Electronic Supplementary Material (ESI) for ChemComm.

Electronic Supporting Information

Remote Difunctionalization of 2*H*-Indazoles Using Koser's Reagents

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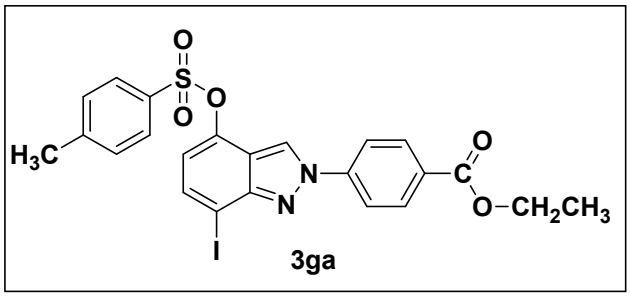
Contents

1. General information:

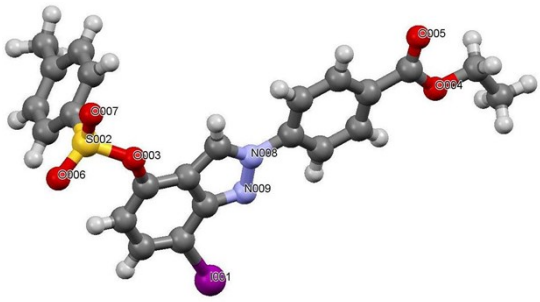
All reagents were purchased from commercial sources and used without further purification. ^{1}H NMR spectra were determined on a 400 MHz spectrometer as solutions in $CDCl_3$. Chemical shifts are expressed in parts per million (δ) and the signals were reported as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), and coupling constants (J) were given in Hz. $^{13}C\{^1H\}$ NMR spectra were recorded at 100 MHz in $CDCl_3$ solution. Chemical shifts are referenced to $CDCl_3$ (δ = 7.26 for ^{1}H and δ = 77.16 for $^{13}C\{^1H\}$ NMR) as internal standard. TLC was done on a silica gel-coated glass slide. All solvents were dried and distilled before use. Commercially available solvents were freshly distilled before the reaction. Melting points (M.p.) were determined after the re-crystallization of solid compounds from a solution of dichloromethane/petroleum ether (1:3). All the 2*H*-indazoles[1] and koser's reagents[2] were prepared by this reported method.

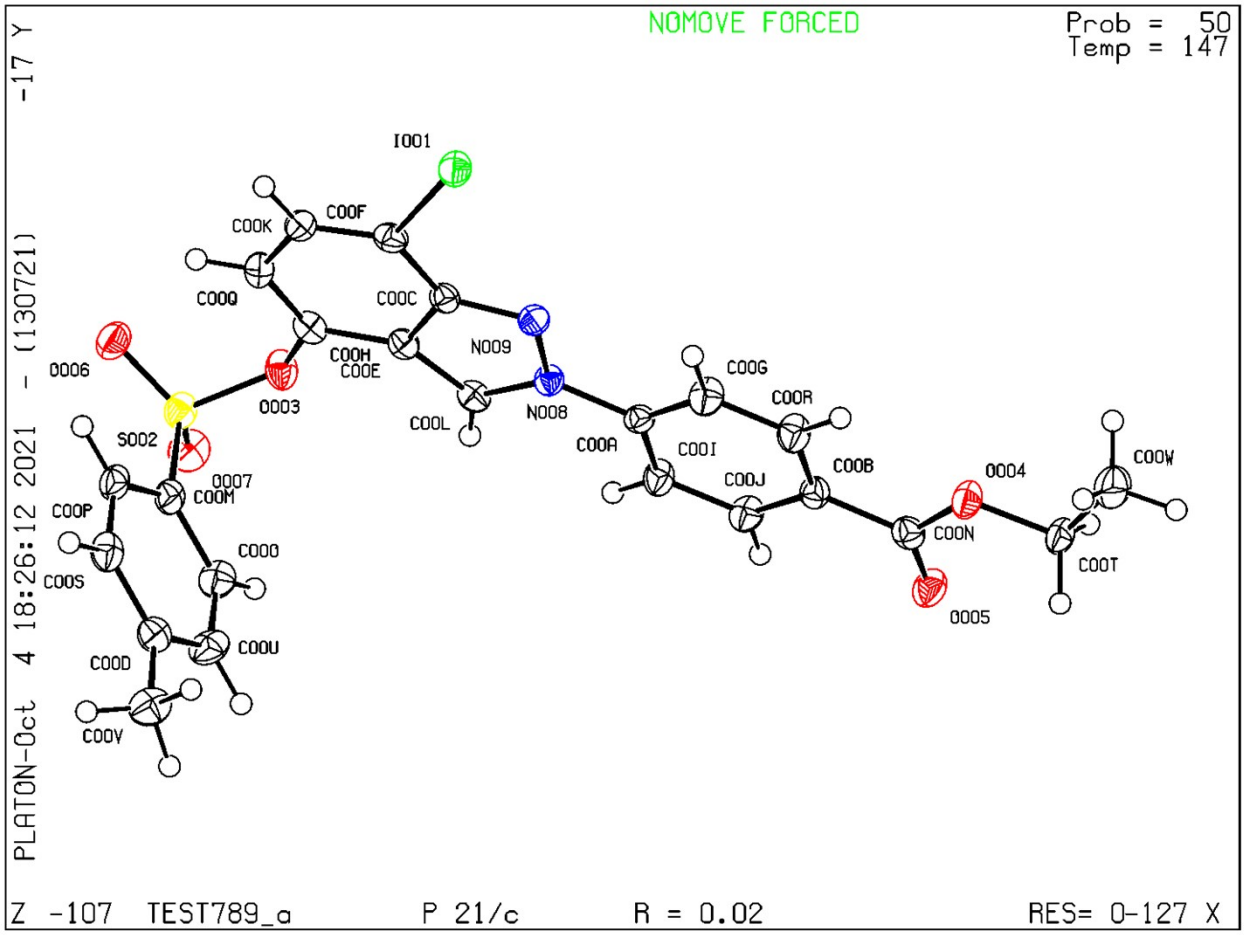
2. Structure determination (X-ray crystallographic data for 3ga):

The brown crystal of **3ga** was obtained by crystallization from a solution in dichloromethane/petroleum ether after purification by column chromatography. Chemical formula: $C_{23}H_{19}IN_2O_5S$.



Mol. formula: $C_{23}H_{19}IN_2O_5S$





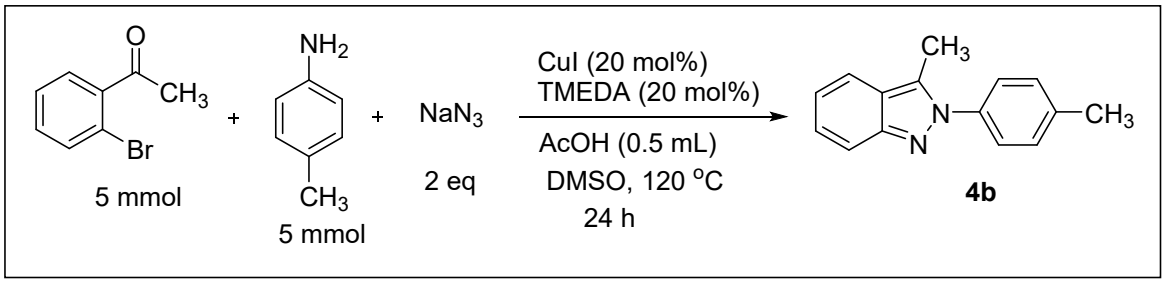
View of ORTEP diagram for the crystal structure of the compound **Ethyl 4-(7-iodo-4-(tosyloxy)-2*H*-indazol-2-yl)benzoate** (**3ga**) (Thermal ellipsoid contour at 50% probability level).

Wavelength	0.71073 Å	
Formula	C_{23} H_{19} I N_2 O_5 S	
Crystal system	Monoclinic	
Space group	P $2_1/c$	
Unit cell dimensions	a = 8.5871(6) Å	α = 90 °
	b = 22.0393(15) Å	β = 90.532(2)°
	c = 11.5720(7) Å	γ = 90 °

Volume	2189.95 Å^3	
Z	4	
R-factor (%)	2.35	

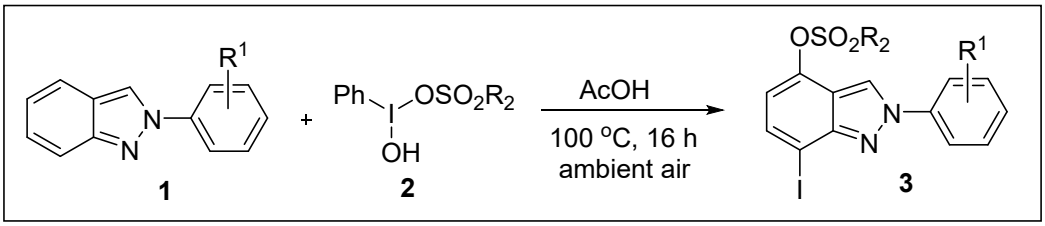
The crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as a supplementary publication with a CCDC reference number CCDC 2113810.

3. Synthetic procedure for 3-Methyl-2-(*p*-tolyl)-2*H*-indazole (4b):



To a stirred solution of 1-(2-bromophenyl)ethan-1-one (5 mmol, 995 mg), *p*-toluidine (5 mmol, 535 mg), and sodium azide (2 eq, 650 mg) in the presence of CuI (20 mol%, 390 mg), TMEDA (20 mol%, 116 mg), and AcOH (0.5 mL) in DMSO (10 mL) were added successively. The resulting solution was heated in a 100 mL round-bottom flask for 24 h at 120 °C. After the completion of the reaction (monitored by TLC), the crude reaction mixture was extracted with ethyl acetate. The organic extract was dried over anhydrous Na_2SO_4 and concentrated. The product was subjected to column chromatography (silica gel, 60-120 mesh), eluting with petroleum ether and ethyl acetate (97:3) to afford the product **4b** (62%, 689 mg) as yellow gummy mass.

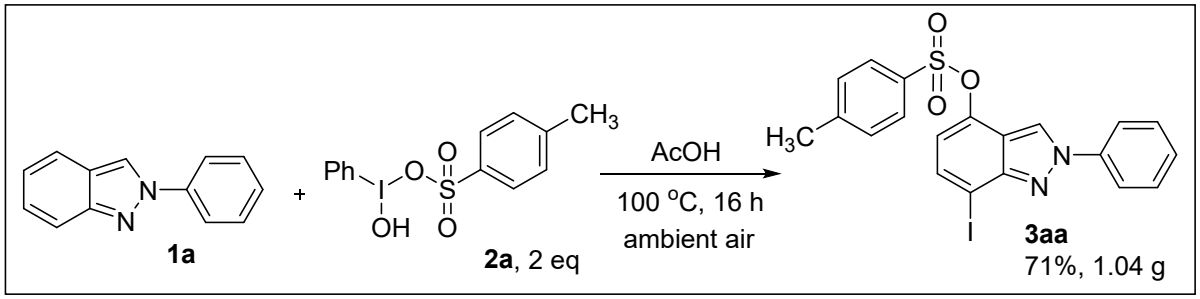
4. General experimental procedure for the synthesis of 3aa-3bf:



2-(*p*-tolyl)-2*H*-indazole (**1b**, 0.2 mmol, 41.2 mg) and HTIB (Koser's reagent) (**2a**, 2.0 equiv, 156.8 mg), in 2.0 mL AcOH solvent were added to an oven-dried reaction tube equipped with

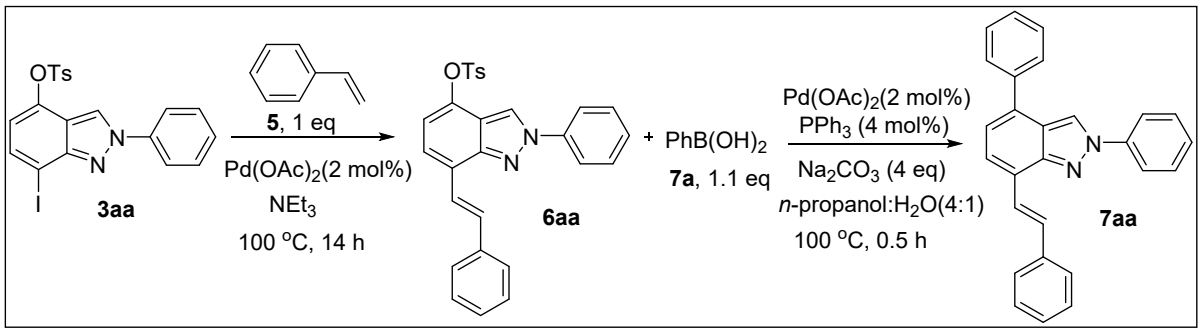
a magnetic stirrer, and the reaction tube was heated in an oil bath at 100 °C for 16 h under ambient air. The progress of the reaction was monitored by TLC. After completion of the reaction, the reaction was cooled to room temperature and extracted with ethyl acetate and a saturated solution of sodium bicarbonate. The combined organic phase was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure to get the crude residue which was purified by column chromatography on silica gel (60−120 mesh) using a mixture of petroleum ether and ethyl acetate (95 : 5) as an eluent to afford the product **3ba** (73%, 73 mg) as black gummy mass.

5. Gram scale synthesis of 7-Iodo-2-phenyl-2*H*-indazol-4-yl 4-methylbenzenesulfonate (3aa):



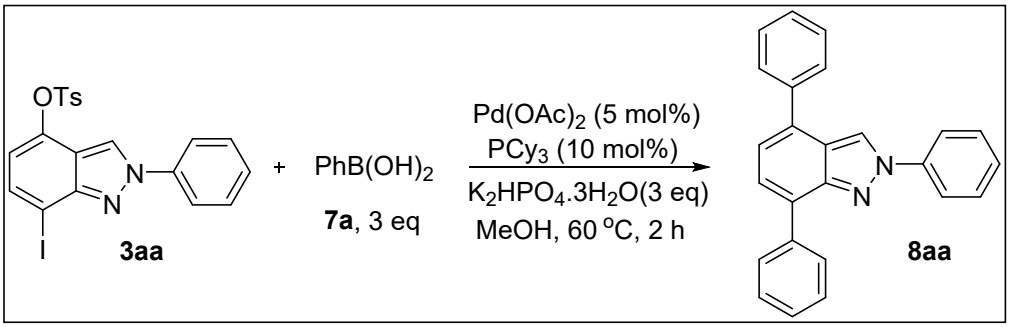
To a 100 mL round bottom flask equipped with a stir bar were charged with 2-phenyl-2*H*-indazole (**1a**, 3.0 mmol, 582.3 mg) and Koser's agent (**2a**, 6.0 mmol, 2353.2 mg), in 30 mL AcOH were added to an oven-dried reaction tube equipped with a magnetic stirrer, and the reaction tube was heated in an oil bath at 100 °C for 16 h under ambient air. The progress of the reaction was monitored by TLC. After completion of the reaction, the reaction was cooled to room temperature and extracted with 50 mL ethyl acetate and a saturated solution of sodium bicarbonate. The combined organic phase was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure to get the crude residue which was purified by column chromatography on silica gel (60−120 mesh) using a mixture of petroleum ether and ethyl acetate (96 : 4) as an eluent to afford the product **3aa** (71%, 1.04 g) as grey solid.

6. Stepwise synthesis of (*E*)-2,4-Diphenyl-7-styryl-2*H*-indazole (7aa):



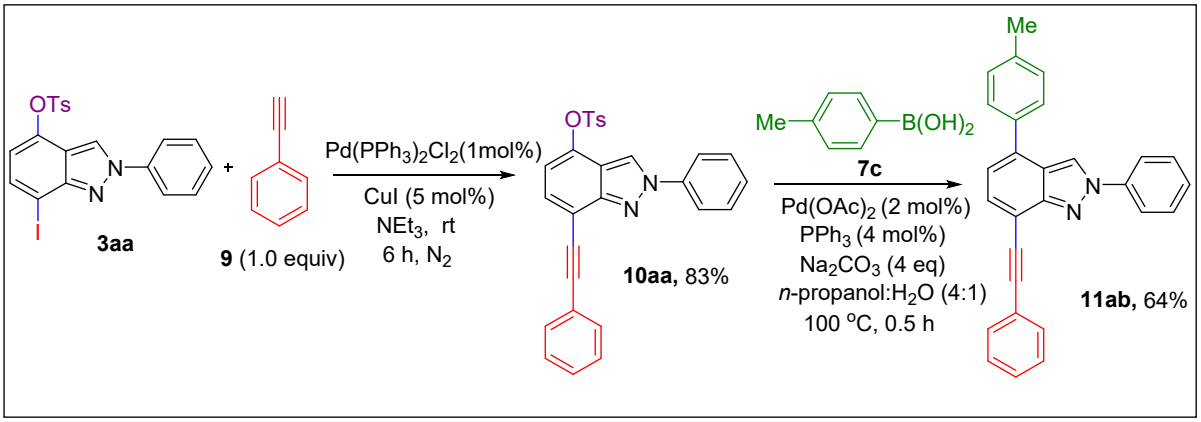
To a stirred solution of 7-Iodo-2-phenyl-2*H*-indazol-4-yl 4-methylbenzenesulfonate (**3aa**) (0.25 mmol, 122.5 mg) and styrene (**5**) (0.25 mmol, 26 mg) in equimolar quantity in the presence of $Pd(OAc)_2$ (2.0 mol%, 1.1 mg) in triethylamine (1 mL) were added successively. The resulting solution was heated in a sealed tube for 14 h at 100 °C under an open atmosphere. After the completion of the reaction (monitored by TLC), the crude reaction mixture was extracted with ethyl acetate. The organic extract was dried over anhydrous Na_2SO_4 and concentrated. The product was subjected to column chromatography (silica gel, 60-120 mesh), eluting with petroleum ether and ethyl acetate (97:3) to afford the product **6aa** (79%, 92.1 mg) as yellow gummy mass**.** After that, a mixture of (*E*)-2-Phenyl-7-styryl-2*H*-indazol-4-yl 4-methylbenzenesulfonate (0.1 mmol, 46.6 mg) (**6aa**) and phenylboronic acid (1.1 equiv, 13.4 mg) was taken in an oven-dried reaction tube in presence of $Pd(OAc)_2$ (2.0 mol%, 0.4 mg), PPh_3 (4 mol%, 1.0 mg), and Na_2CO_3 (4.0 equiv, 42.4 mg) in 2mL *n*-propanol:H_2O (4:1) and stirred at 100 °C under open atmosphere for 0.5 h. After the completion of the reaction (monitored by TLC), the crude reaction mixture was extracted with ethyl acetate. The organic extract was dried over anhydrous Na_2SO_4 and concentrated. The product was subjected to column chromatography (silica gel, 60-120 mesh), eluting with petroleum ether and ethyl acetate (98:2) to afford the product **7aa** (70%, 26 mg) as yellow solid.

7. Synthetic procedure of 2,4,7-triphenyl-2*H*-indazole (8aa):



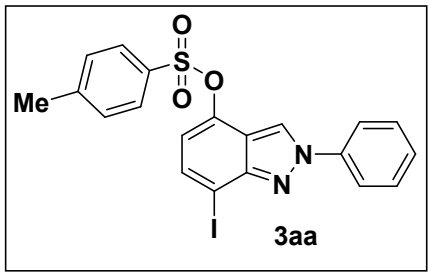
A mixture of 7-Iodo-2-phenyl-2*H*-indazol-4-yl 4-methylbenzenesulfonate (**3aa**) (0.2 mmol, 98 mg) and phenylboronic acid (**7a**) (3 equiv, 73.1 mg) was taken in an oven-dried reaction tube in presence of $Pd(OAc)_2$ (5.0 mol%, 2.2 mg), PCy_3 (10 mol%, 11.2 mg), and $K_2HPO_4.3H_2O$ (3.0 equiv, 136.9 mg) in 2 mL MeOH and stirred at 100 °C for 2 h. After the completion of the reaction (monitored by TLC), the crude reaction mixture was extracted with ethyl acetate. The organic extract was dried over anhydrous Na_2SO_4 and concentrated. The product was subjected to column chromatography (silica gel, 60-120 mesh), eluting with petroleum ether and ethyl acetate (98.5 : 1.5) to afford the product **8aa** (62%, 42 mg) as yellow solid.

8. Stepwise synthetic procedure of 2-Phenyl-7-(phenylethynyl)-4-(*p*-tolyl)-2*H*-indazole (11ab):



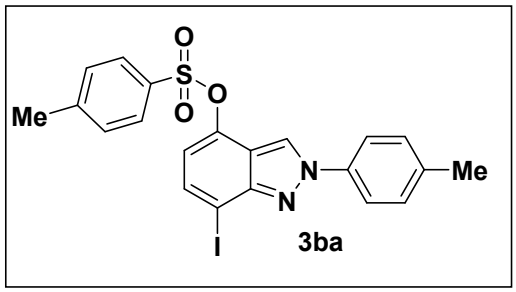
To a stirred solution of 7-Iodo-2-phenyl-2*H*-indazol-4-yl 4-methylbenzenesulfonate (**3aa**) (0.2 mmol, 98 mg) and Phenylacetylene (**9**) (0.2 mmol, 20.4 mg) in equimolar quantity in the presence of $Pd(PPh_3)_2Cl_2$ (1.0 mol%, 1.4 mg) and CuI (5 mol%, 1.9 mg) in triethylamine (1 mL) were added successively under N_2 atmosphere at room temperature for 6 h. After the completion of the reaction (monitored by TLC), the crude reaction mixture was extracted with ethyl acetate. The organic extract was dried over anhydrous Na_2SO_4 and concentrated. The product was subjected to column chromatography (silica gel, 100-200 mesh), eluting with petroleum ether and ethyl acetate (97:3) to afford the product **10aa** (83%, 77 mg) as brown gummy mass**.** After that, a mixture of 2-Phenyl-7-(phenylethynyl)-2H-indazol-4-yl 4-methylbenzenesulfonate (0.1 mmol, 46.1 mg) (**10aa**) and *p*-tolylphenylboronic acid (**7b**) (1.1 equiv, 14.9 mg) was taken in an oven-dried reaction tube in presence of $Pd(OAc)_2$ (2.0 mol%, 0.4 mg), PPh_3 (4 mol%, 1.0 mg), and Na_2CO_3 (4.0 equiv, 42.4 mg) in 2mL *n*-propanol:H_2O (4:1) and stirred at 100 °C under open atmosphere for 0.5 h. After the completion of the reaction (monitored by TLC), the crude reaction mixture was extracted with ethyl acetate. The organic extract was dried over anhydrous Na_2SO_4 and concentrated. The product was subjected to column chromatography (silica gel, 60-120 mesh), eluting with petroleum ether and ethyl acetate (98:2) to afford the product **11ab** (64%, 24 mg) as a white solid.

9. Characterization data of the synthesized compounds (3aa–11ab):



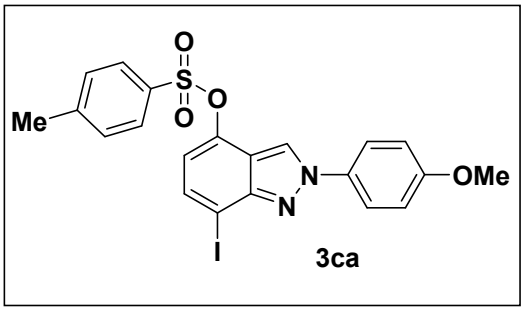
3aa

7-Iodo-2-phenyl-2*H*-indazol-4-yl 4-methylbenzenesulfonate (3aa): Grey solid (77 mg, 79%); M.p. 128–129 °C; R_f = 0.55 (PE : EA = 96 : 4); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.37 (s, 1H), 7.86–7.84 (m, 2H), 7.75 (d, J = 8.4 Hz, 2H), 7.61 (d, J = 7.6 Hz, 1H), 7.53 (t, J = 8.0 Hz, 2H), 7.44 (t, J = 7.2 Hz, 1H), 7.31 (d, J = 8.0 Hz, 2H), 6.38 (d, J = 8.0 Hz, 1H), 2.42 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 151.7, 145.9, 143.0, 139.9, 135.7, 132.1, 130.0, 129.7, 128.8, 121.4, 121.1, 117.6, 116.0, 113.2, 82.3, 21.8; Anal. Calcd for $C_{20}H_{15}IN_2O_3S$: C, 48.99; H, 3.08; N, 5.71%; Found C, 48.78; H, 3.15; N, 5.59%.

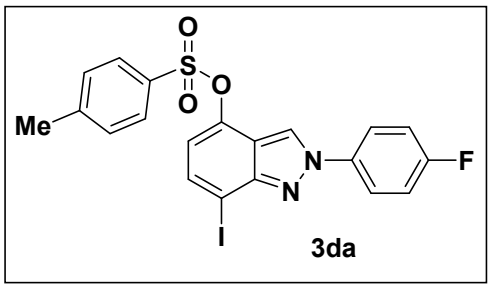


3ba

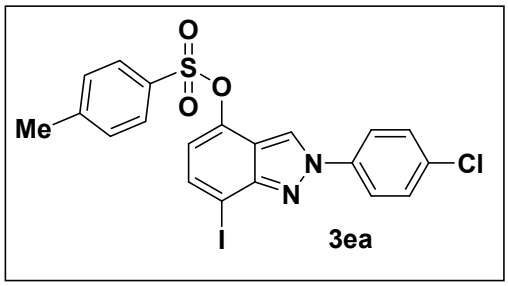
7-Iodo-2-(*p*-tolyl)-2*H*-indazol-4-yl 4-methylbenzenesulfonate (3ba): Black gummy mass (73 mg, 73%); R_f = 0.5 (PE : EA = 95 : 5); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.32 (s, 1H), 7.76-7.71 (m, 4H), 7.60 (d, J = 7.6 Hz, 1H), 7.32–7.30 (m, 4H), 6.38 (d, J = 7.6 Hz, 1H), 2.43 (s, 3H), 2.42 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 151.6, 145.9, 143.0, 138.9, 137.7, 135.5, 132.1, 130.2, 130.0, 128.8, 121.2, 120.9, 117.5, 115.9, 82.2, 21.8, 21.2; Anal. Calcd for $C_{21}H_{17}IN_2O_3S$: C, 50.01; H, 3.40; N, 5.55%; Found C, 50.19; H, 3.34; N, 5.79%.



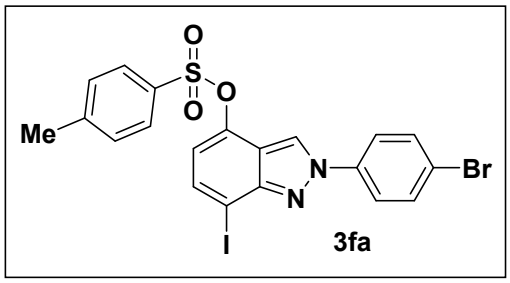
7-Iodo-2-(4-methoxyphenyl)-2*H*-indazol-4-yl 4-methylbenzenesulfonate (3ca): Brown gummy mass (72 mg, 70%); R_f = 0.45 (PE : EA = 94 : 6); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.29 (s, 1H), 7.76-7.74 (m, 4H), 7.59 (d, J = 8.0 Hz, 1H), 7.31 (d, J = 8.4 Hz, 2H), 7.03-7.01 (m, 2H), 6.37 (d, J = 8.0 Hz, 1H), 3.88 (s, 3H), 2.43 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 160.0, 145.9, 136.0, 133.4, 130.1, 130.0, 128.8, 127.1, 125.3, 122.8, 120.9, 115.8, 115.2, 114.8, 82.1, 55.8, 21.8; Anal. Calcd for $C_{21}H_{17}IN_2O_4S$: C, 48.47; H, 3.29; N, 5.38%; Found C, 48.30; H, 3.37; N, 5.28%.



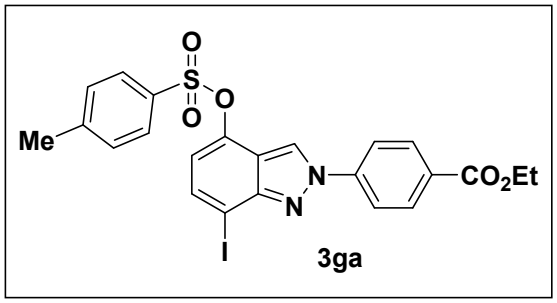
2-(4-Fluorophenyl)-7-iodo-2*H*-indazol-4-yl 4-methylbenzenesulfonate (3da): Brown solid (90 mg, 89%); M.p. 176-177 ^{o}C; R_f = 0.5 (PE : EA = 95 : 5); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.37 (s, 1H), 7.85-7.82 (m, 2H), 7.75 (d, J = 8.4 Hz, 2H), 7.60 (d, J = 7.6 Hz, 1H), 7.31 (d, J = 8.0 Hz, 2H), 7.24-7.19 (m, 2H), 6.35 (d, J = 8.0 Hz, 1H), 2.42 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 162.6 ($J_{C\text{-}F}$ = 248 Hz), 151.8, 145.9, 142.9, 136.2 ($J_{C\text{-}F}$ = 3 Hz), 135.8, 132.0, 130.0, 128.8, 123.2 ($J_{C\text{-}F}$ = 9 Hz), 121.3, 117.7, 123.7 ($J_{C\text{-}F}$ = 23 Hz), 116.1, 82.2, 21.8; Anal. Calcd for $C_{20}H_{14}FIN_2O_3S$: C, 47.26; H, 2.78; N, 5.51%; Found C, 47.04; H, 2.83; N, 5.60%.



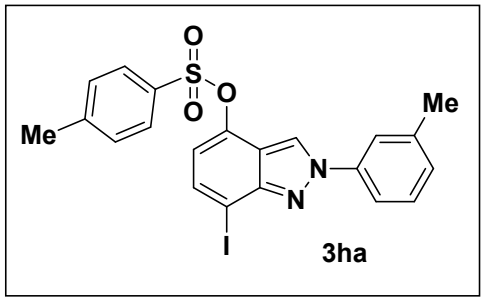
2-(4-Chlorophenyl)-7-iodo-2*H*-indazol-4-yl 4-methylbenzenesulfonate (3ea): Brown solid (85 mg, 81%); M.p. 172-173 °C; R_f = 0.5 (PE : EA = 96 : 4); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.40 (s, 1H), 7.83-7.81 (m, 2H), 7.75 (d, J = 8.0 Hz, 2H), 7.61 (d, J = 7.6 Hz, 1H), 7.52-7.48 (m, 2H), 7.32 (d, J = 8.0 Hz, 2H), 6.34 (d, J = 7.6 Hz, 1H), 2.43 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 151.8, 146.0, 142.9, 138.4, 136.0, 134.6, 131.9, 130.0, 129.9, 128.8, 122.4, 121.1, 117.8, 116.2, 82.3, 21.8; Anal. Calcd for $C_{20}H_{14}ClIN_2O_3S$: C, 45.78; H, 2.69; N, 5.34%; Found C, 45.96; H, 2.63; N, 5.22%.



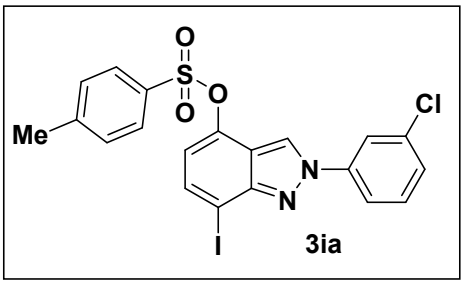
2-(4-Bromophenyl)-7-iodo-2*H*-indazol-4-yl 4-methylbenzenesulfonate (3fa): Brown gummy mass (84 mg, 74%); R_f = 0.55 (PE : EA = 96 : 4); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.41 (s, 1H), 7.78-7.74 (m, 4H), 7.67-7.65 (m, 2H), 7.61 (d, J = 7.6 Hz, 1H), 7.32 (d, J = 8.4 Hz, 2H), 6.35 (d, J = 8.0 Hz, 1H), 2.43 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 151.8, 146.0, 142.9, 138.8, 136.0, 132.9, 131.9, 130.0, 128.8, 122.7, 122.6, 121.1, 117.8, 116.2, 82.3, 21.8; Anal. Calcd for $C_{20}H_{14}BrIN_2O_3S$: C, 42.20; H, 2.48; N, 4.92%; Found C, 42.39; H, 2.55; N, 5.06%.



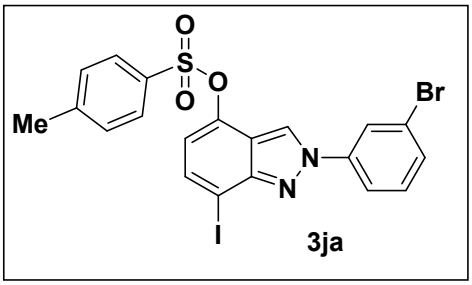
Ethyl 4-(7-iodo-4-(tosyloxy)-2*H*-indazol-2-yl)benzoate (3ga): Brown solid (78 mg, 70%); M.p. 159-160 °C; R_f = 0.45 (PE : EA = 94 : 6); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.47 (s, 1H), 8.21 (d, J = 8.8 Hz, 2H), 7.96 (d, J = 8.8 Hz, 2H), 7.76 (d, J = 8.0 Hz, 2H), 7.63 (d, J = 7.6 Hz, 1H), 7.32 (d, J = 8.0 Hz, 2H), 6.38 (d, J = 8.0 Hz, 1H), 4.43 (q, J = 7.2 Hz, 2H), 2.43 (s, 3H), 1.44 (t, J = 7.2 Hz, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 165.6, 152.0, 146.0, 143.0, 142.9, 136.3, 132.0, 131.2, 130.6, 130.0, 128.8, 121.3, 120.8, 117.9, 116.4, 82.4, 61.5, 21.8, 14.4; Anal. Calcd for $C_{23}H_{19}IN_2O_5S$: C, 49.12; H, 3.41; N, 4.98%; Found C, 48.92; H, 3.49; N, 4.89%.



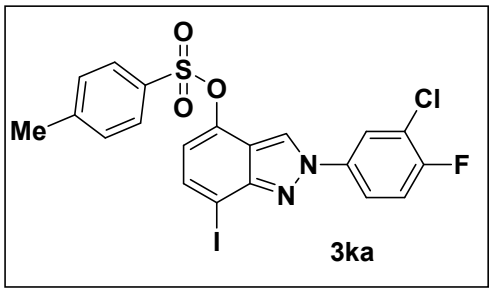
7-Iodo-2-(*m*-tolyl)-2*H*-indazol-4-yl 4-methylbenzenesulfonate (3ha): Brown solid (87 mg, 87%); M.p. 118-119 °C; R_f = 0.5 (PE : EA = 95 : 5); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.36 (s, 1H), 7.75 (d, J = 8.4 Hz, 2H), 7.68 (s, 1H), 7.61 (d, J = 7.6 Hz, 2H), 7.39 (t, J = 8.0 Hz, 1H), 7.31 (d, J = 8.4 Hz, 2H), 7.24 (d, J = 7.6 Hz, 1H), 6.38 (d, J = 7.6 Hz, 1H), 2.47 (s, 3H), 2.42 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 151.7, 145.9, 143.0, 140.0, 139.8, 135.6, 132.1, 130.0, 129.6, 129.5, 128.8, 122.1, 121.2, 118.4, 117.5, 116.0, 82.3, 21.8, 21.6; Anal. Calcd for $C_{21}H_{17}IN_2O_3S$: C, 50.01; H, 3.40; N, 5.55%; Found C, 50.23; H, 3.32; N, 5.66%.



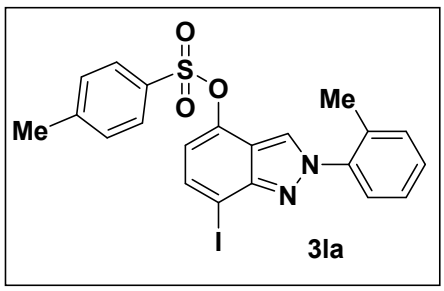
2-(3-Chlorophenyl)-7-iodo-2*H*-indazol-4-yl 4-methylbenzenesulfonate (3ia): Yellow gummy mass (68 mg, 65%); R_f = 0.55 (PE : EA = 96 : 4); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.35 (s, 1H), 7.88 (t, J = 2.0 Hz, 1H), 7.76 (d, J = 7.6 Hz, 3H), 7.63 (d, J = 7.6 Hz, 1H), 7.47 (t, J = 8.0 Hz, 1H), 7.42-7.40 (m, 1H), 7.33 (d, J = 8.0 Hz, 2H), 6.38 (d, J = 7.6 Hz, 1H), 2.44 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 151.9, 146.1, 142.9, 140.7, 136.1, 135.6, 131.9, 130.8, 130.0, 128.9, 128.8, 121.6, 121.2, 119.3, 117.7, 116.4, 82.4, 21.9; HRMS (ESI-TOF) m/z: [M + H]+ Calcd for $[C_{20}H_{15}ClIN_2O_3S]^+$: 524.9531; found: 524.9534.



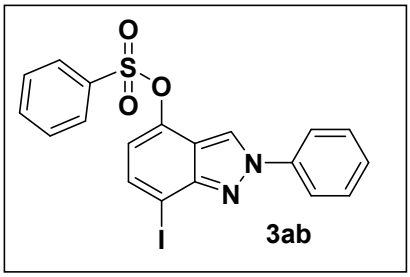
2-(3-Bromophenyl)-7-iodo-2*H*-indazol-4-yl 4-methylbenzenesulfonate (3ja): Brown gummy mass (95 mg, 84%); R_f = 0.5 (PE : EA = 95 : 5); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.35 (s, 1H), 8.02 (t, J = 2.4 Hz, 1H), 7.82-7.79 (m, 1H), 7.75 (d, J = 8.4 Hz, 2H), 7.63 (d, J = 7.6 Hz, 1H), 7.56 (d, J = 8.0 Hz, 1H), 7.40 (t, J = 8.0 Hz, 1H), 7.32 (d, J = 8.0 Hz, 2H), 6.39 (d, J = 7.6 Hz, 1H), 2.44 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 151.9, 146.0, 142.9, 140.8, 136.1, 132.0, 131.8, 131.0, 130.0, 128.8, 124.4, 123.3, 121.2, 119.8, 117.7, 116.4, 82.3, 21.8; Anal. Calcd for $C_{20}H_{14}BrIN_2O_3S$: C, 42.20; H, 2.48; N, 4.92%; Found C, 42.04; H, 2.41; N, 4.78%.



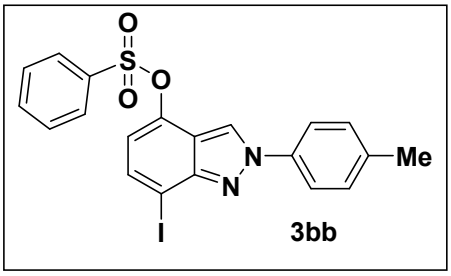
2-(3-Chloro-4-fluorophenyl)-7-iodo-2*H*-indazol-4-yl 4-methylbenzenesulfonate (3ka): White solid (93 mg, 86%); M.p. 145-146 °C; R_f = 0.45 (PE : EA = 95 : 5); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.37 (s, 1H), 7.96-7.94 (m, 1H), 7.78-7.74 (m, 3H), 7.62 (d, J = 7.6 Hz, 1H), 7.34-7.28 (m, 3H), 6.36 (d, J = 8.0 Hz, 1H), 2.44 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 158.1 ($J_{C\text{-}F}$ = 251 Hz), 151.9, 146.0, 142.9, 136.5, 136.2, 132.0, 130.0, 128.8, 123.8, 122.5 ($J_{C\text{-}F}$ = 19 Hz), 121.3, 120.9 ($J_{C\text{-}F}$ = 7 Hz), 117.8 ($J_{C\text{-}F}$ = 15 Hz), 117.6 ($J_{C\text{-}F}$ = 23 Hz), 116.4, 82.2, 21.8; Anal. Calcd for $C_{20}H_{13}ClFIN_2O_3S$: C, 44.26; H, 2.41; N, 5.16%; Found C, 44.07; H, 2.46; N, 5.25%.



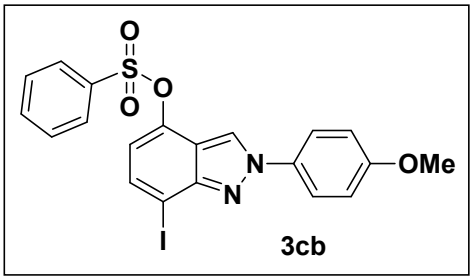
7-Iodo-2-(*o*-tolyl)-2*H*-indazol-4-yl 4-methylbenzenesulfonate (3la): Brown gummy mass (72 mg, 72%); R_f = 0.5 (PE : EA = 96 : 4); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.06 (s, 1H), 7.74 (d, J = 8.4 Hz, 2H), 7.65 (d, J = 7.6 Hz, 1H), 7.42-7.40 (m, 1H), 7.39-7.33 (m, 3H), 7.31–7.29 (m, 2H), 6.47 (d, J = 7.6 Hz, 1H), 2.42 (s, 3H), 2.18 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 151.4, 145.8, 143.0, 139.7, 135.5, 134.0, 132.2, 131.5, 130.0, 129.8, 128.8, 126.8, 126.6, 125.0, 116.7, 115.9, 82.2, 21.8, 17.9; HRMS (ESI-TOF) m/z: [M + H]+ Calcd for $[C_{21}H_{18}IN_2O_3S]^+$: 505.0077; found: 505.0083.



7-Iodo-2-phenyl-2*H*-indazol-4-yl benzenesulfonate (3ab): Brown solid (79 mg, 83%); M.p. 124-125 ^{o}C; R_f = 0.5 (PE : EA = 94 : 6); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.42 (s, 1H), 7.90-7.85 (m, 4H), 7.68 (t, J = 7.6 Hz, 1H), 7.61 (d, J = 7.6 Hz, 1H), 7.56-7.51 (m, 4H), 7.46-7.42 (m, 1H), 6.37 (d, J = 7.6 Hz, 1H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 151.7, 142.9, 139.9, 135.6, 135.1, 134.6, 129.7, 129.4, 128.8, 128.7, 121.4, 121.1, 117.5, 116.0, 82.5; Anal. Calcd for $C_{19}H_{13}IN_2O_3S$: C, 47.91; H, 2.75; N, 5.88%; Found C, 47.73; H, 2.81; N, 5.74%.

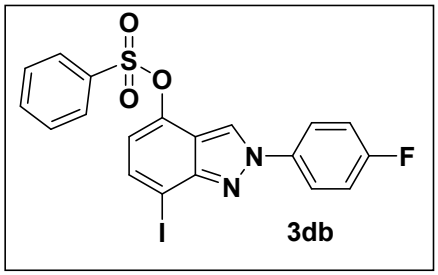


7-Iodo-2-(*p*-tolyl)-2*H*-indazol-4-yl benzenesulfonate (3bb): Yellow gummy mass (73 mg, 75%); R_f = 0.5 (PE : EA = 95 : 5); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.37 (s, 1H), 7.88 (d, J = 7.6 Hz, 2H), 7.43 (d, J = 8.4 Hz, 2H), 7.69-7.65 (m, 1H), 7.60 (d, J = 7.6 Hz, 1H), 7.53 (t, J = 8.0 Hz, 1H), 7.32 (d, J = 8.0 Hz, 2H), 6.36 (d, J = 8.0 Hz, 1H), 2.43 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 151.6, 142.9, 139.0, 137.6, 135.5, 135.1, 134.6, 130.2, 129.4, 128.7, 121.2, 120.9, 117.4, 115.9, 82.4, 21.2; Anal. Calcd for $C_{20}H_{15}IN_2O_3S$: C, 48.99; H, 3.08; N, 5.71%; Found C, 48.77; H, 3.01; N, 5.80%.



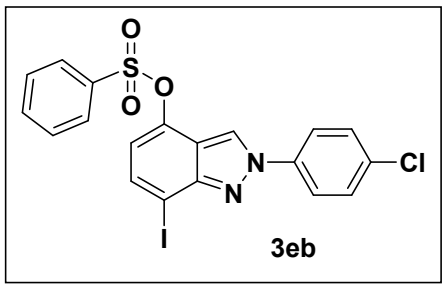
7-Iodo-2-(4-methoxyphenyl)-2*H*-indazol-4-yl benzenesulfonate (3cb): Black gummy mass (71 mg, 71%); R_f = 0.45 (PE : EA = 94 : 6); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.33 (s, 1H),

7.90-7.87 (m, 2H), 7.78-7.74 (m, 2H), 7.69-7.66 (m, 1H), 7.59 (d, *J* = 7.6 Hz, 1H), 7.53 (t, *J* = 8.0 Hz, 2H), 7.04-7.00 (m, 2H), 6.35 (d, *J* = 8.0 Hz, 1H), 3.88 (s, 3H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz): δ 160.0, 142.8, 135.3, 135.1, 134.6, 133.4, 129.4, 128.8, 122.9, 120.9, 115.8, 114.8, 114.6, 111.2, 82.3, 55.8; Anal. Calcd for $C_{20}H_{15}IN_2O_4S$: C, 47.44; H, 2.99; N, 5.53%; Found C, 47.63; H, 2.91; N, 5.44%.



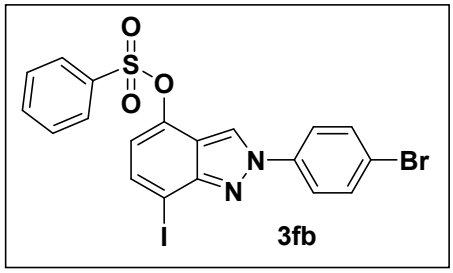
3db

2-(4-Fluorophenyl)-7-iodo-2*H*-indazol-4-yl benzenesulfonate (3db): White solid (75 mg, 76%); M.p 128-129 ^{o}C; R_f = 0.5 (PE : EA = 95 : 5); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.40 (s, 1H), 7.90-7.83 (m, 4H), 7.69 (t, *J* = 7.6 Hz, 1H), 7.61 (d, *J* = 7.6 Hz, 1H), 7.54 (t, J = 8.0 Hz, 2H), 7.25-7.21 (m, 2H), 6.34 (d, *J* = 7.6 Hz, 1H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz): δ 162.6 (J_{C-F} = 248 Hz), 151.8, 142.8 (J_{C-F} = 14 Hz), 135.8, 135.1, 134.7, 131.5, 129.4, 128.8, 123.3 (J_{C-F} = 9 Hz), 121.3, 117.6, 116.7 (J_{C-F} = 23 Hz), 116.1, 82.4; Anal. Calcd for $C_{19}H_{12}FIN_2O_3S$: C, 46.17; H, 2.45; N, 5.67%; Found C, 46.37; H, 2.50, N, 5.78%.

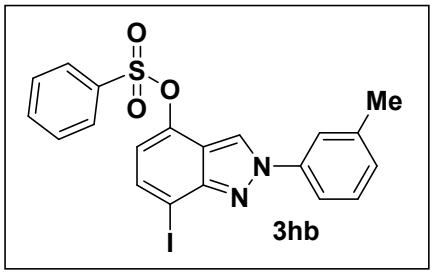


3eb

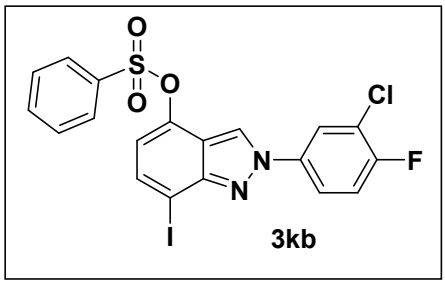
2-(4-Chlorophenyl)-7-iodo-2*H*-indazol-4-yl benzenesulfonate (3eb): Brown solid (79 mg, 78%); M.p 162-163 ^{o}C; R_f = 0.45 (PE : EA = 94 : 6); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.43 (s, 1H), 7.89 (d, *J* = 7.6 Hz, 2H), 7.85-7.81 (m, 2H), 7.68 (t, *J* = 7.6 Hz, 1H), 7.61 (d, *J* = 7.6 Hz, 1H), 7.56-7.49 (m, 4H), 6.34 (d, *J* = 8.0 Hz, 1H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz): δ 151.8, 142.9, 140.4, 138.4, 135.9, 135.0, 134.7, 129.9, 129.4, 128.8, 122.5, 121.1, 117.7, 116.2, 82.4; Anal. Calcd for $C_{19}H_{12}ClIN_2O_3S$: C, 44.68; H, 2.37; N, 5.49%; Found C, 44.47; H, 2.44; N, 5.39%.



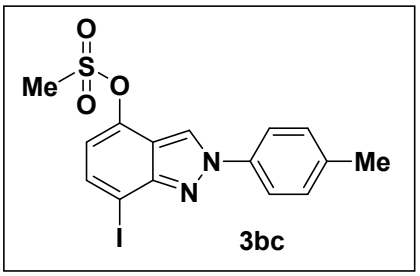
2-(4-Bromophenyl)-7-iodo-2*H*-indazol-4-yl benzenesulfonate (3fb): Brown solid (85 mg, 77%); M.p. 164-165 °C; R_f = 0.5 (PE : EA = 95 : 5); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.43 (s, 1H), 7.90-7.88 (m, 2H), 7.79-7.75 (m, 2H), 7.70-7.64 (m, 3H), 7.61 (d, J = 8.0 Hz, 1H), 7.56-7.52 (m, 2H), 6.34 (d, J = 7.6 Hz, 1H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 151.9, 142.9, 138.9, 136.0, 135.0, 134.7, 132.9, 129.4, 128.8, 122.7, 122.6, 121.0, 117.7, 116.2, 82.4; Anal. Calcd for $C_{19}H_{12}BrIN_2O_3S$: C, 41.11; H, 2.18; N, 5.05%; Found C, 41.30; H, 2.10; N, 5.17%.



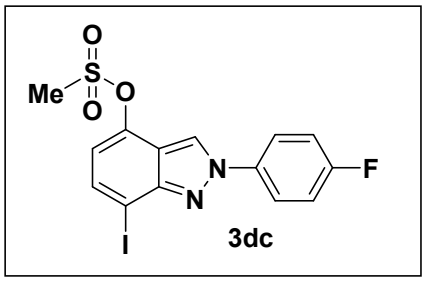
7-Iodo-2-(*m*-tolyl)-2*H*-indazol-4-yl benzenesulfonate (3hb): Black solid (65 mg, 67%); M.p. 96-97 °C; R_f = 0.6 (PE : EA = 96 : 4); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.40 (s, 1H), 7.90-7.88 (m, 2H), 7.69-7.66 (m, 2H), 7.63-7.59 (m, 2H), 7.56-7.52 (m, 2H), 7.40 (t, J = 8.0 Hz, 1H), 7.23 (s, 1H), 6.36 (d, J = 7.6 Hz, 1H), 2.47 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 151.7, 142.9, 140.0, 139.8, 135.6, 135.1, 134.6, 129.6, 129.5, 129.4, 128.7, 122.1, 121.2, 118.5, 117.4, 115.9, 82.5, 21.6; Anal. Calcd for $C_{20}H_{15}IN_2O_3S$: C, 48.99; H, 3.08; N, 5.71%; Found C, 48.79; H, 3.13; N, 5.62%.



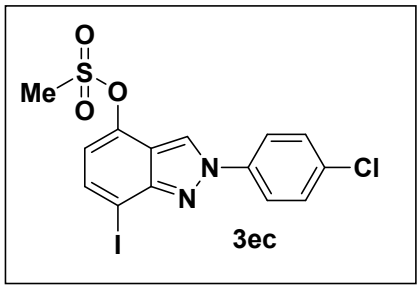
2-(3-Chloro-4-fluorophenyl)-7-iodo-2*H*-indazol-4-yl benzenesulfonate (3kb): Grey solid (84 mg, 80%); M.p. 207-208 °C; R_f = 0.5 (PE : EA = 95 : 5); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.40 (s, 1H), 8.00-7.97 (m, 1H), 7.90-7.88 (m, 2H), 7.77-7.74 (m, 1H), 7.72-7.68 (m, 1H), 7.62 (d, J = 7.6 Hz, 1H), 7.55 (t, J = 8.0 Hz, 2H), 7.31 (t, J = 7.6 Hz, 1H), 6.34 (d, J = 7.6 Hz, 1H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 158.1 ($J_{C\text{-}F}$ = 250 Hz), 151.9, 142.8, 136.5, 136.1, 135.0, 134.9, 134.7, 129.4, 128.8, 123.9, 121.4, 120.9 ($J_{C\text{-}F}$ = 8 Hz), 117.8 ($J_{C\text{-}F}$ = 10 Hz), 117.6 ($J_{C\text{-}F}$ = 23 Hz), 116.4, 82.4; Anal. Calcd for $C_{19}H_{11}ClFIN_2O_3S$: C, 43.16; H, 2.10; N, 5.30%; Found C, 43.33; H, 2.04; N, 5.43%.



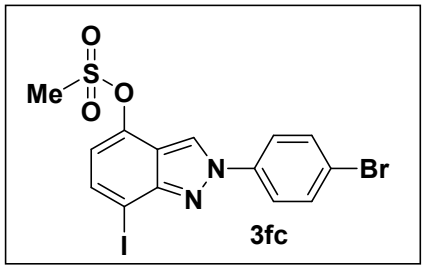
7-Iodo-2-(*p*-tolyl)-2*H*-indazol-4-yl methanesulfonate (3bc): Brown solid (63 mg, 74%); M.p. 102-103 °C; R_f = 0.4 (PE : EA = 92 : 8); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.67 (s, 1H), 7.81 (d, J = 7.6 Hz, 2H), 7.75 (d, J = 7.6 Hz, 1H), 7.33 (d, J = 8.4 Hz, 2H), 6.80 (d, J = 7.6 Hz, 1H), 3.24 (s, 3H), 2.43 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 142.6, 139.1, 137.7, 135.6, 130.3, 129.2, 121.4, 117.3, 116.3, 115.2, 82.6, 37.7, 21.2; Anal. Calcd for $C_{15}H_{13}IN_2O_3S$: C, 42.07; H, 3.06; N, 6.54%; Found C, 41.89; H, 3.11; N, 6.44%.



2-(4-Fluorophenyl)-7-iodo-2*H*-indazol-4-yl methanesulfonate (3dc): Grey solid (71 mg, 83%); M.p. 158-159 °C; R_f = 0.45 (PE : EA = 93 : 7); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.65 (s, 1H), 7.93-7.90 (m, 2H), 7.77 (d, J = 8.0 Hz, 1H), 7.25-7.21 (m, 2H), 6.81 (d, J = 8.0 Hz, 1H), 3.26 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 162.7 ($J_{C\text{-}F}$ = 248 Hz), 142.5, 135.9, 131.2, 123.4 ($J_{C\text{-}F}$ = 8 Hz), 121.5, 117.7, 117.5, 116.7 ($J_{C\text{-}F}$ = 23 Hz), 115.4 ($J_{C\text{-}F}$ = 14 Hz), 82.6, 37.7; Anal. Calcd for $C_{14}H_{10}FIN_2O_3S$: C, 38.91; H, 2.33; N, 6.48%; Found C, 39.13; H, 2.26; N, 6.59%.

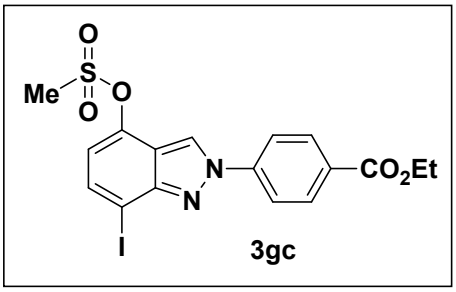


2-(4-Chlorophenyl)-7-iodo-2*H*-indazol-4-yl methanesulfonate (3ec): Brown solid (78 mg, 88%); M.p. 151-152 °C; R_f = 0.4 (PE : EA = 90 : 10); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.68 (s, 1H), 7.91-7.88 (m, 2H), 7.77 (d, J = 8.0 Hz, 1H), 7.53-7.49 (m, 2H), 6.80 (d, J = 8.0 Hz, 1H), 3.26 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 152.0, 142.5, 138.4, 136.0, 134.7, 129.9, 122.6, 121.3, 117.6, 115.6, 82.7, 37.7; Anal. Calcd for $C_{14}H_{10}ClIN_2O_3S$: C, 37.48; H, 2.25; N, 6.24%; Found C, 37.27; H, 2.20; N, 6.36%.

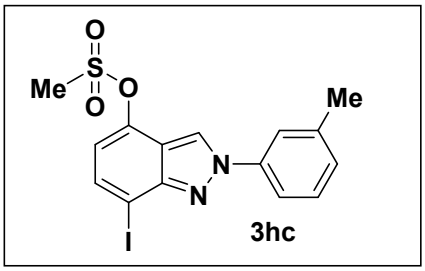


2-(4-Bromophenyl)-7-iodo-2*H*-indazol-4-yl methanesulfonate (3fc): Brown solid (80 mg, 82%); M.p. 161-162 °C; R_f = 0.45 (PE : EA = 92 : 8); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.69

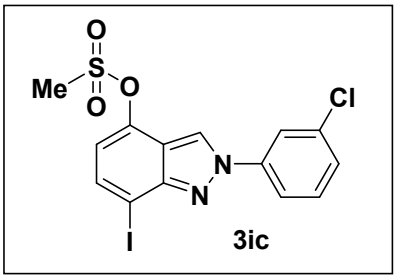
(s, 1H), 7.85-7.82 (m, 2H), 7.77 (d, J = 7.6 Hz, 1H), 7.68-7.65 (m, 2H), 6.81 (d, J = 7.6 Hz, 1H), 3.26 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 152.0, 142.5, 138.9, 136.0, 132.9, 122.8, 122.7, 121.3, 117.6, 115.6, 82.7, 37.7; Anal. Calcd for $C_{14}H_{10}BrIN_2O_3S$: C, 34.10; H, 2.04; N, 5.68%; Found C, 33.83; H, 2.12; N, 5.59%.



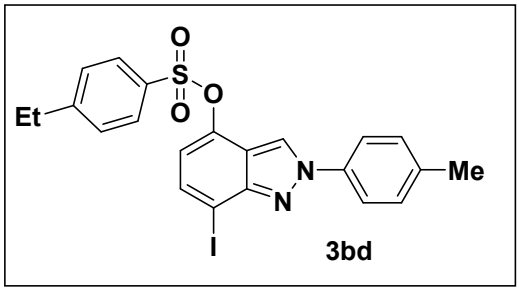
Ethyl 4-(7-iodo-4-((methylsulfonyl)oxy)-2*H*-indazol-2-yl)benzoate (3gc): Brown solid (66 mg, 68%); M.p. 160-161 ^oC; R_f = 0.4 (PE : EA = 88 : 12); ^1H NMR ($CDCl_3$, 400 MHz): δ 8.78 (s, 1H), 8.22 (d, J = 8.8 Hz, 2H), 8.05 (d, J = 8.8 Hz, 2H), 7.79 (d, J = 8.0 Hz, 1H), 6.82 (d, J = 7.6 Hz, 1H), 4.43 (q, J = 7.2 Hz, 2H), 3.27 (s, 3H), 1.43 (t, J = 7.2 Hz, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 165.6, 142.9, 142.5, 136.3, 131.3, 130.7, 121.67, 121.62, 120.9, 117.7, 115.8, 82.8, 61.5, 37.8, 14.4; Anal. Calcd for $C_{17}H_{15}IN_2O_5S$: C, 41.99; H, 3.11; N, 5.76%; Found C, 42.15; H, 3.05; N, 5.64%.



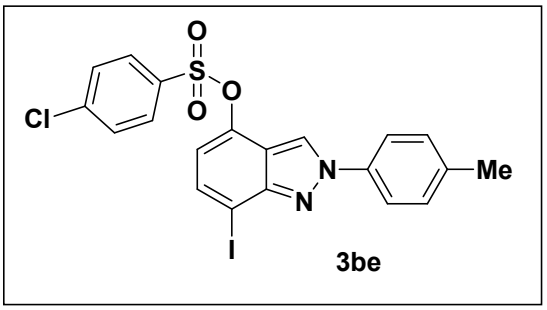
7-Iodo-2-(*m*-tolyl)-2*H*-indazol-4-yl methanesulfonate (3hc): Yellow solid (56 mg, 66%); M.p. 120-121 ^oC; R_f = 0.45 (PE : EA = 92 : 8); ^1H NMR ($CDCl_3$, 400 MHz): δ 8.69 (s, 1H), 7.77-7.75 (m, 2H), 7.71 (d, J = 8.0 Hz, 1H), 7.41 (t, J = 8.0 Hz, 1H), 7.26-7.24 (m, 1H), 6.81 (d, J = 8.0 Hz, 1H), 3.25 (s, 3H), 2.47 (s, 3H), $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): 142.6, 140.0, 139.9, 135.7, 129.7, 129.6, 122.2, 121.6, 121.4, 118.6, 117.3, 115.3, 82.7, 37.7, 21.6; Anal. Calcd for $C_{15}H_{13}IN_2O_3S$: C, 42.07; H, 3.06; N, 6.54%; Found C, 41.85; H, 2.99; N, 6.68%.



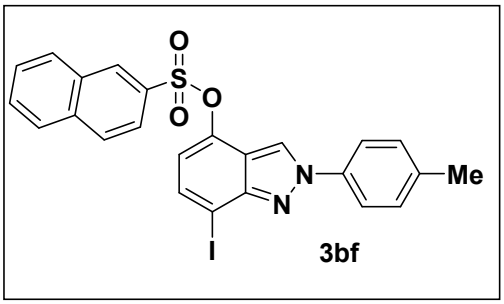
2-(3-Chlorophenyl)-7-iodo-2*H*-indazol-4-yl methanesulfonate (3ic): Brown solid (69 mg, 77%); M.p. 146-147 °C; R_f = 0.45 (PE : EA = 92 : 8); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.70 (s, 1H), 8.00 (t, J = 2.0 Hz, 1H), 7.84-7.81 (m, 1H), 7.78 (d, J = 8.0 Hz, 1H), 7.48 (t, J = 8.0 Hz, 1H), 7.43-7.41 (m, 1H), 6.81 (d, J = 7.6 Hz, 1H), 3.26 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): 152.0, 142.5, 139.0, 136.1, 130.8, 129.0, 127.4, 121.8, 121.5, 119.4, 117.6, 115.7, 82.8, 37.7; HRMS (ESI-TOF) m/z: [M + H]+ Calcd for $[C_{14}H_{11}ClIN_2O_3S]^+$: 448.9218; found: 448.9221.



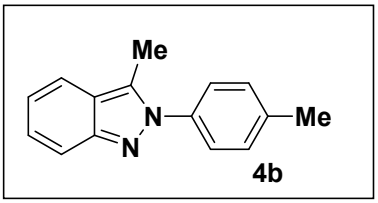
7-Iodo-2-(*p*-tolyl)-2*H*-indazol-4-yl 4-ethylbenzenesulfonate (3bd): Brown gummy mass (86 mg, 83%); R_f = 0.50 (PE : EA = 96 : 4); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.29 (s, 1H), 7.78 (d, J = 8.0 Hz, 2H), 7.71 (d, J = 8.4 Hz, 2H), 7.61 (d, J = 8.0 Hz, 1H), 7.34-7.29 (m, 4H), 6.41 (d, J = 8.0 Hz, 1H), 2.71 (q, J = 7.6 Hz, 2H), 2.42 (s, 3H), 1.22 (t, J = 7.6 Hz, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): 152.0, 151.6, 143.0, 138.9, 137.6, 135.6, 132.4, 130.2, 128.9, 128.8, 121.2, 120.9, 117.5, 116.0, 82.2, 29.0, 21.2, 15.0; Anal. Calcd for $C_{22}H_{19}IN_2O_3S$: C, 50.98; H, 3.69; N, 5.40%; Found C, 51.18; H, 3.76; N, 5.26%.



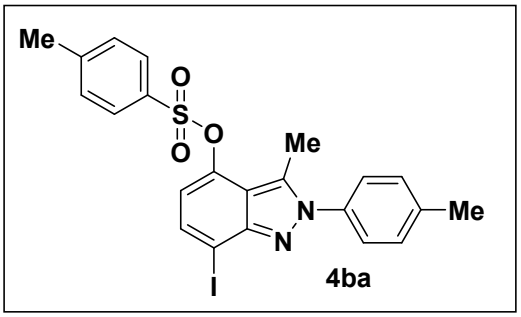
7-Iodo-2-(*p*-tolyl)-2*H*-indazol-4-yl 4-chlorobenzenesulfonate (3be): Brown solid (71 mg, 68%); M.p. 131-132 ^{o}C; R_f = 0.5 (PE : EA = 95 : 5); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.39 (s, 1H), 7.83-7.80 (m, 2H), 7.73 (d, J = 8.8 Hz, 2H), 7.61 (d, J = 8.0 Hz, 1H), 7.53-7.49 (m, 2H), 7.33 (d, J = 8.0 Hz, 2H), 6.35 (d, J = 7.6 Hz, 1H), 2.43 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): 151.7, 142.7, 141.6, 139.1, 137.6, 135.4, 133.5, 131.8, 130.3, 130.2, 129.8, 121.3, 120.9, 115.8, 82.7, 21.2; Anal. Calcd for $C_{20}H_{14}ClIN_2O_3S$: C, 45.78; H, 2.69; N, 5.34%; Found C, 45.57; H, 2.75; N, 5.47%.



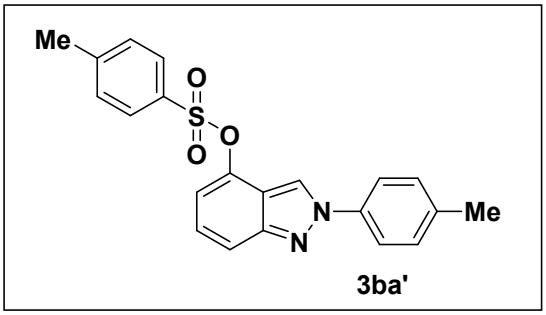
7-Iodo-2-(*p*-tolyl)-2*H*-indazol-4-yl naphthalene-2-sulfonate (3bf): Brown gummy mass (61 mg, 57%); R_f = 0.5 (PE : EA = 95 : 5); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.44 (s, 1H), 8.21 (s, 1H), 7.99 (d, J = 8.8 Hz, 1H), 7.94 (d, J = 8.8 Hz, 2H), 7.89-7.86 (m, 1H), 7.74-7.72 (m, 1H), 7.70-7.62 (m, 1H), 7.57 (d, J = 8.0 Hz, 1H), 7.51 (d, J = 8.4 HZ, 2H), 7.24 (d, J = 8.4 Hz, 2H), 6.34 (d, J = 8.0 HZ, 1H), 2.41(s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): 156.8, 148.9, 142.9, 138.9, 135.6, 135.5, 132.1, 131.9, 130.8, 130.2, 130.0, 129.79, 129.70, 128.2, 128.1, 123.1, 121.2, 120.9, 117.4, 116.1, 82.4, 21.2; Anal. Calcd for $C_{24}H_{17}IN_2O_3S$: C, 53.35; H, 3.17; N, 5.18%; Found C, 53.16; H, 3.22; N, 5.07%.



3-Methyl-2-(*p*-tolyl)-2*H*-indazole (4b): Yellow gummy mass (689 mg, 62%); R_f = 0.6 (PE : EA = 97 : 3); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.72 (d, J = 8.8 Hz, 2H), 7.61 (d, J = 8.4 Hz, 1H), 7.44 (d, J = 8.4 Hz, 2H), 7.33-7.29 (m, 3H), 7.09-7.05 (m, 1H), 2.62 (s, 3H), 2.45 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): 148.5, 138.7, 137.5, 131.9, 129.8, 126.7, 125.5, 121.6, 120.8, 120.0, 117.5, 21.2, 11.1; Anal. Calcd for $C_{15}H_{14}N_2$: C, 81.05; H, 6.35; N, 12.60%; Found C, 81.27; H, 6.43; N, 12.46%.

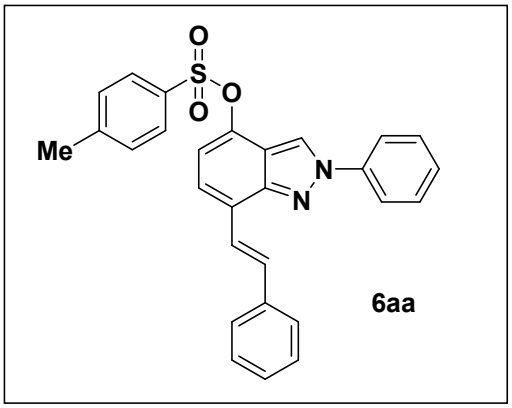


7-Iodo-3-methyl-2-(*p*-tolyl)-2*H*-indazol-4-yl 4-methylbenzenesulfonate (4ba): Black gummy mass (66 mg, 64%); R_f = 0.55 (PE : EA = 96 : 4); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.79 (d, J = 8.4 Hz, 2H), 7.55 (d, J = 8.0 Hz, 1H), 7.39-7.31 (m, 6H), 6.21 (d, J = 7.6 Hz, 1H), 2.63 (s, 3H), 2.47 (s, 3H), 2.44 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): 151.7, 150.8, 146.9, 145.9, 144.3, 139.6, 136.6, 135.2, 132.6, 130.0, 129.9, 128.8, 126.2, 114.1, 82.1, 21.9, 21.3, 12.9; Anal. Calcd for $C_{22}H_{19}IN_2O_3S$: C, 50.98; H, 3.69; N, 5.40%; Found C, 50.78; H, 3.62; N, 5.52%.

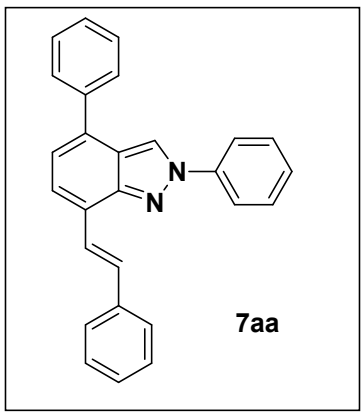


2-(p-tolyl)-2*H*-indazol-4-yl 4-methylbenzenesulfonate (3ba'): Yellow gummy mass (59 mg, 78%); R_f = 0.45 (PE : EA = 95 : 5); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.18 (s, 1H), 7.76 (d,

J = 8.4 Hz, 2H), 7.69 (d, *J* = 8.4 Hz, 2H), 7.65 (d, *J* = 8.8 Hz, 1H), 7.32-7.29 (m, 4H), 7.16-7.12 (m, 1H), 6.59 (d, *J* = 7.2 Hz, 1H), 2.429 (s, 3H), 2.424 (s, 3H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz): 151.2, 145.7, 142.1, 138.6, 137.9, 132.5, 130.2, 129.9, 128.8, 126.3, 121.0, 119.3, 118.4, 117.2, 114.6, 21.8, 21.2; Anal. Calcd for $C_{21}H_{18}N_2O_3S$: C, 66.65; H, 4.79; N, 7.40%; Found C, 66.82; H, 4.87; N, 7.26%.

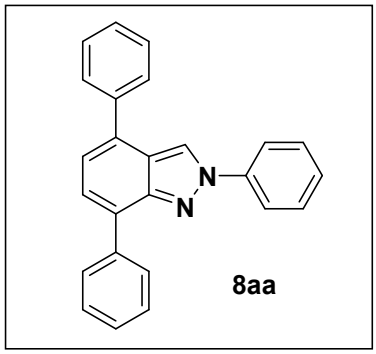


(*E*)-2-Phenyl-7-styryl-2*H*-indazol-4-yl 4-methylbenzenesulfonate (6aa): Yellow gummy mass (92 mg, 79%); R_f = 0.7 (PE : EA = 97 : 3); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.24 (s, 1H), 8.11 (d, *J* = 16.4 Hz, 1H), 7.91-7.89 (m, 2H), 7.78 (d, *J* = 8.4 Hz, 2H), 7.62 (d, J = 7.2 Hz, 2H), 7.58-7.47 (m, 2H), 7.46-7.36 (m, 4H), 7.32-7.27 (m, 3H), 7.21 (d, *J* = 8.0 Hz, 1H), 6.62 (d, *J* = 8.0 Hz, 1H), 2.42 (s, 3H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz): 149.0, 145.7, 141.2, 140.2, 138.0, 133.1, 132.4, 129.9, 129.7, 128.8, 128.7, 128.4, 127.8, 127.2, 126.9, 125.5, 125.1, 121.0, 119.4, 119.1, 115.2, 21.8; Anal. Calcd for $C_{28}H_{22}N_2O_3S$: C, 72.08; H, 4.75; N, 6.00%; Found C, 72.30; H, 4.67; N, 6.12%.

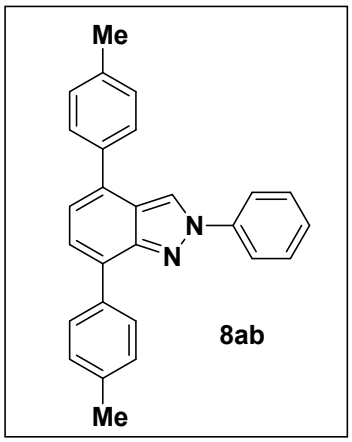


(*E*)-2,4-Diphenyl-7-styryl-2*H*-indazole (7aa): Yellow solid (26 mg, 70%); M.p. 90–91 °C; R_f = 0.8 (PE : EA = 98 : 2); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.61 (s, 1H), 8.26 (d, *J* = 16.0 Hz, 1H), 8.02-8.00 (m, 2H), 7.74-7.72 (m, 2H), 7.68 (d, *J* = 7.6 Hz, 2H), 7.60-7.48 (m, 6H), 7.44-

7.38 (m, 4H), 7.28 (d, J = 7.6 Hz, 1H), 7.21 (d, J = 7.2 Hz, 1H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): 140.6, 140.3, 138.4, 134.0, 132.4, 129.7, 129.0, 128.7, 128.2, 128.0, 127.8, 127.5, 126.9, 126.8, 126.6, 126.0, 123.1, 122.0, 121.08, 121.02, 120.8; Anal. Calcd for $C_{27}H_{20}N_2$: C, 87.07; H, 5.41; N, 7.52%; Found C, 86.86; H, 5.48; N, 7.39%.

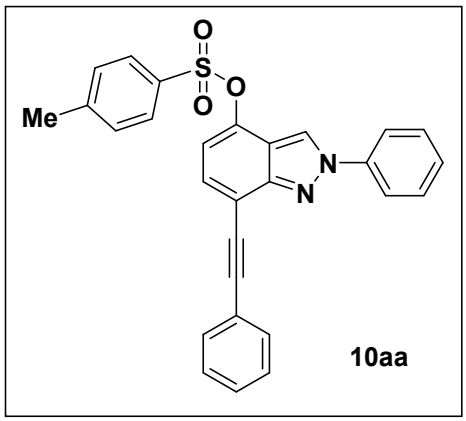


2,4,7-triphenyl-2*H*-indazole (8aa): White solid (42 mg, 62%); M.p. 82–83 °C; R_f = 0.85 (PE : EA = 98.5 : 1.5); ^1H NMR ($CDCl_3$, 400 MHz): δ 8.63 (s, 1H), 8.19-8.17 (m, 2H), 7.98-7.95 (m, 2H), 7.77-7.75 (m, 2H), 7.59-7.50 (m, 7H), 7.44-7.39 (m, 3H), 7.29 (d, J = 7.2 Hz, 1H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): 148.5, 140.6, 140.3, 138.2, 134.0, 130.0, 129.6, 129.1, 129.0, 128.5, 128.2, 128.0, 127.8, 127.7, 125.9, 123.3, 122.0, 121.1, 120.7; Anal. Calcd for $C_{25}H_{18}N_2$: C, 86.68; H, 5.24; N, 8.09%; Found C, 86.49; H, 5.19; N, 8.23%.

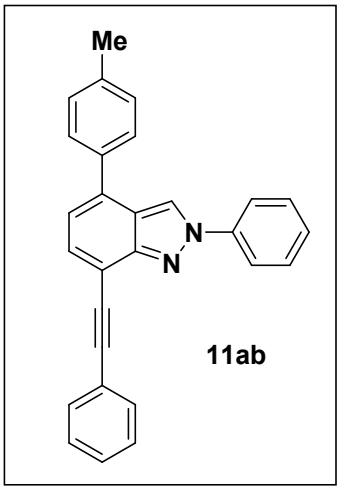


2-Phenyl-4,7-di-*p*-tolyl-2*H*-indazole (8ab): White solid (50 mg, 68%); M.p. 157–158 °C; R_f = 0.80 (PE : EA = 98 : 2); ^1H NMR ($CDCl_3$, 400 MHz): δ 8.61 (s, 1H), 8.06 (d, J = 8.0 Hz, 2H), 7.95 (d, J = 7.6 Hz, 2H), 7.65 (d, J = 8.0 Hz, 2H), 7.55-7.49 (m, 3H), 7.40-7.33 (m, 5H), 7.25 (d, J = 7.2 Hz, 1H), 2.45 (s, 3H), 2.44 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): 148.6, 142.0, 140.7, 137.6, 137.5, 137.4, 135.3, 133.6, 129.7, 129.6, 129.3, 128.9, 128.0, 127.9,

125.5, 123.3, 121.8, 121.0, 120.7, 21.46, 21.42; Anal. Calcd for $C_{27}H_{22}N_2$: C, 86.60; H, 5.92; N, 7.48%; Found C, 86.97; H, 5.84; N, 7.61%.



2-Phenyl-7-(phenylethynyl)-2*H*-indazol-4-yl 4-methylbenzenesulfonate (10aa): Brown gummy mass (77 mg, 83%); R_f = 0.5 (PE : EA = 96 : 4); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.25 (s, 1H), 7.88 (d, J = 7.6 Hz, 2H), 7.65-7.63 (m, 2H), 7.53 (t, J = 8.0 Hz, 2H), 7.44-7.35 (m, 5H), 7.29 (d, J = 8.0 Hz, 2H), 6.63 (d, J = 7.6 Hz, 1H), 2.40 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): 150.7, 145.9, 142.2, 140.0, 132.0, 131.9, 130.7, 129.9, 129.7, 128.8, 128.67, 128.63, 128.4, 123.2, 121.2, 120.2, 118.3, 114.9, 112.5, 95.0, 85.3, 21.8; Anal. Calcd for $C_{28}H_{20}N_2O_3S$: C, 72.40; H, 4.34; N, 6.03%; Found C, 72.61; H 4.27; N, 6.16%.



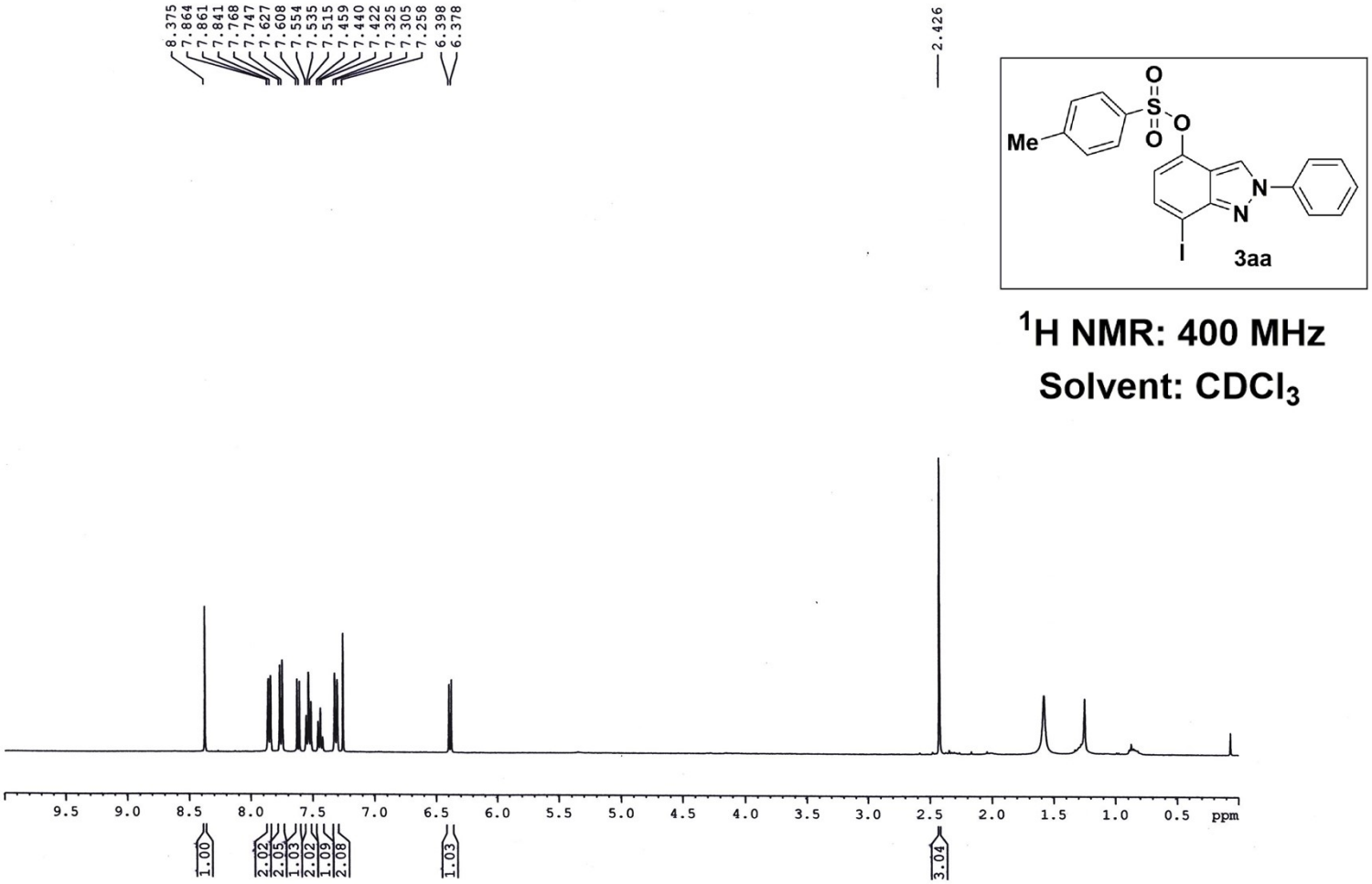
2-Phenyl-7-(phenylethynyl)-4-(*p*-tolyl)-2*H*-indazole (11ab): White Solid (24 mg, 64%); M.p. 120–121 ^{o}C; R_f = 0.8 (PE : EA = 98 : 2); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.60 (s, 1H), 8.00-7.98 (m, 2H), 7.70-7.68 (m, 2H), 7.65-7.62 (m, 3H), 7.55-7.51 (m, 2H), 7.42-7.32 (m, 6H), 7.18 (d, J = 7.2 Hz, 1H), 2.45 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): 150.1, 140.5,

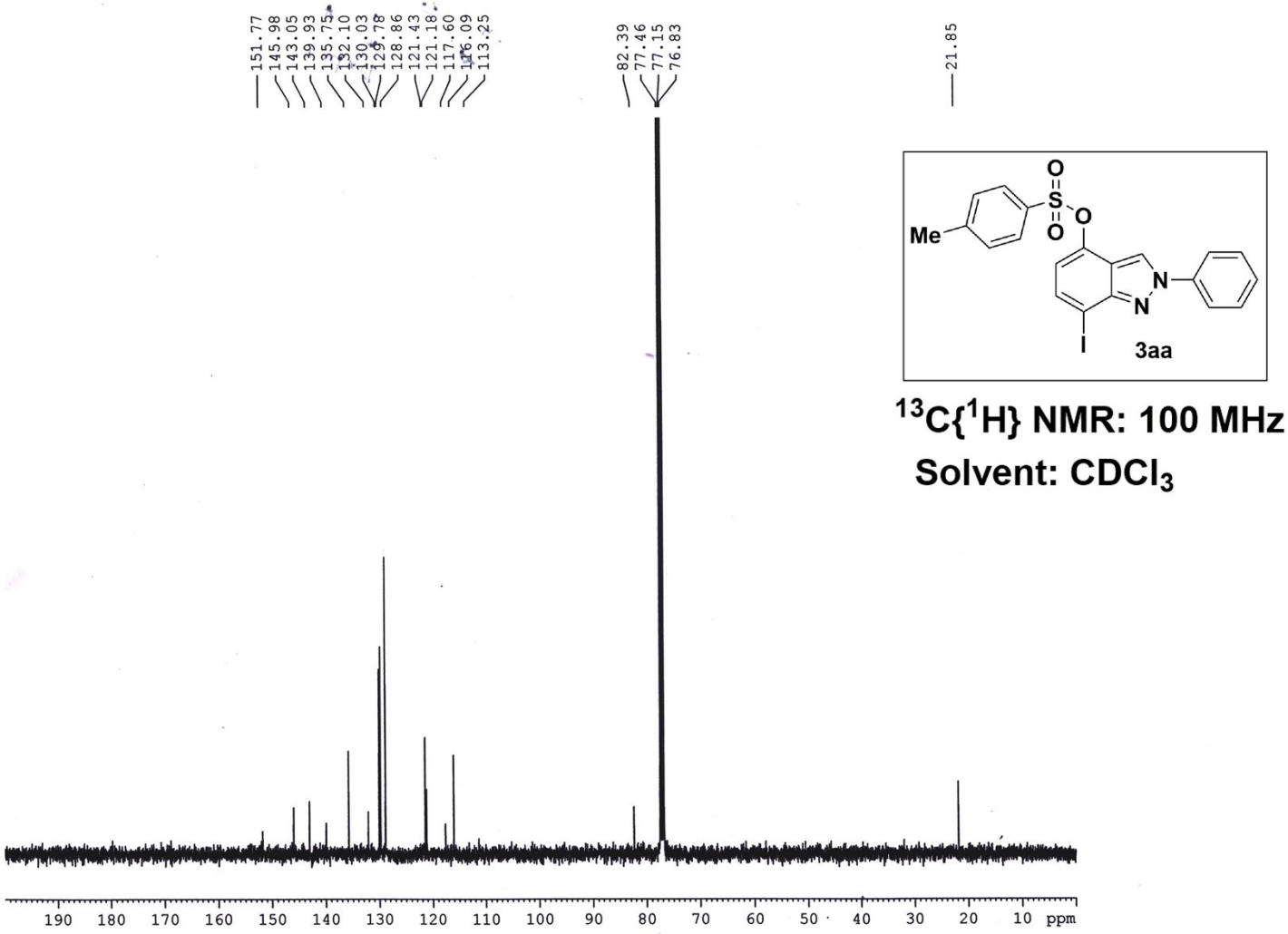
138.1, 137.1, 135.5, 132.0, 131.7, 129.8, 129.6, 128.3, 128.2, 128.0, 126.9, 123.8, 122.3, 121.6, 121.3, 121.2, 111.7, 94.6, 86.6, 21.4; Anal. Calcd for $C_{28}H_{20}N_2$: C, 87.47; H, 5.24; N, 7.29%; Found C, 87.25; H, 5.32; N, 7.17%.

10. References:

1. (a) M. R. Kumar, A. Park, N. Park and S. Lee, *Org. Lett*., 2011, **13**, 3542-3545; (b) P. Ghosh, S. Mondal and A. Hajra, *J. Org. Chem.,* 2018, **83**, 13618-13623.
2. M. S. Yusubov and T. Wirth, *Org. Lett.,* 2005, **7**, 519-521.

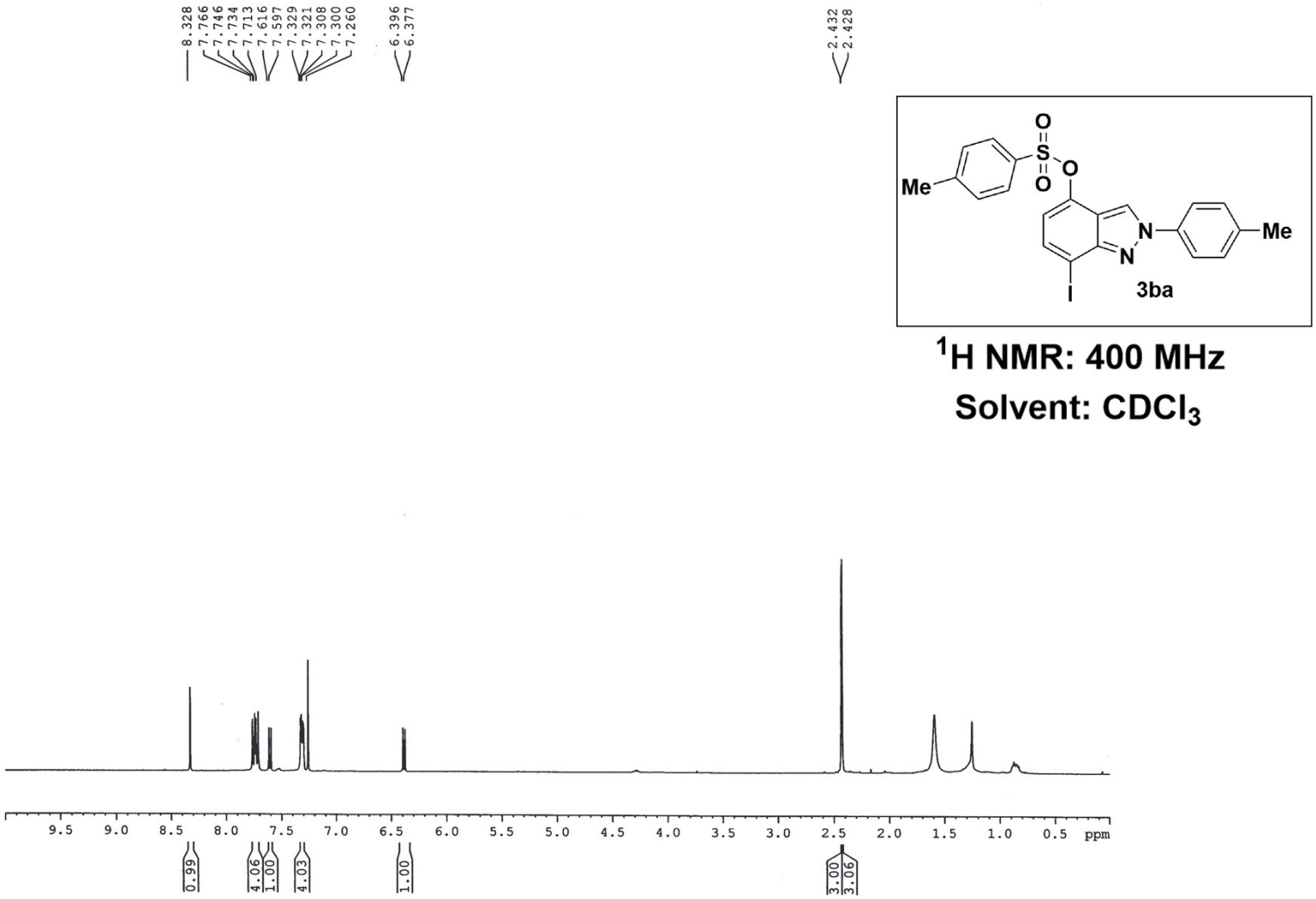
11. NMR spectra [^{1}H, and ^{13}C{^{1}H}] of synthesized products


8.375
7.864
7.861
7.841
7.768
7.747
7.627
7.608
7.554
7.535
7.515
7.459
7.440
7.422
7.325
7.305
7.258
6.398
6.378
2.426
Me
O
S
O
O
O
N
N
I
3aa
1H NMR: 400 MHz
Solvent: CDCl3
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.00
2.02
2.05
1.03
2.02
1.09
2.08
1.03
3.04



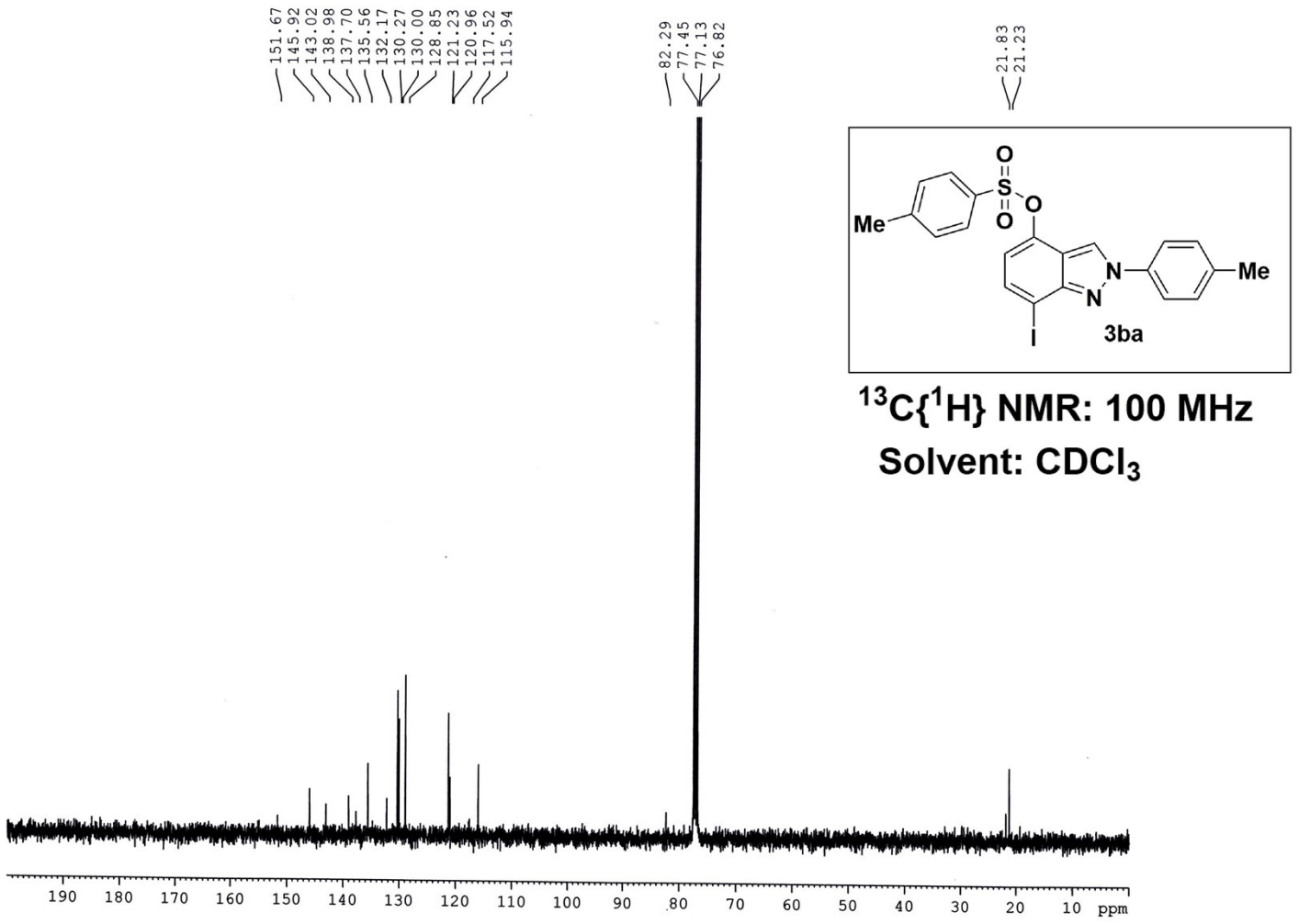
$^{13}C\{^{1}H\}$ NMR: 100 MHz

Solvent: $CDCl_3$



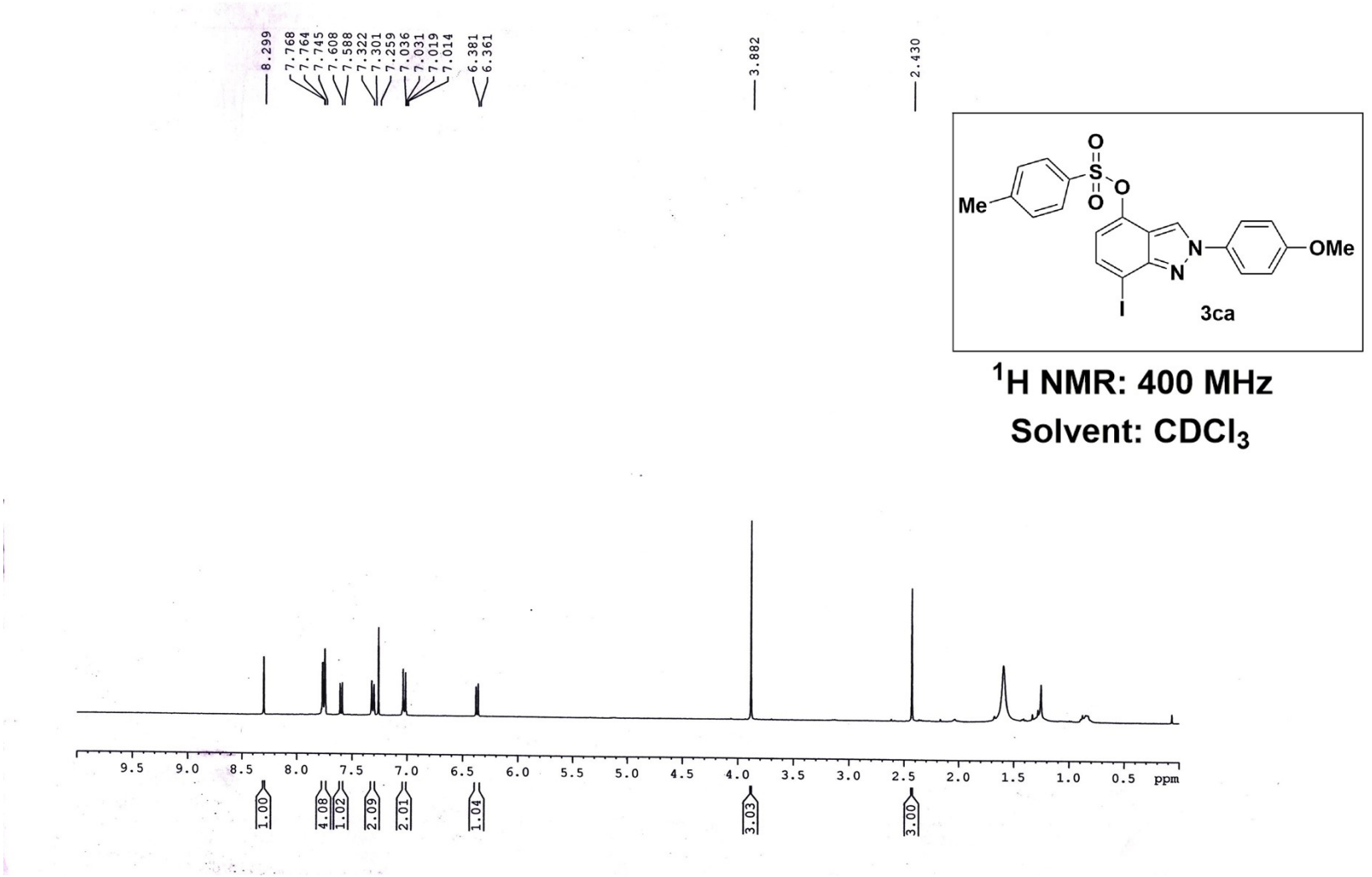
^{1}H NMR: 400 MHz

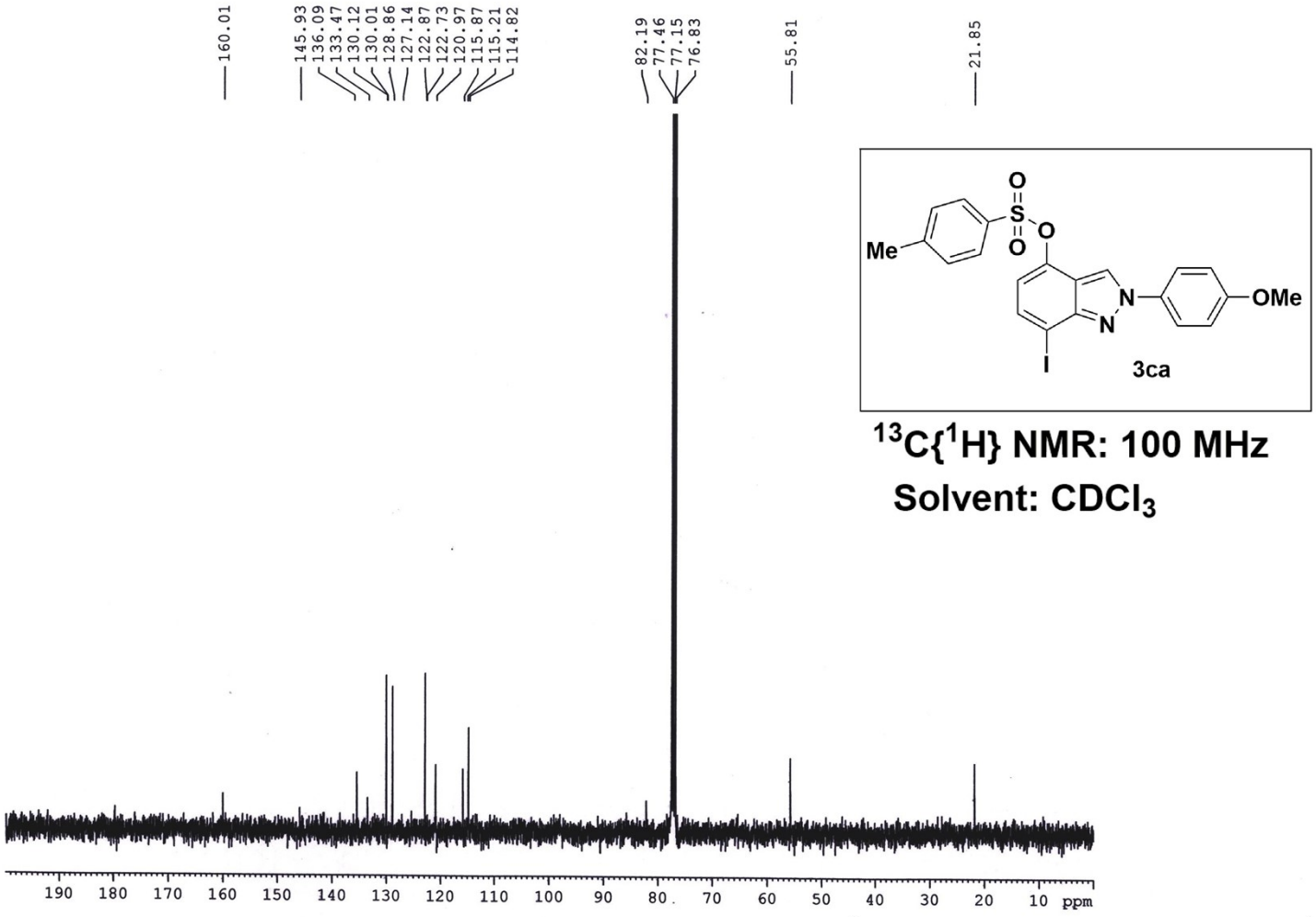
Solvent: $CDCl_3$



$^{13}C\{^{1}H\}$ NMR: 100 MHz

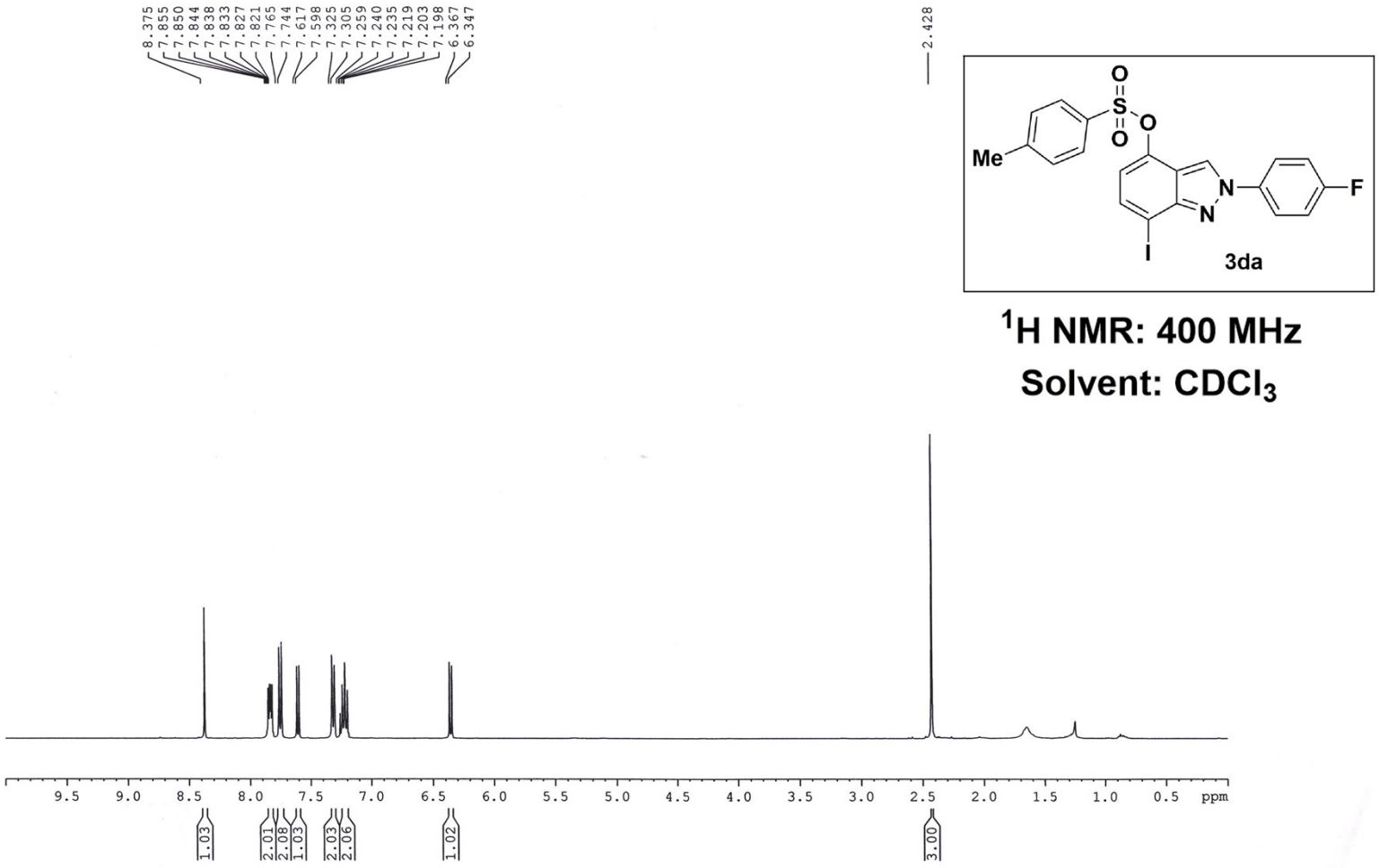
Solvent: $CDCl_3$

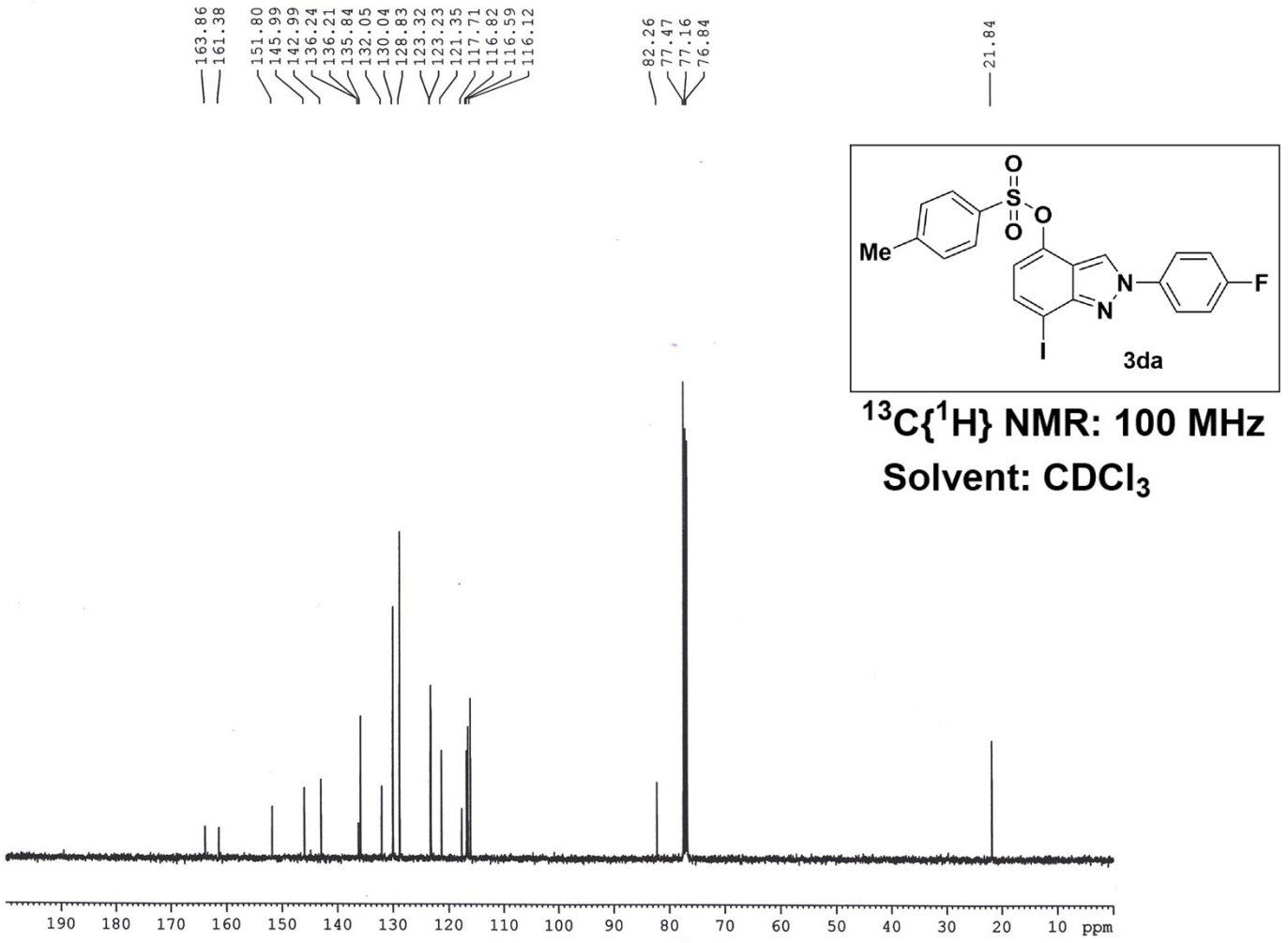

8.299
7.768
7.764
7.745
7.608
7.588
7.322
7.301
7.259
7.036
7.031
7.019
7.014
6.381
6.361
3.882
2.430
Me
O
S
O
O
N
N
OMe
I
3ca
1H NMR: 400 MHz
Solvent: CDCl3
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.00
4.08
1.02
2.09
2.01
1.04
3.03
3.00

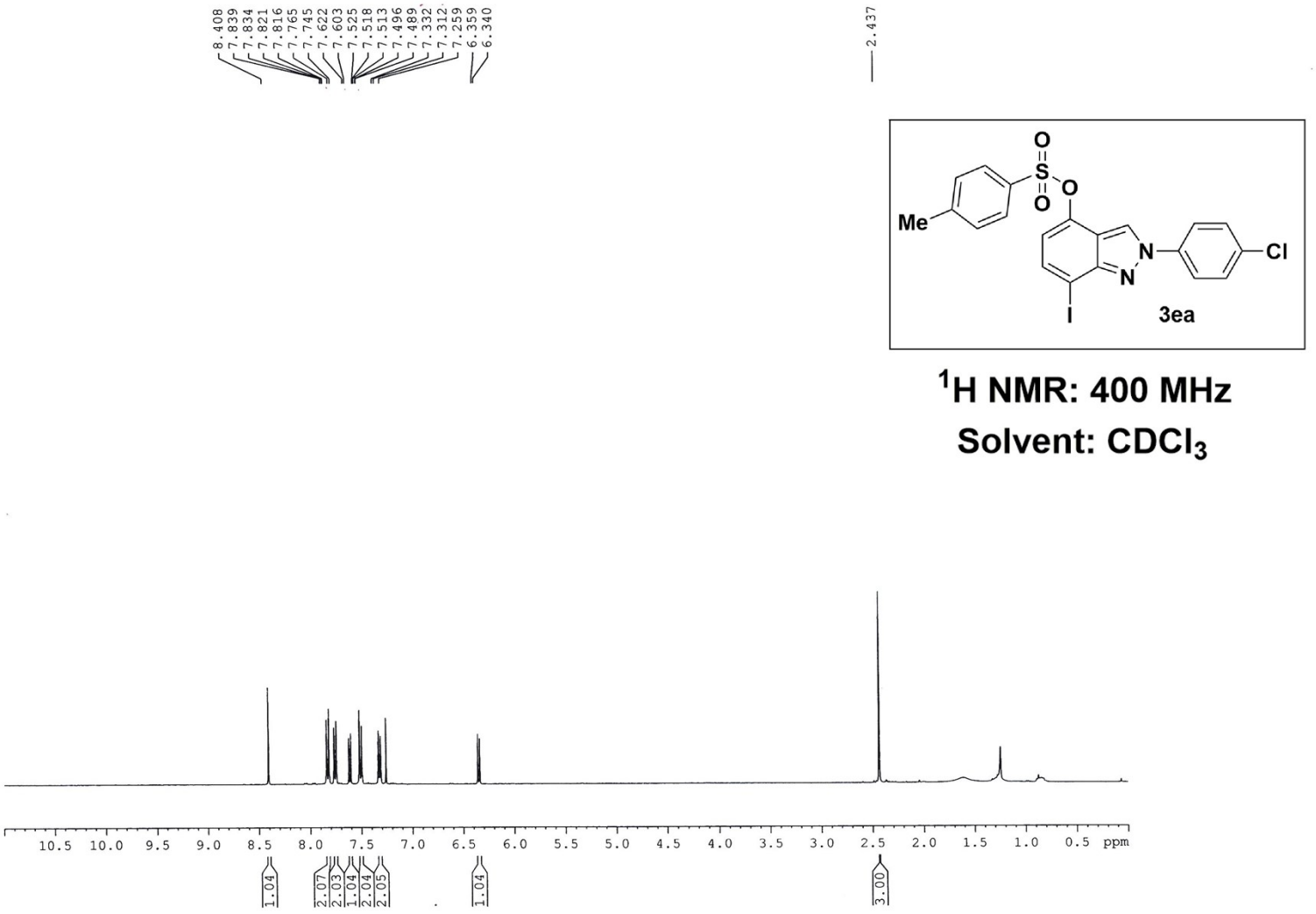


$^{13}C\{^{1}H\}$ NMR: 100 MHz

Solvent: $CDCl_3$

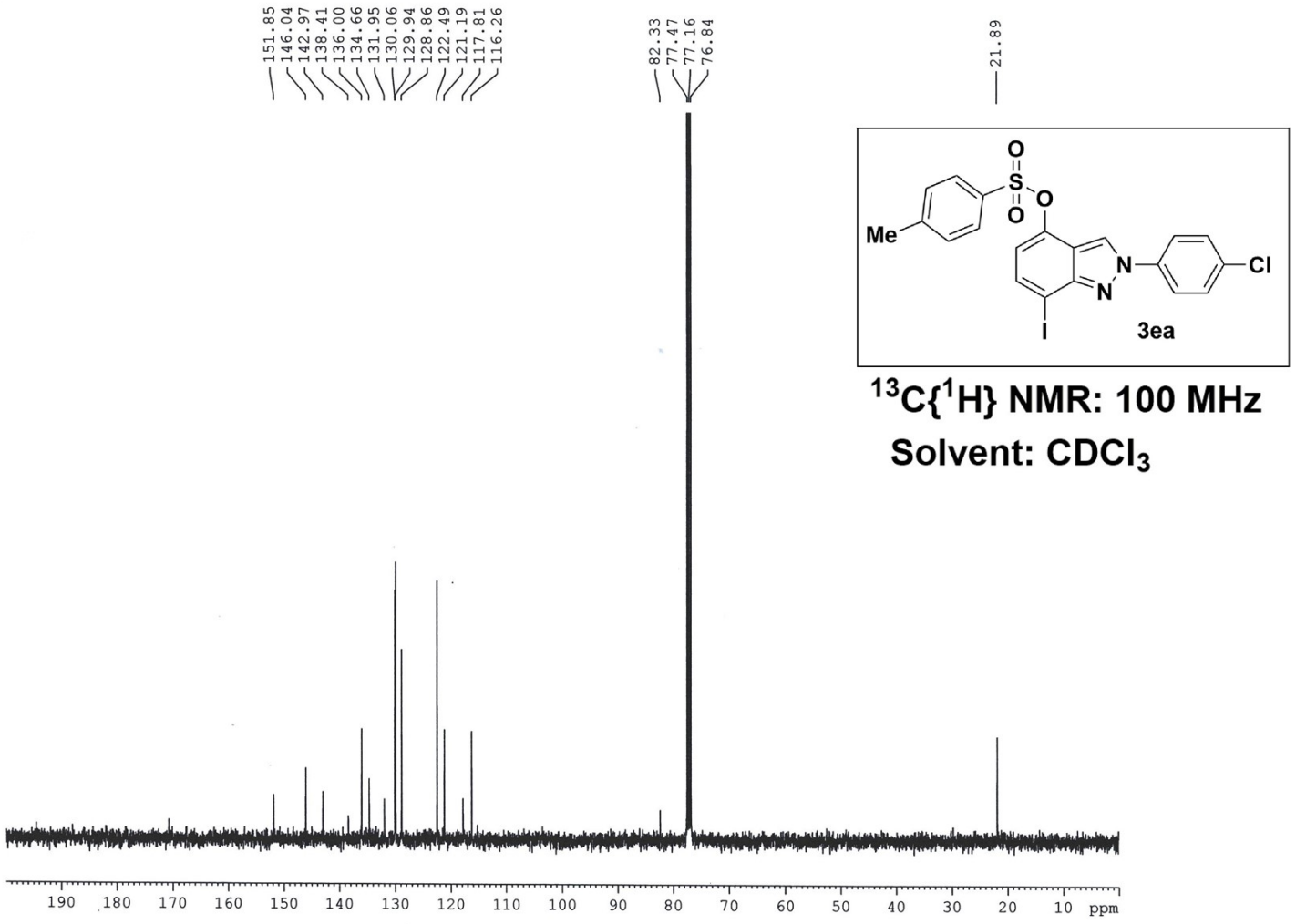

8.375
7.855
7.850
7.844
7.838
7.833
7.827
7.821
7.765
7.744
7.617
7.598
7.325
7.305
7.259
7.240
7.235
7.219
7.203
7.198
6.367
6.347
2.428
Me
F
I
3da
1H NMR: 400 MHz
Solvent: CDCl3
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.03
2.01
2.08
1.03
2.03
2.06
1.02
3.00


163.86
161.38
151.80
145.99
142.99
136.24
136.21
135.84
132.05
130.04
128.83
123.32
123.23
121.35
117.71
116.82
116.59
116.12
82.26
77.47
77.16
76.84
21.84
Me
O
S
O
O
O
N
N
F
I
3da
13C{1H} NMR: 100 MHz
Solvent: CDCl3
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm



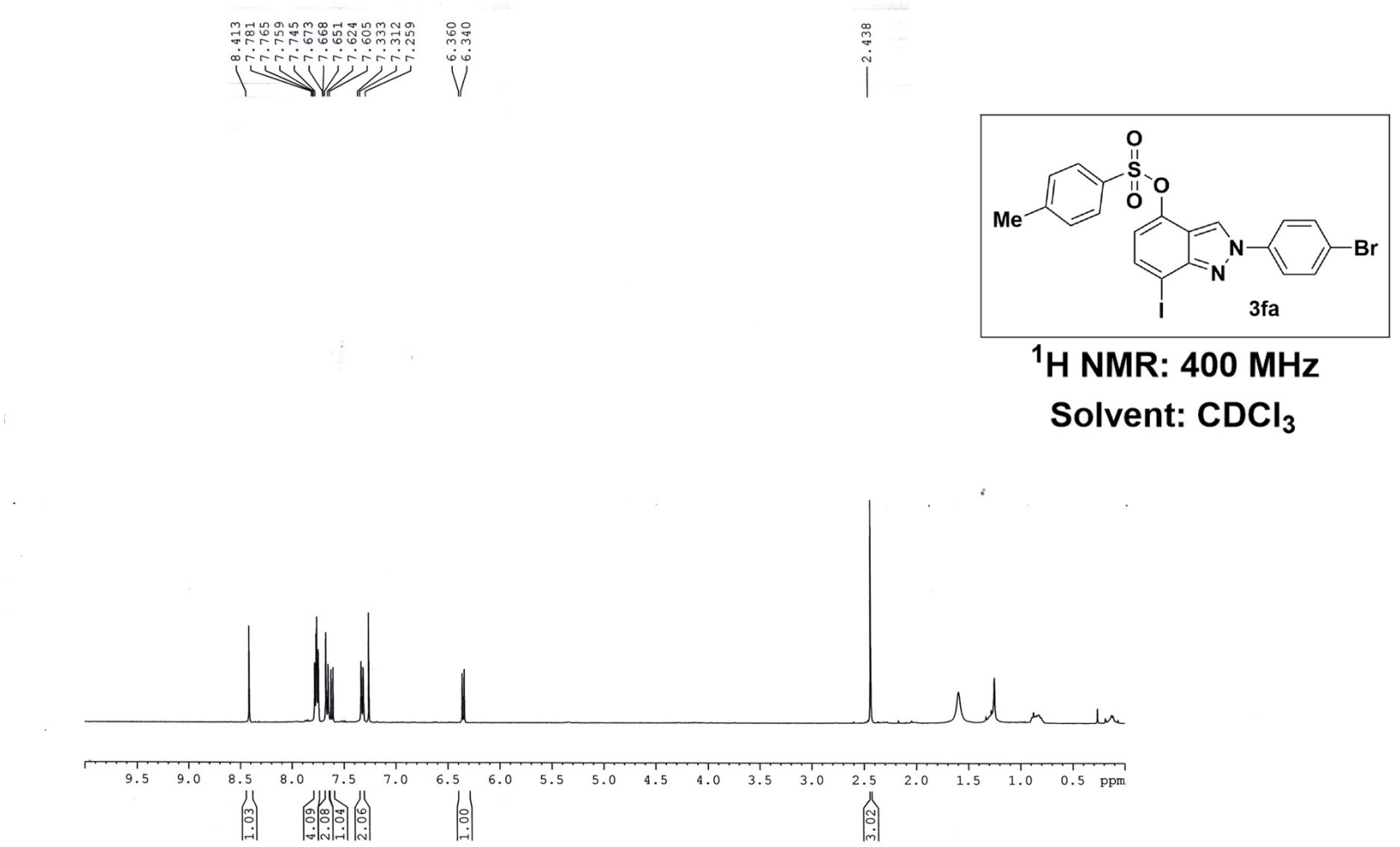
^{1}H NMR: 400 MHz

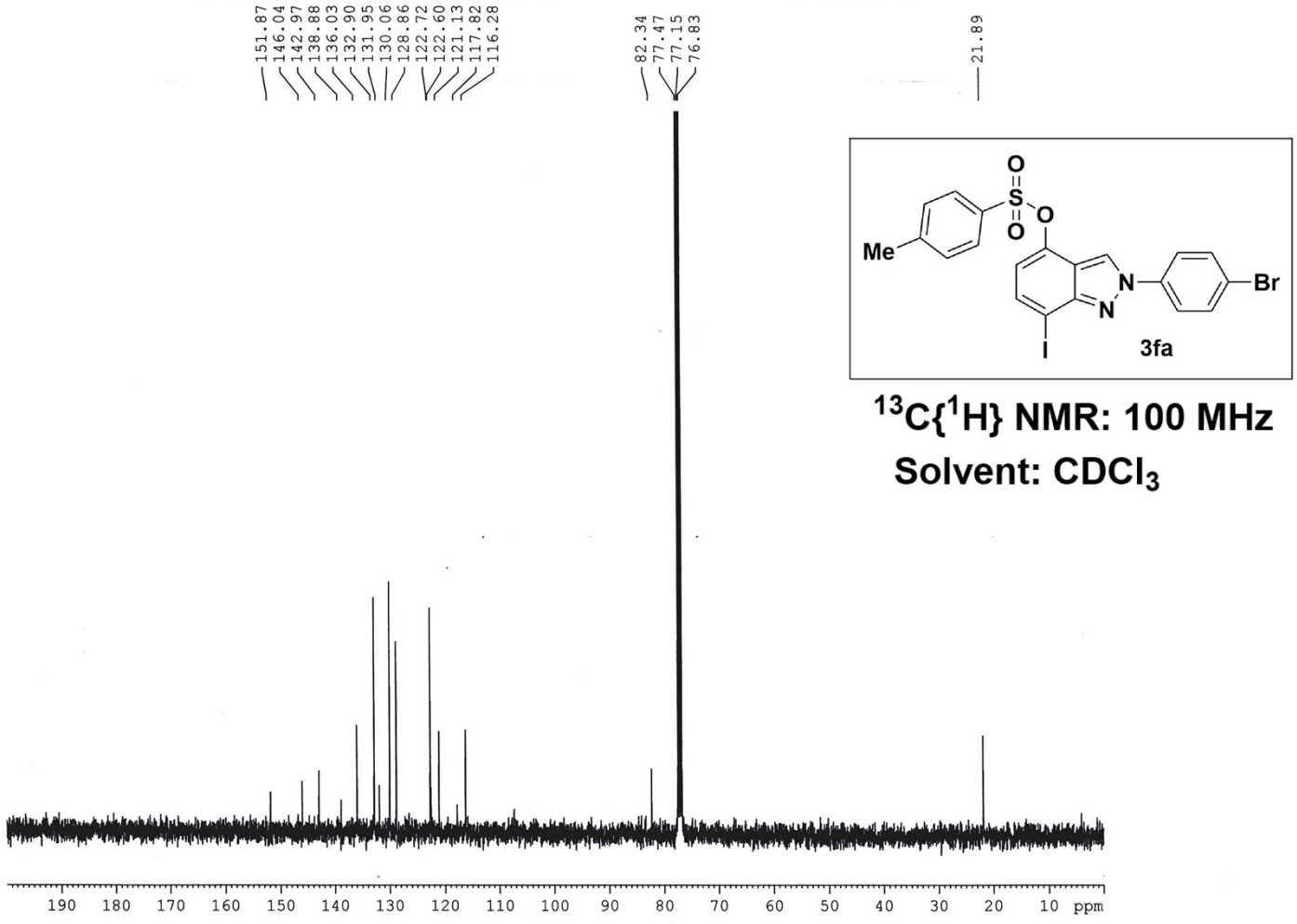
Solvent: $CDCl_3$

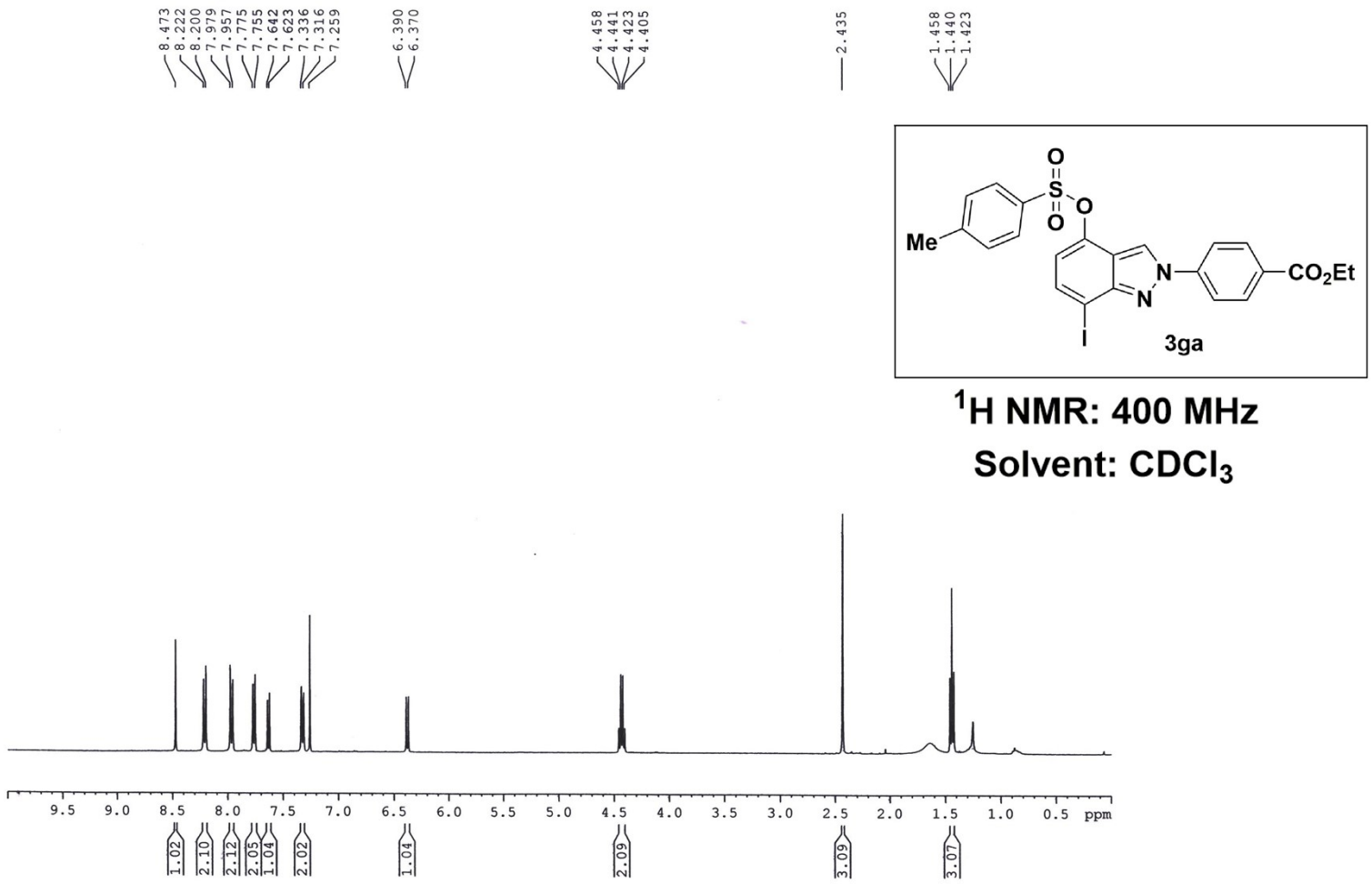


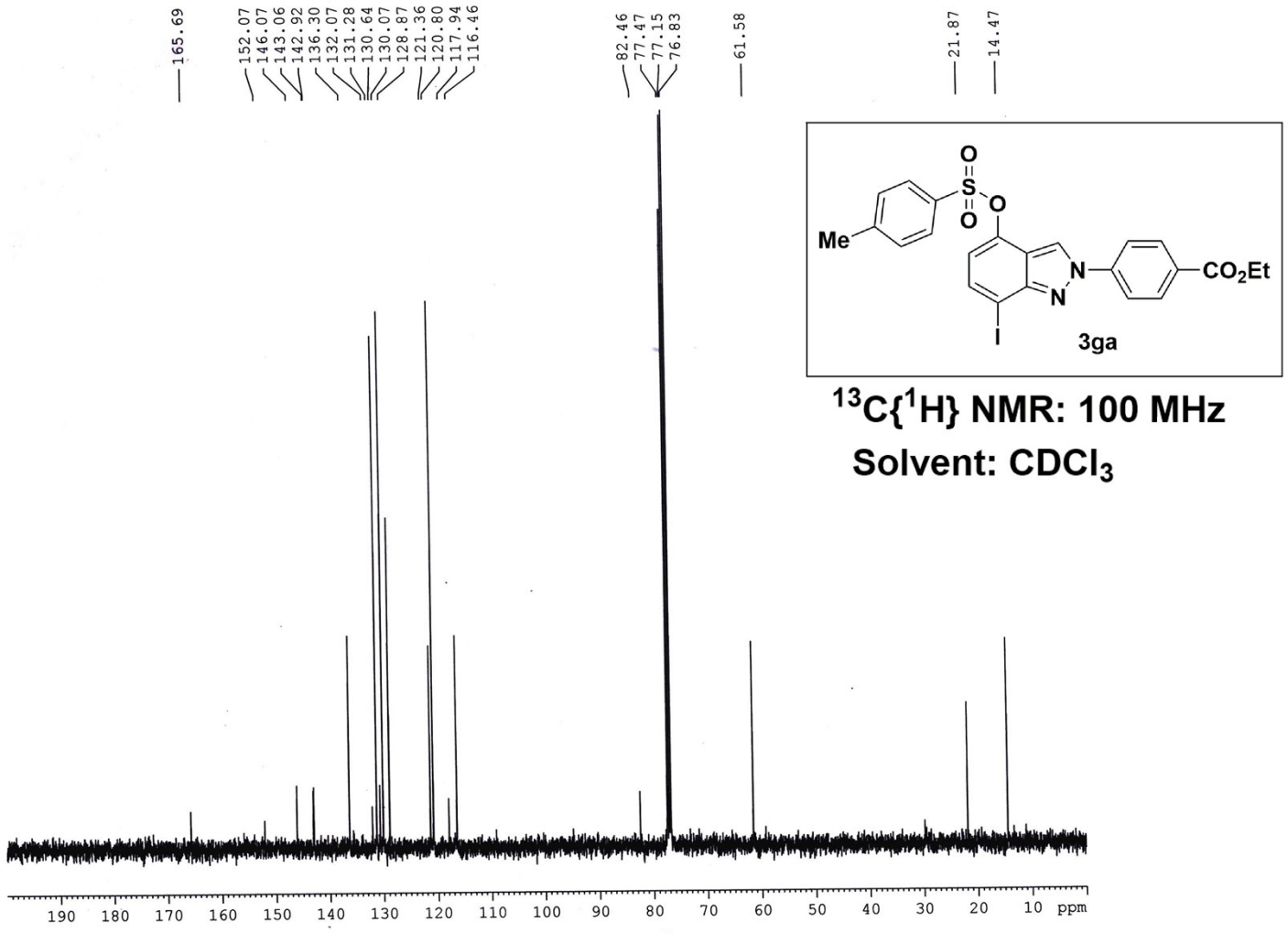
$^{13}C\{^{1}H\}$ NMR: 100 MHz

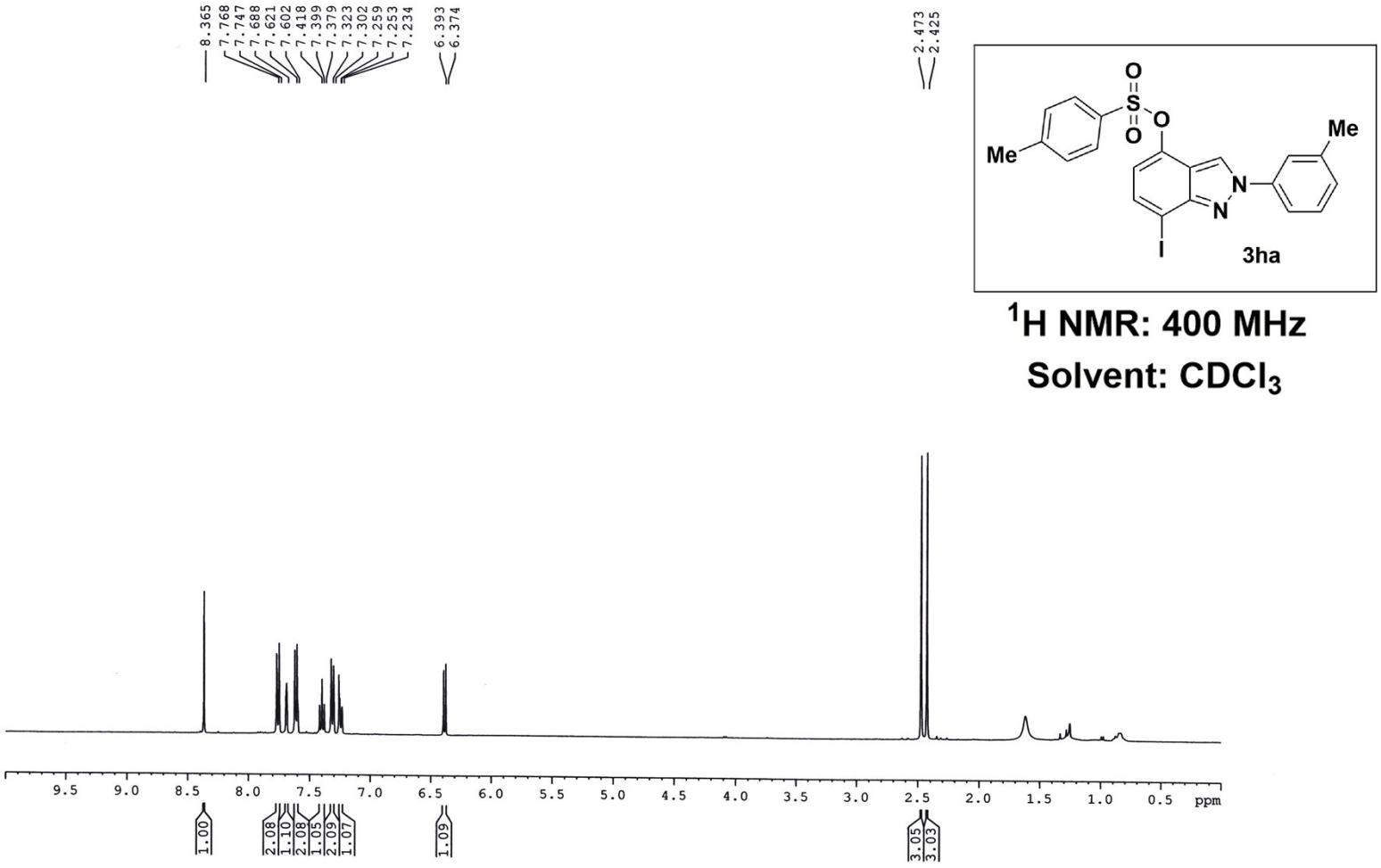
Solvent: $CDCl_3$

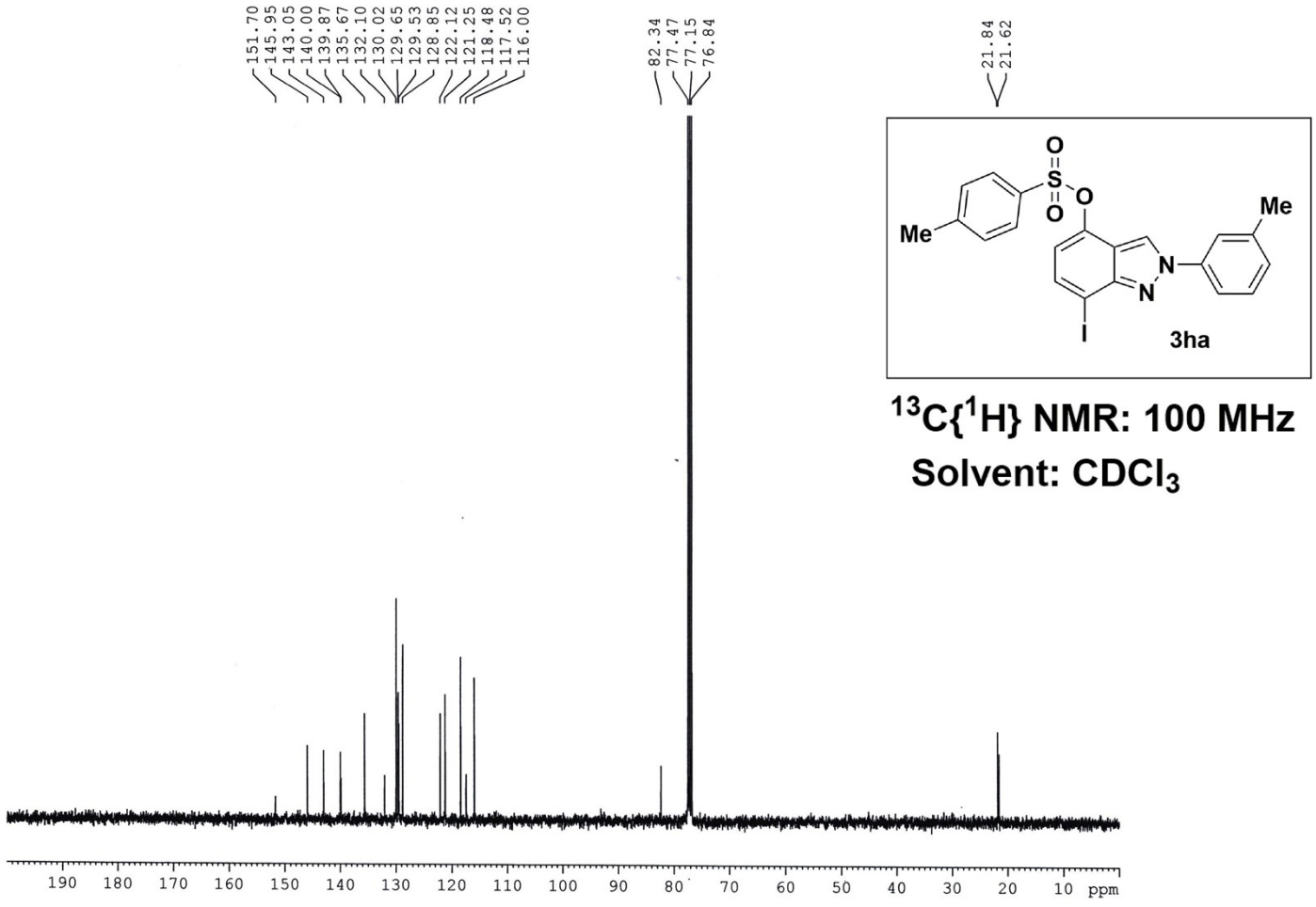

8.413
7.781
7.765
7.759
7.745
7.673
7.668
7.651
7.624
7.605
7.333
7.312
7.259
6.360
6.340
2.438
Me
Br
I
3fa
1H NMR: 400 MHz
Solvent: CDCl3
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.03
4.09
2.08
1.04
2.06
1.00
3.02

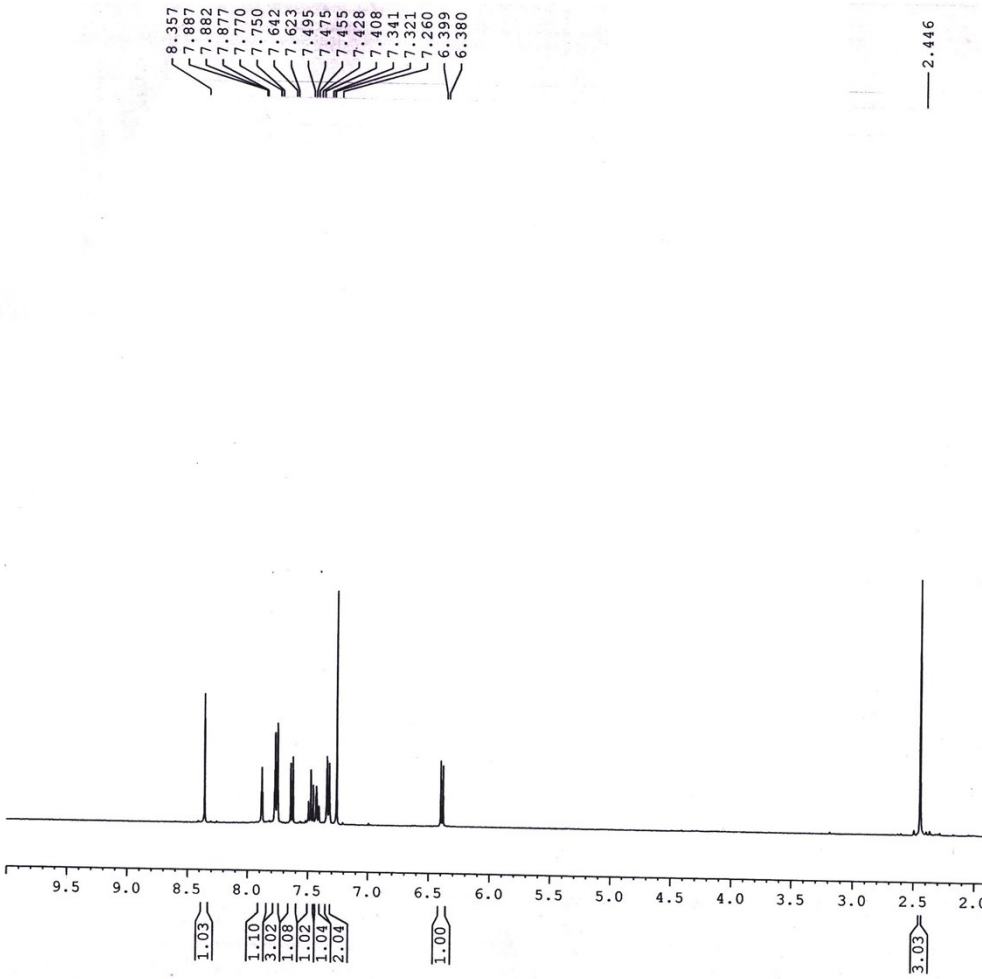

151.87
146.04
142.97
138.88
136.03
132.90
131.95
130.06
128.86
122.72
122.60
121.13
117.82
116.28
82.34
77.47
77.15
76.83
21.89
Me
Br
I
3fa
$^{13}C\{^{1}H\}$ NMR: 100 MHz
Solvent: $CDCl_3$
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

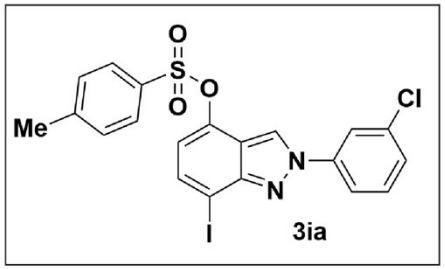

8.473
8.222
8.200
7.979
7.957
7.775
7.755
7.642
7.623
7.336
7.316
7.259
6.390
6.370
4.458
4.441
4.423
4.405
2.435
1.458
1.440
1.423
Me
CO2Et
I
3ga
1H NMR: 400 MHz
Solvent: CDCl3
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.02
2.10
2.12
2.05
1.04
2.02
1.04
2.09
3.09
3.07


165.69
152.07
146.07
143.06
142.92
136.30
132.07
131.28
130.64
130.07
128.87
121.36
120.80
117.94
116.46
82.46
77.47
77.15
76.83
61.58
21.87
14.47
Me
CO2Et
3ga
13C{1H} NMR: 100 MHz
Solvent: CDCl3
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


8.365
7.768
7.747
7.688
7.621
7.602
7.418
7.399
7.379
7.323
7.302
7.259
7.253
7.234
6.393
6.374
2.473
2.425
Me
Me
3ha
1H NMR: 400 MHz
Solvent: CDCl3
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.00
2.08
1.10
2.08
1.05
2.09
1.07
1.09
3.05
3.03

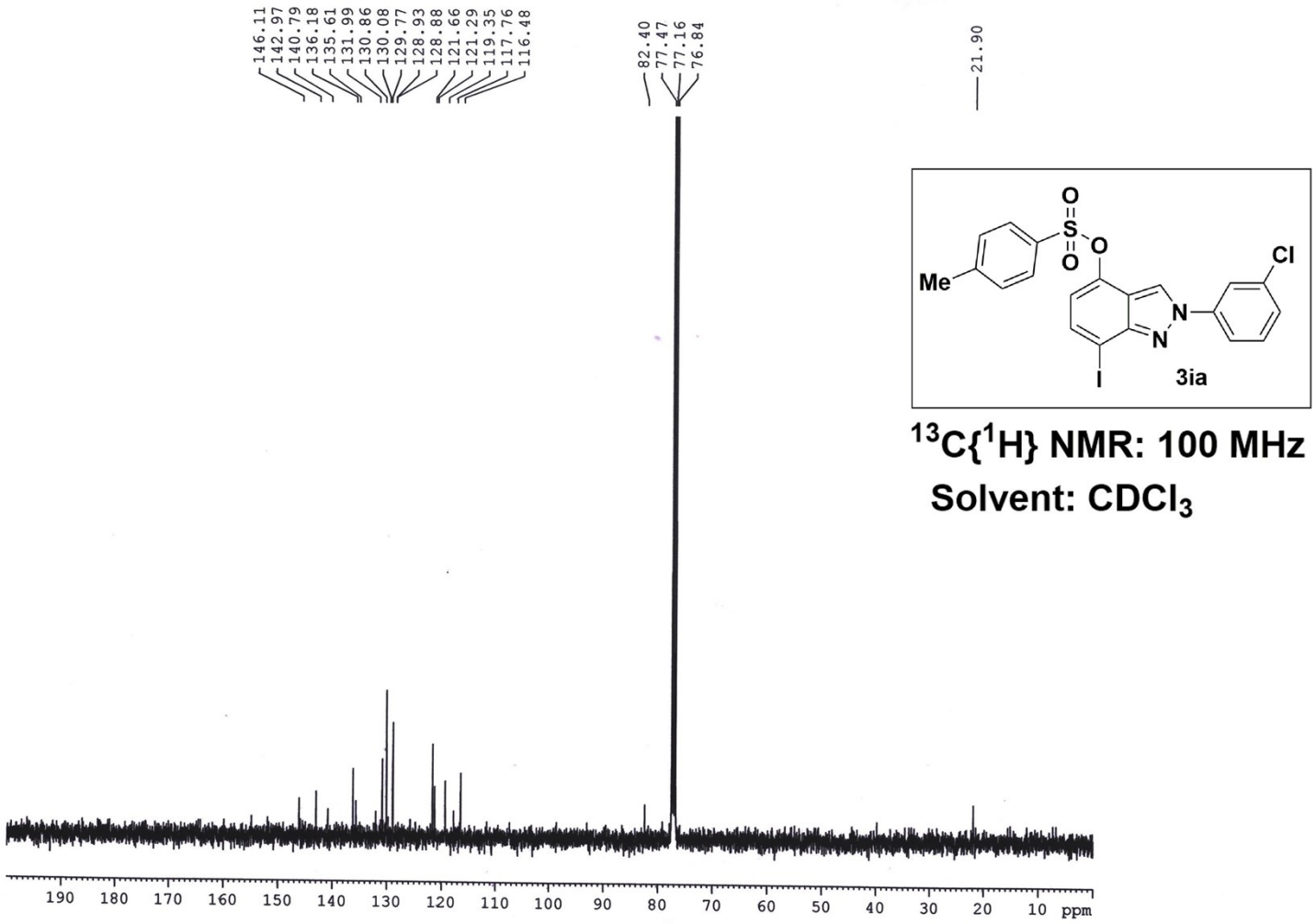

151.70
145.95
143.05
140.00
139.87
135.67
132.10
130.02
129.65
129.53
128.85
122.12
121.25
118.48
117.52
116.00
82.34
77.47
77.15
76.84
21.84
21.62
Me
Me
N
N
I
3ha
13C{1H} NMR: 100 MHz
Solvent: CDCl3
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm





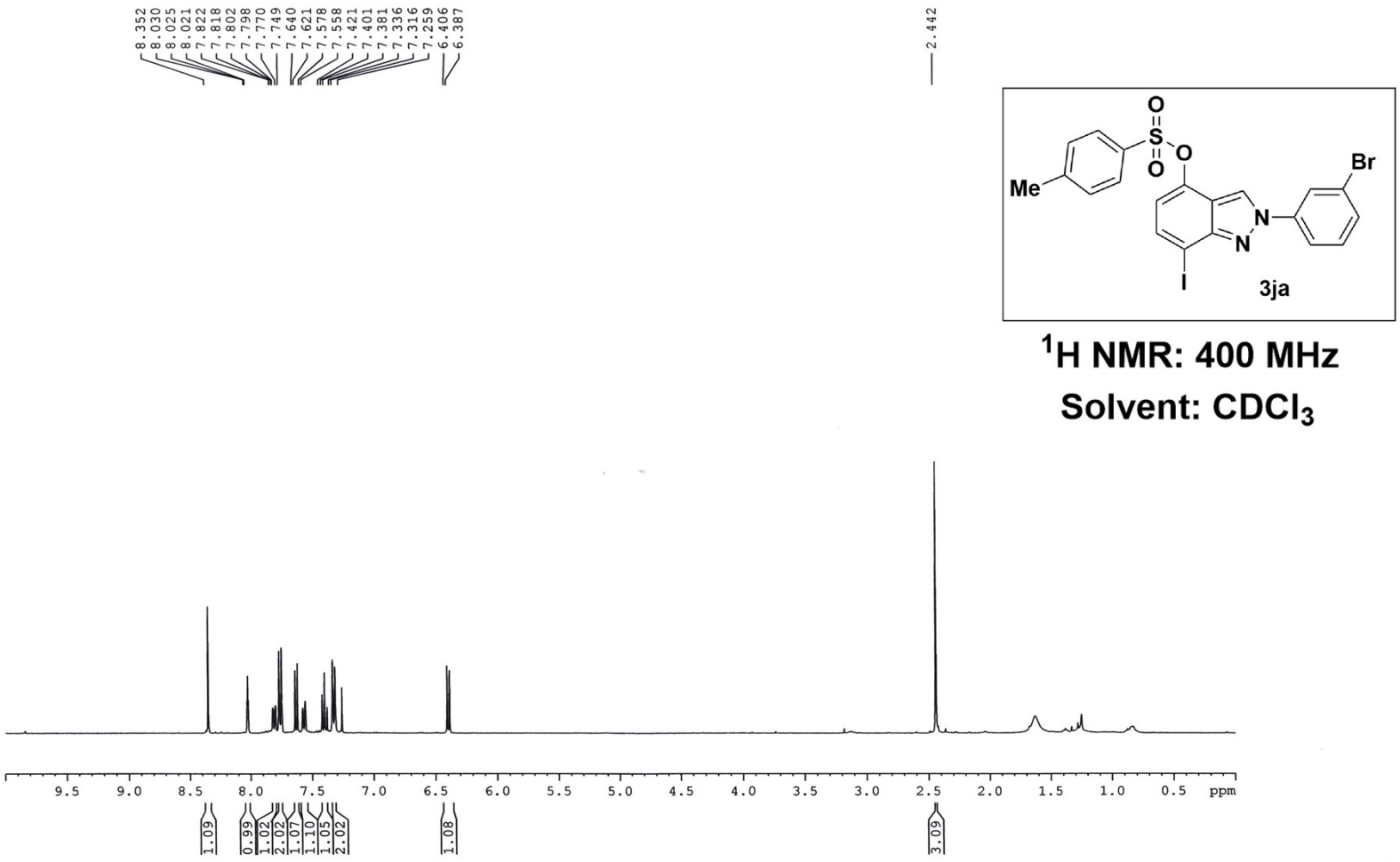
^{1}H NMR: 400 MHz

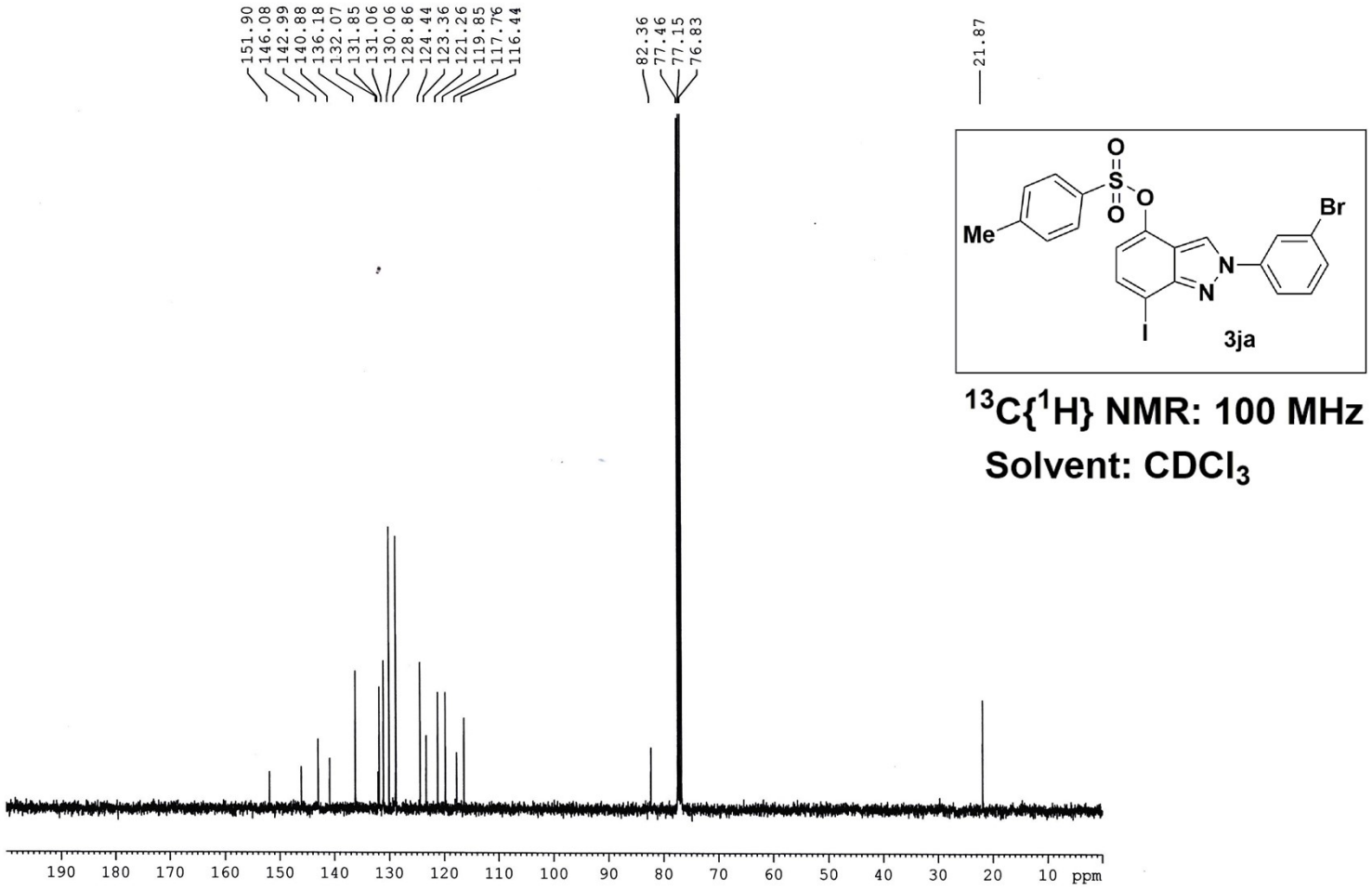
Solvent: $CDCl_3$



$^{13}C\{^{1}H\}$ NMR: 100 MHz

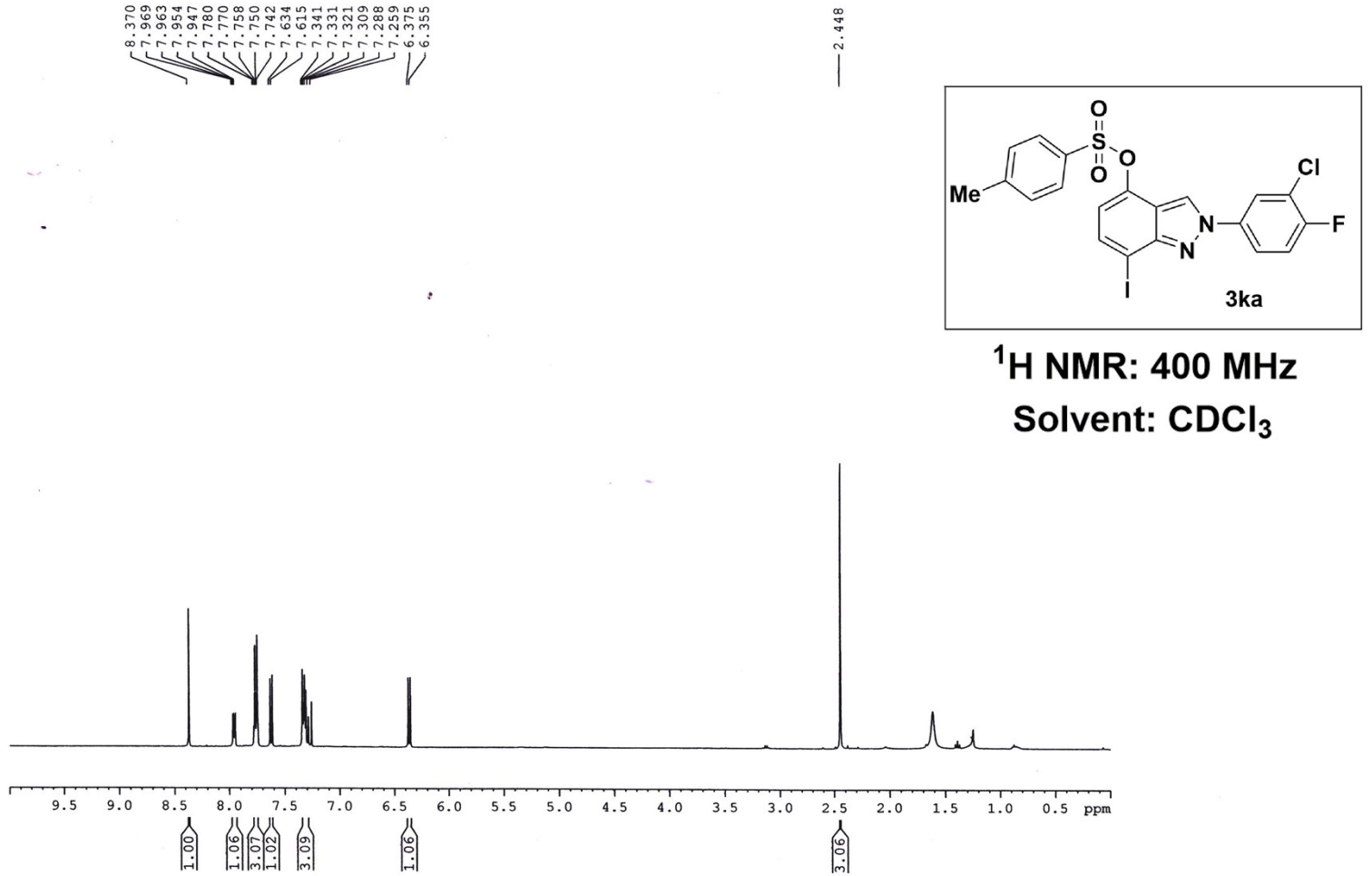
Solvent: $CDCl_3$

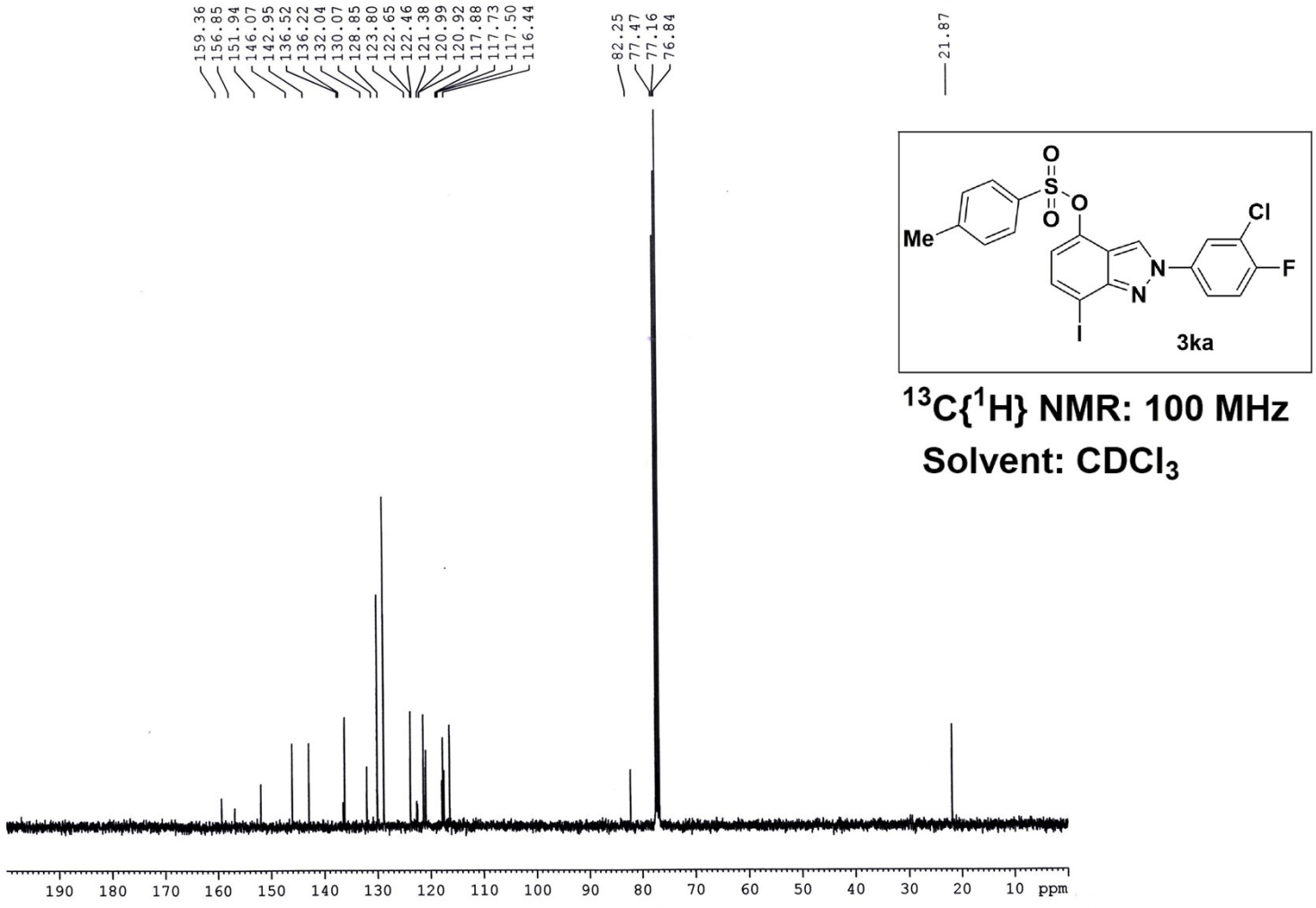

8.352
8.030
8.025
8.021
7.822
7.818
7.802
7.798
7.770
7.749
7.640
7.621
7.578
7.558
7.421
7.401
7.381
7.336
7.316
7.259
6.406
6.387
2.442
Me
Br
N
N
I
3ja
1H NMR: 400 MHz
Solvent: CDCl3
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.09
0.99
1.02
2.02
1.07
1.10
1.05
2.02
1.08
3.09

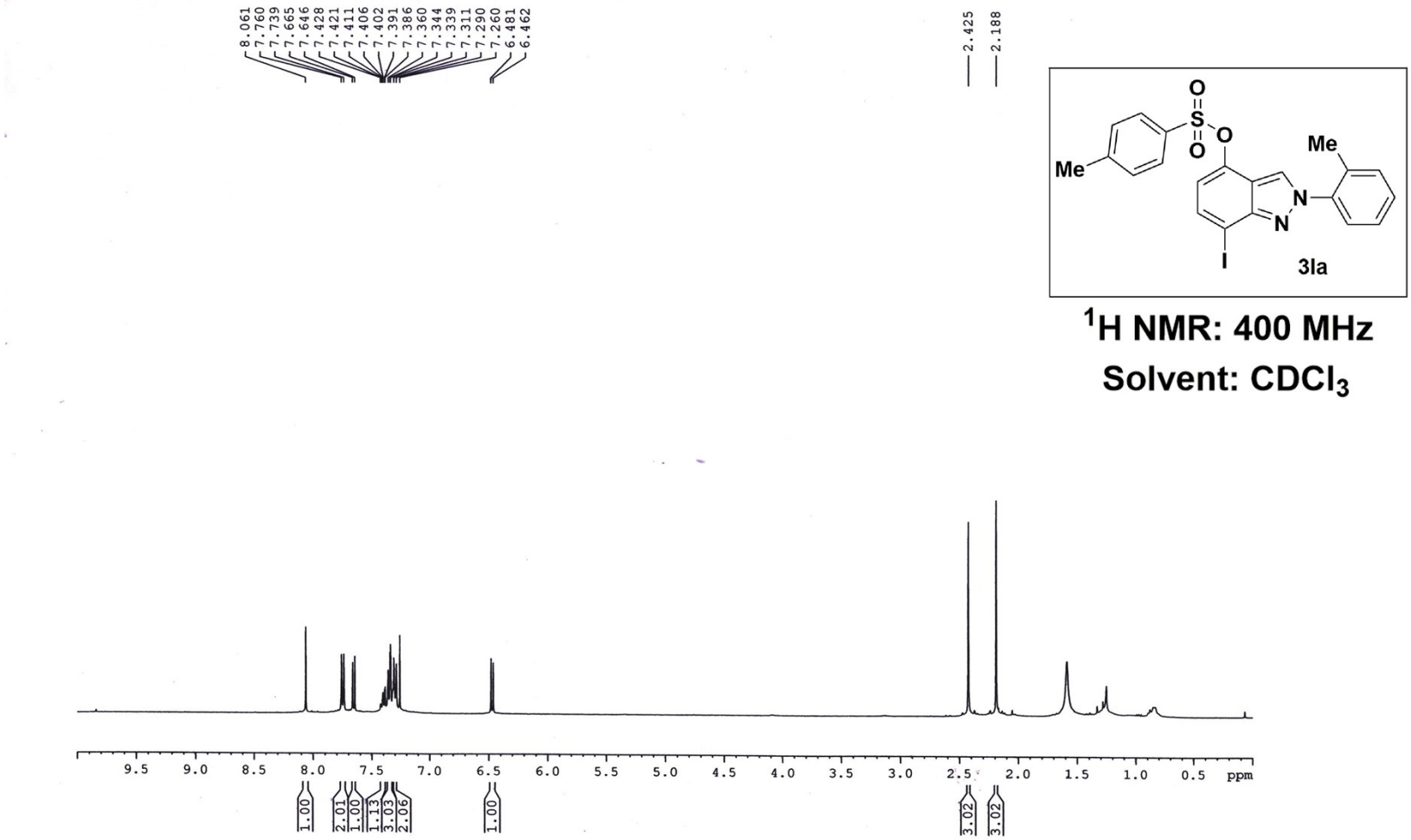


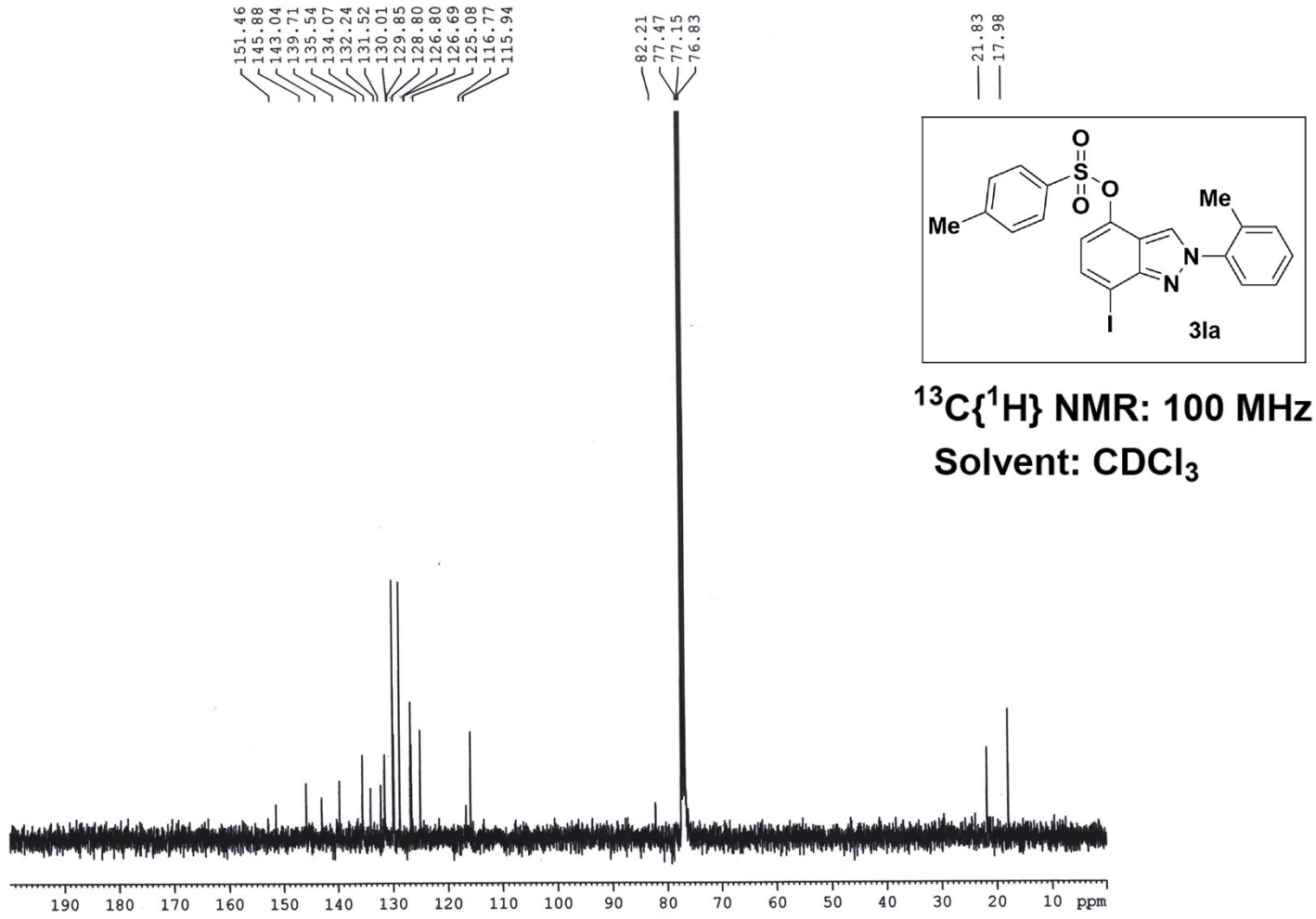
$^{13}C\{^{1}H\}$ NMR: 100 MHz

Solvent: $CDCl_3$


8.370
7.969
7.963
7.954
7.947
7.780
7.770
7.758
7.750
7.742
7.634
7.615
7.341
7.331
7.321
7.309
7.288
7.259
6.375
6.355
2.448
Me
Cl
F
N
N
I
3ka
1H NMR: 400 MHz
Solvent: CDCl3
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.00
1.06
3.07
1.02
3.09
1.06
3.06

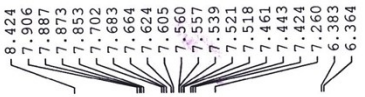

159.36
156.85
151.94
146.07
142.95
136.52
136.22
132.04
130.07
128.85
123.80
122.65
122.46
121.38
120.99
120.92
117.88
117.73
117.50
116.44
82.25
77.47
77.16
76.84
21.87
Me
O
S
O
O
O
N
N
Cl
F
I
3ka
$^{13}C\{^{1}H\}$ NMR: 100 MHz
Solvent: $CDCl_3$
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

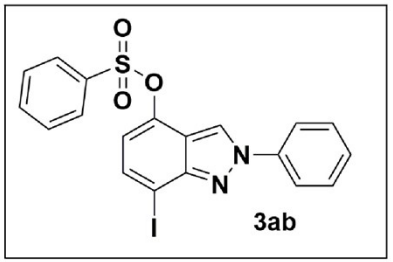

8.061
7.760
7.739
7.665
7.646
7.428
7.421
7.411
7.406
7.402
7.391
7.386
7.360
7.344
7.339
7.311
7.290
7.260
6.481
6.462
2.425
2.188
Me
Me
3la
1H NMR: 400 MHz
Solvent: CDCl3
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.00
2.01
1.00
1.13
3.03
2.06
1.00
3.02
3.02



$^{13}C\{^{1}H\}$ NMR: 100 MHz

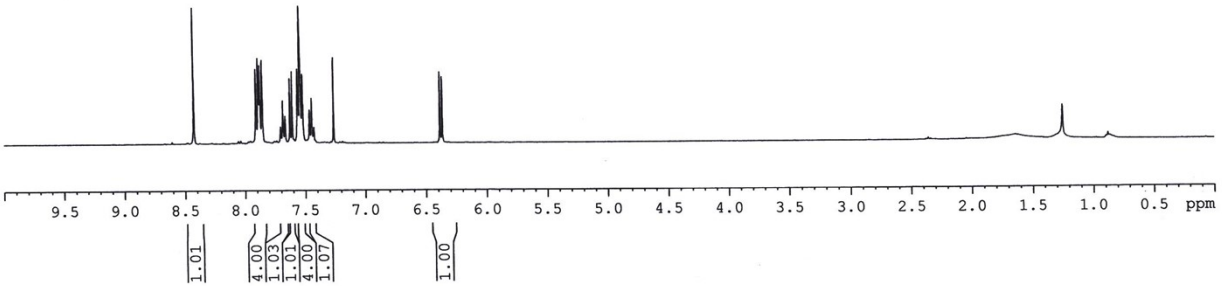
Solvent: $CDCl_3$

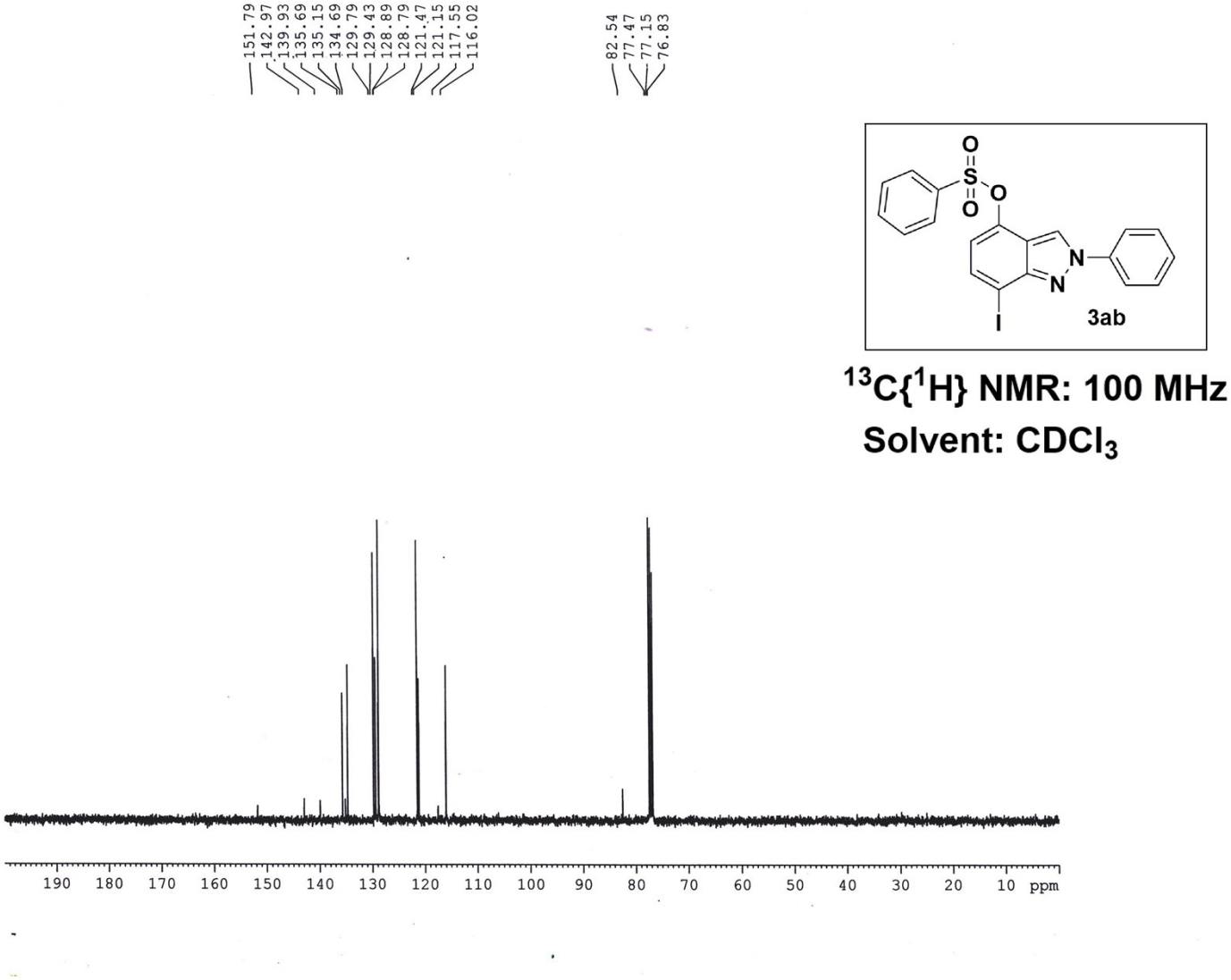




^{1}H NMR: 400 MHz

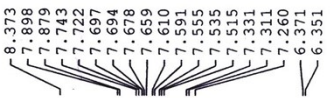
Solvent: $CDCl_3$

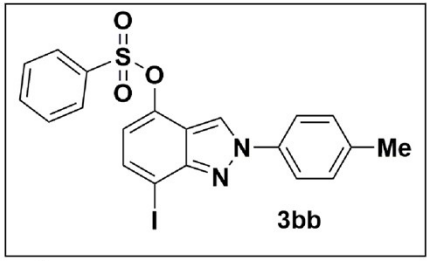




$^{13}C\{^{1}H\}$ NMR: 100 MHz

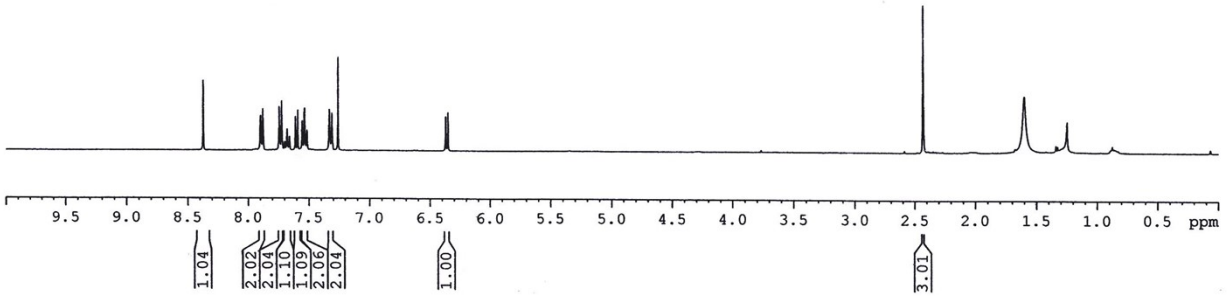
Solvent: $CDCl_3$

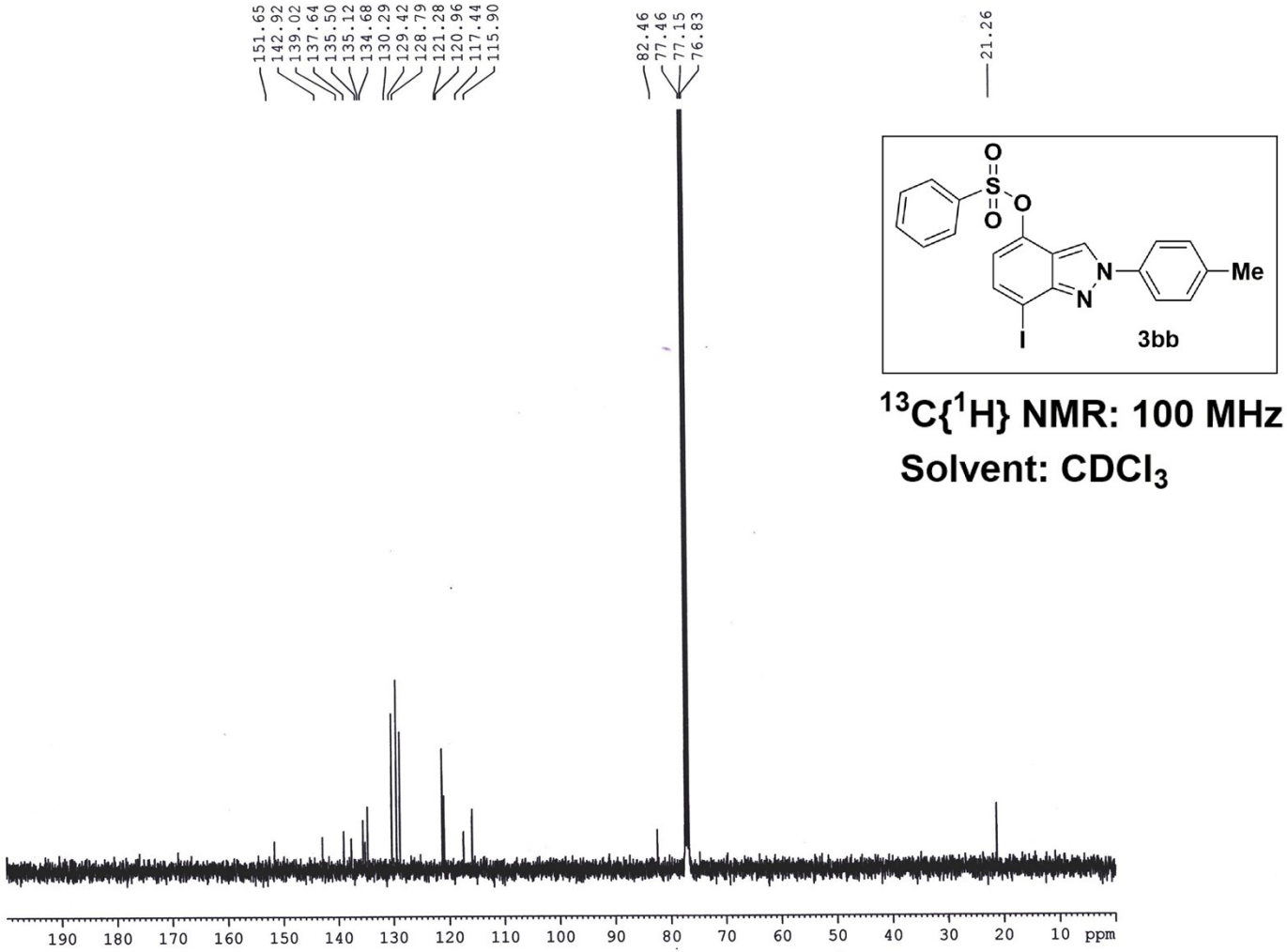


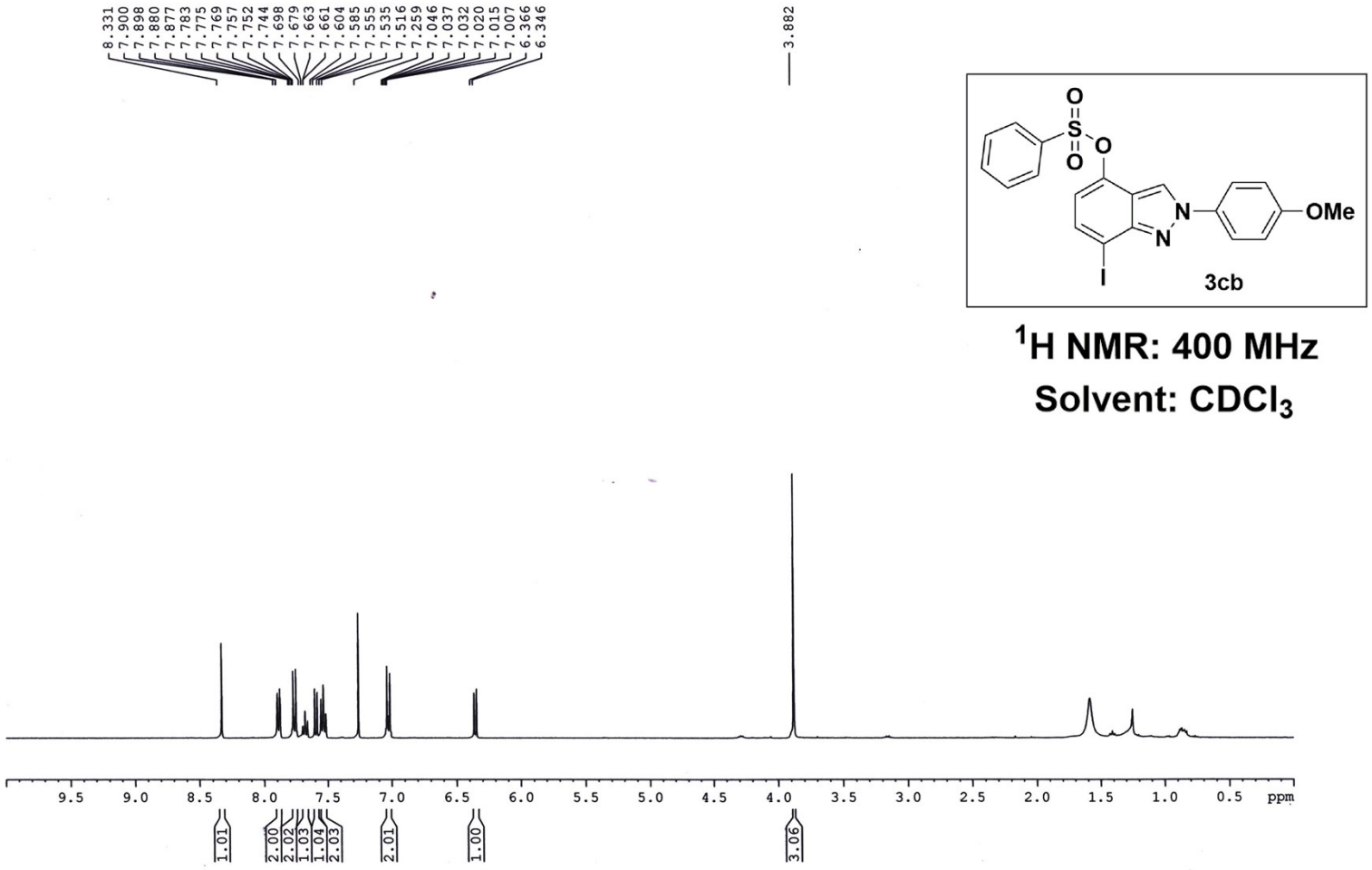


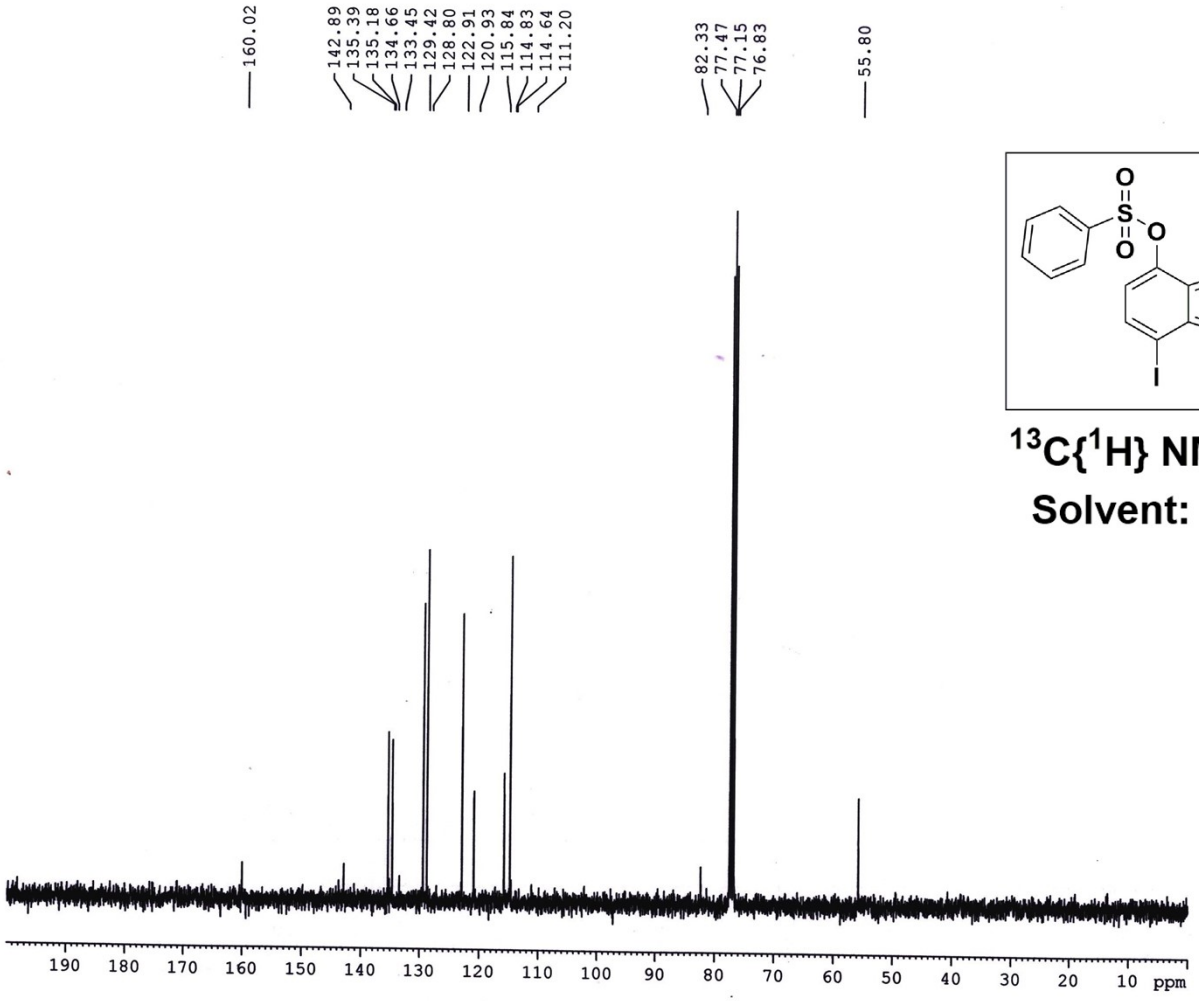
^{1}H NMR: 400 MHz

Solvent: $CDCl_3$



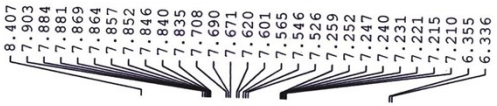

151.65
142.92
139.02
137.64
135.50
135.12
134.68
130.29
129.42
128.79
121.28
120.96
117.44
115.90
82.46
77.46
77.15
76.83
21.26
O
S
O
O
O
N
N
Me
I
3bb
13C{1H} NMR: 100 MHz
Solvent: CDCl3
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

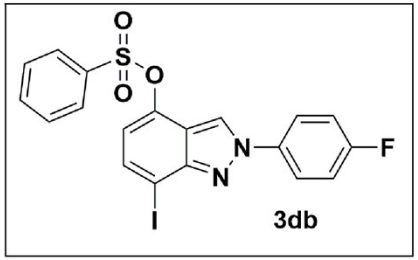

8.331
7.900
7.898
7.880
7.877
7.783
7.775
7.769
7.757
7.752
7.744
7.698
7.679
7.663
7.661
7.604
7.585
7.555
7.535
7.516
7.259
7.046
7.037
7.032
7.020
7.015
7.007
6.366
6.346
3.882
O
S
O
O
O
N
N
OMe
I
3cb
1H NMR: 400 MHz
Solvent: CDCl3
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.01
2.00
2.02
1.03
1.04
2.03
2.01
1.00
3.06



$^{13}C\{^{1}H\}$ NMR: 100 MHz

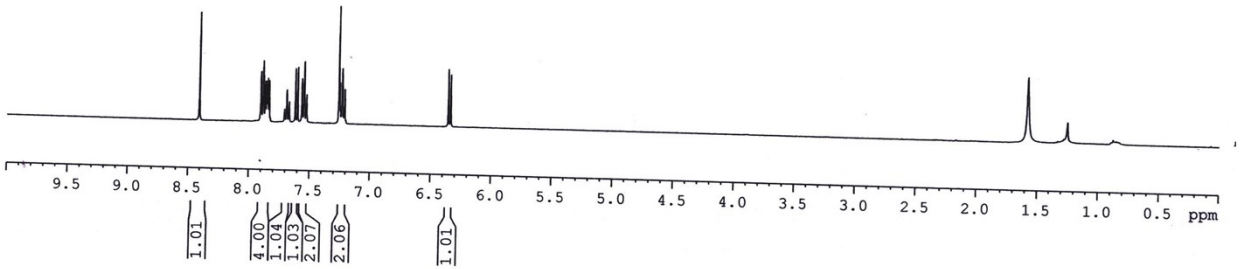
Solvent: $CDCl_3$

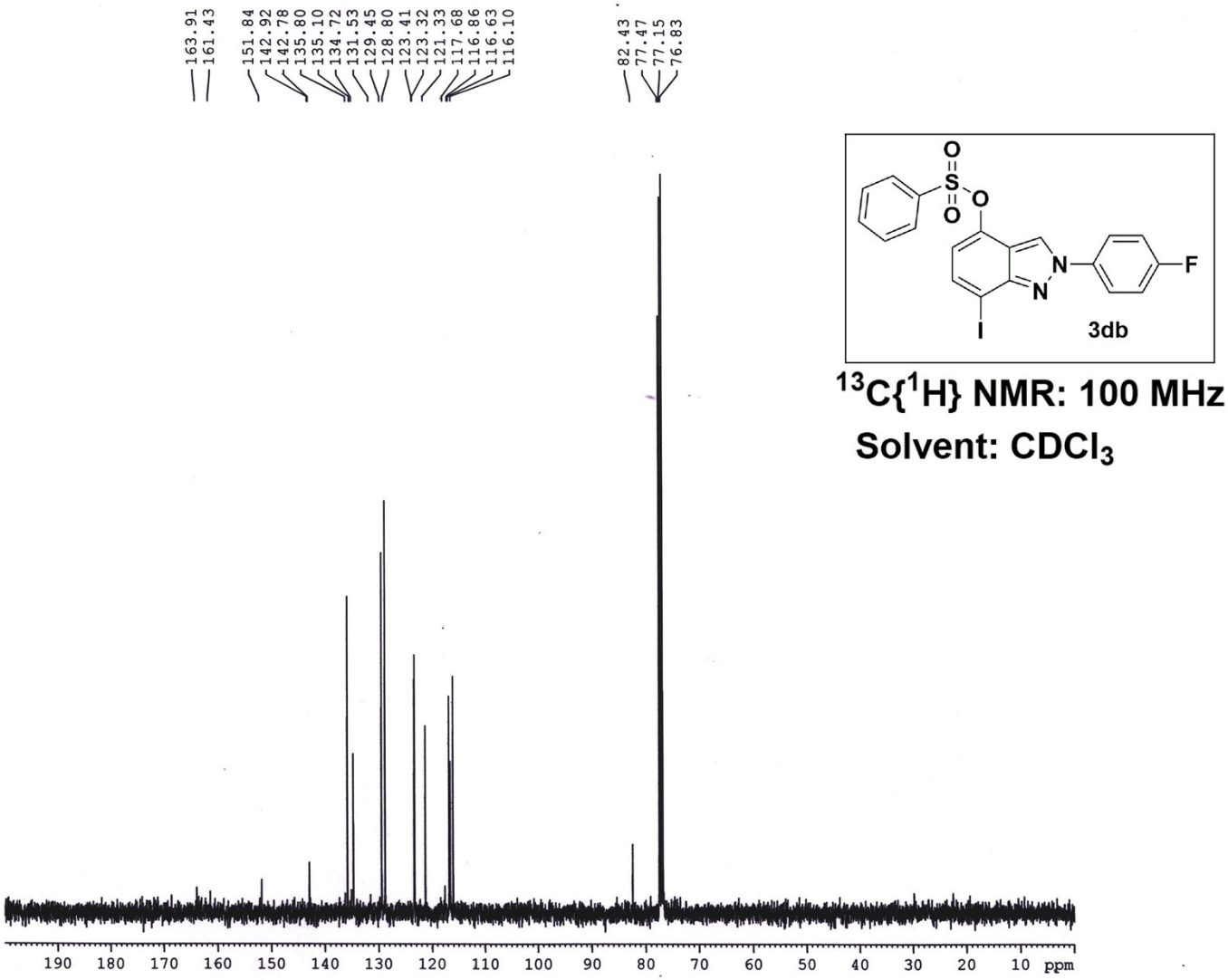


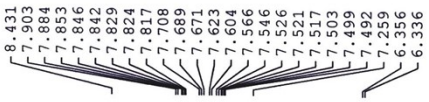


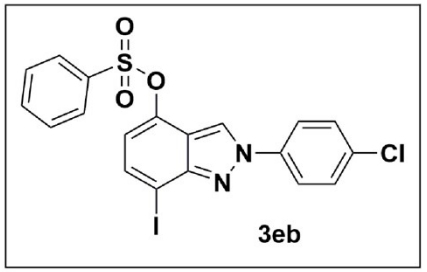
^{1}H NMR: 400 MHz

Solvent: $CDCl_3$



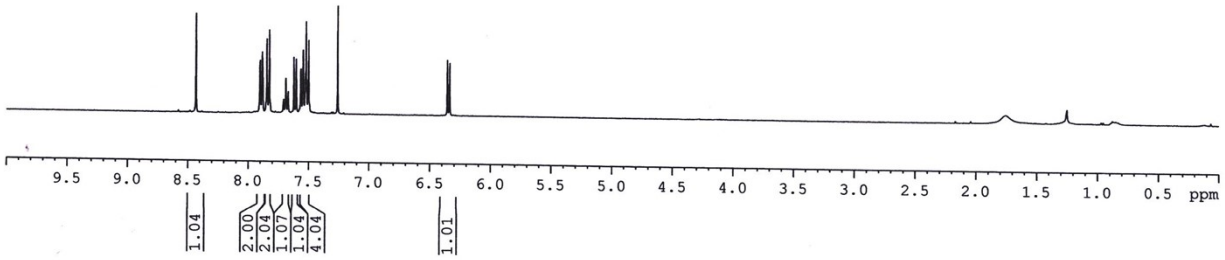

163.91
161.43
151.84
142.92
142.78
135.80
135.10
134.72
131.53
129.45
128.80
123.41
123.32
121.33
117.68
116.86
116.63
116.10
82.43
77.47
77.15
76.83
O
S
O
O
N
N
F
I
3db
$^{13}C\{^{1}H\}$ NMR: 100 MHz
Solvent: $CDCl_3$
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

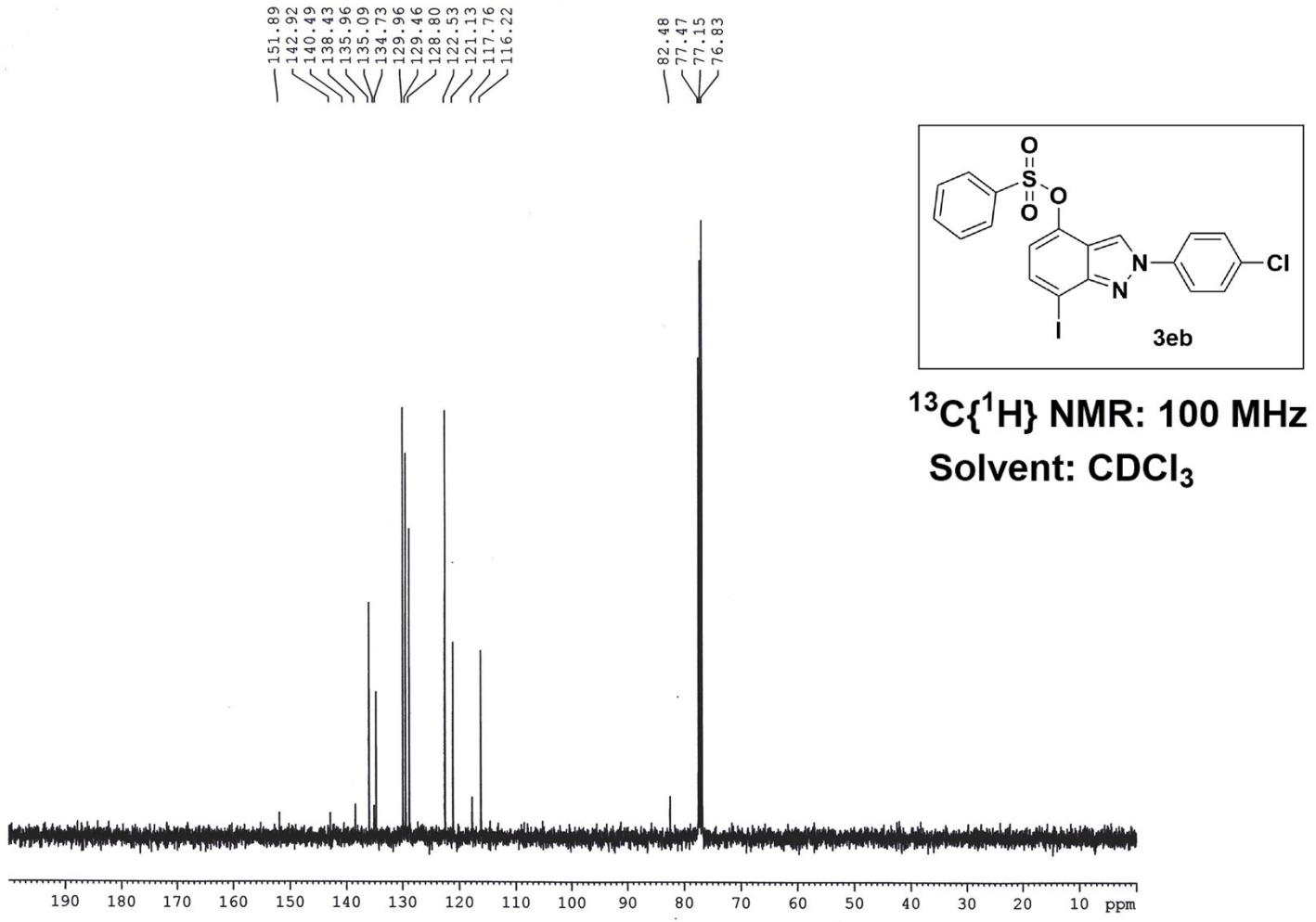




^{1}H NMR: 400 MHz

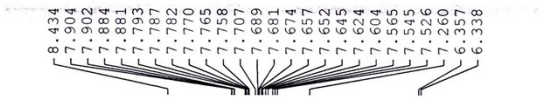
Solvent: $CDCl_3$

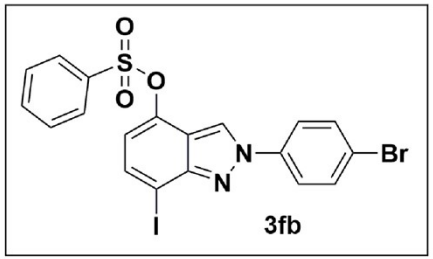




$^{13}C\{^{1}H\}$ NMR: 100 MHz

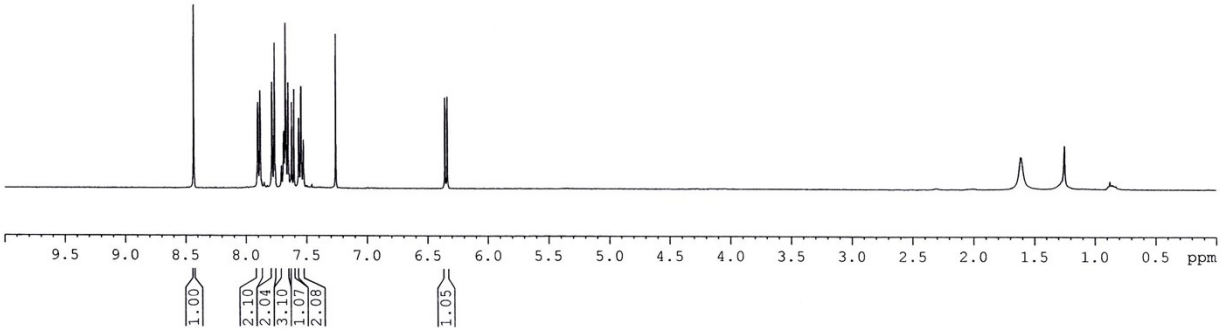
Solvent: $CDCl_3$

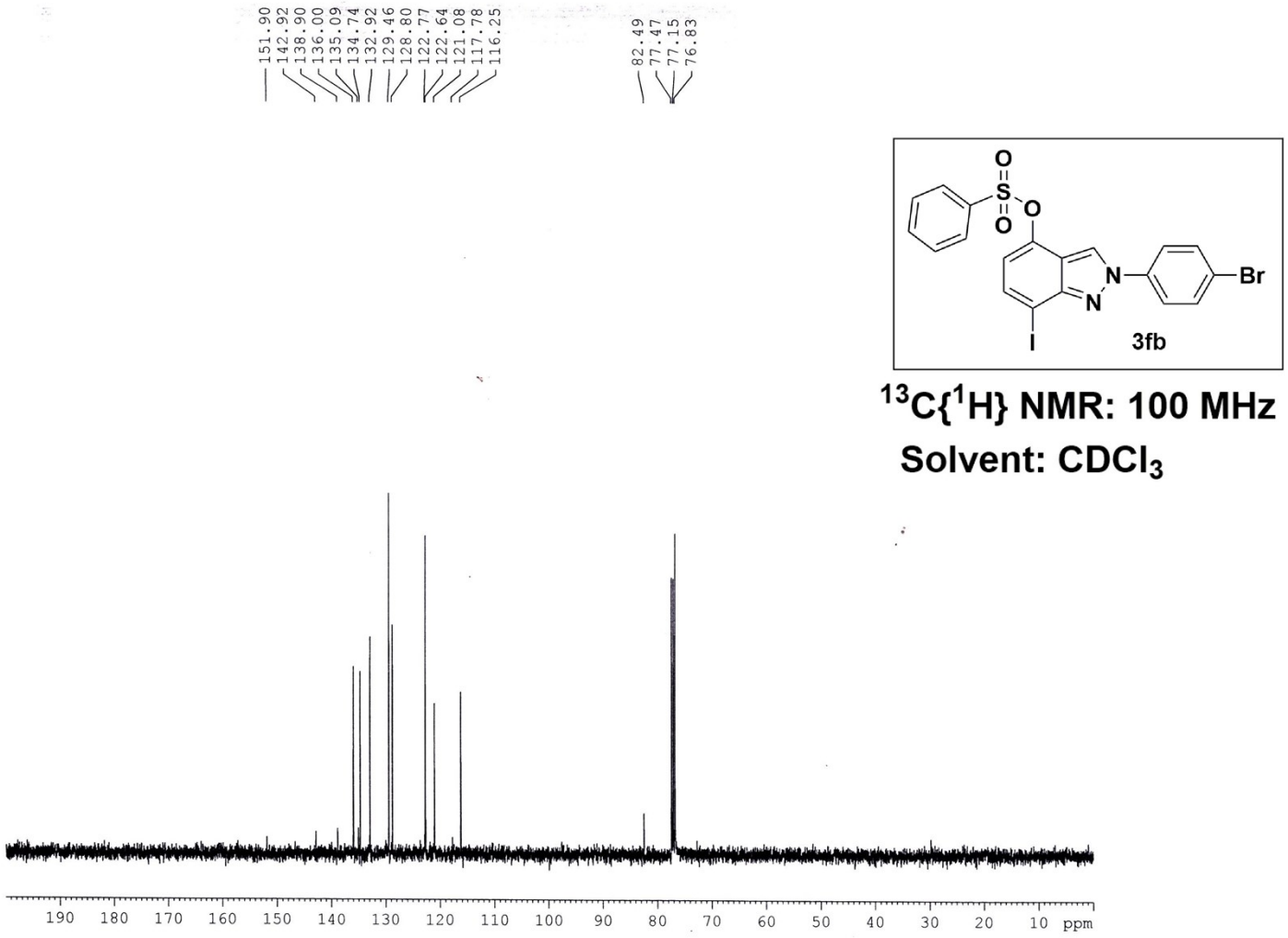


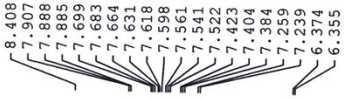


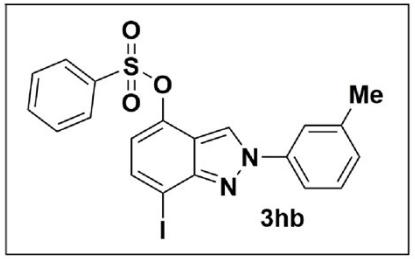
^{1}H NMR: 400 MHz

Solvent: $CDCl_3$



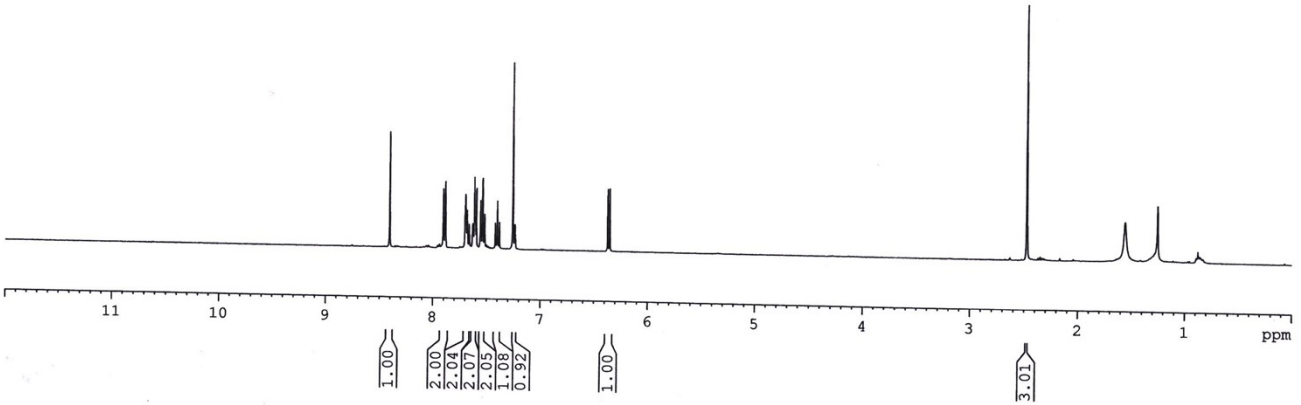

151.90
142.92
138.90
136.00
135.09
134.74
132.92
129.46
128.80
122.77
122.64
121.08
117.78
116.25
82.49
77.47
77.15
76.83
O
S
O
O
N
N
Br
I
3fb
13C{1H} NMR: 100 MHz
Solvent: CDCl3
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

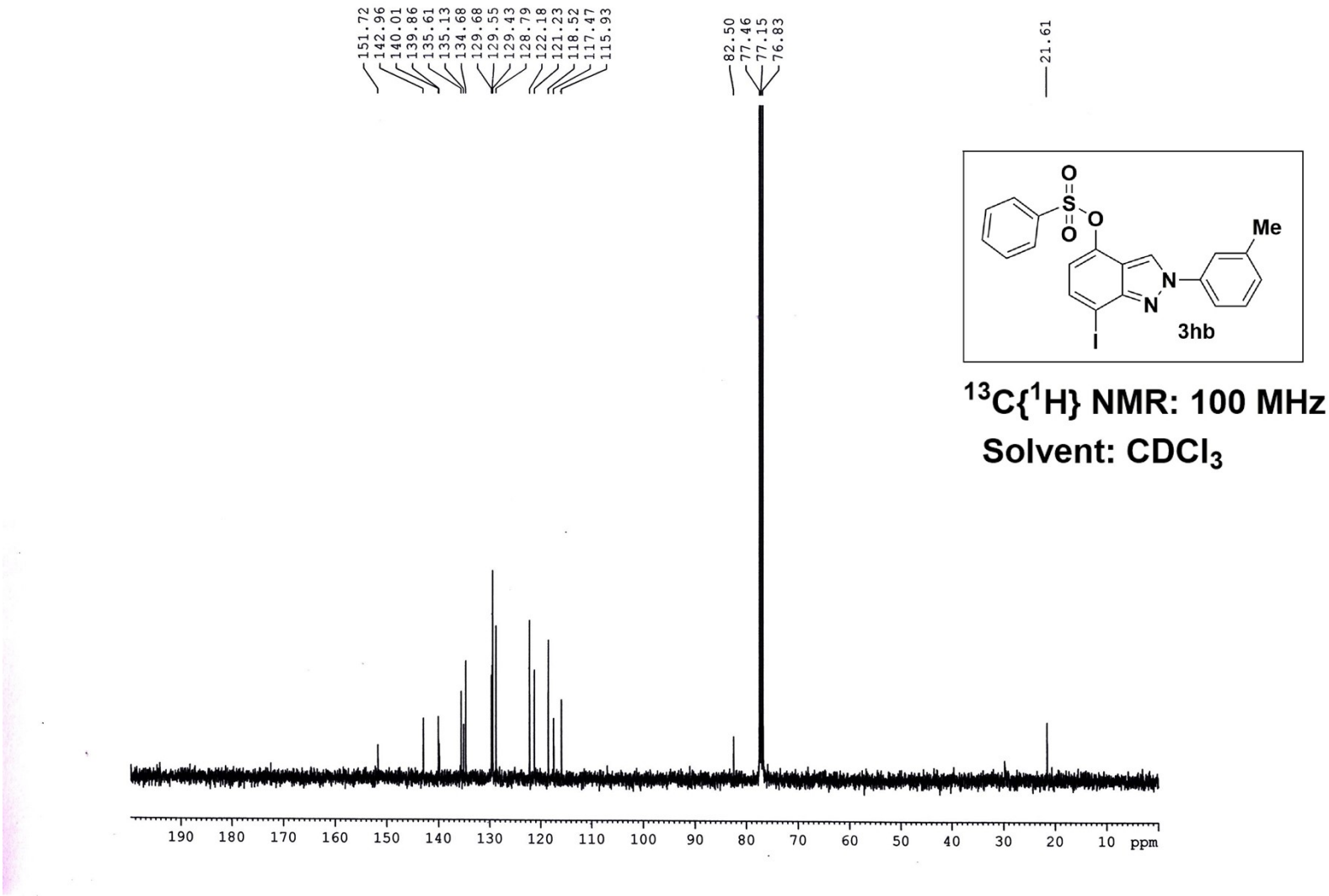


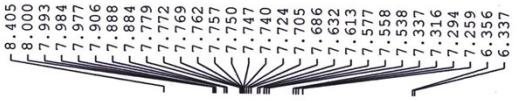


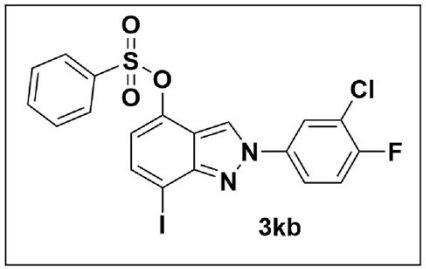
^{1}H NMR: 400 MHz

Solvent: $CDCl_3$



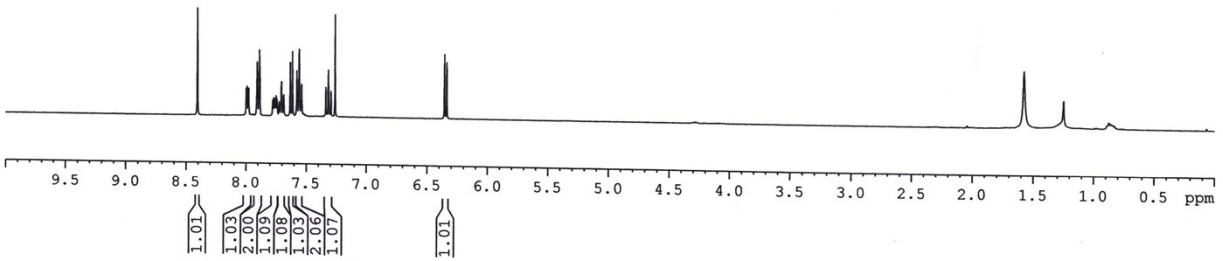

151.72
142.96
140.01
139.86
135.61
135.13
134.68
129.68
129.55
129.43
128.79
122.18
121.23
118.52
117.47
115.93
82.50
77.46
77.15
76.83
21.61
O
S
O
O
O
Me
N
N
I
3hb
$^{13}C\{^{1}H\}$ NMR: 100 MHz
Solvent: $CDCl_3$
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

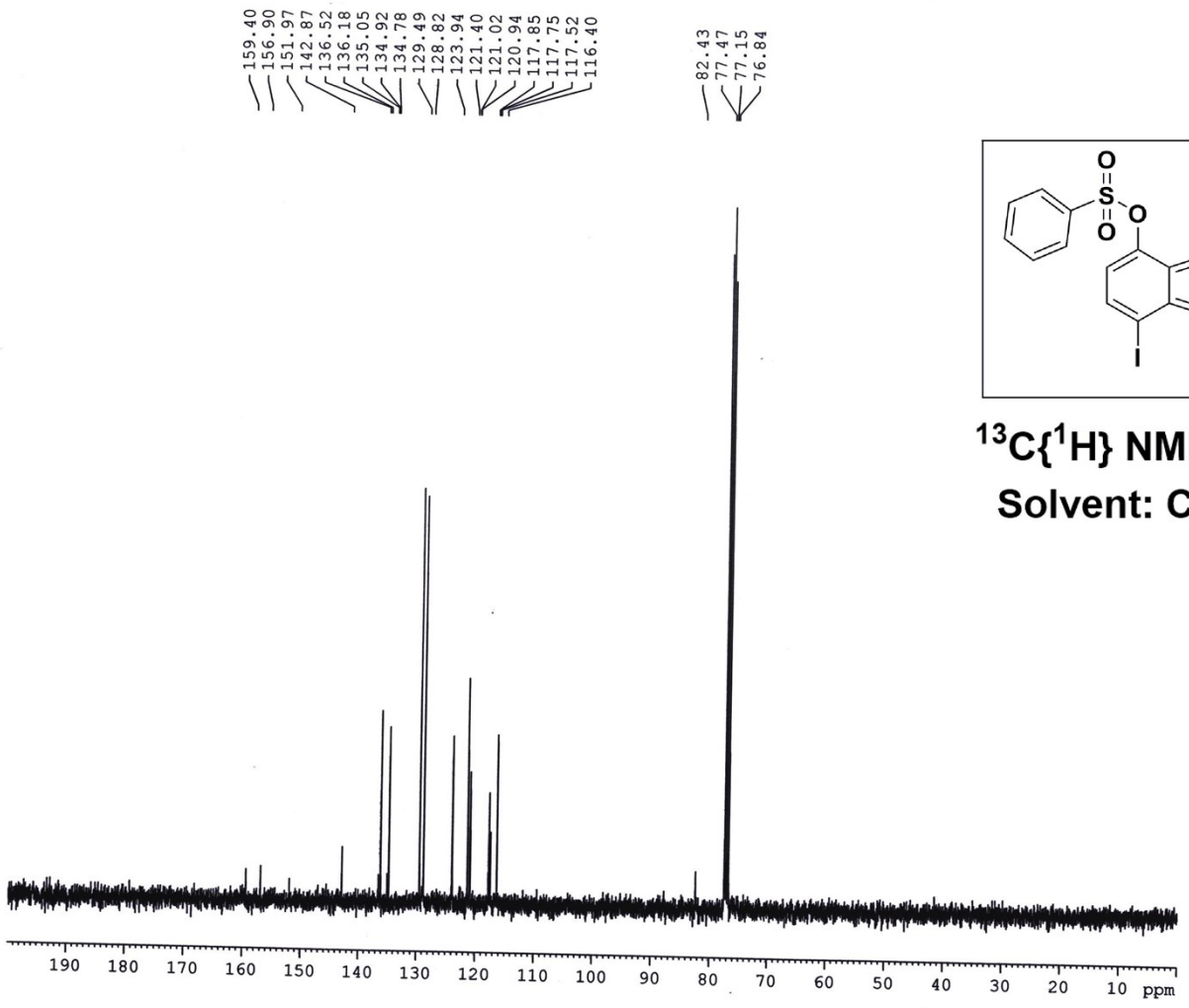


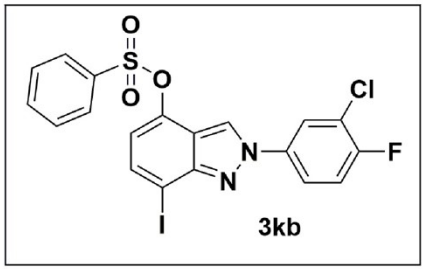


^{1}H NMR: 400 MHz

Solvent: $CDCl_3$

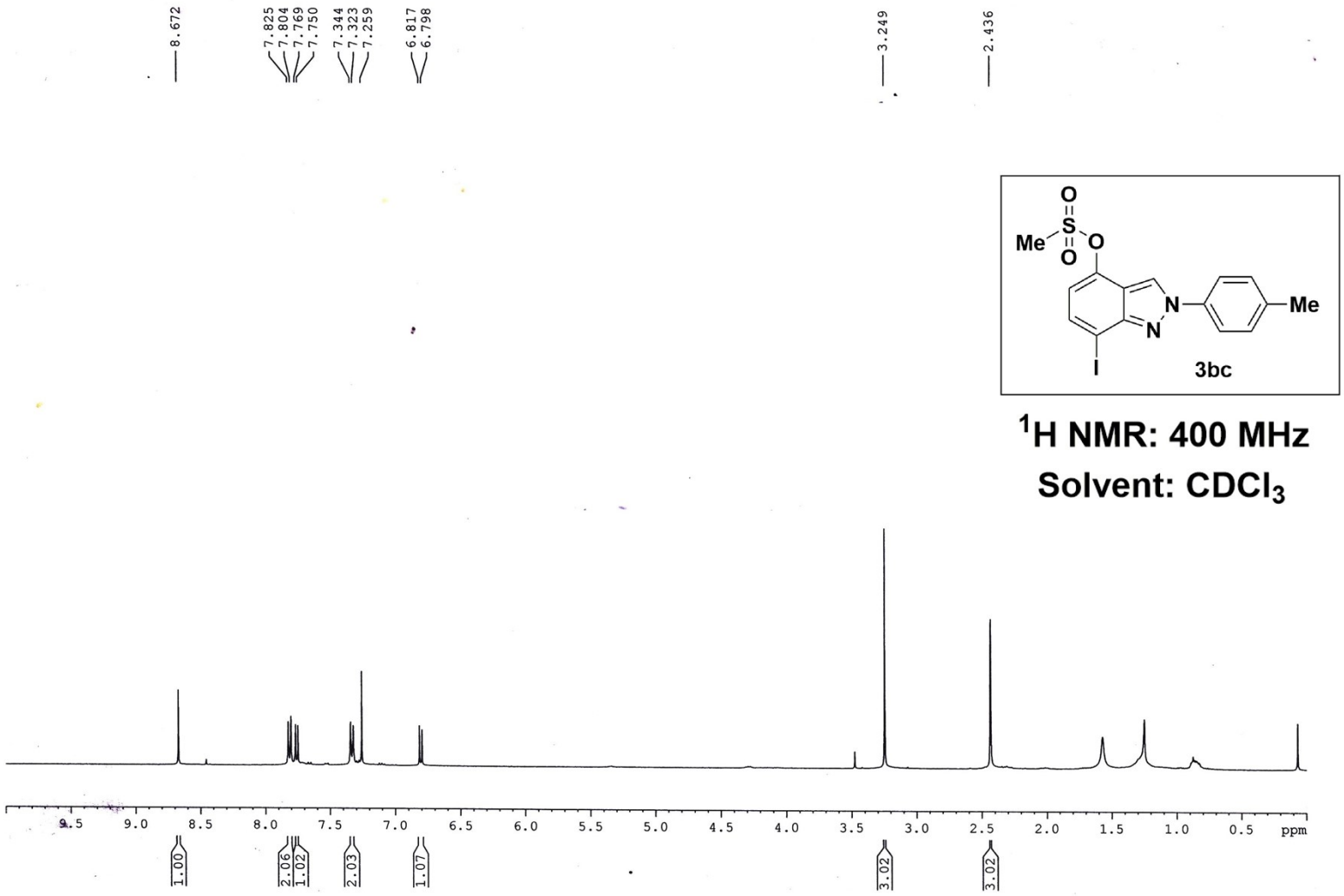


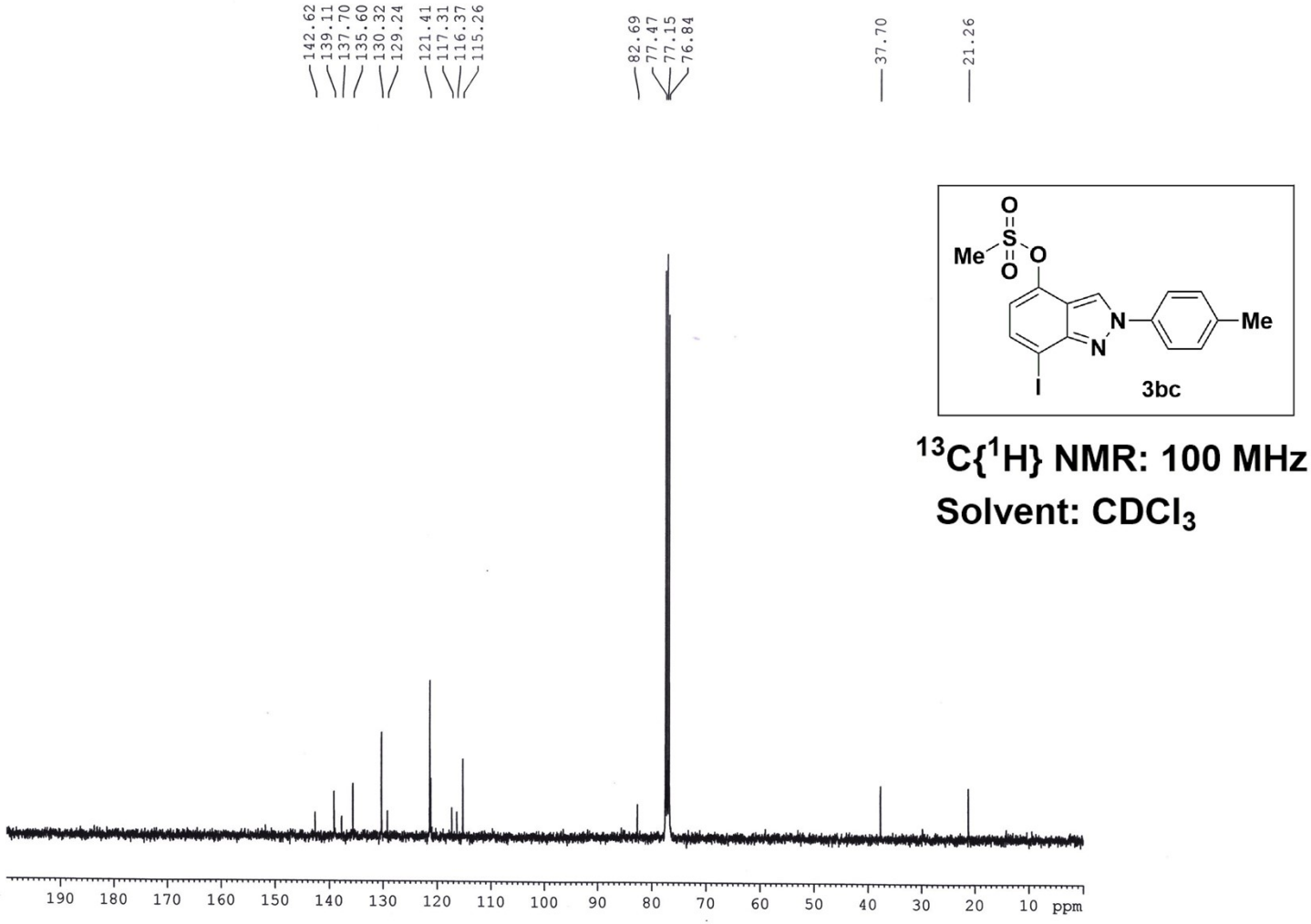




$^{13}C\{^{1}H\}$ NMR: 100 MHz

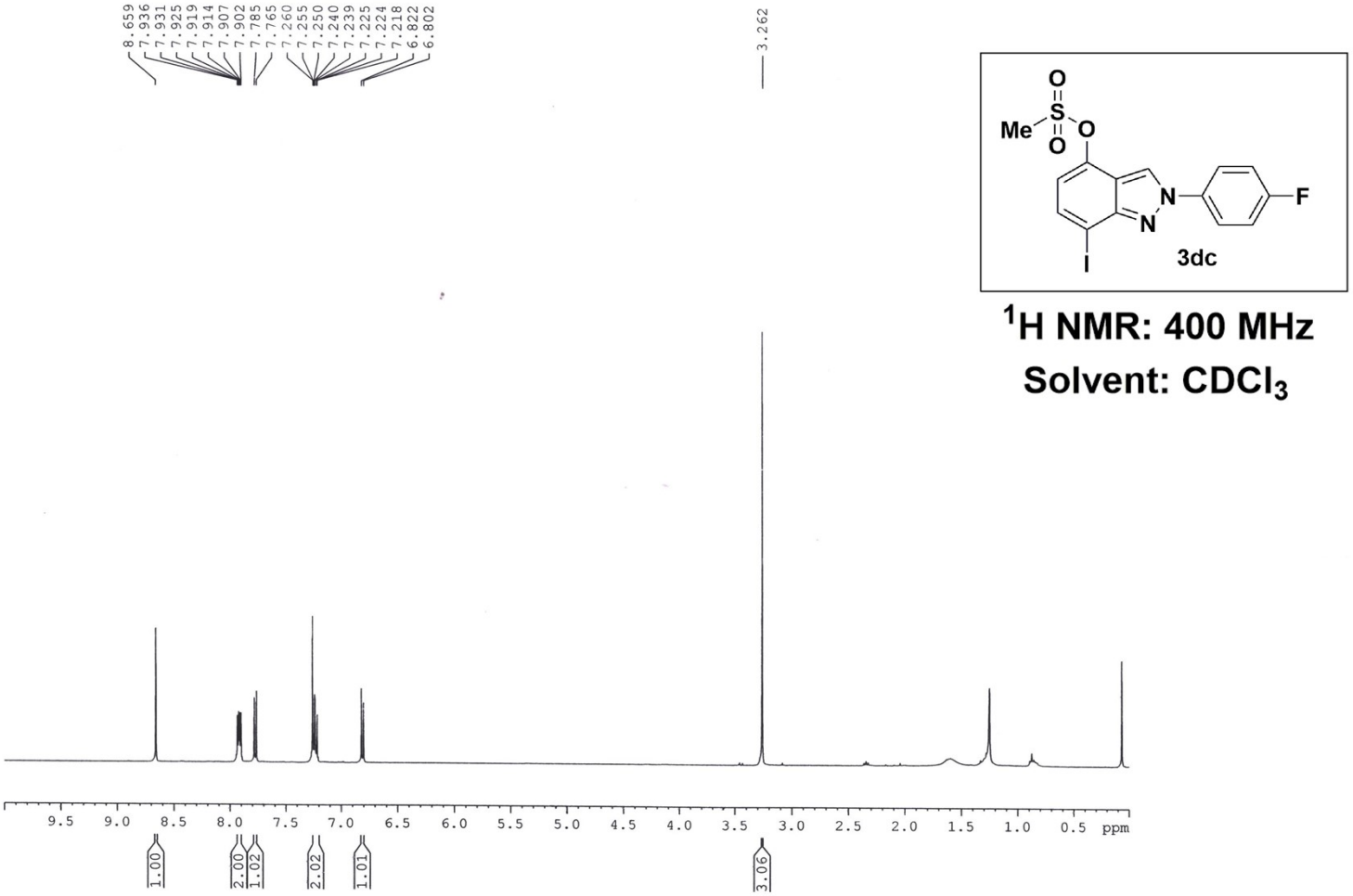
Solvent: $CDCl_3$

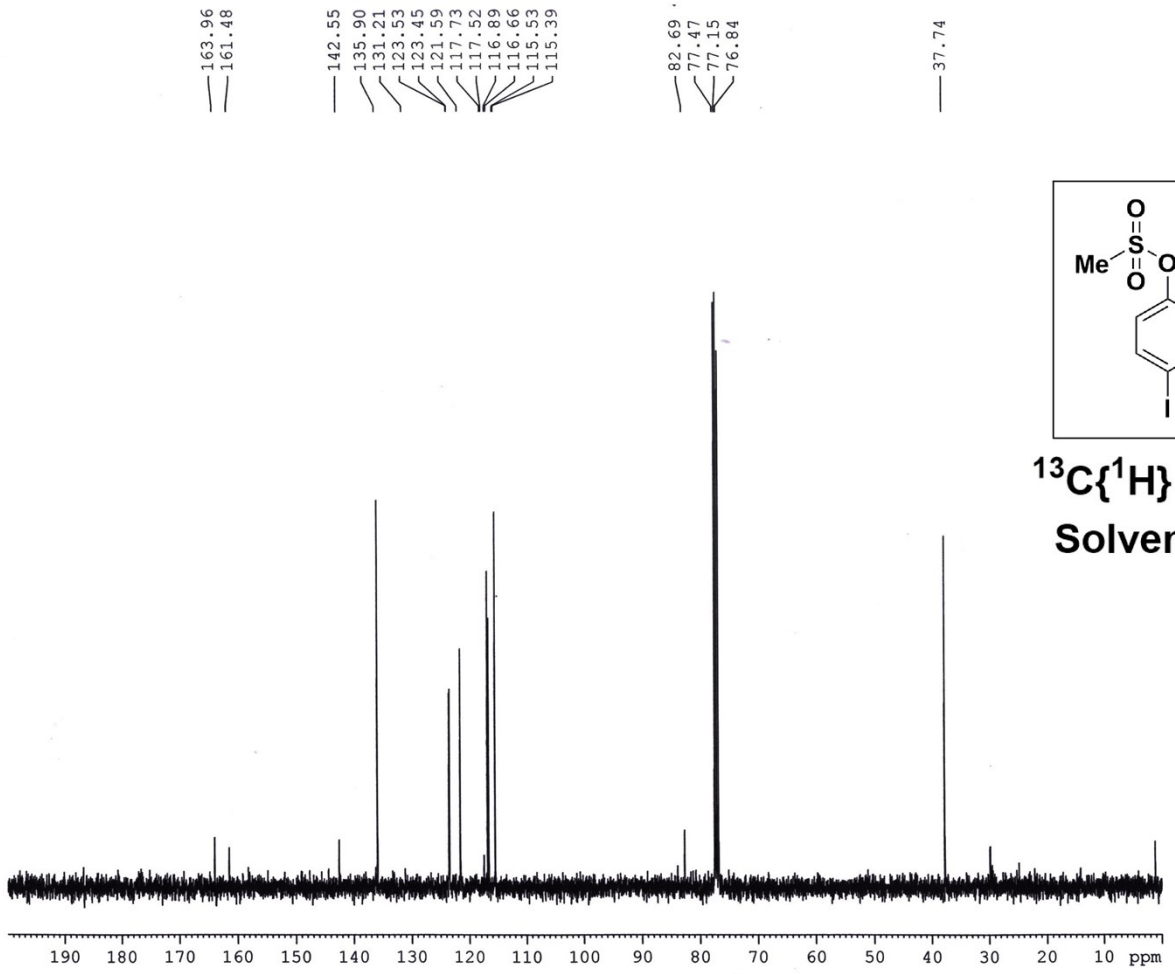

8.672
7.825
7.804
7.769
7.750
7.344
7.323
7.259
6.817
6.798
3.249
2.436
Me
O
S
O
O
O
N
N
Me
I
3bc
1H NMR: 400 MHz
Solvent: CDCl3
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.00
2.06
1.02
2.03
1.07
3.02
3.02

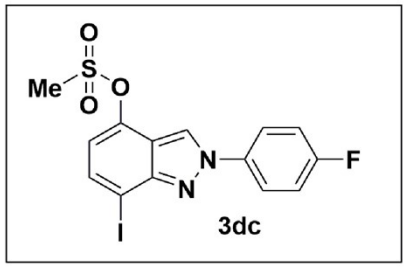


$^{13}C\{^{1}H\}$ NMR: 100 MHz

Solvent: $CDCl_3$

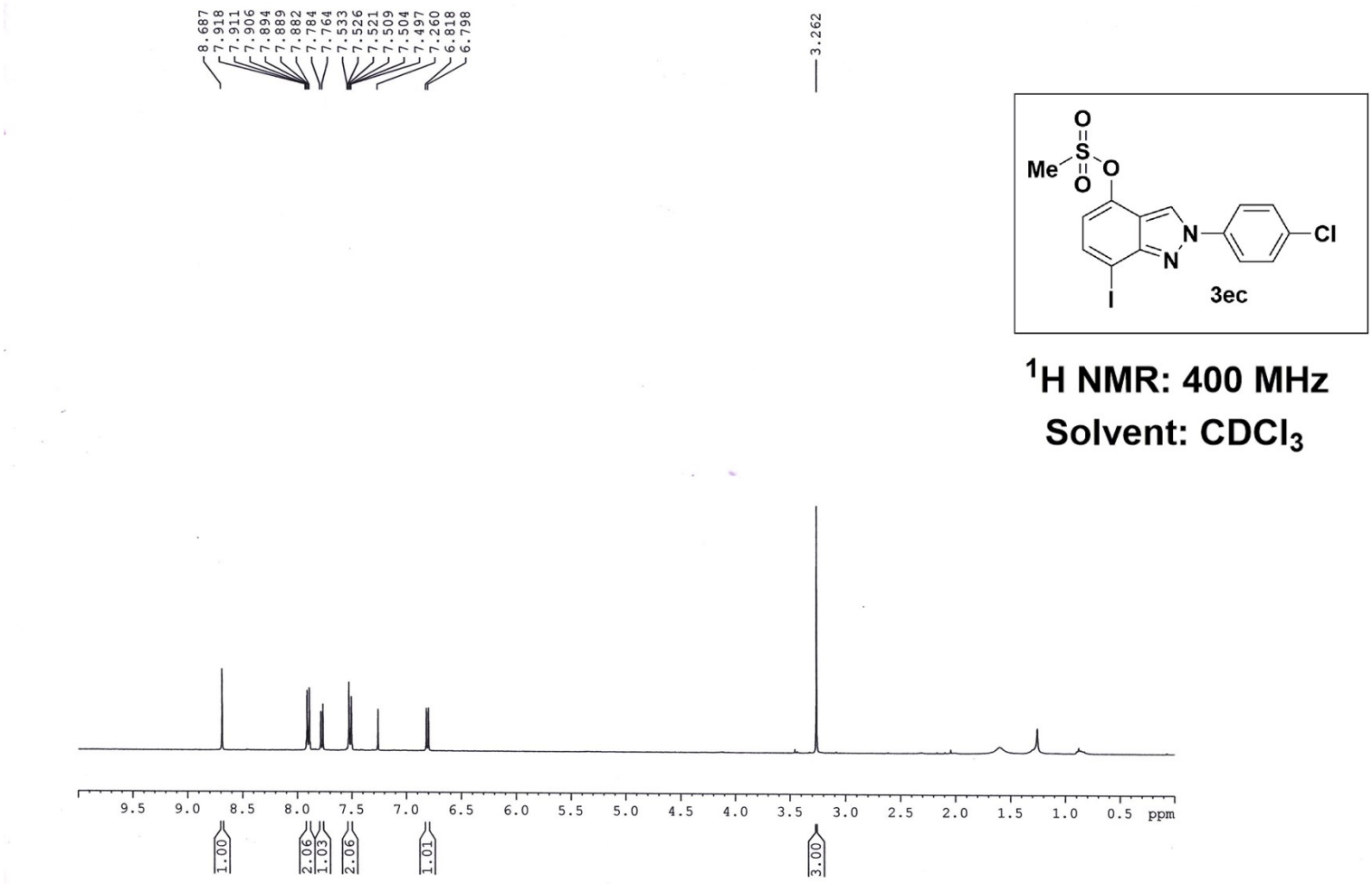

8.659
7.936
7.931
7.925
7.919
7.914
7.907
7.902
7.785
7.765
7.260
7.255
7.250
7.240
7.239
7.225
7.224
7.218
6.822
6.802
3.262
Me
O
S
O
O
N
N
F
I
3dc
1H NMR: 400 MHz
Solvent: CDCl3
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.00
2.00
1.02
2.02
1.01
3.06

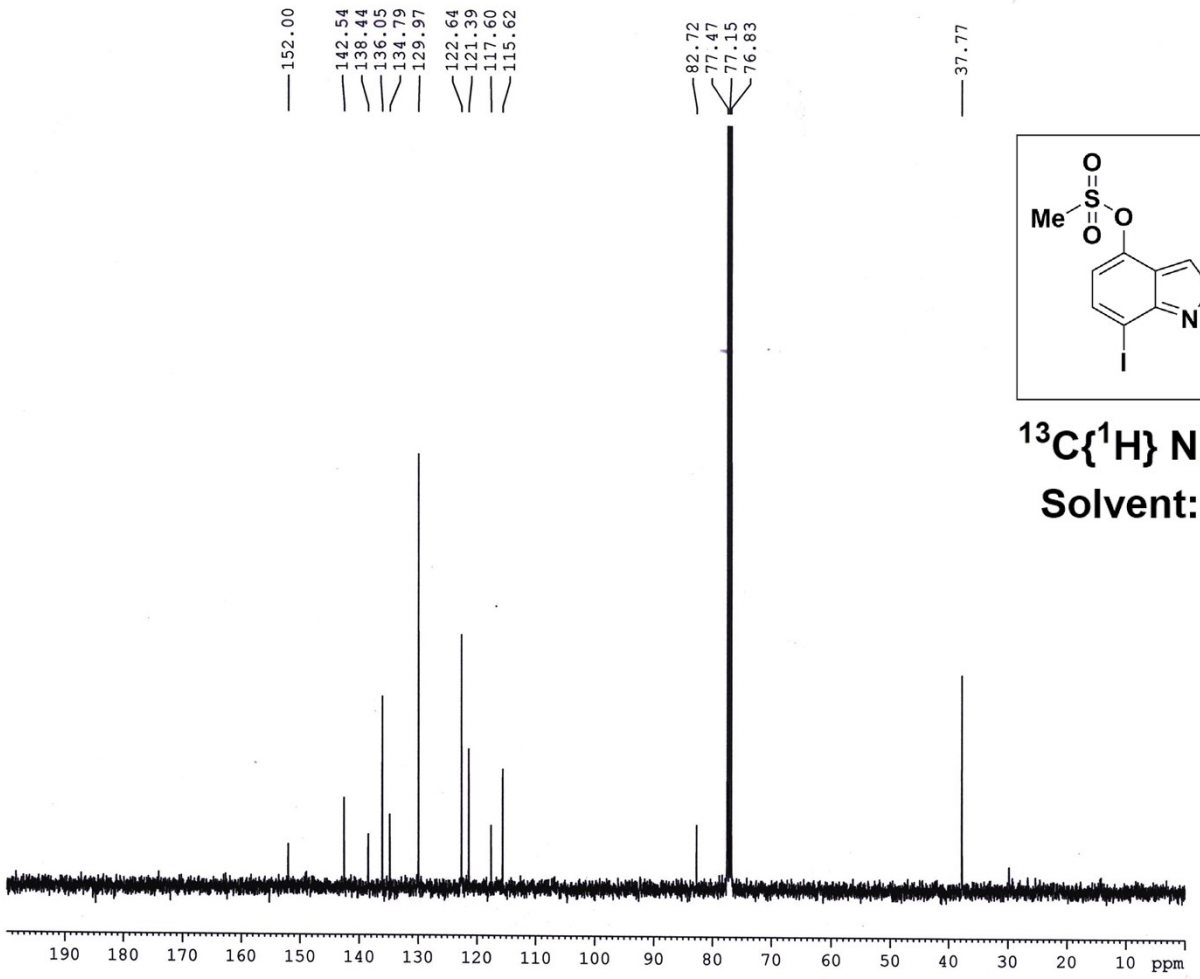


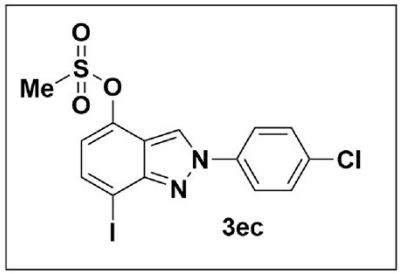


$^{13}C\{^{1}H\}$ NMR: 100 MHz

Solvent: $CDCl_3$

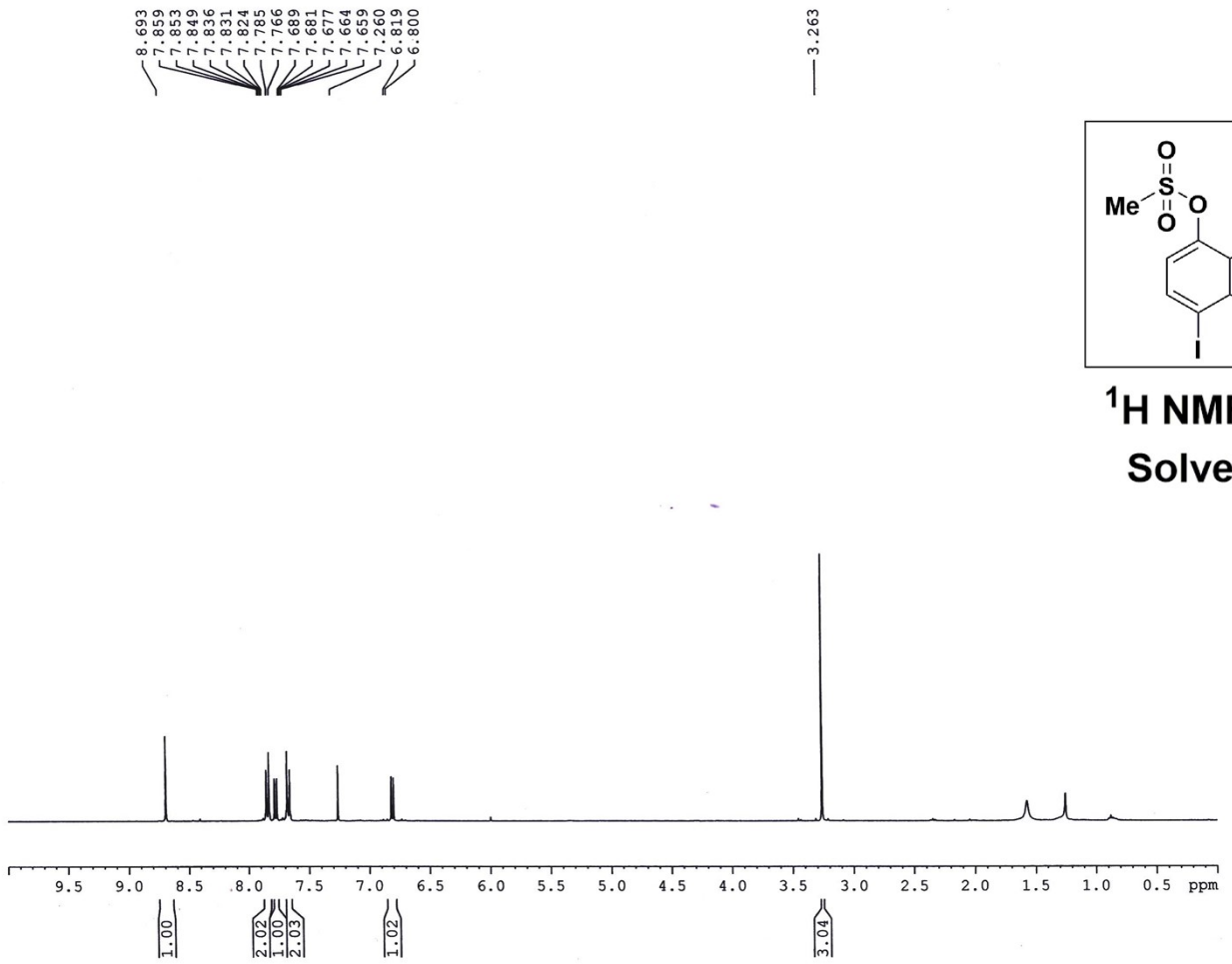

8.687
7.918
7.911
7.906
7.894
7.889
7.882
7.784
7.764
7.533
7.526
7.521
7.509
7.504
7.497
7.260
6.818
6.798
3.262
Me
O
S
O
O
O
N
N
Cl
I
3ec
1H NMR: 400 MHz
Solvent: CDCl3
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.00
2.06
1.03
2.06
1.01
3.00

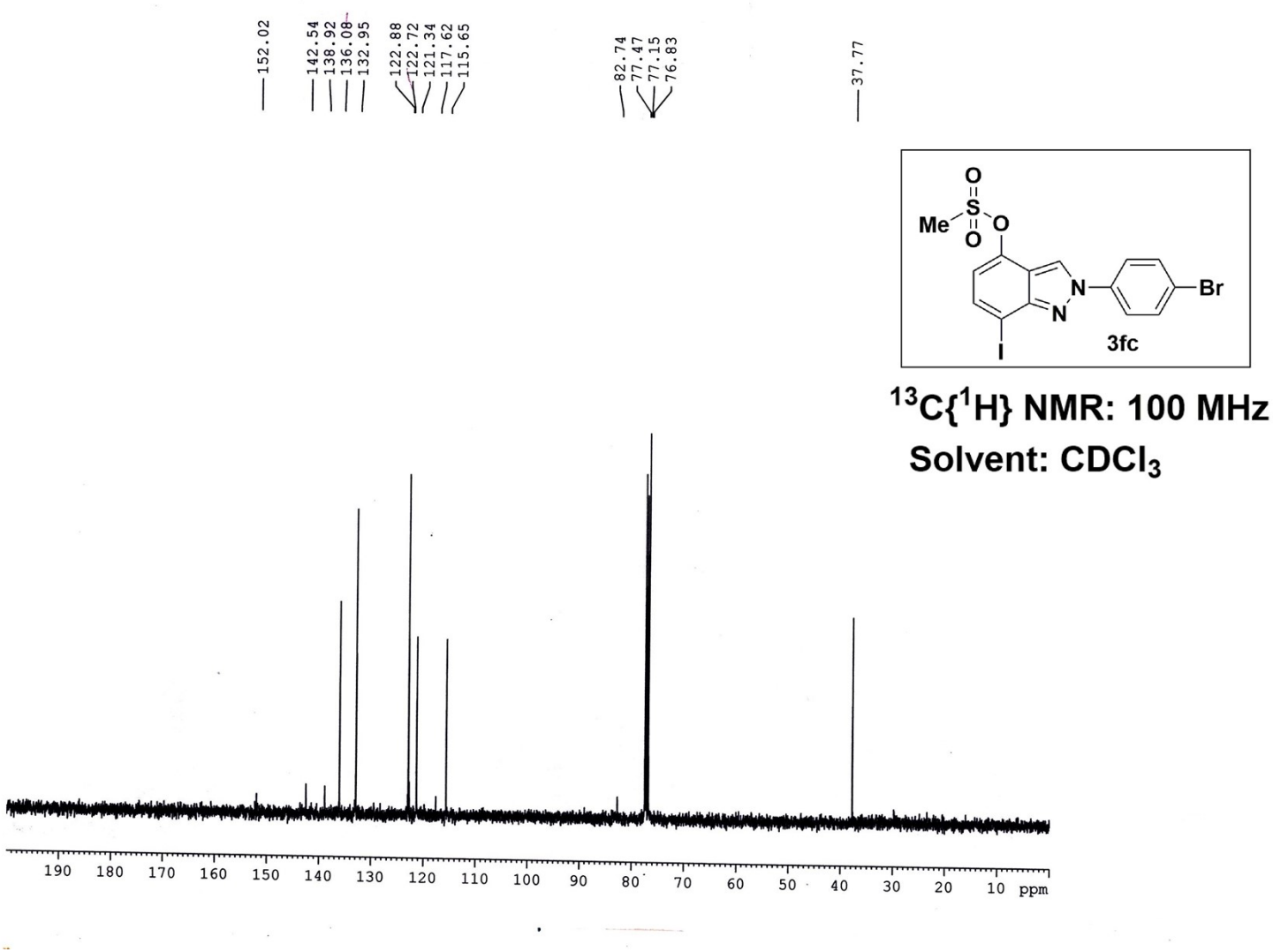


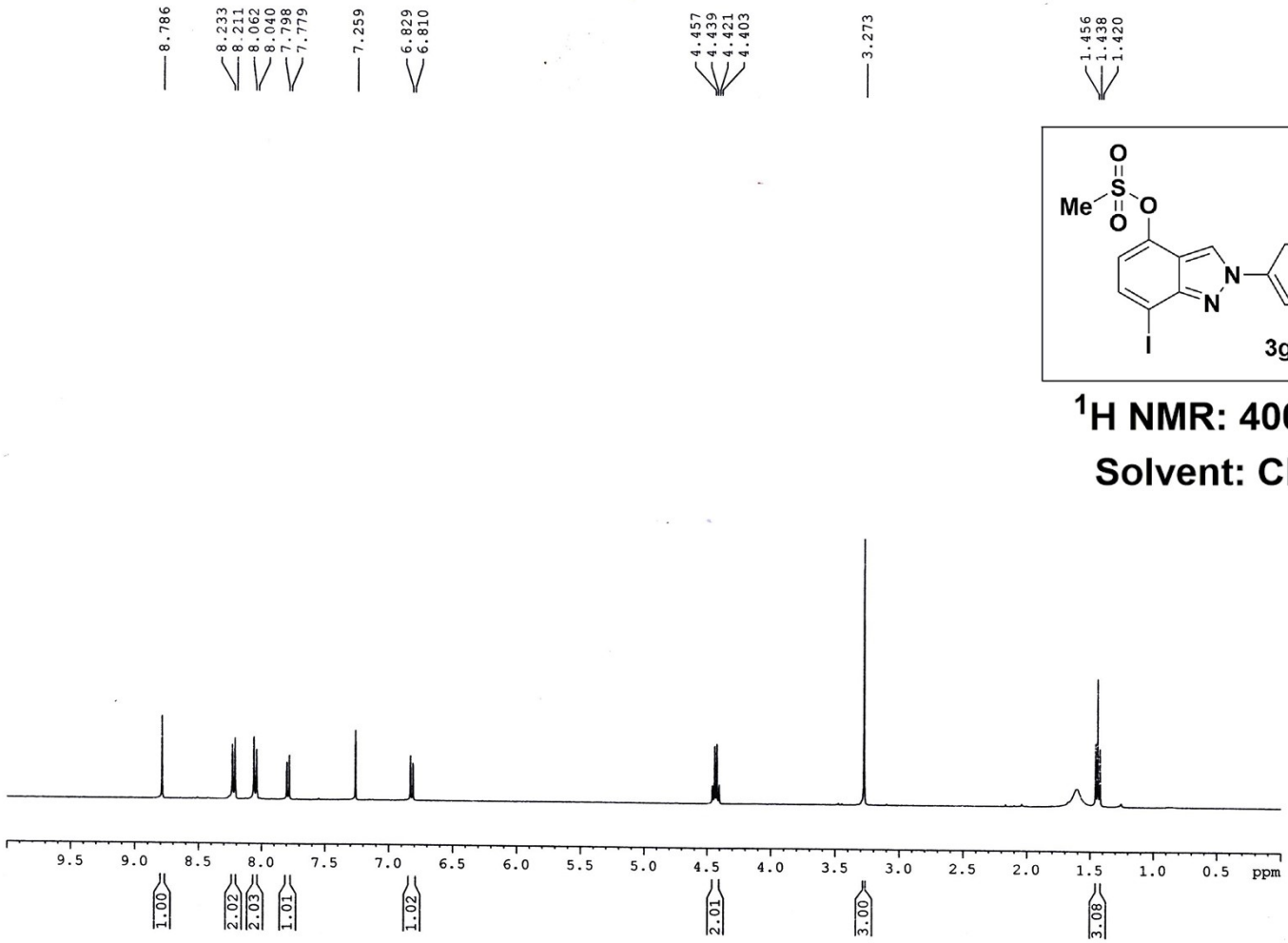


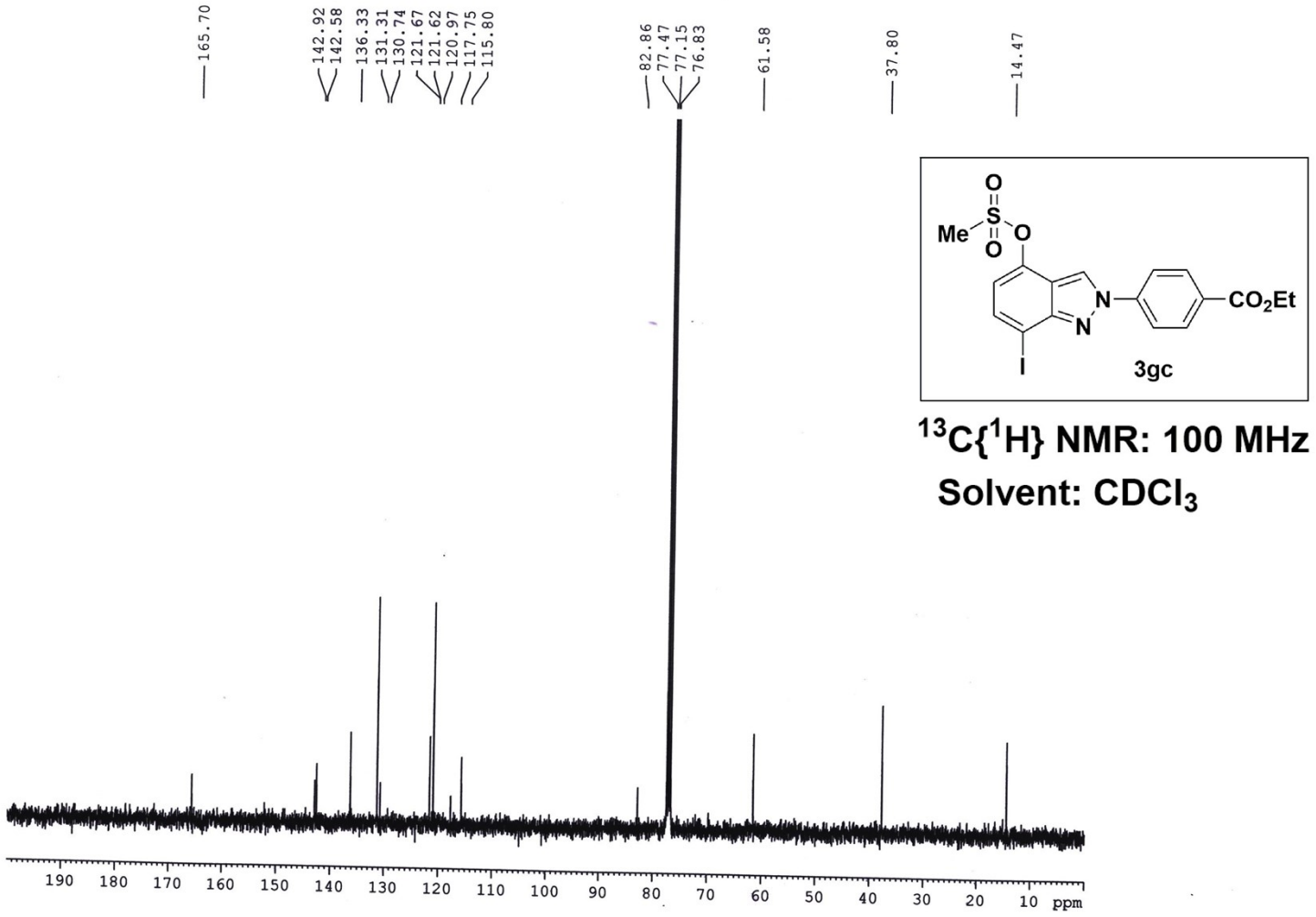
$^{13}C\{^{1}H\}$ NMR: 100 MHz

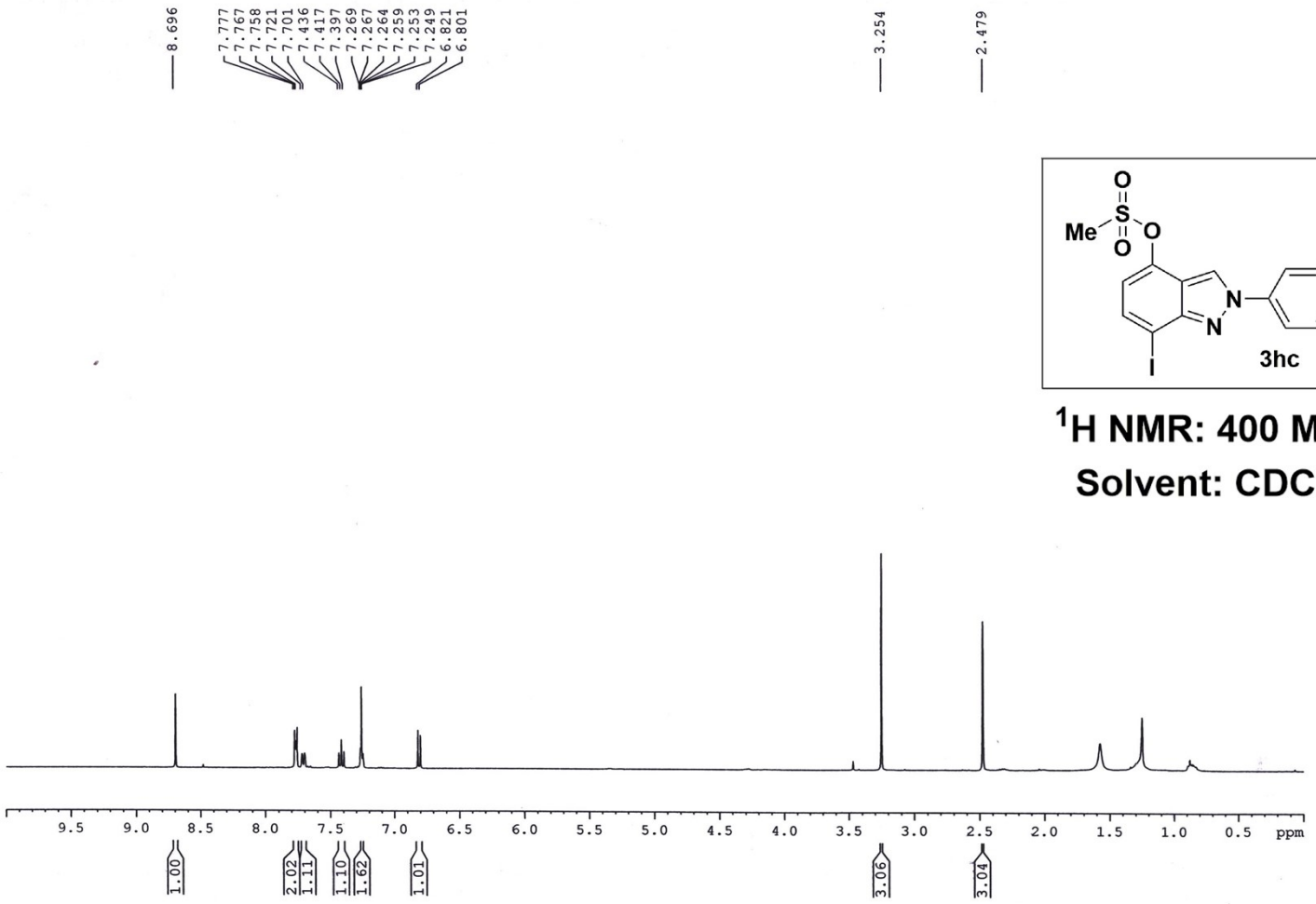
Solvent: $CDCl_3$

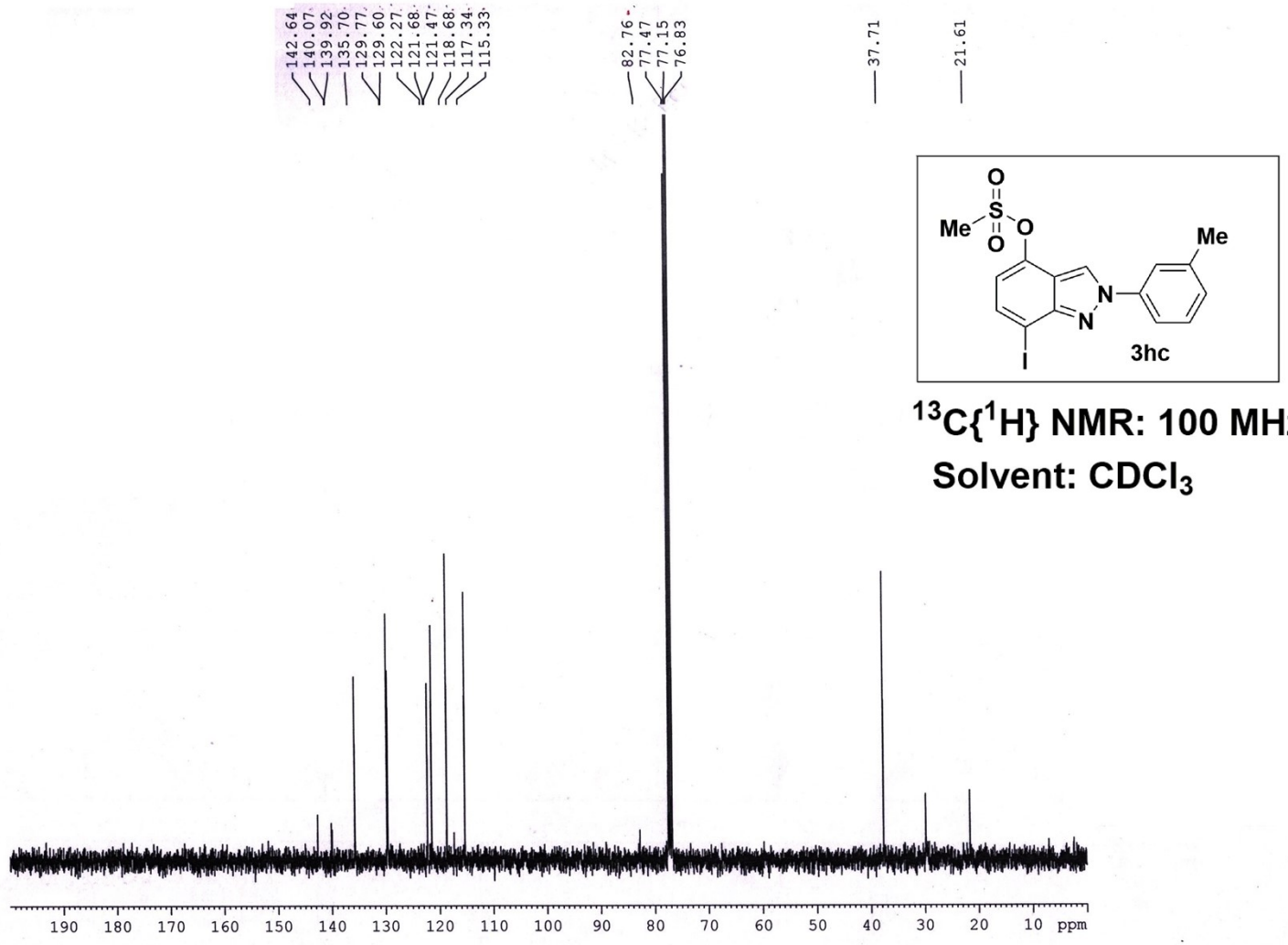

8.693
7.859
7.853
7.849
7.836
7.831
7.824
7.785
7.766
7.689
7.681
7.677
7.664
7.659
7.260
6.819
6.800
3.263
Me
O
S
O
O
O
N
N
Br
I
3fc
1H NMR: 400 MHz
Solvent: CDCl3
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.00
2.02
1.00
2.03
1.02
3.04

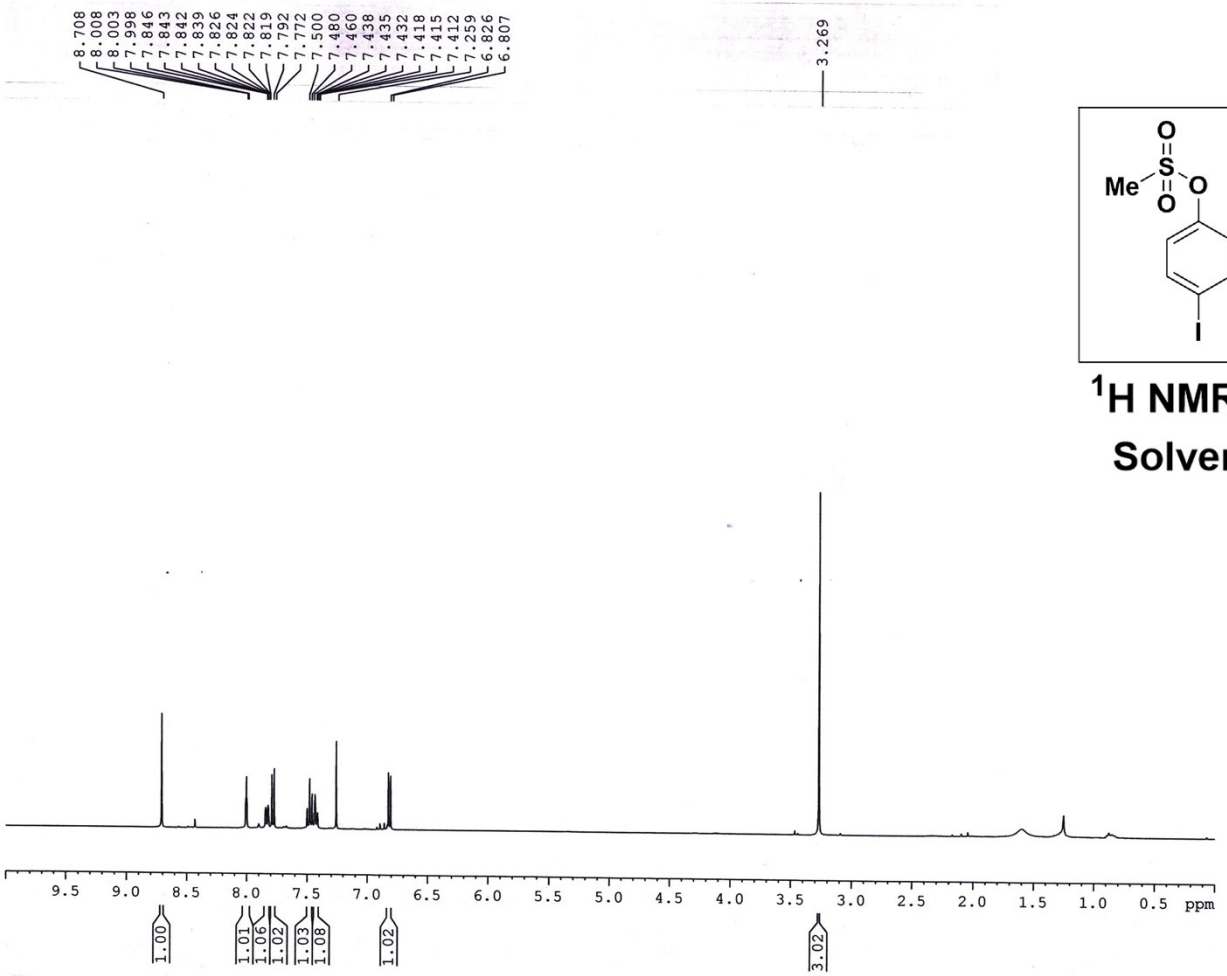

152.02
142.54
138.92
136.08
132.95
122.88
122.72
121.34
117.62
115.65
82.74
77.47
77.15
76.83
37.77
Me
O
S
O
O
O
N
N
Br
I
3fc
13C{1H} NMR: 100 MHz
Solvent: CDCl3
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

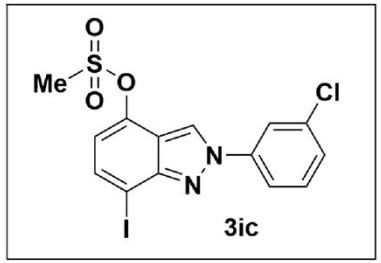

8.786
8.233
8.211
8.062
8.040
7.798
7.779
7.259
6.829
6.810
4.457
4.439
4.421
4.403
3.273
1.456
1.438
1.420
Me
O
S
O
O
O
N
N
CO2Et
I
3gc
1H NMR: 400 MHz
Solvent: CDCl3
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.00
2.02
2.03
1.01
1.02
2.01
3.00
3.08


165.70
142.92
142.58
136.33
131.31
130.74
121.67
121.62
120.97
117.75
115.80
82.86
77.47
77.15
76.83
61.58
37.80
14.47
Me
O
S
O
O
O
N
N
I
CO2Et
3gc
13C{1H} NMR: 100 MHz
Solvent: CDCl3
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


8.696
7.777
7.767
7.758
7.721
7.701
7.436
7.417
7.397
7.269
7.267
7.264
7.259
7.253
7.249
6.821
6.801
3.254
2.479
Me
Me
3hc
1H NMR: 400 MHz
Solvent: CDCl3
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.00
2.02
1.11
1.10
1.62
1.01
3.06
3.04

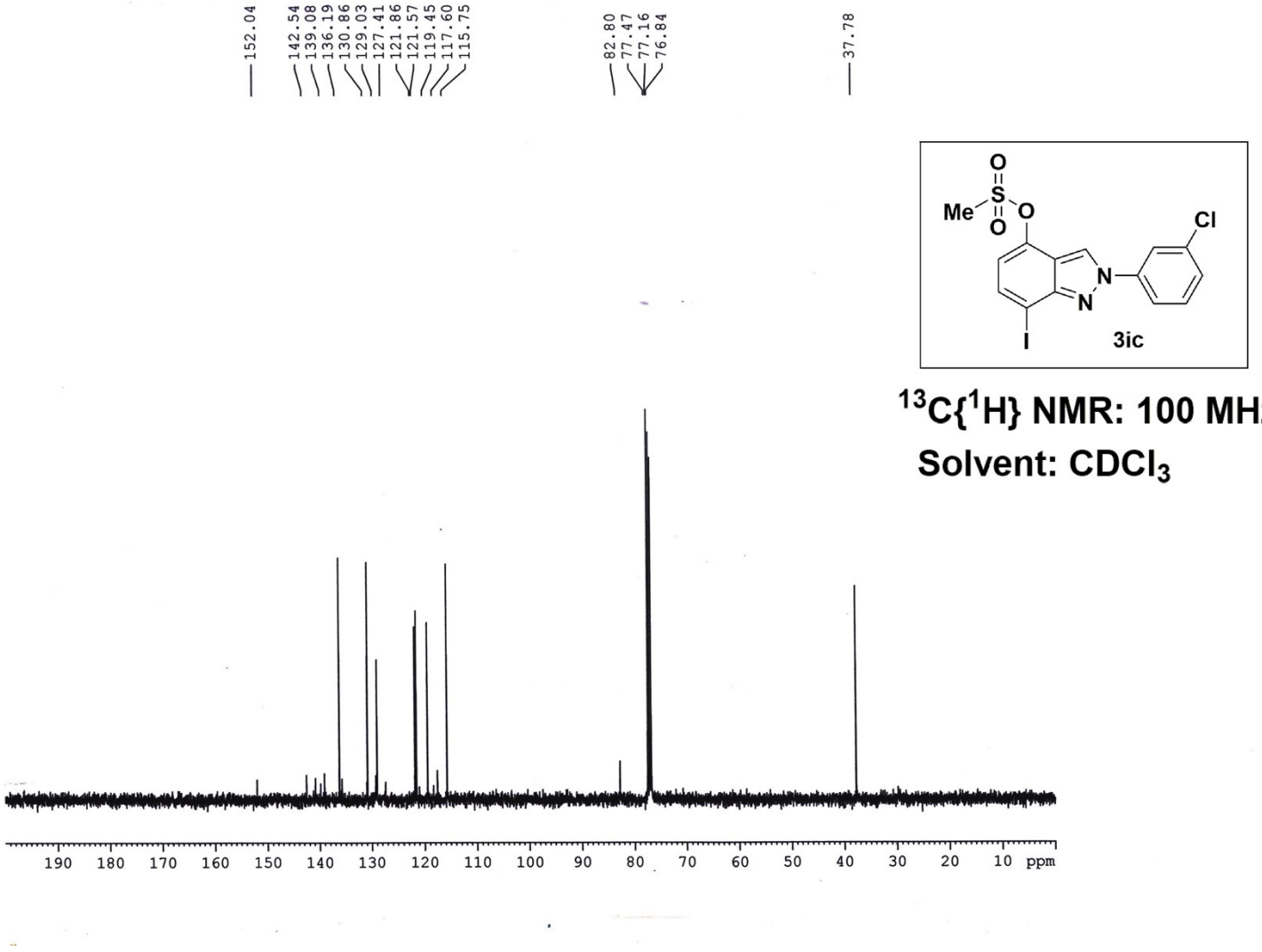

142.64
140.07
139.92
135.70
129.77
129.60
122.27
121.68
121.47
118.68
117.34
115.33
82.76
77.47
77.15
76.83
37.71
21.61
Me
O
S
O
O
O
Me
N
N
I
3hc
13C{1H} NMR: 100 MHz
Solvent: CDCl3
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

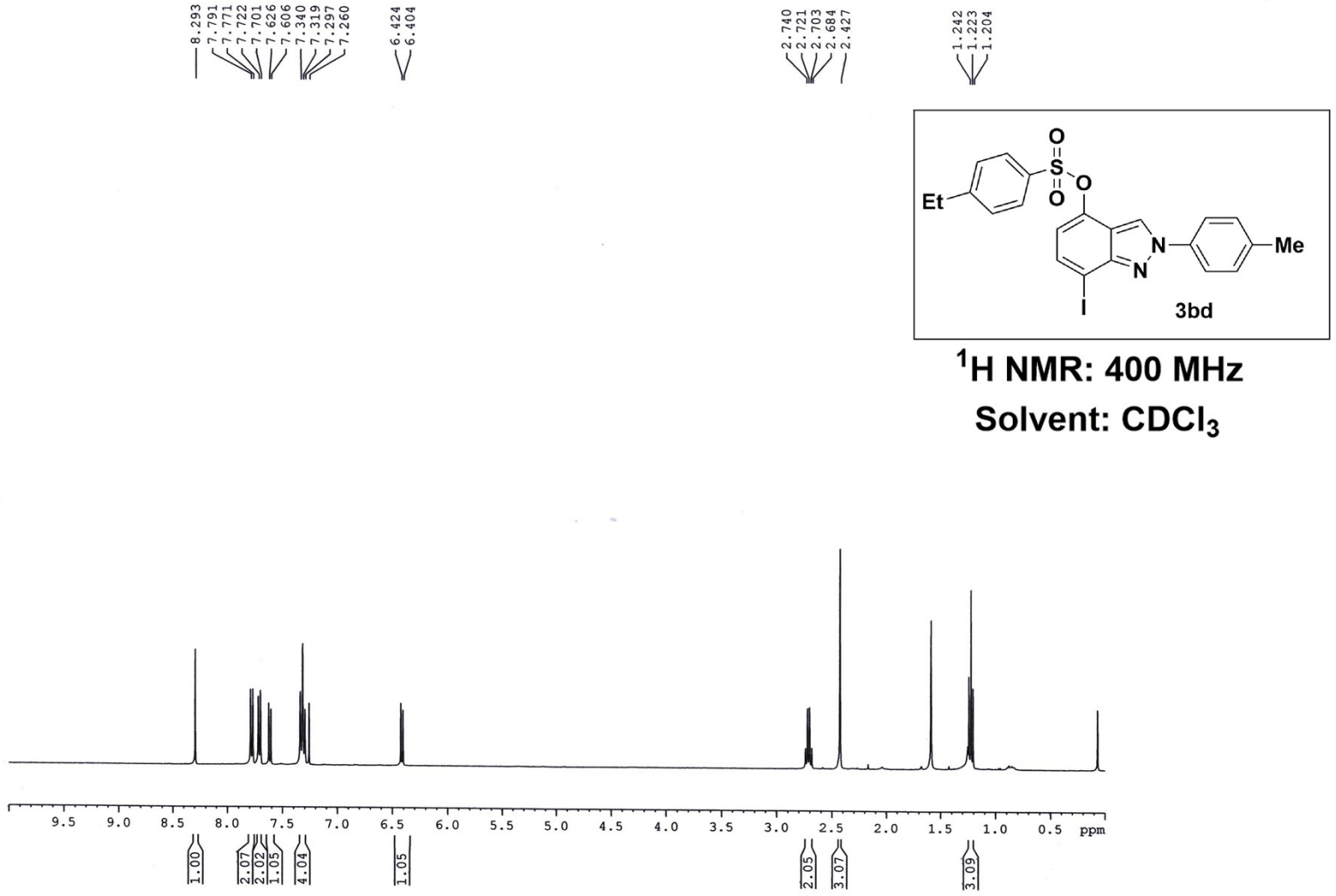


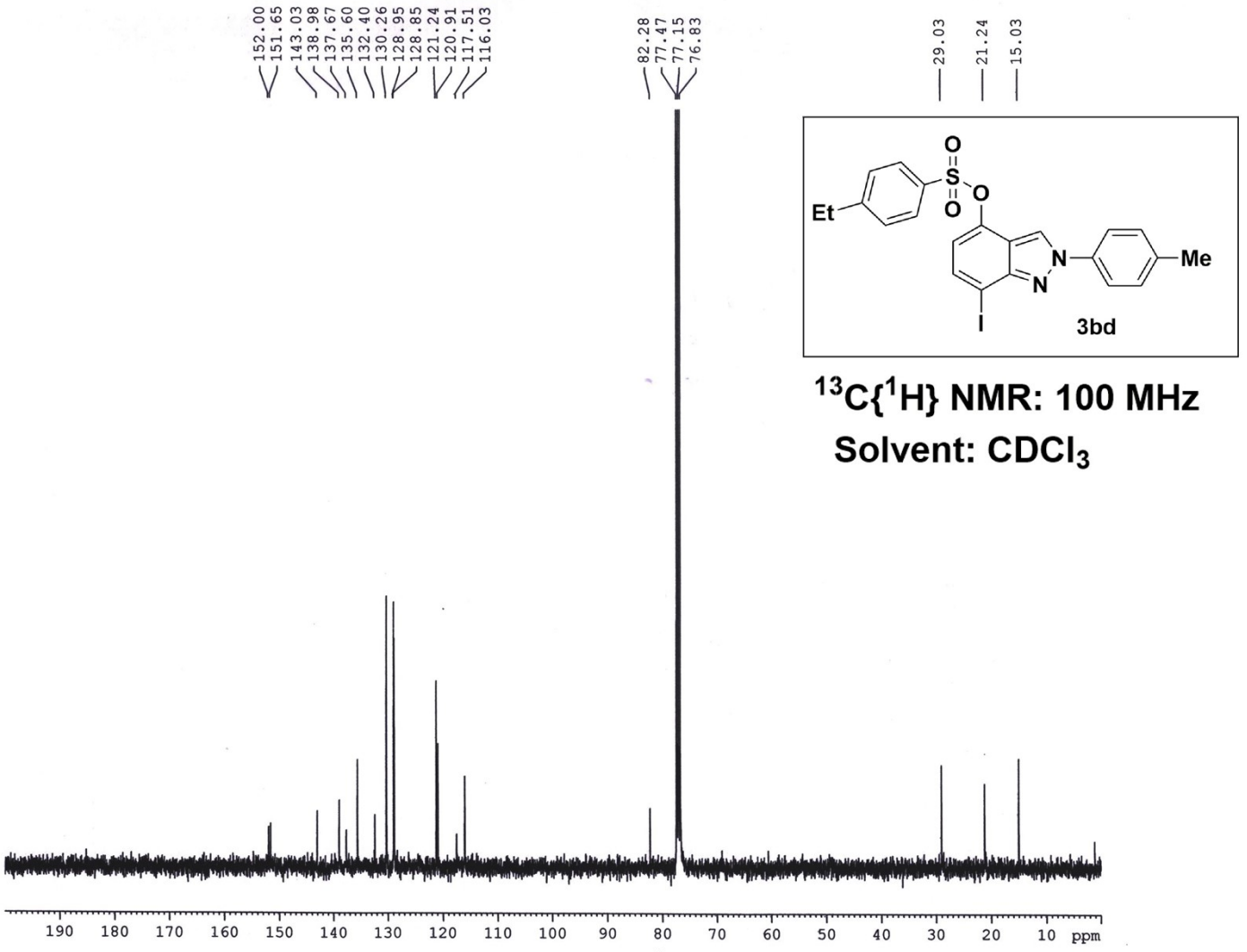


^{1}H NMR: 400 MHz

Solvent: $CDCl_3$

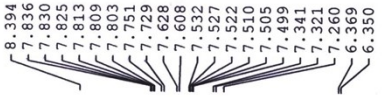

152.04
142.54
139.08
136.19
130.86
129.03
127.41
121.86
121.57
119.45
117.60
115.75
82.80
77.47
77.16
76.84
37.78
Me
O
S
O
O
O
Cl
N
N
I
3ic
13C{1H} NMR: 100 MHz
Solvent: CDCl3
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

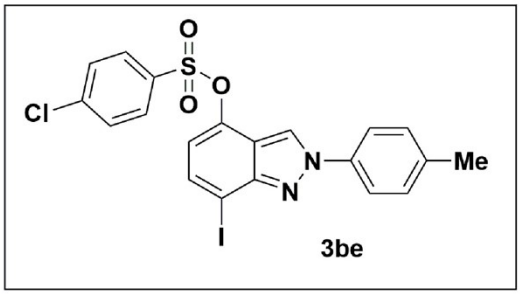

8.293
7.791
7.771
7.722
7.701
7.626
7.606
7.340
7.319
7.297
7.260
6.424
6.404
2.740
2.721
2.703
2.684
2.427
1.242
1.223
1.204
Et
Me
I
3bd
1H NMR: 400 MHz
Solvent: CDCl3
ppm
1.00
2.07
2.02
1.05
4.04
1.05
2.05
3.07
3.09



$^{13}C\{^{1}H\}$ NMR: 100 MHz

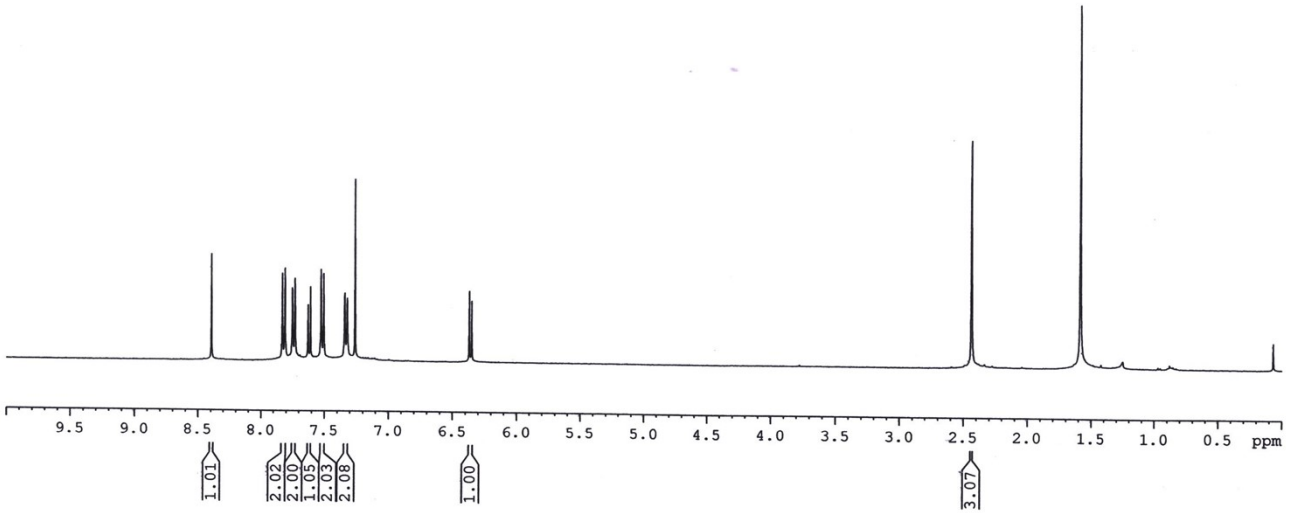
Solvent: $CDCl_3$

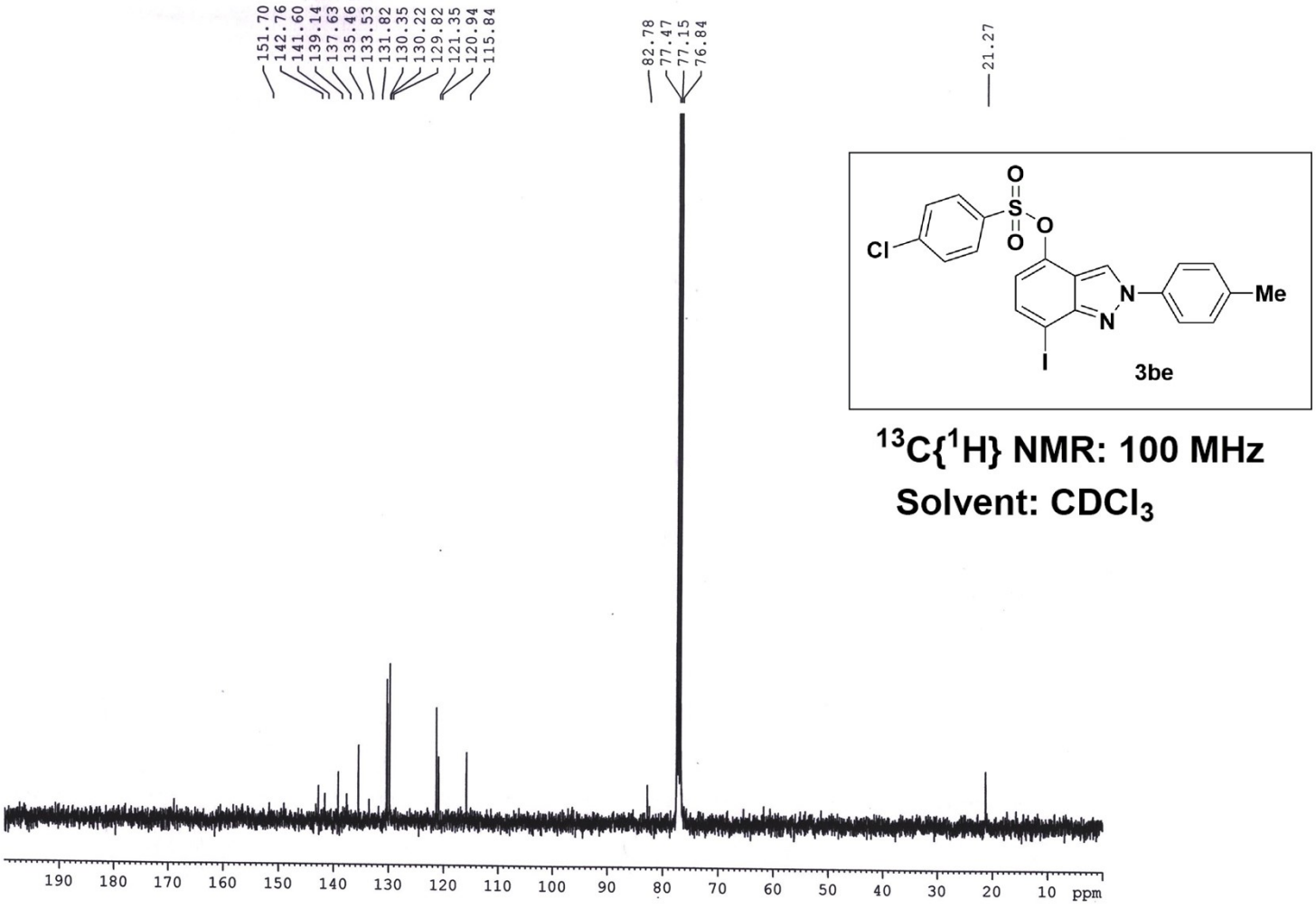




^{1}H NMR: 400 MHz

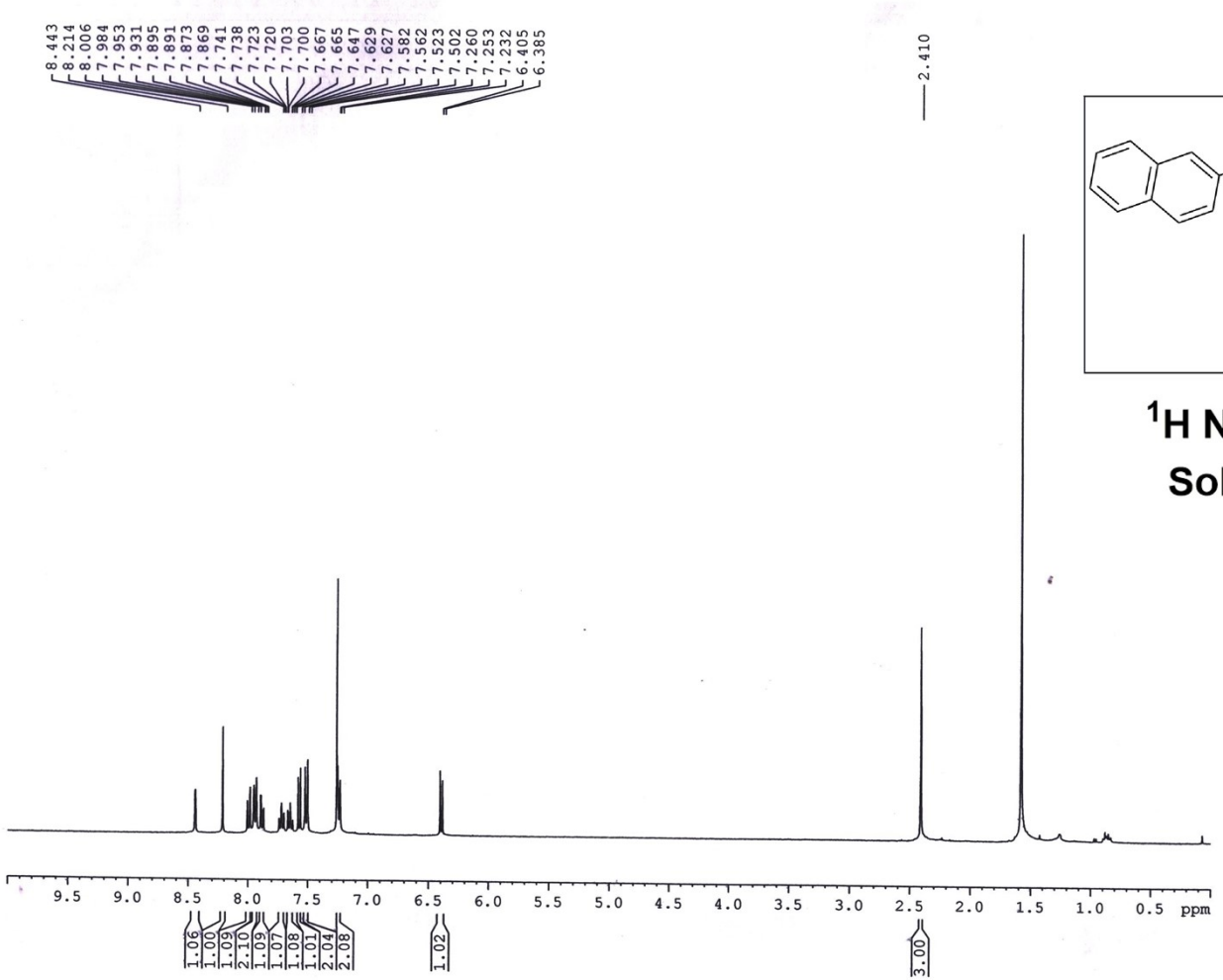
Solvent: $CDCl_3$

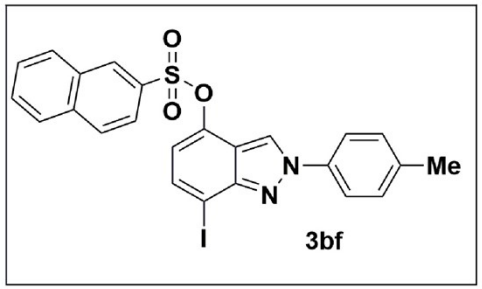




$^{13}C\{^{1}H\}$ NMR: 100 MHz

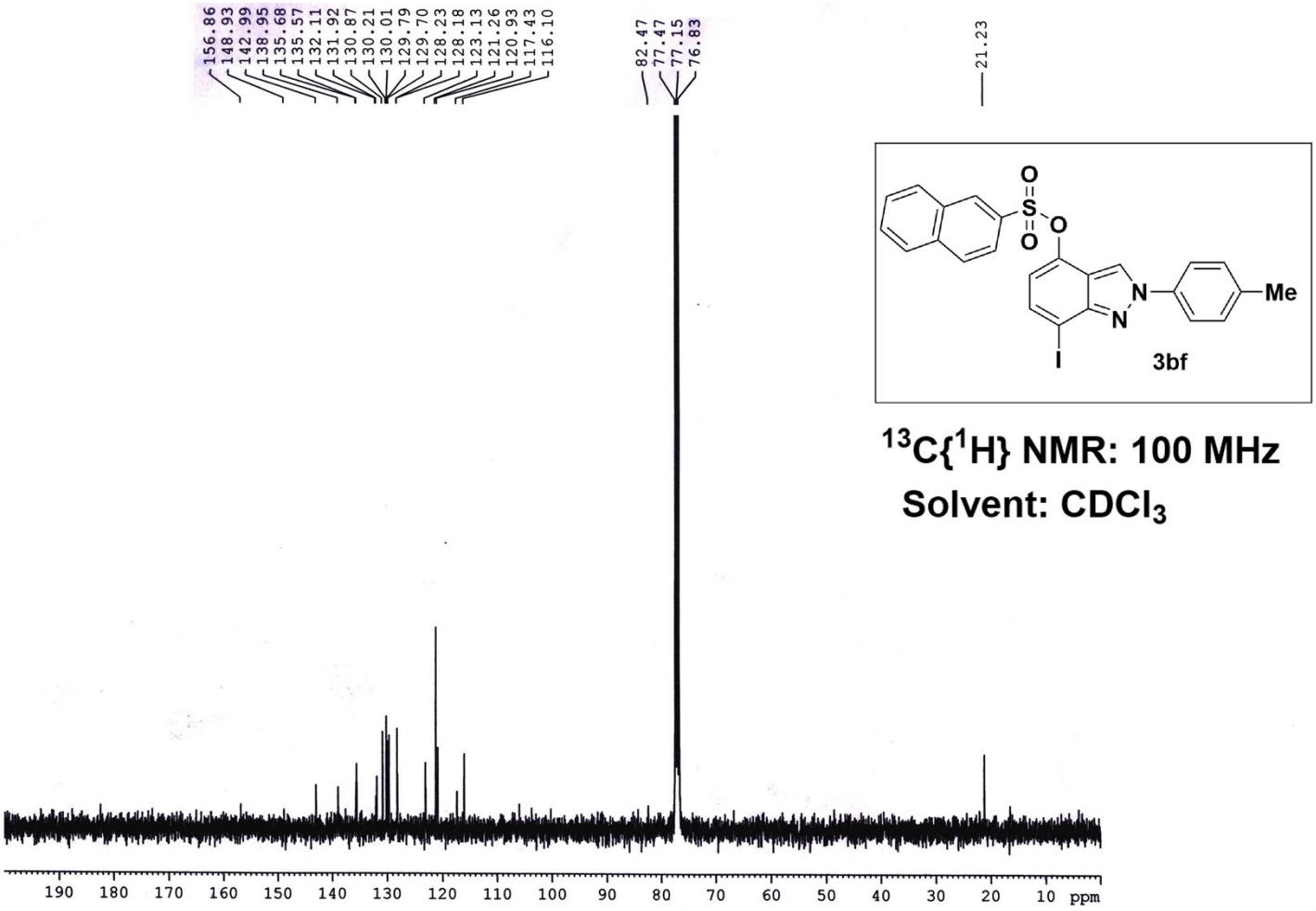
Solvent: $CDCl_3$





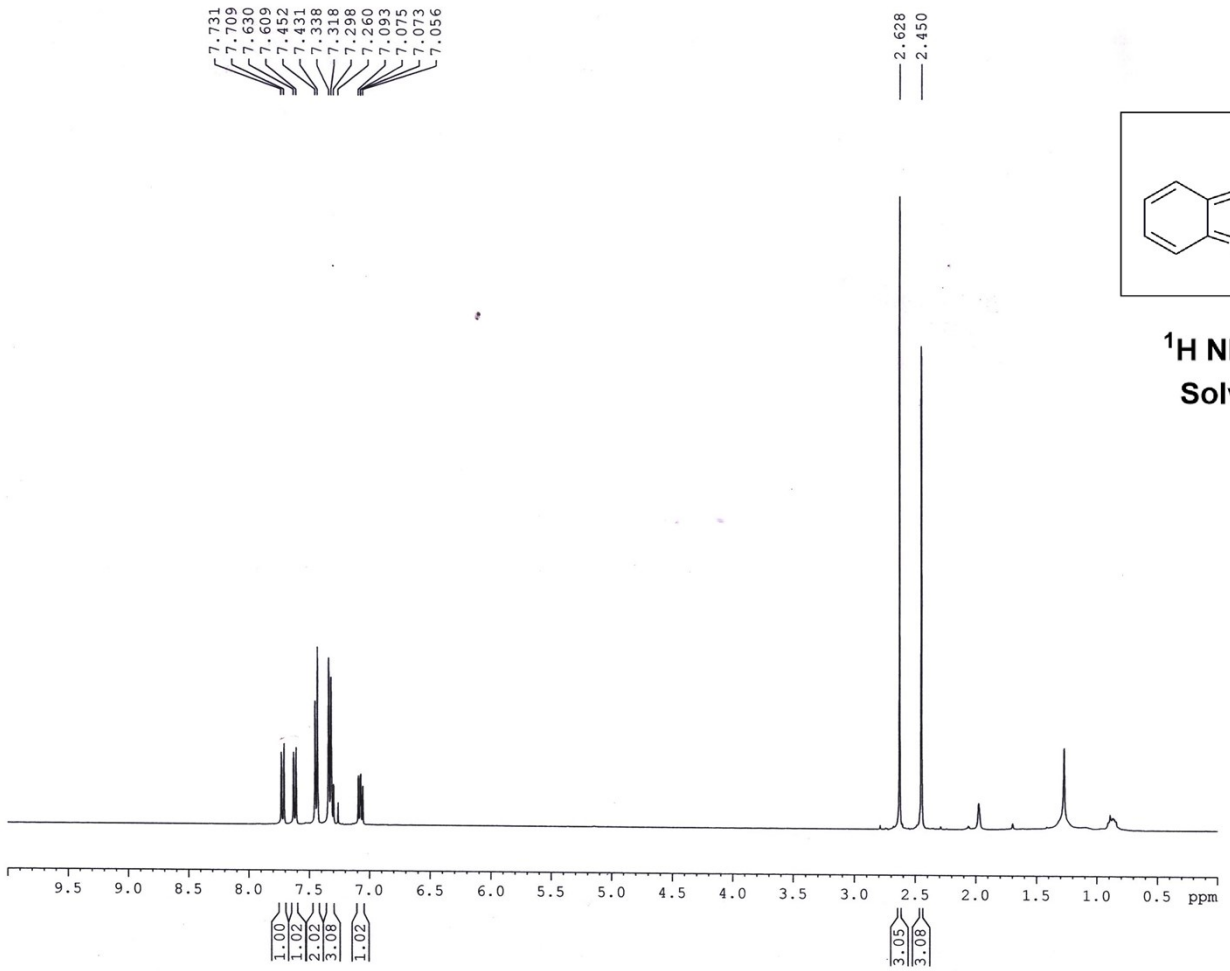
^{1}H NMR: 400 MHz

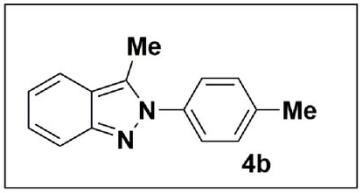
Solvent: $CDCl_3$



$^{13}C\{^{1}H\}$ NMR: 100 MHz

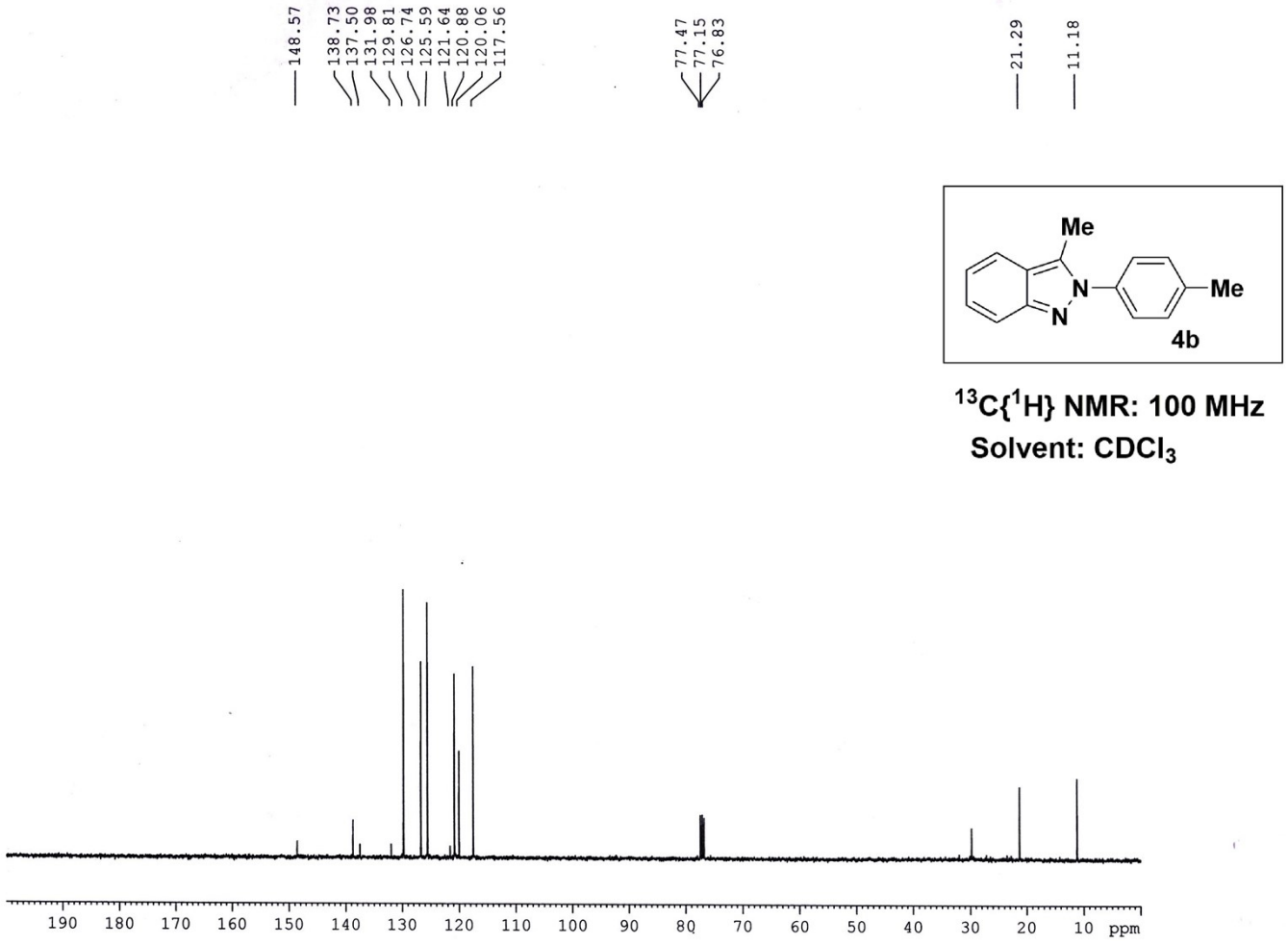
Solvent: $CDCl_3$

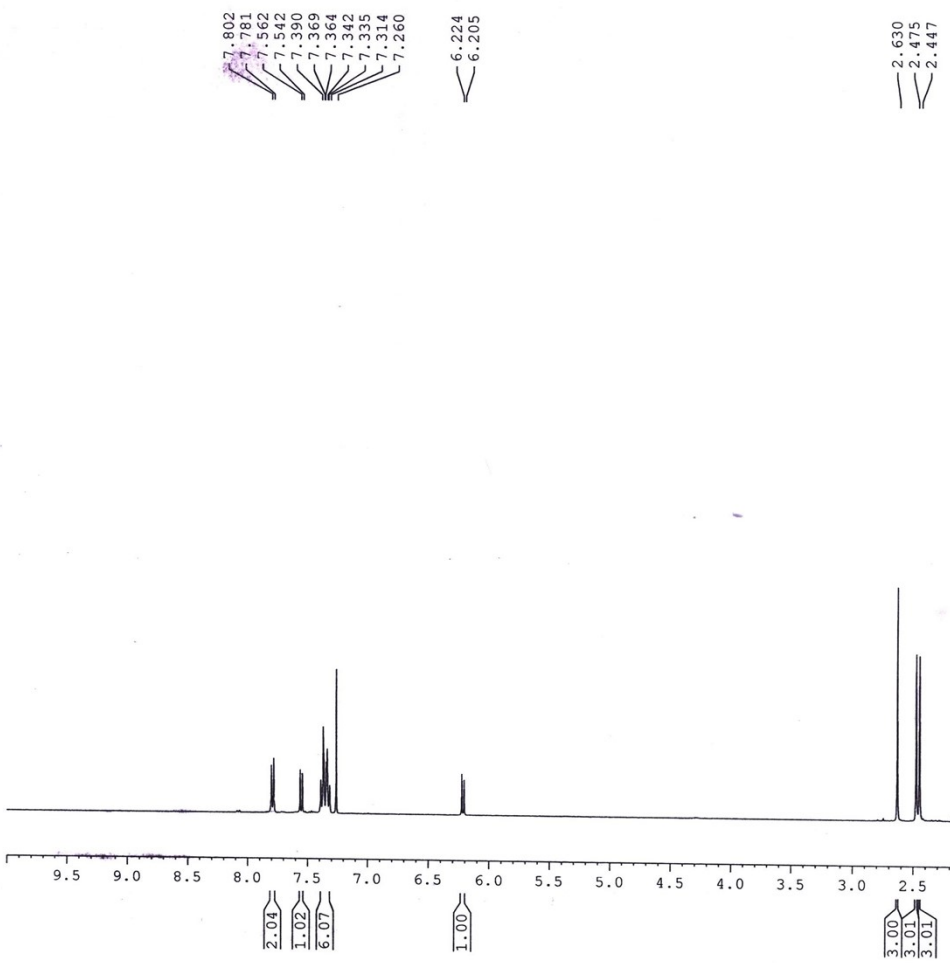


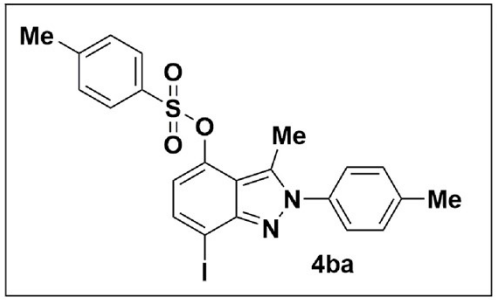


4b

^{1}H NMR: 400 MHz
Solvent: $CDCl_3$

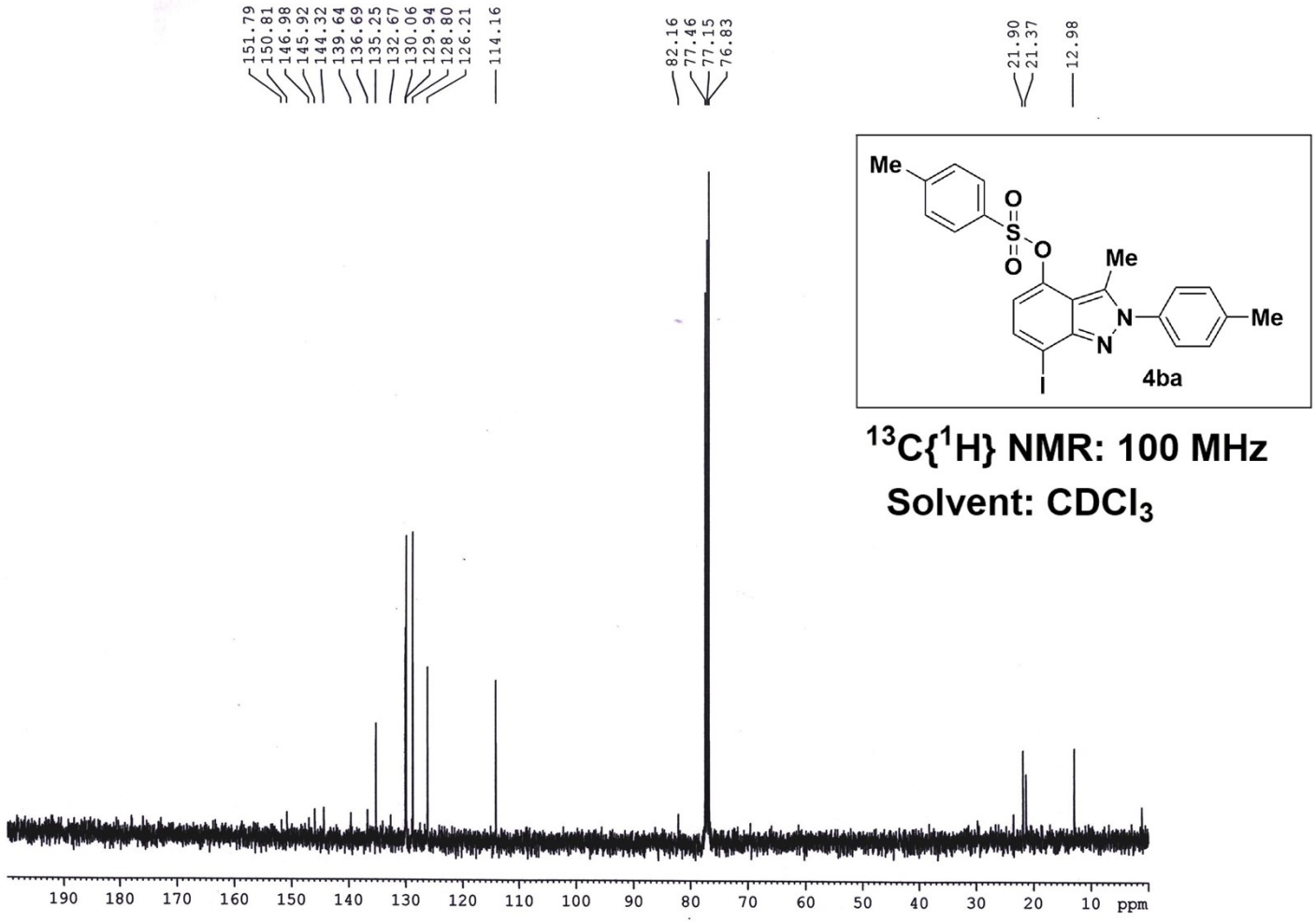

148.57
138.73
137.50
131.98
129.81
126.74
125.59
121.64
120.88
120.06
117.56
77.47
77.15
76.83
21.29
11.18
Me
N
N
Me
4b
13C{1H} NMR: 100 MHz
Solvent: CDCl3
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

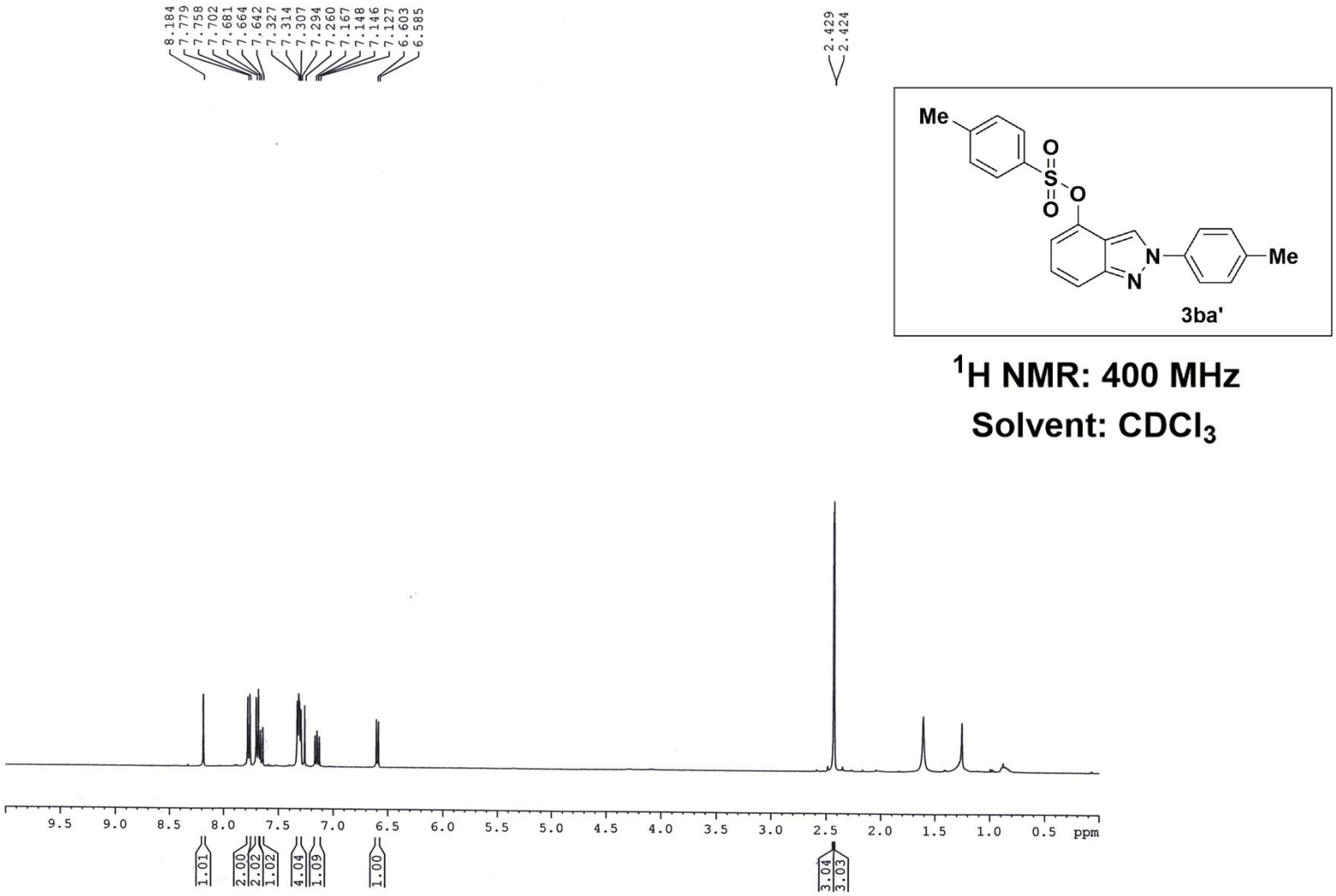


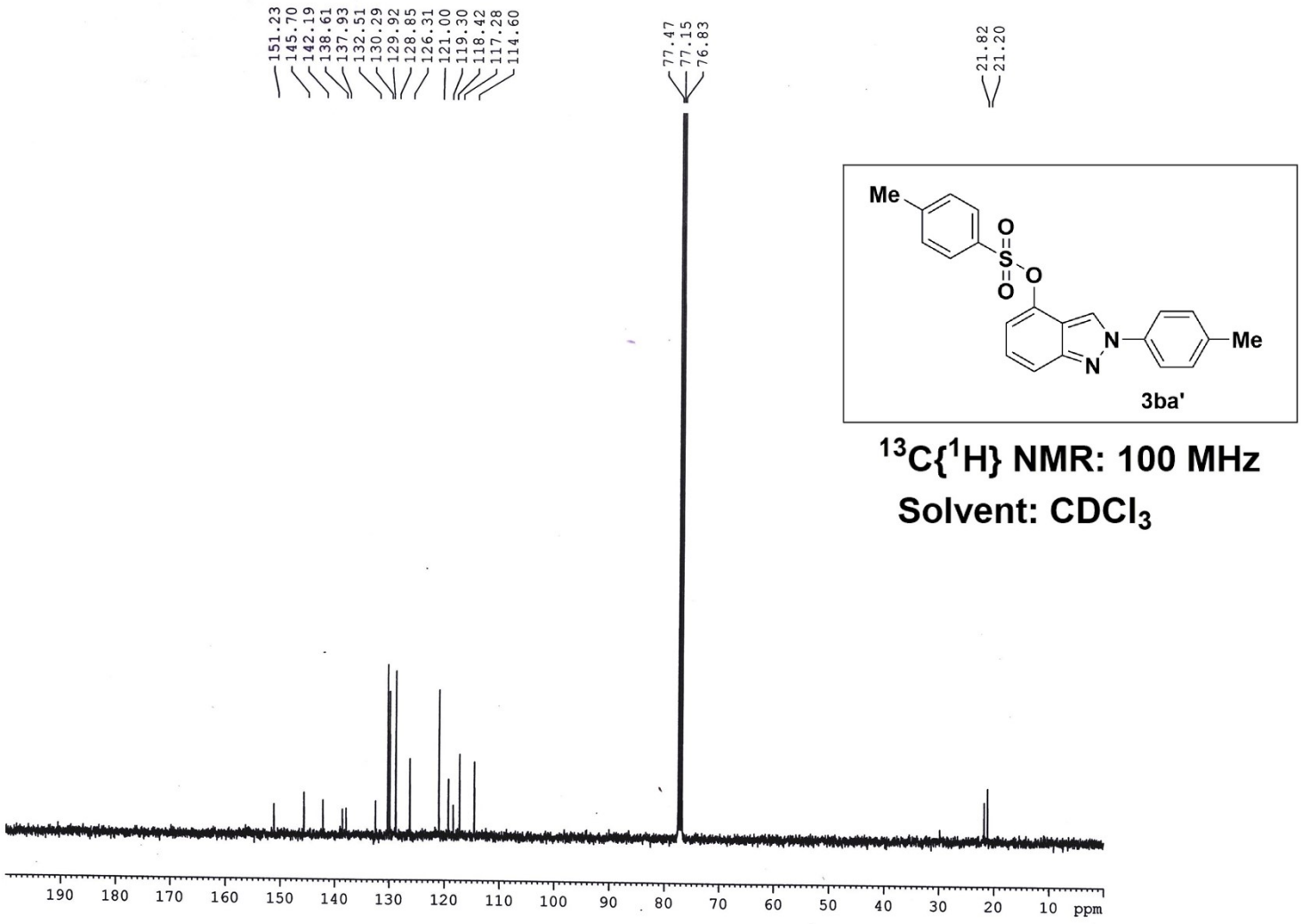


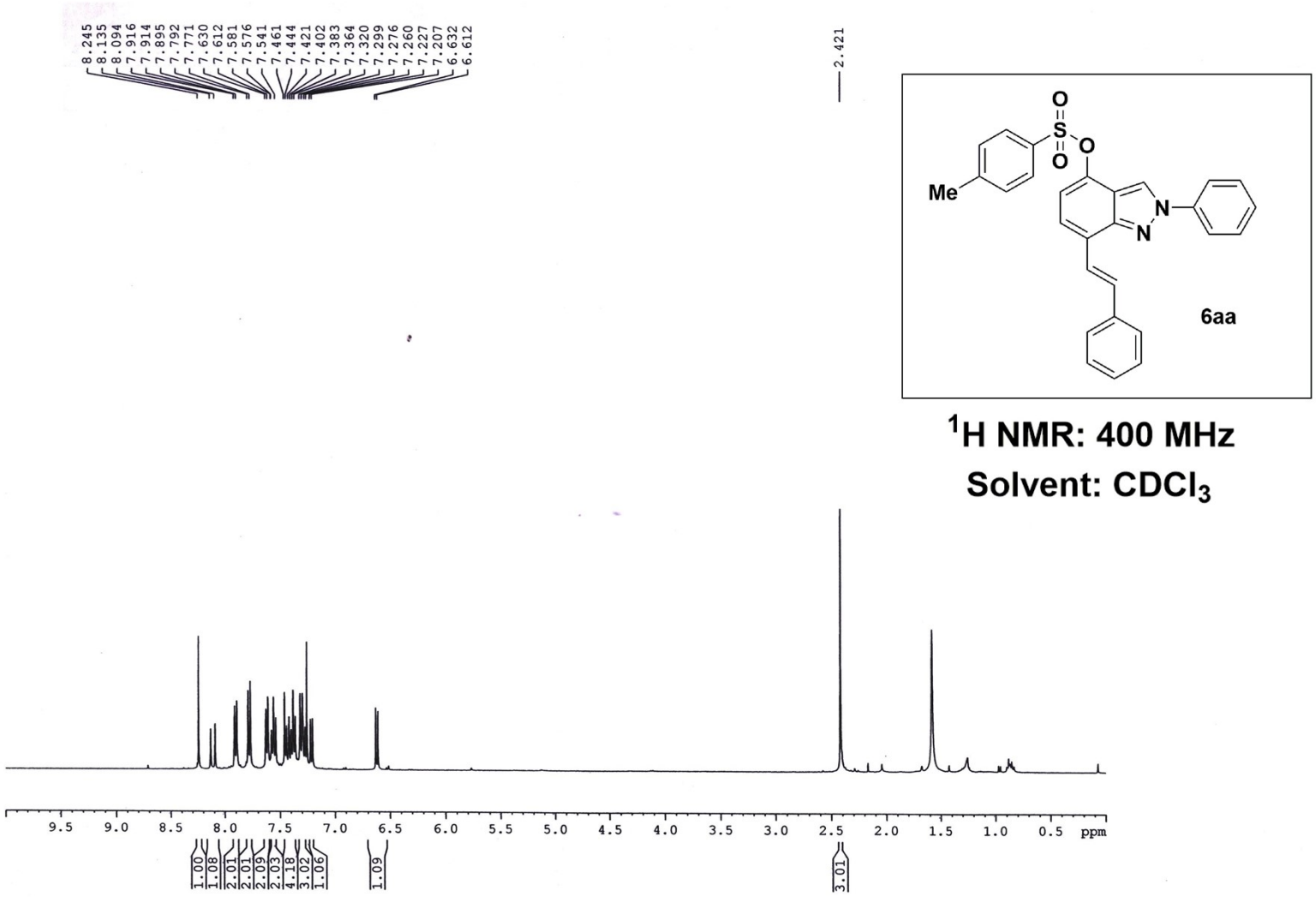
^{1}H NMR: 400 MHz

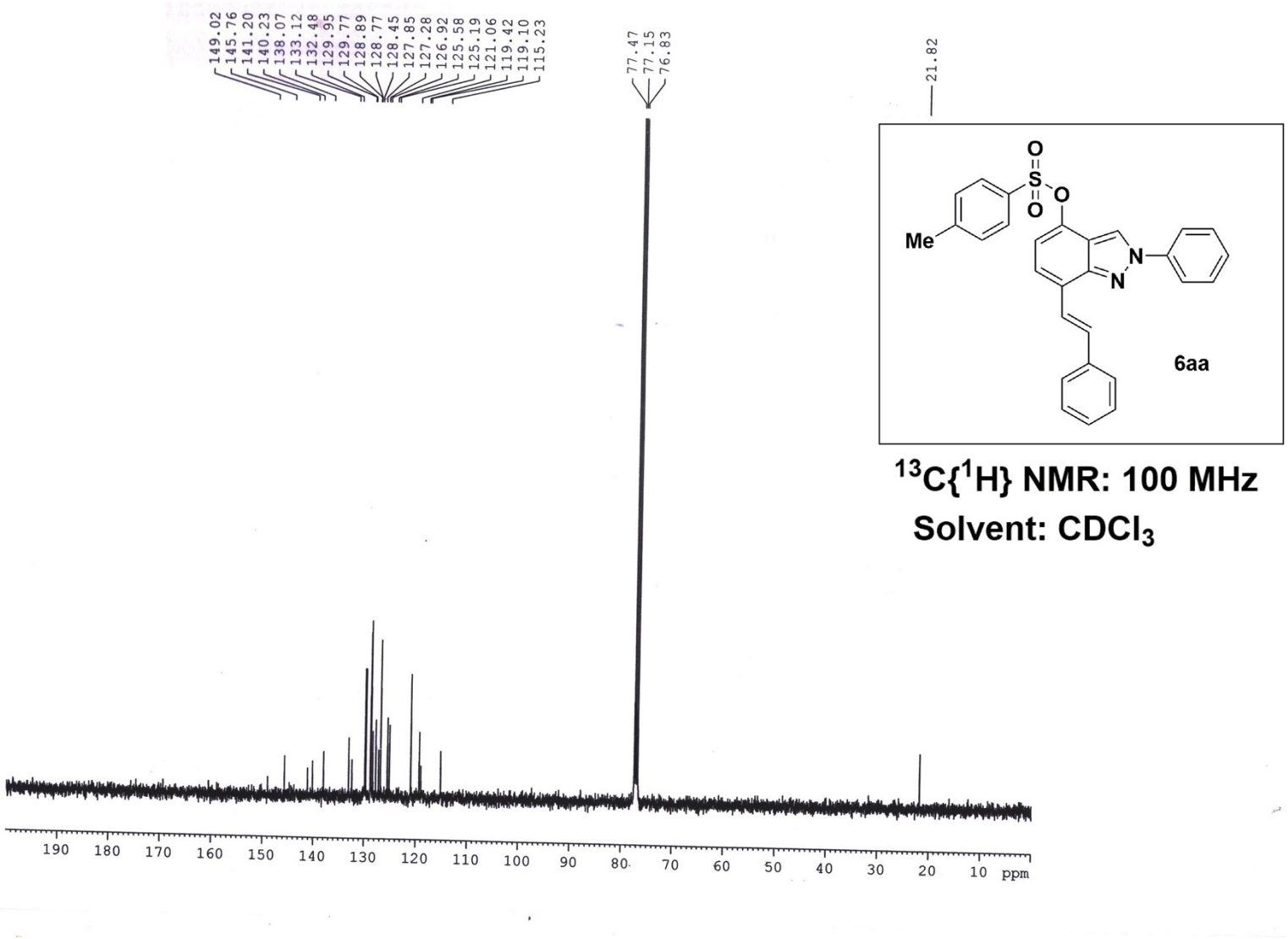
Solvent: $CDCl_3$


151.79
150.81
146.98
145.92
144.32
139.64
136.69
135.25
132.67
130.06
129.94
128.80
126.21
114.16
82.16
77.46
77.15
76.83
21.90
21.37
12.98
Me
O
S
O
O
Me
N
N
Me
I
4ba
13C{1H} NMR: 100 MHz
Solvent: CDCl3
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


8.184
7.779
7.758
7.702
7.681
7.664
7.642
7.327
7.314
7.307
7.294
7.260
7.167
7.148
7.146
7.127
6.603
6.585
2.429
2.424
Me
O
S
O
O
O
N
N
Me
3ba'
1H NMR: 400 MHz
Solvent: CDCl3
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.01
2.00
2.02
1.02
4.04
1.09
1.00
3.04
3.03

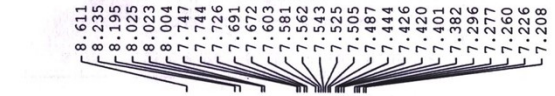

151.23
145.70
142.19
138.61
137.93
132.51
130.29
129.92
128.85
126.31
121.00
119.30
118.42
117.28
114.60
77.47
77.15
76.83
21.82
21.20
Me
O
S
O
O
O
N
N
Me
3ba'
13C{1H} NMR: 100 MHz
Solvent: CDCl3
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

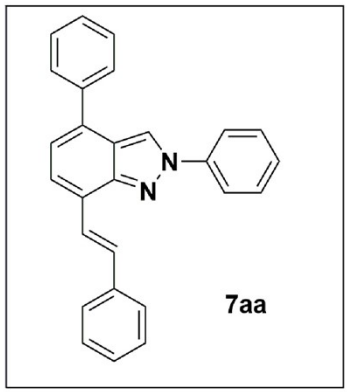

8.245
8.135
8.094
7.916
7.914
7.895
7.792
7.771
7.630
7.612
7.581
7.576
7.541
7.461
7.444
7.421
7.402
7.383
7.364
7.320
7.299
7.276
7.260
7.227
7.207
6.632
6.612
2.421
Me
6aa
1H NMR: 400 MHz
Solvent: CDCl3
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.00 1.08 2.01 2.01 2.09 2.03 4.18 3.02 1.06
1.09
3.01



$^{13}C\{^{1}H\}$ NMR: 100 MHz

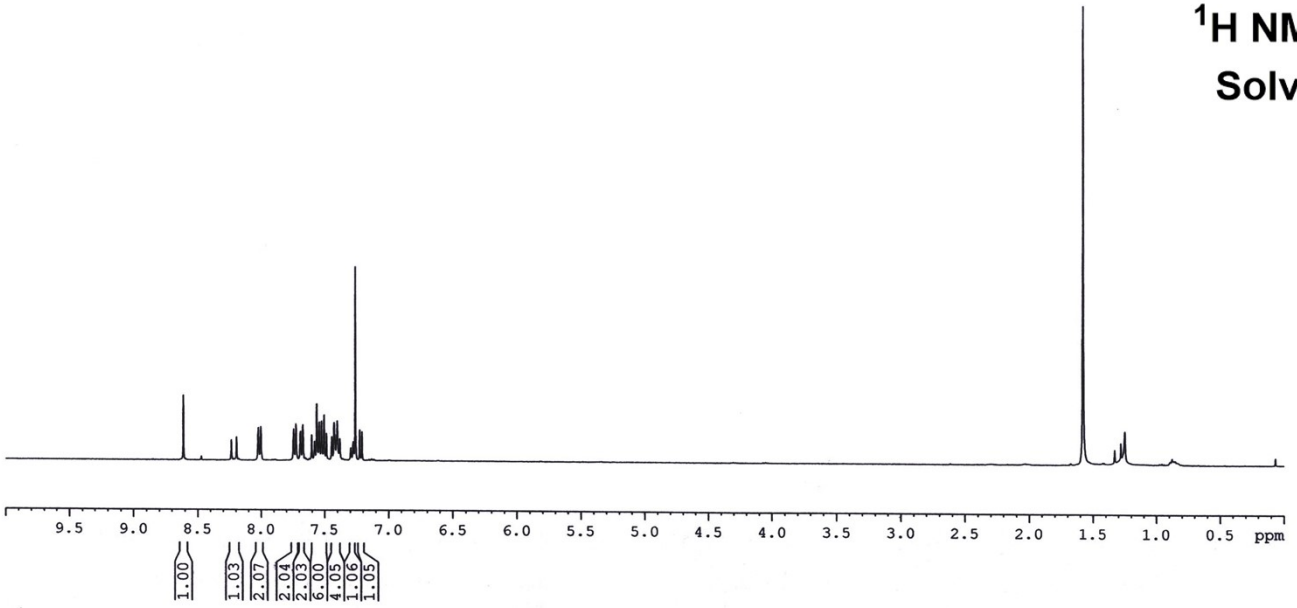
Solvent: $CDCl_3$

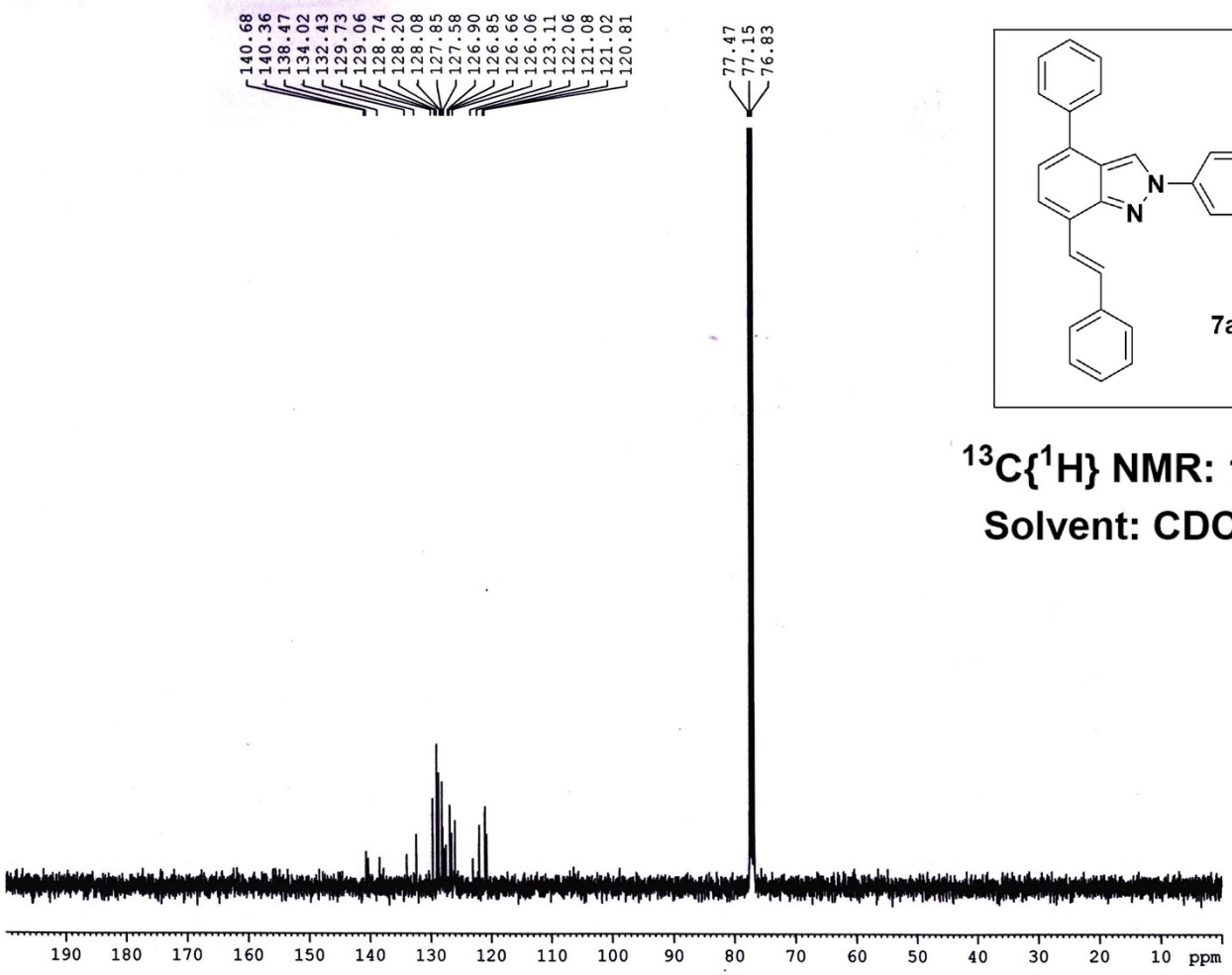




^{1}H NMR: 400 MHz

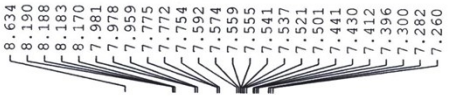
Solvent: $CDCl_3$

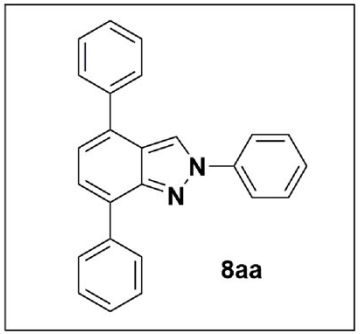




$^{13}C\{^{1}H\}$ NMR: 100 MHz

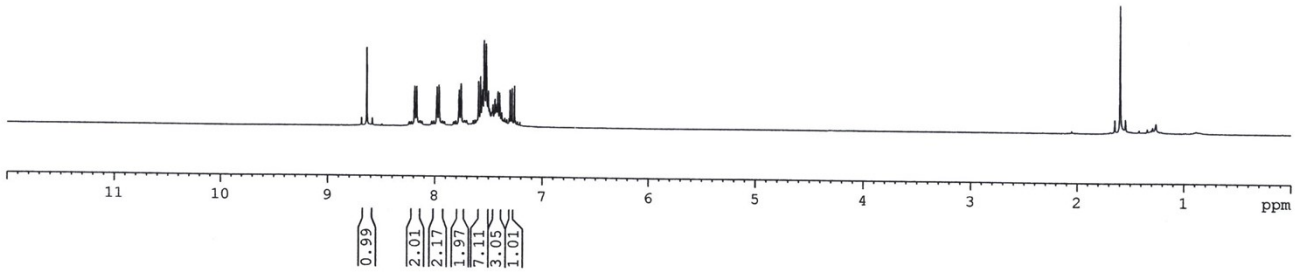
Solvent: $CDCl_3$

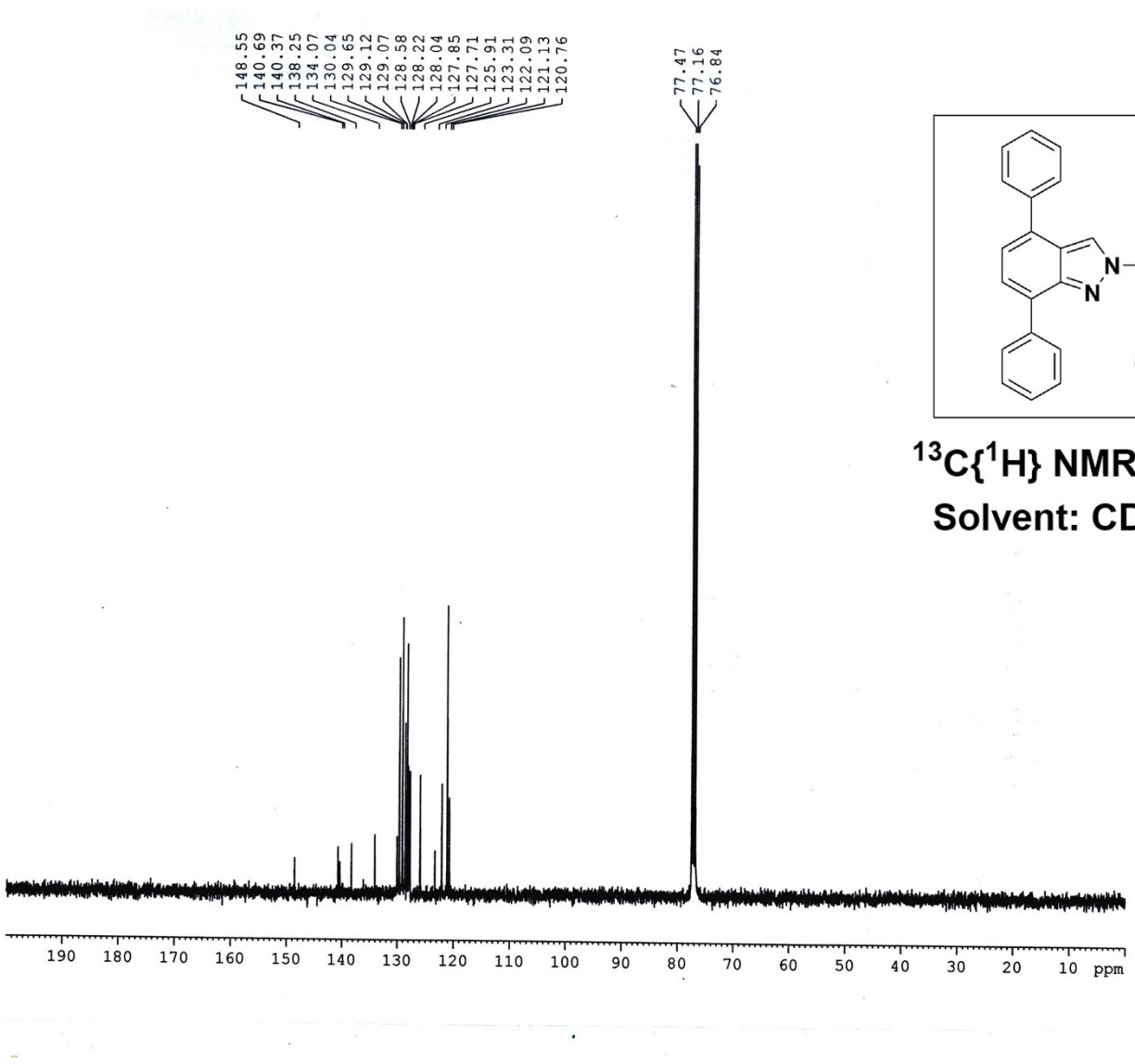




^{1}H NMR: 400 MHz

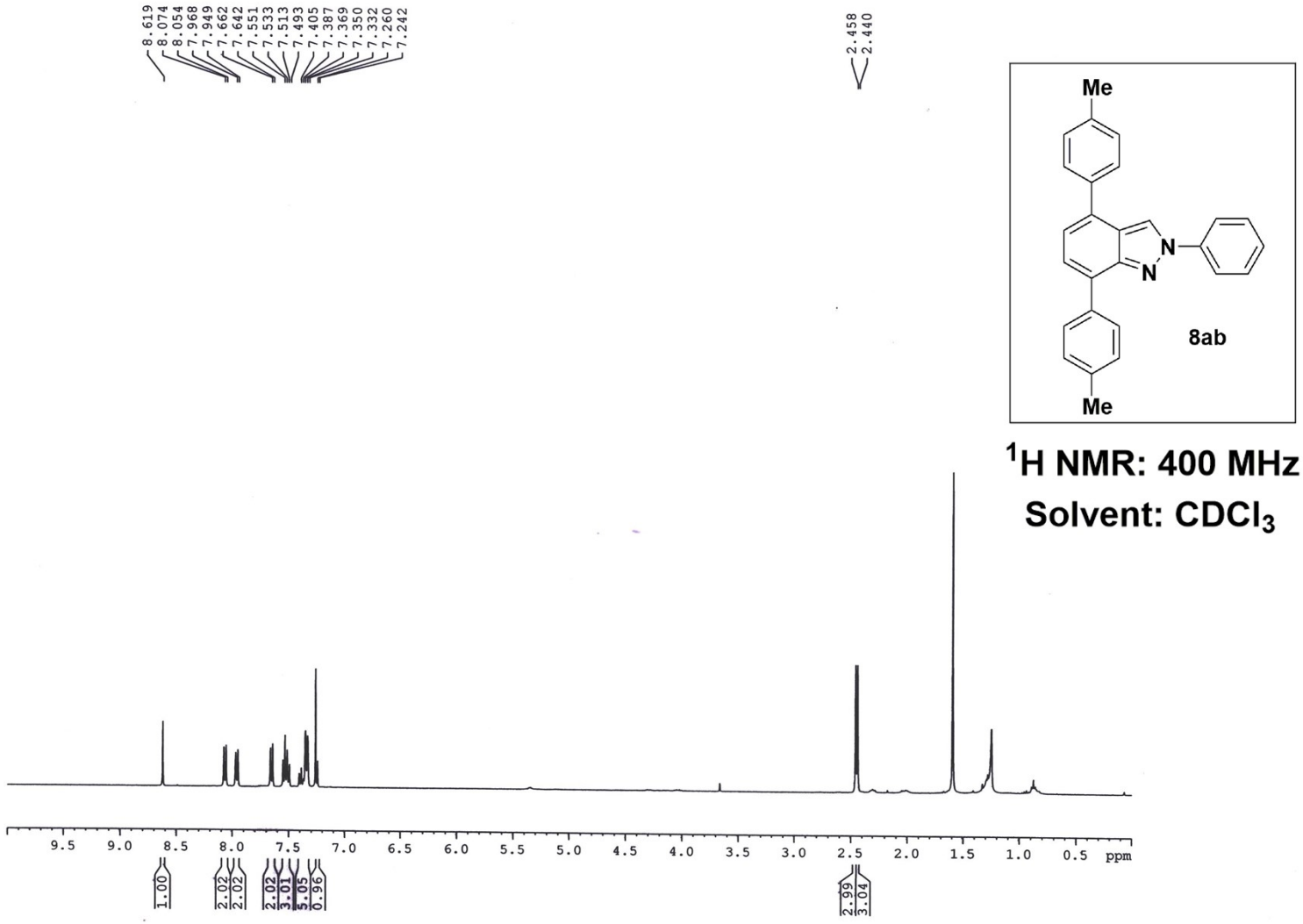
Solvent: $CDCl_3$

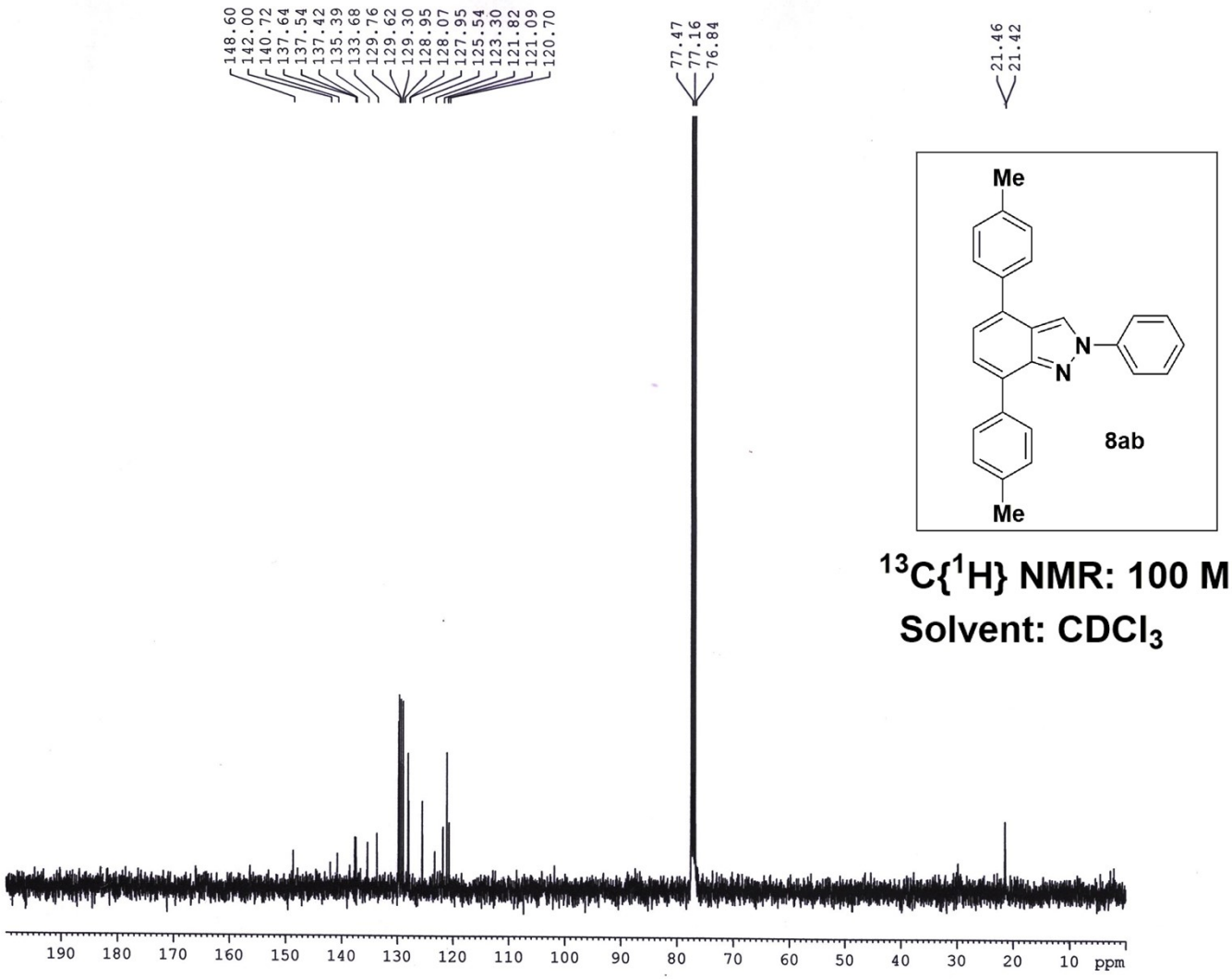


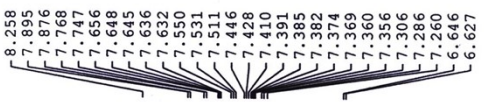


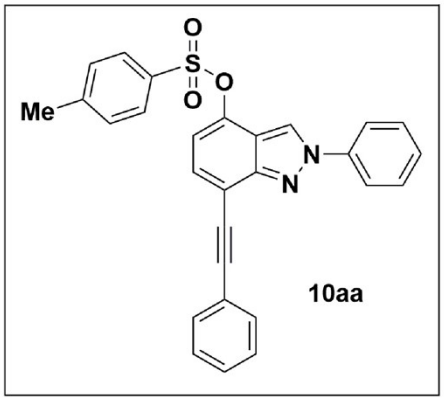
$^{13}C\{^{1}H\}$ NMR: 100 MHz

Solvent: $CDCl_3$


8.619
8.074
8.054
7.968
7.949
7.662
7.642
7.551
7.533
7.513
7.493
7.405
7.387
7.369
7.350
7.332
7.260
7.242
2.458
2.440
Me
N
N
8ab
Me
1H NMR: 400 MHz
Solvent: CDCl3
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.00
2.02
2.02
2.02
3.01
3.05
0.96
2.99
3.04

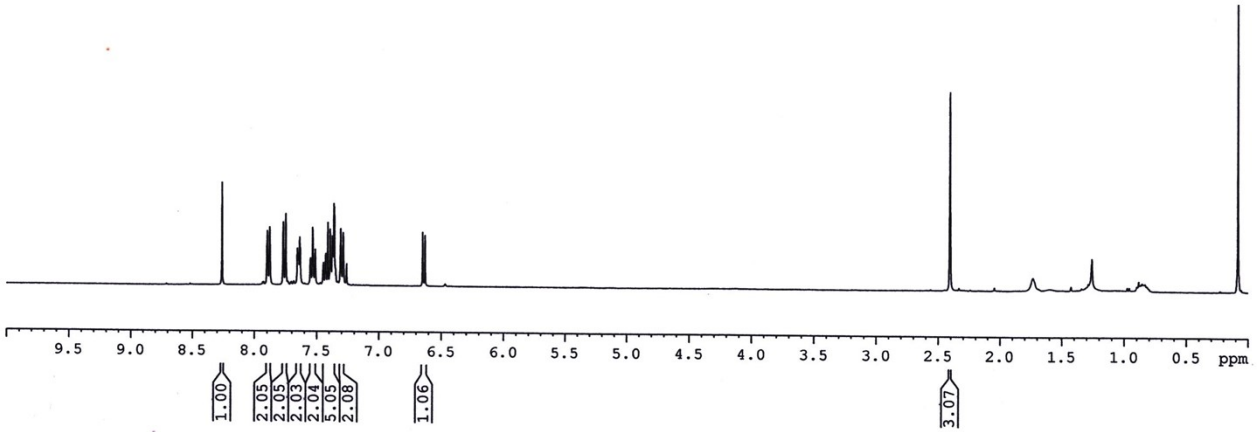

148.60
142.00
140.72
137.64
137.54
137.42
135.39
133.68
129.76
129.62
129.30
128.95
128.07
127.95
125.54
123.30
121.82
121.09
120.70
77.47
77.16
76.84
21.46
21.42
Me
N
N
Me
8ab
$^{13}C\{^{1}H\}$ NMR: 100 MHz
Solvent: $CDCl_3$
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

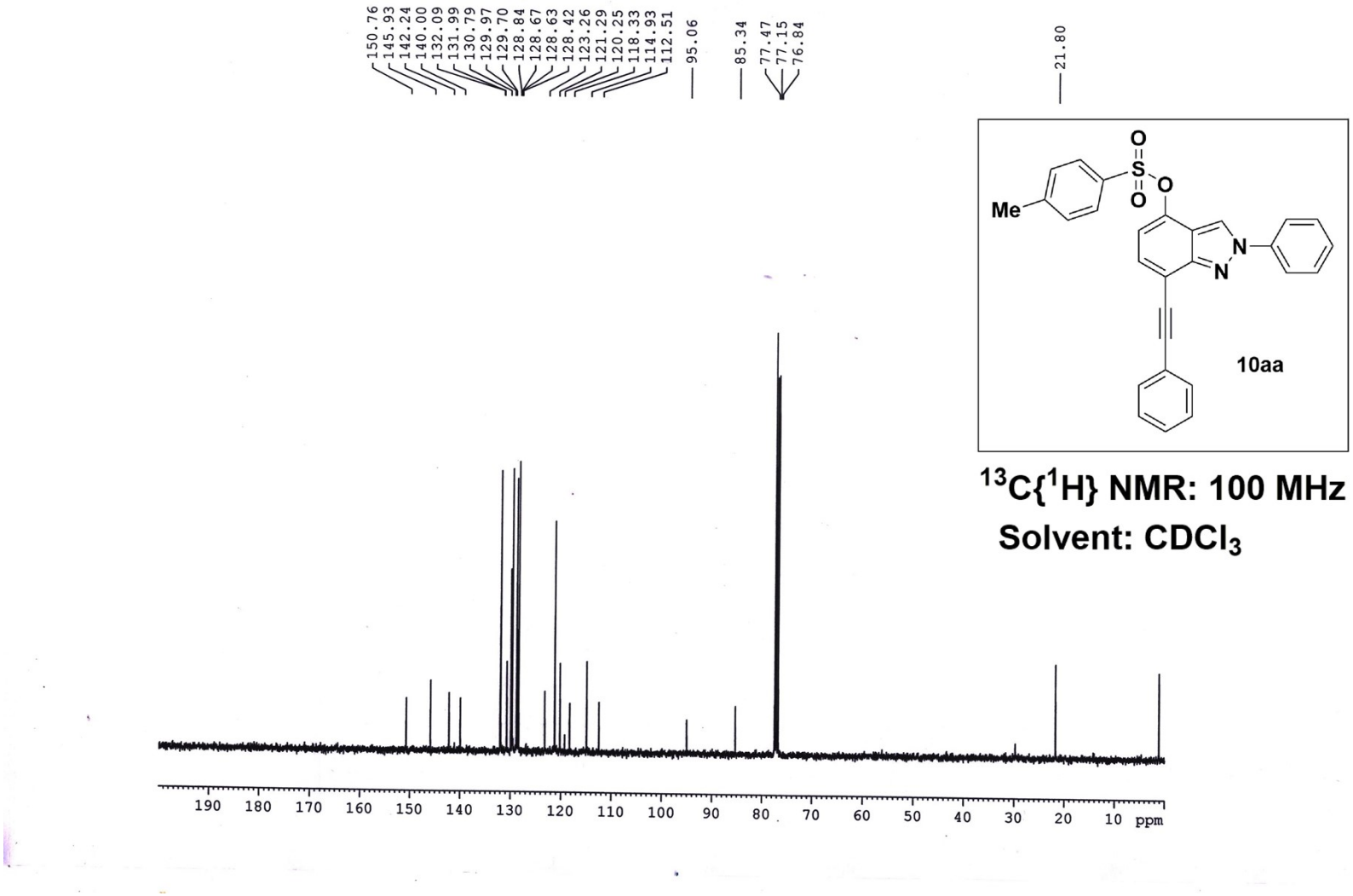


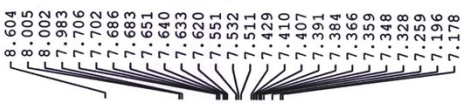


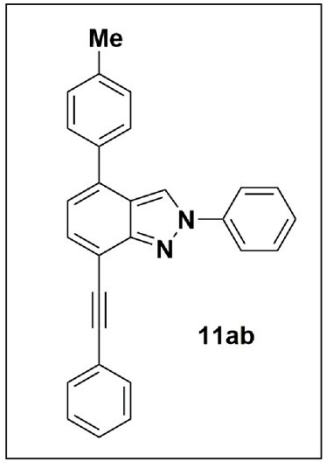
^{1}H NMR: 400 MHz

Solvent: $CDCl_3$



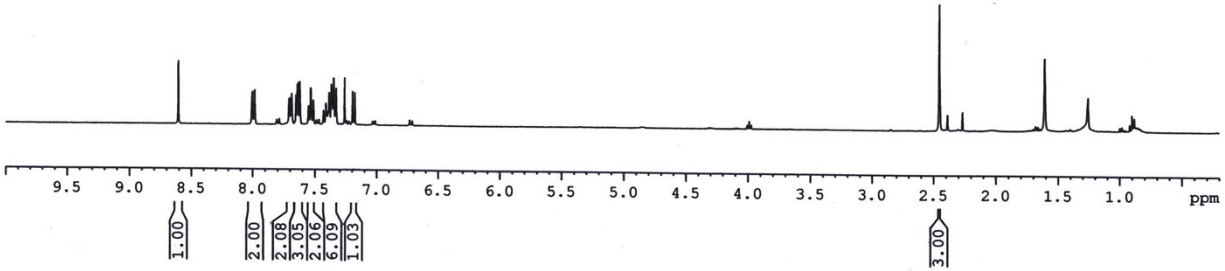

150.76
145.93
142.24
140.00
132.09
131.99
130.79
129.97
129.70
128.84
128.67
128.63
128.42
123.26
121.29
120.25
118.33
114.93
112.51
95.06
85.34
77.47
77.15
76.84
21.80
Me
10aa
13C{1H} NMR: 100 MHz
Solvent: CDCl3
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

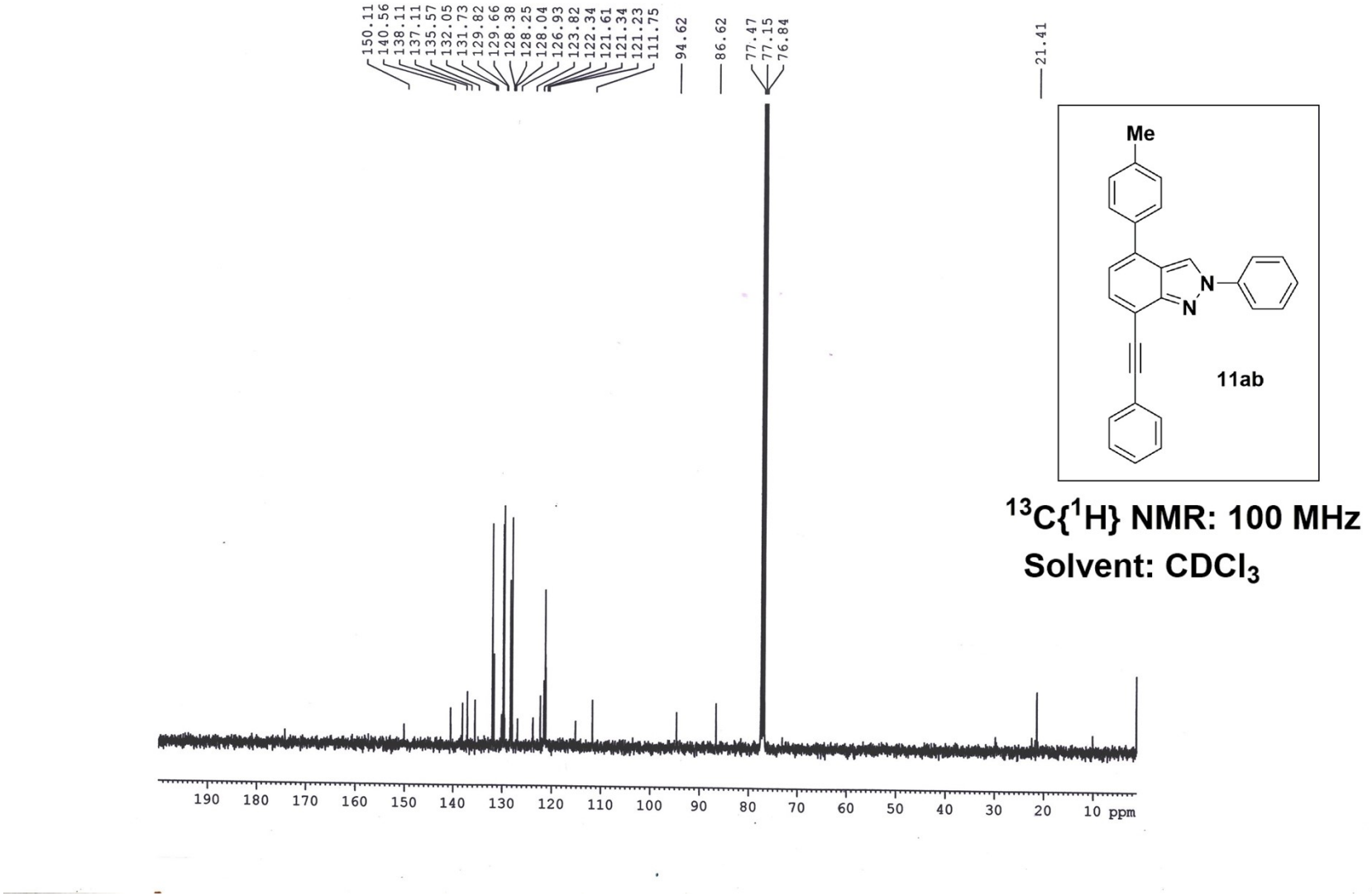




^{1}H NMR: 400 MHz

Solvent: $CDCl_3$





$^{13}C\{^{1}H\}$ NMR: 100 MHz

Solvent: $CDCl_3$