A Facile Iron-Catalyzed Dual C-C Bond Cleavage: An Approach towards Triaryl Methanes

Dipankar Paul,[a] Snehadrinarayan Khatua[b] and Paresh Nath Chatterjee[a,]*

[a] Department of Chemistry, National Institute of Technology Meghalaya, Bijni Complex, Laitumkhrah, Shillong 793003, Meghalaya, INDIA

[b] Centre for Advanced Studies, Department of Chemistry, North Eastern Hill University, Shillong 793022, Meghalaya, INDIA

*Corresponding author:

Email: paresh.chatterjee@nitm.ac.in

Supporting Information

Table of contents **Page**

1. General remarks:

All reagents and solvents are of AR grade and were procured from Sigma Aldrich, Alfa Aesar, Spectrochem and Sisco Research Laboratories Pvt. Ltd. and used without further purification. All the reactions were done in oven-dried glass apparatus in an air atmosphere unless otherwise noted. Reactions were monitored by thin-layer chromatography (TLC) on silica gel 60 F_{254} using UV light and *p*-anisaldehyde stain as visualizing agents. Organic products were purified by dry column vacuum chromatography[1] using silica gel G as the stationary phase and petroleum ether 60-80 °C/ethyl acetate as the eluent. ^{1}H and ^{13}C NMR spectra were measured on a Bruker Avance II (^{1}H NMR: 400 MHz and ^{13}C NMR: 100 MHz) spectrometer. Chemical shifts are reported in ppm from tetramethylsilane, with the solvent resonance as the internal standard (unless otherwise mentioned, chloroform: δ 7.26 ppm). Data are reported as follows: chemical shifts, multiplicity (s=singlet, d=doublet, t=triplet, q=quartet, br=broad, dd=double doublet, m=multiplet), coupling constant (in Hz), integration. ^{13}C NMR spectra were recorded at 100 MHz with proton decoupling. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard (unless otherwise mentioned, chloroform: δ 77.0 ppm). Elemental analyses were carried out using a CHNS Analyzer Perkin Elmer 2400 Series II instrument. The starting substrates **1** were prepared from reported procedures[2,3] after minor modifications. The ^{1}H NMR and ^{13}C NMR spectra of the synthesized starting substrates **1** were satisfactory and in good agreement with reported data.

2. General procedure for the optimization of reaction conditions:

A 25 mL round-bottom flask equipped with a magnetic bar and water condenser were charged with **1a** (480 mg, 1.0 mmol), **2a** (258 mg, 2.2 mmol), solvent (5 mL) and catalyst (10 mol% or as specified in Table 1 of the manuscript) in an air atmosphere. The flask was placed in a constant temperature bath at 80 °C (or as specified in Table 1 of the manuscript) and the progress of the reaction was monitored by TLC. After the specified time as mentioned in Table 1 of the mauscript, the solvent was removed under reduced pressure and the crude product was purified by dry column vacuum chromatography (silica gel G, petroleum ether 60-80 °C/EtOAc) to obtain the desired product **3aa**.

3. General procedure for the synthesis of symmetrical TRAMs 3:

A 25 mL round-bottom flask equipped with a magnetic bar and water condenser were charged with **1** (1.0 mmol), **2** (2.2 mmol), MeCN (5 mL) and $FeCl_3$ (10 mol%) in an air atmosphere. The flask was placed in a constant temperature bath at 80 °C and the progress of the reaction was monitored by TLC. After the completion of the reaction, the solvent was removed under reduced pressure and the crude product was purified by dry column vacuum chromatography (silica gel G, petroleum ether 60-80 °C/EtOAc) to obtain the desired product **3**.

4. Typical procedure for the isolation of intermediate 4a:

A 25 mL round-bottom flask equipped with a magnetic bar and water condenser were charged with **1a** (480 mg, 1.0 mmol), **2a** (117 mg, 1.0 mmol), MeCN (5 mL) and $FeCl_3$ (5 mol%) in an air atmosphere. The flask was placed into a constant temperature bath at 50 °C and the progress of the reaction was monitored by TLC. After 1 h, the solvent was removed under reduced pressure and the crude product was purified by dry column vacuum chromatography (silica gel G, petroleum ether 60-80 °C/EtOAc) to obtain the intermediate **4a** in 62% yield.

5. Typical procedure for the conversion of intermediate 4a to final product 3aa:

A 25 mL round-bottom flask equipped with a magnetic bar and water condenser were charged with **4a** (186 mg, 0.5 mmol), **2a** (58.5 mg, 0.5 mmol), MeCN (3 mL) and $FeCl_3$ (10 mol%) in an air atmosphere. The flask was placed into a constant temperature bath at 80 °C and the progress of the reaction was monitored by TLC. After the completion of the reaction, the solvent was removed under reduced pressure and the crude product was purified by dry column vacuum chromatography (silica gel G, petroleum ether 60-80 °C/EtOAc) to obtain the desired product **3aa** in 93% yield.

6. General procedure for the synthesis of 4 from substrate 1 via $ZnCl_2$ catalyzed C_{sp3}-C_{sp3} bond cleavage:

A 25 mL round-bottom flask equipped with a magnetic bar and water condenser were charged with **1** (1.0 mmol), **2** (1.0 mmol), MeCN (5 mL) and $ZnCl_2$ (10 mol%) in air atmosphere. The flask was placed into a constant temperature bath at 80 °C and the progress of the reaction was monitored by TLC. After the completion of the reaction, the solvent was removed under reduced pressure and the crude product was purified by dry column vacuum

chromatography (silica gel G, petroleum ether 60-80 °C/EtOAc) to obtain the desired product **4**.

7. General procedure for the synthesis of unsymmetrical TRAMs 5 from intermediate 4 via $FeCl_3$ catalyzed C_{sp3}-C_{sp2} bond cleavage:

A 25 mL round-bottom flask equipped with a magnetic bar and water condenser was charged with **4** (0.5 mmol), **2** (0.5 mmol), MeCN (3 mL) and $FeCl_3$ (10 mol%) in air atmosphere. The flask was placed into a constant temperature bath at 80 °C and the progress of the reaction was monitored by TLC. After the completion of the reaction, the solvent was removed under reduced pressure and the crude product was purified by dry column vacuum chromatography (silica gel G, petroleum ether 60-80 °C/EtOAc) to obtain the desired product **5**.

8. General procedure for the one-pot synthesis of unsymmetrical TRAMs 5 from substrate 1:

A 25 mL round-bottom flask equipped with a magnetic bar and water condenser was charged with **1** (1.0 mmol), Nu^1-H **2** (1.0 mmol), MeCN (5 mL) and $ZnCl_2$ (10 mol%) in air atmosphere. The flask was placed into a constant temperature bath at 80 °C and the progress of the reaction was monitored by TLC. After the full consumption of the starting materials, 1.0 mmol of the Nu^2-H **2** as well as $FeCl_3$ (10 mol%) were added to the reaction mixture and the reaction mixture was allowed to stir for 1 h at 80 °C. The progress of the reaction was monitored by TLC. On completion of the reaction, the solvent was removed under reduced pressure and the crude product was purified by dry column vacuum chromatography (silica gel G, petroleum ether 60-80 °C/EtOAc) to obtain the desired product **5**.

9. Analytical data of products 3, 4 and 5:

3,3'-(Phenylmethylene)bis(1*H*-indole) (3aa):[4] White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.71 (br, 2H), 7.30 (d, J = 8.0 Hz, 2H), 7.27-7.12 (m, 7H), 7.08 (t, J = 7.6 Hz, 2H), 6.92 (d, J = 7.6 Hz, 2H), 6.50 (d, J = 2.4 Hz, 2H), 5.79 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 144.0, 136.7, 128.7, 128.2, 127.0, 126.2, 123.7, 121.9, 119.9, 119.6, 119.2, 111.1, 40.2.

3,3'-((4-Chlorophenyl)methylene)bis(1*H*-indole) (3ga):[5] White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.67 (d, J = 2.0 Hz, 2H), 7.25 (d, J = 8.0 Hz, 2H), 7.19 (d, J = 8.0 Hz, 2H), 7.14-7.13 (m, 4H), 7.08-7.04 (m, 2H), 6.90 (t, J = 7.6 Hz, 2H), 6.42 (d, J = 2.4 Hz, 2H), 5.72 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 142.6, 136.7, 131.8, 130.1, 128.4, 126.9, 123.7, 122.1, 119.8, 119.4, 119.1, 111.2, 39.6.

3,3'-((3-Chlorophenyl)methylene)bis(1*H*-indole) (3ha):[6] White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.92 (br, 2H), 7.37 (t, J = 7.4 Hz, 4H), 7.25-7.16 (m, 6H), 7.01 (t, J = 7.6 Hz, 2H), 6.65 (d, J = 2.8 Hz, 2H), 5.86 (d, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 146.2, 136.7, 134.0, 129.5, 128.8, 126.9, 126.4, 123.6, 122.1, 119.8, 119.4, 118.9, 111.1, 39.9.

3,3'-((2-Chlorophenyl)methylene)bis(1*H*-indole) (3ia):[5] White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.70-7.67 (m, 2H), 7.32-7.30 (m, 3H), 7.22 (d, J = 8.0 Hz, 2H), 7.14-7.03 (m, 4H), 6.99 (td, J = 7.6 Hz and 1.6 Hz, 1H), 6.93 (t, J = 7.6 Hz, 2H), 6.46 (d, J = 2.8 Hz, 2H), 6.24 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 140.3, 135.7, 132.9, 128.3, 128.5, 126.5, 125.9, 125.6, 122.8, 120.9, 118.8, 118.3, 117.3, 110.1, 35.6.

3,3'-((4-Bromophenyl)methylene)bis(1*H*-indole) (3ja):[7] Light pink solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.83 (d, J = 1.6 Hz, 2H), 7.37-7.29 (m, 6H), 7.19-7.14 (m, 4H), 6.99 (t, J = 7.0 Hz, 2H), 6.55 (d, J = 2.8 Hz, 2H), 5.81 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 142.03, 135.6, 130.3, 129.4, 125.8, 122.6, 121.0, 118.9, 118.7, 118.3, 117.9, 110.1, 38.6.

3,3'-((4-Nitrophenyl)methylene)bis(1*H*-indole) (3ka):[5] Yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 10.51-10.46 (m, 2H), 8.11 (d, J = 8.8 Hz, 2H), 7.54 (d, J = 8.8 Hz, 2H), 7.36 (d, J = 8.4 Hz, 2H), 7.27 (d, J = 8.0 Hz, 2H), 7.08 (t, J = 7.6 Hz, 2H), 6.93-6.88 (m, 2H), 6.74 (d, J = 2.4 Hz, 2H), 5.97 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 152.4, 145.7, 136.5, 129.1, 126.1, 123.6, 122.9, 120.9, 118.6, 118.2, 116.5, 111.2, 35.7.

3,3'-(*p*-Tolylmethylene)bis(1*H*-indole) (3la):[5] White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.76 (br, 2H), 7.31 (d, J = 8.0 Hz, 2H), 7.25 (d, J = 8.0 Hz, 2H), 7.16-7.14 (m, 2H), 7.10-7.06 (m, 2H), 6.99 (d, J = 8.4 Hz, 2H), 6.92 (td, J = 7.4 Hz and 1.2 Hz, 2H), 6.55 (d, J = 2.4 Hz, 2H), 5.77 (s, 1H), 2.24 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 139.9, 135.6, 134.4, 127.9, 127.5, 126.0, 122.5, 120.8, 118.9, 118.9, 118.1, 109.9, 38.7, 20.0.

3,3'-((4-Methoxyphenyl)methylene)bis(1*H*-indole) (3ma):[5] Light orange solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.75 (d, J = 10.4 Hz, 2H), 7.30 (d, J = 8.0 Hz, 2H), 7.17-7.15 (m, 2H), 7.04-7.02 (m, 2H), 6.93-6.69 (m, 4H), 6.73 (d, J = 8.8 Hz, 2H), 6.51 (d, J = 1.6 Hz, 2H), 5.74 (s, 1H), 3.69 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 159.0, 136.7, 136.1, 129.5, 127.8, 123.5, 121.8, 121.3, 119.9, 119.8, 114.4, 112.7, 55.8, 39.3.

3,3'-(Naphthalen-1-ylmethylene)bis(1*H*-indole) (3na):[8] White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 8.15 (d, J = 8.4 Hz, 1H), 7.89-7.85 (m, 3H), 7.74 (d, J = 8.0 Hz, 1H), 7.46-7.24 (m, 8H), 7.18 (t, J = 7.6 Hz, 2H), 6.99 (t, J = 7.6 Hz, 2H), 6.65 (s, 1H), 6.54 (d, J = 2.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 139.5, 136.7, 136.9, 131.8, 128.6,

127.1, 126.9, 126.1, 125.8, 125.5, 125.3, 124.3, 124.3, 121.9, 119.8, 119.3, 119.2, 111.0, 35.8.

3,3'-(Thiophen-2-ylmethylene)bis(1*H*-indole) (3oa):[5] Light orange solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.89 (br, 2H), 7.48 (d, J = 7.6 Hz, 2H), 7.35 (d, J = 8.0 Hz, 2H), 7.21-7.15 (m, 3H), 7.04 (t, J = 7.4 Hz, 2H), 6.94-6.90 (m, 2H), 6.82 (s, 2H), 6.17 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 148.6, 136.6, 126.7, 126.4, 125.1, 123.6, 123.2, 122.0, 119.8, 119.7, 119.4, 111.1, 35.3.

3,3'-(Phenylmethylene)bis(1-methyl-1*H*-indole) (3ab):[9] White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.31-7.25 (m, 4H), 7.18 (d, J = 7.6 Hz, 4H), 7.13-7.09 (m, 3H), 6.92-6.88 (m, 2H), 6.44 (s, 2H), 5.80 (s, 1H), 3.56 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 144.5, 137.4, 128.7, 128.3, 128.2, 127.5, 126.1, 121.5, 120.1, 118.7, 118.3, 109.1, 40.1, 32.7.

3,3'-(Phenylmethylene)bis(2-methyl-1*H*-indole) (3ac):[8] White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.67-7.63 (m, 2H), 7.21-7.14 (m, 7H), 6.96 (t, J = 7.8 Hz, 2H), 6.89 (d, J = 8.0 Hz, 2H), 6.77 (t, J = 7.4 Hz, 2H), 5.92 (s, 1H), 1.98 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 143.7, 135.0, 131.8, 130.9, 129.1, 128.1, 125.9, 120.6, 119.3, 119.0, 113.4, 109.9, 39.2, 29.7.

3,3'-(Phenylmethylene)bis(1-benzyl-1*H*-indole) (3ad):[10] White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.42-7.36 (m, 4H), 7.29-7.18 (m, 12H), 7.13-7.11 (m, 2H), 7.02-6.97 (m, 5H), 6.65 (s, 2H), 5.93 (s, 1H), 5.19 (s, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 143.6, 137.4, 136.5, 128.3, 128.2, 127.8, 127.5, 127.3, 126.9, 125.9, 125.7, 121.2, 119.7, 118.5, 118.3, 109.3, 49.5, 39.8.

3,3'-(Phenylmethylene)bis(5-methoxy-1*H*-indole) (3ae):[10] Pale yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.82-7.74 (m, 2H), 7.30-7.25 (m, 2H), 7.19-7.16 (m, 5H), 6.79-6.70 (m, 4H), 6.60 (d, J = 2.1 Hz, 2H), 5.70 (s, 1H), 3.62 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 153.6, 143.9, 131.9, 128.7, 128.7, 127.9, 126.4, 124.4, 119.3, 111.9, 111.7, 101.9, 55.6, 40.3.

3,3'-(Phenylmethylene)bis(5-bromo-1*H*-indole) (3af):[11] Pale yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 8.13 (br, 2H), 7.47 (s, 2H), 7.30-7.29 (m, 4H), 7.27 (s, 2H), 7.24 (d, J = 0.4 Hz, 3H), 6.65 (t, J = 1.2 Hz, 2H), 5.75 (s, 1H).

3,3'-(Phenylmethylene)bis(5-nitro-1*H*-indole) (3ag):[10] Yellow solid. ^{1}H NMR (600 MHz, DMSO-d_6): δ (ppm) = 11.68 (br, 2H), 8.32 (s, 2H), 7.97 (d, J = 7.7 Hz, 2H), 7.54 (d, J = 8.5 Hz, 2H), 7.46-7.29 (m, 4H), 7.23 (d, J = 7.0 Hz, 1H), 7.14 (s, 2H), 6.21 (s, 1H). ^{13}C NMR (150 MHz, DMSO-d_6): δ (ppm) = 143.8, 140.2, 139.9, 128.5, 128.3, 127.7, 126.46, 125.8, 120.6, 116.7, 116.3, 112.2, 54.9.

5,5'-(Phenylmethylene)bis(2-methylfuran) (3ah):[12] Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.22 (t, J = 7.2 Hz, 2H), 7.16 (d, J = 7.2 Hz, 3H), 5.78 (d, J = 3.2 Hz, 4H), 5.25 (s, 1H), 2.16 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 152.9, 151.5, 140.0, 128.5, 128.4, 126.9, 108.2, 106.1, 45.1, 13.7.

3,3'-(Phenylmethylene)bis(2,5-dimethylfuran) (3ai):[7] Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.20-7.17 (m, 2H), 7.11 (d, J = 6.8 Hz, 3H), 5.64 (s, 2H), 5.84 (s, 1H), 2.11 (s, 6H), 2.05 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 149.2, 145.4, 143.9, 128.2, 128.1, 126.0, 121.9, 107.3, 37.9, 13.6, 11.7.

4,4'-(Phenylmethylene)bis(1,3-dimethoxybenzene) (3aj):[13] Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.25-7.20 (m, 2H), 7.17-7.13 (m, 1H), 7.04 (d, J = 7.2 Hz, 2H), 6.68 (d, J = 8.4 Hz, 2H), 6.45 (d, J = 2.4 Hz, 2H), 6.37-6.35 (m, 2H), 6.01 (s, 1H), 3.77 (s, 6H), 3.68 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 158.2, 157.1, 143.6, 129.4, 128.1, 126.8, 124.5, 124.3, 102.5, 97.8, 54.7, 54.2, 41.1.

(Phenylmethylene)bis((4-methoxyphenyl)sulfane) (3ak):[14] Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.28-7.20 (m, 9H), 6.75 (d, J = 8.8 Hz, 4H), 5.15 (s, 1H), 3.73 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 159.9, 140.2, 135.9, 128.3, 127.9, 127.8, 124.8, 114.3, 62.9, 55.3.

3-(Phenyl(2,4,6-trimethoxyphenyl)methyl)-1*H*-indole (4a):[15] Light pink solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.84 (s, 1H), 7.29 (d, J = 6.7, 4H), 7.25-7.18 (m, 5H), 6.86 (d, J = 2.6, 1H), 6.28 (s, 1H), 6.15 (s, 2H), 3.79 (s, 3H), 3.57 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 159.7, 159.0, 144.6, 136.0, 128.2, 126.9, 124.9, 121.8, 121.4, 119.1, 118.9, 117.9, 114.3, 110.8, 91.7, 55.7, 55.2, 53.4, 36.3.

2-Bromo-5-(phenyl(2,4,6-trimethoxyphenyl)methyl)thiophene (4b):[14] Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.14-7.12 (m, 5H), 6.77 (d, J = 4.0 Hz, 1H), 6.57 (d, J = 3.6 Hz, 1H), 6.09 (s, 1H), 6.06 (s, 2H), 3.72 (s, 3H), 3.60 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 160.4, 158.7, 149.0, 143.7, 128.6, 127.7, 127.6, 126.4, 125.7, 112.5, 110.1, 91.3, 55.6, 55.3, 41.1.

1,3,5-Trimethoxy-2-((4-methoxyphenyl)(phenyl)methyl)benzene (4c):[14] Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.23-7.19 (m, 2H), 7.15 (t, J = 8.4 Hz, 5H), 6.78 (d, J = 8.8 Hz, 2H), 6.14 (s, 2H), 5.99 (s, 1H), 3.80 (s, 3H), 3.78 (s, 3H), 3.59 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 159.4, 158.6, 156.9, 144.1, 135.5, 129.7, 128.4, 126.9, 124.7, 112.5, 91.1, 55.3, 54.8, 54.7, 43.8.

1,3,5-Trimethoxy-2-(1-phenylbut-3-en-1-yl)benzene (4d):[14] Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.32 (d, J = 7.6 Hz, 2H), 7.20 (t, J = 7.6 Hz, 2H), 7.09 (t, J = 7.2

Hz, 1H), 6.10 (s, 2H), 5.79-5.69 (m, 1H), 4.99 (dd, *J* = 16.8 Hz and 1.8 Hz, 1H), 4.86 (dd, *J* = 10.2 Hz and 1.4 Hz, 1H), 4.67 (t, *J* = 8.2 Hz, 1H), 3.76 (s, 3H), 3.71 (s, 6H), 3.03-2.90 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 159.5, 159.2, 145.2, 138.5, 127.9, 127.6, 125.2, 114.9, 113.5, 91.2, 55.7, 55.2, 39.3, 36.5.

3-((2,6-Dimethoxy-4-methylphenyl)(phenyl)methyl)-1*H*-indole (4e): White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.78 (s, 1H), 7.30 (d, *J* = 7.9 Hz, 1H), 7.22 (d, *J* = 8.1 Hz, 1H), 7.16 (d, *J* = 7.5 Hz, 2H), 7.10-6.98 (m, 4H), 6.92 (t, *J* = 7.5 Hz, 1H), 6.81 (d, *J* = 1.7 Hz, 1H), 6.32 (s, 2H), 6.26 (s, 1H), 3.50 (s, 6H), 2.25 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 158.34, 144.65, 137.73, 136.15, 128.58, 128.07, 127.37, 125.01, 123.80, 121.43, 119.84, 118.98, 118.86, 117.85, 110.82, 106.21, 55.88, 36.48, 21.99. Anal. Cacld (%) for $C_{24}H_{23}NO_2$: C 80.64; H 6.49; Found: C 80.59; H 6.42.

1-Methyl-3-(phenyl(2,4,6-trimethoxyphenyl)methyl)-1*H*-indole (4f):[14] Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.29 (d, *J* = 8.0 Hz, 1H), 7.19-7.13 (m, 3H), 7.11-7.06 (m, 3H), 7.01 (t, *J* = 7.8 Hz, 1H), 6.93-6.89 (m, 1H), 6.67 (s, 1H), 6.20 (s, 1H), 6.08 (s, 2H), 3.71 (s, 3H), 3.62 (s, 3H), 3.50 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 159.8, 159.1, 144.9, 136.8, 128.5, 128.5, 128.4, 127.3, 124.9, 120.9, 119.9, 118.4, 116.3, 114.7, 108.9, 91.9, 55.9, 55.3, 36.3, 32.7.

2-Methyl-3-(phenyl(2,4,6-trimethoxyphenyl)methyl)-1*H*-indole (4g):[14] Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.53 (s, 1H), 7.17-7.07 (m, 6H), 7.01 (d, *J* = 7.9 Hz, 1H), 6.94-6.88 (m, 1H), 6.79 (t, *J* = 7.5 Hz, 1H), 6.25 (s, 1H), 6.08 (s, 2H), 3.71 (s, 3H), 3.52 (s, 6H), 2.02 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 159.7, 159.1, 143.3, 134.8, 132.5, 129.5, 128.4, 127.6, 125.1, 120.5, 119.5, 118.4, 113.9, 112.4, 109.6, 91.2, 55.5, 55.2, 36.3, 12.6.

2-Methyl-5-(phenyl(2,4,6-trimethoxyphenyl)methyl)furan (4h): Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) =7.22 (d, *J* = 4.3 Hz, 4H), 7.14 (dd, *J* = 8.5 Hz and 4.0 Hz, 1H), 6.15 (s, 2H), 5.95 (s, 1H), 5.86 (s, 1H), 5.79 (s, 1H), 3.81 (s, 3H), 3.65 (s, 6H), 2.25 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 160.06, 159.07, 155.12, 149.88, 142.99, 128.40, 127.57, 125.56, 107.33, 105.88, 91.57, 55.85, 55.25, 39.54, 13.70. Anal. Cacld (%) for $C_{21}H_{22}O_4$: C 74.54; H 6.55; Found: C 74.59; H 6.49.

(4-Methoxyphenyl)(phenyl(2,4,6-trimethoxyphenyl)methyl)sulfane (4i): Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) =7.49 (d, *J* = 7.5 Hz, 2H), 7.33-7.28 (m, 2H), 7.22 (t, *J* = 7.6 Hz, 2H), 7.13 (t, *J* = 7.3 Hz, 1H), 6.76 (d, *J* = 8.8 Hz, 2H), 6.11 (s, 2H), 5.91 (s, 1H), 3.78 (s, 3H), 3.75 (s, 3H), 3.71 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 160.41, 158.71, 142.77, 133.44, 129.18, 127.86, 127.68, 125.99, 116.03, 114.79, 114.23, 112.46,

91.32, 55.87, 55.33, 55.29, 49.08. Anal. Cacld (%) for $C_{23}H_{24}O_4S$: C 69.67; H 6.10; Found: C 69.70; H 6.15.

3-((4-Chlorophenyl)(2,4,6-trimethoxyphenyl)methyl)-1-methyl-1*H*-indole (4j):[14] Pale yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.32 (d, J = 8.0 Hz, 1H), 7.27 (d, J = 8.4 Hz, 1H), 7.19-7.10 (m, 5H), 7.00 (dt, J = 7.8 Hz , 1H), 6.67 (s, 1H), 6.20 (s, 1H), 6.08 (s, 2H), 3.71 (s, 3H), 3.62 (s, 3H), 3.50 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 159.8, 159.1, 144.9, 136.8, 128.5, 125.5, 128.4, 127.3, 124.9, 120.9, 119.9, 118.4, 116.3, 114.7, 108.9, 91.9, 55.9, 55.3, 36.3, 32.7.

1-Methyl-3-(p-tolyl(2,4,6-trimethoxyphenyl)methyl)-1*H*-indole (4k):[14] Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.35 (d, J = 7.9 Hz, 1H), 7.25 (d, J = 8.2 Hz , 1H), 7.18-7.10 (m, 3H), 6.97 (dd, J = 7.1 Hz and 6.2 Hz, 3H), 6.74 (s, 1H), 6.24 (s, 1H), 6.15 (s, 2H), 3.79 (s, 3H), 3.70 (s, 3H), 3.60 (s, 6H), 2.28 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) = 159.7, 159.1, 141.7, 136.8, 134.2, 128.4, 128.4, 128.1, 120.9, 119.9, 118.3, 116.7, 114.7, 108.8, 91.9, 55.9, 55.3, 35.9, 32.7, 21.1.

3-((1*H*-indol-3-yl)(phenyl)methyl)-1-benzyl-1*H*-indole (5a): Light pink solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.89 (s, 1H), 7.43-7.17 (m, 12H), 7.13 (dd, J = 14.8, 7.9, 2H), 7.04-6.94 (m, 4H), 6.64 (d, J = 4.5, 2H), 5.91 (s, 1H), 5.20 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 144.05, 137.90, 137.01, 136.68, 132.51, 128.74, 128.66, 128.25, 127.95, 127.78, 127.38, 127.20, 127.07, 126.43, 126.13, 123.62, 121.92, 121.69, 120.12, 120.02, 119.80, 119.21, 118.96, 118.72, 111.03, 109.73, 49.92, 40.21. Anal. Cacld (%) for $C_{30}H_{24}N_2$: C 87.35; H 5.86; Found: C 87.31; H 5.90.

2-Methyl-3-((1-methyl-1*H*-indol-3-yl)(phenyl)methyl)-1*H*-indole (5b): Light pink solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.74 (d, J =10.4, 1H), 7.33-7.17 (m, 11H), 7.07-7.02 (m, 1H), 7.00-6.94 (m, 1H), 6.92-6.87 (m, 1H), 6.55–6.49 (m, 1H), 5.90 (s, 1H), 3.66 (s, 3H), 2.23 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 144.15, 142.72, 137.35, 135.18, 131.40, 130.14, 128.78, 128.42, 128.15, 128.04, 125.83, 121.41, 120.67, 119.94, 119.49, 119.02, 118.66, 117.42, 114.15, 110.02, 109.06, 39.24, 38.64, 32.70. Anal. Cacld (%) for $C_{25}H_{22}N_2$: C 85.68; H 6.33; Found: C 58.70; H 6.30.

3-((5-methylfuran-2-yl)(phenyl)methyl)-5-nitro-1*H*-indole (5c): Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 8.45 (s, 1H), 8.35 (d, J = 2.3 Hz, 1H), 7.44 (d, J = 9.0 Hz, 1H), 7.36-7.23 (m, 5H), 6.79-6.70 (m, 1H), 5.89 (d, J = 3.2 Hz, 1H), 5.82 (d, J = 3.3 Hz, 1H), 5.63 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 153.90, 151.58, 141.17, 139.45, 127.33, 126.99, 126.29, 120.36, 118.04, 117.74, 117.04, 111.14, 111.02, 108.45, 106.10, 105.11, 42.40, 13.69. Anal. Cacld (%) for $C_{20}H_{16}N_2O_3$: C 72.28; H 4.85; Found: C 72.22; H 4.82.

5-Bromo-3-((5-methylfuran-2-yl)(phenyl)methyl)-1*H*-indole (5d): Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 8.02 (s, 1H), 7.51 (s, 1H), 7.31-7.18 (m, 7H), 6.78 (s, 1H), 5.88 (s, 1H), 5.80 (s, 1H), 5.54 (s, 1H), 2.26 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 154.49, 151.29, 141.68, 135.08, 128.49, 128.44, 128.39, 126.72, 124.99, 124.49, 122.15, 117.45, 112.53, 108.25, 106.01, 42.46, 13.71. Anal. Cacld (%) for $C_{20}H_{16}BrNO$: C 65.59; H 4.40; Found: C 65.65; H 4.37.

5-Bromo-3-(((4-methoxyphenyl)thio)(phenyl)methyl)-1*H*-indole (5e): Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 8.05 (s, 1H), 7.73 (s, 1H), 7.38 (d, J = 7.4 Hz, 2H), 7.30-7.18 (m, 7H), 7.06 (s, 1H), 6.70 (d, J = 8.3 Hz, 2H), 5.51 (s, 1H), 3.73 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 159.35, 141.19, 135.12, 134.80, 128.39, 128.37, 128.07, 127.21, 126.04, 125.24, 124.75, 122.42, 116.34, 114.26, 112.95, 112.64, 55.26, 51.44. Anal. Cacld (%) for $C_{22}H_{18}BrNOS$: C 62.27; H 4.28; Found: C 62.32; H 4.31.

5-Bromo-3-((1-methyl-1*H*-indol-3-yl)(phenyl)methyl)-1*H*-indole (5f): Light yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.83 (s, 1H), 7.44 (s, 1H), 7.28-7.20 (m, 6H), 7.16-7.08 (m, 4H), 6.91 (t, J = 7.4 Hz, 1H), 6.56 (s, 1H), 6.39 (s, 1H), 5.73 (s, 1H), 3.59 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 143.74, 137.46, 135.26, 128.79, 128.61, 128.33, 128.21, 127.28, 126.29, 124.86, 124.82, 122.30, 121.56, 119.94, 119.53, 118.73, 117.76, 112.59, 112.52, 109.18, 39.95, 32.71. Anal. Cacld (%) for $C_{24}H_{19}BrN_2$: C 69.41; H 4.61; Found: C 69.44; H 4.64.

5-Bromo-3-((4-chlorophenyl)(1-methyl-1*H*-indol-3-yl)methyl)-1*H*-indole (5g): Light yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.98 (s, 1H), 7.50 (s, 1H), 7.31 (d, J = 8.3 Hz, 2H), 7.27-7.20 (m, 6H), 7.00 (t, J = 7.4 Hz, 1H), 6.66 (s, 1H), 6.46 (s, 1H), 5.79 (s, 1H) 3.69 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 142.27, 137.46, 135.26, 131.93, 129.95, 128.60, 128.47, 128.19, 127.07, 125.00, 124.83, 122.20, 121.69, 119.80, 119.06, 118.85, 117.20, 112.72, 112.58, 109.26, 39.35, 32.75. Anal. Cacld (%) for $C_{24}H_{18}BrClN_2$: C 64.09; H 4.03; Found: C 64.05; H 4.10.

5-Bromo-3-((1-methyl-1*H*-indol-3-yl)(p-tolyl)methyl)-1*H*-indole (5h): Light yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.88 (s, 1H), 7.56 (s, 1H), 7.36 (d, J = 8.3 Hz, 1H), 7.31 (d, J = 8.1 Hz, 1H), 7.26-7.16 (m, 5H), 7.11 (d, J = 7.5 Hz, 2H), 7.01 (t, J = 7.3 Hz, 1H), 6.65 (s, 1H), 6.49 (s, 1H), 5.80 (s, 1H), 3.68 (s, 3H), 2.35 (s, 3H). ^{13}C NMR (100 MHz,

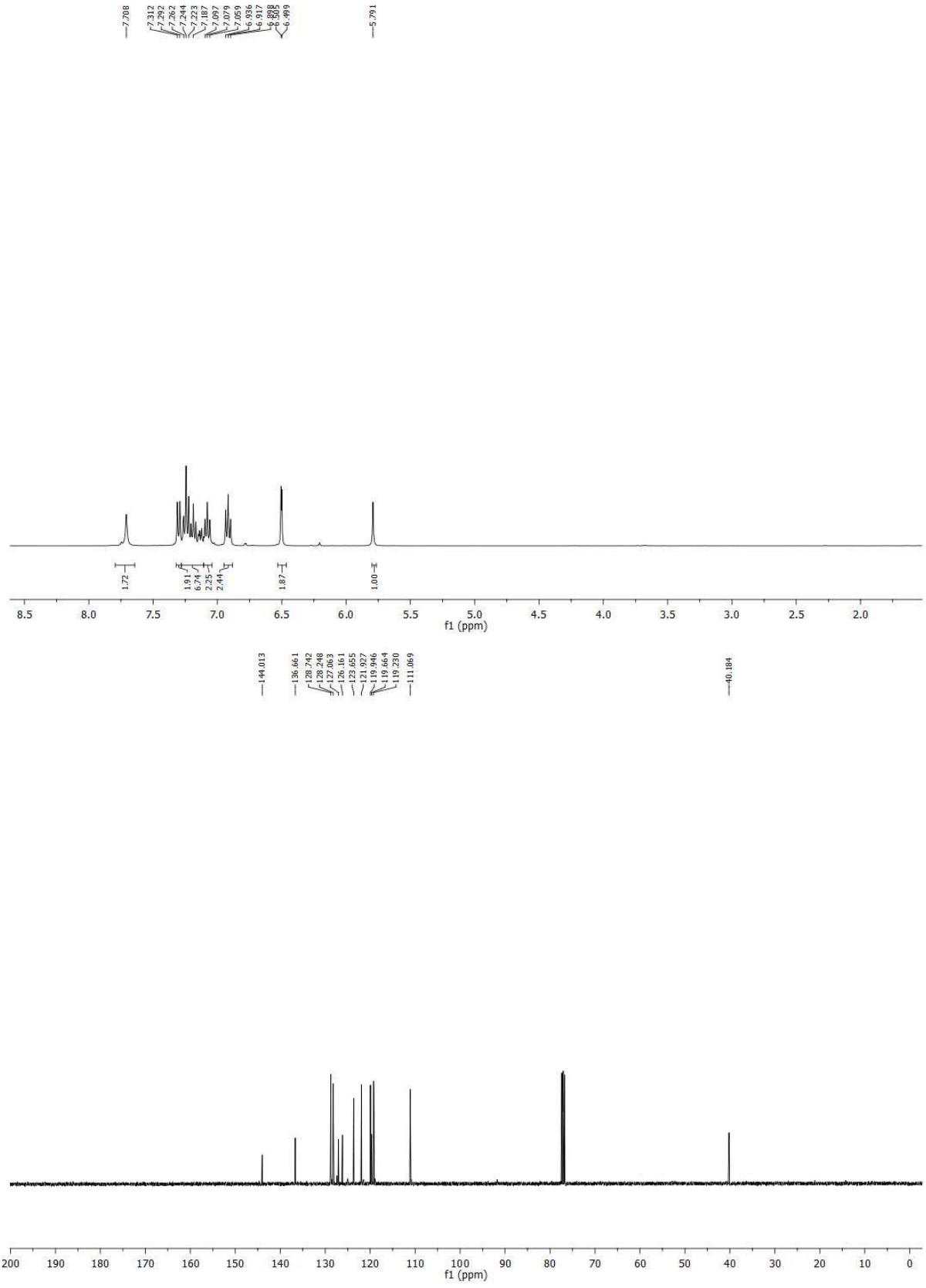
$CDCl_3$) δ (ppm) = 140.73, 137.46, 135.69, 135.26, 129.04, 128.81, 128.46, 128.18, 127.31, 124.80, 124.77, 122.32, 121.52, 119.99, 119.73, 118.70, 117.97, 112.56, 112.52, 109.18, 39.53, 32.71, 21.13. Anal. Cacld (%) for $C_{25}H_{21}BrN_2$: C 69.94; H 4.93; Found: C 69.90; H 5.01.

10. References:

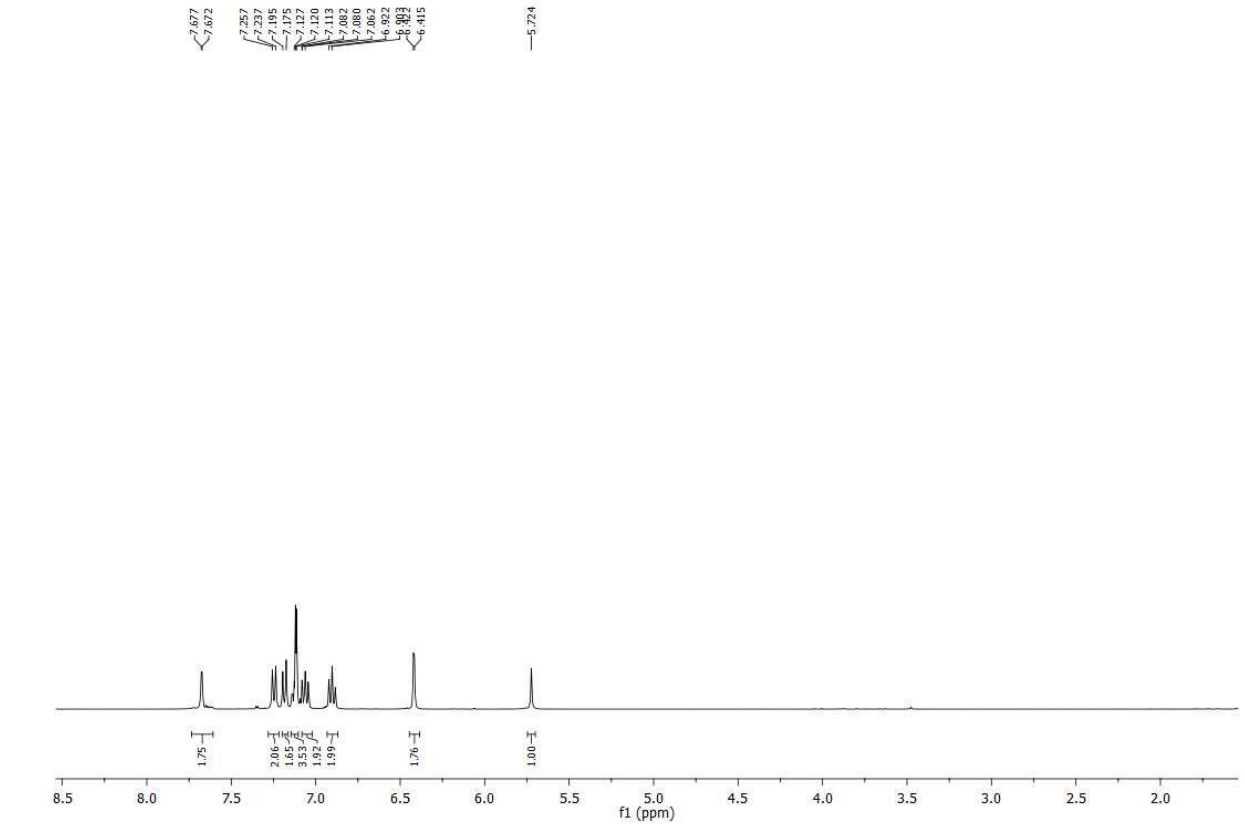
1. D. S. Pedersen and C. Rosenbohm, *Synthesis*, 2001, **2001**, 2431-2434.
2. D. Paul and P. N. Chatterjee, *ChemistrySelect*, 2018, **3**, 12150-12154.
3. K. Jette, M. Kristin, M. Dirk, Z. Alexander and B. Matthias, *Adv. Synth. Catal.*, 2007, **349**, 865-870.
4. P. Thirupathi and S. Soo Kim, *J. Org. Chem.*, 2010, **75**, 5240-5249.
5. S. J. Ji, M. F. Zhou, D. G. Gu, Z. Q. Jiang and T. P. Loh, *Eur. J. Org. Chem.*, 2004, **2004**, 1584-1587.
6. Z.-H. Zhang, L. Yin and Y.-M. Wang, *Synthesis*, 2005, **2005**, 1949-1954.
7. P. N. Chatterjee, A. K. Maity, S. S. Mohapatra and S. Roy, *Tetrahedron*, 2013, **69**, 2816-2826.
8. X. L. Shi, H. Lin, P. Li and W. Zhang, *ChemCatChem*, 2014, **6**, 2947-2953.
9. N. Azizi, E. Gholibeghlo and Z. Manocheri, *Scientia Iranica*, 2012, **19**, 574-578.
10. K. Gopalaiah, S. Chandrudu and A. Devi, *Synthesis*, 2015, **47**, 1766-1774.
11. K. Tabatabaeian, M. Mamaghani, N. Mahmoodi and A. Khorshidi, *Can. J. Chem.*, 2006, **84**, 1541-1545.
12. V. Nair, K. G. Abhilash and N. Vidya, *Org. Lett.*, 2005, **7**, 5857-5859.
13. A. Wang, P. Xing, X. Zheng, H. Cao, G. Yang and X. Zheng, *RSC Advances*, 2015, **5**, 59022-59026.
14. D. Paul, S. Khatua and P. N. Chatterjee, *ChemistrySelect*, 2018, **3**, 11649-11656.
15. F. L. Sun, X. J. Zheng, Q. Gu, Q. L. He and S. L. You, *Eur. J. Org. Chem.*, 2010, **2010**, 47-50.

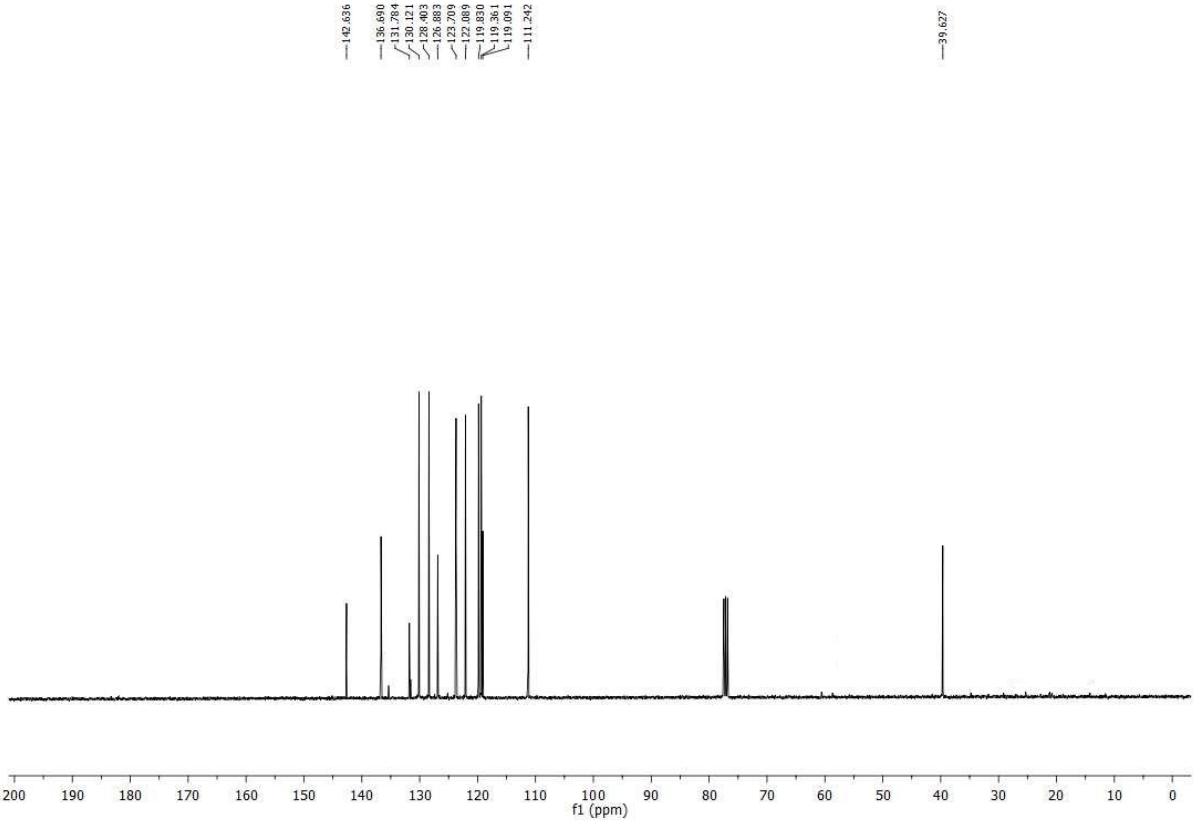
11. ^{1}H and ^{13}C NMR spectra of the products 3, 4 and 5:

3,3'-(Phenylmethylene)bis(1*H*-indole) (3aa):

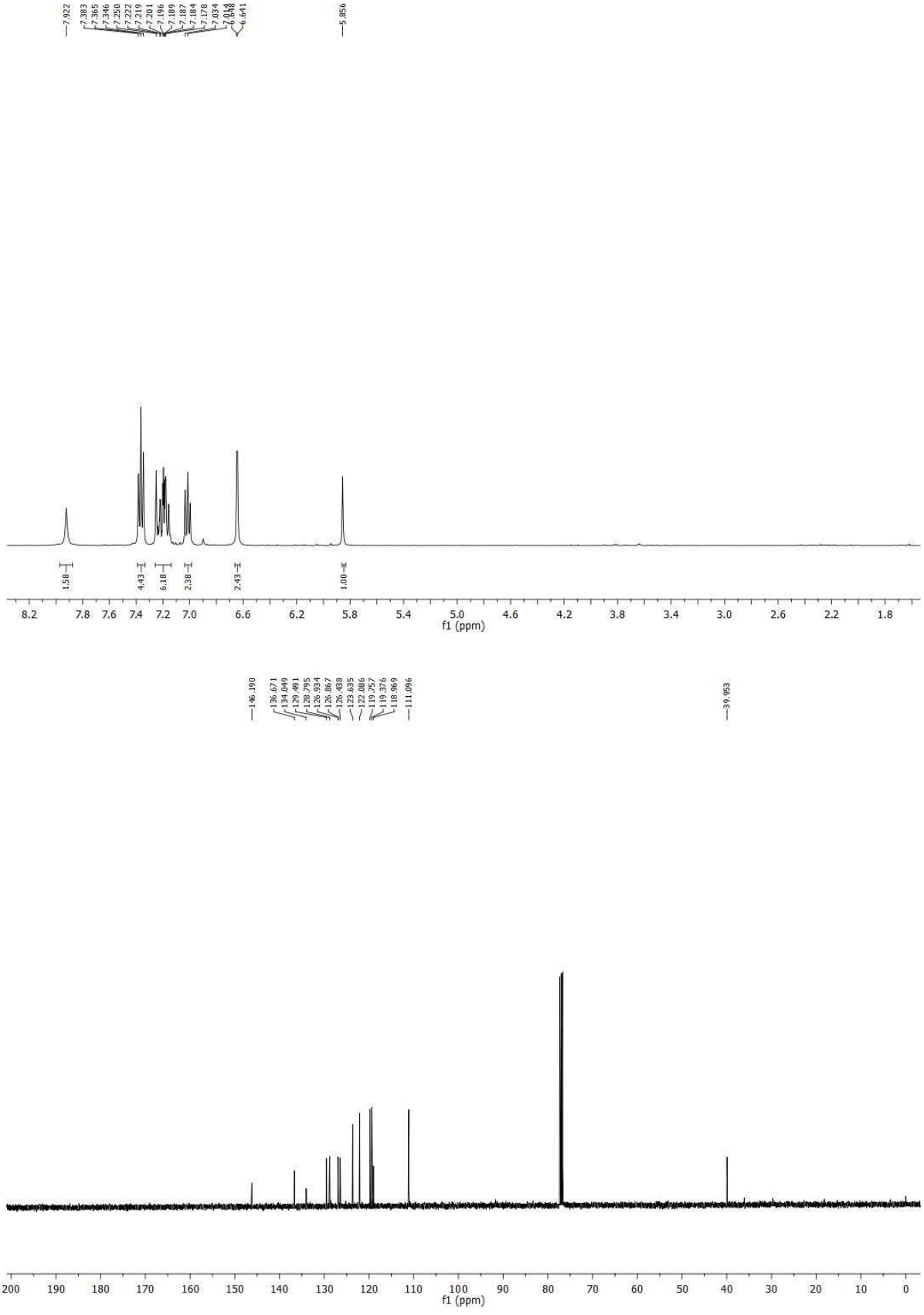


3,3'-((4-Chlorophenyl)methylene)bis(1*H*-indole) (3ga):

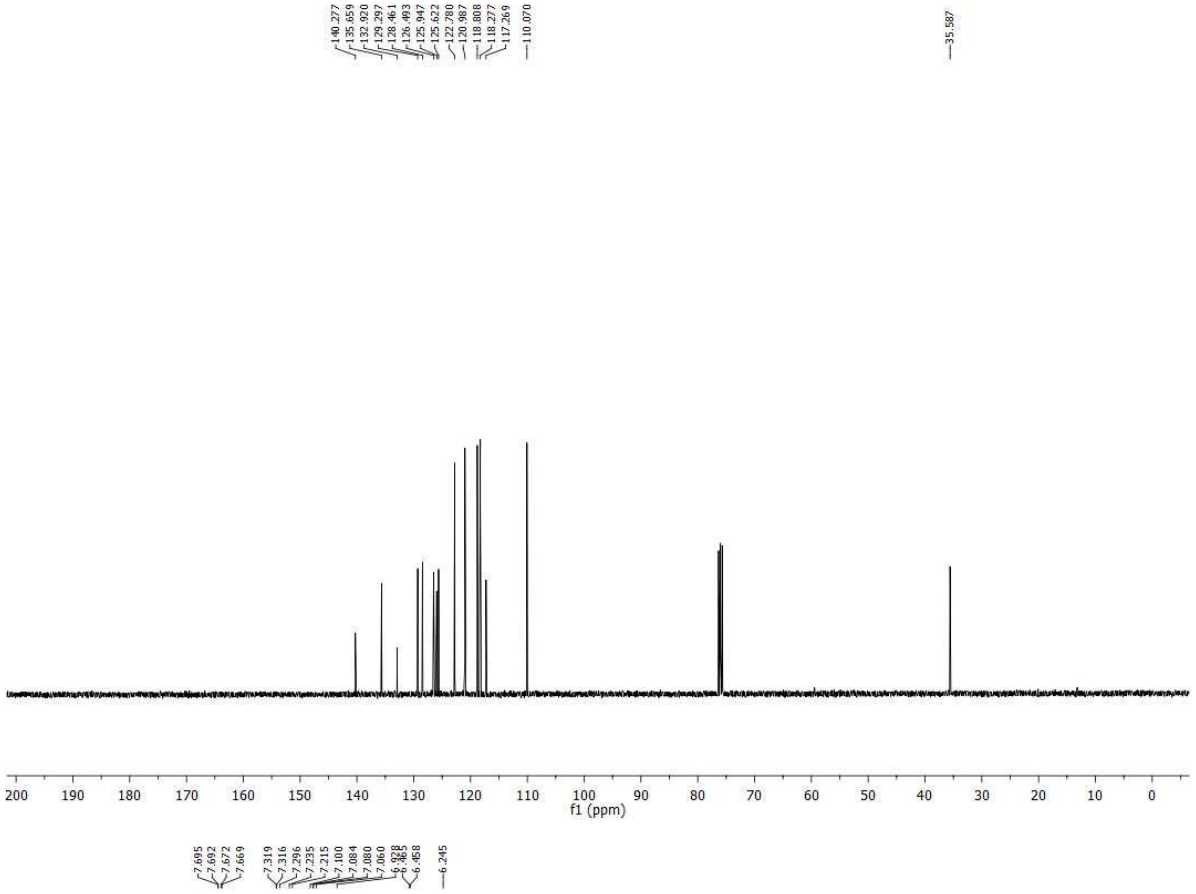


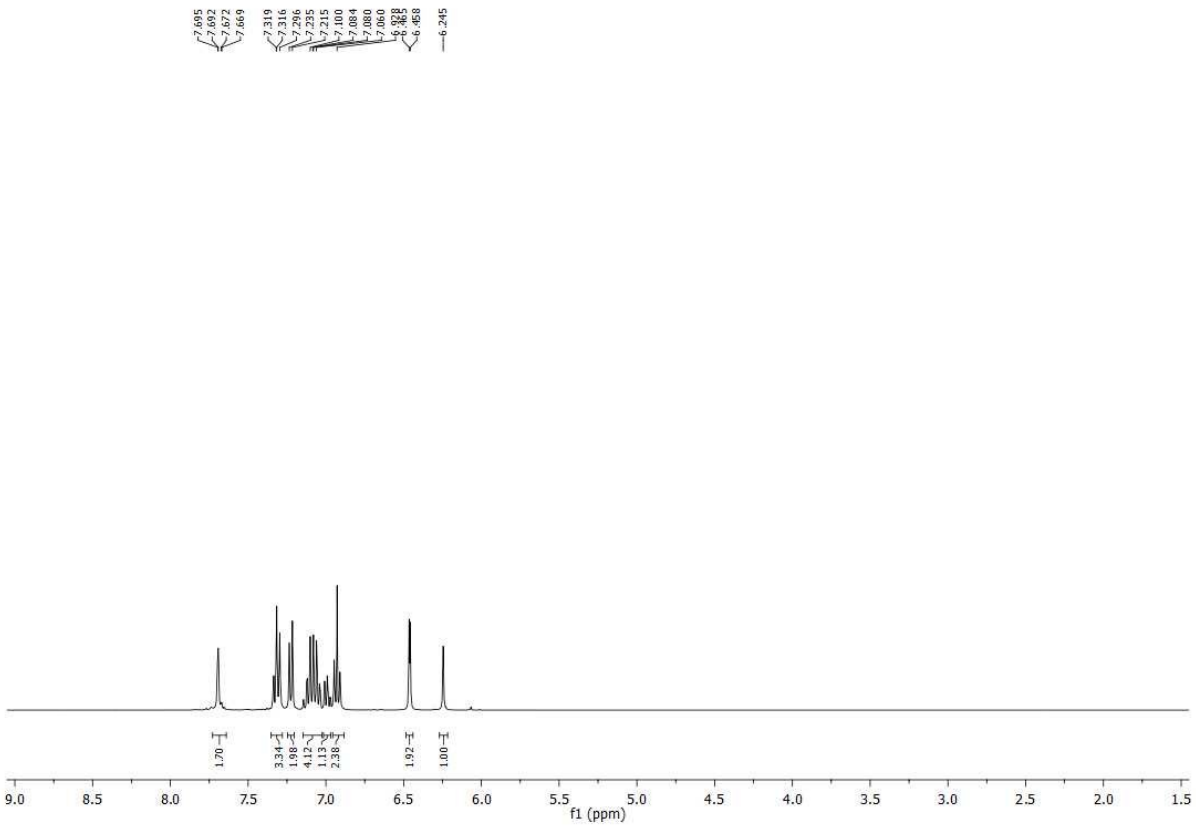


3,3'-((3-Chlorophenyl)methylene)bis(1*H*-indole) (3ha)

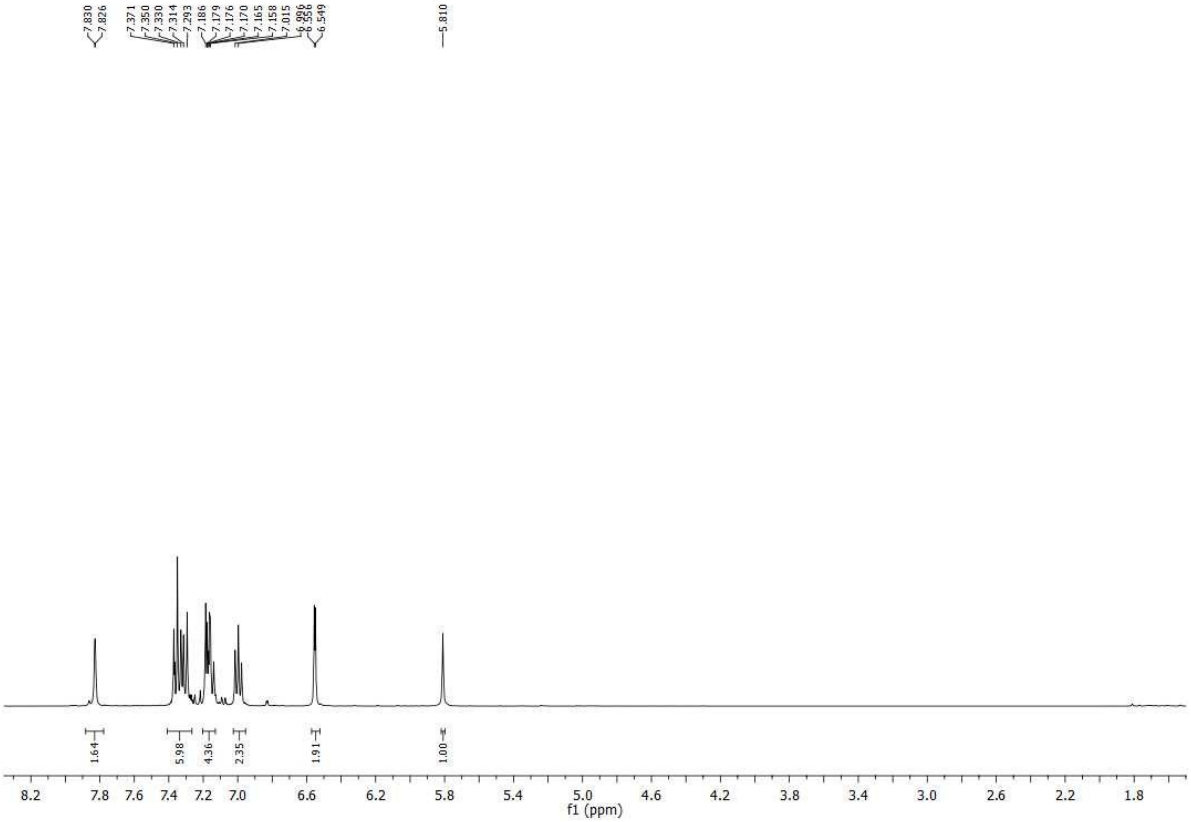


3,3'-((2-Chlorophenyl)methylene)bis(1*H*-indole) (3ia)

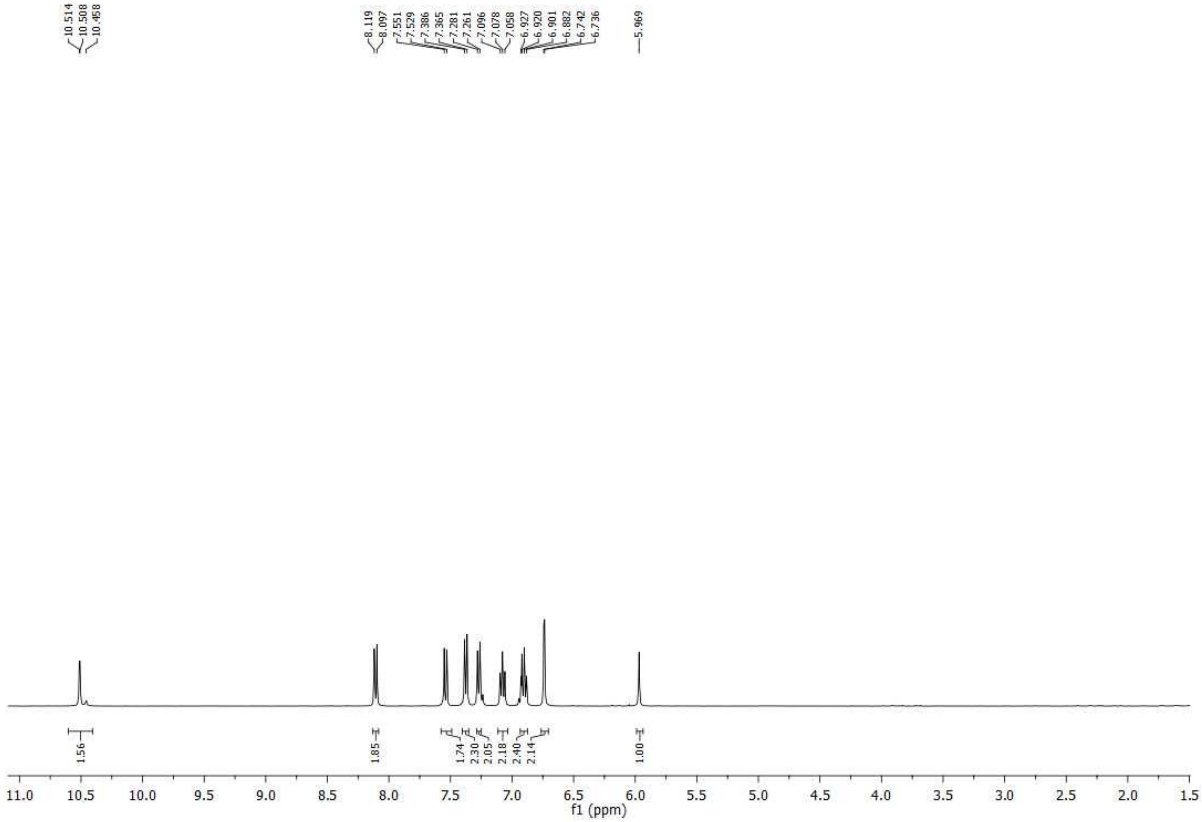


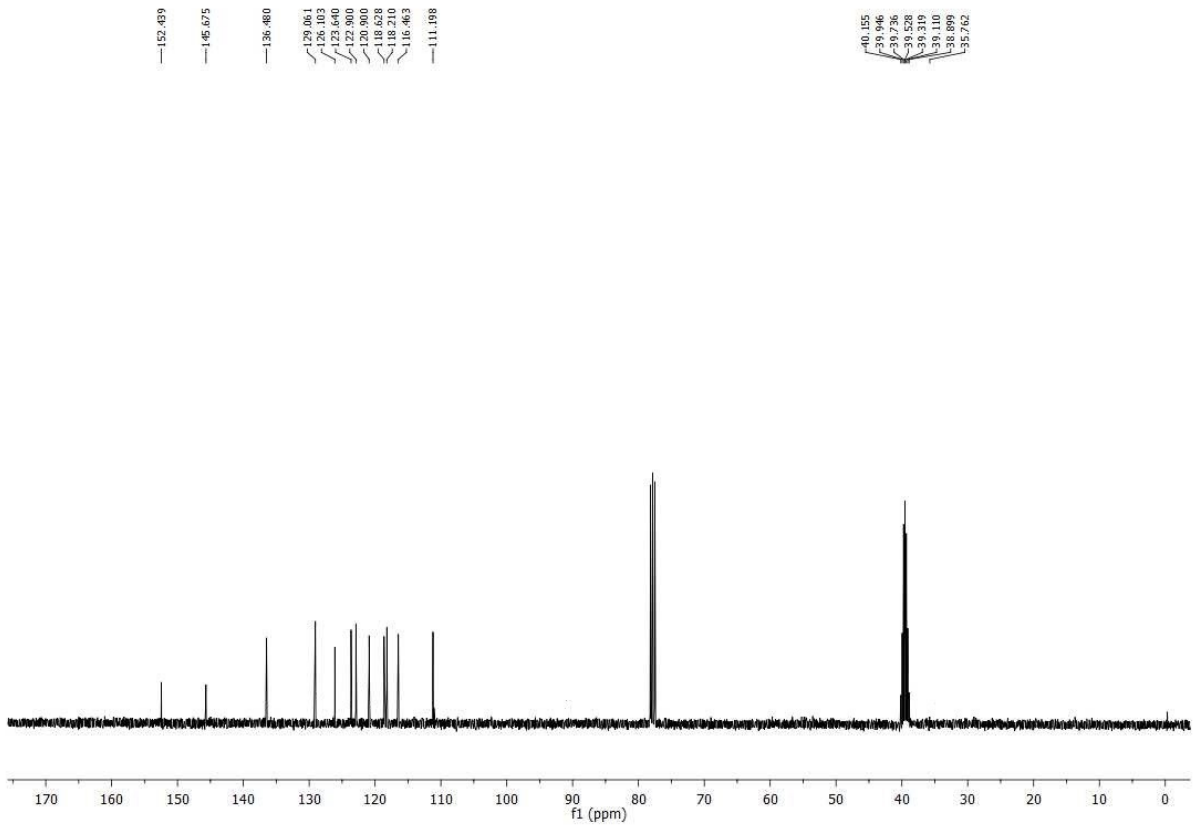


3,3'-((4-Bromophenyl)methylene)bis(1*H*-indole) (3ja)

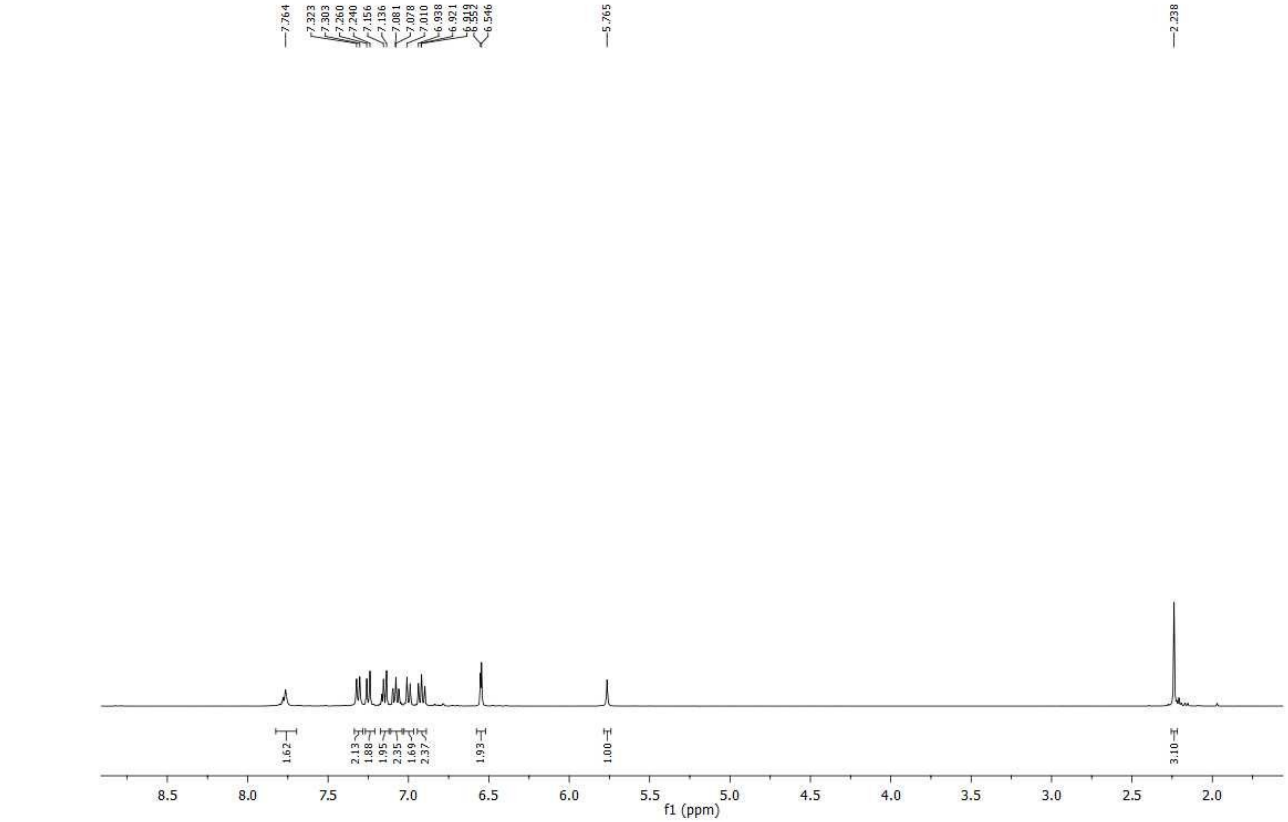


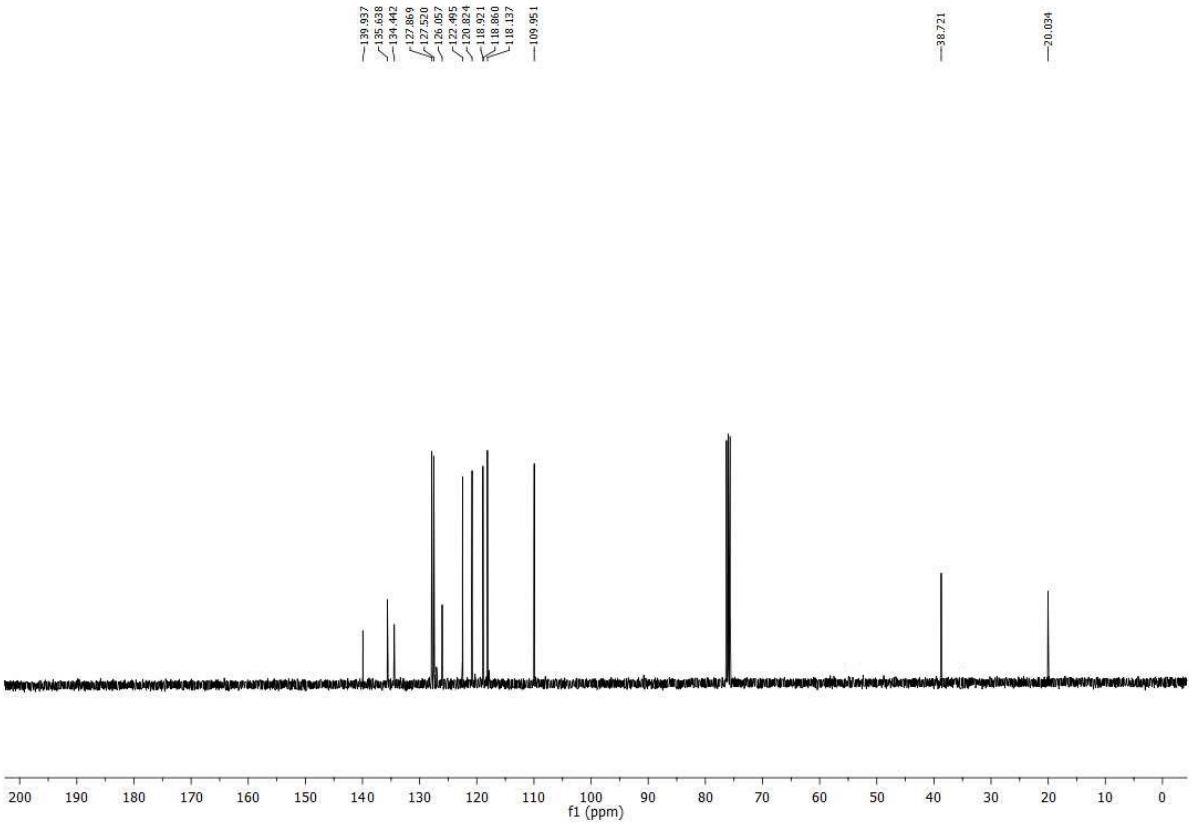
3,3'-((4-Nitrophenyl)methylene)bis(1*H*-indole) (3ka)



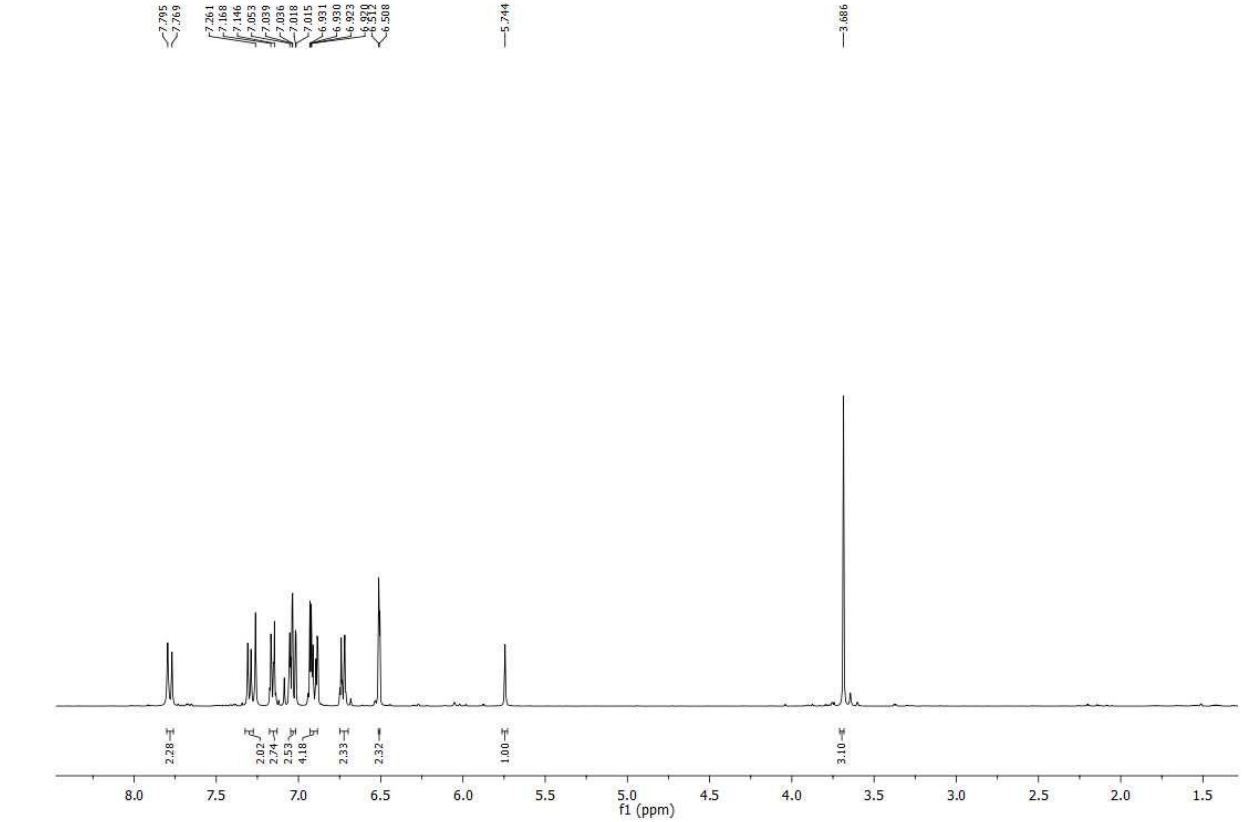


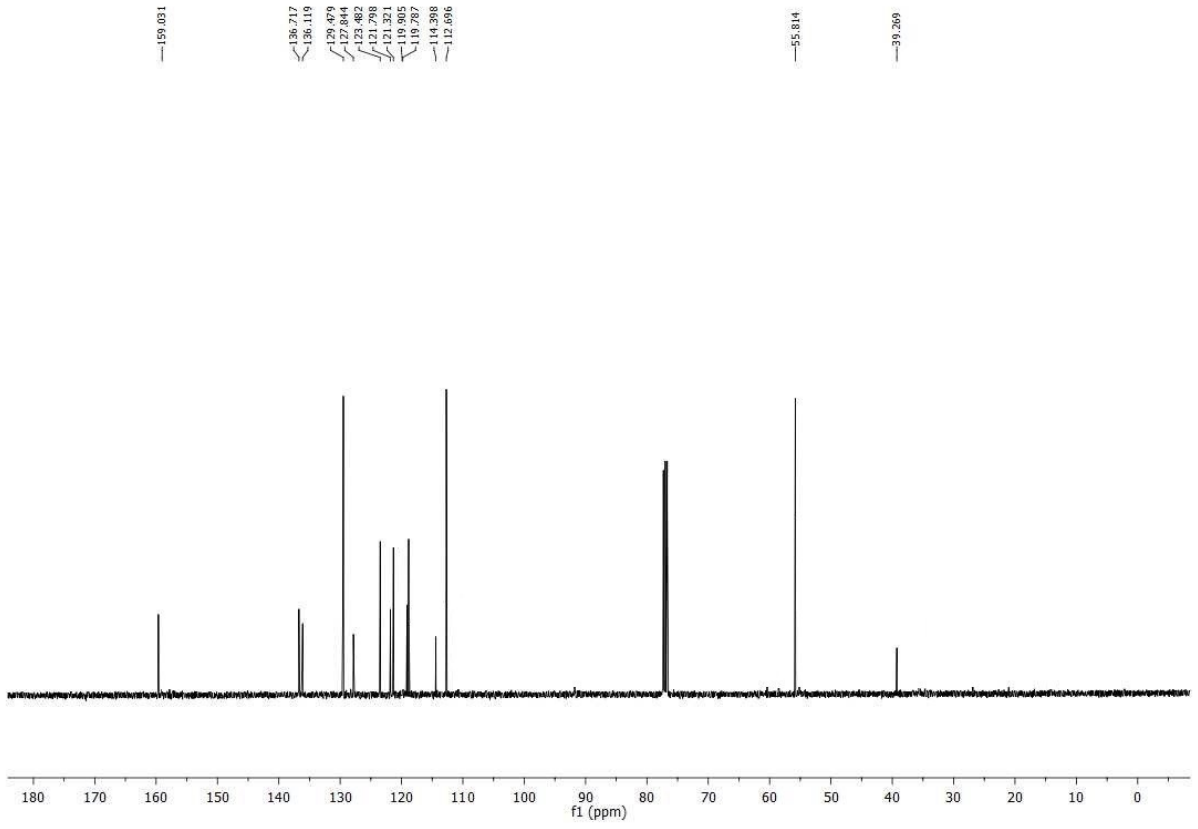
3,3'-(*p*-Tolylmethylene)bis(1*H*-indole) (3la)



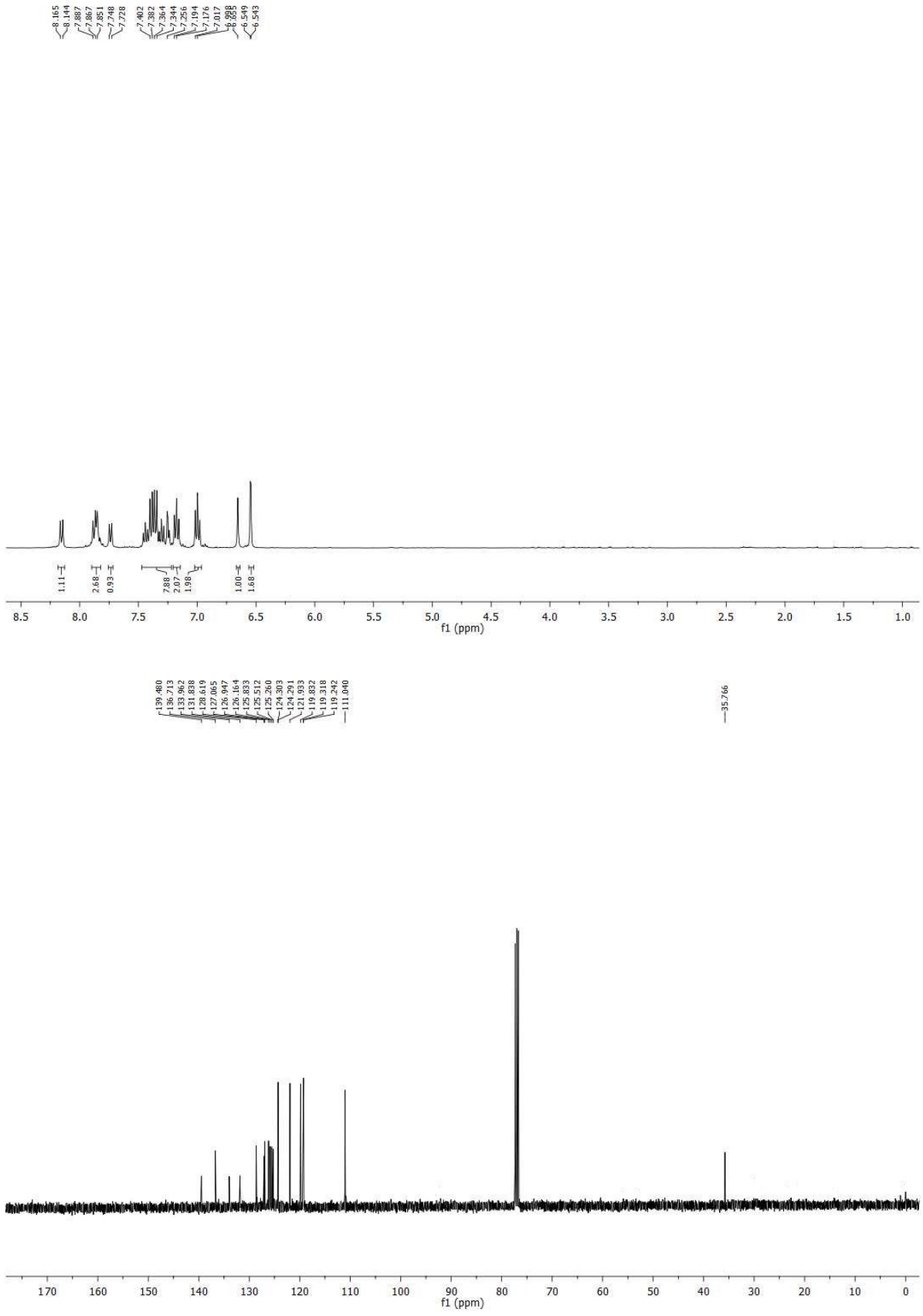


3,3'-((4-Methoxyphenyl)methylene)bis(1*H*-indole) (3ma)

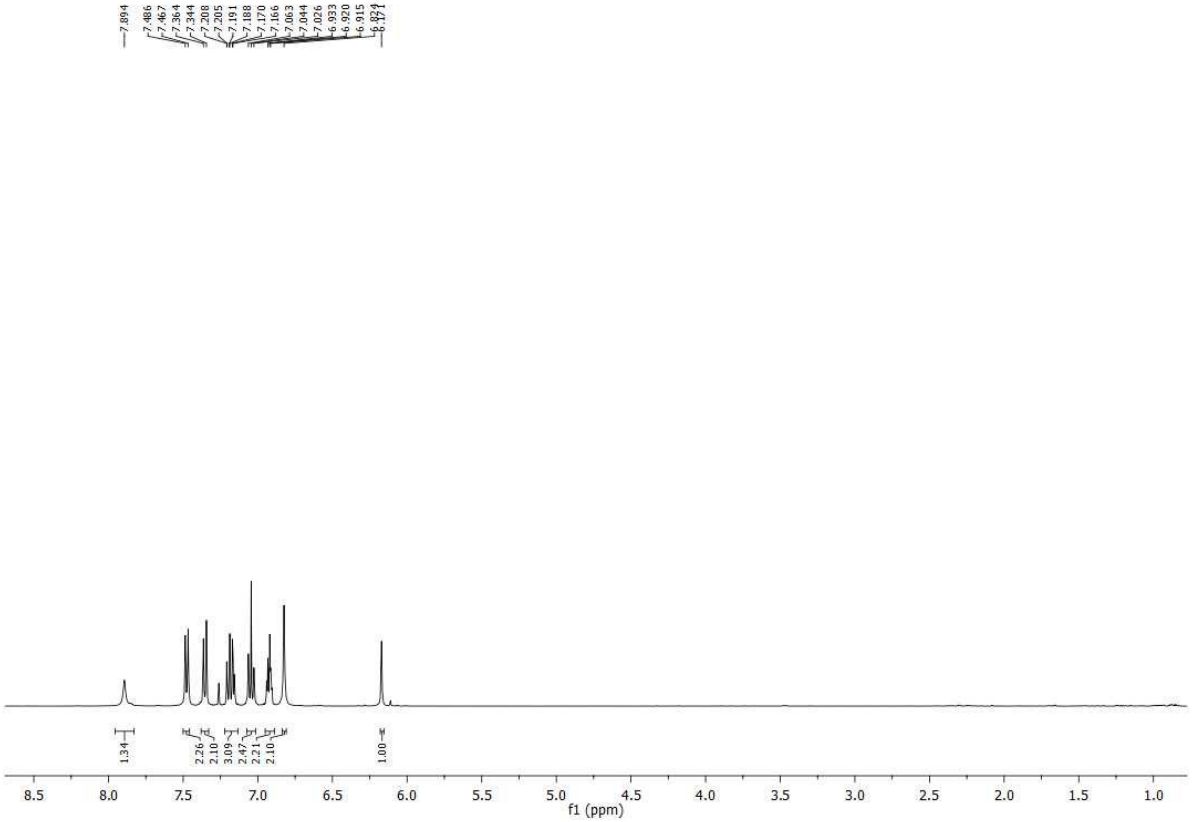


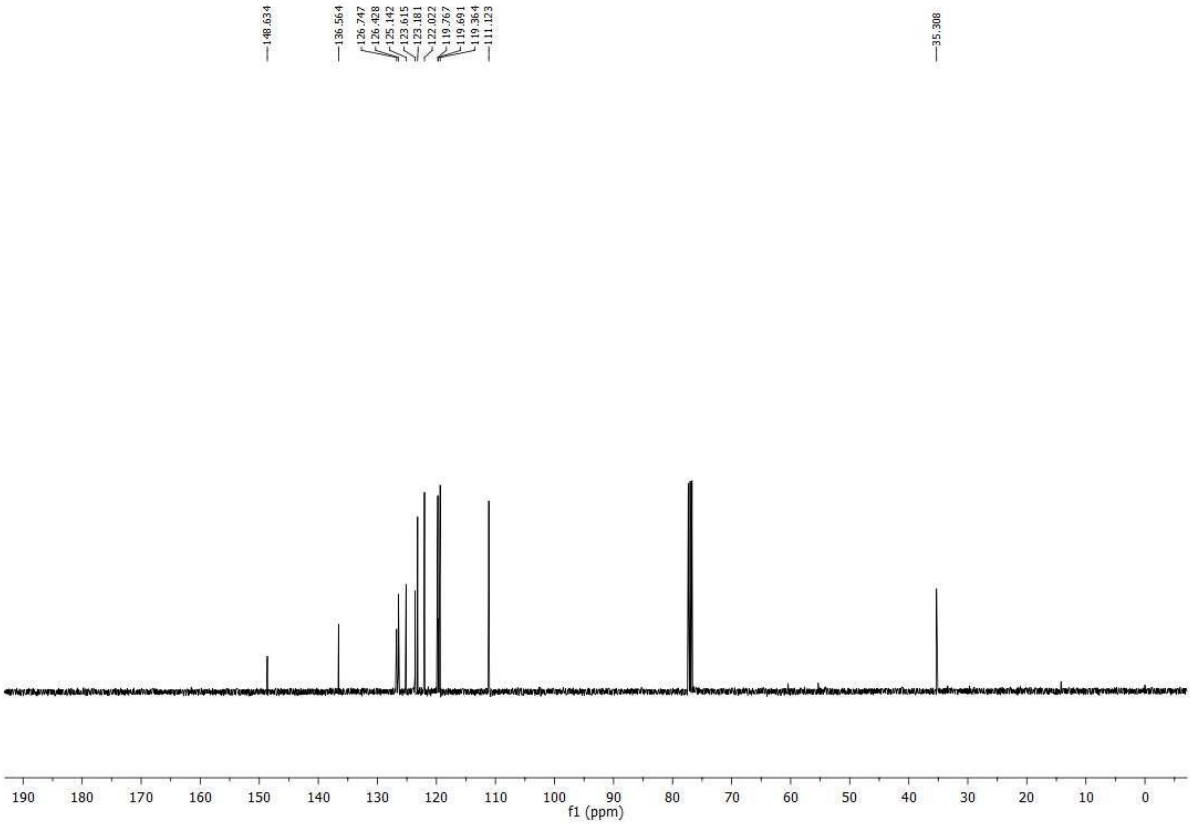


3,3'-(Naphthalen-1-ylmethylene)bis(1*H*-indole) (3na)

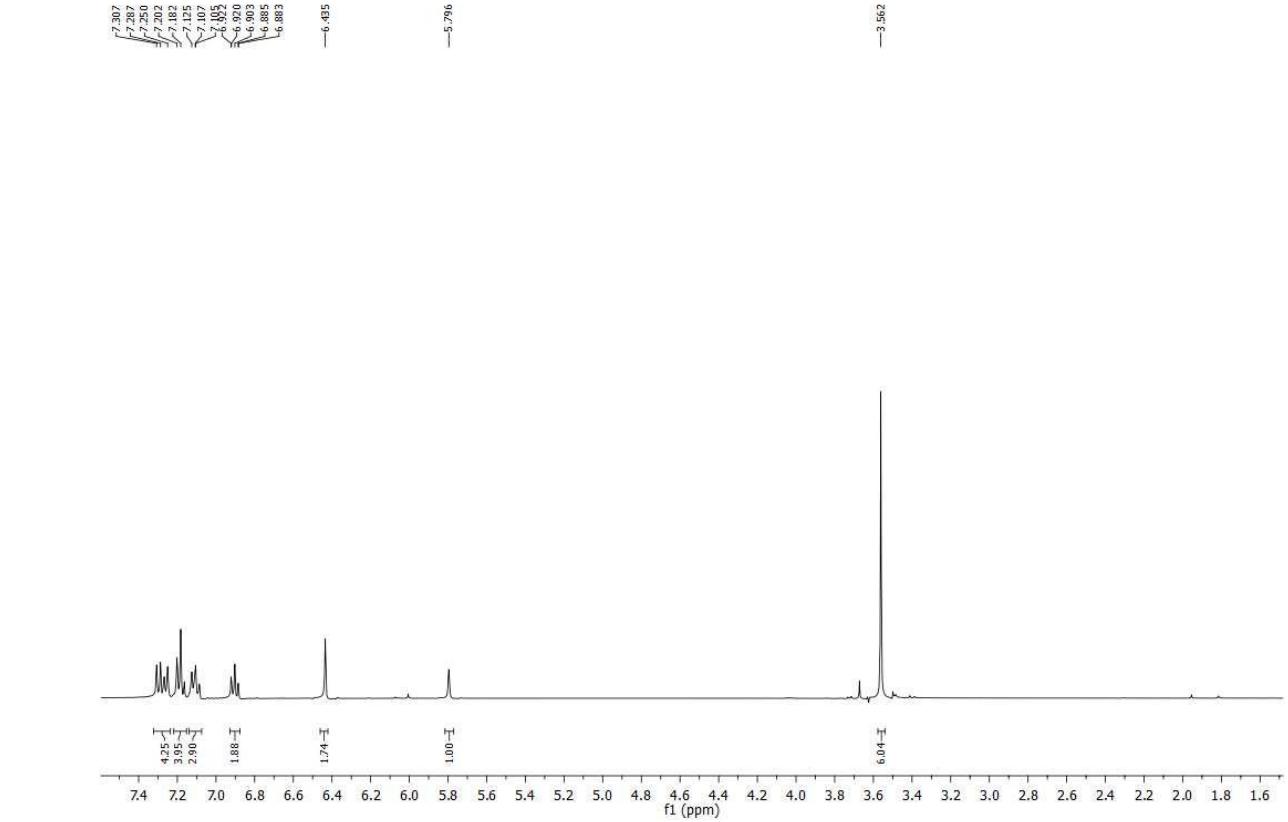


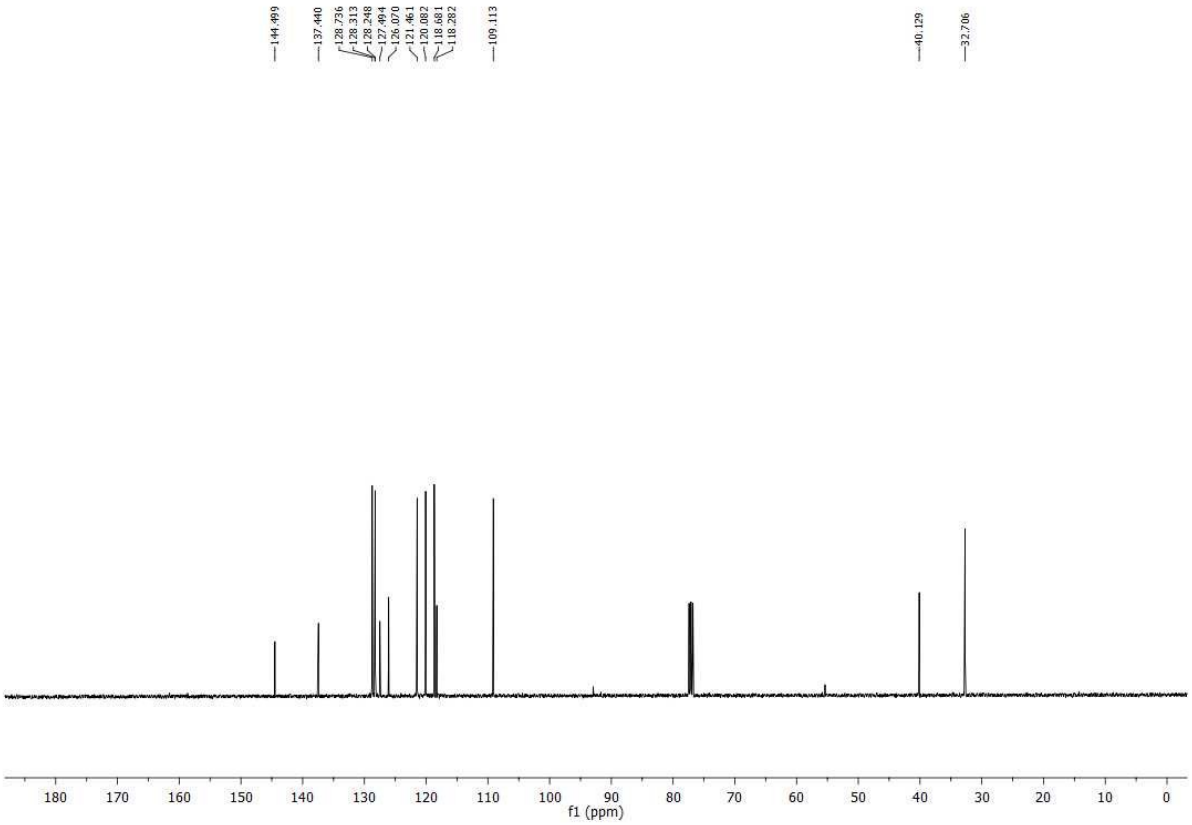
3,3'-(Thiophen-2-ylmethylene)bis(1*H*-indole) (3oa)



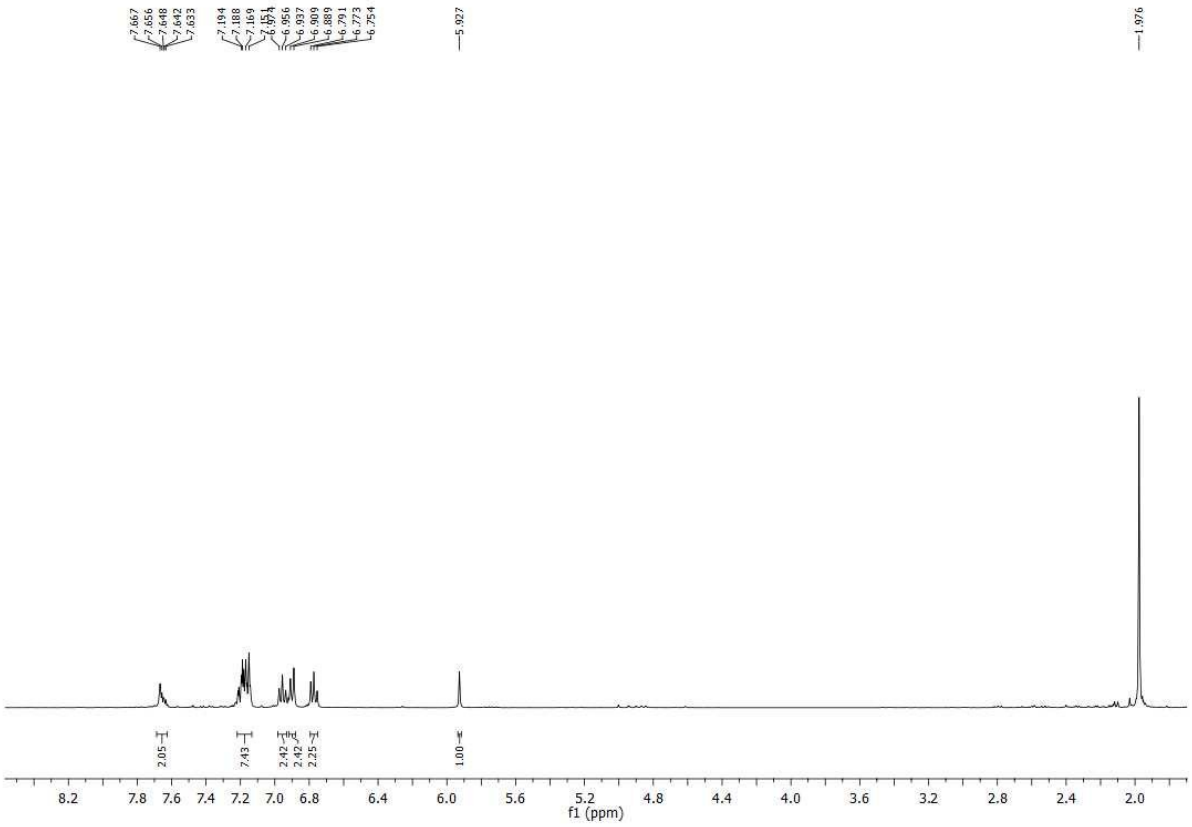


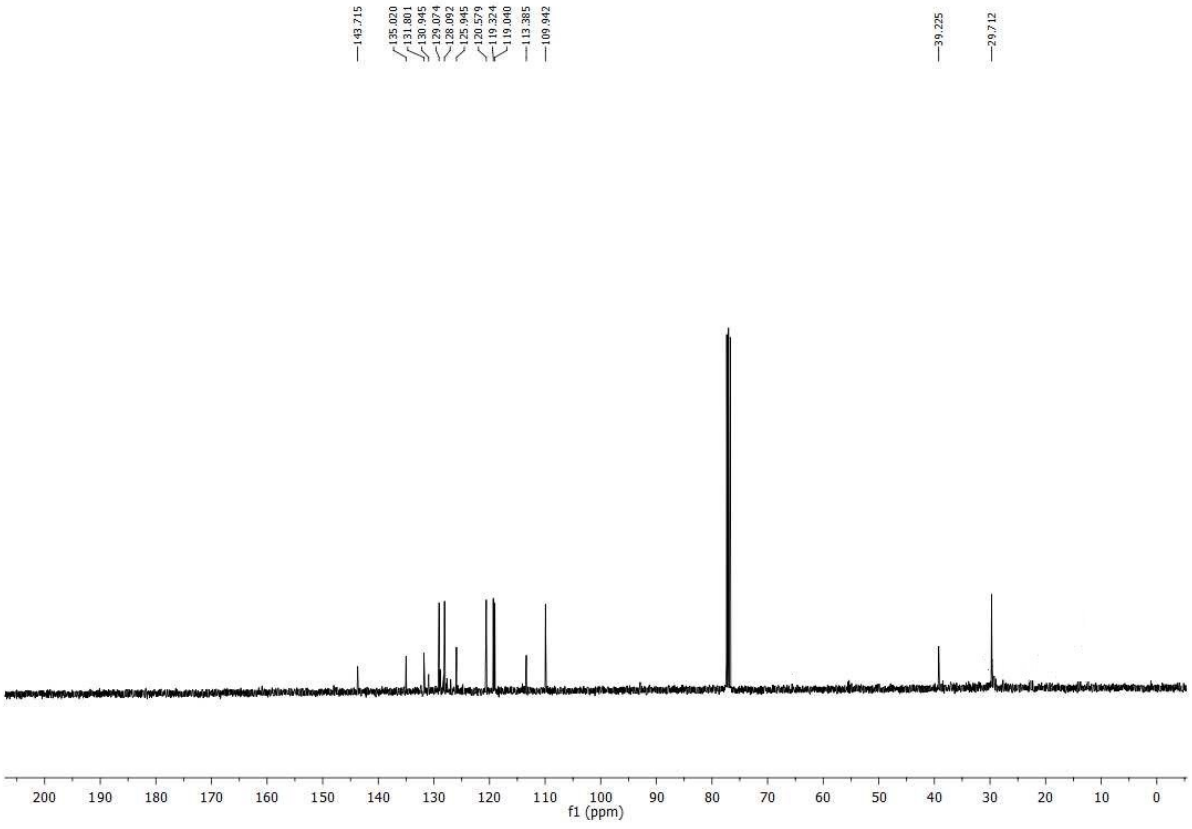
3,3'-(Phenylmethylene)bis(1-methyl-1*H*-indole) (3ab)



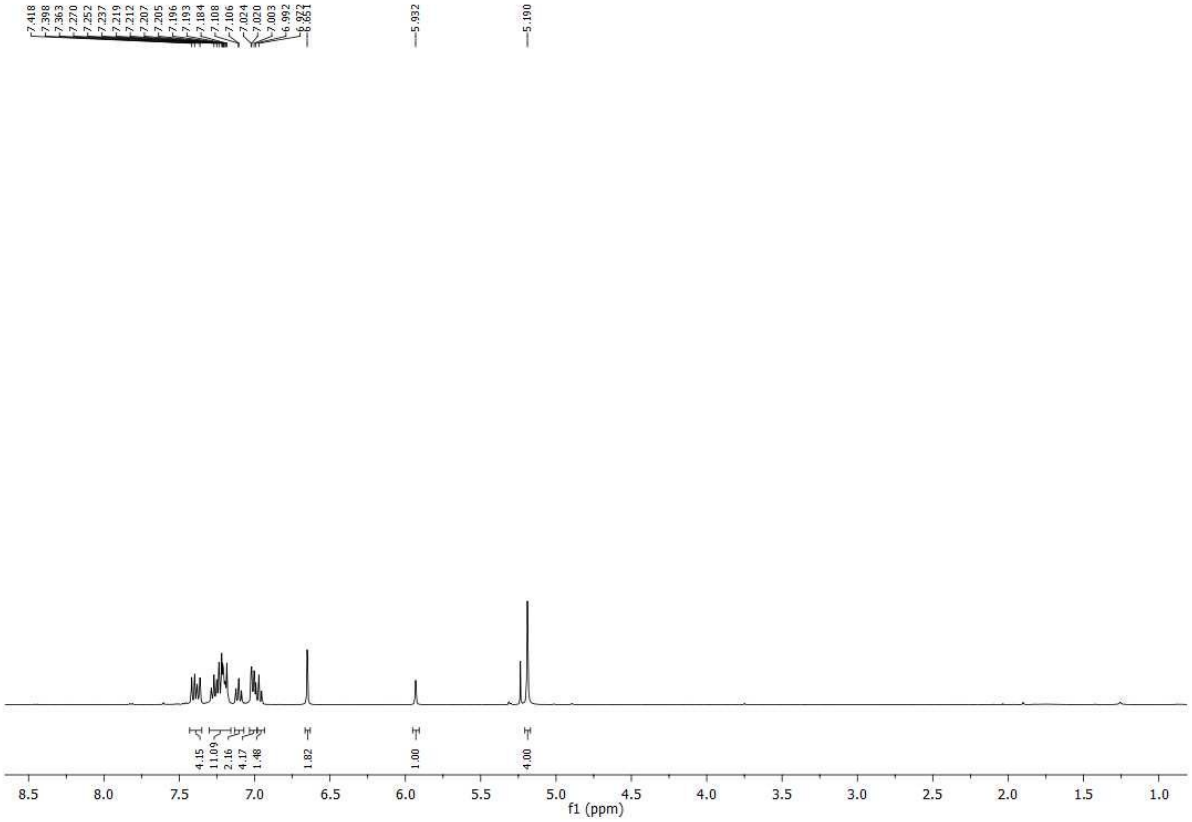


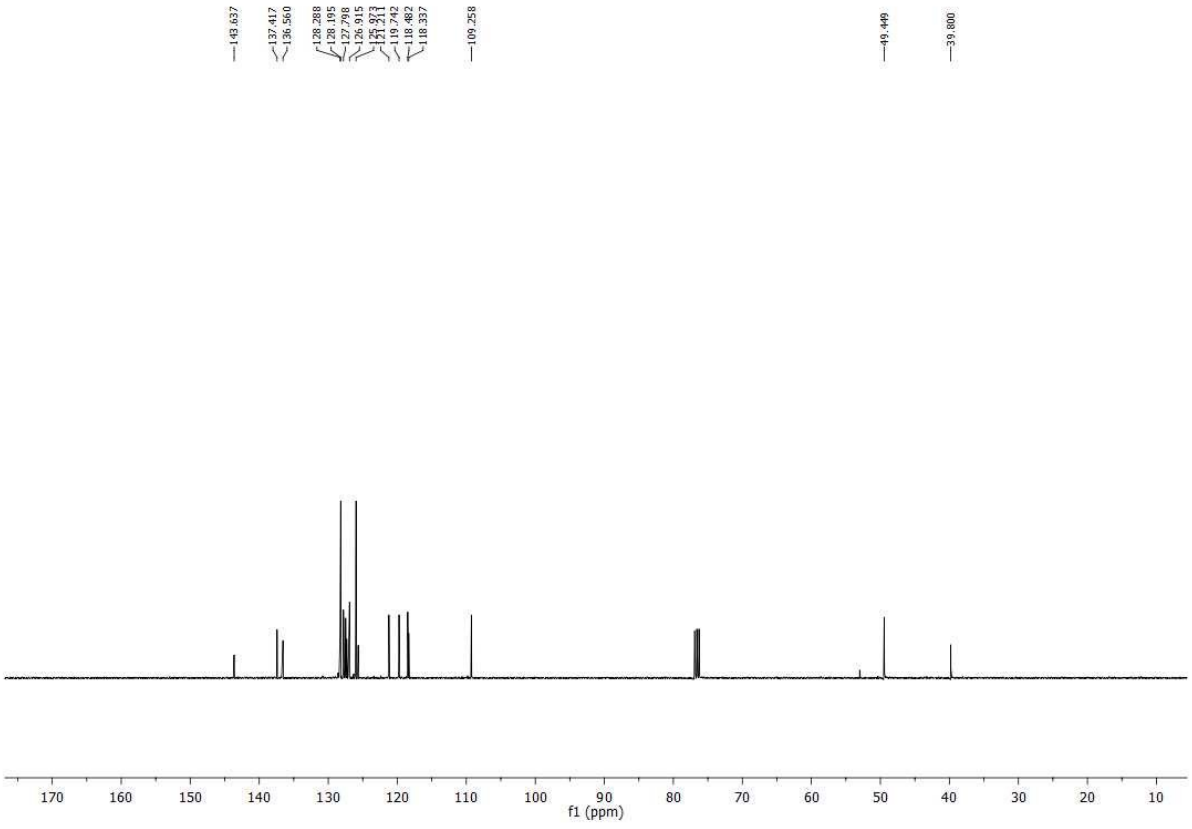
3,3'-(Phenylmethylene)bis(2-methyl-1*H*-indole) (3ac)



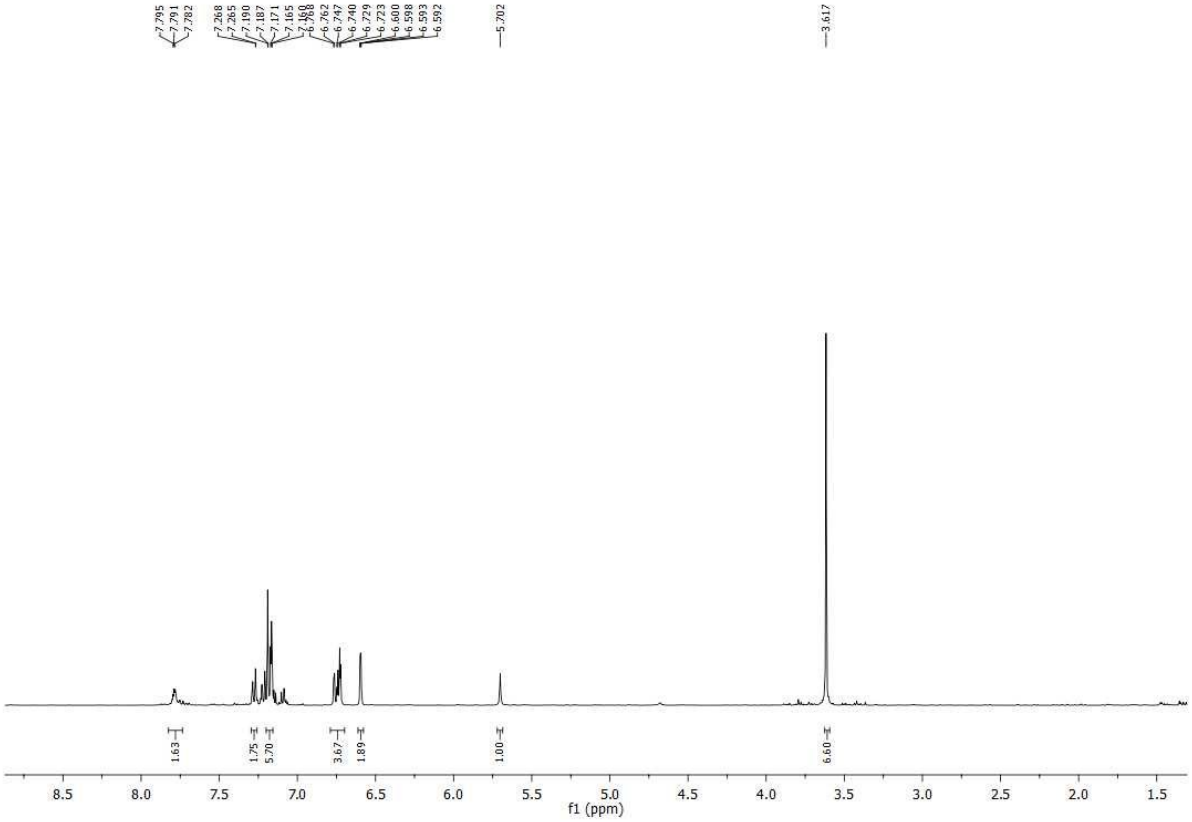


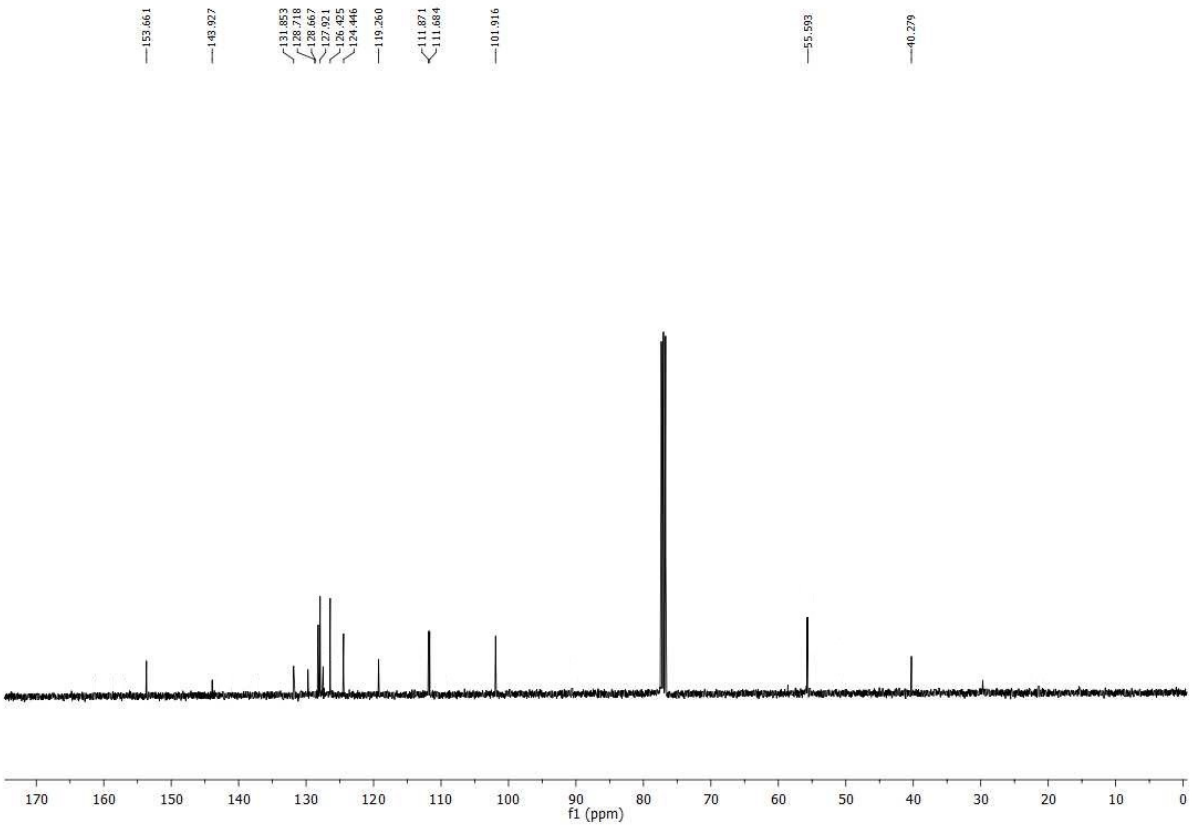
3,3'-(Phenylmethylene)bis(1-benzyl-1*H*-indole) (3ad)



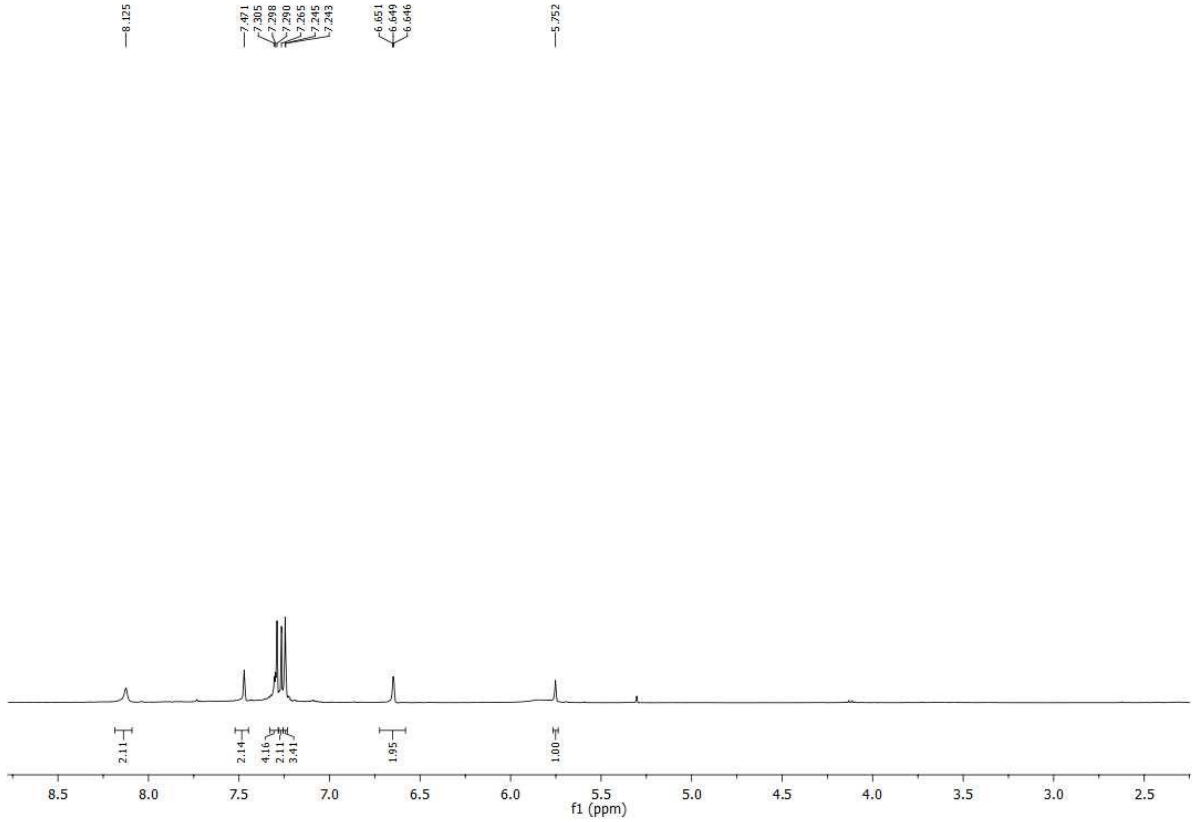


3,3'-(Phenylmethylene)bis(5-methoxy-1*H*-indole) (3ae)

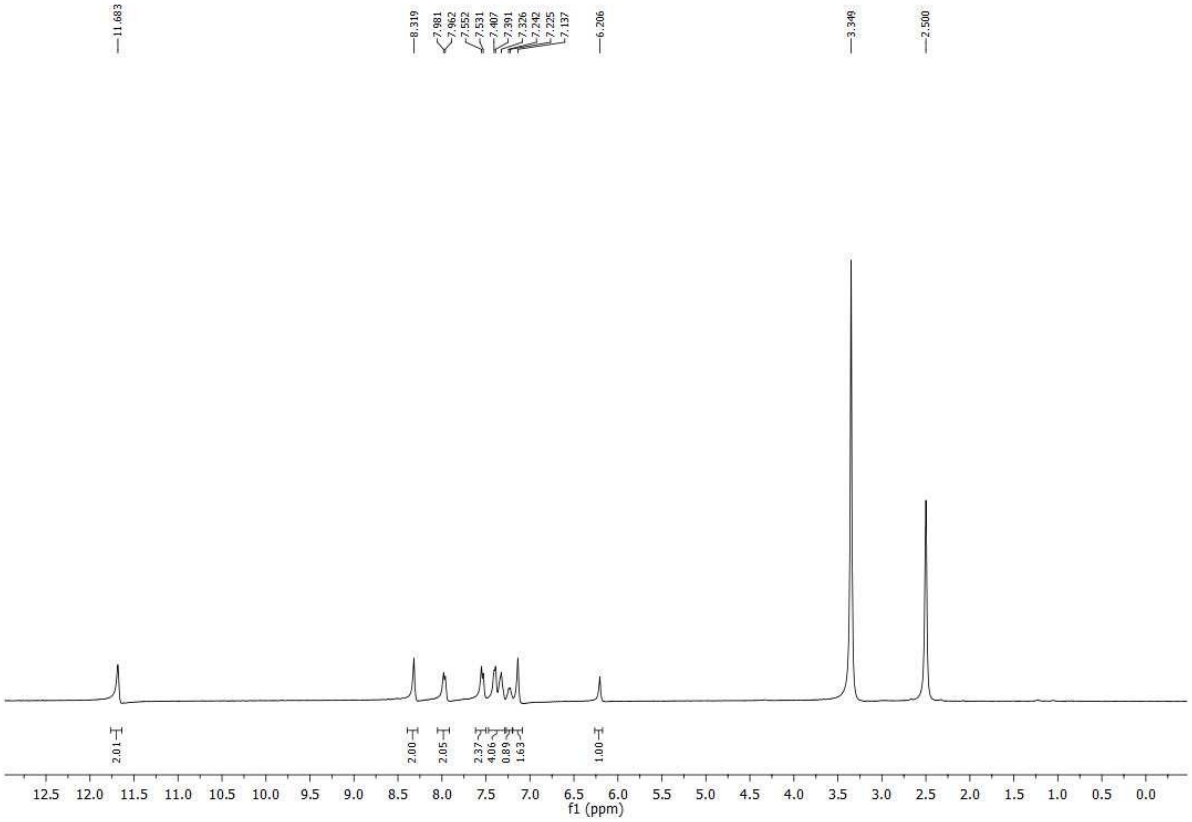


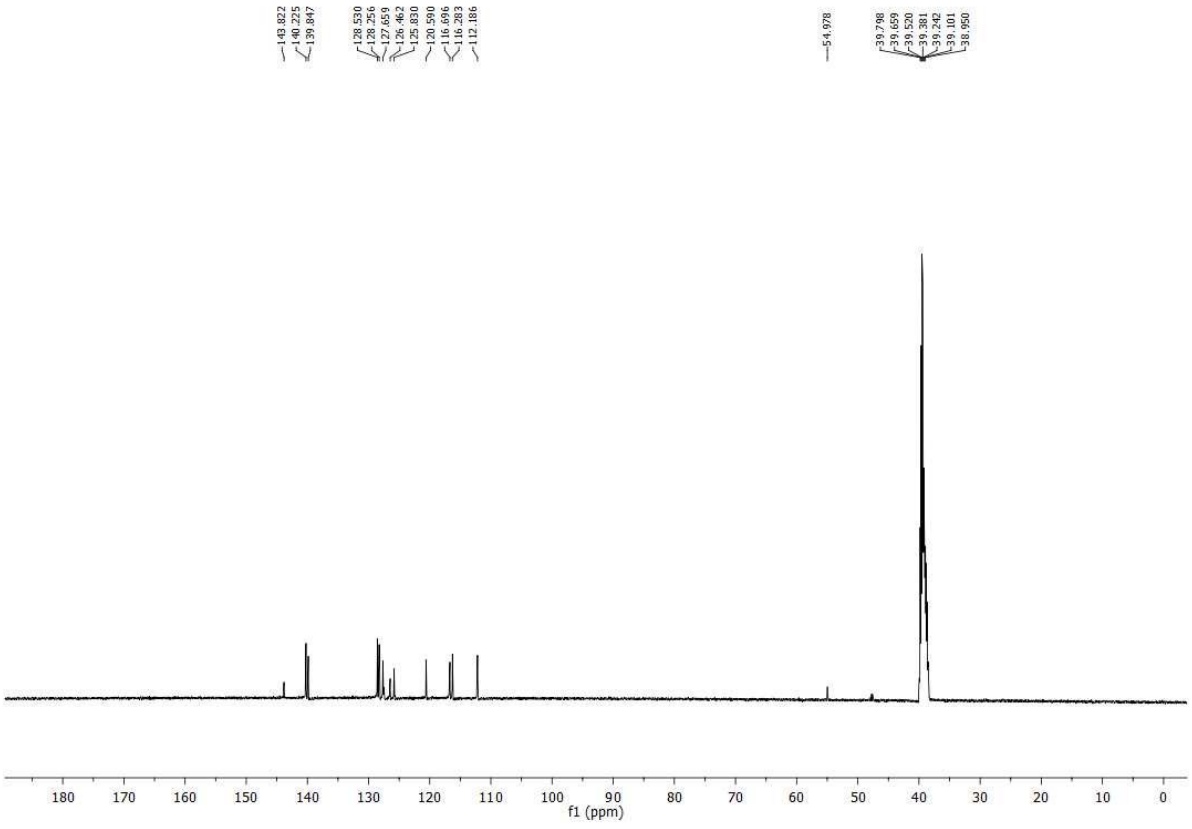


3,3'-(Phenylmethylene)bis(5-bromo-1*H*-indole) (3af)

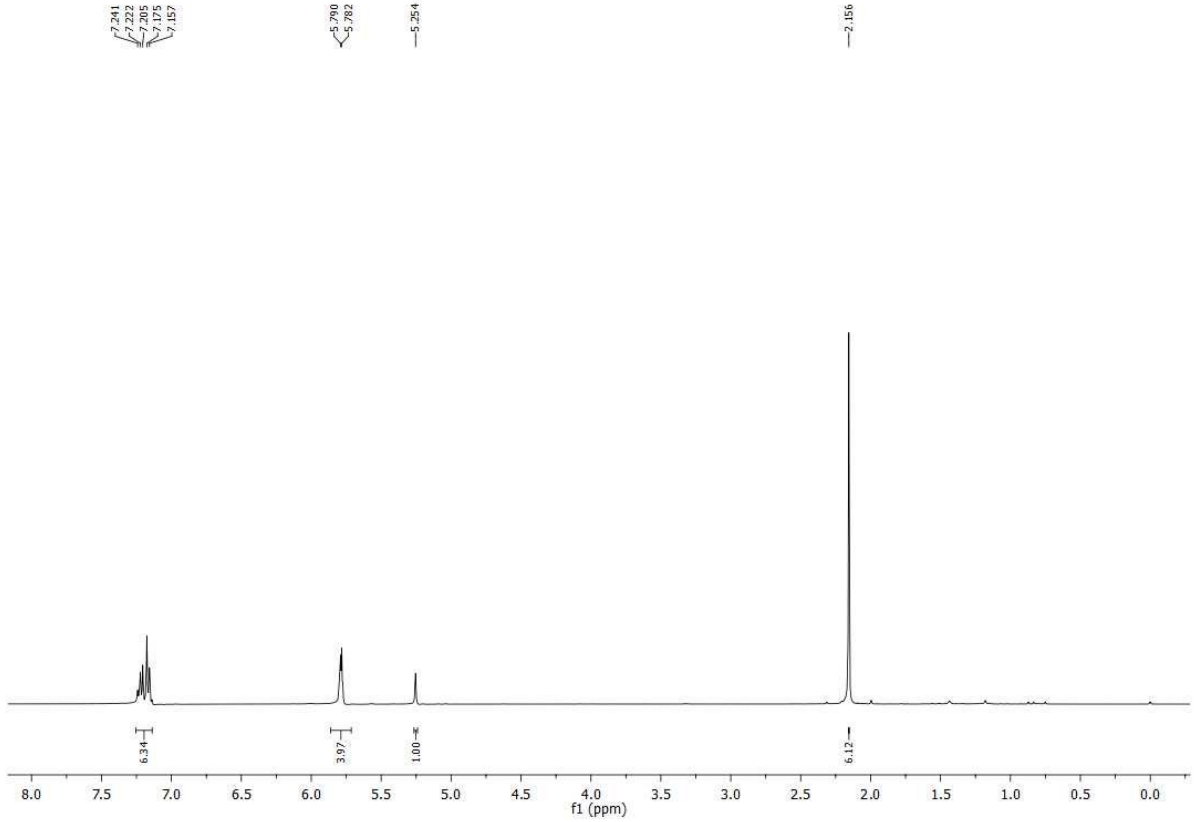


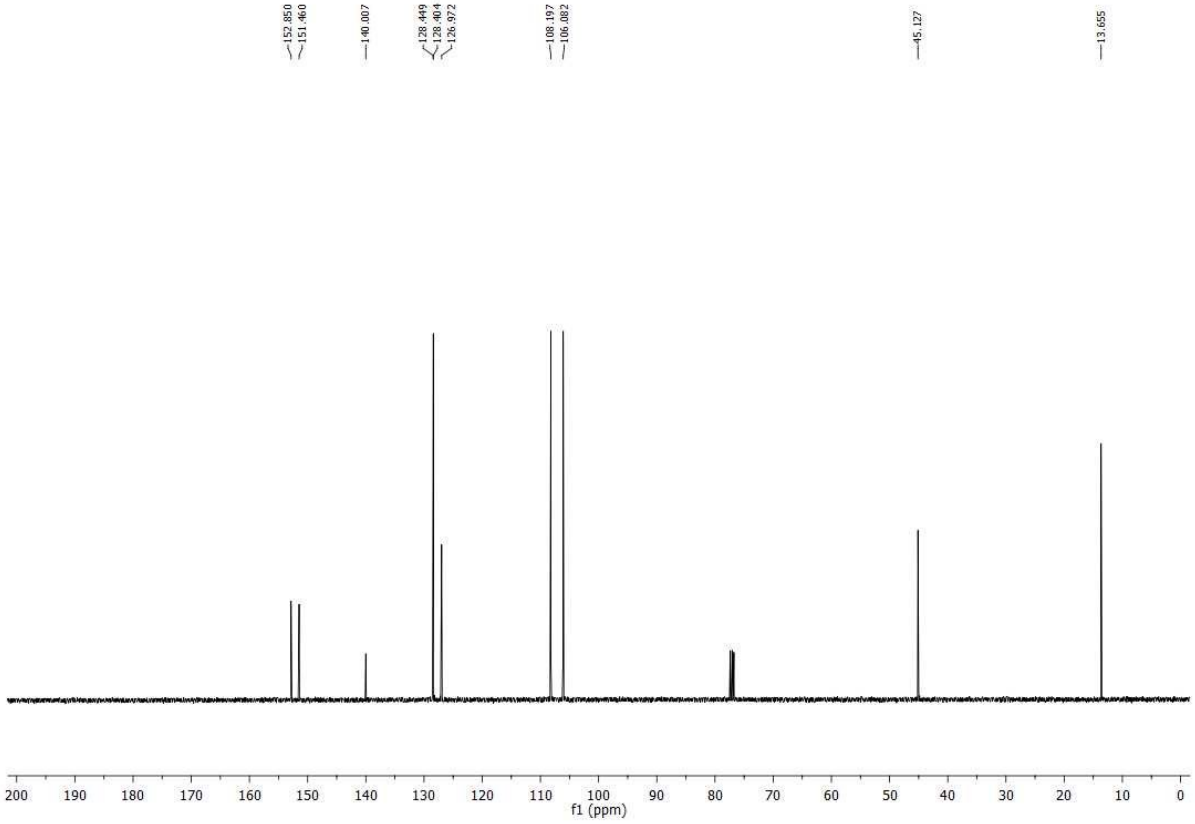
3,3'-(Phenylmethylene)bis(5-nitro-1*H*-indole) (3ag)



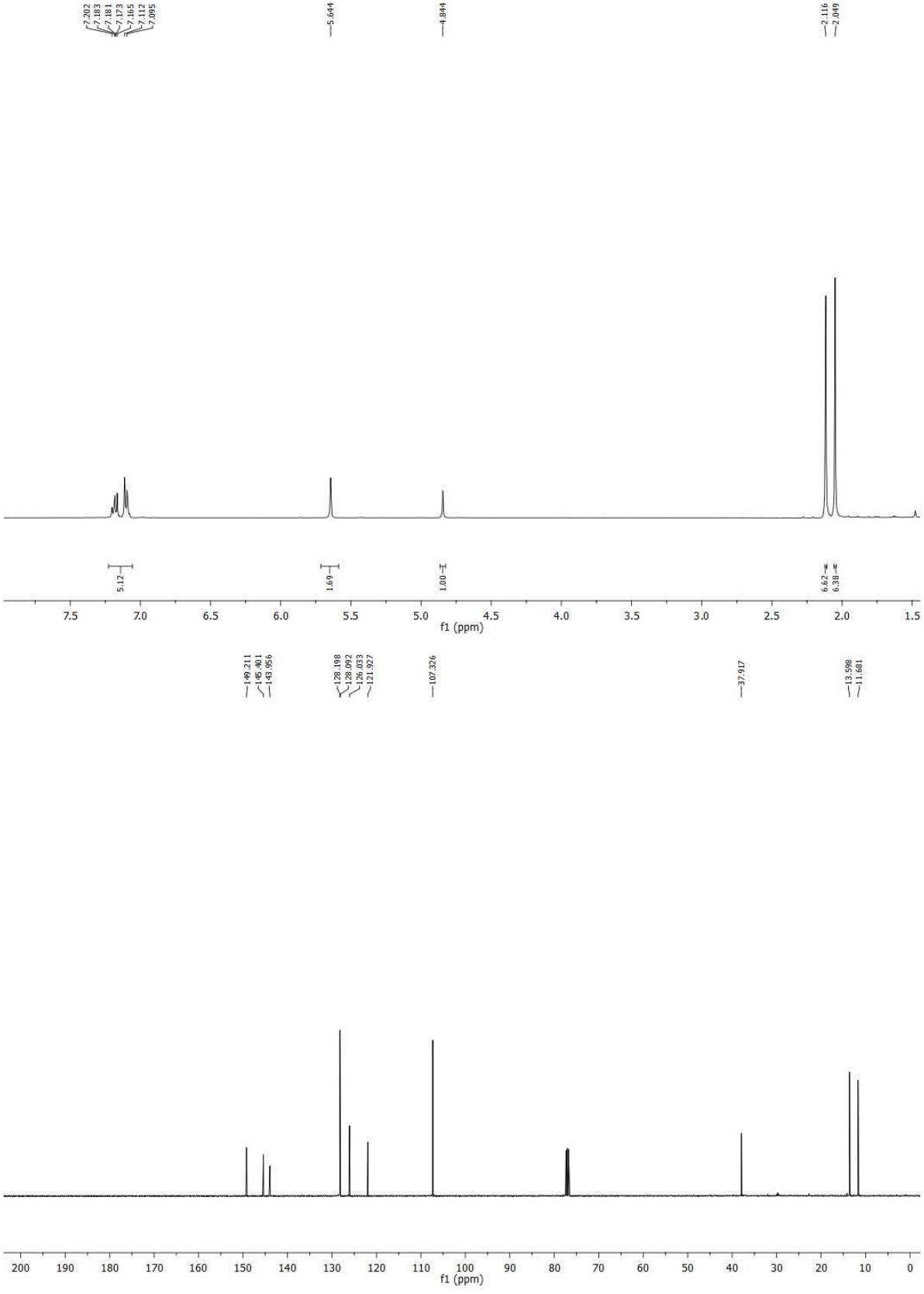


5,5'-(Phenylmethylene)bis(2-methylfuran) (3ah)

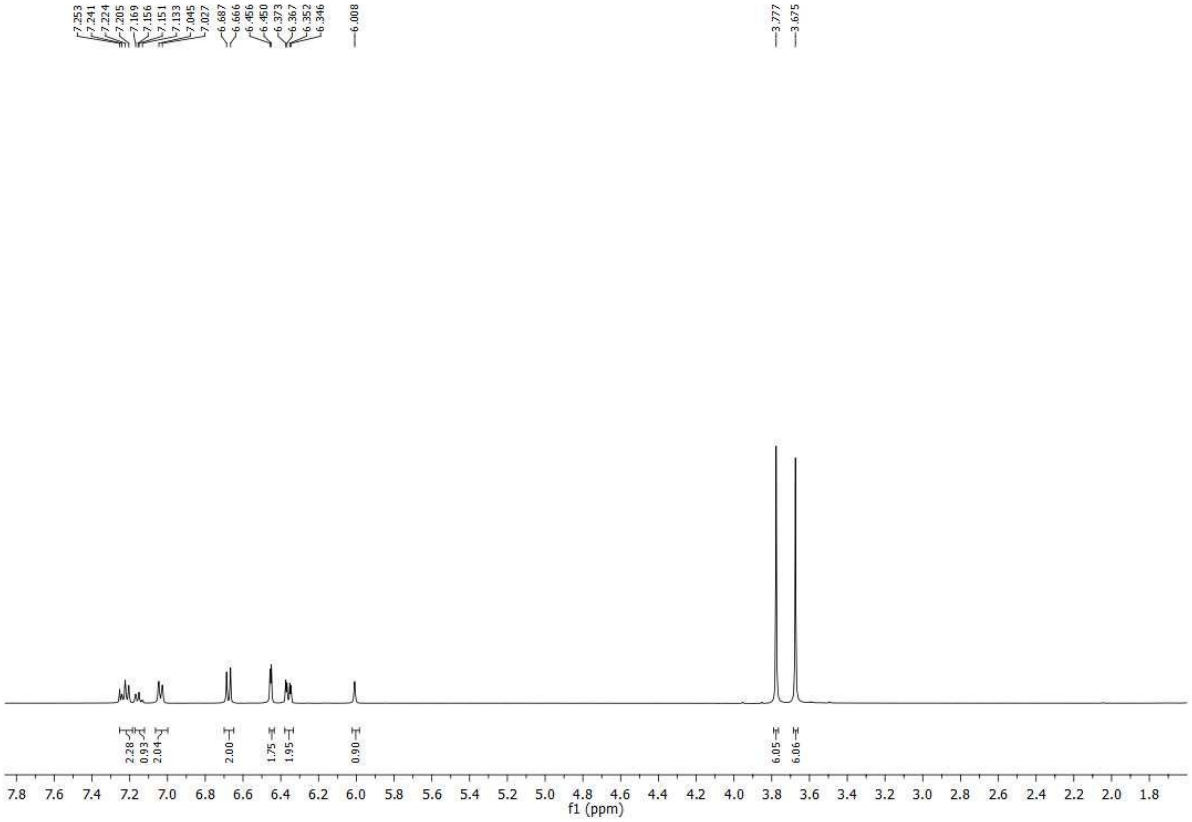


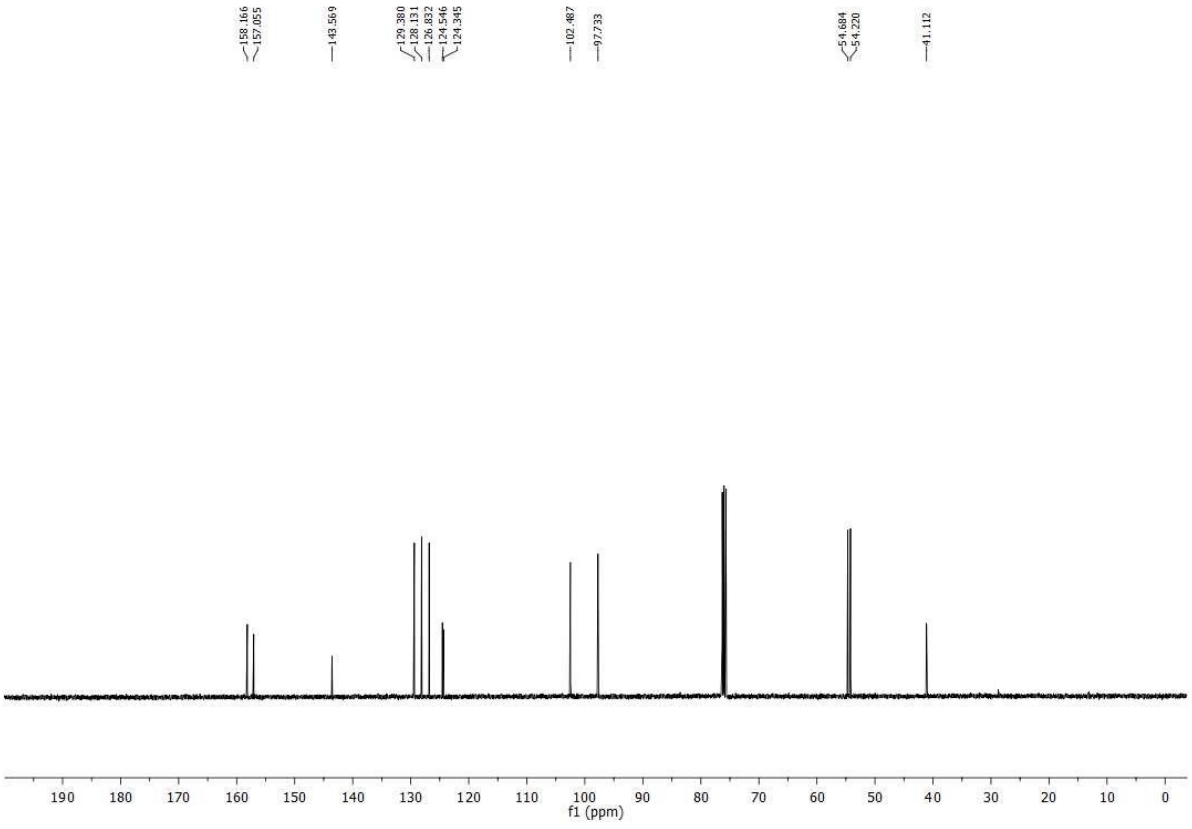


3,3'-(Phenylmethylene)bis(2,5-dimethylfuran) (3ai)

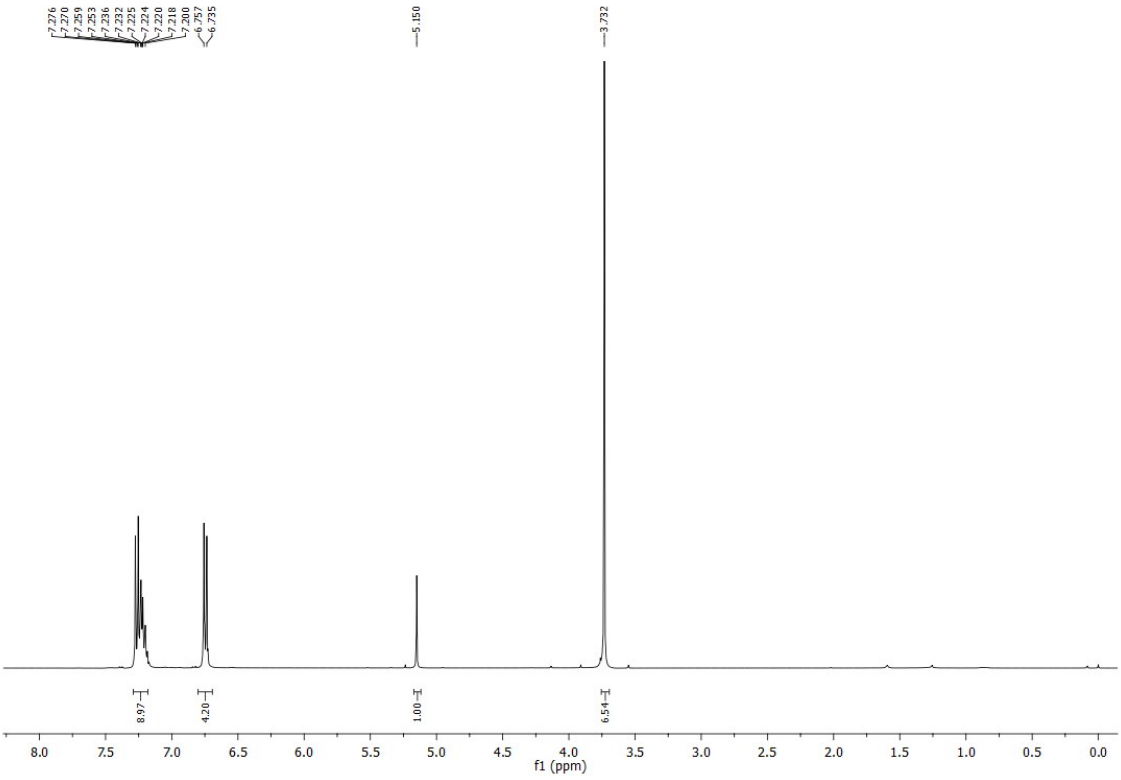


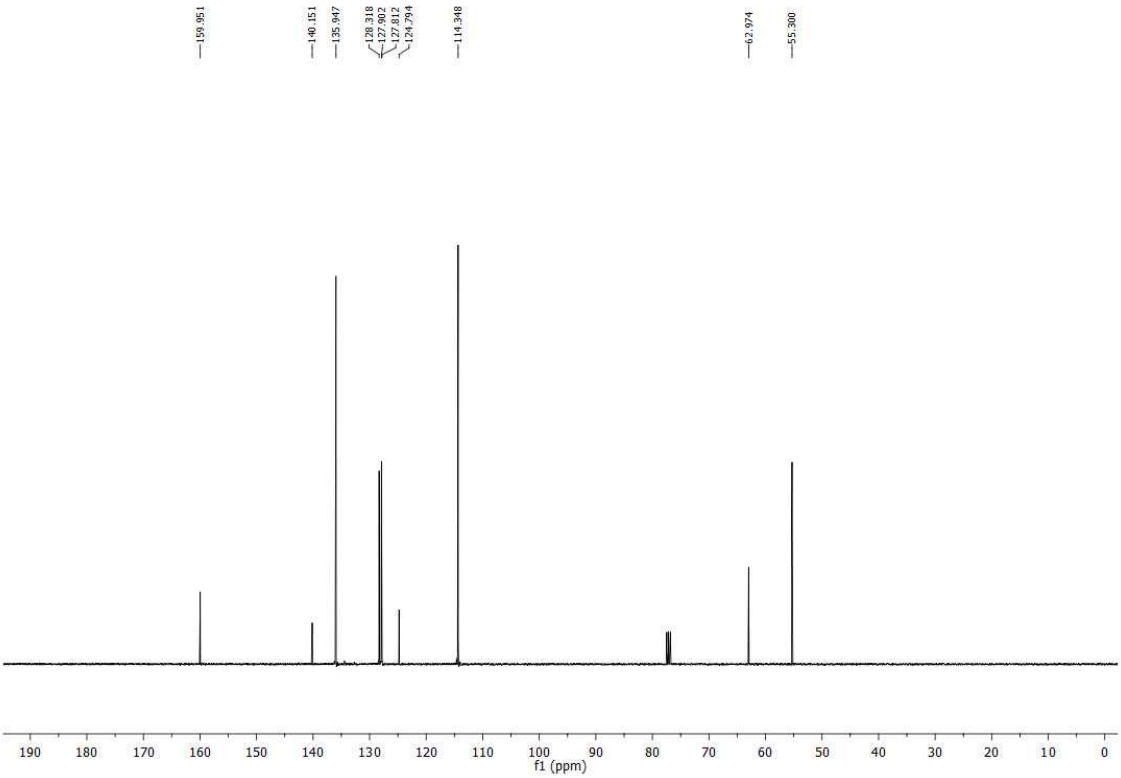
4,4'-(Phenylmethylene)bis(1,3-dimethoxybenzene) (3aj)



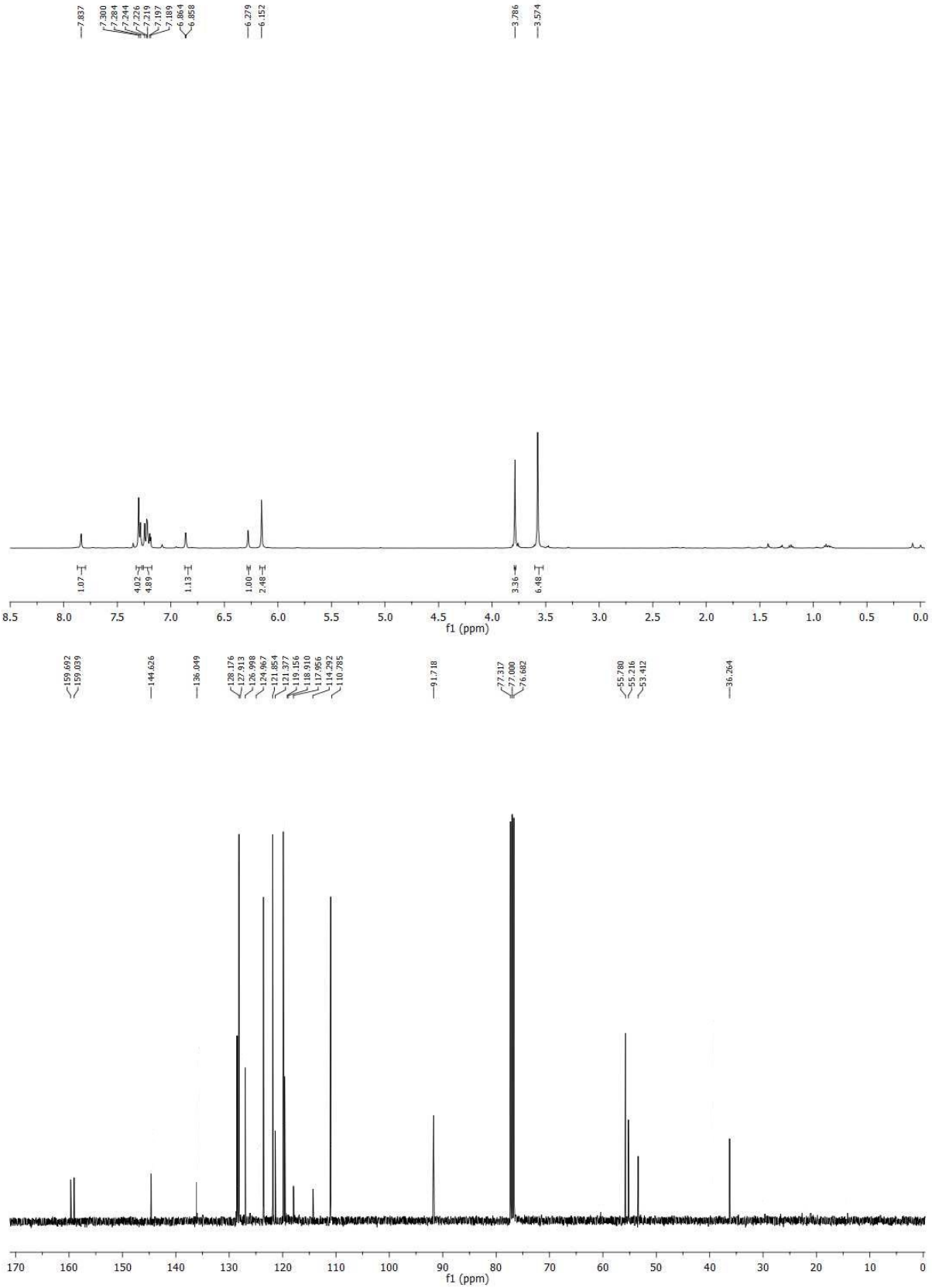


(Phenylmethylene)bis((4-methoxyphenyl)sulfane) (3ak)

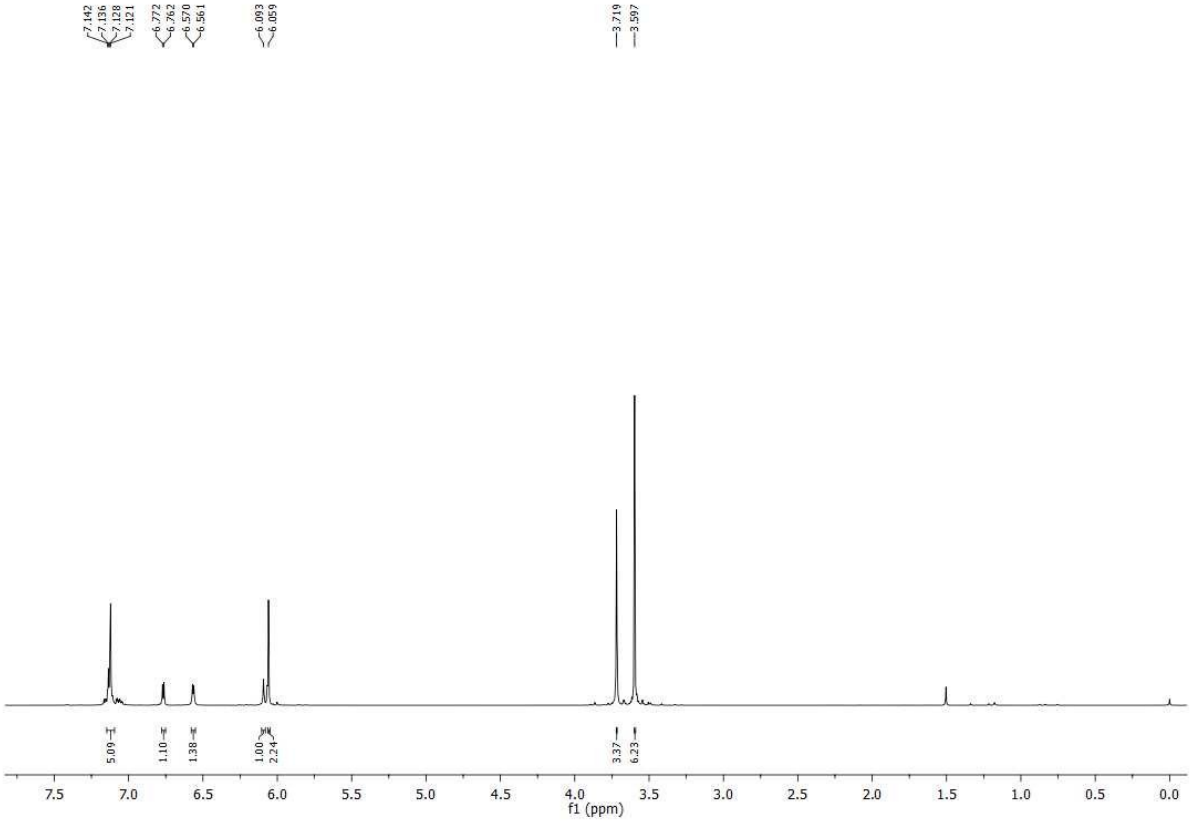


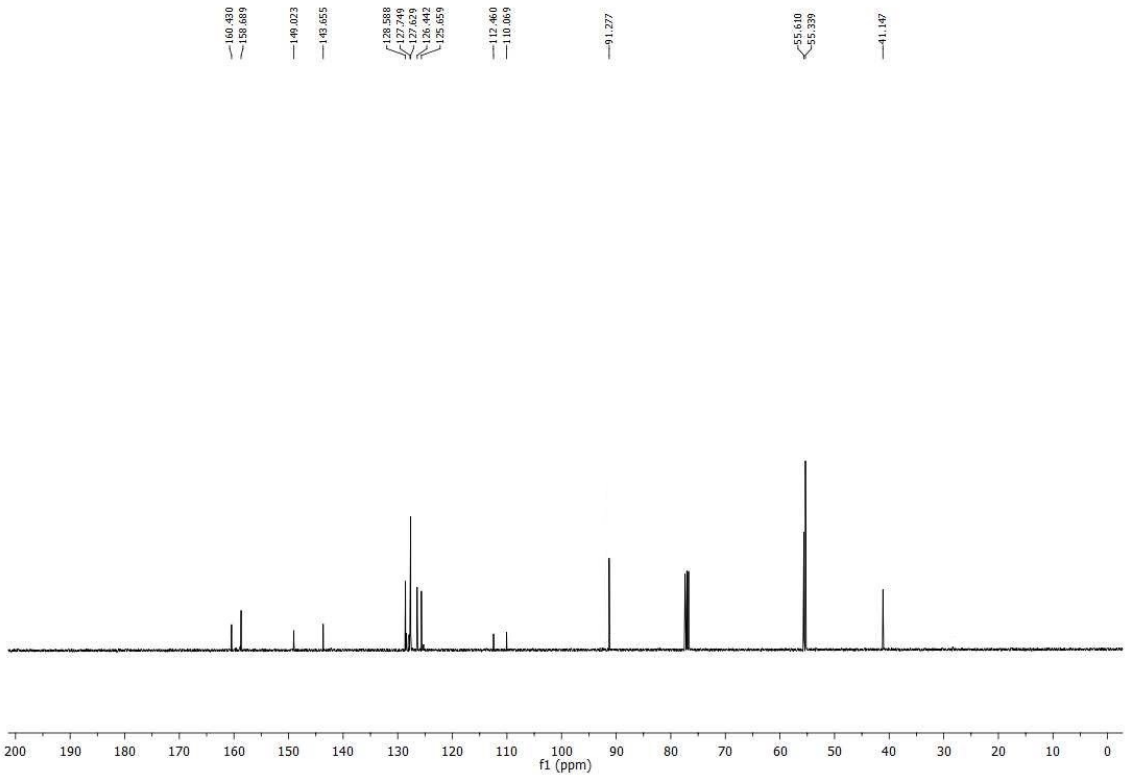


3-(Phenyl(2,4,6-trimethoxyphenyl)methyl)-1*H*-indole (4a)

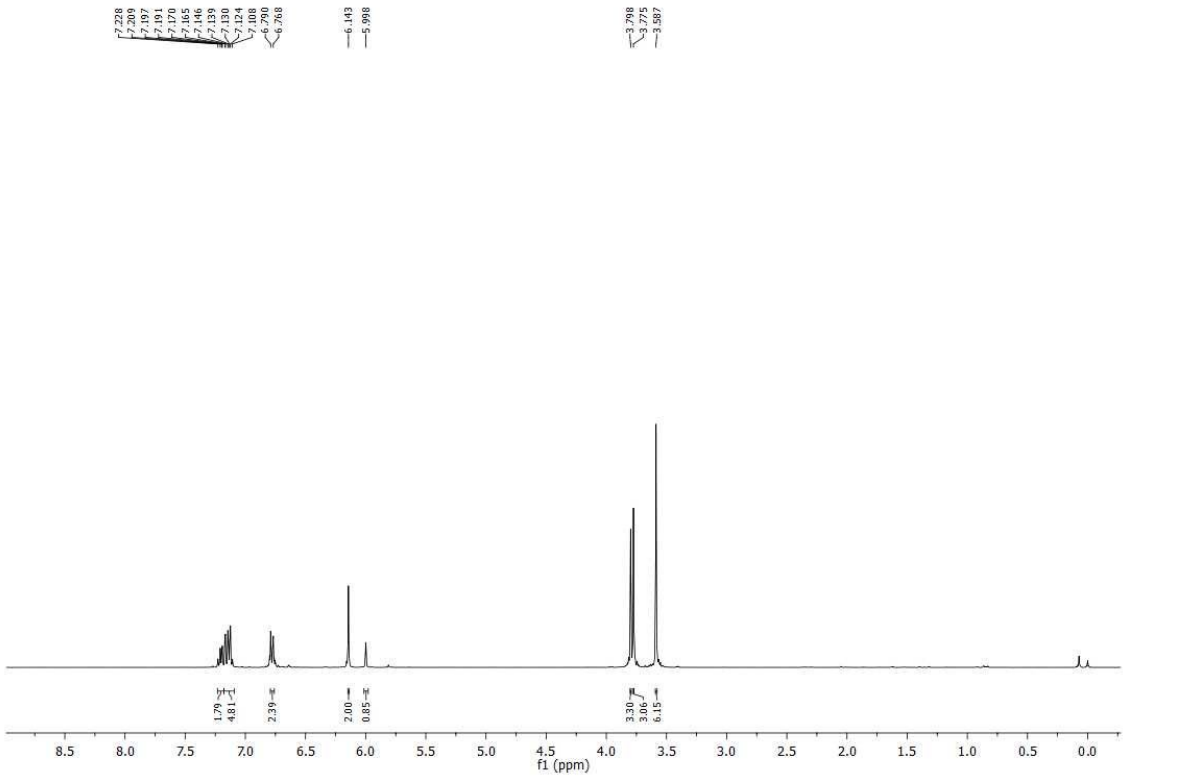


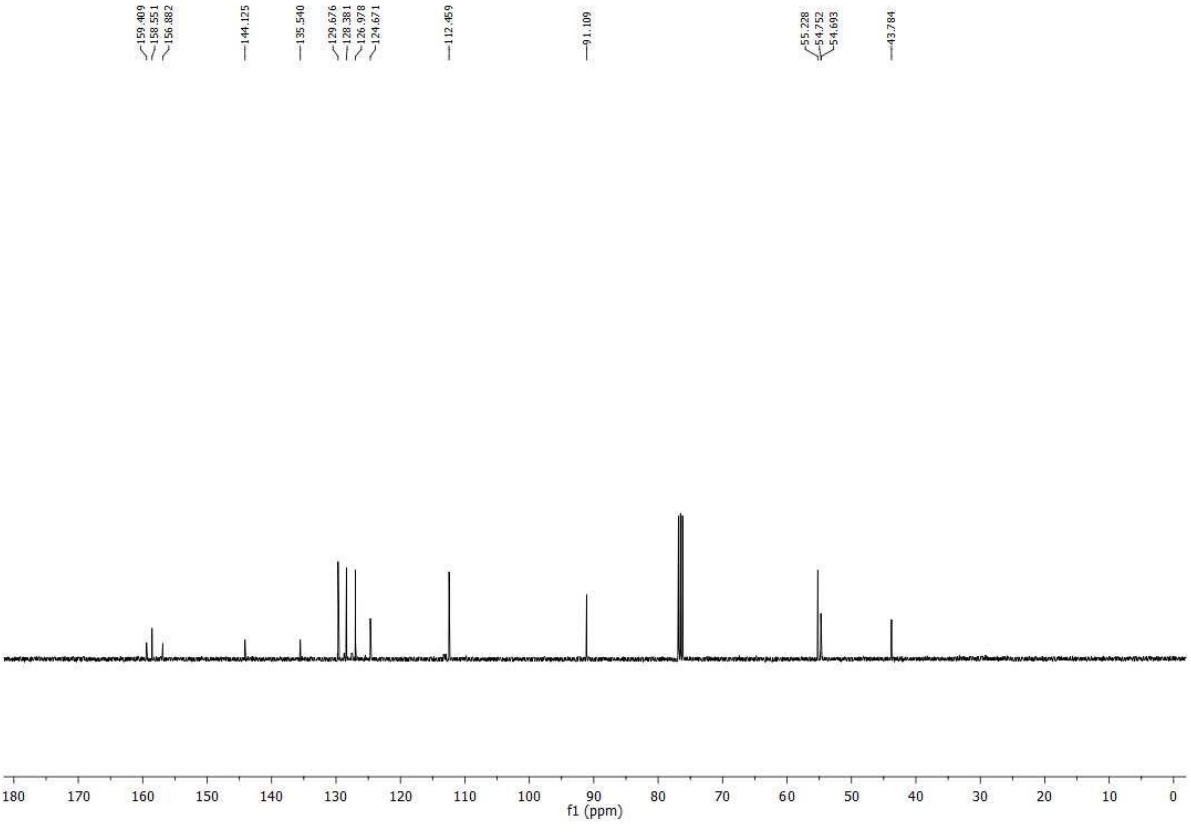
2-Bromo-5-(phenyl(2,4,6-trimethoxyphenyl)methyl)thiophene (4b)



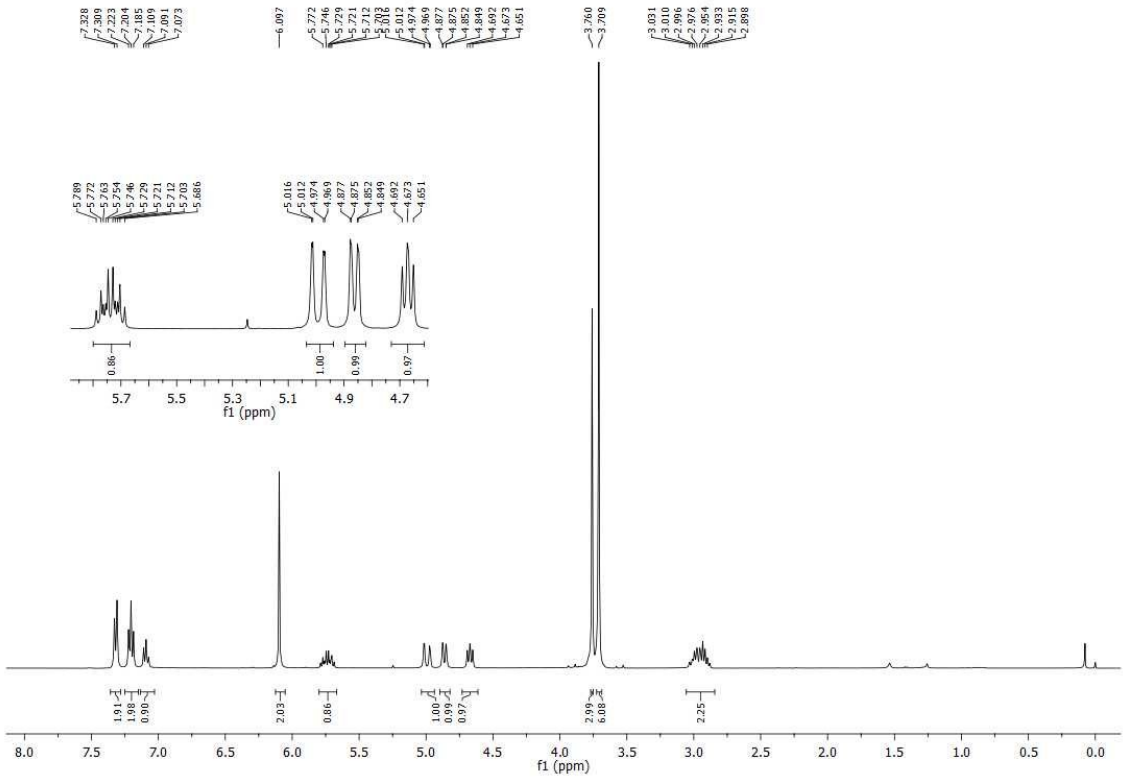


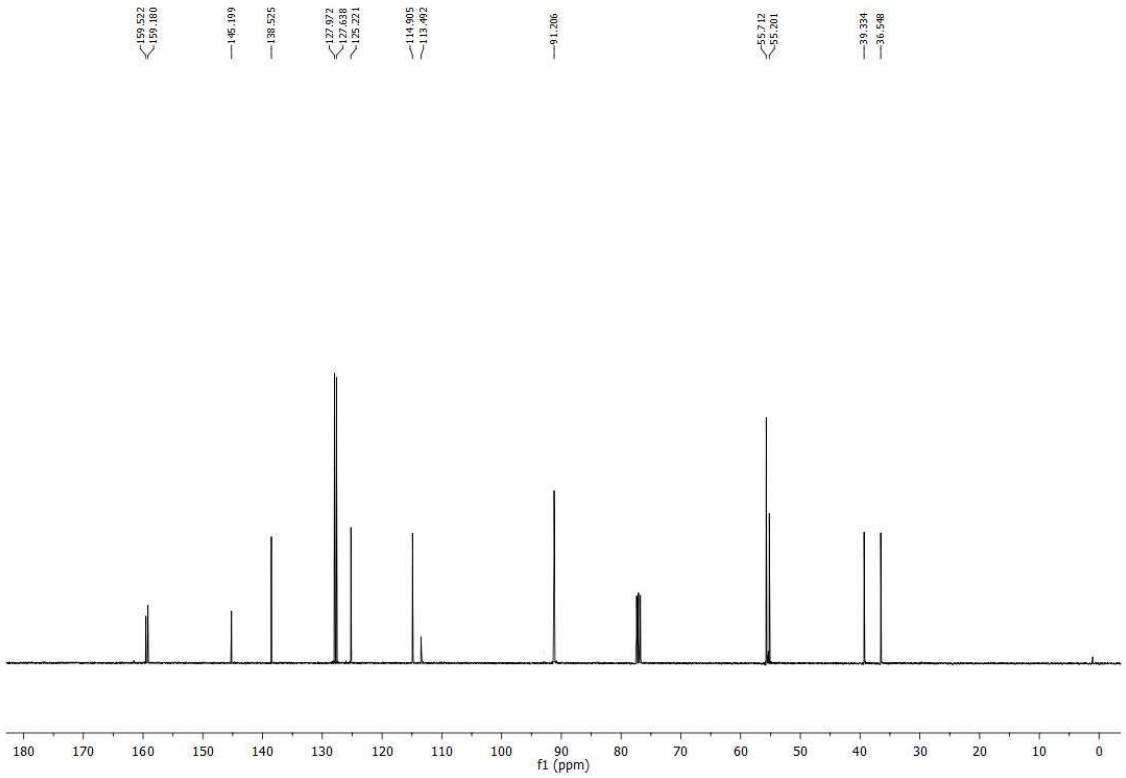
1,3,5-Trimethoxy-2-((4-methoxyphenyl)(phenyl)methyl)benzene (4c)



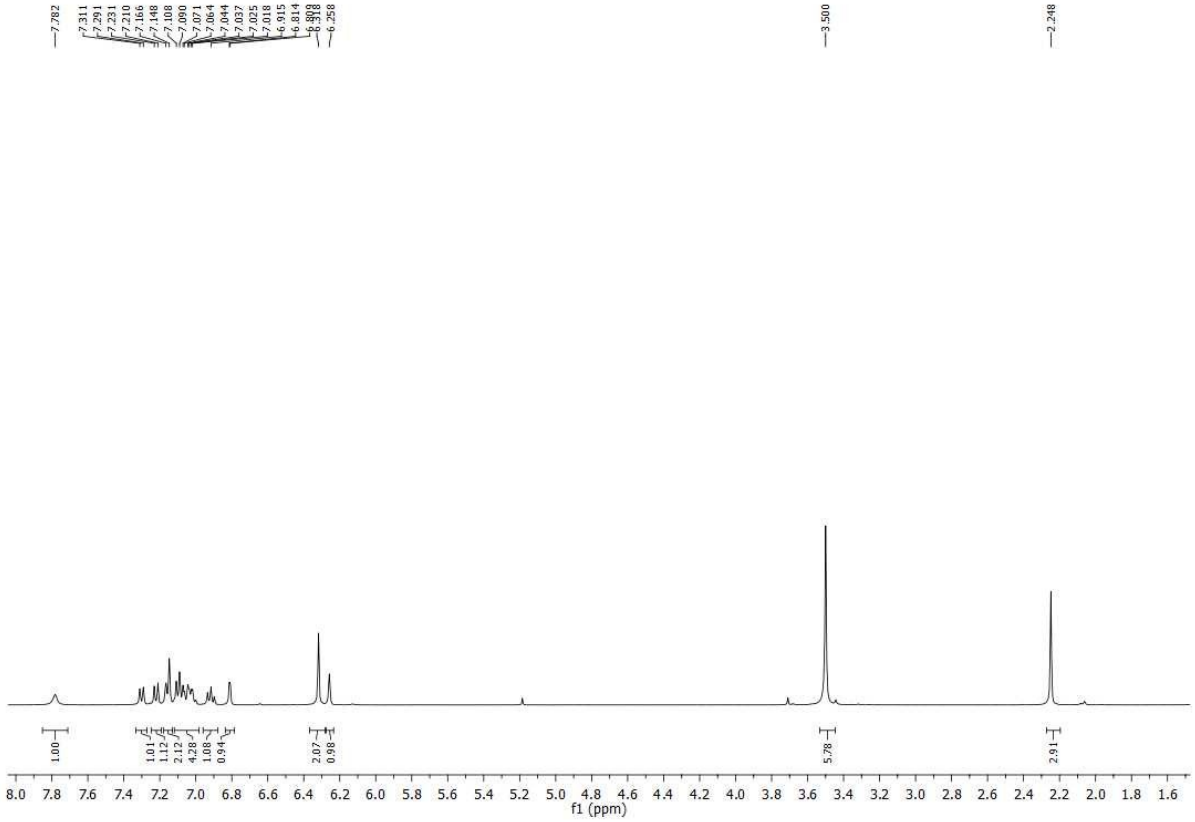


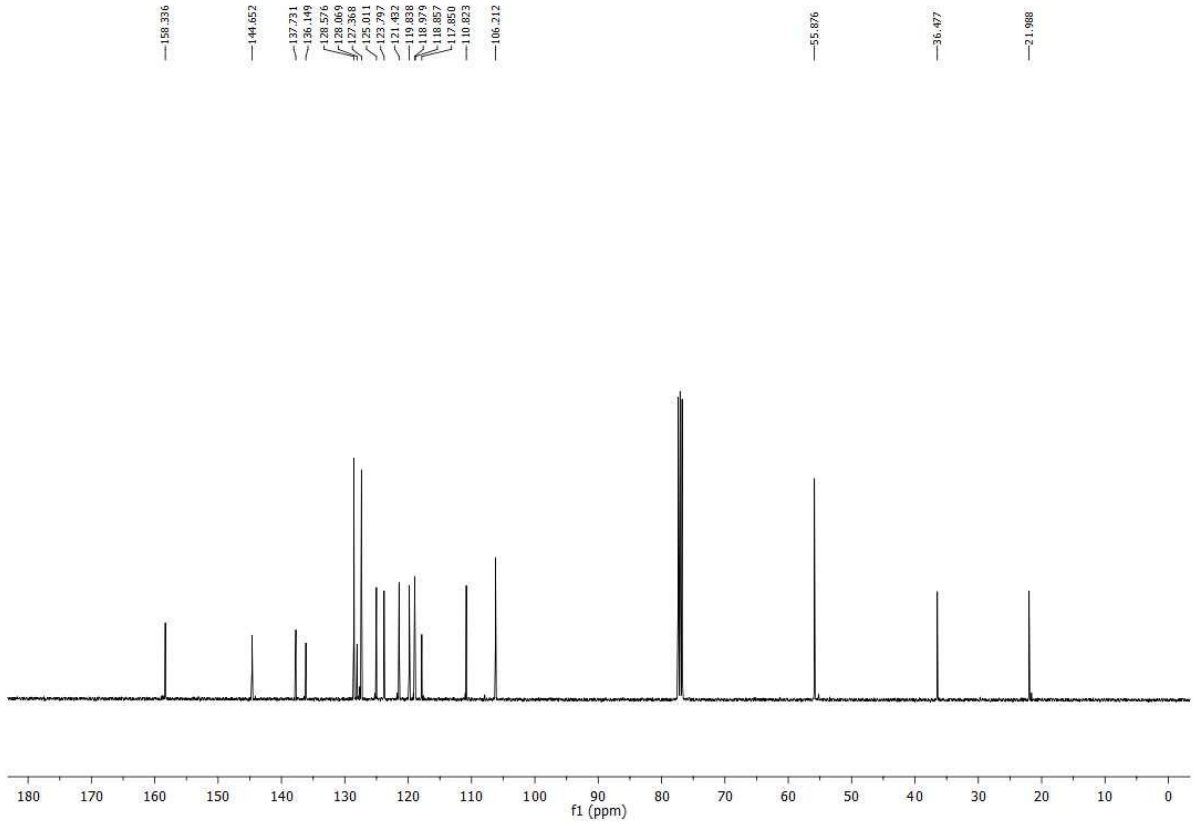
1,3,5-Trimethoxy-2-(1-phenylbut-3-en-1-yl)benzene (4d)



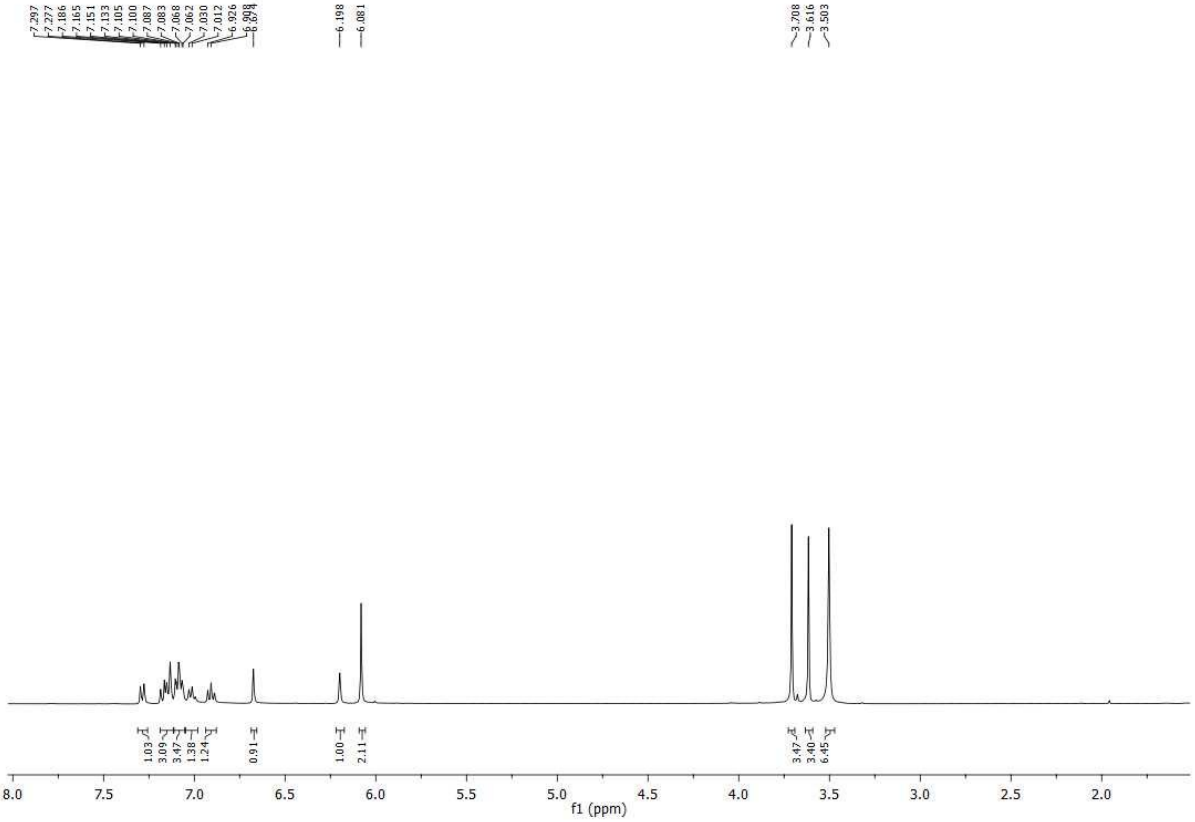


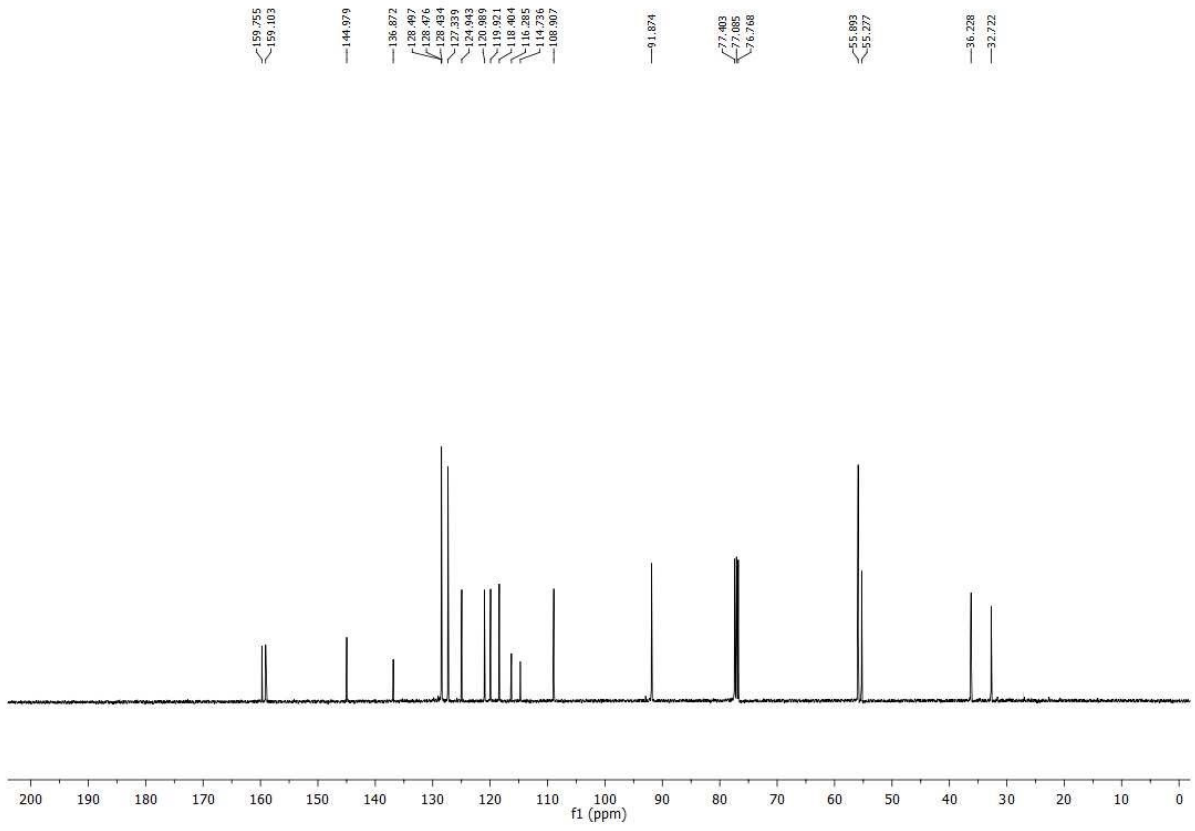
3-((2,6-Dimethoxy-4-methylphenyl)(phenyl)methyl)-1*H*-indole (4e)



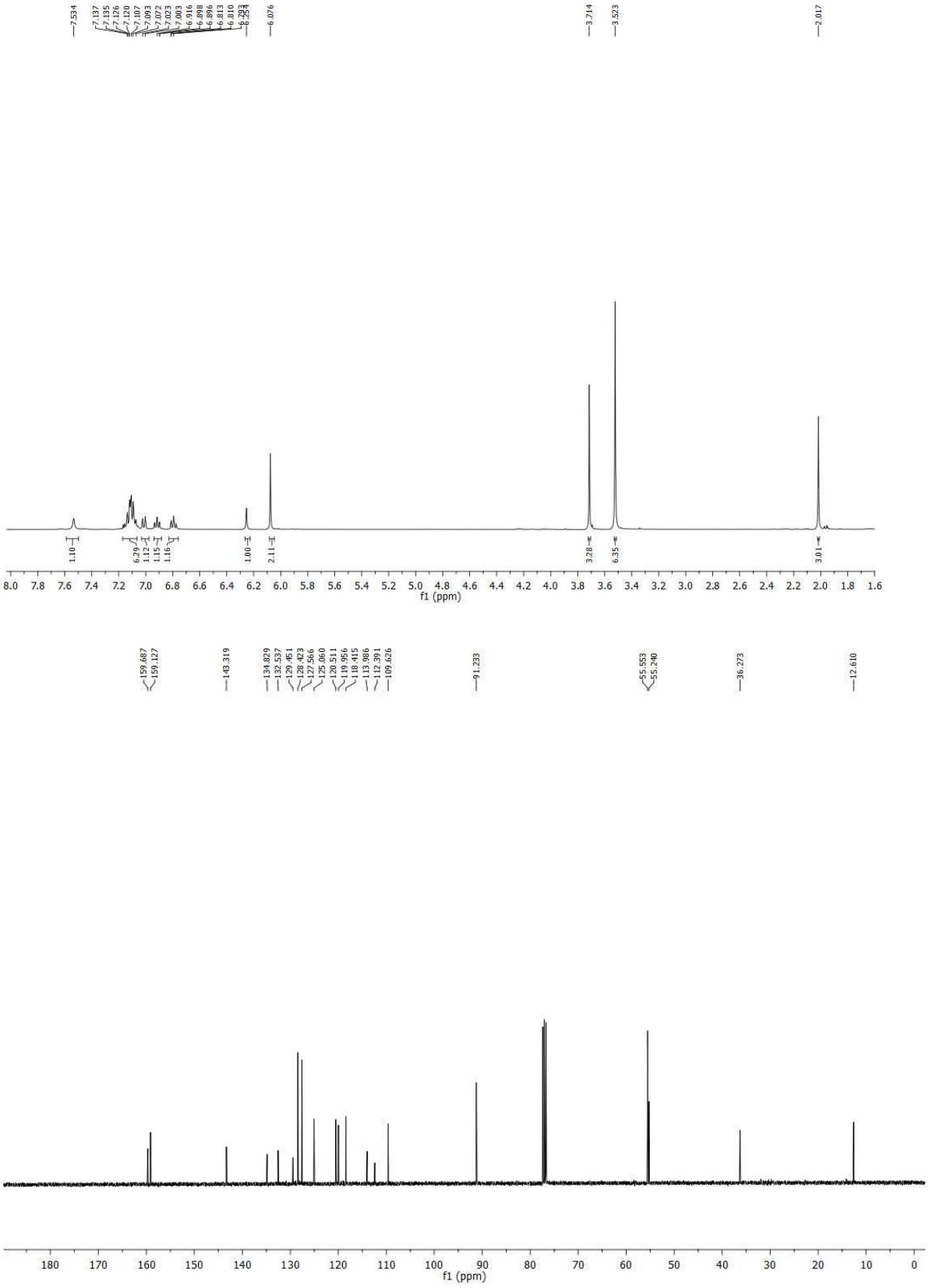


1-Methyl-3-(phenyl(2,4,6-trimethoxyphenyl)methyl)-1*H*-indole (4f)

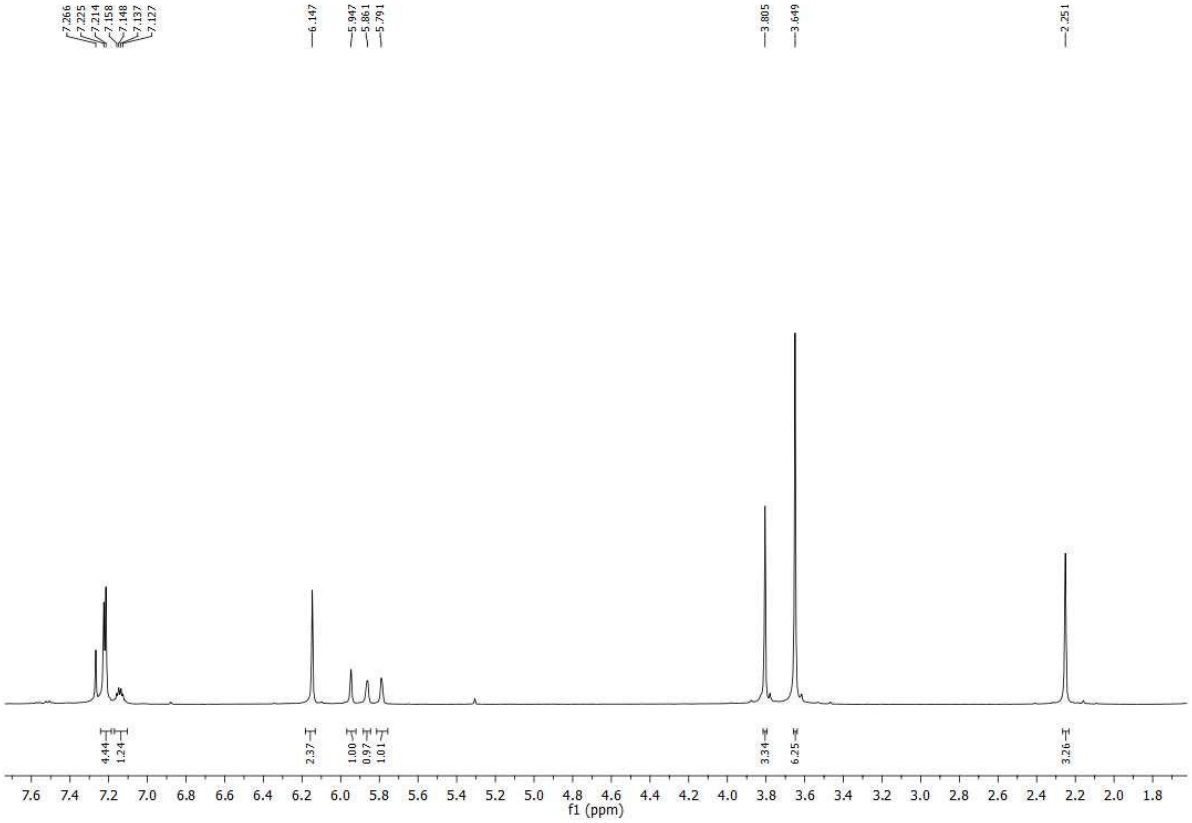


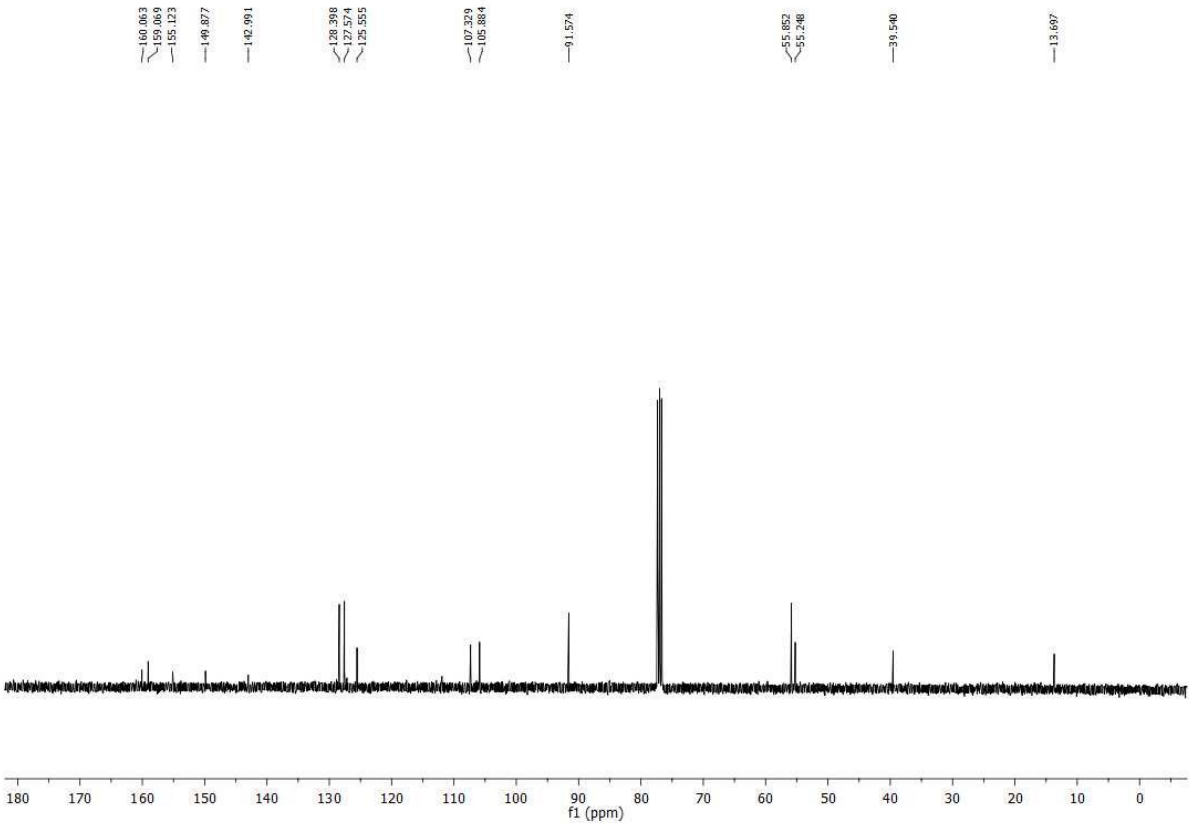


2-Methyl-3-(phenyl(2,4,6-trimethoxyphenyl)methyl)-1*H*-indole (4g)

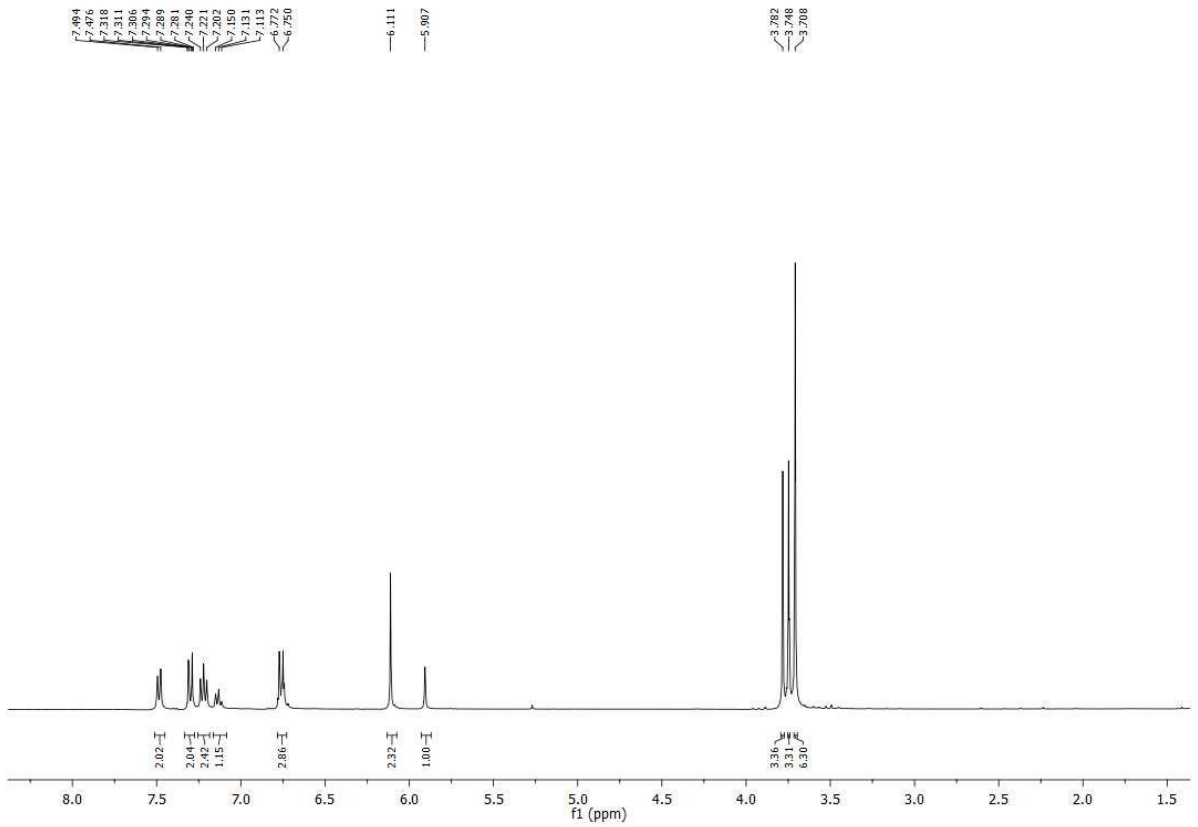


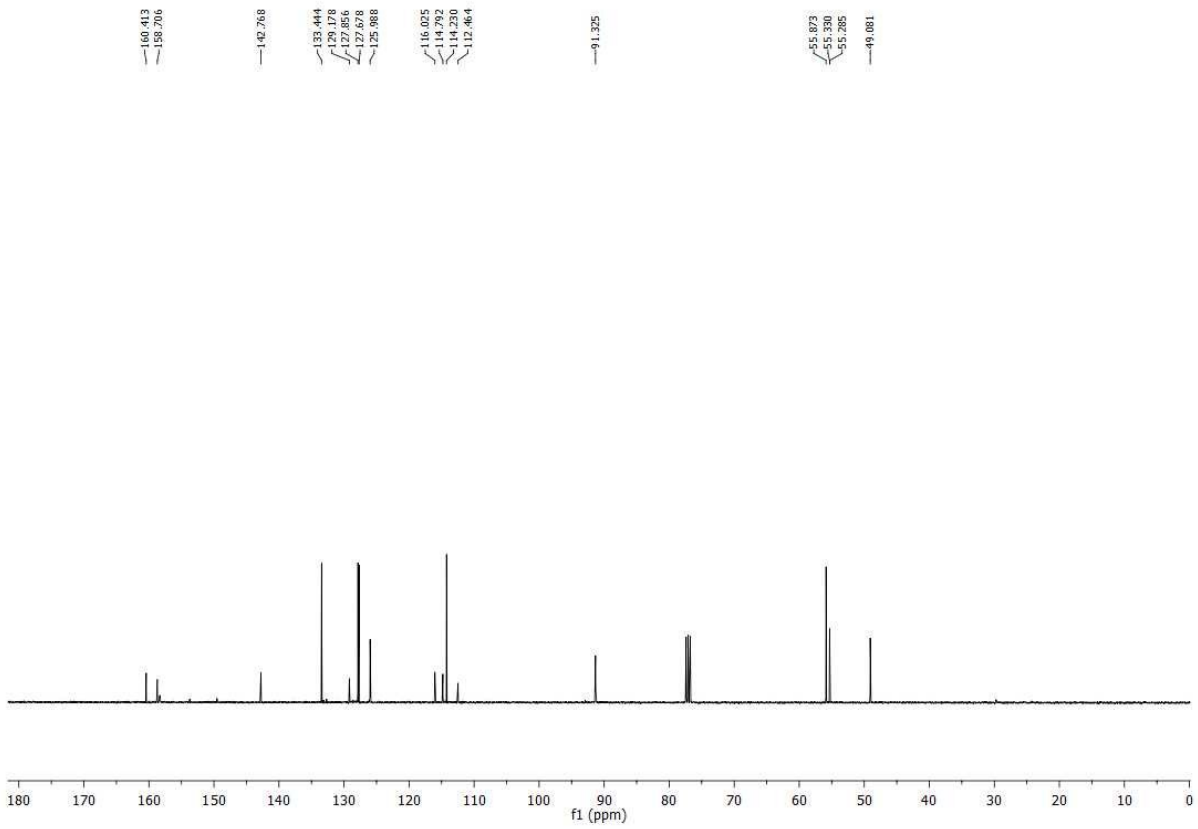
2-Methyl-5-(phenyl(2,4,6-trimethoxyphenyl)methyl)furan (4h)



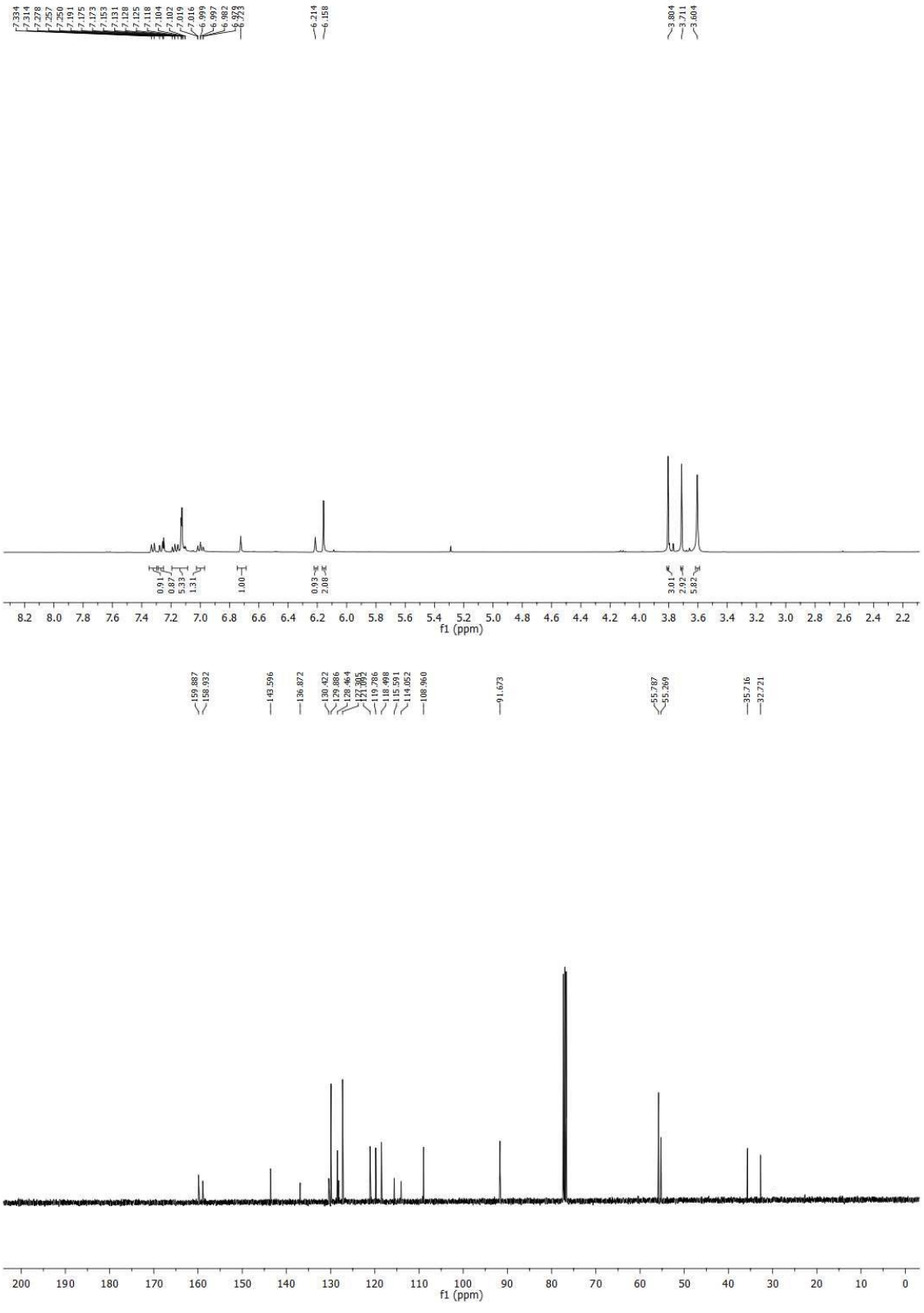


(4-Methoxyphenyl)(phenyl(2,4,6-trimethoxyphenyl)methyl)sulfane (4i)

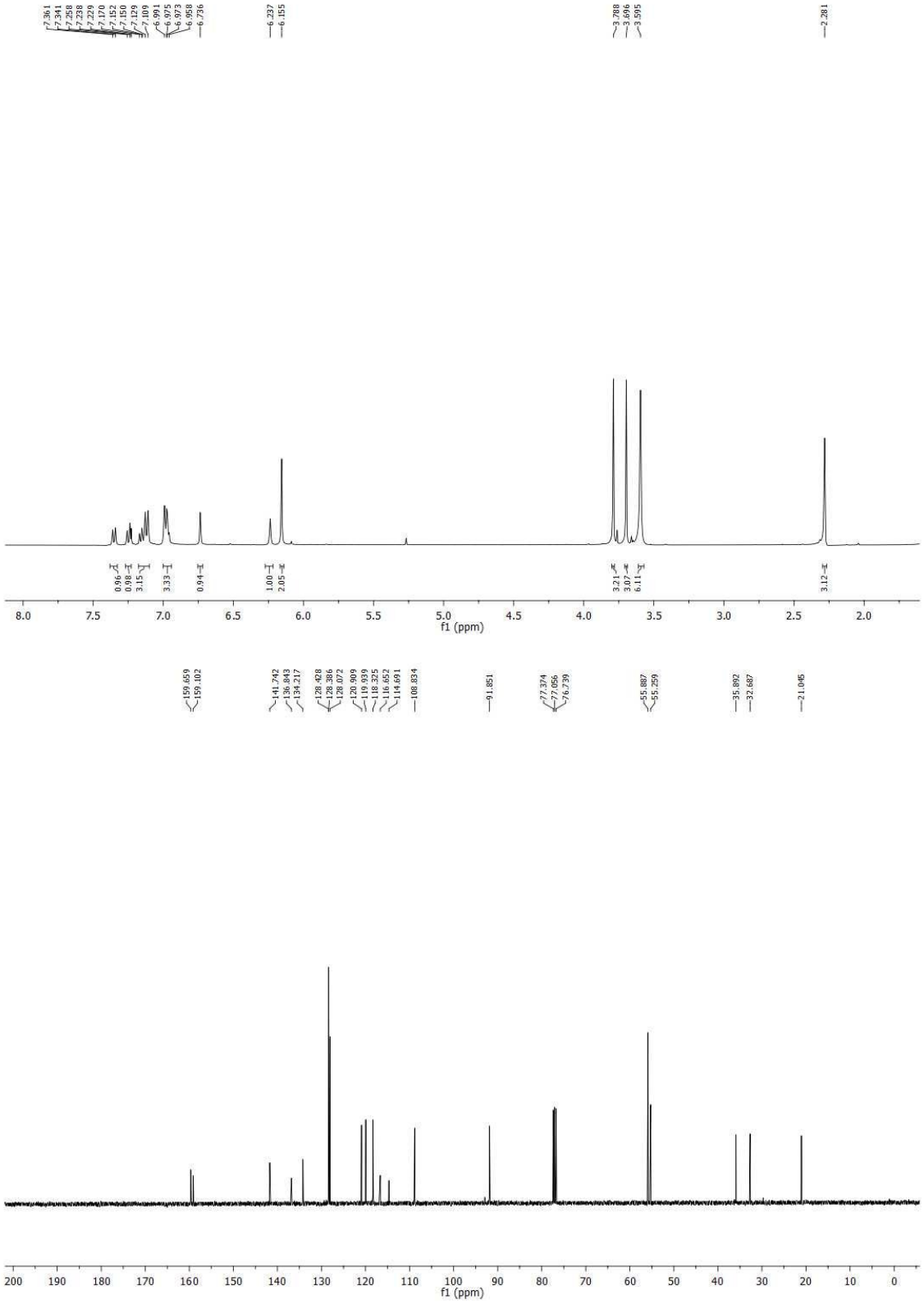




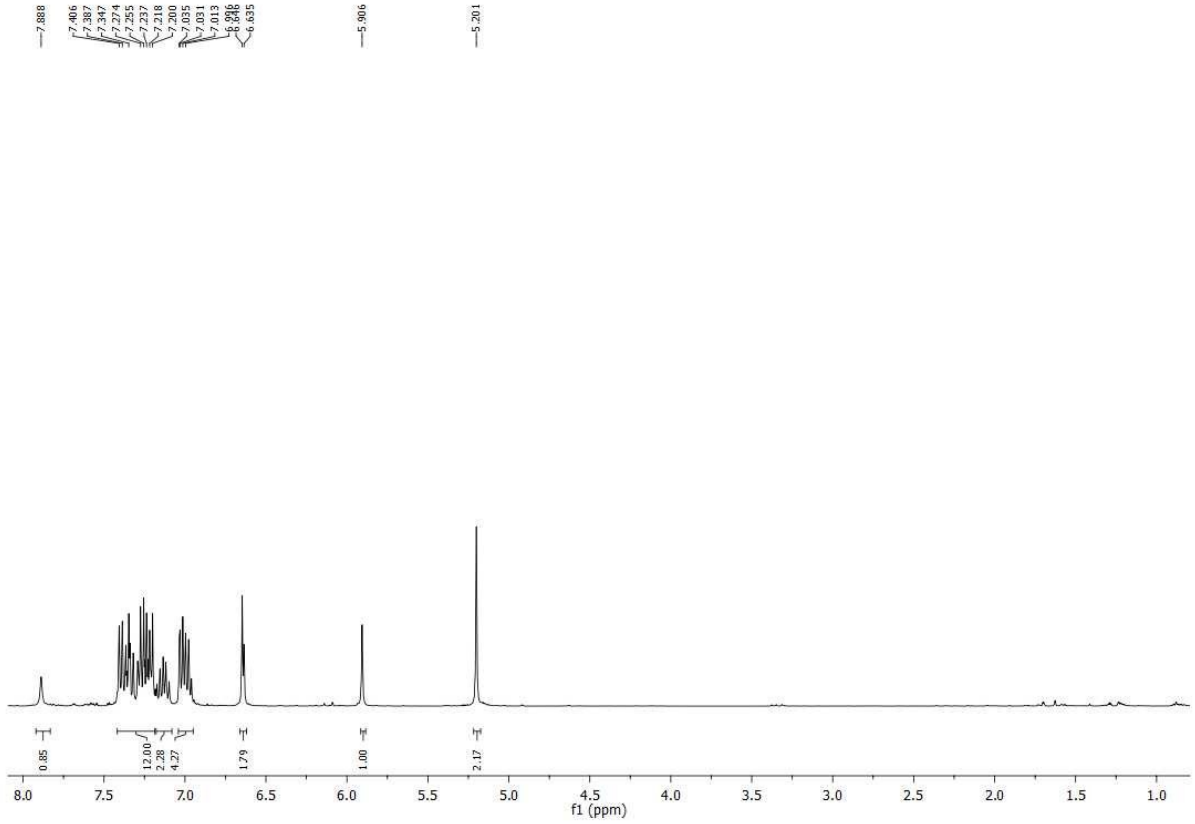
3-((4-chlorophenyl)(2,4,6-trimethoxyphenyl)methyl)-1-methyl-1*H*-indole (4j)

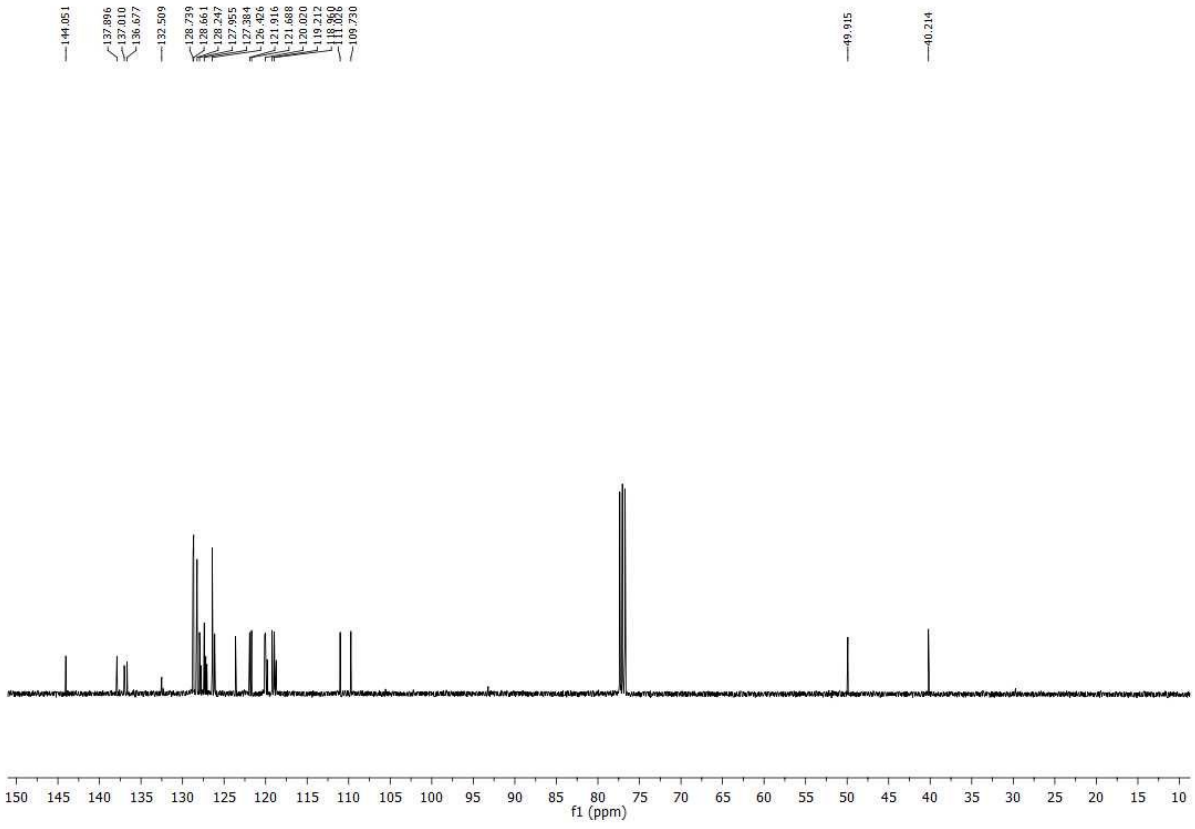


1-methyl-3-(p-tolyl(2,4,6-trimethoxyphenyl)methyl)-1*H*-indole (4k)

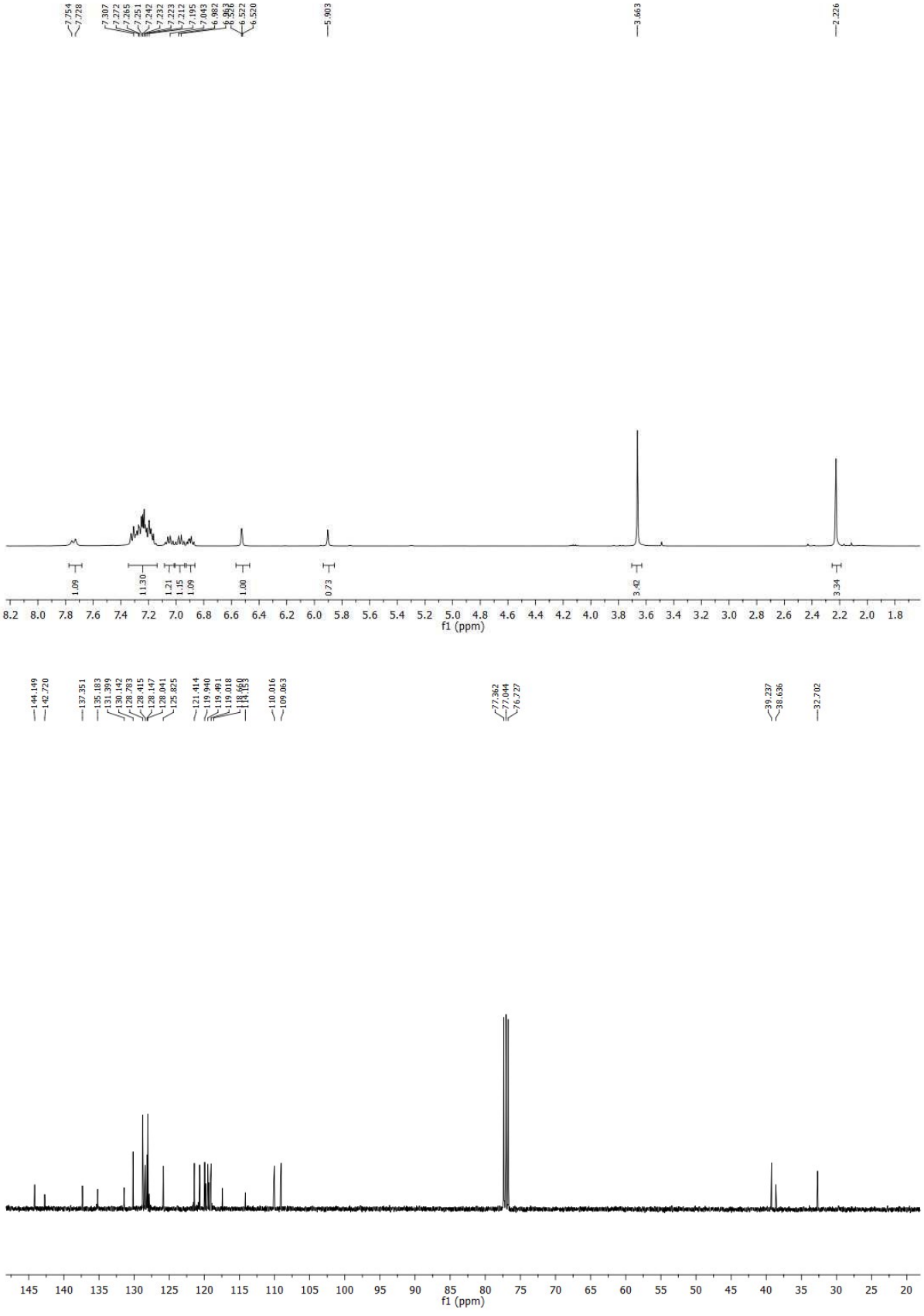


3-((1*H*-Indol-3-yl)(phenyl)methyl)-1-benzyl-1*H*-indole (5a)

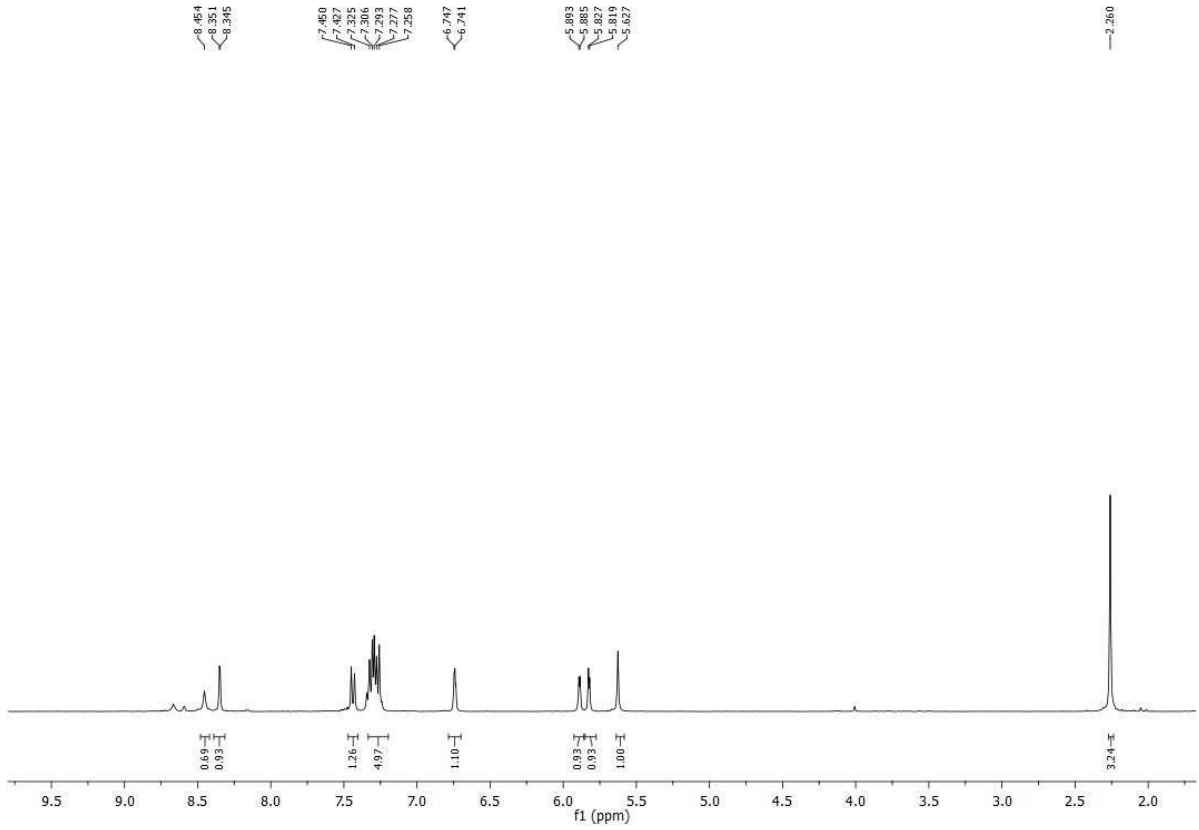


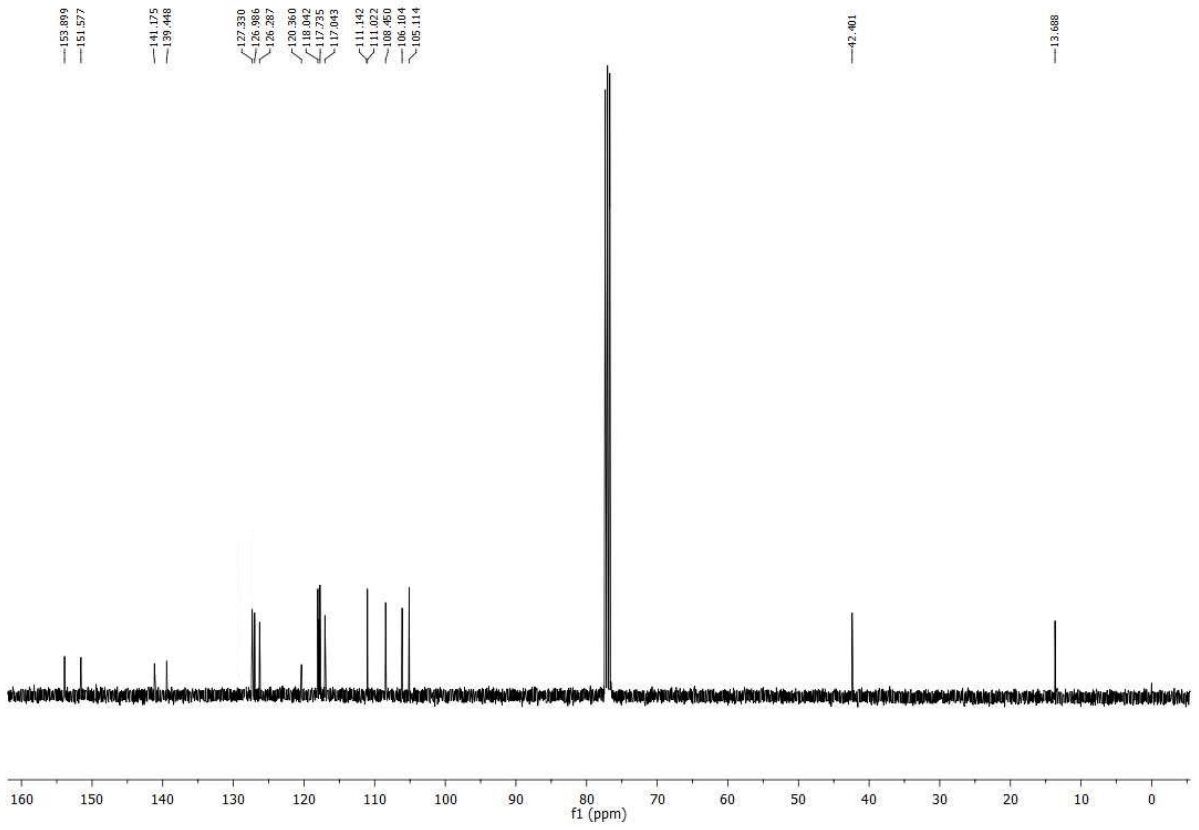


2-Methyl-3-((1-methyl-1*H*-indol-3-yl)(phenyl)methyl)-1*H*-indole (5b)

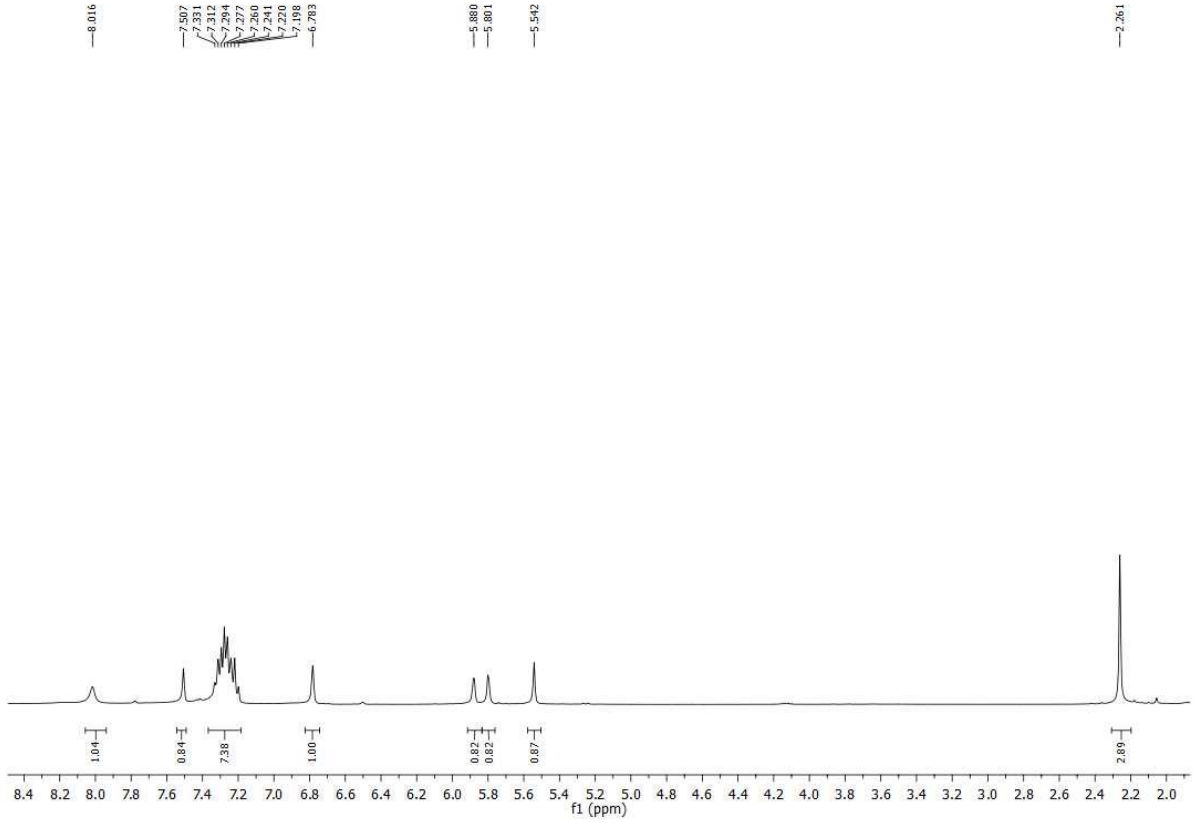


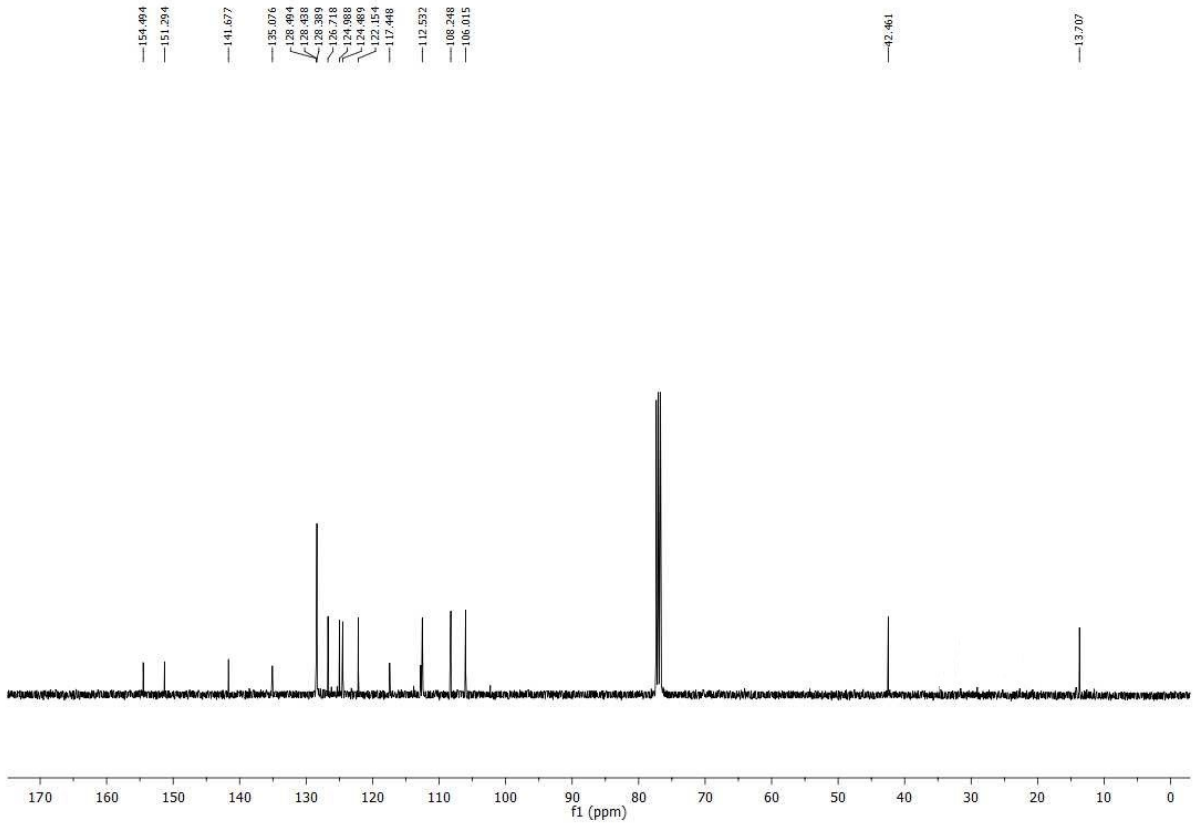
3-((5-methylfuran-2-yl)(phenyl)methyl)-5-nitro-1*H*-indole (5c)



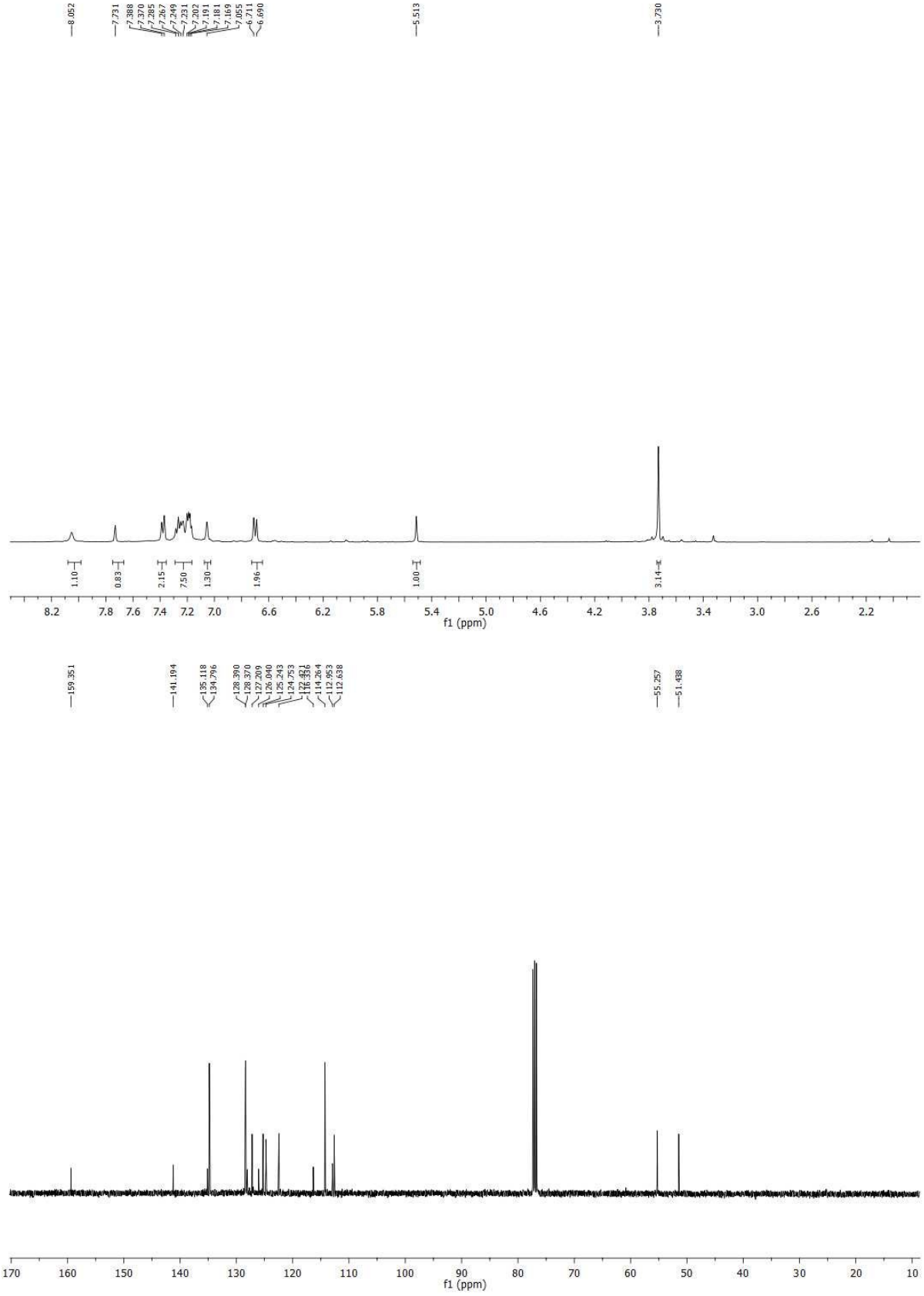


5-bromo-3-((5-methylfuran-2-yl)(phenyl)methyl)-1*H*-indole (5d)

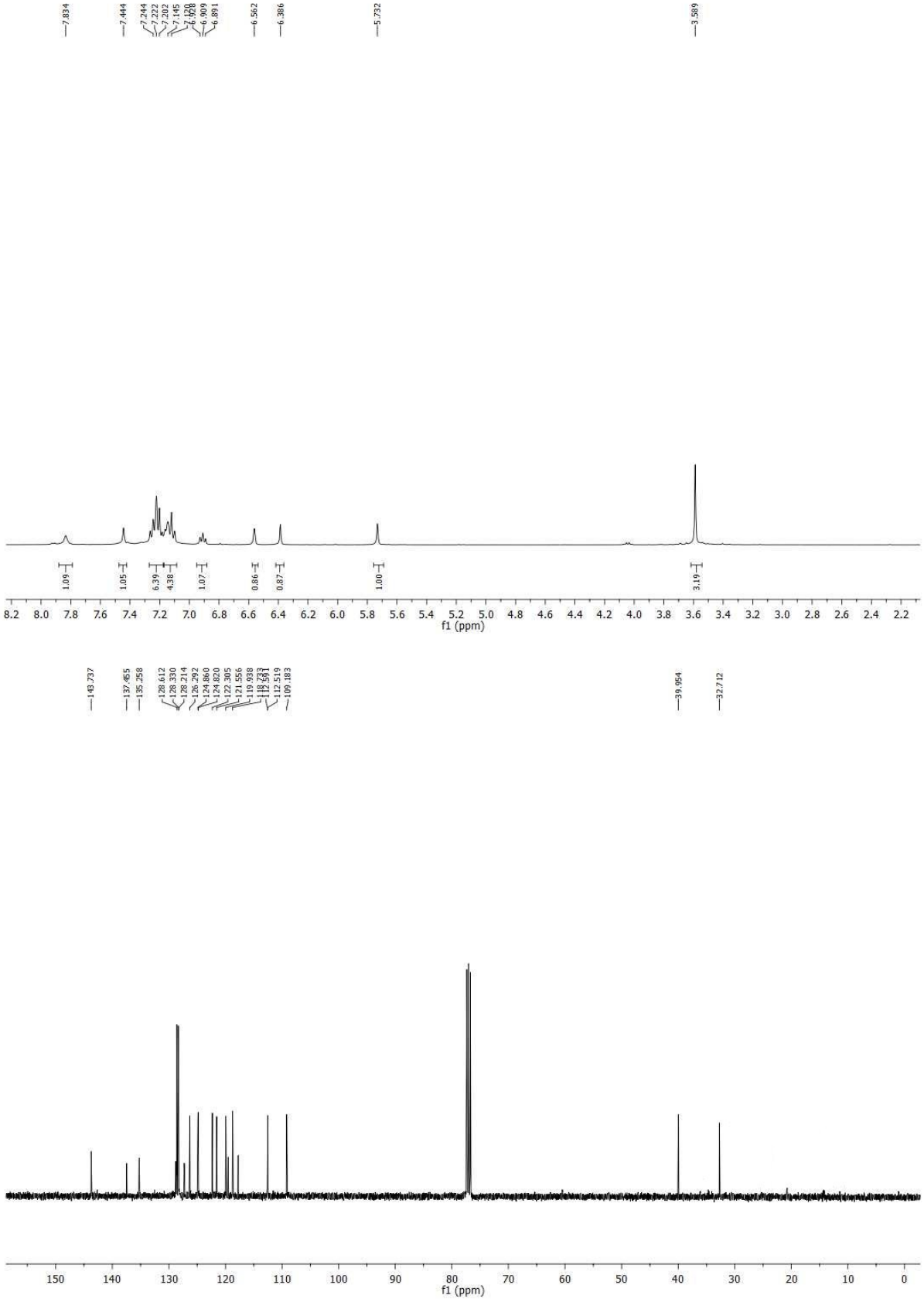




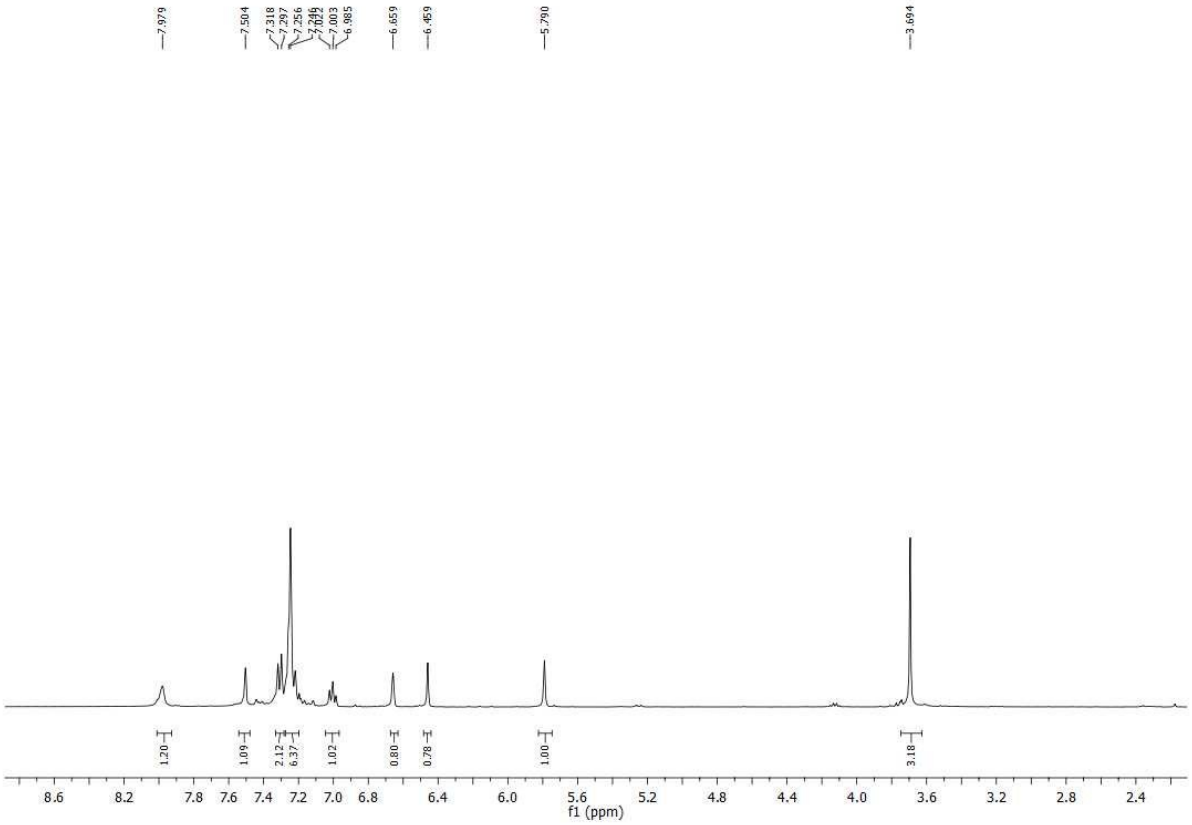
5-bromo-3-(((4-methoxyphenyl)thio)(phenyl)methyl)-1*H*-indole (5e)

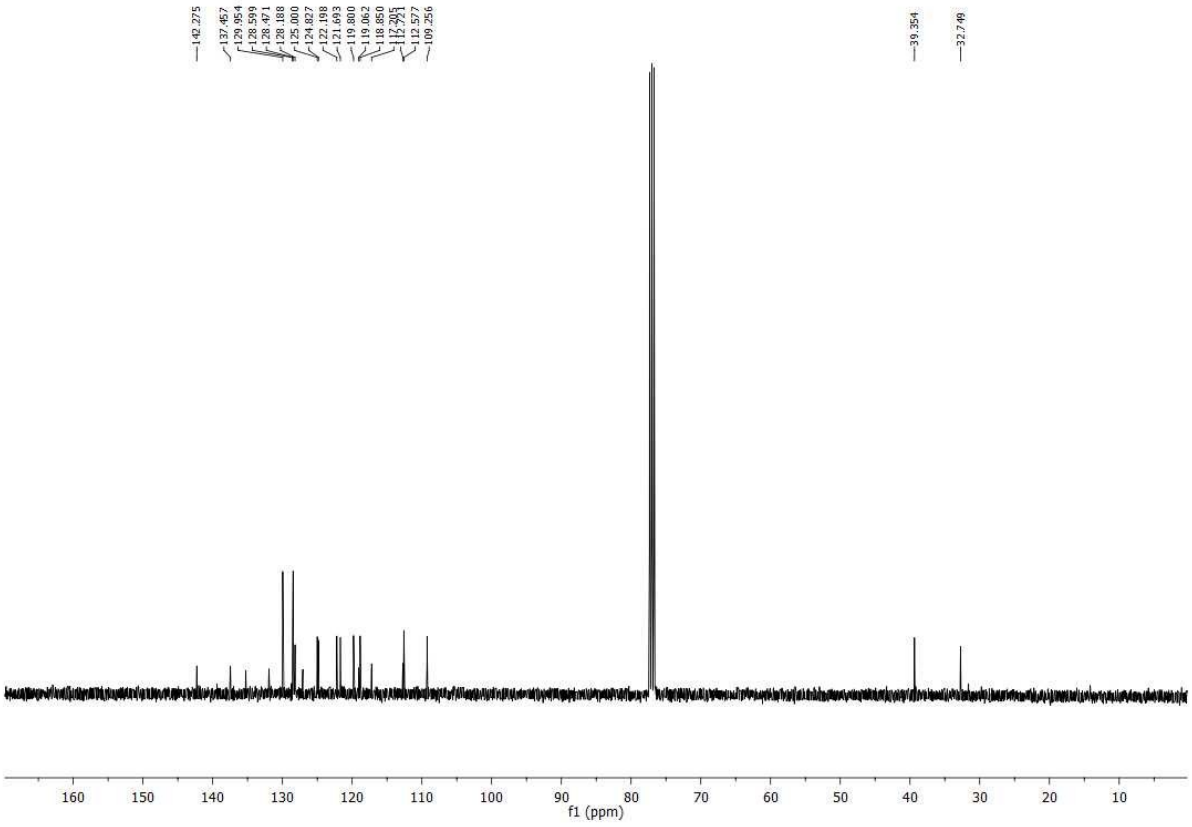


5-bromo-3-((1-methyl-1*H*-indol-3-yl)(phenyl)methyl)-1*H*-indole (5f)



5-bromo-3-((4-chlorophenyl)(1-methyl-1*H*-indol-3-yl)methyl)-1*H*-indole (5g)





5-bromo-3-((1-methyl-1*H*-indol-3-yl)(p-tolyl)methyl)-1*H*-indole (5h)