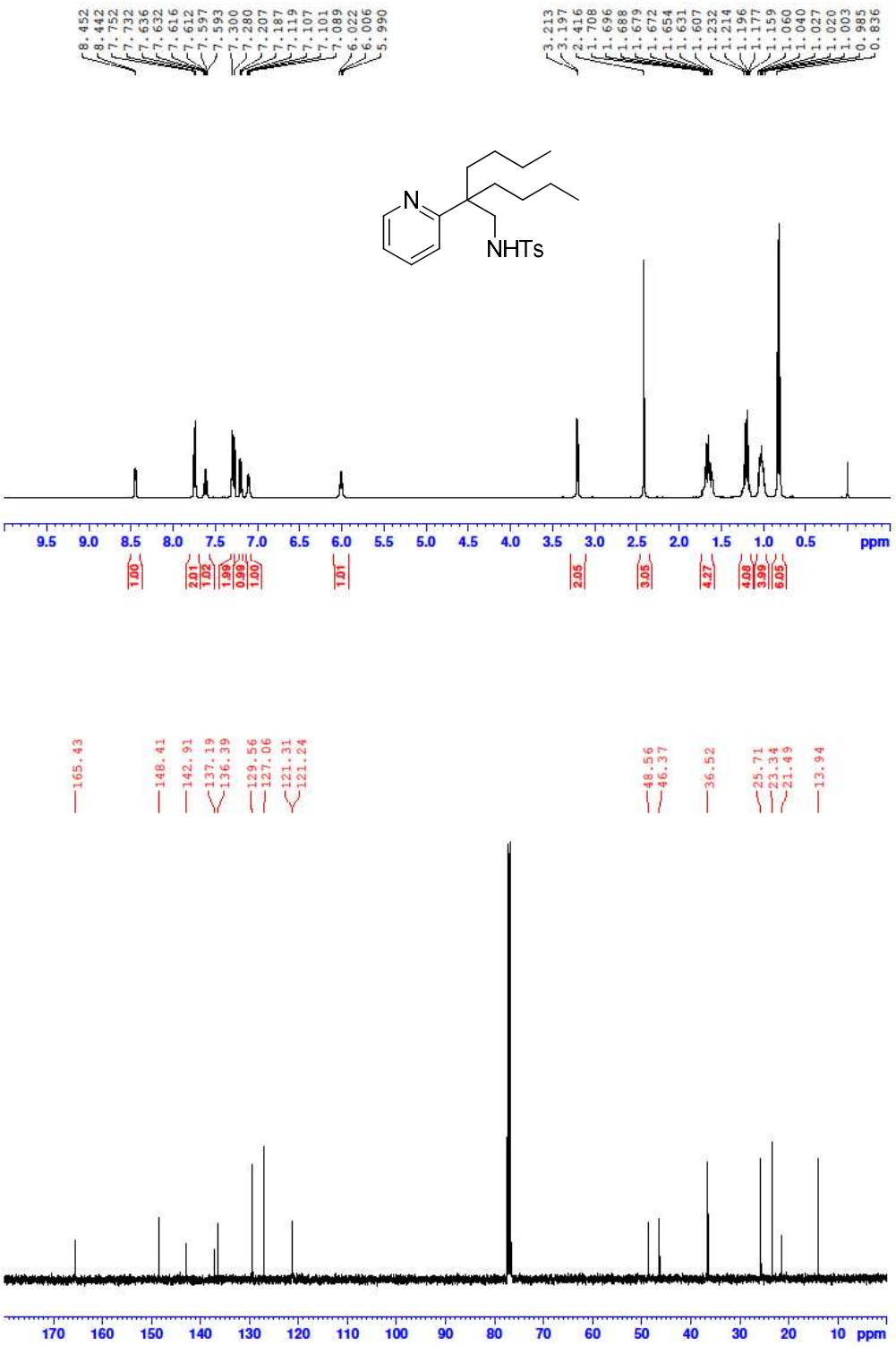
^{1}H and ^{13}C NMR spectra for product 6ka ($CDCl_3$)



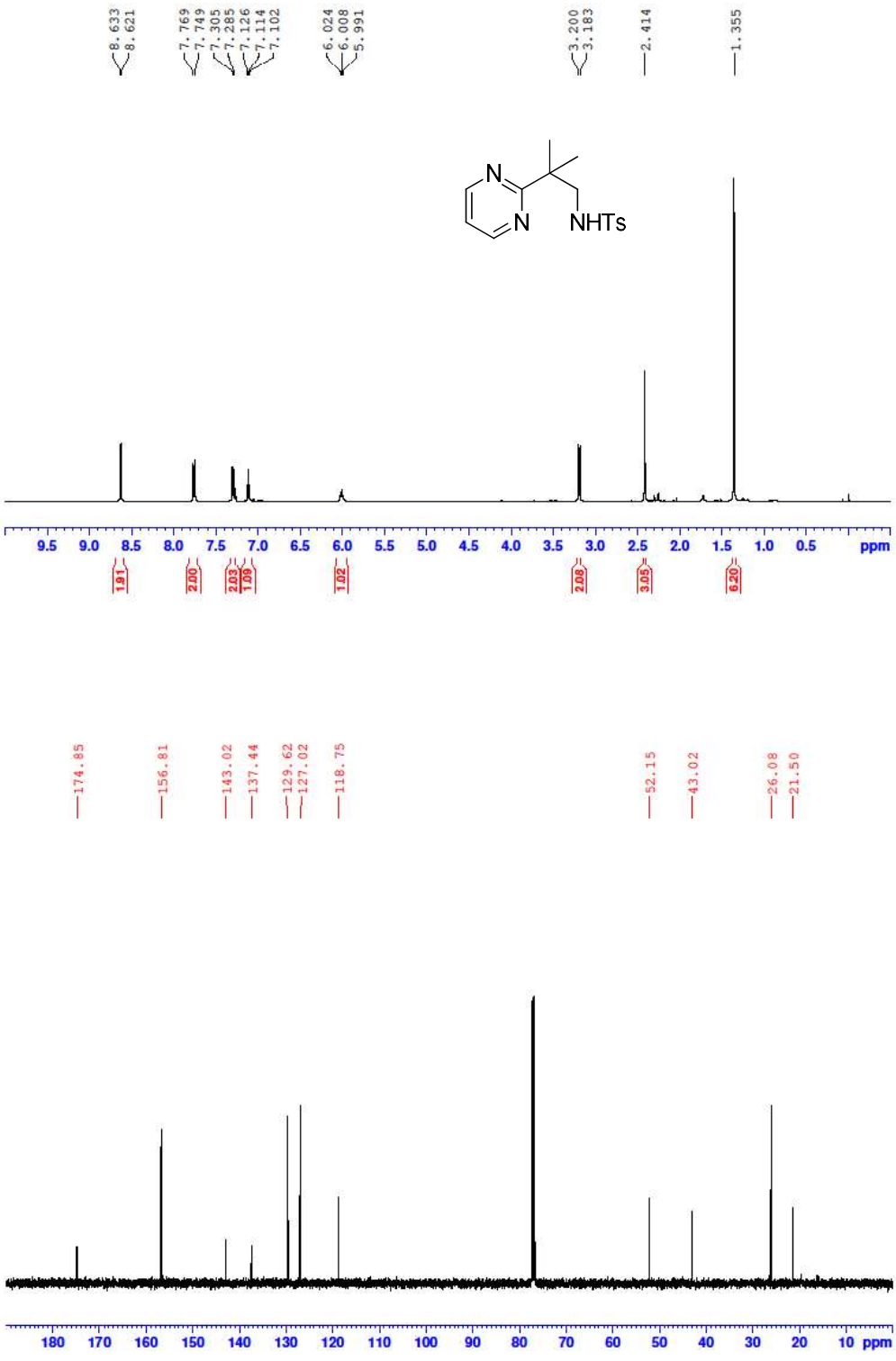
^{1}H and ^{13}C NMR spectra for product 6la ($CDCl_3$)



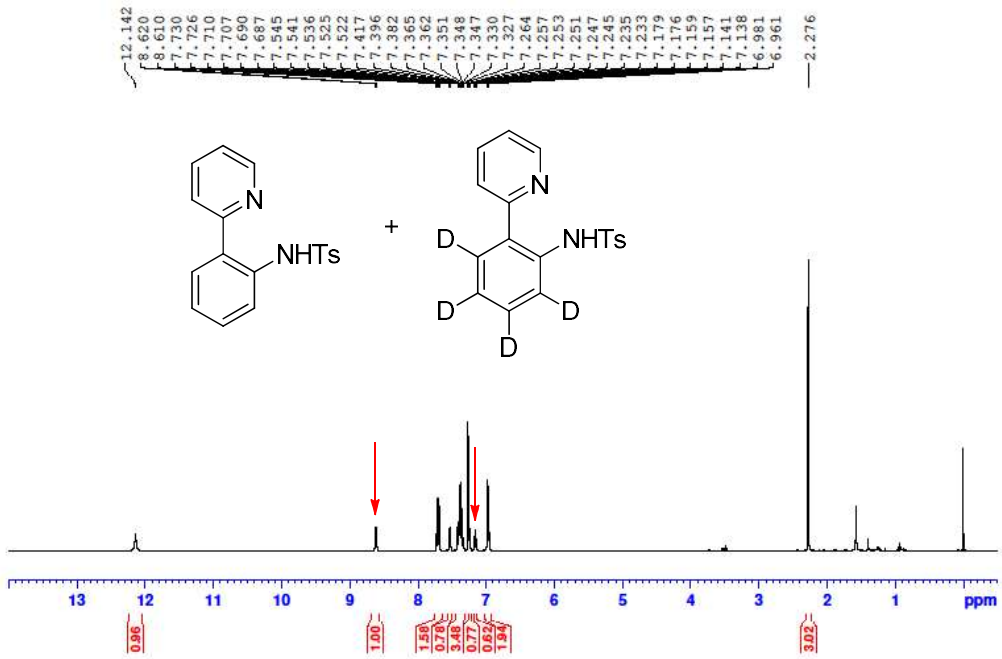
^{1}H and ^{13}C NMR spectra for product 6ma ($CDCl_3$)



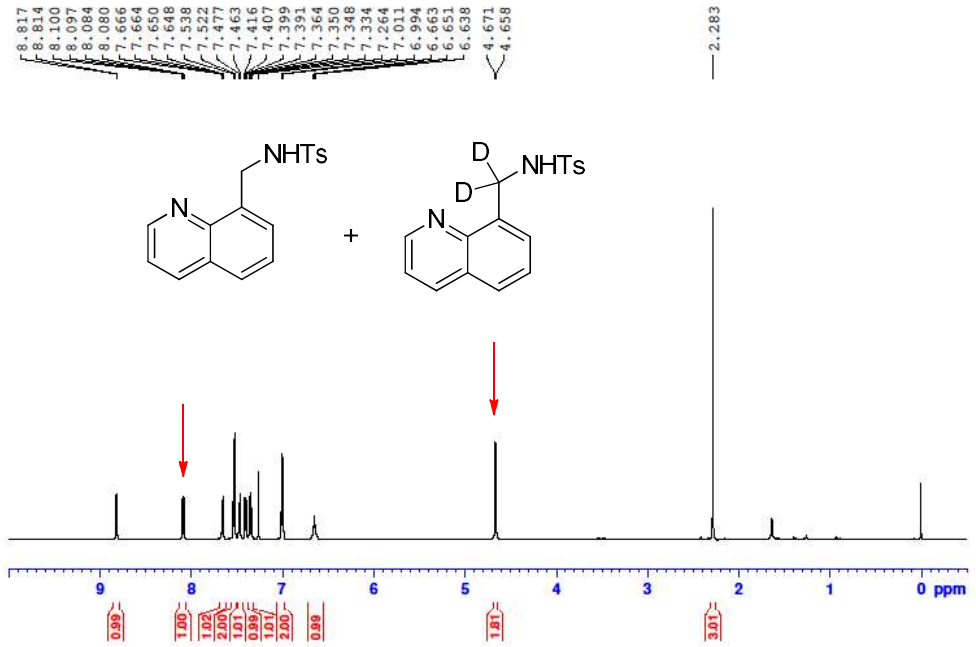
^{1}H and ^{13}C NMR spectra for product 6na ($CDCl_3$)



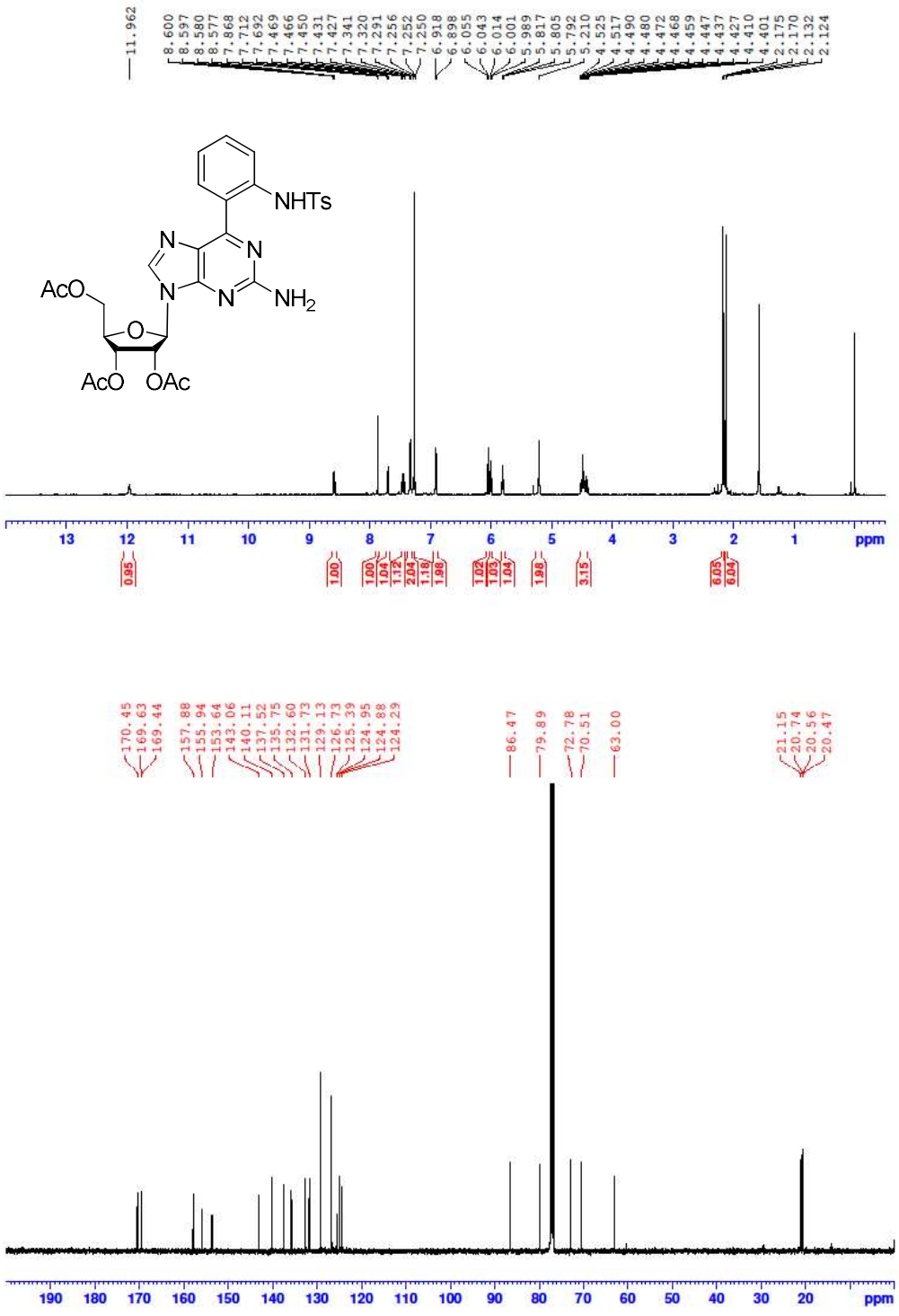
^{1}H and ^{13}C NMR spectra for product 6oa ($CDCl_3$)



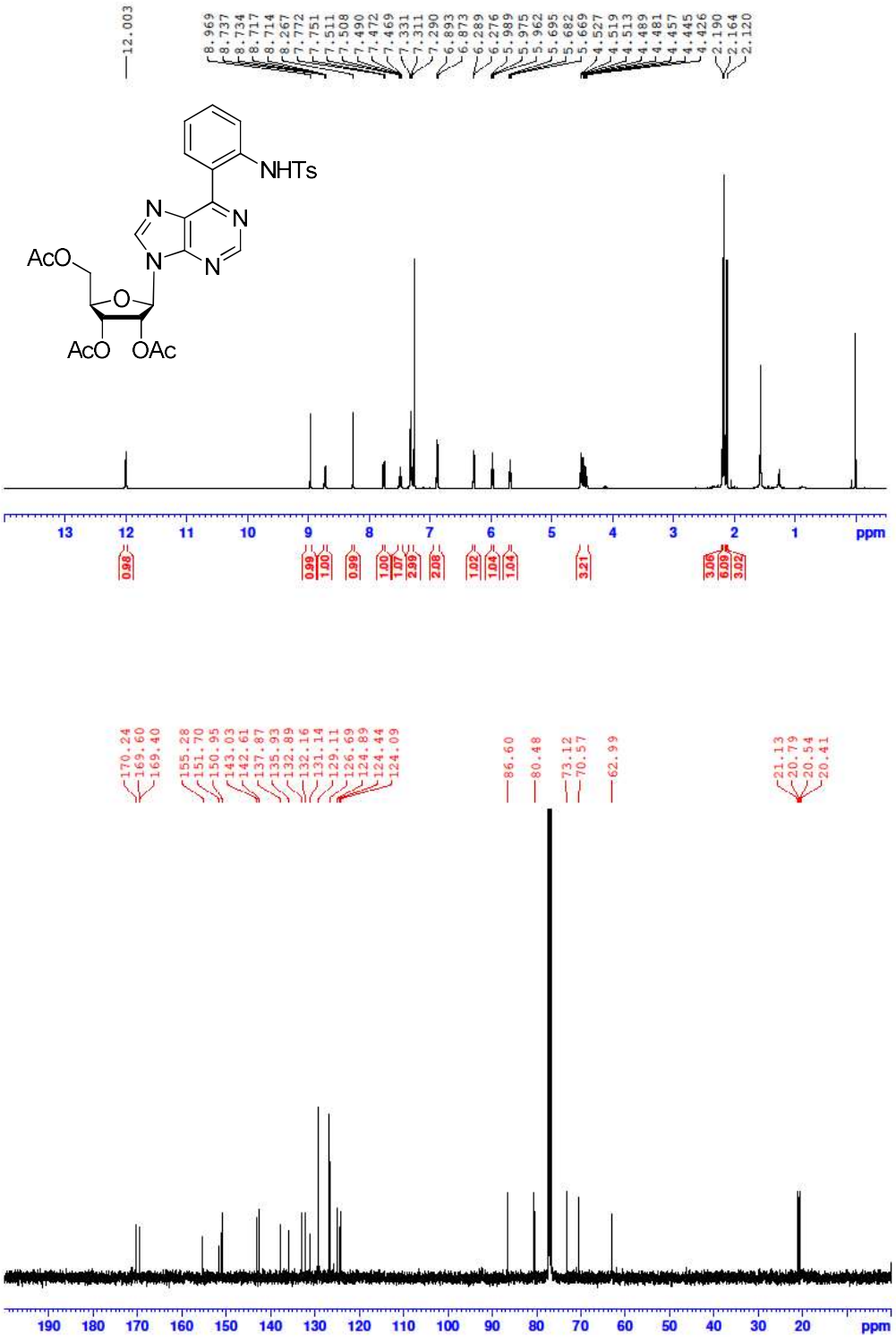
KIE experiment 1H NMR spectrum for product 3aa/3aa-d_4 ($CDCl_3$)



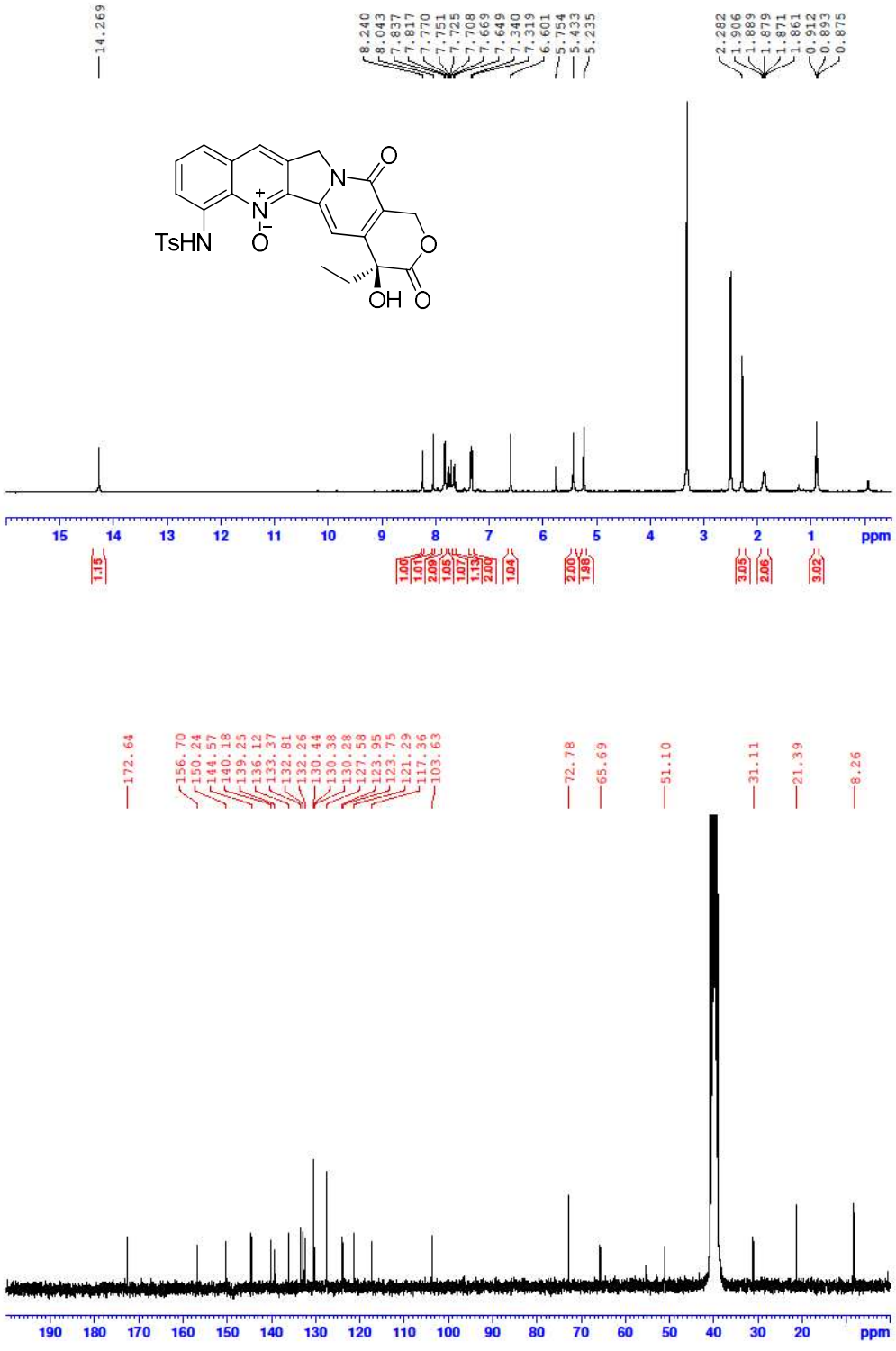
KIE experiment 1H NMR spectrum for product 6aa/6aa-d_2 ($CDCl_3$)



^{1}H and ^{13}C NMR spectra for product 7aa ($CDCl_3$)



^{1}H and ^{13}C NMR spectra for product 7ba ($CDCl_3$)



^{1}H and ^{13}C NMR spectra for product 8 (DMSO-*d*$_6$)