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Supporting Information

Br_2-Catalyzed Regioselective Dehydrative Coupling of Indoles with Acyloins: Direct Synthesis of α-(3-Indolyl) Ketones

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I. General information

Chemicals were all purchased from commercial sources and used without treatment. Thin-layer chromatography (TLC) was carried out using silica gel GF254 plates. Products were purified by column chromatography over silica gel. ^{1}H NMR and ^{13}C NMR spectra were recorded at 25 °C on a Bruker Ascend^{TM} 400 spectrometer in $CDCl_3$/DMSO using TMS as internal standard. The following abbreviations were used to indicate the multiplicity in NMR spectra: s, singlet; d, doublet; t, triplet; q, quartet; quint, quintet; sext, sextet; oct, octet; m, multiplet; bs, broad signal. ^{13}C NMR spectra were acquired on a broad band decoupled mode. High-resolution mass spectra (HRMS) were obtained using a Bruker microTOF II Focus spectrometer (ESI). The key products **3b1**,[1] **3d1**,[1] **5a**,[2] **5b**[3] and **7**[4] are known compounds, and their spectral data match well with literatures.

Optimization of all molecular geometries and vibrational analyses were calculated at M06-2X[5] functions with the def2TZVP[6] or 6-31G(d) basis sets by using Gaussian 09 program.[7] A natural bonding orbital (NBO) analysis for structures was also performed to determine the natural population atomic (NPA) charges by using the NBO 3.1 package implemented in Gaussian 09. The Gibbs free energy changes (ΔG) of formation of different benzyl cations were used to compare their stabilities. Solvent effect at M06-2X/6-31G(d) level was calculated using the solvation model density (SMD) approach.[8] Stationary points were characterized as minima by full vibration frequency calculations (no imaginary frequency). The minimum energy nature of the optimized structures was verified from vibrational frequency analyses at the same level of theory, and the intrinsic reaction coordinate calculations (IRC) were performed to ensure that transition-state structures connect their respective reactants and products.

[1] Y. Li, F. Shi, Q. He, S. You, *Org. Lett.* **2009**, *11*, 3182–3185.
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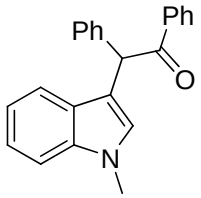
[3] T. P. Pathak, M. S. Sigman, *Org. Lett.* **2011**, *13*, 2774–2777.
[4] A. Berlin, A. Canavesi, *Tetrahedron* **1996**, *52*, 7947–7960.
[5] Y. Zhao, D. G. Truhlar, *Theor. Chem. Acc.* **2008**, *120*, 215–241.
[6] F. Weigend, R. Ahlrichs, *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297–3305.
[7] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, *Gaussian 09*, Gaussian, Inc., Wallingford CT, 2009.
[8] A. V. Marenich, C. J. Cramer, D. G. Truhlar, *J. Phys. Chem. B* **2009**, *113*, 6378–6396.

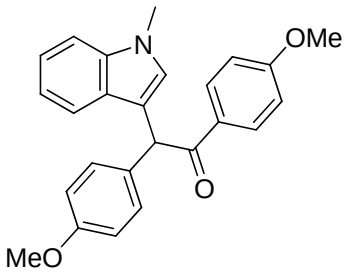
II. General procedure

3a1 as example: To a stirred solution of 1-methyl indole **1a** (66 mg, 0.5 mmol) and benzoin **2a** (117 mg, 0.55 mmol) in MeCN (4.0 mL) was added a solution of Br_2 (0.00077 mL) in MeCN (1.0 mL), and the mixture was stirred for 12 h at 50 °C. After **1a** was consumed, as indicated by TLC, the reaction mixture was quenched with saturated aqueous $Na_2S_2O_3$ (0.2 mL) and water (10.0 mL), and extracted with CH_2Cl_2 three times. The residue obtained after evaporation of the solvent was purified by column chromatography on silica gel (petroleum ether–ethyl acetate = 20:1, v/v) to afford 2-(1-methyl-1*H*-indol-3-yl)-1,2-diphenylethanone **3a1** as a white solid (153 mg, 94% yield).

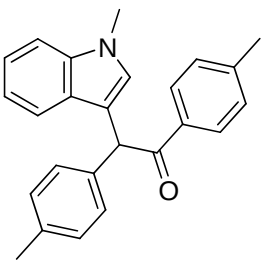
III. Spectral data of all products



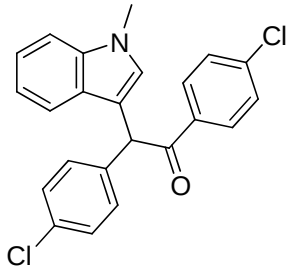
3a1, 2-(1-methyl-1*H*-indol-3-yl)-1,2-diphenylethanone, yellow solid: mp 120-121 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 3.73 (s, 3H), 6.28 (s, 1H), 6.89 (s, 1H), 7.08 (ddd, *J* = 1.0, 7.0, 7.9 Hz, 1H), 7.20-7.25 (m, 2H), 7.28-7.32 (m, 3H), 7.36-7.43 (m, 4H), 7.49-7.54 (m, 2H), 8.04-8.07 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 198.4, 139.2, 137.3, 136.9, 133.0, 129.1, 128.9, 128.7, 128.6, 128.5, 127.1, 122.0, 119.4, 118.9, 112.8, 109.5, 50.6, 32.8; HRMS (ESI-TOF) Calcd for $C_{23}H_{20}NO^+$ ($[M+H]^+$) 326.1539. Found 326.1537.



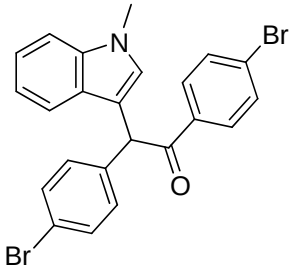
3a2, 1,2-bis(4-methoxyphenyl)-2-(1-methyl-1*H*-indol-3-yl)ethanone, yellow solid: mp 108-110 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 3.72 (s, 3H), 3.76 (s, 3H), 3.83 (s, 3H), 6.18 (s, 1H), 6.82-6.90 (m, 5H), 7.07 (ddd, *J* = 1.0, 7.0, 8.0 Hz, 1H), 7.21 (ddd, *J* = 1.0, 7.0, 8.0 Hz, 1H), 7.27-7.29 (m, 3H), 7.47 (d, *J* = 7.9 Hz, 1H), 8.05 (ddd, *J* = 2.9, 2.0, 9.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 197.2, 163.3, 158.5, 137.2, 131.5, 131.2, 129.9, 129.8, 128.3, 127.0, 121.8, 119.2, 118.9, 113.9, 113.7, 113.4, 109.4, 55.4, 55.2, 49.4, 32.8; HRMS (ESI-TOF) Calcd for $C_{25}H_{24}NO_3^+$ ($[M+H]^+$) 386.1751. Found 386.1754.



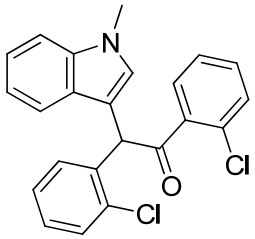
3a3, 2-(1-methyl-1*H*-indol-3-yl)-1,2-di-*p*-tolylethanone, white solid: mp 94-95 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 2.29 (s, 3H), 2.37 (s, 3H), 3.71 (s, 3H), 6.22 (s, 1H), 6.87 (s, 1H), 7.05-7.11 (m, 3H), 7.19-7.29 (m, 6H), 7.48 (d, J = 7.9 Hz, 1H), 7.96 (d, J = 8.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 198.2, 143.7, 137.2, 136.5, 136.2, 134.4, 129.3, 129.2, 129.0, 128.8, 128.4, 127.0, 121.8, 119.2, 118.9, 113.1, 109.4, 50.0, 32.8, 21.6, 21.1; HRMS (ESI-TOF) Calcd for $C_{25}H_{24}NO^+$ ($[M+H]^+$) 354.1852. Found 354.1849.



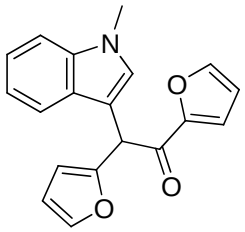
3a4, 1,2-bis(4-chlorophenyl)-2-(1-methyl-1*H*-indol-3-yl)ethanone, white solid: mp 110-112 °C. ^{1}H NMR (400 MHz, DMSO) δ = 3.72 (s, 3H), 6.57 (s, 1H), 7.02 (ddd, J = 0.8, 7.0, 7.9 Hz, 1H), 7.13-7.17 (m, 2H), 7.34-7.40 (m, 5H), 7.54-7.57 (m, 3H), 8.09 (ddd, J = 2.4, 1.9, 8.7 Hz, 2H); ^{13}C NMR (100 MHz, DMSO) δ = 197.0, 138.9, 138.6, 137.2, 135.3, 131.8, 131.4, 131.0, 129.3, 128.9, 128.5, 126.8, 122.0, 119.5, 119.2, 111.7, 110.3, 49.1, 32.9; HRMS (ESI-TOF) Calcd for $C_{23}H_{18}Cl_2NO^+$ ($[M+H]^+$) 394.0760. Found 394.0762.



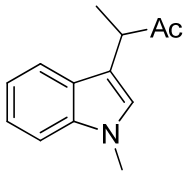
3a5, 1,2-bis(4-bromophenyl)-2-(1-methyl-1*H*-indol-3-yl)ethanone, pale yellow solid: mp 134-135 °C. ^{1}H NMR (400 MHz, DMSO) δ = 3.72 (s, 3H), 6.55 (s, 1H), 7.02 (dd, J = 7.4, 7.5 Hz, 1H), 7.13-7.17 (m, 2H), 7.33 (d, J = 8.4 Hz, 2H), 7.39 (d, J = 8.2 Hz, 1H), 7.49 (d, J = 8.4 Hz, 2H), 7.55 (d, J = 7.9 Hz, 1H), 7.69 (d, J = 8.5 Hz, 2H), 8.01 (d, J = 8.5 Hz, 2H); ^{13}C NMR (100 MHz, DMSO) δ = 197.2, 139.3, 137.2, 135.6, 132.2, 131.8, 131.4, 131.1, 128.9, 127.8, 126.8, 122.1, 120.4, 119.5, 119.2, 111.6, 110.3, 49.1, 32.9; HRMS (ESI-TOF) Calcd for $C_{23}H_{18}Br_2NO^+$ ($[M+H]^+$) 481.9750. Found 481.9756.



3a6, 1,2-bis(2-chlorophenyl)-2-(1-methyl-1*H*-indol-3-yl)ethanone, white solid: mp 142-143 °C. ^{1}H NMR (400 MHz, DMSO) δ = 3.77 (s, 3H), 6.59 (s, 1H), 7.02 (ddd, *J* = 0.8, 7.1, 7.9 Hz, 1H), 7.14-7.19 (m, 2H), 7.23-7.31 (m, 2H), 7.33 (s, 1H), 7.37-7.50 (m, 6H), 7.92 (dd, *J* = 1.6, 7.9 Hz, 1H); ^{13}C NMR (100 MHz, DMSO) δ = 197.8, 137.9, 137.2, 137.0, 133.5, 133.0, 131.4, 131.33, 131.29, 130.0, 129.8, 129.6, 129.3, 127.7, 127.5, 127.2, 122.1, 119.7, 119.0, 110.5, 108.5, 50.9, 33.0; HRMS (ESI-TOF) Calcd for $C_{23}H_{18}Cl_2NO^+$ ($[M+H]^+$) 394.0760. Found 394.0762.

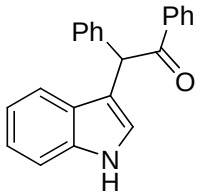


3a7, 1,2-di(furan-2-yl)-2-(1-methyl-1*H*-indol-3-yl)ethanone, yellow solid: mp 124-125 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 3.75 (s, 3H), 6.13 (s, 1H), 6.20 (d, *J* = 3.2 Hz, 1H), 6.31 (dd, *J* = 1.9, 3.2 Hz, 1H), 6.50 (dd, *J* = 1.7, 3.6 Hz, 1H), 7.10-7.14 (m, 2H), 7.23 (ddd, *J* = 1.0, 7.2, 8.1 Hz, 1H), 7.28-7.31 (m, 2H), 7.38 (dd, *J* = 0.6, 1.6 Hz, 1H), 7.57 (d, *J* = 1.1 Hz, 1H), 7.65 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 184.9, 152.3, 151.9, 146.8, 142.1, 137.0, 128.5, 127.0, 121.9, 119.5, 119.1, 118.4, 112.5, 110.4, 109.5, 108.9, 108.4, 44.4, 32.9; HRMS (ESI-TOF) Calcd for $C_{19}H_{16}NO_3^+$ ($[M+H]^+$) 306.1125. Found 306.1127.

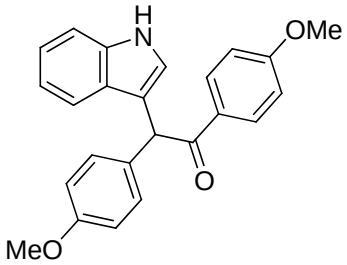


3a8, 3-(1-methyl-1*H*-indol-3-yl)butan-2-one, yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.39 (d, *J* = 7.0 Hz, 3H), 1.98 (s, 3H), 3.65 (s, 3H), 3.90 (q, *J* = 7.0 Hz, 1H), 6.83 (s, 1H), 7.03 (dd, *J* = 7.1, 7.8 Hz, 1H), 7.14 (dd, *J* = 7.3, 7.5 Hz, 1H), 7.20 (d, *J* = 8.2 Hz, 1H), 7.48 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 208.8,

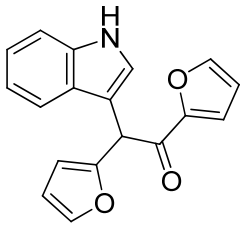
136.1, 125.8, 125.5, 120.9, 118.2, 118.0, 112.9, 108.4, 43.8, 31.7, 26.6, 15.7; HRMS (ESI-TOF) Calcd for $C_{13}H_{16}NO^+$ ([M+H]$^+$) 202.1226. Found 202.1231.



3b1, 2-(1*H*-indol-3-yl)-1,2-diphenylethanone, white semi-solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.27 (s, 1H), 6.89 (s, 1H), 7.07 (dd, J = 6.8, 6.8 Hz, 1H), 7.16 (dd, J = 7.2, 7.0 Hz, 1H), 7.22-7.40 (m, 8H), 7.48 (d, J = 4.7 Hz, 2H), 8.04 (d, J = 5.2 Hz, 2H), 8.15 (bs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 198.6, 138.9, 136.9, 136.5, 133.1, 129.1, 128.9, 128.7, 128.6, 127.1, 126.6, 124.0, 122.4, 119.8, 118.8, 114.3, 111.5, 50.8; HRMS (ESI-TOF) Calcd for $C_{22}H_{18}NO^+$ ([M+H]$^+$) 312.1383. Found 312.1387.

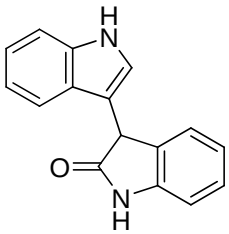


3b2, 2-(1*H*-indol-3-yl)-1,2-bis(4-methoxyphenyl)ethanone, white solid: mp 171-173 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 3.75 (s, 3H), 3.82 (s, 3H), 6.17 (s, 1H), 6.83 (ddd, J = 3.0, 2.0, 8.7 Hz, 2H), 6.87 (ddd, J = 2.9, 2.0, 9.0 Hz, 2H), 6.97 (d, J = 1.5 Hz, 1H), 7.07 (ddd, J = 0.9, 7.1, 8.0 Hz, 1H), 7.17 (ddd, J = 1.0, 7.1, 8.0 Hz, 1H), 7.27 (ddd, J = 3.0, 2.0, 8.7 Hz, 2H), 7.33 (d, J = 8.2 Hz, 1H), 7.47 (d, J = 8.0 Hz, 1H), 8.04 (ddd, J = 2.9, 2.0, 9.0 Hz, 2H), 8.09 (bs, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 197.3, 163.4, 158.6, 136.4, 131.3, 131.2, 130.0, 129.8, 126.6, 123.7, 122.3, 119.7, 118.8, 115.0, 114.0, 113.8, 111.3, 55.5, 55.2, 49.5; HRMS (ESI-TOF) Calcd for $C_{24}H_{22}NO_3^+$ ([M+H]$^+$) 372.1594. Found 372.1596.

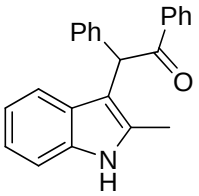


3b3, 1,2-di(furan-2-yl)-2-(1*H*-indol-3-yl)ethanone, dark brown semi-solid. ^{1}H NMR

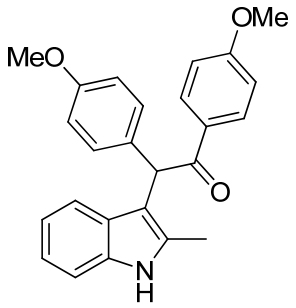
(400 MHz, $CDCl_3$) δ = 6.01 (s, 1H), 6.06 (d, J = 3.2 Hz, 1H), 6.16 (dd, J = 1.8, 2.9 Hz, 1H), 6.29 (dd, J = 1.5, 3.4 Hz, 1H), 6.97-7.06 (m, 3H), 7.11-7.16 (m, 2H), 7.23 (d, J = 0.7 Hz, 1H), 7.37 (d, J = 0.7 Hz, 1H), 7.53 (d, J = 7.7 Hz, 1H), 8.35 (bs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 184.1, 151.1, 150.7, 145.9, 141.1, 135.2, 125.4, 123.1, 121.2, 118.8, 117.8, 117.7, 111.4, 110.5, 109.4, 109.1, 107.6, 43.7; HRMS (ESI-TOF) Calcd for $C_{18}H_{14}NO_3^+$ ($[M+H]^+$) 292.0968. Found 292.0970.



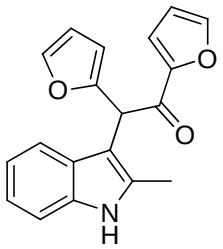
3c, 3-(1*H*-indol-3-yl)indolin-2-one, brown solid: mp 122-123 °C. ^{1}H NMR (400 MHz, DMSO) δ = 4.91 (s, 1H), 6.84-6.95 (m, 3H), 7.01-7.06 (m, 3H), 7.21 (dd, J = 7.1, 6.7 Hz, 1H), 7.28 (s, 1H), 7.37 (d, J = 7.8 Hz, 1H), 10.56 (bs, 1H), 11.03 (bs, 1H); ^{13}C NMR (100 MHz, DMSO) δ = 178.2, 143.0, 137.0, 130.9, 128.3, 126.5, 124.9, 124.9, 121.9, 121.6, 119.0, 119.0, 112.1, 110.5, 109.7, 44.9; HRMS (ESI-TOF) Calcd for $C_{16}H_{13}N_2O^+$ ($[M+H]^+$) 249.1022. Found 249.1017.



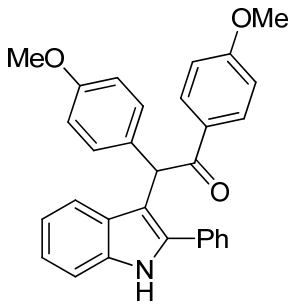
3d1, 2-(2-methyl-1*H*-indol-3-yl)-1,2-diphenylethanone, white crystal: 153-154 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 2.20 (s, 3H), 6.10 (s, 1H), 6.94-7.03 (m, 2H), 7.11-7.24 (m, 8H), 7.36 (dd, J = 7.4, 7.3 Hz, 1H), 7.44 (d, J = 7.7 Hz, 1H), 7.81 (bs, 1H), 7.91 (d, J = 7.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 197.7, 138.2, 136.1, 134.2, 131.8, 131.7, 128.1, 127.5, 127.4, 127.2, 127.0, 125.7, 120.3, 118.8, 117.6, 109.3, 107.5, 49.7, 11.4; HRMS (ESI-TOF) Calcd for $C_{23}H_{20}NO^+$ ($[M+H]^+$) 326.1539. Found 326.1533.



3d2, 1,2-bis(4-methoxyphenyl)-2-(2-methyl-1*H*-indol-3-yl)ethanone, orange solid: mp 138-139 °C (dec.). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 2.32 (s, 3H), 3.76 (s, 3H), 3.79 (s, 3H), 6.08 (s, 1H), 6.79-6.84 (m, 4H), 7.02-7.16 (m, 4H), 7.25 (d, J = 8.0 Hz, 1H), 7.51 (d, J = 7.9 Hz, 1H), 7.86 (bs, 1H), 7.97 (ddd, J = 2.8, 2.0, 9.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 197.6, 163.2, 158.3, 135.2, 132.5, 131.7, 130.9, 130.1, 130.1, 128.1, 121.3, 119.8, 118.7, 113.7, 113.6, 110.3, 109.4, 55.4, 55.2, 49.7, 12.5; HRMS (ESI-TOF) Calcd for $C_{25}H_{24}NO_3^+$ ($[M+H]^+$) 386.1751. Found 386.1753.

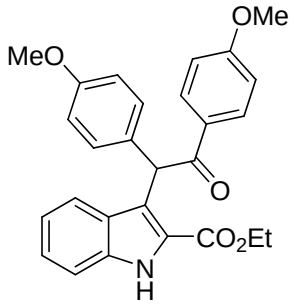


3d3, 1,2-di(furan-2-yl)-2-(2-methyl-1*H*-indol-3-yl)ethanone, yellow solid: mp 184-185 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 2.49 (s, 3H), 6.04 (s, 1H), 6.15 (d, J = 3.2 Hz, 1H), 6.30 (dd, J = 1.8, 3.2 Hz, 1H), 6.43 (dd, J = 1.7, 3.6 Hz, 1H), 7.06-7.13 (m, 2H), 7.16 (dd, J = 0.6, 3.6 Hz, 1H), 7.25-7.27 (m, 1H), 7.39 (d, J = 1.4 Hz, 1H), 7.49 (dd, J = 0.6, 1.6 Hz, 1H), 7.65 (dd, J = 1.3, 7.5 Hz, 1H), 7.97 (bs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 184.4, 152.2, 151.9, 146.2, 141.9, 135.1, 133.6, 127.7, 121.4, 119.9, 119.2, 117.6, 112.3, 110.2, 108.8, 105.7, 44.6, 12.3; HRMS (ESI-TOF) Calcd for $C_{19}H_{16}NO_3^+$ ($[M+H]^+$) 306.1125. Found 306.1120.

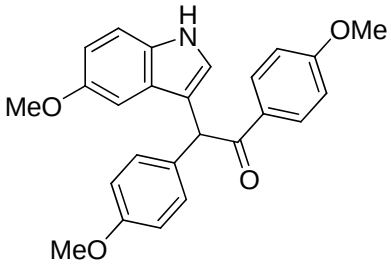


3e, 1,2-bis(4-methoxyphenyl)-2-(2-phenyl-1*H*-indol-3-yl)ethanone, yellow solid: mp

228-230 °C. ^{1}H NMR (400 MHz, DMSO) δ = 3.70 (s, 3H), 3.74 (s, 3H), 6.15 (s, 1H), 6.73-6.77 (m, 2H), 6.86-6.93 (m, 3H), 7.05 (ddd, J = 1.0, 7.0, 7.1 Hz, 1H), 7.14-7.17 (m, 2H), 7.32-7.35 (m, 2H), 7.45-7.50 (m, 3H), 7.53-7.59 (m, 4H), 11.53 (bs, 1H); ^{13}C NMR (100 MHz, DMSO) δ = 196.8, 163.1, 158.3, 136.7, 136.5, 132.7, 132.6, 130.7, 130.6, 129.6, 129.4, 128.64, 128.60, 127.9, 121.9, 120.4, 119.8, 113.98, 113.95, 111.9, 108.8, 55.8, 55.4, 50.2; HRMS (ESI-TOF) Calcd for $C_{30}H_{26}NO_3^+$ ($[M+H]^+$) 448.1907. Found 448.1908.

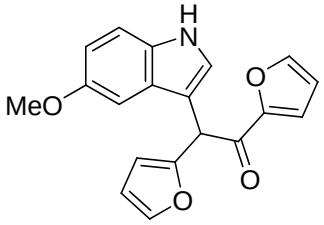


3f, ethyl 3-(1,2-bis(4-methoxyphenyl)-2-oxoethyl)-1*H*-indole-2-carboxylate, pink solid: mp 138-139 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.38 (t, J = 7.0 Hz, 3H), 3.75 (s, 3H), 3.79 (s, 3H), 4.38-4.46 (m, 2H), 6.82 (dd, J = 3.8, 8.5 Hz, 4H), 7.01 (dd, J = 7.0, 7.8 Hz, 1H), 7.16 (s, 1H), 7.24 (d, J = 8.1 Hz, 3H), 7.30 (d, J = 8.2 Hz, 1H), 7.55 (d, J = 8.0 Hz, 1H), 8.07 (d, J = 8.7 Hz, 2H), 8.91 (bs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 197.5, 163.2, 161.9, 158.3, 136.1, 131.5, 131.1, 130.3, 130.0, 127.2, 125.5, 123.1, 123.1, 121.6, 120.7, 113.8, 113.7, 111.8, 61.1, 55.4, 55.2, 49.8, 14.4; HRMS (ESI-TOF) Calcd for $C_{27}H_{26}NO_5^+$ ($[M+H]^+$) 444.1805. Found 444.1803.

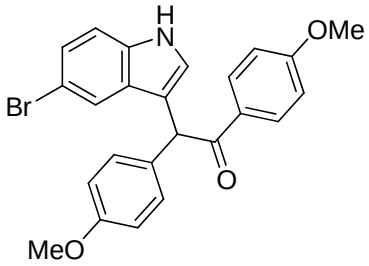


3g1, 2-(5-methoxy-1*H*-indol-3-yl)-1,2-bis(4-methoxyphenyl)ethanone, white solid: mp 157-158 °C. ^{1}H NMR (400 MHz, DMSO) δ = 3.69 (s, 3H), 3.70 (s, 3H), 3.79 (s, 3H), 6.36 (s, 1H), 6.72 (dd, J = 2.4, 8.8 Hz, 1H), 6.84 (d, J = 8.7 Hz, 2H), 6.99 (d, J = 9.0 Hz, 2H), 7.04 (d, J = 2.4 Hz, 1H), 7.08 (d, J = 2.4 Hz, 1H), 7.23 (d, J = 8.7 Hz, 1H), 7.31 (d, J = 8.7 Hz, 2H), 8.09 (d, J = 8.9 Hz, 2H), 10.82 (d, J = 2.0 Hz, 1H); ^{13}C NMR (100 MHz, DMSO) δ = 197.2, 163.4, 158.3, 153.6, 132.4, 131.8, 131.4, 130.4,

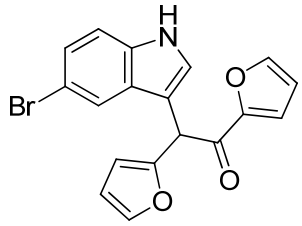
129.7, 127.1, 125.0, 114.3, 113.9, 113.6, 112.6, 111.4, 101.3, 55.9, 55.8, 55.4, 48.6; HRMS (ESI-TOF) Calcd for $C_{25}H_{24}NO_4^+$ ([M+H]$^+$) 402.1700. Found 402.1703.



3g2, 1,2-di(furan-2-yl)-2-(5-methoxy-1*H*-indol-3-yl)ethanone, brown semi-solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 3.82 (s, 3H), 6.07 (s, 1H), 6.19 (s, 1H), 6.31 (s, 1H), 6.49 (s, 1H), 6.85 (d, J = 8.0 Hz, 1H), 7.08 (s, 1H), 7.21-7.26 (m, 3H), 7.38 (s, 1H), 7.56 (s, 1H), 8.16 (bs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 184.8, 154.3, 152.1, 151.9, 146.7, 142.1, 131.4, 127.0, 124.6, 118.4, 112.6, 112.5, 112.1, 110.5, 110.3, 108.6, 101.0, 55.9, 44.8; HRMS (ESI-TOF) Calcd for $C_{19}H_{16}NO_4^+$ ([M+H]$^+$) 322.1074. Found 322.1078.

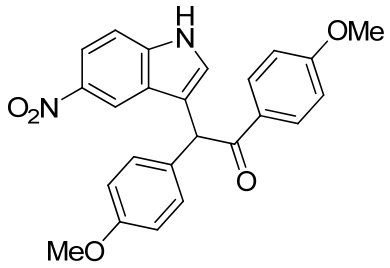


3h1, 2-(5-bromo-1*H*-indol-3-yl)-1,2-bis(4-methoxyphenyl)ethanone, white solid: 212-213 °C. ^{1}H NMR (400 MHz, DMSO) δ = 3.69 (s, 3H), 3.81 (s, 3H), 6.44 (s, 1H), 6.85 (d, J = 8.7 Hz, 2H), 7.00 (d, J = 8.9 Hz, 2H), 7.15-7.20 (m, 2H), 7.28-7.32 (m, 3H), 7.72 (d, J = 1.7 Hz, 1H), 8.11 (d, J = 8.9 Hz, 2H), 11.19 (bs, 1H); ^{13}C NMR (100 MHz, DMSO) δ = 197.0, 163.5, 158.4, 135.3, 132.2, 131.5, 130.3, 129.5, 128.6, 126.0, 124.1, 121.5, 114.3, 114.08, 114.00, 113.9, 111.7, 55.9, 55.4, 48.2; HRMS (ESI-TOF) Calcd for $C_{24}H_{21}BrNO_3^+$ ([M+H]$^+$) 450.0699. Found 450.0692.

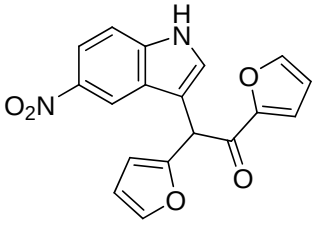


3h2, 2-(5-bromo-1*H*-indol-3-yl)-1,2-di(furan-2-yl)ethanone, dark brown semi-solid.

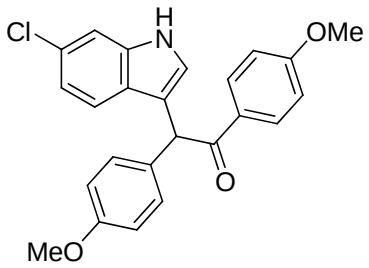
^{1}H NMR (400 MHz, $CDCl_3$) δ = 5.99 (s, 1H), 6.09 (d, J = 3.1 Hz, 1H), 6.22 (dd, J = 1.8, 2.8 Hz, 1H), 6.43 (dd, J = 1.5, 3.4 Hz, 1H), 7.08-7.18 (m, 4H), 7.21 (d, J = 3.5 Hz, 1H), 7.29 (d, J = 0.6 Hz, 1H), 7.50 (s, 1H), 7.67 (s, 1H), 8.38 (bs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 183.7, 150.6, 150.6, 146.0, 141.3, 133.8, 127.2, 124.2, 120.4, 117.8, 112.2, 111.9, 111.6, 109.5, 109.2, 107.5, 43.3; HRMS (ESI-TOF) Calcd for $C_{18}H_{13}BrNO_3^+$ ($[M+H]^+$) 370.0073. Found 370.0076.



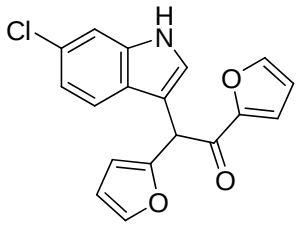
3i1, 1,2-bis(4-methoxyphenyl)-2-(5-nitro-1*H*-indol-3-yl)ethanone, yellow solid: mp 169-170 °C. ^{1}H NMR (400 MHz, DMSO) δ = 3.69 (s, 3H), 3.81 (s, 3H), 6.61 (s, 1H), 6.87 (ddd, J = 3.0, 2.0, 8.8 Hz, 2H), 7.01 (ddd, J = 2.9, 2.0, 9.0 Hz, 2H), 7.33 (ddd, J = 2.9, 2.0, 8.8 Hz, 2H), 7.40 (d, J = 2.1 Hz, 1H), 7.52 (d, J = 9.0 Hz, 1H), 7.98 (dd, J = 2.3, 9.0 Hz, 1H), 8.15 (ddd, J = 2.9, 2.0, 9.0 Hz, 2H), 8.57 (d, J = 2.2 Hz, 1H), 11.73 (bs, 1H); ^{13}C NMR (100 MHz, DMSO) δ = 196.9, 163.6, 158.5, 140.8, 139.8, 131.9, 131.7, 130.3, 129.3, 128.4, 126.2, 117.2, 117.1, 116.7, 114.4, 114.3, 112.5, 56.0, 55.4, 48.1; HRMS (ESI-TOF) Calcd for $C_{24}H_{21}N_2O_5^+$ ($[M+H]^+$) 417.1445. Found 417.1449.



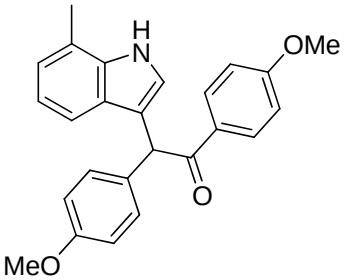
3i2, 1,2-di(furan-2-yl)-2-(5-nitro-1*H*-indol-3-yl)ethanone, orange semi-solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.20 (s, 1H), 6.24 (d, J = 3.2 Hz, 1H), 6.33 (dd, J = 1.8, 3.2 Hz, 1H), 6.57 (dd, J = 1.7, 3.6 Hz, 1H), 7.34-7.39 (m, 4H), 7.64 (dd, J = 0.6, 1.6 Hz, 1H), 8.06 (dd, J = 2.2, 9.0 Hz, 1H), 8.59 (d, J = 2.2 Hz, 1H), 9.03 (bs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 184.5, 151.5, 150.9, 147.4, 142.6, 141.8, 139.2, 127.3, 125.9, 119.3, 117.9, 116.2, 113.1, 112.9, 111.6, 110.7, 108.6, 44.1; HRMS (ESI-TOF) Calcd for $C_{18}H_{13}N_2O_5^+$ ($[M+H]^+$) 337.0819. Found 337.0823.



3j1, 2-(6-chloro-1*H*-indol-3-yl)-1,2-bis(4-methoxyphenyl)ethanone, pale red solid: mp 124-125 °C. ^{1}H NMR (400 MHz, DMSO) δ = 3.69 (s, 3H), 3.79 (s, 3H), 6.40 (s, 1H), 6.85 (d, J = 8.7 Hz, 2H), 6.96-7.01 (m, 3H), 7.14 (d, J = 2.3 Hz, 1H), 7.29 (d, J = 8.6 Hz, 2H), 7.40 (d, J = 1.8 Hz, 1H), 7.49 (d, J = 8.5 Hz, 1H), 8.09 (d, J = 8.9 Hz, 2H), 11.13 (bs, 1H); ^{13}C NMR (100 MHz, DMSO) δ = 197.1, 163.5, 158.4, 137.0, 132.1, 131.5, 130.4, 129.5, 126.4, 125.6, 125.6, 120.6, 119.4, 114.6, 114.4, 114.1, 111.6, 56.0, 55.4, 48.5; HRMS (ESI-TOF) Calcd for $C_{24}H_{21}ClNO_3^+$ ($[M+H]^+$) 406.1204. Found 406.1201.

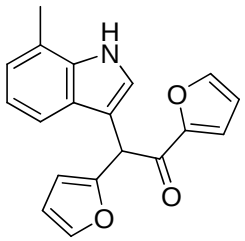


3j2, 2-(6-chloro-1*H*-indol-3-yl)-1,2-di(furan-2-yl)ethanone, yellow semi-solid. ^{1}H NMR (400 MHz, DMSO) δ = 6.16 (s, 1H), 6.27 (s, 1H), 6.38 (s, 1H), 6.70 (d, J = 1.6 Hz, 1H), 7.03 (d, J = 8.3 Hz, 1H), 7.44 (s, 2H), 7.59 (s, 1H), 7.63 (d, J = 8.4 Hz, 1H), 7.74 (d, J = 2.9 Hz, 1H), 7.99 (s, 1H), 11.30 (bs, 1H); ^{13}C NMR (100 MHz, DMSO) δ = 184.4, 152.8, 151.2, 149.0, 142.9, 137.1, 126.6, 126.5, 125.4, 121.0, 120.6, 119.7, 113.2, 111.8, 110.9, 110.0, 108.6, 44.7; HRMS (ESI-TOF) Calcd for $C_{18}H_{13}ClNO_3^+$ ($[M+H]^+$) 326.0578. Found 326.0572.

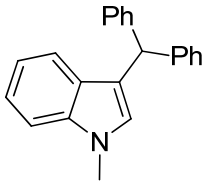


3k1, 1,2-bis(4-methoxyphenyl)-2-(7-methyl-1*H*-indol-3-yl)ethanone, white solid: 70-71 °C (dec.). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 2.46 (s, 3H), 3.76 (s, 3H), 3.83 (s,

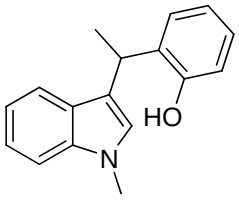
3H), 6.17 (s, 1H), 6.81-6.89 (m, 4H), 6.98-7.03 (m, 3H), 7.25-7.28 (m, 2H), 7.34 (dd, J = 2.1, 6.7 Hz, 1H), 8.04 (d, J = 8.9 Hz, 2H), 8.07 (bs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 197.2, 163.3, 158.6, 136.0, 131.4, 131.2, 130.0, 129.9, 126.2, 123.3, 122.9, 120.4, 120.0, 116.6, 115.7, 113.9, 113.8, 55.4, 55.2, 49.6, 16.6; HRMS (ESI-TOF) Calcd for $C_{25}H_{24}NO_3^+$ ($[M+H]^+$) 386.1751. Found 386.1752.



3k2, 1,2-di(furan-2-yl)-2-(7-methyl-1*H*-indol-3-yl)ethanone, dark brown semi-solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 2.30 (s, 3H), 6.02 (s, 1H), 6.07 (d, J = 2.9 Hz, 1H), 6.18 (s, 1H), 6.33 (dd, J = 1.4, 3.3 Hz, 1H), 6.88 (d, J = 7.0 Hz, 1H), 6.94 (dd, J = 7.7, 7.3 Hz, 1H), 7.07 (d, J = 2.0 Hz, 1H), 7.15 (d, J = 3.4 Hz, 1H), 7.25 (s, 1H), 7.40 (d, J = 7.6 Hz, 1H), 7.41 (s, 1H), 8.23 (bs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 184.0, 151.2, 150.8, 145.8, 141.1, 134.7, 125.0, 122.7, 121.8, 119.7, 119.0, 117.5, 115.5, 111.4, 109.8, 109.4, 107.5, 43.7, 15.4; HRMS (ESI-TOF) Calcd for $C_{19}H_{16}NO_3^+$ ($[M+H]^+$) 306.1125. Found 306.1127.

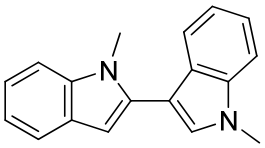


5a, 3-benzhydryl-1-methyl-1*H*-indole, white crystal: 147-148 °C. ^{1}H NMR (400 MHz, DMSO) δ = 3.70 (s, 3H), 5.69 (s, 1H), 6.71 (s, 1H), 6.90 (dd, J = 6.9, 6.9 Hz, 1H), 7.12 (dd, J = 7.3, 7.3 Hz, 2H), 7.18-7.31 (m, 10H), 7.39 (d, J = 7.8 Hz, 1H); ^{13}C NMR (100 MHz, DMSO) δ = 144.7, 137.6, 129.1, 128.9, 128.7, 127.3, 126.6, 121.7, 119.7, 118.9, 117.6, 110.1, 48.5, 32.7; HRMS (ESI-TOF) Calcd for $C_{22}H_{20}N^+$ ($[M+H]^+$) 298.1590. Found 298.1592.



5b, 2-(1-(1-methyl-1*H*-indol-3-yl)ethyl)phenol, yellow oil. ^{1}H NMR (400 MHz,

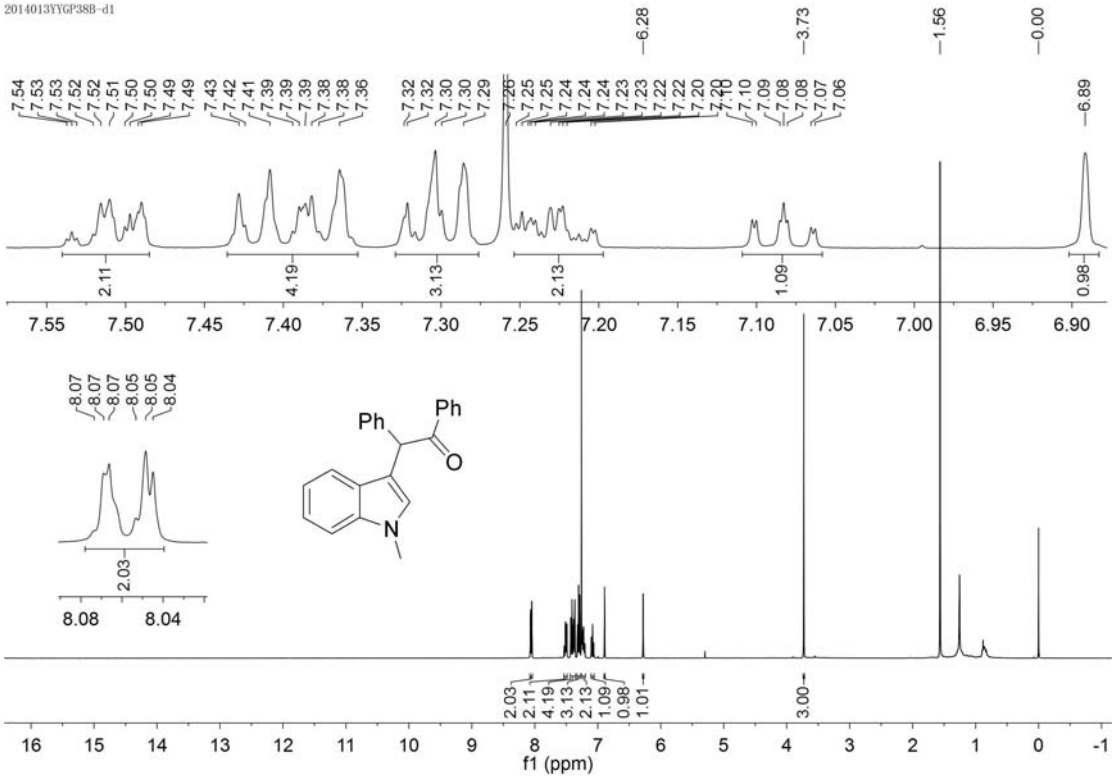
$CDCl_3$) δ = 1.71 (d, J = 7.2 Hz, 3H), 3.72 (s, 3H), 4.50 (q, J = 7.1 Hz, 1H), 5.20 (s, 1H), 6.75 (dd, J = 1.1, 8.0 Hz, 1H), 6.88 (s, 1H), 6.92 (ddd, J = 1.2, 7.5, 7.4 Hz, 1H), 7.00 (ddd, J = 0.9, 7.0, 7.0 Hz, 1H), 7.12 (ddd, J = 1.6, 7.8, 7.6 Hz, 1H), 7.18-7.22 (m, 1H), 7.26-7.30 (m, 2H), 7.37 (d, J = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 154.2, 137.8, 131.6, 128.3, 127.6, 127.1, 126.1, 122.2, 120.8, 119.8, 119.2, 117.8, 116.4, 109.4, 32.8, 32.2, 20.5; HRMS (ESI-TOF) Calcd for $C_{17}H_{18}NO^+$ ($[M+H]^+$) 252.1383. Found 252.1382.

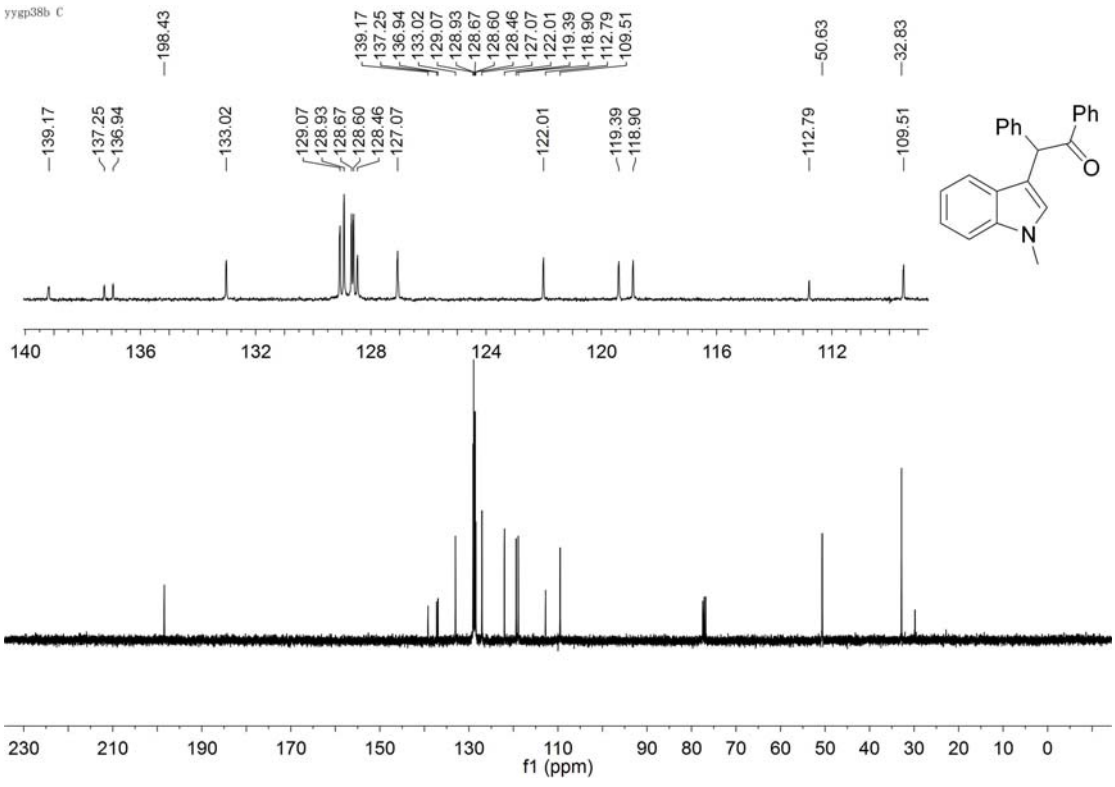


7, 1,1'-dimethyl-1*H*,1'*H*-2,3'-biindole, white solid: 130-131 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 3.76 (s, 3H), 3.89 (s, 3H), 6.62 (s, 1H), 7.13-7.23 (m, 4H), 7.32 (dd, J = 7.5, 6.8 Hz, 1H), 7.37-7.42 (m, 2H), 7.64 (d, J = 7.5 Hz, 1H), 7.70 (d, J = 7.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 138.0, 137.0, 135.1, 128.4, 127.7, 122.4, 121.0, 120.4, 120.2, 120.0, 119.6, 109.6, 109.4, 107.4, 101.4, 33.0, 31.0; HRMS (ESI-TOF) Calcd for $C_{18}H_{17}N_2^+$ ($[M+H]^+$) 261.1386. Found 261.1401.

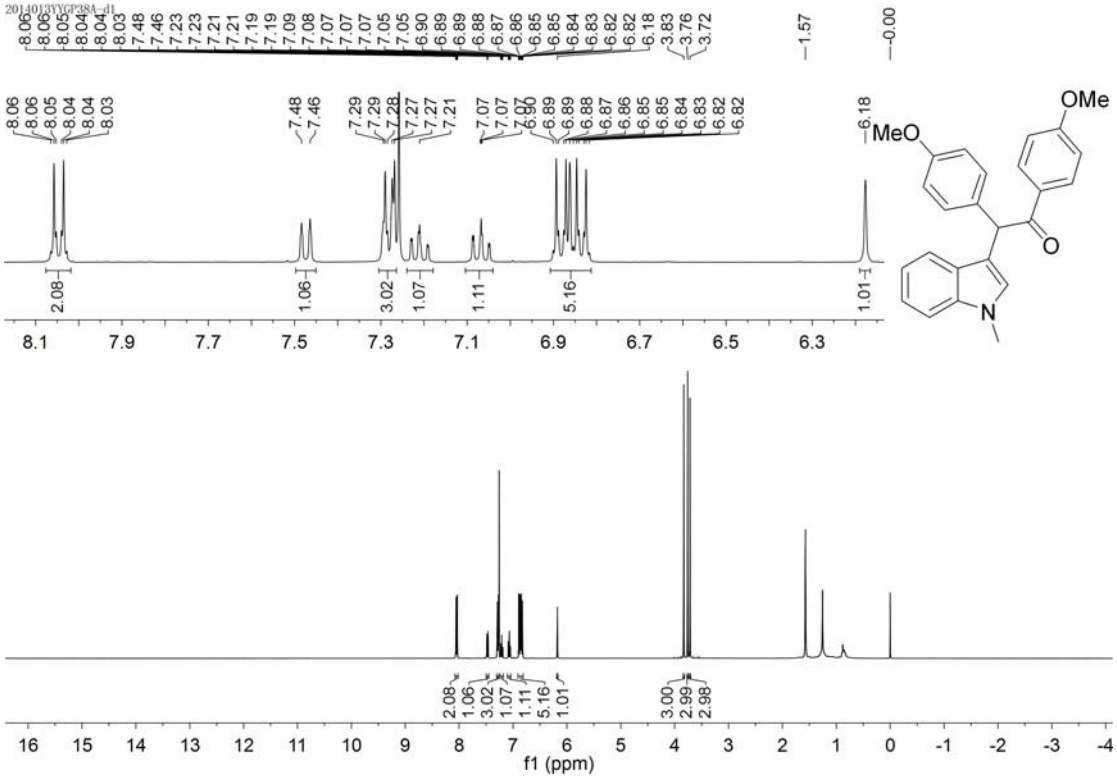
IV. Copies of NMR spectra for all products

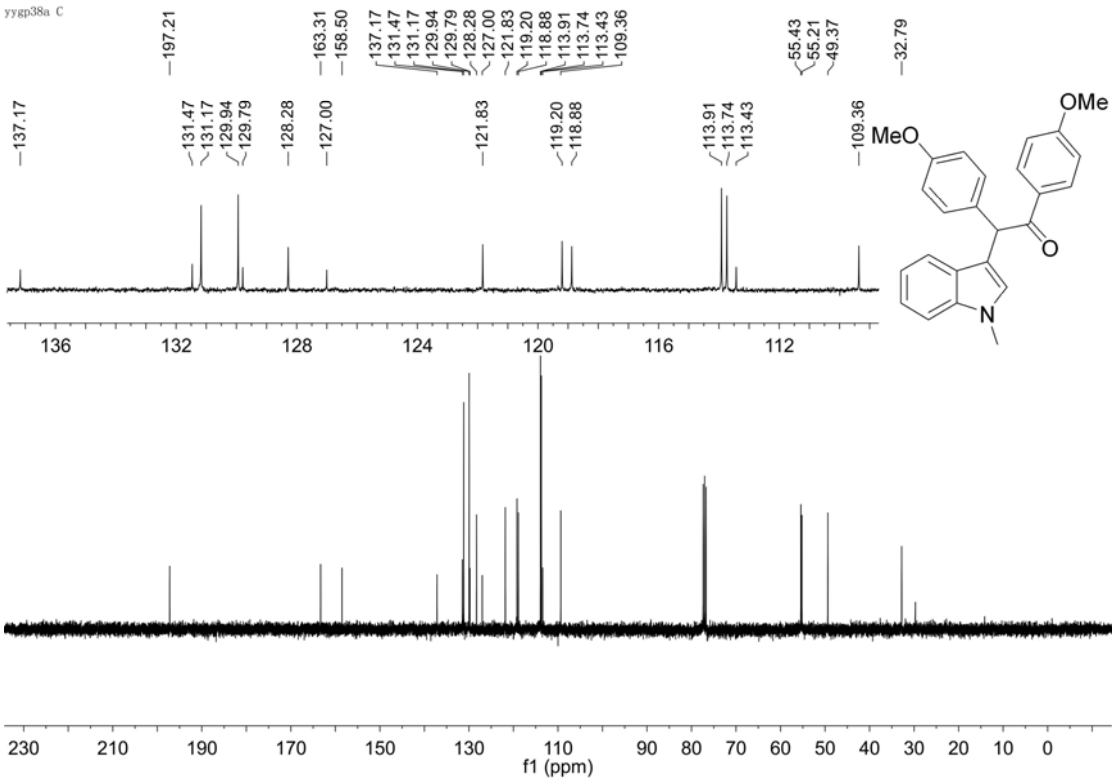
3a1



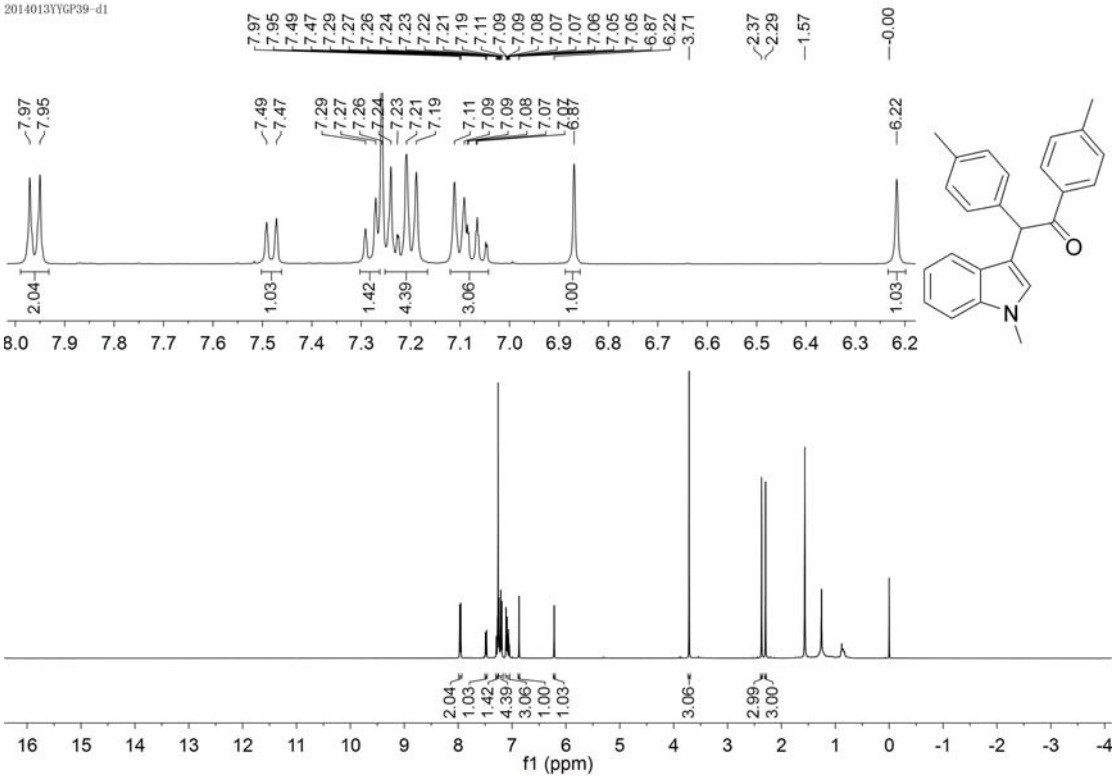


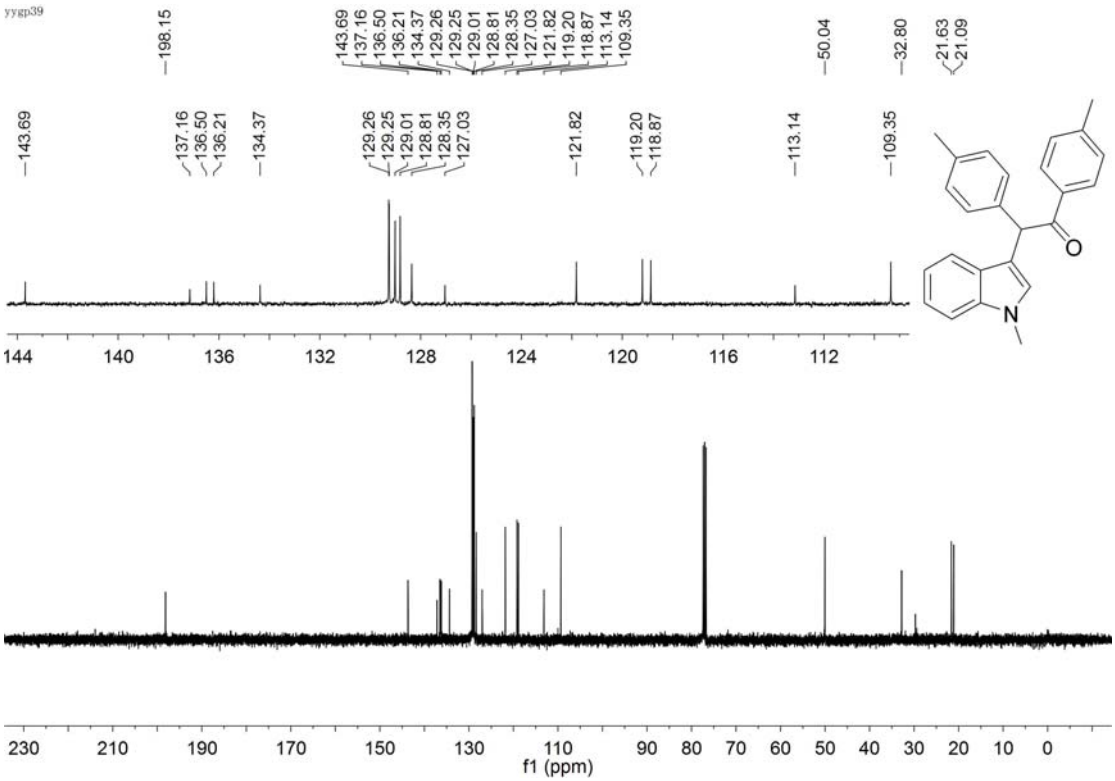
3a2



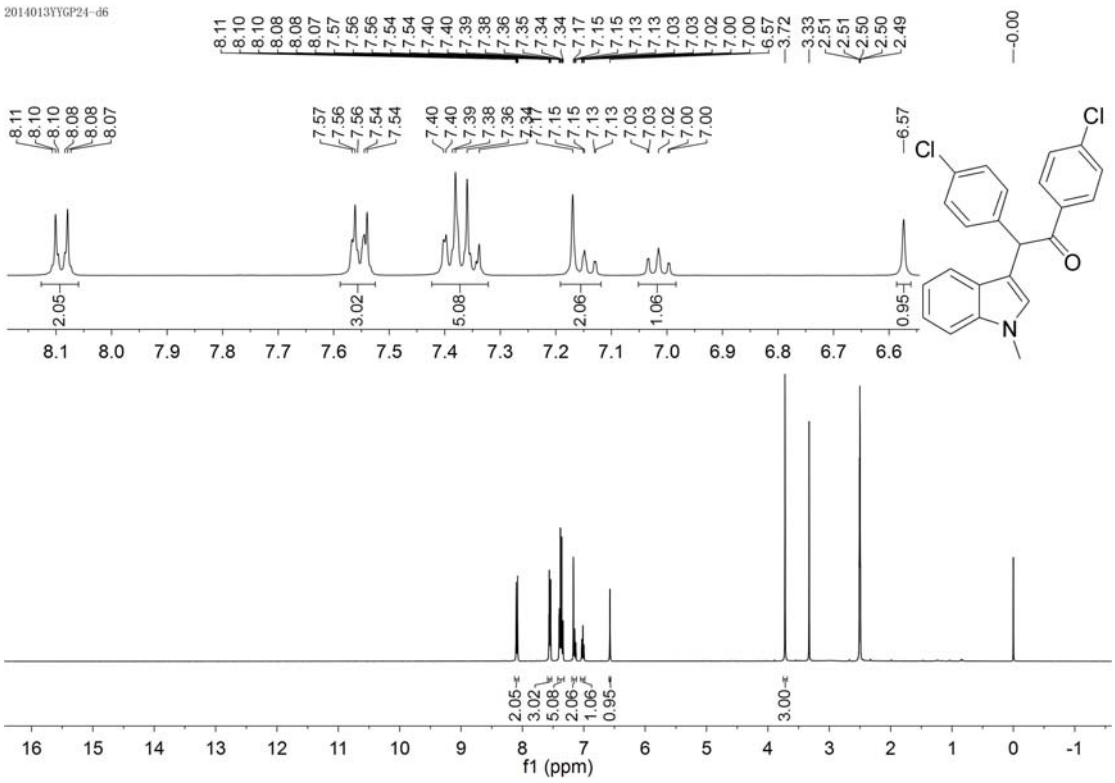


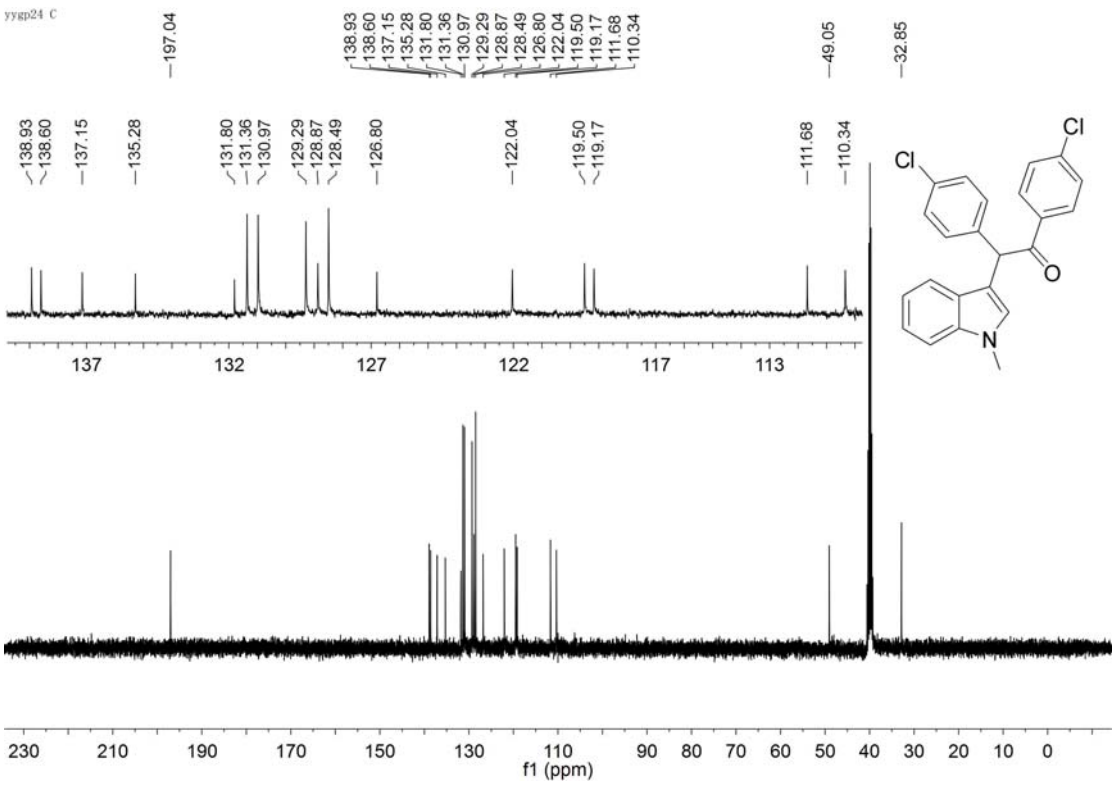
3a3



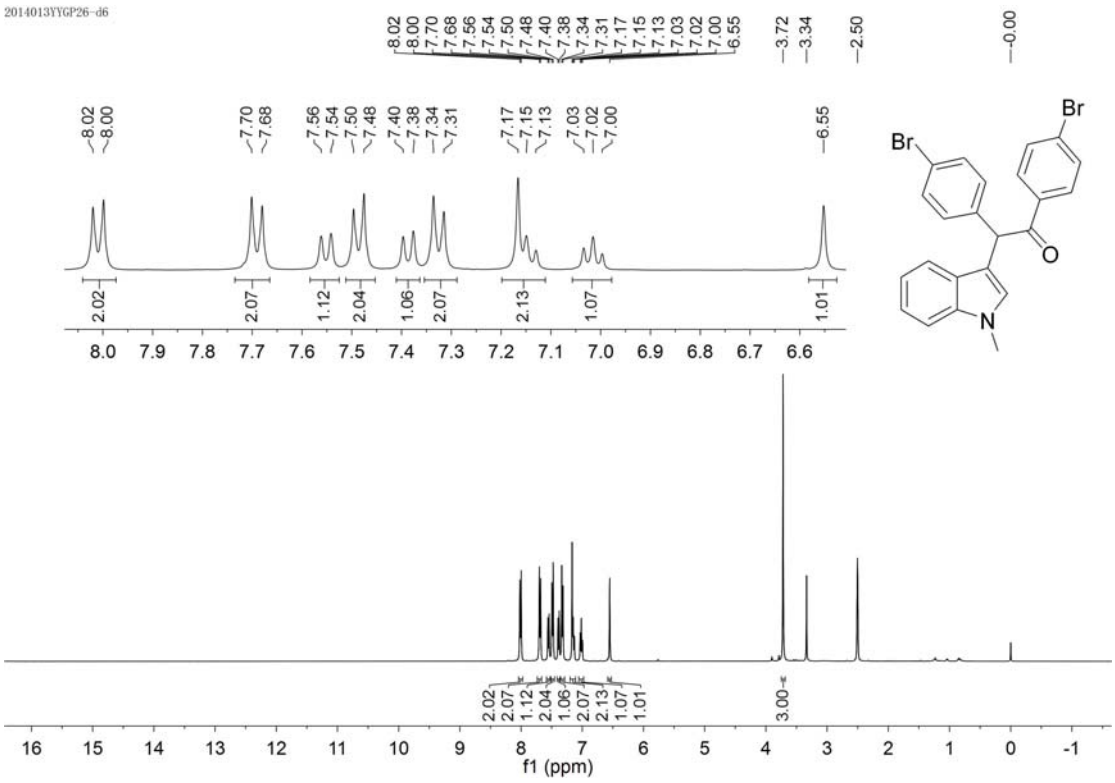


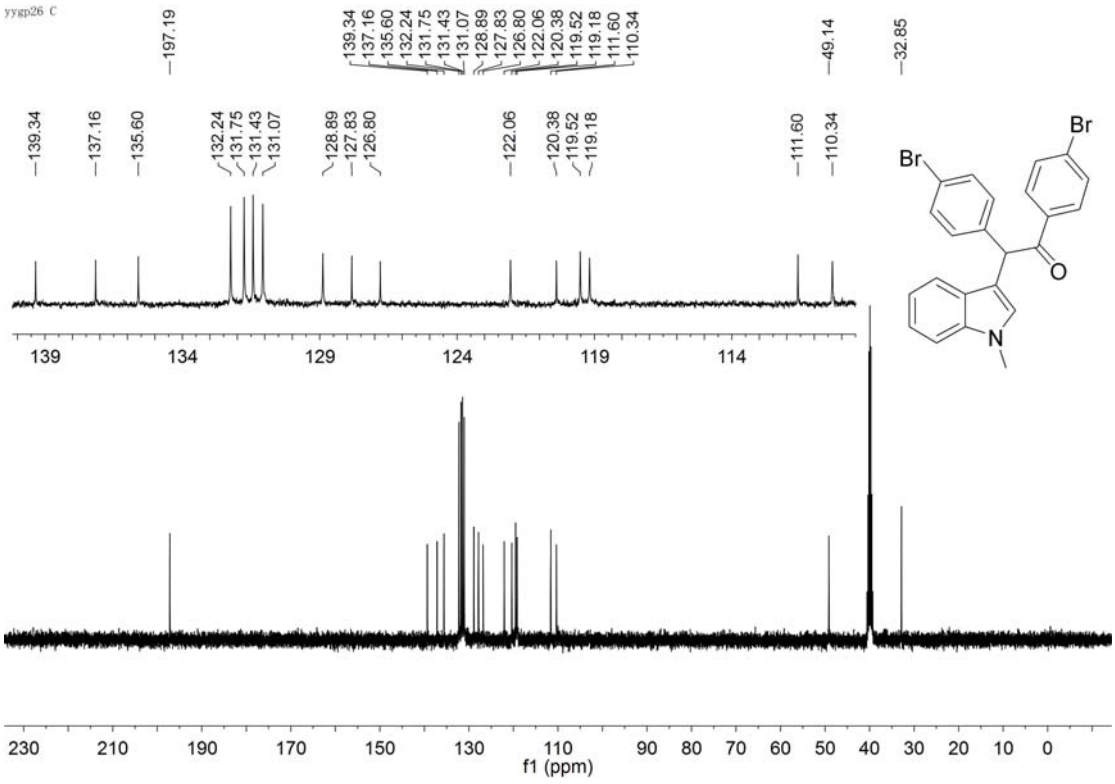
3a4



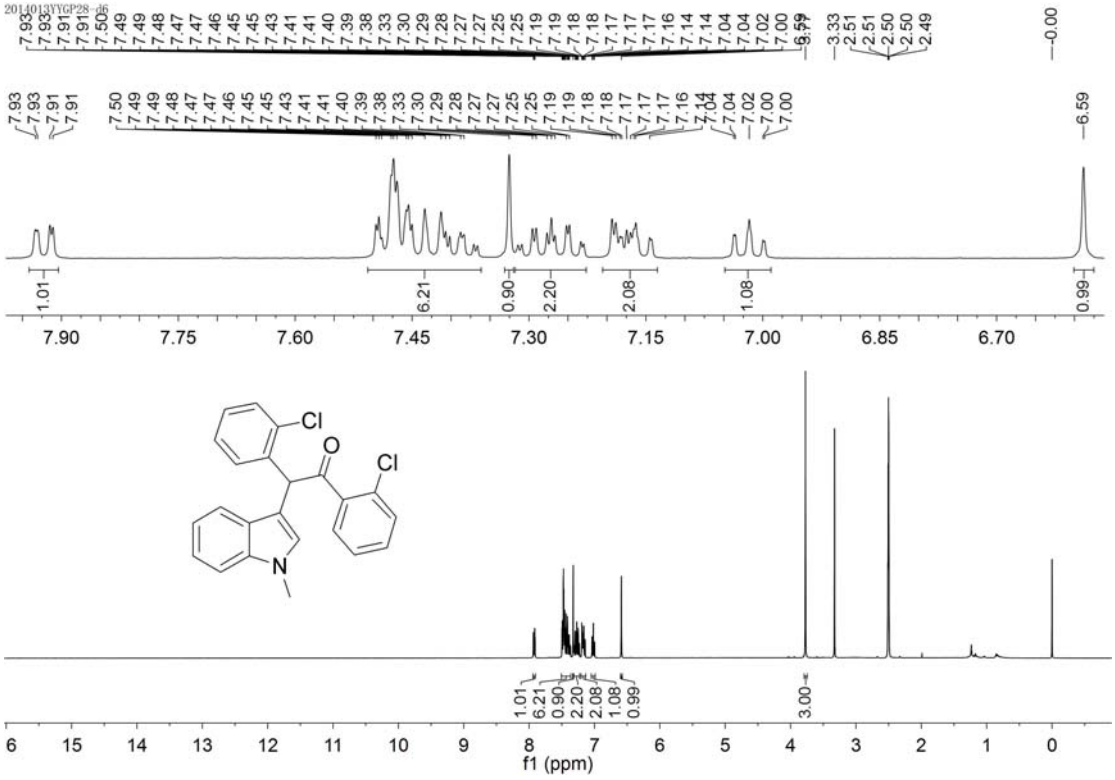


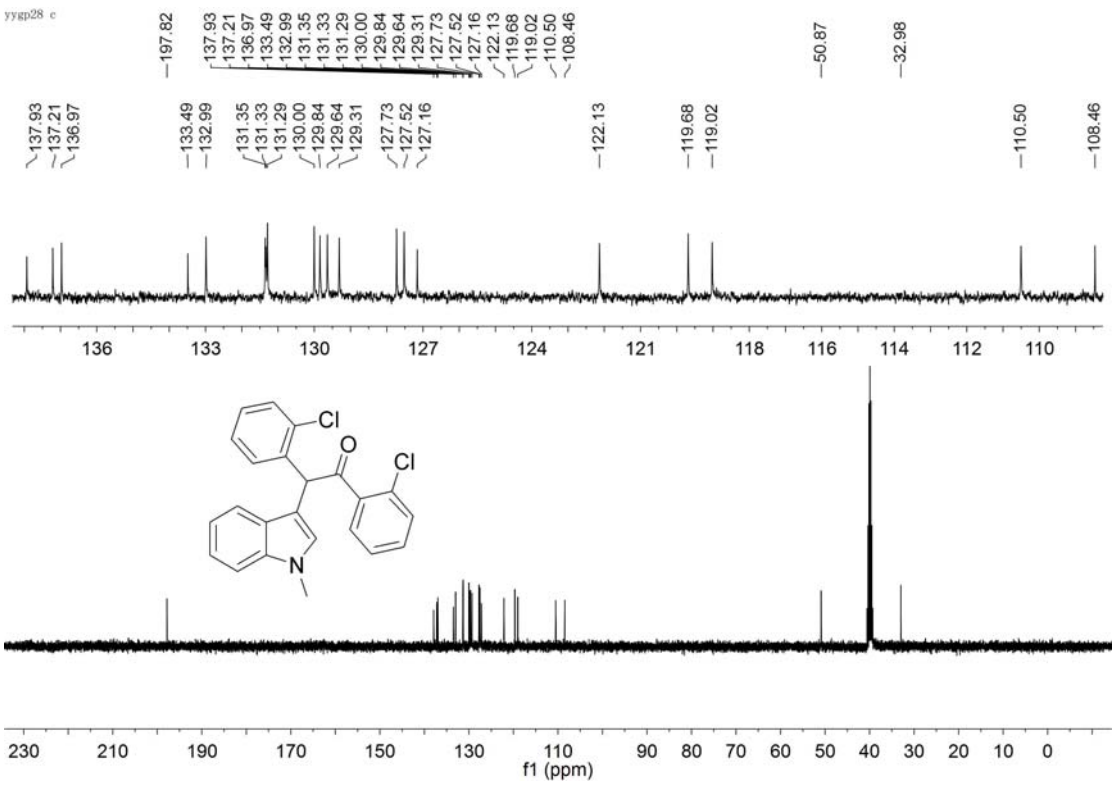
3a5


2014013YYGP26-d6
8.02
8.00
7.70
7.68
7.56
7.54
7.50
7.48
7.40
7.38
7.34
7.31
7.17
7.15
7.13
7.03
7.02
7.00
6.55
3.72
3.34
2.50
0.00
Br
Br
O
N
2.02
2.07
1.12
2.04
1.06
2.07
2.13
1.07
1.01
3.00
f1 (ppm)

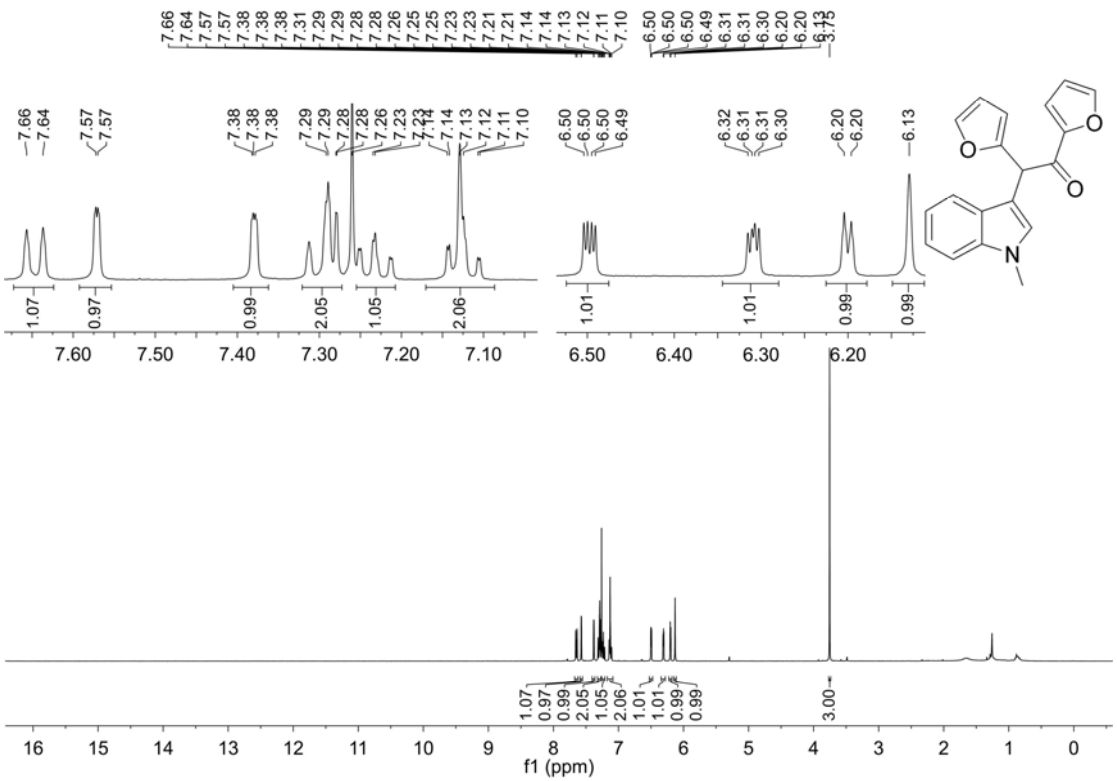

yygp26 C
197.19
139.34
137.16
135.60
132.24
131.75
131.43
131.07
128.89
127.83
126.80
122.06
120.38
119.52
119.18
111.60
110.34
49.14
32.85
Br
Br
O
N
f1 (ppm)

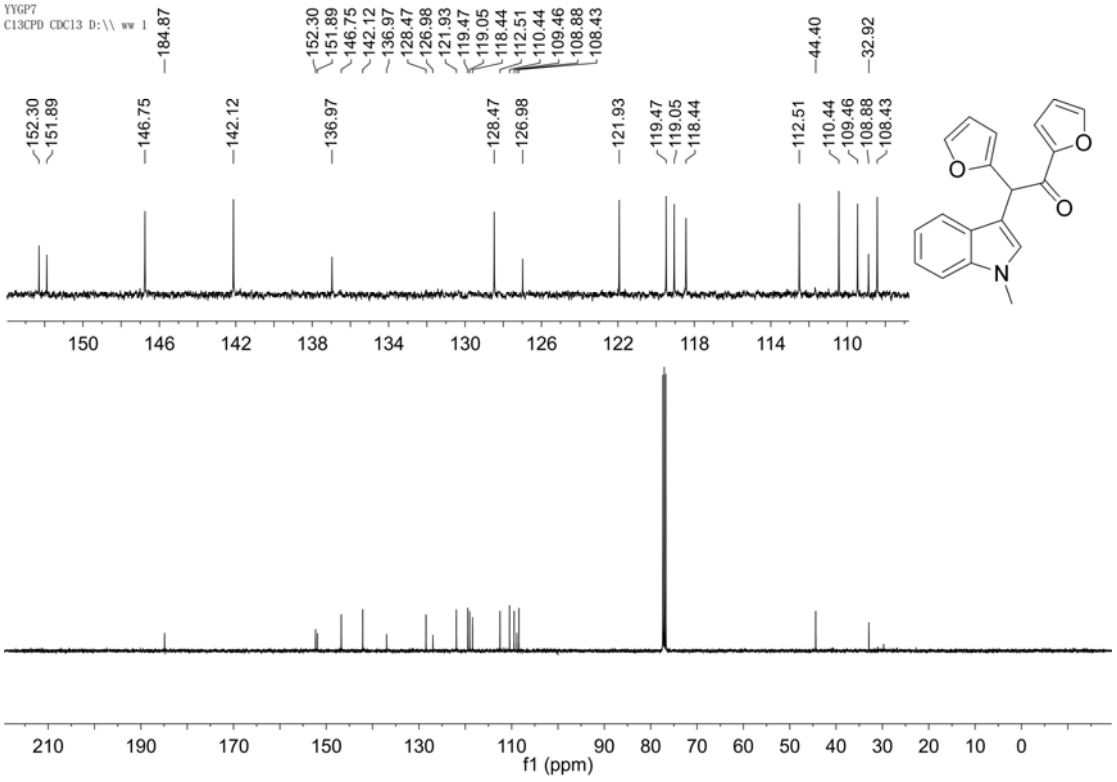
3a6



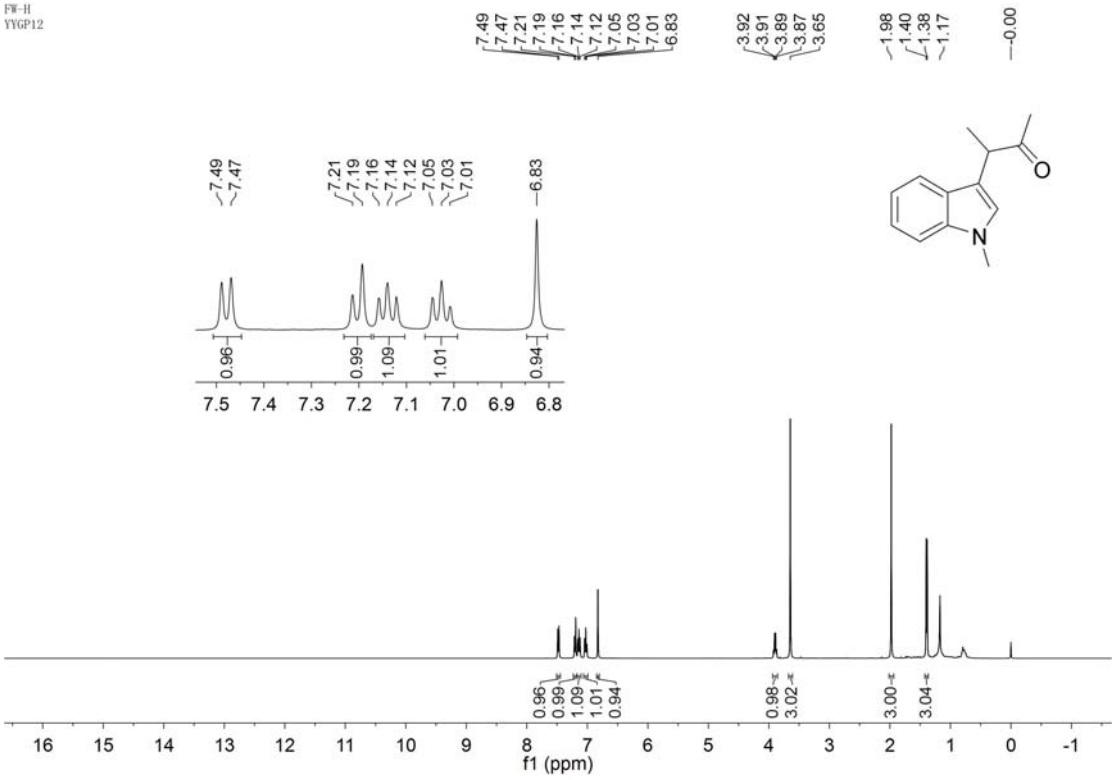


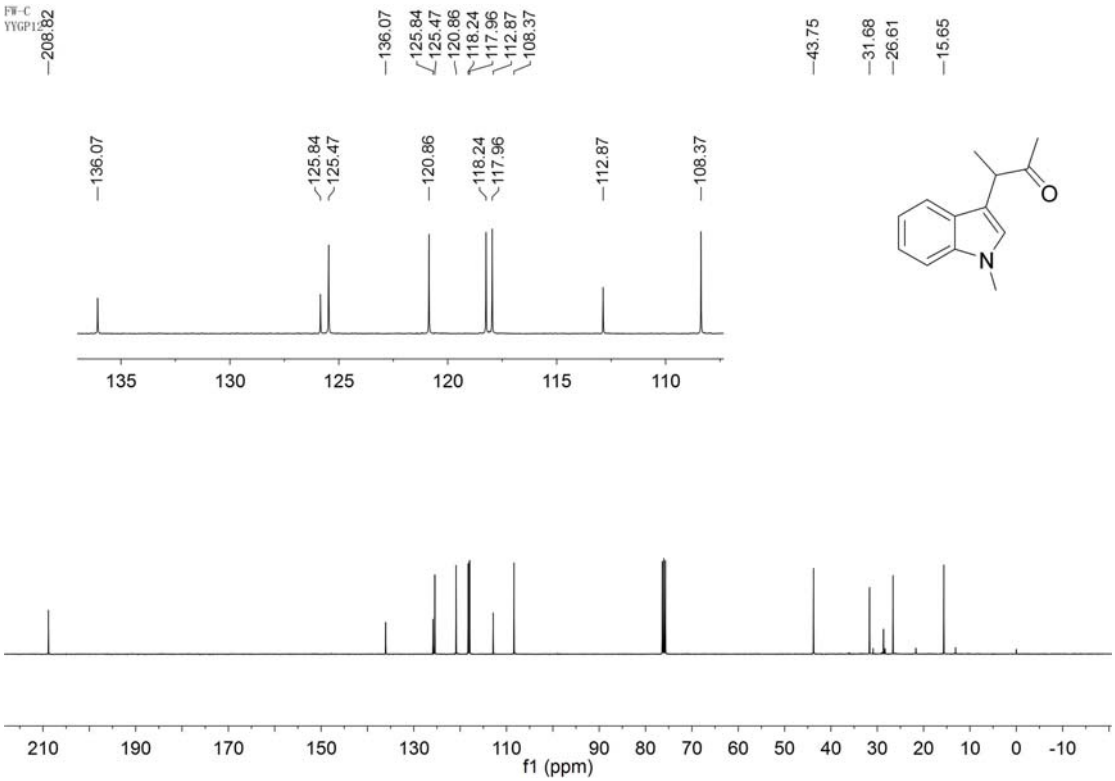
3a7


7.66
7.64
7.57
7.57
7.38
7.38
7.38
7.31
7.29
7.29
7.28
7.28
7.26
7.25
7.23
7.23
7.21
7.21
7.14
7.14
7.13
7.12
7.11
7.10
6.50
6.50
6.50
6.49
6.32
6.31
6.31
6.30
6.20
6.20
6.13
3.75
1.07
0.97
0.99
2.05
1.05
2.06
1.01
1.01
0.99
0.99
3.00
f1 (ppm)

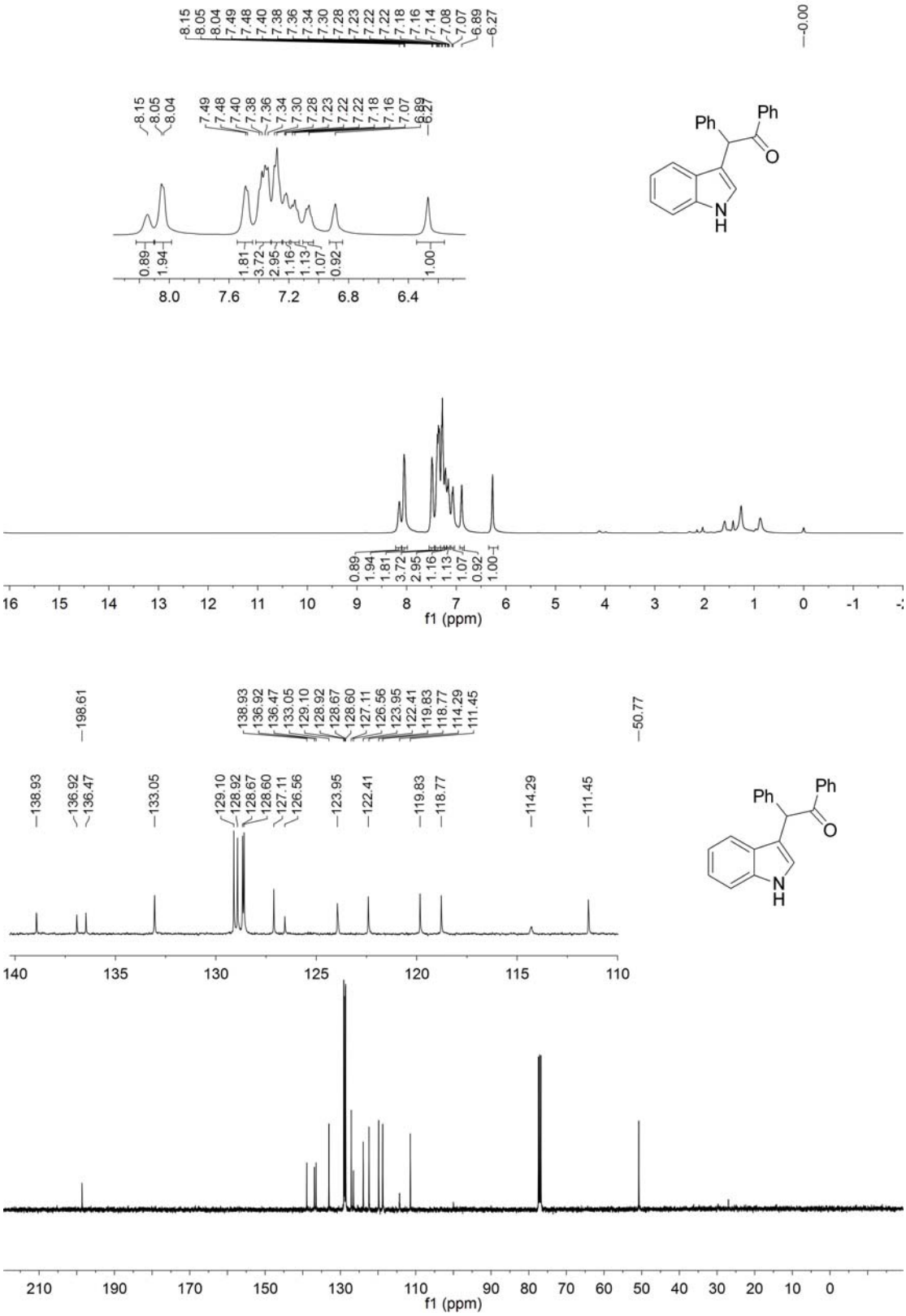

YYGP7
C13CPD CDCl3 D:\\ ww 1
184.87
152.30
151.89
146.75
142.12
136.97
128.47
126.98
121.93
119.47
119.05
118.44
112.51
110.44
109.46
108.88
108.43
44.40
32.92
f1 (ppm)

3a8

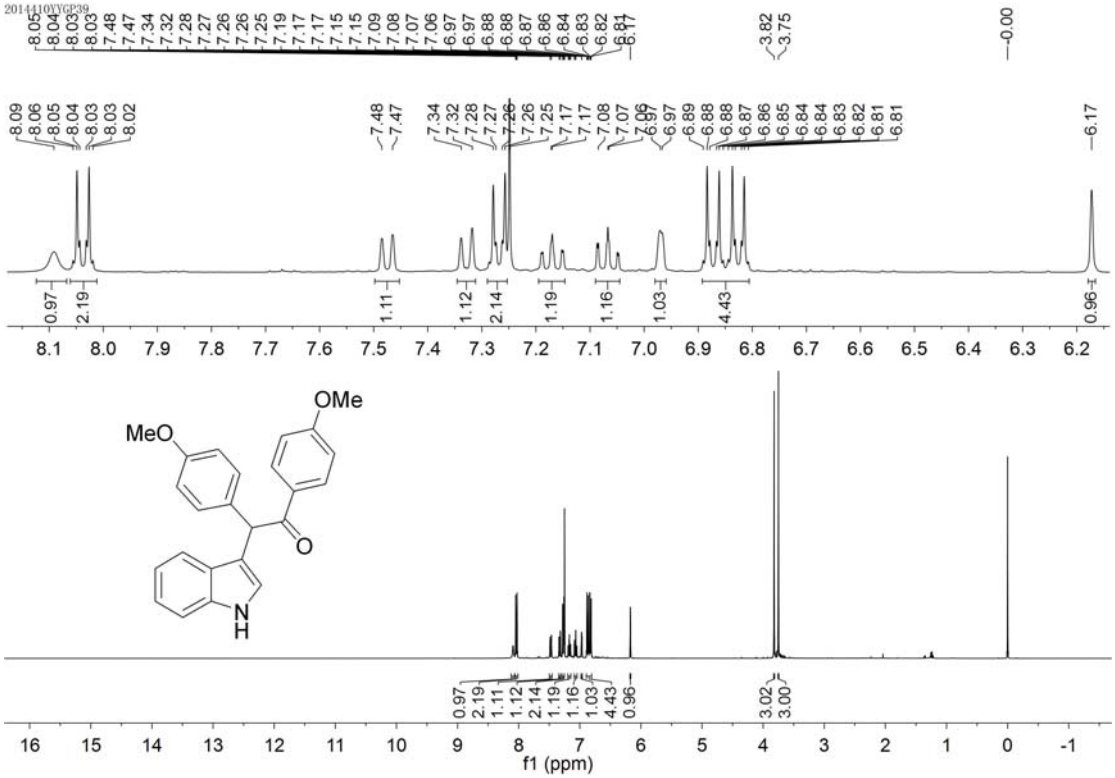

FW-H
YYGP12
7.49
7.47
7.21
7.19
7.16
7.14
7.12
7.05
7.03
7.01
6.83
3.92
3.91
3.89
3.87
3.65
1.98
1.40
1.38
1.17
0.00
0.96
0.99
1.09
1.01
0.94
0.98
3.02
3.00
3.04
f1 (ppm)

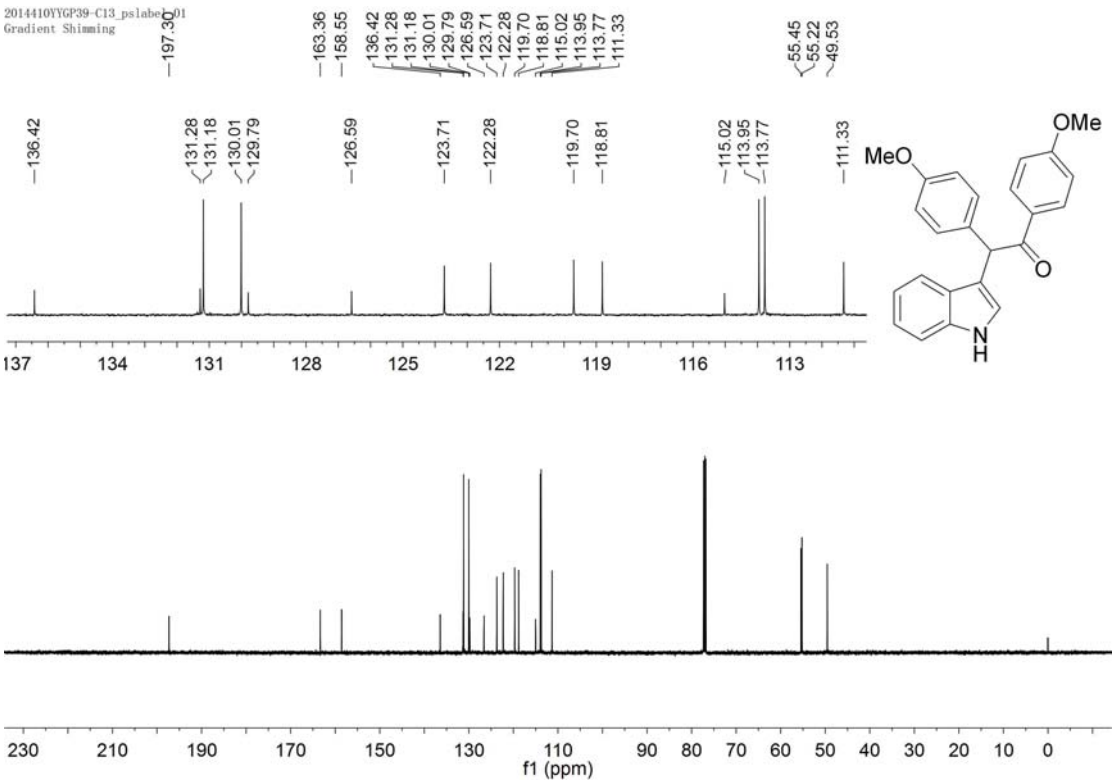

FW-C
YYGP12
208.82
136.07
125.84
125.47
120.86
118.24
117.96
112.87
108.37
43.75
31.68
26.61
15.65
f1 (ppm)

3b1

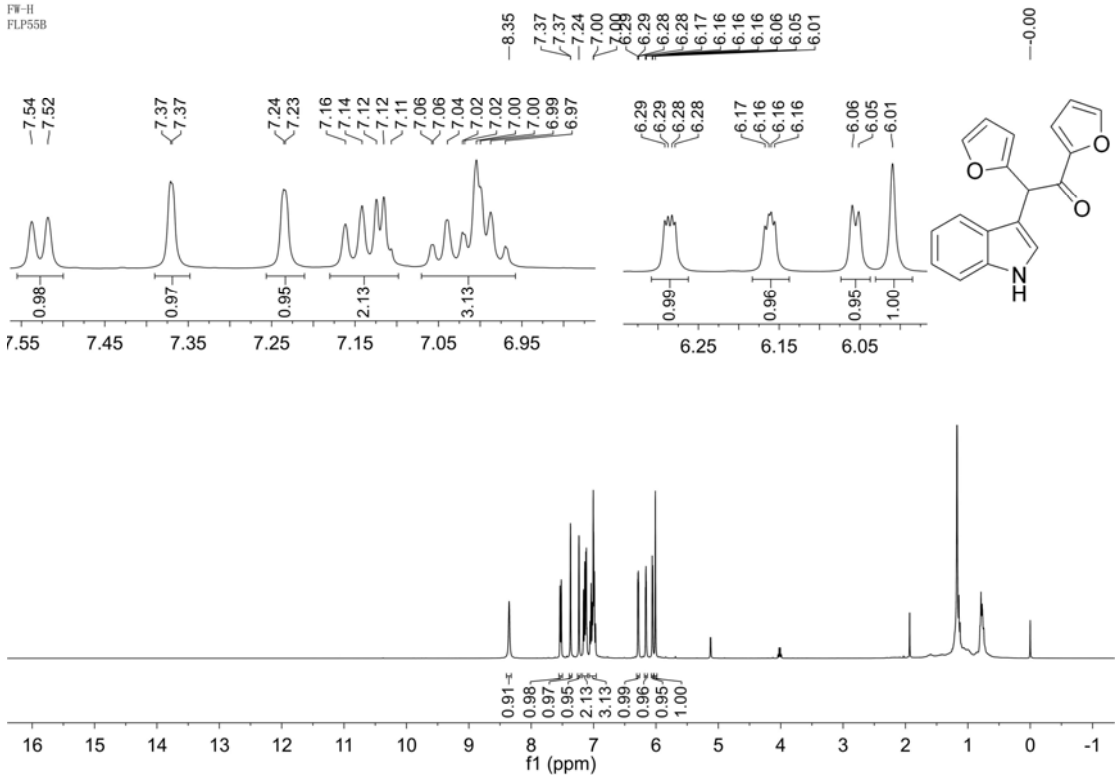

8.15
8.05
8.04
7.49
7.48
7.40
7.38
7.36
7.34
7.30
7.28
7.23
7.22
7.22
7.18
7.16
7.14
7.08
7.07
6.89
6.27
0.00
Ph
Ph
O
N
H
0.89
1.94
1.81
3.72
2.95
1.16
1.13
1.07
0.92
1.00
f1 (ppm)
198.61
138.93
136.92
136.47
133.05
129.10
128.92
128.67
128.60
127.11
126.56
123.95
122.41
119.83
118.77
114.29
111.45
50.77
f1 (ppm)

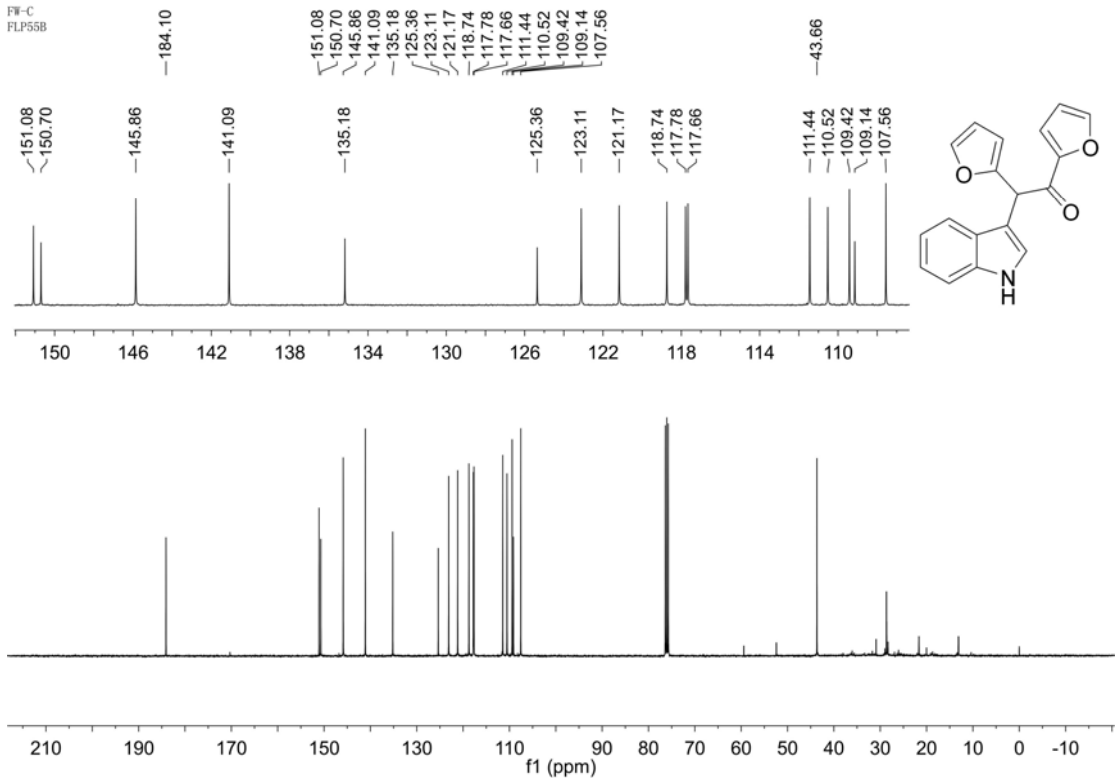
3b2



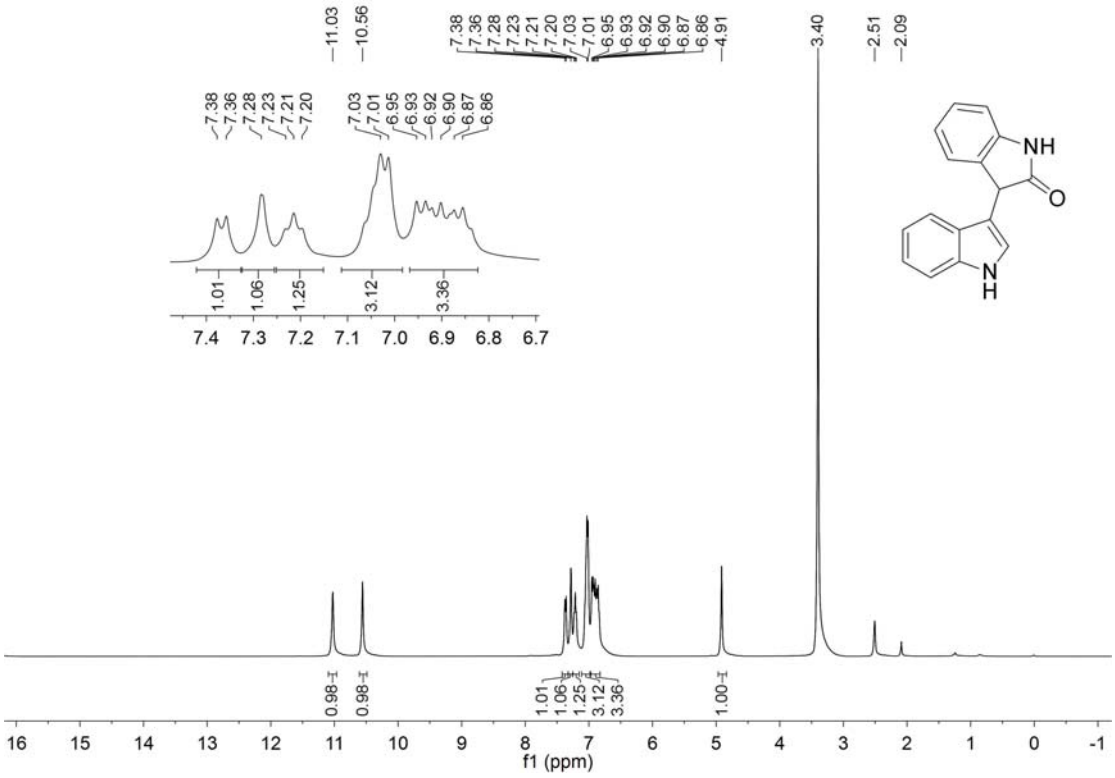


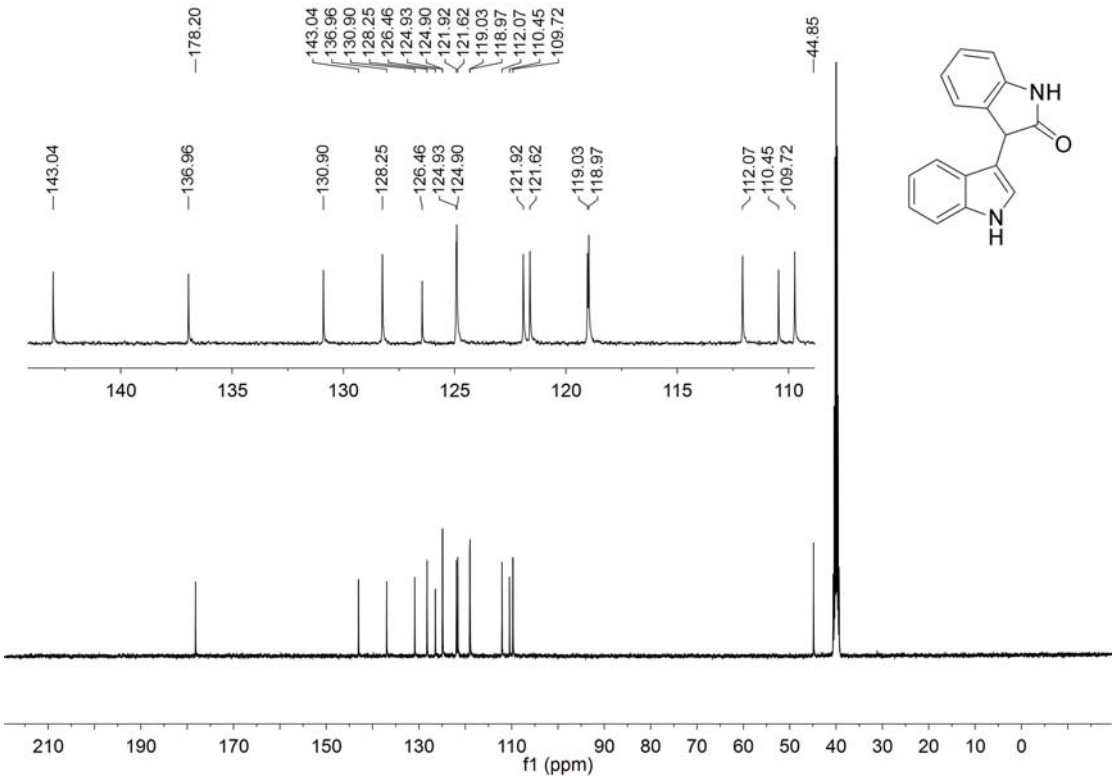
3b3


FW-H
FLP55B
8.35
7.37
7.37
7.24
7.00
6.29
6.28
6.28
6.17
6.16
6.16
6.06
6.05
6.01
0.00
7.54
7.52
7.37
7.37
7.24
7.23
7.16
7.14
7.12
7.12
7.11
7.06
7.06
7.04
7.02
7.02
7.00
7.00
6.99
6.97
6.29
6.29
6.28
6.28
6.17
6.16
6.16
6.16
6.06
6.05
6.01
0.98
0.97
0.95
2.13
3.13
0.99
0.96
0.95
1.00
7.55
7.45
7.35
7.25
7.15
7.05
6.95
6.25
6.15
6.05
O
O
N
H
0.91
0.98
0.97
0.95
2.13
3.13
0.99
0.96
0.95
1.00
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)

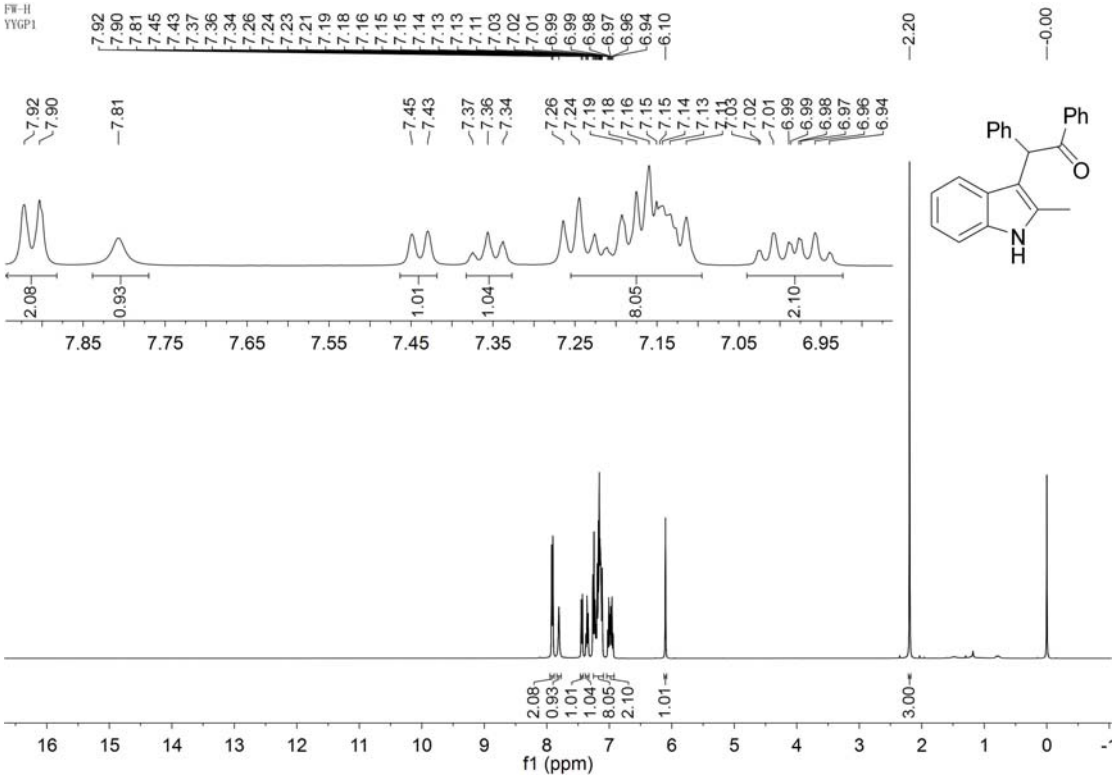

FW-C
FLP55B
184.10
151.08
150.70
145.86
141.09
135.18
125.36
123.11
121.17
118.74
117.78
117.66
111.44
110.52
109.42
109.14
107.56
43.66
151.08
150.70
145.86
141.09
135.18
125.36
123.11
121.17
118.74
117.78
117.66
111.44
110.52
109.42
109.14
107.56
150
146
142
138
134
130
126
122
118
114
110
O
O
N
H
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

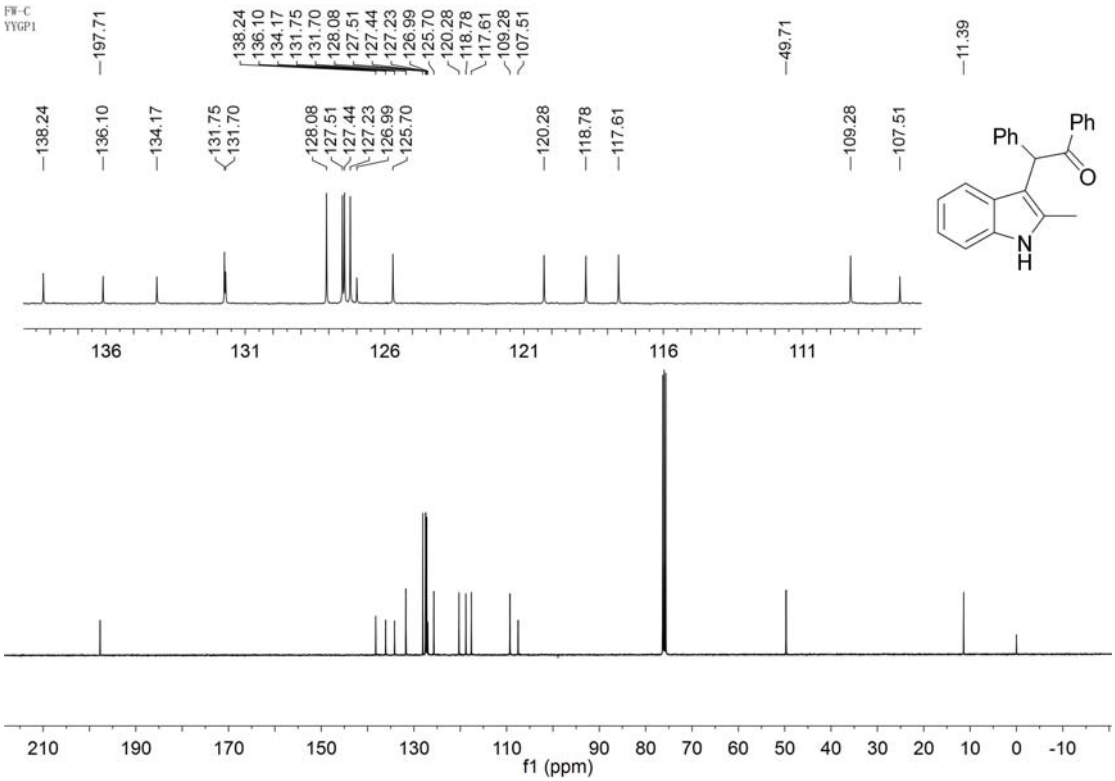
3c


11.03
10.56
7.38
7.36
7.28
7.23
7.21
7.20
7.03
7.01
6.95
6.93
6.92
6.90
6.87
6.86
4.91
3.40
2.51
2.09
NH
O
N
H
0.98
0.98
1.01
1.06
1.25
3.12
3.36
1.00
f1 (ppm)

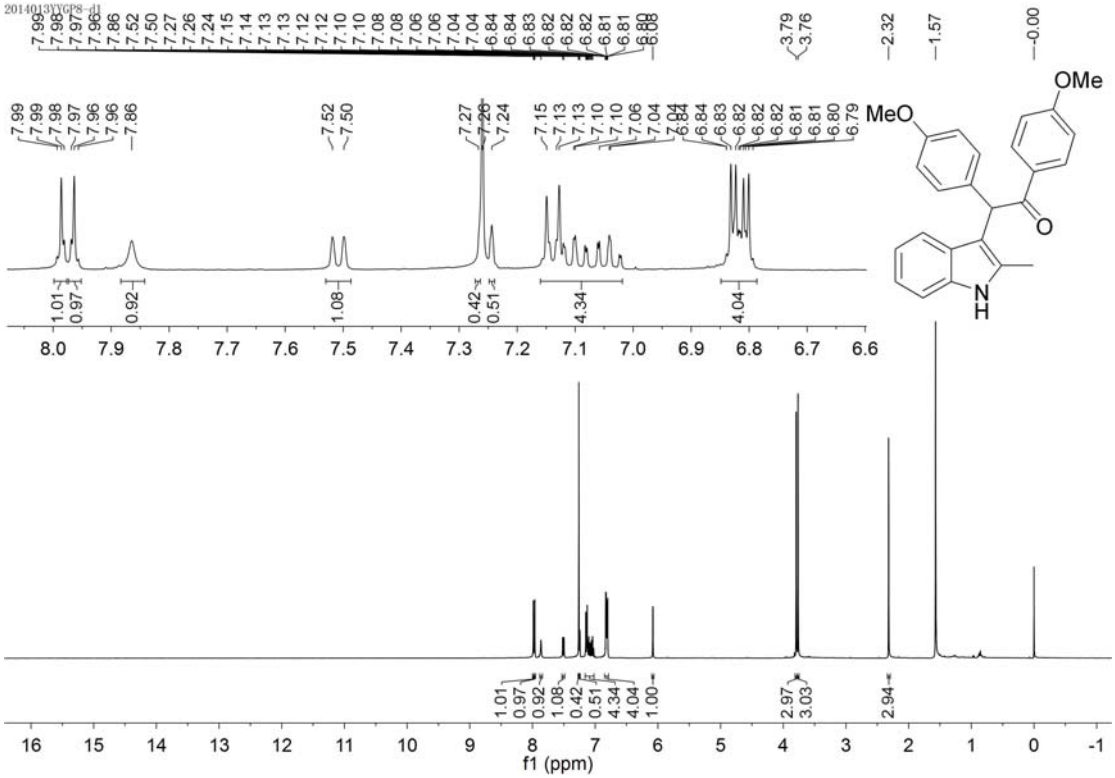

178.20
143.04
136.96
130.90
128.25
126.46
124.93
124.90
121.92
121.62
119.03
118.97
112.07
110.45
109.72
44.85
NH
O
N
H
f1 (ppm)

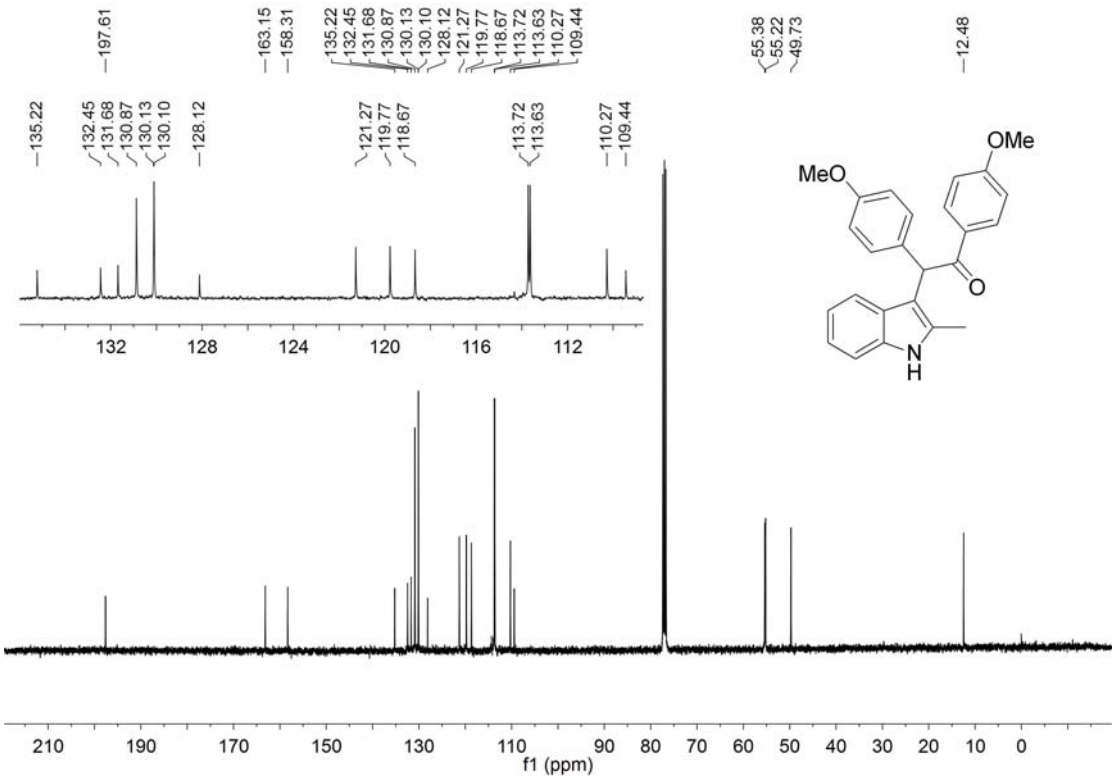
3d1



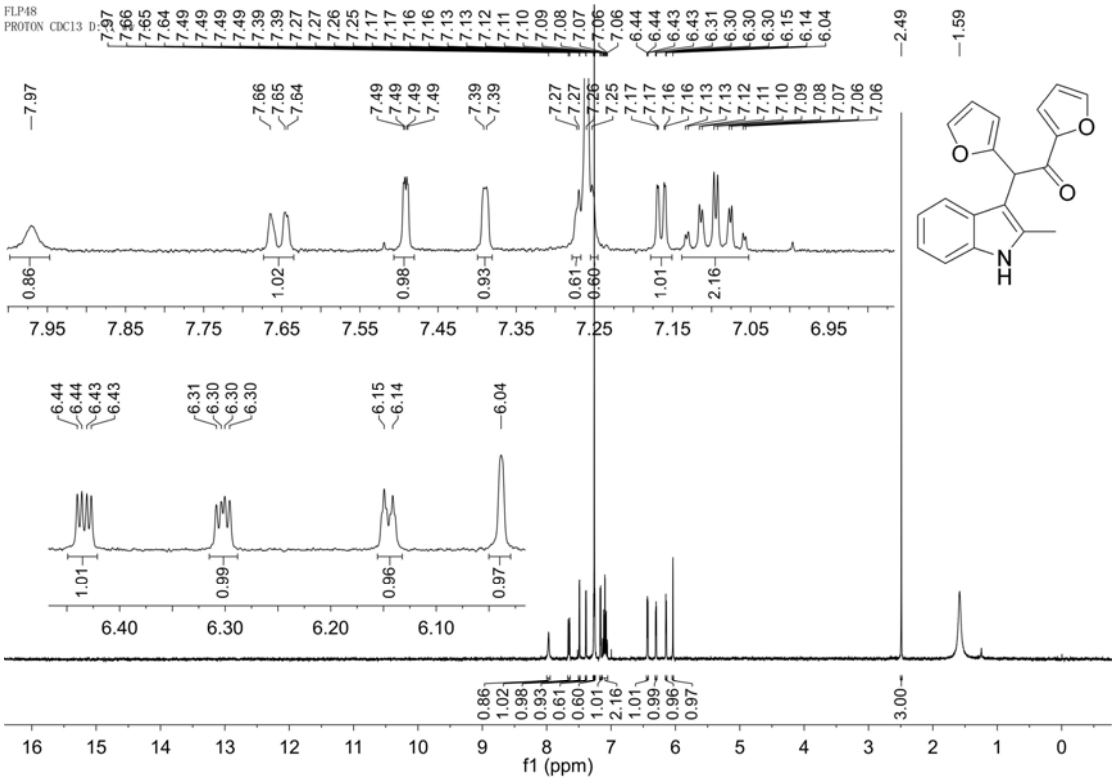


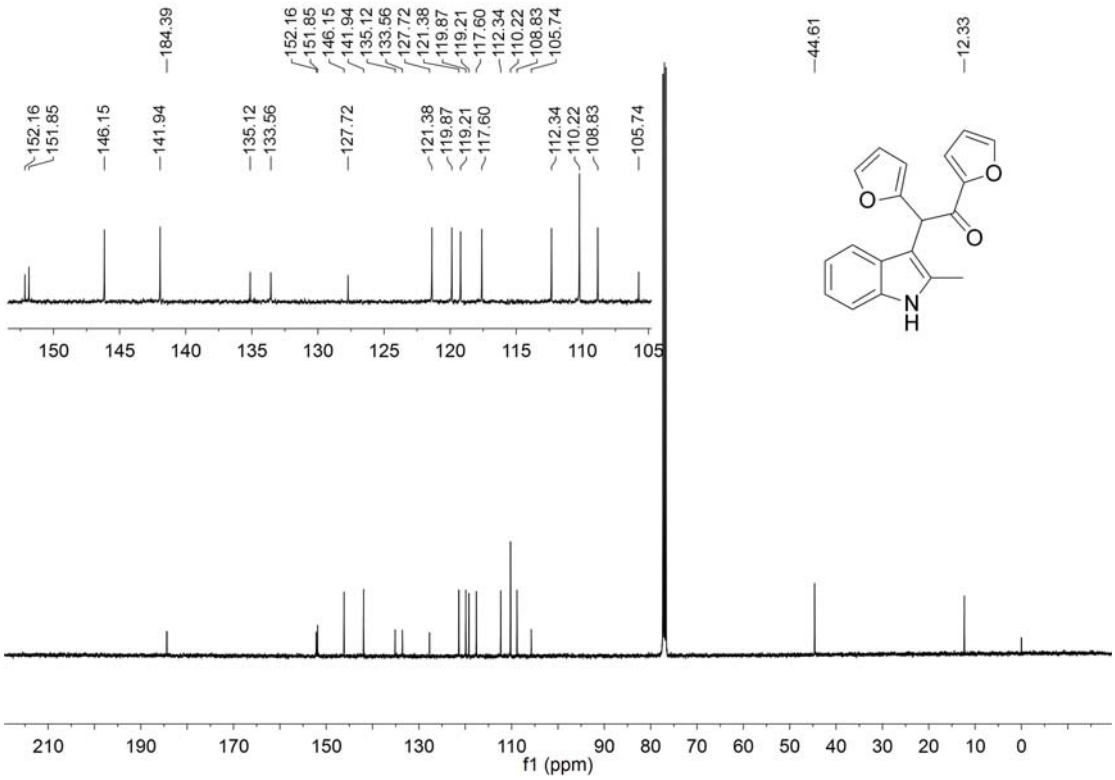
3d2



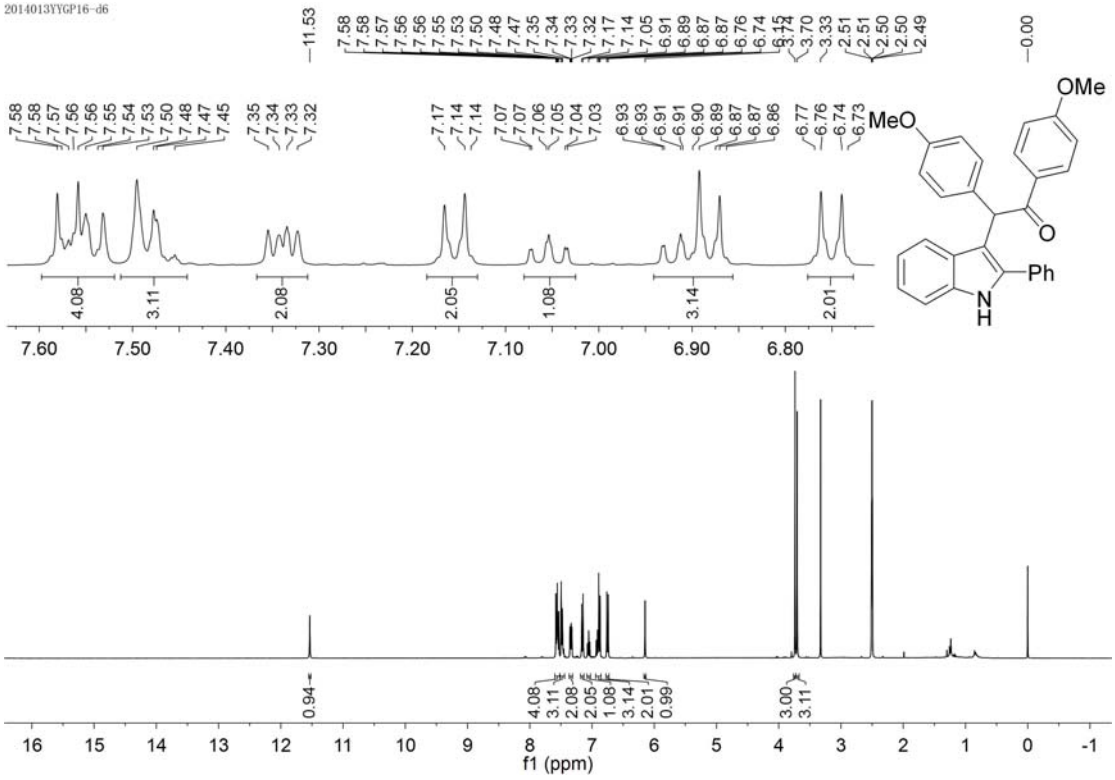


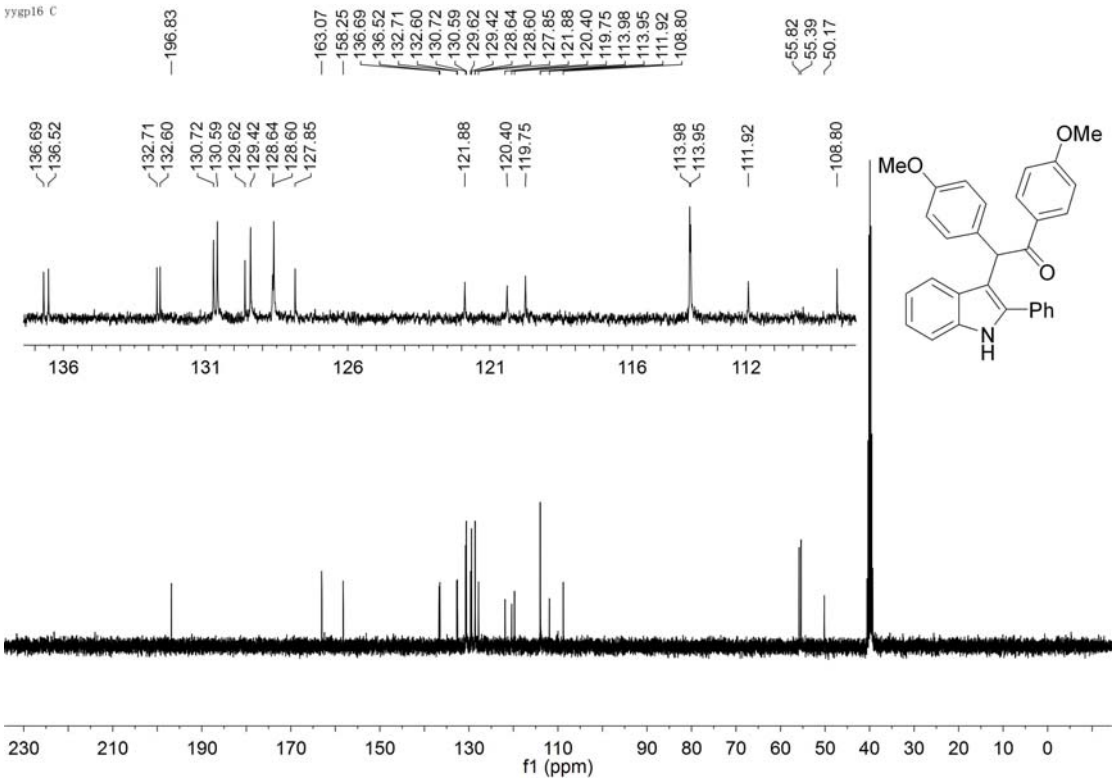
3d3



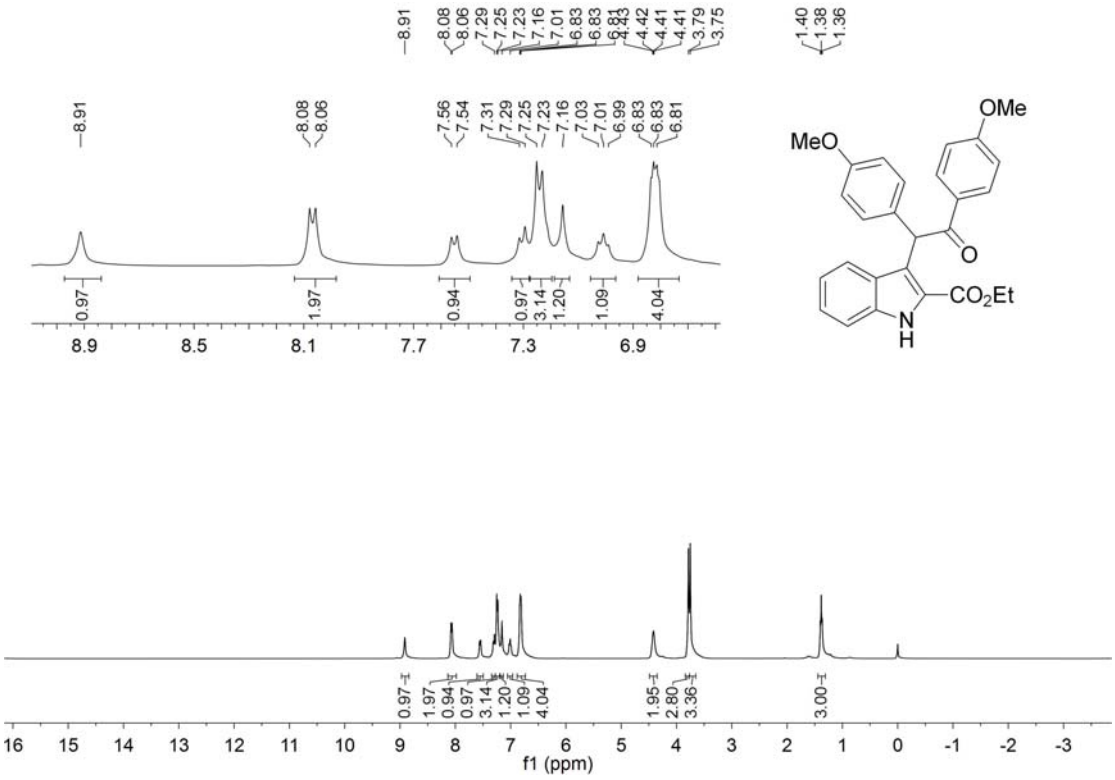


3e

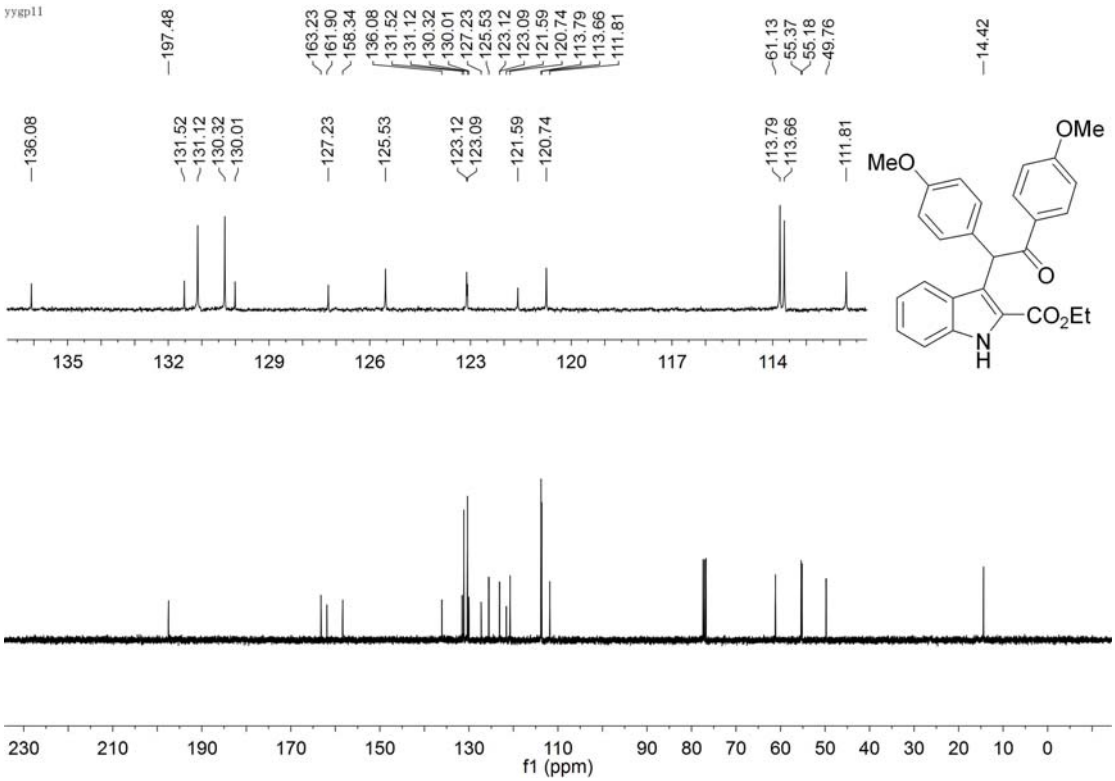

2014013YYGP16-d6
OMe
MeO
O
Ph
N
H
f1 (ppm)


yygp16 C
OMe
MeO
O
Ph
N
H
f1 (ppm)

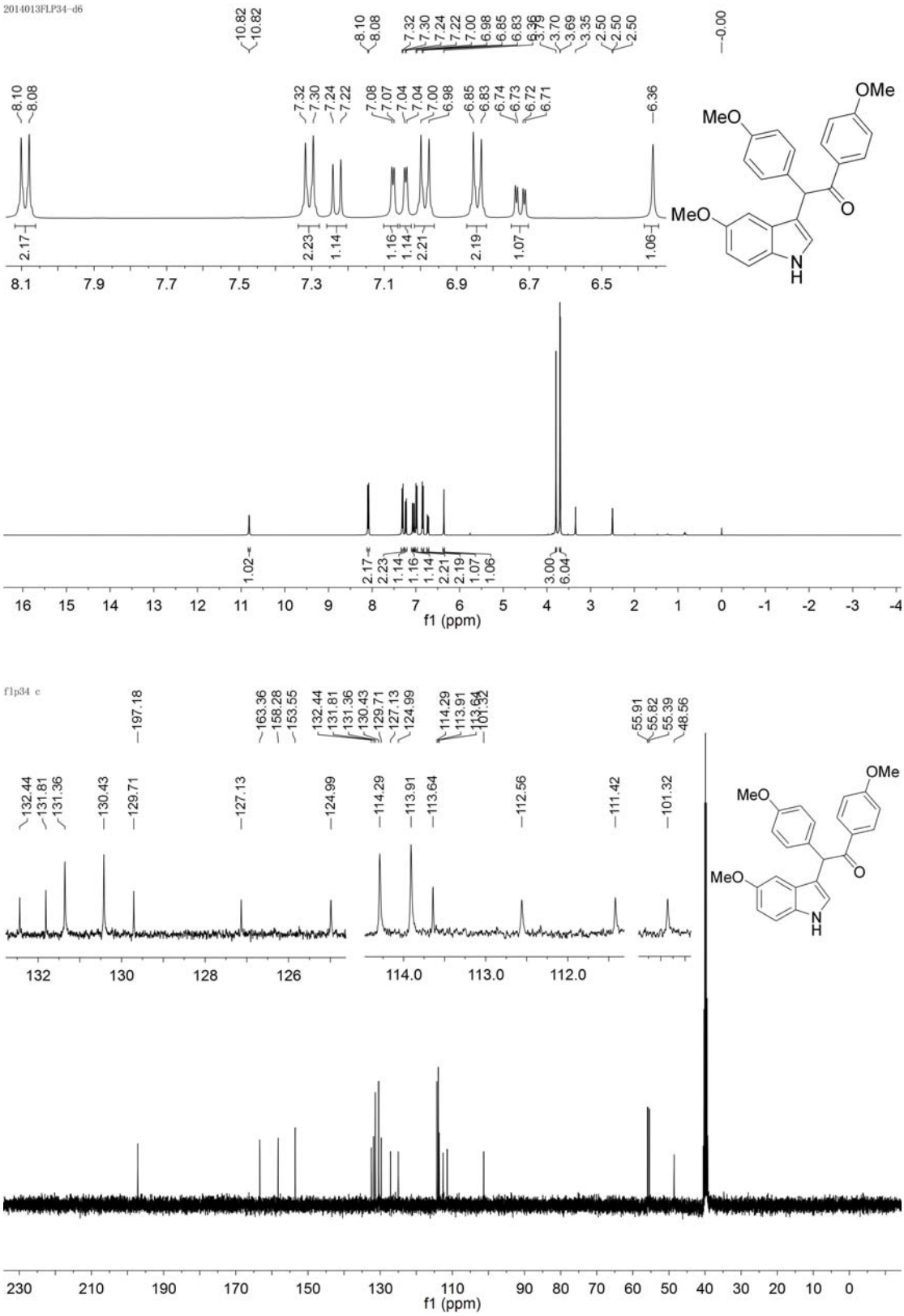
3f


8.91
8.08
8.06
7.56
7.54
7.31
7.29
7.25
7.23
7.16
7.03
7.01
6.99
6.83
6.81
0.97
1.97
0.94
0.97
3.14
1.20
1.09
4.04
8.9
8.5
8.1
7.7
7.3
6.9
OMe
MeO
O
CO2Et
N
H

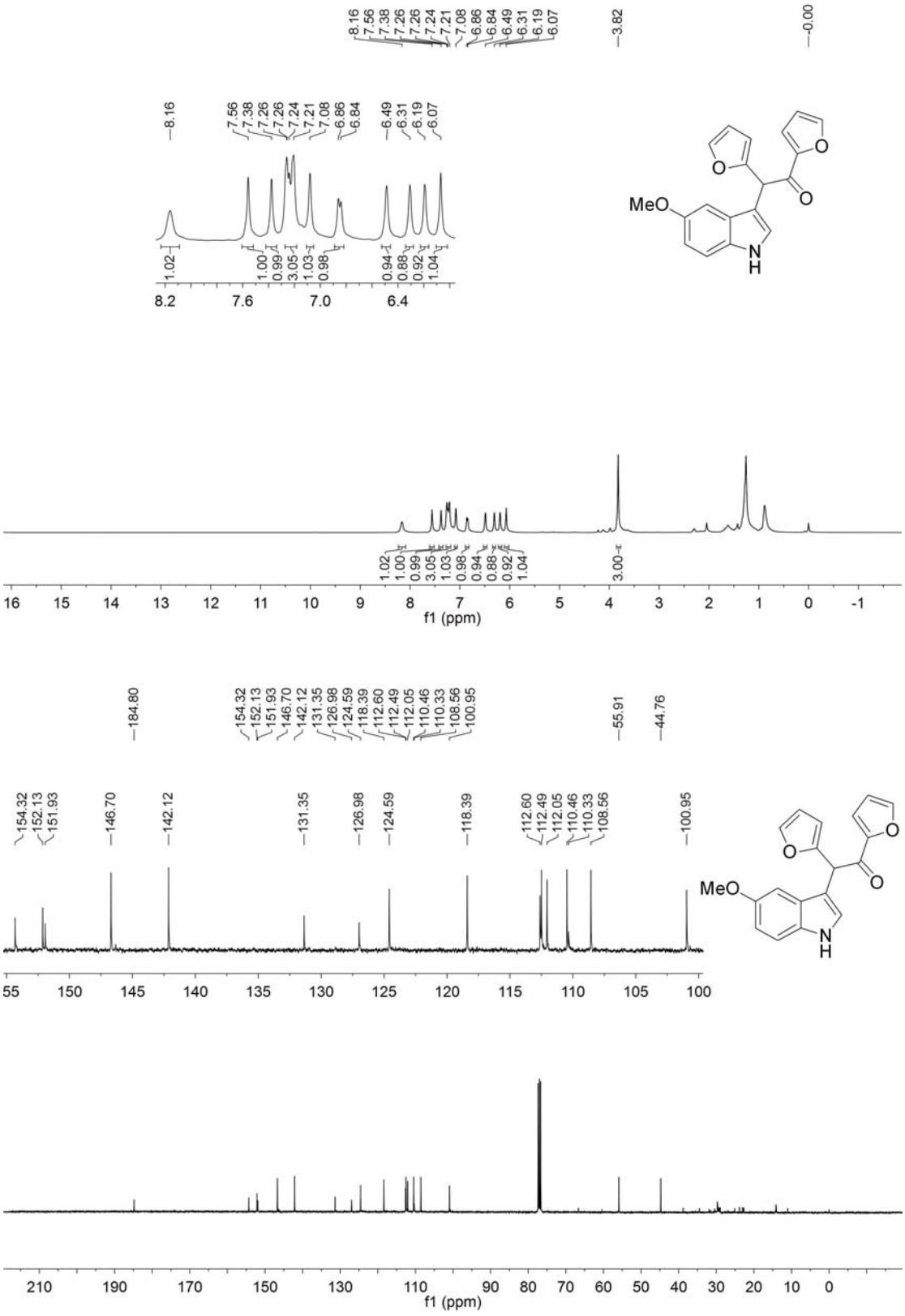
0.97
1.97
0.94
0.97
3.14
1.20
1.09
4.04
1.95
2.80
3.36
3.00
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)


yygp11
197.48
163.23
161.90
158.34
136.08
131.52
131.12
130.32
130.01
127.23
125.53
123.12
123.09
121.59
120.74
113.79
113.66
111.81
61.13
55.37
55.18
49.76
14.42
135 132 129 126 123 120 117 114
OMe
MeO
O
CO2Et
N
H
230 210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

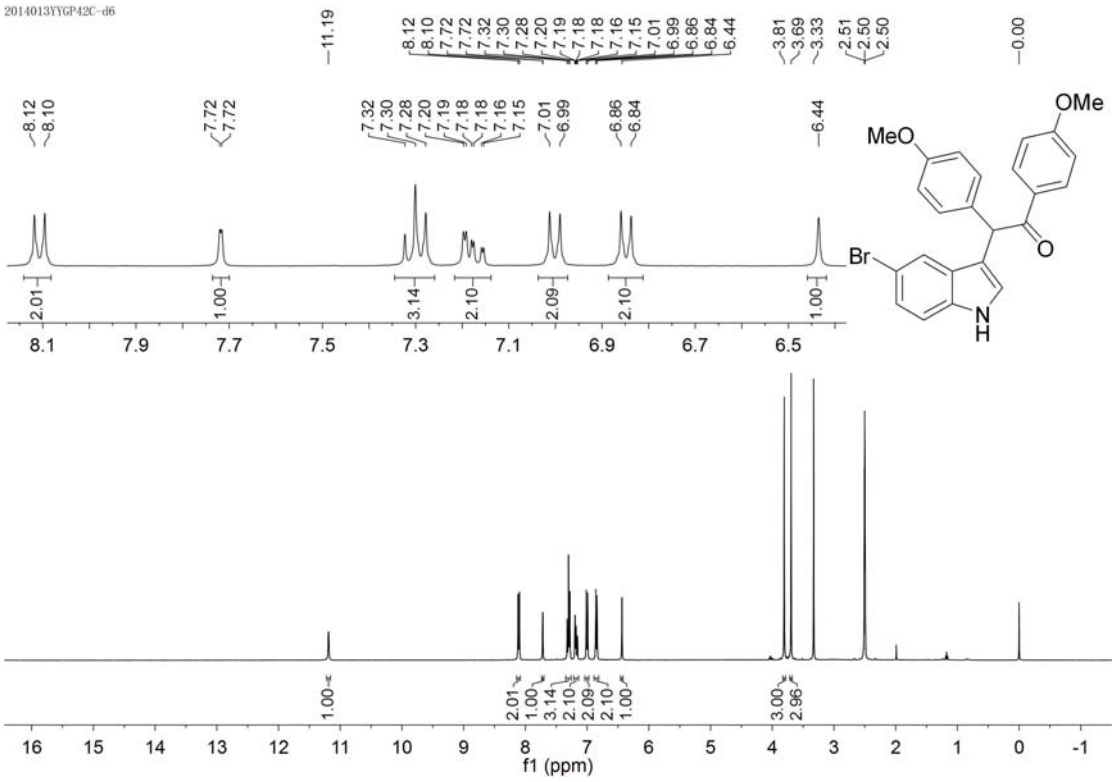
3g1

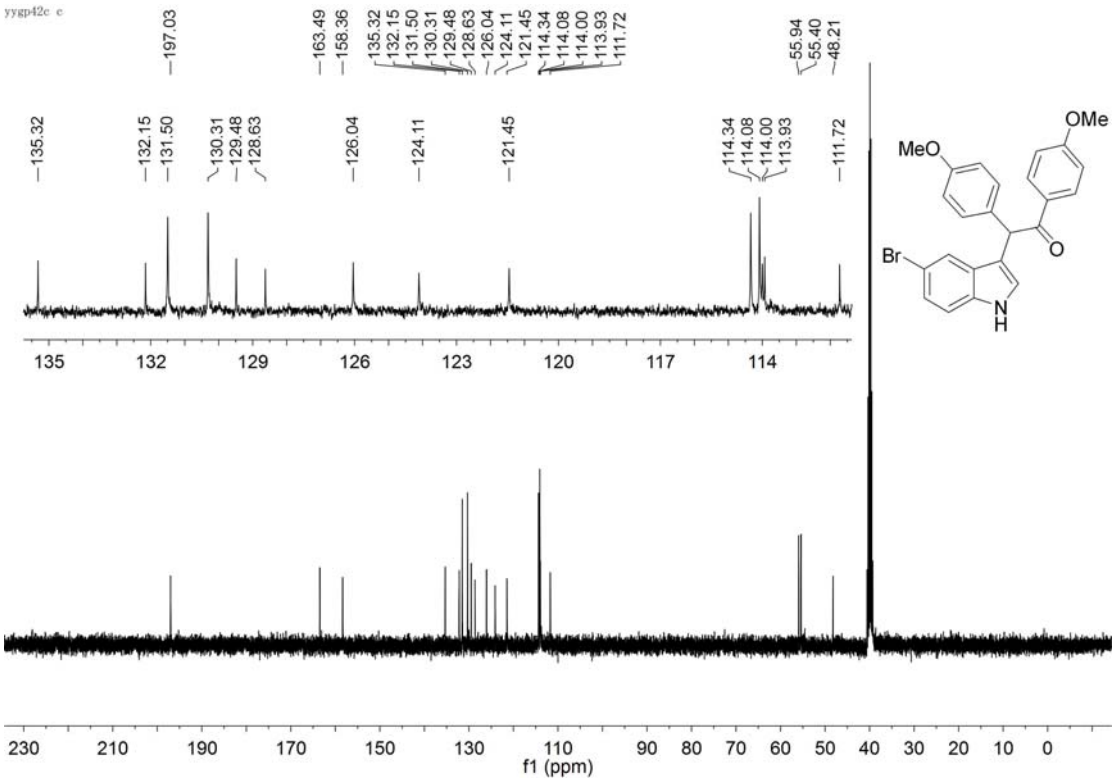


3g2

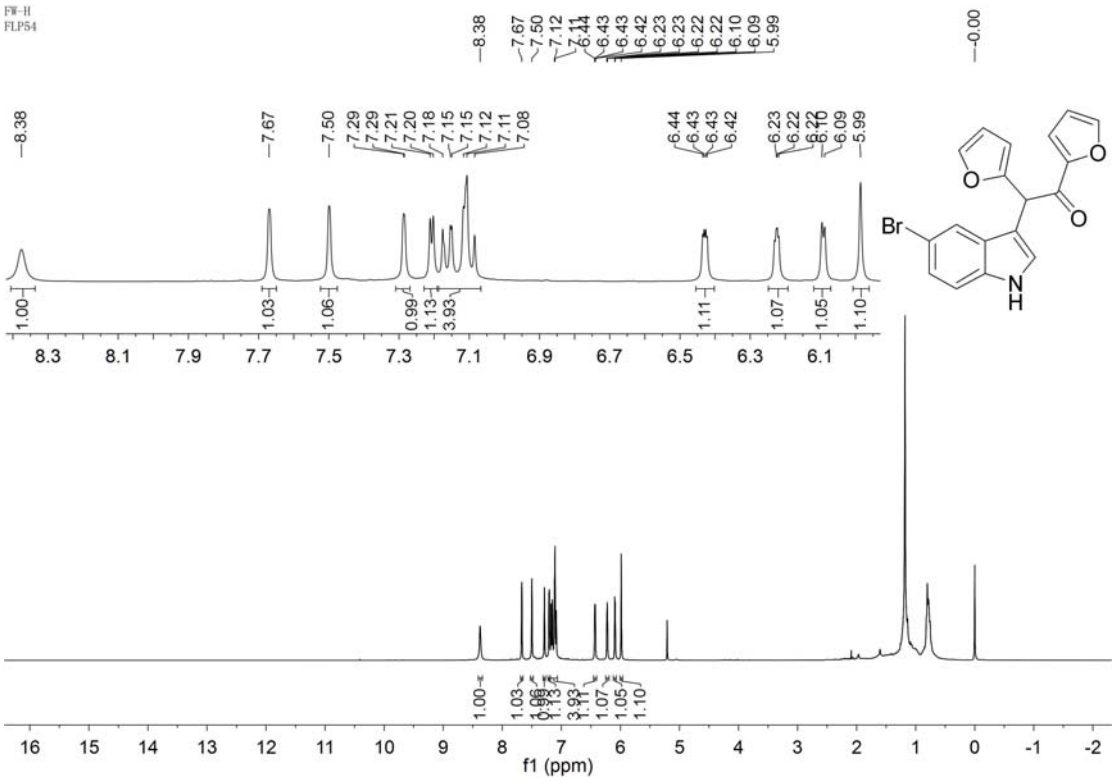

8.16
7.56
7.38
7.26
7.26
7.24
7.21
7.08
6.86
6.84
6.49
6.31
6.19
6.07
3.82
0.00
MeO
N
H
O
O
O
1.02
1.00
0.99
3.05
1.03
0.98
0.94
0.88
0.92
1.04
3.00
f1 (ppm)
184.80
154.32
152.13
151.93
146.70
142.12
131.35
126.98
124.59
118.39
112.60
112.49
112.05
110.46
110.33
108.56
100.95
55.91
44.76

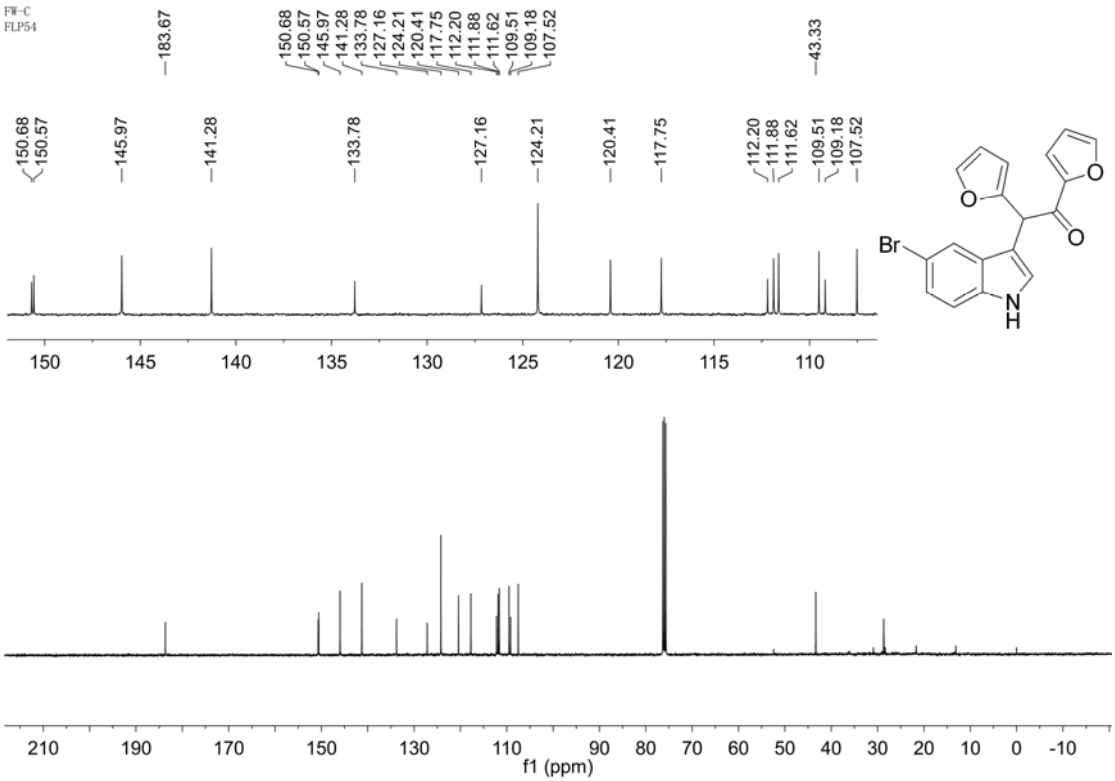
3h1





3h2


FW-H
FLP54
8.38
7.67
7.50
7.29
7.29
7.21
7.20
7.18
7.15
7.15
7.12
7.11
7.08
6.44
6.43
6.43
6.42
6.23
6.22
6.22
6.10
6.09
5.99
0.00
1.00
1.03
1.06
0.99
1.13
3.93
1.11
1.07
1.05
1.10
Br
O
O
O
N
H
f1 (ppm)


FW-C
FLP54
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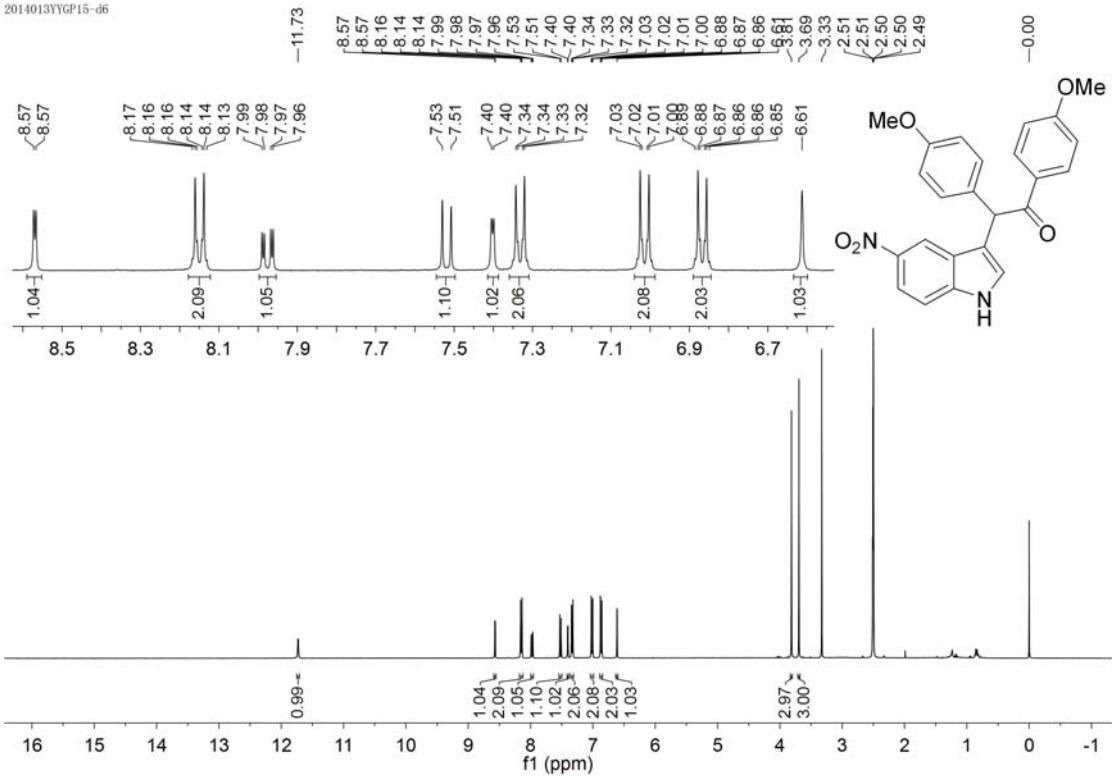
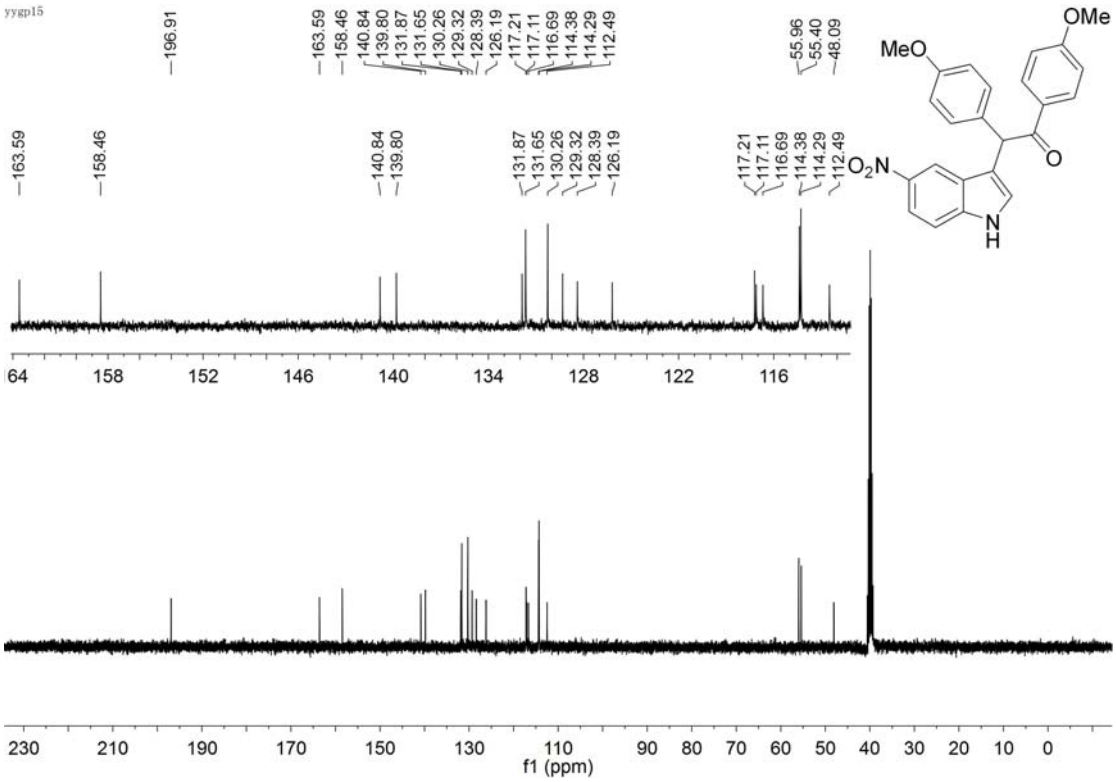
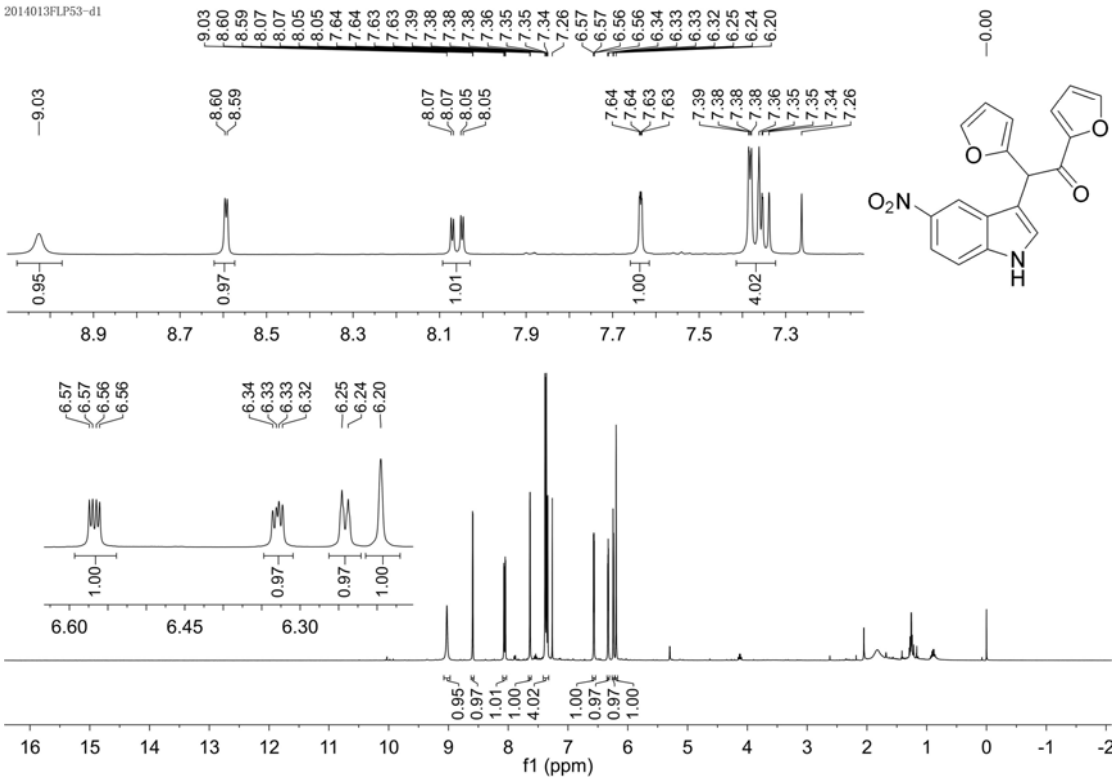
150.68
150.57
145.97
141.28
133.78
127.16
124.21
120.41
117.75
112.20
111.88
111.62
109.51
109.18
107.52
43.33
Br
O
O
O
N
H
f1 (ppm)

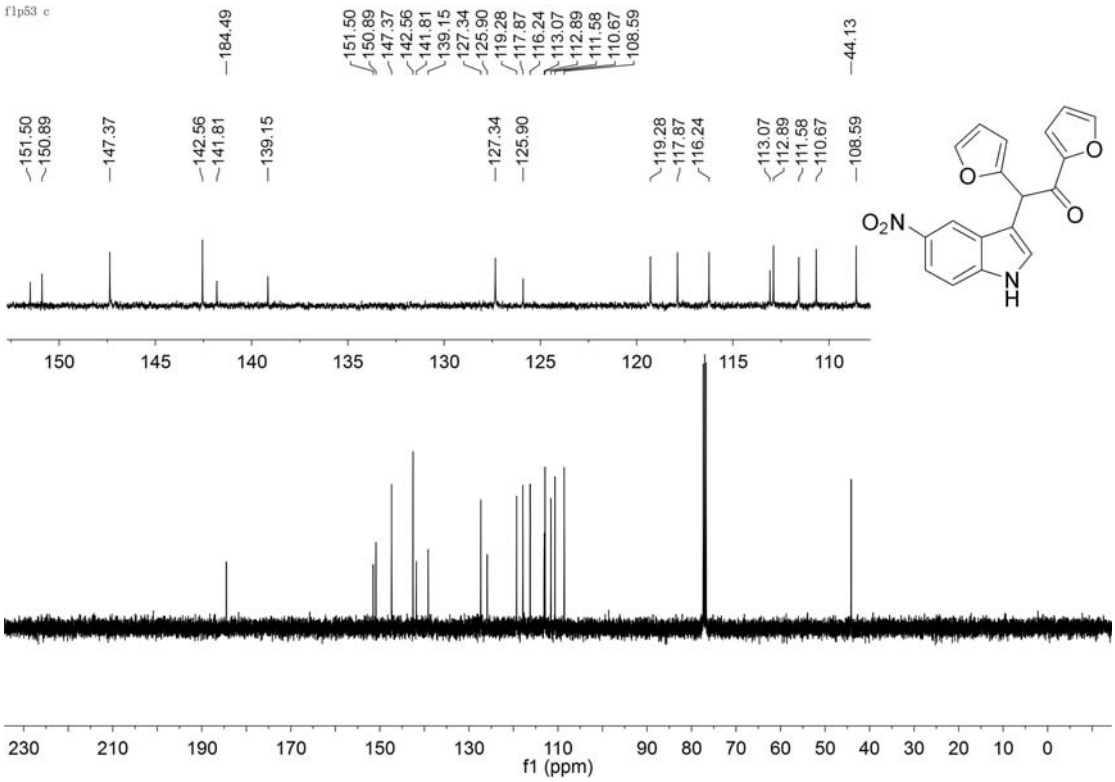
3i1



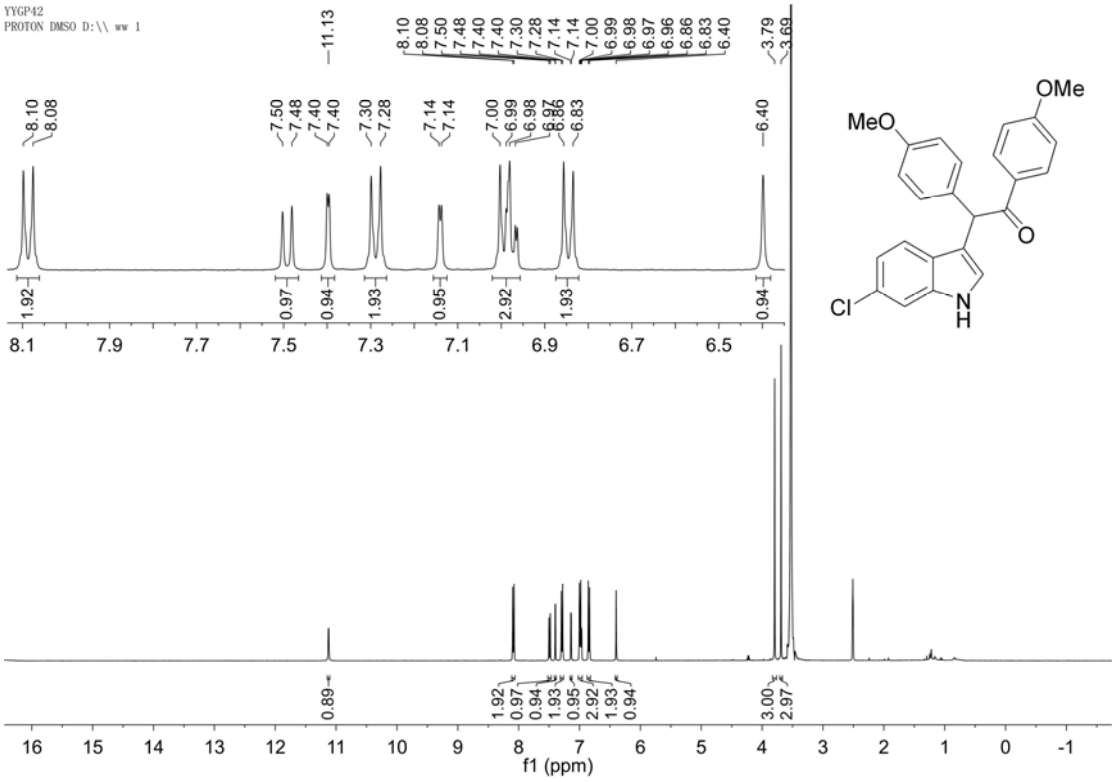


3i2





3j1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PROTON DMSO D:\\ ww 1
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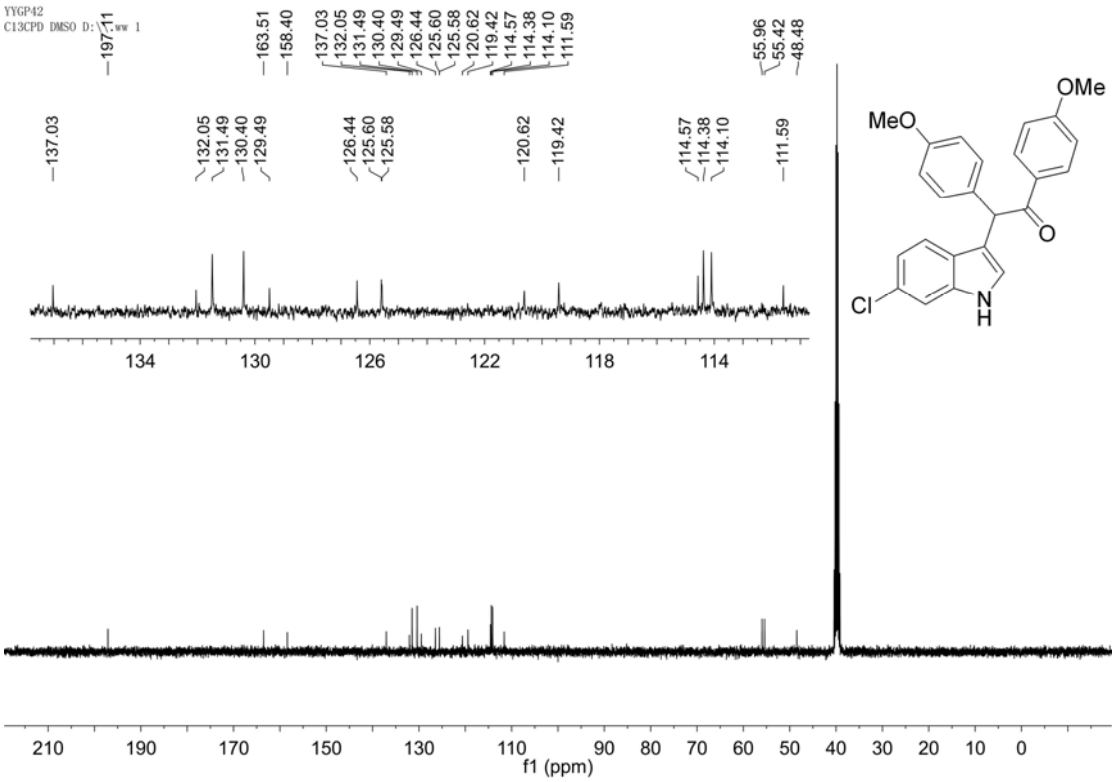
8.08
7.50
7.48
7.40
7.40
7.30
7.28
7.14
7.14
7.00
6.99
6.98
6.97
6.96
6.86
6.83
6.40
3.79
3.69
1.92
0.97
0.94
1.93
0.95
2.92
1.93
0.94
0.89
3.00
2.97
MeO
OMe
O
Cl
N
H
f1 (ppm)


YYGP42
C13CPD DMSO D:\ww 1
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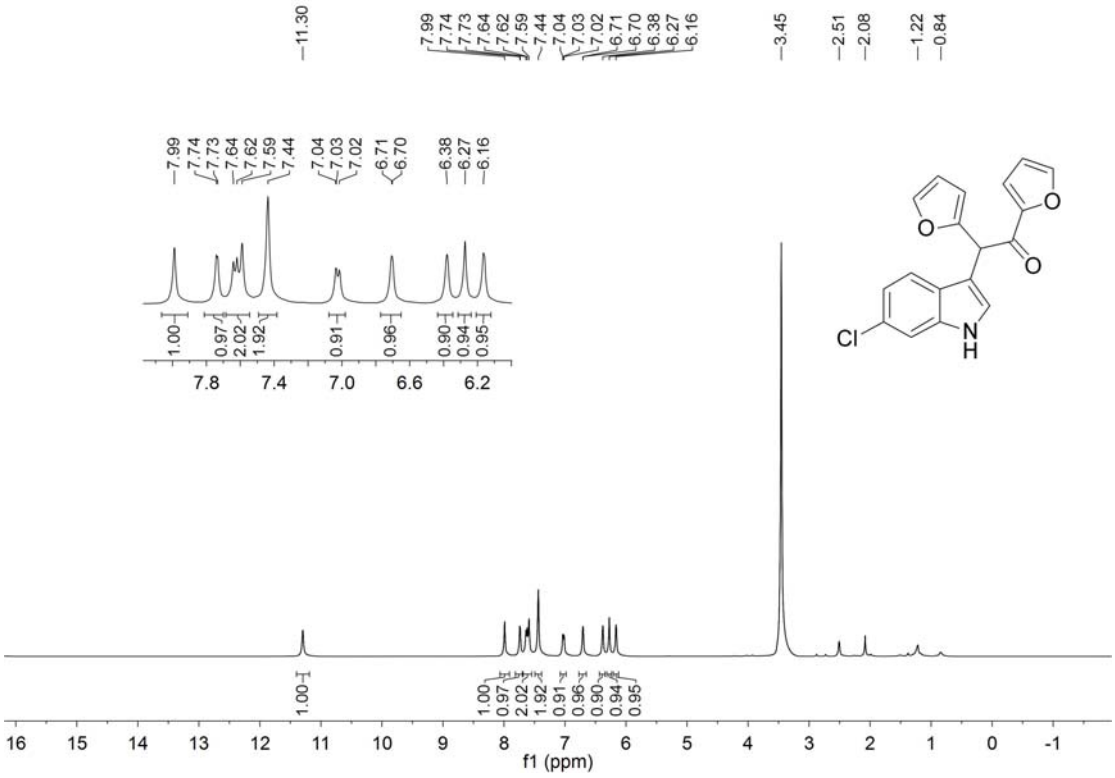
158.40
137.03
132.05
131.49
130.40
129.49
126.44
125.60
125.58
120.62
119.42
114.57
114.38
114.10
111.59
55.96
55.42
48.48
MeO
OMe
O
Cl
N
H
f1 (ppm)

3j2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7.59
7.44
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7.03
7.02
6.71
6.70
6.38
6.27
6.16
3.45
2.51
2.08
1.22
0.84
1.00
0.97
2.02
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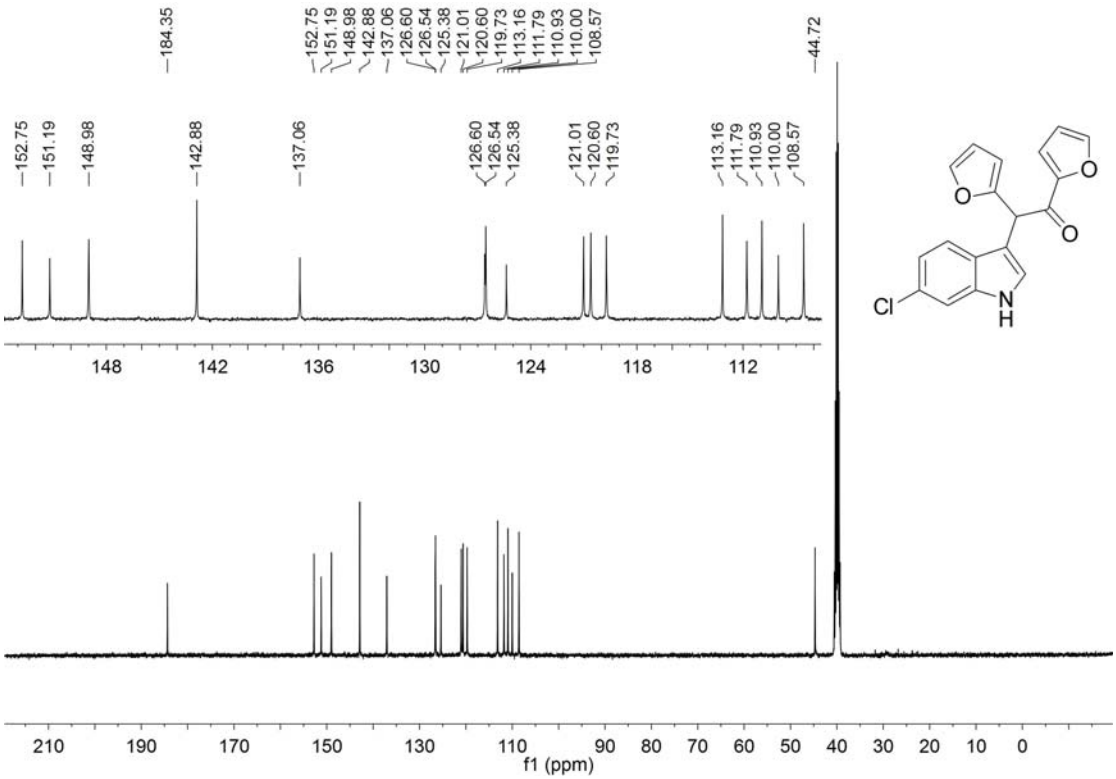
0.91
0.96
0.90
0.94
0.95
Cl
N
H
O
f1 (ppm)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152.75
151.19
148.98
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137.06
126.60
126.54
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120.60
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111.79
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110.00
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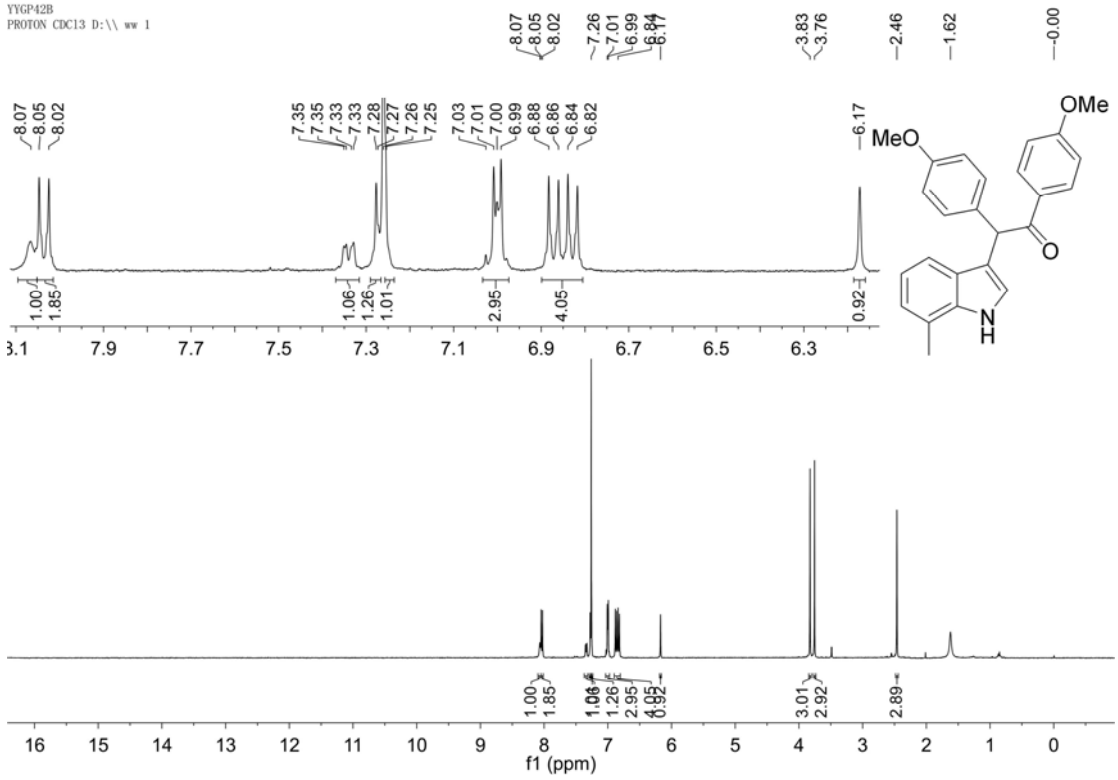
Cl
N
H
O
f1 (ppm)

3k1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PROTON CDC13 D:\\ ww 1
f1 (ppm)
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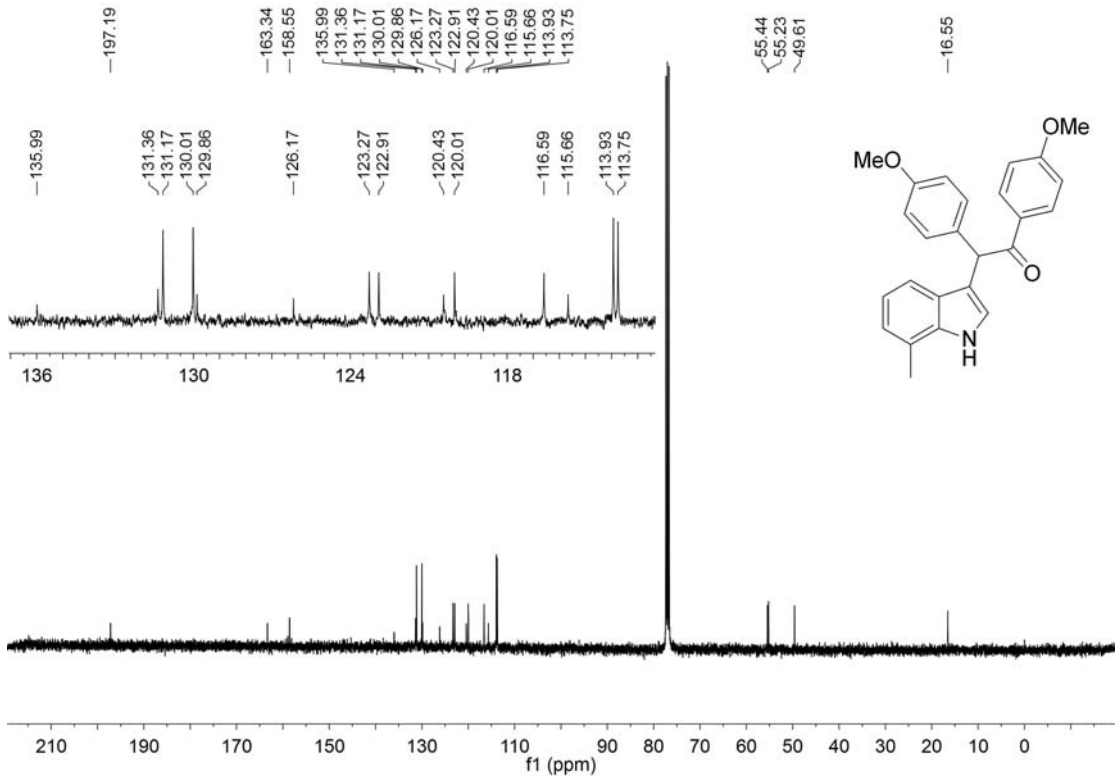
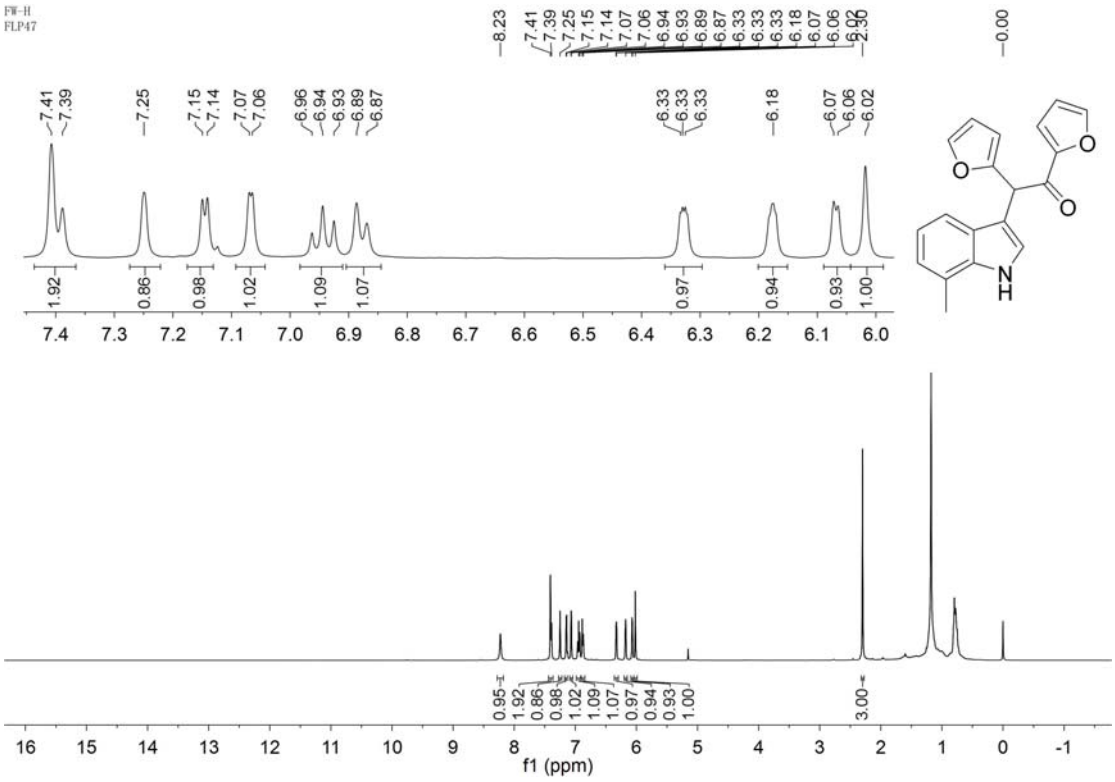
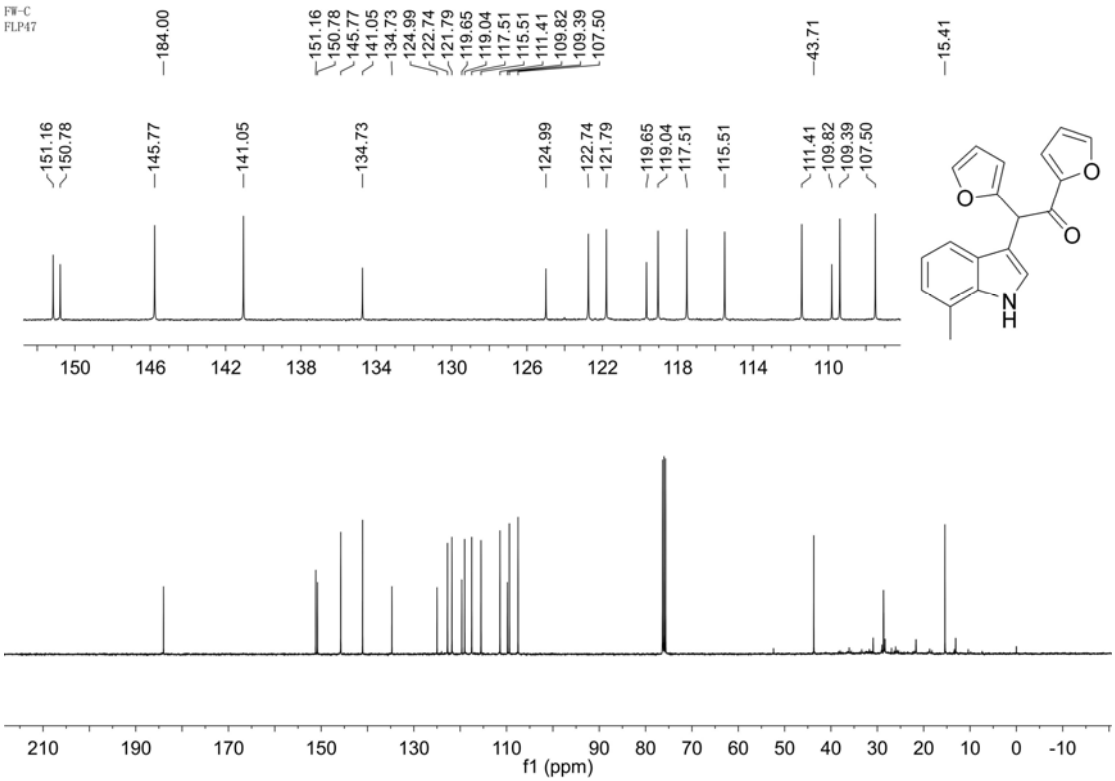
OMe
O
N
H

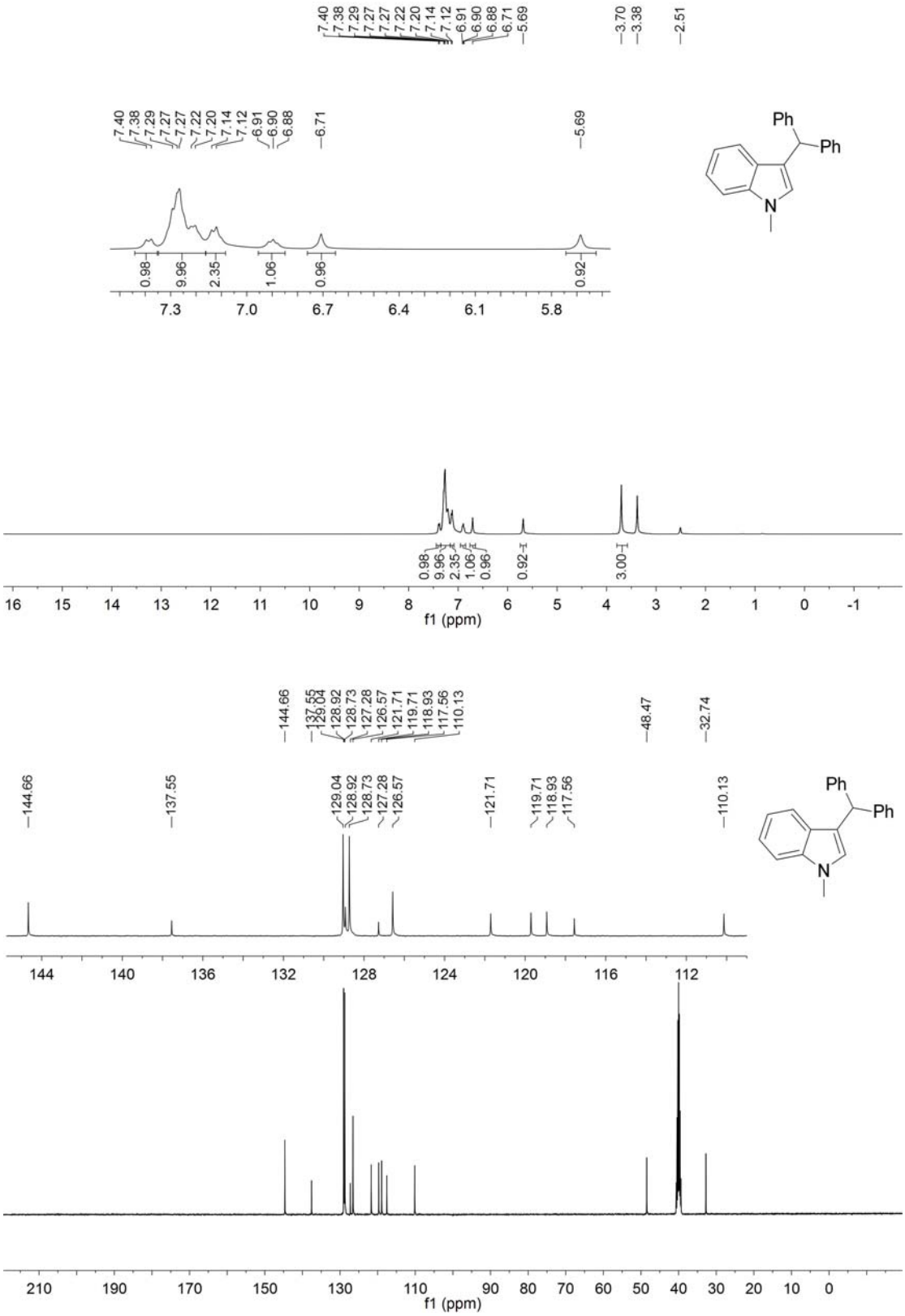

f1 (ppm)
MeO
OMe
O
N
H

3k2





5a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7.38
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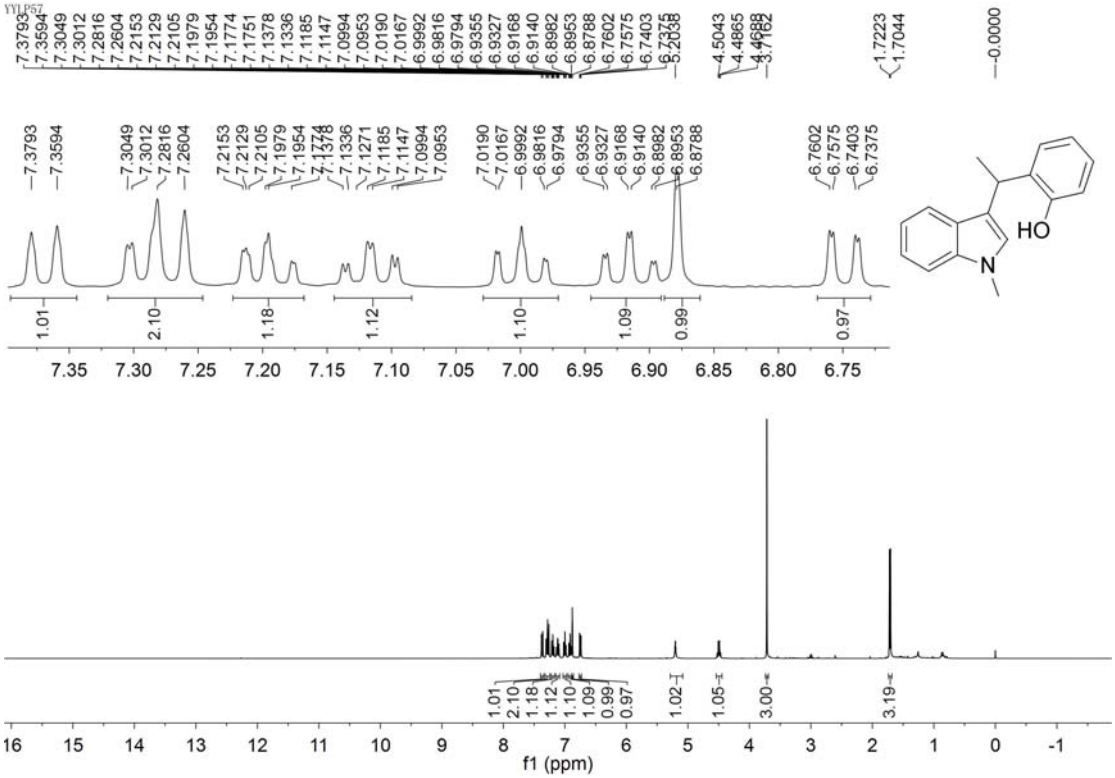
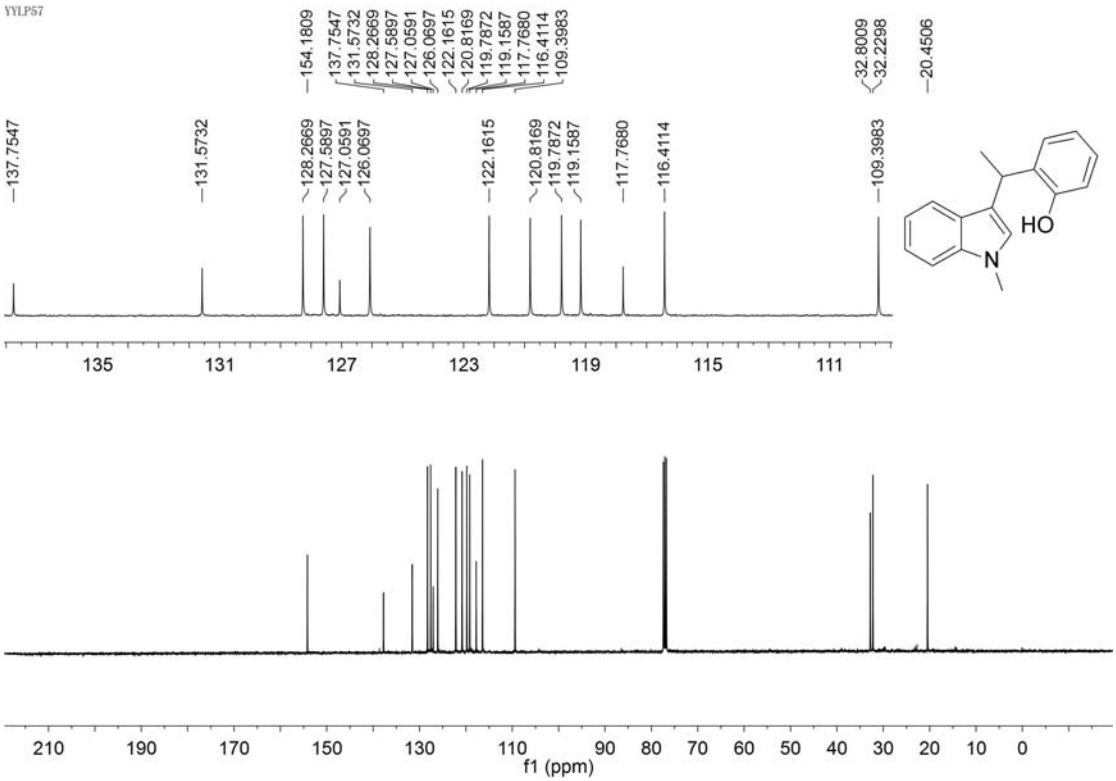
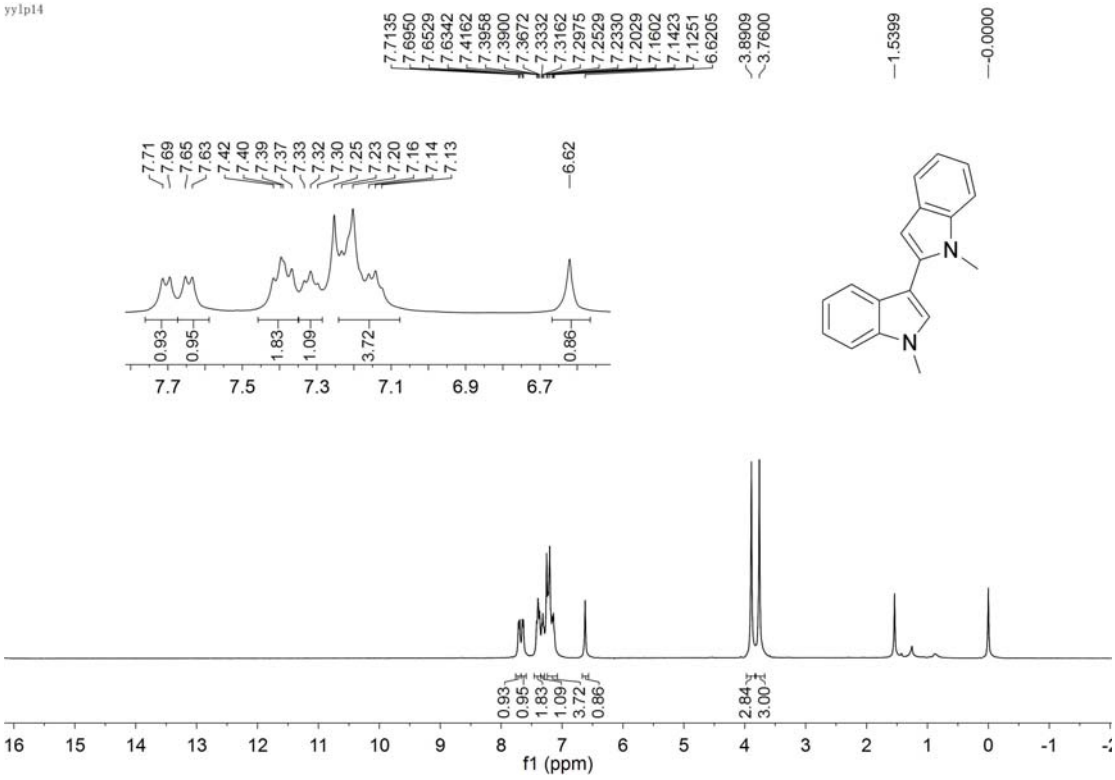
7.27
7.27
7.22
7.20
7.14
7.12
6.91
6.90
6.88
6.71
5.69
3.70
3.38
2.51
Ph
Ph
N
0.98
9.96
2.35
1.06
0.96
0.92
3.00
f1 (ppm)
144.66
137.55
129.04
128.92
128.73
127.28
126.57
121.71
119.71
118.93
117.56
110.13
48.47
32.74

5b





7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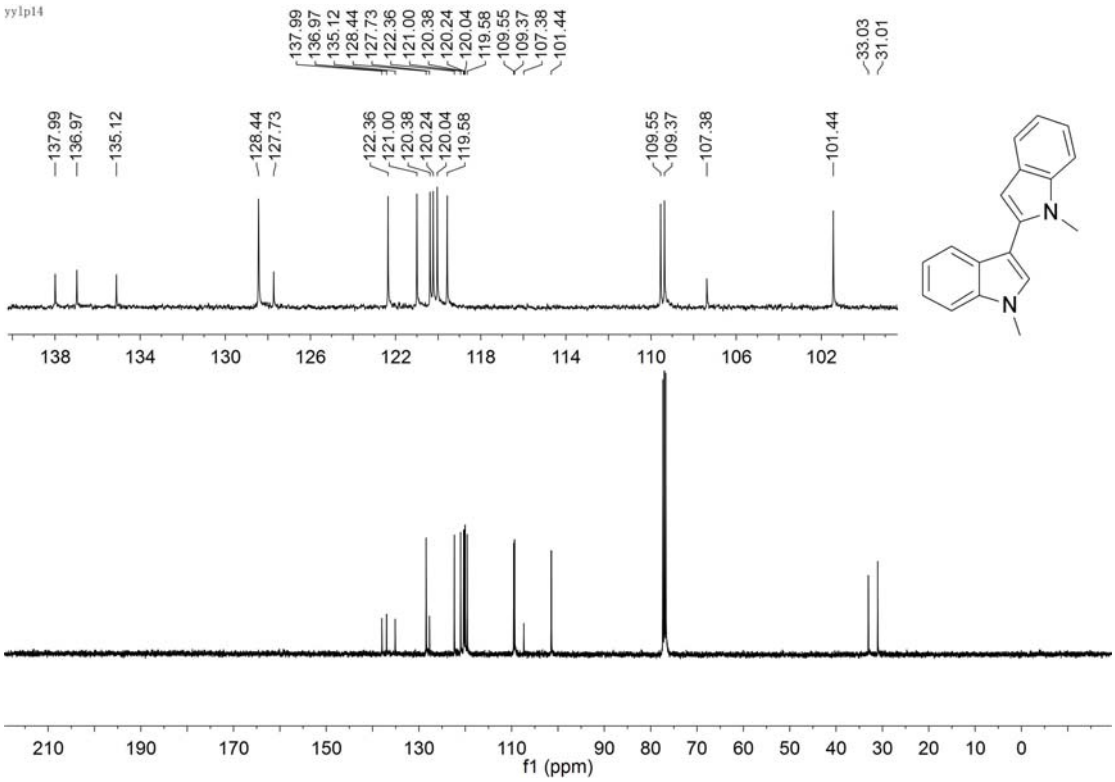
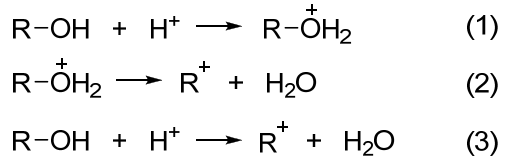
7.6529
7.6342
7.4162
7.3958
7.3900
7.3672
7.3332
7.3162
7.2975
7.2529
7.2330
7.2029
7.1602
7.1423
7.1251
6.6205
3.8909
3.7600
1.5399
0.0000
7.71
7.69
7.65
7.63
7.42
7.40
7.39
7.37
7.33
7.32
7.30
7.25
7.23
7.20
7.16
7.14
7.13
6.62
0.93
0.95
1.83
1.09
3.72
0.86
2.84
3.00
f1 (ppm)

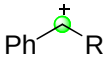

yylp14
137.99
136.97
135.12
128.44
127.73
122.36
121.00
120.38
120.24
120.04
119.58
109.55
109.37
107.38
101.44
33.03
31.01
f1 (ppm)

V. Stability and charge calculations



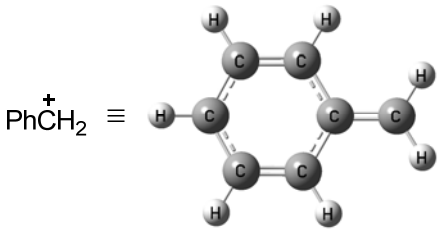
Benzyl cations are usually formed by reaction (1) and reaction (2). According to Hess's law states, the enthalpy of an overall reaction is the sum of the enthalpies of the individual reactions into which a reaction may be divided. The sum of enthalpies of reaction (1) and reaction (2) is equal to the enthalpy of reaction (3). So is Gibbs free energy. We use the Gibbs free energy change (ΔG) of reaction (3) to compare the stabilities of different benzyl cations, and cations with lower energy are more stable.

Table S1. Stabilities and natural population atomic charges (NPA) of the benzyl cations at the M062X/def2TZVP level of theory.

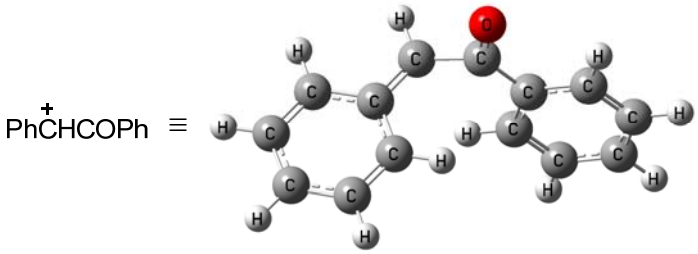


	R = H	R = COPh	R = CO_2Me	R = CN	R = CF_3
ΔG (kJ/mol)	−754.69	−771.37	−746.11	−725.52	−694.09
NBO charge	0.029	0.140	0.114	0.041	0.087

Coordinates of optimised geometries



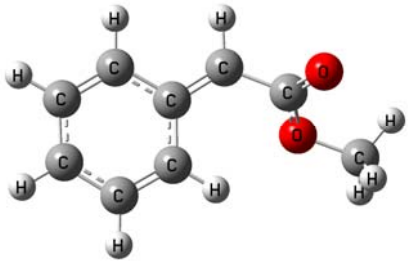
C	-2.73855800	1.36401300	-0.02350200
C	-1.31052400	1.31264800	0.10348700
C	-0.55943100	2.53276700	0.17417900
C	-1.20928800	3.73377900	0.12057400
C	-2.60657100	3.74767600	-0.00417700
C	-3.37176200	2.57396700	-0.07588100
H	-3.29472400	0.43568200	-0.07608300
H	0.51856900	2.48105800	0.26988900
H	-0.66276700	4.66511000	0.17211100
H	-3.11580900	4.70408500	-0.04736500
H	-4.44689000	2.63541200	-0.17174500
C	-0.67125600	0.11244100	0.15595700
H	-1.22048000	-0.82179000	0.10443700
H	0.40782200	0.05199600	0.25101900



C	-4.26327353	4.40005439	2.75107181
C	-3.27203453	3.74474239	1.96245581
C	-1.99421253	4.35435139	1.77991281
C	-1.73013653	5.56148039	2.36991881
C	-2.72018553	6.17857439	3.14588081
C	-3.98094853	5.60460639	3.34059281
H	-5.23244053	3.93184639	2.87432981
H	-1.24780353	3.85741839	1.17125081

H	-0.76966153	6.04044039	2.24004681
H	-2.50313253	7.13460539	3.60822581
H	-4.72060153	6.11289639	3.94315181
C	-3.56159853	2.52334639	1.39790181
H	-4.54640253	2.08513039	1.54441081
C	-1.58192753	0.97203339	0.70535981
C	-1.21455253	0.77162039	2.03721281
C	-0.89160753	0.33659639	-0.33036819
C	-0.15235453	-0.06464761	2.33473981
H	-1.75560753	1.26205839	2.83948381
C	0.16824347	-0.49470961	-0.02538619
H	-1.20342053	0.50312539	-1.35373619
C	0.53545347	-0.69283861	1.30345681
H	0.13928647	-0.23013561	3.36278281
H	0.70950347	-0.99486461	-0.81693919
H	1.36574647	-1.34681061	1.53694081
C	-2.70792453	1.83253539	0.37234581
O	-3.12738653	2.11982839	-0.72316819

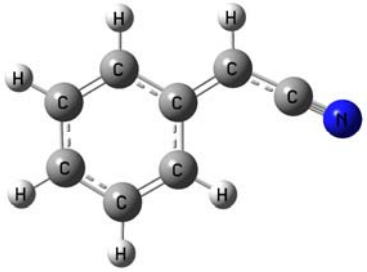
$PhC\overset{+}{H}CO_2Me$ ≡



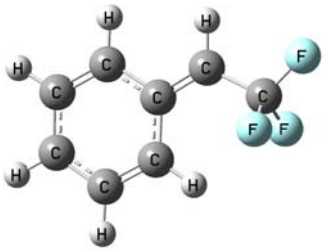
C	-0.89729392	2.63440433	4.07521248
C	-0.89134345	1.62062706	3.06183342
C	-1.49434639	1.88824572	1.78958776
C	-2.06332598	3.10919029	1.55641312
C	-2.04711942	4.08141876	2.56740640
C	-1.46826856	3.85106503	3.82193258
H	-0.44390679	2.41818380	5.03524374
H	-1.48322451	1.12200839	1.02592550
H	-2.52314354	3.33148693	0.60361225
H	-2.50020897	5.04651464	2.37081617
H	-1.47979290	4.62701868	4.57448723

C	-0.30296946	0.41835084	3.34419770
H	0.12705416	0.24738261	4.32756391
C	-0.32579204	-0.80165652	2.47368261
O	-0.84616396	-1.77949037	2.92126210
O	0.22819896	-0.64306009	1.29539797
C	0.26313315	-1.82692870	0.46035183
H	-0.75288987	-2.15599972	0.25438436
H	0.77294489	-1.52245758	-0.44627711
H	0.80993974	-2.61388929	0.97520598

PhCHCN ≡



C	-3.37541115	2.11433621	3.29168457
C	-2.89216215	1.52939821	2.07367757
C	-2.98292915	2.26117321	0.84179457
C	-3.53181615	3.51088121	0.84301457
C	-3.99686715	4.05678521	2.05131557
C	-3.92083115	3.36633921	3.27083757
H	-3.30083215	1.54994521	4.21364457
H	-2.61341615	1.80893821	-0.07142743
H	-3.61041715	4.08118521	-0.07220043
H	-4.43102015	5.05055421	2.04043557
H	-4.29170015	3.82575321	4.17648657
C	-2.35265815	0.27172521	2.11975557
H	-2.29229915	-0.26935079	3.06065857
C	-1.85017615	-0.39982079	0.97939857
N	-1.44251315	-0.94721679	0.05446857

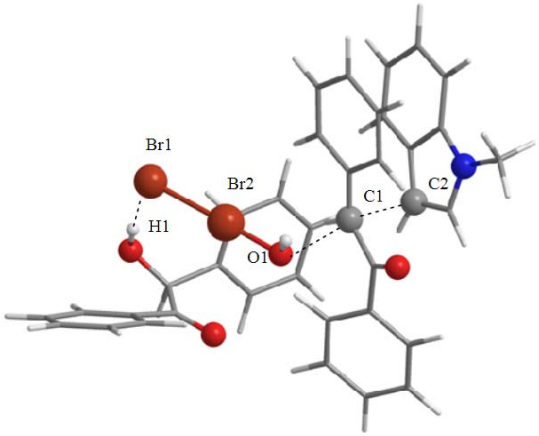
$PhCHCF_3^+$ ≡ 

C	-2.07543600	1.69040500	1.45329100
C	-1.67547400	1.05013100	0.22687700
C	-1.84588000	1.74518100	-1.02430700
C	-2.38426900	2.99866500	-1.02580800
C	-2.76346600	3.59117000	0.19077000
C	-2.61253000	2.94480400	1.42671600
H	-1.94260800	1.15802100	2.38760100
H	-1.54697300	1.27033100	-1.94967900
H	-2.52108400	3.53863800	-1.95241500
H	-3.18969300	4.58839100	0.17220400
H	-2.91900400	3.43939100	2.33788100
C	-1.15114900	-0.20071100	0.30389800
H	-1.03768700	-0.69559200	1.26438100
C	-0.68819600	-1.01607800	-0.89789200
F	-0.22617200	-2.18373500	-0.49905100
F	-1.70626100	-1.21038500	-1.72902200
F	0.27253000	-0.36461200	-1.54415700

VI. Calculations of the reaction mechanism

Geometries of molecules (**1a**, **2a**, **3a1**, and Br_2) and complexes (**Com**, **Int1**, **Int2**, and **TS**) involved in the reaction pathway have been fully optimized by using density functional theory (DFT) in its M062X formulation with the 6-31G(d) basis sets.

Table S2. The crucial bond distances of complexes involved in the raction pathway calculated at the SMD-M062X/6-31G(d) level.



TS

Species	Bond distance (angstroms)				
	R_{H1-Br1}	$R_{Br1-Br2}$	R_{Br2-O1}	R_{O1-C1}	R_{C1-C2}
Com	2.474	2.316	2.513	1.442	3.885
TS	2.323	2.607	1.983	2.243	2.515
Int1	2.291	2.838	1.904	3.052	1.575

Table S3. The natural population (e) analysis (NPA) for the involved atoms calculated at the SMD-M062X/6-31G(d) level.

Species	NBO charge					
	H1	Br1	Br2	O1	C1	C2
Com	0.488	-0.097	0.066	-0.758	0.004	-0.361
TS	0.496	-0.537	0.169	-0.856	-0.016	-0.321
Int1	0.494	-0.705	0.217	-0.863	-0.316	-0.323

Coordinates of optimised geometries

1a

M062X/6-31g(d), SCRF=(smd,solvent=Acetonitrile), Int=UltraFine, E(RM062X) =-402.967393189

C	0.72971600	1.88937300	0.00000700
C	-0.38690800	0.98779300	-0.00000300
C	1.85843800	1.11348600	-0.00000400
C	0.15327800	-0.32529300	-0.00001000
C	-1.78476200	1.14281100	0.00001200
H	2.90240400	1.39877200	0.00000700
C	-0.65327300	-1.47088300	0.00000300
C	-2.58682400	0.01328600	0.00000100
H	-2.22664200	2.13563500	0.00001100
C	-2.02593100	-1.28189800	-0.00000400
H	-0.21821100	-2.46611900	0.00000100
H	-3.66737700	0.12173700	-0.00000100
H	-2.68339300	-2.14618800	-0.00001000
N	1.52250500	-0.21935700	-0.00002100
C	2.44357600	-1.33809900	0.00001800
H	2.29569900	-1.95512700	0.89112500
H	2.29517400	-1.95557200	-0.89069300
H	3.46320700	-0.95115900	-0.00040300
H	0.69775100	2.97007300	-0.00000700

2a

M062X/6-31g(d), SCRF=(smd,solvent=Acetonitrile), Int=UltraFine, E(RM062X) =-690.880449905

O	-0.16504900	1.85460700	-0.44747300
C	-0.47856900	0.67254400	0.26550800
C	-1.93961100	0.28032300	0.18016200
H	-0.23763800	0.88987100	1.31330900
C	-2.39626000	-0.84020800	0.88254200
C	-2.84828900	1.03510000	-0.55889500
C	-3.73747300	-1.20371200	0.83637400
H	-1.69463000	-1.42929100	1.46756900
C	-4.19476800	0.66946200	-0.60823900
H	-2.51090500	1.92085700	-1.08788600

C	-4.64234700	-0.44994100	0.08617700
H	-4.07900700	-2.07606400	1.38578700
H	-4.89235700	1.26694800	-1.18785600
H	-5.68987500	-0.73370200	0.04924700
H	-0.29806400	1.67739300	-1.39548800
C	0.47088000	-0.45297100	-0.20056100
C	1.94356300	-0.22042700	-0.05555100
C	2.47414100	0.89329600	0.60634500
C	2.80932900	-1.18426100	-0.58637700
C	3.85323500	1.03287800	0.73729800
H	1.82007100	1.65667700	1.01293100
C	4.18540400	-1.03983700	-0.45975300
H	2.38512600	-2.04372800	-1.09574000
C	4.70886100	0.06999400	0.20473000
H	4.26032900	1.89653000	1.25380300
H	4.85072700	-1.79003100	-0.87584900
H	5.78398300	0.18426000	0.30683900
O	0.04675800	-1.47875200	-0.69317900

3a1

M062X/6-31g(d), SCRF=(smd,solvent=Acetonitrile), Int=UltraFine, E(RM062X) =-1017.48021572

C	-0.08650000	0.90958300	-0.31565200
C	0.89372000	2.06088600	-0.18336500
C	1.48883400	2.36646000	1.04422900
C	1.21384500	2.83449400	-1.30017800
C	2.38306400	3.42730800	1.15149000
H	1.25316100	1.76303300	1.91656600
C	2.11342200	3.89583500	-1.19732000
H	0.75629700	2.60244600	-2.25932400
C	2.69985600	4.19491900	0.02960000
H	2.83833300	3.65413000	2.11127600
H	2.35634000	4.48453600	-2.07714700
H	3.40287200	5.01846300	0.11311000
C	-1.42772600	1.20990000	0.36365200
C	-2.63956400	0.44492400	-0.08432900

C	-2.57785700	-0.59812600	-1.01564600
C	-3.87491100	0.80173000	0.46777900
C	-3.73831100	-1.27253000	-1.38568400
H	-1.62851600	-0.90064700	-1.44726900
C	-5.03361500	0.13145500	0.09300500
H	-3.90983500	1.61070200	1.19058700
C	-4.96588500	-0.90836400	-0.83454700
H	-3.68308200	-2.08366900	-2.10504200
H	-5.98876900	0.41736100	0.52270000
H	-5.86934100	-1.43525500	-1.12696600
O	-1.51111900	2.02203000	1.26405700
C	0.43983700	-0.39159200	0.23734900
C	1.28688800	-1.31888900	-0.46153500
C	0.23609400	-0.92381300	1.48653700
C	1.54907000	-2.38743500	0.43213200
C	1.84205500	-1.35029100	-1.75156400
N	0.89791900	-2.12120800	1.61190000
H	-0.34710400	-0.54423400	2.31704800
C	2.34485300	-3.48236300	0.07246300
C	2.62946000	-2.43199500	-2.11172100
H	1.65815800	-0.53743300	-2.45002200
C	0.91377500	-2.97392100	2.78399500
C	2.87732900	-3.48685600	-1.20736700
H	2.53579600	-4.29368300	0.76879900
H	3.06689000	-2.47234300	-3.10471500
H	0.52151300	-3.96502300	2.53904600
H	1.93243000	-3.07719300	3.16904400
H	0.28596000	-2.52194700	3.55259400
H	3.49952700	-4.31962300	-1.52136800
H	-0.28350200	0.76468700	-1.38461400

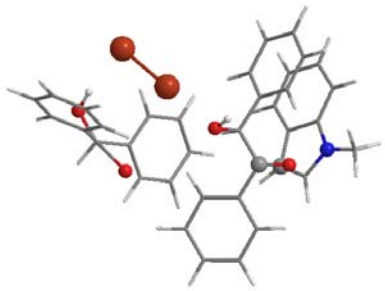
Br_2

M062X/6-31g(d), SCRF=(smd,solvent=Acetonitrile), Int=UltraFine, E(RM062X) =-5143.53969222

Br	0.00000000	0.00000000	1.14289800

Br	0.00000000	0.00000000	-1.14289800

Com



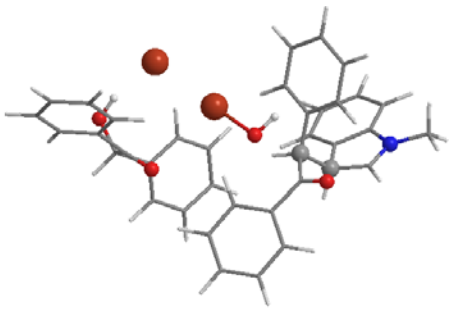
M062X/6-31g(d), SCRF=(smd,solvent=Acetonitrile), Int=UltraFine, E(RM062X) =-6928.31349375

C	1.30435800	0.08057500	-1.17922100
C	1.97259300	-1.26853900	-1.23337800
H	3.40804600	2.06171400	1.94828100
C	2.65036200	-1.72232700	-2.37121800
C	1.79179500	-2.13866800	-0.15278500
C	3.15033000	-3.02304600	-2.41367400
H	2.79033800	-1.06186400	-3.22015400
C	2.27930500	-3.44181600	-0.20306000
H	1.25128000	-1.79048600	0.72502100
C	2.96374600	-3.88464300	-1.33369900
H	3.68033000	-3.36541200	-3.29758600
H	2.13208500	-4.10681000	0.64273400
H	3.35029900	-4.89877500	-1.37368900
C	2.10325100	1.29125700	-1.68647100
C	1.55493000	2.63923200	-1.33970200
C	0.32602900	2.80794900	-0.68997100
C	2.31530900	3.76311100	-1.68749800
C	-0.13143900	4.09022600	-0.39657200
H	-0.30443400	1.96094500	-0.43341200
C	1.86173600	5.03964200	-1.38070000
H	3.26217200	3.61686200	-2.19864900
C	0.63511100	5.20381300	-0.73391400
H	-1.09364400	4.20653300	0.09222700
H	2.45880300	5.90676400	-1.64574900
H	0.27710200	6.20149300	-0.49733600

O	3.09706100	1.16926400	-2.37492500
O	-4.07894500	0.09880900	2.45912400
C	-3.37726600	1.20898600	1.94835600
C	-1.91011800	1.20738800	2.34191500
H	-3.85011500	2.09529200	2.39285500
C	-1.24734500	2.41581800	2.55937500
C	-1.21092600	0.00753500	2.48778600
C	0.09651000	2.42969100	2.92631200
H	-1.79375100	3.34973000	2.45379900
C	0.13382500	0.01807100	2.85562900
H	-1.71670600	-0.94226500	2.33695600
C	0.78754300	1.22902200	3.08134700
H	0.60025500	3.37614400	3.10147500
H	0.66736000	-0.92039600	2.98277300
H	1.82586100	1.23689600	3.39649300
H	-3.93946200	-0.66096700	1.87091500
C	-3.52417900	1.41274800	0.42261700
C	-4.62616200	0.74342700	-0.33783600
C	-5.85304100	0.38366700	0.23336900
C	-4.39884500	0.50427600	-1.69974200
C	-6.83258000	-0.21869000	-0.55224600
H	-6.04500000	0.57890300	1.28192100
C	-5.36886300	-0.12050300	-2.47236400
H	-3.44645400	0.79660500	-2.13040600
C	-6.58797400	-0.48327500	-1.89798700
H	-7.78671900	-0.48674000	-0.10912500
H	-5.18016000	-0.32037700	-3.52267200
H	-7.34876600	-0.96874300	-2.50216500
O	-2.73953600	2.14372100	-0.15057400
Br	-1.64730800	-1.26102100	-0.72474600
Br	-3.27288700	-2.50341700	0.36000600
C	3.96002700	1.34167200	1.36106700
C	4.19626500	-0.04411100	1.66035900
C	4.59873100	1.59857200	0.17658600
C	4.98801200	-0.55509800	0.59601700

C	3.84239800	-0.91196300	2.70963400
N	5.21431600	0.46638200	-0.29313900
H	4.66263800	2.51628900	-0.39371600
C	5.42864100	-1.88326400	0.55280000
C	4.27581800	-2.22860500	2.67160800
H	3.24774300	-0.55449600	3.54624100
C	5.91315000	0.33069900	-1.55413000
C	5.06418800	-2.70873700	1.60500500
H	6.03049000	-2.25066400	-0.27372500
H	4.00939900	-2.90415900	3.47927900
H	6.93916800	-0.00996600	-1.38684500
H	5.39244900	-0.38302500	-2.19956600
H	5.93255800	1.30260500	-2.04783300
H	5.38411000	-3.74676000	1.60459000
H	0.99936300	0.27978500	-0.14641000
O	0.08315800	0.09124200	-1.94544600
H	0.26472500	-0.33284800	-2.80574300

Int1



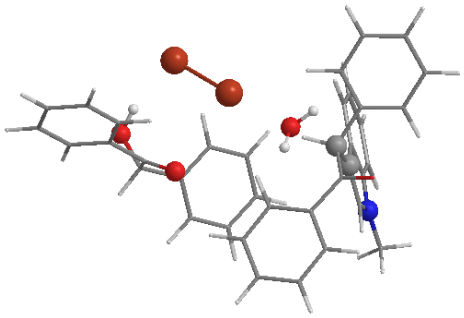
M062X/6-31g(d), SCRF=(smd,solvent=Acetonitrile), Int=UltraFine, E(RM062X) =-6928.29410551

C	2.46979600	0.51003100	-0.51452900
C	2.54943500	-0.96624500	-0.85621900
H	3.72748800	2.08718700	0.33075800
C	3.27949500	-1.45775400	-1.94754200
C	1.91446300	-1.87899900	-0.00779200
C	3.36587800	-2.83041500	-2.17765000
H	3.76556300	-0.77088600	-2.63284600
C	2.00463400	-3.24956100	-0.23600700
H	1.32306100	-1.50676300	0.82459300

C	2.73400100	-3.72992300	-1.32087300
H	3.93055800	-3.19437400	-3.03090700
H	1.49573300	-3.93921500	0.43079900
H	2.80577300	-4.79818600	-1.50212800
C	2.15989500	1.45988500	-1.67766400
C	1.21268500	2.59342100	-1.44922800
C	0.02142600	2.46099400	-0.72776800
C	1.55545500	3.82694000	-2.01582200
C	-0.82146800	3.56211800	-0.59238300
H	-0.29181100	1.49578500	-0.33461400
C	0.72683900	4.93041900	-1.84641900
H	2.47859000	3.90956100	-2.58169200
C	-0.46537500	4.79602400	-1.13509100
H	-1.76456700	3.43719600	-0.07179400
H	1.00474300	5.88907300	-2.27381300
H	-1.12279700	5.65194300	-1.01250800
O	2.81102100	1.39750800	-2.70585700
O	-4.16900500	-0.29469300	2.52622800
C	-3.69496800	0.86787100	1.89079300
C	-2.27178000	1.23292200	2.27012800
H	-4.35357000	1.68840800	2.21366600
C	-1.95107900	2.54567200	2.61584500
C	-1.26647700	0.26110800	2.27550900
C	-0.64398200	2.89559000	2.95673500
H	-2.73233600	3.30309600	2.61852300
C	0.03466300	0.60658000	2.62998000
H	-1.50190800	-0.76137500	1.99106400
C	0.35378900	1.92392200	2.96649100
H	-0.40961000	3.92290000	3.22074100
H	0.80033000	-0.16456400	2.65047800
H	1.37073100	2.19028300	3.24320300
H	-3.83994200	-1.06431600	2.01151100
C	-3.85249700	0.80626300	0.36087900
C	-5.06988200	0.14725400	-0.20840300
C	-6.29731700	0.15449300	0.45676100

C	-4.96272400	-0.43521800	-1.47501700
C	-7.42137200	-0.39682300	-0.15658300
H	-6.37565300	0.58890700	1.44858000
C	-6.08128100	-0.99758000	-2.07757500
H	-3.98409800	-0.47124300	-1.94609000
C	-7.31403000	-0.97232800	-1.42125000
H	-8.37918300	-0.38041600	0.35481000
H	-5.99651200	-1.46176800	-3.05578400
H	-8.18926200	-1.40842200	-1.89420200
O	-3.04441400	1.33854800	-0.37287500
Br	-1.08787400	-1.05207200	-1.17934000
Br	-2.85627700	-2.48949300	0.51217100
C	3.83263600	1.02031600	0.08849000
C	4.30896300	0.19546600	1.25498900
C	4.95978800	0.83597000	-0.87760400
C	5.50523400	-0.42099100	0.89660100
C	3.77086900	-0.05186100	2.50788900
N	5.84972900	0.02304500	-0.41679800
H	5.06415400	1.27802600	-1.86167500
C	6.20581500	-1.29270000	1.71209000
C	4.45337700	-0.92539000	3.35818600
H	2.85025900	0.42615100	2.82361500
C	7.04450200	-0.43524800	-1.11896700
C	5.64636200	-1.53924700	2.96616100
H	7.13509500	-1.75696900	1.39937700
H	4.04940500	-1.13059100	4.34424900
H	7.91770400	-0.20959000	-0.50497800
H	6.95814900	-1.51370400	-1.26666700
H	7.10228200	0.08001700	-2.07590300
H	6.15082300	-2.21522400	3.64847100
H	1.72911900	0.64883200	0.27962800
O	0.11022900	-0.13393000	-2.33999100
H	0.74161900	-0.83357100	-2.58286000

Int2



M062X/6-31g(d), SCRF=(smd,solvent=Acetonitrile), Int=UltraFine, E(RM062X) =-6928.32803126

C	2.44148100	0.65100300	0.79879900
C	2.91425500	2.09119400	0.70879200
C	4.24816900	2.42187600	0.96842200
C	2.02604400	3.10969800	0.35918000
C	4.68014700	3.74246600	0.88772700
H	4.94984500	1.63436700	1.22871300
C	2.45607700	4.43422000	0.27313000
H	0.98920200	2.86378400	0.14467200
C	3.78470300	4.75455400	0.53933500
H	5.71934300	3.98309100	1.09297600
H	1.75156900	5.21209100	-0.00682100
H	4.12330100	5.78415600	0.47111100
C	2.38431800	0.17891500	2.25888000
C	1.52701000	-1.00420800	2.61265200
C	0.33994400	-1.33624400	1.95028200
C	1.96559600	-1.79731700	3.68155500
C	-0.39530400	-2.44677700	2.36526500
H	-0.05392200	-0.71807300	1.14579900
C	1.24368800	-2.91749000	4.07464600
H	2.88471900	-1.52402600	4.19084900
C	0.05822800	-3.24257500	3.41483300
H	-1.32809900	-2.67450300	1.86157100
H	1.59979100	-3.53281200	4.89541000
H	-0.51509900	-4.11199800	3.72313400
O	3.10688300	0.67013400	3.10255700
O	-3.70410200	-1.37713400	-2.42384200

C	-3.17368100	-1.97892600	-1.25700300
C	-1.67095600	-2.16256600	-1.31456400
H	-3.64655600	-2.96787400	-1.18766600
C	-1.09253100	-3.37485500	-0.94139800
C	-0.84509700	-1.11948900	-1.74310900
C	0.29135800	-3.54801200	-0.99277600
H	-1.73039600	-4.19208600	-0.61212900
C	0.53453600	-1.28823200	-1.79459000
H	-1.27533400	-0.17116200	-2.05218800
C	1.10866200	-2.50439500	-1.41962400
H	0.72686500	-4.49972800	-0.70255700
H	1.16440100	-0.47192800	-2.13633600
H	2.18688900	-2.63512200	-1.47081200
H	-3.55278000	-0.42083500	-2.36114000
C	-3.59663000	-1.21261000	0.01073400
C	-4.98454300	-0.66151900	0.08544600
C	-6.05197500	-1.22177100	-0.62281600
C	-5.20403400	0.43361600	0.92899900
C	-7.33379600	-0.69917300	-0.46939500
H	-5.88497300	-2.06332900	-1.28713500
C	-6.48017900	0.96593700	1.06327400
H	-4.35803400	0.86834600	1.45509900
C	-7.54745800	0.39451300	0.36815500
H	-8.16530500	-1.14261500	-1.00826800
H	-6.64628600	1.82386400	1.70748400
H	-8.54666800	0.80578700	0.47673700
O	-2.82159000	-1.06084500	0.93474200
Br	-1.55523900	1.73803500	0.36899800
Br	-3.01339300	1.91328100	-1.41612600
C	3.34592400	-0.29246000	0.03472100
C	3.75890700	-0.13271300	-1.33587000
C	3.93170600	-1.45493200	0.47239400
C	4.57698600	-1.24660400	-1.65194000
C	3.52036100	0.83636700	-2.32748800
N	4.66502200	-2.03745200	-0.53299000

H	3.88418100	-1.94171800	1.43855700
C	5.15280600	-1.42215800	-2.91696500
C	4.08668200	0.66662400	-3.58072800
H	2.90057600	1.70322600	-2.11274700
C	5.42150000	-3.27017500	-0.43797600
C	4.89575700	-0.45227500	-3.87216000
H	5.77546700	-2.28448300	-3.13688900
H	3.90930500	1.40744600	-4.35455600
H	5.04552500	-4.00593500	-1.15501500
H	6.48098500	-3.08502800	-0.63746200
H	5.31325500	-3.66900000	0.57128600
H	5.32532800	-0.55389100	-4.86423800
H	1.43029900	0.59615200	0.37199700
O	0.05020900	1.67808700	2.36545600
H	0.21449100	2.58395600	2.68088200
H	-0.38809600	1.22301100	3.10584700

TS

M062X/6-31g(d), SCRF=(smd,solvent=Acetonitrile), Int=UltraFine, E(RM062X) =-6928.25169681

C	1.73166900	0.35307700	-0.78081800
C	2.27884900	-0.93944300	-1.05283500
H	2.76209400	1.84648600	1.31316500
C	3.17425700	-1.21194500	-2.11126800
C	1.92872100	-1.97727900	-0.15784200
C	3.70033900	-2.48763200	-2.25617800
H	3.44542300	-0.42249800	-2.80097800
C	2.45813600	-3.24729800	-0.31295300
H	1.23021500	-1.76268600	0.64621900
C	3.35296000	-3.49888100	-1.35659000
H	4.38996700	-2.69715900	-3.06775300
H	2.18935300	-4.03834200	0.37946300
H	3.77800600	-4.49155100	-1.47288700
C	1.82600100	1.58004500	-1.65387100
C	1.19917700	2.82924400	-1.13036700
C	0.05388800	2.82026900	-0.32629100

C	1.79041800	4.04414100	-1.49709400
C	-0.49557300	4.02862100	0.09466300
H	-0.45727100	1.89111400	-0.08174000
C	1.25459700	5.24490300	-1.04660200
H	2.67218000	4.03327900	-2.13141100
C	0.10784600	5.23657800	-0.25150200
H	-1.40645700	4.01286000	0.68382100
H	1.72419900	6.18493500	-1.31931900
H	-0.32045700	6.17410600	0.09063400
O	2.41934600	1.56596100	-2.71679900
O	-4.07898500	-0.46610400	2.35302000
C	-3.53140900	0.77055700	1.97477400
C	-2.09205200	0.95355000	2.42553600
H	-4.14378000	1.54071300	2.46585800
C	-1.63977100	2.20210100	2.85283000
C	-1.20097800	-0.12130900	2.39397200
C	-0.31064000	2.38566300	3.23242500
H	-2.33577300	3.03699800	2.89044100
C	0.12746200	0.06076200	2.77060500
H	-1.54020700	-1.10366000	2.07795200
C	0.57923800	1.31335600	3.18951300
H	0.02714700	3.36360600	3.56344200
H	0.80582000	-0.78758000	2.74740100
H	1.61389600	1.44984800	3.49379600
H	-3.76735900	-1.15817800	1.73426500
C	-3.64962800	1.09072900	0.46732600
C	-4.66860800	0.40250200	-0.38588800
C	-5.87440100	-0.09900800	0.11547800
C	-4.40617400	0.33695000	-1.75973100
C	-6.80839800	-0.65636900	-0.75488400
H	-6.08259700	-0.05005900	1.17802500
C	-5.33011000	-0.24141200	-2.62089700
H	-3.46244800	0.72537600	-2.12902400
C	-6.53502900	-0.73607700	-2.11899000
H	-7.74936000	-1.03342000	-0.36569400

H	-5.11711400	-0.30344500	-3.68392600
H	-7.26061500	-1.18275600	-2.79263800
O	-2.93829800	1.95331200	-0.01107300
Br	-1.33353200	-1.04754200	-0.93722300
Br	-2.84784200	-2.75615700	0.32179900
C	3.46153400	1.15731000	0.85819400
C	3.95668200	-0.08042700	1.40199200
C	4.26473500	1.43741900	-0.24931600
C	4.97060100	-0.52823900	0.52342600
C	3.63710800	-0.86988200	2.51641400
N	5.12743500	0.42834500	-0.47335900
H	4.26431900	2.30486500	-0.89688900
C	5.65212500	-1.73165000	0.69583600
C	4.31265900	-2.06870100	2.70296600
H	2.89126100	-0.54284000	3.23371800
C	6.11048600	0.35549600	-1.54136500
C	5.30203100	-2.49872600	1.80031700
H	6.42257600	-2.05216100	0.00122100
H	4.07746700	-2.68540800	3.56482200
H	7.11843900	0.45167400	-1.12960300
H	6.01936200	-0.60196200	-2.05970600
H	5.92068900	1.16788600	-2.24306500
H	5.80887800	-3.44279900	1.97486900
H	1.10923200	0.43840700	0.10514800
O	-0.20080300	0.25413200	-1.91529300
H	0.08640000	-0.24698100	-2.70100700