Supporting Information

The Concise Synthesis of Spiro-Cyclopropane Compounds *via* the Dearomatization of Indole Derivatives

Jing Luo,[a] Bo Wu,[b] Mu-Wang Chen,[b] Guo-Fang Jiang[a,*] and Yong-Gui Zhou[b,*]

[a] *State Key Laboratory of Chemo/Biosensing and Chemometrics, College of Chemistry and Chemical Engineering, Hunan University, Changsha 410082, China and* [b]*State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, 457 Zhongshan Road, Dalian 116023, China.*

Email: gfjiang@hnu.edu.cn & ygzhou@dicp.ac.cn

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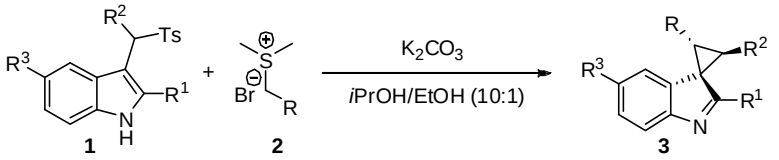
1. General:

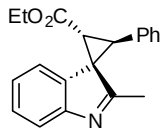
All reactions were carried out under an atmosphere of nitrogen using standard Schlenk techniques, unless otherwise noted. Commercially available reagents were used without further purification. Solvents were treated prior to use according to the standard methods. ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra were recorded at room temperature in $CDCl_3$ on 400 MHz instrument with tetramethylsilane (TMS) as internal standard. Flash column chromatography was performed on silica gel (200-300 mesh). All reactions were monitored by TLC analysis. Arylsulfonyl indoles **1** were prepared according to the known methods.[1]

2. General Procedure for Synthesis of Spiro-Cyclopropanes 3



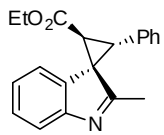
A reaction mixture of arylsulfonyl indole **1** (0.25 mmol), sulfonium salt **2** (0.375 mmol) and K_2CO_3 (104 mg, 0.75 mmol) in *i*PrOH (3.0 mL) and EtOH (0.3 mL) was stirred at room temperature for 12 h. Then water (20 mL) was added to the mixture. The organic layer was separated and the aqueous layer was extracted with dichloromethane (30 mL×3). The combined organic layer was dried by anhydrous sodium sulfate, concentrated in *vacuo*. The crude products were purified by flash chromatography on silica gel using petroleum ether and ethyl acetate to give the corresponding product spiro-cyclopropanes **3**.

Ethyl 2'-methyl-3-phenylspiro[cyclopropane-1,3'-indole]-2-carboxylate (3a): 83% yield, unknown compound, white solid, mp = 106-108 °C, R_f = 0.58 (petroleum ether/ethyl acetate 10/1).



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 7.7 Hz, 1H), 7.55 (d, *J* = 7.6 Hz, 1H), 7.42-7.29 (m, 4H), 7.25-7.19 (m, 3H), 4.30-4.06 (m, 3H), 3.35 (d, *J* = 8.1 Hz, 1H), 1.58 (s, 3H), 1.24 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.6, 168.1, 155.4, 136.0, 134.4, 129.4, 128.9, 128.2, 127.7, 124.9, 121.8, 120.3, 61.8, 48.0, 38.3, 35.6, 18.1, 14.3. HRMS Calculated for $C_{20}H_{20}NO_2$ $[M+H]^+$ 306.1494, found 306.1482.

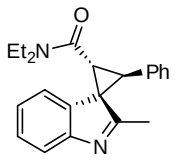
Ethyl 2'-methyl-3-phenylspiro[cyclopropane-1,3'-indole]-2-carboxylate (3a'): unknown compound, white solid, mp = 103-104 °C, R_f = 0.52 (petroleum ether/ethyl acetate 10/1). ^{1}H NMR



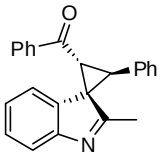
(400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 7.7 Hz, 1H), 7.28-7.21 (m, 4H), 7.15-7.04 (m, 2H), 6.85 (t, *J* = 7.5 Hz, 1H), 6.11 (d, *J* = 7.5 Hz, 1H), 4.28-4.22 (m, 2H), 4.09 (d, *J* = 8.3 Hz, 1H), 3.25 (d, *J* = 8.3 Hz, 1H), 2.39 (s, 3H), 1.30 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.9, 168.5, 154.7, 135.9, 133.7, 129.8, 128.7, 128.1, 127.5, 124.4, 120.6, 120.2, 62.0, 48.8, 37.7, 37.4, 18.2, 14.4. HRMS Calculated for $C_{20}H_{20}NO_2$ $[M+H]^+$ 306.1494, found 306.1492.

(1) (a) Palmieri, A.; Petrini, M. *J. Org. Chem.* **2007**, *72*, 1863. (b) Motokura, K.; Nakagiri, N.; Mizugaki, T.; Ebitani, K.; Kaneda, K. *J. Org. Chem.* **2007**, *72*, 6006.

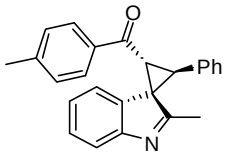
***N*, *N*-Diethyl-2'-methyl-3-phenylspiro[cyclopropane-1,3'-indole]-2-carboxamide (3b):** 78% yield, unknown compound, white solid, mp = 152-154 °C, R_f = 0.37 (petroleum ether/ethyl acetate 5/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 7.7 Hz, 1H), 7.38-7.22 (m, 7H), 7.16 (t, *J* = 7.5 Hz, 1H), 4.24 (d, *J* = 7.9 Hz, 1H), 3.51-3.46 (m, 1H), 3.40 (d, *J* = 7.9 Hz, 1H), 3.20-3.15 (m, 1H), 2.88 (dd, *J* = 7.2 Hz, 2H), 1.59 (s, 3H), 0.98 (t, *J* = 7.1 Hz, 3H), 0.80 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.5, 165.3, 155.0, 136.4, 135.2, 129.5, 128.8, 128.0, 127.5, 124.9, 120.6, 120.2, 47.2, 41.7, 40.6, 38.2, 36.3, 18.0, 13.8, 13.3. HRMS Calculated for $C_{22}H_{25}N_2O$ $[M+H]^+$ 333.1967, found 333.1961.



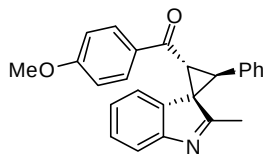
(2'-Methyl-2-phenylspiro[cyclopropane-1,3'-indole]-3-yl)(phenyl)methanone (3c): 60% yield, unknown compound, yellow solid, mp = 127-128 °C, R_f = 0.45 (petroleum ether/ethyl acetate 10/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74-7.67 (m, 2H), 7.59 (d, *J* = 7.7 Hz, 1H), 7.51 (t, *J* = 7.4 Hz, 1H), 7.40-7.32 (m, 5H), 7.31-7.27 (m, 3H), 7.24 (d, *J* = 7.3 Hz, 1H), 7.13 (t, *J* = 7.5 Hz, 1H), 4.45 (d, *J* = 8.2 Hz, 1H), 4.20 (d, *J* = 8.2 Hz, 1H), 1.78 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.6, 177.0, 155.1, 137.2, 135.5, 134.8, 133.7, 129.6, 129.0, 129.0, 128.3, 128.2, 127.7, 125.2, 121.1, 120.4, 49.5, 40.0, 37.4, 18.2. HRMS Calculated for $C_{24}H_{20}NO$ $[M+H]^+$ 338.1545, found 338.1543.



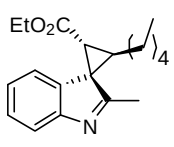
(2'-Methyl-2-phenylspiro[cyclopropane-1,3'-indole]-3-yl)(*p*-tolyl)methanone (3d): 55% yield, unknown compound, yellow solid, mp = 167-169 °C, R_f = 0.45 (petroleum ether/ethyl acetate 10/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63-7.54 (m, 3H), 7.37-7.27 (m, 6H), 7.21 (d, *J* = 7.4 Hz, 1H), 7.18-7.06 (m, 3H), 4.41 (d, *J* = 8.2 Hz, 1H), 4.17 (d, *J* = 8.2 Hz, 1H), 2.34 (s, 3H), 1.75 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.1, 177.1, 155.1, 144.7, 135.6, 134.9, 134.7, 129.7, 129.6, 128.9, 128.4, 128.2, 127.6, 125.1, 121.1, 120.3, 49.4, 40.0, 37.4, 21.8, 18.2. HRMS Calculated for $C_{25}H_{22}NO$ $[M+H]^+$ 352.1701, found 352.1698.



(4-Methoxyphenyl)(2'-methyl-2-phenylspiro[cyclopropane-1,3'-indole]-3-yl)methanone (3e): 71% yield, unknown compound, white solid, mp = 158-159 °C, R_f = 0.25 (petroleum ether/ethyl acetate 3/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76-7.66 (m, 2H), 7.58 (d, *J* = 7.7 Hz, 1H), 7.37-7.28 (m, 6H), 7.22 (d, *J* = 7.2 Hz, 1H), 7.16-7.08 (m, 1H), 6.89-6.80 (m, 2H), 4.42 (d, *J* = 8.2 Hz, 1H), 4.17 (d, *J* = 8.2 Hz, 1H), 3.82 (s, 3H), 1.77 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.8, 177.2, 164.1, 155.1, 135.7, 135.0, 130.6, 130.2, 129.6, 128.9, 128.1, 127.5, 125.1, 121.0, 120.3, 114.2, 55.6, 49.2, 39.8, 37.4, 18.2. HRMS Calculated for $C_{25}H_{22}NO_2$ $[M+H]^+$ 368.1651, found 368.1646.

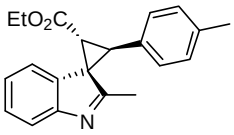


Ethyl 2'-methyl-3-pentylspiro[cyclopropane-1,3'-indole]-2-carboxylate (3f): 56% yield, unknown compound, orange oil, R_f = 0.55 (petroleum ether/ethyl acetate 10/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 7.6 Hz, 1H), 7.40 (d, *J* = 7.5 Hz, 1H), 7.31 (t, *J* = 7.5 Hz, 1H), 7.16 (t, *J* = 7.5 Hz, 1H), 4.30-3.86 (m, 2H), 2.81 (d, *J* = 8.1 Hz, 1H), 2.75-2.60 (m, 1H), 2.31 (s, 3H), 1.93-1.85 (m, 1H), 1.80-1.71 (m, 1H), 1.38-1.22 (m, 6H), 1.16 (t, *J* = 7.1 Hz, 3H), 0.85 (brs, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.6, 168.3, 154.9, 136.7, 127.3, 124.8, 121.6, 120.1, 61.4, 47.4, 38.7, 35.9, 31.4, 29.1, 28.5, 22.6,



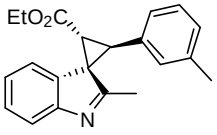
19.2, 14.3, 14.1. HRMS Calculated for $C_{19}H_{26}NO_2$ $[M+H]^+$ 300.1964, found 300.1963.

Ethyl 2'-methyl-3-*p*-tolylspiro[cyclopropane-1,3'-indole]-2-carboxylate (3g): 88% yield, unknown compound, white solid, mp = 123-125 °C, R_f = 0.48 (petroleum ether/ethyl acetate 10/1).

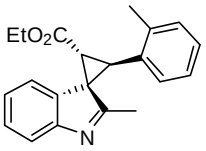


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 7.7 Hz, 1H), 7.53 (d, *J* = 7.6 Hz, 1H), 7.40-7.32 (m, 1H), 7.25-7.19 (m, 1H), 7.15-7.05 (m, 4H), 4.29-4.08 (m, 2H), 4.05 (d, *J* = 8.1 Hz, 1H), 3.32 (d, *J* = 8.1 Hz, 1H), 2.34 (s, 3H), 1.59 (s, 3H), 1.23 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.8, 168.2, 155.4, 138.0, 136.1, 131.3, 129.6, 129.3, 127.7, 124.9, 121.8, 120.3, 61.8, 48.1, 38.2, 35.7, 21.3, 18.2, 14.4. HRMS Calculated for $C_{21}H_{22}NO_2$ $[M+H]^+$ 320.1651, found 320.1649.

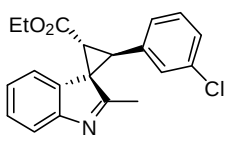
Ethyl 2'-methyl-3-*m*-tolylspiro[cyclopropane-1,3'-indole]-2-carboxylate (3h): 86% yield, unknown compound, colourless oil, R_f = 0.45 (petroleum ether/ethyl acetate 10/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 7.7 Hz, 1H), 7.53 (d, *J* = 7.5 Hz, 1H), 7.39-7.37 (m, 1H), 7.23-7.19 (m, 2H), 7.10 (d, *J* = 7.5 Hz, 1H), 7.03 (brs, 2H), 4.21-4.14 (m, 2H), 4.06 (d, *J* = 8.2 Hz, 1H), 3.33 (d, *J* = 8.2 Hz, 1H), 2.31 (s, 3H), 1.60 (s, 3H), 1.23 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.8, 168.2, 155.4, 138.7, 136.1, 134.3, 130.1, 129.0, 128.8, 127.7, 126.4, 124.9, 121.8, 120.3, 61.8, 48.1, 38.4, 35.7, 21.4, 18.1, 14.4. HRMS Calculated for $C_{21}H_{22}NO_2$ $[M+H]^+$ 320.1651, found 320.1642.



Ethyl 2'-methyl-3-*o*-tolylspiro[cyclopropane-1,3'-indole]-2-carboxylate (3i): 84% yield, unknown compound, white solid, mp = 160-162 °C, R_f = 0.45 (petroleum ether/ethyl acetate 10/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63-7.57 (m, 2H), 7.41-7.32 (m, 2H), 7.25-7.12 (m, 4H), 4.38-4.04 (m, 2H), 3.90 (d, *J* = 8.2 Hz, 1H), 3.38 (d, *J* = 8.2 Hz, 1H), 1.78 (s, 3H), 1.53 (s, 3H), 1.25 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.8, 168.2, 155.3, 138.8, 135.8, 133.1, 130.4, 128.7, 128.3, 127.7, 126.1, 125.0, 121.7, 120.4, 61.8, 48.1, 37.9, 35.8, 19.2, 17.7, 14.3. HRMS Calculated for $C_{21}H_{22}NO_2$ $[M+H]^+$ 320.1651, found 320.1646.



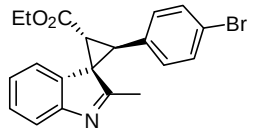
Ethyl 3-(4-chlorophenyl)-2'-methylspiro[cyclopropane-1,3'-indole]-2-carboxylate (3j): 82% yield, unknown compound, white solid, mp = 109-110 °C, R_f = 0.57 (petroleum ether/ethyl acetate 10/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 7.8 Hz, 1H), 7.51 (d, *J* = 7.4 Hz, 1H), 7.45-7.38 (m, 1H), 7.36-7.30 (m, 2H), 7.26-7.19 (m, 3H), 4.26-4.15 (m, 2H), 4.02 (d, *J* = 8.0 Hz, 1H), 3.30 (d, *J* = 8.1 Hz, 1H), 1.58 (s, 3H), 1.23 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.0, 167.9, 155.4, 135.7, 134.2, 133.0, 130.7, 129.2, 127.9, 125.1, 121.8, 120.4, 61.9, 47.9, 37.4, 35.5, 18.1, 14.3. HRMS Calculated for $C_{20}H_{19}ClNO_2$ $[M+H]^+$ 340.1104, found 340.1102.



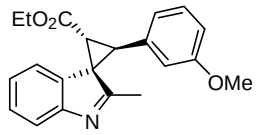
Ethyl 3-(3-chlorophenyl)-2'-methylspiro[cyclopropane-1,3'-indole]-2-carboxylate (3k): 75% yield, unknown compound, yellow solid, mp = 109-110 °C, R_f = 0.55 (petroleum ether/ethyl acetate 10/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 7.6 Hz, 1H), 7.52 (d, *J* = 7.2 Hz, 1H), 7.38 (t, *J* = 7.3 Hz, 1H), 7.35-7.20 (m, 4H), 7.11 (d, *J* = 6.0 Hz, 1H), 4.35-4.07 (m, 2H), 4.03 (d, *J* = 7.9 Hz, 1H), 3.31 (d, *J* = 8.1 Hz, 1H), 1.63 (s, 3H), 1.23 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.9, 167.8, 155.4, 136.5, 135.7, 135.0, 130.2, 129.5, 128.5, 128.0, 127.7, 125.1, 121.8, 120.5,

61.9, 47.9, 37.5, 35.4, 18.1, 14.3. HRMS Calculated for $C_{20}H_{19}ClNO_2$ $[M+H]^+$ 340.1104, found 340.1104.

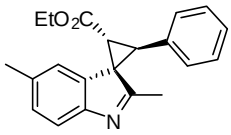
Ethyl 2-(4-bromophenyl)-2'-methylspiro[cyclopropane-1,3'-indole]-3-carboxylate (3l): 81% yield, unknown compound, yellow solid, mp = 130-132 °C R_f = 0.59 (petroleum ether/ethyl acetate 10/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 7.6 Hz, 1H), 7.51 (d, *J* = 7.6 Hz, 1H), 7.46 (d, *J* = 8.2 Hz, 2H), 7.38 (t, *J* = 7.6 Hz, 1H), 7.22 (t, *J* = 7.6 Hz, 1H), 7.11 (d, *J* = 8.2 Hz, 2H), 4.35-4.07 (m, 2H), 4.00 (d, *J* = 8.1 Hz, 1H), 3.29 (d, *J* = 8.1 Hz, 1H), 1.62 (s, 3H), 1.22 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.9, 167.8, 155.3, 135.6, 133.5, 132.1, 131.0, 127.9, 125.0, 122.2, 121.7, 120.4, 61.8, 47.8, 37.4, 35.4, 18.1, 14.3. HRMS Calculated for $C_{20}H_{19}BrNO_2$ $[M+H]^+$ 384.0599, found 384.0597.



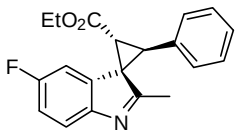
Ethyl 3-(3-methoxyphenyl)-2'-methylspiro[cyclopropane-1,3'-indole]-2-carboxylate (3m): 69% yield, unknown compound, colorless oil, R_f = 0.50 (petroleum ether/ethyl acetate 10/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 7.7 Hz, 1H), 7.53 (d, *J* = 7.6 Hz, 1H), 7.40-7.32 (m, 1H), 7.26-7.18 (m, 2H), 6.85-6.81 (m, 2H), 6.74 (s, 1H), 4.26-4.10 (m, 2H), 4.06 (d, *J* = 8.1 Hz, 1H), 3.76 (s, 3H), 3.32 (d, *J* = 8.1 Hz, 1H), 1.63 (s, 3H), 1.22 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.6, 168.1, 160.1, 155.4, 136.0, 135.9, 130.0, 127.8, 124.9, 121.8, 121.6, 120.3, 115.0, 113.8, 61.8, 55.5, 48.1, 38.3, 35.6, 18.1, 14.3. HRMS Calculated for $C_{21}H_{22}NO_3$ $[M+H]^+$ 336.1600, found 336.1600.



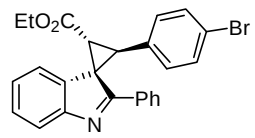
Ethyl 2',5'-dimethyl-3-phenylspiro[cyclopropane-1,3'-indole]-2-carboxylate (3n): 88% yield, unknown compound, white solid, mp = 132-134 °C, R_f = 0.57 (petroleum ether/ethyl acetate 10/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 7.8 Hz, 1H), 7.35-7.26 (m, 4H), 7.25-7.20 (m, 2H), 7.17 (d, *J* = 7.8 Hz, 1H), 4.29-4.09 (m, 2H), 4.04 (d, *J* = 8.1 Hz, 1H), 3.31 (d, *J* = 8.2 Hz, 1H), 2.42 (s, 3H), 1.55 (s, 3H), 1.24 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.6, 168.2, 153.3, 136.2, 134.7, 134.6, 129.4, 128.9, 128.4, 128.2, 122.5, 119.9, 61.8, 47.9, 38.3, 35.5, 21.8, 18.0, 14.3. HRMS Calculated for $C_{21}H_{22}NO_2$ $[M+H]^+$ 320.1651, found 320.1649.



Ethyl 5'-fluoro-2'-methyl-3-phenylspiro[cyclopropane-1,3'-indole]-2-carboxylate (3o): 83% yield, unknown compound, white solid, mp = 132-134 °C, R_f = 0.55 (petroleum ether/ethyl acetate 10/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55-7.50 (m, 1H), 7.35-7.27 (m, 4H), 7.26-7.17 (m, 2H), 7.10-7.01 (m, 1H), 4.31-4.12 (m, 2H), 4.05 (d, *J* = 8.1 Hz, 1H), 3.36 (d, *J* = 8.2 Hz, 1H), 1.56 (s, 3H), 1.26 (t, *J* = 39.5 Hz, 3H); ^{13}C NMR (100 MHz, CDCl3) δ 177.5, 167.9, 160.9 (d, $J_{C\text{-}F}$ = 242.5 Hz), 151.4 (d, $J_{C\text{-}F}$ = 2.0 Hz), 137.9 (d, $J_{C\text{-}F}$ = 10.2 Hz) , 134.1, 129.2, 128.4, 120.8 (d, $J_{C\text{-}F}$ = 8.9 Hz), 114.5 (d, $J_{C\text{-}F}$ = 23.7 Hz), 109.8 (d, $J_{C\text{-}F}$ = 26.5 Hz), 62.0, 48.2, 38.9, 35.7, 18.0, 14.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ -117.05. HRMS Calculated for $C_{20}H_{19}FNO_2$ $[M+H]^+$ 324.1440, found 324.1399.

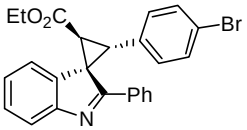


Ethyl 2-(4-bromophenyl)-2'-phenylspiro[cyclopropane-1,3'-indole]-3-carboxylate (3p): 70% yield, unknown compound, yellow solid, mp = 130-132 °C, R_f = 0.55 (petroleum ether/ethyl acetate 10/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 7.7 Hz, 1H), 7.54 (d, *J* = 7.6 Hz, 1H),



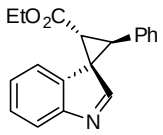
7.36 (t, *J* = 7.5 Hz, 1H), 7.26-7.20 (m, 1H), 7.17 (s, 1H), 7.08 (t, *J* = 7.6 Hz, 2H), 6.99 (d, *J* = 8.3 Hz, 2H), 6.81 (d, *J* = 7.4 Hz, 2H), 6.58 (d, *J* = 8.2 Hz, 2H), 4.32-4.18 (m, 2H), 3.92 (d, *J* = 8.3 Hz, 1H), 3.88 (d, *J* = 8.4 Hz, 1H), 1.21 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.2, 167.9, 155.2, 136.3, 135.1, 132.5, 131.2, 130.2, 128.8, 128.2, 127.9, 127.9, 125.9, 121.6, 121.6, 121.5, 62.0, 48.3, 38.5, 33.1, 14.4. HRMS Calculated for $C_{25}H_{21}BrNO_2$ $[M+H]^+$ found 446.0756, found 440.0747.

Ethyl 2-(4-bromophenyl)-2'-phenylspiro[cyclopropane-1,3'-indole]-3-carboxylate (3p'): unknown compound, white solid, mp = 143-145 °C, R_f = 0.50 (petroleum ether/ethyl acetate 10/1).



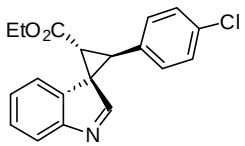
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 7.7 Hz, 1H), 7.60-7.51 (m, 2H), 7.40-7.40 (m, 5H), 7.33 (t, *J* = 7.6 Hz, 1H), 7.12 (d, *J* = 8.1 Hz, 2H), 6.98 (t, *J* = 7.5 Hz, 1H), 6.11 (d, *J* = 7.6 Hz, 1H), 4.60 (d, *J* = 8.1 Hz, 1H), 3.94-3.45 (m, 2H), 3.16 (d, *J* = 8.1 Hz, 1H), 1.01 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.0, 166.6, 154.7, 136.1, 135.1, 132.9, 132.0, 131.6, 129.8, 128.4, 128.3, 127.8, 125.4, 122.2, 121.6, 120.8, 61.6, 47.0, 37.9, 34.6, 13.9. HRMS Calculated for $C_{25}H_{21}BrNO_2$ $[M+H]^+$ 446.0756, found 446.0754.

Ethyl 3-phenylspiro[cyclopropane-1,3'-indole]-2-carboxylate (3q): unknown compound, colorless oil, R_f = 0.65 (petroleum ether/ethyl acetate 5/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ



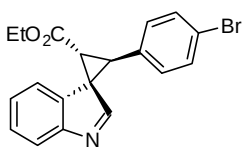
7.77-7.53 (m, 3H), 7.45-7.24 (m, 7H), 4.29-4.08 (m, 2H), 4.05 (d, *J* = 7.6 Hz, 1H), 3.65 (d, *J* = 7.6 Hz, 1H), 1.23 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, CDCl3) δ 170.1, 168.1, 156.5, 135.5, 134.6, 129.0, 128.5, 128.1, 128.0, 125.9, 122.2, 121.7, 61.8, 48.6, 37.3, 33.1, 14.3. HRMS Calculated for $C_{19}H_{18}NO_2$ $[M+H]^+$ 292.1338, found 292.1332.

Ethyl 3-(4-chlorophenyl)spiro[cyclopropane-1,3'-indole]-2-carboxylate (3r): unknown compound, colorless oil, R_f = 0.65 (petroleum ether/ethyl acetate 5/1). ^{1}H NMR (400 MHz,



CDCl3) δ 7.73 (d, *J* = 7.7 Hz, 1H), 7.58 (d, *J* = 7.6 Hz, 1H), 7.54 (s, 1H), 7.46-7.37 (m, 1H), 7.35-7.26 (m, 3H), 7.20 (d, *J* = 8.4 Hz, 2H), 4.27-4.09 (m, 2H), 4.00 (d, *J* = 7.6 Hz, 1H), 3.59 (d, *J* = 7.6 Hz, 1H), 1.22 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, CDCl3) δ 169.6, 167.9, 156.5, 134.4, 134.2, 134.0, 129.9, 129.2, 128.2, 126.1, 122.2, 121.9, 62.0, 48.4, 36.4, 33.0, 14.3. HRMS Calculated for $C_{19}H_{17}ClNO_2$ $[M+H]^+$ 326.0948, found 326.0942.

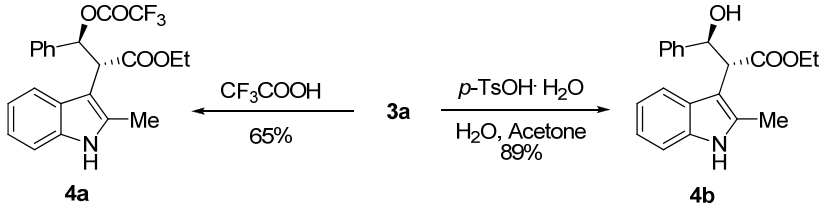
Ethyl 2-(4-bromophenyl)spiro[cyclopropane-1,3'-indole]-3-carboxylate (3s): unknown compound, white solid, mp = 143-145 °C °C, R_f = 0.68 (petroleum ether/ethyl acetate 5/1). ^{1}H



NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 7.8 Hz, 1H), 7.59 (d, *J* = 7.6 Hz, 1H), 7.54 (s, 1H), 7.51-7.38 (m, 3H), 7.30 (d, *J* = 7.5 Hz, 1H), 7.15 (d, *J* = 8.4 Hz, 2H), 4.29-4.06 (m, 2H), 3.99 (d, *J* = 7.6 Hz, 1H), 3.60 (d, *J* = 7.6 Hz, 1H), 1.23 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.6, 167.8, 156.5, 134.5, 134.3, 132.2, 130.2, 128.2, 126.1, 122.2, 122.2, 121.8, 62.0, 48.3, 36.5, 32.9, 14.3. HRMS Calculated for $C_{19}H_{17}BrNO_2$ $[M+H]^+$ 370.0443, found 370.0431.

Ethyl 3-ethylspiro[cyclopropane-1,3'-indole]-2-carboxylate (3t): unknown compound, colorless oil, R_f = 0.65 (petroleum ether/ethyl acetate 5/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (s, 1H), 7.72 (d, *J* = 7.7 Hz, 1H), 7.47 (d, *J* = 7.5 Hz, 1H), 7.37 (td, *J* = 7.6, 1.2 Hz, 1H), 7.23 (td, *J* = 7.6, 0.7 Hz, 1H), 4.19-3.99 (m, 2H), 3.01 (d, *J* = 7.4 Hz, 1H), 2.75 (q, *J* = 7.4 Hz, 1H), 1.98-1.80 (m, 1H), 1.78-1.63 (m, 1H), 1.39-1.21 (m, 6H), 1.17 (t, *J* = 7.1 Hz, 3H), 0.85 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.9, 168.5, 156.3, 135.3, 127.6, 125.8, 122.2, 121.6, 61.5, 47.7, 35.9, 34.8, 31.4, 31.0, 29.0, 22.6, 14.3, 14.1. HRMS Calculated for $[M+H]^+$ $C_{18}H_{24}NO_2$ 286.1807, found 286.1802.

3. General Procedure for Synthesis of Rearomatized Indole Derivatives 4



For the synthesis of **4a**: To a mixture compound of **3a** (75 mg, 0.20 mmol) in dry CH_2Cl_2 (3 mL), CF_3COOH (23 mg, 0.20 mmol) was added. The reaction mixture was stirred for 0.5 h. Filtration and concentration in *vacuo* gave a residue, which was purified by flash chromatography on silica gel using petroleum ether and ethyl acetate to give the rearomatized 2,3-disubstituted indole derivative **4a.**

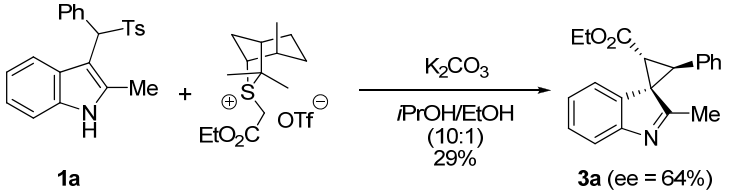
For the synthesis of **4b**: To a mixture compound of **3a** (75 mg, 0.20 mmol) in dry acetone (3 mL), *p*-TsOH·H_2O (32 mg, 0.20 mmol) and water (36μL, 0.20 mmol) was added. The reaction mixture was stirred for 0.5 h. Filtration and concentration in *vacuo* gave a residue, which was purified by flash chromatography on silica gel using petroleum ether and ethyl acetate to give the rearomatized 2,3-disubstituted indole derivative **4b**.

Ethyl 2-(2-methyl-1H-indol-3-yl)-3-phenyl-3-(2,2,2-trifluoroacetoxy)propanoate (4a): 65% yield, unknown compound, orange oil, R_f = 0.53 (petroleum ether/ethyl acetate 10/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89-7.80 (m, 1H), 7.74 (brs, 1H), 7.17-7.01 (m, 8H), 6.80 (d, *J* = 11.2 Hz, 1H), 4.36 (d, *J* = 11.1 Hz, 1H), 4.28-4.20 (m, 1H), 4.14-4.01 (m, 1H), 1.92 (s, 3H), 1.21 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.1, 156.4(q, J_{C-F} = 42.5 Hz) 136.1, 135.3, 134.2, 128.9, 128.3, 126.9, 126.8, 121.5, 120.2, 119.3, 114.8(q, J_{C-F} = 286.0 Hz) 110.7, 110.5, 78.9, 61.5, 49.4, 14.2, 11.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ -75.21. HRMS Calculated for $C_{22}H_{20}F_3NO_4K$ $[M+K]^+$ 458.0981, found 458.0972.

Ethyl 3-hydroxy-2-(2-methyl-1H-indol-3-yl)-3-phenylpropanoate (4b): 89% yield, unknown compound, white solid, mp = 132-134 °C, R_f = 0.48 (petroleum ether/ethyl acetate 10/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72-7.68 (m, 1H), 7.62 (brs, 1H), 7.24-7.16 (m, 1H), 7.17-7.03 (m, 5H), 7.00-6.95 (m, 2H), 5.48 (dd, *J* = 10.1, 3.0 Hz, 1H), 4.30-4.10 (m, 2H), 3.95 (d, *J* = 10.0 Hz, 1H), 3.55 (d, *J* = 2.9 Hz, 1H), 1.81 (s, 3H), 1.19 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.5, 141.5, 135.2, 133.6, 127.8, 127.5, 127.4, 126.6, 121.2, 119.8, 119.2, 110.5, 105.9, 74.1,

61.3, 52.0, 14.3, 11.3. HRMS Calculated for $C_{20}H_{21}NO_3Na$ $[M+Na]^+$ 346.1419, found 346.1409.

4. Enantioselective Synthesis of Spiro-Cyclopropane 3a.



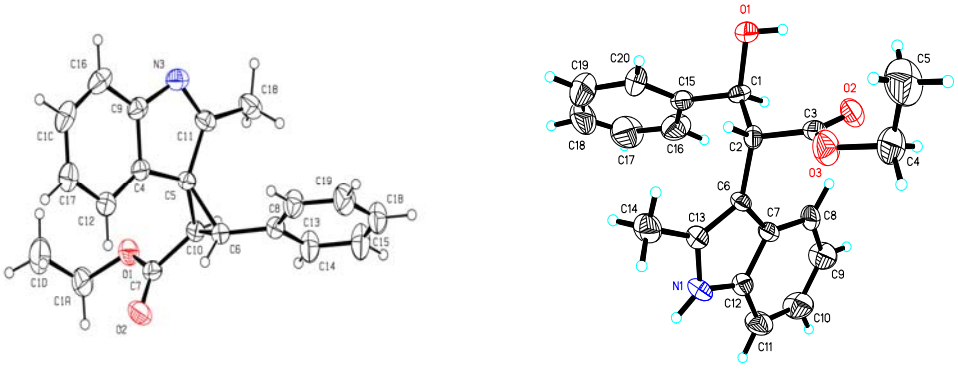
1a **3a** (ee = 64%)

A reaction mixture of methylsulfonyl indole **1a** (0.20 mmol), chiral sulfonium salt[2] (0.24 mmol) and K_2CO_3 (83 mg, 0.60 mmol) in *i*PrOH (3.0 mL) and EtOH (0.3 mL) was stirred at room temperature for 12 h. Then water (20 mL) was added to the mixture. The organic layer was separated and the aqueous layer was extracted with dichloromethane (30 mL×3). The combined organic layer was dried by anhydrous sodium sulfate, concentrated in *vacuo*. The crude product was purified by flash chromatography on silica gel using (petroleum ether/ethyl acetate, 10:1) to give the corresponding product spiro-cyclopropane **3a**.

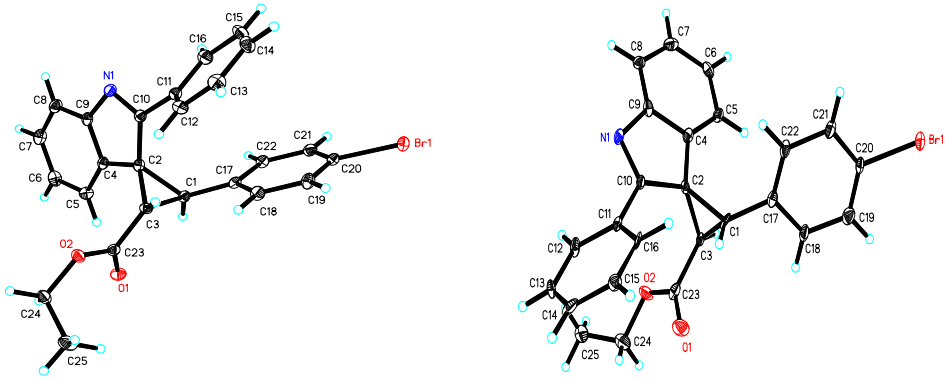
(2) Illa, O.; Arshad, M.; Ros, A.; McGarrigle, E. M.; Aggarwal, V. K. *J. Am. Chem. Soc.* **2010**, *132*, 1828.

5. Crystallographic Data of Compounds 3a, 4b, 3p, 3p'

Procedure for recrystallization of compounds **3a, 4b, 3p, 3p'**: The hexane (2 mL) was slowly added into the solution of target products in dichloromethane (1 mL), then the dichloromethane was evaporated from the mixed solvent system in -20^{o}C and the crystal of **3a, 4b, 3p, 3p'** were obtained after a few days.



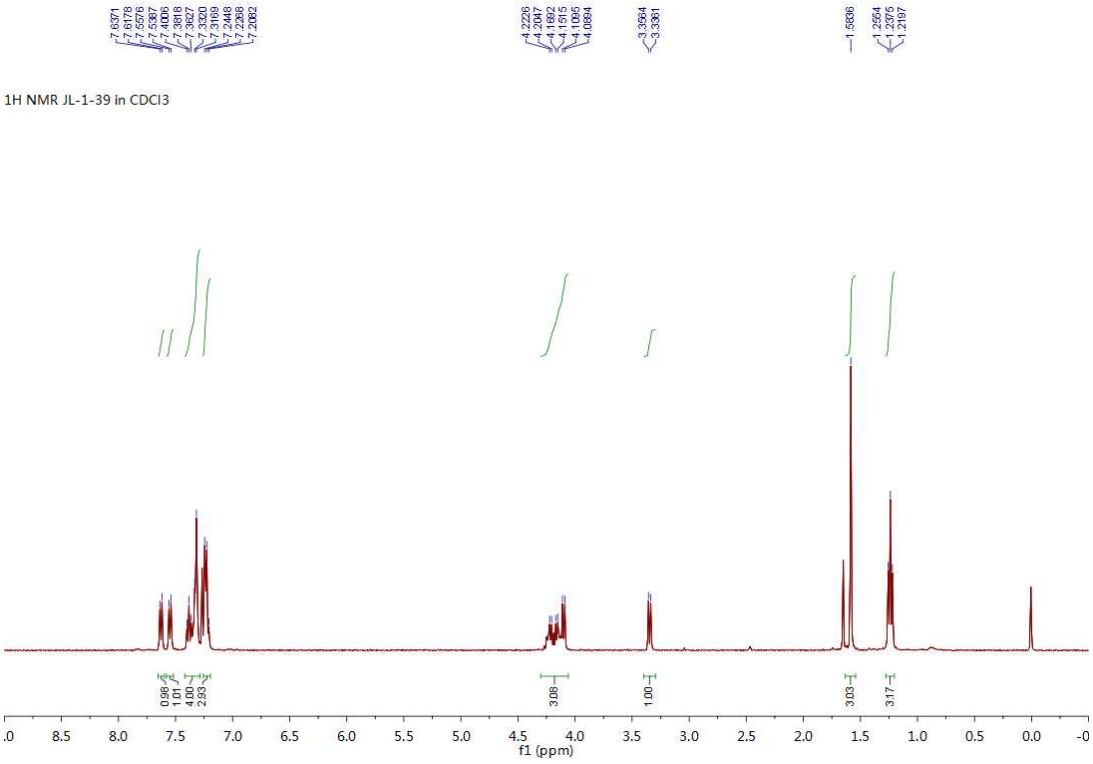
X-ray Single Crystal Structure of **3a, 4b**

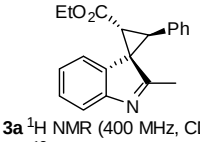


X-ray Single Crystal Structure of **3p, 3p'**

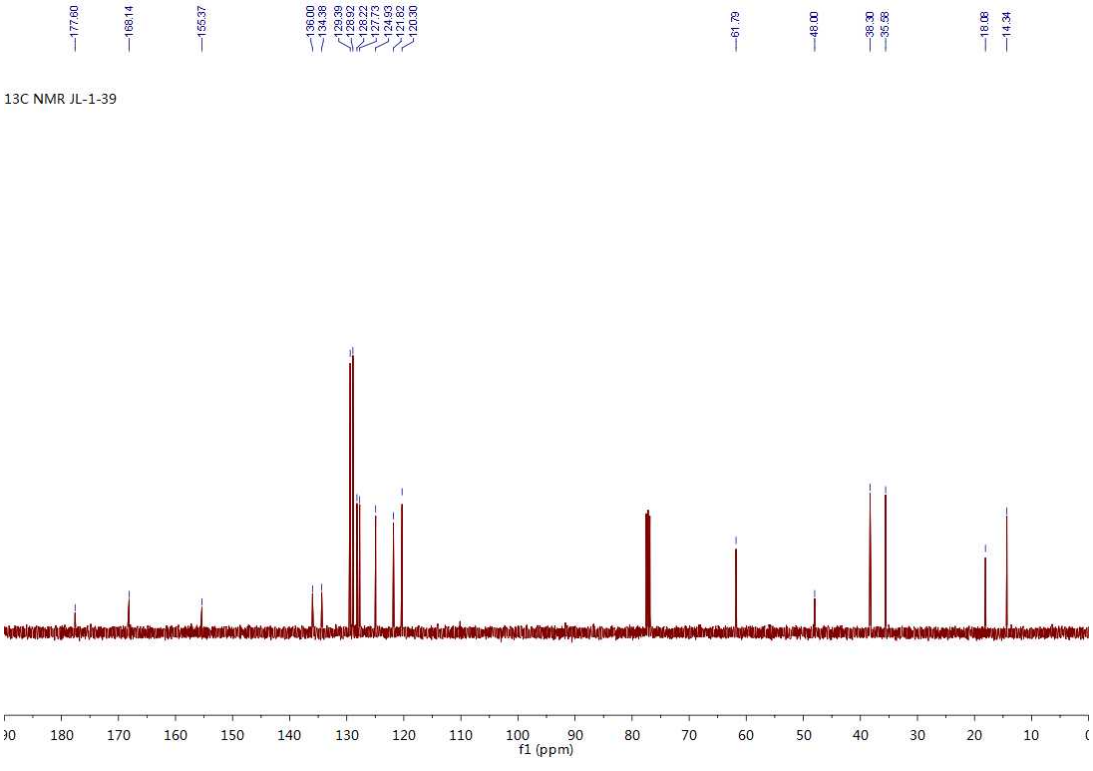
The structure of **3a, 4b, 3p, 3p'** were determined by the single-crystal X-ray diffraction analysis. CCDC 970864 (**3a)**, CCDC 970862 (**4b)**, CCDC 970865 (**3p),** CCDC 970863 (**3p')** contain the structure and supplementary crystallographic data. These data can be obtained free of charge via www.ccdc.com.ac.uk/data_request/cif from the Cambridge Crystallographic Data Center.

6. Copy of NMR

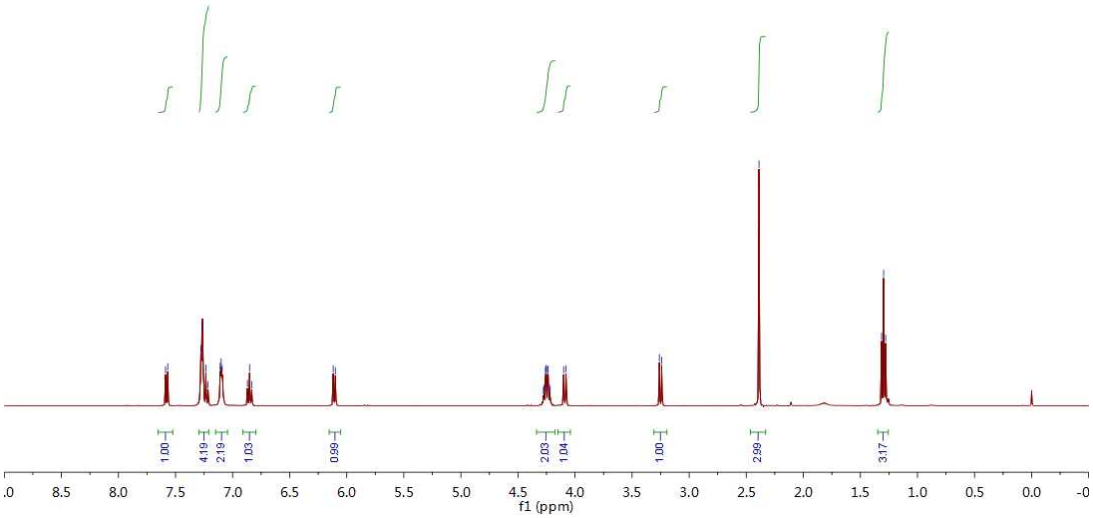


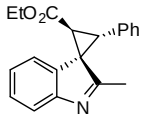


3a ^{1}H NMR (400 MHz, $CDCl_3$)
^{13}C NMR (100 MHz, $CDCl_3$)



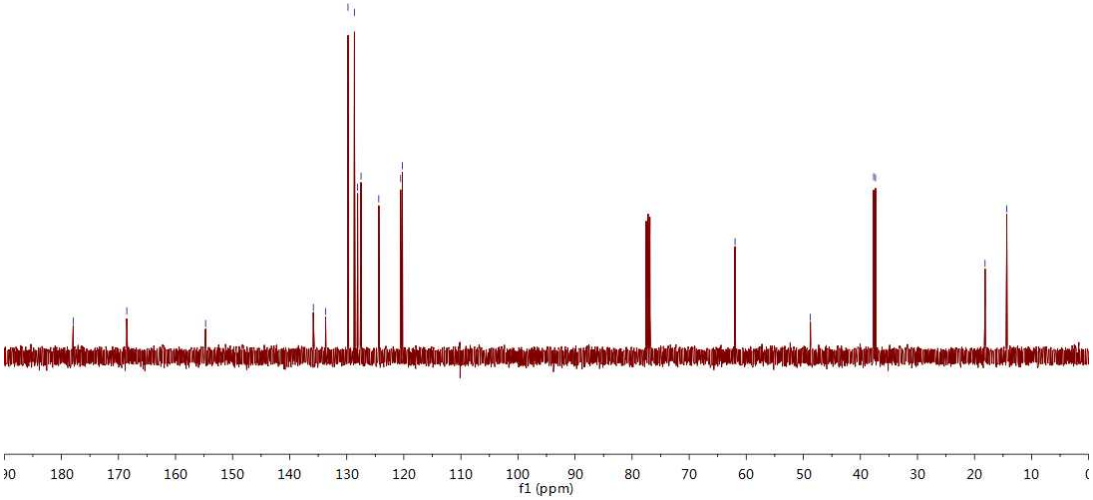
1H NMR JL-1-42A2 in CDCl3



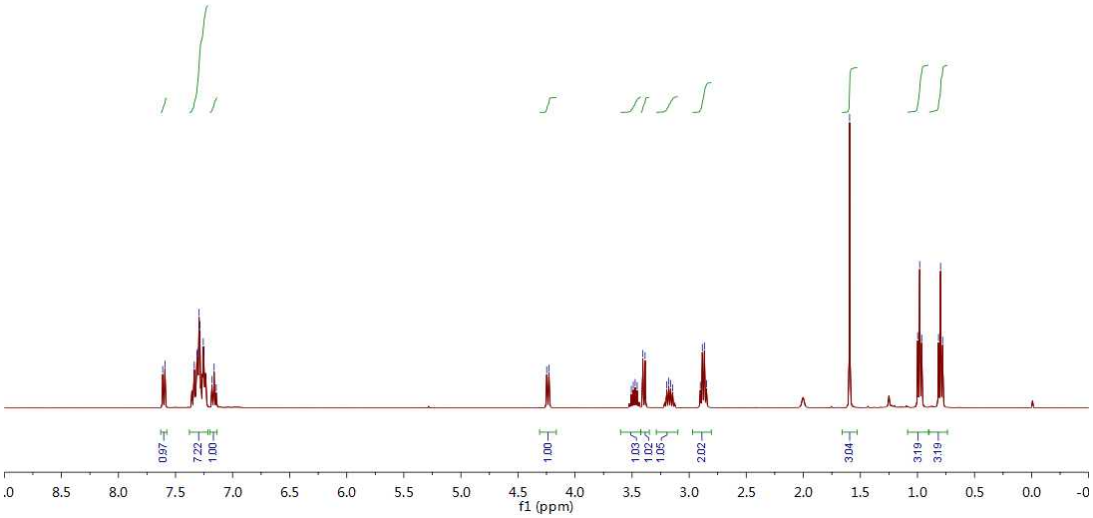


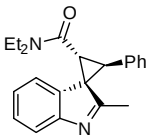
3a' ^{1}H NMR (400 MHz, $CDCl_3$)
^{13}C NMR (100 MHz, $CDCl_3$)

13C NMR JL-1-42A2 in CDCl3



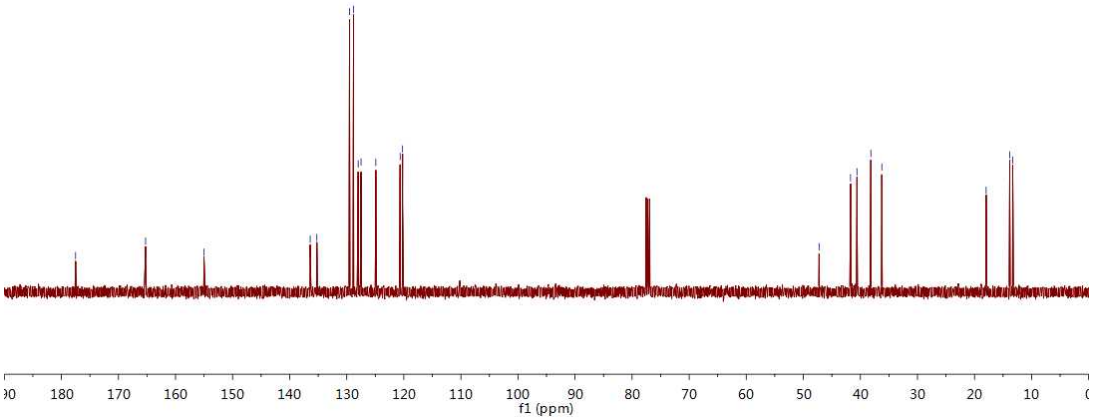
1H NMR JL-2-20C in CDCl3

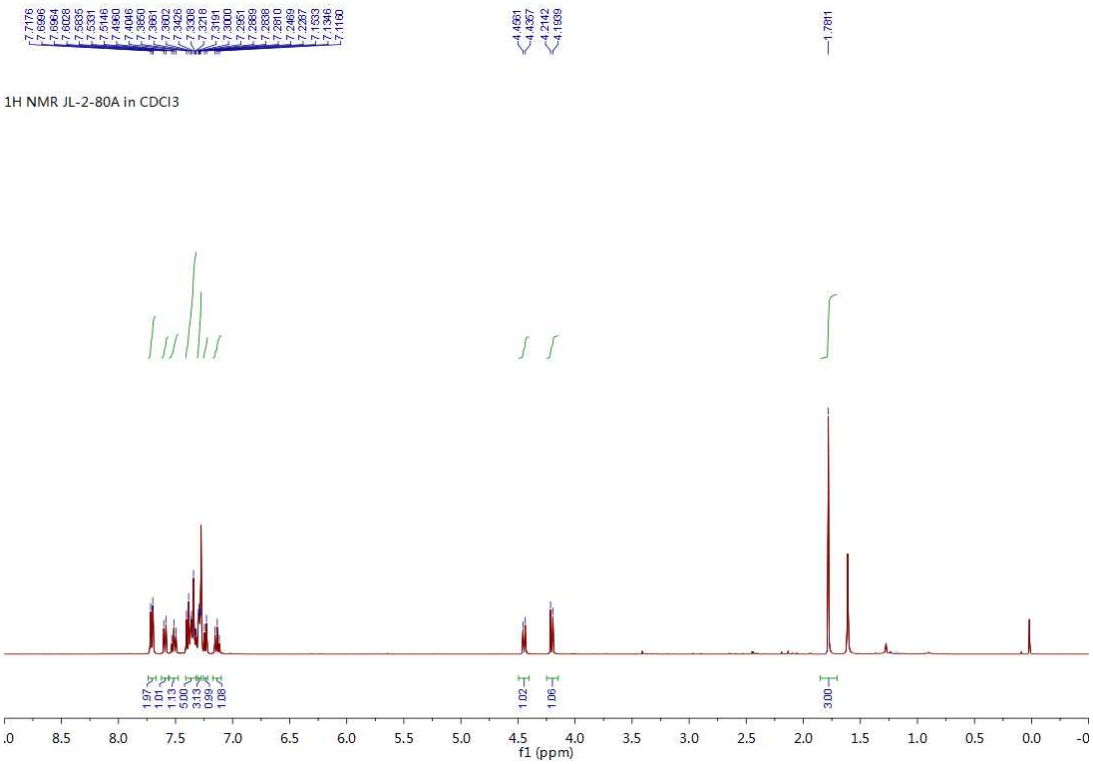




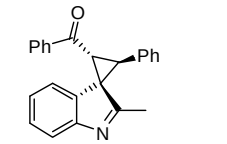
3b ^{1}H NMR (400 MHz, $CDCl_3$)
^{13}C NMR (100 MHz, $CDCl_3$)

13C NMR JL-2-20C in CDCl3

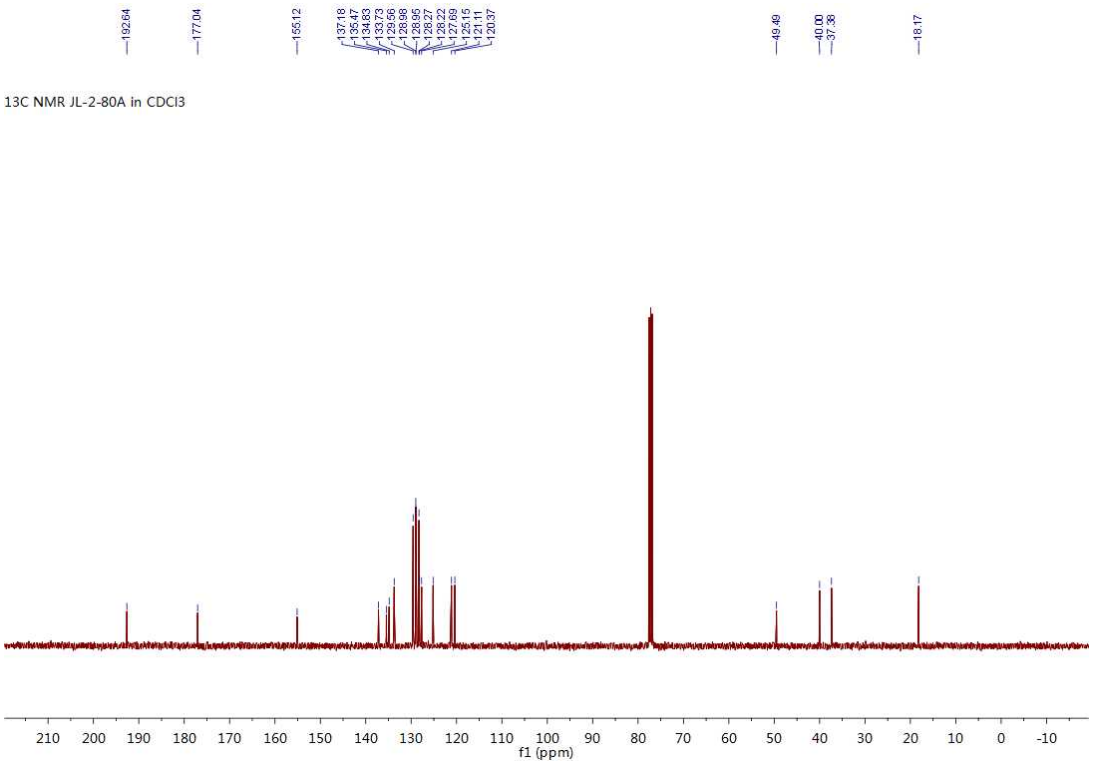




1H NMR JL-2-80A in CDCl3

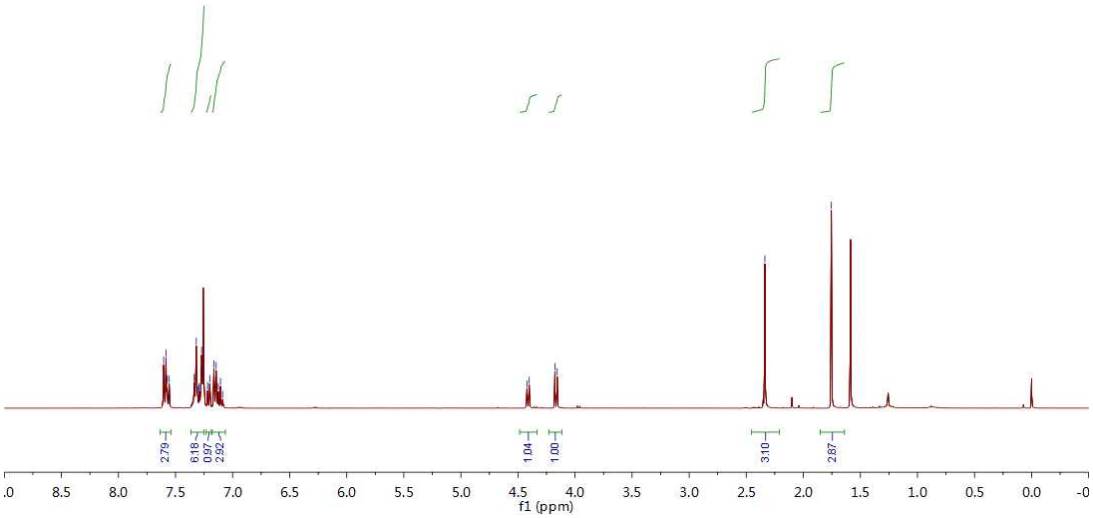


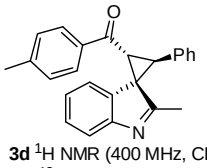
3c ^{1}H NMR (400 MHz, $CDCl_3$)
^{13}C NMR (100 MHz, $CDCl_3$)



13C NMR JL-2-80A in CDCl3

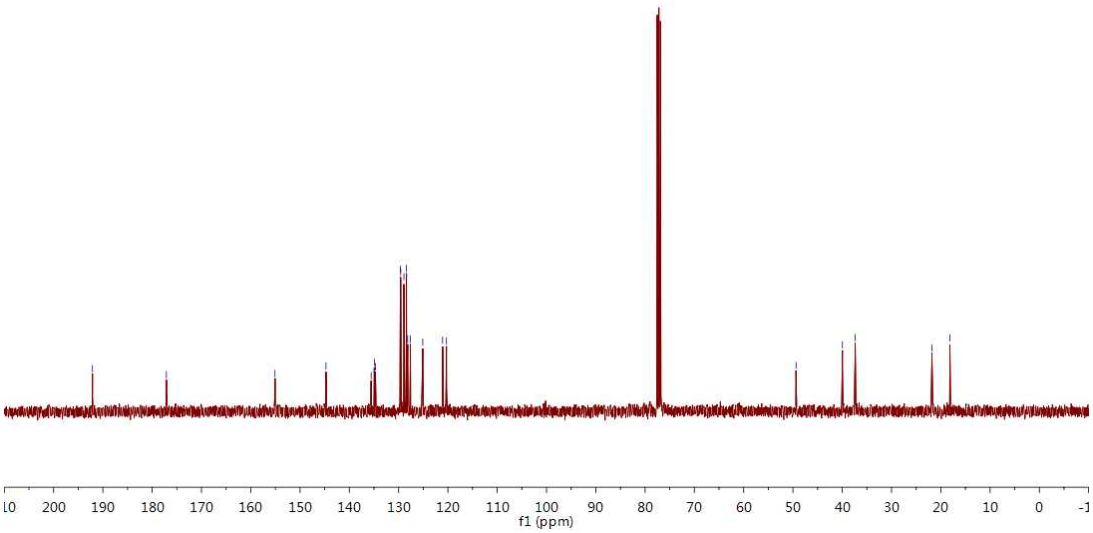
1H NMR JL-2-78A

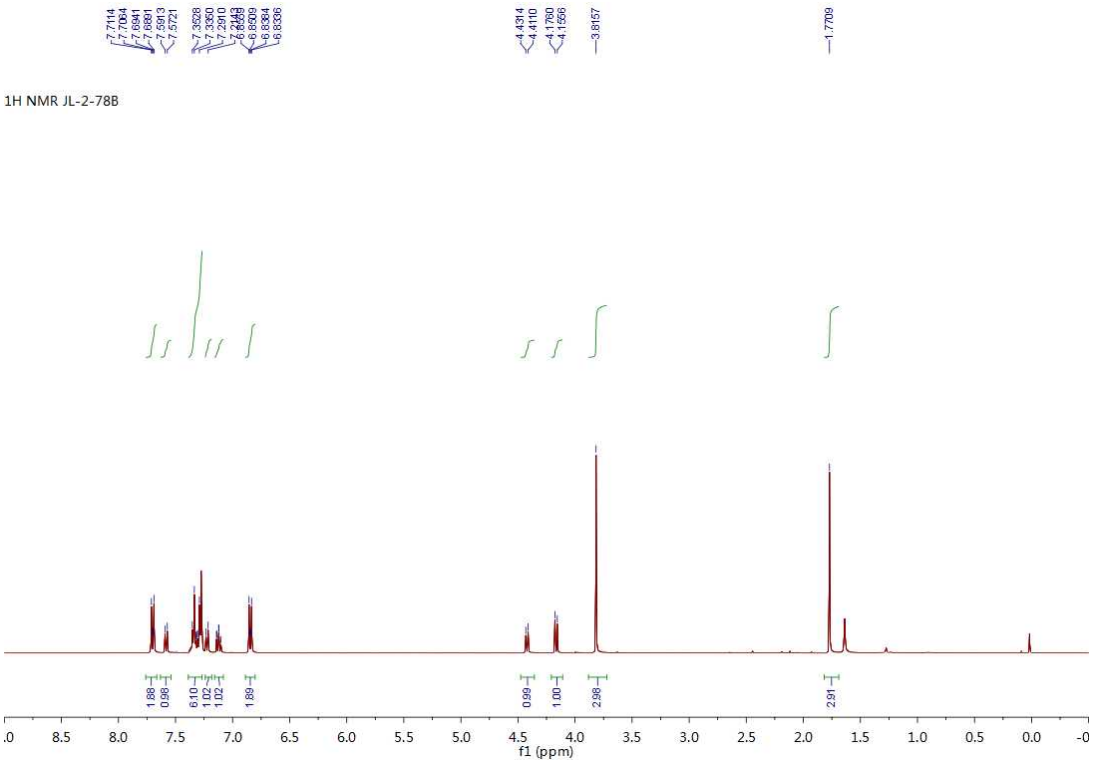




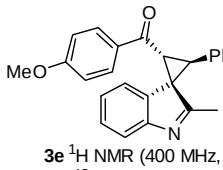
3d ^{1}H NMR (400 MHz, $CDCl_3$)
^{13}C NMR (100 MHz, $CDCl_3$)

13C NMR JL-2-78A

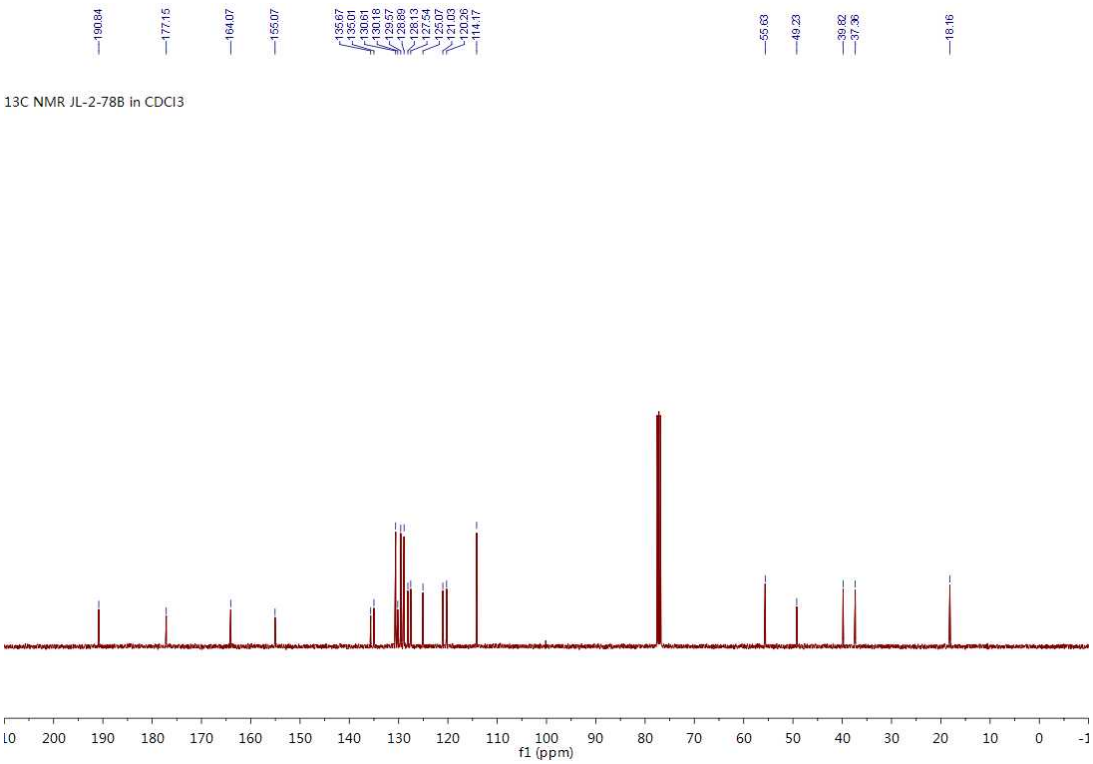




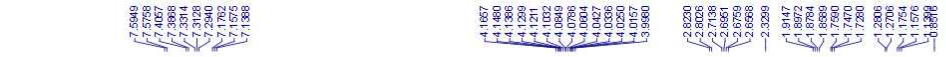
1H NMR JL-2-78B



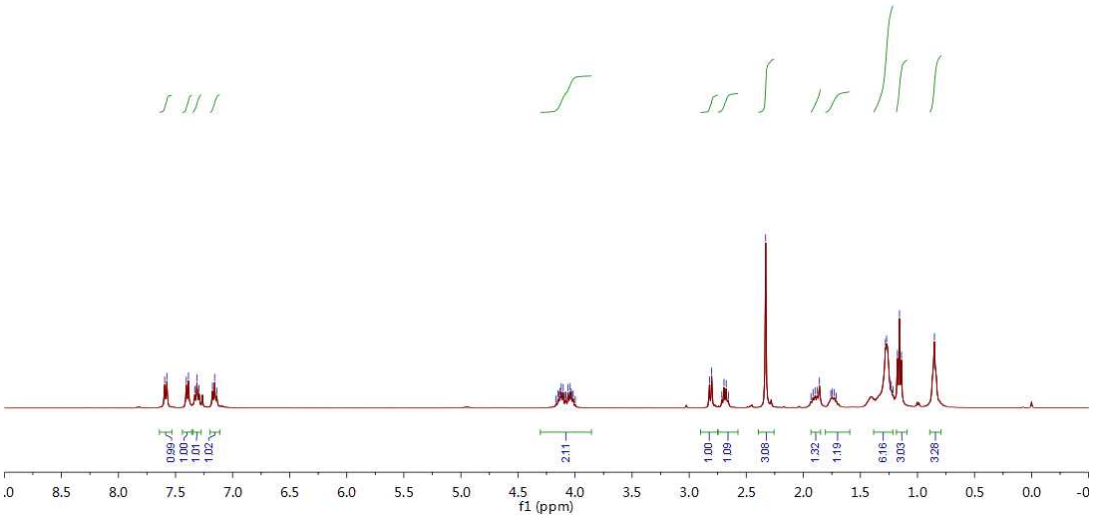
3e ^{1}H NMR (400 MHz, $CDCl_3$)
^{13}C NMR (100 MHz, $CDCl_3$)

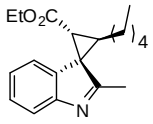


13C NMR JL-2-78B in CDCl3



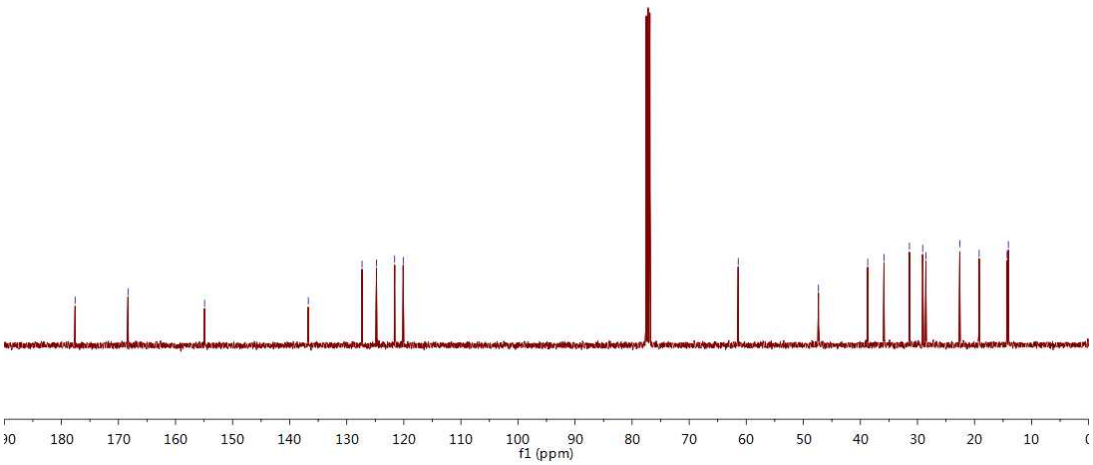
1H NMR JL-2-84



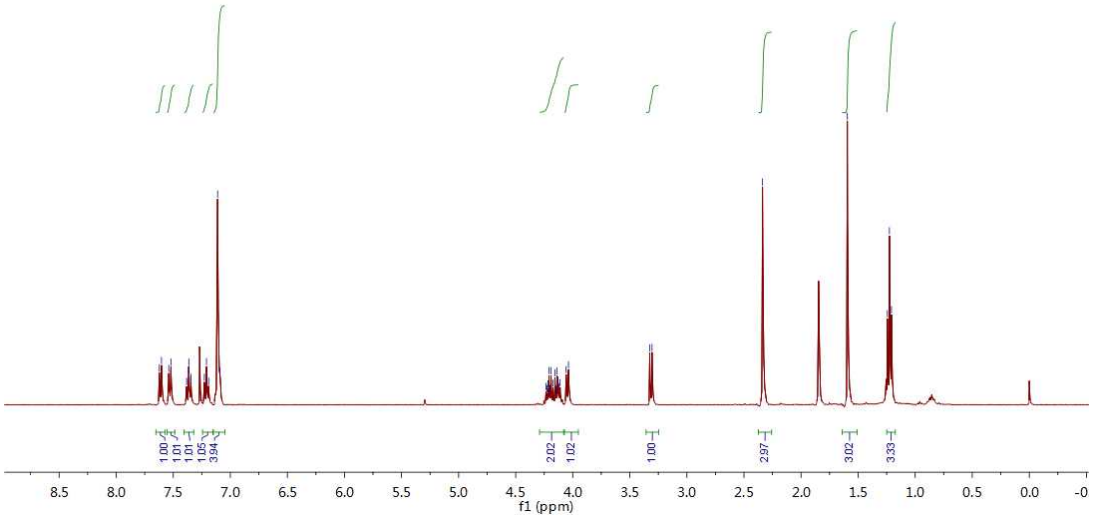


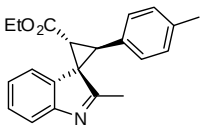
3f ^{1}H NMR (400 MHz, $CDCl_3$)
^{13}C NMR (100 MHz, $CDCl_3$)

13C NMR JL-2-84 in CDCl3



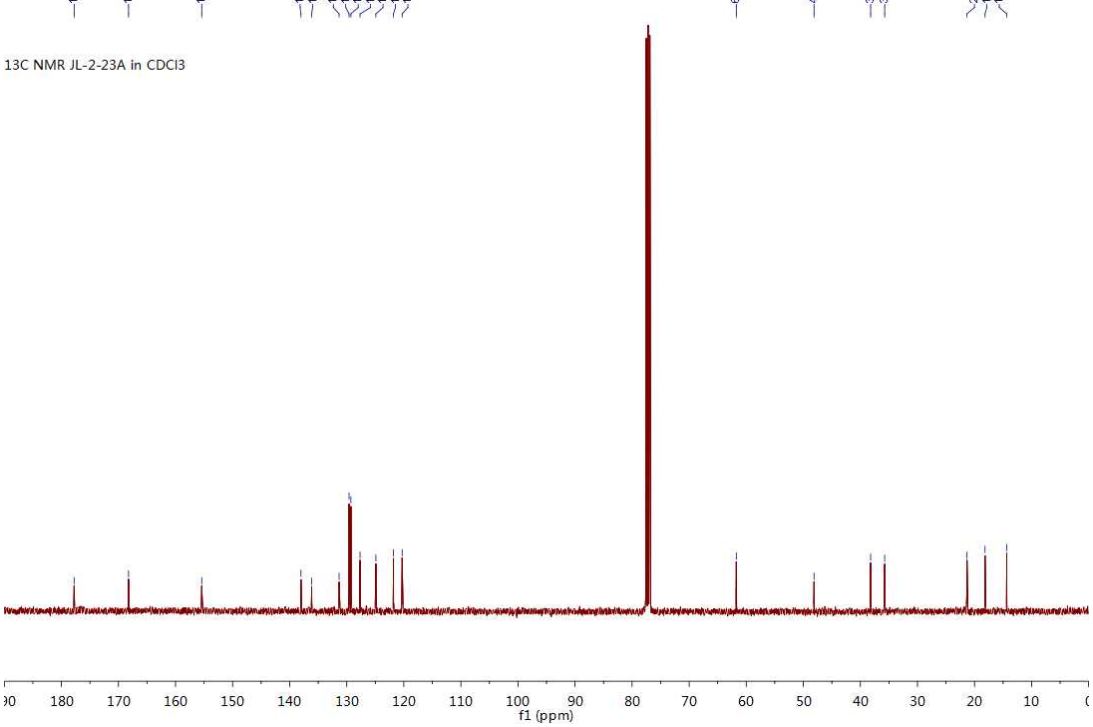
1H NMR JL-2-23A in CDCl3



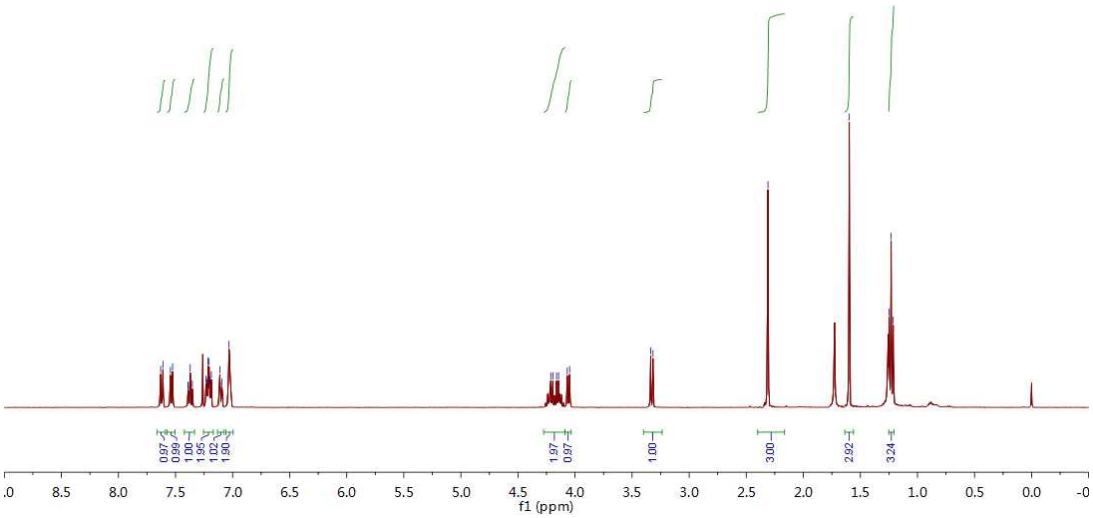


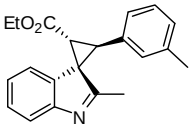
3g ^{1}H NMR (400 MHz, $CDCl_3$)
^{13}C NMR (100 MHz, $CDCl_3$)

13C NMR JL-2-23A in CDCl3



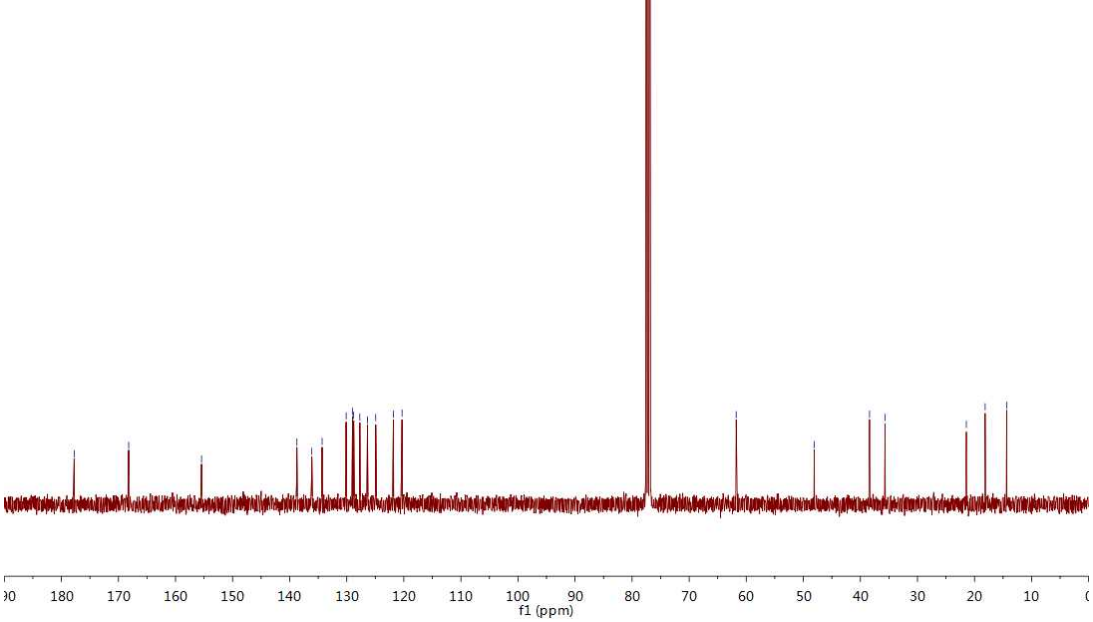
1H NMR JL-2-34B in CDCl3



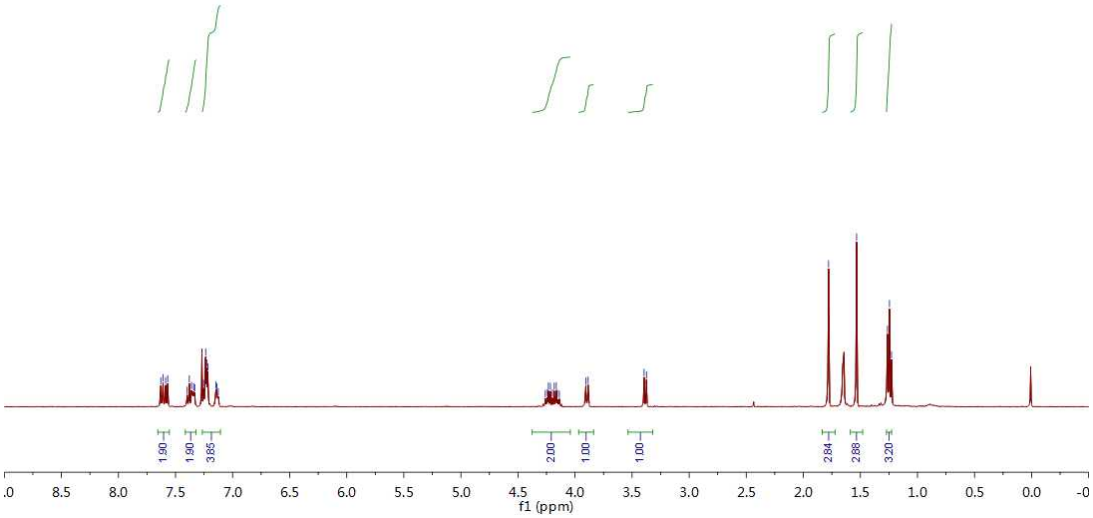


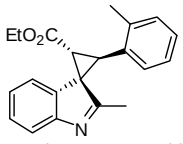
3h ^{1}H NMR (400 MHz, $CDCl_3$)
^{13}C NMR (100 MHz, $CDCl_3$)

13C NMR JL-2-34B in CDCl3



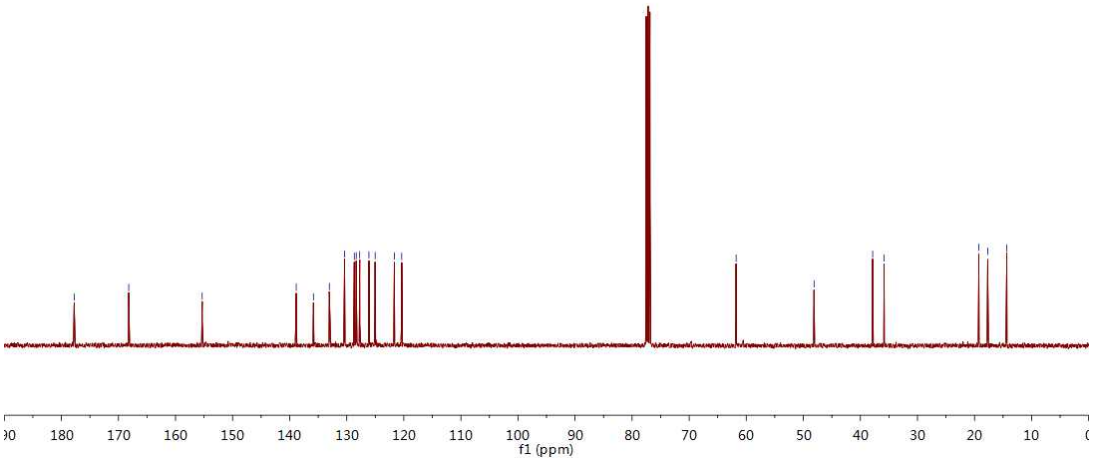
1H NMR JL-2-23B in CDCl3

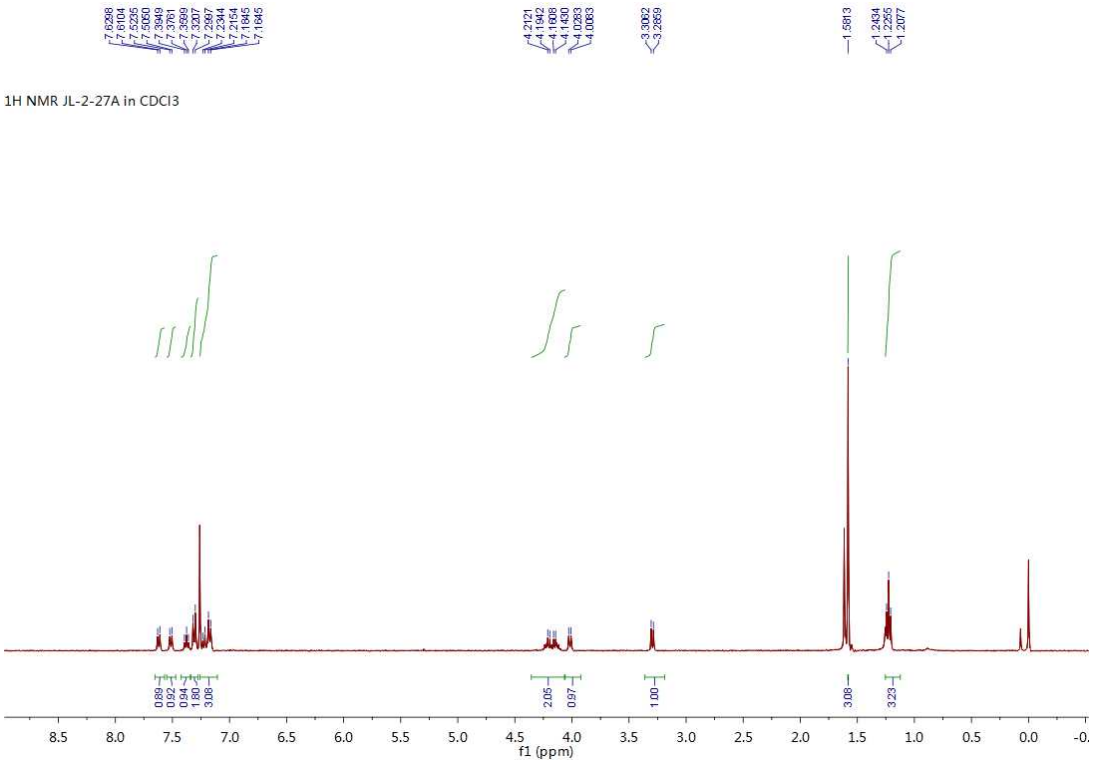




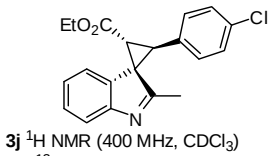
3i ^{1}H NMR (400 MHz, $CDCl_3$)
^{13}C NMR (100 MHz, $CDCl_3$)

13C NMR JL-2-23B in CDCl3

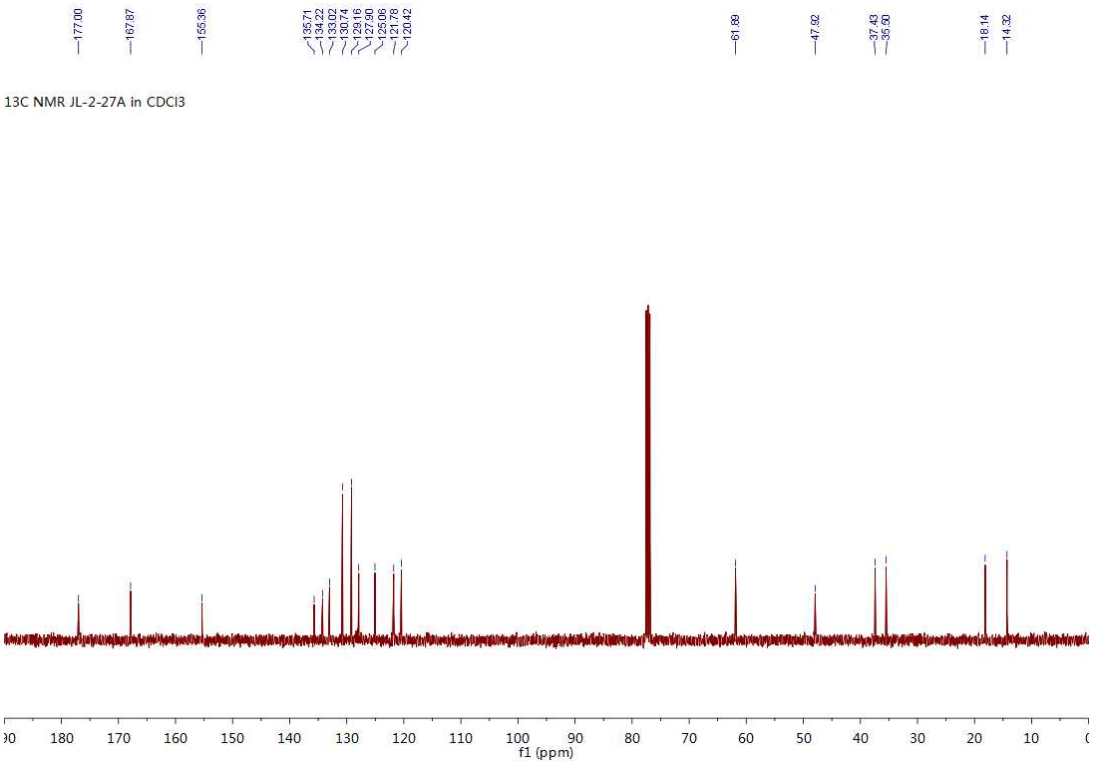




1H NMR JL-2-27A in CDCl3



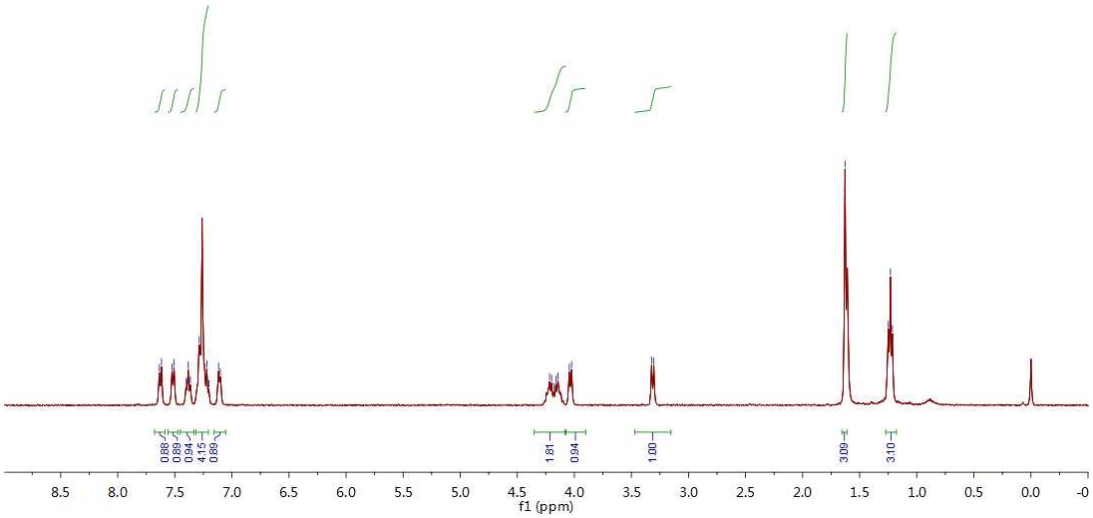
3j ^{1}H NMR (400 MHz, $CDCl_3$)
^{13}C NMR (100 MHz, $CDCl_3$)

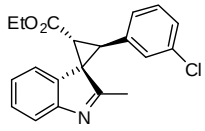


13C NMR JL-2-27A in CDCl3

7.6357
7.6167
7.5287
7.5098
7.4003
7.3826
7.3637
7.2867
7.2198
7.2017
7.1165
7.1014
4.2171
4.1992
4.1806
4.1617
4.1440
4.0443
4.0244
3.3237
3.3034
1.6288
1.2469
1.2310
1.2132

1H NMR JL-2-76A in CDCl3

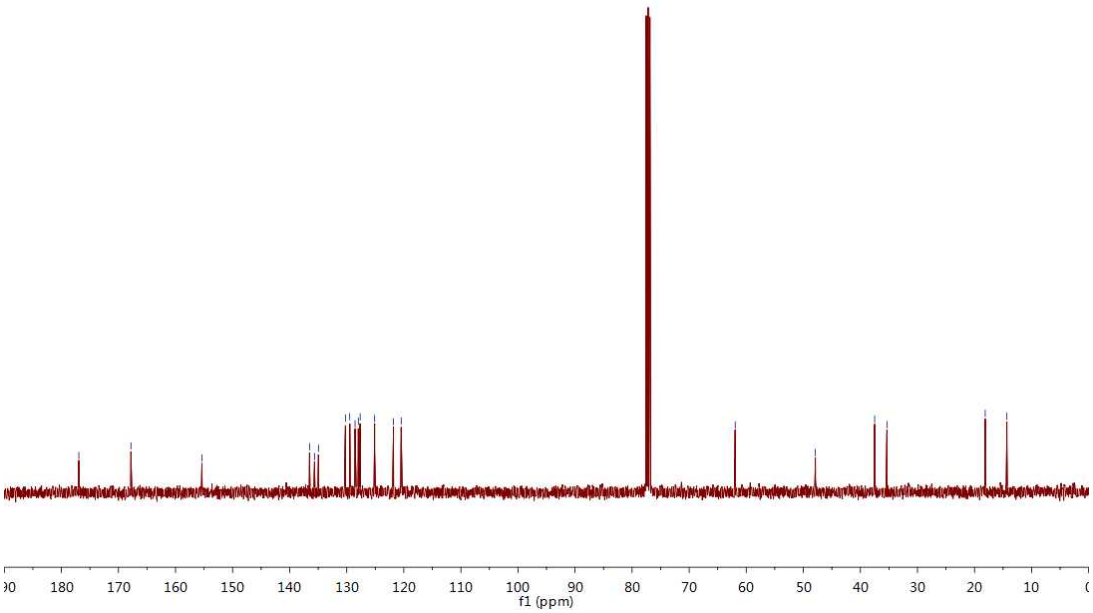


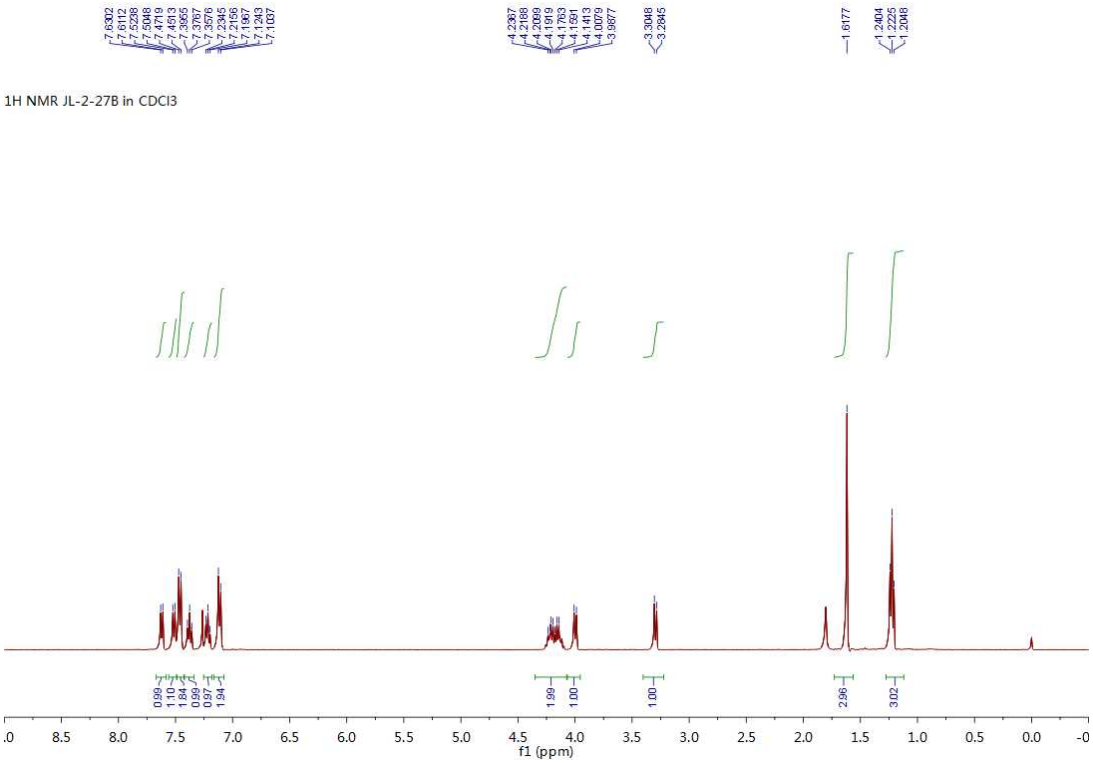


3k ^{1}H NMR (400 MHz, $CDCl_3$)
^{13}C NMR (100 MHz, $CDCl_3$)

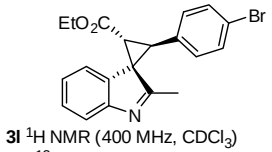
176.94
167.81
155.38
136.52
135.65
134.95
130.23
129.47
128.54
127.97
127.65
125.11
121.81
120.46
61.93
47.88
37.90
35.35
18.12
14.33

13C NMR JL-2-76A in CDCl3

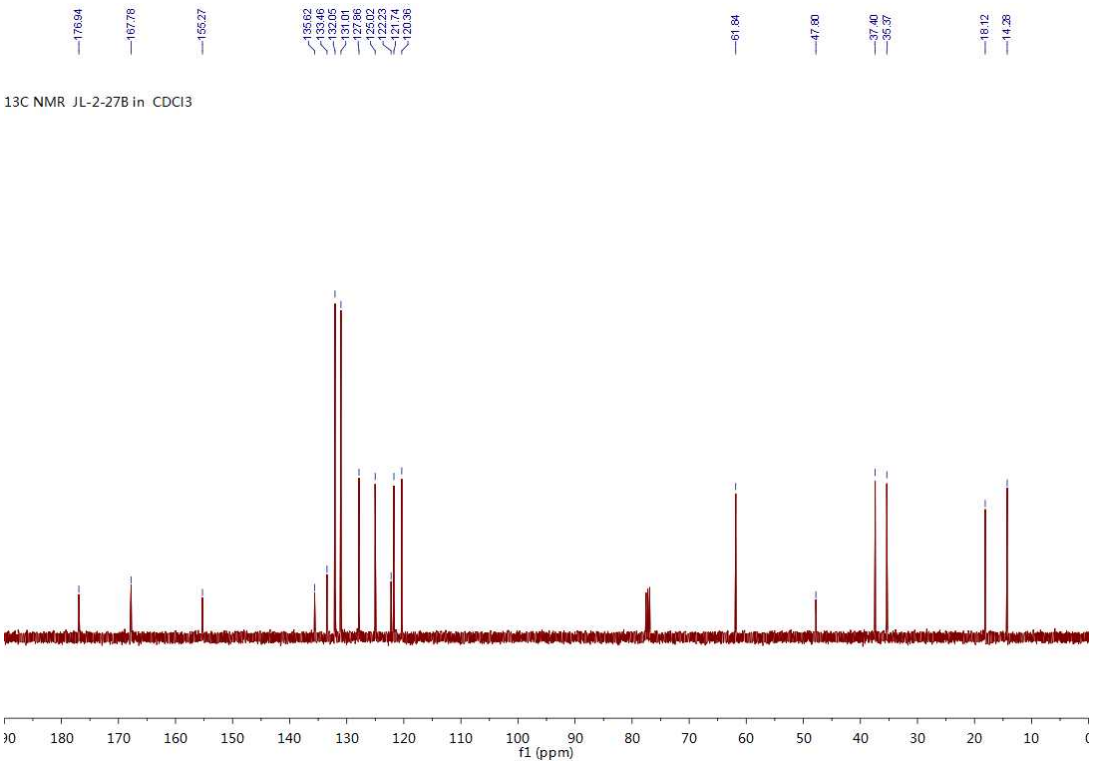




1H NMR JL-2-27B in CDCl3

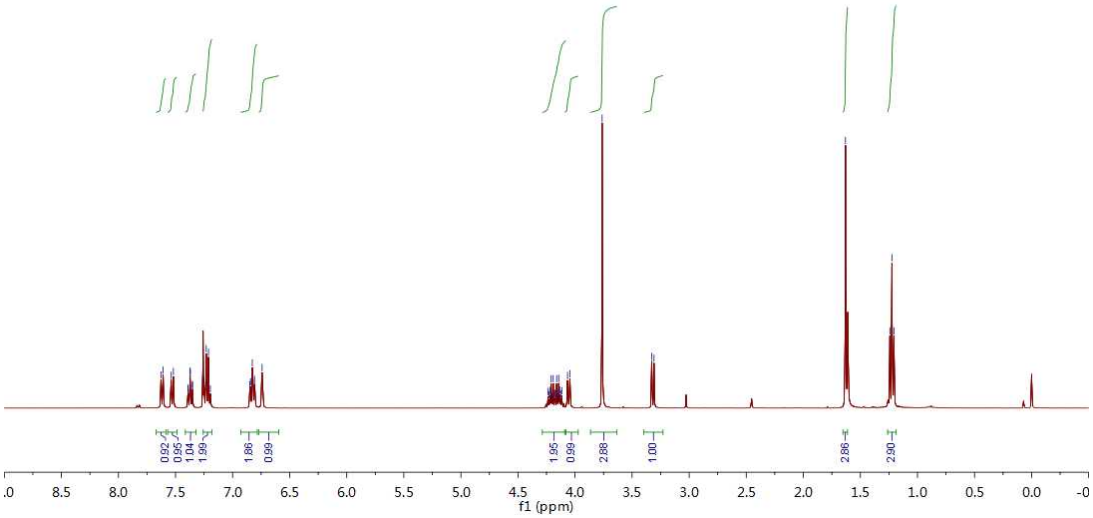


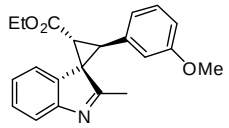
3l ^{1}H NMR (400 MHz, $CDCl_3$)
^{13}C NMR (100 MHz, $CDCl_3$)



13C NMR JL-2-27B in CDCl3

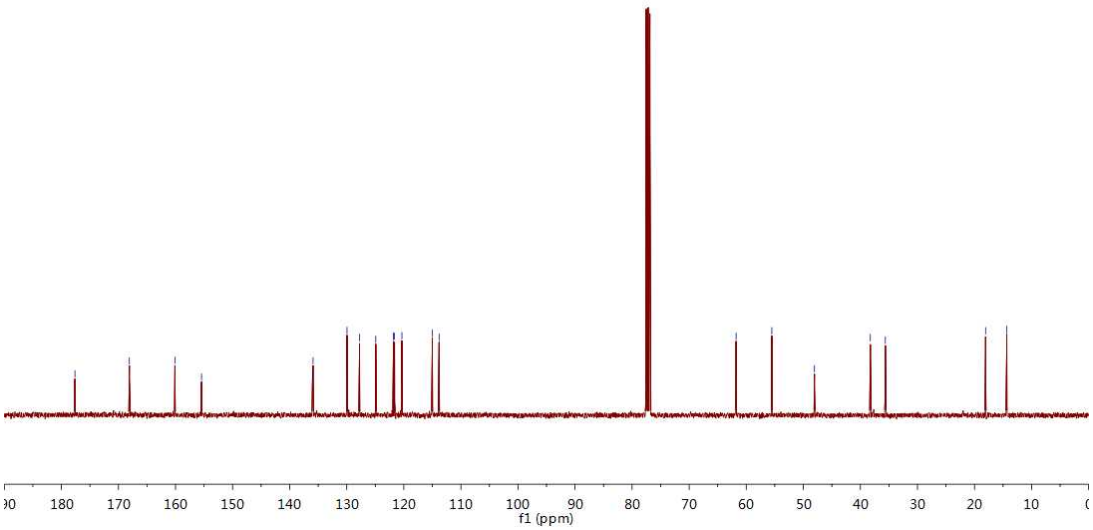
1H NMR JL-2-73B in CDCl3

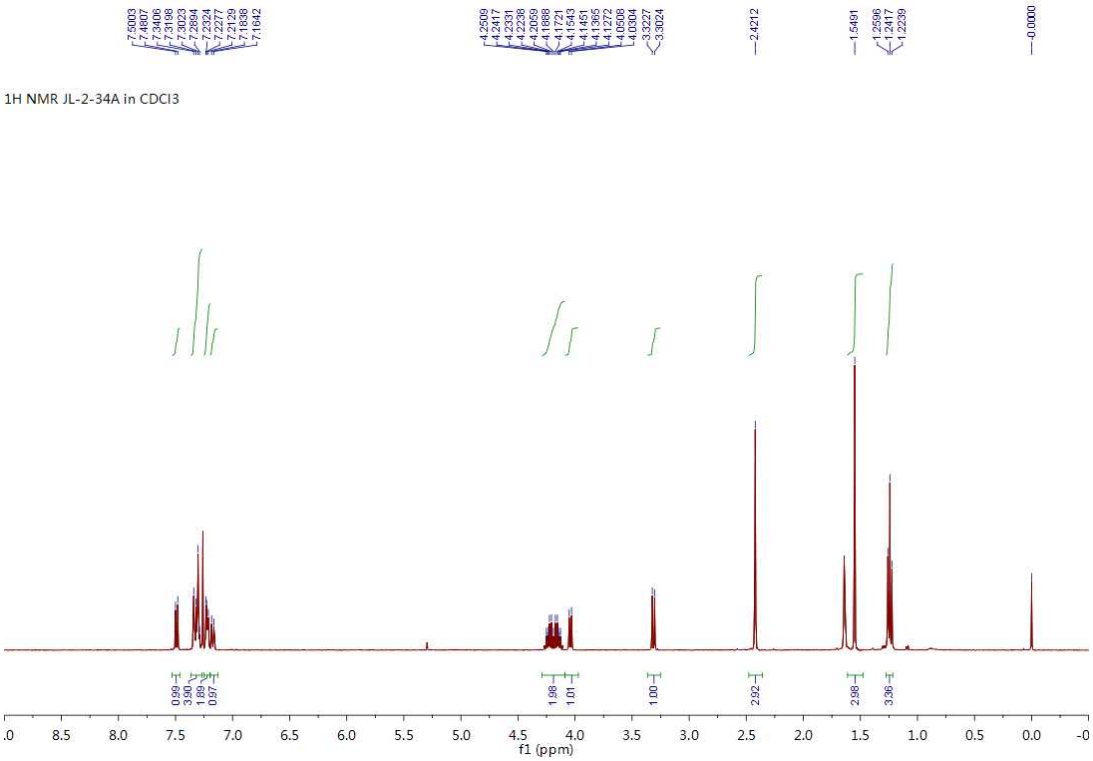


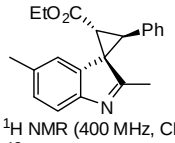


3m ^{1}H NMR (400 MHz, $CDCl_3$)
^{13}C NMR (100 MHz, $CDCl_3$)

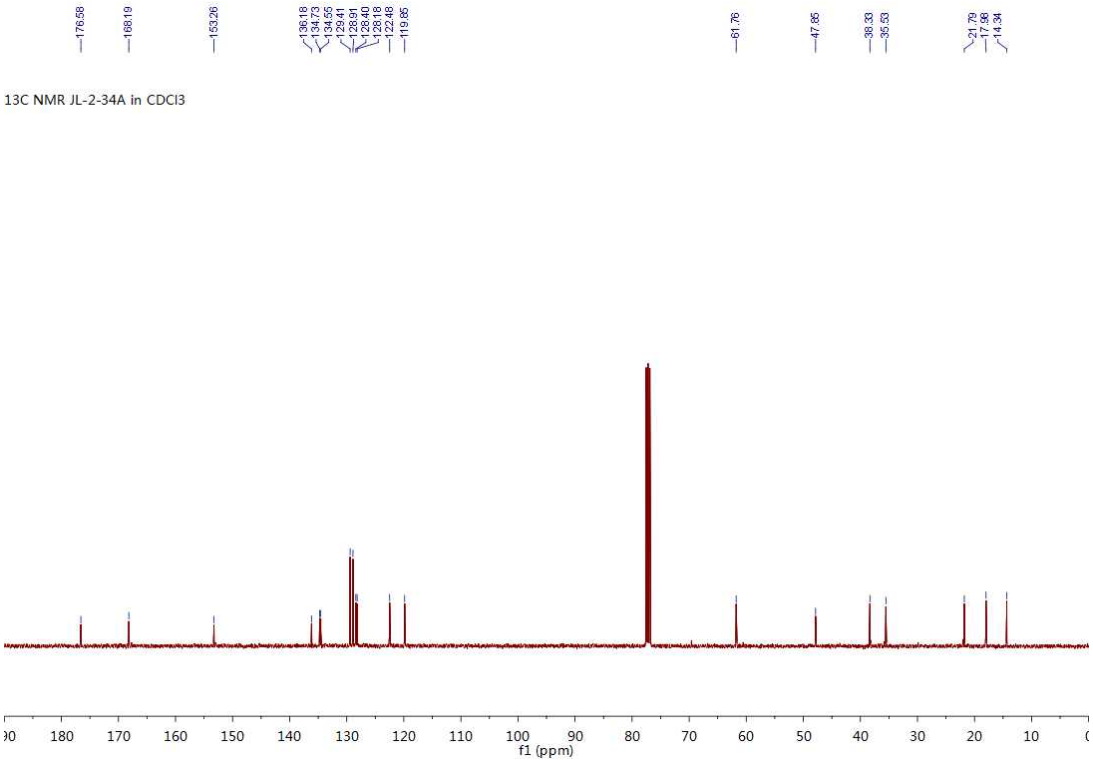
13C NMR JL-2-73B in CDCl3



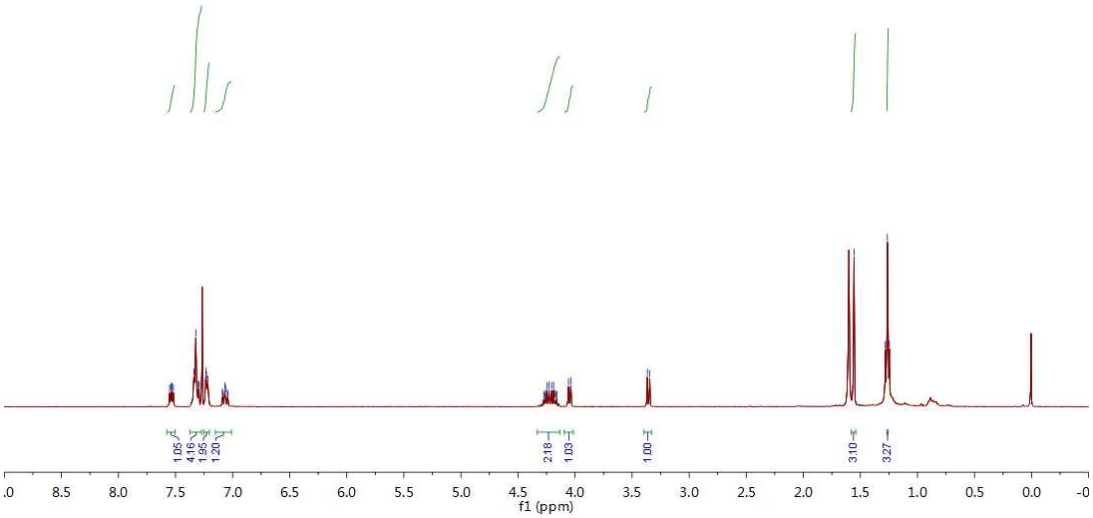


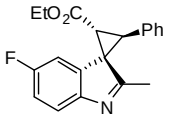


3n ^{1}H NMR (400 MHz, $CDCl_3$)
^{13}C NMR (100 MHz, $CDCl_3$)



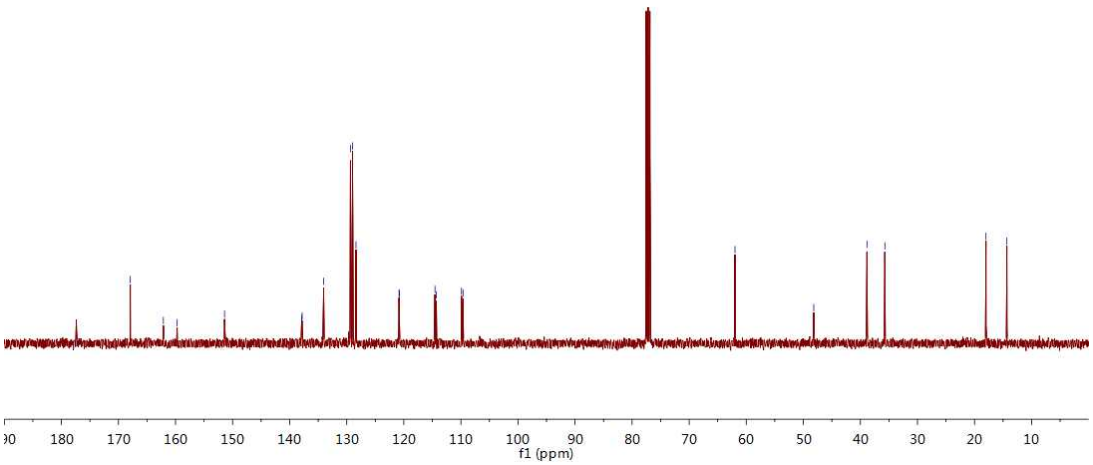
1H NMR JL-2-62A in CDCl3

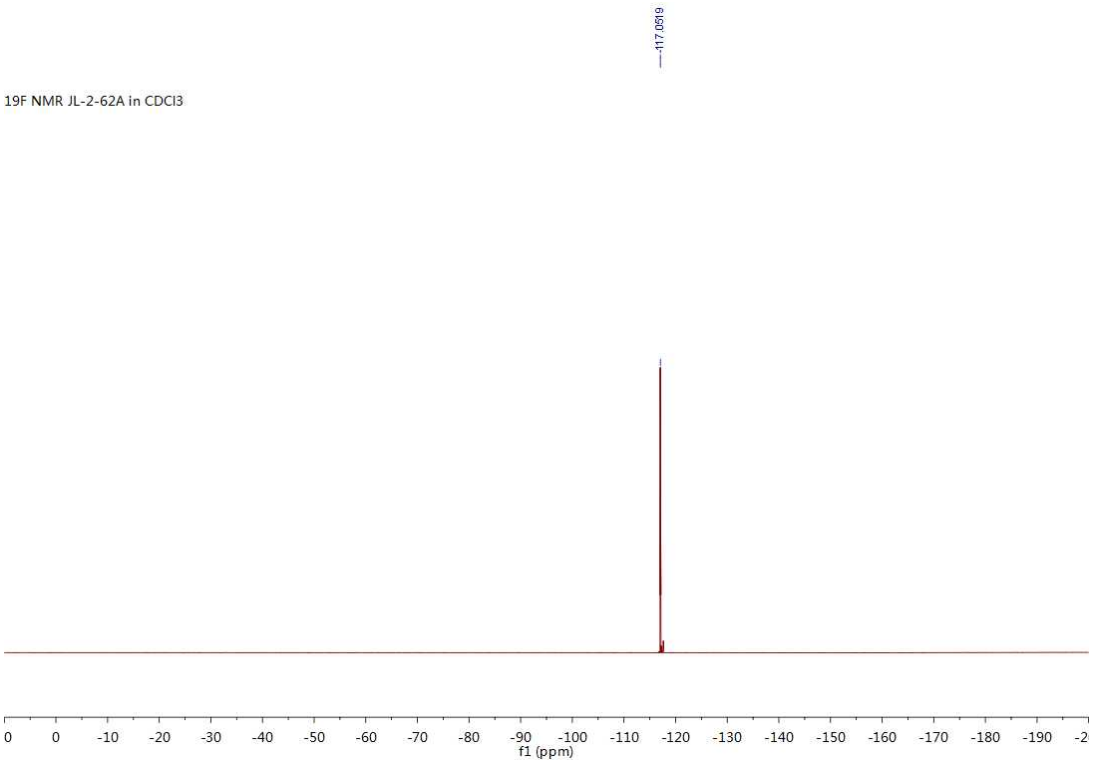


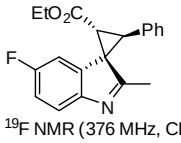


3o ^{1}H NMR (400 MHz, $CDCl_3$)
^{13}C NMR (100 MHz, $CDCl_3$)

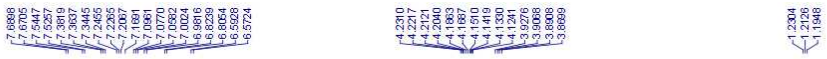
13C NMR JL-2-62A in CDCl3



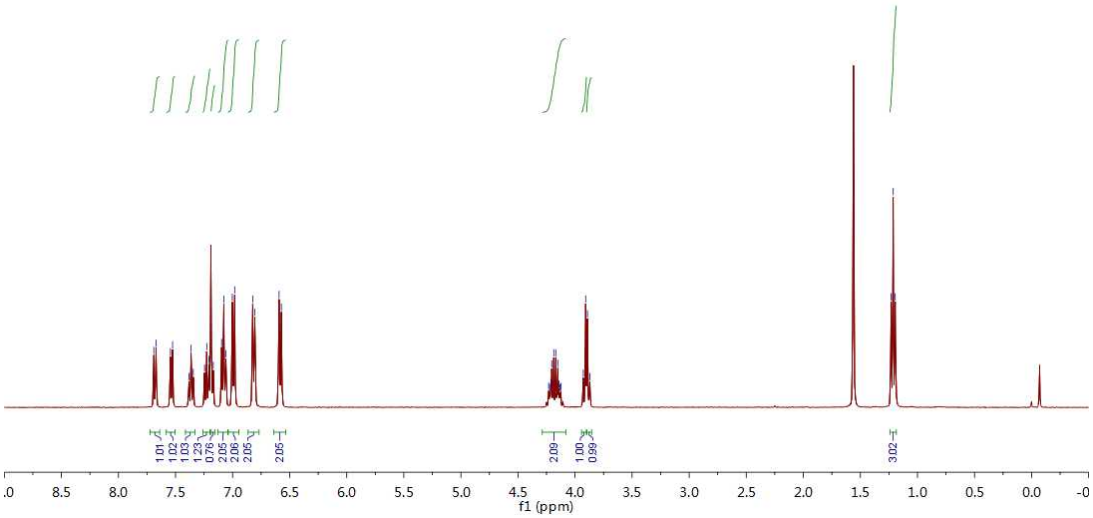


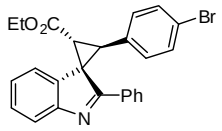


3o ^{19}F NMR (376 MHz, $CDCl_3$)



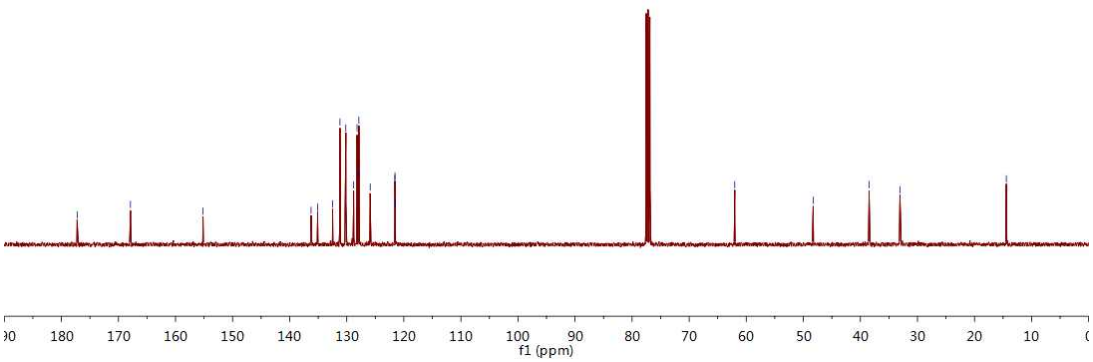
1H NMR JL-2-30B1

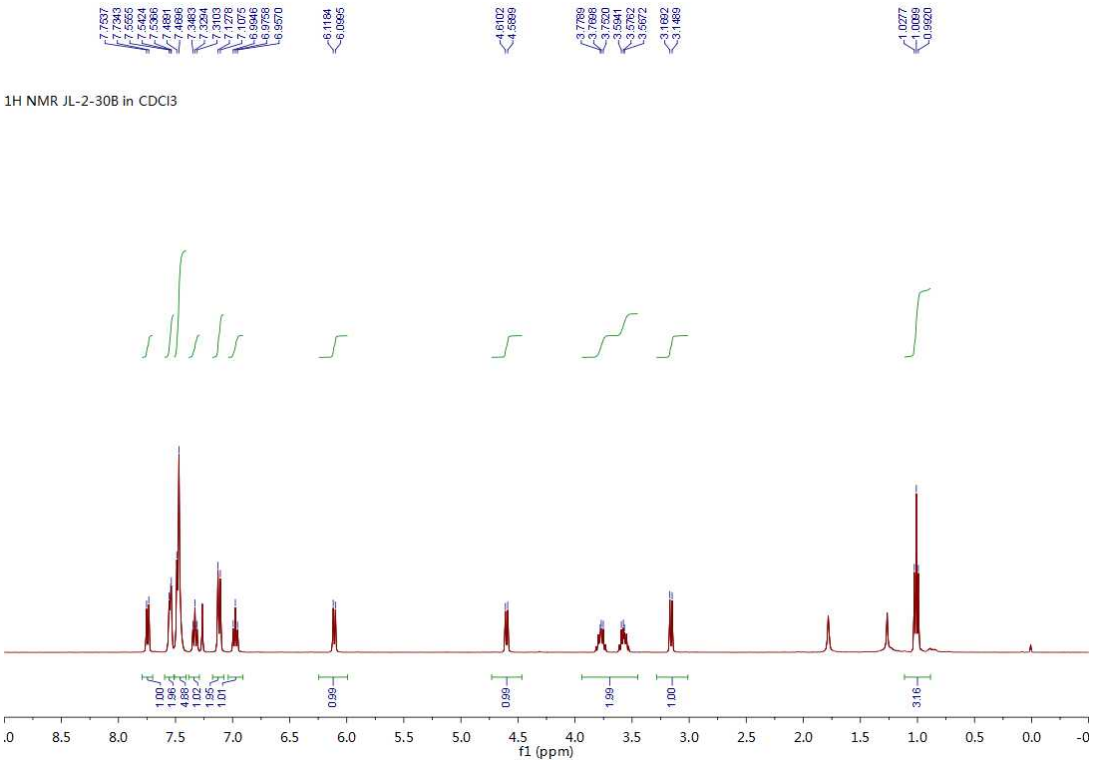




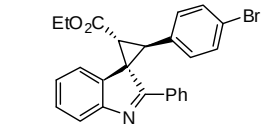
3p ^{1}H NMR (400 MHz, $CDCl_3$)
^{13}C NMR (100 MHz, $CDCl_3$)

13C NMR JL-2-30B1 in CDCl3

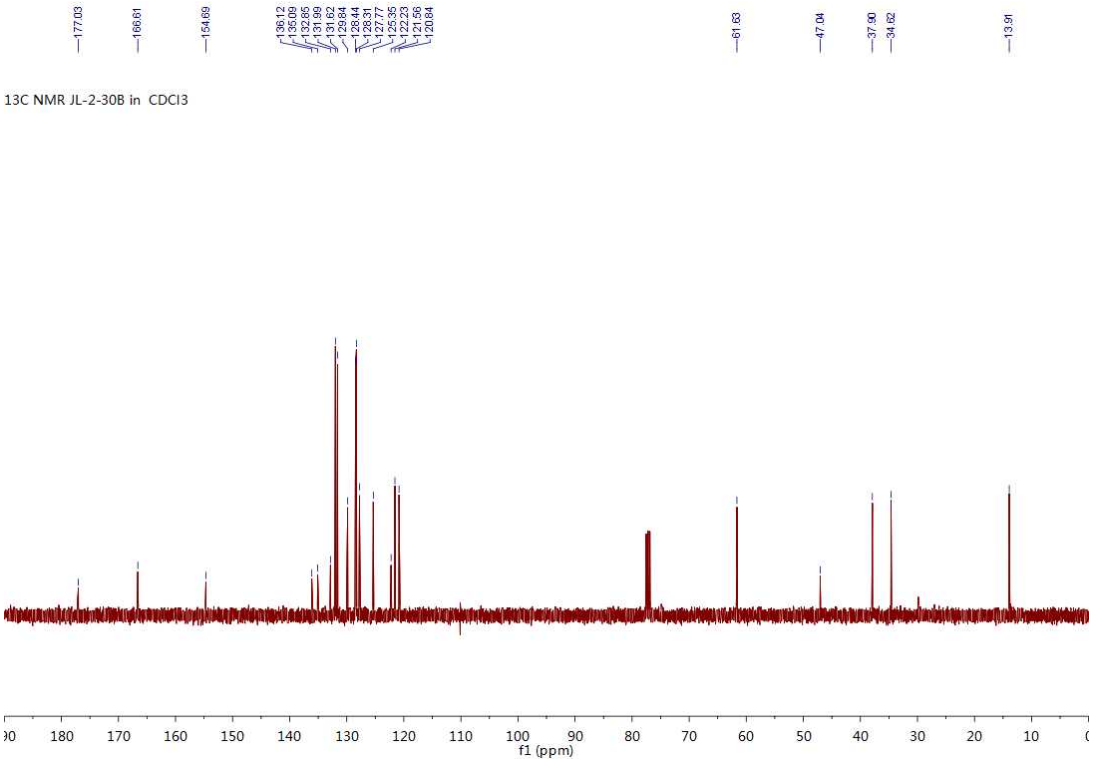




1H NMR JL-2-30B in CDCl3

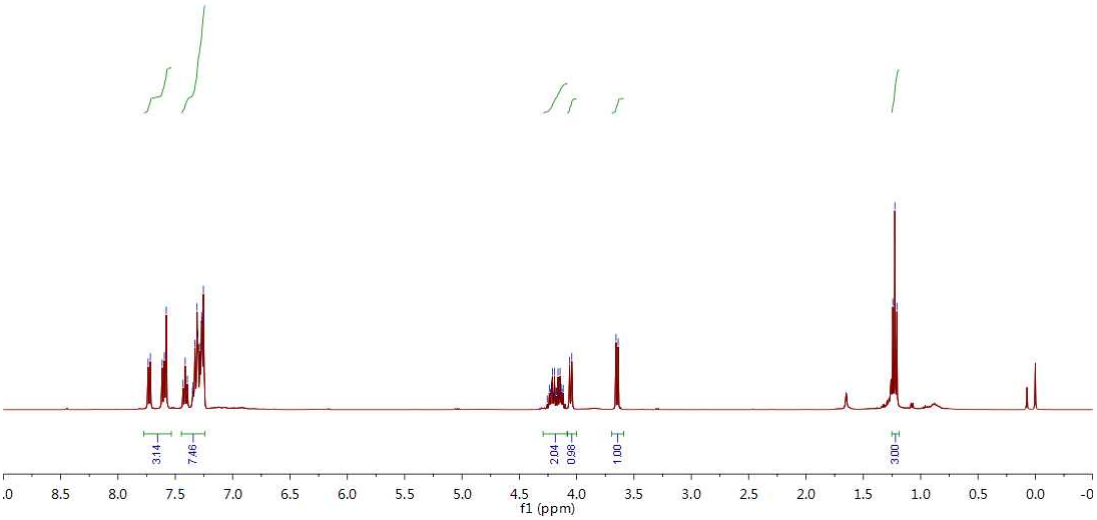


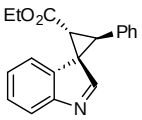
3p' ^{1}H NMR (400 MHz, $CDCl_3$)
^{13}C NMR (100 MHz, $CDCl_3$)



13C NMR JL-2-30B in CDCl3

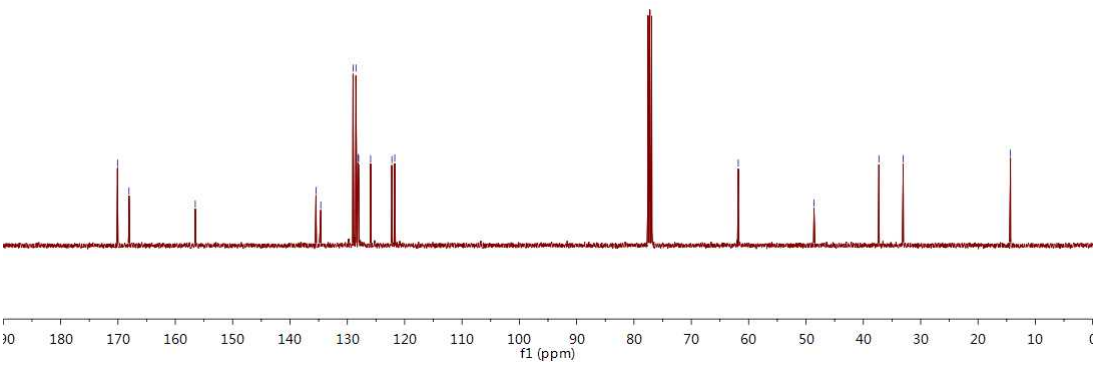
1H NMR BW-4-68b in CDCl3



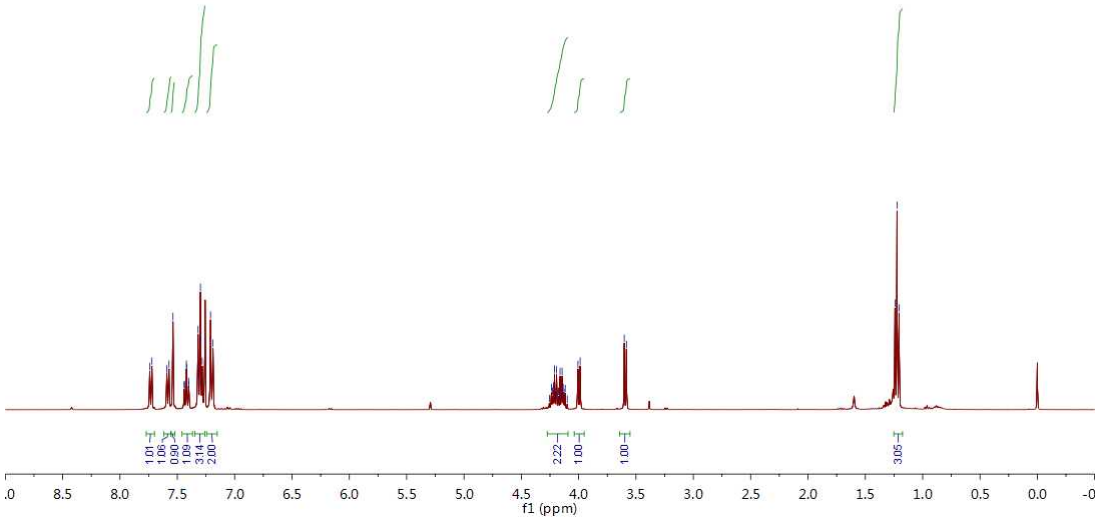


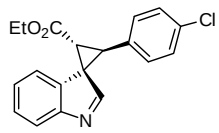
3q ^{1}H NMR (400 MHz, $CDCl_3$)
^{13}C NMR (100 MHz, $CDCl_3$)

13C NMR BW-4-71 in CDCl3



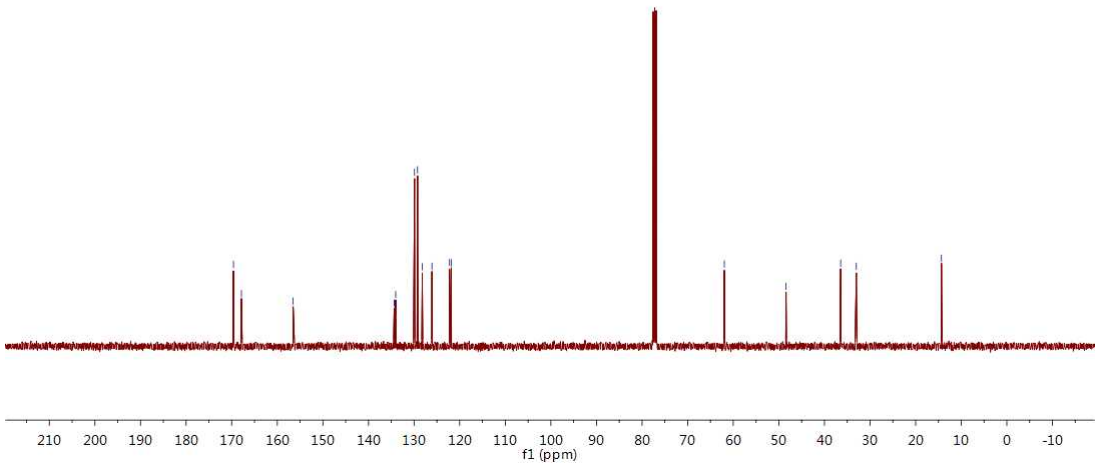
1H NMR BW-4-80 in CDCl3



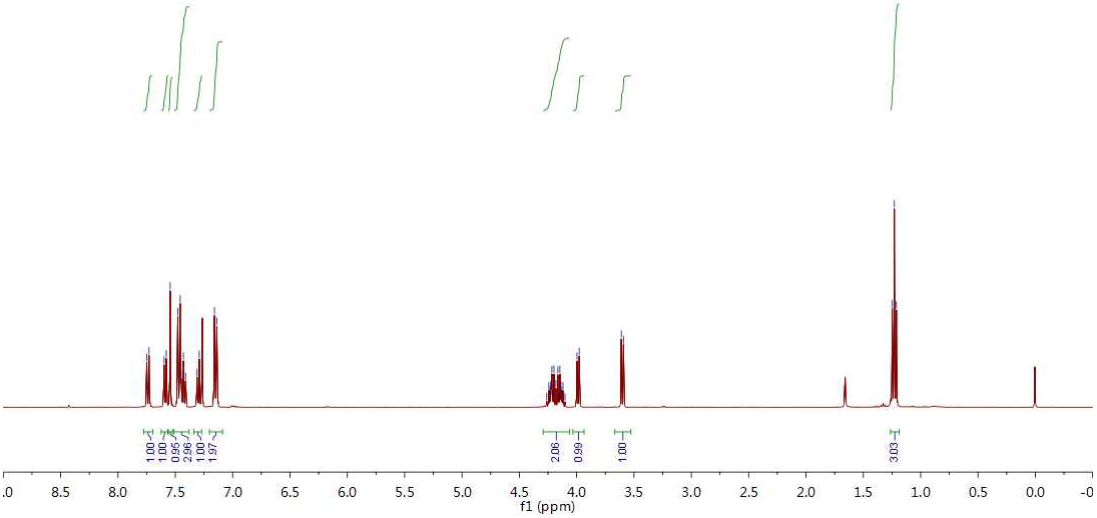


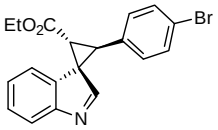
3r ^{1}H NMR (400 MHz, $CDCl_3$)
^{13}C NMR (100 MHz, $CDCl_3$)

13C NMR BW-4-80 in CDCl3



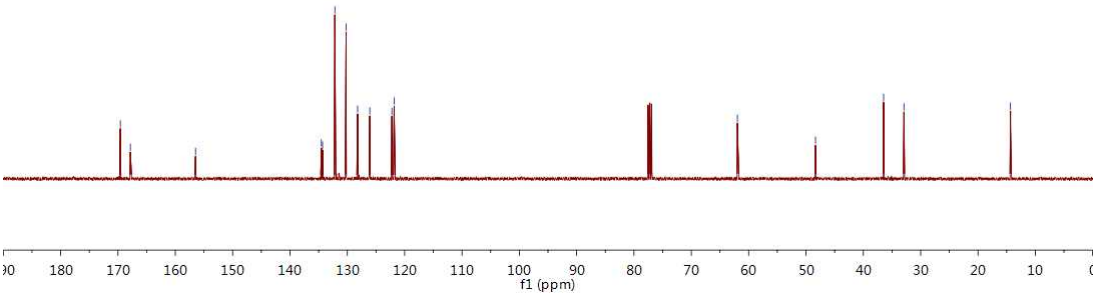
1H NMR BW-4-81in CDCl3



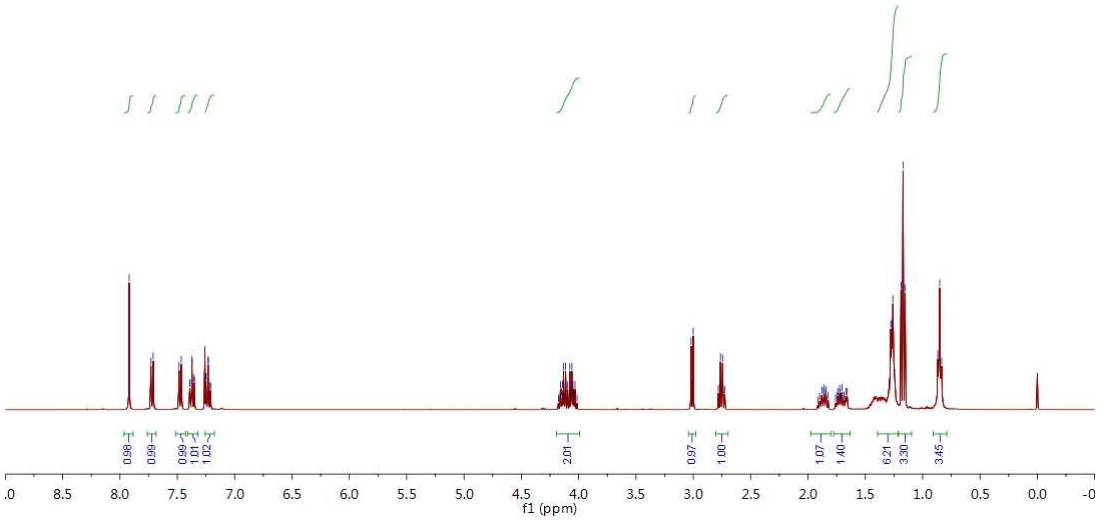


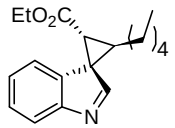
3s ^{1}H NMR (400 MHz, $CDCl_3$)
^{13}C NMR (100 MHz, $CDCl_3$)

13C NMR BW-4-81 in CDCl3

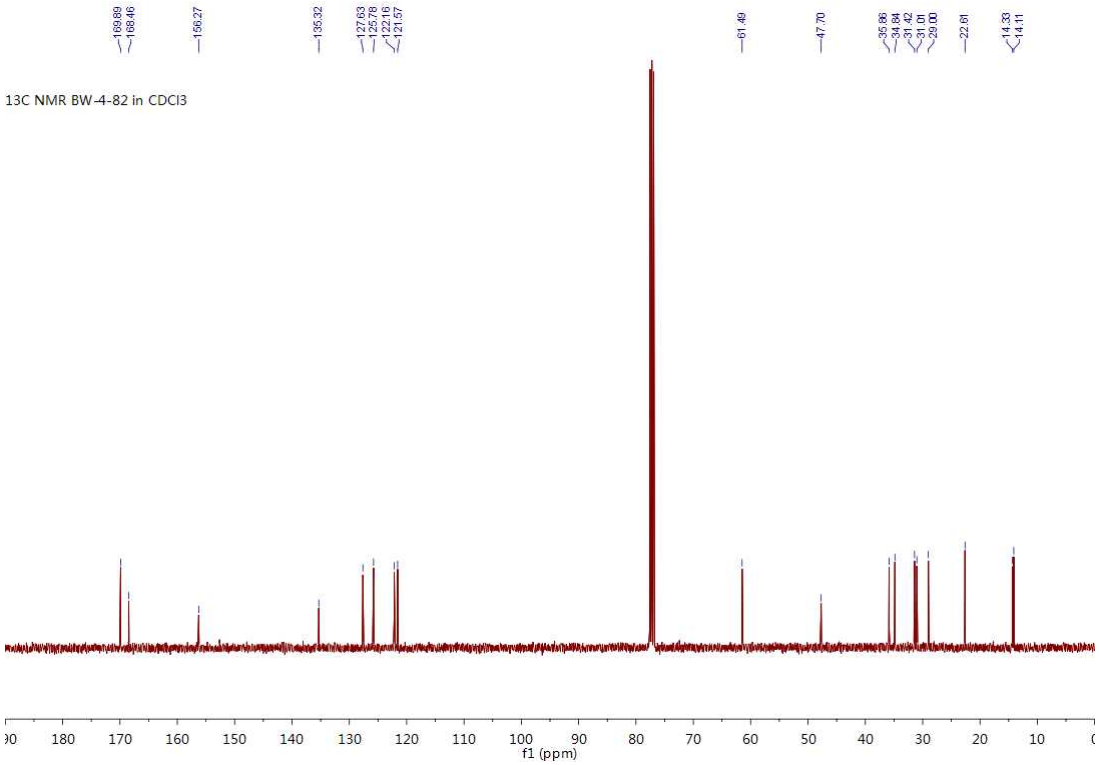


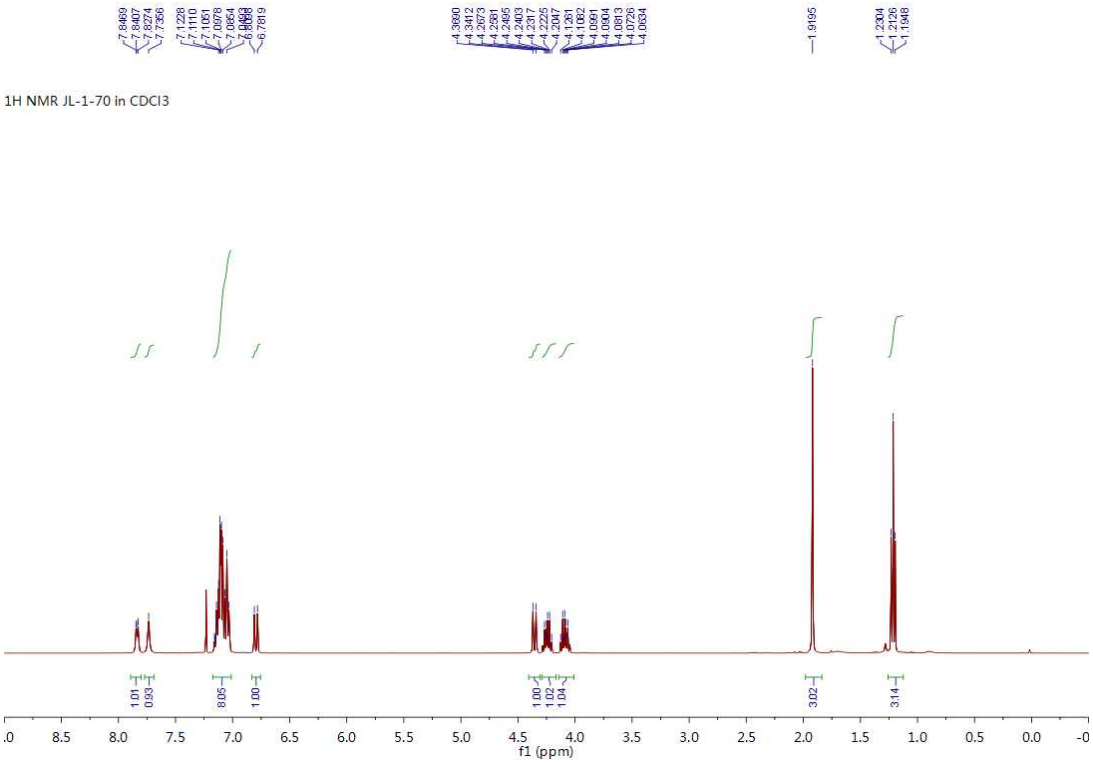
1H NMR BW-4-82 in CDCl3

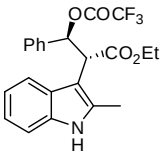




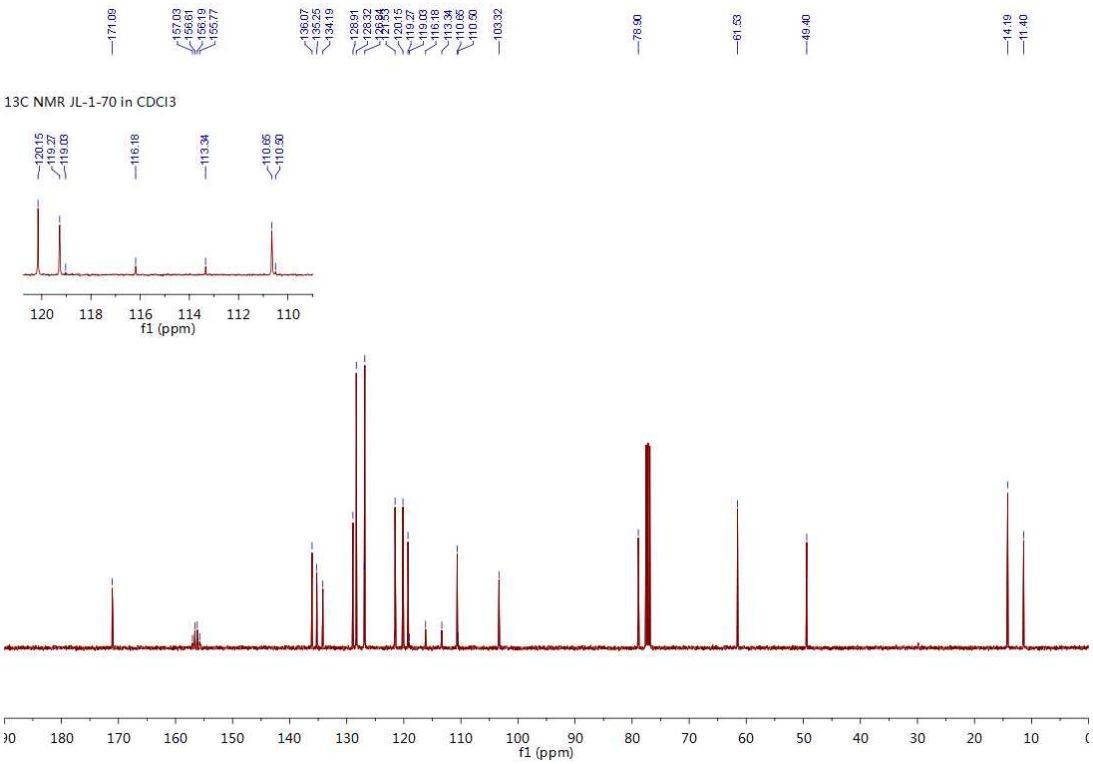
3t ^{1}H NMR (400 MHz, $CDCl_3$)
^{13}C NMR (100 MHz, $CDCl_3$)

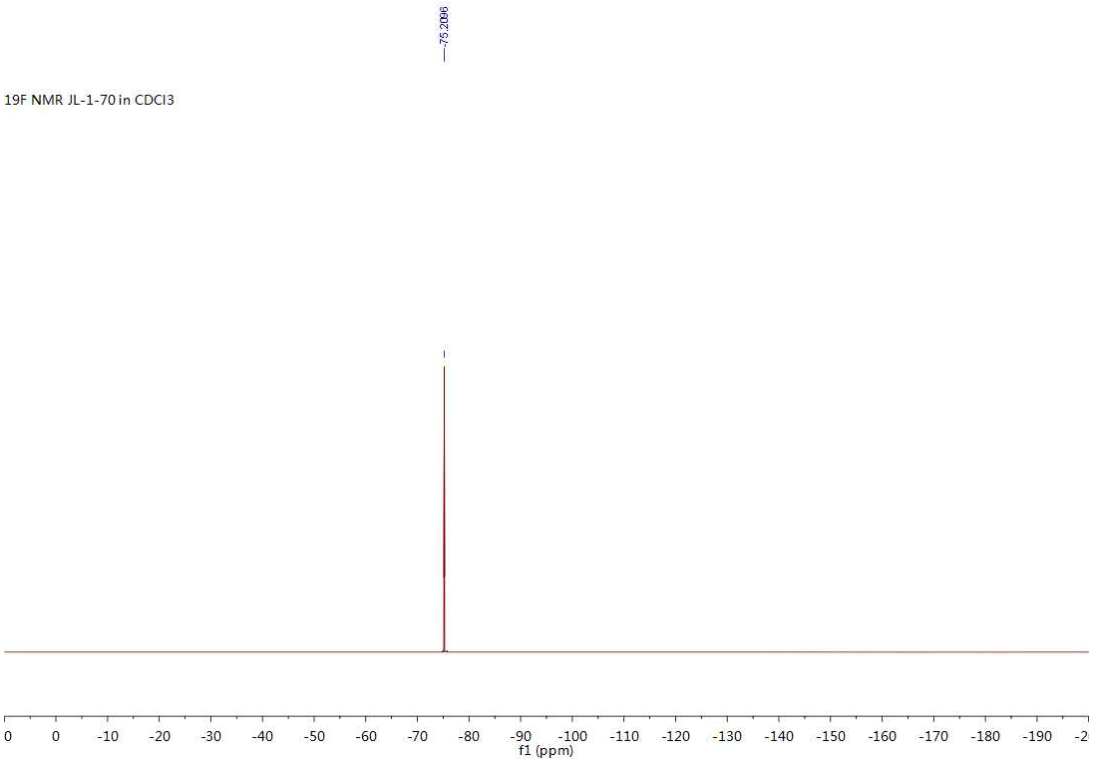


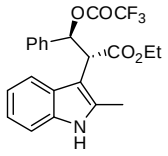




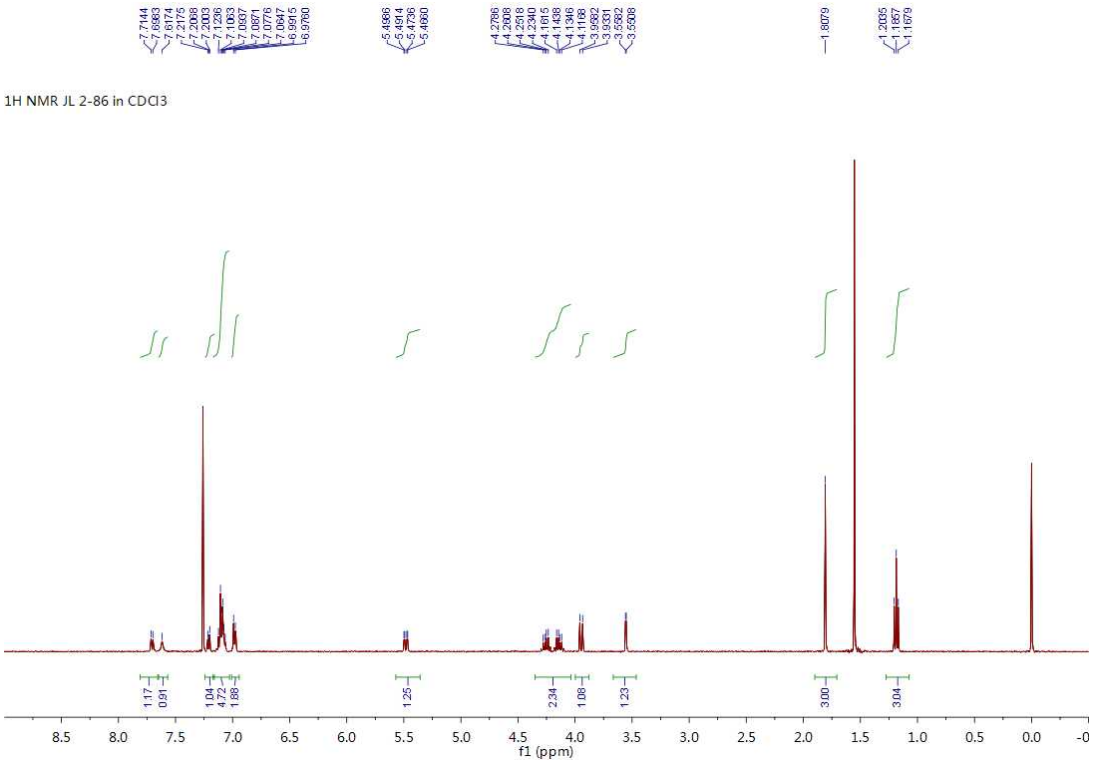
4a ^{1}H NMR (400 MHz, $CDCl_3$)
^{13}C NMR (100 MHz, $CDCl_3$)



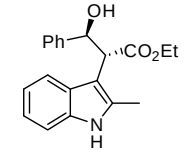




4a ^{19}F NMR (376MHz, $CDCl_3$)



1H NMR JL 2-86 in CDCl3



4b ^{1}H NMR (400 MHz, $CDCl_3$)
^{13}C NMR (100 MHz, $CDCl_3$)

13C NMR JL-2-86 in CDCl3