Supplementary Information

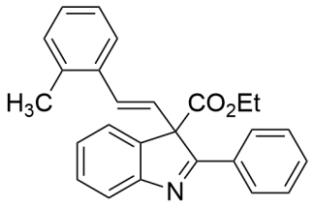
Copper-catalyzed [4+1] Cycloannulation of 2-aminochalcones with ethyl diazophenyl via ester rearrangement

An Li [a], LiPing Hu [a], Tao Yang [a], Zan Yang [a], Yu Liu [a], LiJun Li [a], KeWen Tang [a*] and CongShan Zhou [a*]

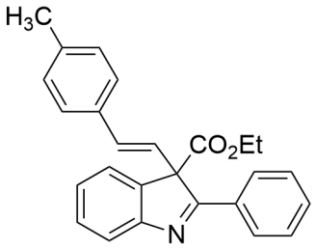
[a] Province Key Laboratory for Fine Petrochemical Catalysis and Separation, College of Chemistry and Chemical Engineering, Hunan Institute of Science and Technology, Yueyang, Hunan, 414000, P. R. China.

**** Corresponding author. Email:*** tangkewen@sina.com and zhoucongsh@126.com.

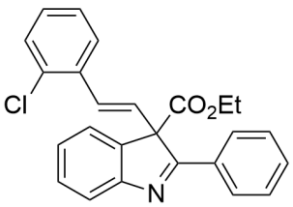
1. Characterization data of products 2aa-2oa



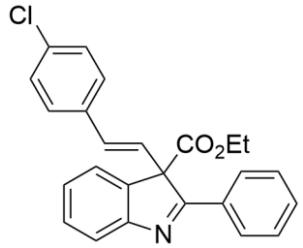
Ethyl (E)-3-(2-methylstyryl)-2-phenyl-3H-indole-3-carboxylate(3ba). The reaction mixture was purified by silica gel column chromatography (petroleum ether /EtOAc =100:1-50:1, V/V) to obtain a yellow solid with a yield of 64% (48.7mg), m. p. 115-117℃. ^{1}H NMR (400 MHz, Chloroform-*d*): δ 8.06 (dd, *J* = 6.5, 3.3 Hz, 2H), 7.75 (d, *J* = 7.7 Hz, 1H), 7.47 – 7.41 (m, 5H), 7.39 – 7.36 (m, 1H), 7.29 (d, *J* = 8.5 Hz, 1H), 7.12 – 7.07 (m, 2H), 7.02 – 6.98 (m, 1H), 6.93 (d, *J* = 16.2 Hz, 1H), 6.32 (d, *J* = 16.2 Hz, 1H), 4.17 – 4.11 (m, 1H), 4.03 – 3.96 (m, 1H), 1.92 (s, 3H), 0.97 (t, *J* = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 176.5, 170.1, 155.2, 140.9, 135.6, 132.2, 131.2, 130.1, 129.9, 129.2, 128.9, 128.7, 127.8, 126.6, 126.5, 126.0, 125.8, 122.3, 121.5, 68.7, 62.1, 19.4, 13.8. HRMS (m/z): [M+H]+ calcd for $C_{26}H_{24}NO_2$: 382.1802; found: 382.1815.



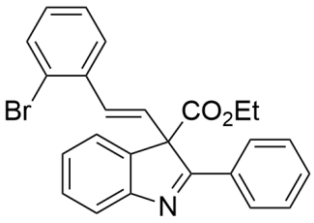
Ethyl (E)-3-(4-methylstyryl)-2-phenyl-3H-indole-3-carboxylate(3ca). The reaction mixture was purified by silica gel column chromatography (petroleum ether /EtOAc =100:1-50:1, V/V) to obtain a yellow solid with a yield of 48% (36.7mg), m. p. 126-128℃. ^{1}H NMR (400 MHz, Chloroform-*d*): δ 8.04 (dd, *J* = 6.6, 3.1 Hz, 2H), 7.74 (d, *J* = 7.4 Hz, 1H), 7.46 – 7.39 (m, 5H), 7.24 (s, 1H), 7.15 (d, *J* = 8.1 Hz, 2H), 7.06 – 7.00 (m, 3H), 6.06 (d, *J* = 16.3 Hz, 1H), 4.13 (ddd, *J* = 11.0, 7.2, 3.8 Hz, 1H), 4.03 – 3.95 (m, 1H), 2.26 (s, 3H), 0.95 (t, *J* = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 176.5, 170.2, 155.3, 140.9, 137.9, 133.6, 132.2, 131.4, 131.1, 129.2, 129.1, 128.9, 128.7, 126.5, 123.8, 122.4, 121.4, 68.5, 62.0, 21.2, 13.7. HRMS (m/z): [M+H]+ calcd for $C_{26}H_{24}NO_2$: 382.1802; found: 382.1812.



Ethyl (E)-3-(2-chlorostyryl)-2-phenyl-3H-indole-3-carboxylate(3da). The reaction mixture was purified by silica gel column chromatography (petroleum ether /EtOAc =100:1-50:1, V/V) to obtain a yellow solid with a yield of 53% (41.5mg), m. p. 111-114℃. ^{1}H NMR (400 MHz, Chloroform-*d*): δ 8.05 (dd, *J* = 6.6, 3.1 Hz, 2H), 7.76 (d, *J* = 7.6 Hz, 1H), 7.48 – 7.45 (m, 5H), 7.29 (t, *J* = 7.4 Hz, 1H), 7.25 – 7.09 (m, 4H), 6.99 (d, *J* = 16.3 Hz, 1H), 6.56 (d, *J* = 16.3 Hz, 1H), 4.19 – 4.11 (m, 1H), 4.05 – 3.98 (m, 1H), 0.98 (t, *J* = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 176.1, 170.0, 155.3, 140.3, 134.7, 133.3, 132.1, 131.2, 129.6, 129.3, 128.92, 128.87, 128.7, 128.4, 127.8, 127.1, 126.7, 126.6, 122.4, 121.5, 68.6, 62.2, 13.7. HRMS (m/z): [M+H]+ calcd for $C_{25}H_{21}ClNO_2$: 402.1255; found: 402.1271.

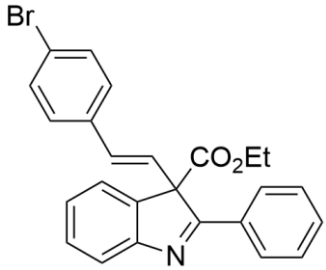


Ethyl (E)-3-(4-chlorostyryl)-2-phenyl-3H-indole-3-carboxylate(3ea). The reaction mixture was purified by silica gel column chromatography (petroleum ether /EtOAc =100:1-50:1, V/V) to obtain a yellow liquid with a yield of 43% (33.8mg). ^{1}H NMR (400 MHz, Chloroform-*d*): δ 8.08 – 7.98 (m, 2H), 7.75 (d, *J* = 7.7 Hz, 1H), 7.48 – 7.40 (m, 5H), 7.33 – 7.26 (m, 1H), 7.18 (d, *J* = 1.6 Hz, 4H), 7.06 (d, *J* = 16.3 Hz, 1H), 6.05 (d, *J* = 16.4 Hz, 1H), 4.17 – 4.11 (m, 1H), 4.04 – 3.95 (m, 1H), 0.96 (t, *J* = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 176.2, 170.1, 155.3, 140.6, 134.8, 133.6, 132.0, 131.3, 130.3, 129.3, 128.8, 128.7, 128.6, 127.8, 126.6, 125.6, 122.3, 121.5, 68.3, 62.2, 13.7. HRMS (m/z): [M+H]+ calcd for $C_{25}H_{21}ClNO_2$: 402.1255; found: 402.1270.

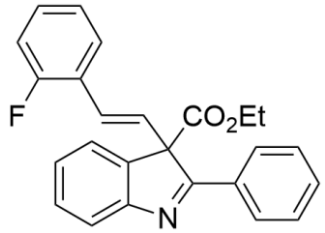


Ethyl (E)-3-(2-bromostyryl)-2-phenyl-3H-indole-3-carboxylate(3fa). The reaction mixture was purified by silica gel column chromatography (petroleum ether /EtOAc =100:1-50:1, V/V) to obtain a yellow solid with a yield of 50% (45.4mg), m. p. 125-127℃. ^{1}H NMR (400 MHz, Chloroform-*d*): δ 8.05 (dd, *J* = 6.8, 3.0 Hz, 2H), 7.76 (d, *J* = 7.7 Hz, 1H), 7.49 – 7.40 (m, 7H), 7.30 (t, *J* = 7.9 Hz, 1H), 7.20 (t, *J* = 7.4 Hz, 1H), 7.05 – 7.00 (m, 1H), 6.92 (d, *J* = 16.2 Hz, 1H), 6.53 (d, *J* = 16.2 Hz, 1H), 4.20 – 4.12 (m, 1H), 4.06 – 3.98 (m, 1H), 0.98 (t, *J* = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 176.0, 170.0, 155.3, 140.3, 136.5, 132.8, 132.1, 131.1, 129.3, 129.2, 128.9,

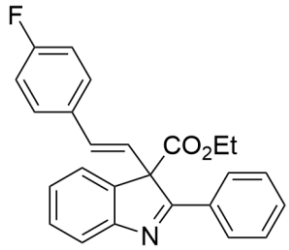
128.7, 128.0, 127.4, 127.3, 126.6, 123.8, 122.4, 121.5, 68.5, 62.2, 13.8. HRMS (m/z): [M+H]+ calcd for $C_{25}H_{21}BrNO_2$: 446.0750; found: 446.0767.



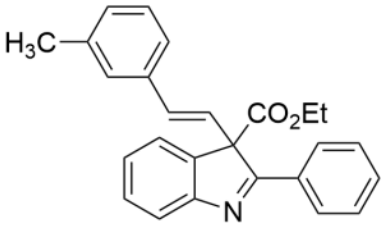
Ethyl (E)-3-(4-bromostyryl)-2-phenyl-3H-indole-3-carboxylate(3ga). The reaction mixture was purified by silica gel column chromatography (petroleum ether /EtOAc =100:1-50:1, V/V) to obtain a yellow liquid with a yield of 51% (44.5mg). ^{1}H NMR (400 MHz, Chloroform-*d*): δ 8.02 (dd, *J* = 7.4, 2.3 Hz, 2H), 7.75 (d, *J* = 7.7 Hz, 1H), 7.48 – 7.40 (m, 5H), 7.34 (d, *J* = 8.5 Hz, 2H), 7.28 (d, *J* = 7.5 Hz, 1H), 7.12 – 7.09 (m, 2H), 7.06 (s, 1H), 6.03 (d, *J* = 16.4 Hz, 1H), 4.18 – 4.10 (m, 1H), 4.04 – 3.95 (m, 1H), 0.96 (t, *J* = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 176.2, 170.0, 155.3, 140.6, 135.3, 132.0, 131.6, 131.3, 130.4, 129.3, 128.78, 128.75, 128.1, 126.7, 125.7, 122.3, 121.8, 121.5, 68.3, 62.2, 13.7. HRMS (m/z): [M+H]+ calcd for $C_{25}H_{21}BrNO_2$: 446.0750; found: 446.0765.



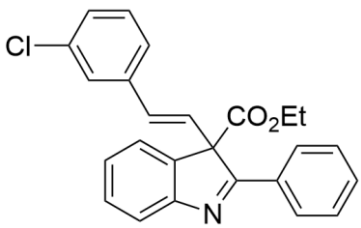
Ethyl (E)-3-(2-fluorostyryl)-2-phenyl-3H-indole-3-carboxylate(3ha). The reaction mixture was purified by silica gel column chromatography (petroleum ether /EtOAc =100:1-50:1, V/V) to obtain a yellow solid with a yield of 52% (40mg), m. p. 95-100℃. ^{1}H NMR (400 MHz, Chloroform-*d*): δ 8.04 (dd, *J* = 6.5, 3.1 Hz, 2H), 7.75 (d, *J* = 7.5 Hz, 1H), 7.48 – 7.41 (m, 5H), 7.38 – 7.34 (m, 1H), 7.28 (t, *J* = 7.5 Hz, 1H), 7.19 – 7.12 (m, 2H), 7.01 (t, *J* = 7.5 Hz, 1H), 6.94 – 6.88 (m, 1H), 6.27 (d, *J* = 16.5 Hz, 1H), 4.15 (dd, *J* = 10.8, 7.1 Hz, 1H), 4.05 – 3.97 (m, 1H), 0.97 (t, *J* = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 176.2, 170.0, 160.2 (d, J = 251.5 Hz), 155.3, 140.5, 132.1, 131.2, 129.2 (d, J = 8.1 Hz), 128.8, 128.7, 127.7 (d, J = 3.0 Hz), 127.6 (d, J = 6.1 Hz), 126.6, 124.4 (d, J = 3.0 Hz), 124.2 (d, J = 12.1 Hz), 124.0 (d, J = 3.0 Hz), 122.4, 121.5, 115.7 (d, J = 22.2 Hz), 68.7, 62.1, 13.7. ^{19}F NMR (376MHz, CDCl3): δ -117.16. HRMS (m/z): [M+H]+ calcd for $C_{25}H_{21}FNO_2$: 386.1551; found: 386.1559.



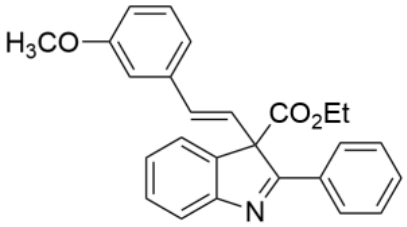
Ethyl (E)-3-(4-fluorostyryl)-2-phenyl-3H-indole-3-carboxylate(3ia). The reaction mixture was purified by silica gel column chromatography (petroleum ether /EtOAc =100:1-50:1, V/V) to obtain a yellow liquid with a yield of 43% (33.2mg). ^{1}H NMR (400 MHz, Chloroform-*d*): δ 8.08 – 7.98 (m, 2H), 7.75 (d, *J* = 7.7 Hz, 1H), 7.48 – 7.40 (m, 5H), 7.28 (d, *J* = 7.5 Hz, 1H), 7.21 (dd, *J* = 8.7, 5.4 Hz, 2H), 7.00 (d, *J* = 16.3 Hz, 1H), 6.91 (t, *J* = 8.7 Hz, 2H), 6.06 (d, *J* = 16.4 Hz, 1H), 4.14 (dq, *J* = 10.8, 7.1 Hz, 1H), 4.03 – 3.95 (m, 1H), 0.96 (t, *J* = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 176.3, 170.1, 162.5 (d, *J* = 248.5 Hz), 155.3, 140.7, 132.5 (d, *J* = 3.0 Hz), 132.1, 131.2, 130.3, 129.2, 128.8, 128.7, 128.1 (d, *J* = 8.1 Hz), 126.6, 124.68, 124.65, 122.3, 121.5, 115.4 (d, *J* = 22.2 Hz), 68.35, 62.11, 13.72. ^{19}F NMR (376MHz, CDCl3): δ -113.72. HRMS (m/z): [M+H]+ calcd for $C_{25}H_{21}FNO_2$: 386.1551; found: 386.1561.



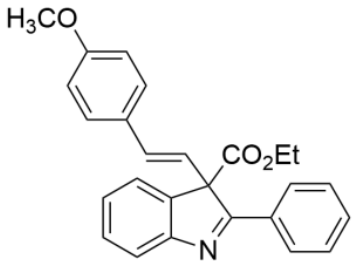
Ethyl (E)-3-(3-methylstyryl)-2-phenyl-3H-indole-3-carboxylate(3ja). The reaction mixture was purified by silica gel column chromatography (petroleum ether /EtOAc =100:1-50:1, V/V) to obtain a yellow solid with a yield of 48% (35.7mg), m. p. 106-109℃. ^{1}H NMR (400 MHz, Chloroform-*d*): δ 8.04 (dd, *J* = 7.1, 2.6 Hz, 2H), 7.74 (d, *J* = 7.6 Hz, 1H), 7.47 – 7.40 (m, 5H), 7.34 – 7.21 (m, 2H), 7.12 – 7.06 (m, 3H), 6.99 (d, *J* = 7.3 Hz, 1H), 6.06 (d, *J* = 16.4 Hz, 1H), 4.17 – 4.10 (m, 1H), 4.03 – 3.96 (m, 1H), 2.26 (s, 3H), 0.96 (t, *J* = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 176.5, 170.2, 155.3, 141.0, 138.1, 136.3, 132.1, 131.6, 131.2, 129.1, 128.9, 128.74, 128.68, 128.4, 127.2, 126.6, 124.7, 123.7, 122.4, 121.4, 68.4, 62.1, 21.3, 13.7. HRMS (m/z): [M+H]+ calcd for $C_{26}H_{24}NO_2$: 382.1802; found: 382.1810.



Ethyl (E)-3-(3-chlorostyryl)-2-phenyl-3H-indole-3-carboxylate(3ka). The reaction mixture was purified by silica gel column chromatography (petroleum ether /EtOAc =100:1-50:1, V/V) to obtain a yellow solid with a yield of 38% (29.9mg), m. p. 117-120℃. ^{1}H NMR (400 MHz, Chloroform-*d*): δ 8.02 (dd, *J* = 7.3, 2.4 Hz, 2H), 7.75 (d, *J* = 7.7 Hz, 1H), 7.48 – 7.40 (m, 5H), 7.35 – 7.19 (m, 3H), 7.15 – 7.12 (m, 2H), 7.09 (s, 1H), 6.04 (d, *J* = 16.4 Hz, 1H), 4.15 (dq, *J* = 10.8, 7.1 Hz, 1H), 4.04 – 3.96 (m, 1H), 0.96 (t, *J* = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 176.1, 170.0, 155.3, 140.6, 138.2, 134.5, 132.0, 131.3, 130.2, 129.7, 129.3, 128.8, 127.9, 126.7, 126.5, 126.4, 124.8, 122.3, 121.5, 68.3, 62.2, 13.7. HRMS (m/z): [M+H]+ calcd for $C_{25}H_{21}ClNO_2$: 402.1255; found: 402.1270.

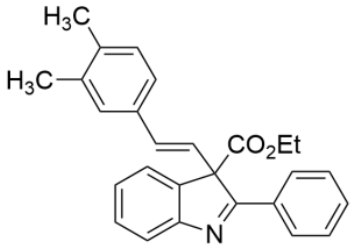


Ethyl (E)-3-(3-methoxystyryl)-2-phenyl-3H-indole-3-carboxylate(3la). The reaction mixture was purified by silica gel column chromatography (petroleum ether /EtOAc =100:1-50:1, V/V) to obtain a yellow solid with a yield of 31% (24.7mg), m. p. 105-110℃. ^{1}H NMR (400 MHz, Chloroform-*d*): δ 8.09 – 7.98 (m, 2H), 7.75 (d, *J* = 7.6 Hz, 1H), 7.48 – 7.39 (m, 5H), 7.27 – 7.25 (m, 1H), 7.16 – 7.06 (m, 2H), 6.85 (d, *J* = 7.7 Hz, 1H), 6.78 (s, 1H), 6.73 (dd, *J* = 7.9, 2.2 Hz, 1H), 6.07 (d, *J* = 16.3 Hz, 1H), 4.15 (dq, *J* = 10.8, 7.1 Hz, 1H), 4.04 – 3.96 (m, 1H), 3.74 (s, 3H), 0.96 (t, *J* = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 176.4, 170.1, 159.7, 155.3, 140.9, 137.8, 132.1, 131.4, 131.2, 129.5, 129.2, 128.8, 128.7, 126.6, 125.2, 122.4, 121.4, 119.2, 113.7, 111.8, 68.4, 62.1, 55.2, 13.7. HRMS (m/z): [M+H]+ calcd for $C_{26}H_{24}NO_3$: 398.1751; found: 398.1760.

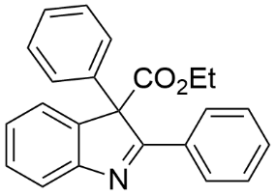


Ethyl (E)-3-(4-methoxystyryl)-2-phenyl-3H-indole-3-carboxylate(3ma). The reaction mixture was purified by silica gel column chromatography (petroleum ether /EtOAc =100:1-50:1, V/V) to obtain a yellow liquid with a yield of 39% (30.4mg). ^{1}H NMR (400 MHz, Chloroform-*d*): δ 8.04 (dd, *J* = 6.6, 3.2 Hz, 2H), 7.74 (d, *J* = 7.3 Hz, 1H), 7.46 – 7.41 (m, 5H), 7.25 (s, 1H), 7.18 (d, *J* = 8.7 Hz, 2H), 6.94 (d, *J* = 16.3 Hz, 1H), 6.76 (d, *J* = 8.8 Hz, 2H), 6.03 (d, *J* = 16.3 Hz, 1H), 4.14 (ddd, *J* = 10.8, 7.2, 3.6 Hz, 1H), 3.99 (dq, *J* = 10.8, 7.1 Hz, 1H), 3.74 (s, 3H), 0.96 (t, *J* = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 176.6, 170.3, 159.5, 155.3, 141.0, 132.2, 131.1, 130.9,

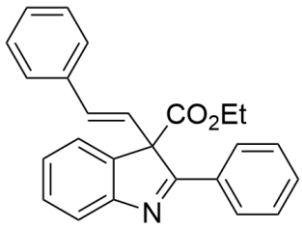
129.12, 129.08, 128.8, 128.7, 128.6, 127.8, 126.54, 126.52, 122.4, 121.4, 113.9, 68.5, 62.0, 55.3, 13.7. HRMS (m/z): [M+H]+ calcd for $C_{26}H_{24}NO_3$: 398.1751; found: 398.1761.



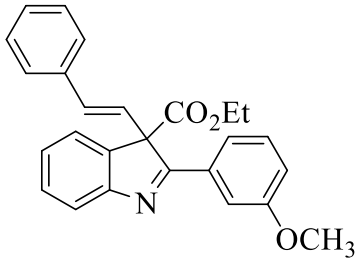
Ethyl (E)-3-(3,4-dimethylstyryl)-2-phenyl-3H-indole-3-carboxylate(3na). The reaction mixture was purified by silica gel column chromatography (petroleum ether /EtOAc =100:1-50:1, V/V) to obtain a yellow solid with a yield of 51% (40.2mg), m. p. 115-120℃. ^{1}H NMR (400 MHz, Chloroform-*d*): δ 8.05 – 8.02 (m, 2H), 7.74 (d, *J* = 8.4 Hz, 1H), 7.50 (t, *J* = 7.7 Hz, 1H), 7.45 – 7.39 (m, 5H), 7.24 (d, *J* = 2.1 Hz, 1H), 7.05 (d, *J* = 4.1 Hz, 1H), 6.98 (s, 2H), 6.04 (d, *J* = 16.4 Hz, 1H), 4.16 – 4.10 (m, 1H), 4.03 – 3.95 (m, 1H), 2.17 (s, 6H), 0.95 (t, *J* = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 176.6, 170.3, 155.3, 141.1, 136.61, 136.57, 134.9, 134.0, 132.2, 131.5, 131.1, 130.1, 129.7, 129.1, 128.91, 128.86, 128.7, 127.7, 126.5, 124.0, 123.6, 122.4, 121.4, 68.5, 62.4, 62.0, 19.7, 19.5, 14.2, 13.7. HRMS (m/z): [M+H]+ calcd for $C_{27}H_{26}NO_2$: 396.1958; found: 396.1971.



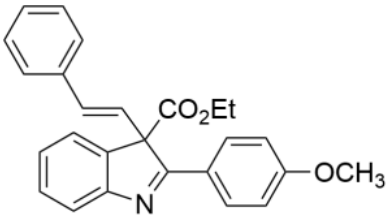
Ethyl 2,3-diphenyl-3H-indole-3-carboxylate(3oa). The reaction mixture was purified by silica gel column chromatography (petroleum ether /EtOAc =100:1-50:1, V/V) to obtain a yellow solid with a yield of 31% (21.8mg), m. p. 105-110℃. ^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.92 (d, *J* = 7.1 Hz, 2H), 7.73 (d, *J* = 7.7 Hz, 1H), 7.41 – 7.36 (m, 3H), 7.34 (d, *J* = 7.7 Hz, 3H), 7.26 – 7.18 (m, 5H), 4.20 – 4.14 (m, 1H), 4.08 – 4.00 (m, 1H), 0.99 (t, *J* = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 177.2, 169.3, 154.7, 142.4, 136.7, 132.6, 130.9, 129.2, 129.1, 128.8, 128.3, 127.7, 127.4, 126.7, 123.3, 121.2, 71.6, 62.0, 13.7. HRMS (m/z): [M+H]+ calcd for $C_{23}H_{20}NO_2$: 342.1489; found: 342.1498.



Ethyl (E)-2-phenyl-3-styryl-3H-indole-3-carboxylate(3aa). The reaction mixture was purified by silica gel column chromatography (petroleum ether /EtOAc =100:1-50:1, V/V) to obtain a yellow solid with a yield of 92% (67.3mg), m. p. 90-95℃. ^{1}H NMR (400 MHz, Chloroform-*d*): δ 8.04 (dd, *J* = 6.5, 3.3 Hz, 2H), 7.77 – 7.72 (m, 1H), 7.47 – 7.40 (m, 5H), 7.28 – 7.16 (m, 6H), 7.10 (d, *J* = 16.4 Hz, 1H), 6.10 (d, *J* = 16.4 Hz, 1H), 4.14 (dq, *J* = 10.8, 7.1 Hz, 1H), 3.99 (dq, *J* = 10.8, 7.1 Hz, 1H), 0.95 (t, *J* = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 176.4, 170.2, 155.3, 140.9, 136.3, 132.1, 131.5, 131.2, 129.2, 128.9, 128.7, 128.5, 128.0, 126.62, 126.56, 124.9, 122.4, 121.5, 68.4, 62.1, 13.8. HRMS (m/z): [M+H]+ calcd for $C_{25}H_{22}NO_2$: 368.1645; found: 368.1656.

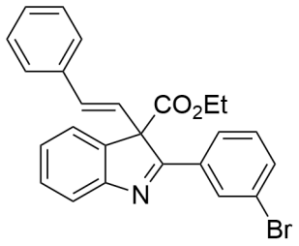


Ethyl (E)-2-(3-methoxyphenyl)-3-styryl-3H-indole-3-carboxylate(3ab). The reaction mixture was purified by silica gel column chromatography (petroleum ether /EtOAc =100:1-50:1, V/V) to obtain a yellow liquid with a yield of 66% (51.8mg). ^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.78 – 7.70 (m, 2H), 7.50 (d, *J* = 7.8 Hz, 1H), 7.43 (t, *J* = 8.1 Hz, 2H), 7.33 (t, *J* = 8.0 Hz, 1H), 7.30 – 7.23 (m, 4H), 7.21 (d, *J* = 7.7 Hz, 1H), 7.19 – 7.14 (m, 1H), 7.09 (d, *J* = 16.4 Hz, 1H), 7.01 (dd, *J* = 7.9, 2.9 Hz, 1H), 6.10 (d, *J* = 16.4 Hz, 1H), 4.14 (dq, *J* = 10.8, 7.1 Hz, 1H), 4.00 (dq, *J* = 10.8, 7.1 Hz, 1H), 3.86 (s, 3H), 0.97 (t, *J* = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 176.4, 170.2, 159.8, 155.3, 140.9, 136.4, 133.5, 131.5, 129.6, 129.2, 128.5, 128.0, 126.64, 126.55, 125.0, 122.4, 121.7, 121.5, 118.0, 112.8, 68.5, 62.1, 55.4, 13.8. HRMS (m/z): [M+H]+ calcd for $C_{26}H_{24}NO_3$: 398.1751; found: 398.1761.

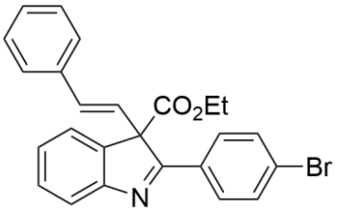


Ethyl (E)-2-(4-methoxyphenyl)-3-styryl-3H-indole-3-carboxylate(3ac). The reaction mixture was purified by silica gel column chromatography (petroleum ether /EtOAc =100:1-50:1, V/V) to obtain a yellow solid with a yield of 56% (44.5mg), m. p. 90-95℃. ^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.99 (d, *J* = 8.9 Hz, 2H), 7.70 (d, *J* = 7.5 Hz, 1H), 7.40 (d, *J* = 7.5 Hz, 2H), 7.22 (dq, *J* = 10.8, 7.4 Hz, 6H), 7.09 (d, *J* = 16.4 Hz, 1H), 6.95 (d, *J* = 8.9 Hz, 2H), 6.09 (d, *J* = 16.4 Hz, 1H), 4.17 – 4.10 (m, 1H), 4.03 – 3.96 (m, 1H), 3.83 (s, 3H), 0.97 (t, *J* = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 175.9, 170.3, 162.1, 155.5, 140.8, 136.4, 131.5, 130.7, 129.1, 128.5, 127.9,

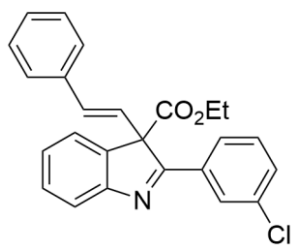
126.5, 126.0, 125.3, 124.9, 122.3, 121.0, 114.1, 68.3, 62.0, 55.4, 13.8. HRMS (m/z): [M+H]+ calcd for $C_{26}H_{24}NO_3$: 398.1751; found: 398.1765.



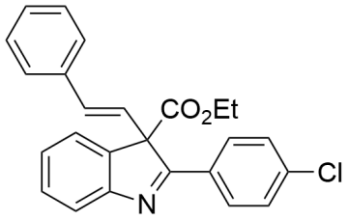
Ethyl (E)-2-(3-bromophenyl)-3-styryl-3H-indole-3-carboxylate(3ad). The reaction mixture was purified by silica gel column chromatography (petroleum ether /EtOAc =100:1-50:1, V/V) to obtain a yellow solid with a yield of 70% (62.3mg), m. p. 136-138℃. ^{1}H NMR (400 MHz, Chloroform-*d*): δ 8.35 (t, *J* = 1.8 Hz, 1H), 7.82 (d, *J* = 7.9 Hz, 1H), 7.78 – 7.73 (m, 1H), 7.57 (d, *J* = 7.0 Hz, 1H), 7.44 (t, *J* = 7.2 Hz, 2H), 7.29 (t, *J* = 7.5 Hz, 2H), 7.26 – 7.15 (m, 5H), 7.04 (d, *J* = 16.4 Hz, 1H), 6.09 (d, *J* = 16.4 Hz, 1H), 4.17 (dq, *J* = 10.8, 7.1 Hz, 1H), 4.00 (dq, *J* = 10.8, 7.1 Hz, 1H), 0.99 (t, *J* = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 174.9, 169.8, 154.9, 140.9, 136.2, 134.2, 134.0, 131.8, 131.4, 130.1, 129.3, 128.5, 128.1, 127.5, 127.0, 126.6, 124.4, 123.0, 122.5, 121.7, 68.5, 62.2, 13.8. HRMS (m/z): [M+H]+ calcd for $C_{25}H_{21}BrNO_2$: 446.0750; found: 446.0765.



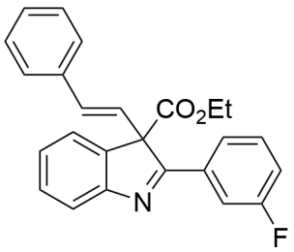
Ethyl (E)-2-(4-bromophenyl)-3-styryl-3H-indole-3-carboxylate(3ae). The reaction mixture was purified by silica gel column chromatography (petroleum ether /EtOAc =100:1-50:1, V/V) to obtain a yellow liquid with a yield of 65% (58.4mg). ^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.91 (d, *J* = 8.6 Hz, 2H), 7.74 (d, *J* = 7.4 Hz, 1H), 7.58 (d, *J* = 8.6 Hz, 2H), 7.43 (t, *J* = 7.1 Hz, 2H), 7.29 – 7.17 (m, 6H), 7.05 (d, *J* = 16.4 Hz, 1H), 6.08 (d, *J* = 16.4 Hz, 1H), 4.14 (dq, *J* = 10.8, 7.1 Hz, 1H), 4.00 (dq, *J* = 10.8, 7.1 Hz, 1H), 0.98 (t, *J* = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 175.3, 169.9, 155.0, 140.9, 136.1, 132.0, 131.7, 131.1, 130.2, 129.3, 128.5, 128.1, 126.9, 126.5, 125.9, 124.5, 122.4, 121.6, 68.4, 62.2, 13.8. HRMS (m/z): [M+H]+ calcd for $C_{25}H_{21}BrNO_2$: 446.0750; found: 446.0766.



Ethyl (E)-2-(3-chlorophenyl)-3-styryl-3H-indole-3-carboxylate(3af). The reaction mixture was purified by silica gel column chromatography (petroleum ether /EtOAc =100:1-50:1, V/V) to obtain a yellow solid with a yield of 33% (26.1mg), m. p. 130-133℃. ^{1}H NMR (400 MHz, Chloroform-*d*): δ 8.16 (s, 1H), 7.77 (dd, *J* = 14.9, 7.7 Hz, 2H), 7.48 – 7.41 (m, 3H), 7.36 (t, *J* = 7.9 Hz, 1H), 7.30 (d, *J* = 6.7 Hz, 1H), 7.26 – 7.18 (m, 5H), 7.04 (d, *J* = 16.4 Hz, 1H), 6.09 (d, *J* = 16.4 Hz, 1H), 4.17 (dq, *J* = 10.8, 7.1 Hz, 1H), 4.01 (dq, *J* = 10.8, 7.1 Hz, 1H), 1.00 (t, *J* = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 175.0, 169.8, 154.9, 140.9, 136.2, 134.9, 133.9, 131.7, 131.1, 129.9, 129.3, 128.5, 128.3, 127.0, 126.6, 124.4, 122.5, 121.7, 68.5, 62.2, 13.8. HRMS (m/z): [M+H]+ calcd for $C_{25}H_{21}ClNO_2$: 402.1255; found: 402.1269.

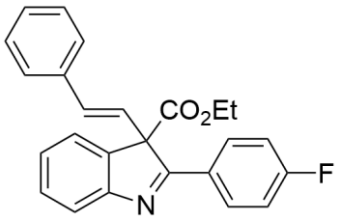


Ethyl (E)-2-(4-chlorophenyl)-3-styryl-3H-indole-3-carboxylate(3ag). The reaction mixture was purified by silica gel column chromatography (petroleum ether /EtOAc =100:1-50:1, V/V) to obtain a yellow solid with a yield of 64% (52.1mg), m. p. 105-110℃. ^{1}H NMR (400 MHz, Chloroform-*d*): δ 8.01 – 7.96 (m, 2H), 7.77 – 7.70 (m, 1H), 7.42 (dd, *J* = 8.0, 3.3 Hz, 4H), 7.28 (d, *J* = 6.6 Hz, 1H), 7.25 – 7.17 (m, 5H), 7.06 (d, *J* = 16.4 Hz, 1H), 6.09 (d, *J* = 16.4 Hz, 1H), 4.18 – 4.10 (m, 1H), 4.00 (dq, *J* = 10.8, 7.1 Hz, 1H), 0.98 (t, *J* = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 175.2, 169.9, 155.0, 140.9, 137.4, 136.2, 131.7, 130.7, 130.1, 129.3, 129.0, 128.5, 128.1, 126.8, 126.5, 124.6, 122.4, 121.5, 68.4, 62.2, 13.8; HRMS (m/z): [M+H]+ calcd for $C_{25}H_{21}ClNO_2$: 402.1255; found: 402.1270.

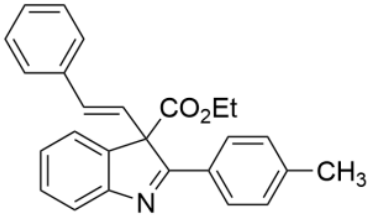


Ethyl (E)-2-(3-fluorophenyl)-3-styryl-3H-indole-3-carboxylate(3ah). The reaction mixture was purified by silica gel column chromatography (petroleum ether /EtOAc =100:1-50:1, V/V) to obtain a yellow solid with a yield of 79% (62.9mg), m. p. 90-95℃. ^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.84 (d, *J* = 10.1 Hz, 1H), 7.74 (t, *J* = 7.1 Hz, 2H), 7.46 – 7.37 (m, 3H), 7.30 – 7.27 (m, 1H), 7.25 – 7.12 (m, 6H), 7.06 (d, *J* = 16.4 Hz, 1H), 6.10 (d, *J* = 16.4 Hz, 1H), 4.16 (dq, *J* = 10.8, 7.1 Hz, 1H), 4.01 (dq, *J* = 10.8, 7.1 Hz, 1H), 0.98 (t, *J* = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 175.2, 169.8, 162.9 (d, *J* = 247.5 Hz), 154.9, 140.9, 136.2, 134.4 (d, *J* = 8.1 Hz), 131.7, 130.2 (d, *J* = 8.1 Hz), 129.3, 128.5, 128.1, 127.0, 126.6, 124.6 (d, *J* = 2.0 Hz),

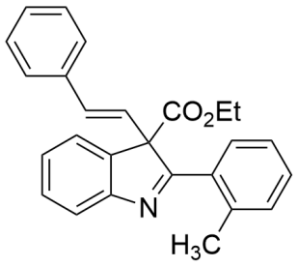
124.5, 122.5, 121.7, 118.1 (d, *J* = 21.2 Hz), 115.3 (d, *J* = 23.2 Hz), 68.5, 62.2, 13.8. ^{19}F NMR (367 MHz, $CDCl_3$): δ -111.97. HRMS (m/z): [M+H]+ calcd for $C_{25}H_{21}FNO_2$: 386.1551; found: 386.1556.



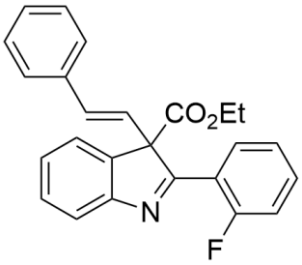
Ethyl (E)-2-(4-fluorophenyl)-3-styryl-3H-indole-3-carboxylate(3ai). The reaction mixture was purified by silica gel column chromatography (petroleum ether /EtOAc =100:1-50:1, V/V) to obtain a yellow liquid with a yield of 35% (26.7mg). ^{1}H NMR (400 MHz, Chloroform-*d*): δ 8.08 – 8.01 (m, 2H), 7.73 (d, *J* = 7.6 Hz, 1H), 7.43 (t, *J* = 7.6 Hz, 2H), 7.26 (q, *J* = 7.3 Hz, 5H), 7.21 – 7.18 (m, 1H), 7.16 – 7.10 (m, 2H), 7.07 (d, *J* = 16.4 Hz, 1H), 6.09 (d, *J* = 16.4 Hz, 1H), 4.15 (dq, *J* = 10.8, 7.1 Hz, 1H), 4.00 (dq, *J* = 10.8, 7.1 Hz, 1H), 0.98 (t, *J* = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 175.1, 170.0, 164.5 (d, *J* = 253.5 Hz), 155.1, 140.9, 136.2, 131.7, 131.0 (d, *J* = 9.1 Hz), 129.2, 128.5, 128.1, 126.6 (d, *J* = 9.1 Hz), 124.7, 122.4, 121.4, 115.9 (d, *J* = 21.2 Hz), 68.4, 62.2, 13.8. ^{19}F NMR (367 MHz, $CDCl_3$): δ -108.04. HRMS (m/z): [M+H]+ calcd for $C_{25}H_{21}FNO_2$: 386.1551; found: 386.1559.



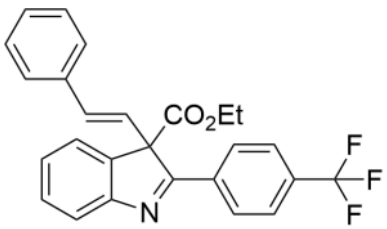
Ethyl (E)-3-styryl-2-(p-tolyl)-3H-indole-3-carboxylate(3aj). The reaction mixture was purified by silica gel column chromatography (petroleum ether /EtOAc =100:1-50:1, V/V) to obtain a yellow solid with a yield of 79% (59.8mg), m. p. 100-104℃. ^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.93 (d, *J* = 8.2 Hz, 2H), 7.73 (d, *J* = 8.4 Hz, 1H), 7.44 – 7.39 (m, 2H), 7.29 – 7.21 (m, 6H), 7.21 – 7.15 (m, 2H), 7.09 (d, *J* = 16.3 Hz, 1H), 6.08 (d, *J* = 16.4 Hz, 1H), 4.13 (dq, *J* = 10.8, 7.1 Hz, 1H), 3.99 (dq, *J* = 10.8, 7.1 Hz, 1H), 2.38 (s, 3H), 0.96 (t, *J* = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 176.5, 170.3, 155.5, 141.7, 140.8, 136.4, 131.5, 129.5, 129.4, 129.1, 128.9, 128.5, 127.9, 126.5, 126.3, 125.1, 122.4, 121.2, 68.4, 62.0, 21.6, 13.80. HRMS (m/z): [M+H]+ calcd for $C_{26}H_{24}NO_2$: 382.1802; found: 382.1812.



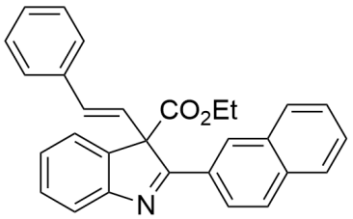
Ethyl (E)-3-styryl-2-(o-tolyl)-3H-indole-3-carboxylate(3ak). The reaction mixture was purified by silica gel column chromatography (petroleum ether /EtOAc =100:1-50:1, V/V) to obtain a yellow solid with a yield of 27% (20.2mg), m. p. 125-128℃. ^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.75 (d, *J* = 7.7 Hz, 1H), 7.50 – 7.41 (m, 3H), 7.33 – 7.28 (m, 3H), 7.25 – 7.19 (m, 6H), 6.89 (d, *J* = 16.3 Hz, 1H), 6.15 (d, *J* = 16.3 Hz, 1H), 4.14 (dq, *J* = 10.8, 7.1 Hz, 1H), 4.05 (dq, *J* = 10.8, 7.1 Hz, 1H), 2.65 (s, 3H), 1.02 (t, *J* = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 177.1, 170.0, 156.2, 139.7, 136.4, 132.1, 132.0, 131.3, 129.7, 129.6, 129.1, 128.5, 127.9, 126.6, 126.5, 125.5, 124.5, 122.9, 121.6, 71.1, 62.0, 22.6, 13.8. HRMS (m/z): [M+H]+ calcd for $C_{26}H_{24}NO_2$: 382.1802; found: 382.1813.



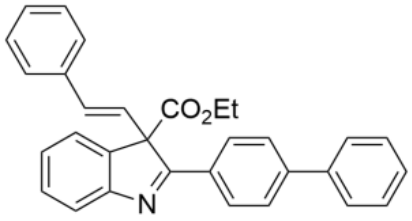
Ethyl (E)-2-(2-fluorophenyl)-3-styryl-3H-indole-3-carboxylate(3ao). The reaction mixture was purified by silica gel column chromatography (petroleum ether /EtOAc =100:1-50:1, V/V) to obtain a yellow liquid with a yield of 38% (28.7mg). ^{1}H NMR (400 MHz, Chloroform-*d*): δ 8.47 (td, *J* = 7.8, 1.8 Hz, 1H), 7.75 (d, *J* = 7.7 Hz, 1H), 7.49 – 7.42 (m, 3H), 7.34 – 7.26 (m, 2H), 7.23 (dd, *J* = 8.6, 7.2 Hz, 4H), 7.19 – 7.11 (m, 2H), 7.05 (dd, *J* = 16.4, 2.0 Hz, 1H), 6.04 (d, *J* = 16.4 Hz, 1H), 4.23 – 4.15 (m, 1H), 4.01 (dq, *J* = 10.7, 7.1 Hz, 1H), 1.04 (t, *J* = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 173.4, 169.5, 160.8 (d, *J* = 254.5 Hz), 154.2, 140.0, 136.5, 133.1 (d, *J* = 10.1 Hz), 130.8 (d, *J* = 3.0 Hz), 130.6 (d, *J* = 2.0 Hz), 129.2, 128.4, 127.8, 126.9, 126.5, 124.7 (d, *J* = 3.0 Hz), 124.1 (d, *J* = 4.0 Hz), 122.8, 121.5, 120.4 (d, *J* = 10.1 Hz), 116.6 (d, *J* = 24.2 Hz), 70.1, 61.9, 13.8. ^{19}F NMR (367 MHz, $CDCl_3$): δ -110.24. HRMS (m/z): [M+H]+ calcd for $C_{25}H_{21}FNO_2$: 386.1551; found: 386.1562.



Ethyl (E)-3-styryl-2-(4-(trifluoromethyl)phenyl)-3H-indole-3-carboxylate(3ap). The reaction mixture was purified by silica gel column chromatography (petroleum ether /EtOAc =100:1-50:1, V/V) to obtain a yellow liquid with a yield of 65% (56.1mg). ^{1}H NMR (400 MHz, Chloroform-*d*) δ: 8.17 (d, *J* = 8.3 Hz, 2H), 7.78 (d, *J* = 8.1 Hz, 1H), 7.70 (d, *J* = 8.4 Hz, 2H), 7.46 (dt, *J* = 6.9, 3.5 Hz, 2H), 7.31 (t, *J* = 7.5 Hz, 1H), 7.28 – 7.22 (m, 4H), 7.21 – 7.18 (m, 1H), 7.07 (d, *J* = 17.2 Hz, 1H), 6.10 (d, *J* = 16.4 Hz, 1H), 4.15 (dq, *J* = 10.8, 7.1 Hz, 1H), 4.02 (dq, *J* = 10.8, 7.1 Hz, 1H), 0.98 (t, *J* = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 174.9, 169.7, 154.8, 141.0, 136.0, 135.4, 132.6, 132.3, 131.8, 129.4, 129.0, 128.6, 128.2, 127.3, 126.5, 125.6(q, J = 4 Hz), 124.2, 122.5, 121.9, 68.5, 62.3, 13.8. ^{19}F NMR (376 MHz, $CDCl_3$): δ -62.91. HRMS (m/z): [M+H]+ calcd for $C_{26}H_{21}F_3NO_2$: 436.1519; found: 436.1531.

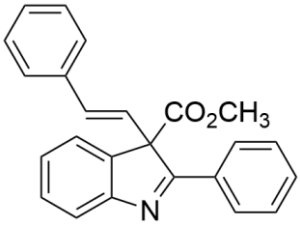


Ethyl (E)-2-(naphthalen-2-yl)-3-styryl-3H-indole-3-carboxylate(3aq). The reaction mixture was purified by silica gel column chromatography (petroleum ether /EtOAc =100:1-50:1, V/V) to obtain a yellow solid with a yield of 67% (56.6mg), m. p. 75-80℃. ^{1}H NMR (400 MHz, Chloroform-*d*): δ 8.41 (s, 1H), 8.27 (dd, *J* = 8.7, 1.7 Hz, 1H), 7.94 – 7.88 (m, 2H), 7.81 (dd, *J* = 16.1, 7.6 Hz, 2H), 7.48 (dt, *J* = 20.4, 7.2 Hz, 4H), 7.31 – 7.26 (m, 1H), 7.25 – 7.20 (m, 3H), 7.19 – 7.16 (m, 2H), 7.14 (dt, *J* = 5.9, 2.3 Hz, 1H), 6.14 (d, *J* = 16.4 Hz, 1H), 4.14 (dq, *J* = 10.8, 7.1 Hz, 1H), 4.04 – 3.96 (m, 1H), 0.93 (t, *J* = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 176.4, 170.3, 155.3, 141.0, 136.3, 134.7, 133.0, 131.6, 129.7, 129.6, 129.2, 128.5, 128.0, 127.8, 126.7, 126.6, 126.6, 125.3, 125.1, 122.4, 121.5, 68.5, 62.2, 13.8. HRMS (m/z): [M+H]+ calcd for $C_{29}H_{24}NO_2$: 418.1802; found: 418.1810.

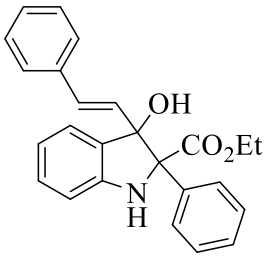


Ethyl (E)-2-([1,1'-biphenyl]-4-yl)-3-styryl-3H-indole-3-carboxylate(3ar). The reaction mixture was purified by silica gel column chromatography (petroleum ether /EtOAc =100:1-50:1, V/V) to obtain a yellow solid with a yield of 65% (56.3mg), m. p. 80-85℃. ^{1}H NMR (400 MHz, Chloroform-*d*): δ 8.12 (d, *J* = 8.6 Hz, 2H), 7.76 (d, *J* = 8.3 Hz, 1H), 7.68 (d, *J* = 8.6 Hz, 2H), 7.65 – 7.61 (m, 2H), 7.47 – 7.41 (m, 4H), 7.36 (t, *J* = 7.3 Hz, 1H), 7.31 – 7.25 (m, 3H), 7.25 – 7.21 (m, 2H), 7.19 (d, *J* = 8.0 Hz, 1H), 7.13 (d, *J* = 16.3 Hz, 1H), 6.14 (d, *J* = 16.4 Hz, 1H), 4.16 (dq, *J* = 10.8, 7.1 Hz, 1H), 4.07 – 3.99 (m, 1H), 0.99 (t, *J* = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$):

δ 176.1, 170.2, 155.4, 143.8, 140.9, 140.0, 136.4, 131.6, 131.0, 129.4, 129.2, 128.9, 128.5, 128.0, 127.3, 127.1, 126.6, 125.0, 122.4, 121.4, 68.5, 62.2, 13.8. HRMS (m/z): [M+H]+ calcd for $C_{31}H_{26}NO_2$: 444.1958; found: 444.1972.



Methyl (E)-2-phenyl-3-styryl-3H-indole-3-carboxylate(3as). The reaction mixture was purified by silica gel column chromatography (petroleum ether /EtOAc =100:1-50:1, V/V) to obtain a yellow solid with a yield of 42% (30.9mg), m. p. 135-140℃. ^{1}H NMR (400 MHz, Chloroform-*d*): δ 8.03 (dd, *J* = 7.3, 2.5 Hz, 2H), 7.76 (d, *J* = 7.7 Hz, 1H), 7.47 – 7.41 (m, 5H), 7.29 (d, *J* = 6.6 Hz, 1H), 7.25 – 7.18 (m, 5H), 7.09 (d, *J* = 16.4 Hz, 1H), 6.09 (d, *J* = 16.4 Hz, 1H), 3.58 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 176.3, 170.8, 155.3, 140.7, 136.3, 132.0, 131.6, 131.3, 129.7, 129.3, 128.8, 128.8, 128.5, 128.0, 126.7, 126.6, 124.7, 122.5, 121.5, 68.2, 53.3. HRMS (m/z): [M+H]+ calcd for $C_{24}H_{20}NO_2$: 354.1313; found: 354.1316.



Ethyl (E)-3-hydroxy-2-phenyl-3-styrylindoline-2-carboxylate(4). The reaction mixture was purified by silica gel column chromatography (petroleum ether /EtOAc =100:1-50:1, V/V) to obtain a yellow solid with a yield of 61% (237mg), m. p. 125-130℃. ^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.60 (d, *J* = 6.9 Hz, 2H), 7.28 (dd, *J* = 10.8, 7.3 Hz, 3H), 7.22 – 7.06 (m, 6H), 7.02 (d, *J* = 6.9 Hz, 2H), 6.89 – 6.79 (m, 2H), 6.45 (d, *J* = 15.9 Hz, 1H), 5.75 (d, *J* = 15.9 Hz, 1H), 5.29 (s, 1H), 4.16 – 4.09 (m, 2H), 1.13 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 174.3, 147.7, 137.0, 136.7, 132.0, 130.1, 129.6, 128.9, 128.4, 128.3, 128.3, 127.3, 126.6, 126.3, 124.3, 120.6, 110.3, 85.9, 79.5, 62.2, 13.9. HRMS (m/z): [M+H]+ calcd for $C_{25}H_{23}NO_3$: 386.1577; found: 386.1581.

2.^{1}H and ^{13}C NMR spectra for all products

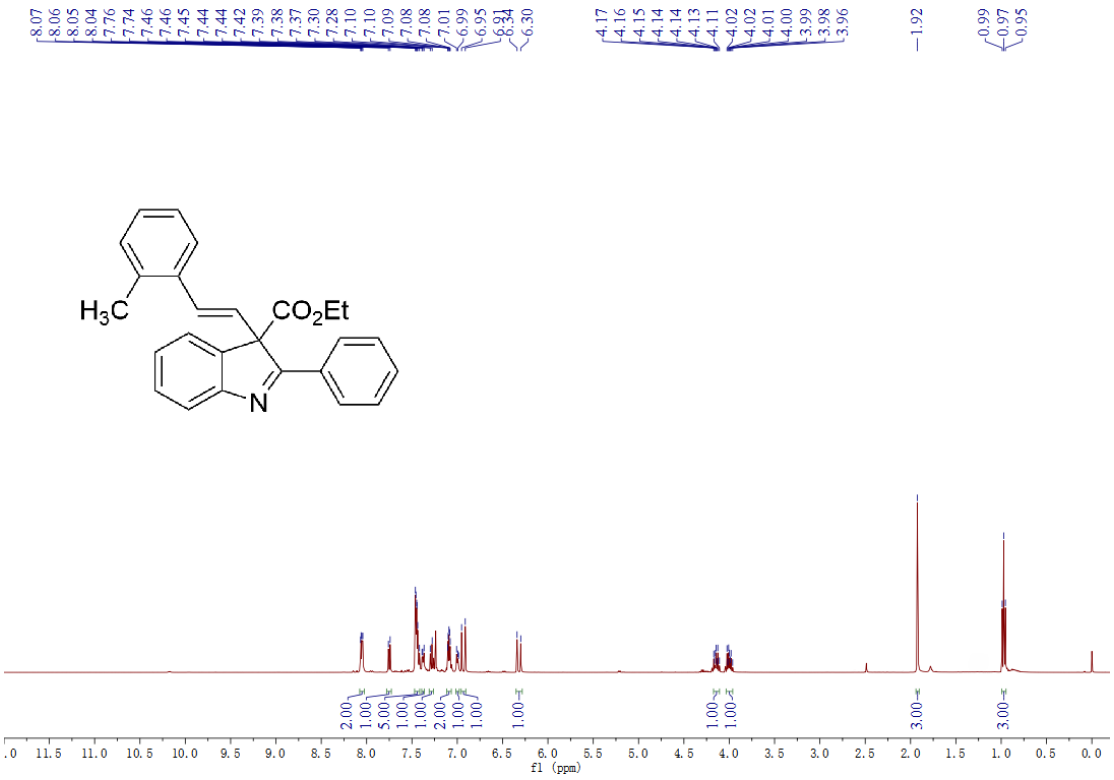


Figure S1 ^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3ba**

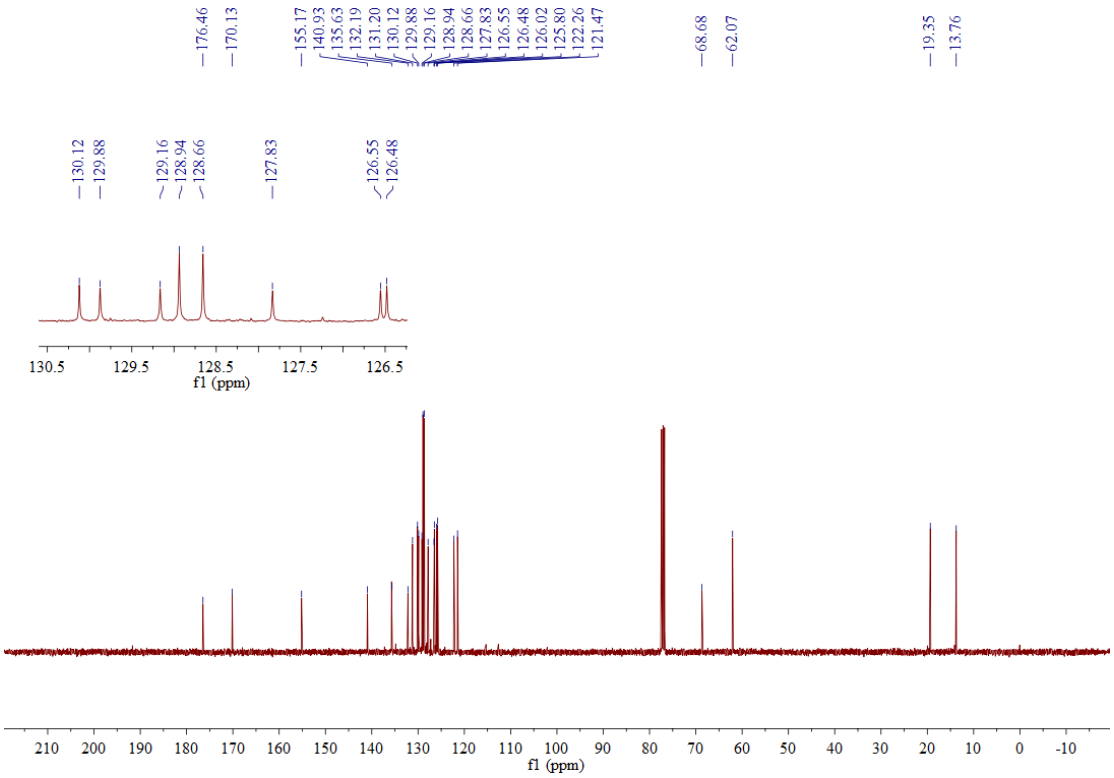


Figure S2 ^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3ba**

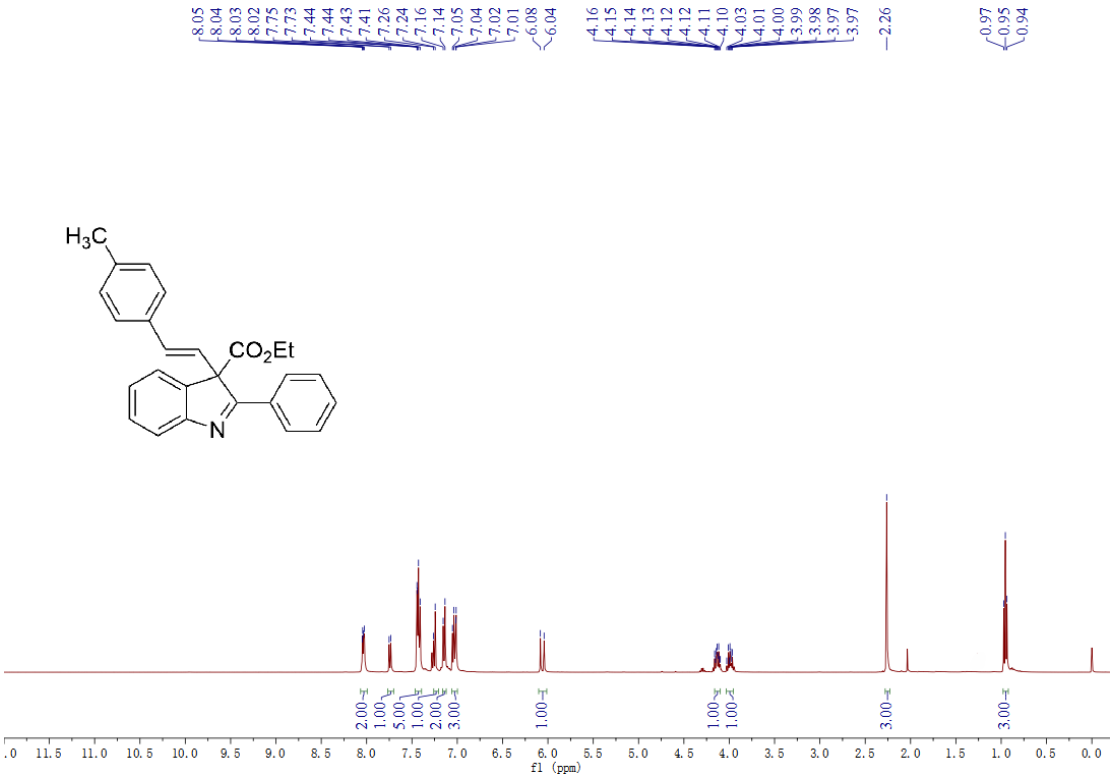


Figure S3 ^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3ca**

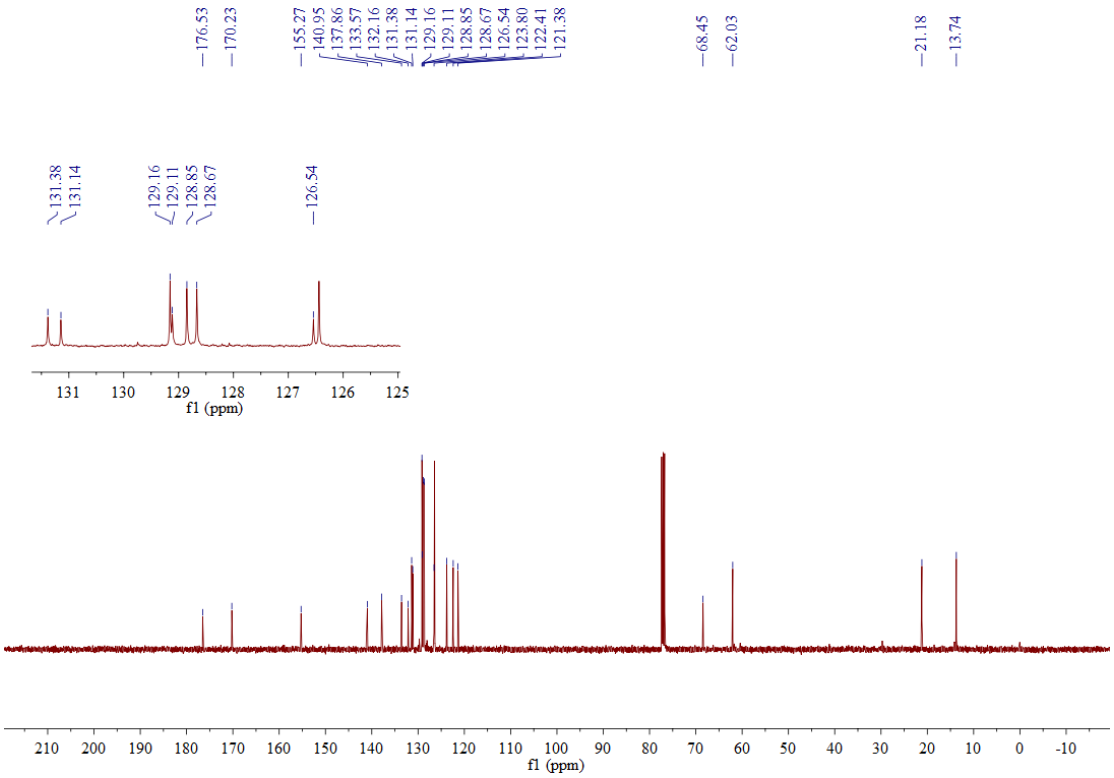


Figure S4 ^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3ca**

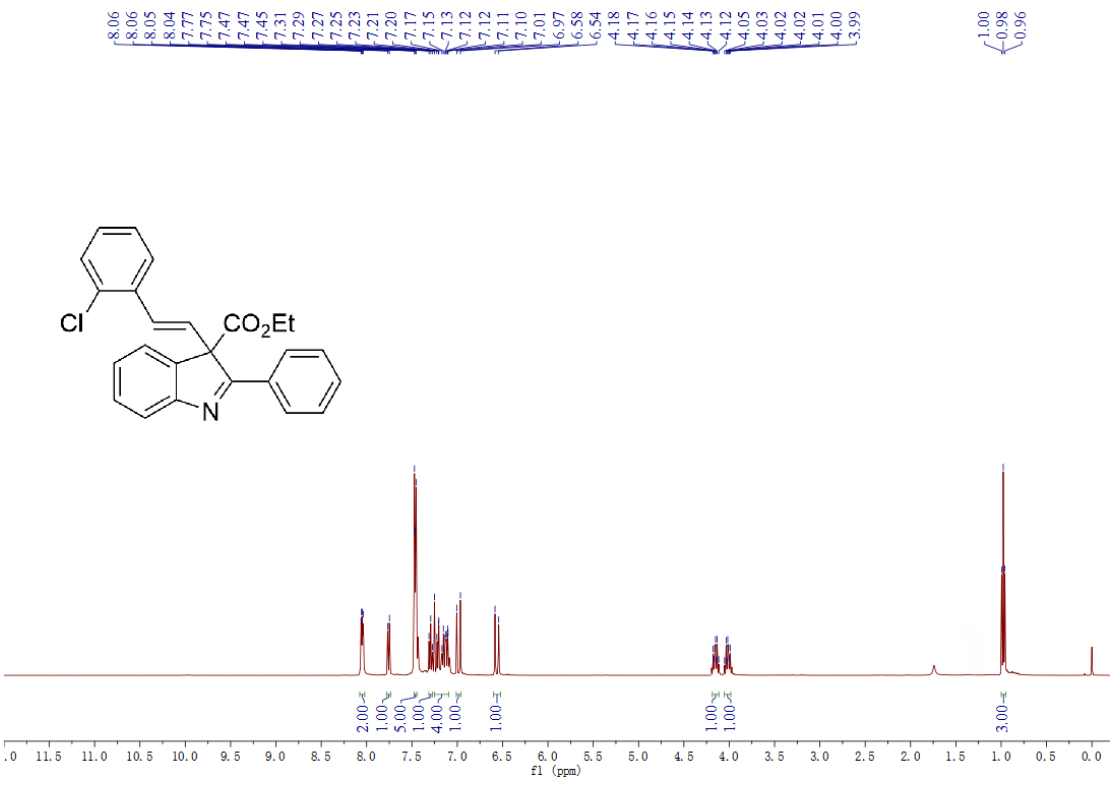


Figure S5 ^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3da**

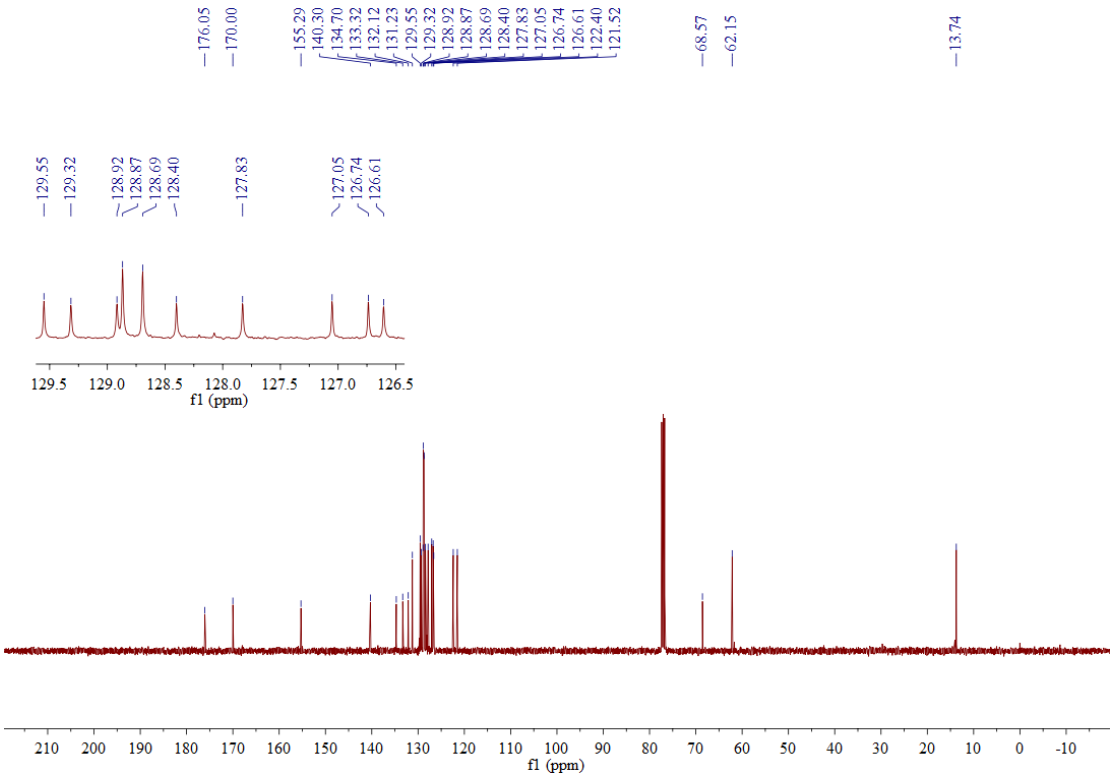


Figure S6 ^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3da**

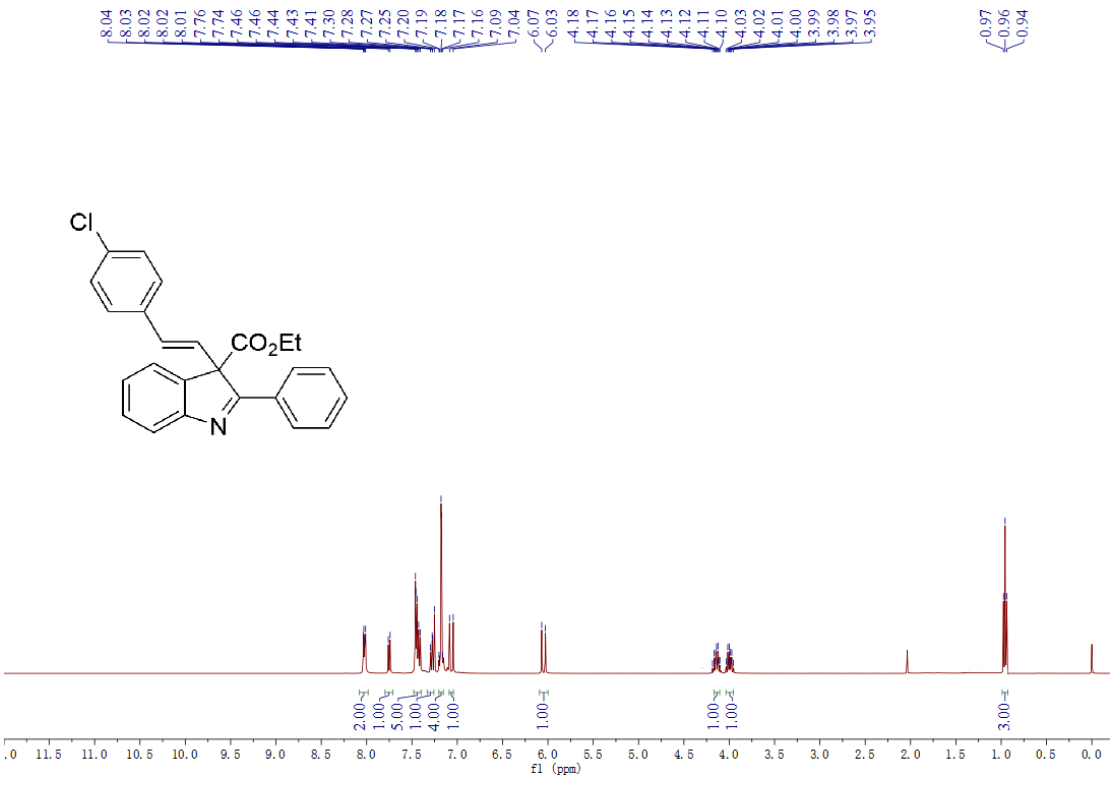


Figure S7 ^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3ea**

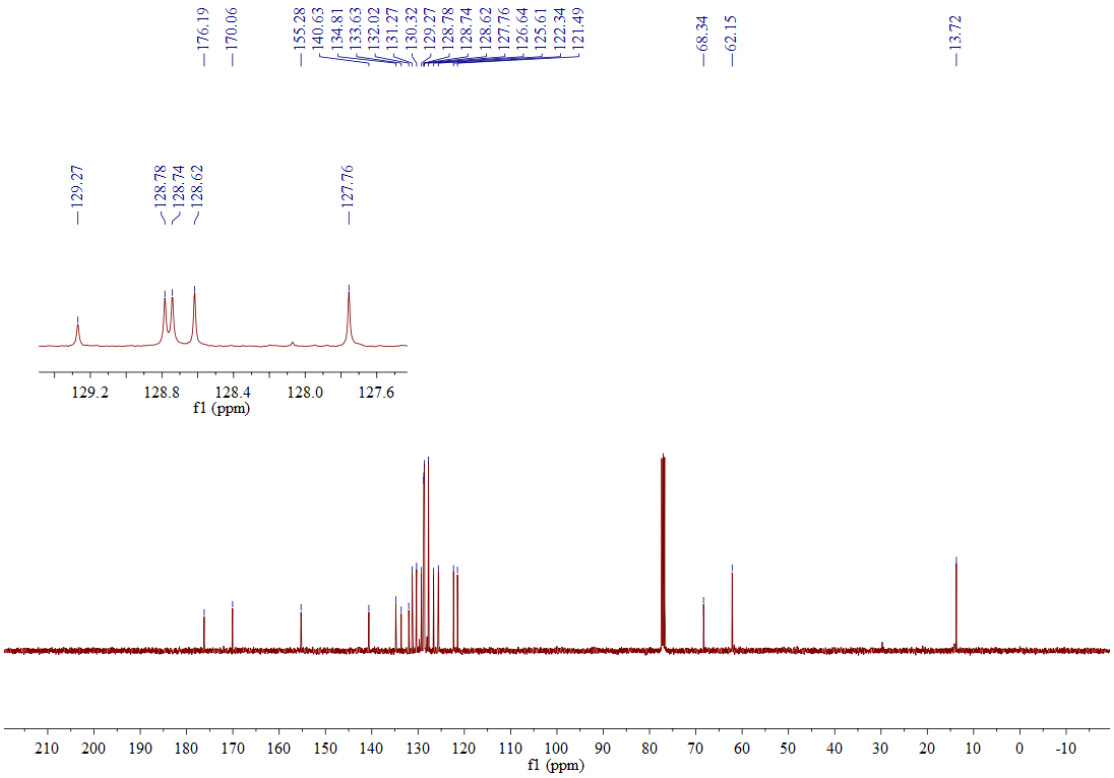


Figure S8 ^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3ea**

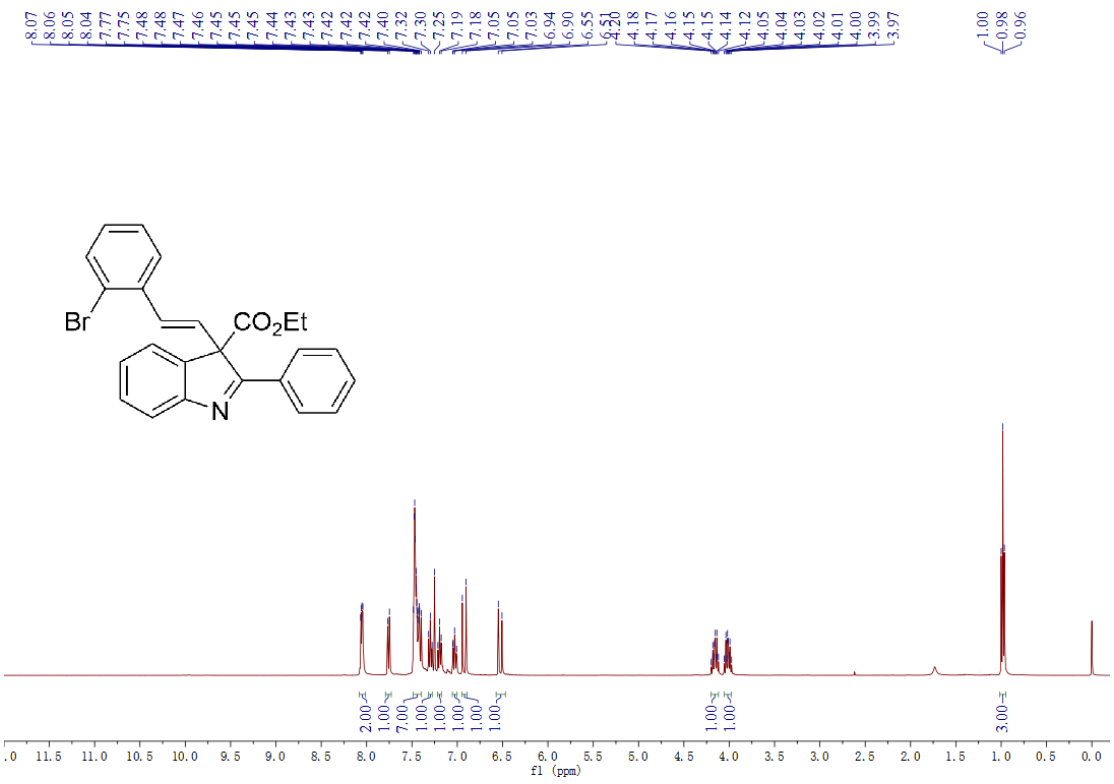


Figure S9 ^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3fa**

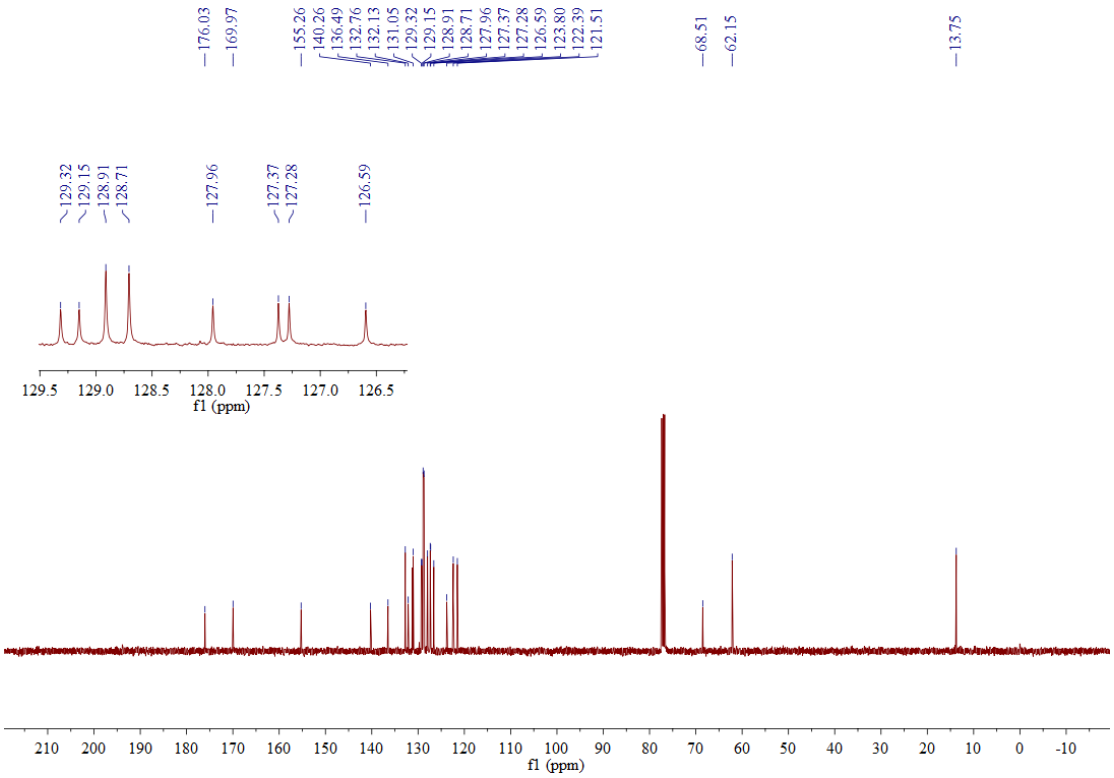


Figure S10 ^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3fa**

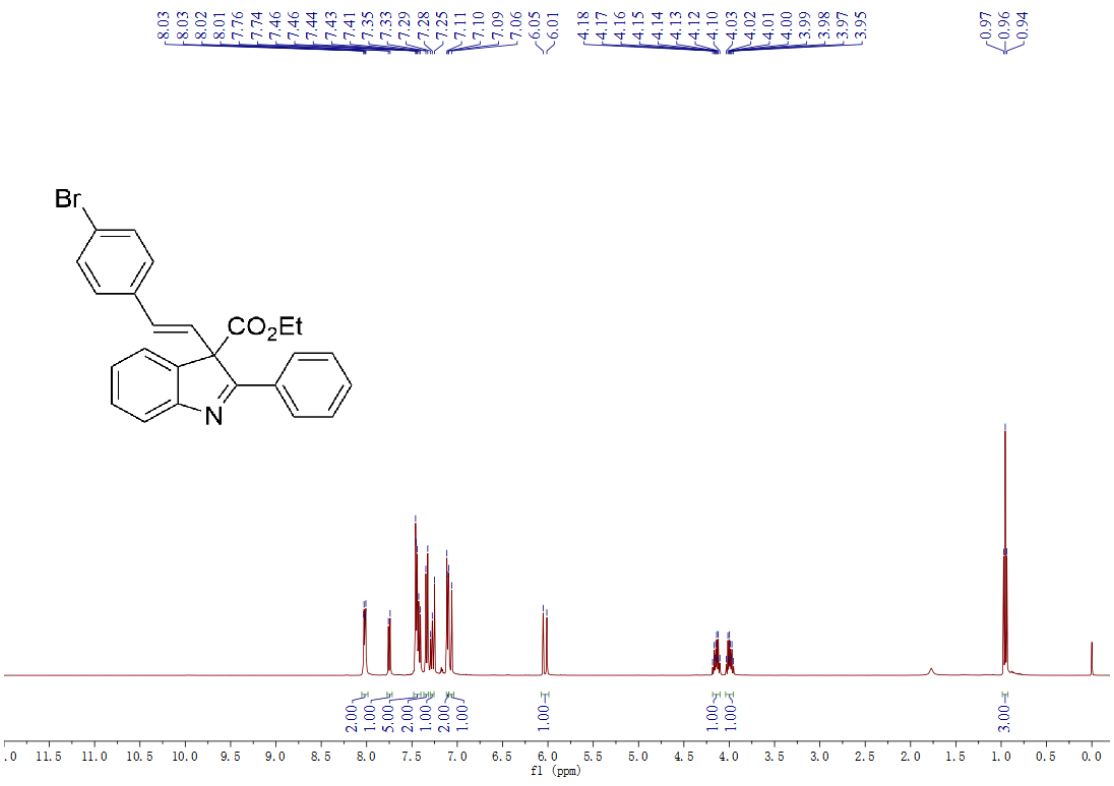


Figure S11 ^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3ga**

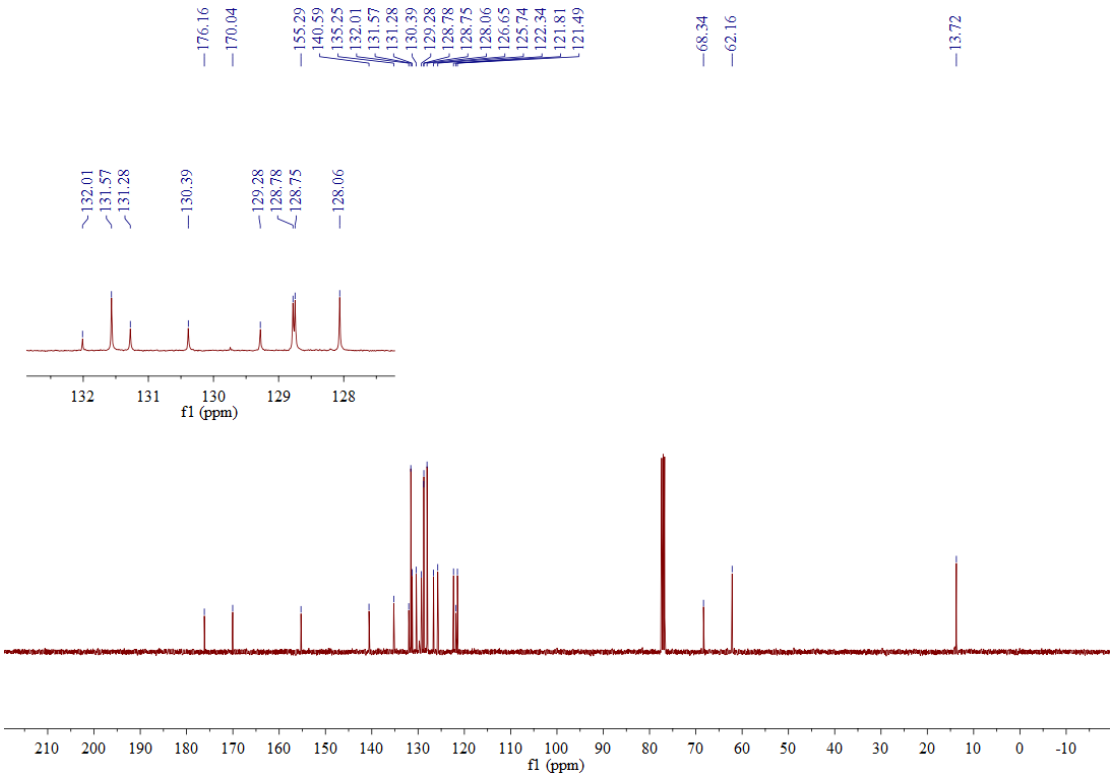


Figure S12 ^{13}H NMR (101 MHz, $CDCl_3$) spectra of **3ga**

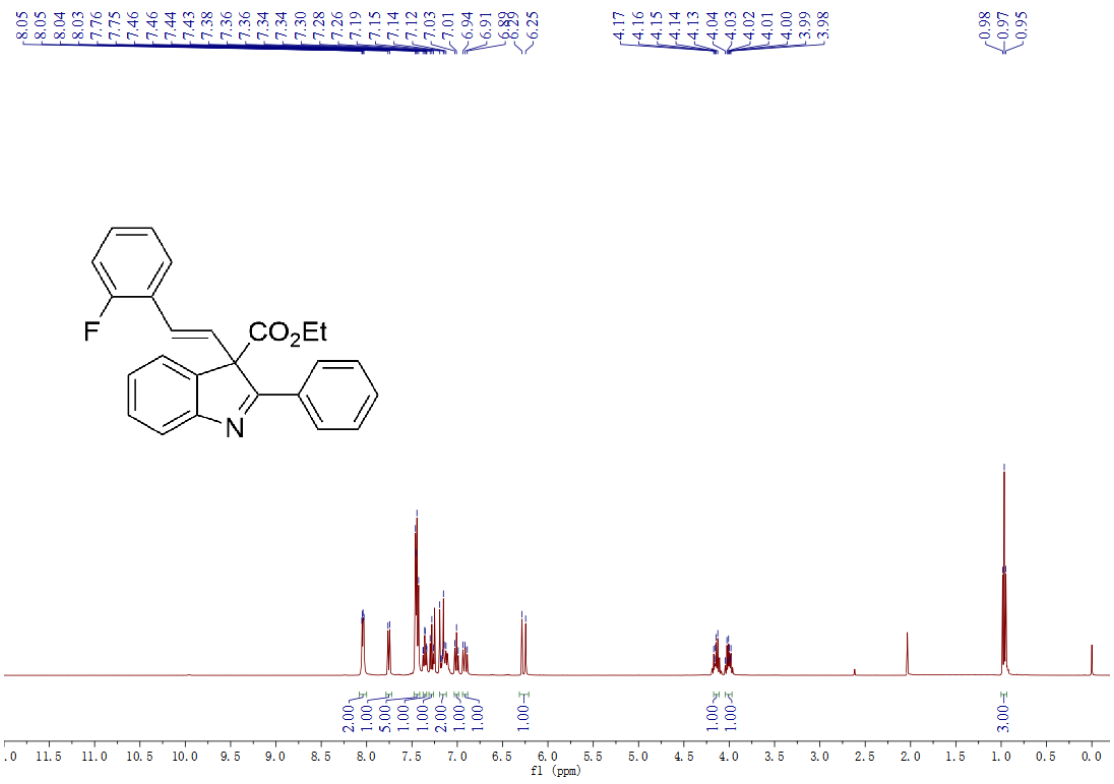


Figure S13 ^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3ha**

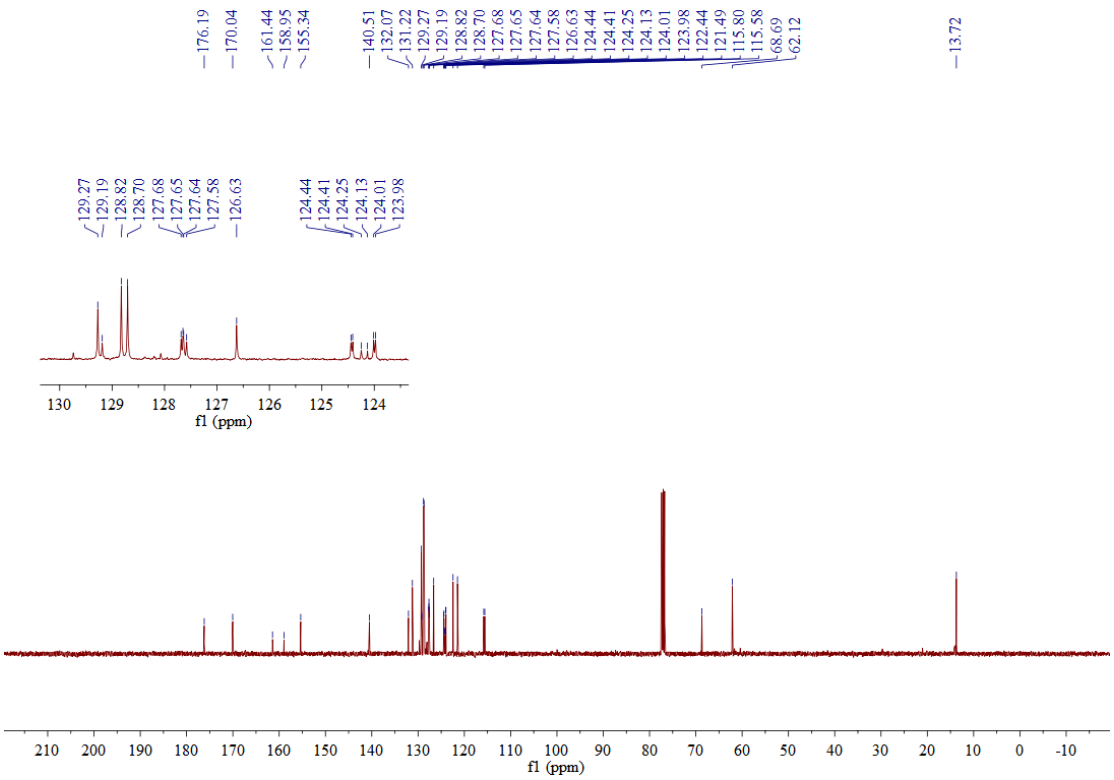


Figure S14 ^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3ha**

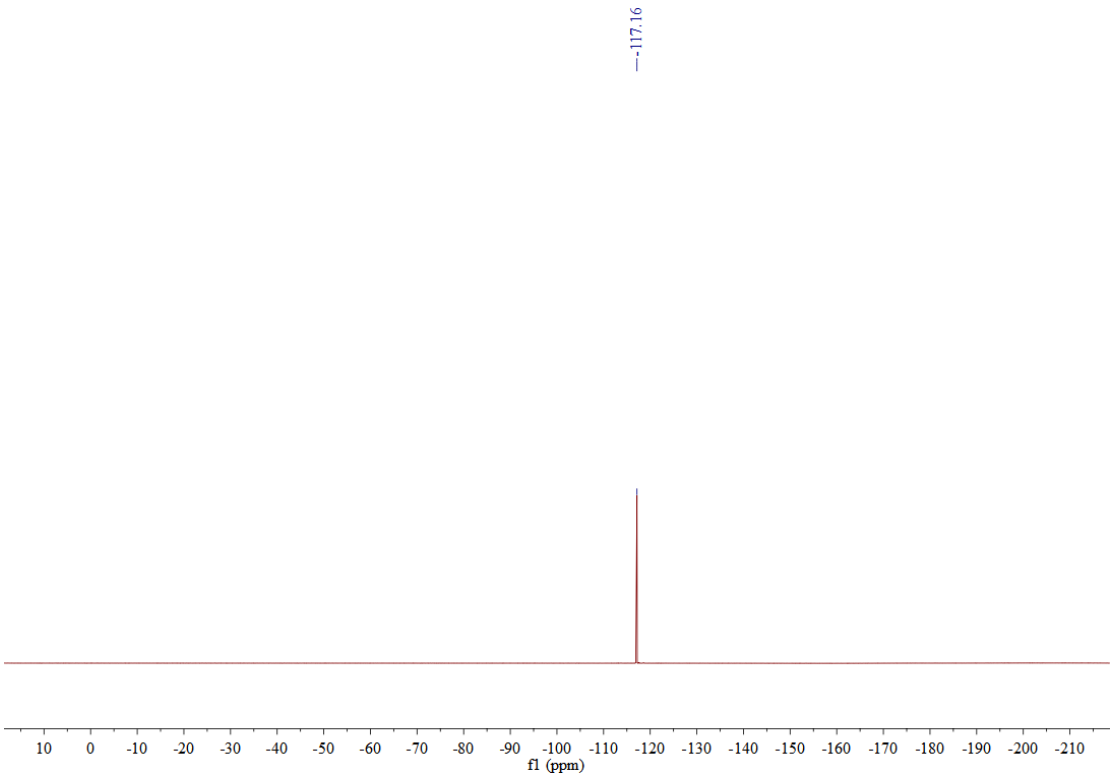


Figure S15 ^{19}F NMR (376 MHz, $CDCl_3$) spectra of **3ha**

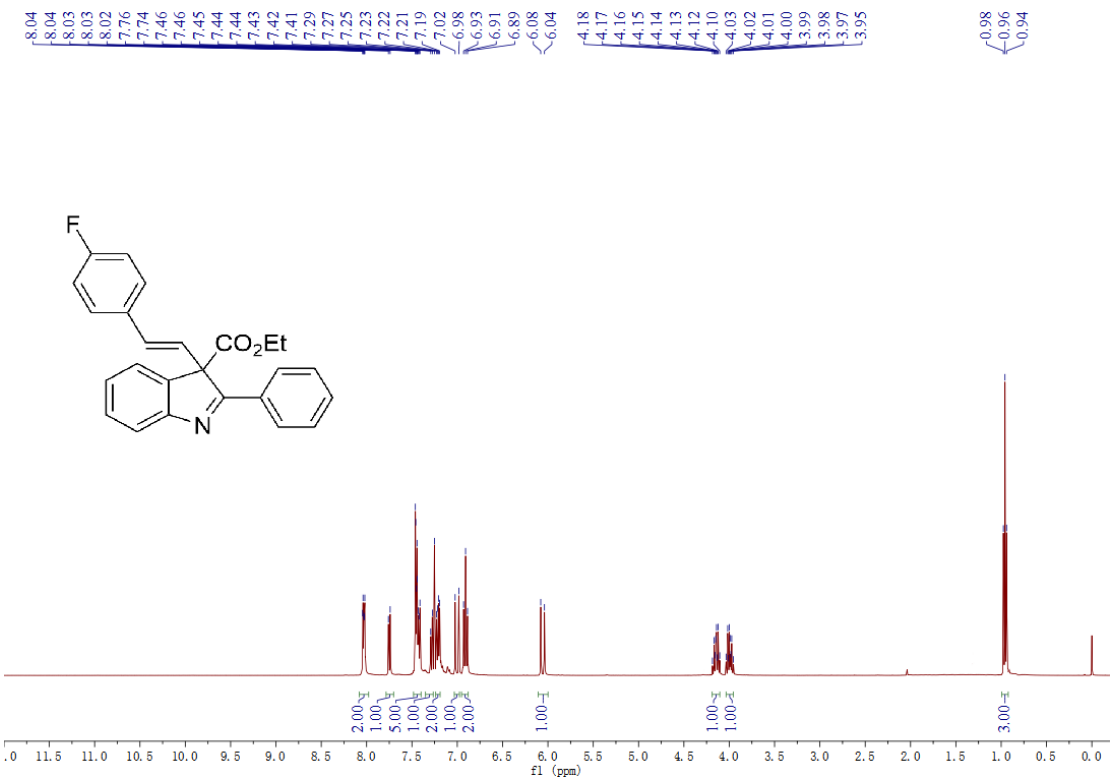


Figure S16 ^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3ia**

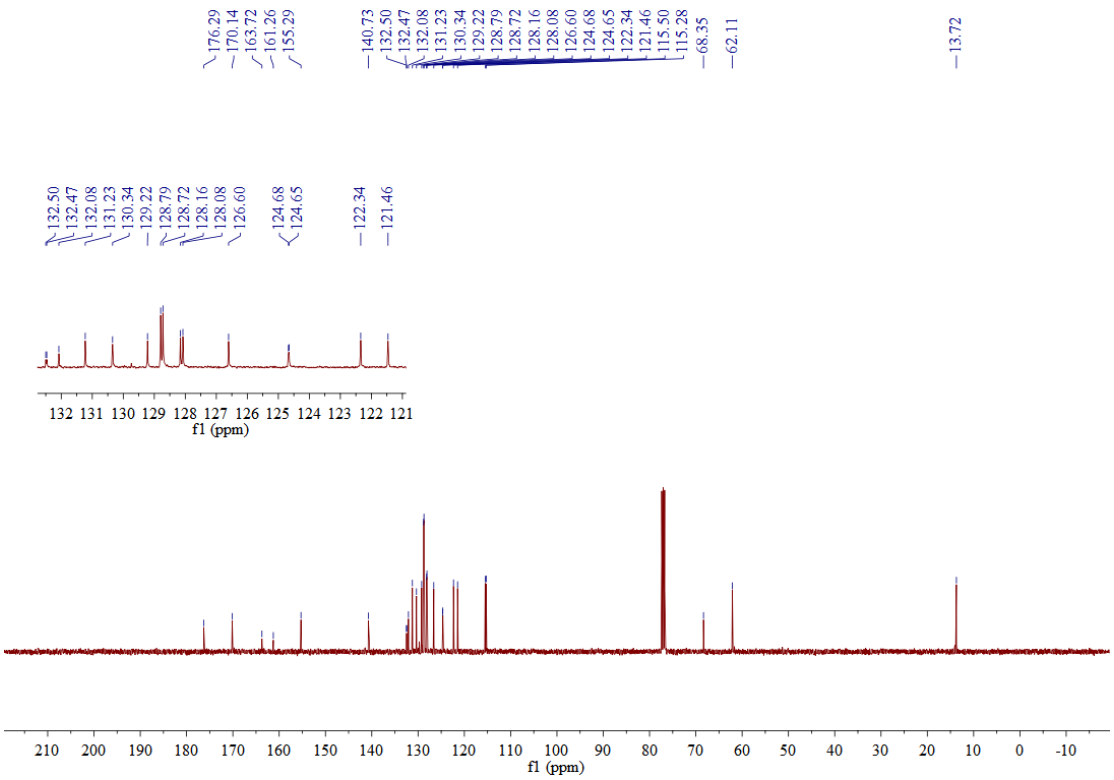


Figure S17 ^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3ia**

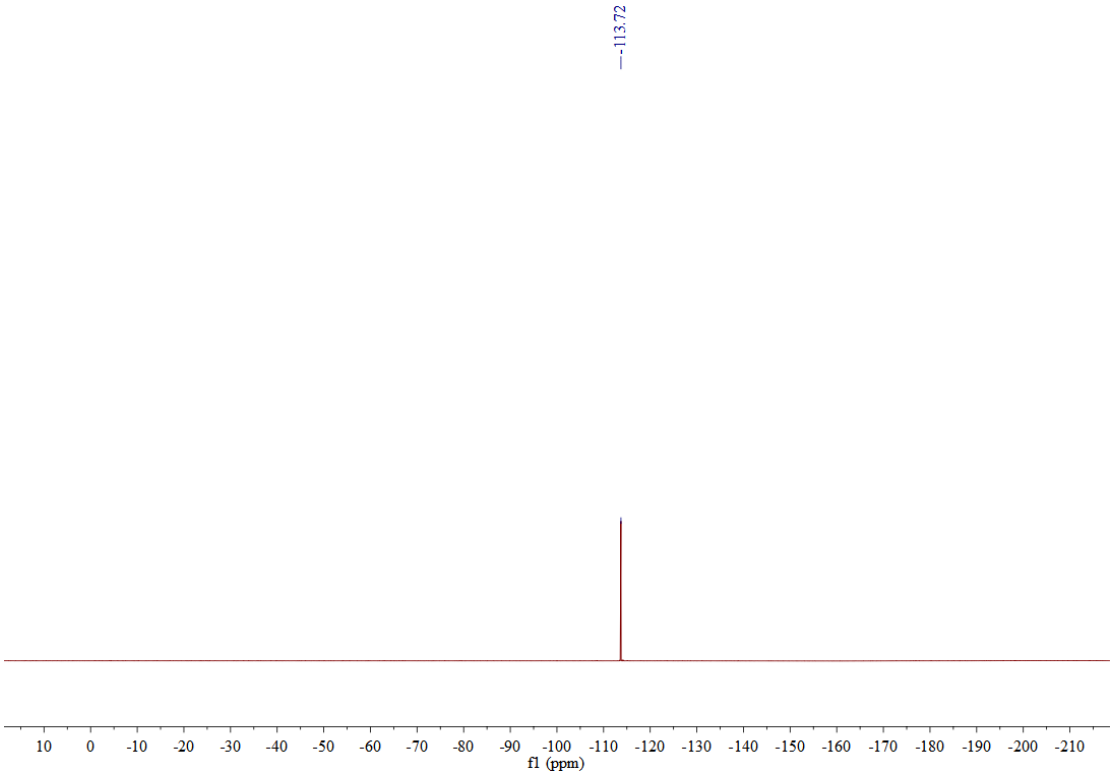


Figure S18 ^{19}F NMR (376 MHz, $CDCl_3$) spectra of **3ia**

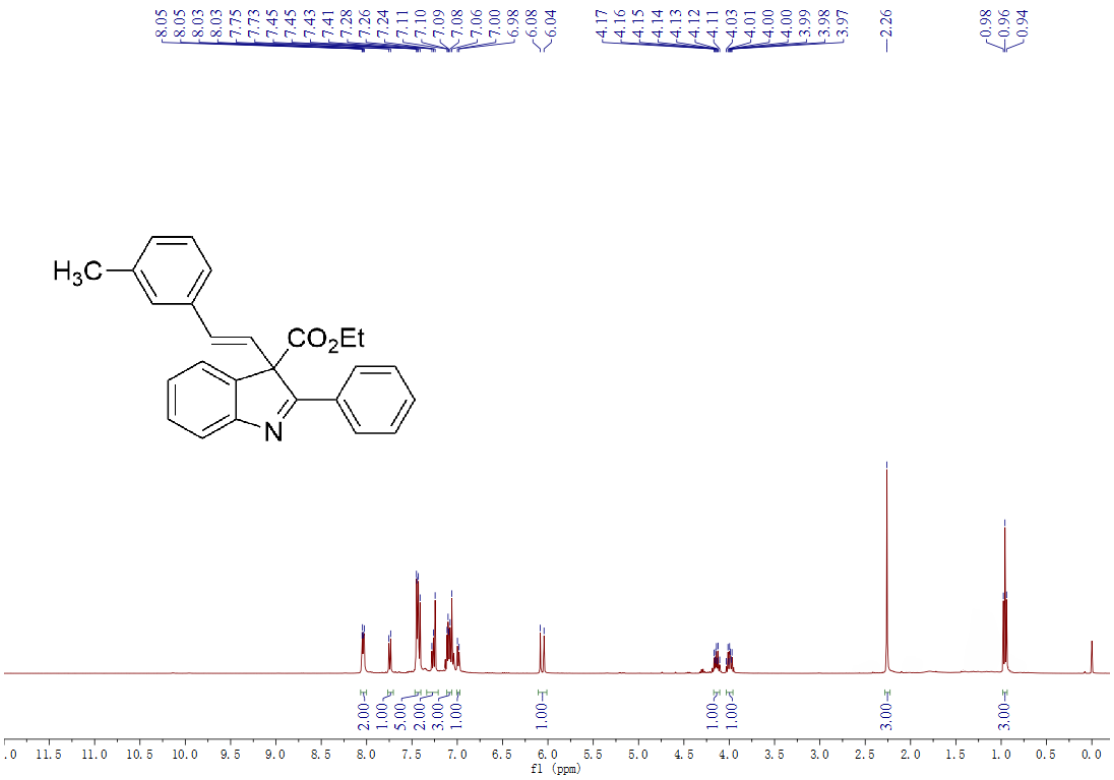


Figure S19 ^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3ja**

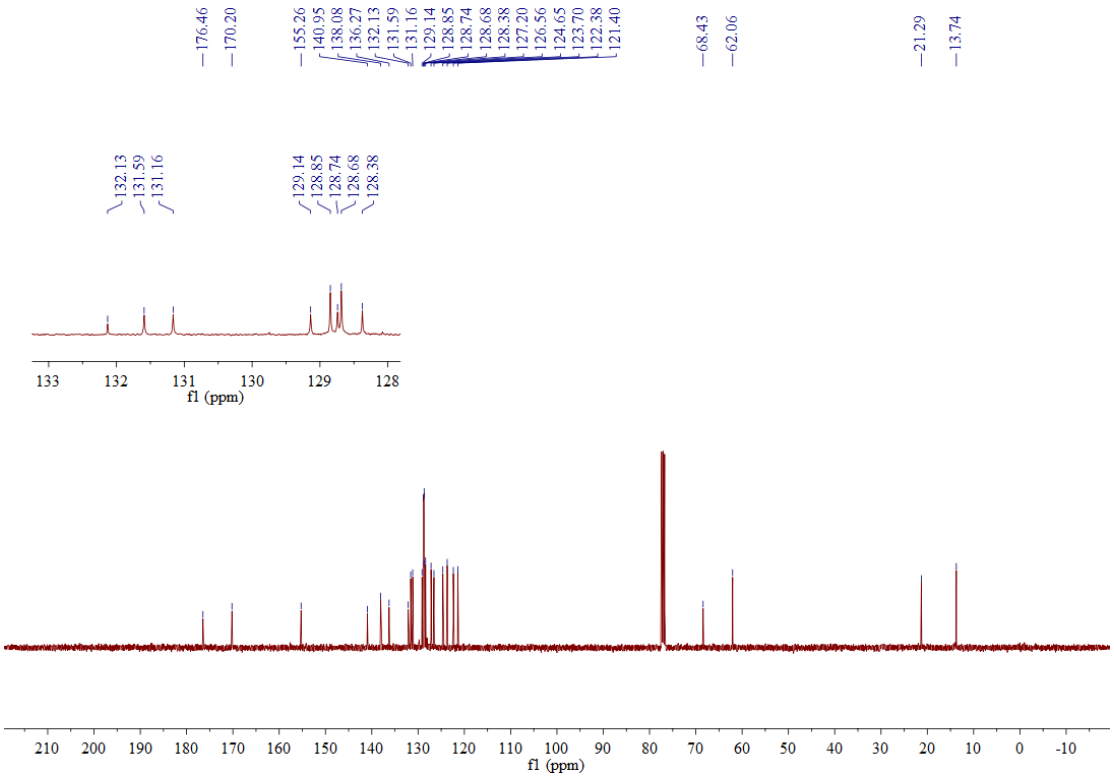


Figure S20 ^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3ja**

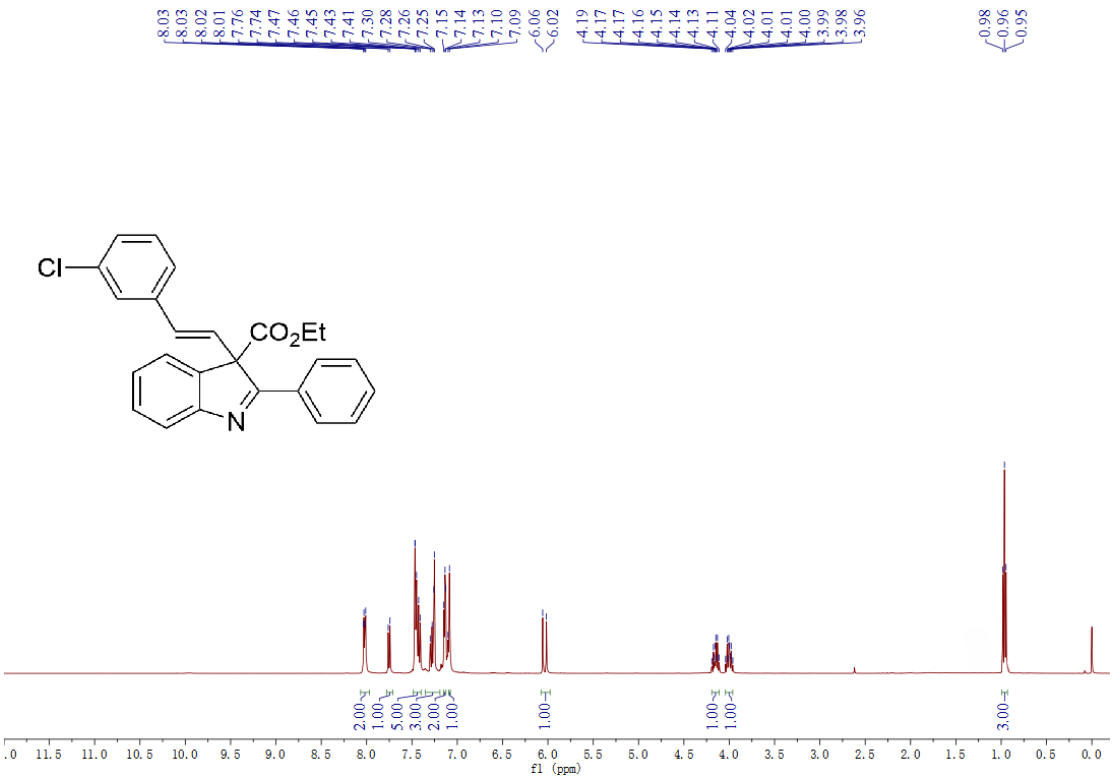


Figure S21 ^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3ka**

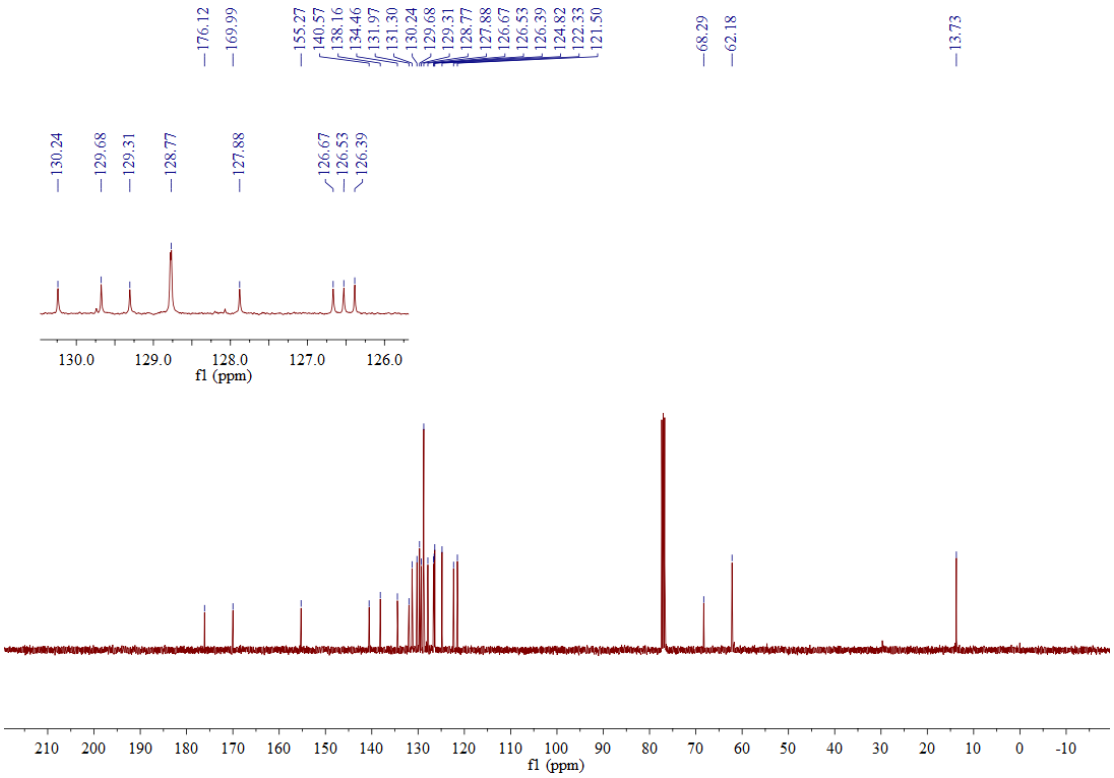


Figure S22 ^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3ka**

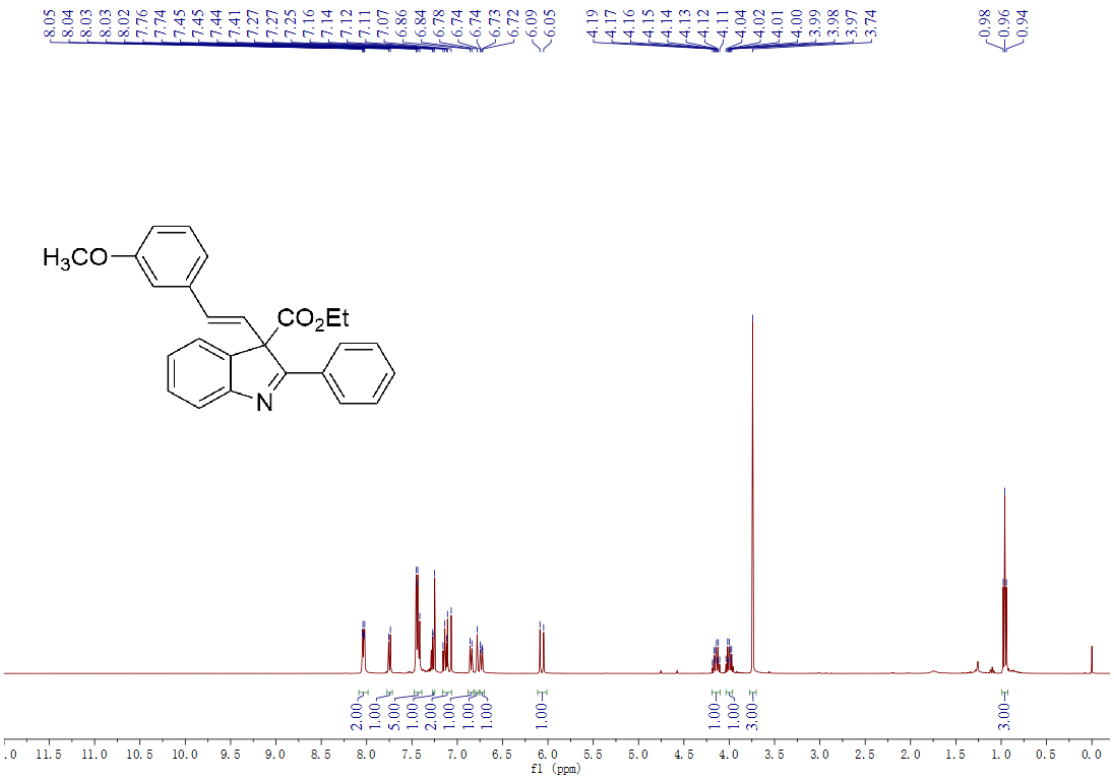


Figure S23 ^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3la**

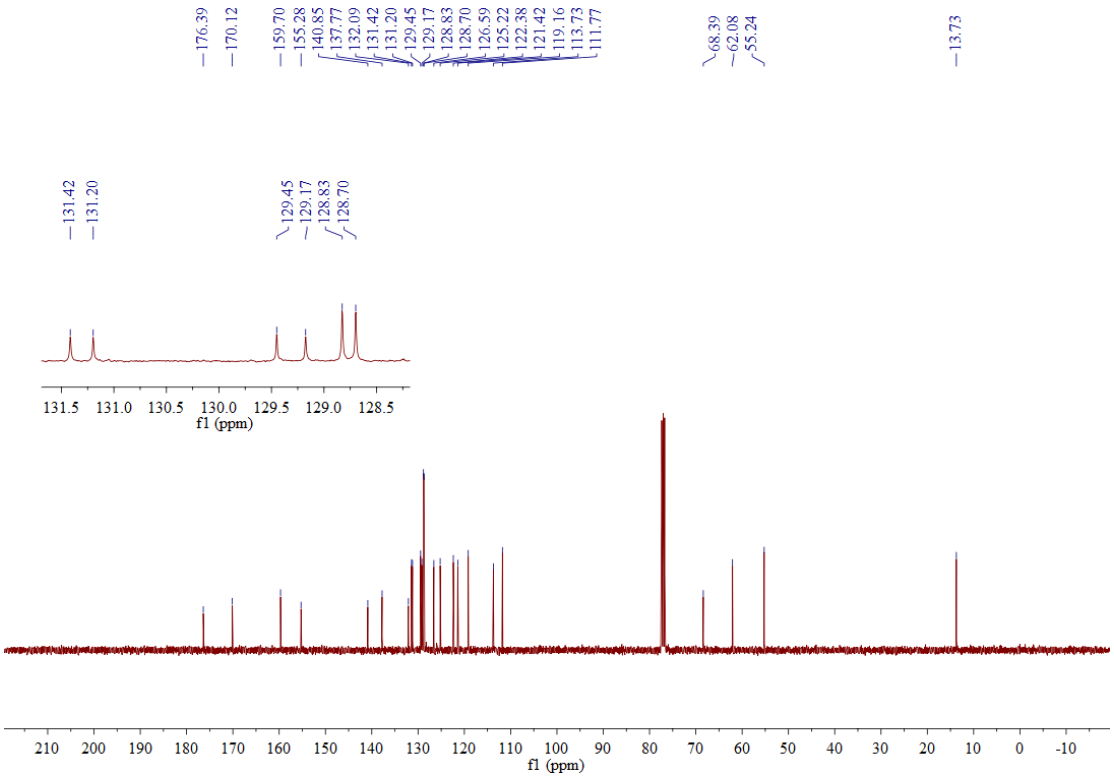


Figure S24 ^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3la**

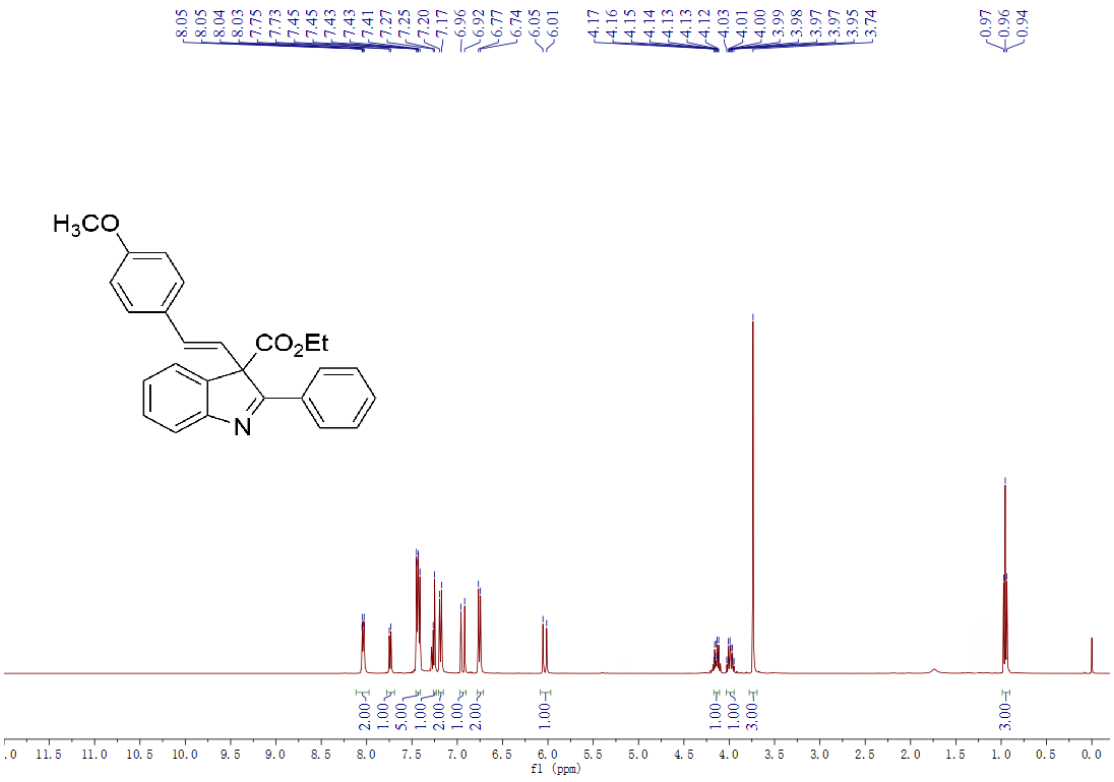


Figure S25 ^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3ma**

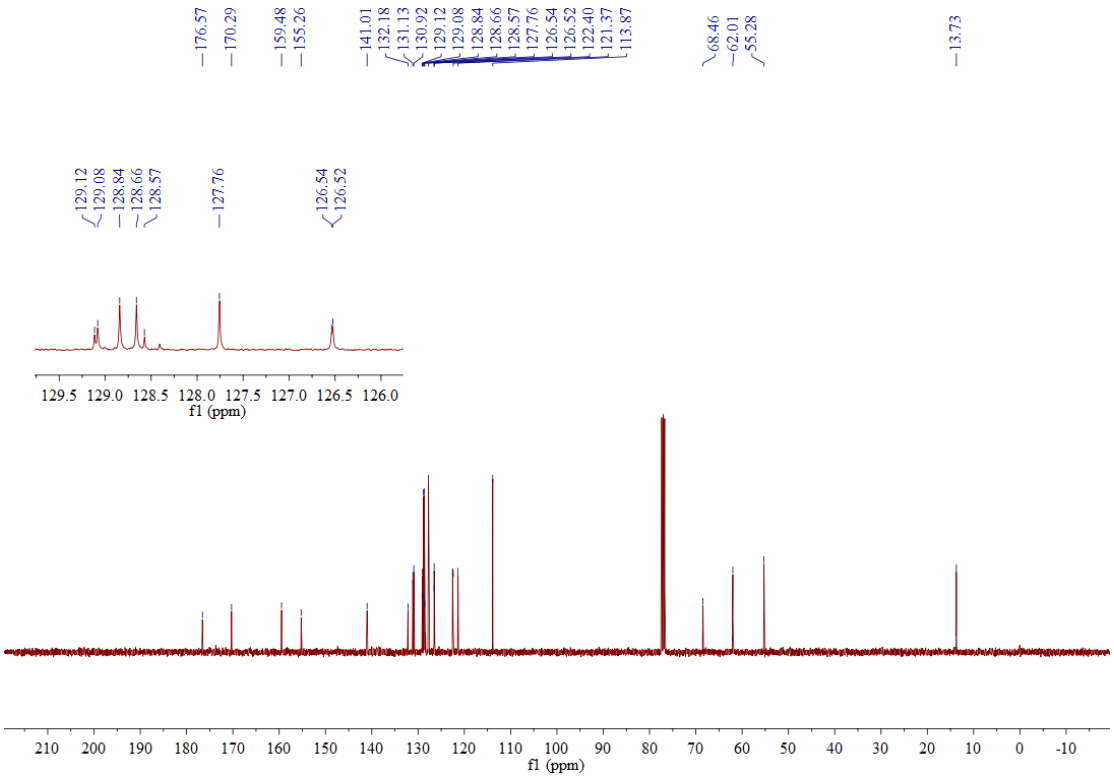


Figure S26 ^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3ma**

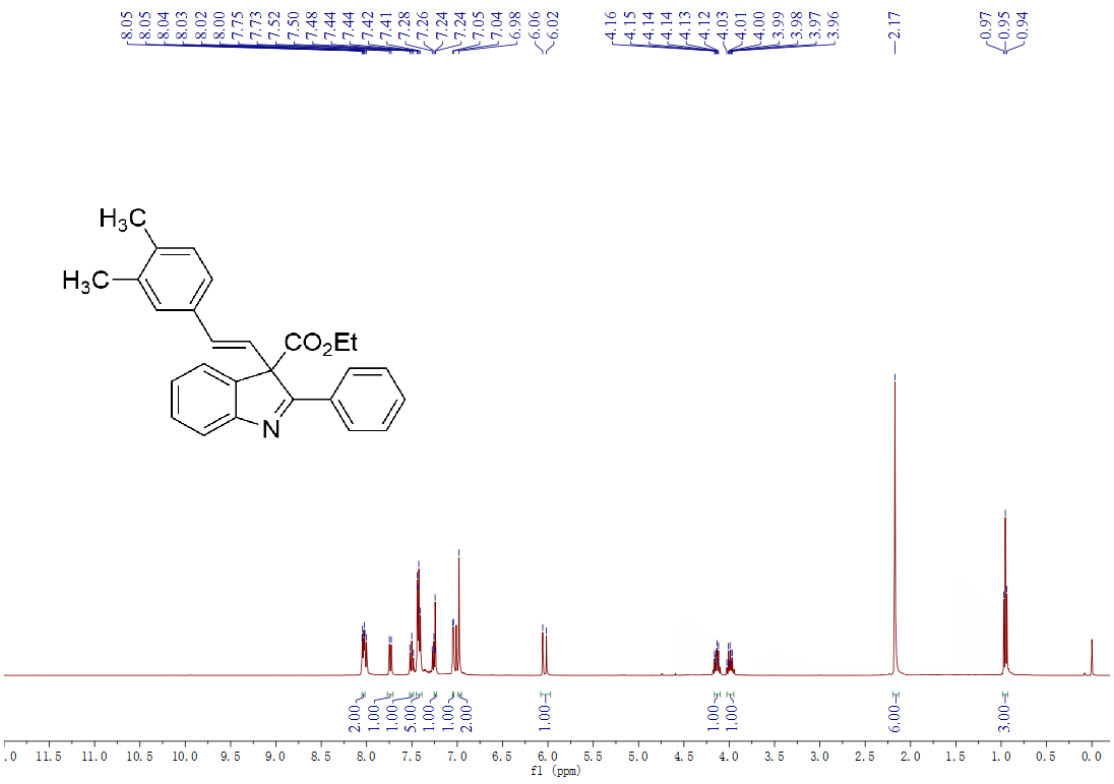


Figure S27 ^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3na**

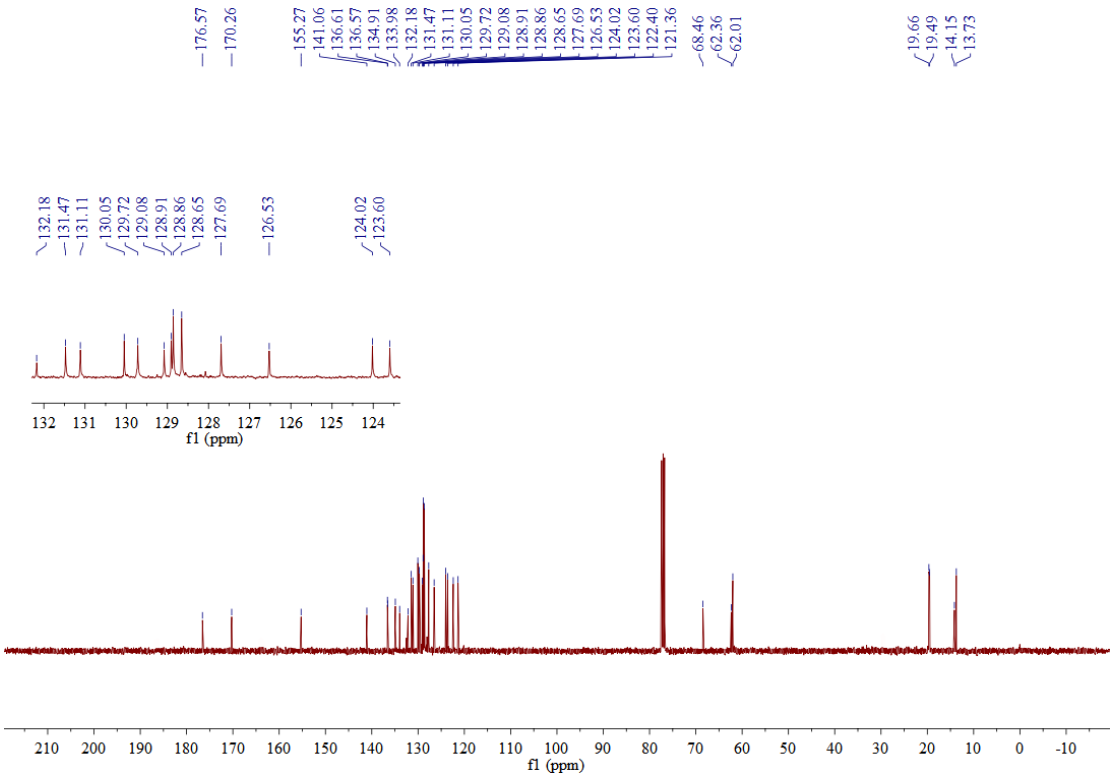


Figure S28 ^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3na**

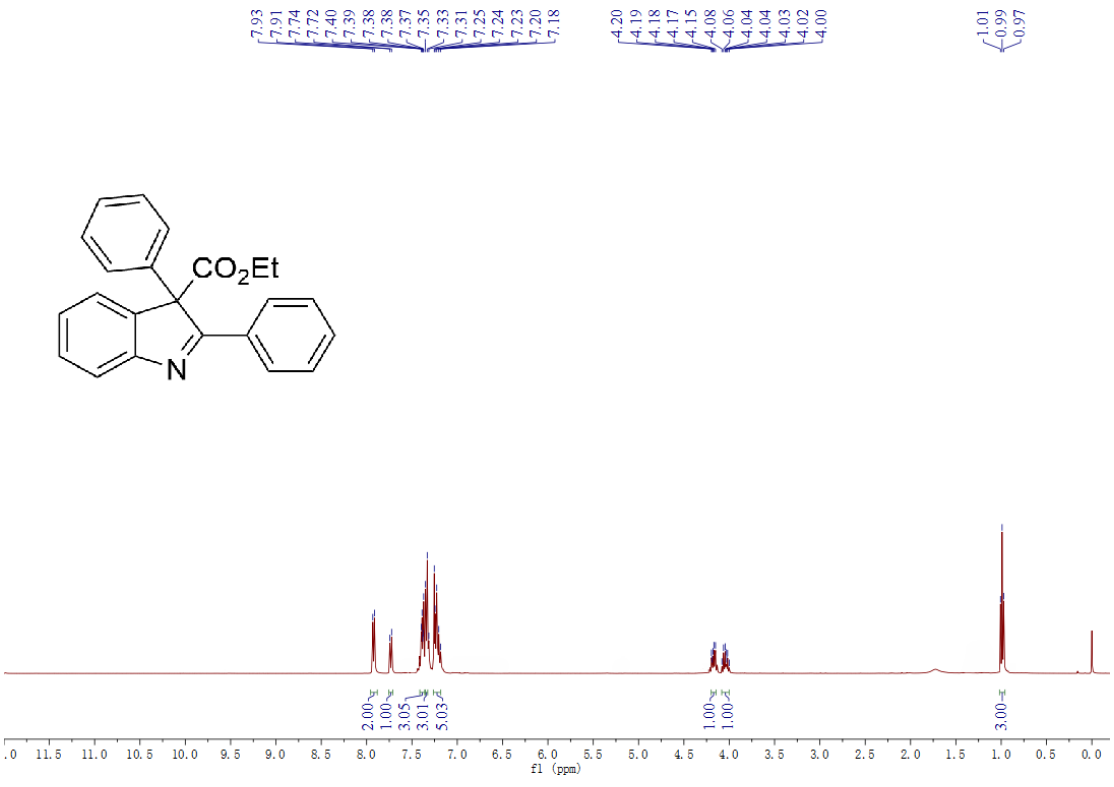


Figure S29 ^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3oa**

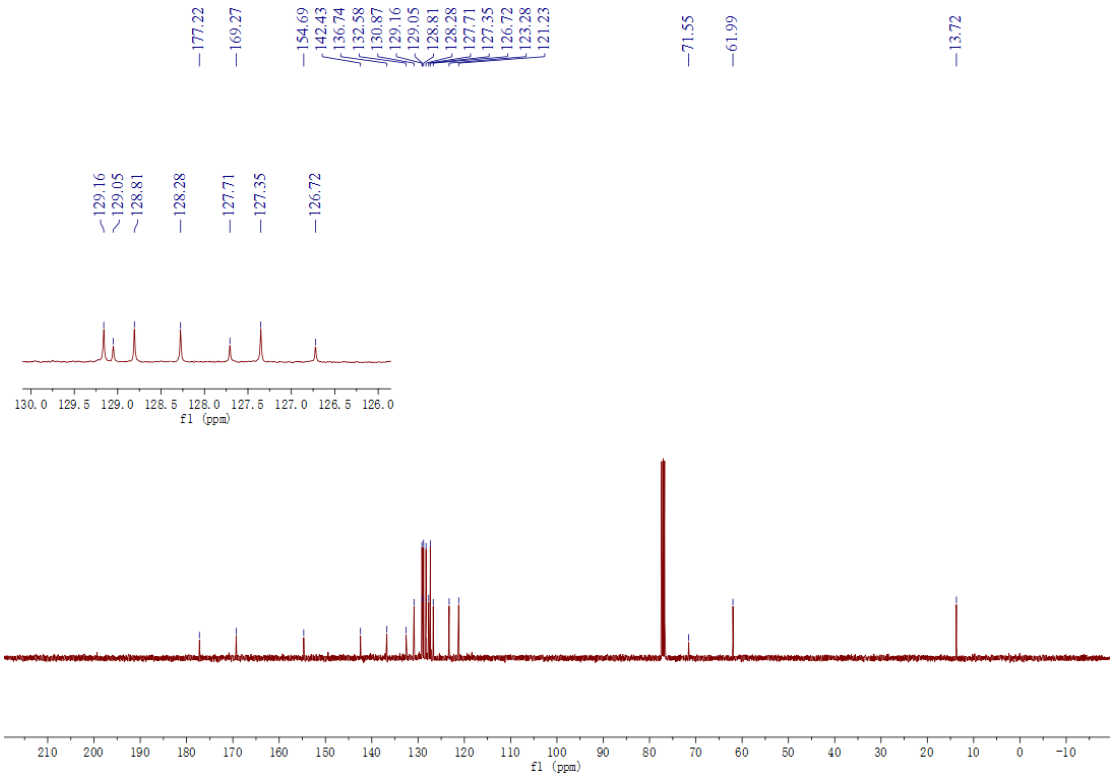


Figure S30 ^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3oa**

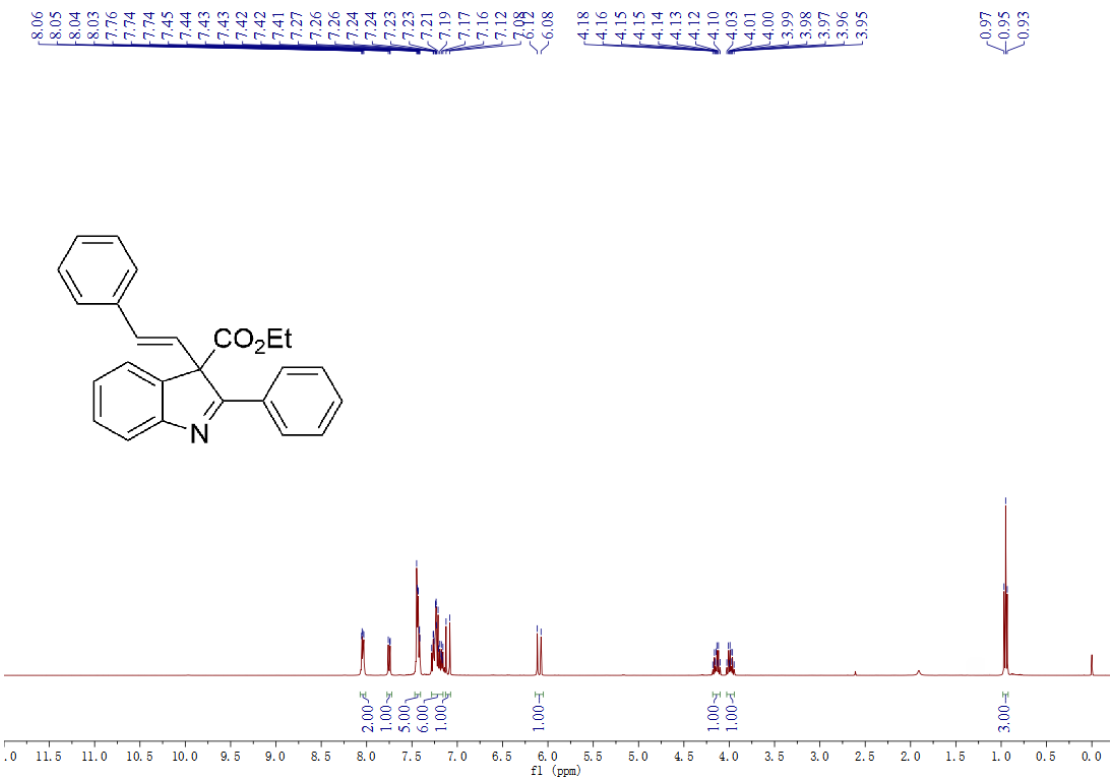


Figure S31 ^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3aa**

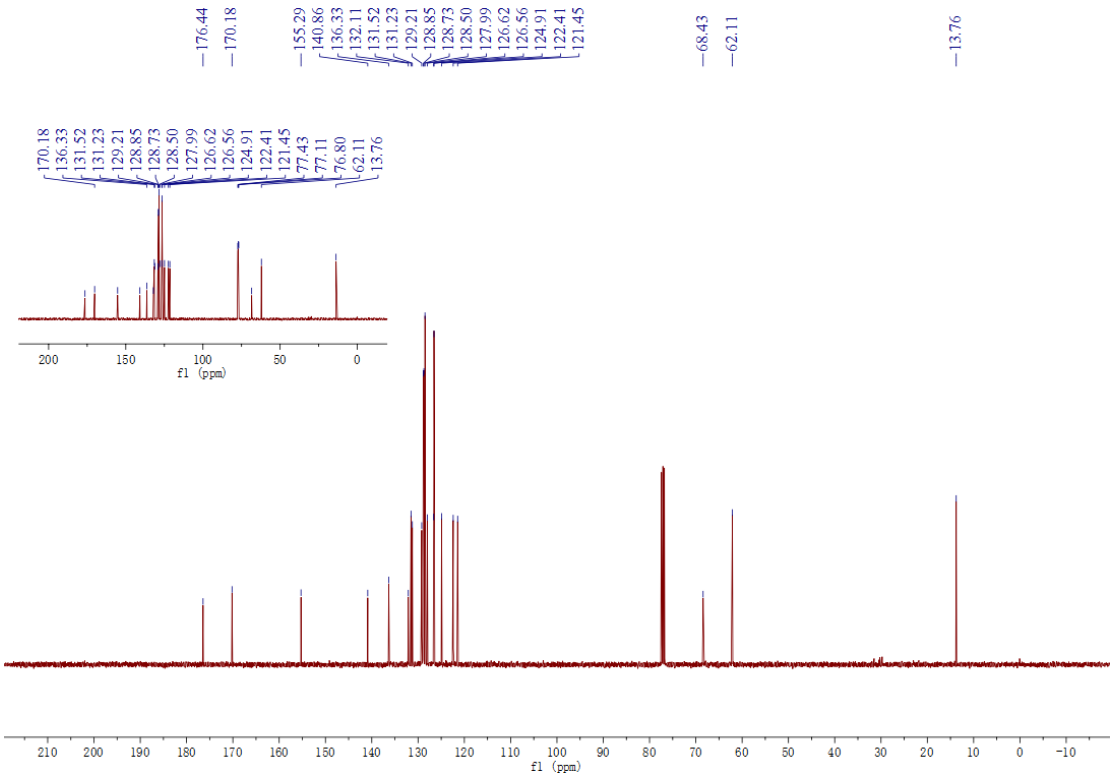


Figure S32 ^{13}H NMR (101 MHz, $CDCl_3$) spectra of **3aa**

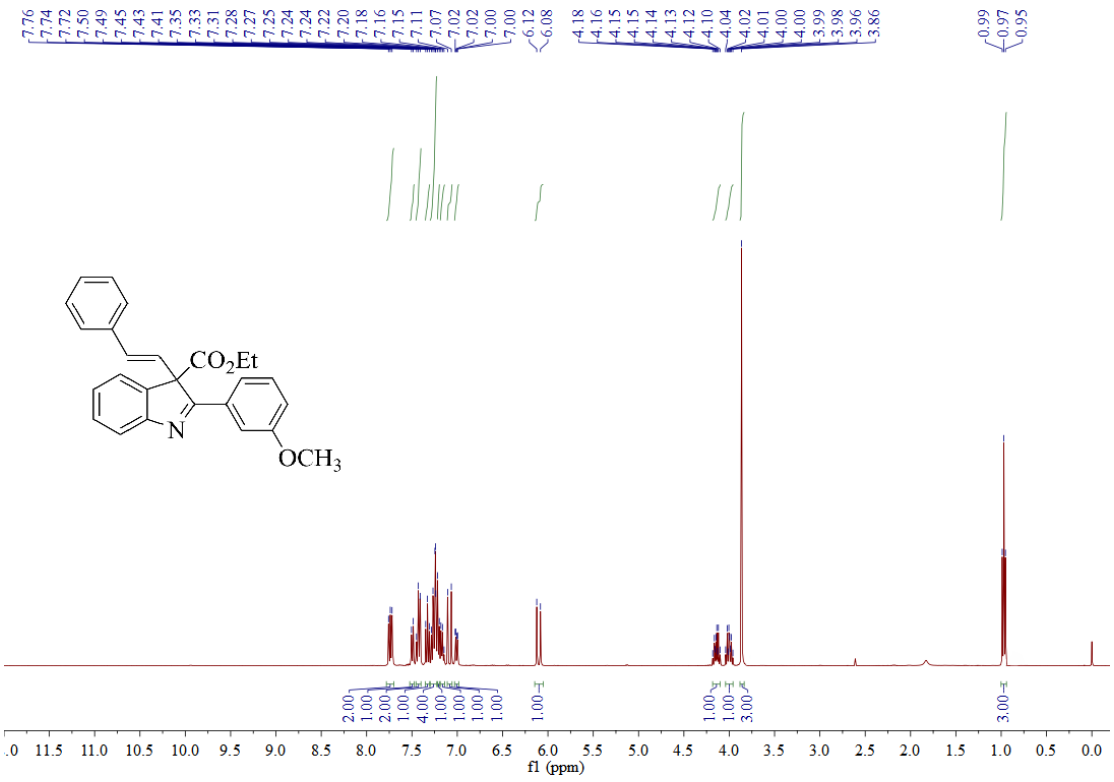


Figure S33 ^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3ab**

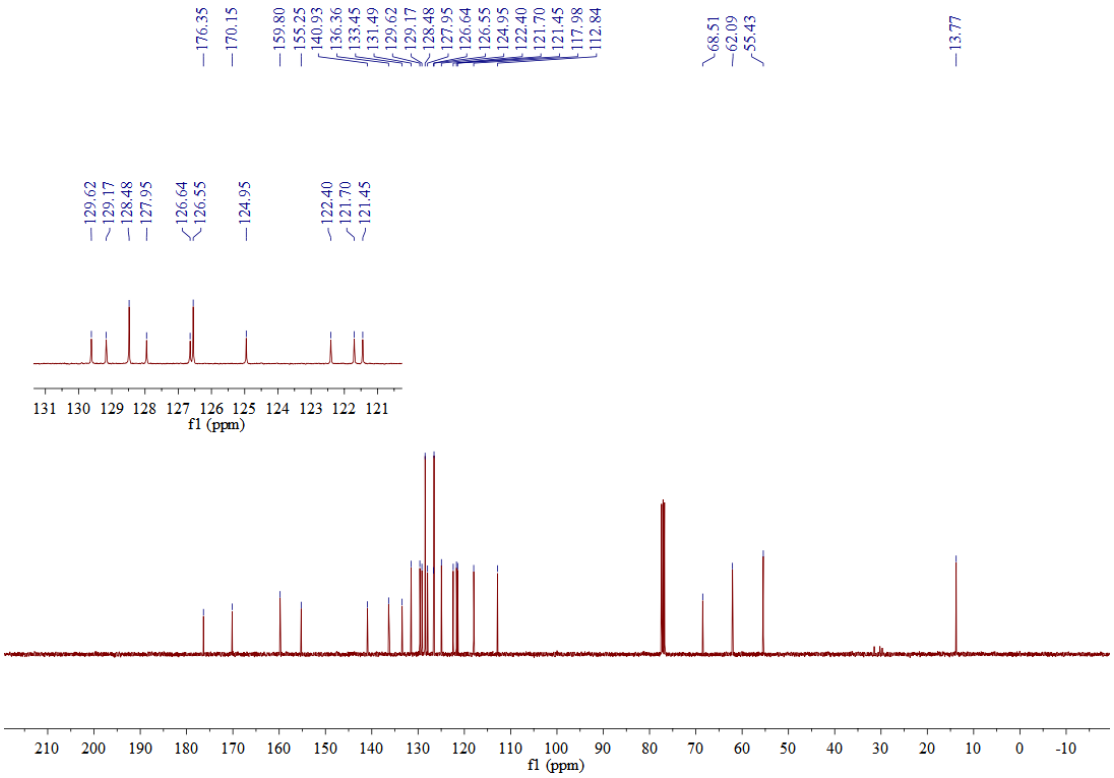


Figure S34 ^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3ab**

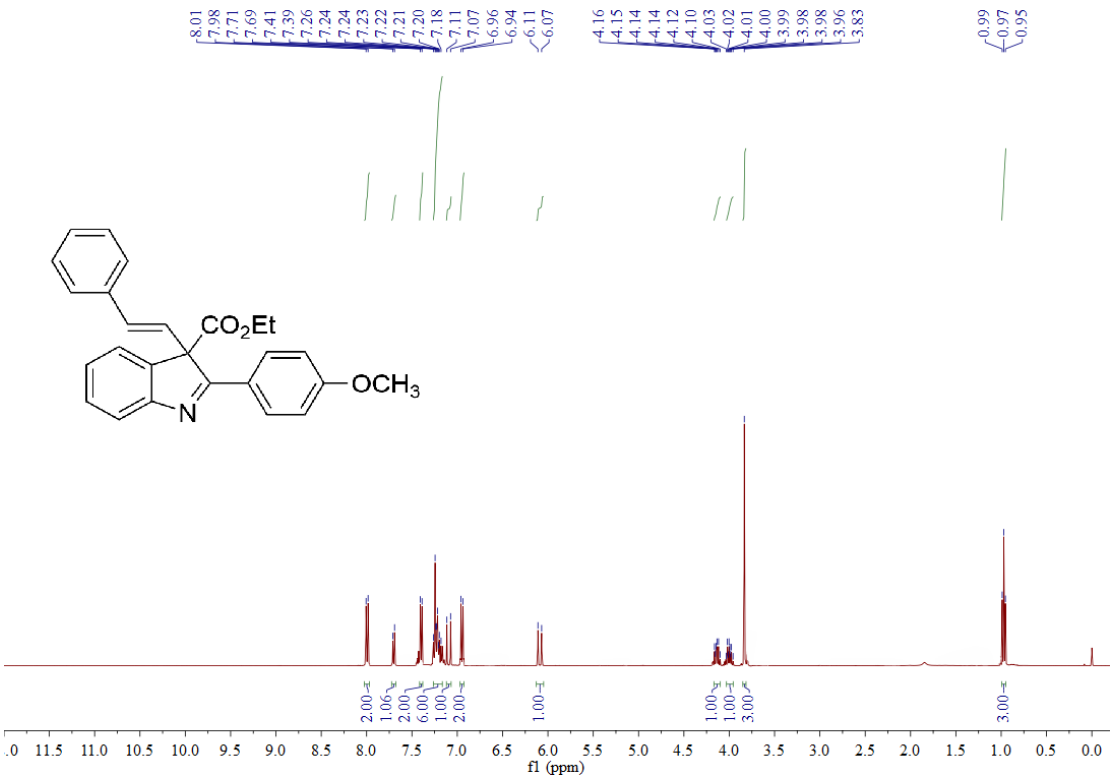


Figure S35 ^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3ac**

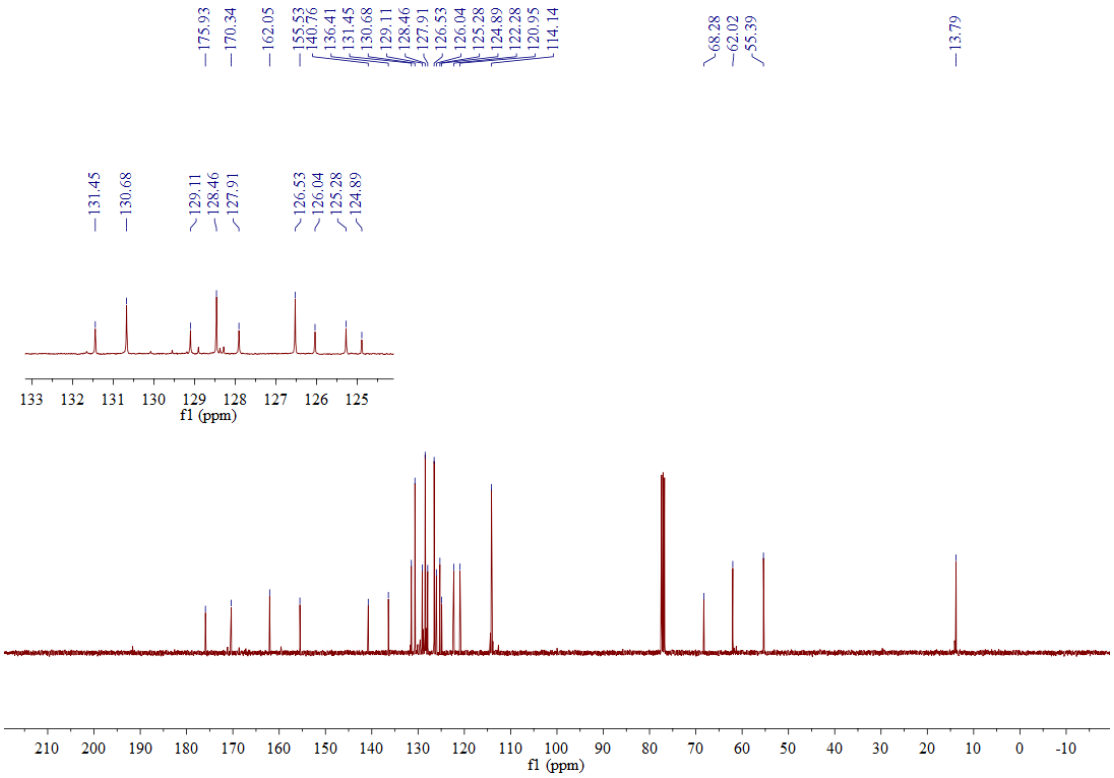


Figure S36 ^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3ac**

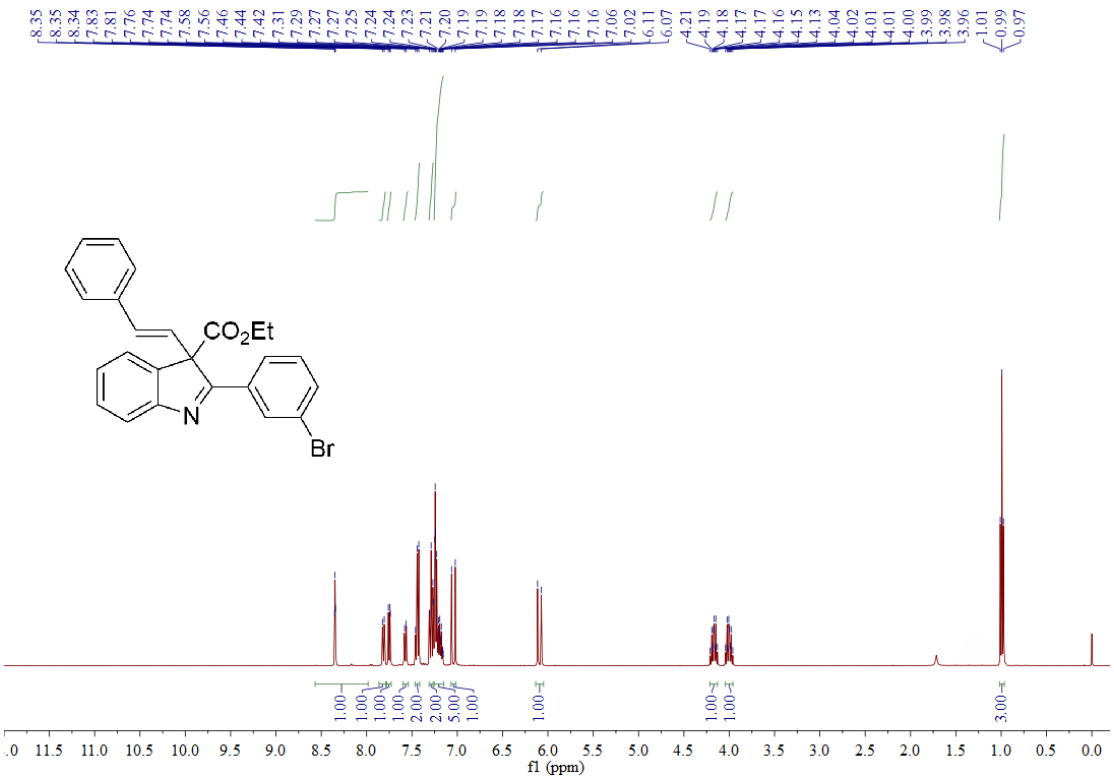


Figure S37 ^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3ad**

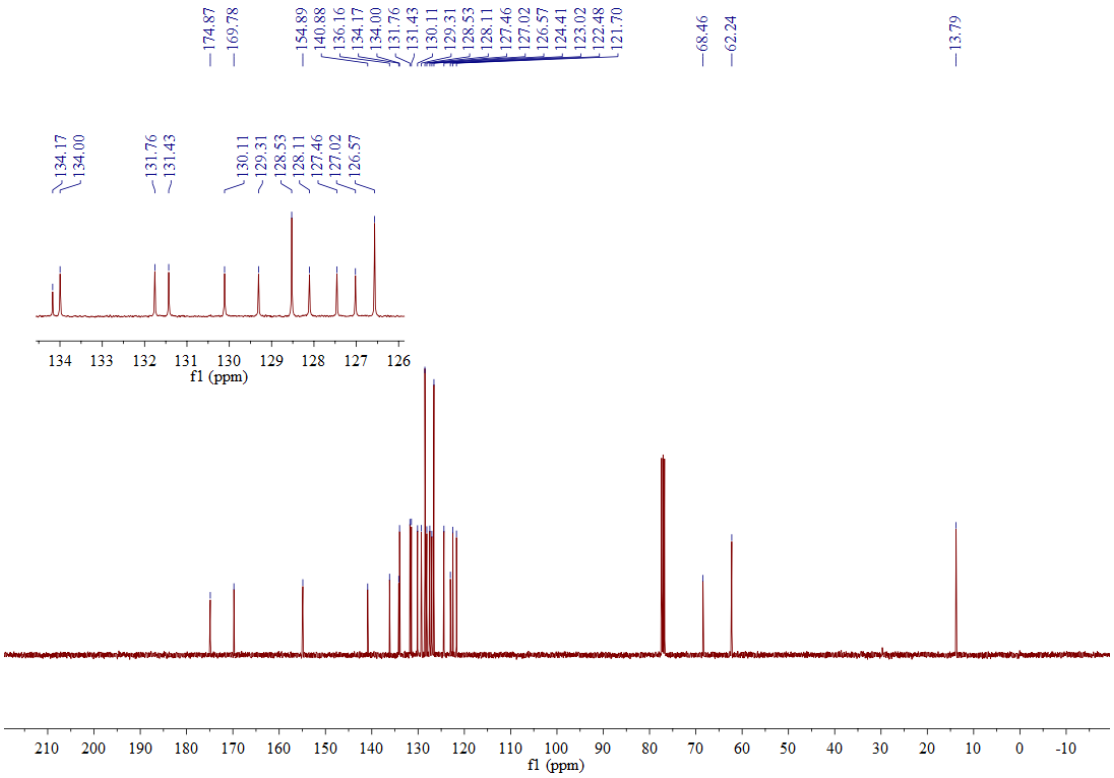


Figure S38 ^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3ad**

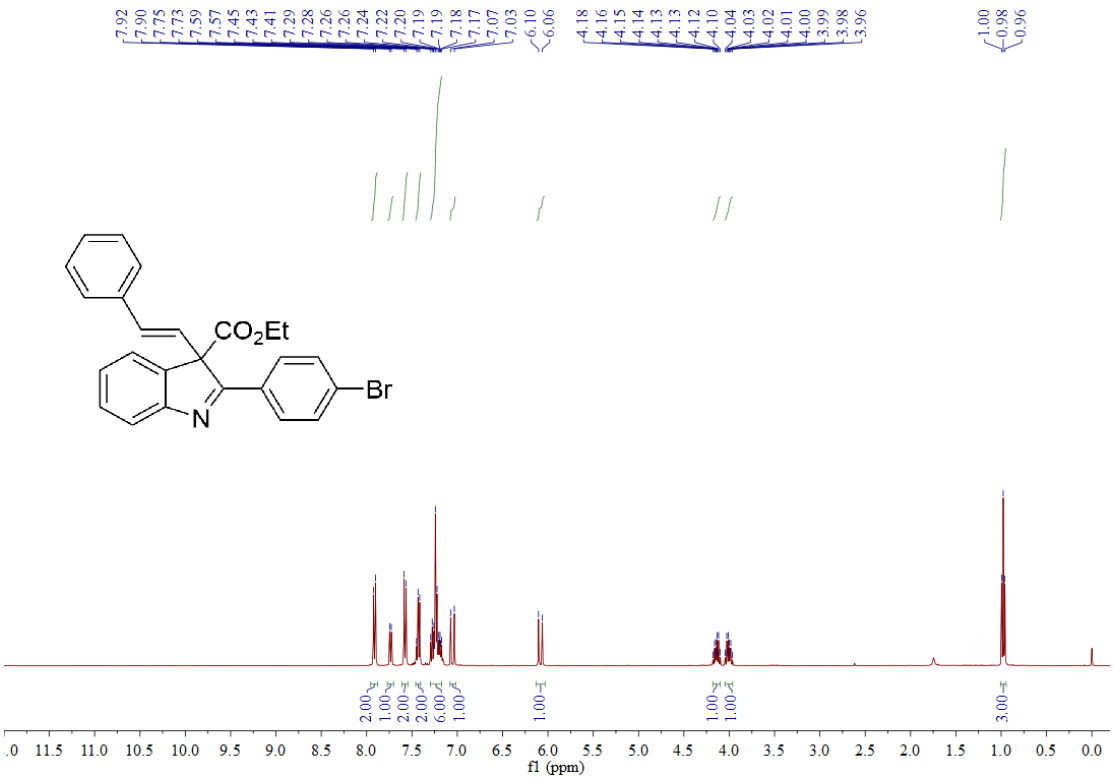


Figure S39 ^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3ae**

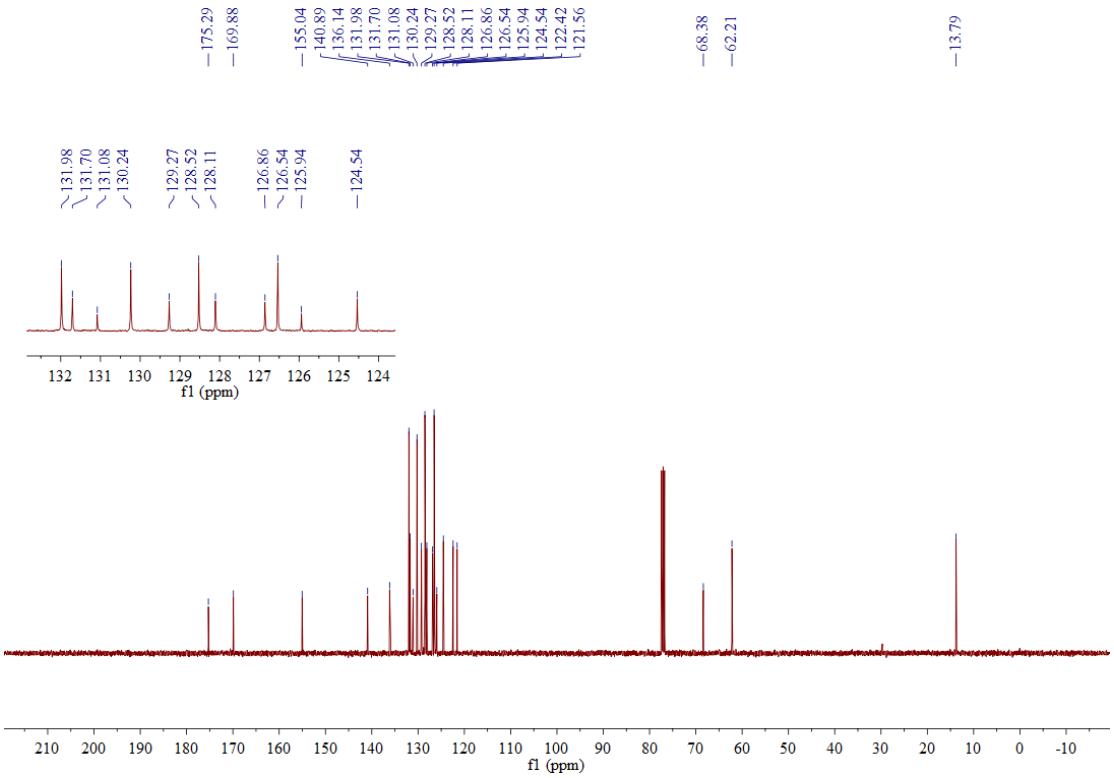


Figure S40 ^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3ae**

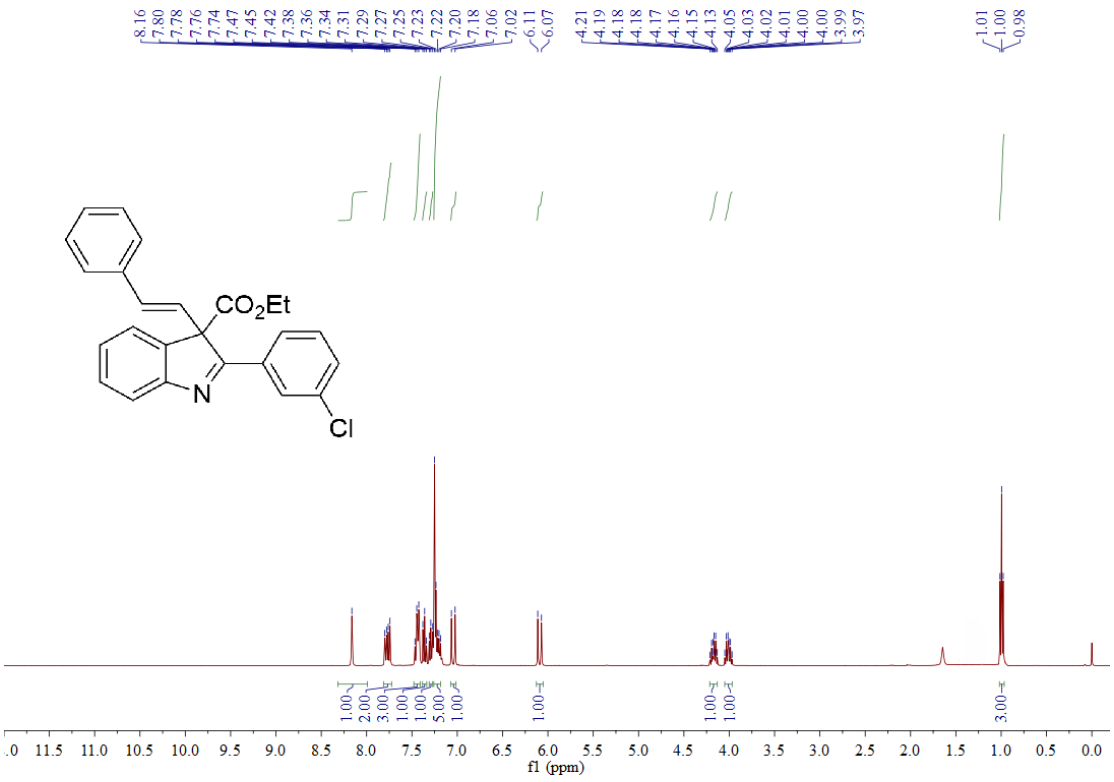


Figure S41 ^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3af**

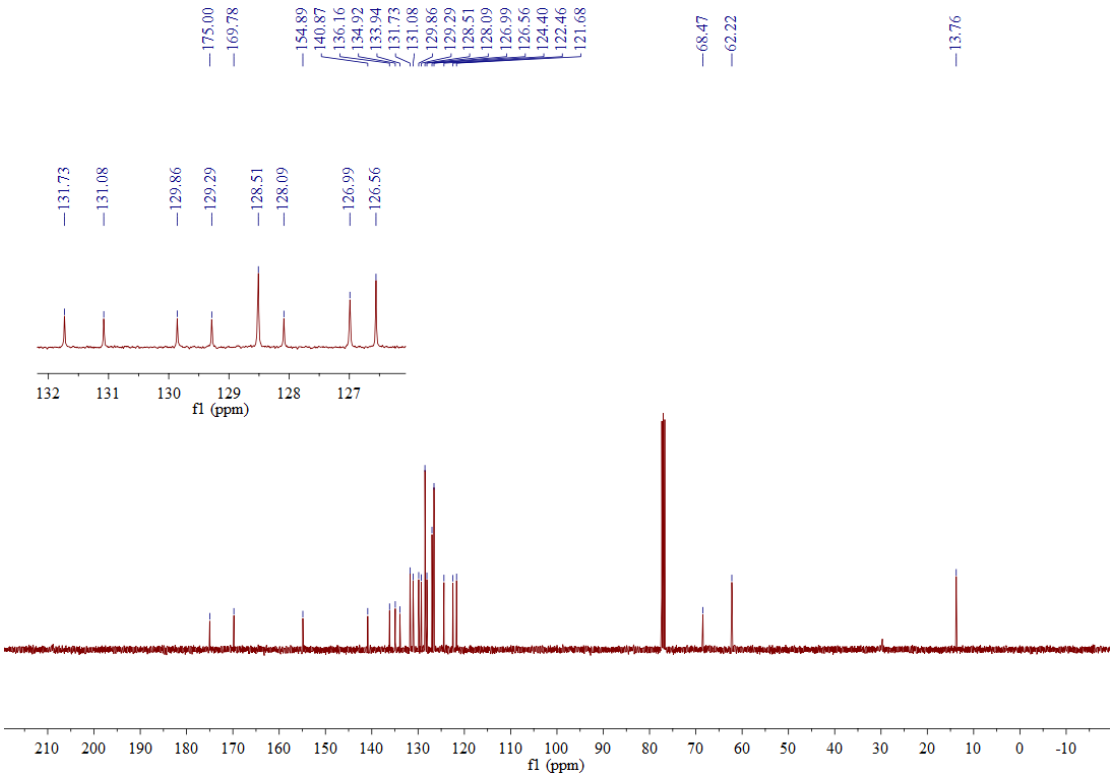


Figure S42 ^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3af**

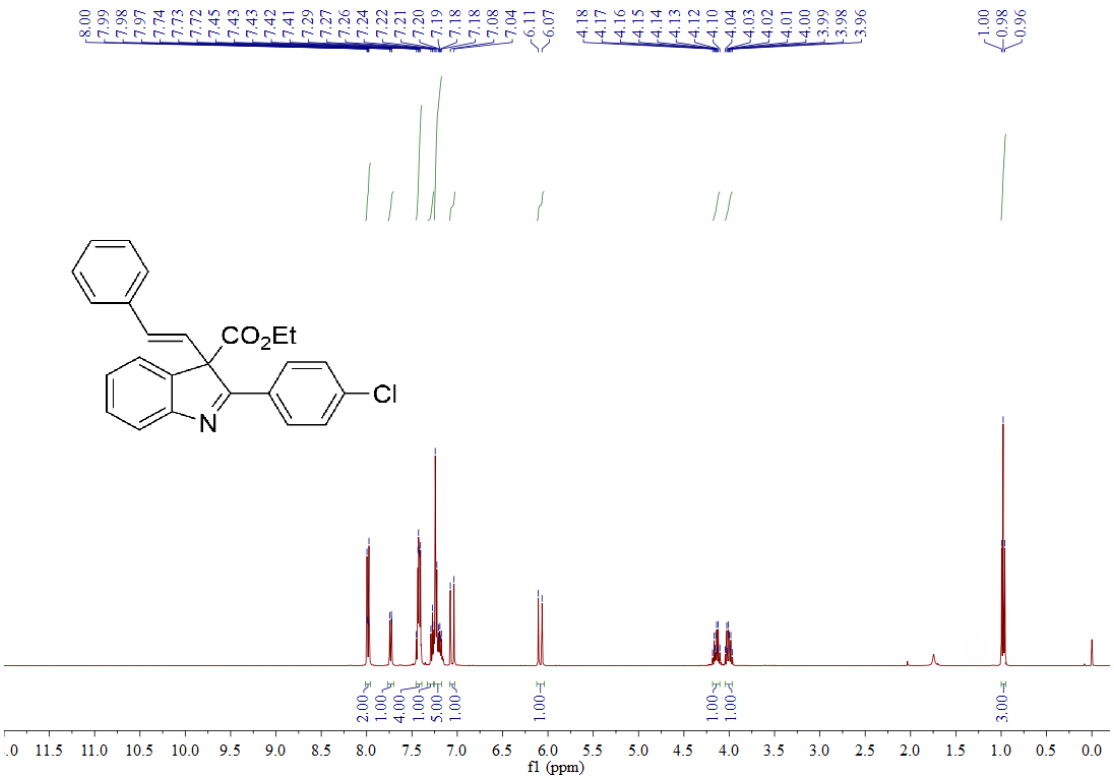


Figure S43 ^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3ag**

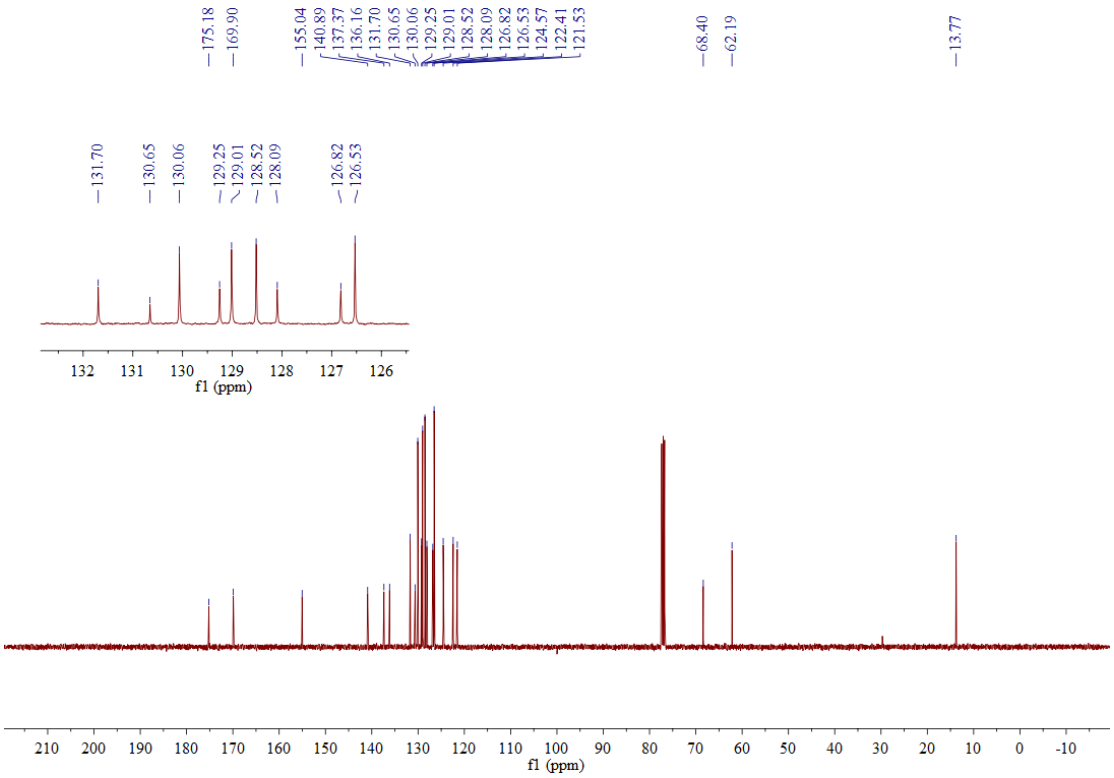


Figure S44 ^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3ag**

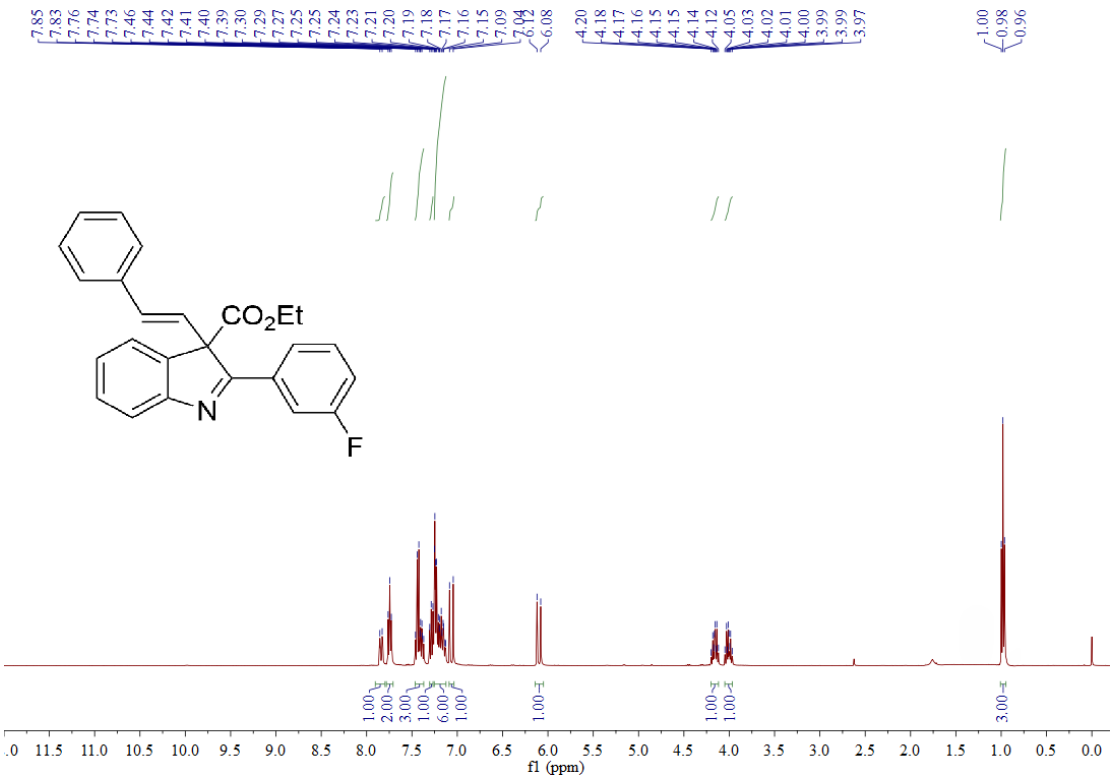


Figure S45 ^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3ah**

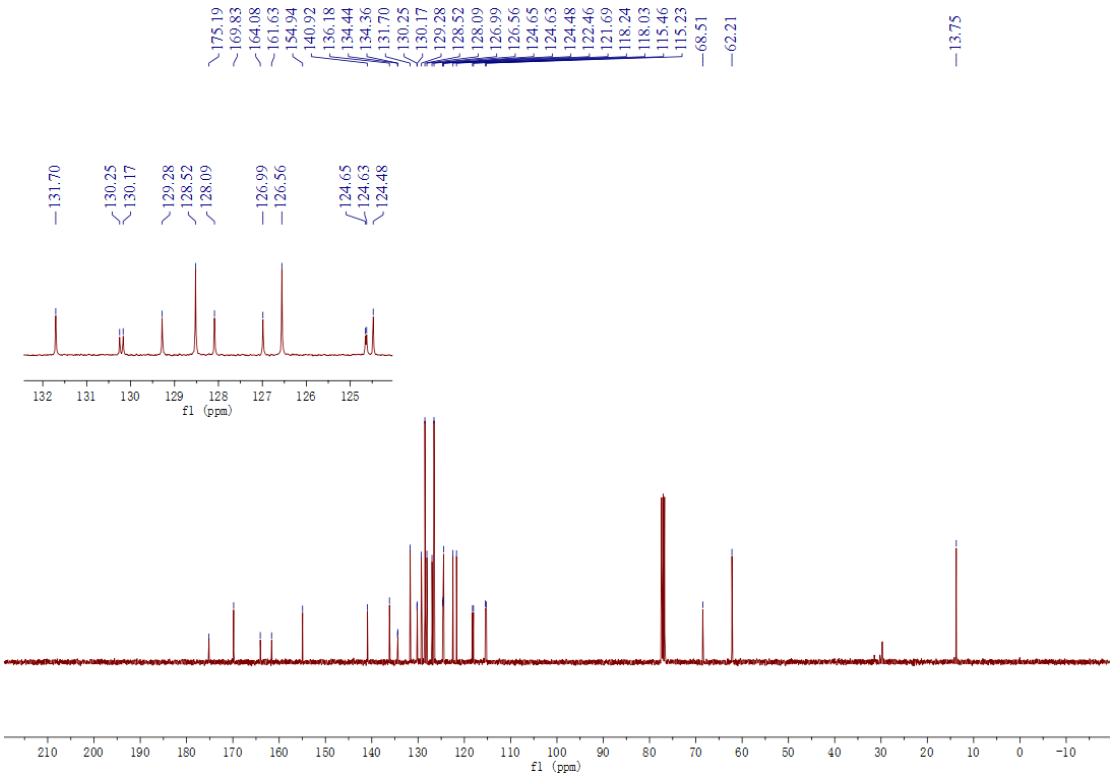


Figure S46 ^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3ah**

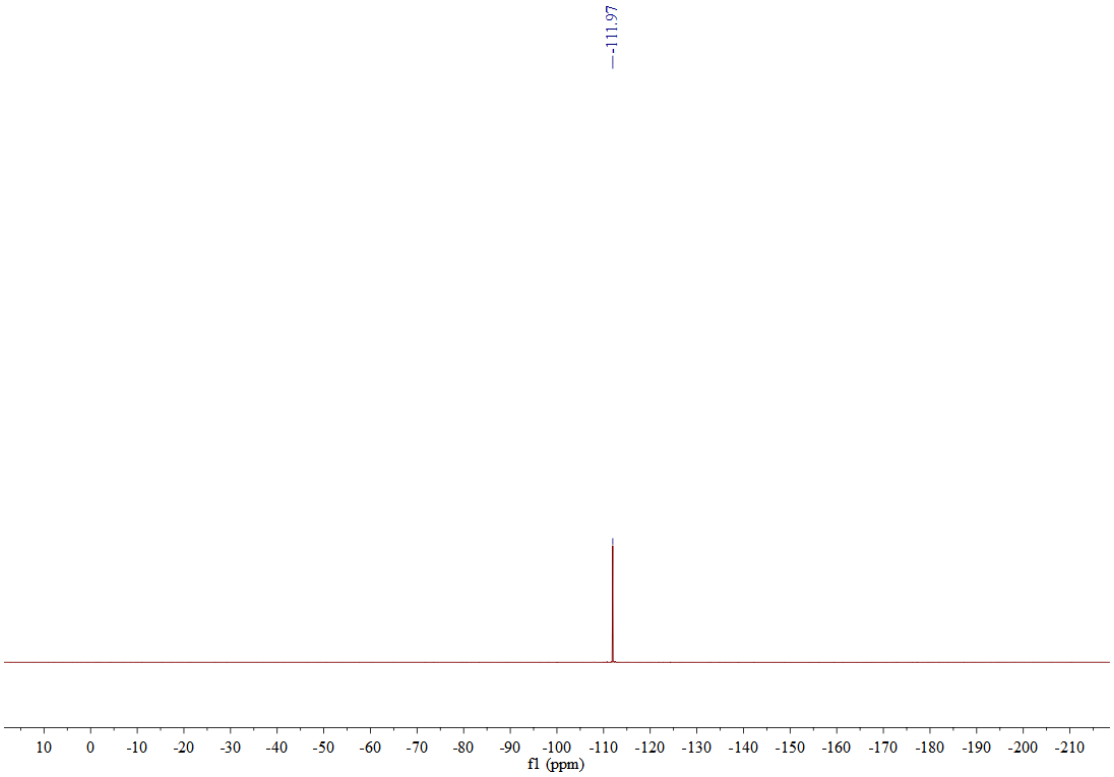


Figure S47 ^{19}F NMR (376 MHz, $CDCl_3$) spectra of **3ah**

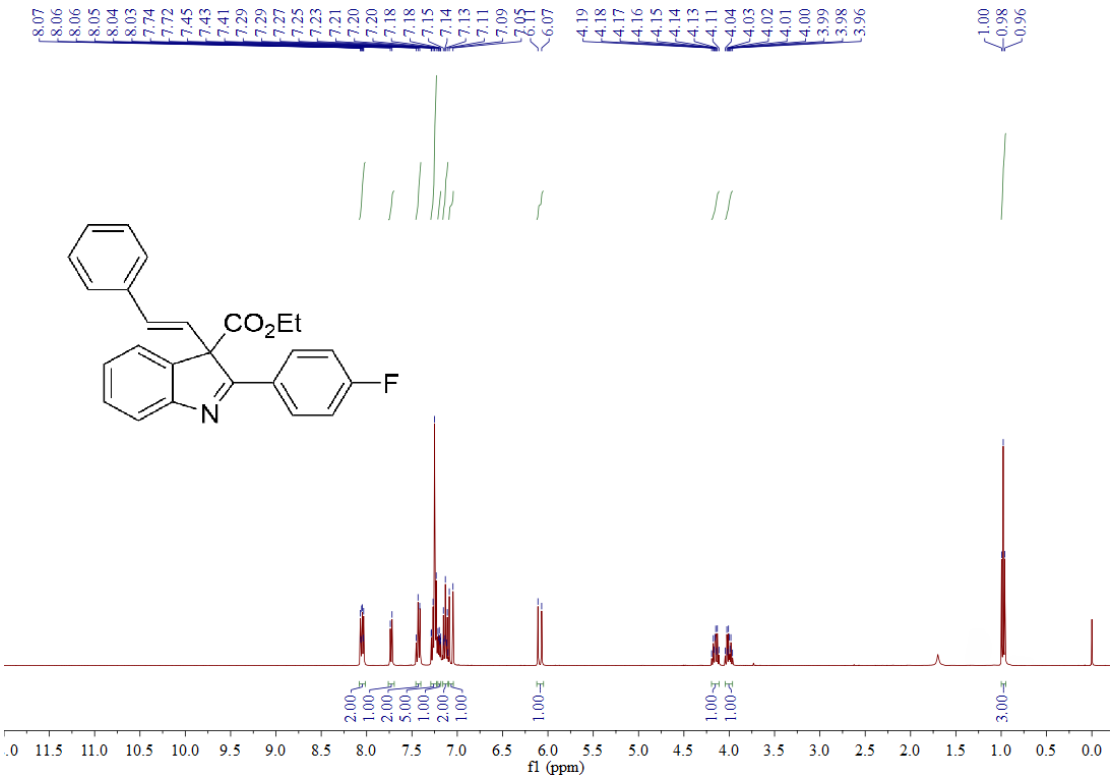


Figure S48 ^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3ai**

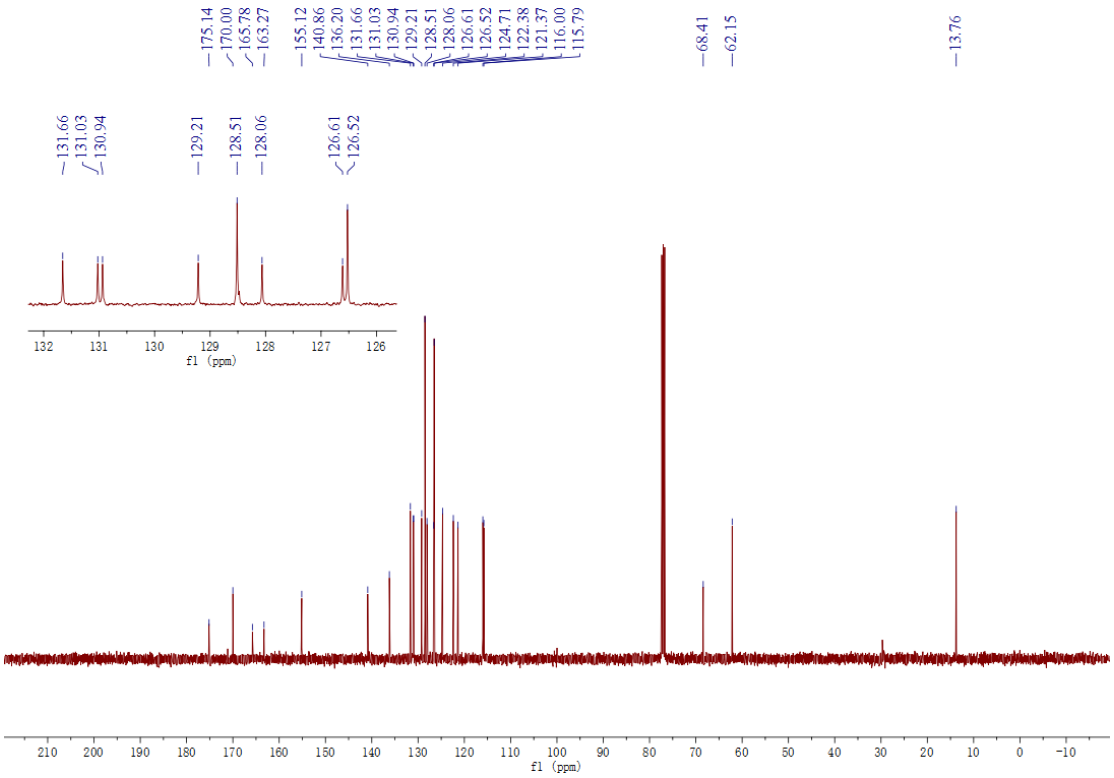


Figure S49 ^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3ai**

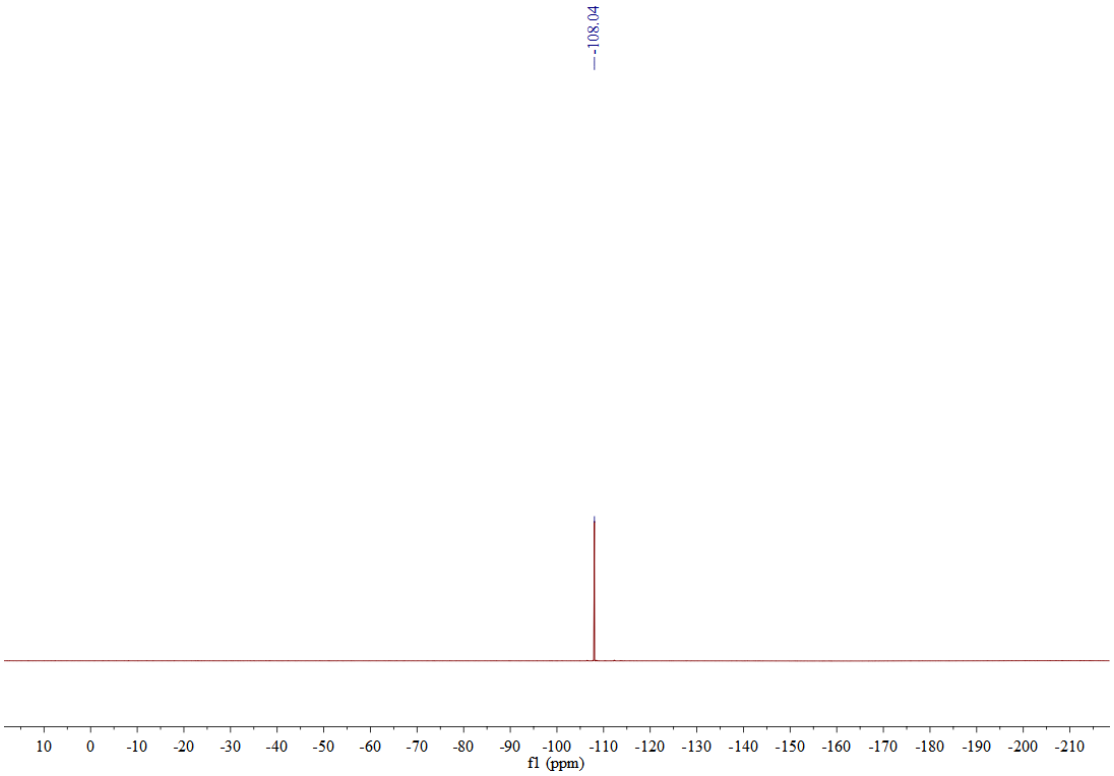


Figure S50 ^{19}F NMR (376 MHz, $CDCl_3$) spectra of **3ai**

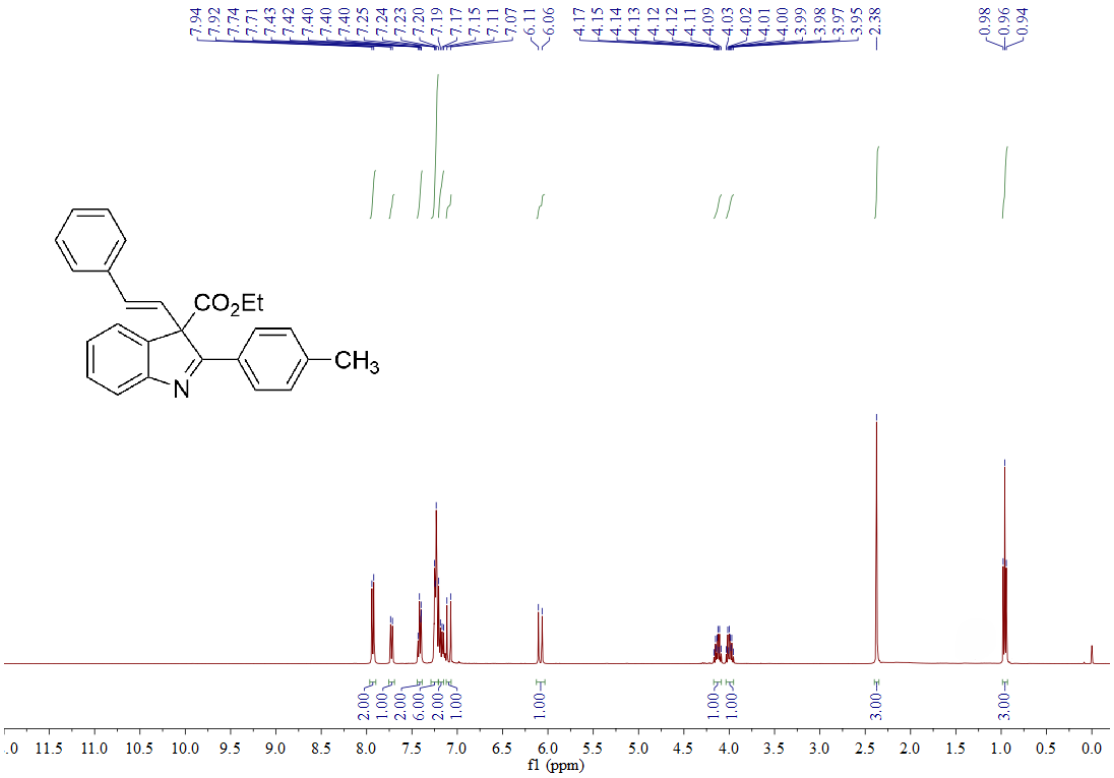


Figure S51 ^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3aj**

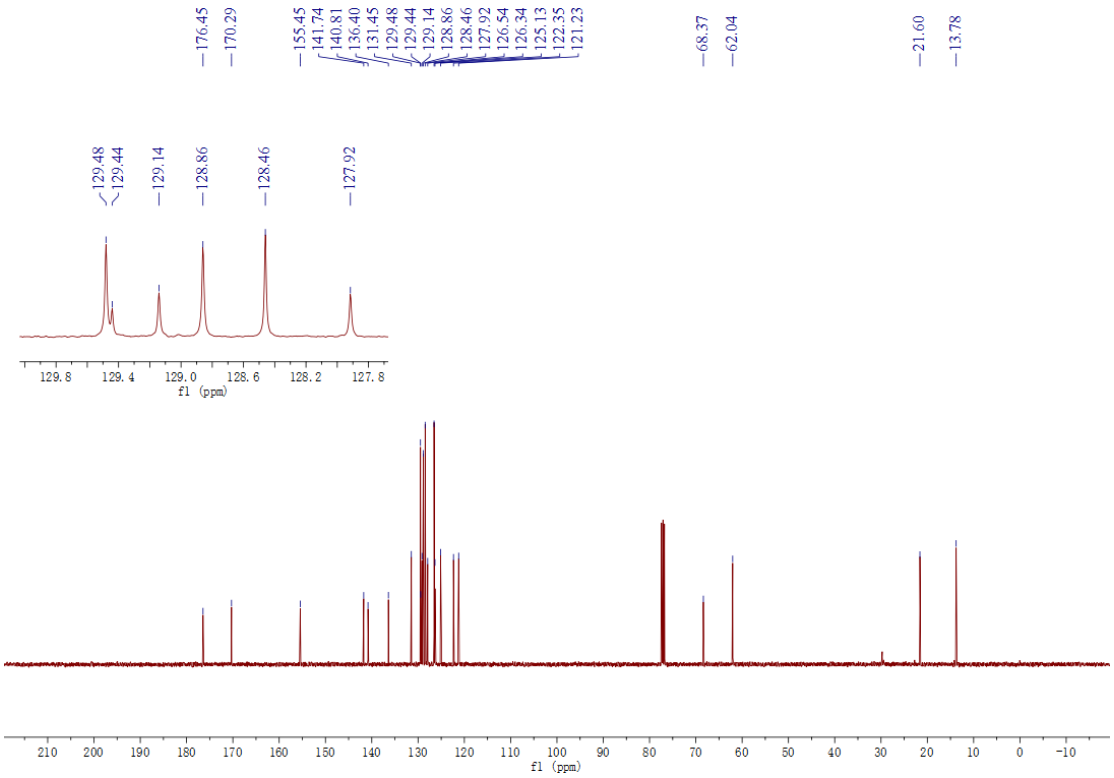


Figure S52 ^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3aj**

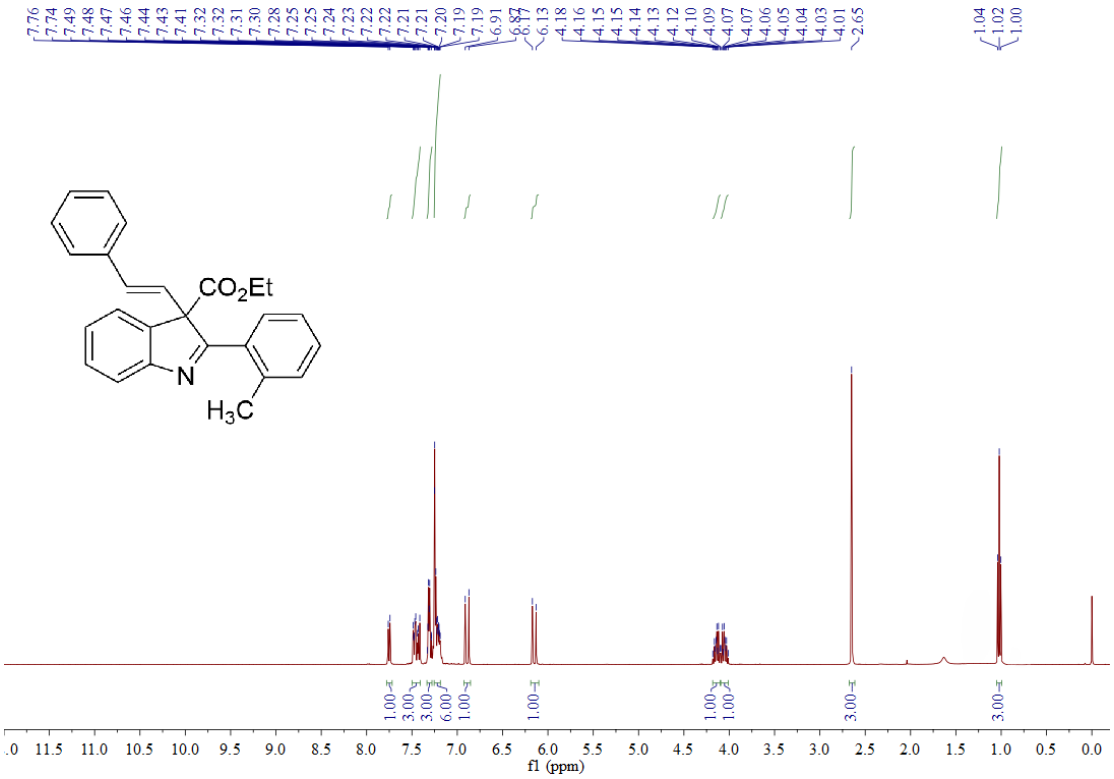


Figure S53 ^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3ak**

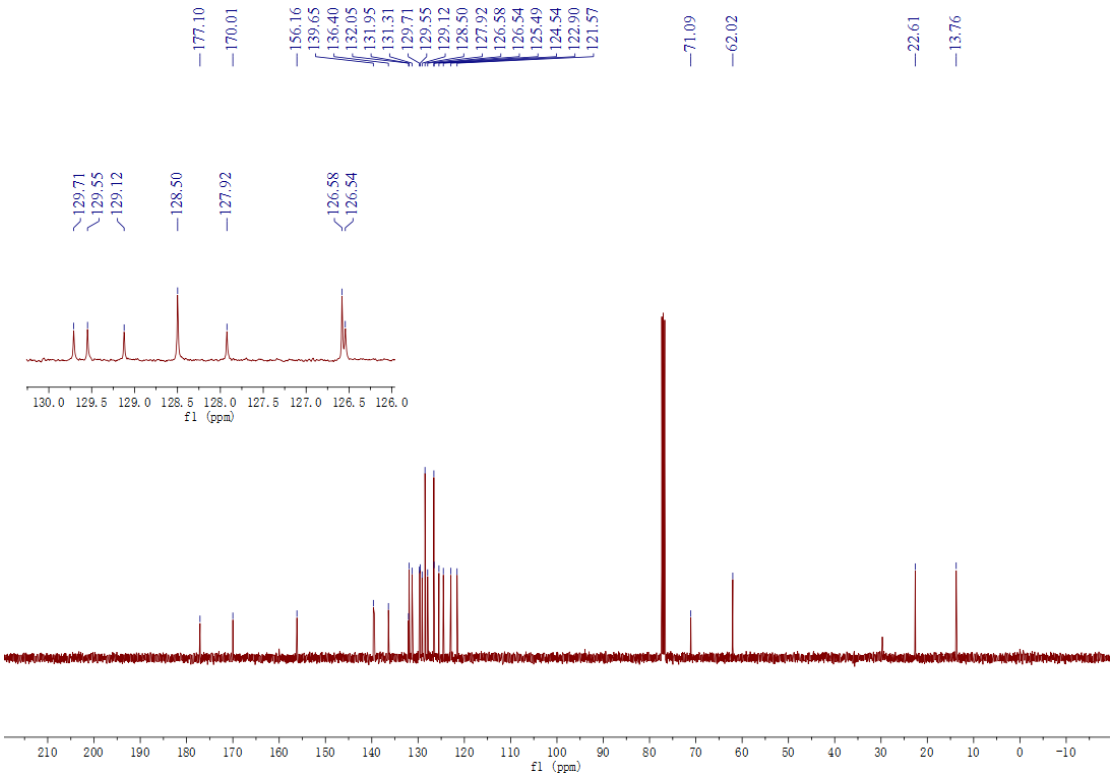


Figure S54 ^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3ak**

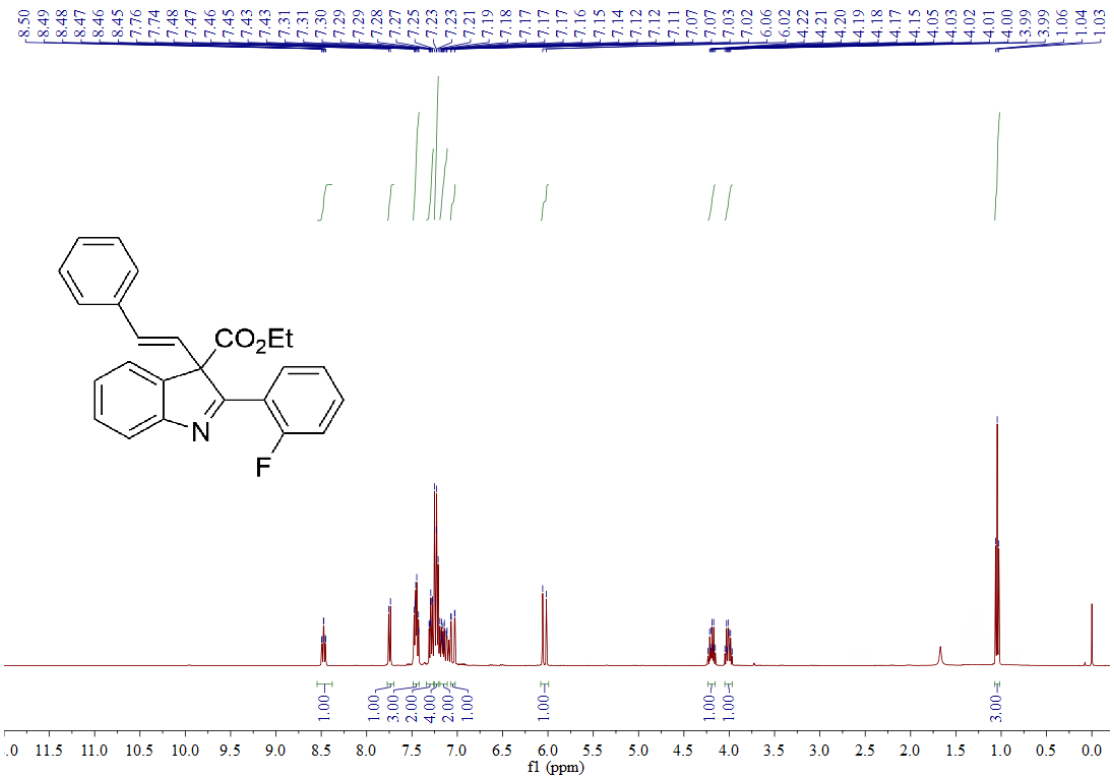


Figure S55 ^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3ao**

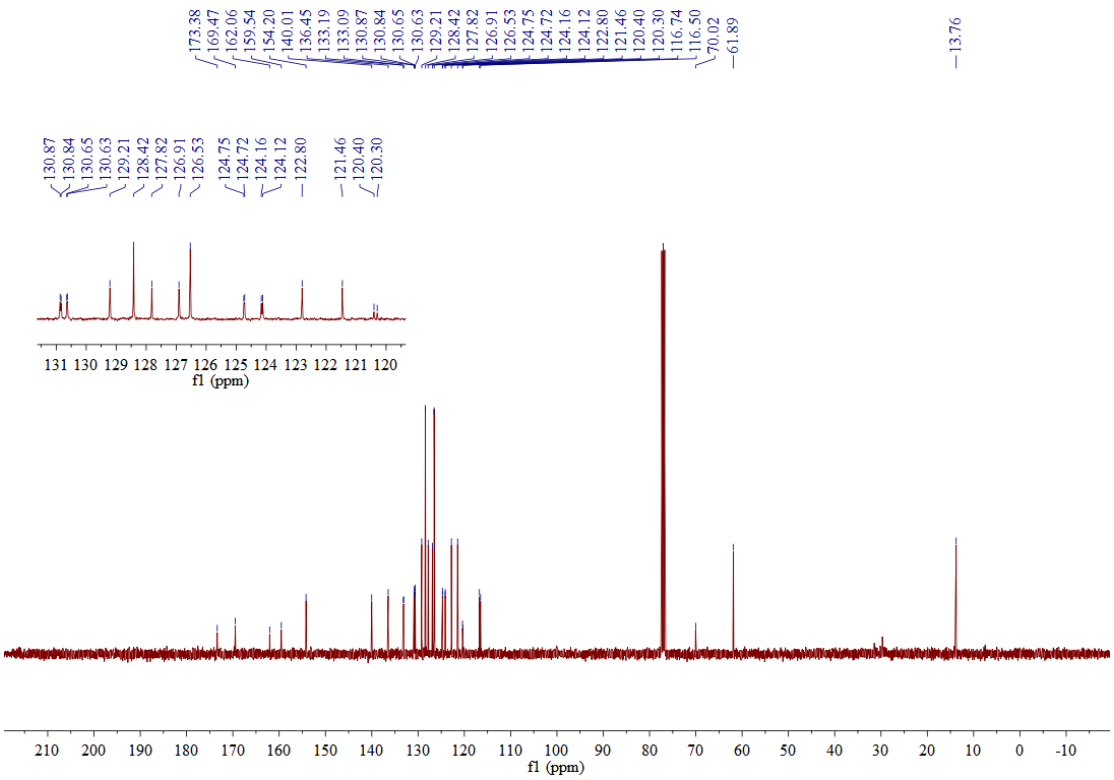


Figure S56 ^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3ao**

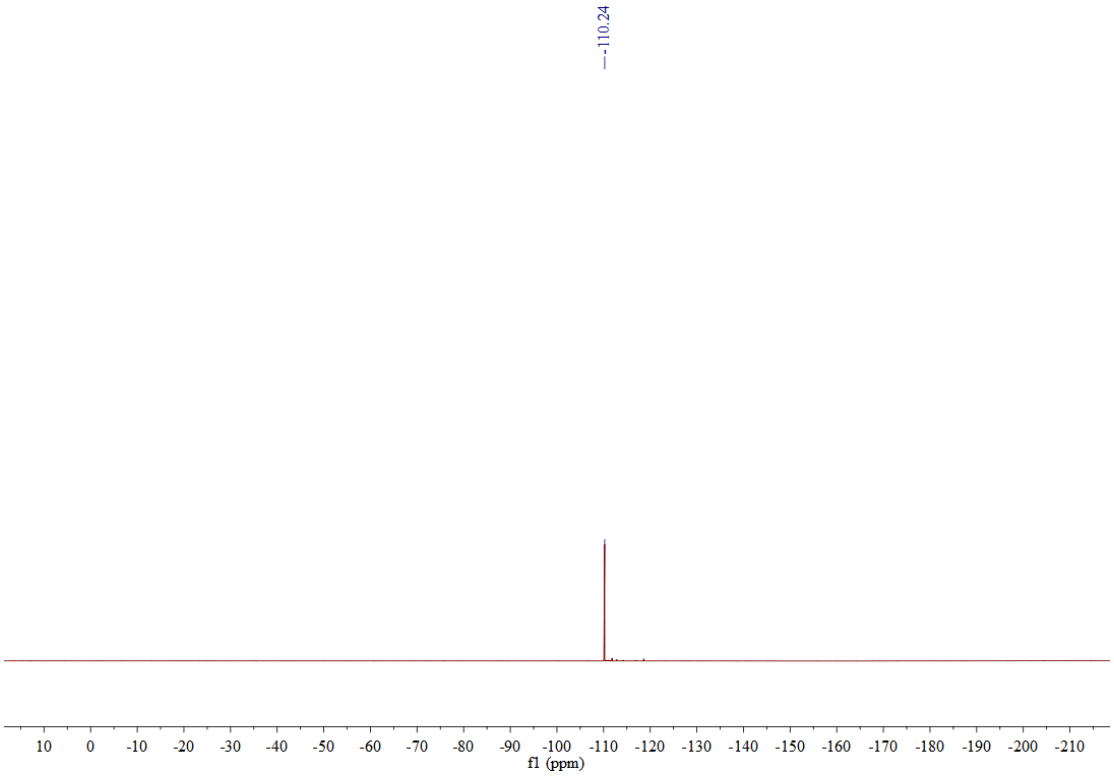


Figure S57 ^{19}F NMR (376 MHz, $CDCl_3$) spectra of **3ao**

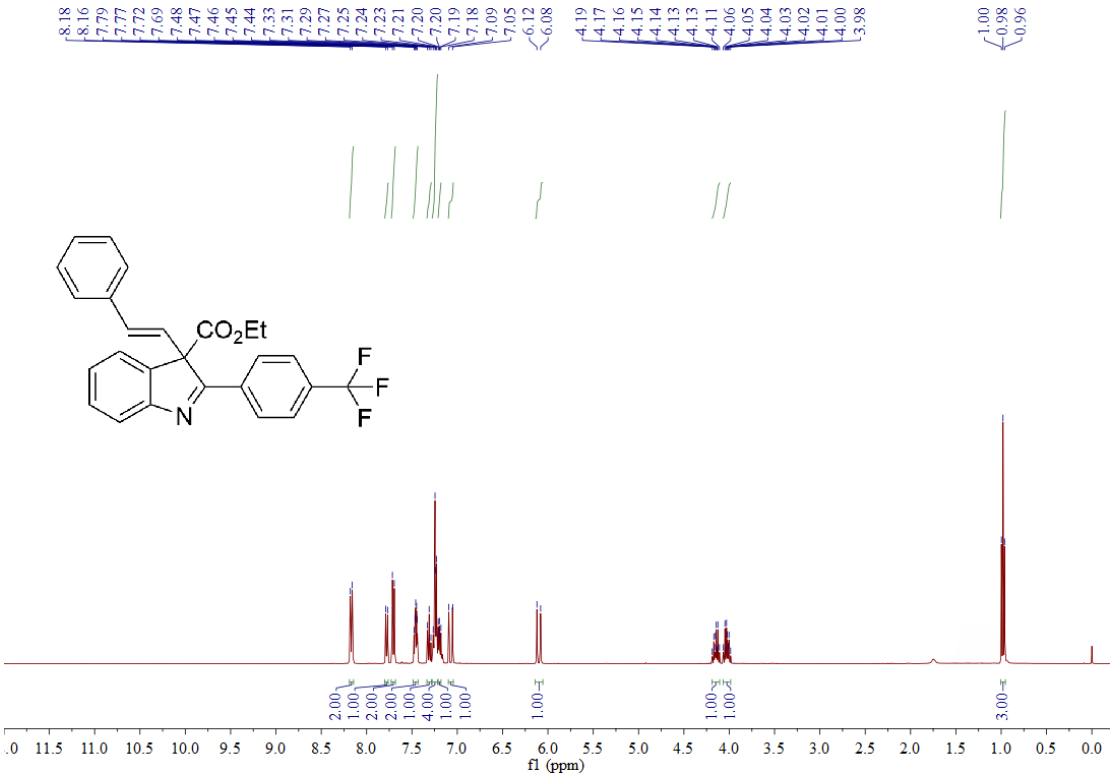


Figure S58 ^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3ap**

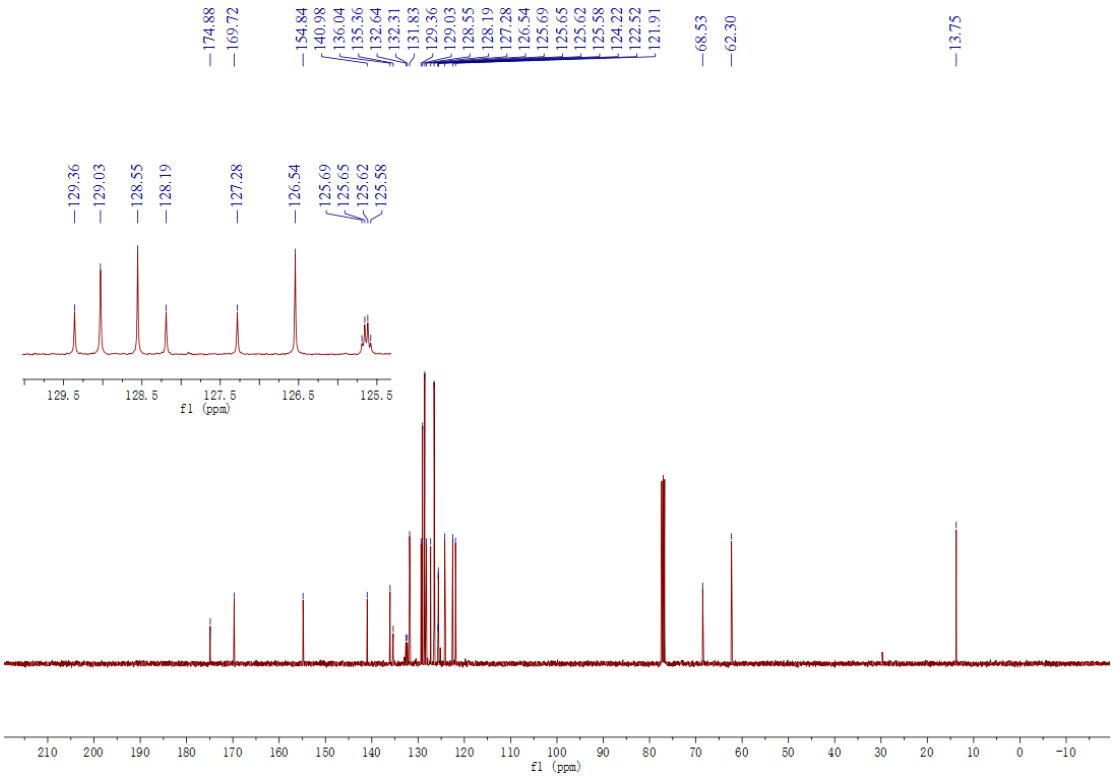


Figure S59 ^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3ap**

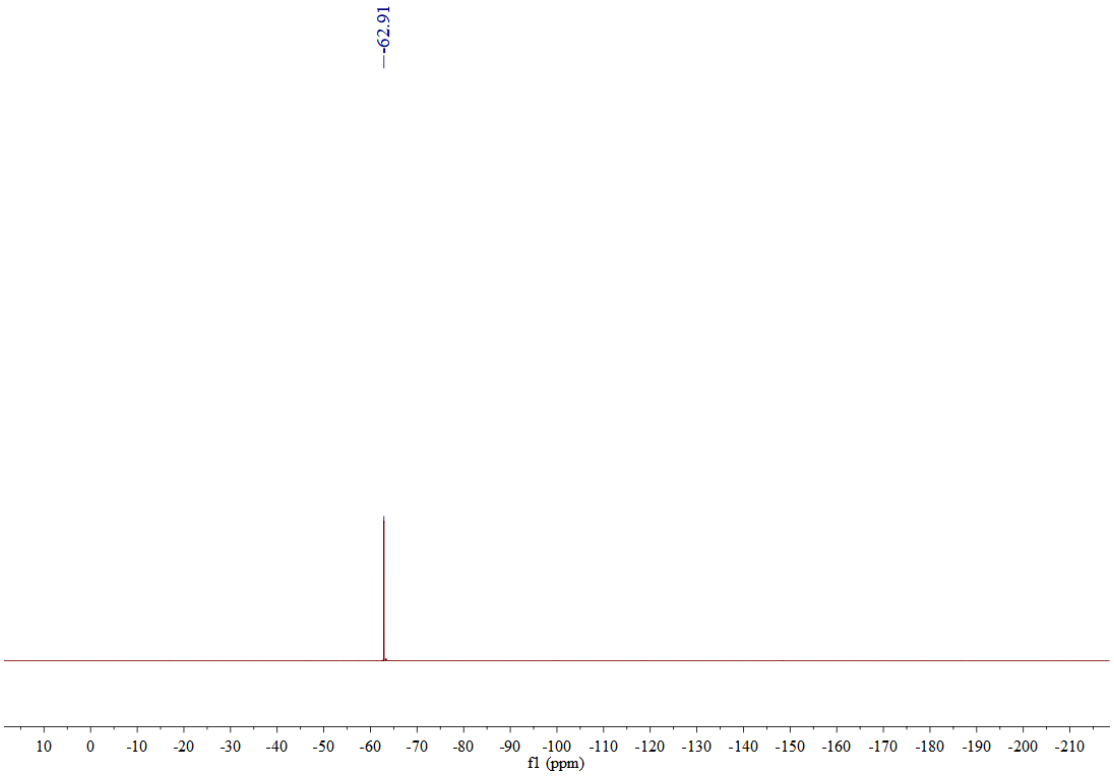


Figure S60 ^{19}F NMR (376 MHz, $CDCl_3$) spectra of **3ap**

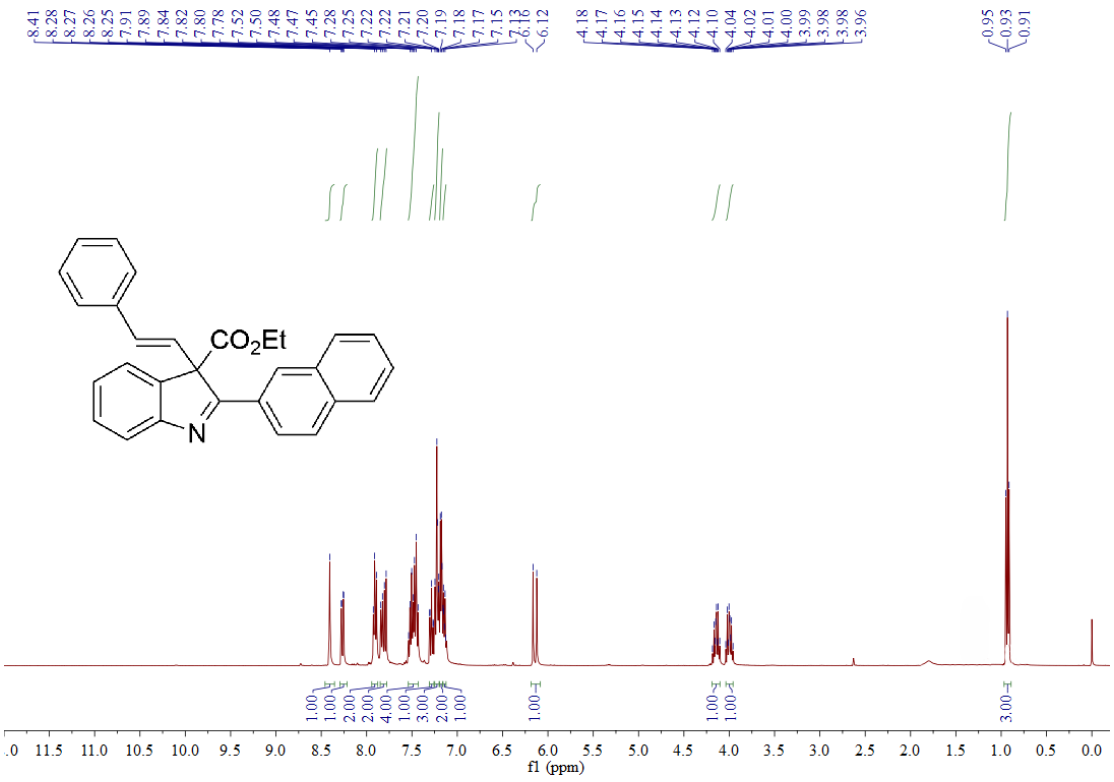


Figure S61 ^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3aq**

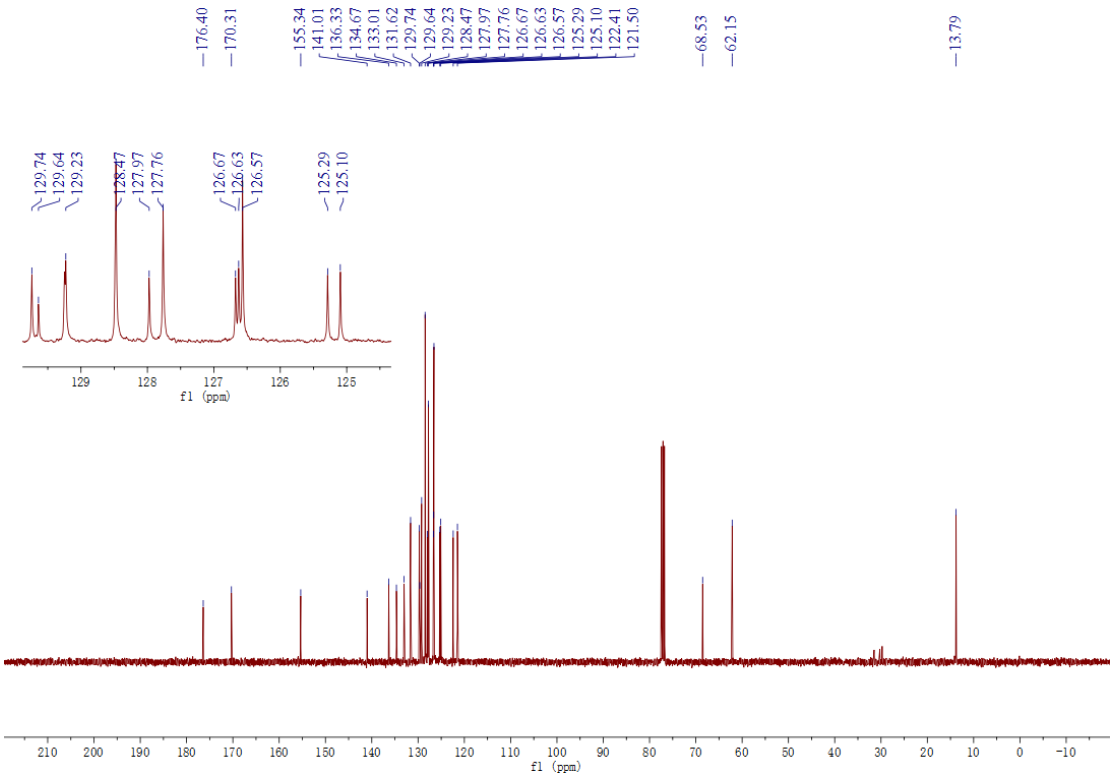


Figure S62 ^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3aq**

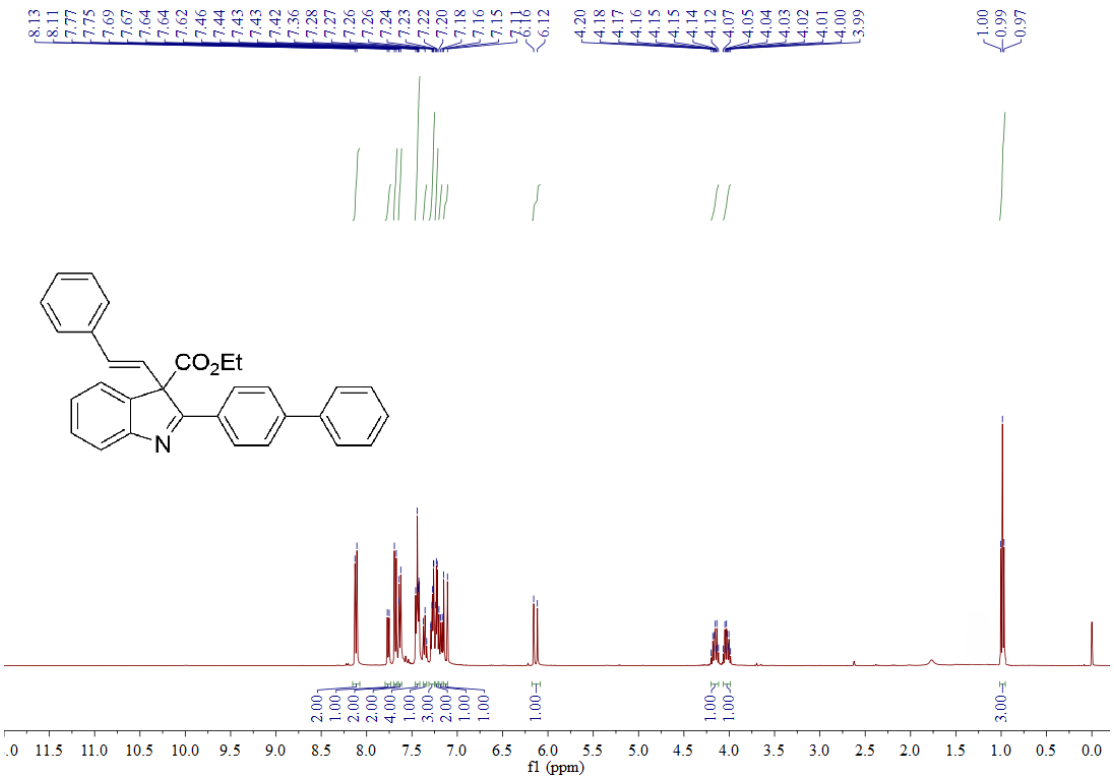


Figure S63 ^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3ar**

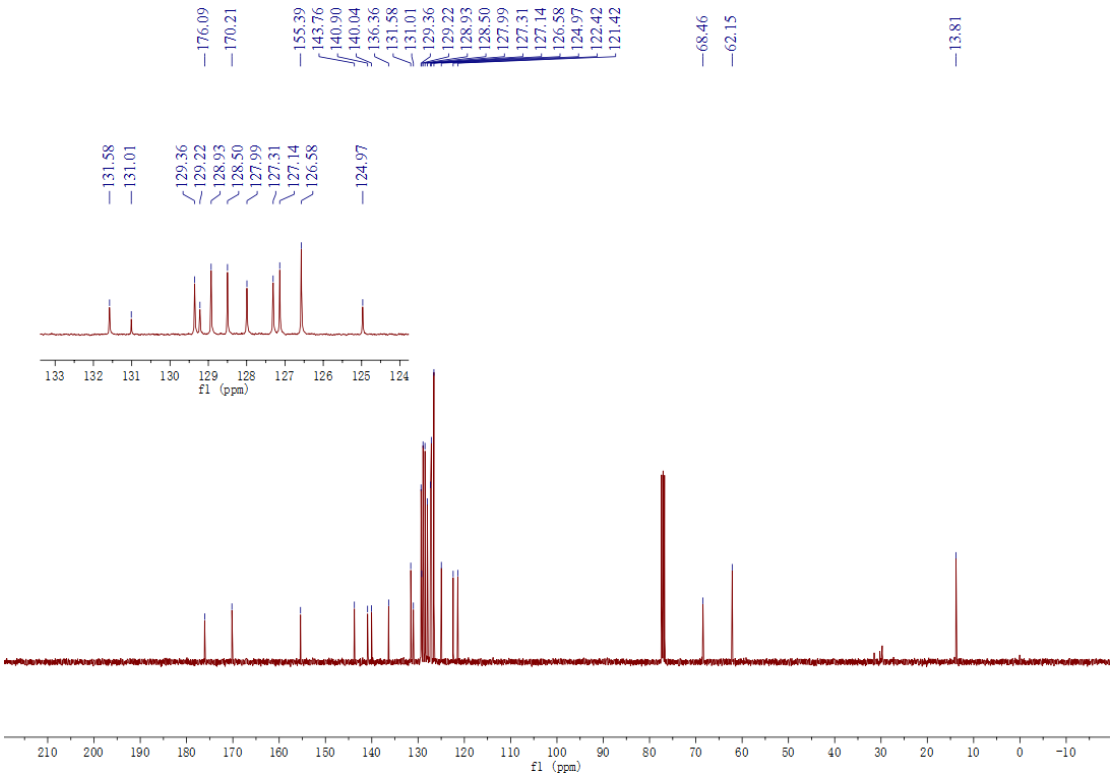


Figure S64 ^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3ar**

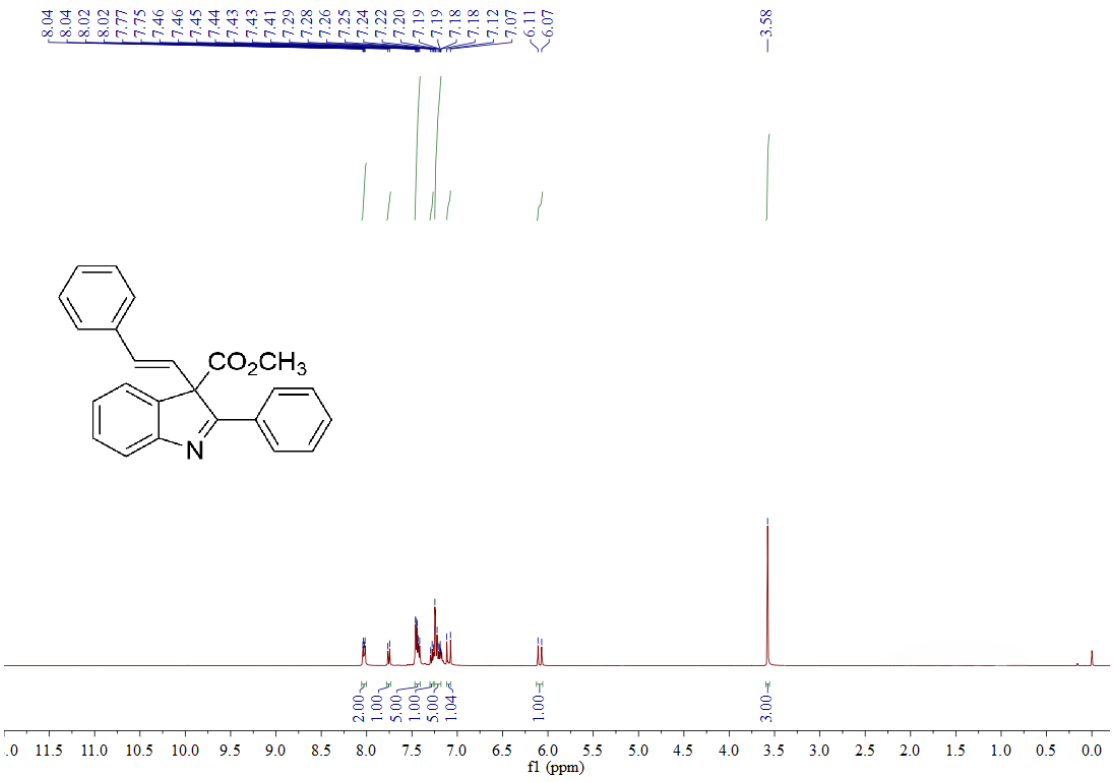


Figure S65 ^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3as**

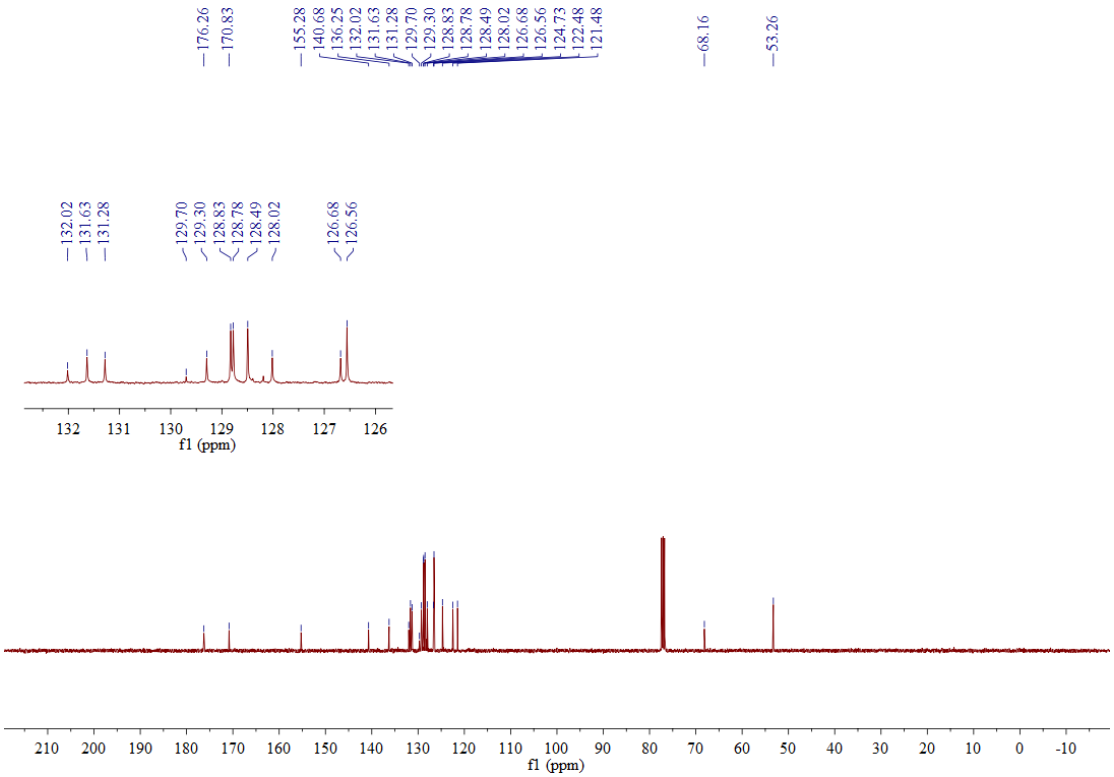


Figure S66 ^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3as**

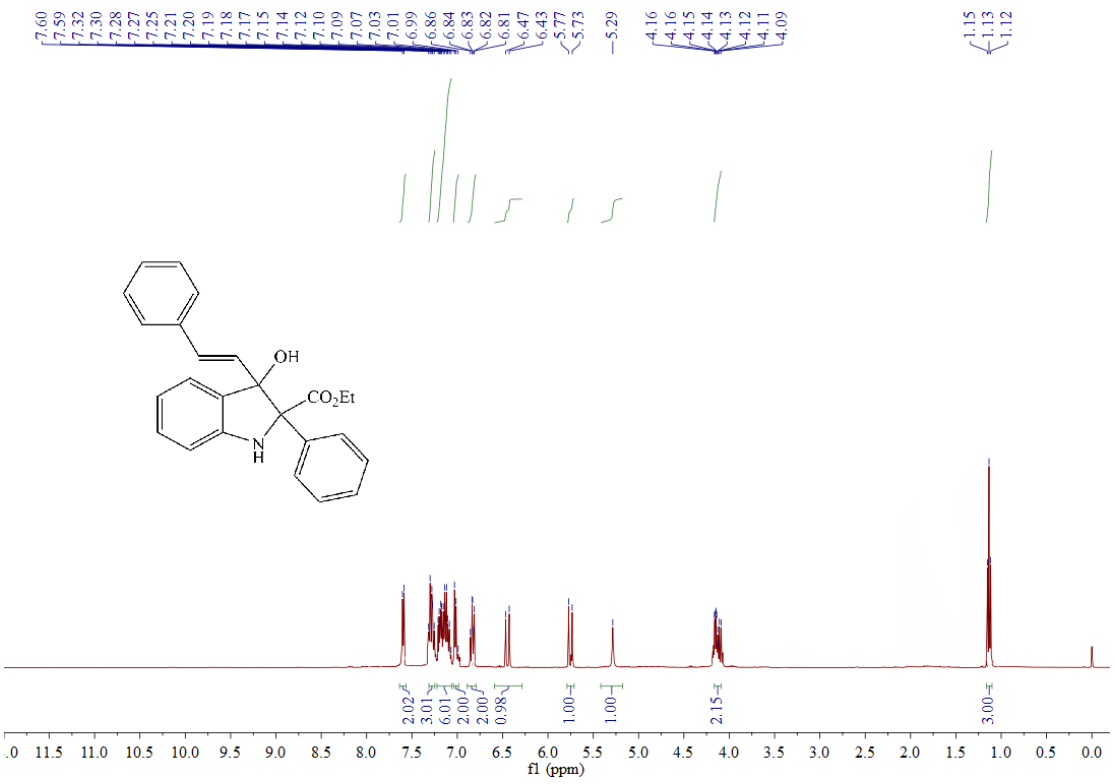


Figure S67 ^{1}H NMR (400 MHz, $CDCl_3$) spectra of **4**

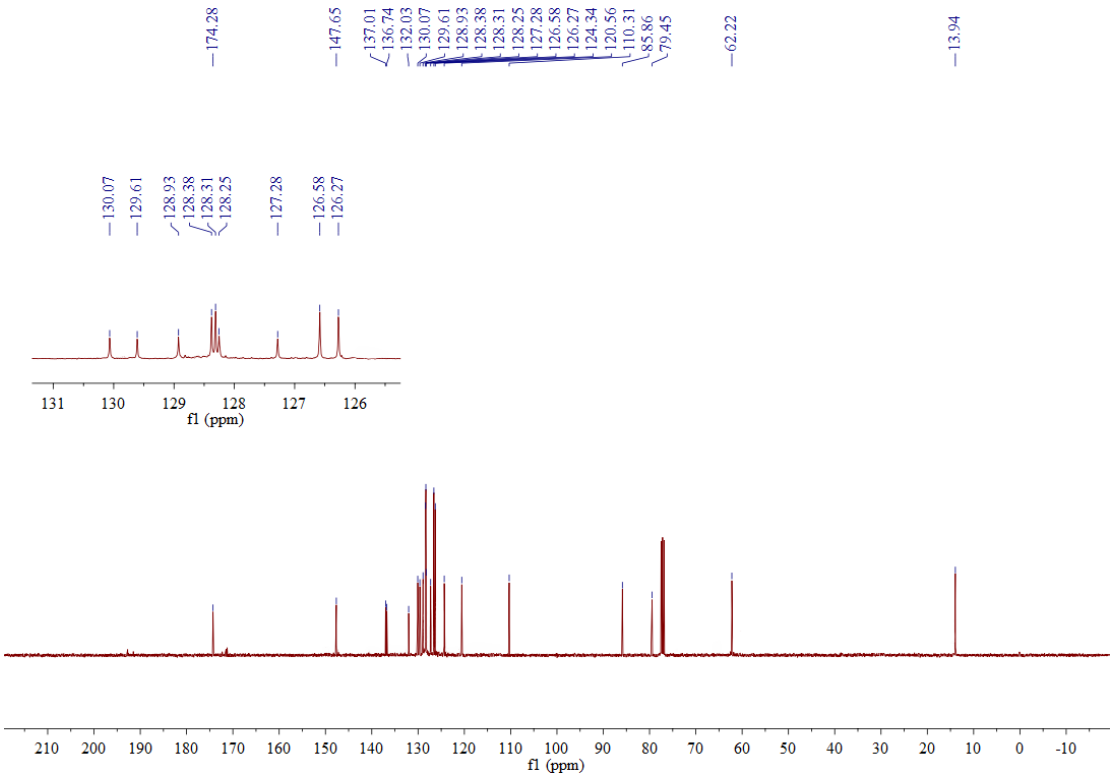


Figure S68 ^{13}C NMR (101 MHz, $CDCl_3$) spectra of **4**