Electronic Supplementary Information

Dibenzo[*a*,*c*]carbazoles from 2-(2-bromoaryl)-3-arylindoles via a palladium-catalyzed intramolecular C-H functionalization/C-C bond formation process

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Contents

GENERAL INFORMATION

Melting points were determined with a Büchi B-545 apparatus and are uncorrected. All of the reagents, catalysts, and solvents are commercially available and were used as purchased, without further purification. 2-Alkynyltrifluoroacetanilides **1** were prepared, usually in high yields, from 2-iodoaniline via a two-step process involving a Sonogashira cross-coupling with terminal alkynes followed by a trifluoracetylation step.[1] Starting materials were purified by chromatography on axially compressed columns, packed with SiO_2 25-40 μm, connected to a solvent delivery system and to a refractive index detector, and eluting with *n*-hexane/EtOAc mixtures.
Carbazoles were purified by flash chromatography, using neutral Al_2O_3 Brockmann activity II (Fluka) as stationary phase, eluting with *n*-hexane/ethyl acetate mixtures. ^{1}H NMR (400.13. MHz), ^{13}CNMR (100.6 MHz), and ^{19}F NMR (376.5 MHz) spectra were recorded with a Bruker Avance 400 spectrometer. Splitting patterns are designed as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), or bs (broad singlet). IR spectra were recorded with a Jasco FT/IR-430 spectrometer.

[1] S. Cacchi, G. Fabrizi, P. Pace, *J.Org. Chem.* 1998, **63**, 1001-1011; A.Arcadi, S. Cacchi, F. Marinelli, *TetrahedronLett.*, 1989, **30**, 2581.

GENERAL PROCEDURES.

***Typical procedure for the preparation of 2-(2-bromophenyl-)3-(4-methoxyphenyl)-1H-indole* 3a.**
In a 50 mL Carousel Tube Reactor (Radleys Discovery Technology) containing a magnetic stirring bar *N*-(2-((2-bromophenyl)ethynyl)phenyl)-2,2,2-trifluoroacetamide **1a** (368.1 mg, 1.0mmol), 4-iodoanisole (468.0 mg, 2.0 mmol), and $Pd(PPh_3)_4$ (57.8 mg, 0.05 mmol) were dissolved in 5 mL of anhydrous MeCN. Then,Cs_2CO_3 (651.6 mg, 2.0 mmol) was added and the mixture was stirred for 40 min at 80°C. After this time the reaction mixture was cooled to room temperature, diluted with EtOAc, and washed with brine. The organic layer was separated, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by chromatography (silica gel, *n*-hexane/EtOAc 85/15 v/v) to afford 302.6 mg (80% yield) of **3a**: mp: 101-103 °C;^{1}H NMR (400.13 MHz, $CDCl_3$): δ 8.34 (bs, 1 H), 7.84 (d, J = 8.0 Hz, 1 H), 7.71 (d, J = 6.4 Hz, 1 H), 7.46 (d, J = 8.0 Hz, 1 H), 7.34-6.92 (m, 7 H), 6.91 (d, J = 8.7 Hz, 2 H), 3.84 (s, 3 H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 135.7, 134.1, 133.5, 133.3, 132.6, 130.7, 129.8, 127.4, 127.3, 127.2, 123.9, 122.8, 120.3, 119.9, 116.4, 113.9, 111.0, 108.2, 55.2.

***Typical procedure for the preparation of 2-(2-bromophenyl)3-(4-methoxyphenyl)-1-(2-((trimethylsilyl)methoxy)ethyl)-1H-indole* 6a**.
To a solution of pre-activated NaH (60 % in mineral oil, 99.9 mg, 2.5 mmol; anhydrous DMF, 6 mL) 2-(2-bromophenyl)3-(4-methoxyphenyl)-1*H*-indole **3a** (472.6 mg, 1.25 mmol), dissolved in 6 mL of anhydrous DMF, was added dropwise under argon at 0°C.
After stirring for 30 min at room temperature, the solution was cooled down in a ice bath, SEM-Cl (330 μL, 1.88 mmol) was added and the mixture was stirred at room temperature until completion. Then, the reaction mixture was diluted with Et_2O and washed with brine. The organic layer was dried over Na_2SO_4 and concentrated under reduced pressure to give 603 mg (95% yield) of **6a**: yellow solid; mp: 228-231 °C. ^{1}H NMR (400.13 MHz, DMSO d_6): δ 7.79 (d, J = 8.0 Hz, 1 H), 7.66-7.61 (m, 2 H), 7.47-7.39 (m, 3 H), 7.31-7.30 (m, 1 H), 7.29-7.14 (m, 3 H), 6.87 (d, J = 8.8 Hz, 2 H), 5.54 (d, J = 11.1 Hz, 1 H), 5.10 (d, J = 11.1 Hz, 1 H), 3.72 (s, 3 H), 3.28 (m, 2 H), 0.70-0.65 (m, 2 H), -0.14 (s. 9 H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 158.0, 136.8, 135.2, 134.2, 133.5, 132.8, 130.2, 127.6, 127.2, 127.0, 126.4, 122.8, 120.7, 119.9, 116.8, 113.8, 110.6, 73.3, 65.7, 55.1, 17.8, -1.48.

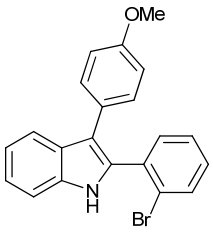
***Typical procedure for the preparation of 3-methoxy-9-((2-(trimethylsilyl)ethoxy)methyl)-9H-dibenzo[a,c]carbazole* 7a.**

In a 50 mL Carousel Tube Reactor (Radleys Discovery Technology) containing a magnetic stirring bar $Pd(OAc)_2$ (2.2 mg, 0.01 mmol) and PPh_3 (10.5 mg, 0.04 mmol) were dissolved under argon in 2 mL of anhydrous DMF. Then, 2-(2-bromophenyl)-3-(4-methoxyphenyl)-1-(2-((trimethylsilyl)methoxy) ethyl)-1*H*-indole **6a** (101.7 mg, 0.2 mmol), CsOAc (77 mg, 0.4 mmol), and 2 mL of solvent were added and the mixture was stirred for 30 min at 120°C under argon. After cooling, the reaction mixture was diluted with Et_2O, washed with $NaHCO_3$, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash chromatography using neutral Al_2O_3Brockmann activity II (Fluka) as stationary phase, eluting with *n*-hexane/ethyl acetate 95/5 to give 83.3 mg (97% yield) of **7a**: oil; IR (neat): 2923, 1616, 1467, 1247, 1028, 1004, 808, 738 (cm^{-1}).^{1}H NMR (400.13 MHz, $CDCl_3$): δ 8.80 (d, *J* = 9.2 Hz, 1 H), 8.79-8.73 (m, 2 H), 8.58 (d, *J* = 8.0 Hz, 1 H), 8.20 (d, *J* = 2.4 Hz, 1 H), 7.70-7.65 (m, 3 H), 7.56-7.48 (m, 1 H), 7.48-7.40 (m, 2 H), 5.96 (s, 2 H), 4.08 (s, 3 H), 3.93 (t, *J* = 8.0 Hz, 1 H), 1.10 (t, *J* = 8.4 Hz, 1 H), 0.03 (s, 9 H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 156.5, 141.4, 133.9, 130.3, 128.9, 126.8, 125.6, 125.1, 124.2, 124.1, 124.0, 123.98, 123.77, 123.76, 121.9, 120.9, 116.5, 114.6, 109.7, 105.8, 74.7, 66.0, 55.5, 18.1, -1.3. Anal calcd for $C_{27}H_{29}NO_2Si$: C, 75.84; H, 6.84; N, 3.28. Found: C, 75.92; H, 6.82; N, 3.25.

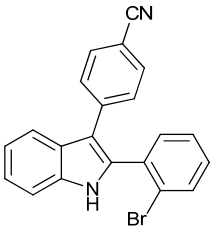
***Typical procedure for the preparation of 3-methoxy-9H-dibenzo[a,c]carbazole* 4a.**

In a 50 mL Carousel Tube Reactor (Radleys Discovery Technology) containing a magnetic stirring bar $Pd(OAc)_2$ (2.2 mg, 0.01 mmol) and PPh_3 (10.5 mg, 0.04 mmol) were dissolved under argon in 2 mL of anhydrous DMF. Then, 2-(2-bromophenyl)-3-(4-methoxyphenyl)-1-(2-((trimethylsilyl)methoxy) ethyl)-1*H*-indole **6a** (101.7 mg, 0.2 mmol), CsOAc (77 mg, 0.4 mmol) and 2 mL of solvent were added and the mixture was stirred for 30 min at 120°C under argon. After cooling, the reaction mixture was diluted with Et_2O, washed with $NaHCO_3$, dried over Na_2SO_4, and concentrated under reduced pressure. To the solution of the crude in anhydrous THF (2 mL) 2 mL of TBAF (THF solution, 1M, 10 eq.) were added and the mixture was stirred at 60°C until completion. The reaction mixture was cooled, diluted with EtOAc, washed with $NaHCO_3$;the organic layer was separated, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash chromatography using neutral Al_2O_3 Brockmann activity II (Fluka) as stationary phase, eluting with *n*-hexane/ethyl acetate 95/5 to give 42 mg (70% yield) of **4a**: mp: 195-198 °C. IR (KBr): 3425, 2923, 1531, 1461, 1257, 1043, 808, 738 (cm^{-1}).^{1}H NMR (400.13 MHz, $CDCl_3$): δ 8.78 (bs, 1 H), 8.73-8.69 (m, 2 H), 8.50 (d, *J* = 7.8 Hz, 1 H), 8.19 (s, 1 H), 8.09-8.03 (m, 1 H), 7.71-7.60 (m, 3 H), 7.49-7.38 (m, 3 H), 4.07 (s, 3 H); ^{13}C NMR (100.6 MHz, DMSO): δ 156.4, 139.0, 133.4, 129.3, 128.2, 127.5, 126.5, 125.3, 124.8, 124.3, 124.0, 123.9, 123.5, 122.7, 121.7, 120.3, 117.3, 112.2, 111.9, 106.8, 55.9. Anal calcd for $C_{21}H_{15}NO$: C, 84.82; H, 5.08; N, 4.71. Found: C, 84.71; H, 5.07; N, 4.74.

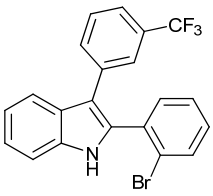
CHARACTERIZATION DATA



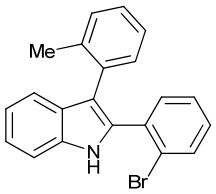
3a 2-(2-bromophenyl)-3-(4-methoxyphenyl)-1*H*-indole: ^{1}H NMR (400.13 MHz, $CDCl_3$): δ 8.34 (bs, 1 H), 7.84 (d, *J* = 8.0 Hz, 1 H), 7.71 (d, *J* = 6.4 Hz, 1 H), 7.46 (d, *J* = 8.0 Hz, 1 H), 7.34-6.92 (m, 7 H), 6.91 (d, *J* = 8.7 Hz, 2 H), 3.84 (s, 3 H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 135.7, 134.1, 133.5, 133.3, 132.6, 130.7, 129.8, 127.4, 127.3, 127.2, 123.9, 122.8, 120.3, 119.9, 116.4, 113.9, 111.0, 108.2, 55.2.



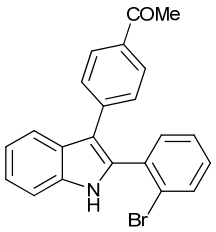
3b 4-(2-(2-bromophenyl)-1*H*-indol-3-yl)benzonitrile: ^{1}H NMR (400.13 MHz, $CDCl_3$): δ 8.66 (bs, 1 H), 8.18 (s, 1 H), 7.73-7.70 (m, 1 H), 7.53 (s, 2 H), 7.39-7.28 (m, 8 H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 137.2, 135.0, 133.4, 133.3, 133.2, 132.8, 130.5, 129.5, 128.7, 127.6, 127.1, 126.8, 125.8, 125.7, 123.6, 120.6, 117.4, 112.0, 103.6.



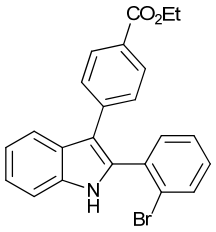
3c 2-(2-bromophenyl)-3-(3-(trifluoromethyl)phenyl)-1*H*-indole: ^{1}H NMR (400.13 MHz, $CDCl_3$): δ 8.36 (bs, 1 H), 7.89 (d, *J* = 8.0 Hz, 1 H), 7.75 (s, 2 H), 7.57-7.44 (m, 4 H), 7.40-7.20 (m, 5 H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 135.8, 135.7, 133.8, 133.4, 133.2, 132.67, 132.65, 130.8 (q, J_{CF} = 32.0 Hz), 130.4, 128.9, 127.5, 126.8, 126.0 (q, J_{CF} = 4.0 Hz), 124.3 (q, J_{CF} = 272.4 Hz), 124.0, 123.3, 122.7 (q, J_{CF} = 4.0 Hz), 120.9, 119.5, 115.3, 111.3.



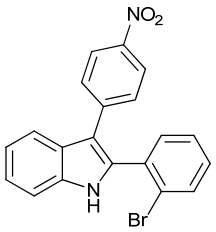
3d 2-(2-bromophenyl)-3-*o*-tolyl-1*H*-indole:^{1}H NMR (400.13 MHz, $CDCl_3$): δ 8.47 (bs, 1 H), 7.71-7.68 (m, 1 H), 7.51 (d, *J* = 8.0 Hz, 2 H), 7.38-7.17 (m, 9 H), 2.14 (s, 3 H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 137.7, 135.5, 134.7, 133.9, 133.4, 133.2, 133.1, 131.8, 130.2, 129.6, 128.2, 127.3, 127.0, 125.5, 123.9, 122.8, 120.3, 120.1, 116.5, 111.0, 20.2.



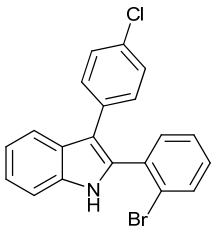
3e 1-(4-(2-(2-bromophenyl)-1*H*-indol-3-yl)phenyl)ethanone: ^{1}H NMR (400.13 MHz, $CDCl_3$): δ 8.49 (bs, 1 H), 7.92 (d, *J* = 8.0 Hz, 2 H), 7.87 (d, *J* = 8.0 Hz, 1 H), 7.72-7.70 (m, 1 H), 7.51-7.46 (m, 3 H), 7.36-7.26 (m, 5 H), 2.61 (s, 3 H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 197.8, 140.3, 135.8, 134.7, 134.2, 133.7, 133.4, 133.2, 130.2, 129.3, 128.6, 127.5, 126.8, 123.9, 123.2, 120.9, 119.7, 115.7, 111.2, 26.4.



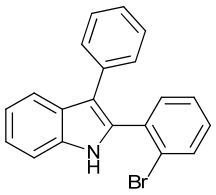
3f ethyl 4-(2-(2-bromophenyl)-1*H*-indol-3-yl)benzoate: ^{1}H NMR (400.13 MHz, $CDCl_3$): δ 8.49 (bs, 1 H), 8.01 (d, *J* = 8.4 Hz, 2 H), 7.86 (d, *J* = 8.0 Hz, 1 H), 7.71-7.69 (m, 1 H), 7.51-7.43 (m, 3 H), 7.35-7.24 (m, 5 H), 4.39 (q, *J* = 7.2 Hz, 2 H) 1.41 (t, *J* = 7.2 Hz, 3 H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 166.8, 139.9, 135.8, 133.9, 133.6, 133.4, 133.3, 130.2, 129.7, 129.2, 127.8, 127.5, 126.8, 123.9, 123.2, 120.8, 119.7, 115.8, 111.2, 60.8, 14.4.



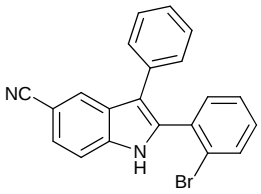
3g 2-(2-bromophenyl)-3-(4-nitrophenyl)-1*H*-indole: ^{1}H NMR (400.13 MHz, $CDCl_3$): δ 8.50 (bs, 1 H), 8.18 (d, *J* = 8.8 Hz, 2 H), 7.86 (d, *J* = 8.0 Hz, 1 H), 7.74-7.71 (m, 1 H), 7.52-7.50 (m, 3 H), 7.38-7.25 (m, 5 H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 145.8, 142.4, 135.8, 134.7, 133.6, 133.2, 133.0, 130.7, 129.6, 27.7, 126.5, 123.91, 123.89, 123.6, 121.3, 119.4, 114.7, 111.5.



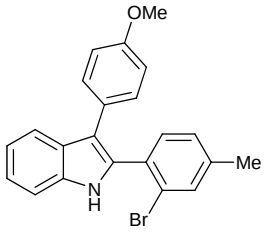
3h 2-(2-bromophenyl)-3-(4-chlorophenyl)-1*H*-indole: ^{1}H NMR (400.13 MHz, $CDCl_3$): δ 8.36 (bs, 1 H), 7.81 (d, *J* = 8.0 Hz, 1 H), 7.72-7.70 (m, 1 H), 7.48 (d, *J* = 8.0 Hz, 1 H), 7.35-7-22 (m, 9 H); ^{13}C NMR (100.6 MHz, $CdCl_3$): δ 135.7, 133.7, 133.38, 133.37, 133.3, 133.2, 131.8, 130.7, 130.1, 128.6, 127.5, 127.0, 123.9, 123.1, 120.6, 119.6, 115.5, 111.2.



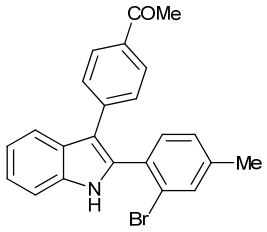
3i 2-(2-bromophenyl)-3-phenyl-1*H*-indole: ^{1}H NMR (400.13 MHz, $CDCl_3$): δ 8.29 (bs, 1 H), 7.95 (d, *J* = 7.6 Hz, 1 H), 7.76-7.73 (m, 1 H), 7.51-7.23 (m, 11 H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 135.8, 134.9, 134.1, 133.5, 133.3, 133.1, 129.9, 129.7, 128.5, 127.4, 127.3, 126.1, 124.0, 123.0, 120.5, 120.0, 116.7, 111.2.



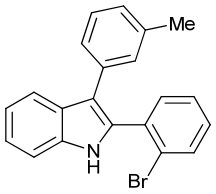
3j 2-(2-bromophenyl)-3-phenyl-1*H*-indole-5-carbonitrile: ^{1}H NMR (400.13 MHz, $CDCl_3$): δ 8.66 (bs, 1 H), 8.17 (s, 3 H), 7.72-7.60 (m, 1 H), 7.42-7.26 (m, 8 H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 137.1, 134.9, 133.4, 133.3, 133.2, 132.8, 130.5, 129.5, 128.7, 127.6, 127.1, 126.8, 125.8, 125.7, 123.6, 120.6, 117.4, 111.9, 103.6.



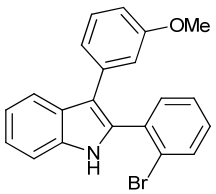
3k 2-(2-bromo-4-methylphenyl)-3-(4-methoxyphenyl)-1*H*-indole: ^{1}H NMR (400.13 MHz, $CDCl_3$): δ 8.40 (bs, 1 H), 7.84 (d, *J* = 8.0 Hz, 1 H), 7.54 (s, 1 H), 7.45 (d, *J* = 8.0 Hz, 1 H), 7.36-7.15 (m, 5 H), 7.06 (d, *J* = 7.6 Hz, 1 H), 6.91 (d, *J* = 8.8 Hz, 2 H), 3.84 (s, 3 H), 2.39 (s, 3 H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 157.8, 140.1, 135.6, 133.7, 133.1, 132.7, 131.1, 130.6, 128.2, 127.5, 127.4, 123.6, 122.6, 120.2, 119.8, 116.1, 113.9, 111.1, 55.2, 20.9.



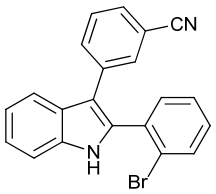
3l 1-(4-(2-(2-bromo-4-methylphenyl)-1*H*-indol-3-yl)phenyl)ethanone: ^{1}H NMR (400.13 MHz, $CDCl_3$): δ 8.42 (bs, 1 H), 7.92 (d, *J* = 8.0 Hz, 2 H), 8.86 (d, *J* = 7.2 Hz, 1 H), 7.54-7.40 (m, 4 H), 7.35-7.21 (m, 2 H), 7.16 (d, *J* = 7.6 Hz, 1 H), 7.08 (d, *J* = 7.2 Hz, 1 H), 2.61 (s, 3 H), 2.40 (s, 3 H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 197.9, 140.8, 140.4, 135.7, 134.5, 134.1, 133.9, 132.9, 130.5, 129.3, 128.6, 128.4, 126.8, 123.5, 123.1, 120.8, 119.6, 115.4, 111.2, 26.5, 20.9.



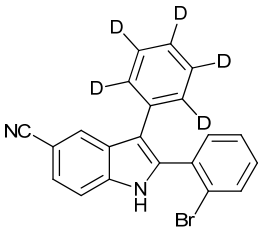
3m 2-(2-bromophenyl)-3-*m*-tolyl-1*H*-indole: ^{1}H NMR (400.13 MHz, $CDCl_3$): δ 8,27 (bs, 1 H), 7.97 (d, *J* = 8.0 Hz, 1 H), 7.78 (d, *J* = 4.4 Hz, 2 H), 7.49 (d, *J* = 8.0 Hz, 2 H), 7.40-7.10 (m, 7 H), 2.44 (s, 3 H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 137.9, 135.8, 134.8, 134.2, 133.6, 133.3, 133.1, 130.3, 129.9, 128.4, 127.4, 127.3, 126.9, 126.8, 124.0, 122.9, 120.4, 120.1, 116.8, 111.2, 21.7.



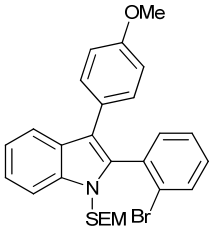
3n 2-(2-bromophenyl)-3-(3-methoxyphenyl)-1*H*-indole: ^{1}H NMR (400.13 MHz, $CDCl_3$): δ 8,35 (bs, 1 H), 7.90 (d, *J* = 8.0 Hz, 1 H), 7.71-7.68 (m, 1 H), 7.48 (d, *J* = 8.0 Hz, 1 H), 7.34-7.20 (m, 6 H), 7.02-6.93 (m, 2 H), 6.81 (dd, J_1= 8.0 Hz, J_2= 1.6 Hz, 1 H), 3.72 (s, 3 H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 159.5, 136.2, 135.7, 134.0, 133.4, 133.2, 133.1, 130.0, 129.3, 127.4, 127.1, 124.0, 122.9, 122.1, 120.5, 120.0, 116.5, 114.7, 112.0, 111.1, 55.1.



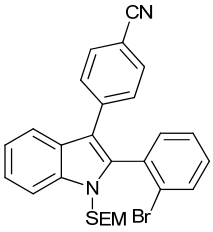
3o 3-(2-(2-bromophenyl)-1*H*-indol-3-yl)benzonitrile: ^{1}H NMR (400.13 MHz, $CDCl_3$): δ 8,51 (bs, 1 H), 7.80 (d, *J* = 8.0 Hz, 1 H), 7.72-7.70 (m, 2 H), 7.69-7.48 (m, 3 H), 7.44-7.25 (m, 6 H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 136.5, 135.7, 133.9, 133.8, 133.6, 133.2, 133.1, 133.0, 132.6, 130.5, 129.5, 129.3, 127.6, 126.5, 123.9, 123.3, 121.0, 119.2, 114.3, 112.5, 111.4.



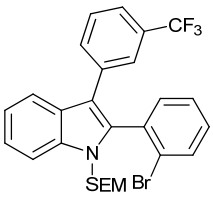
3jD 2-(2-bromophenyl)-3-pentadeuterophenyl-1*H*-indole-5-carbonitrile: ^{1}H NMR (400.13 MHz, $CDCl_3$): δ 8.67 (bs, 1 H), 8.17 (s, 1 H), 7.65-7.38 (m, 6 H).



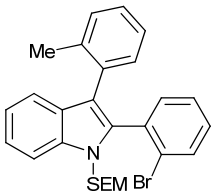
6a 2-(2-bromophenyl)-3-(4-methoxyphenyl)-1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-indole: ^{1}H NMR (400.13 MHz, DMSO d_6): δ 7.79 (d, J = 8.0 Hz, 1 H), 7.66-7.61 (m, 2 H), 7.47-7.39 (m, 3 H), 7.31-7.30 (m, 1 H), 7.29-7.14 (m, 3 H), 6.87 (d, J = 8.8 Hz, 2 H), 5.54 (d, J = 11.1 Hz, 1 H), 5.10 (d, J = 11.1 Hz, 1 H), 3.72 (s, 3 H), 3.28 (m, 2 H), 0.70-0.65 (m, 2 H), -0.14 (s, 9 H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 158.0, 136.8, 135.2, 134.2, 133.5, 132.8, 130.22,130.24, 127.6, 127.2, 127.0, 126.4, 122.8, 120.7, 119.9, 116.8, 113.8, 110.6, 73.3, 65.7, 55.1, 17.8, -1.48.



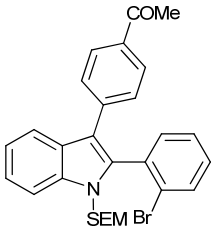
6b 2-(2-bromophenyl)-1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-indol-3yl)benzonitrile: ^{1}H NMR (400.13 MHz, DMSO d_6): δ 7.81-7.73 (m, 5 H), 7.52-7.40 (m, 3 H), 7.41 -7.33 (m, 3 H), 7.27-7.23 (m, 1 H), 5.56 (d, J = 11.2 Hz, 1 H), 5.18 (d, J = 11.2 Hz, 1 H), 3.30-3.26 (m, 2 H), 0.71-0.69 (m, 2 H), -0.13 (9 H); ^{13}C NMR (100.6 MHz, DMSO d_6): δ 140.0, 137.1, 137.0, 134.3, 133.3, 132.8, 132.1, 131.9, 129.6, 128.4, 126.2, 125.6, 123.6, 121.9, 119.4, 119.3, 115.0, 111.7, 108.8, 72.9, 65.7, 17.7, -0.9.



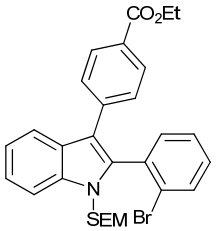
6c 2-(2-bromophenyl)-3-(3-(trifluoromethyl)phenyl)-1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-indole: ^{1}H NMR (400.13 MHz, $CDCl_3$): δ 7.91 (d, J = 8.0 Hz, 1 H), 7.79-7.60 (m, 3 H), 7.59 (d, J = 7.6 Hz, 1 H), 7.53 -7.35 (m, 7 H), 5.58 (d, J = 11.2 Hz, 1 H), 5.30 (d, J = 11.2 Hz, 1 H), 3.49-3.36 (m, 2 H), 0.92-0.87 (m, 2 H), 0.02 (9 H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 136.9, 136.3, 135.7, 134.0, 133.0, 132.7, 132.4, 130.8, 130.7 (q, J_{CF} = 31 Hz), 128.8, 127.5, 126.9, 126.2, 126.0 (q, J_{CF} = 4 Hz), 124.3 (q, J_{CF} = 272 Hz), 123.3, 122.6(q, J_{CF} = 4 Hz), 121.4, 119.5, 115.7, 111.0, 73.3, 65.9, 17.8, -1.4.^{19}F (376.5 MHz) δ -62.6.



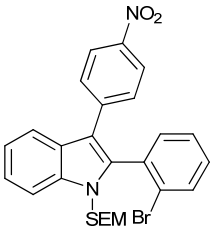
6d 2-(2-bromophenyl)-3-*o*-tolyl-1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-indole: ^{1}H NMR (400.13 MHz, $CDCl_3$) (stereoisomeric mixture): δ 7.65-7.60 (m, 4 H), 7.40-7.31 (m, 6 H), 7.25-7.14 (m, 14 H), 5.68 (d, *J* = 11.2 Hz, 1 H), 5.64 (d, *J* = 11.2 Hz, 1 H), 5.23 (d, *J* = 11.2 Hz, 1 H), 5.15 (d, *J* = 11.2 Hz, 1 H), 3.33-3.24 (m, 4 H), 2.25 (s, 3 H), 2.15 (s, 3 H), 0.79-0.75 (m, 4 H), -0.08 (9 H), -0.1 (s, 9 H).



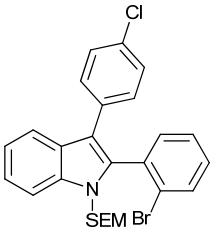
6e 1-(4-(2-(2-bromophenyl)-1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-indol-3-yl)phenyl)ethanone: ^{1}H NMR (400.13 MHz, $CDCl_3$): δ 7.91-7.86 (m, 3 H), 7.74-7.72 (m, 1 H), 7.67 (d, *J* = 8.0 Hz, 1 H), 7.45 -7.30 (m, 7 H), 5.60 (d, *J* = 11.2 Hz, 1 H), 5.21 (d, *J* = 11.2 Hz, 1 H), 3.41-3.28 (m, 2 H), 2.60 (s, 3 H), 0.82-0.78 (m, 2 H), -0.06 (9 H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 197.7, 140.0, 136.9, 136.4, 134.6, 133.8, 133.0, 132.8, 130.7, 129.1, 128.4, 127.4, 126.9, 126.1, 123.2, 121.3, 119.7, 116.0, 111.9, 73.3, 65.8, 26.4, 17.8, -1.5.



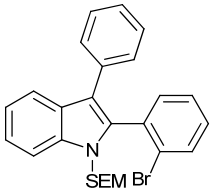
6f ethyl 4-(2-(2-bromophenyl)-1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-indol-3-yl)benzoate: ^{1}H NMR (400.13 MHz, $CDCl_3$): δ 8.01 (d, *J* = 8.4 Hz, 2 H), 7.89 (d, *J* = 8.0 Hz, 1 H), 7.74 (d, *J* = 7.2 Hz, 1 H), 7.69 (d, *J* = 8.4 Hz, 1 H), 7.38-7.28 (m, 7 H), 5.63 (d, *J* = 10.8 Hz, 1 H), 5.23 (d, *J* = 11.2 Hz, 1 H), 4.40 (q, *J* = 7.2 Hz, 2 H), 3.42-3.29 (m, 2 H), 1.44-1.40 (m, 3 H), 0.82 (t, *J* = 8.4 Hz, 2 H), -0.04 (9 H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 166.7, 139.7, 136.9, 136.4, 134.0, 133.0, 132.9, 130.7, 129.6, 129.0, 127.8, 127.4, 127.0, 126.2, 123.2, 121.3, 119.7, 116.2, 110.9, 73.3, 65.9, 60.1, 17.8, 14.4, -1.4.



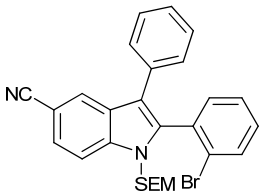
6g 2-(2-bromophenyl)-3-(4-nitrophenyl)-1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-indole: ^{1}H NMR (400.13 MHz, $CDCl_3$): δ 8.15 (d, *J* = 8.8 Hz, 2 H), 7.85 (d, *J* = 7.6 Hz, 1 H), 7.76-7.74 (m, 1 H), 7.69 (d, *J* = 8.0 Hz, 1 H), 7.48 (d, *J* = 8.8 Hz, 2 H), 7.44-7.31 (m, 5 H), 5.59 (d, *J* = 11.2 Hz, 1 H), 5.22 (d, *J* = 11.2 Hz, 1 H), 3.42-3.30 (m, 2 H), 0.82 (t, *J* = 8.0 Hz, 2 H), -0.05 (9 H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 145.7, 142.2, 137.1, 137.0, 133.8, 133.2, 132.4, 131.0, 129.4, 127.6, 126.5, 126.0, 123.7, 123.5, 121.7, 119.4, 115.2, 111.1, 73.3, 66.0, 17.8, -1.4.



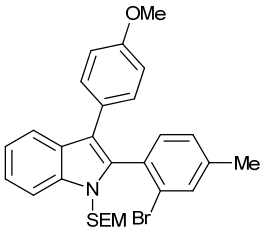
6h 2-(2-bromophenyl)-3-(4-chlorophenyl)-1-((2-(triethylsilyl)ethoxy)methyl)-1*H*-indole: ^{1}H NMR (400.13 MHz, $CDCl_3$): δ 7.84 (d, *J* = 8.0 Hz, 1 H), 7.75 (d, *J* = 7.6 Hz, 2 H), 7.43-7.31 (m, 9 H), 5.63 (d, *J* = 11.2 Hz, 1 H), 5.23 (d, *J* = 11.2 Hz, 1 H), 3.44-3.30 (m, 2 H), 0.84 (t, *J* = 8.4 Hz, 2 H), -0.03 (9 H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 136.8, 135.8, 134.0, 133.2, 133.2, 133.0, 131.8, 130.62, 132.56, 128.5, 127.4, 127.1, 126.2, 123.1, 121.1, 119.6, 115.9, 110.8, 73.3, 65.8, 17.8, -1.4.



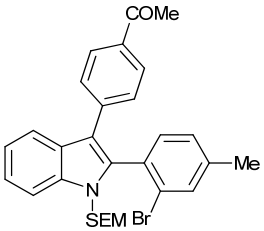
6i 2-(2-bromophenyl)-3-phenyl-1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-indole: ^{1}H NMR (400.13 MHz, DMSO d_6): δ 7.77 (d, *J* = 7.6 Hz, 1 H), 7.79 (d, *J* = 7.6 Hz, 1 H), 7.70 -7.67 (m, 2 H), 7.48-7.42 (m, 3 H), 7.34-7.17 (m, 7 H), 5.56 (d, *J* = 11.2 Hz, 1 H), 5.13 (d, *J* = 11.2 Hz, 1 H), 3.29-3.22 (m, 2 H), 0.71-0.65 (m, 2 H), -0.13 (9 H); ^{13}C NMR (100.6 MHz, DMSO d_6): δ 137.0, 135.9, 134.6, 134.5, 133.0, 132.8, 131.5, 129.2, 128.8, 128.1, 126.9, 126.5, 125.9, 123.1, 121.2, 119.5, 116.5, 111.3, 72.8, 65.6, 17.7, -0.9.



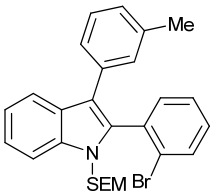
6j 2-(2-bromophenyl)-3-phenyl-1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-indole-5-carbonitrile: ^{1}H NMR (400.13 MHz, DMSO d_6): δ 8.12 (s, 1 H), 7.93 (d, J = 8.8 Hz, 1 H), 7.79 (d, J = 7.6 Hz, 1 H), 7.70 (d, J = 8.4 Hz, 1 H), 7.51-7.43 (m, 3 H), 7.36-7.23 (m, 5 H), 5.63 (d, J = 11.2 Hz, 1 H), 5.20 (d, J = 11.2 Hz, 1 H), 3.30-3.24 (m, 2 H), 0.71-0.65 (m, 2 H), -0.13 (9 H); ^{13}C NMR (100.6 MHz, DMSO d_6): δ 138.6, 138.2, 134.4, 133.22, 133.17, 131.9, 131.8, 129.3, 129.1, 128.3, 127.1, 126.7, 126.0, 125.6, 125.1, 120.6, 117.1, 112.8, 103.6, 73.0, 65.9, 17.6, -0.9.



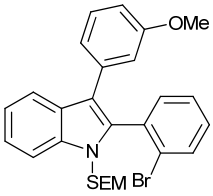
6k 2-(2-bromo-4-methylphenyl)-3-(4-methoxyphenyl)-1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-indole: ^{1}H NMR (400.13 MHz, DMSO d_6): δ 7.67-7.60 (m, 3 H), 7.30-7.25 (m, 3 H), 7.19-7.15 (m, 3 H), 6.88 (d, J = 8.4 Hz, 2 H), 5.53 (d, J = 11.2 Hz, 1 H), 5.10 (d, J = 11.2 Hz, 1 H),3.73 (s, 3 H), 3.29-3.20 (m, 2 H), 2.37 (s, 3 H), 0.68 (t, J = 6.4 Hz, 2 H), -0.13 (s, 3 H);); ^{13}C NMR (100.6 MHz, DMSO d_6): δ 158.0, 141.4, 136.9, 135.4, 134.2, 133.3, 130.3, 129.9, 128.8, 127.1, 126.9, 125.7, 122.9, 121.0, 119.5, 116.2, 114.4, 111.2, 72.7, 65.5, 55.4, 20.9, 17.7, -0.89.



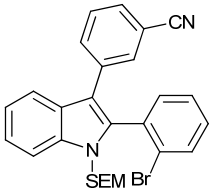
6l 1-(4-2-(2-bromo-4-methylphenyl)-1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-indol-3-yl)phenyl)ethanone: ^{1}H NMR (400.13 MHz, DMSO d_6): δ 7.89 (d, J = 8.0 Hz, 2 H), 7.72 (t, J = 8.0 Hz, 2 H), 7.64 (s, 1 H), 7.40-7.20 (m, 5 H), 7.23 (t, J = 7.6 Hz, 1 H), 5.55 (d, J = 11.6 Hz, 1 H), 5.16 (d, J = 11.6 Hz, 1 H), 3.27 (t, J = 7.6 Hz, 2 H), 2.54 (s, 3 H), 2.38 (s, 3 H), 0.71 (t, J = 7.6 Hz, 2 H), -0.13 (9 H); ^{13}C NMR (100.6 MHz, DMSO d_6): δ 197.7, 141.8, 139.9, 137.0, 136.8, 134.7, 134.0, 133.5, 129.4, 129.0, 128.9, 126.5, 125.5, 123.3, 121.6, 121.1, 119.4, 115.5, 111.5, 72.8, 65.6, 27.0, 20.9, 17.7,-0.99.



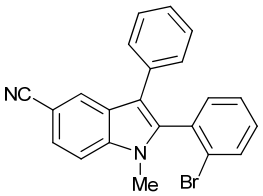
6m 2-(2-bromophenyl)-3-*m*-tolyl-1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-indole: ^{1}H NMR (400.13 MHz, DMSO d_6): δ 7.77 (d, J = 7.6 Hz, 2 H), 7.69 (d, J = 8.4 Hz, 2 H), 7.47-7.40 (m. 3 H), 7.30 (t, J = 7.2 Hz, 2 H), 7.20-7.10 (m, 3 H), 7.01-6.95 (m, 2 H), 5.57 (d, J = 11.2 Hz, 2 H), 5.11 (d, J = 11.2 Hz, 2 H), 3.30-3.20 (m, 2 H), 2.23 (s, 3 H), 0.71-0.67 (m, 2 H), -0.13 (s, 9 H). ^{13}C NMR (100.6 MHz, DMSO d_6): δ 137.7, 137.0, 135.9, 134.53, 134.50, 133.0, 132.9, 131.4, 129.9, 128.7, 128.1, 127.2, 126.9, 126.3, 126.0, 123.1, 121.2, 119.6, 116.4, 111.3, 72.8, 65.6, 21.5, 17.7, -0.9.



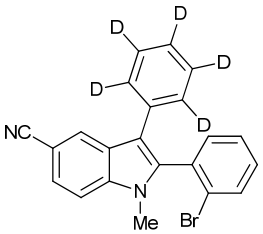
6n 2-(2-bromophenyl)-3-(3-methoxyphenyl)-1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-indole: ^{1}H NMR (400.13 MHz, $CDCl_3$): δ 7.93 (d, J = 7.6 Hz, 1 H), 7.75 (d, J = 7.6 Hz, 1 H), 7.68 (d, J = 8.4 Hz, 1 H), 7.40-7.20 (m, 6 H), 7.03 (d, J = 7.6 Hz, 1 H), 6.92 (s, 1 H), 6.80 (dd, J_1= 8.0 Hz, J_2= 1.6 Hz, 1 H), 5.64 (d, J = 11.2 Hz, 1 H), 5.22 (d, J = 11.2 Hz, 1 H), 3.71 (s, 3 H), 3.41-3.30 (m, 2 H), 0.85 (t, J = 8.1 Hz, 2 H), -0.04 (s, 9 H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 159.4, 136.8, 135.9, 135.7, 134.1, 133.4, 132.8, 130.5, 129.2, 127.4, 127.2, 126.4, 122.9, 121.8, 121.0, 120.0, 116.9, 114.3, 112.2, 110.7, 73.3, 65.8, 55.0, 17.8, -1.4.



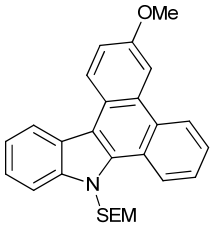
6o 3-(2-(2-bromophenyl)-1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-indol-3-yl)benzonitrile: ^{1}H NMR (400.13 MHz, $CDCl_3$): δ 7.80-7.60 (m, 4 H), 7.55 (d, J = 8.0 Hz, 1 H), 7.49 (d, J = 8.0 Hz, 1 H), 7.40-7.29 (m, 6 H), 5.59 (d, J = 11.2 Hz, 1 H), 5.21 (d, J = 11.2 Hz, 1 H), 3.38-3.26 (m, 2 H), 0.80 (d, J = 8.4 Hz, 2 H), -0.07 (s, 9 H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 136.8, 136.4, 136.2, 133.8, 133.6, 133.1, 132.5, 132.3, 131.0, 129.5, 129.1, 127.5, 126.6, 126.0, 123.4, 121.4, 119.2, 119.1, 114.9, 112.4, 110.9, 73.2, 65.9, 17.8, -1.41.



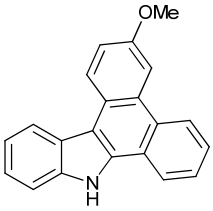
8j 2-(2-bromophenyl)-1-methyl-3-phenyl-1*H*-indole-5-carbonitrile: ^{1}H NMR (400.13 MHz, $CDCl_3$): δ 8.12 (s, 1 H), 7.86-7.80 (m, 2 H), 7.65 (d, *J* = 8.8 Hz, 1 H), 7.51-7.42 (m, 3 H), 7.36-7.19 (m, 5 H), 3.58 (s, 3 H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 138.4, 138.3, 133.4, 133.2, 132.9, 132.6, 130.9, 129.2, 128.5, 127.7, 126.55, 126.51, 125.6, 125.1, 120.8, 116.6.1, 110.4, 103.2, 30.7.



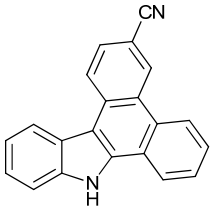
8jD 2-(2-bromophenyl)-1-methyl-3-pentadeuterophenyl-1*H*-indole-5-carbonitrile: ^{1}H NMR (400.13 MHz, DMSO d_6): δ 8.12 (s, 1 H), 7.86-7.79 (m, 2 H), 7.65 (d, *J* = 8.4 Hz, 1 H), 7.51-7.43 (m, 3 H), 3.58 (s, 3 H).



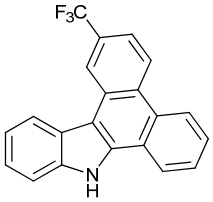
7a 3-methoxy-9-((2-(trimethylsilyl)ethoxy)methyl)-9*H*-dibenzo[*a*,*c*]carbazole: oil. IR (neat): 2923, 1616, 1467, 1247, 1028, 1004, 808, 738 (cm^{-1}).^{1}H NMR (400.13 MHz, $CDCl_3$): δ 8.80 (d, *J* = 9.2 Hz, 1 H), 8.79-8.73 (m, 2 H), 8.58 (d, *J* = 8.0 Hz, 1 H), 8.20 (d, *J* = 2.4 Hz, 1 H), 7.70-7.65 (m, 3 H), 7.56-7.48 (m, 1 H), 7.48-7.40 (m, 2 H), 5.96 (s, 2 H), 4.08 (s, 3 H), 3.93 (t, *J* = 8.0 Hz, 1 H), 1.10 (t, *J* = 8.4 Hz, 1 H), 0.03 (s, 9 H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 156.5, 141.4, 133.9, 130.3, 128.9, 126.8, 125.6, 125.1, 124.2, 124.1, 124.0, 123.98, 123.77, 123.76, 121.9, 120.9, 116.5, 114.6, 109.7, 105.8, 74.7, 66.0, 55.5, 18.1, -1.3. Anal calcd for $C_{27}H_{29}NO_2Si$: C, 75.84; H, 6.84; N, 3.28;. Found: C, 75.92; H, 6.82; N, 3.25.



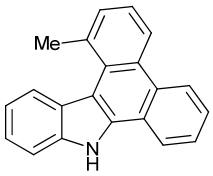
4a 3-methoxy-9*H*-dibenzo[*a*,*c*]carbazole: white solid; mp: 195-198 °C. IR (KBr): 3425, 2923, 1531, 1461, 1257, 1043, 808, 738 (cm^{-1}).^{1}H NMR (400.13 MHz, $CDCl_3$): δ 8.78 (bs, 1 H), 8.73-8.69 (m, 2 H), 8.50 (d, *J* = 7.8 Hz, 1 H), 8.19 (s, 1 H), 8.09-8.03 (m, 1 H), 7.71-7.60 (m, 3 H), 7.49-7.38 (m, 3 H), 4.07 (s, 3 H); ^{13}C NMR (100.6 MHz, DMSO): δ 156.4, 139.0, 133.4, 129.3, 128.2, 127.5, 126.5, 125.3, 124.8, 124.3, 124.0, 123.9, 123.5, 122.7, 121.7, 120.3, 117.3, 112.2, 111.9, 106.8, 55.9. ESI MS: 298 (M^{+1}, 100). Analcalcd for $C_{21}H_{15}NO$: C, 84.82; H, 5.08; N, 4.71. Found: C, 84.71; H, 5.07; N, 4.74.



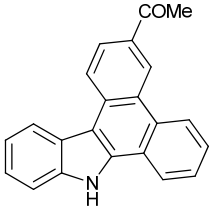
4b 9*H*-dibenzo[*a*,*c*]carbazole-3-carbonitrile: white solid; mp: 334-337 °C. IR (KBr): 3311, 2223, 1531, 1448 (cm^{-1}).^{1}H NMR (400.13 MHz, DMSO d_6): δ 12.69 (bs, 1 H), 9.41 (s, 1 H), 9.04 (d, *J* = 8.2 Hz, 1 H), 8.89 (d, *J* = 8.4 Hz, 1 H), 8.63 (d, *J* = 8.0 Hz, 1 H), 8.56 (d, *J* = 7.9 Hz, 1 H), 8.05 (d, *J* = 8.0 Hz, 1 H), 7.89-7.82 (m, 1 H), 7.81-7.73 (m, 2 H), 7.49 (t, *J* = 7.6 Hz, 1 H), 7.37 (t, *J* = 7.6 Hz, 1 H); ^{13}C NMR (100.6 MHz, DMSO d_6): δ 139.1, 136.5, 132.7, 129.9, 129.74, 129.71, 128.9, 128.5, 127.7, 126.5, 124.9, 124.7, 123.8, 123.3, 122.9, 121.8, 121.2, 120.4, 112.6, 111.1, 105.8. ESI MS: 293 (M^{+1}, 100). Anal calcd for $C_{21}H_{12}N_2$: C, 86.28; H, 4.14; N, 9.58. Found: C, 86.20; H, 4.13; N, 9.60.



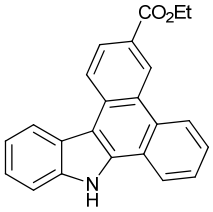
4c 2-(trifluoromethyl)-9*H*-dibenzo[*a*,*c*]carbazole: yellow solid; mp: 203-207 °C. IR (KBr): 3418, 1531, 1446, 1111 (cm^{-1}). ^{1}H NMR (400.13 MHz, DMSO d_6): δ 12.62 (bs, 1 H), 9.13 (d, J = 8.8 Hz, 1 H), 9.01- 8.95 (m, 2 H), 8.66 (d, J = 8.0 Hz, 1 H), 8.49 (d, J = 8.0 Hz, 1 H), 7.92-7.74 (m, 4 H), 7.51-7.39 (m, 2 H); ^{13}C NMR (100.6 MHz, DMSO d_6): 139.0, 135.5, 129.6, 129.2, 128.9, 128.8, 128.0 (q, J = 31.0 Hz), 127.5, 125.6, 125.2, 124.6, 124.1 (q, J = 278.0 Hz), 123.8, 123.6, 122.9, 121.4, 121.1, 120.1(q, J = 4.0 Hz),119.5 (q, J = 4.0 Hz),118.8, 112.6,111. ^{19}F (376.5 MHz, DMSO d_6) δ -60.3.ESI MS: 336 (M^{+1}, 100). Anal calcd for $C_{21}H_{12}F_3N$: C, 75.22; H, 3.61; N, 4.18. Found: C, 75.29; H, 3.60; N, 4.15.



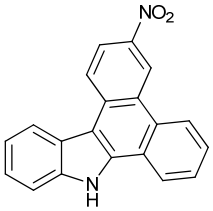
4d 1-methyl-9*H*-dibenzo[*a*,*c*]carbazole: yellow solid; mp: 173-176 °C. IR (KBr): 3440, 2923, 1436, 736 (cm^{-1})**.** ^{1}H NMR (400.13 MHz, $CDCl_3$): δ 8.87 (bs, 1 H), 8.74 (d, J = 8.0 Hz, 1 H), 8.64 (d, J = 8.0 Hz, 1 H), 8.30 (d, J = 8.2 Hz, 1 H), 8.00 (d, J = 7.6 Hz, 1 H), 7.69-7.53 (m, 5 H), 7.45-7.30 (m, 2 H), 3.13 (s, 3 H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 138.3, 135.1, 133.2, 130.6, 130.2, 129.4, 128.4, 126.7, 126.5, 125.6, 124.8, 124.1, 123.7, 123.4, 122.3, 120.9, 120.5, 119.5, 113.0, 111.1, 24.8. ESI MS: 282 (M^{+1}, 100). Anal calcd for $C_{21}H_{15}N$: C, 89.65; H, 5.37; N, 4.98. Found: C,89.71; H, 5.35; N, 5.00.



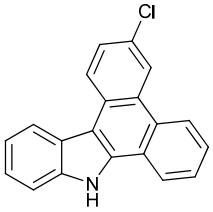
4e 1-(9*H*-dibenzo[*a*,*c*]carbazole-3-yl)ethanone: yellow solid; mp: 208-211 °C. IR (KBr): 3248, 2923, 1646, 1608, 1531, 1460,1330, 738 (cm^{-1}).^{1}H NMR (400.13 MHz, DMSO d_6): δ 12.63 (bs, 1 H), 9.47 (s, 1 H), 9.09 (d, J = 8.0 Hz, 1 H), 8.90 (d, J = 8.6 Hz, 1 H), 8.67-8.59 (m, 2 H), 8.30 (dd, J_1= 8.6 Hz, J_2= 1.2 Hz 1 H), 7.88-7.78 (m, 2 H), 7.76 (d, J = 8.0 Hz, 1 H), 7.48 (t, J = 7.6 Hz, 1 H), 7.38 (t, J = 7.6 Hz, 1 H), 2.84 (s, 3 H); ^{13}C NMR (100.6 MHz, DMSO d_6): δ 198.2, 139.1, 136.3, 133.2, 132.2, 129.9, 128.1, 127.5, 126.8, 125.9, 125.6, 124.7, 124.6, 124.0, 123.9, 123.2, 122.9, 121.9, 121.0, 112.5, 111.5, 27.3. ESI MS: 310 (M^{+1}, 100). Anal calcd for $C_{22}H_{15}NO$: C, 85.41; H, 4.89; N, 4.53. Found: C, 85.37; H, 4.90; N, 4.50.



4f ethyl 9*H*-dibenzo[*a*,*c*]carbazole-3-carboxylate: yellow solid; mp: 200-204 °C. IR (KBr): 3421, 2918, 1521, 1459, 1360, 738 (cm^{-1}). ^1H NMR (400.13 MHz, DMSO d_6): δ 12.62 (bs, 1 H), 9.44 (s, 1 H), 8.95-8.88 (m, 2 H), 8.64 (d, J = 7.5 Hz, 1 H), 8.60 (d, J = 8.1 Hz, 1 H), 8.30 (d, J = 8.5 Hz, 1 H), 7.89-7.73 (m, 3 H), 7.50-7.45 (m, 1 H), 7.38 (t, J = 7.4 Hz, 1 H), 4.45 (q, J = 7.0 Hz, 2 H), 1.44 (t, J = 7.0 Hz, 3 H); ^{13}C NMR (100.6 MHz, DMSO d_6): δ 166.6, 139.1, 136.2, 133.2, 129.6, 128.1, 127.8, 127.6, 126.0, 125.7, 124.9, 124.6, 124.3, 124.1, 123.9, 123.2, 122.9, 121.9, 121.0, 112.5, 111.4, 61.2, 14.8. ESI MS: 340 (M^{+1}, 100). Anal calcd for $C_{23}H_{17}NO_2$: C, 81.40; H, 5.05; N, 4.13. Found:C, 81.50; H, 5.04; N, 4.12.

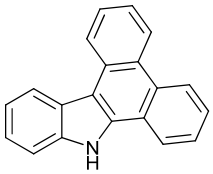


4g 3-nitro-9*H*-dibenzo[*a*,*c*]carbazole: orange solid; mp: 292-295 °C. IR (KBr): 3350, 1606, 1498, 1321, 735 (cm^{-1}). ^1H NMR (400.13 MHz, DMSO d_6): δ 12.81 (bs, 1 H), 9.54 (d, J = 2.2 Hz, 1 H), 8.90 (d, J = 8.2 Hz, 1 H), 8.82 (d, J = 8.8 Hz, 1 H), 8.57 (d, J = 7.8 Hz, 1 H), 8.50 (d, J = 8.1 Hz, 1 H), 8.41 (dd, J_1= 9.0 Hz, J_2= 2.1 Hz, 1 H), 7.87-7.71 (m, 3 H), 7.48 (t, J = 7.6 Hz, 1 H), 7.37 (t, J = 7.5 Hz, 1 H); ^{13}C NMR (100.6 MHz, DMSO d_6): δ 143.1, 139.1, 137.1, 134.2, 129.4, 128.7, 127.9, 125.9, 124.9, 124.7, 124.6, 123.7, 123.3, 123.0, 121.8, 121.7, 121.4, 120.2, 112.7, 111.2. ESI MS: 313 (M^{+1}, 100). Anal calcd for $C_{20}H_{12}N_2O_2$: C, 76.91; H, 3.87; N, 8.97. Found: C, 76.83; H, 3.88; N, 8.99.

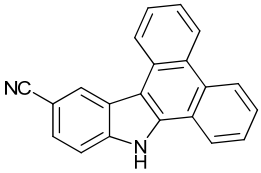


4h 3-chloro-9*H*-dibenzo[*a*,*c*]carbazole: yellow solid; mp: 240-243 °C. IR (KBr): 3338, 2918, 1685, 1608, 1240 (cm^{-1}).^1H NMR (400.13 MHz, DMSO d_6): δ 12.49 (bs, 1 H), 8.98-8.90 (m, 2 H), 8.82 (d, J = 8.8 Hz, 1 H), 8.62 (d, J = 7.9 Hz, 1 H), 8.54 (d, J = 7.9 Hz, 1 H), 7.86-7.70 (m, 4 H), 7.46 (t, J = 7.2 Hz, 1 H), 7.35 (t, J = 7.6 Hz, 1 H); ^{13}C NMR (100.6 MHz, DMSO d_6): δ 139.0, 134.8, 133.1, 128.8, 128.7, 128.5, 128.2, 128.0, 127.2, 125.7, 124.9, 124.3, 123.9, 123.8, 123.4, 122.8, 121.7,

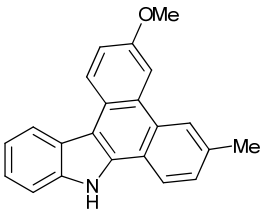
120.7, 112.4, 111.3. ESI MS: 302 (M^{+1}, 100). Anal calcd for $C_{20}H_{12}ClN$: C, 79.60; H, 4.01; N, 4.64. Found: C, 79.66; H, 3.99; N, 4.65.



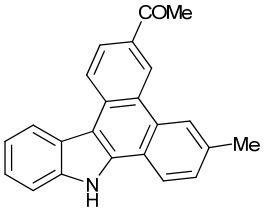
4i 9*H*-dibenzo[*a*,*c*]carbazole: white solid; mp: 185-188 °C. ^{1}H NMR (400.13 MHz, DMSO d_6): δ 12.51 (bs, 1 H) 8.94-8.86 (m, 3 H), 8.65 (d, J = 8.0 Hz, 1 H), 8.57 (d, J = 7.6 Hz, 1 H), 7.83-7.65 (m, 4 H), 7.59 (t, J = 7.6 Hz, 1 H), 7.44 (t, J = 7.6 Hz, 1 H), 7.34 (t, J = 7.6 Hz, 1 H); ^{13}C NMR (100.6 MHz, DMSO d_6): δ139.0, 134.7, 130.1, 129.8, 128.0, 127.4, 126.9, 126.7, 125.2, 124.4, 124.1, 124.0, 123.84, 123.82, 123.1, 122.8, 121.8, 120.5, 112.3, 111.7. ESI MS: 268 (M^{+1}, 100). Anal calcd for $C_{20}H_{13}N$: C, 89.86; H, 4.90; N, 5.24. Found: C, 89.80; H, 4.93; N, 5.20



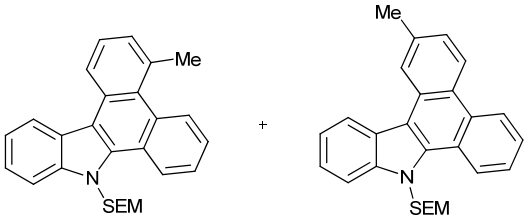
4j 9*H*-dibenzo[*a*,*c*]carbazole-12-carbonitrile: white solid; mp: 305-308 °C.IR (KBr): 3336, 2360, 2223, 1531, 1448, 757 (cm^{-1}).^{1}H NMR (400.13 MHz, DMSO d_6): δ 12.95 (bs, 1 H), 9.12 (s, 1 H), 8.94-8.85 (m, 3 H), 8.59 (d, J = 7.6 Hz, 1 H), 7.87-7.72 (m, 5 H), 7.62 (t, J = 7.6 Hz, 1 H); ^{13}C NMR (100.6 MHz, DMSO d_6): δ 140.8, 136.2, 130.3, 129.1, 128.3, 127.73, 127.70, 127.1, 127.0, 126.9, 124.8, 124.5, 124.4, 124.3, 123.9, 122.9, 122.6, 121.1, 113.3, 111.7, 102.6. ESI MS: 293 (M^{+1}, 100). Anal calcd for $C_{21}H_{12}N_2$; C, 86.28; H, 4.14; N, 9.58. Found: C, 86.19; H, 4.15; N, 9.60.



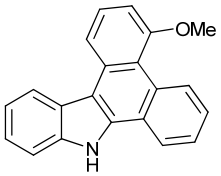
4k 3-methoxy-6-methyl-9*H*-dibenzo[*a*,*c*]carbazole: yellow solid; mp. 283-287 °C.IR (KBr): 3426, 1529, 1450, 1249, 1176, 1089, 738^{1}H NMR (400.13 MHz, DMSO d_6): δ 12.76 (bs, 1 H), 8.83 (s, 1 H), 8.80 (s, 1 H), 8.72 (d, J = 8.8 Hz, 1 H), 8.60 (d, J = 8.0 Hz, 1 H), 8.32 (s, 1 H), 7.97 (d, J = 8.0 Hz, 1 H), 7.57 (d, J = 8.4 Hz, 1 H), 7.49 (t, J = 7.6 Hz, 1 H), 7.46-7.34 (m, 2 H), 4.04 (s, 3 H), 2.64 (s, 3 H); ^{13}C NMR (100.6 MHz, DMSO d_6): δ 156.8, 141.2, 135.9, 133.5, 130.4, 128.9, 128.6, 125.4, 124.54, 124.49, 124.3, 123.7, 123.3, 121.81, 121.80, 121.4, 117.5, 113.3, 110.9, 106.4, 55.9, 21.8. ESI MS: 312 (M^{+1}, 100). Anal calcd for $C_{22}H_{17}NO$; C, 84.86; H, 5.50; N, 4.50. Found: C, 84.78; H, 5.49; N, 4.52.



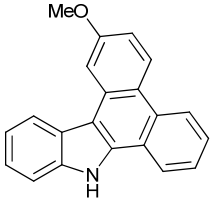
4l 1-(6-methyl-9*H*-dibenzo[*a*,*c*]carbazol-3-yl)ethanone: white solid, mp: 313-318 °C. ^{1}H NMR (400.13 MHz, DMSO d_6): δ 12.63 (bs, 1 H), 9.39 (s, 1 H), 8.90-8.85 (m, 2 H), 8.72 (d, J = 8.4 Hz, 1 H), 8.64 (d, J = 8.0 Hz, 1 H), 8.25 (d, J = 8.0 Hz, 1 H), 8.01 (d, J = 8.0 Hz, 1 H), 7.61 (d, J = 8.8 Hz, 1 H), 7.55 (t, J = 7.2 Hz, 1 H), 7.44 (t, J = 7.2 Hz, 1 H), 2.83 (s, 3 H), 2.66 (s, 3 H); ^{13}C NMR (100.6 MHz, DMSO d_6): δ 198.2, 141.2, 136.9, 136.2, 132.7, 132.5, 131.0, 129.4, 126.7, 126.3, 125.2, 124.9, 124.6, 124.3, 124.0, 123.3, 122.0, 121.9, 121.1, 112.9, 111.1, 27.3, 21.9. ESI MS: 324 (M^{+1}, 100). Anal calcd for $C_{23}H_{17}NO$; C, 85.42; H, 5.30; N, 4.33. Found: C, 85.35; H, 5.29; N, 4.32.



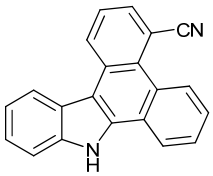
7m+7m': oil**;** IR (neat): 3396, 2950, 1465, 1076, 835, 734 (cm^{-1}). ^{1}H NMR (400.13 MHz, DMSO d_6) (unselected signals): δ 8.92-8.63 (m, 4.4 H), 8.03-7.95 (m, 1.0 H), 7.70-7.60 (m, 2.7 H), 7.57-7.38 (m, 3.3 H), 6.11 (s, 0.9 H), 6.06 (s, 0.9 H), 3.86 (q, J = 8.0 Hz, 2 H), 3.09 (s, 1.4 H), 2.67 (s, 1.4 H), 1.10-0.92 (m, 2 H), -0.06 (s, 4.5 H), -0.09 (s, 4.5 H); ^{13}C NMR (100.6 MHz, DMSO d_6) (unselected signals): δ 141.6, 141.3, 137.7, 135.7, 134.69, 134.66, 131.4, 130.8, 129.5, 129.3, 129.0, 127.6, 127.3, 126.9, 126.8, 126.7, 126.4, 125.3, 125.1, 124.8, 124.5, 124.3, 124.2, 124.1, 123.6, 123.5, 123.4, 122.8, 122.3, 122.1, 121.9, 121.7, 121.6, 114.3, 113.7, 111.2, 111.0, 74.7, 74.5, 65.85, 65.81, 27.3, 21.9, 17.95, 17.93, -0.88. Anal calcd for $C_{27}H_{29}NOSi$: C, 78.79; H, 7.10; N, 3.40. Found: C, 78.68; H, 7.13; N, 3.42.



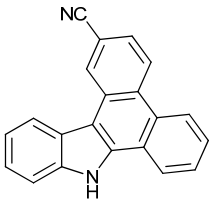
4n 4-methoxy-9*H*-dibenzo[*a*,*c*]carbazole: white solid, mp: 200-203 °C. IR (KBr): 3409, 2254, 1484, 1252, 1025, 873 (cm^{-1}).^{1}H NMR (400.13 MHz, DMSO d_6): δ 12.69 (bs, 1 H), 9.85 (d, J = 7.6 Hz, 1 H), 8.93-8.87 (m, 1 H), 8.65 (d, J = 8.0 Hz, 1 H), 8.58 (d, J = 7.6 Hz, 1 H), 8.01 (d, J = 8.4 Hz, 1 H), 7.79-7.60 (m, 3 H), 7.54 (t, J = 7.2 Hz, 1 H), 7.43 (t, J = 7.2 Hz, 1 H), 4.15 (s, 3 H); ^{13}C NMR (100.6 MHz, DMSO d_6): δ 159.1, 141.7, 135.2, 131.6, 130.6, 129.4, 128.6, 126.6, 126.3, 124.9, 124.0, 123.5, 123.4, 122.2, 121.8, 117.2, 116.7, 114.0, 111.8, 107.8, 56.4. ESI MS: 298 (M^{+1}, 100). Anal calcd for $C_{21}H_{15}NO$: C, 84.82; H, 5.08; N, 4.71. Found: C, 84.75; H, 5.10; N, 4.69.



4n' 2-methoxy-9*H*-dibenzo[*a*,*c*]carbazole: yellow solid, mp: 210-213 °C. IR (KBr): 3423, 1467, 1247, 1027, 825, 730 (cm^{-1}). ^{1}H NMR (400.13 MHz, DMSO d_6): δ 12.48 (bs, 1 H), 8.89-8.82 (m, 3 H), 8.61 (d, J = 7.6 Hz, 1 H), 8.21 (d, J = 2.4 Hz, 1 H), 8.04 (d, J = 8.0 Hz, 1 H), 7.75-7.65 (m, 2 H), 7.55 (t, J = 7.2 Hz, 1 H), 7.45 (t, J = 7.2 Hz, 1 H), 7.30-7.25 (m, 1 H), 4.08 (s, 3 H); ^{13}C NMR (100.6 MHz, DMSO d_6): δ 159.4, 141.3, 135.1, 130.9, 130.7, 126.9, 126.3, 126.1, 124.8, 124.5, 123.9, 123.3, 122.0, 121.9, 121.8, 121.3, 114.2, 113.6, 111.0, 105.3, 55.8. ESI MS: 298 (M^{+1}, 100). Anal calcd for $C_{21}H_{15}NO$: C, 84.82; H, 5.08; N, 4.71. Found: C, 84.74; H, 5.06; N, 4.69.



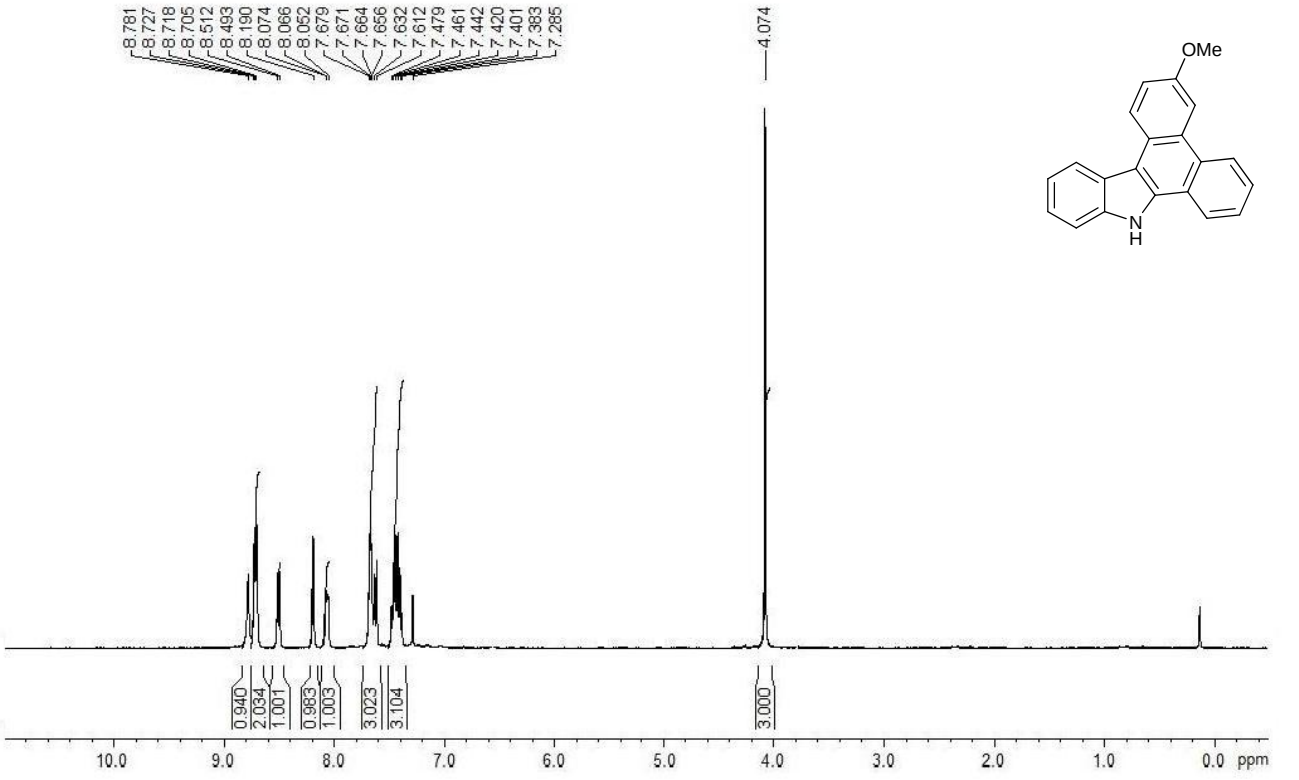
4o 9*H*-dibenzo[*a*,*c*]carbazole-4-carbonitrile: IR (KBr): 3423, 2227, 1523, 1467, 1438, 1070 (cm^{-1}).^{1}H NMR (400.13 MHz, DMSO d_6): δ 12.73 (bs, 1 H), 9.65 (d, J = 8.0 Hz, 1 H), 9.20 (d, J = 8.0 Hz, 1 H), 8.88 (d, J = 8.0 Hz, 1 H), 8.63 (d, J = 8.0 Hz, 1 H), 8.13 (d, J = 7.2 Hz, 1 H), 8.02 (d, J = 8.4 Hz, 1 H), 7.92-7.77 (m, 4 H), 7.72 (d, J = 8.0 Hz, 1 H). ESI MS: 293 (M^{+1}, 100).

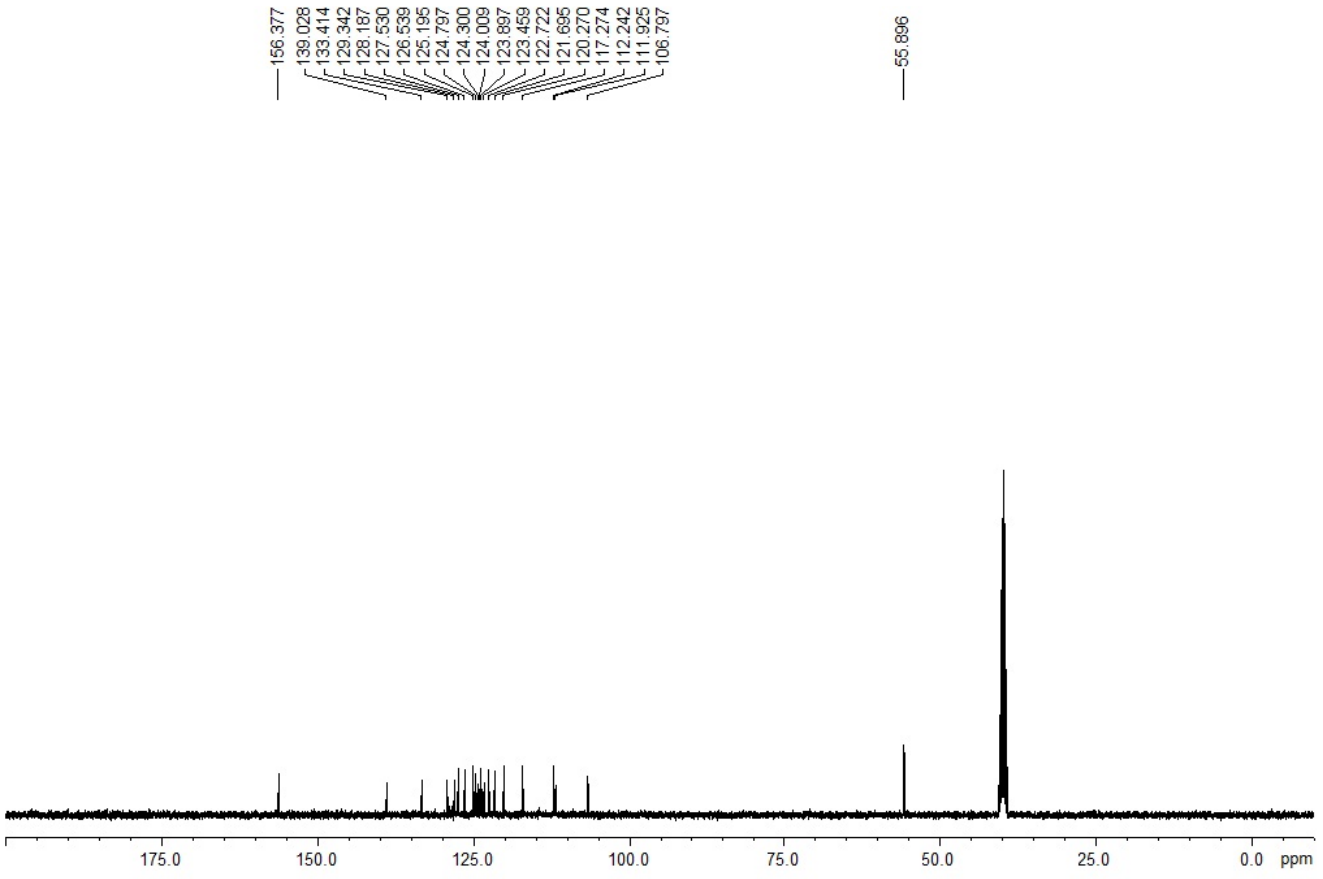


4o' 9*H*-dibenzo[*a*,*c*]carbazole-4-carbonitrile: white solid, mp: 299-302 °C. IR (KBr): 3421, 2228, 1467, 1438, 1068, 837, 734 (cm^{-1}).^{1}H NMR (400.13 MHz, DMSO d_6): δ 12.99 (bs, 1 H), 9.26 (s, 1 H), 9.10 (d, J = 8.8 Hz, 1 H), 9.07 (d, J = 8.0 Hz, 1 H), 8.89 (d, J = 8.4 Hz, 1 H), 7.78 (d, J = 8.0 Hz, 1 H), 8.06 (d, J = 8.0 Hz, 1 H), 7.96 (d, J = 8.4 Hz, 1 H), 7.89-7.80 (m, 1 H), 7.58 (t, J = 7.2 Hz, 1 H), 7.46 (d, J = 7.2 Hz, 1 H); ^{13}C NMR (100.6 MHz, DMSO d_6): δ 141.3, 135.2, 130, 129.6, 129.1, 128.9, 128.3, 127.4, 126.5, 125.7, 125.44, 125.37, 124.8, 124.1, 122.7, 122.3, 122.1, 119.8, 113.0, 11.2, 110.6. ESI MS: 293 (M^{+1}, 100). Anal calcd for $C_{21}H_{12}N_2$: C, 86.28; H, 4.14; N, 9.58. Found: C, 86.22; H, 4.13; N, 9.56.

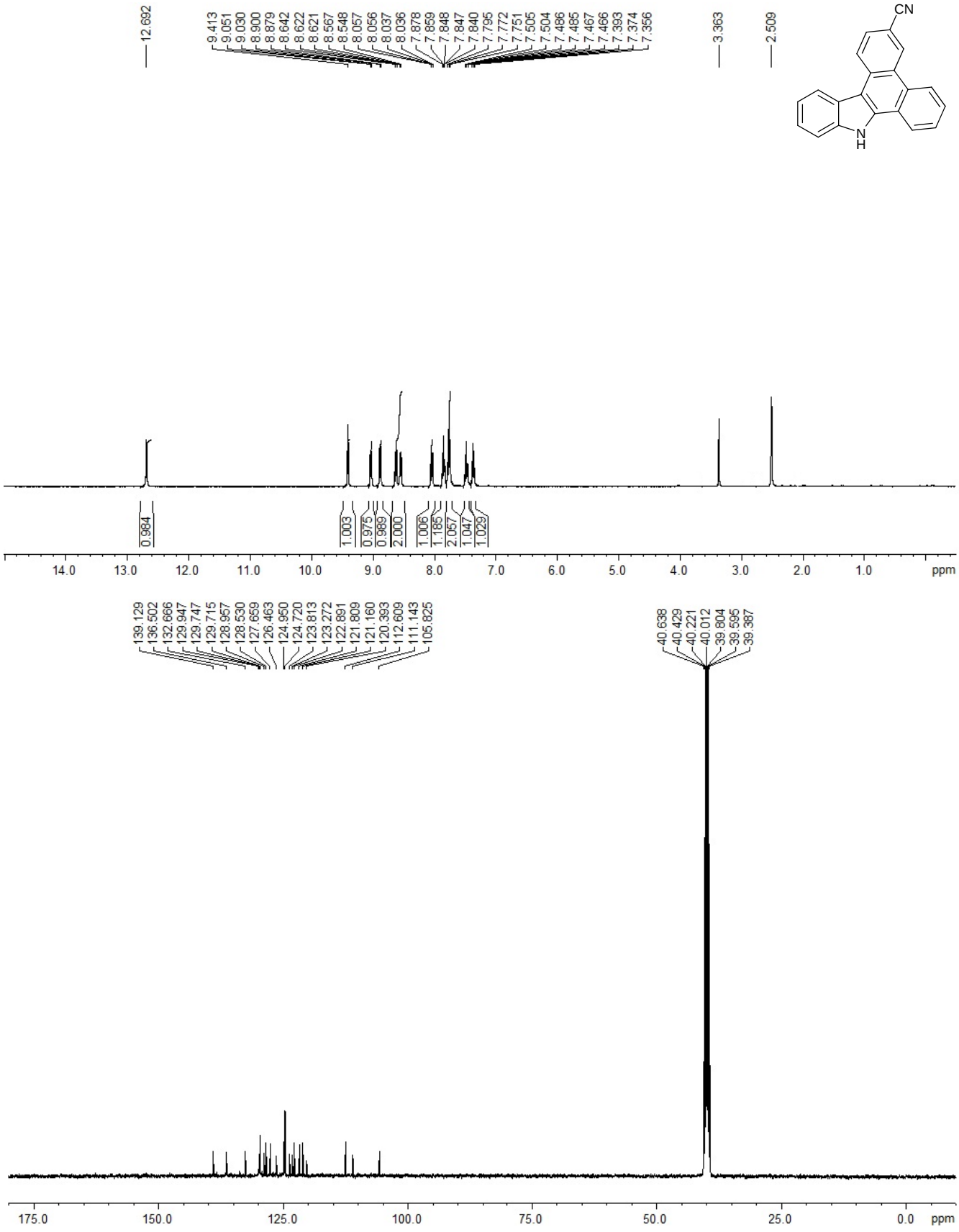
NMR Spectra

4a

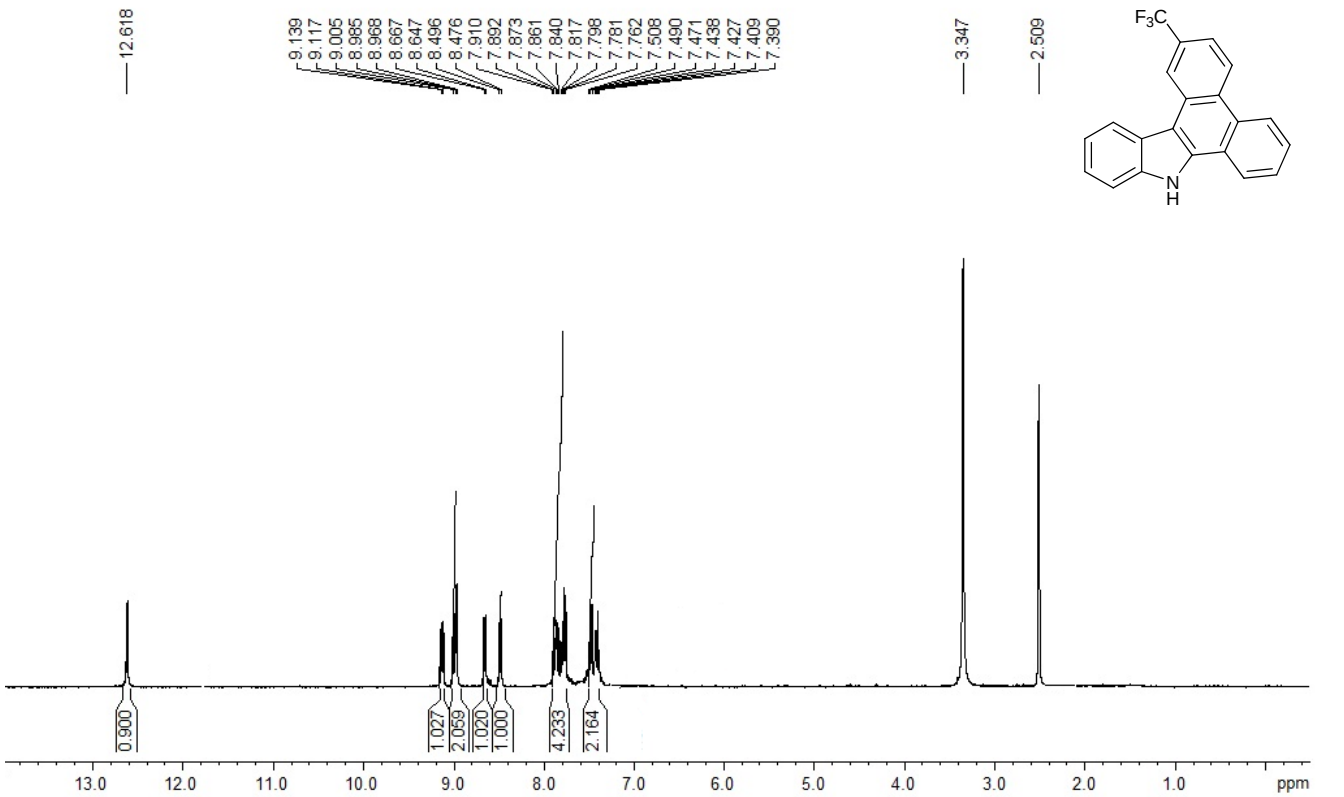


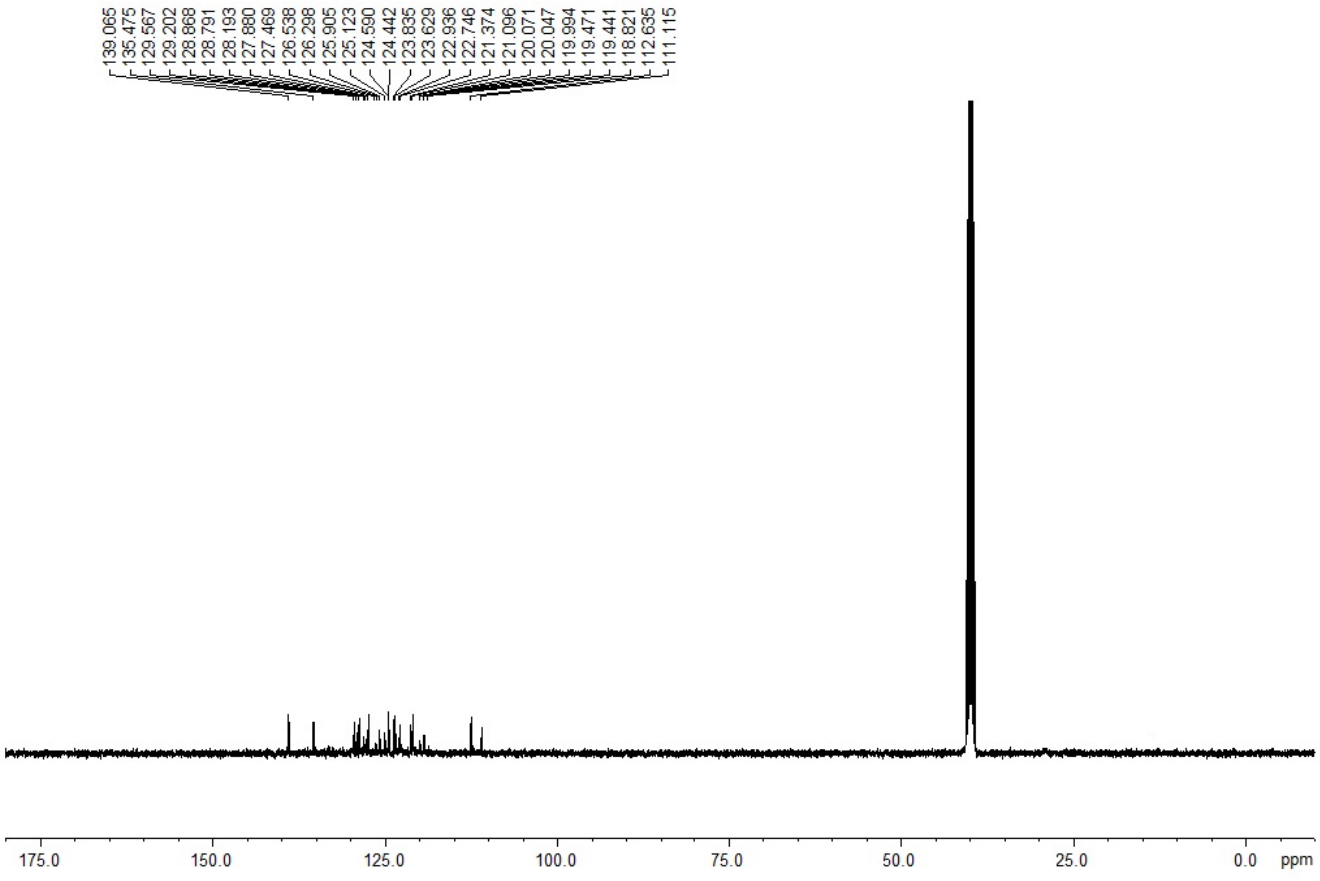


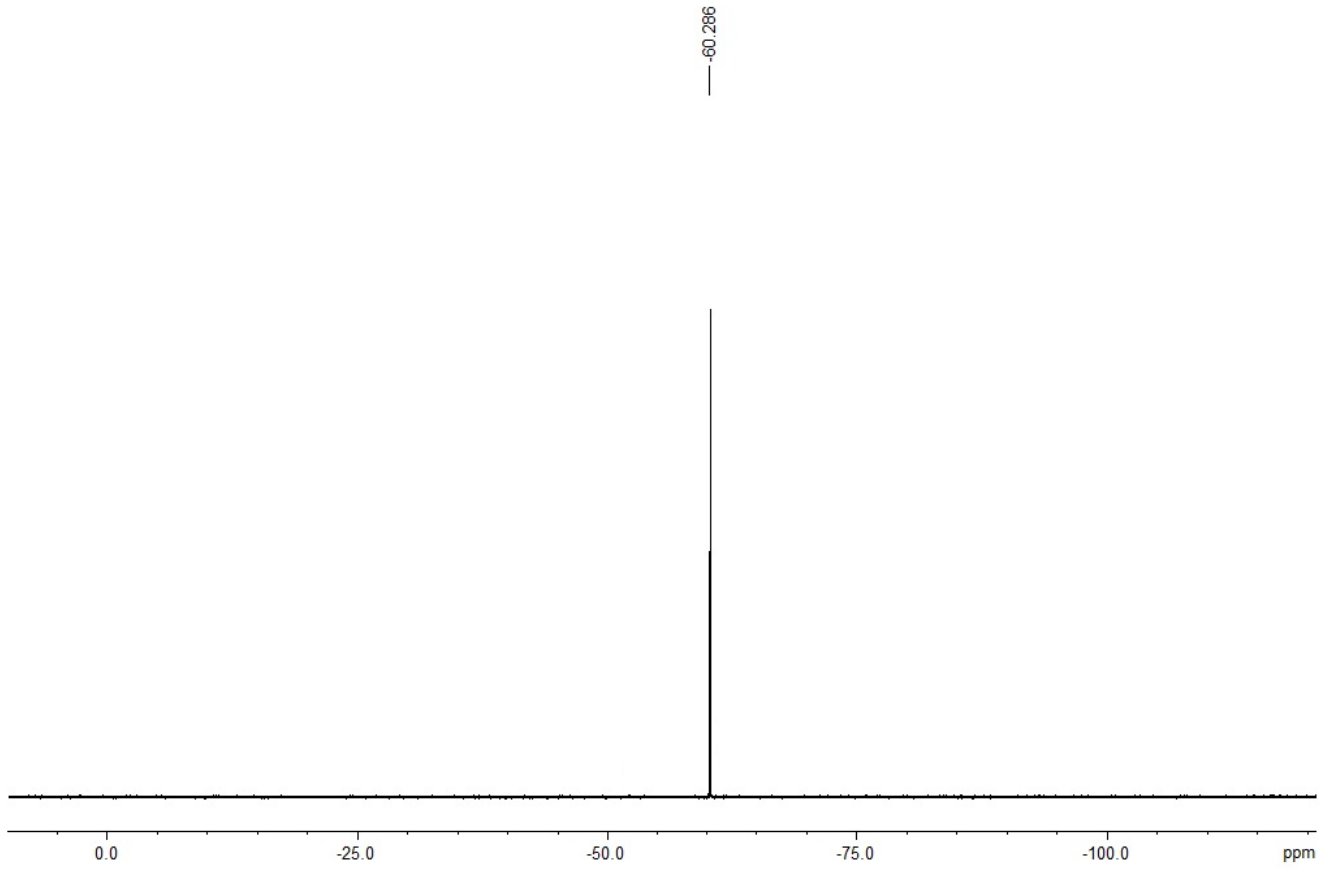
4b



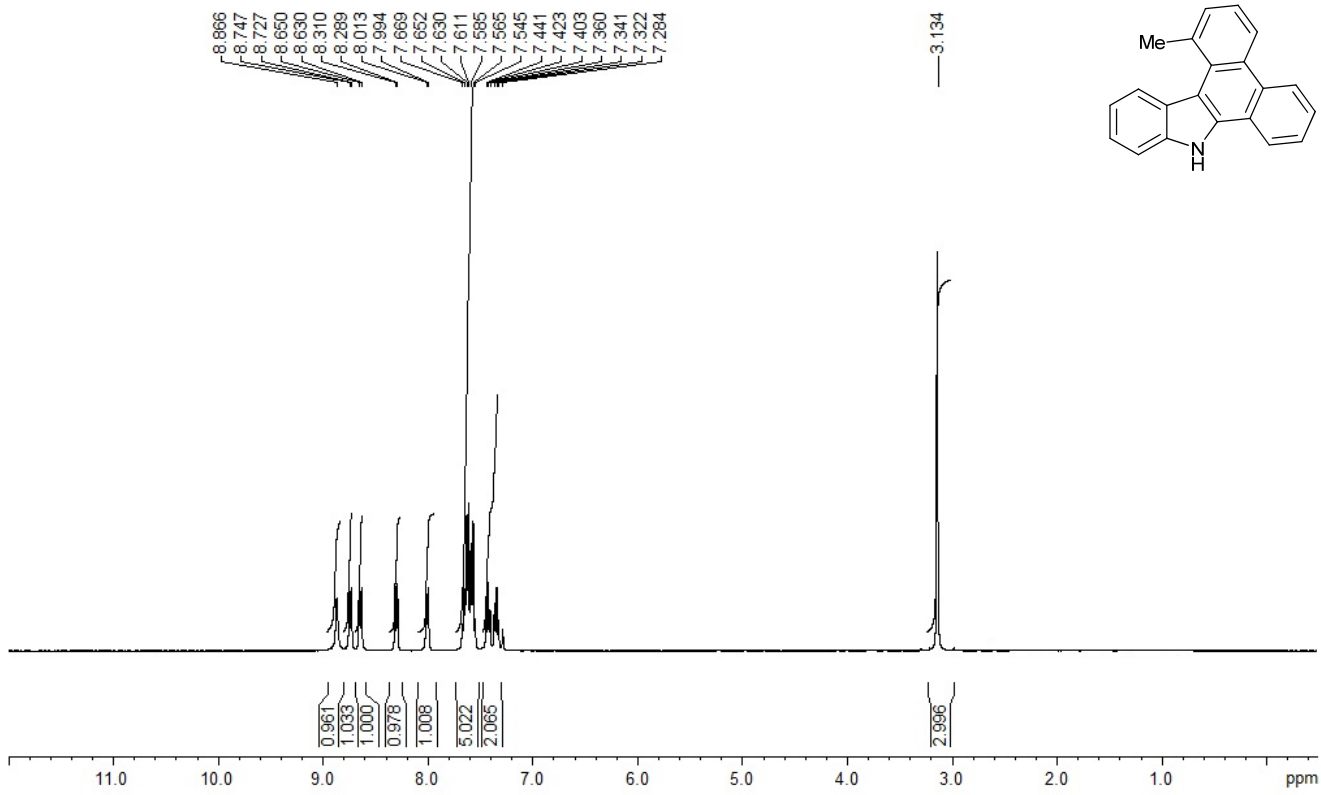
4c







4d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8.727
8.650
8.630
8.310
8.289
8.013
7.994
7.669
7.652
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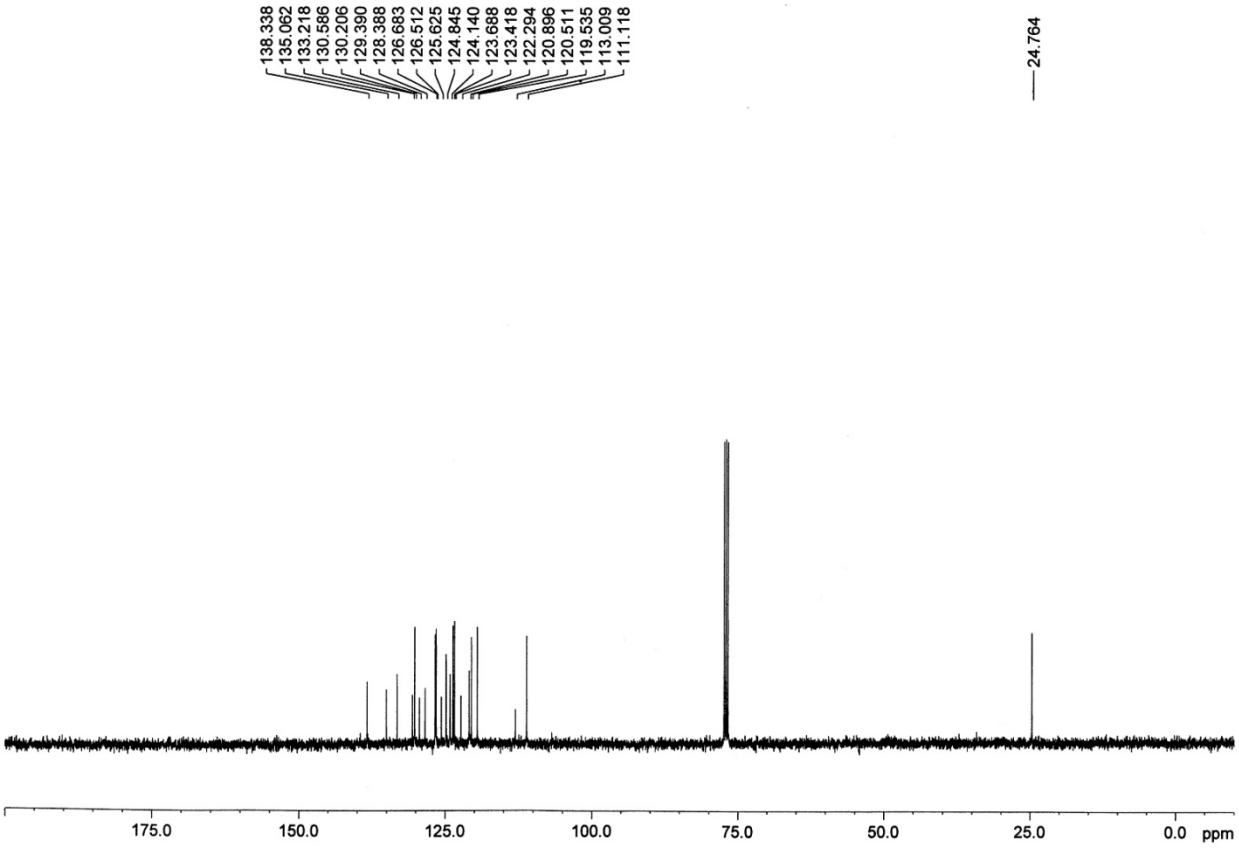
7.585
7.565
7.545
7.441
7.423
7.403
7.360
7.341
7.322
7.284
3.134
Me
N
H
0.961
1.033
1.000
0.978
1.008
5.022
2.065
2.996
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm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133.218
130.586
130.206
129.390
128.388
126.683
126.512
125.625
124.845
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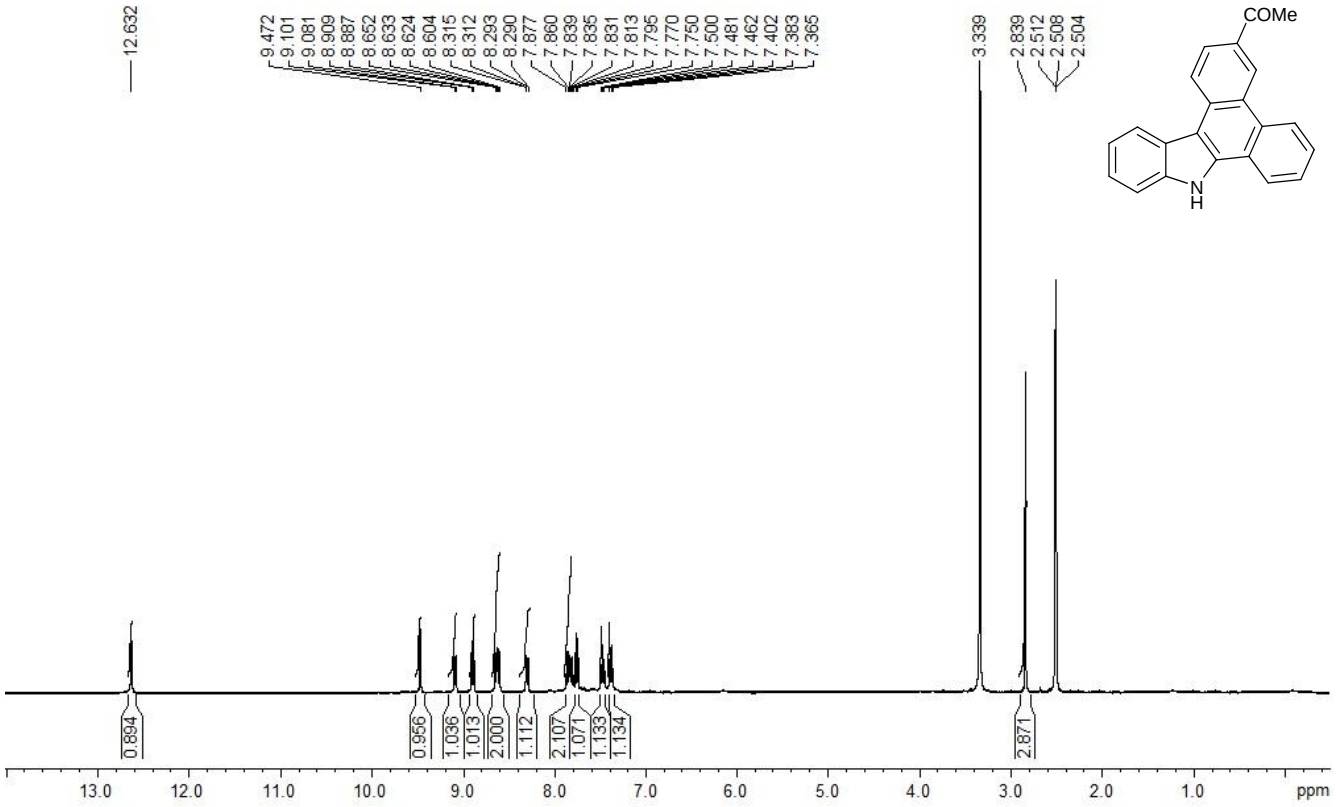
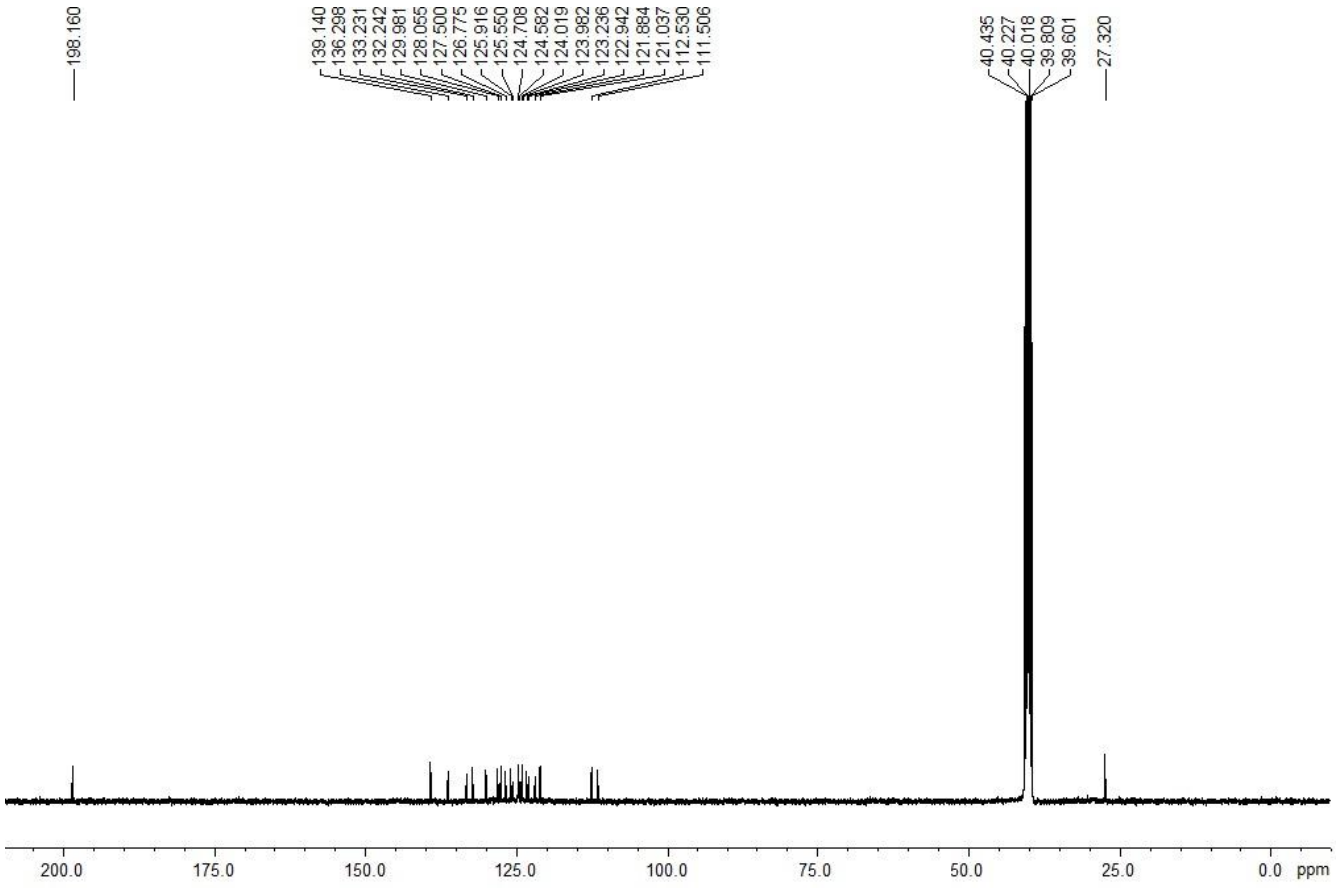
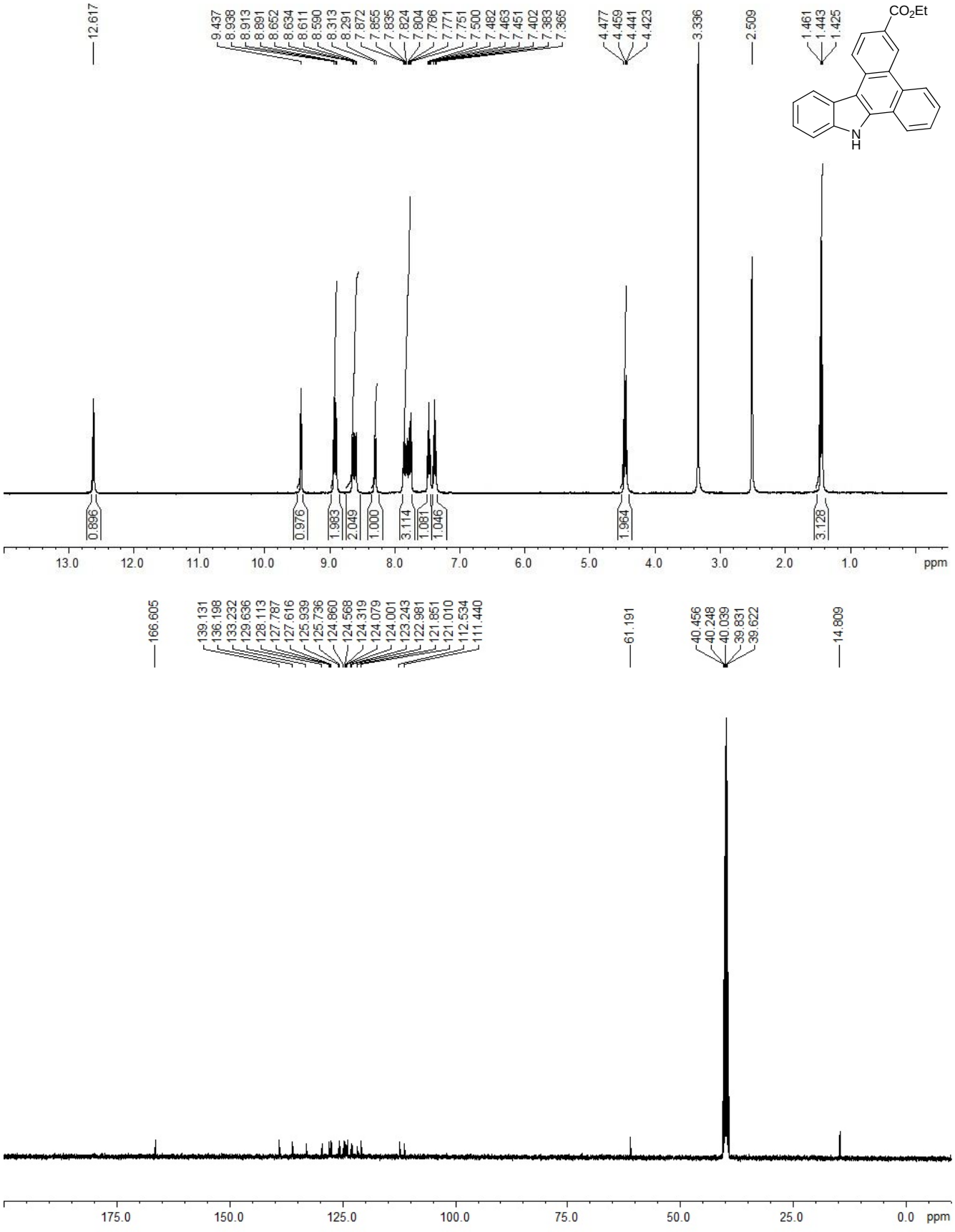
123.418
122.294
120.896
120.511
119.535
113.009
111.118
24.764
175.0
150.0
125.0
100.0
75.0
50.0
25.0
0.0
ppm

4e





4f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8.611
8.590
8.313
8.291
7.872
7.855
7.835
7.824
7.804
7.786
7.771
7.751
7.500
7.482
7.463
7.451
7.402
7.383
7.365
4.477
4.459
4.441
4.423
3.336
2.509
1.461
1.443
1.425
CO2Et
N
H
0.896
0.976
1.963
2.049
1.000
3.114
1.081
1.046
1.964
3.128
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm
166.605
139.131
136.198
133.232
129.636
128.113
127.787
127.616
125.939
125.736
124.860
124.568
124.319
124.079
124.001
123.243
122.981
121.851
121.010
112.534
111.440
61.191
40.456
40.248
40.039
39.831
39.622
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125.0
100.0
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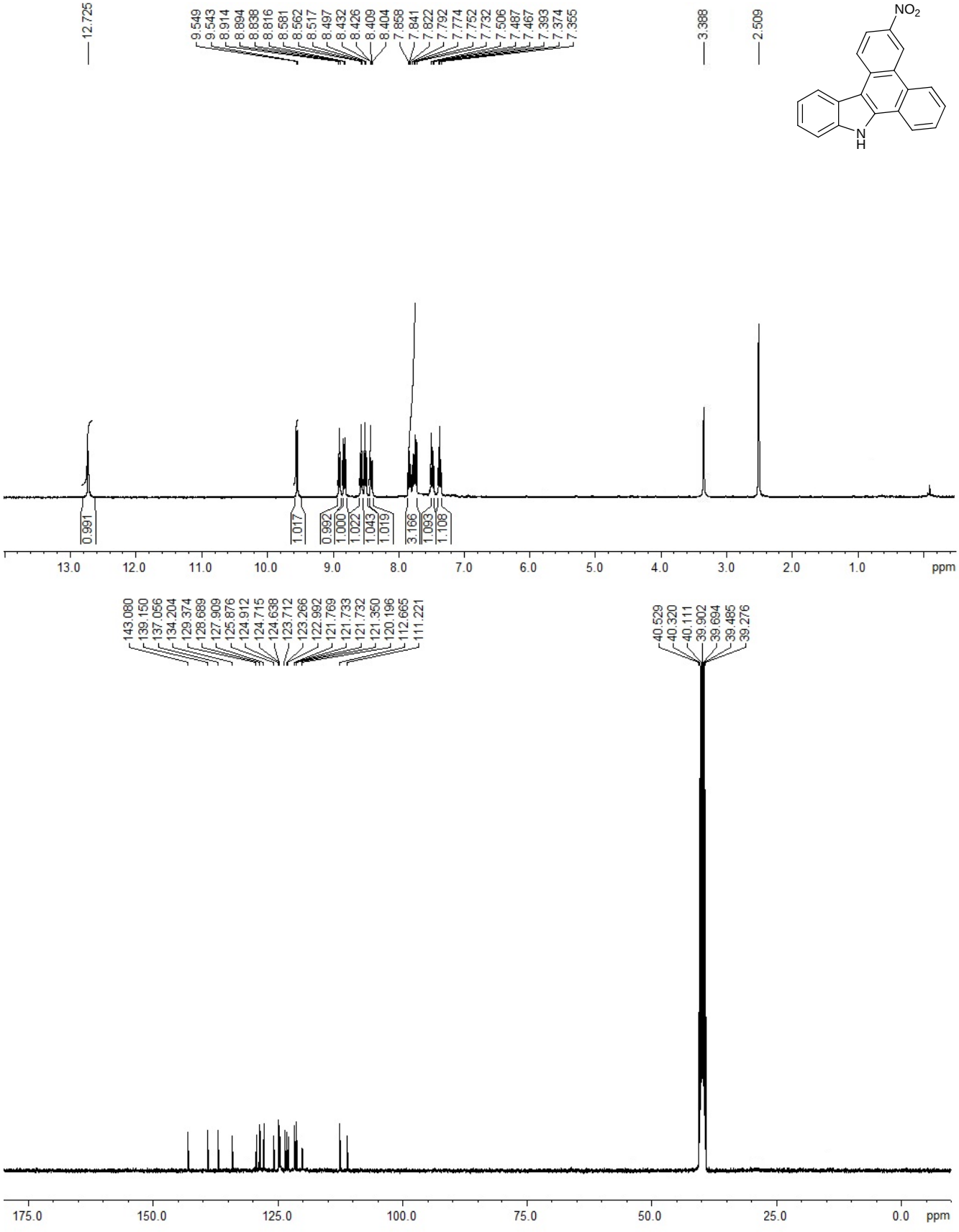
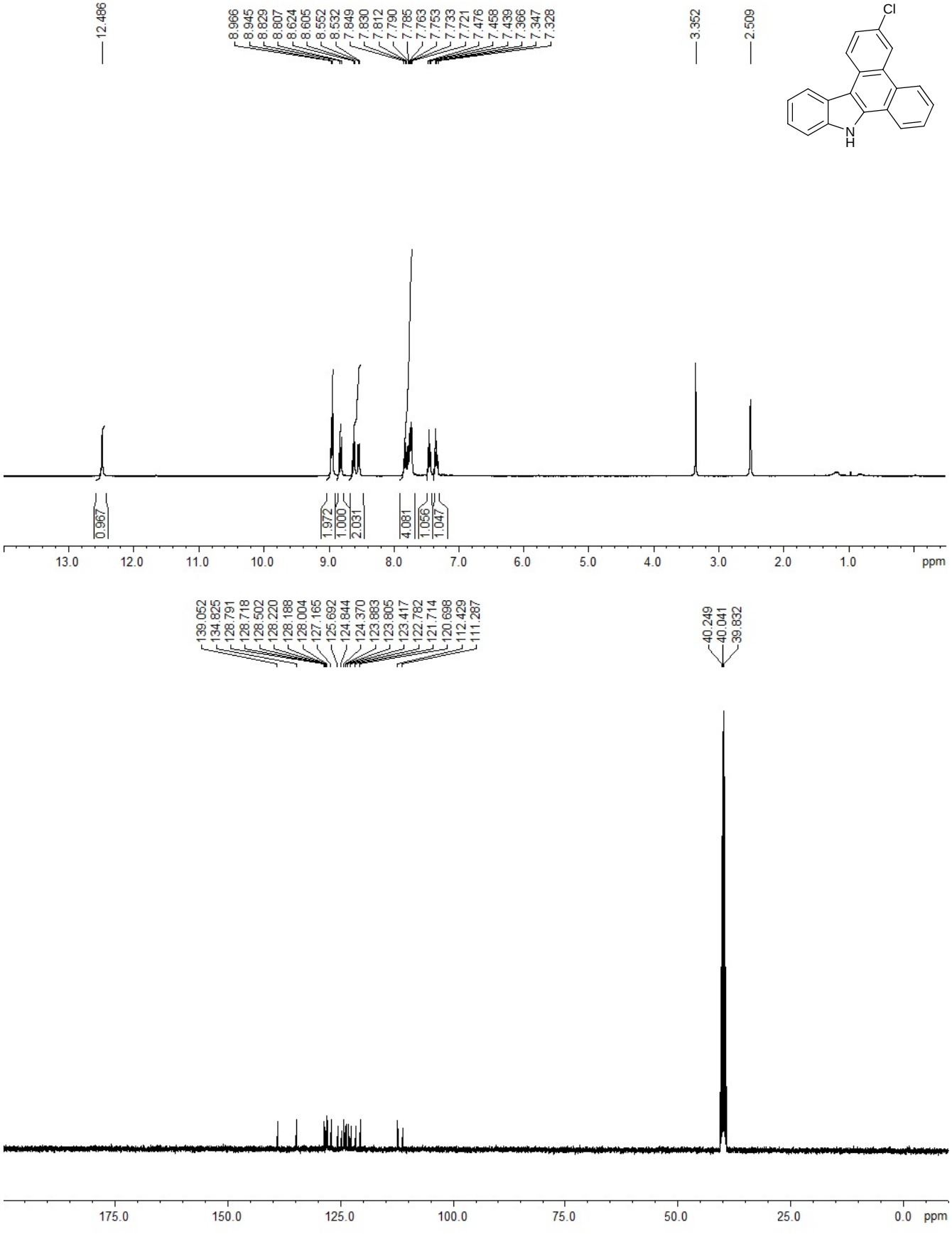
50.0
25.0
0.0
ppm

4g



4h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8.829
8.807
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8.605
8.552
8.532
7.849
7.830
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7.790
7.785
7.763
7.753
7.733
7.721
7.476
7.458
7.439
7.366
7.347
7.328
3.352
2.509
Cl
N
H
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1.972
1.000
2.031
4.081
1.056
1.047
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm
139.052
134.825
128.791
128.718
128.502
128.220
128.188
128.004
127.165
125.692
124.844
124.370
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123.805
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120.698
112.429
111.287
40.249
40.041
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125.0
100.0
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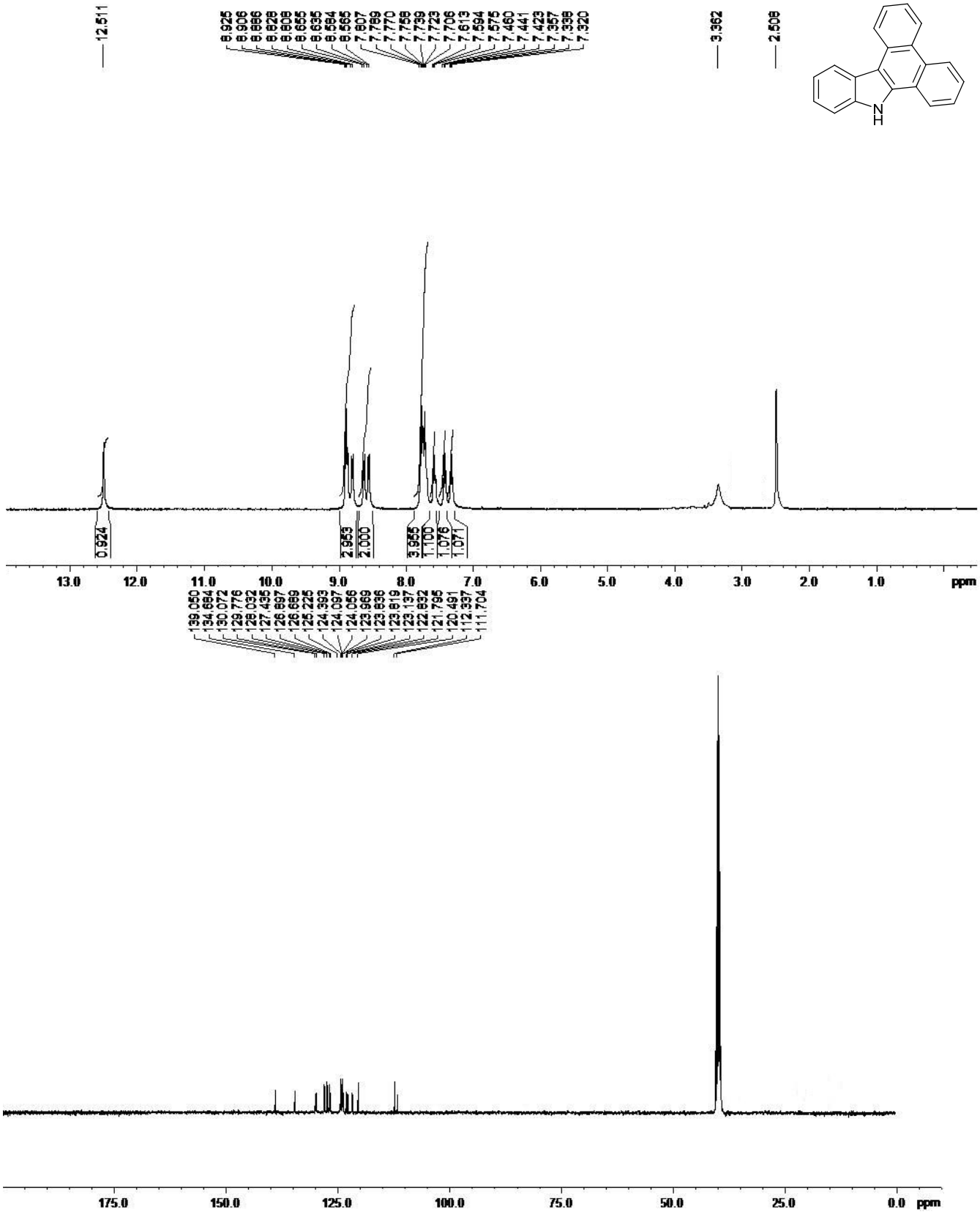
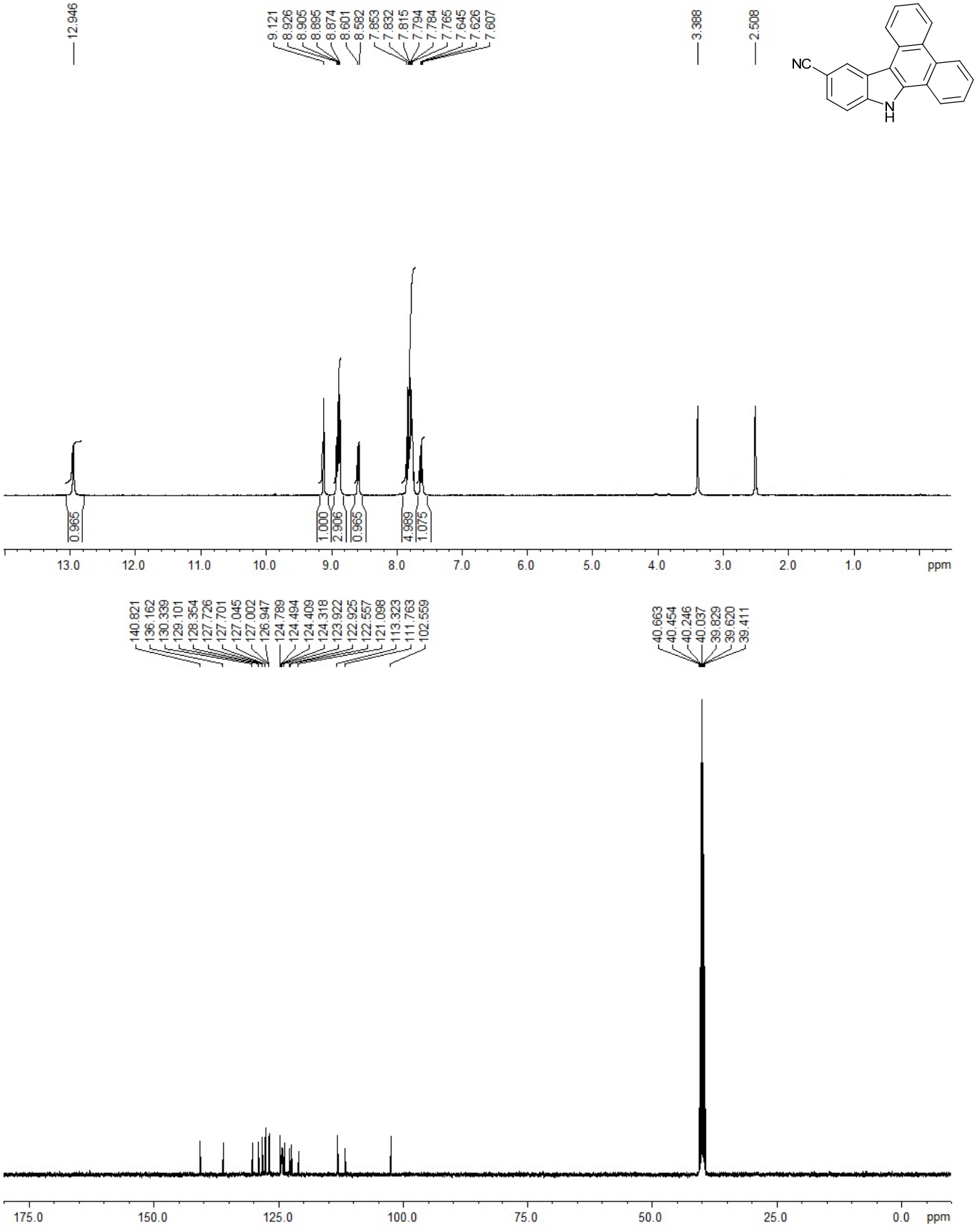
25.0
0.0
ppm

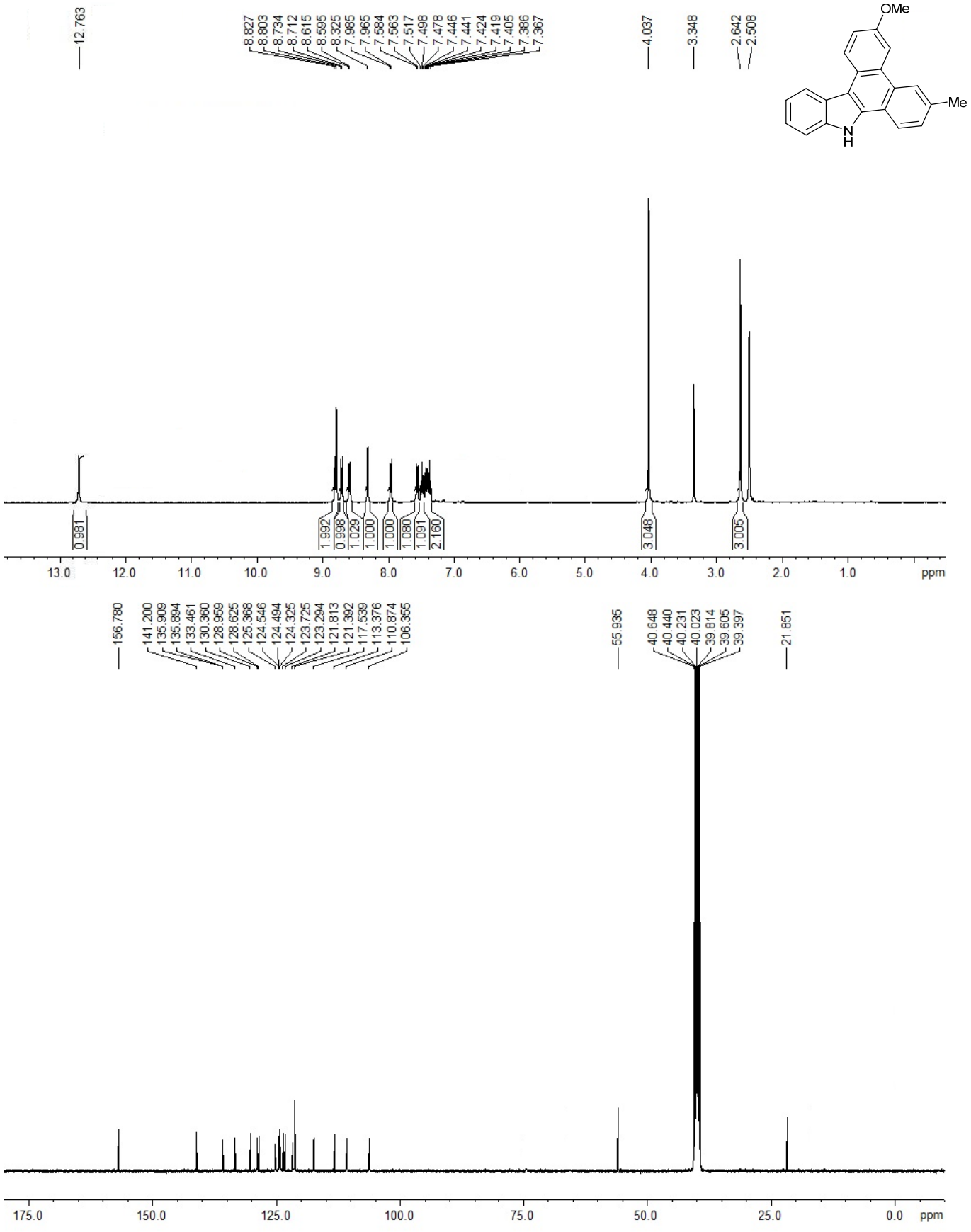
4i



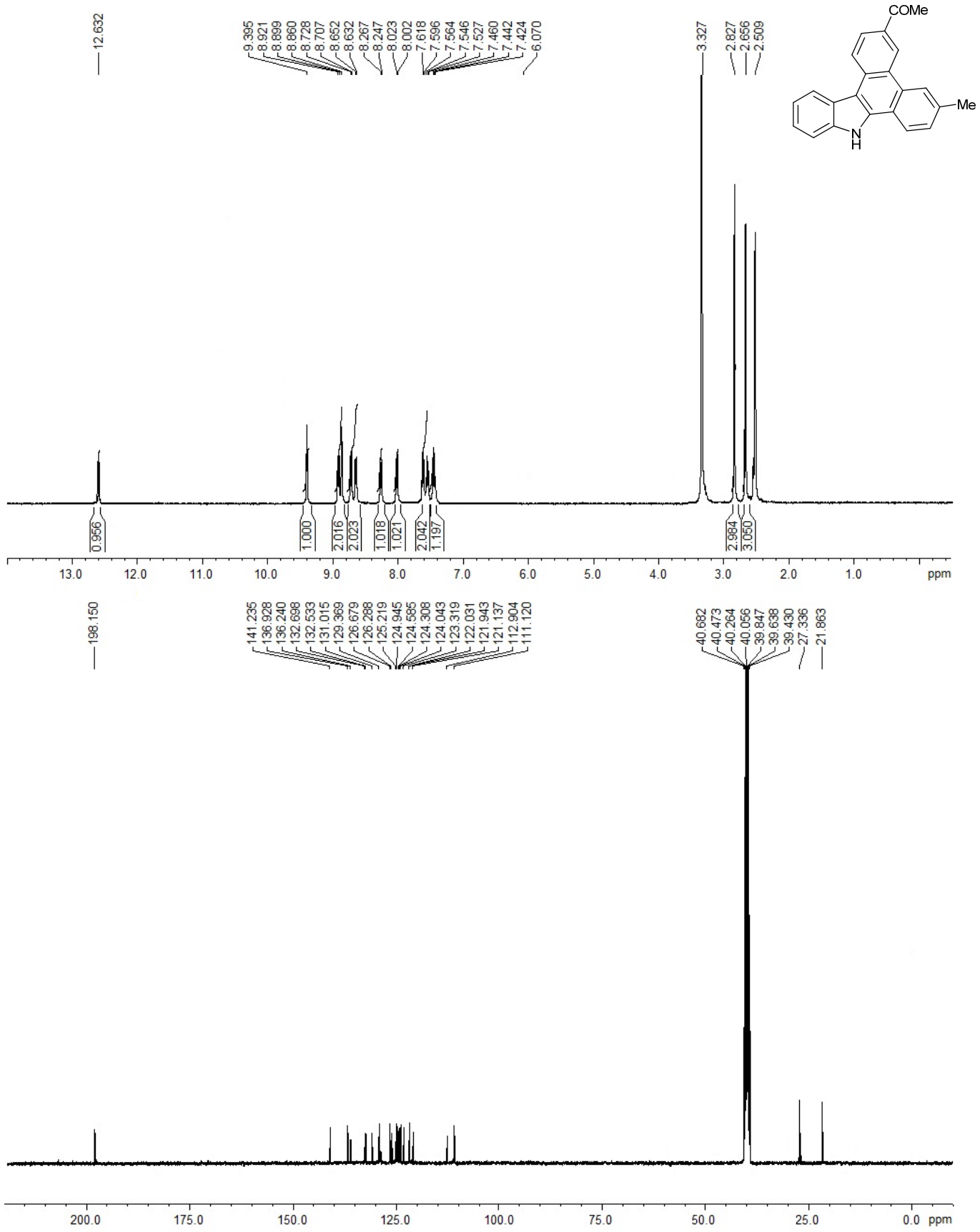
4j



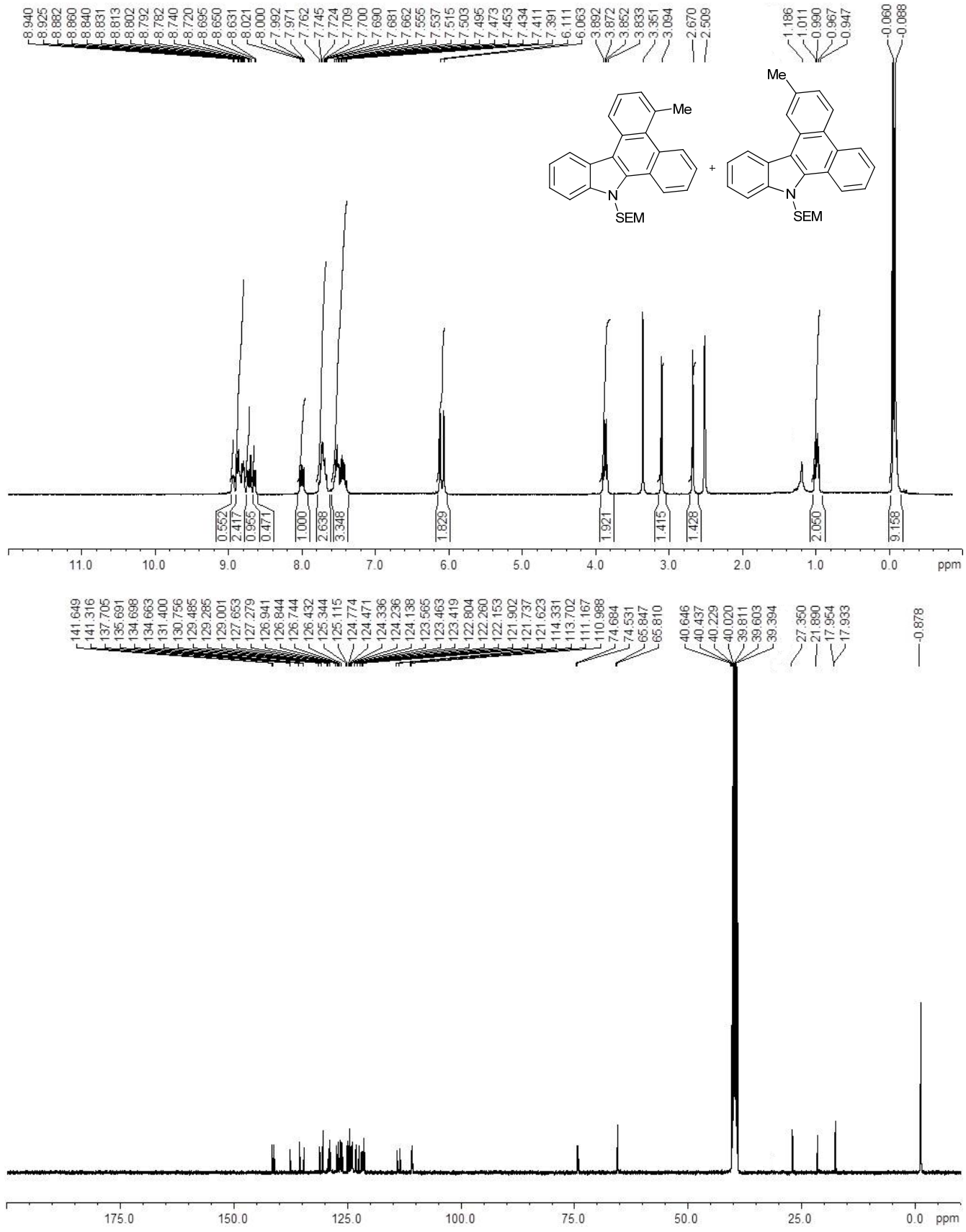
4k



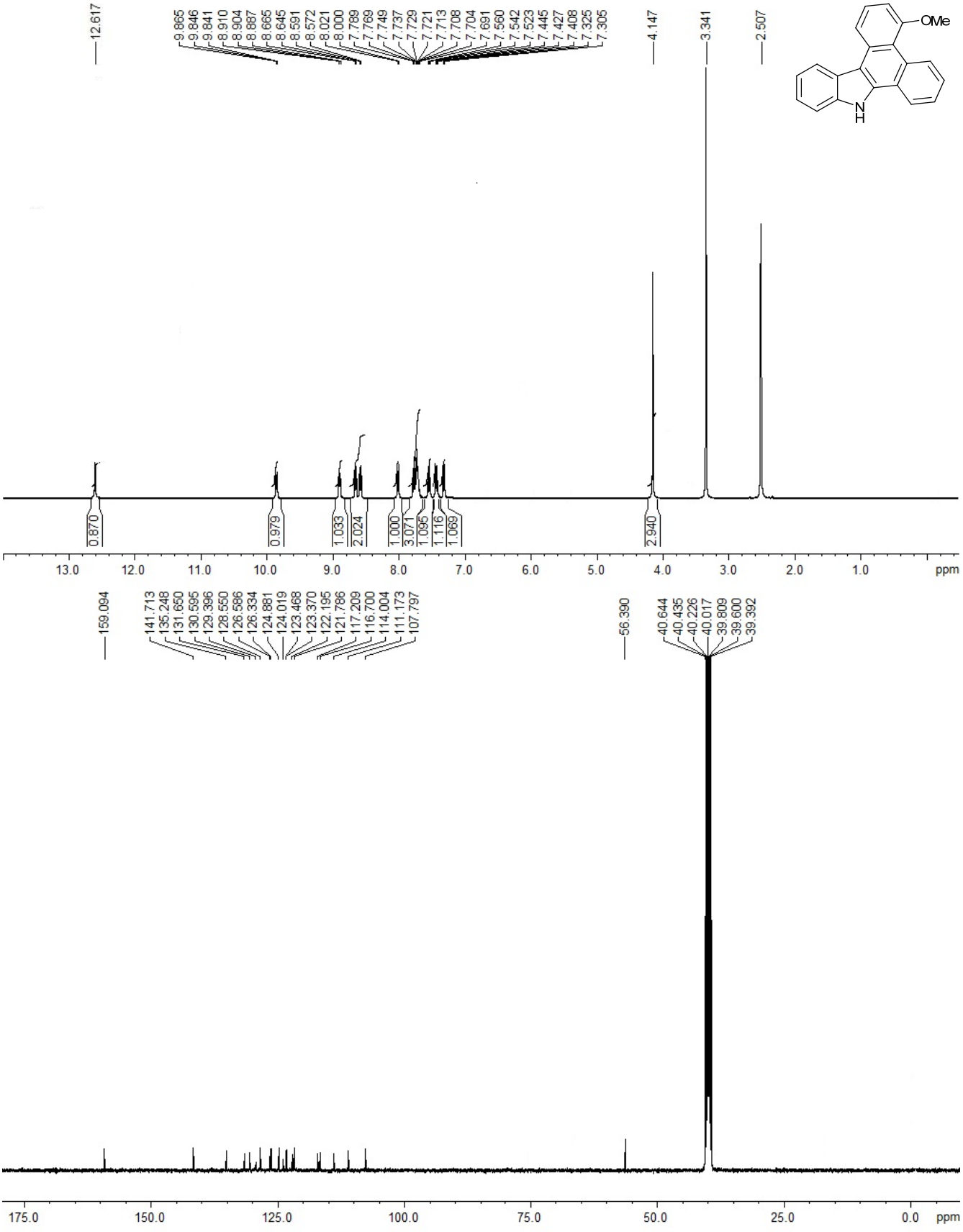
4l



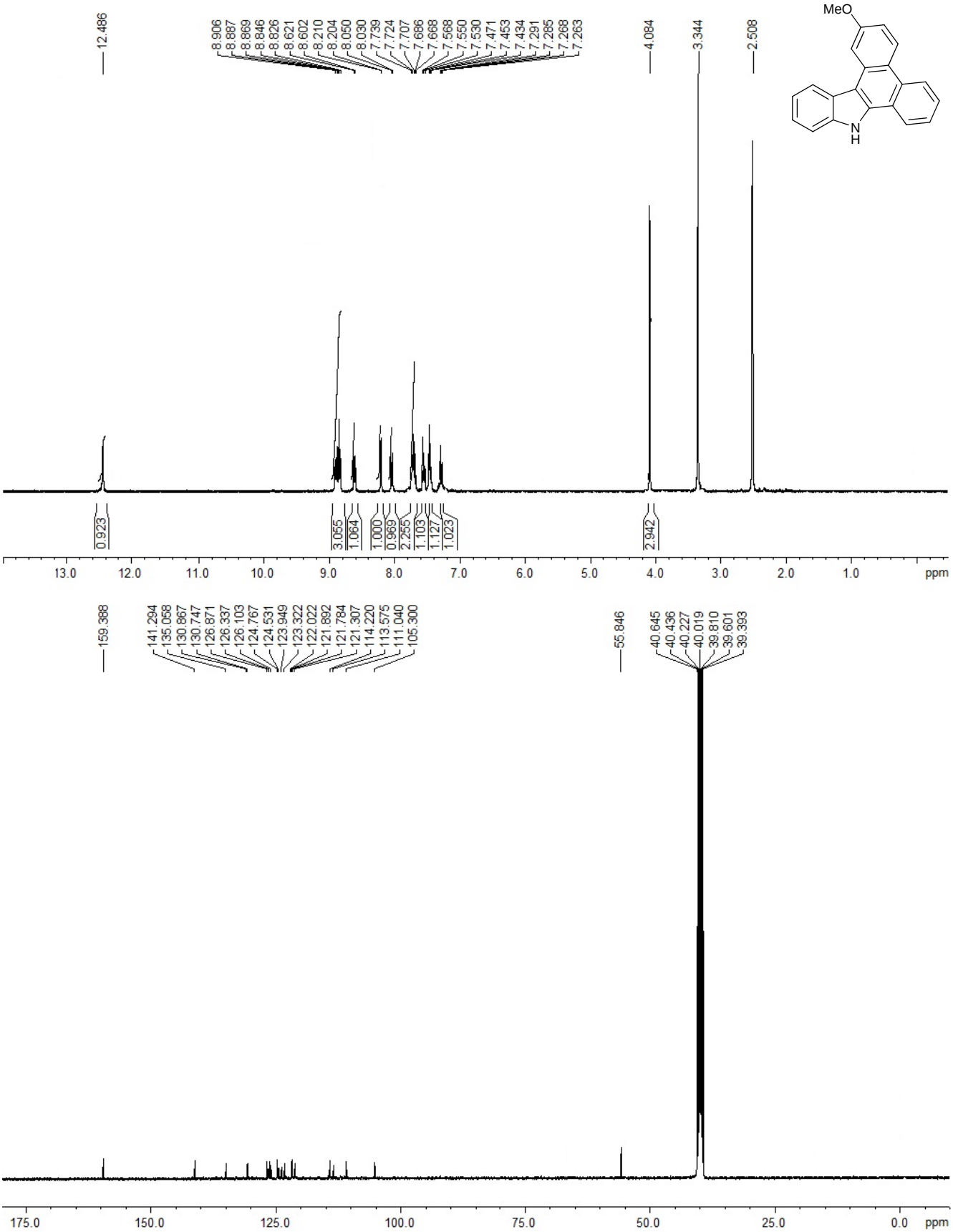
7m + 7m'



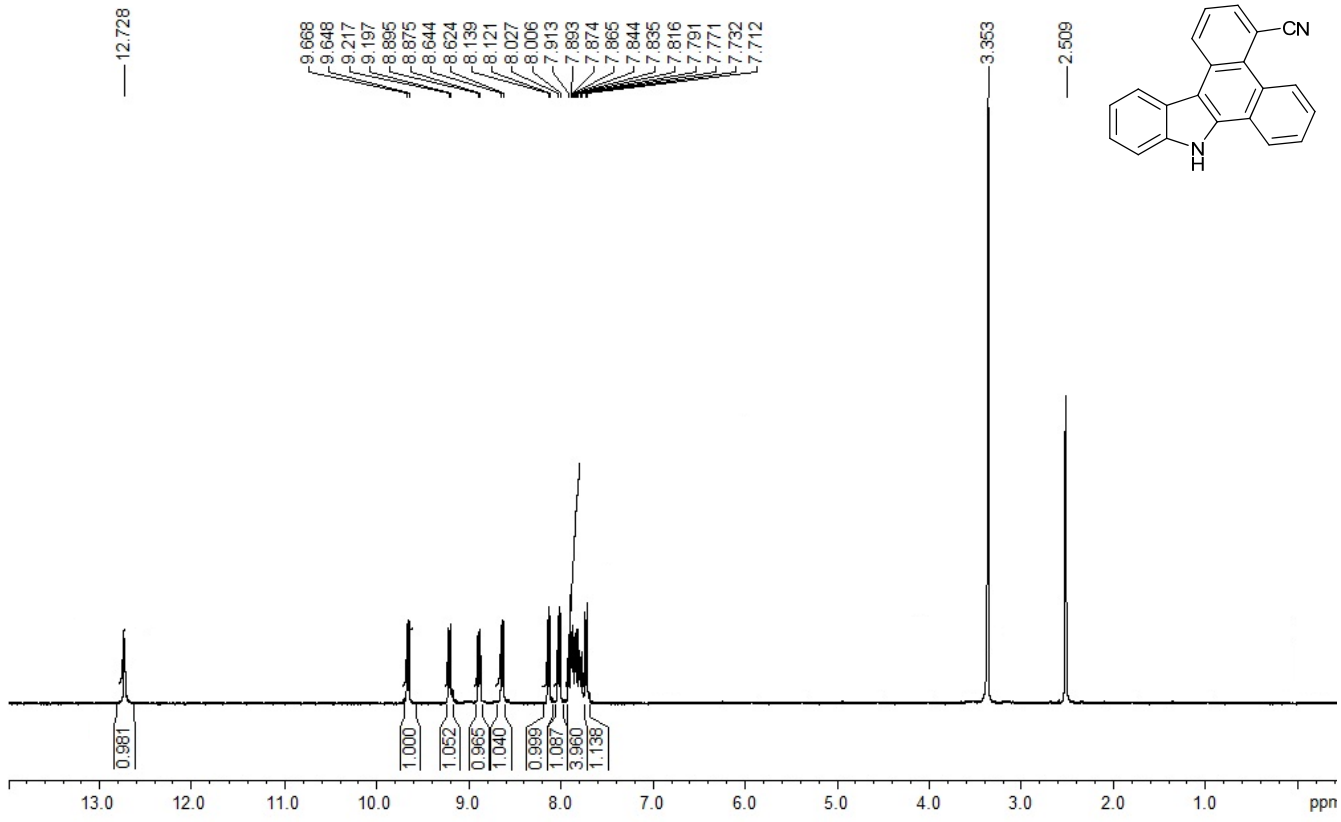
4n



4n'



4o



4o'