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Supporting information

$B(C_6F_5)_3$-Catalyzed Markovnikov Addition of Indoles to Aryl Alkynes: An Approach Toward Bis(indolyl)alkanes

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I. General Information

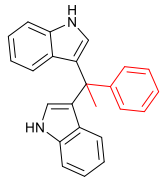
All commercial materials were used as received unless otherwise noted. Commercially available chemicals were obtained from Energy Chemical, TCI, Alfa Aesar, J&K. ^{1}H NMR spectra were recorded at 400 MHz and 600 MHz using TMS as internal standard, ^{13}C NMR spectra were recorded at 100 MHz, 125 MHz and 150 MHz using TMS as internal standard. The multiplicities are reported as follows: singlet (s), doublet (d), doublet of doublets (dd), multiplet (m), triplet (t) and broad resonances (br). Mass spectroscopy data of the products were collected on an HRMS-TOF instrument.

II. General procedure for the synthesis of 3

A mixture of 1*H*-indole (**1a,** 117.0 mg, 1.0 mmol), ethynylbenzene (**2a,** 204.2 mg, 2.0 mmol) and $B(C_6F_5)_3$ (25.6 mg, 0.05 mmol) was heated at 60 ℃ for 6 hours. After the reaction was completed, the residue was purified by chromatography on silica gel (*n*-hexane/EtOAc = 20:1) to obtain product **3a** (142.9 mg, 85 %) as a white solid. **3b–w** were synthesized in a similar way.

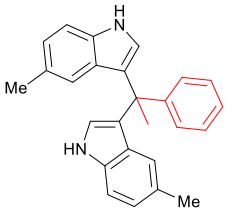
Analytic Data of Products 3

3,3'-(1-Phenylethane-1,1-diyl)bis(1*H*-indole) (3a).



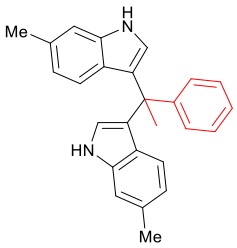
White solid (142.9 mg, 85%; 1.36 g, 81% for 10 mmol scale experiment), Mp 190−192 ℃. **^{1}H NMR** (600 MHz, $CDCl_3$, ppm) δ 7.64 (s, 2H), 7.36 (d, *J* = 7.2 Hz, 2H), 7.29 (d, *J* = 7.8 Hz, 2H), 7.26 (d, *J* = 7.8 Hz, 2H), 7.23−7.19 (m, 2H), 7.18−7.14 (m, 1H), 7.10 (t, *J* = 7.8 Hz, 2H), 6.91 (t, *J* = 7.8 Hz, 2H), 6.50 (d, *J* = 2.4 Hz, 2H), 2.33 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$, ppm) δ 148.0, 137.1, 128.1, 127.8, 126.5, 125.9, 124.7, 123.4, 122.1, 121.6, 119.0, 111.2, 43.8, 28.9. **HRMS** (ESI-TOF) calcd for $C_{24}H_{20}KN_2$ $[M + K]^+$: 375.1258, found: 375.1256. The analytic data were in accordance with ref 1.

3,3'-(1-Phenylethane-1,1-diyl)bis(5-methyl-1*H*-indole) (3b).



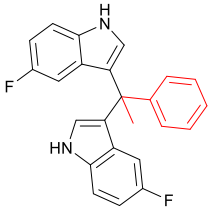
White solid (113.0 mg, 62%), Mp 101−103 ℃. **^{1}H NMR** (600 MHz, $CDCl_3$, ppm) δ 7.69 (s, 2H), 7.41 (d, *J* = 7.8 Hz, 2H), 7.28 (t, *J* = 7.8 Hz, 2H), 7.25−7.20 (m, 3H), 7.16 (s, 2H), 6.99 (d, *J* = 8.4 Hz, 2H), 6.65 (d, *J* = 2.4 Hz, 2H), 2.39 (s, 3H), 2.33 (s, 6H). **^{13}C NMR** (150 MHz, $CDCl_3$, ppm) δ 148.2, 135.5, 128.1, 128.0, 127.8, 126.7, 125.7, 124.3, 123.8, 123.2, 121.8, 110.8, 43.8, 28.6, 21.7. **HRMS** (ESI-TOF) calcd for $C_{26}H_{24}KN_2$ $[M + K]^+$: 403.1571, found: 403.1563.

3,3'-(1-Phenylethane-1,1-diyl)bis(6-methyl-1*H*-indole) (3c).



White solid (149.4 mg, 82%), Mp 177−179 ℃. **^{1}H NMR** (600 MHz, $CDCl_3$, ppm) δ 7.54 (s, 2H), 7.36 (d, *J* = 7.2 Hz, 2H), 7.23−7.13 (m, 5H), 7.05 (s, 2H), 6.75 (d, *J* = 8.4 Hz, 2H), 6.45 (d, *J* = 2.4 Hz, 2H), 2.39 (s, 6H), 2.30 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$, ppm) δ 148.2, 137.6, 131.3, 128.1, 127.8, 125.8, 124.7, 124.4, 122.8, 121.7, 120.7, 111.2, 43.7, 28.8, 21.6. **HRMS** (ESI-TOF) calcd for $C_{26}H_{24}KN_2$ $[M + K]^+$: 403.1571, found: 403.1567.

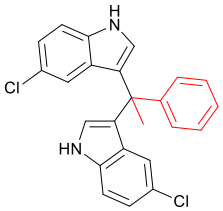
3,3'-(1-Phenylethane-1,1-diyl)bis(5-fluoro-1*H*-indole) (3d).



White solid (135.9 mg, 73%), Mp 139−140 ℃. **^{1}H NMR** (600 MHz, $CDCl_3$, ppm) δ 7.85 (s, 2H), 7.35−7.32 (m, 2H), 2.25 (t, *J* = 7.8 Hz, 2H), 7.23−7.18 (m, 3H), 6.90−6.83 (m, 4H), 6.69 (d, *J* =

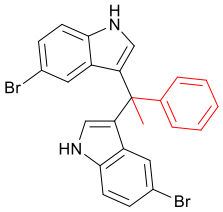
1.8 Hz, 2H), 2.27 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$, ppm) δ 157.1 ($J_{C\text{-}F}$ = 232.2 Hz), 147.2 ($J_{C\text{-}F}$ = 1.4 Hz), 133.6, 128.0, 127.9, 126.7 ($J_{C\text{-}F}$ = 9.8 Hz), 126.1, 124.9 ($J_{C\text{-}F}$ = 1.5 Hz), 124.5 ($J_{C\text{-}F}$ = 4.5 Hz), 111.6 ($J_{C\text{-}F}$ = 7.7 Hz), 110.1 ($J_{C\text{-}F}$ = 26.3 Hz), 106.7 ($J_{C\text{-}F}$ = 23.9 Hz), 43.5, 28.7. **HRMS** (ESI-TOF) calcd for $C_{24}H_{18}F_2KN_2$ $[M + K]^+$: 411.1070, found: 411.1073.

5-Chloro-3-(1-(5-chloro-1H-inden-3-yl)-1-phenylethyl)-1*H*-indole (3e).



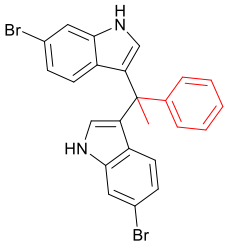
White solid (184.4 mg, 91%), Mp 175−177 ℃. **^{1}H NMR** (600 MHz, $CDCl_3$, ppm) δ 7.92 (s, 2H), 7.34 (d, *J* = 7.8 Hz, 2H), 7.30−7.26 (m, 3H), 7.25−7.21 (m, 4H), 7.09 (dd, *J* = 9.0 Hz, *J* = 1.8 Hz, 2H), 6.66 (d, *J* = 2.4 Hz, 2H), 2.31 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$, ppm) δ 147.1, 135.6, 128.0, 127.9, 127.8, 126.2, 124.7, 124.6, 124.2, 122.1, 121.1, 112.2, 43.5, 28.7. **HRMS** (ESI-TOF) calcd for $C_{24}H_{18}C_{l2}KN_2$ $[M + K]^+$: 443.0479, found: 443.0477.

3,3'-(1-Phenylethane-1,1-diyl)bis(5-bromo-1*H*-indole) (3f).



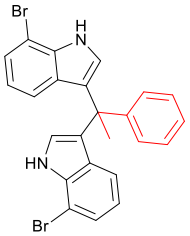
White solid (160.6 mg, 65%), Mp 184−186 ℃. **^{1}H NMR** (600 MHz, DMSO-d_6, ppm) δ 11.10 (s, 2H), 7.33 (d, *J* = 9.0 Hz, 2H), 7.29−7.24 (m, 4H), 7.23−7.17 (m, 1H), 7.13−7.06 (m, 4H), 6.84 (s, 2H), 2.18 (s, 3H). **^{13}C NMR** (150 MHz, DMSO-d_6, ppm) δ 148.0, 136.2, 128.3, 128.2, 128.0, 126.4, 125.6, 123.6, 123.2, 122.6, 114.2, 111.1, 43.4, 29.8. **HRMS** (ESI-TOF) calcd for $C_{24}H_{18}Br_2KN_2$ $[M + K]^+$: 530.9468, found: 530.9480. The analytic data were in accordance with ref 2.

3,3'-(1-Phenylethane-1,1-diyl)bis(6-bromo-1*H*-indole) (3g).



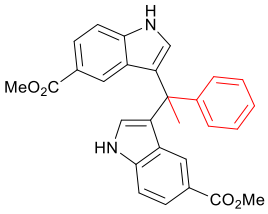
White solid (175.5 mg, 71%), Mp 181−182 ℃. **^{1}H NMR** (600 MHz, $CDCl_3$, ppm) δ 7.89 (s, 2H), 7.48 (s, 2H), 7.33 (d, *J* = 7.8 Hz, 2H), 7.26−7.23 (m, 2H), 7.22−7.18 (m, 1H), 7.10 (d, *J* = 8.4 Hz, 2H), 7.00 (d, *J* = 8.4 Hz, 2H), 6.63 (s, 2H), 2.29 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$, ppm) δ 147.3, 137.9, 128.0, 127.9, 126.2, 125.3, 124.7, 123.7, 123.1, 122.4, 115.4, 114.1, 43.5, 28.9. **HRMS** (ESI-TOF) calcd for $C_{24}H_{18}Br_2KN_2$ $[M + K]^+$: 530.9468, found: 530.9472.

7-Bromo-3-(1-(7-bromo-1*H*-indol-2-yl)-1-phenylethyl)-1*H*-indole (3h).



White solid (160.6 mg, 65%), Mp 168−170 ℃. **^{1}H NMR** (600 MHz, $CDCl_3$, ppm) δ 8.05 (s, 2H), 7.34 (d, *J* = 7.2 Hz, 2H), 7.28 (d, *J* = 7.2 Hz, 2H), 7.26−7.23 (m, 2H), 7.22−7.18 (m, 3H), 6.80 (t, *J* = 7.8 Hz, 2H), 6.67 (d, *J* = 1.8 Hz, 2H), 2.32 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$, ppm) δ 147.3, 135.7, 127.9, 127.9, 127.6, 126.2, 125.7, 124.1, 123.8, 121.2, 120.3, 104.8, 44.0, 28.9. **HRMS** (ESI-TOF) calcd for $C_{24}H_{18}Br_2KN_2$ $[M + K]^+$: 530.9468, found: 530.9475.

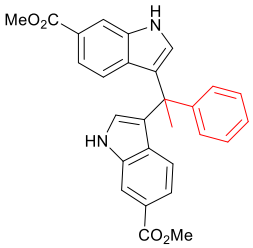
Dimethyl 3,3'-(1-phenylethane-1,1-diyl)bis(1*H*-indole-5-carboxylate) (3i).



White solid (142.6 mg, 63%), Mp 190−192 ℃. **^{1}H NMR** (600 MHz, DMSO-d_6, ppm) δ 11.31 (s, 2H), 7.83 (s, 2H), 7.67 (d, *J* = 8.4 Hz, 2H), 7.46 (d, *J* = 8.4 Hz, 2H), 7.31 (d, *J* = 7.8 Hz, 2H), 7.26

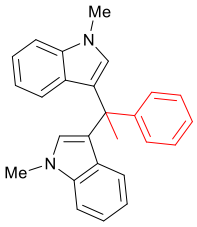
(t, *J* = 7.2 Hz, 2H), 7.19 (t, *J* = 7.2 Hz, 1H), 6.86 (d, *J* = 1.8 Hz, 2H), 3.71 (s, 6H), 2.28 (s, 3H). **^{13}C NMR** (150 MHz, DMSO-d_6) δ 167.6, 148.1, 140.2, 128.3, 128.0, 126.5, 126.0, 125.8, 124.5, 124.0, 122.2, 120.1, 112.2, 52.0, 43.6, 29.9. **HRMS** (ESI-TOF) calcd for $C_{28}H_{24}KN_2O_4$ $[M + K]^+$: 491.1368, found: 491.1374.

Dimethyl 3,3'-(1-phenylethane-1,1-diyl)bis(1*H*-indole-6-carboxylate) (3j)



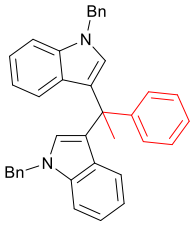
White solid (196.6 mg, 87%), Mp 253−254 ℃. **^{1}H NMR** (400 MHz, DMSO-d_6, ppm) δ 11.30 (s, 2H), 8.05 (s, 2H), 7.39 (d, *J* = 8.4 Hz, 2H), 7.35–7.22 (m, 4H), 7.21–7.15 (m, 1H), 7.10 (d, *J* = 8.4 Hz, 2H), 7.01 (d, *J* = 1.6 Hz ,2H), 3.81 (s, 6H), 2.27 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$, ppm) δ 167.6, 148.1, 136.8, 129.9, 128.3, 128.0, 127.9, 126.3, 123.6, 122.1, 1210, 119.2, 114.2, 52.2, 43.5, 29.7. **HRMS** (ESI-TOF) calcd for $C_{28}H_{24}KN_2O_4$ $[M + K]^+$: 491.1368, found: 491.1372.

3,3'-(1-Phenylethane-1,1-diyl)bis(1-methyl-1*H*-indole) (3k).



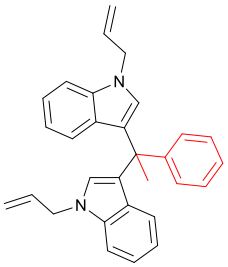
White solid (76.5 mg, 42%), Mp 196−197 ℃. **^{1}H NMR** (600 MHz, $CDCl_3$, ppm) δ 7.46 (d, *J* = 7.2 Hz, 2H), 7.37 (d, *J* = 8.4 Hz, 2H), 7.33 (d, *J* = 8.4 Hz, 2H), 7.30 (t, *J* = 7.8 Hz, 2H), 7.26−7.18 (m, 3H), 6.98 (t, *J* = 7.8 Hz, 2H), 6.54 (s, 2H), 3.70 (s, 6H), 2.41 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$, ppm) δ 148.4, 137.8, 128.1, 128.1, 127.8, 126.9, 125.7, 123.4, 122.2, 121.1, 118.4, 109.2, 43.7, 32.7, 29.2. **HRMS** (ESI-TOF) calcd for $C_{26}H_{24}KN_2$ $[M + K]^+$: 403.1571, found: 403.1582. The analytic data were in accordance with ref 3.

3,3'-(1-Phenylethane-1,1-diyl)bis(1-benzyl-1*H*-indole) (3l).



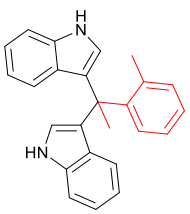
White solid (142.3 mg, 55%), Mp 143−144 ℃. **^{1}H NMR** (600 MHz, $CDCl_3$, ppm) δ 7.57 (d, *J* = 7.2 Hz, 2H), 7.34 (d, *J* = 7.8 Hz, 2H), 7.30−7.26 (m, 6H), 7.26−7.21 (m, 5H), 7.09 (t, *J* = 7.2 Hz, 2H), 7.06 (d, *J* = 7.2 Hz, 4H), 6.91 (t, *J* = 7.6 Hz, 2H), 6.71 (s, 2H), 5.25 (s, 4H), 2.40 (s, 3H).**^{13}C NMR** (150 MHz, $CDCl_3$, ppm) δ 148.1, 137.9, 137.4, 128.7, 128.1, 127.8, 127.7, 127.4, 127.2, 126.5, 125.8, 123.8, 122.3, 121.3, 118.6, 109.8, 49.9, 43.8, 29.3. **HRMS** (ESI-TOF) calcd for $C_{38}H_{32}KN_2$ $[M + K]^+$: 555.2197, found: 555.2191. The analytic data were in accordance with ref 4.

3,3'-(1-Phenylethane-1,1-diyl)bis(1-allyl-1*H*-indole) (3m).



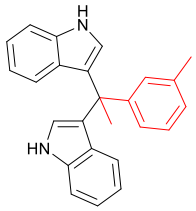
White solid (127.0 mg, 61%), Mp 52−54 ℃. **^{1}H NMR** (600 MHz, $CDCl_3$, ppm) δ 7.52 (d, *J* = 7.8 Hz, 2H), 7.42 (d, *J* = 7.8 Hz, 2H), 7.39−3.33 (m, 4H), 7.29 (t, *J* = 7.2 Hz, 1H), 7.23 (t, *J* = 7.8 Hz, 2H), 7.01 (t, *J* = 7.8 Hz, 2H), 6.68 (s, 2H), 6.10−5.95 (m, 2H), 5.22 (d, *J* = 10.2 Hz, 2H), 5.07 (d, *J* = 17.4 Hz, 2H), 4.69 (d, *J* = 4.8 Hz, 4H), 2.48 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$, ppm) δ 148.3, 137.3, 133.9, 128.2, 127.9, 127.4, 127.2, 125.9, 123.7, 122.4, 121.2, 118.6, 116.9, 109.7, 48.7, 43.9, 29.3. **HRMS** (ESI-TOF) calcd for $C_{30}H_{28}KN_2$ $[M + K]^+$: 455.1884, found: 455.1877.

3,3'-(1-(o-Tolyl)ethane-1,1-diyl)bis(1*H*-indole) (3n).



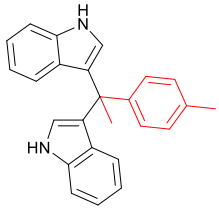
White solid (136.6 mg, 78%), Mp 168−170 ℃. **^{1}H NMR** (600 MHz, $CDCl_3$, ppm) δ 7.77 (s, 2H), 7.55 (d, *J* = 6.6 Hz, 1H), 7.42−7.31 (m, 4H), 7.24−7.13 (m, 4H), 7.07 (d, *J* = 5.4 Hz, 1H), 6.60 (s, 2H), 7.00 (t, *J* = 7.2 Hz, 2H), 2.44 (s, 3H), 1.97 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$, ppm) δ 145.5, 138.1, 137.1, 132.6, 128.4, 126.5, 126.4, 125.6, 124.1, 123.4, 122.1, 121.5, 119.0, 111.2, 44.4, 28.9, 22.5. **HRMS** (ESI-TOF) calcd for $C_{25}H_{22}KN_2$ $[M + K]^+$: 389.1415, found: 389.1423.

3,3'-(1-(*m*-Tolyl)ethane-1,1-diyl)bis(1*H*-indole) (3o).



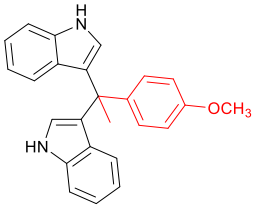
White solid (122.6 mg, 70%), Mp 160−162 ℃. **^{1}H NMR** (600 MHz, $CDCl_3$, ppm) δ 7.81 (s, 2H), 7.36−7.72 (m, 4H), 7.25 (s, 1H), 7.18 (d, *J* = 7.8 Hz, 1H), 7.16−7.12 (m, 3H), 7.02 (d, *J* = 7.8 Hz, 1H), 6.95 (t, *J* = 7.8 Hz , 2H), 6.61 (d, *J* =1.8 Hz, 2H), 2.36 (s, 3H), 2.28 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$, ppm) δ 147.9, 137.1, 137.0, 128.6, 127.6, 126.6, 126.6, 125.3, 124.8, 123.4, 122.1, 121.5, 118.9, 111.1, 43.6, 28.7, 21.7. **HRMS** (ESI-TOF) calcd for $C_{25}H_{22}KN_2$ $[M + K]^+$: 389.1415, found: 389.1424. The analytic data were in accordance with ref 5.

3,3'-(1-(*p*-Tolyl)ethane-1,1-diyl)bis(1*H*-indole) (3p).



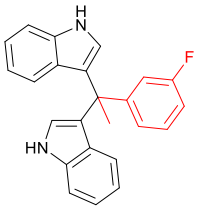
White solid (134.6 mg, 77%), Mp 190−192 ℃. **^{1}H NMR** (600 MHz, $CDCl_3$, ppm) δ 7.74 (s, 2H), 7.36 (d, *J* = 8.4 Hz, 2H), 7.33 (d, *J* = 7.8 Hz, 2H), 7.30 (d, *J* = 8.4 Hz, 2H), 7.16 (dt, *J* = 7.8 Hz, *J* = 0.6 Hz, 2H), 7.07 (d, *J* = 7.8 Hz, 2H), 6.96 (dt, *J* = 7.8 Hz, *J* = 0.6 Hz, 2H), 6.65−6.57 (m, 2H), 2.36 (s, 3H), 2.34 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$, ppm) δ 145.1, 137.1, 135.2, 128.5, 128.0, 126.5, 124.9, 123.4, 122.2, 121.5, 118.91, 111.2, 43.4, 28.8, 21.0. **HRMS** (ESI-TOF) calcd for $C_{25}H_{22}KN_2$ $[M + K]^+$: 389.1415, found: 389.1426. The analytic data were in accordance with ref1.

3,3'-(1-(4-Methoxyphenyl)ethane-1,1-diyl)bis(1*H*-indole) (3q).



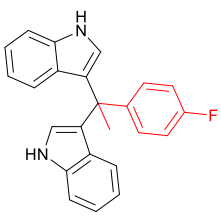
White solid (162.9 mg, 89%), Mp 119−121 ℃. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.82 (s, 2H), 7.37−7.33 (m, 4H), 7.30 (d, *J* = 9.0 Hz, 2H), 7.14 (t, *J* = 7.8 Hz, 2H), 6.95 (t, *J* = 7.8 Hz, 2H), 6.79 (d, *J* = 8.4 Hz, 2H), 6.60 (s, 2H), 3.78 (s, 3H), 2.34 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$, ppm) δ 157.5, 140.4, 137.1, 129.1, 126.5, 125.0, 123.3, 122.1, 121.5, 118.9, 113.1, 111.2, 55.2, 43.1, 28.9. **HRMS** (ESI-TOF) calcd for $C_{25}H_{22}KN_2O$ $[M + K]^+$: 405.1364, found: 405.1369. The analytic data were in accordance with ref 6.

3,3'-(1-(3-Fluorophenyl)ethane-1,1-diyl)bis(1*H*-indole) (3r).



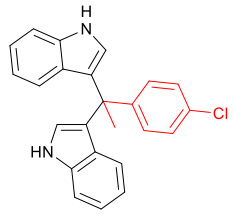
White solid (136.4 mg, 77%), Mp 145−147 ℃. **^{1}H NMR** (600 MHz, $CDCl_3$, ppm) δ 7.78 (s, 2H), 7.35 (d, *J* = 8.4 Hz, 4H), 7.23−7.16 (m, 4H), 7.14−7.11 (m, 1H), 6.98 (t, *J* = 8.4 Hz 2H), 6.94−6.89 (m, 1H), 6.59 (d, *J* = 2.4 Hz, 2H), 2.36 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$, ppm) δ 162.3 ($J_{C\text{-}F}$ = 242.4 Hz), 151.0 ($J_{C\text{-}F}$ = 6.3 Hz), 137.1, 129.1 (d, $J_{C\text{-}F}$ =8.1 Hz), 126.3, 124.1, 123.8 ($J_{C\text{-}F}$ = 2.4 Hz), 123.4, 122.0, 121.7, 119.1, 115.2 ($J_{C\text{-}F}$ = 21.8 Hz), 112.8($J_{C\text{-}F}$ = 21.0 Hz), 111.3, 43.8, 28.7. **HRMS** (ESI-TOF) calcd for $C_{24}H_{19}FKN_2$ $[M + K]^+$: 393.1164, found: 393.1156.

3,3'-(1-(4-Fluorophenyl)ethane-1,1-diyl)bis(1*H*-indole) (3s).



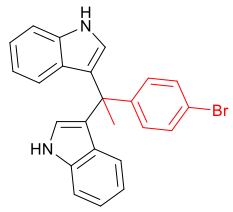
White solid (120.4 mg, 68%), Mp 110−112 ℃. **^{1}H NMR** (600 MHz, $CDCl_3$, ppm) δ 7.85 (s, 2H), 7.37−7.34 (m, 4H), 7.32 (d, *J* = 8.4 Hz, 2H), 7.16 (t, *J* = 7.8 Hz, 2H), 6.6 (t, *J* = 7.8 Hz, 2H), 6.93 (t, *J* = 8.4 Hz, 2H), 6.61 (d, *J* = 2.4 Hz, 2H), 2.35 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$, ppm) δ 161.1 ($J_{C\text{-}F}$ = 242.6 Hz), 160.33, 143.8 ($J_{C\text{-}F}$ = 3.2 Hz), 137.1, 129.6 ($J_{C\text{-}F}$ =7.6 Hz), 126.3, 124.6, 123.3, 122.0, 121.7, 119.1, 114.5 ($J_{C\text{-}F}$ = 20.9 Hz), 111.2, 43.3, 28.9. **HRMS** (ESI-TOF) calcd for $C_{24}H_{19}FKN_2$ $[M + K]^+$: 393.1164, found: 393.1159. The analytic data were in accordance with ref 1.

3,3'-(1-(4-Chlorophenyl)ethane-1,1-diyl)bis(1*H*-indole) (3t).



White solid (150.0 mg, 81%), Mp 175−172 ℃. **^{1}H NMR** (600 MHz, $CDCl_3$, ppm) δ 7.84 (s, 2H), 7.36−7.30 (m, 6H), 7.21 (d, *J* = 8.4 Hz, 2H), 7.16 (t, *J* =7.8 Hz, 2H), 6.97 (t, *J* =7.8 Hz, 2H), 6.62 (d, *J* = 2.4 Hz, 2H), 2.34 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$, ppm) δ 146.6, 137.1, 131.6, 129.6, 127.9, 126.2, 124.2, 123.3, 121.9, 121.7, 119.1, 111.3, 43.5, 28.8. **HRMS** (ESI-TOF) calcd for $C_{24}H_{19}ClKN_2$ $[M + K]^+$: 409.0868, found: 409.0874. The analytic data were in accordance with ref 1.

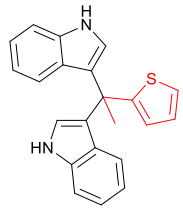
3,3'-(1-(4-Bromophenyl)ethane-1,1-diyl)bis(1*H*-indole) (3u).



White solid (130.8 mg, 63%), Mp 150−151 ℃. **^{1}H NMR** (600 MHz, $CDCl_3$, ppm) δ 7.81 (s, 2H), 7.36 (d, *J* = 8.4 Hz, 2H), 7.34 (d, *J* = 8.4 Hz, 2H), 7.32 (d, *J* = 8.4 Hz, 2H), 7.28 (d, *J* = 9.0 Hz, 2H), 7.17 (t, *J* = 7.8 Hz, 2H), 6.98 (t, *J* = 7.8 Hz, 2H), 6.60 (d, *J* = 2.4 Hz, 2H), 2.34 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$, ppm) δ 147.2, 137.1, 130.9, 130.0, 126.2, 124.1, 123.4, 122.0, 121.7,

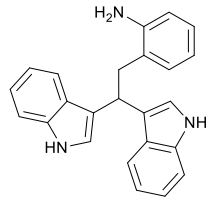
119.8, 119.1, 111.3, 43.5, 28.7. **HRMS** (ESI-TOF) calcd for $C_{24}H_{19}BrKN_2$ $[M + K]^+$: 453.0363, found: 453.0369. The analytic data were in accordance with ref 1.

3,3'-(1-(Thiophen-2-yl)ethane-1,1-diyl)bis(1*H*-indole) (3v).



White solid (149.0 mg, 87%), Mp 111−113 ℃. **^{1}H NMR** (600 MHz, $CDCl_3$, ppm) δ 7.80 (s, 2H), 7.41 (d, *J* = 7.8 Hz, 2H), 7.34 (d, *J* = 7.8 Hz, 2H), 7.18−7.14 (m, 3H), 6.99−6.95 (m, 2H), 6.94−6.90 (m, 2H), 6.72 (d, *J* = 2.4 Hz, 2H), 2.43 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$, ppm) δ 154.5, 137.1, 126.1, 126.0, 125.0, 124.6, 123.6, 123.1, 121.9, 121.6, 119.1, 111.3, 41.9, 30.3. **HRMS** (ESI-TOF) calcd for $C_{22}H_{18}KN_2S$ $[M + K]^+$: 381.0822, found: 381.0835. The analytic data were in accordance with ref 7.

2-(2-(1*H*-indol-3-yl)-2-phenylethyl)aniline (5a)



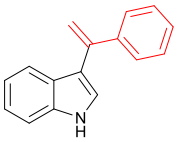
White solid, Mp 168−169 ℃. **^{1}H NMR** (600 MHz, $CDCl_3$, ppm) δ 7.73 (s, 2H), 7.45 (d, *J* = 8.4 Hz, 2H), 7.25–7.20 (m, 2H), 7.13–7.07 (m, 2H), 6.99–6.91 (m, 4H), 6.83 (d, *J* = 2.4 Hz, 2H), 6.60 (td, *J* = 7.2, 1.2 Hz, 1H), 6.51 (dd, *J* = 8.4, 0.6 Hz, 1H), 4.81 (t, *J* = 7.8 Hz, 1H), 3.36 (d, *J* = 7.3 Hz, 2H), 3.12 (s, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$, ppm) δ 144.7, 136.6, 130.4, 126.9, 126.0, 121.9, 121.8, 119.6, 119.5, 119.1, 118.8, 115.8, 111.2, 37.1, 34.4. **HRMS** (ESI-TOF) calcd for $C_{24}H_{21}KN_3$ $[M + K]^+$: 390.1367, found: 390.1361. The analytic data were in accordance with ref 8.

III. Typical procedure for the Preparation of 4a

4a was prepared according the according the literature.[9] 1) A mixture of 3-acetylindole (10 mml, 1.6 g) and dry THF (40 mL) at 0 ℃ was added PhMgBr (25 mmol, 1.0 M solution in THF, 2.5 equiv.) dropwise. The reaction mixture was warmed to 50 ℃ and stirred at the same temperature overnight. Upon completion, the reaction mixture was cooled to 0 ℃. A saturated aqueous NH_4Cl solution (40 mL) was added dropwise. The organic layer was separated. The aqueous layer was extracted with Et_2O (3 × 50 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated. 2) The residue was dissolved in CH_2Cl_2 (50 mL), to which was added anhydrous $MgSO_4$ (5.0 g) followed by silica gel (200-300 mesh particle size, 5.0 g). The mixture was then stirred at room temperature, and the reaction progress was monitored by thin layer chromatography. Upon completion, the reaction mixture was filtered and washed with Et_2O. The filtrate was concentrated and the residue was purified by silica gel chromatography. to obtain product **4a** (1.40 g, 65%) as a brown solid

Analytic Data of Products 4a

3-(1-Phenylvinyl)-1*H*-indole (4a).



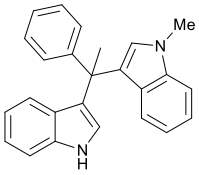
^{1}H NMR (600 MHz, DMSO-d_6, ppm) δ 11.28 (s, 1H), 7.45−7.39 (m, 3H), 7.39−7.33 (m, 3H), 7.30 (d, *J* = 7.8 Hz, 1H), 7.26 (d, *J* = 2.4 Hz, 1H), 7.11 (t, *J* = 7.8 Hz, 1H), 6.96 (t, *J* = 7.8 Hz, 1H), 5.51 (d, *J* = 1.2 Hz, 1H), 5.31 (d, J = 1.8 Hz, 1H).

IV. Typical procedure for the Preparation of 3x

A mixture of 1-methyl-1*H*-indole (**1j,** 65.6 mg, 0.5 mmol), 3-(1-phenylvinyl)-1*H*-indole (**4a,** 109.6 mg, 0.5 mmol), and $B(C_6F_5)_3$ (12.8 mg, 0.025 mmol) in toluene (2 mL) were heated at 60 ℃ for 30 min. After the reaction was completed, the solvent was removed under vacuum, and the residue was purified by chromatography on silica gel (*n*-hexane/EtOAc = 20:1) to obtain product **3x** (132.9 mg, 87%) as a white solid.

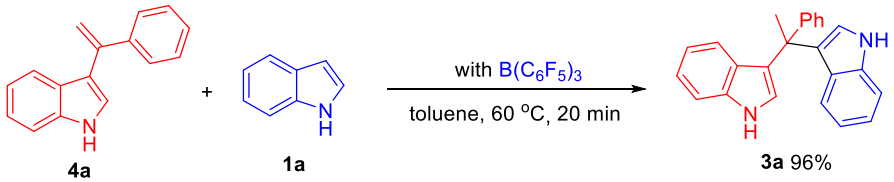
Analytic Data of Products 3x

3-(1-(1*H*-Indol-3-yl)-1-phenylethyl)-1-methyl-1*H*-indole (3x).

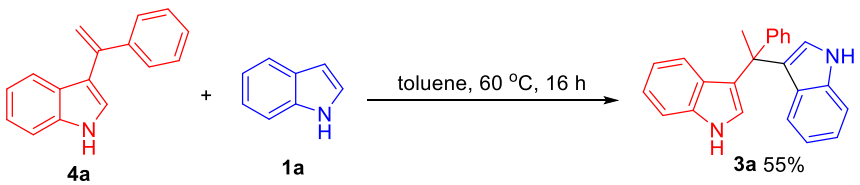


White solid (132.9 mg, 87%), Mp 186−187 ℃. **^{1}H NMR** (600 MHz, $CDCl_3$, ppm) δ 7.70 (s, 1H), 7.49 (d, *J* = 7.8 Hz, 2H), 7.44−7.39 (m, 2H), 7.39−7.35 (m, 2H), 7.33 (t, *J* = 7.8 Hz, 2H), 7.30−7.25 (m, 2H), 7.22 (t, *J* = 7.8 Hz, 1H), 7.03 (t, *J* = 7.8 Hz, 2H), 6.63 (d, *J* = 2.4 Hz, 1H), 6.54 (s, 1H), 3.69 (s, 3H), 2.45 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 148.3, 137.9, 137.1, 128.2, 127.9, 126.9, 126.5, 125.9, 124.8, 123.5, 123.4, 122.3, 122.1, 121.6, 121.2, 119.0, 118.5, 111.2, 109.3, 43.8, 32.6, 29.0. **HRMS** (ESI-TOF) calcd for $C_{25}H_{22}KN_2$ $[M + K]^+$: 389.1415, found: 389.1421.

V. Control experiments



A mixture of **4a** (109.6 mg, 0.5 mmol), **1a** (58.5 mg, 0.5 mol), and $B(C_6F_5)_3$ (12.8 mg, 0.025 mmol) in toluene (2 mL) were heated at 60 ℃ for 20 min. After the reaction was completed, the solvent was removed under vacuum, and the residue was purified by chromatography on silica gel (*n*-hexane/EtOAc = 20:1) to obtain product **3a** (161.5 mg, 96%) as a white solid.



A mixture of **4a** (109.6 mg, 0.5 mmol) and **1a** (58.5 mg, 0.5 mol) in toluene (2 mL) were heated at 60 ℃ for 16 h. Then, the solvent was removed under vacuum, and the residue was purified by chromatography on silica gel (*n*-hexane/EtOAc = 20:1) to obtain product **3a** (92.5 mg, 55%) as a white solid.

VI. References

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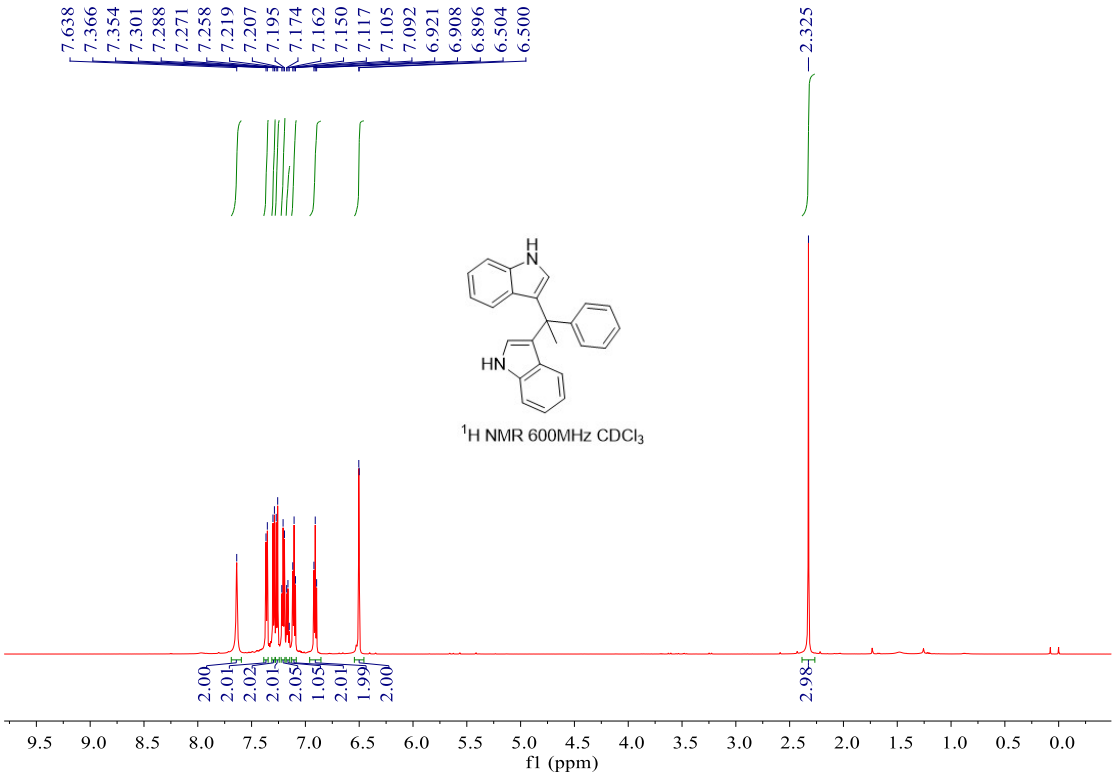
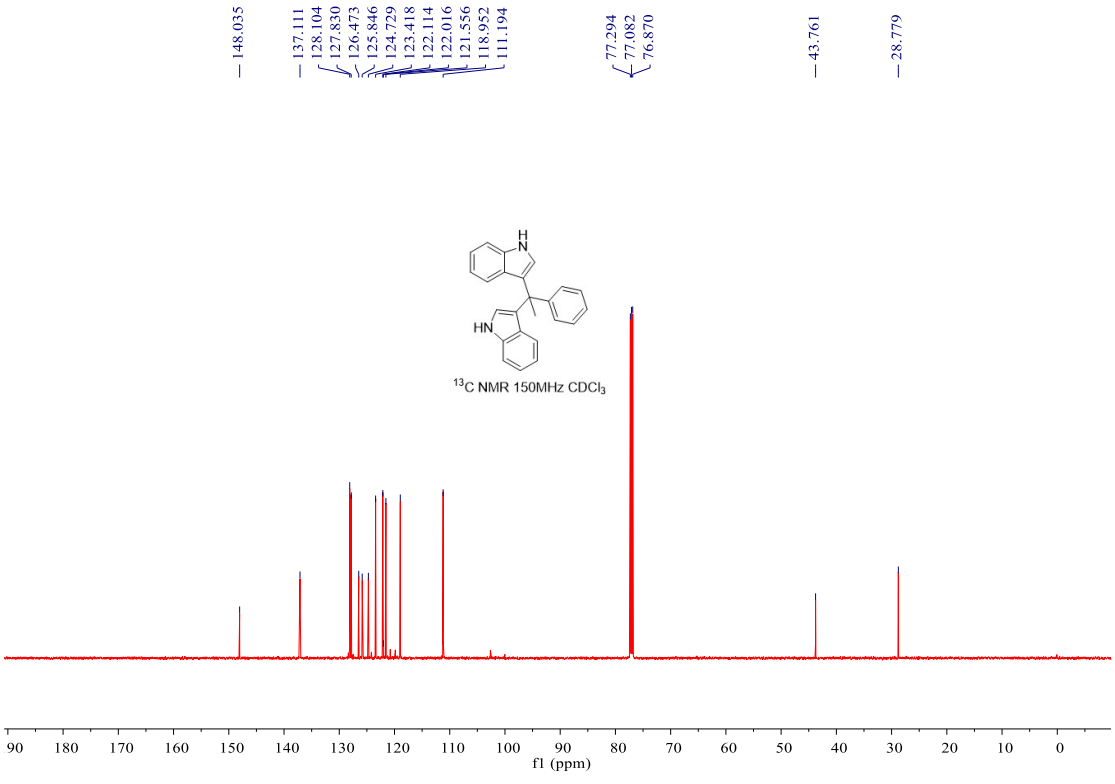
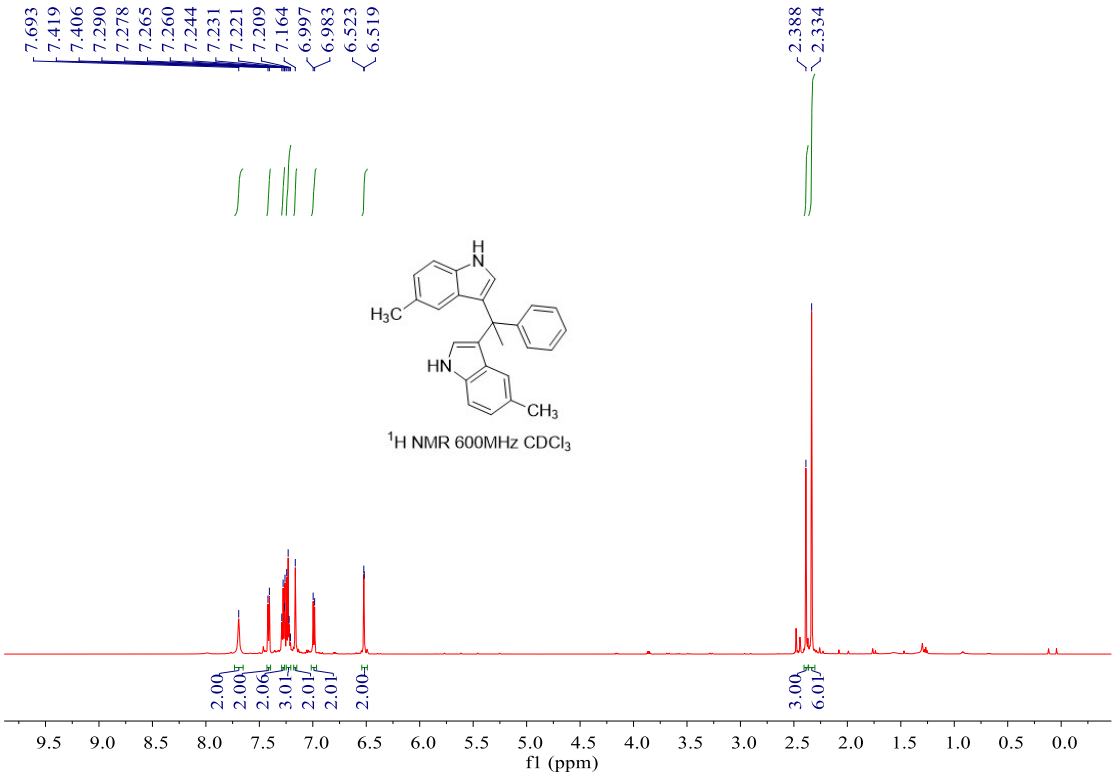
VII. Copies of ^{1}H and ^{13}C NMR Spectra

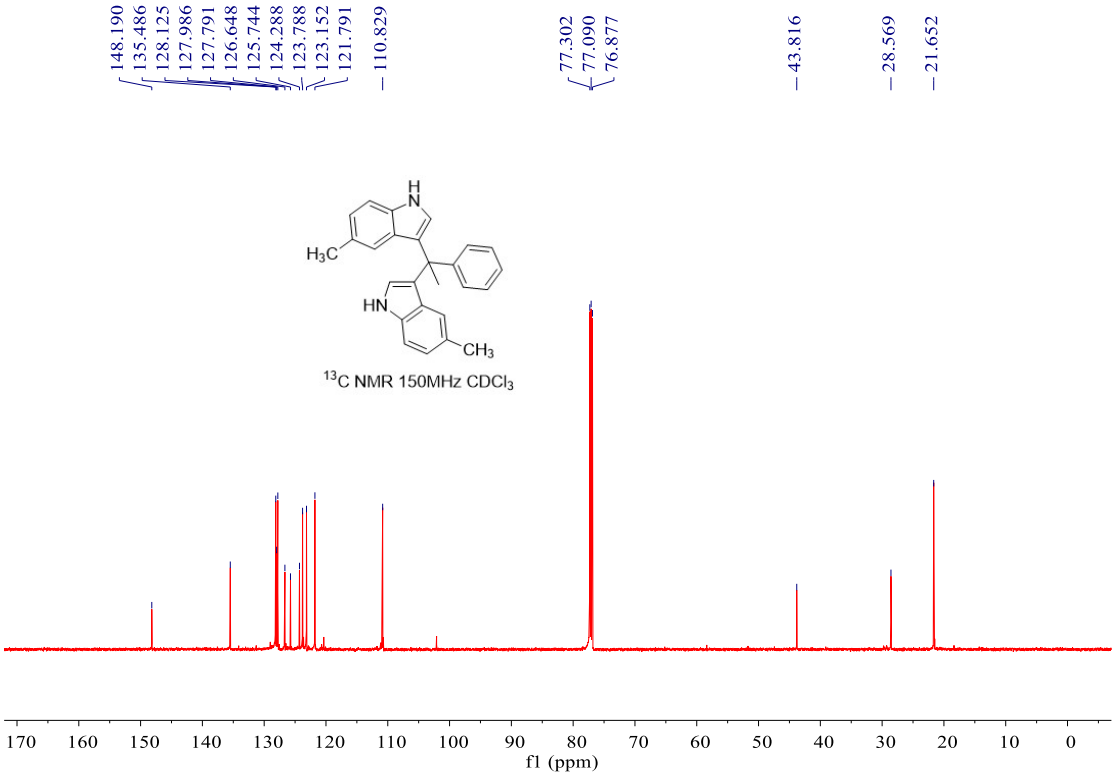
3,3'-(1-Phenylethane-1,1-diyl)bis(1*H*-indole) (3a)



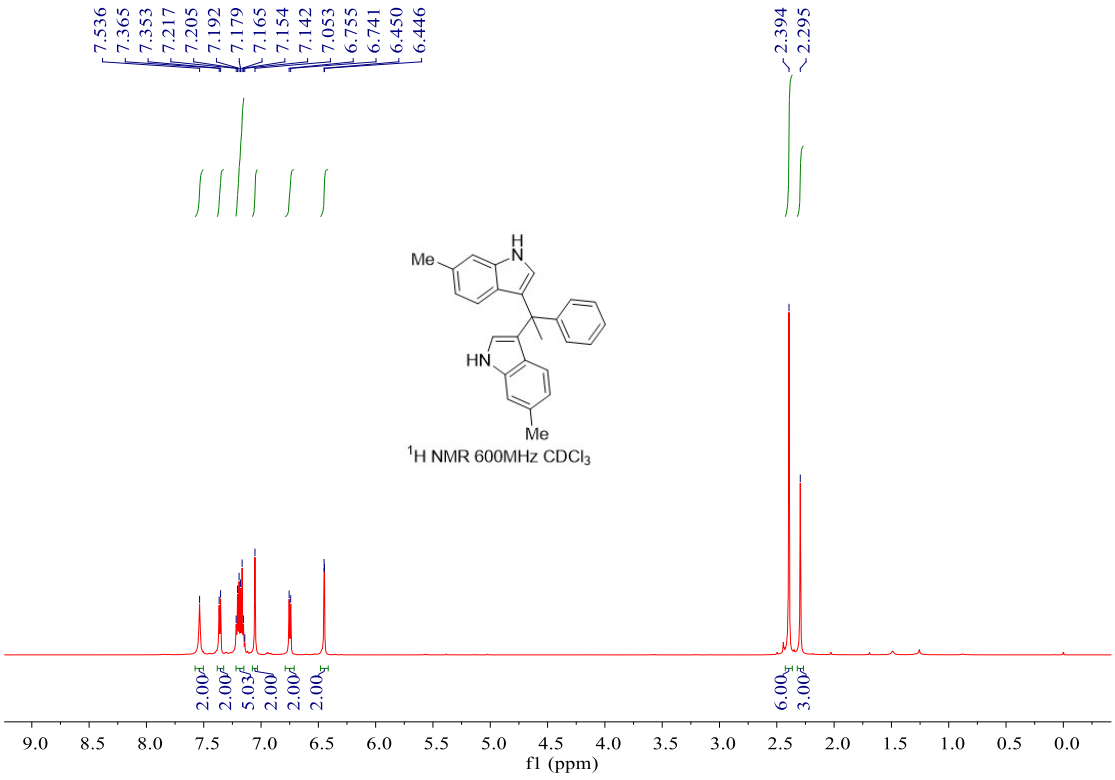


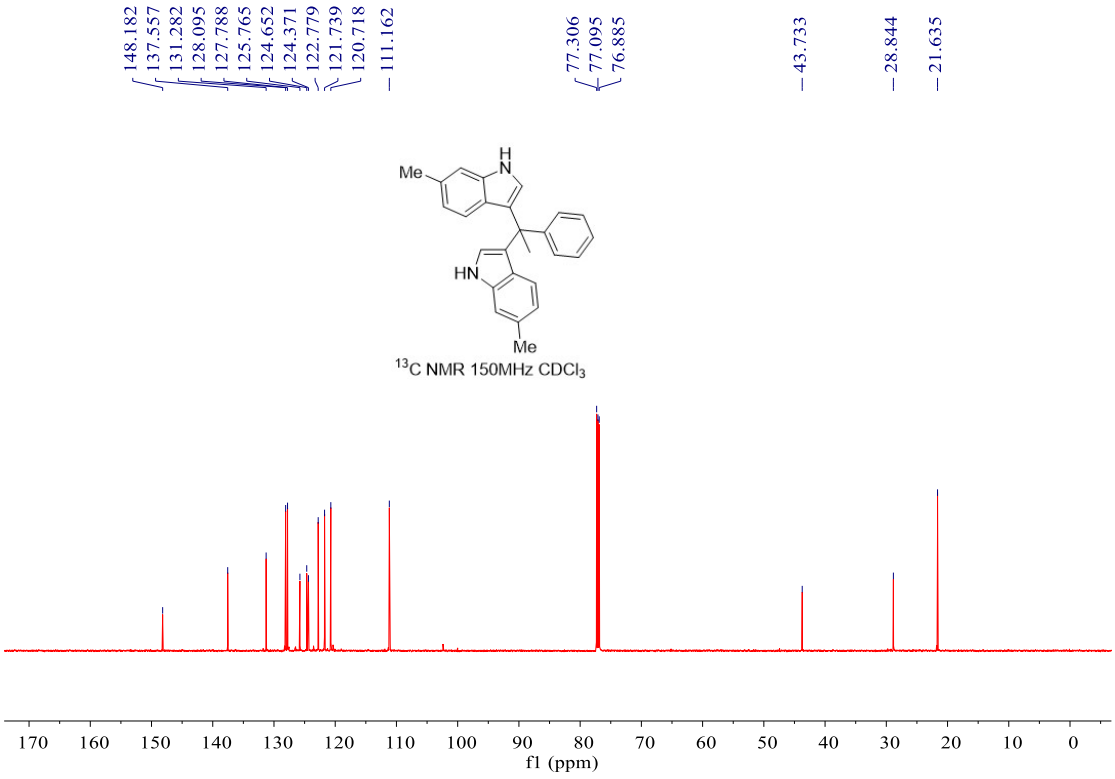
3,3'-(1-Phenylethane-1,1-diyl)bis(5-methyl-1*H*-indole) (3b)



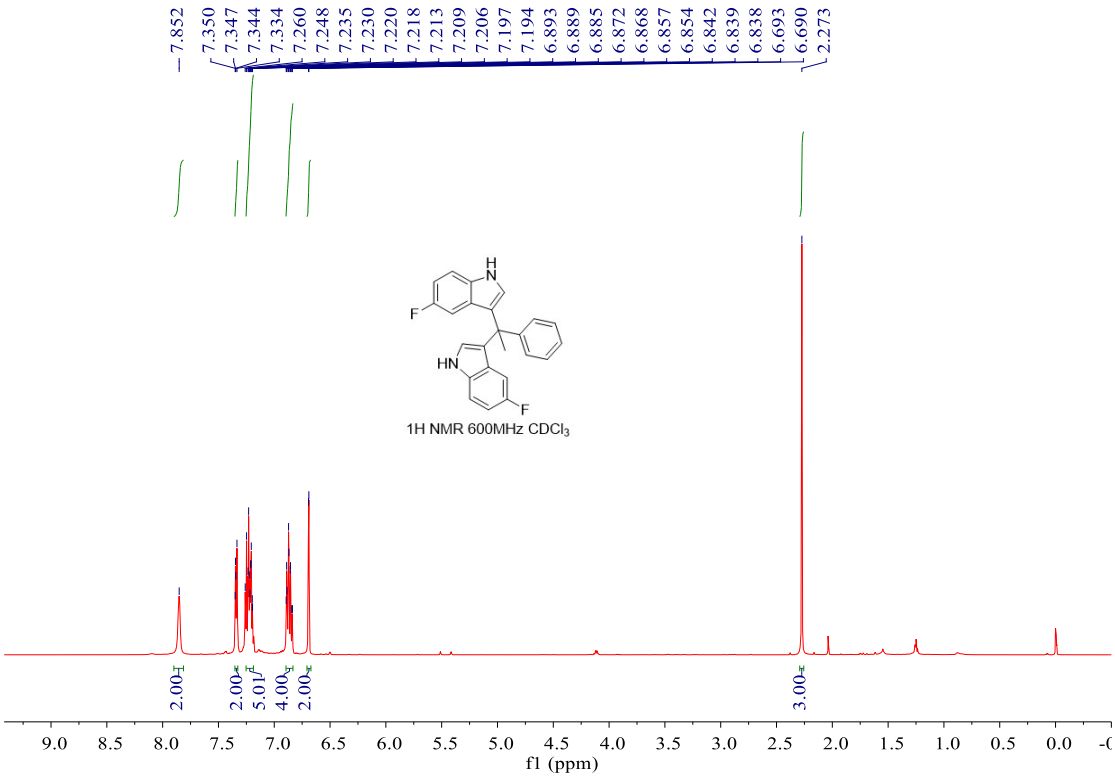


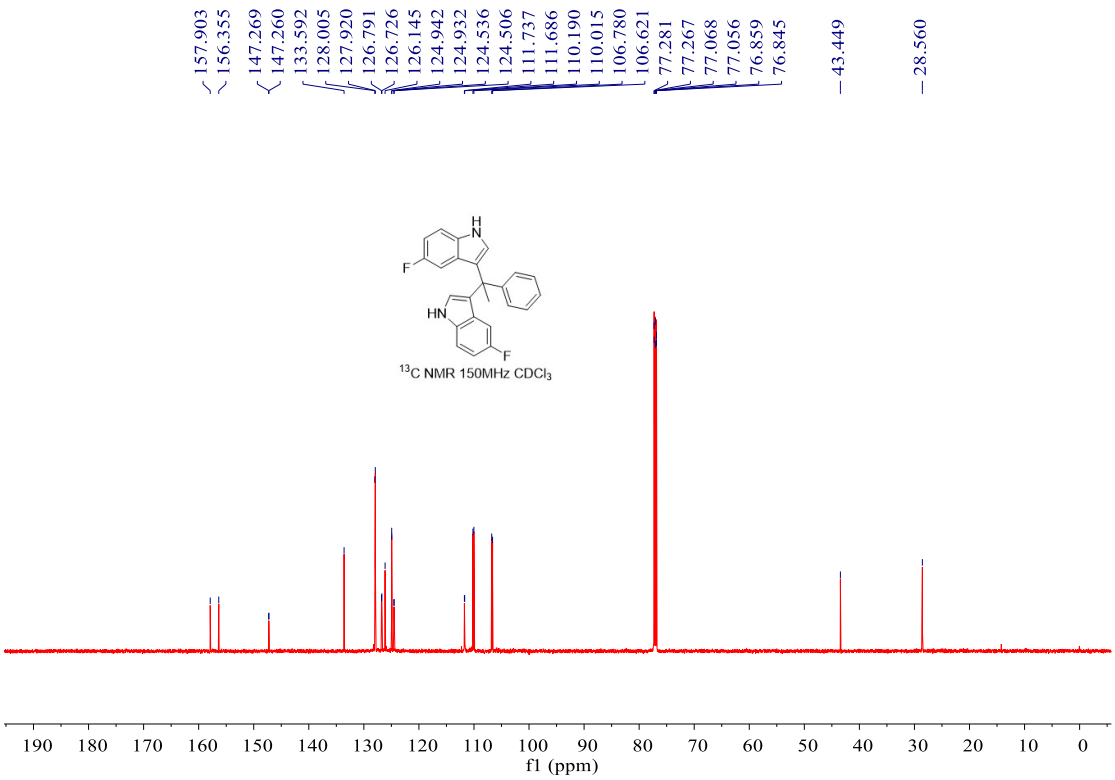
3,3'-(1-Phenylethane-1,1-diyl)bis(6-methyl-1*H*-indole) (3c)



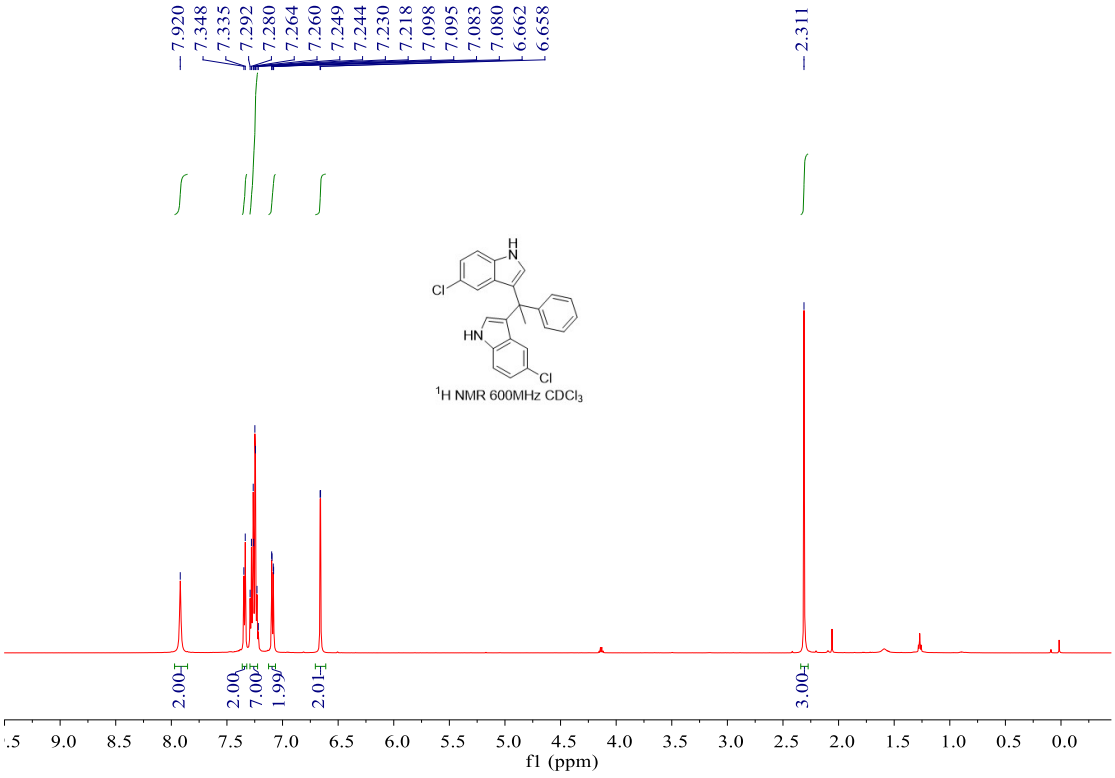


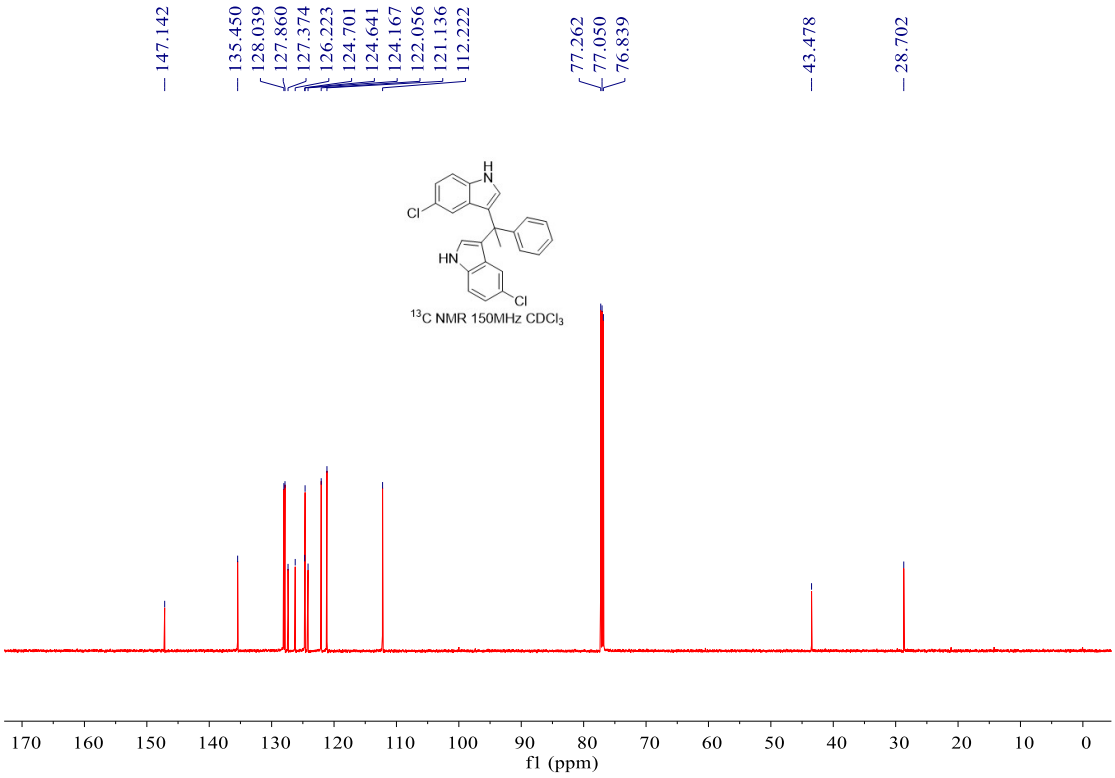
3,3'-(1-Phenylethane-1,1-diyl)bis(5-fluoro-1*H*-indole) (3d)



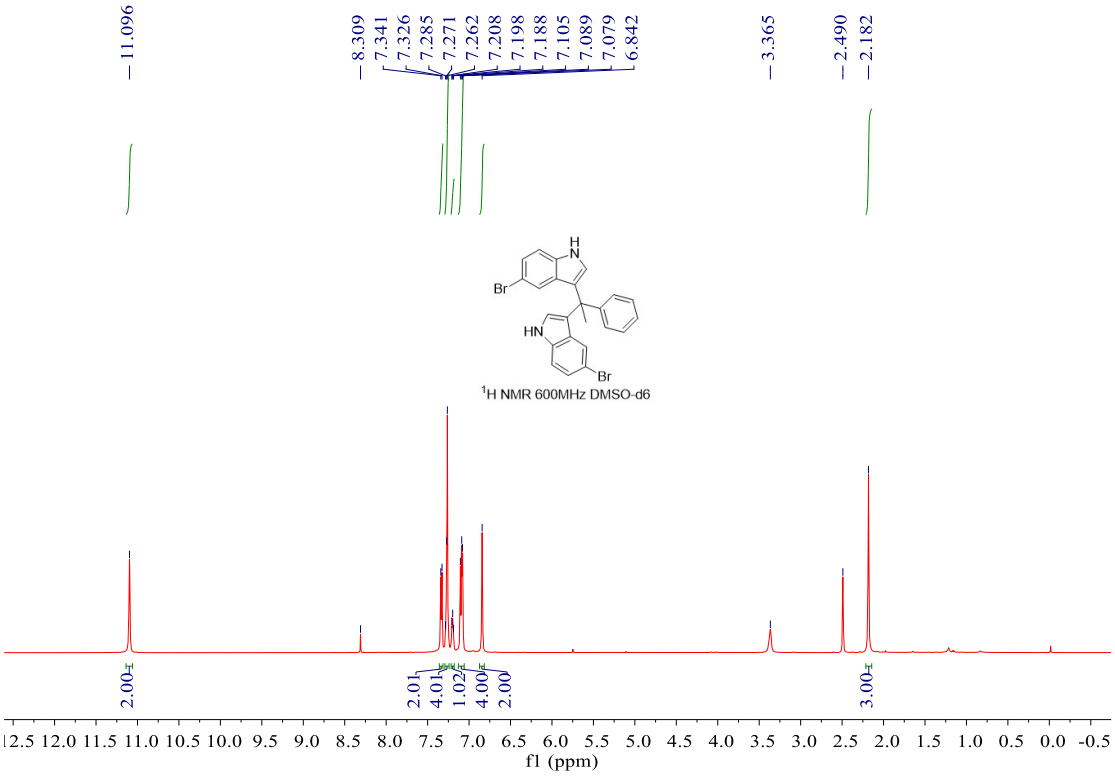


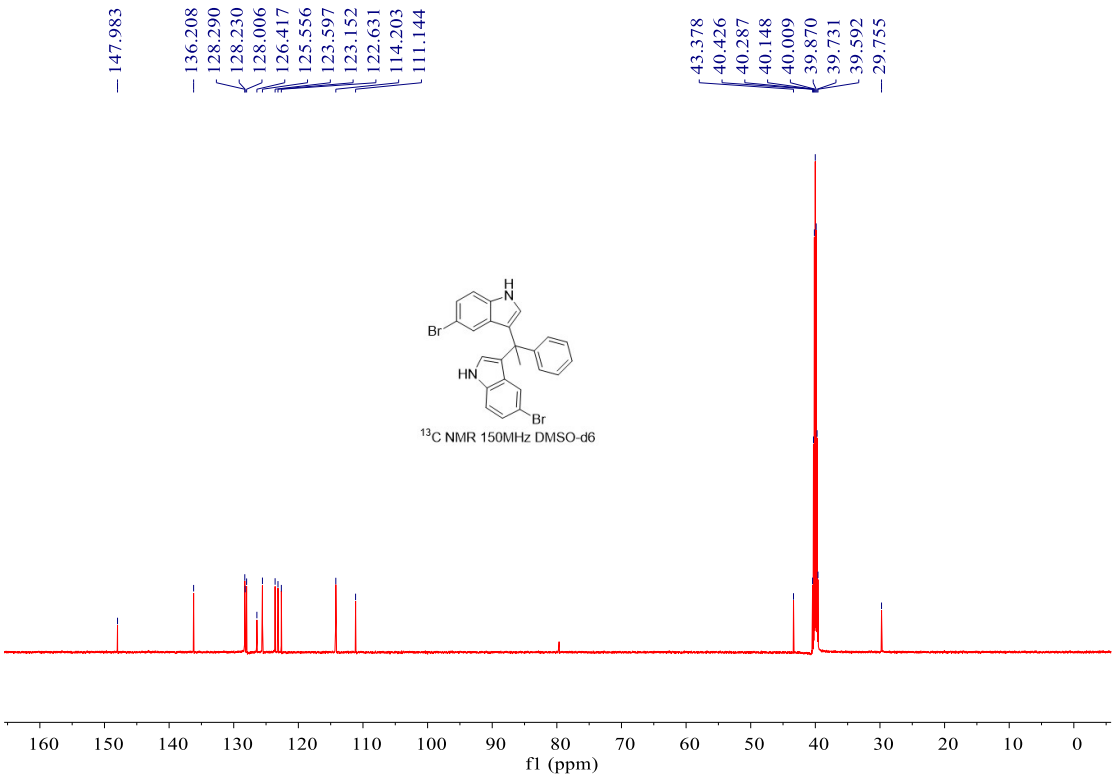
5-Chloro-3-(1-(5-chloro-1*H*-inden-3-yl)-1-phenylethyl)-1*H*-indole (3e)



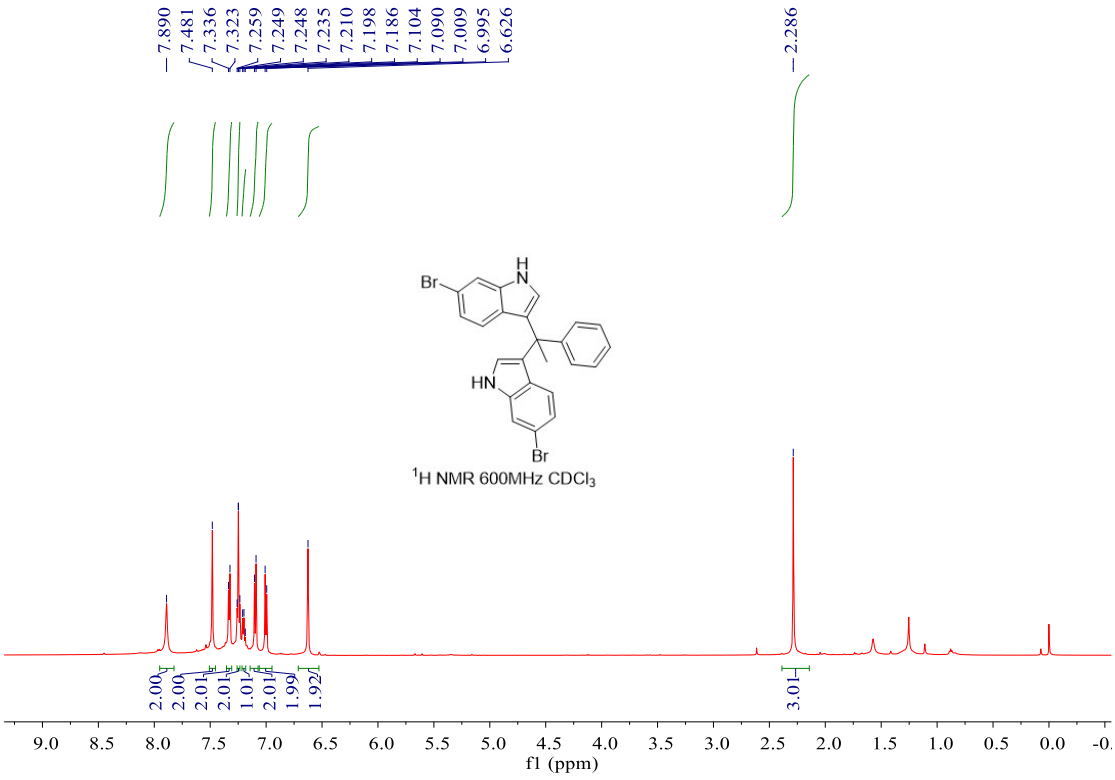


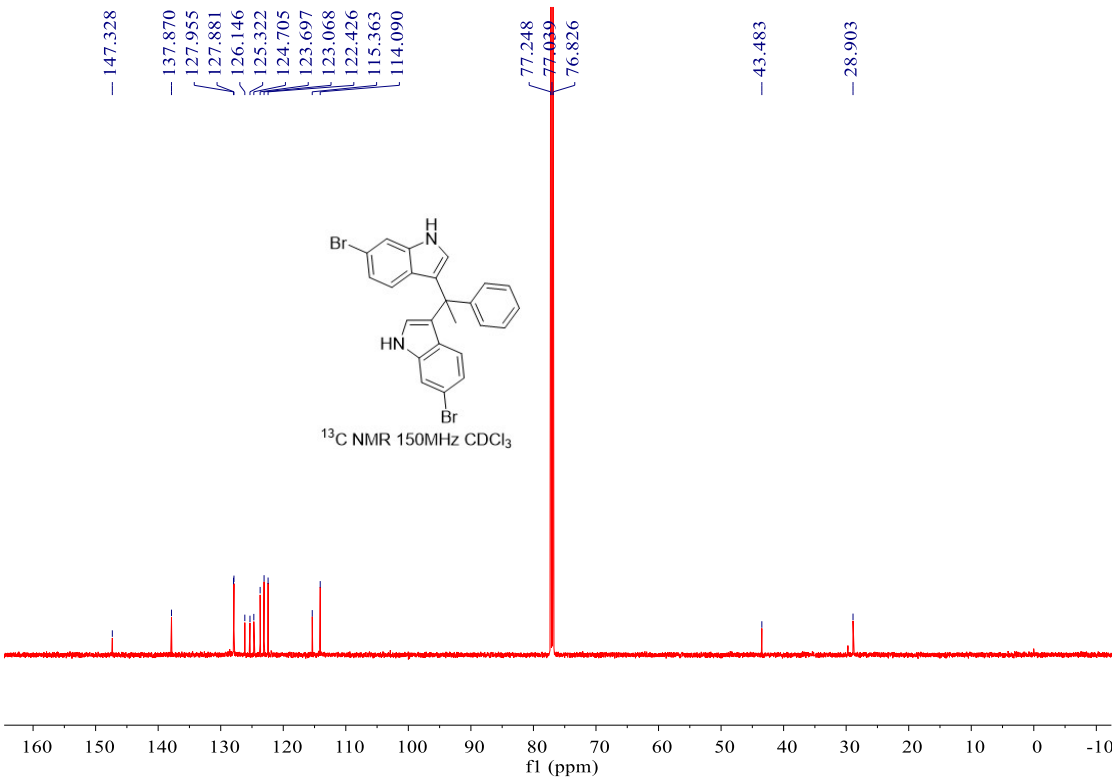
3,3'-(1-Phenylethane-1,1-diyl)bis(5-bromo-1*H*-indole) (3f)



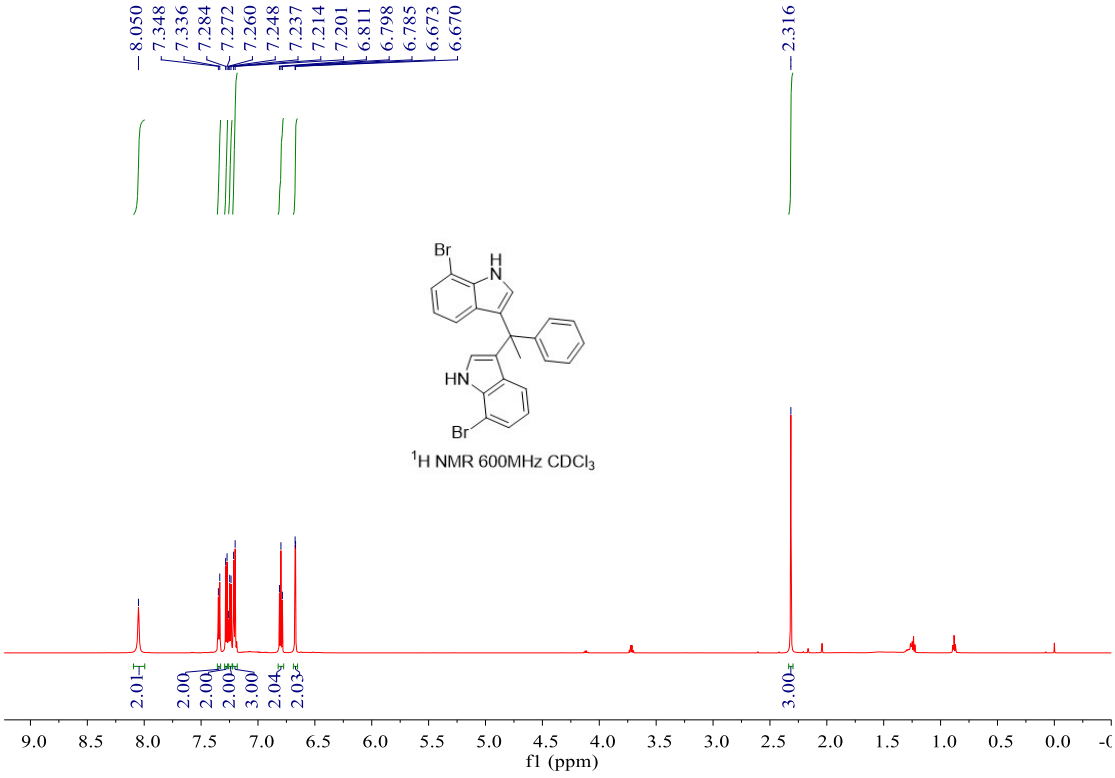


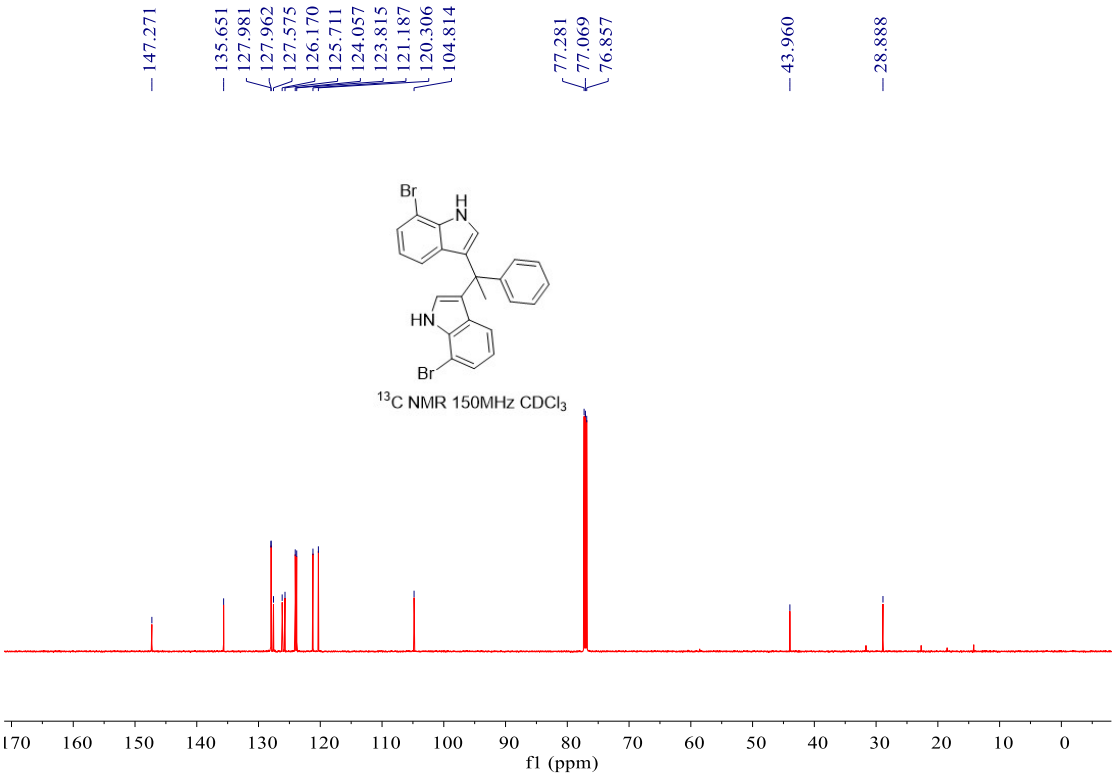
3,3'-(1-Phenylethane-1,1-diyl)bis(6-bromo-1*H*-indole) (3g)



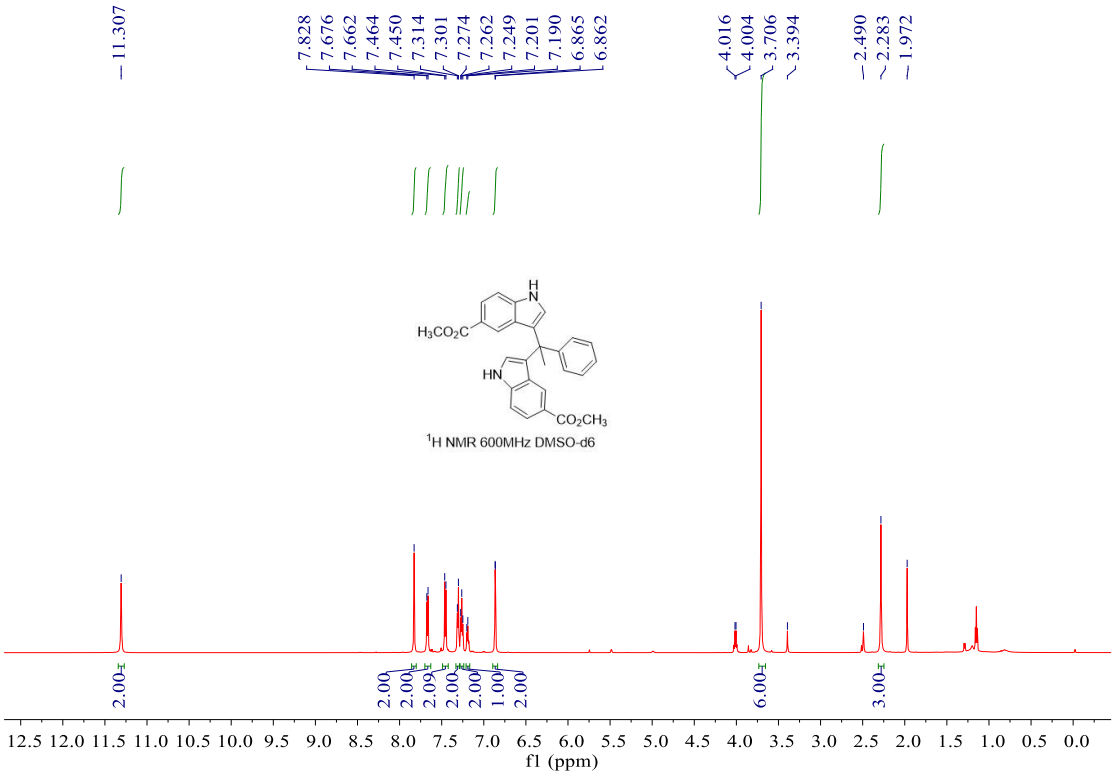


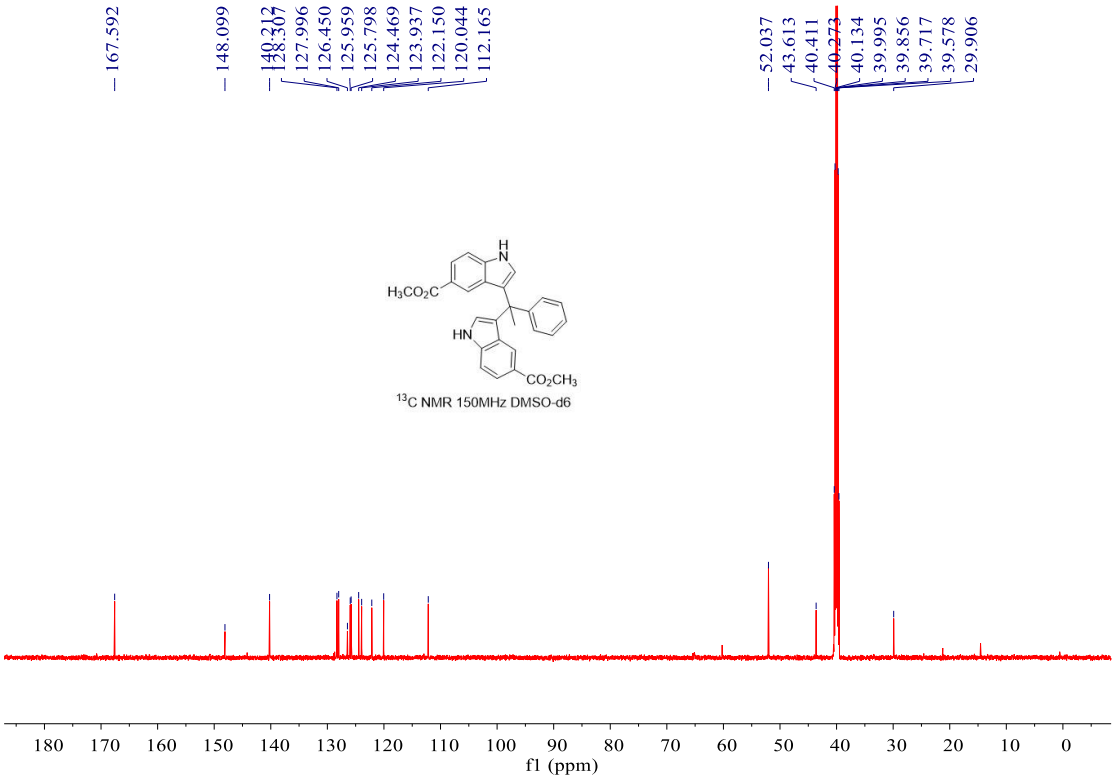
7-Bromo-3-(1-(7-bromo-1*H*-indol-2-yl)-1-phenylethyl)-1*H*-indole (3h)



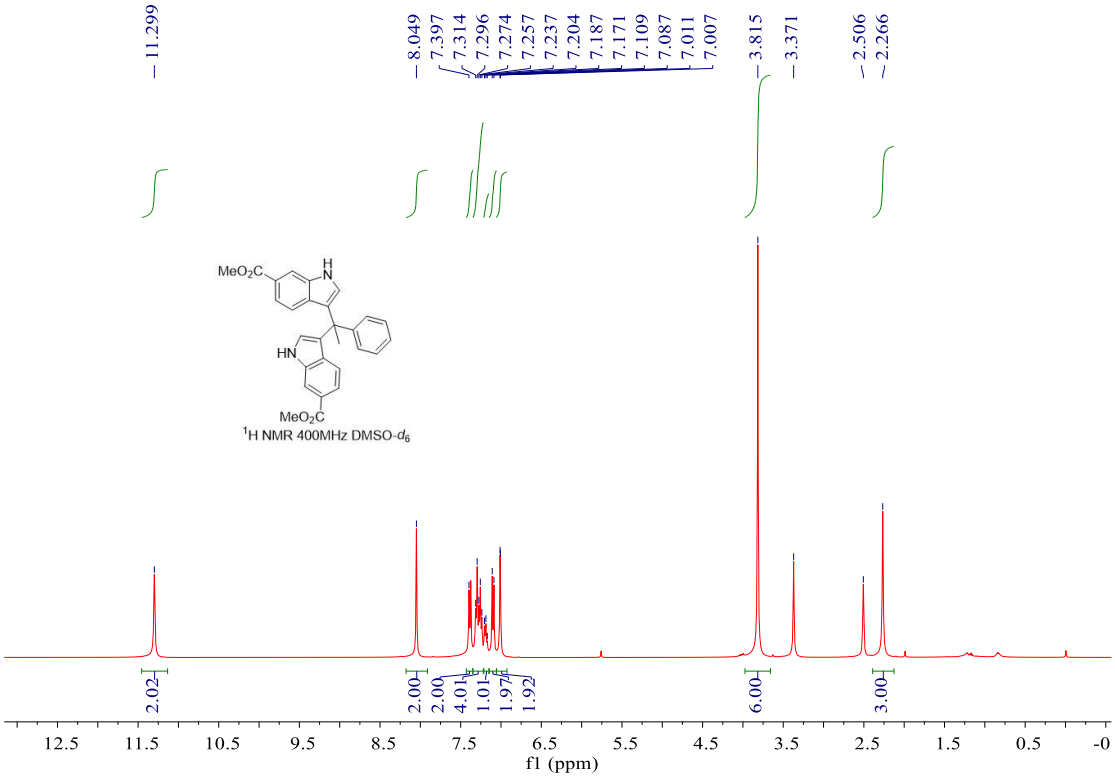


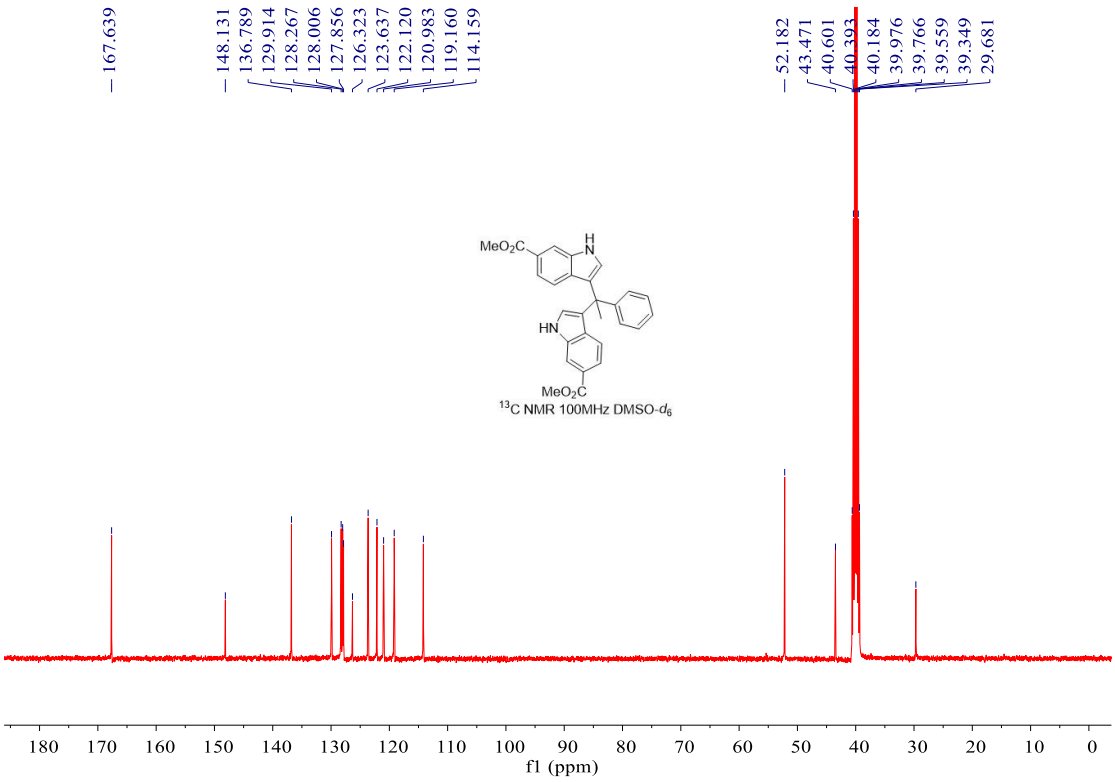
Dimethyl 3,3'-(1-phenylethane-1,1-diyl)bis(1*H*-indole-5-carboxylate) (3i)



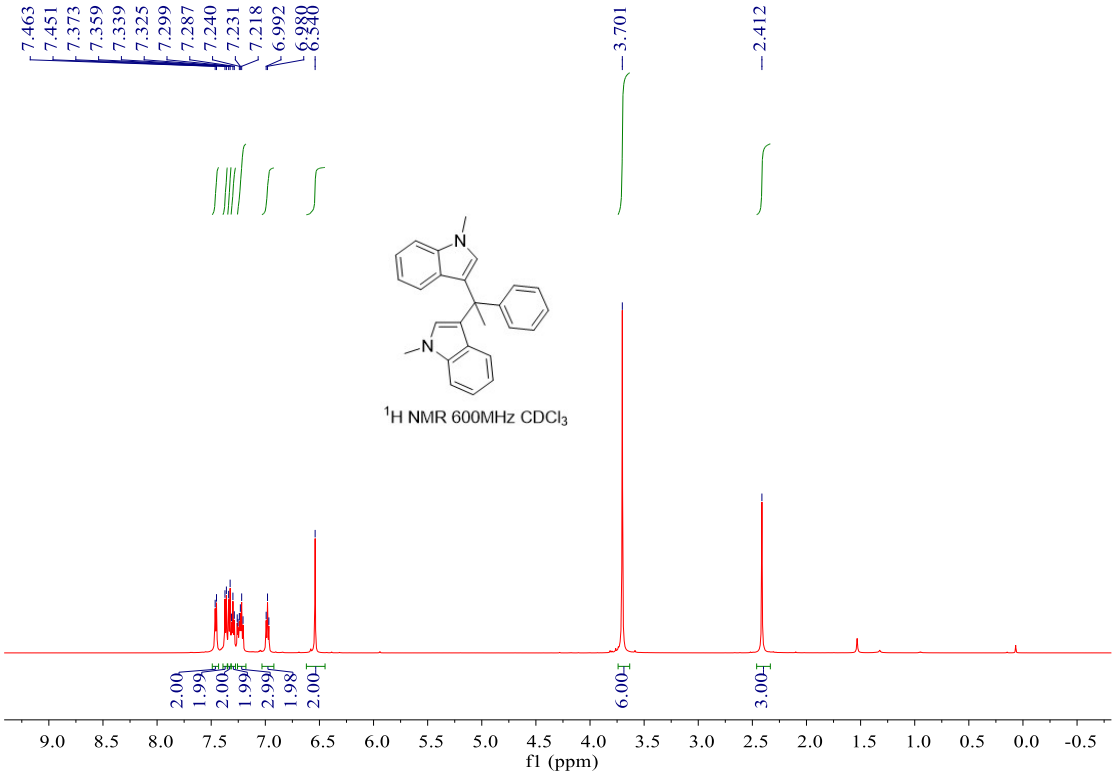


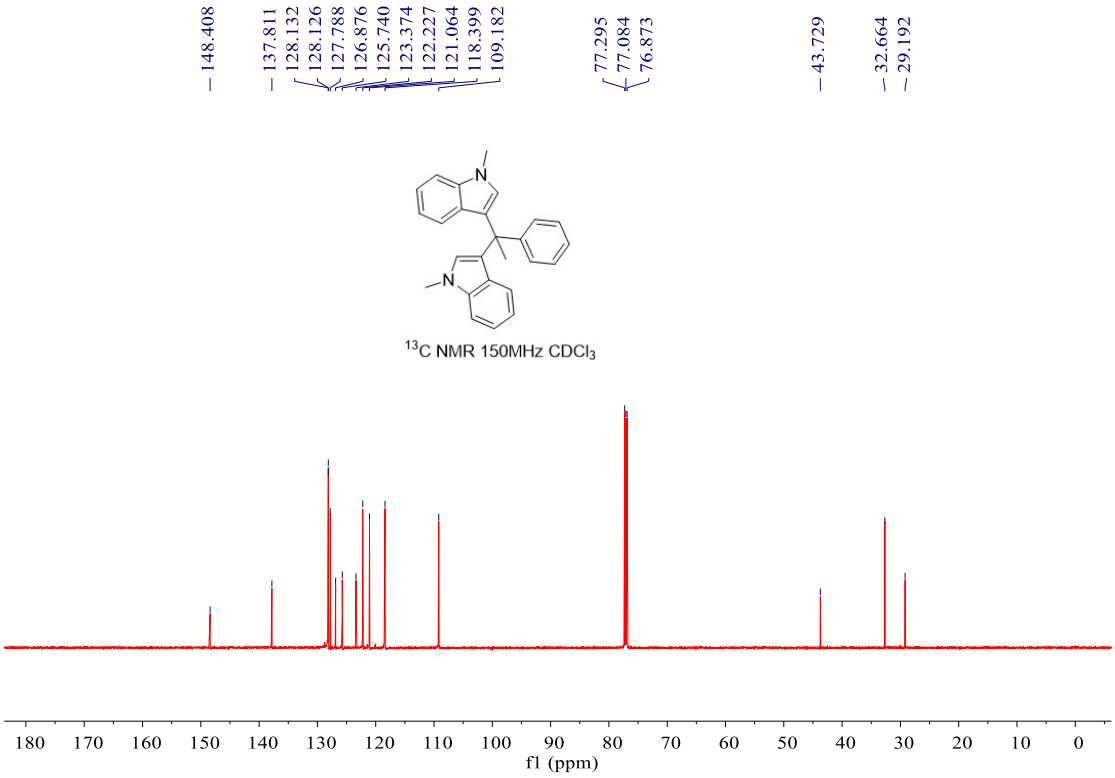
Dimethyl 3,3'-(1-phenylethane-1,1-diyl)bis(1H-indole-6-carboxylate) (3j)



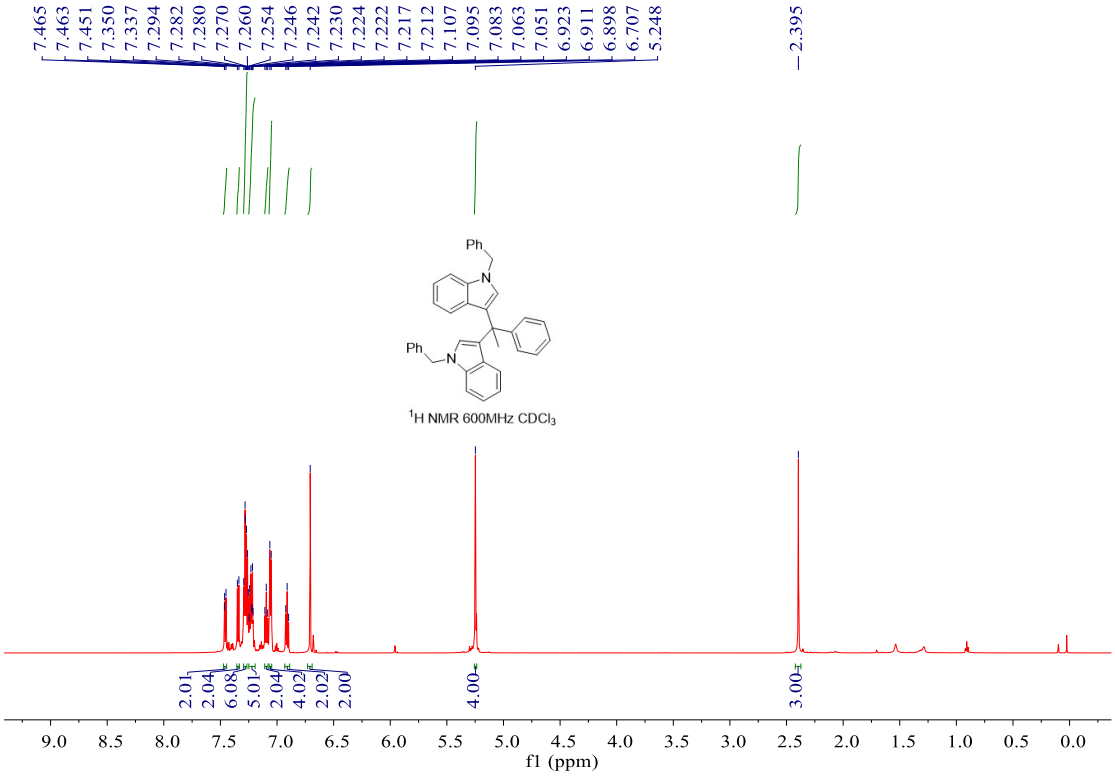


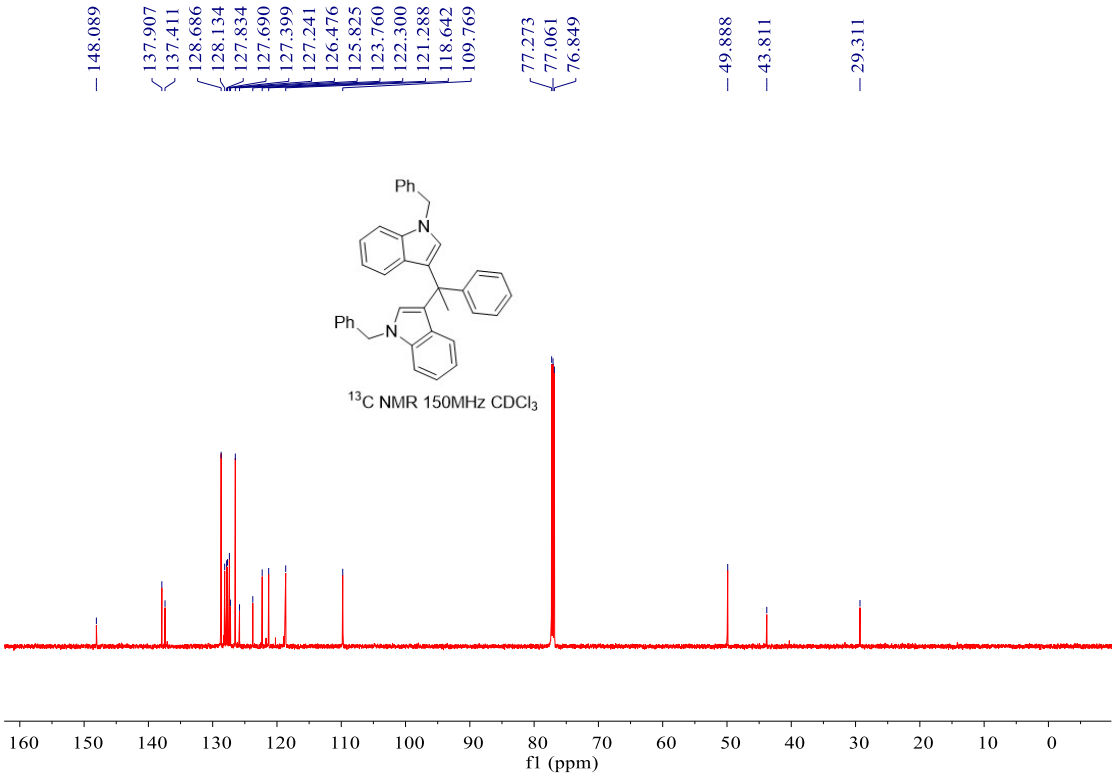
3,3'-(1-Phenylethane-1,1-diyl)bis(1-methyl-1*H*-indole) (3k)



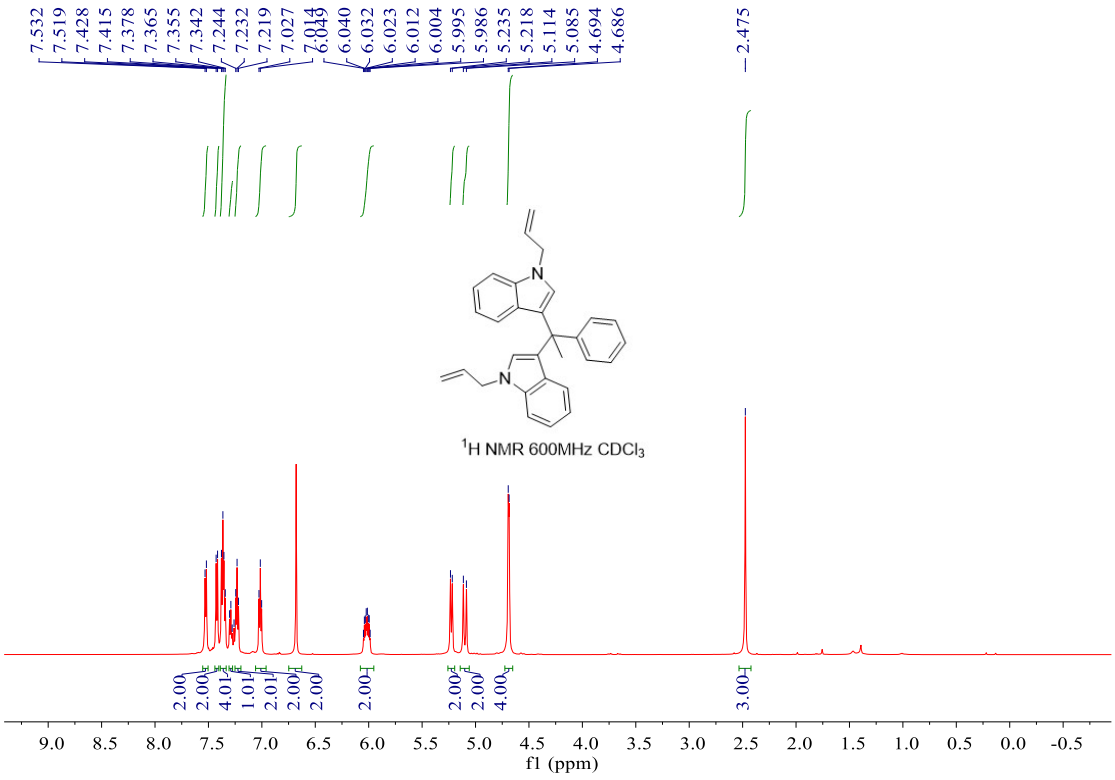


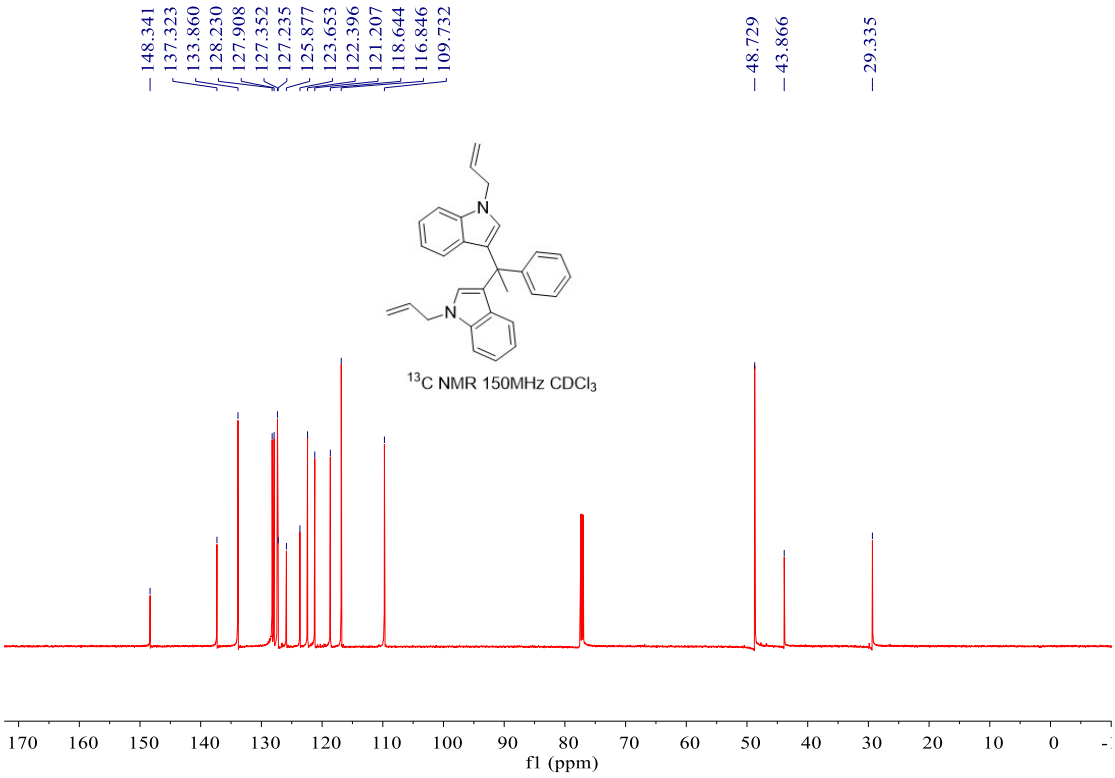
3,3'-(1-Phenylethane-1,1-diyl)bis(1-benzyl-1*H*-indole) (3l)



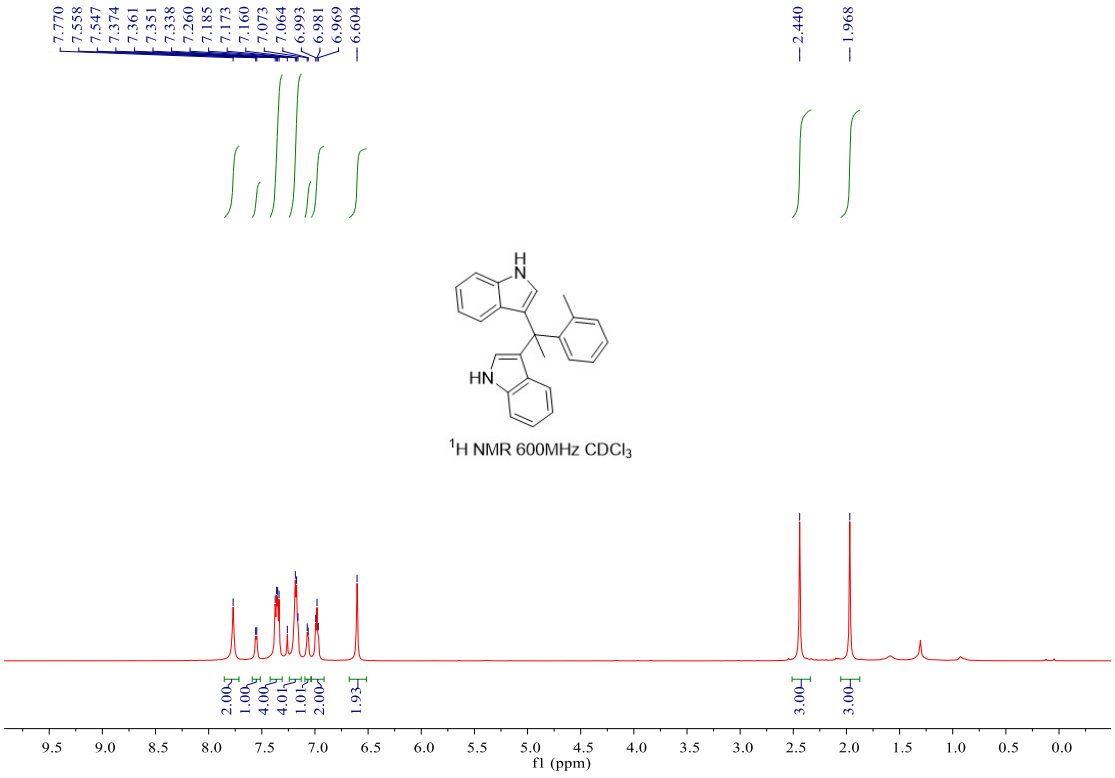


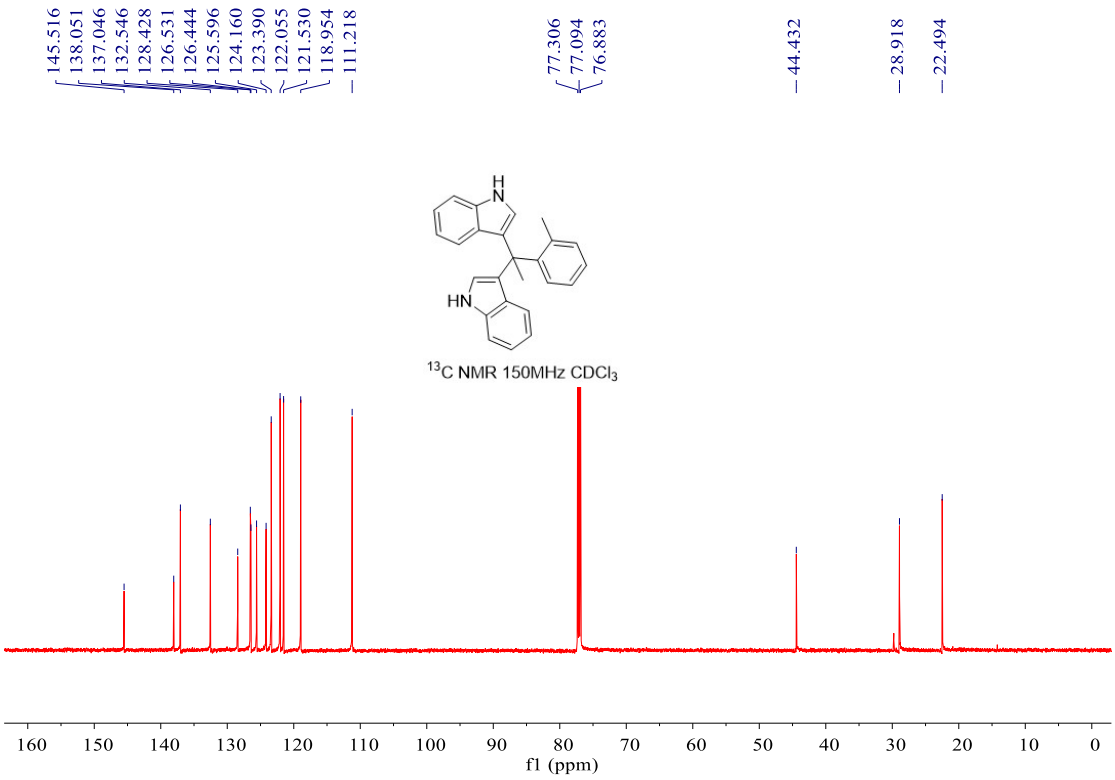
3,3'-(1-Phenylethane-1,1-diyl)bis(1-allyl-1*H*-indole) (3m)



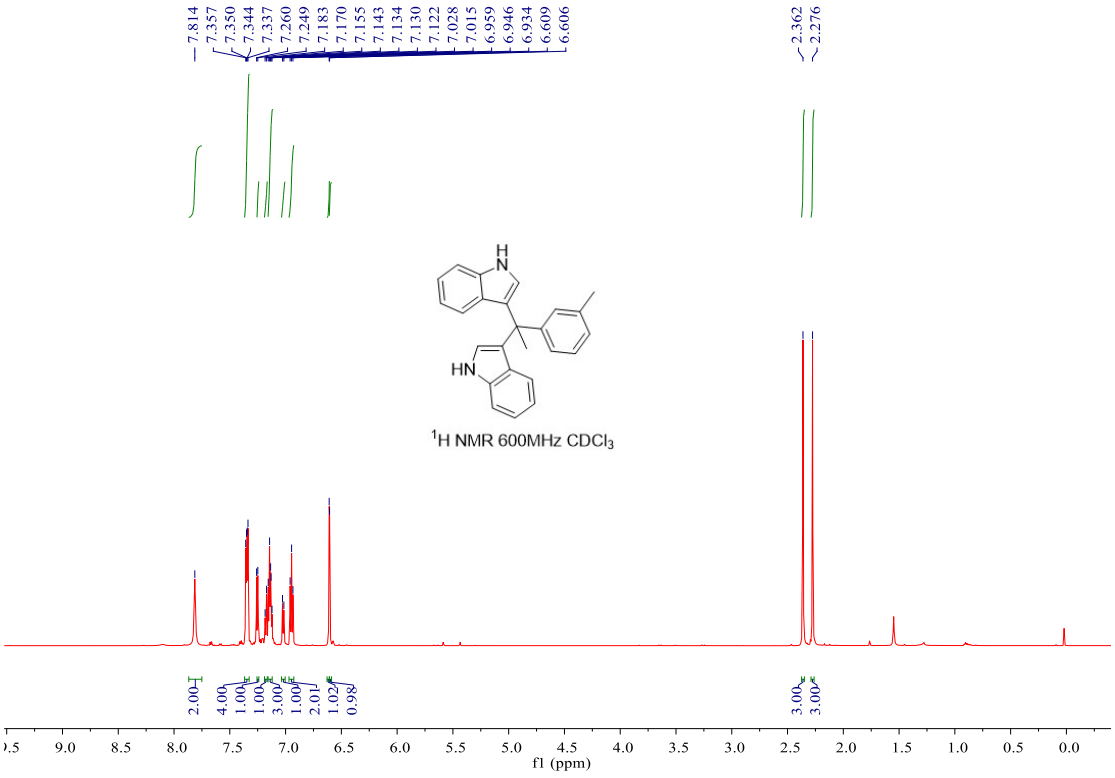


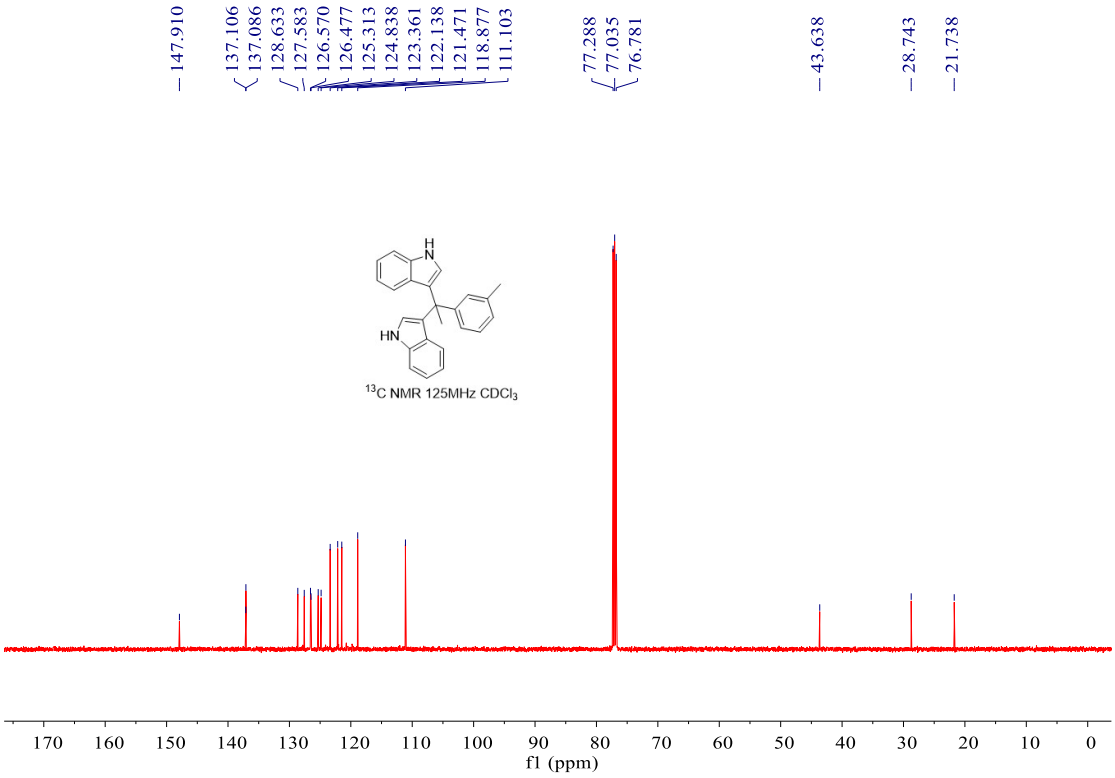
3,3'-(1-(*o*-Tolyl)ethane-1,1-diyl)bis(1*H*-indole) (3n)



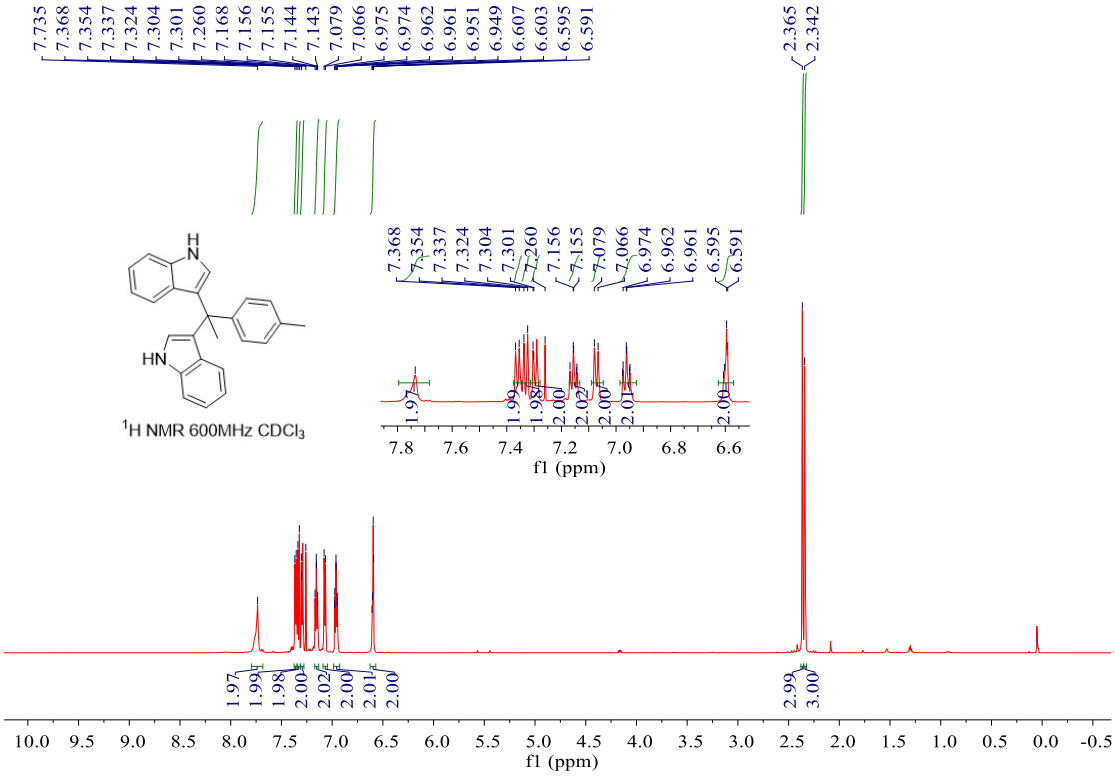


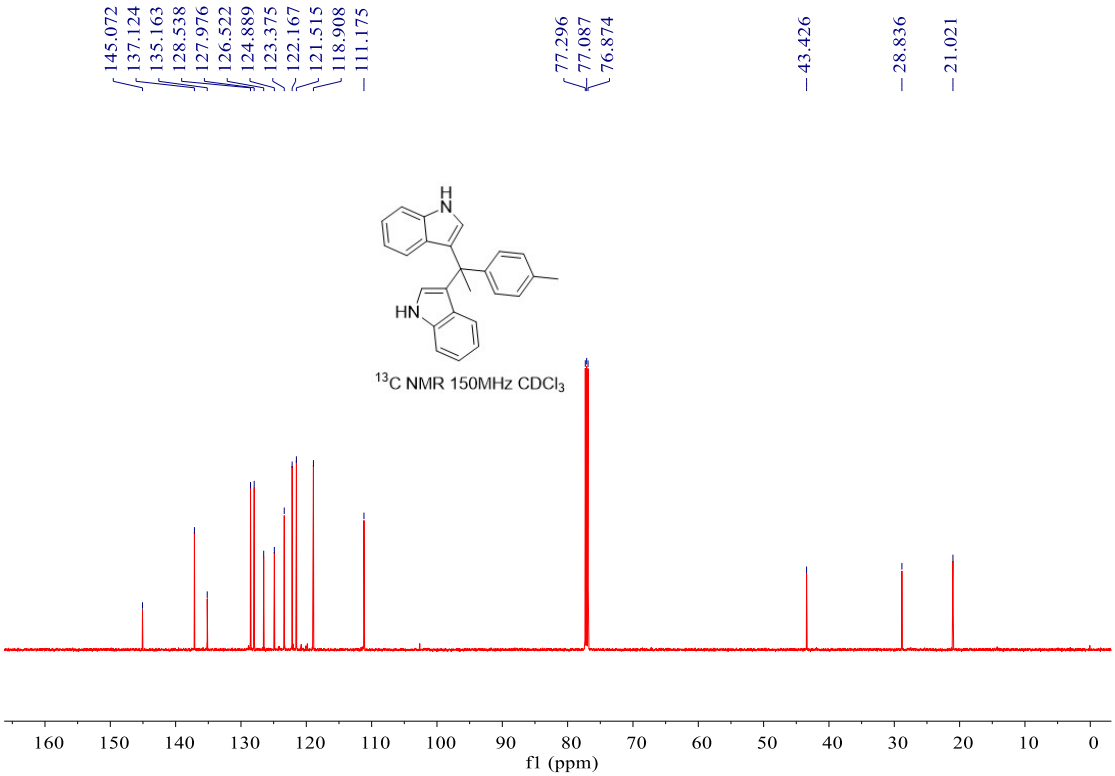
3,3'-(1-(*m*-Tolyl)ethane-1,1-diyl)bis(1*H*-indole) (3o)



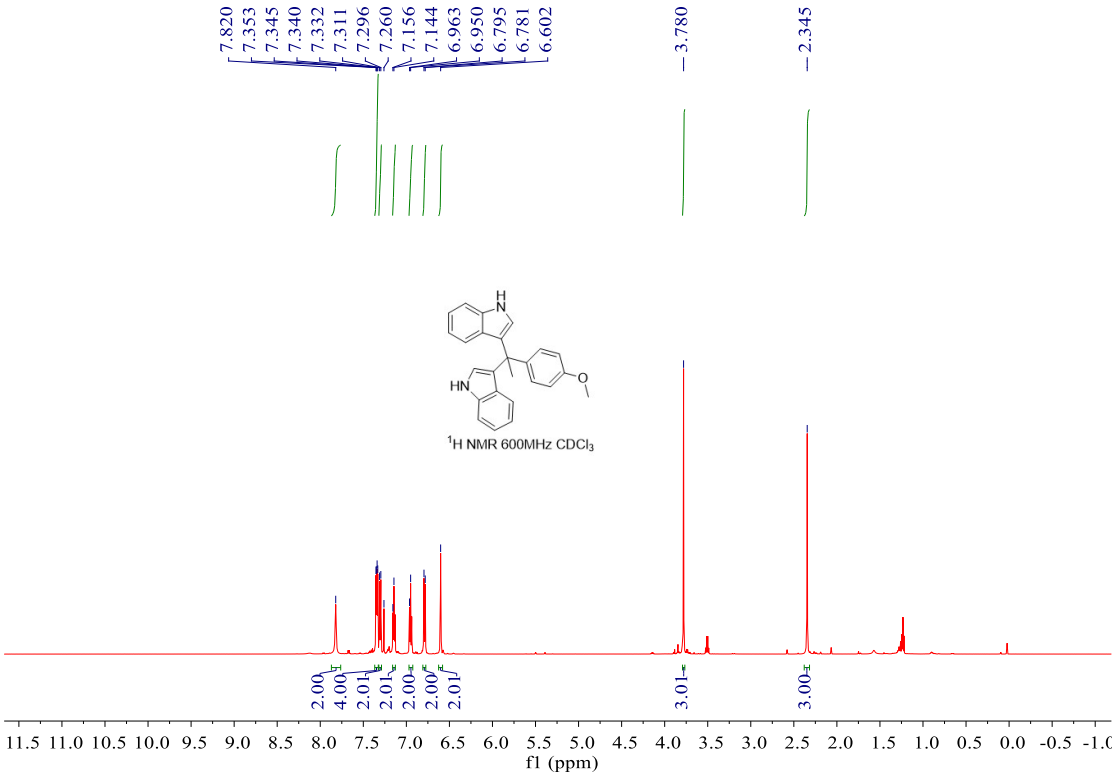


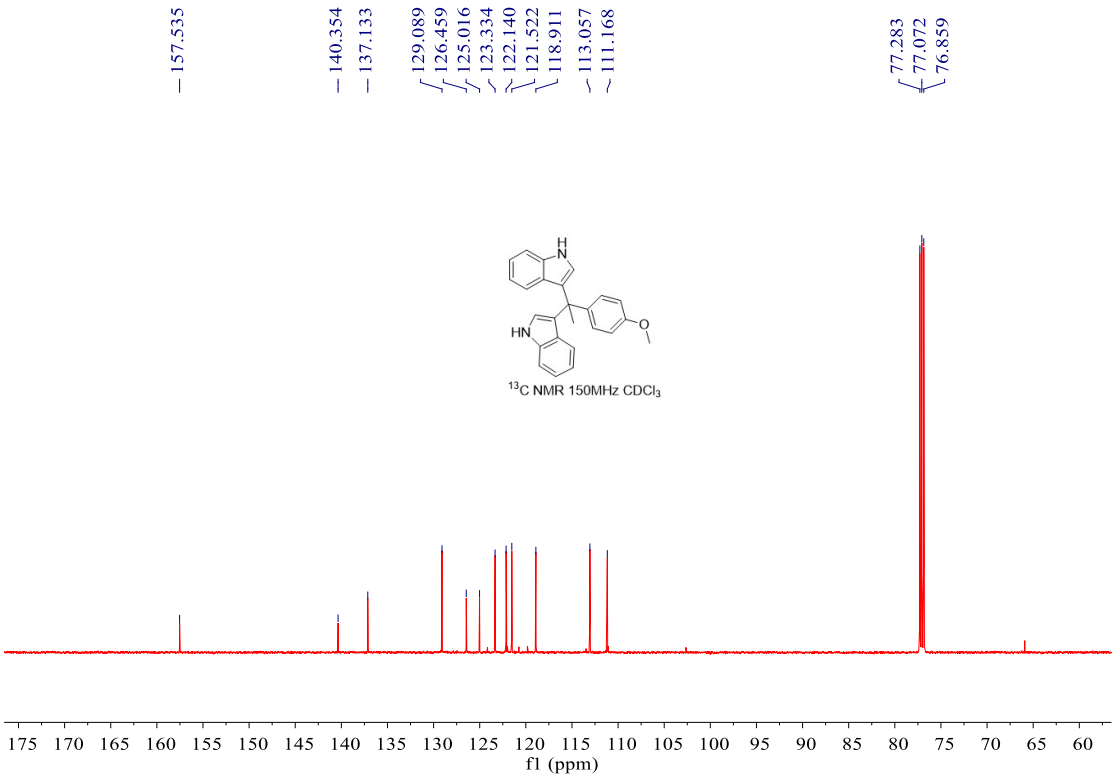
3,3'-(1-(p-Tolyl)ethane-1,1-diyl)bis(1*H*-indole) (3p)



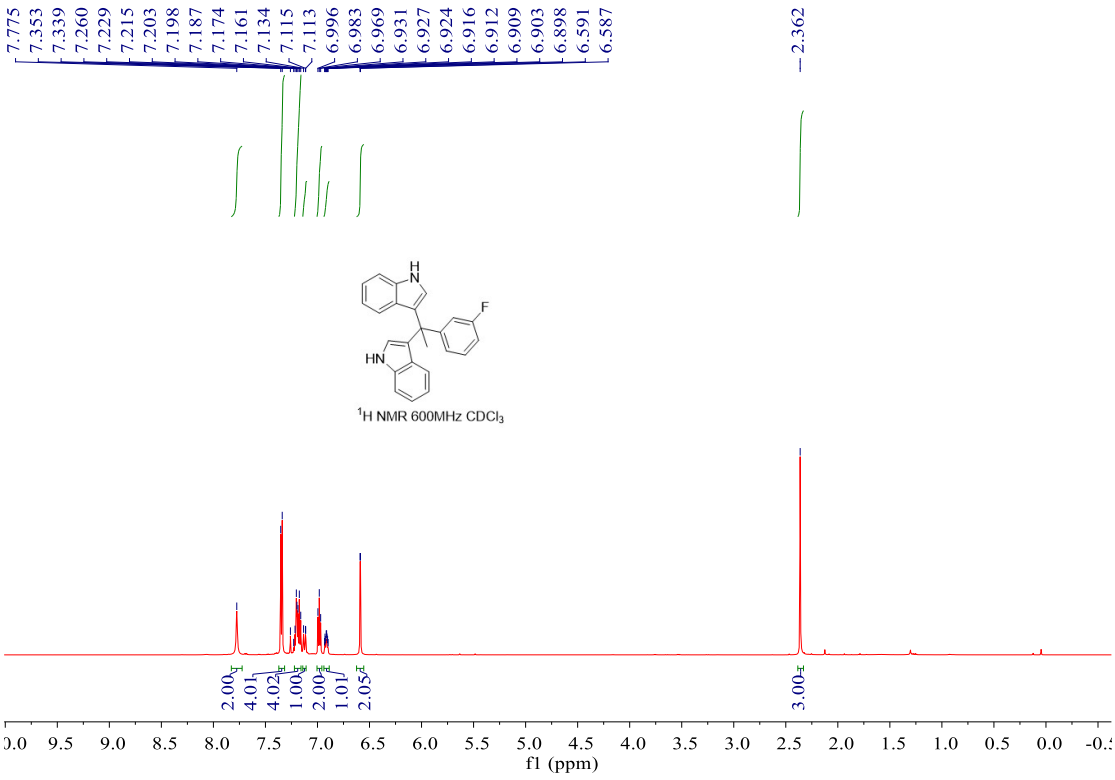


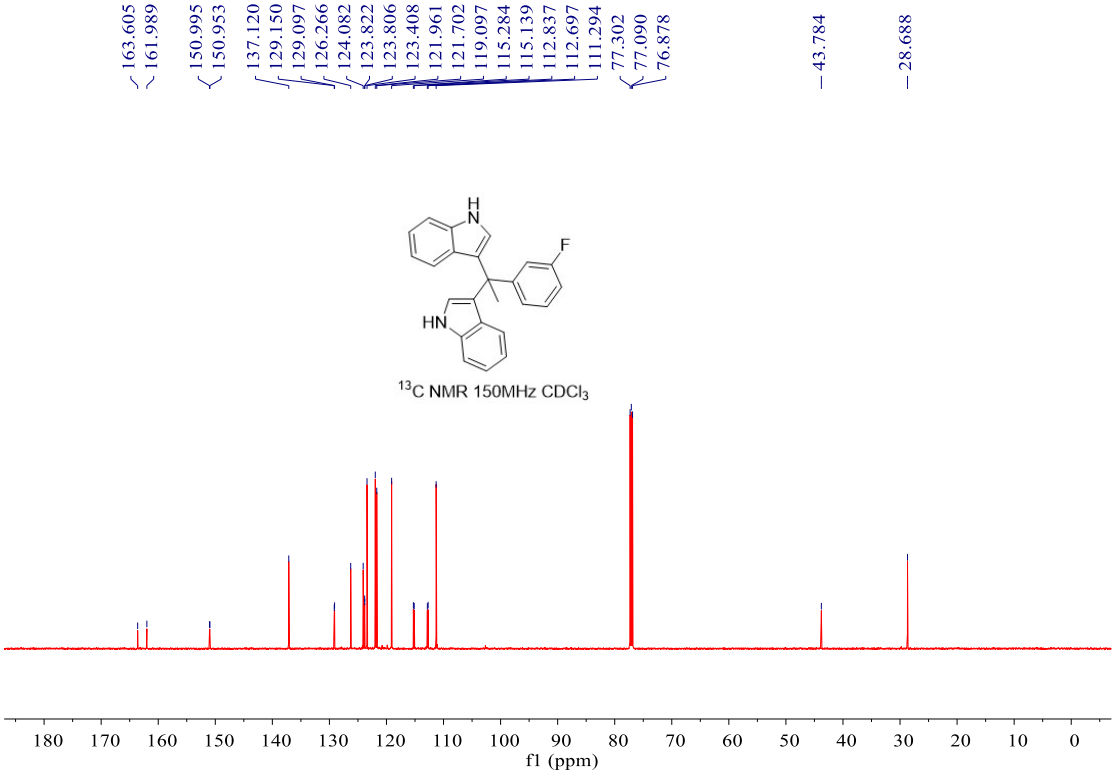
3,3'-(1-(4-Methoxyphenyl)ethane-1,1-diyl)bis(1*H*-indole) (3q)



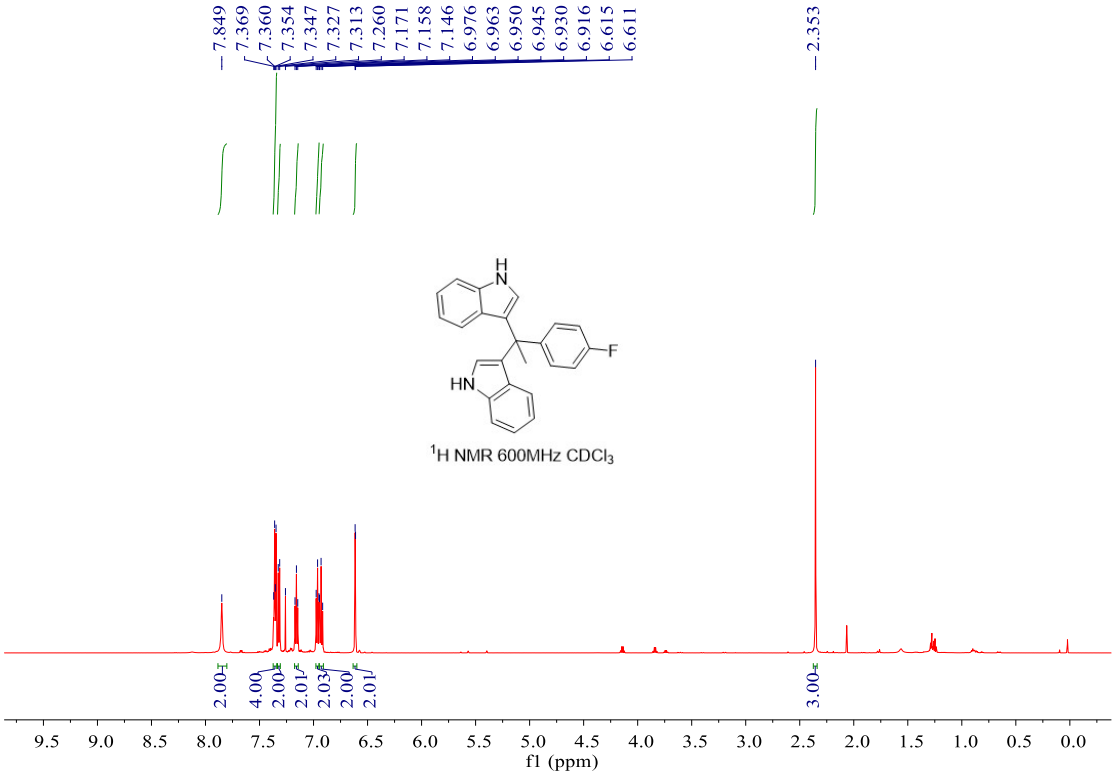


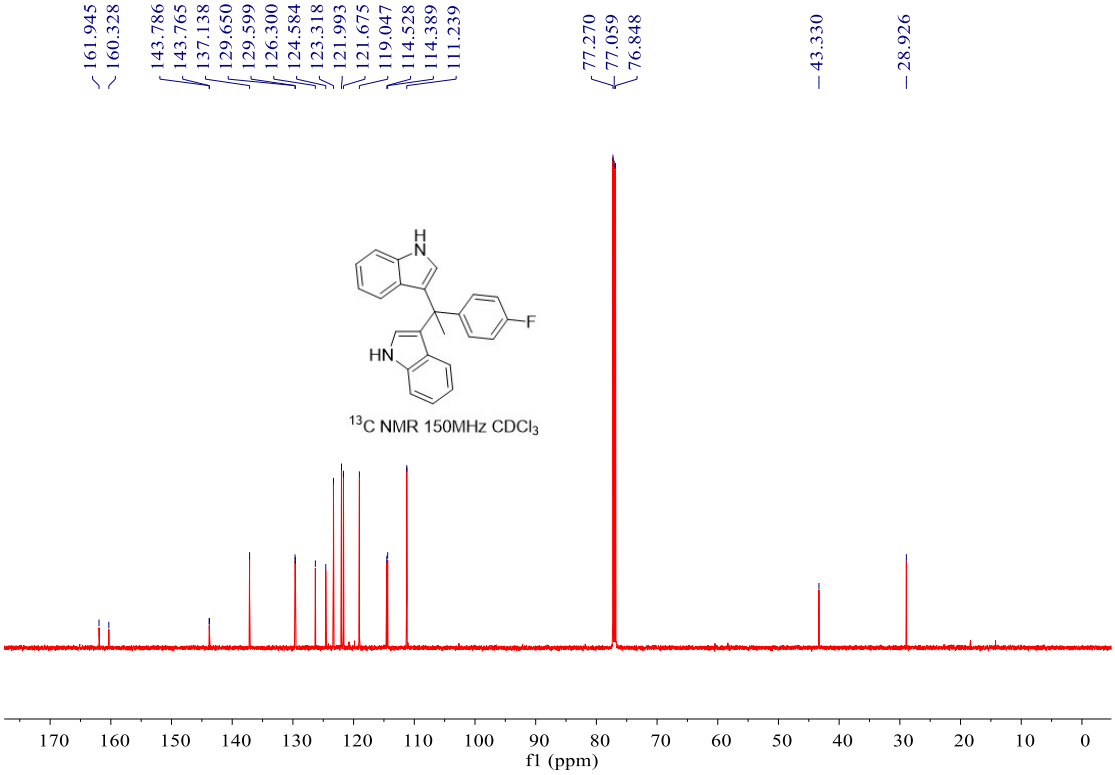
3,3'-(1-(3-Fluorophenyl)ethane-1,1-diyl)bis(1*H*-indole) (3r)



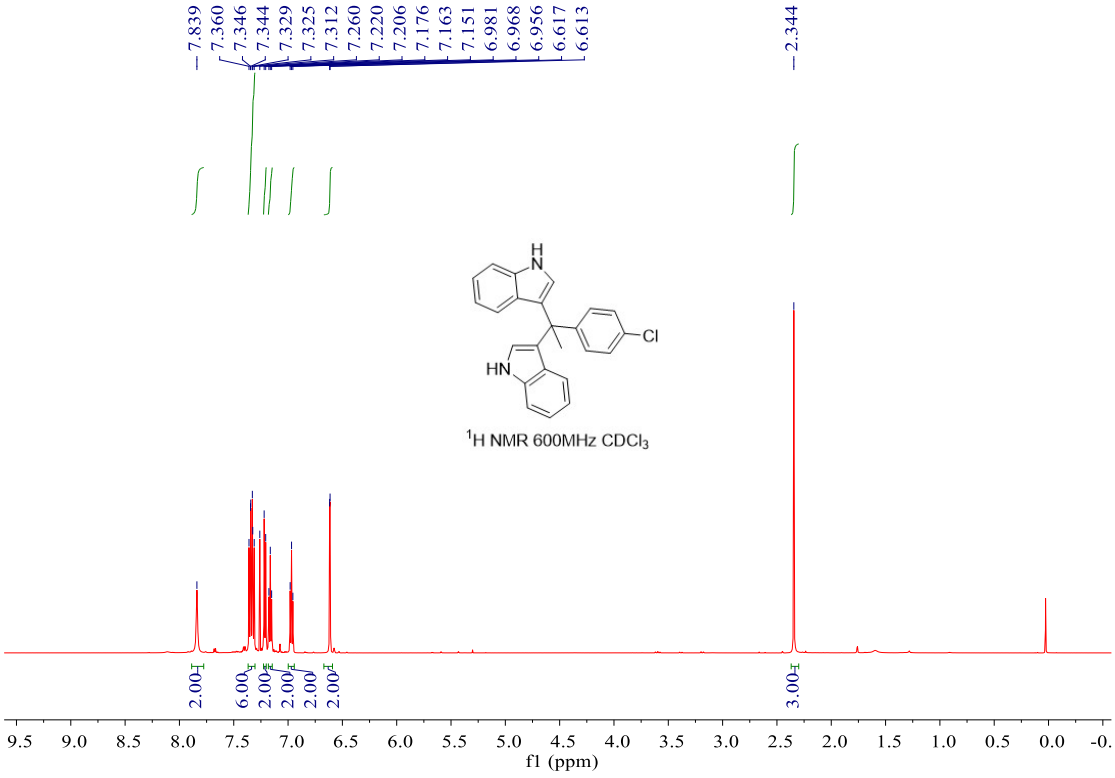


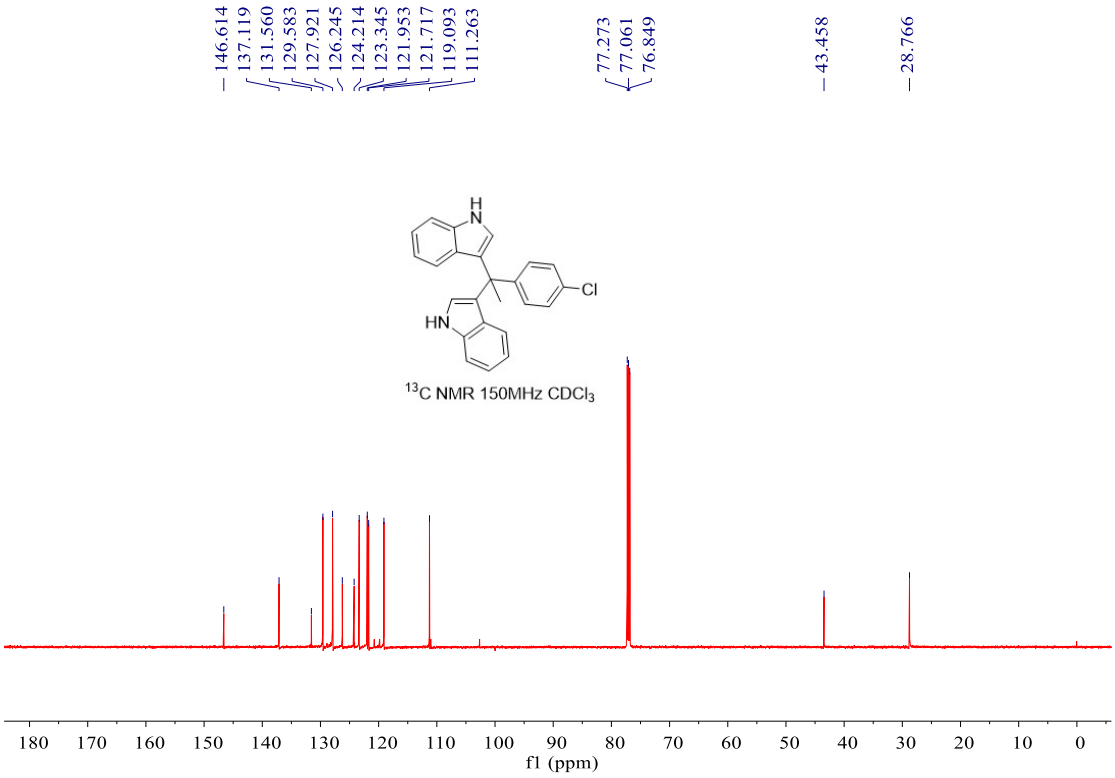
3,3'-(1-(4-Fluorophenyl)ethane-1,1-diyl)bis(1*H*-indole) (3s)



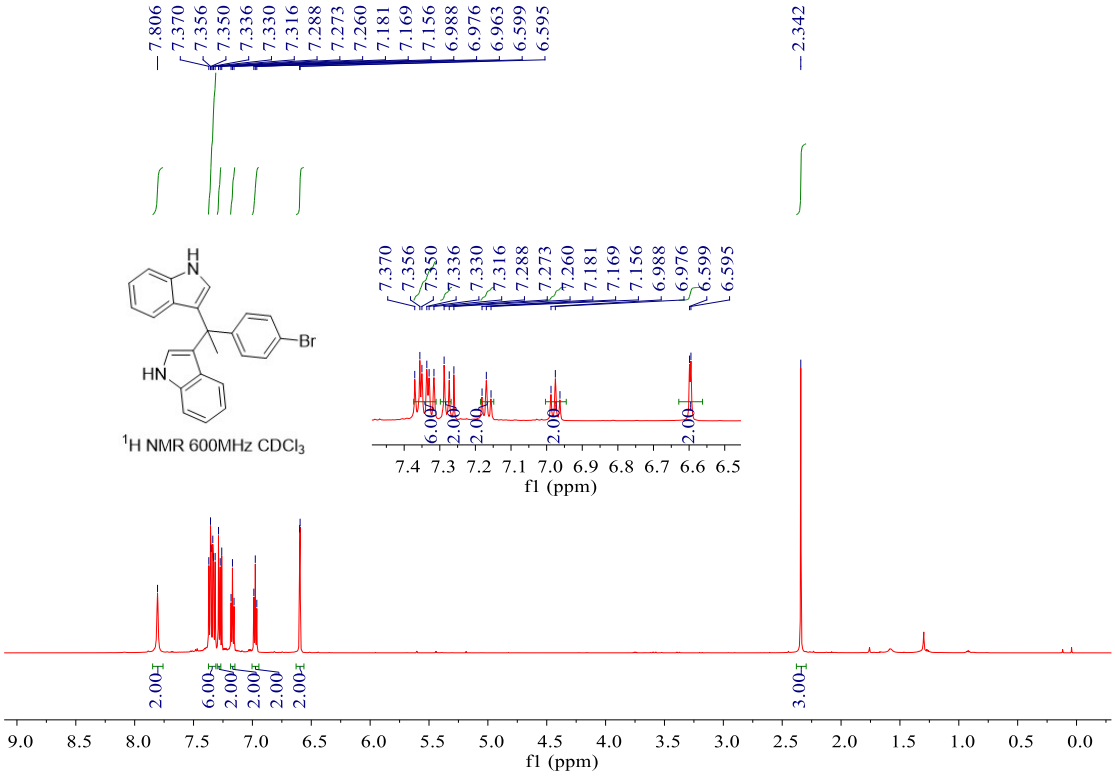


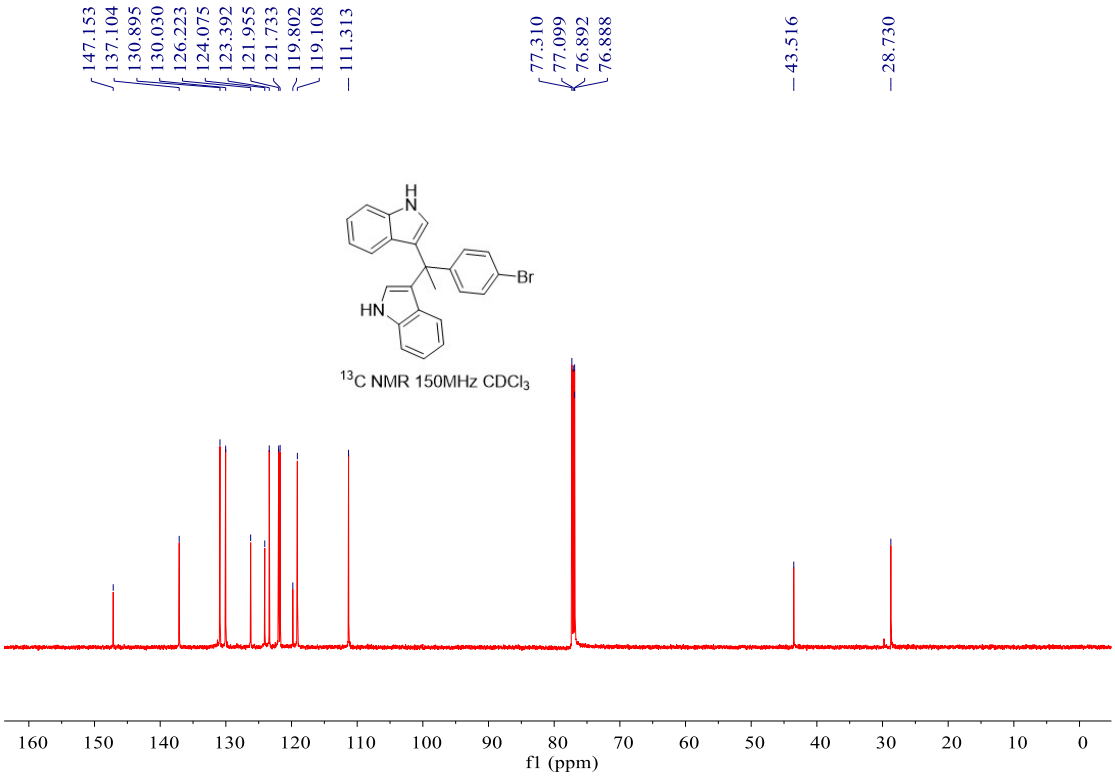
3,3'-(1-(4-Chlorophenyl)ethane-1,1-diyl)bis(1*H*-indole) (3t)



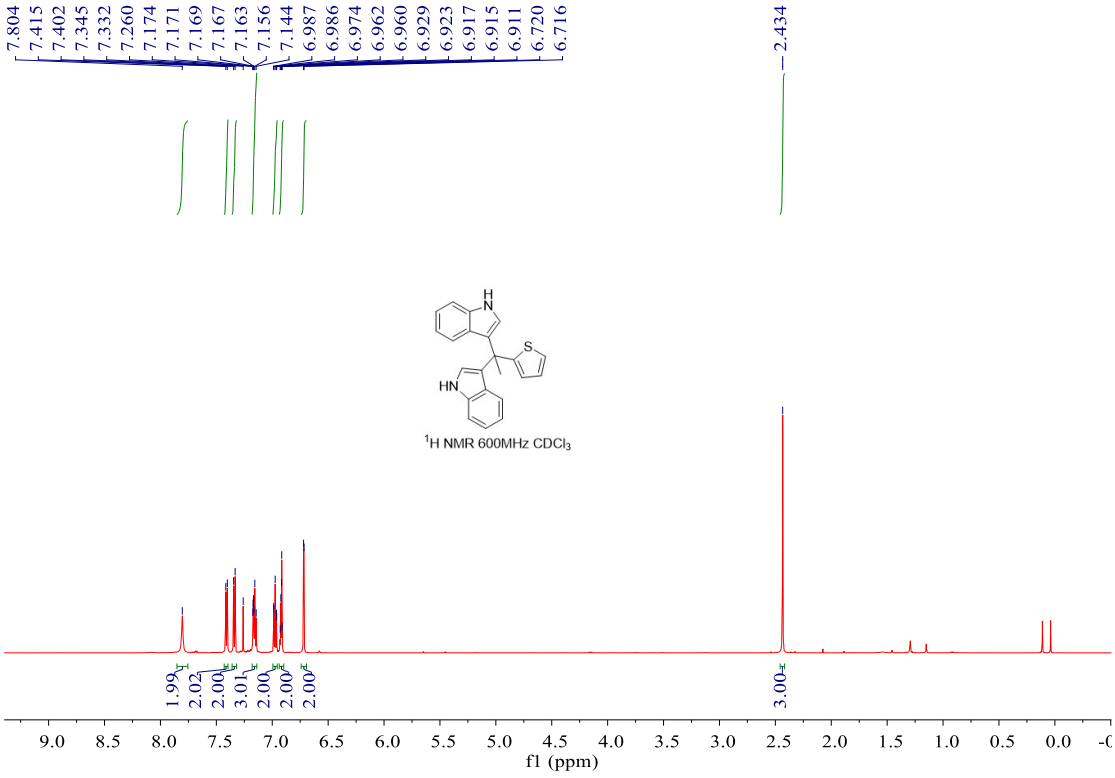


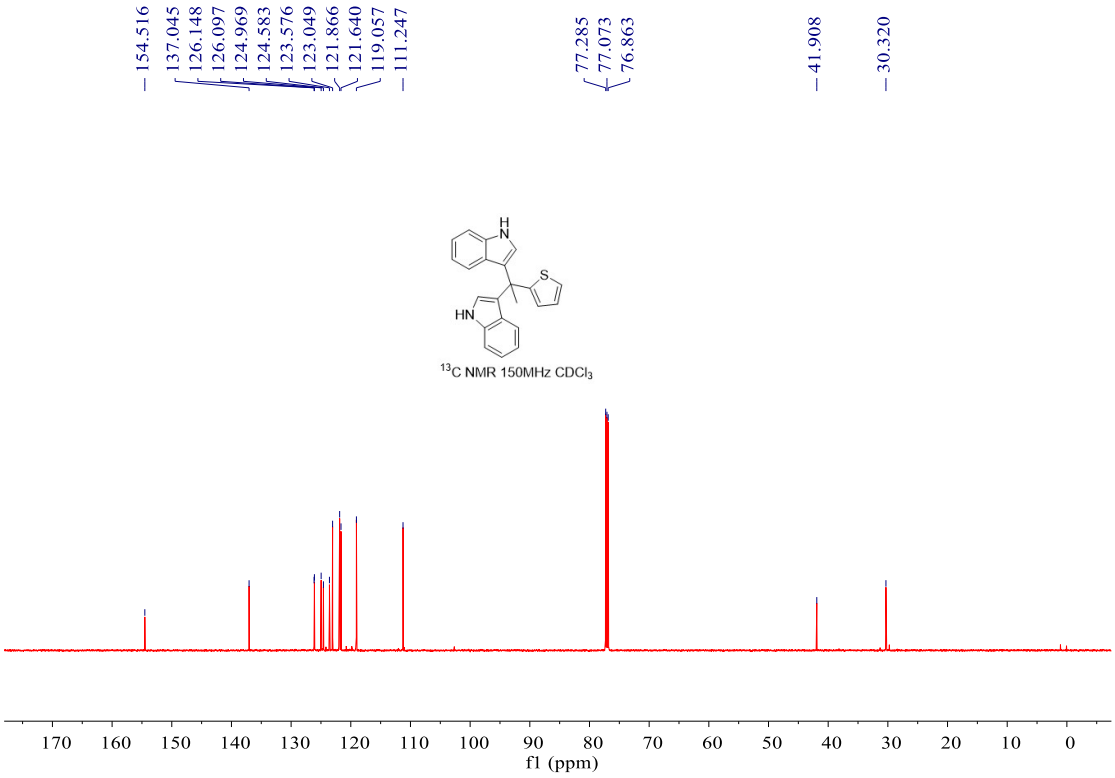
3,3'-(1-(4-Bromophenyl)ethane-1,1-diyl)bis(1*H*-indole) (3u)



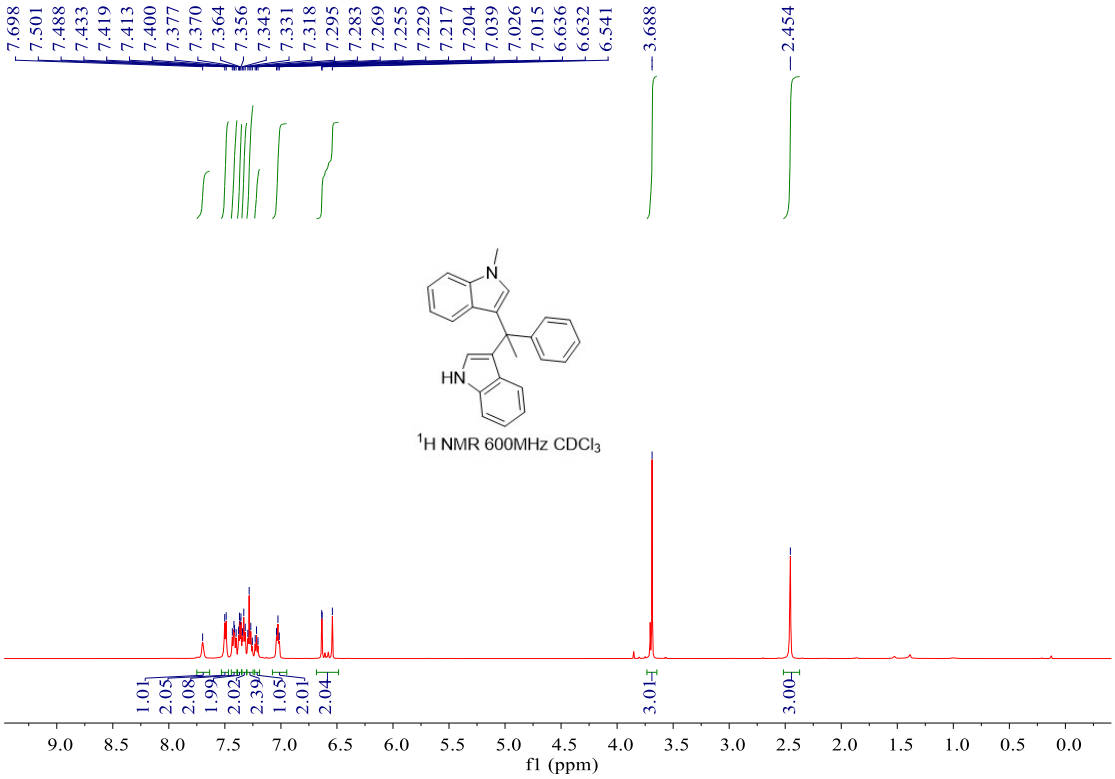


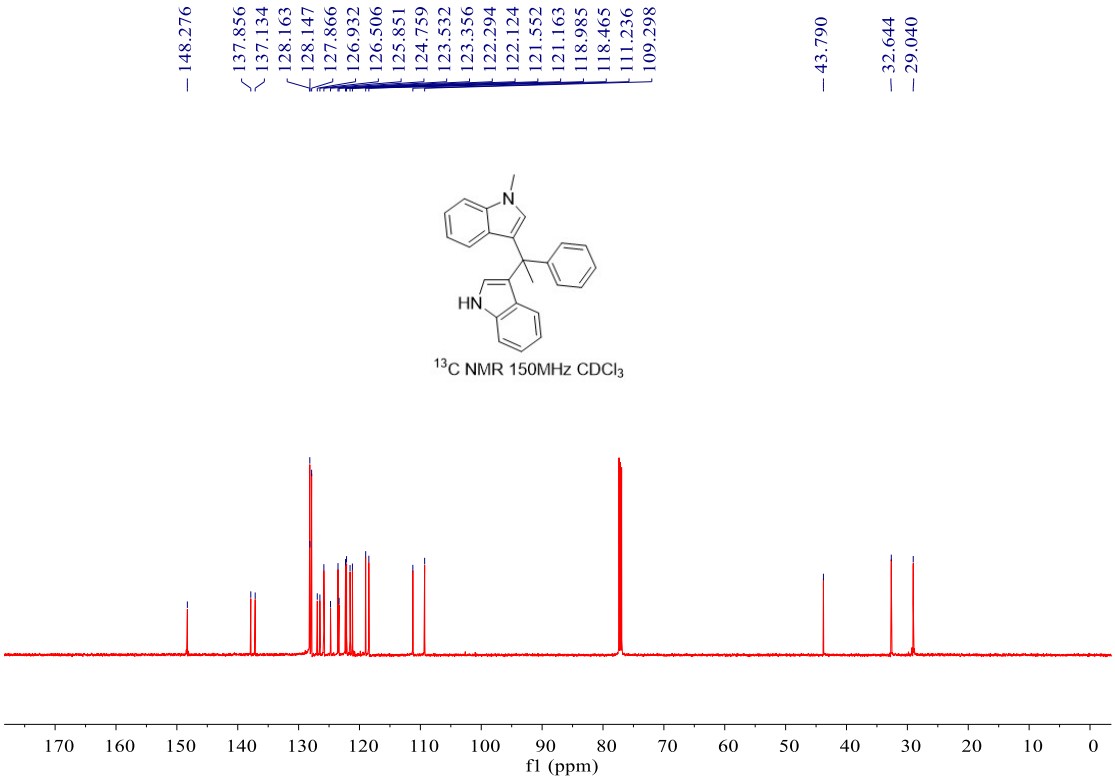
3,3'-(1-(Thiophen-2-yl)ethane-1,1-diyl)bis(1*H*-indole) (3v)



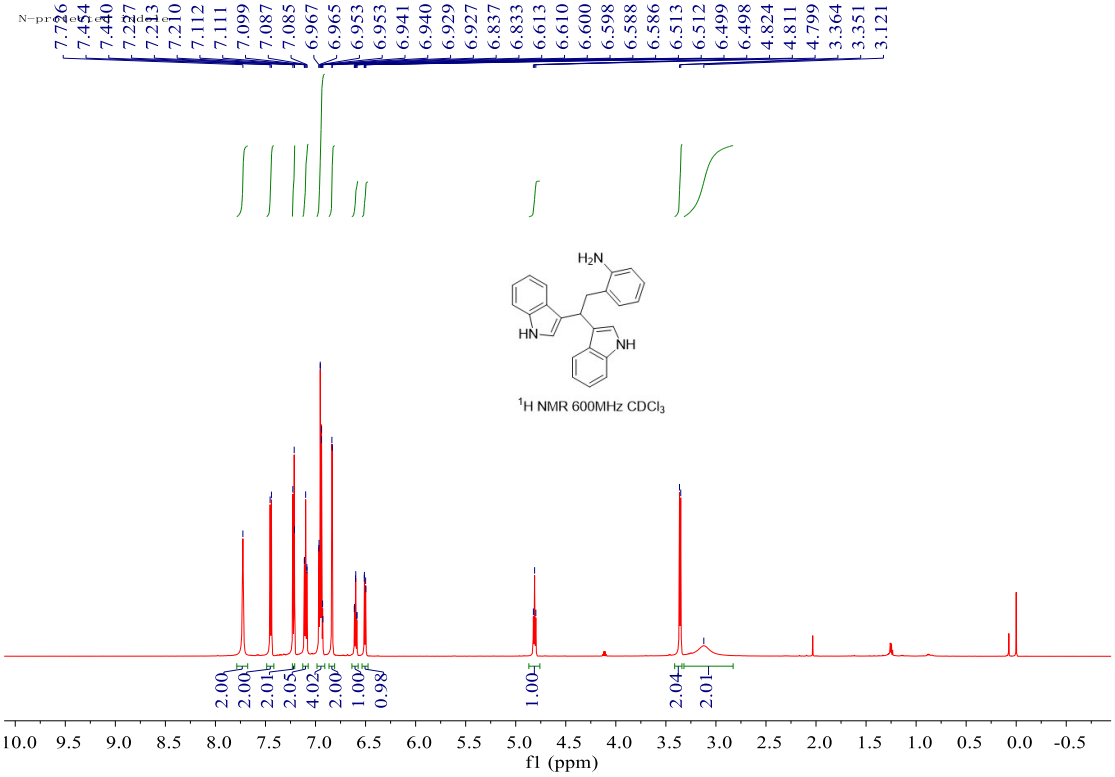


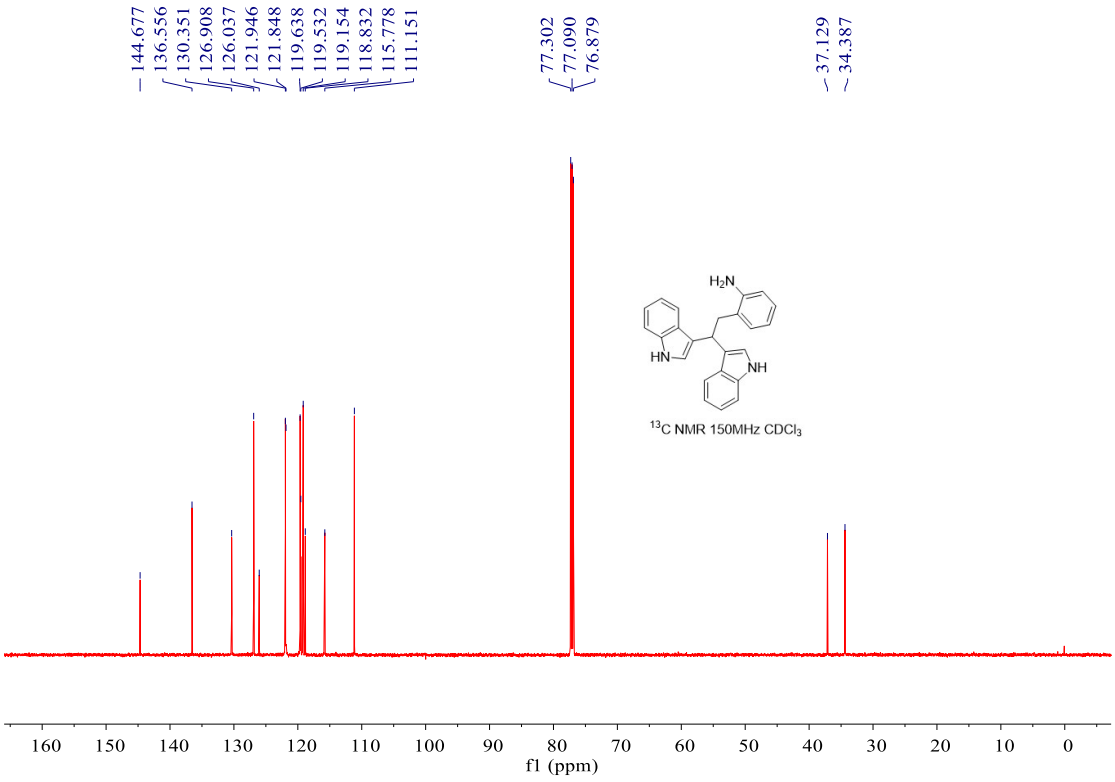
3-(1-(1*H*-Indol-3-yl)-1-phenylethyl)-1-methyl-1*H*-indole (3w)



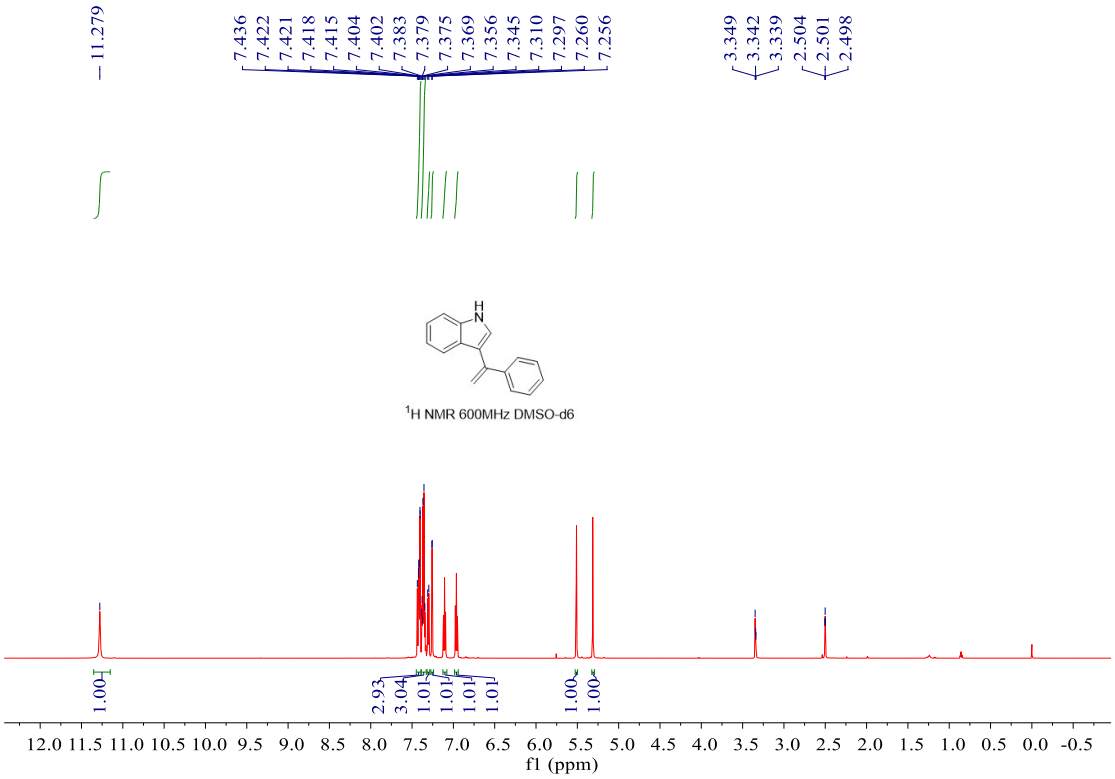


2-(2-(1H-indol-3-yl)-2-phenylethyl)aniline (5a)





3-(1-Phenylvinyl)-1*H*-indole (4a)



VIII. X-ray parameters and structures

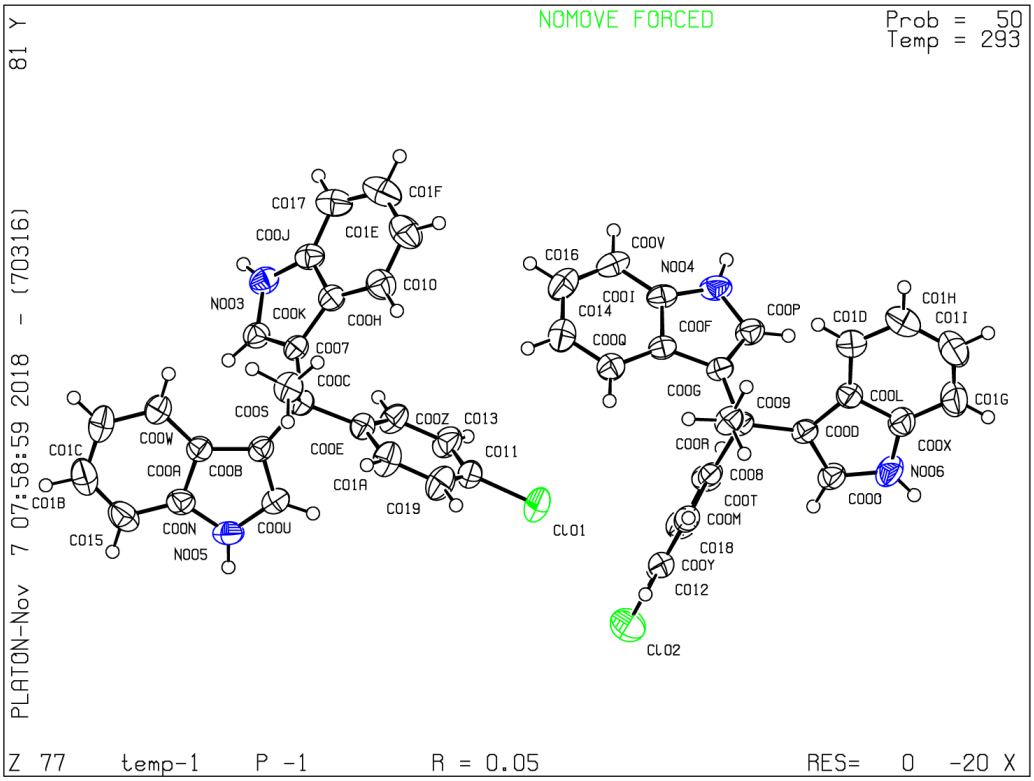


Figure S1 Thermal ellipsoid ORTEP diagram of **3t**

Table S1 Crystal and Structure Refinement Data for 3t

Date	3t
CCDC	**1877500**
Empirical formula	$C_{24}H_{19}ClN_2$
Formula weight	370.86
Temperature/K	293
Crystal system	triclinic
Space group	P-1
a/Å	10.4828(5)
b/Å	13.6099(6)
c/Å	13.9679(5)
α/°	76.703(4)
β/°	79.086(4)
γ/°	80.640(4)
Volume/$Å^3$	1889.45(15)
Z	31
$\rho_{calc}g/cm^3$	1.702
μ/mm^{-1}	1.164
F(000)	961.0
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.318 to 59.002
Index ranges	$-13 \leq h \leq 14$, $-18 \leq k \leq 18$, $-18 \leq l \leq 19$
Reflections collected	30140
Independent reflections	9108 [R_{int} = 0.0393, R_{sigma} = 0.0432]
Data/restraints/parameters	9108/0/489
Goodness-of-fit on F^2	1.028
Final R indexes [I>=2σ (I)]	R_1 = 0.0495, wR_2 = 0.1115
Final R indexes [all data]	R_1 = 0.0868, wR_2 = 0.1329
Largest diff. peak/hole / e $Å^{-3}$	0.20/-0.39