Supporting Information for

Rh(III)-Catalyzed Spiroannulation of 3-Arylquinoxalin-2(1*H*)-ones with Alkynes: Practical Access to Spiroquinoxalinones

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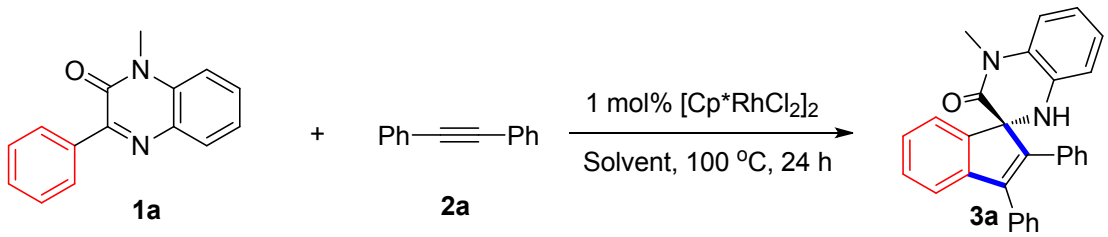
I. General Information

All reactions were performed under Argon. The reagents used for experiments were purchased from Adamas, Aladdin, Accela, Sigma-Aldrich, Acros Organics, TCI, and Alfa Aesar and used as received unless otherwise noted. DMF, DCE, Toluene, PhCl, 1,4-Dioxane, Aceton and CH_3CN were distilled from CaH_2 under Argon. ^1H, ^{13}C and ^{19}F NMR spectra were recorded on Bruker Avance 400 MHz and 300 MHz spectrometer. Chemical shifts were reported in the scale relative to TMS (0.00 ppm). Data were reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz), integration. High resolution mass spectroscopy (HRMS) was recorded on a TOF MS mass spectrometer. Column chromatography was carried out on silica gel (300-400 mesh). X-Ray single-crystal diffraction data were collected on Bruker D8 VENTURE X-ray single crystal diffractometer at Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences. 1-Methyl-3-phenylquinoxalin-2(1*H*)-one derivatives[1-3] and internal alkynes[4,5] were prepared according to the literature procedures.

35 mL Schlenk tubes were used for all reactions:

II. Optimization of the reaction conditions

Table S1. Seleced results from optimization studies[a]



Entry	$AgSbF_6$ (mol%)	Solvent	Additive	Yield (%)[b]
1	4	DCE	-	< 10
2	4	Dioxane	-	< 10
3	4	CH_3CN	-	62
4	4	PhCl	-	< 10
5	4	Aceton	-	16
6	4	Toluene	-	Trace
7	4	^{t}BuOH	-	< 10
8	4	DMF	-	< 10

9[c]	4	CH_3CN	PivOH	86
10	5	CH_3CN	PivOH	91
11	**6**	**CH_3CN**	PivOH	**97**
12	6	CH_3CN	Phenol	59
13	6	CH_3CN	TFA	< 10
14	6	CH_3CN	MsOH	0
15[c]	3	CH_3CN	PivOH	76
16[d]	1.5	CH_3CN	PivOH	60
17[c,e]	3	CH_3CN	PivOH	78
18[d,e]	1.5	CH_3CN	PivOH	65
19	0	CH_3CN	PivOH	0
20[f]	6	CH_3CN	PivOH	0

[a] Reaction conditions: **1a** (0.2 mmol, 0.0473 g), **2a** (0.22 mmol, 0.0393 g), $[Cp^*RhCl_2]_2$ (1 mol%, 0.0013 g) , $AgSbF_6$ (4 mol%, 0.0028 g), additive (1 equiv), 2 mL of solvent, 100 °C, 24 h. [b] Isolated yields. [c] 0.5 mmol scale, 0.5 mol% of $[Cp^*RhCl_2]_2$ was used. [d] 0.5 mmol scale, 0.25 mol% of $[Cp^*RhCl_2]_2$ was used. [e] The reaction ran at 120 °C for 24 h. [f] In the absence of $[Cp^*RhCl_2]_2$

III. General Procedure:

An oven dried 35 mL Schlenk tube equipped with a stir bar was fitted with a rubber septum and cooled under vacuum. After cooling, the tube was charged with $[Cp^*RhCl_2]_2$ (1 mol%), $AgSbF_6$ (6 mol%), 1-methyl-3-phenylquinoxalin-2(1*H*)-one (0.2 mmol), 1,2-diphenylethyne (1.1 equiv), PivOH (1 equiv), and CH_3CN (2 mL) under Argon, and was evacuted and refilled with Argon for three times. Then, the septum was replaced by a Teflon screwcap under Argon flow. The reaction mixture was stirred at 100 °C for 24 h. Upon completion, the reaction mixture was diluted with 10 mL of ethyl acetate, filtered through a pad of silica gel, followed by washing the pad of the silica gel with the ethyl acetate (30 mL). The filtrate was concentrated under reduced pressure. The residue was then purified by chromatography on silica gel to provide the corresponding product **3** or **4**.

VI. Graphical Information:

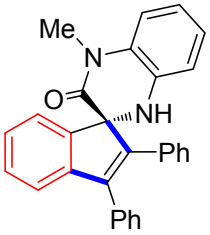
Left to Right: $[Cp^*RhCl_2]_2$, 1,2-Diphenylethyne, 1-Methyl-3-phenylquinoxalin-2(1*H*)-one, Pivalic acid,

Schlenk tube cooled under vacuum

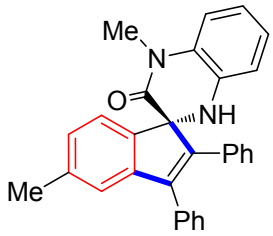
After the addition of catalyst, additive and SM

Septum replaced by Teflon screwcap

V. Characterization data for the spirocyclic products:

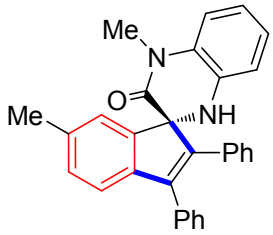


4'-Methyl-2,3-diphenyl-1'*H*-spiro[indene-1,2'-quinoxalin]-3'(4'*H*)-one (3a): The title compound was prepared according to the general procedure. White solid (80.5 mg, 97%; eluent: 5%-15% ethyl acetate/hexane). Mp: 231-233 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51-7.35 (m, 7H), 7.33-7.25 (m, 2H), 7.18-7.15 (dd, *J* = 7.4, 4.4 Hz, 4H), 7.09 (td, *J* = 7.3, 1.7 Hz, 1H), 7.01 (dd, *J* = 7.5, 1.5 Hz, 1H), 6.94 (pd, *J* = 7.4, 1.5 Hz, 2H), 6.65 (dd, *J* = 7.3, 1.6 Hz, 1H), 4.25 (s, 1H), 3.51 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.34, 146.99, 144.20, 143.16, 143.01, 134.46, 134.34, 134.09, 129.93, 129.42, 129.20, 128.70, 128.67, 127.89, 127.84, 127.35, 126.73, 123.72, 122.02, 121.41, 119.59, 114.71, 114.43, 73.25, 29.61. HRMS (ESI): calcd for $C_{29}H_{23}N_2O$ $[M+H]^+$: 415.1810, found 415.1802.

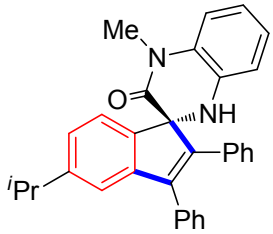


4',5-Dimethyl-2,3-diphenyl-1'*H*-spiro[indene-1,2'-quinoxalin]-3'(4'*H*)-one (3b): The title compound was prepared according to the general procedure. White solid (79.7 mg, 93%; eluent: 5%-15% ethyl acetate/hexane). Mp: 225-227 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47-7.40 (m, 7H), 7.19-7.17 (m, 3H), 7.12 (s, 1H), 7.09-7.00 (m, 2H), 6.98-6.91 (m, 3H), 6.65 (dd, *J* = 7.2, 1.8 Hz, 1H), 4.25 (s, 1H), 3.52 (s, 3H), 2.36 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.50, 144.46,

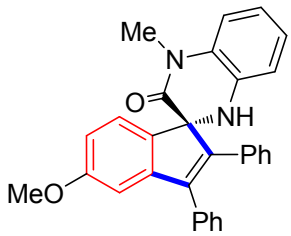
144.23, 143.41, 143.06, 139.24, 134.66, 134.47, 134.18, 129.97, 129.48, 128.77, 128.71, 127.84, 127.31, 127.27, 123.68, 122.21, 121.80, 119.55, 114.72, 114.41, 72.95, 29.60, 21.67. HRMS (ESI): calcd for $C_{30}H_{25}N_2O$ $[M+H]^+$: 429.1967, found 429.1975.



4',6-Dimethyl-2,3-diphenyl-1'*H*-spiro[indene-1,2'-quinoxalin]-3'(4'*H*)-one (3c): The title compound was prepared according to the general procedure. White solid (81.6 mg, 95%; eluent: 5%-15% ethyl acetate/hexane). Mp: 230-232 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49-7.37 (m, 7H), 7.23-7.15 (m, 5H), 7.04 (s, 1H), 7.01-6.90 (m, 3H), 6.64 (d, J = 7.2 Hz, 1H), 4.31 (s, 1H), 3.52 (s, 3H), 2.31 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.43, 147.53, 143.62, 142.78, 140.61, 136.77, 134.65, 134.31, 129.93, 129.77, 129.44, 128.64, 128.50, 127.83, 127.23, 123.73, 123.05, 121.18, 119.40, 114.54, 114.41, 73.25, 29.59, 21.60. HRMS (ESI): calcd for $C_{30}H_{25}N_2O$ $[M+H]^+$: 429.1967, found 429.1953.

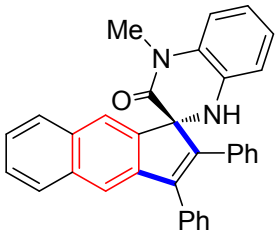


5-Isopropyl-4'-methyl-2,3-diphenyl-1'*H*-spiro[indene-1,2'-quinoxalin]-3'(4'*H*)-one (3d): The title compound was prepared according to the general procedure. White solid (82.2 mg, 90%; eluent: 5%-15% ethyl acetate/hexane). Mp: 183-185 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53-7.39 (m, 7H), 7.24-7.16 (m, 4H), 7.11 (d, J = 7.7 Hz, 1H), 7.04-6.92 (m, 4H), 6.66 (dd, J = 7.2, 1.7 Hz, 1H), 4.28 (s, 1H), 3.53 (s, 3H), 2.93 (hept, J = 6.9 Hz, 1H), 1.27 (d, J = 6.9 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.60, 150.36, 144.61, 144.45, 143.31, 143.25, 134.69, 134.53, 134.25, 130.00, 129.51, 128.81, 128.73, 127.85, 127.30, 124.68, 123.70, 121.95, 119.79, 119.57, 114.78, 114.42, 72.95, 34.43, 29.62, 24.22, 24.12. HRMS (ESI): calcd for $C_{32}H_{29}N_2O$ $[M+H]^+$: 457.2280, found 457.2282.

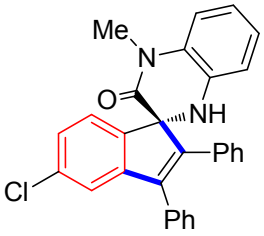


5-Methoxy-4'-methyl-2,3-diphenyl-1'*H*-spiro[indene-1,2'-quinoxalin]-3'(4'*H*)-one (3e): The title compound was prepared according to the general procedure. White solid (46.1 mg, 52%; eluent: 5%-15% ethyl acetate/hexane). Mp: 214-216 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46-7.34 (m, 7H), 7.17-7.15 (m, 3H), 7.04-6.99 (m, 2H), 6.95-6.91 (m, 2H), 6.82 (d, J = 2.3 Hz, 1H), 6.66 (dd, J = 7.4, 1.5 Hz, 1H), 6.58 (dd, J = 8.2, 2.3 Hz, 1H), 4.19 (s, 1H), 3.76 (s, 3H), 3.51 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.49, 160.94, 144.95, 142.73, 139.14, 134.43, 134.37, 129.91,

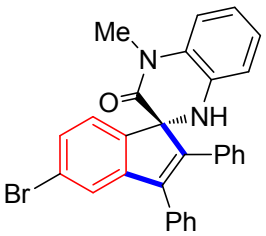
129.39, 128.76, 128.67, 127.88, 127.79, 127.35, 123.64, 122.69, 119.57, 114.71, 114.37, 111.25, 108.02, 72.60, 55.55, 29.58. HRMS (ESI): calcd for $C_{30}H_{25}N_2O_2$ $[M+H]^+$: 445.1916, found 445.1913.



4'-Methyl-2,3-diphenyl-1'*H*-spiro[cyclopenta[*b*]naphthalene-1,2'-quinoxalin]-3'(4'*H*)-one (3f): The title compound was prepared according to the general procedure. White solid (75.3 mg, 81%; eluent: 5%-15% ethyl acetate/hexane). Mp: 211-213 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 7.9 Hz, 1H), 7.66-7.61 (m, 2H), 7.56-7.50 (m, 3H), 7.49-7.38 (m, 7H), 7.23-7.15 (m, 3H), 7.07-7.05 (m, 1H), 7.01-6.92 (m, 2H), 6.66 (dd, *J* = 6.0, 3.0 Hz, 1H), 4.32 (s, 1H), 3.53 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.45, 144.83, 143.23, 141.51, 134.51, 134.31, 134.13, 134.08, 132.58, 129.99, 129.52, 128.74, 128.58, 128.33, 128.24, 128.01, 127.85, 127.49, 126.42, 125.78, 123.80, 121.01, 119.87, 119.62, 114.77, 114.48, 72.83, 29.62. HRMS (ESI): calcd for $C_{33}H_{25}N_2O$ $[M+H]^+$: 465.1967, found 465.1966.

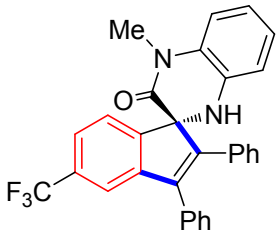


5-Chloro-4'-methyl-2,3-diphenyl-1'*H*-spiro[indene-1,2'-quinoxalin]-3'(4'*H*)-one (3g): The title compound was prepared according to the general procedure. White solid (77.9 mg, 87%; eluent: 5%-15% ethyl acetate/hexane). Mp: 221-223 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46-7.32 (m, 7H), 7.24 (s, 1H), 7.20-7.15 (m, 3H), 7.05 (s, 2H), 7.01-6.90 (m, 3H), 6.68-6.62 (m, 1H), 4.23 (s, 1H), 3.50 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.83, 145.81, 145.18, 145.10, 142.04, 135.31, 133.97, 133.79, 133.61, 129.87, 129.27, 128.83, 128.53, 128.17, 127.89, 127.65, 126.43, 123.85, 122.96, 121.67, 119.83, 114.72, 114.51, 72.86, 29.65. HRMS (ESI): calcd for $C_{29}H_{22}ClN_2O$ $[M+H]^+$: 449.1421, found 449.1423.

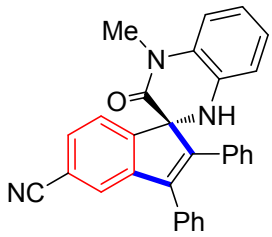


5-Bromo-4'-methyl-2,3-diphenyl-1'*H*-spiro[indene-1,2'-quinoxalin]-3'(4'*H*)-one (3h): The title compound was prepared according to the general procedure. White solid (69.1 mg, 70%; eluent: 5%-15% ethyl acetate/hexane). Mp: 240-242 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46-7.32 (m, 8H), 7.22-7.16 (m, 4H), 7.03-6.89 (m, 4H), 6.65 (d, *J* = 7.0 Hz, 1H), 4.23 (s, 1H), 3.50 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) 165.75, 145.70, 145.61, 145.43, 142.00, 133.94, 133.77, 133.56, 129.87, 129.36, 129.26, 128.84, 128.52, 128.17, 127.88, 127.66, 124.53, 123.86, 123.46, 123.33, 119.84,

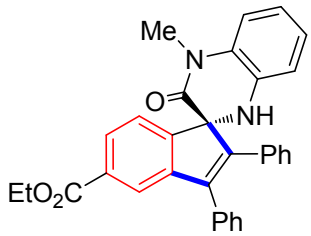
114.72, 114.51, 72.93, 29.65. HRMS (ESI): calcd for $C_{29}H_{22}BrN_2O$ $[M+H]^+$: 493.0916, found 493.0894.



4'-Methyl-2,3-diphenyl-5-(trifluoromethyl)-1'*H*-spiro[indene-1,2'-quinoxalin]-3'(4'*H*)-one (3i): The title compound was prepared according to the general procedure. White solid (70.4 mg, 73%; eluent: 5%-15% ethyl acetate/hexane). Mp: 221-223 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (s, 1H), 7.50-7.36 (m, 8H), 7.29 (d, *J* = 7.7 Hz, 1H), 7.25-7.12 (m, 3H), 7.05-7.00 (m, 1H), 6.99-6.89 (m, 2H), 6.62 (dd, *J* = 5.8, 3.2 Hz, 1H), 4.42 (s, 1H), 3.48 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.65, 150.39, 146.09, 144.23, 141.97, 133.89, 133.65, 133.53, 131.58 (q, *J* = 32.1 Hz), 129.92, 129.28, 129.00, 128.43, 128.35, 127.97, 127.81, 123.90 (q, *J* = 3.9 Hz), 124.20 (q, *J* = 273.6 Hz), 124.01, 122.29, 119.95, 117.97 (q, *J* = 3.7Hz), 114.78, 114.62, 73.26, 29.64. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.17 (s, 3F). HRMS (ESI): calcd for $C_{30}H_{22}F_3N_2O$ $[M+H]^+$: 483.1684, found 483.1668.

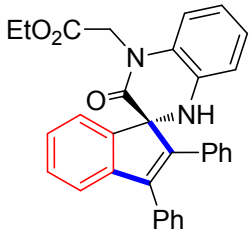


4'-Methyl-3'-oxo-2,3-diphenyl-3',4'-dihydro-1'*H*-spiro[indene-1,2'-quinoxaline]-5-carbonitrile (3j): The title compound was prepared according to the general procedure using $[Cp^*RhCl_2]_2$ (2 mol%) and $AgSbF_6$ (12 mol%). White solid (44.9 mg, 51%; eluent: 5%-20% ethyl acetate/hexane). Mp: 227-229 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (s, 1H), 7.47-7.36 (m, 6H), 7.35-7.30 (m, 2H), 7.24-7.13 (m, 4H), 7.03-6.91 (m, 3H), 6.67 (dd, *J* = 7.4, 1.4 Hz, 1H), 4.24 (s, 1H), 3.50 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.14, 151.16, 146.28, 144.41, 141.43, 133.48, 133.16, 133.12, 130.93, 129.80, 129.14, 128.99, 128.48, 128.32, 127.98, 124.32, 124.07, 122.61, 120.14, 118.89, 114.75, 114.66, 112.97, 73.43, 29.75. HRMS (ESI): calcd for $C_{30}H_{22}N_3O$ $[M+H]^+$: 440.1763, found 440.1756.

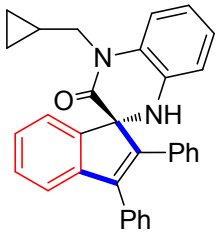


Ethyl-4'-methyl-3'-oxo-2,3-diphenyl-3',4'-dihydro-1'H-spiro[indene-1,2'-quinoxaline]-5-carboxylate (3k): The title compound was prepared according to the general procedure. White solid (86.7 mg, 89%; eluent: 5%-25% ethyl acetate/hexane). Mp: 210-212 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (s, 1H), 7.82 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.48-7.31 (m, 7H), 7.23-7.11 (m, 4H), 7.01-6.90 (m, 3H), 6.65 (d, *J* = 7.2 Hz, 1H), 4.42-4.25 (m, 3H), 3.49 (s, 3H), 1.36 (t, *J* = 7.1 Hz, 3H).

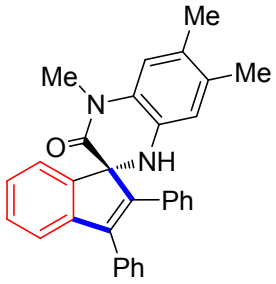
^{13}C NMR (101 MHz, $CDCl_3$) δ 166.39, 165.71, 151.37, 145.14, 143.58, 142.39, 133.93, 133.87, 133.74, 131.51, 129.88, 129.35, 128.81, 128.61, 128.51, 128.11, 127.87, 127.58, 123.88, 122.08, 121.84, 119.82, 114.71, 114.52, 73.19, 61.09, 29.66, 14.33. HRMS (ESI): calcd for $C_{32}H_{27}N_2O_3$ $[M+H]^+$: 487.2022, found 487.2013.



Ethyl 2-(3'-oxo-2,3-diphenyl-1'*H*-spiro[indene-1,2'-quinoxalin]-4'(3'*H*)-yl)acetate (3l): The title compound was prepared according to the general procedure. White solid (86.5 mg, 89%; eluent: 5%-25% ethyl acetate/hexane). Mp: 181-183 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50-7.37 (m, 7H), 7.34-7.26 (m, 3H), 7.24-7.17 (m, 3H), 7.13-7.06 (m, 1H), 7.01-6.88 (m, 2H), 6.85 (d, J = 7.7 Hz, 1H), 6.67 (dd, J = 7.6, 1.2 Hz, 1H), 5.15 (d, J = 17.5 Hz, 1H), 4.50 (d, J = 17.5 Hz, 1H), 4.35-4.16 (m, 3H), 1.27 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.30, 166.91, 146.51, 143.57, 143.35, 143.01, 134.55, 134.23, 133.88, 130.01, 129.42, 129.33, 128.78, 127.99, 127.93, 127.74, 127.43, 126.77, 124.15, 122.46, 121.40, 119.82, 115.34, 114.09, 72.92, 61.70, 44.23, 14.22. HRMS (ESI): calcd for $C_{32}H_{27}N_2O_3$ $[M+H]^+$: 487.2022, found 487.2027.

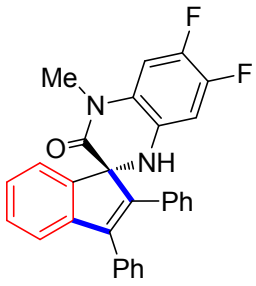


4'-(Cyclopropylmethyl)-2,3-diphenyl-1'*H*-spiro[indene-1,2'-quinoxalin]-3'(4'*H*)-one (3m): The title compound was prepared according to the general procedure. White solid (83.7 mg, 92%; eluent: 5%-15% ethyl acetate/hexane). Mp: 183-185 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55-7.38 (m, 7H), 7.38-7.29 (m, 2H), 7.26 (d, J = 7.4 Hz, 1H), 7.20 (d, J = 2.8 Hz, 3H), 7.12 (t, J = 6.7 Hz, 1H), 6.96 (dd, J = 8.9, 5.3 Hz, 2H), 6.69-6.60 (m, 1H), 4.25 (s, 1H), 4.13 (dd, J = 14.5, 6.3 Hz, 1H), 4.02 (dd, J = 14.5, 7.3 Hz, 1H), 1.40-1.27 (m, 1H), 0.58-0.51 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.23, 147.20, 144.27, 143.19, 142.89, 134.62, 134.49, 134.10, 130.03, 129.49, 129.20, 128.75, 127.95, 127.84, 127.36, 126.74, 123.64, 122.03, 121.44, 119.50, 115.08, 114.85, 73.13, 46.05, 9.84, 4.04. HRMS (ESI): calcd for $C_{32}H_{27}N_2O$ $[M+H]^+$: 455.2123, found 455.2112.

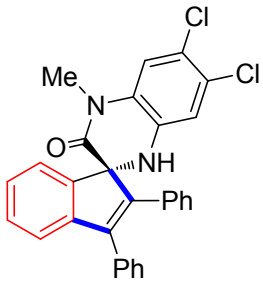


4',6',7'-Trimethyl-2,3-diphenyl-1'*H*-spiro[indene-1,2'-quinoxalin]-3'(4'*H*)-one (3n): The title compound was prepared according to the general procedure. White solid (66.4 mg, 75%; eluent: 5%-15% ethyl acetate/hexane). Mp: 257-259 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51-7.36 (m, 7H),

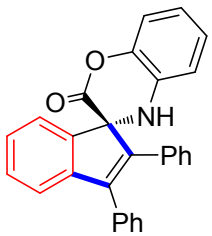
7.29 (t, *J* = 8.0 Hz, 2H), 7.19-7.15 (m, 4H), 7.08 (td, *J* = 7.3, 1.6 Hz, 1H), 6.83 (s, 1H), 6.47 (s, 1H), 4.06 (s, 1H), 3.52 (s, 3H), 2.32 (s, 3H), 2.21 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.24, 147.13, 144.14, 143.12, 142.95, 134.68, 134.15, 131.86, 131.67, 129.94, 129.45, 129.10, 128.69, 127.86, 127.81, 127.39, 127.25, 126.61, 126.58, 121.95, 121.32, 116.32, 115.84, 73.30, 29.58, 19.43, 19.22. HRMS (ESI): calcd for $C_{31}H_{27}N_2O$ $[M+H]^+$: 443.2123, found 443.2120.



6',7'-Difluoro-4'-methyl-2,3-diphenyl-1'*H*-spiro[indene-1,2'-quinoxalin]-3'(4'*H*)-one (3o): The title compound was prepared according to the general procedure. Pale yellow solid (74.8 mg, 83%; eluent: 5%-15% ethyl acetate/hexane). Mp: 216-218 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44-7.27 (m, 9H), 7.20-7.12 (m, 5H), 6.78 (dd, *J* = 11.5, 7.3 Hz, 1H), 6.40 (dd, *J* = 10.7, 7.3 Hz, 1H), 4.29 (s, 1H), 3.39 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.98, 147.22 (d, *J* = 13.3 Hz), 146.45, 145.09-144.65 (m), 143.97, 143.23, 143.1, 142.56 (d, *J* = 13.5 Hz), 133.99 (d, *J* = 13.5 Hz), 130.72 (d, *J* = 8.2 Hz), 129.85, 129.46, 129.34, 128.65, 128.00, 127.90, 127.53, 126.89, 124.65 (d, *J* = 5.0 Hz), 122.09, 121.61, 104.09 (d, *J* = 23.1 Hz), 103.26 (d, *J* = 21.8 Hz), 73.04, 29.85. ^{19}F NMR (376 MHz, $CDCl_3$) δ -144.03 (d, *J* = 22.4 Hz, 1F), -149.04 (d, *J* = 22.4 Hz, 1F). HRMS (ESI): calcd for $C_{29}H_{21}F_2N_2O$ $[M+H]^+$: 451.1622, found 451.1621.

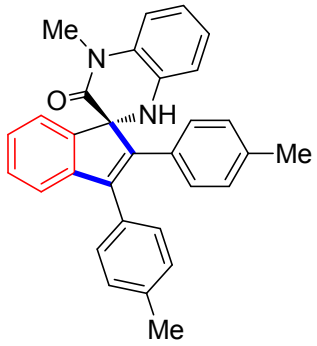


6',7'-Dichloro-4'-methyl-2,3-diphenyl-1'*H*-spiro[indene-1,2'-quinoxalin]-3'(4'*H*)-one (3p): The title compound was prepared according to the general procedure. Pale yellow solid (83.2 mg, 86%; eluent: 5%-15% ethyl acetate/hexane). Mp: 239-241 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45-7.24 (m, 9H), 7.22-7.11 (m, 5H), 7.00 (s, 1H), 6.61 (s, 1H), 4.33 (s, 1H), 3.41 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.63, 146.52, 143.76, 143.30, 143.10, 134.01, 133.87, 133.79, 129.83, 129.55, 129.34, 128.71, 128.23, 128.08, 128.01, 127.59, 126.97, 126.50, 122.01, 121.94, 121.67, 115.77, 115.26, 72.96, 29.74. HRMS (ESI): calcd for $C_{29}H_{21}Cl_2N_2O$ $[M+H]^+$: 483.1031, found 483.1029.

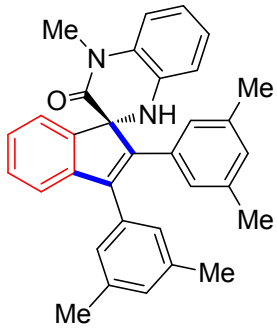


2',3'-Diphenylspiro[benzo[*b*][1,4]oxazine-3,1'-inden]-2(4*H*)-one (3q): The title compound was

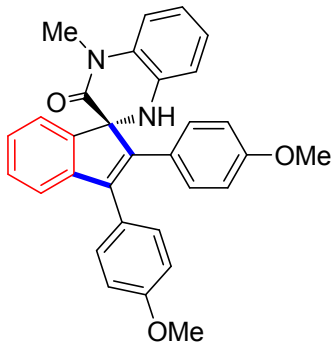
prepared according to the general procedure. White solid (70.9 mg, 88%; eluent: 5%-10% ethyl acetate/hexane). Mp: 180-182 °C. ^{1}H NMR (400 MHz, CDCl3) δ 7.49-7.30 (m, 9H), 7.25-7.20 (m, 4H), 7.16-7.09 (m, 2H), 7.04 (td, *J* = 7.7, 1.2 Hz, 1H), 6.93 (t, *J* = 7.7 Hz, 1H), 6.74 (d, *J* = 7.8 Hz, 1H), 4.16 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.19, 145.42, 143.88, 143.27, 142.52, 141.18, 133.88, 133.27, 131.87, 129.89, 129.81, 129.32, 128.80, 128.24, 128.09, 127.77, 127.15, 125.34, 122.18, 121.85, 120.33, 116.74, 115.54, 71.88. HRMS (ESI): calcd for $C_{28}H_{20}NO_2$ $[M+H]^+$: 402.1494, found 402.1488.



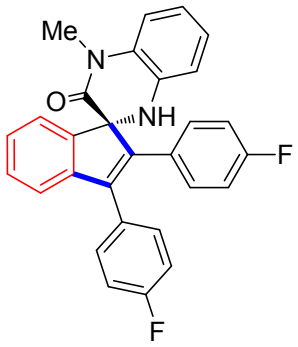
4'-Methyl-2,3-di-p-tolyl-1'*H*-spiro[indene-1,2'-quinoxalin]-3'(4'*H*)-one (4a): The title compound was prepared according to the general procedure. White solid (86.0 mg, 97%; eluent: 5%-15% ethyl acetate/hexane). Mp: 209-211 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.0 Hz, 2H), 7.34-7.28 (m, 4H), 7.26 (d, *J* = 7.9 Hz, 2H), 7.14 (d, *J* = 7.4 Hz, 1H), 7.09-6.99 (m, 4H), 6.98-6.91 (m, 2H), 6.65 (dt, *J* = 6.8, 3.3 Hz, 1H), 4.22 (s, 1H), 3.53 (s, 3H), 2.45 (s, 3H), 2.31 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.52, 146.96, 143.68, 143.42, 142.45, 137.55, 137.01, 134.47, 131.67, 131.23, 129.78, 129.44, 129.33, 129.16, 128.79, 128.67, 126.49, 123.69, 121.87, 121.32, 119.52, 114.79, 114.40, 73.10, 29.62, 21.47, 21.32. HRMS (ESI): calcd for $C_{31}H_{27}N_2O$ $[M+H]^+$: 443.2123, found 443.2113.



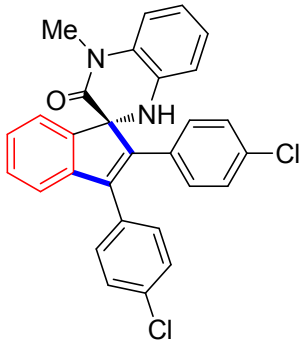
2,3-Bis(3,5-dimethylphenyl)-4'-methyl-1'*H*-spiro[indene-1,2'-quinoxalin]-3'(4'*H*)-one (4b): The title compound was prepared according to the general procedure. White solid (66.8 mg, 71%; eluent: 5%-15% ethyl acetate/hexane). Mp: 171-173 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30-7.23 (m, 2H), 7.14 (d, *J* = 7.3 Hz, 1H), 7.10-7.04 (m, 3H), 7.01-6.87 (m, 6H), 6.78 (s, 1H), 6.65 (d, *J* = 6.9 Hz, 1H), 4.18 (s, 1H), 3.51 (s, 3H), 2.32 (s, 6H), 2.15 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.67, 146.90, 144.09, 143.62, 142.76, 137.88, 136.78, 134.56, 134.43, 133.77, 129.37, 129.07, 129.03, 128.80, 127.67, 126.99, 126.46, 123.55, 121.95, 121.41, 119.41, 114.62, 114.29, 73.14, 29.55, 21.40, 21.35. HRMS (ESI): calcd for $C_{33}H_{31}N_2O$ $[M+H]^+$: 471.2436, found 471.2426.



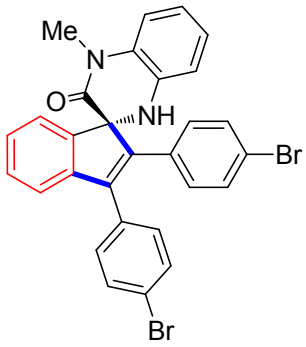
2,3-Bis(4-methoxyphenyl)-4'-methyl-1'*H*-spiro[indene-1,2'-quinoxalin]-3'(4'*H*)-one (4c): The title compound was prepared according to the general procedure. White solid (78.9 mg, 83%; eluent: 5%-15% ethyl acetate/hexane). Mp: 170-172 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.24 (m, 6H), 7.09 (d, *J* = 7.3 Hz, 1H), 7.06-7.00 (m, 2H), 6.99-6.89 (m, 4H), 6.72 (d, *J* = 8.7 Hz, 2H), 6.65 (d, *J* = 7.5 Hz, 1H), 4.17 (s, 1H), 3.87 (s, 3H), 3.76 (s, 3H), 3.52 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.56, 159.12, 158.63, 146.77, 143.47, 142.96, 141.42, 134.43, 131.09, 130.68, 129.11, 128.79, 126.91, 126.59, 126.31, 123.67, 121.79, 121.10, 119.55, 114.72, 114.39, 114.13, 113.38, 72.96, 55.23, 55.09, 29.58. HRMS (ESI): calcd for $C_{31}H_{27}N_2O_3$ $[M+H]^+$: 475.2022, found 475.2027.



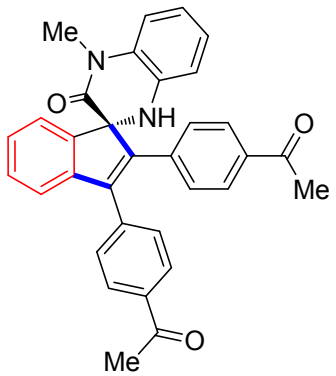
2,3-Bis(4-fluorophenyl)-4'-methyl-1'*H*-spiro[indene-1,2'-quinoxalin]-3'(4'*H*)-one (4d): The title compound was prepared according to the general procedure. White solid (77.4 mg, 86%; eluent: 5%-15% ethyl acetate/hexane). Mp: 233-235 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43-7.28 (m, 5H), 7.25 (d, *J* = 7.4 Hz, 1H), 7.17-7.07 (m, 4H), 7.07-6.91 (m, 3H), 6.88 (t, *J* = 8.7 Hz, 2H), 6.68-6.63 (m, 1H), 4.27 (s, 1H), 3.48 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.09, 163.46 (d, *J* = 37.7 Hz), 161.00 (d, *J* = 37.9 Hz), 146.76, 143.44, 142.75, 142.11, 134.17, 131.62 (d, *J* = 7.9 Hz), 131.16 (d, *J* = 8.0 Hz), 130.09 (d, *J* = 3.3 Hz), 129.31, 128.64, 126.95, 123.85, 122.13, 121.21, 119.85, 115.86 (d, *J* = 21.5 Hz), 115.12, 114.91, 114.78, 114.52, 73.28, 29.60. ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.13 (s, 1F), -113.79 (s, 1F). HRMS (ESI): calcd for $C_{29}H_{21}F_2N_2O$ $[M+H]^+$: 451.1622, found 451.1617.



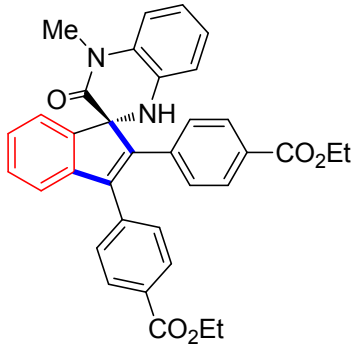
2,3-Bis(4-chlorophenyl)-4'-methyl-1'*H*-spiro[indene-1,2'-quinoxalin]-3'(4'*H*)-one (4e): The title compound was prepared according to the general procedure. White solid (86.1 mg, 89%; eluent: 5%-15% ethyl acetate/hexane). Mp: 232-234 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (q, *J* = 8.5 Hz, 4H), 7.34-7.28 (m, 3H), 7.23 (d, *J* = 7.5 Hz, 1H), 7.16 (d, *J* = 8.6 Hz, 2H), 7.12-7.07 (m, 2H), 7.03-7.01 (m, 1H), 6.99-6.93 (m, 2H), 6.0 (dd, *J* = 7.1, 1.8 Hz, 1H), 4.21 (s, 1H), 3.49 (s, 3H). ^{13}C NMR (101 MHz, CDCl3) δ 165.92, 146.76, 143.43, 142.44, 142.38, 134.02, 133.49, 132.52, 132.39, 131.11, 130.72, 129.35, 129.13, 128.64, 128.27, 127.12, 123.88, 122.12, 121.26, 119.95, 114.83, 114.56, 73.27, 29.63. HRMS (ESI): calcd for $C_{29}H_{21}Cl_2N_2O$ $[M+H]^+$: 483.1031, found 483.1016.



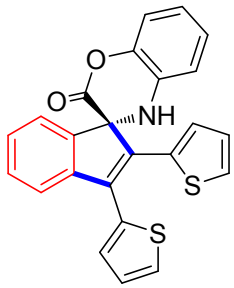
2,3-Bis(4-bromophenyl)-4'-methyl-1'*H*-spiro[indene-1,2'-quinoxalin]-3'(4'*H*)-one (4f): The title compound was prepared according to the general procedure. White solid (101.9 mg, 89%; eluent: 5%-15% ethyl acetate/hexane). Mp: 208-210 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.4 Hz, 2H), 7.35-7.22 (m, 8H), 7.16-7.06 (m, 2H), 7.05-7.00 (m, 1H), 6.99-6.92 (m, 2H), 6.63 (dd, *J* = 5.8, 3.3 Hz, 1H), 4.28 (s, 1H), 3.47 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.89, 146.80, 143.45, 142.50, 142.30, 134.03, 133.01, 132.87, 132.12, 131.42, 131.25, 131.03, 129.39, 128.61, 127.18, 123.93, 122.29, 122.14, 121.87, 121.29, 119.95, 114.87, 114.59, 73.25, 29.65. HRMS (ESI): calcd for $C_{29}H_{21}Br_2N_2O$ $[M+H]^+$: 571.0021, found 571.0018.



1,1'-((4'-Methyl-3'-oxo-3',4'-dihydro-1'*H*-spiro[indene-1,2'-quinoxaline]-2,3-diyl)bis(4,1-phenylene))diethanone (4g): The title compound was prepared according to the general procedure. White solid (74.8 mg, 75%; eluent: 5%-25% ethyl acetate/hexane). Mp: 152-154 °C. ^{1}H NMR (300 MHz, CDCl3) δ 7.95 (d, *J* = 8.3 Hz, 2H), 7.71 (d, *J* = 8.5 Hz, 2H), 7.47-7.42 (m, 4H), 7.32-7.24 (m, 1H), 7.19 (d, *J* = 7.4 Hz, 1H), 7.14-7.05 (m, 2H), 7.03-6.96 (m, 1H), 6.96-6.87 (m, 2H), 6.64-6.62 (m, 1H), 4.62 (s, 1H), 3.44 (s, 3H), 2.60 (s, 3H), 2.48 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.73, 165.83, 147.00, 144.32, 143.72, 142.02, 139.15, 138.99, 136.62, 135.73, 134.05, 130.00, 129.61, 129.42, 128.87, 128.51, 127.97, 127.49, 123.99, 122.23, 121.44, 119.91, 114.92, 114.60, 73.46, 29.64, 26.67, 26.55. HRMS (ESI): calcd for $C_{33}H_{27}N_2O_3$ $[M+H]^+$: 499.2022, found 499.2011.

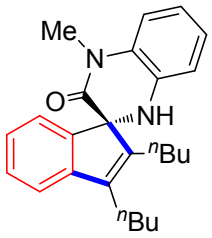


Diethyl-4,4'-(4'-methyl-3'-oxo-3',4'-dihydro-1'*H*-spiro[indene-1,2'-quinoxaline]-2,3-diyl)dibenzoate (4h): The title compound was prepared according to the general procedure. White solid (91.6 mg, 82%; eluent: 5%-30% ethyl acetate/hexane). Mp: 206-208 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.1 Hz, 2H), 7.81 (d, *J* = 8.3 Hz, 2H), 7.44 (dd, *J* = 14.6, 8.2 Hz, 4H), 7.32-7.28 (m, 1H), 7.22 (d, *J* = 7.5 Hz, 1H), 7.16 (d, *J* = 7.3 Hz, 1H), 7.10 (t, *J* = 7.3 Hz, 1H), 7.02-6.97 (m, 1H), 6.95-6.89 (m, 1H), 6.65-6.63 (m, 1H), 4.63 (s, 1H), 4.39 (q, *J* = 7.1 Hz, 2H), 4.31 (q, *J* = 7.1 Hz, 2H), 3.45 (s, 3H), 1.42 (t, *J* = 7.1 Hz, 3H), 1.35 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.31, 166.28, 165.85, 147.10, 144.45, 143.60, 142.14, 138.86, 138.69, 134.12, 130.10, 130.03, 129.80, 129.39, 129.21, 129.11, 128.49, 127.37, 123.94, 122.21, 121.41, 119.79, 114.84, 114.54, 73.47, 61.15, 60.90, 29.60, 14.38, 14.34. HRMS (ESI): calcd for $C_{35}H_{31}N_2O_5$ $[M+H]^+$: 559.2233, found 559.2225.

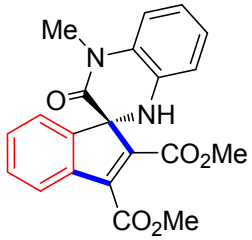


2',3'-Di(thiophen-2-yl)spiro[benzo[*b*][1,4]oxazine-3,1'-inden]-2(4*H*)-one (4i): The title compound was prepared according to the general procedure. Brown oil (67.8 mg, 82%; eluent: 5%-10% ethyl acetate/hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 5.0 Hz, 1H), 7.39-7.19 (m, 7H), 7.15 (d, *J* = 7.3 Hz, 1H), 7.10 (t, *J* = 7.6 Hz, 2H), 6.99 (dd, *J* = 11.7, 6.3 Hz, 2H), 6.78 (d, *J* = 7.7 Hz, 1H), 4.29 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.45, 144.35, 143.34, 141.14, 138.53, 135.40, 134.79, 133.59, 131.40, 130.19, 129.00, 128.76, 127.92, 127.67, 127.47, 127.26, 126.95, 125.57, 121.90, 121.81, 120.64, 116.89, 115.77, 71.46. HRMS (ESI): calcd for

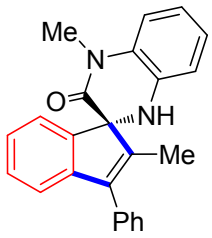
$C_{24}H_{16}NO_2S_2$ $[M+H]^+$: 414.0622, found 414.0608.



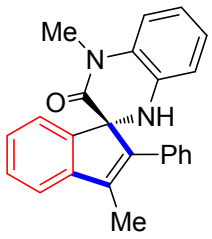
2,3-Dibutyl-4'-methyl-1'*H*-spiro[indene-1,2'-quinoxalin]-3'(4'*H*)-one (4j): The title compound was prepared according to the general procedure. White solid (73.5 mg, 98%; eluent: 5%-15% ethyl acetate/hexane). Mp: 71-73 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31-7.24 (m, 1H), 7.21 (d, *J* = 7.3 Hz, 1H), 7.06-6.92 (m, 5H), 6.67 (dd, *J* = 7.3, 1.5 Hz, 1H), 3.95 (s, 1H), 3.48 (s, 3H), 2.56 (t, *J* = 7.6 Hz, 2H), 2.49 (m, 1H), 2.33 (m, 1H), 1.75-1.44 (m, 6H), 1.43-1.32 (m, 2H), 1.02 (t, *J* = 7.2 Hz, 3H), 0.93 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.80, 146.82, 144.97, 144.07, 141.11, 134.81, 128.87, 128.80, 125.39, 123.60, 121.70, 119.49, 119.28, 114.49, 114.38, 72.83, 31.90, 30.74, 29.50, 26.37, 25.43, 23.47, 23.03, 14.13, 13.91. HRMS (ESI): calcd for $C_{25}H_{31}N_2O$ $[M+H]^+$: 375.2436, found 375.2435.



Dimethyl-4'-methyl-3'-oxo-3',4'-dihydro-1'*H*-spiro[indene-1,2'-quinoxaline]-2,3-dicarboxylate (4k): The title compound was prepared according to the general procedure. White solid (73.4 mg, 97%; eluent: 5%-30% ethyl acetate/hexane). Mp: 92-94 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.52 (d, *J* = 7.5 Hz, 1H), 7.35 (t, *J* = 6.4 Hz, 1H), 7.27-7.16 (m, 2H), 7.03-6.84 (m, 3H), 6.62 (d, *J* = 7.4 Hz, 1H), 4.38 (s, 1H), 3.92 (s, 3H), 3.60 (s, 3H), 3.43 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.40, 164.25, 163.38, 147.45, 142.84, 140.60, 137.38, 132.82, 129.78, 129.73, 128.46, 123.86, 123.57, 123.00, 119.97, 114.77, 114.45, 72.13, 52.62, 52.35, 29.67. HRMS (ESI): calcd for $C_{21}H_{19}N_2O_5$ $[M+H]^+$: 379.1294, found 379.1281.

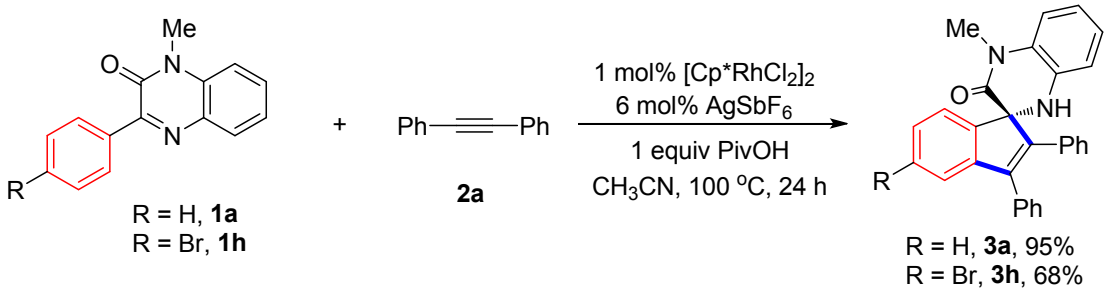


2,4'-Dimethyl-3-phenyl-1'*H*-spiro[indene-1,2'-quinoxalin]-3'(4'*H*)-one (4l): The title compound was prepared according to the general procedure. White solid (45.8 mg, 65%; eluent: 5%-10% ethyl acetate/hexane). Mp: 157-159 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 7.3 Hz, 2H), 7.39-7.26 (m, 5H), 7.10-7.03 (m, 2H), 6.98-6.83 (m, 3H), 6.61 (dd, *J* = 7.4, 1.4 Hz, 1H), 4.08 (s, 1H), 3.46 (s, 3H), 2.24 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.51, 146.72, 144.10, 143.51, 138.92, 134.77, 134.52, 129.51, 129.20, 128.77, 128.06, 127.41, 126.52, 123.55, 121.63, 119.95, 119.50, 114.58, 114.31, 73.32, 29.55, 12.06. HRMS (ESI): calcd for $C_{24}H_{21}N_2O$ $[M+H]^+$: 353.1654, found 353.1641.

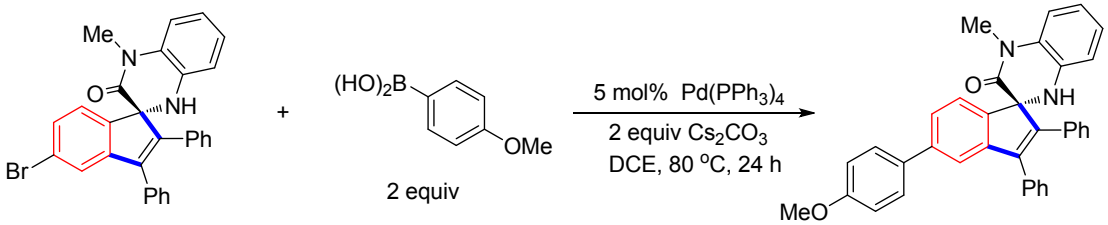


3,4'-Dimethyl-2-phenyl-1'*H*-spiro[indene-1,2'-quinoxalin]-3'(4'*H*)-one (4l'): The title compound was prepared according to the general procedure. White solid (23.8 mg, 34%; eluent: 5%-15% ethyl acetate/hexane). Mp: 169-171 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54-7.48 (m, 4H), 7.47-7.38 (m, 1H), 7.25 (td, *J* = 7.5, 0.8 Hz, 1H), 7.18 (d, *J* = 7.4 Hz, 1H), 7.08 (d, *J* = 8.1 Hz, 2H), 7.03-6.95 (m, 3H), 6.74-6.71 (m, 1H), 4.08 (s, 1H), 3.52 (s, 3H), 2.08 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.17, 146.39, 143.68, 142.91, 140.81, 134.70, 134.01, 129.07, 129.03, 128.97, 128.49, 127.72, 125.65, 123.73, 122.14, 120.33, 119.84, 114.76, 114.54, 72.31, 29.51, 11.35. HRMS (ESI): calcd for $C_{24}H_{21}N_2O$ $[M+H]^+$: 353.1654, found 353.1634.

VI. Gram scale synthesis and synthetic transformations:

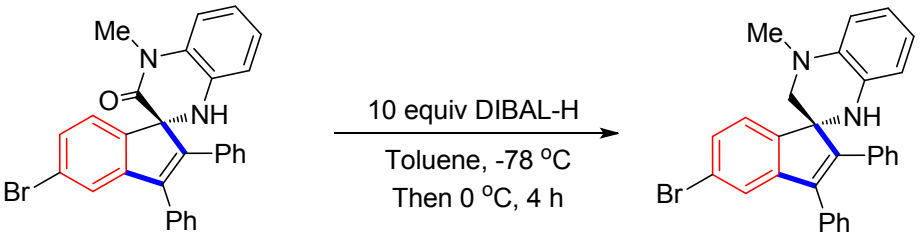


Gram-Scale: An oven dried 75 mL Schlenk tube equipped with a stir bar was fitted with a rubber septum and cooled under vacuum. After cooling, the tube was charged with $[Cp^*RhCl_2]_2$ (1 mol%), $AgSbF_6$ (6 mol%), **1a** (2.0 mmol) or **1h** (2.0 mmol), 1,2-diphenylethyne (1.1 equiv), PivOH (1 equiv), and CH_3CN (20 mL) under Argon, and was evacuated and refilled with Argon for three times. Then, the septum was replaced by a Teflon screwcap under Argon flow. The reaction mixture was stirred at 100 °C for 24 h. Upon completion, the reaction mixture was diluted with 20 mL of ethyl acetate, filtered through a pad of silica gel, followed by washing the pad of the silica gel with the ethyl acetate (50 mL). The filtrate was concentrated under reduced pressure. The residue was then purified by chromatography on silica gel to provide the corresponding product **3a** (0.7876 g, 95%) or **3h** (0.6721 g, 68%).



Procedure: An oven dried 35 mL Schlenk tube equipped with a stir bar was fitted with a rubber septum and cooled under vacuum. After cooling, the tube was charged with **3h** (0.2 mmol), (4-

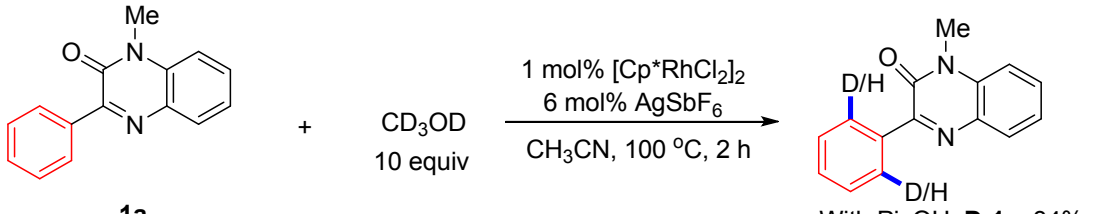
methoxyphenyl)boronic acid (0.4 mmol), Cs_2CO_3 (0.4 mmol), $Pd(PPh_3)_4$ (5 mol%) and DCE (2 mL) under Argon, and was evacuated and refilled with Argon for three times. Then, the septum was replaced by a Teflon screwcap under Argon flow. The reaction mixture was stirred at 80 °C for 24 h. Upon completion, the reaction mixture was diluted with 10 mL of ethyl acetate, filtered through a pad of silica gel, followed by washing the pad of the silica gel with the ethyl acetate (30 mL). The filtrate was concentrated under reduced pressure. The residue was then purified by chromatography on silica gel to afford **4m** as white solid (93.9 mg, 90%, eluent: 5%-15% ethyl acetate/hexane). Mp: 241-243 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53-7.37 (m, 10H), 7.29-7.25 (m, 1H), 7.21 (dd, *J* = 7.0, 3.7 Hz, 4H), 7.04 (dd, *J* = 7.4, 1.6 Hz, 1H), 6.97 (ddd, *J* = 12.9, 6.3, 4.3 Hz, 4H), 6.68 (dd, *J* = 7.1, 1.7 Hz, 1H), 4.33 (s, 1H), 3.86 (s, 3H), 3.55 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.40, 159.28, 145.33, 144.84, 143.83, 142.99, 142.31, 134.48, 134.40, 134.07, 133.77, 129.99, 129.49, 128.79, 128.73, 128.36, 127.97, 127.89, 127.42, 125.38, 123.78, 122.25, 120.00, 119.65, 114.77, 114.49, 114.23, 73.05, 55.39, 29.66. HRMS (ESI): calcd for $C_{36}H_{29}N_2O_2$ $[M+H]^+$: 521.2229, found 521.2227.



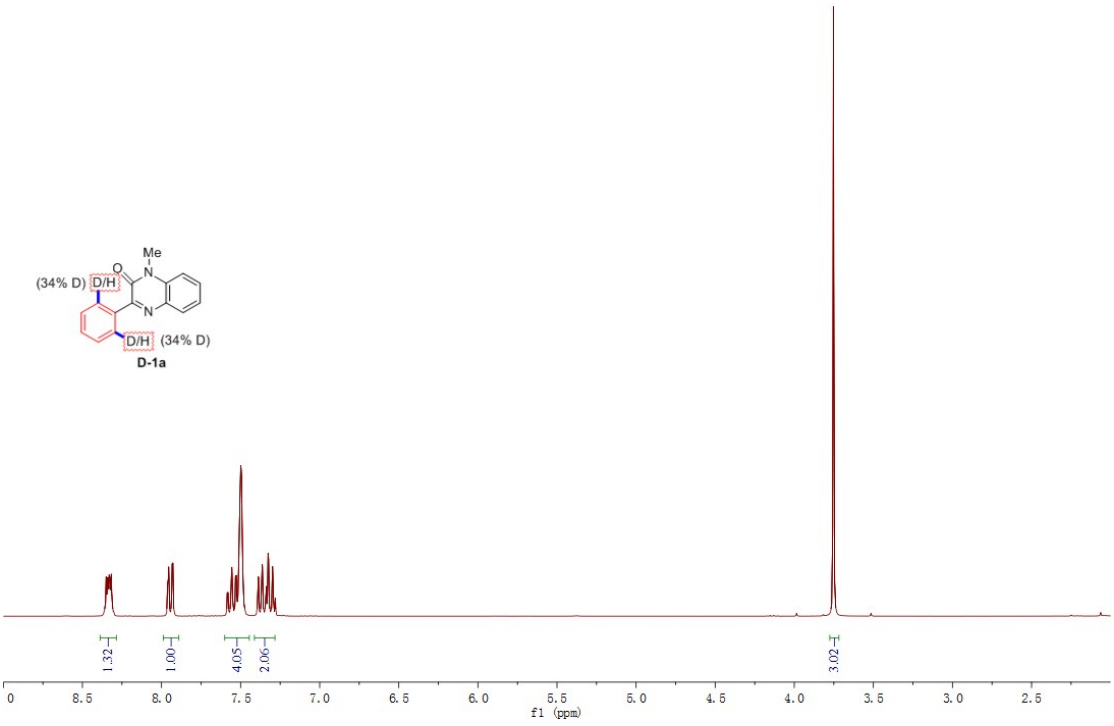
Procedure: An oven dried 35 mL Schlenk tube equipped with a stir bar was fitted with a rubber septum and cooled under vacuum. After cooling, the tube was charged with **3h** (0.2 mmol) and was evacuated and refilled with Argon for three times, and dry toluene (2 mL) was added. Then, the reaction mixture was cooled to -78 °C and DIBAL-H (2 mL, 1M in Hexane) was added. The reaction mixture was stirred at 0 °C for 4 h. Upon completion, the reaction mixture was diluted with 10 mL of ethyl acetate, filtered through a pad of silica gel, followed by washing the pad of the silica gel with the ethyl acetate (30 mL). The filtrate was concentrated under reduced pressure. The residue was then purified by chromatography on silica gel to afford **4n** as white solid (83.4 mg, 87%). Mp: 221-223 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.53-7.31 (m, 8H), 7.31-7.08 (m, 5H), 6.84 (t, *J* = 7.5 Hz, 1H), 6.77-6.54 (m, 3H), 3.99 (s, 1H), 3.51 (d, *J* = 11.2 Hz, 1H), 2.93 (s, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ149.22, 144.98, 144.02, 140.60, 134.86, 134.42, 134.14, 132.25, 129.35, 129.28, 128.80, 127.99, 127.94, 127.72, 124.93, 123.55, 121.85, 119.18, 118.50, 114.54, 111.25, 65.48, 54.76, 38.79. HRMS (ESI): calcd for $C_{29}H_{24}BrN_2$ $[M+H]^+$: 479.1117, found 479.1129.

VII. Mechanistic studies

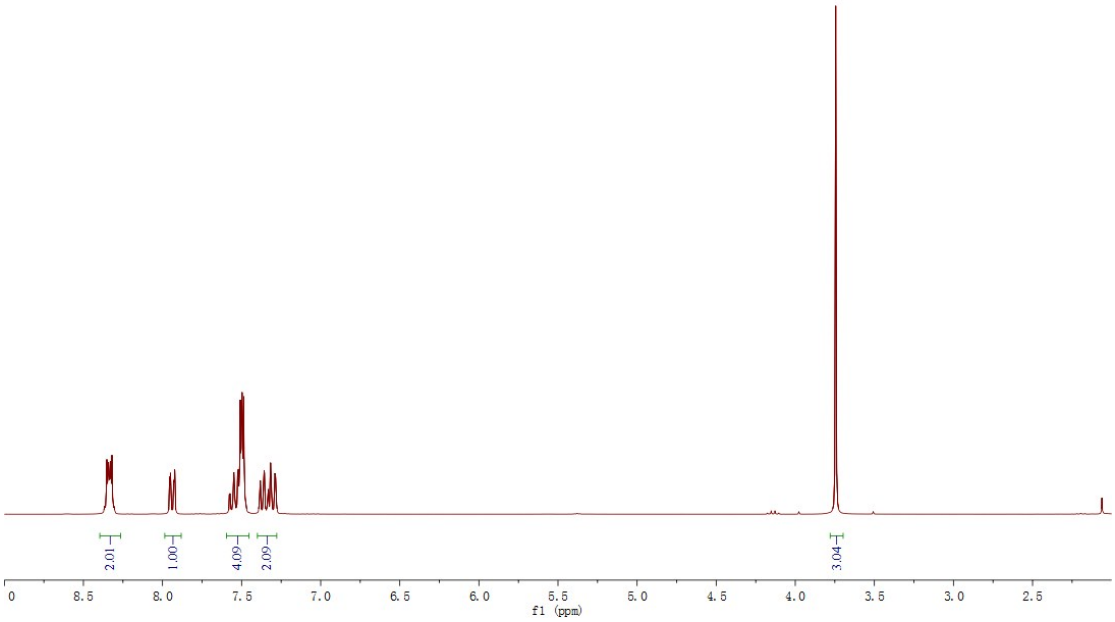
H/D exchange experiment



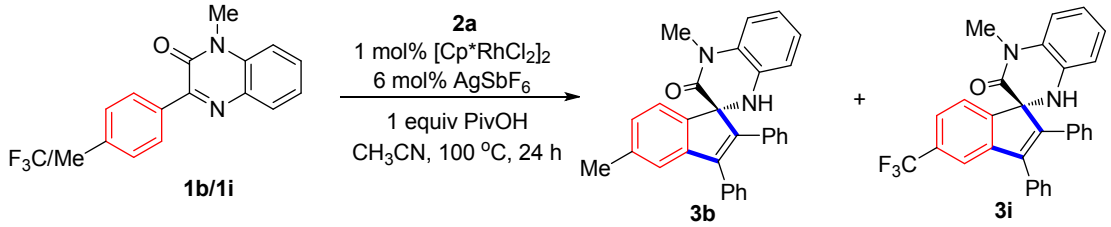
Procedure: An oven dried 35 mL Schlenk tube equipped with a stir bar was fitted with a rubber septum and cooled under vacuum. After cooling, the tube was charged with $[Cp^*RhCl_2]_2$ (1 mol%), $AgSbF_6$ (6 mol%), **1a** (0.2 mmol), CD_3OD (10 equiv), PivOH (1 equiv), and CH_3CN (2 mL) under Argon, and was evacuated and refilled with Argon for three times. Then, the septum was replaced by a Teflon screwcap under Argon flow. The reaction mixture was stirred at 100 °C for 2 h. Upon completion, the reaction mixture was diluted with 10 mL of ethyl acetate, filtered through a pad of silica gel, followed by washing the pad of the silica gel with the ethyl acetate (30 mL). The filtrate was concentrated under reduced pressure. The crude ^1H NMR showed 34% D was incorporated into the two *ortho* positions of **1a**.



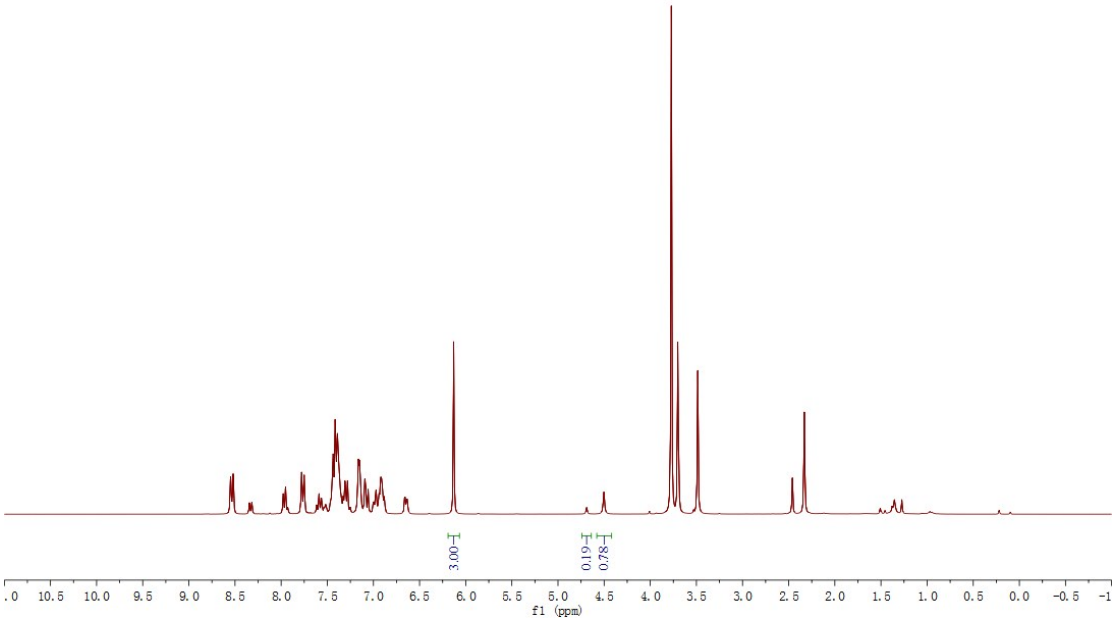
However, we did not observe D incorporation into **1a** in the absence of PivOH indicating PivOH would accerate C-H cyclorhodation.



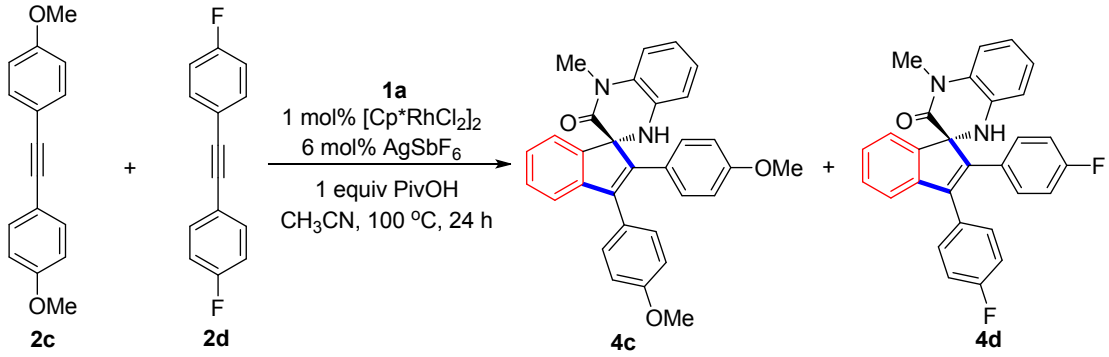
Competition experiment between 3-phenylquinoxalin-2(1*H*)-ones



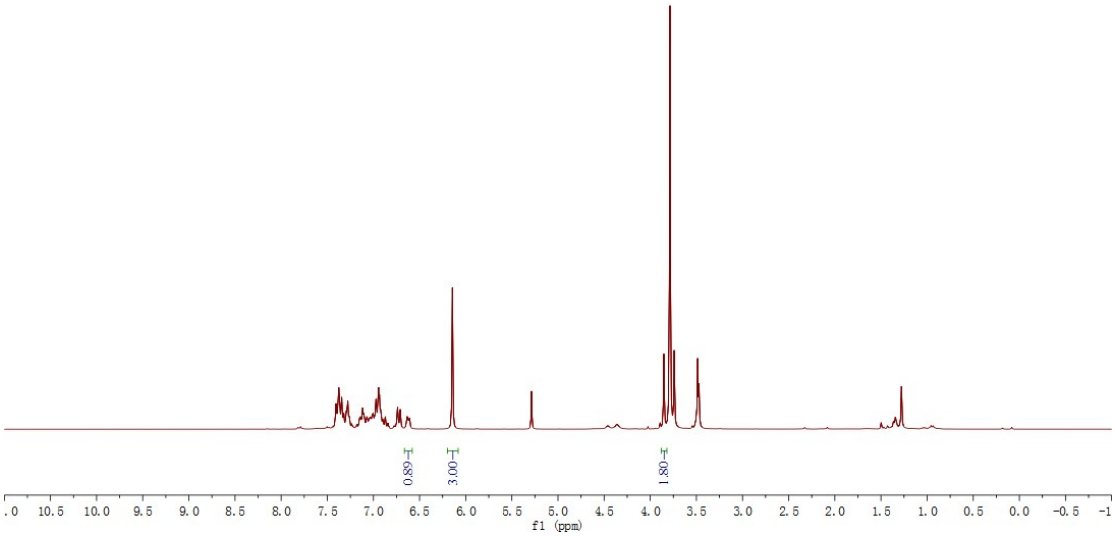
Procedure: An oven dried 35 mL Schlenk tube equipped with a stir bar was fitted with a rubber septum and cooled under vacuum. After cooling, the tube was charged with $[Cp^*RhCl_2]_2$ (1 mol%), $AgSbF_6$ (6 mol%), **1b** (0.2 mmol), **1i** (0.2 mmol), **2a** (0.2 mmol), PivOH (1 equiv), and CH_3CN (2 mL) under Argon, and was evacuated and refilled with Argon for three times. Then, the septum was replaced by a Teflon screwcap under Argon flow. The reaction mixture was stirred at 100 °C for 24 h. Upon completion, the reaction mixture was diluted with 10 mL of ethyl acetate, filtered through a pad of silica gel, followed by washing the pad of the silica gel with the ethyl acetate (30 mL). The filtrate was concentrated under reduced pressure and the residue was then purified by chromatography on silica gel to afford amixture of **3b** and **3i**. The crude ^1H NMR was measured to determine the conversions to the products **3b** (78%) and **3i** (19%) using the 1,3,5-trimethoxybenzene as the internal standard.



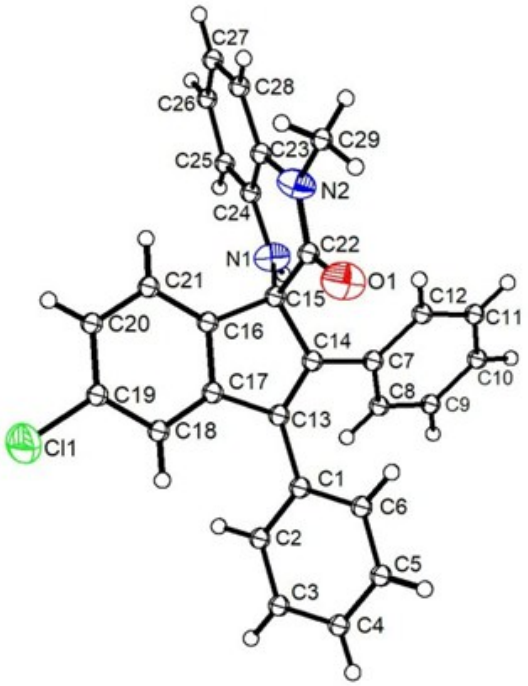
Competition experiment between alkynes



Procedure: An oven dried 35 mL Schlenk tube equipped with a stir bar was fitted with a rubber septum and cooled under vacuum. After cooling, the tube was charged with $[Cp^*RhCl_2]_2$ (1 mol%), $AgSbF_6$ (6 mol%), **1a** (0.2 mmol), **2c** (0.2 mmol), **2d** (0.2 mmol), PivOH (1 equiv), and CH_3CN (2 mL) under Argon, and was evacuated and refilled with Argon for three times. Then, the septum was replaced by a Teflon screwcap under Argon flow. The reaction mixture was stirred at 100 °C for 24 h. Upon completion, the reaction mixture was diluted with 10 mL of ethyl acetate, filtered through a pad of silica gel, followed by washing the pad of the silica gel with the ethyl acetate (30 mL). The filtrate was concentrated under reduced pressure and the residue was then purified by chromatography on silica gel to afford amixture of **4c** and **4d**. The crude ^1H NMR was measured to determine the conversions to the products **4c** (60%) and **4d** (29%) using the 1,3,5-trimethoxybenzene as the internal standard.



VIII. X-ray crystallographic analysis of 3g (CCDC: 1993099)



Identification code	**3g**
Empirical formula	$C_{29}H_{21}ClN_2O$
Formula Mass	448.93
Temperature / K	150(2)
Wavelength / Å	0.71073
Crystal system	orthorhombic
Space group	$Pca2_1$
a / Å	23.099(7)
b / Å	10.570(3)
c / Å	9.121(2)
V / Å^3	2226.8
Z	4
μ / mm^{-1}	0.197
Flack parameter	0.03(9)
F(000)	936.0
Crystal size / mm	0.25 x 0.1 x 0.08
Theta range for data collection / °	2.612 to 26.372
Index ranges	-28<=h<=28, -13<=k<=13, -11<=l<=11
ρ_{calcd} /g cm^{-3}	1.339
Measured refls.	17396
Independent refls.	4372
Completeness to theta = 25.242°	99.5%
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4372 / 1 / 304
R_{int}	0.0570
[a]R indices [$I > 2\sigma(I)$] R_1, $wR2$	0.0372, 0.0811
R indices (all data) R_1, $wR2$	0.0540, 0.0918
GOF	1.026
Largest diff. peak and hole / e.Å^{-3}	0.125 and -0.198
CCDC reference numbers	1993099

IX. References

[1] Xue, Z.-Y.; Jiang, Y.; Peng, X.-Z.; Yuan, W.-C.; Zhang, X.-M., *Adv. Synth. Catal.* **2010**, *352*, 2132-2136.

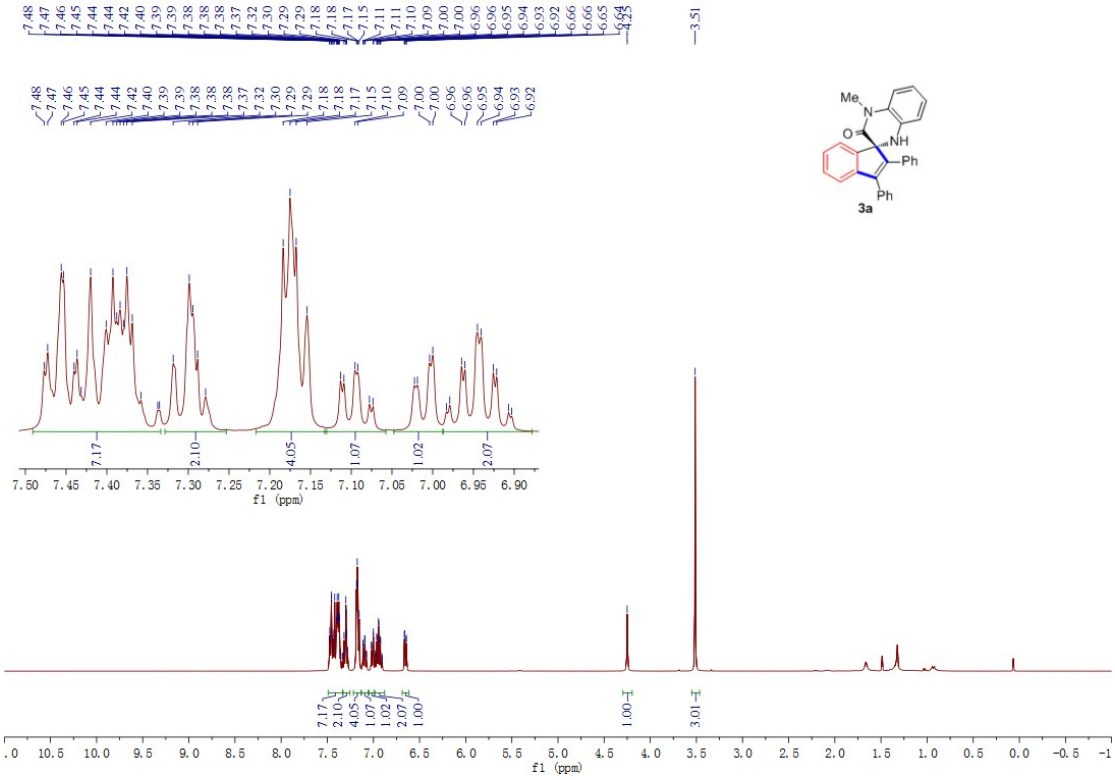
[2] Núñez-Rico, J. L.; Vidal-Ferran, A., *Org. Lett.* **2013**, *15*, 2066-2069.

[3] Carrër, A.; Brion, J.-D.; Messaoudi, S.; Alami, M., *Org. Lett.* **2013**, *15*, 5606-5609.

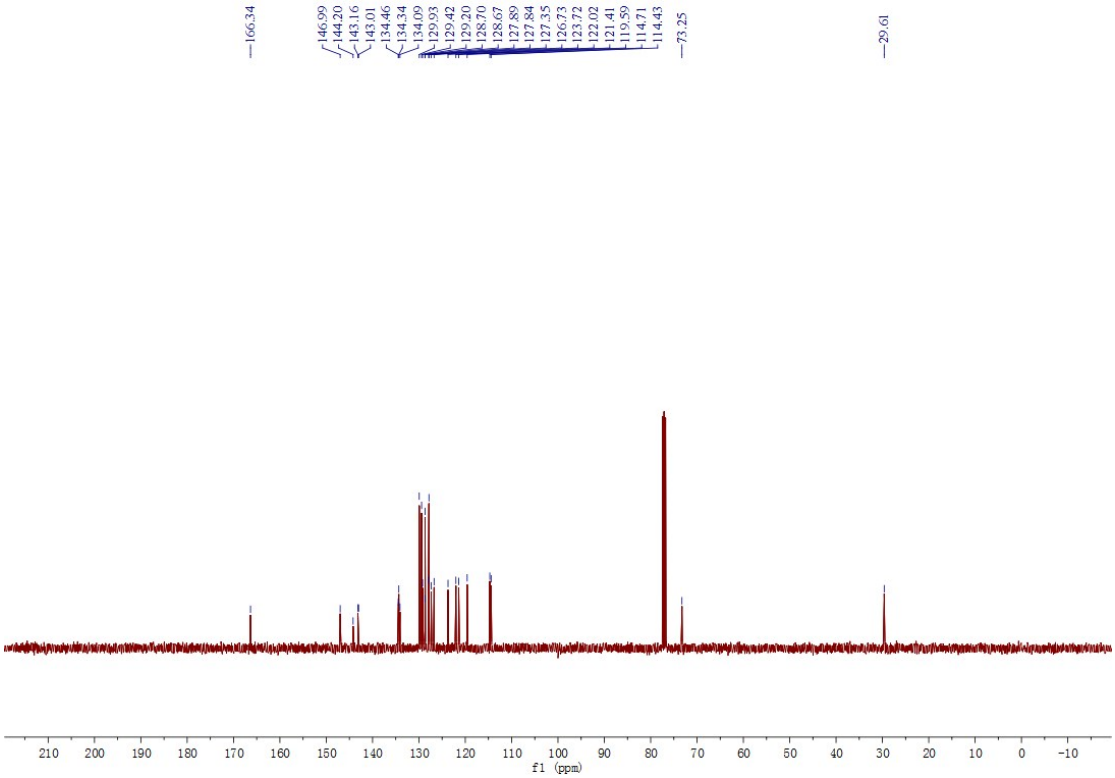
[4] Chuentragoola, P.; Vongnamb, K.; Rashatasakhona, P.; Sukwattanasinitta, M.; Wacharasindhu, S. *Tetrahedron* **2011**, *67*, 8177-8182.

[5] Leadbeater, N. E.; Tominack, B. J., *Tetrahedron Lett* **2003**, *44*, 8653-8656.

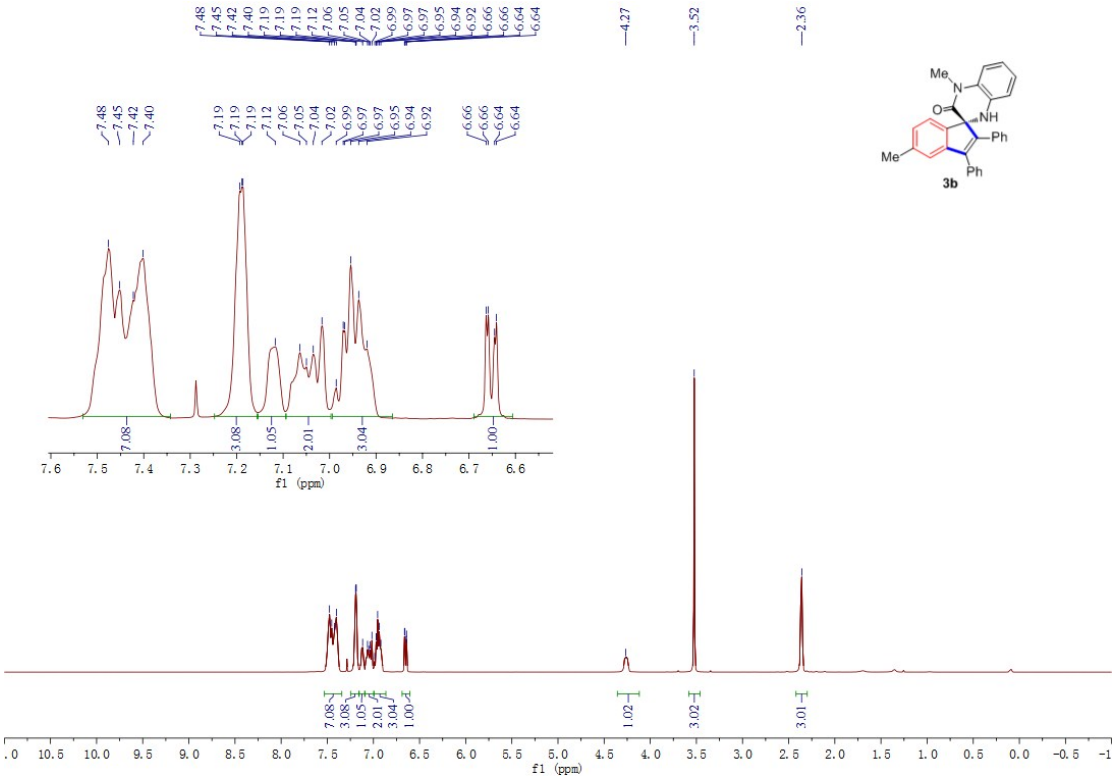
X. ^{1}H, ^{13}C and ^{19}F NMR spectra



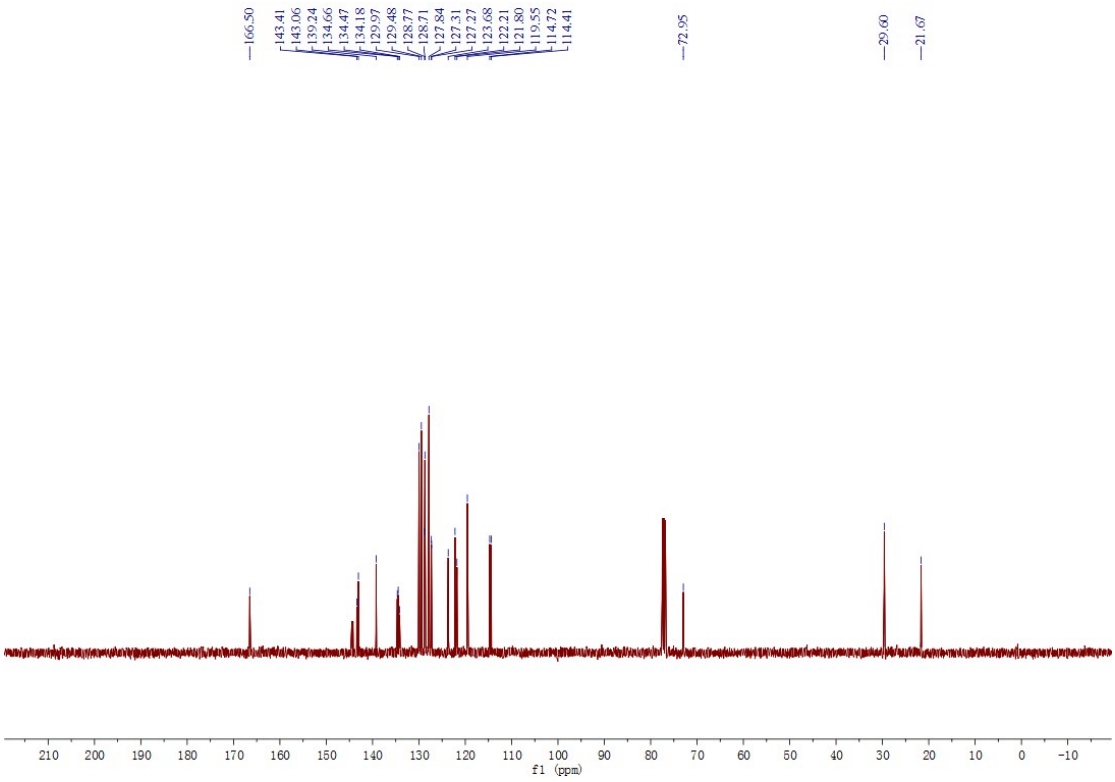
^{1}H NMR spectra of 3a ($CDCl_3$)



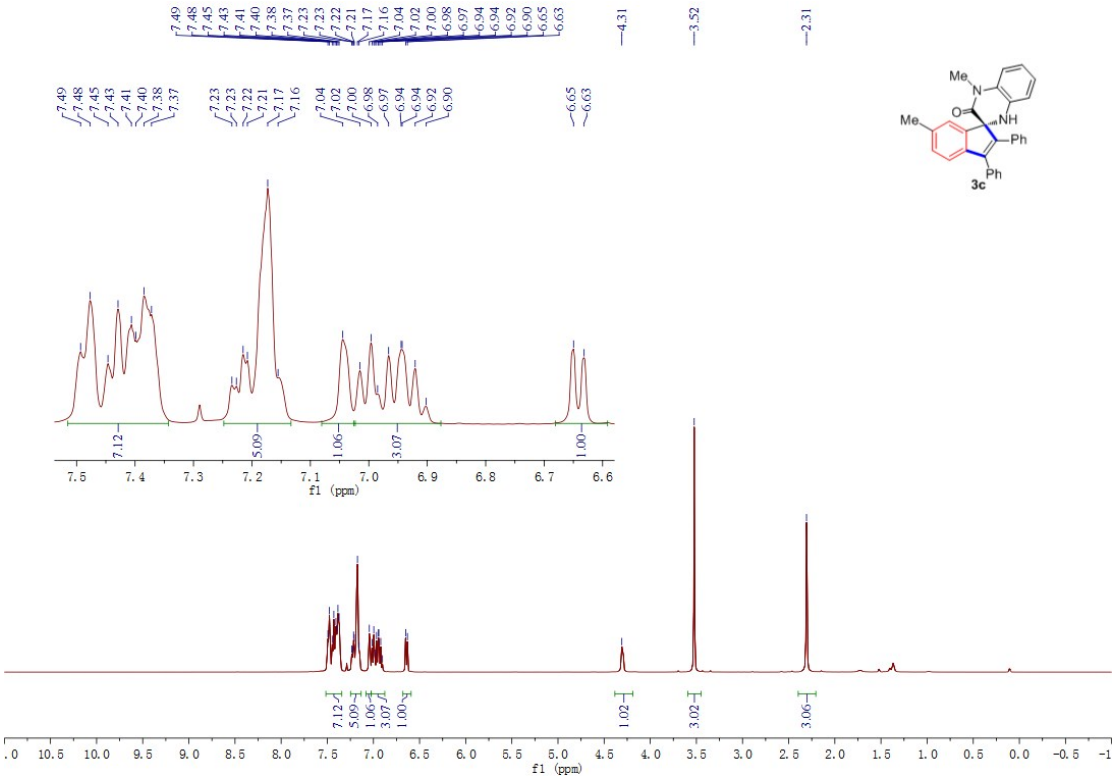
^{13}C NMR spectra of 3a ($CDCl_3$)



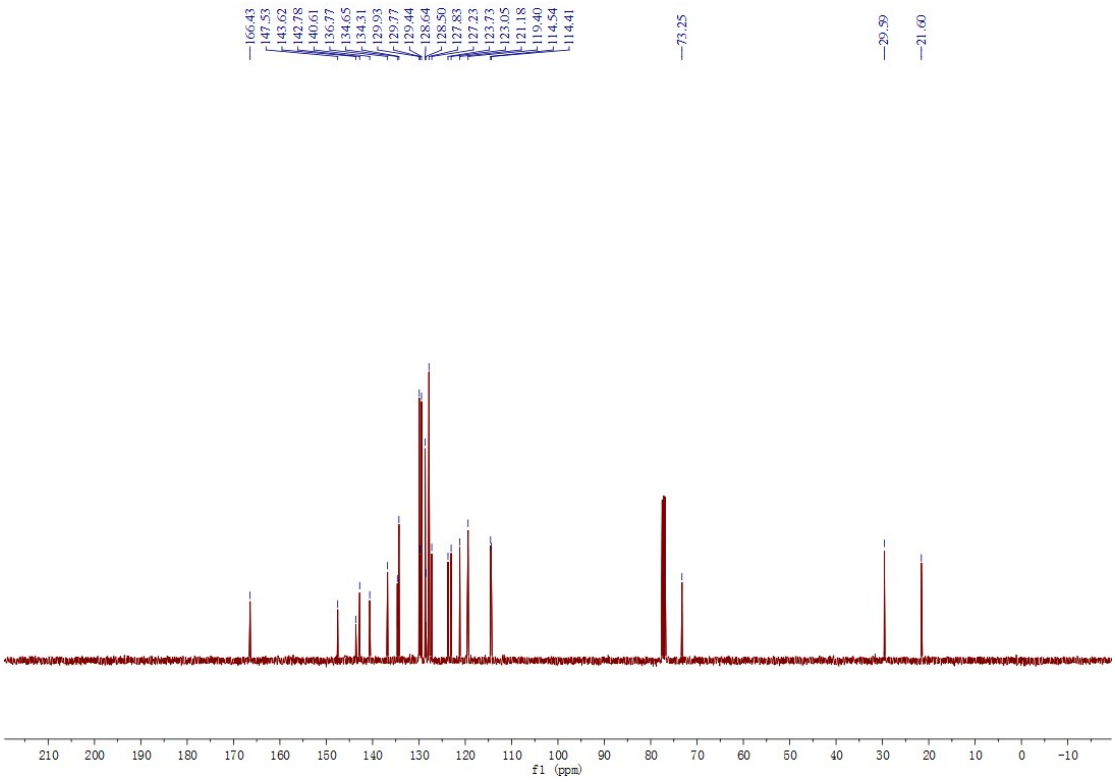
^{1}H NMR spectra of 3b ($CDCl_3$)



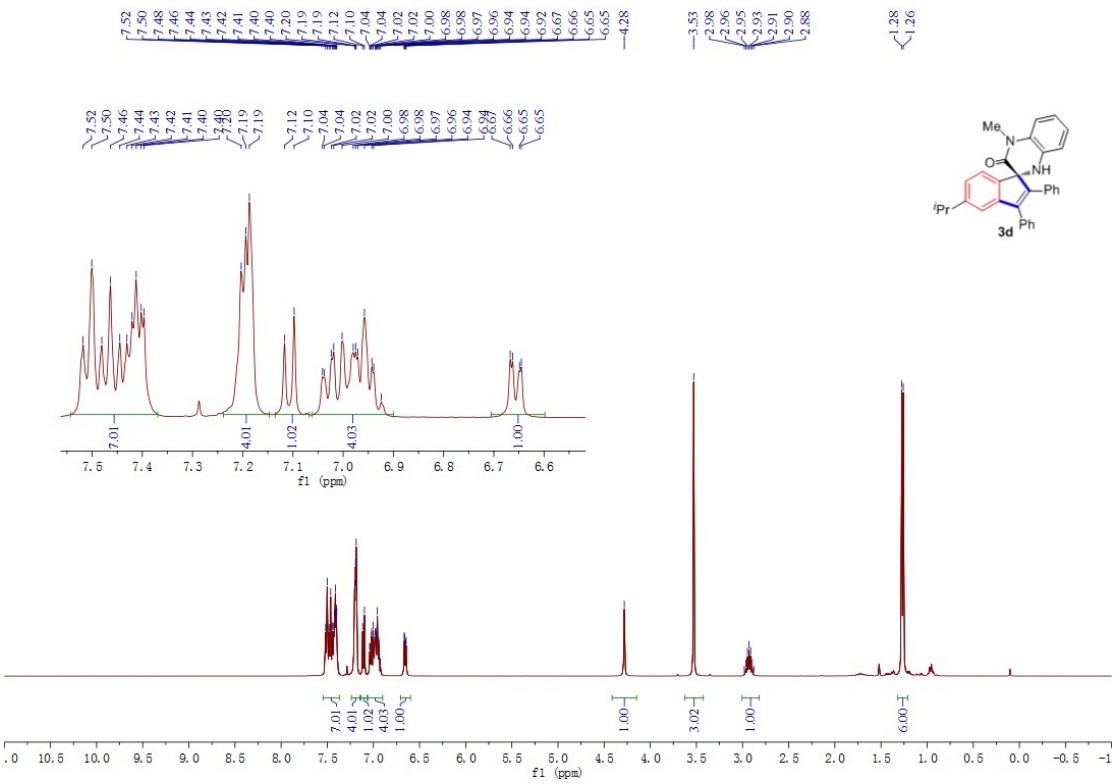
^{13}C NMR spectra of 3b ($CDCl_3$)



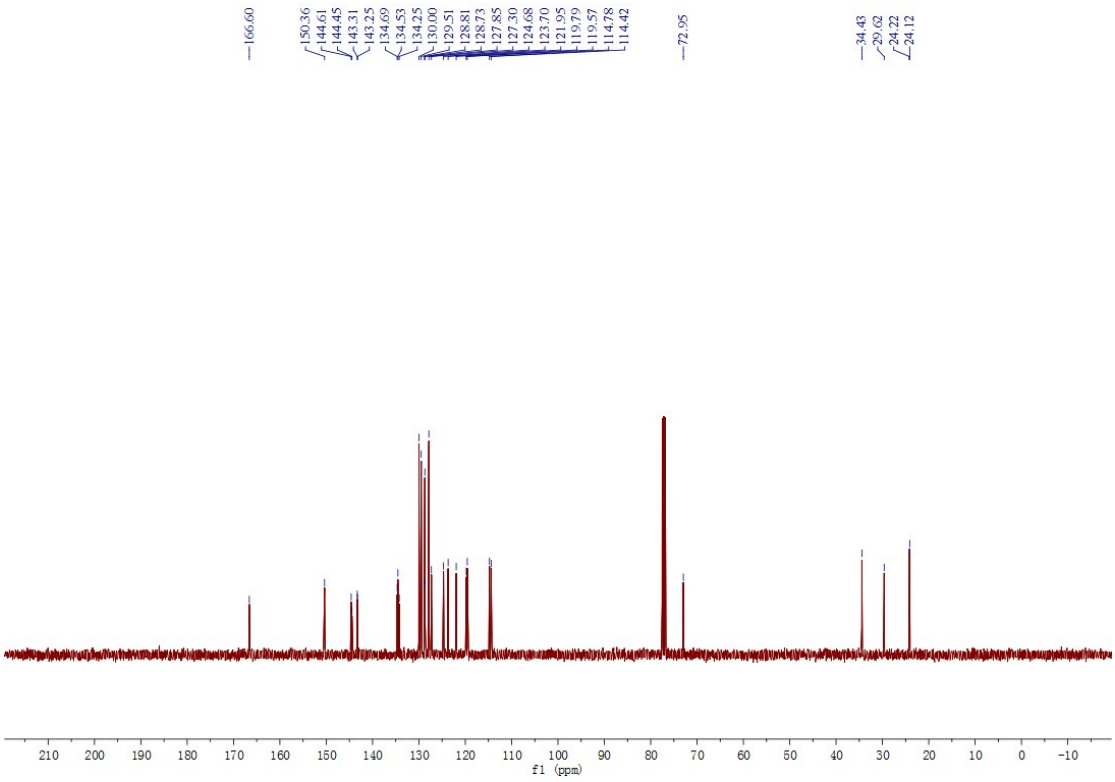
^{1}H NMR spectra of 3c ($CDCl_3$)



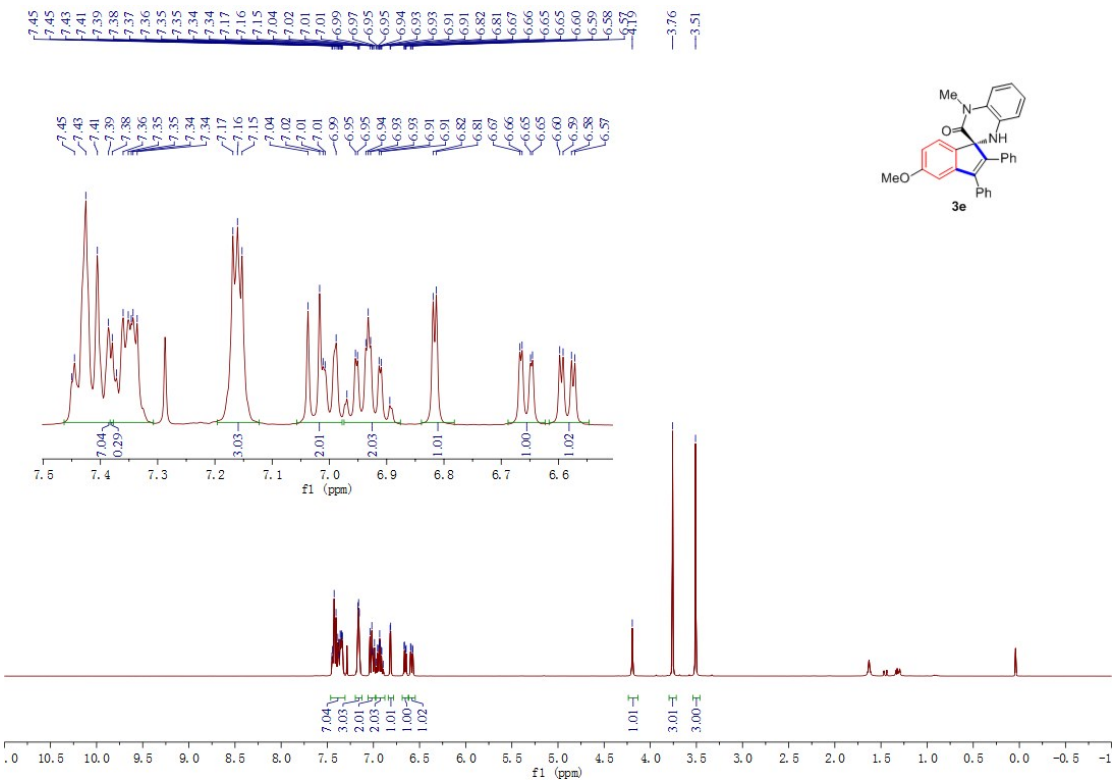
^{13}C NMR spectra of 3c ($CDCl_3$)



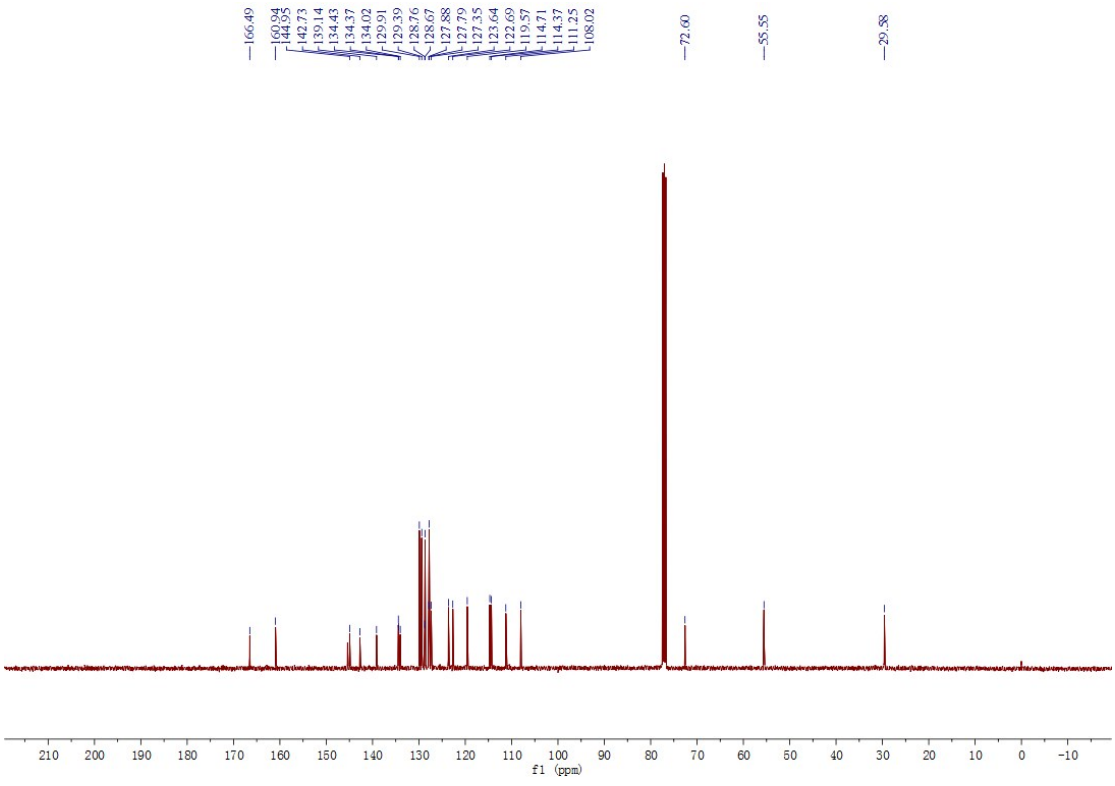
^{1}H NMR spectra of 3d ($CDCl_3$)



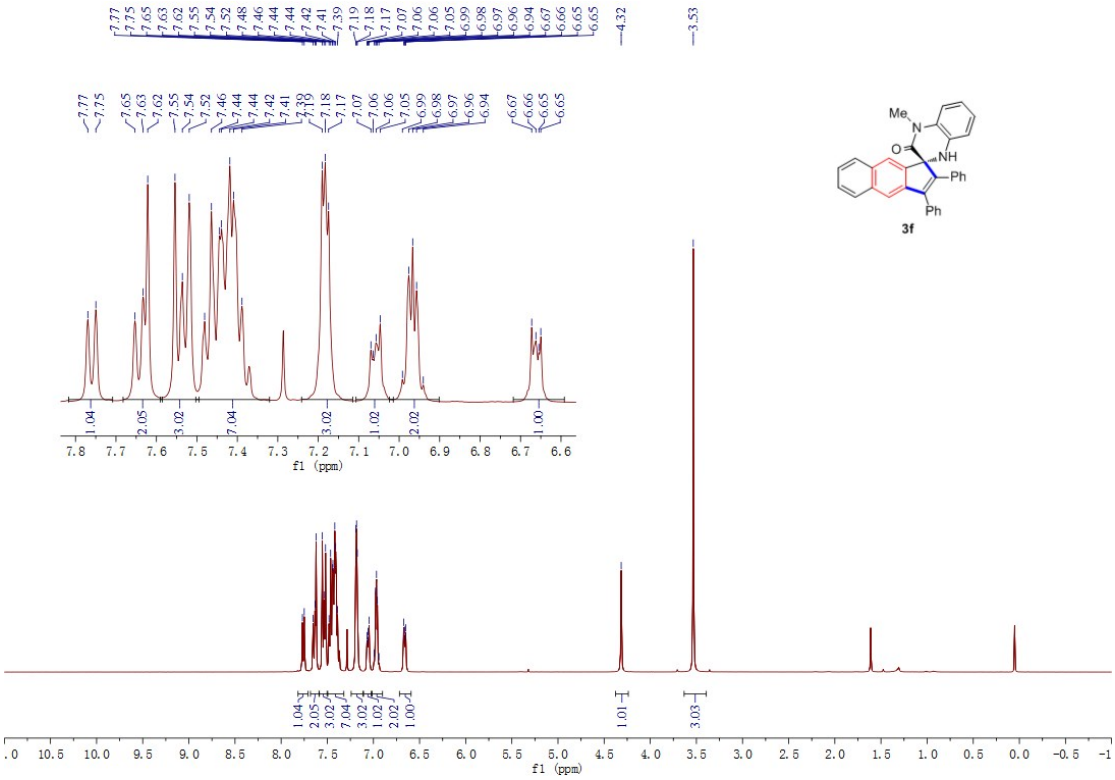
^{13}C NMR spectra of 3d ($CDCl_3$)



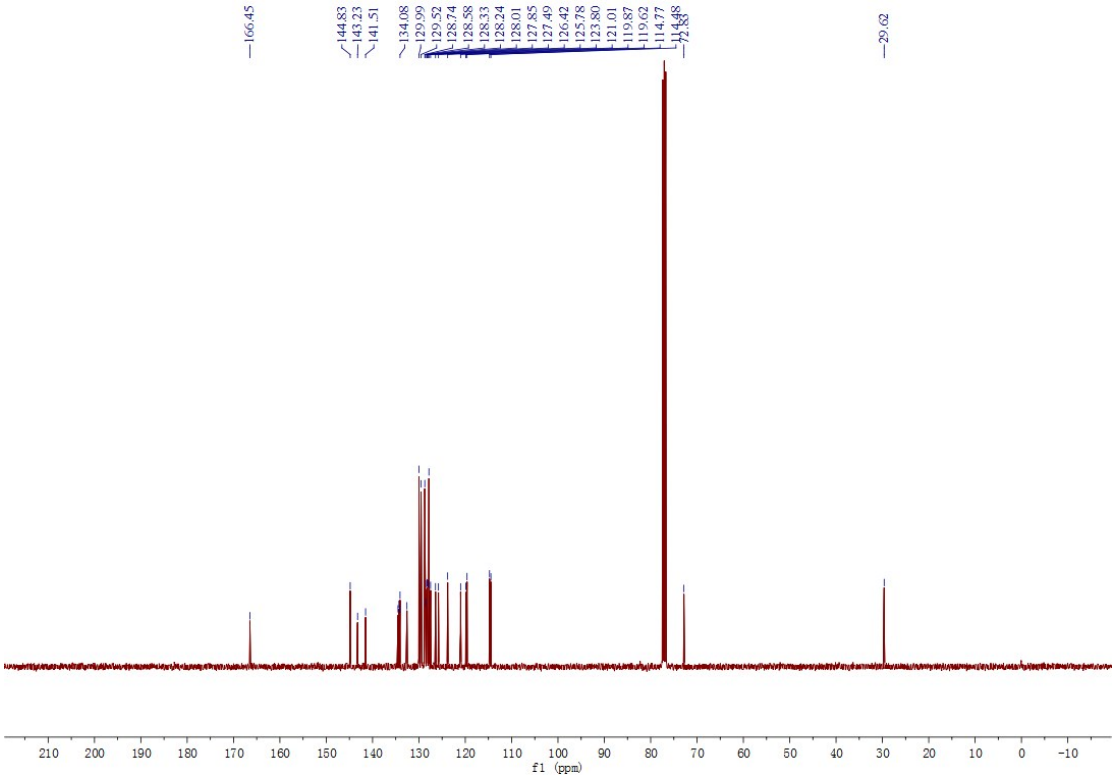
^{1}H NMR spectra of 3e ($CDCl_3$)



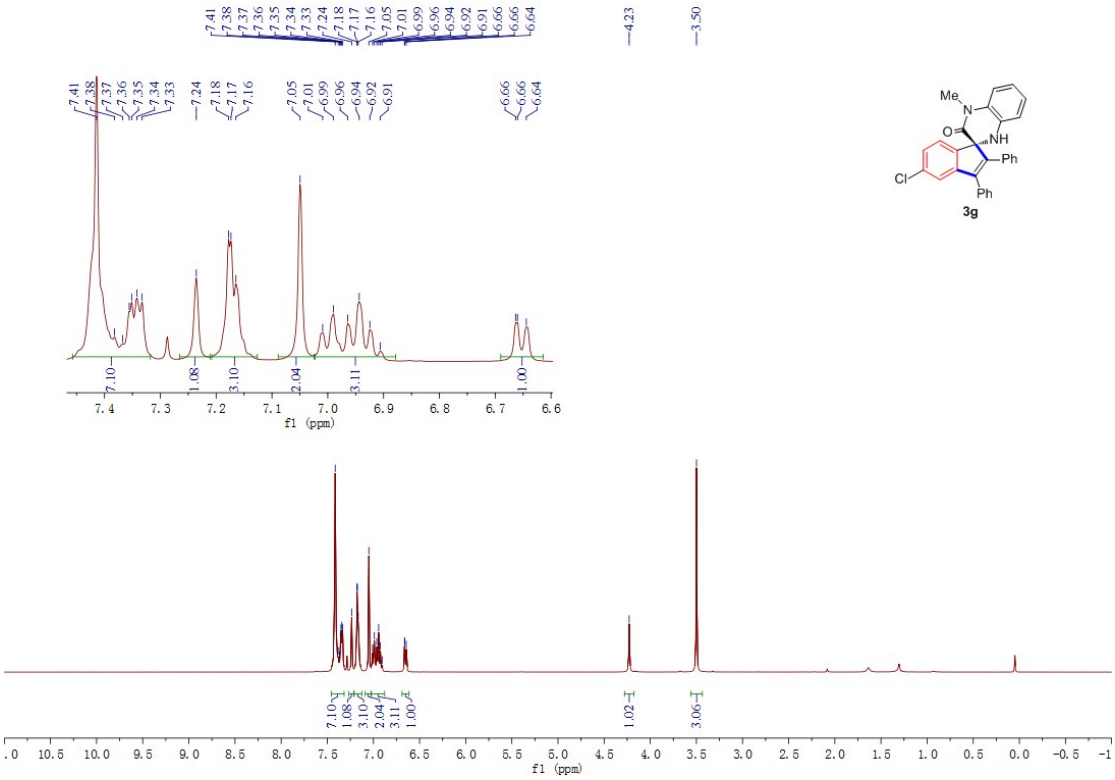
^{13}C NMR spectra of 3e ($CDCl_3$)



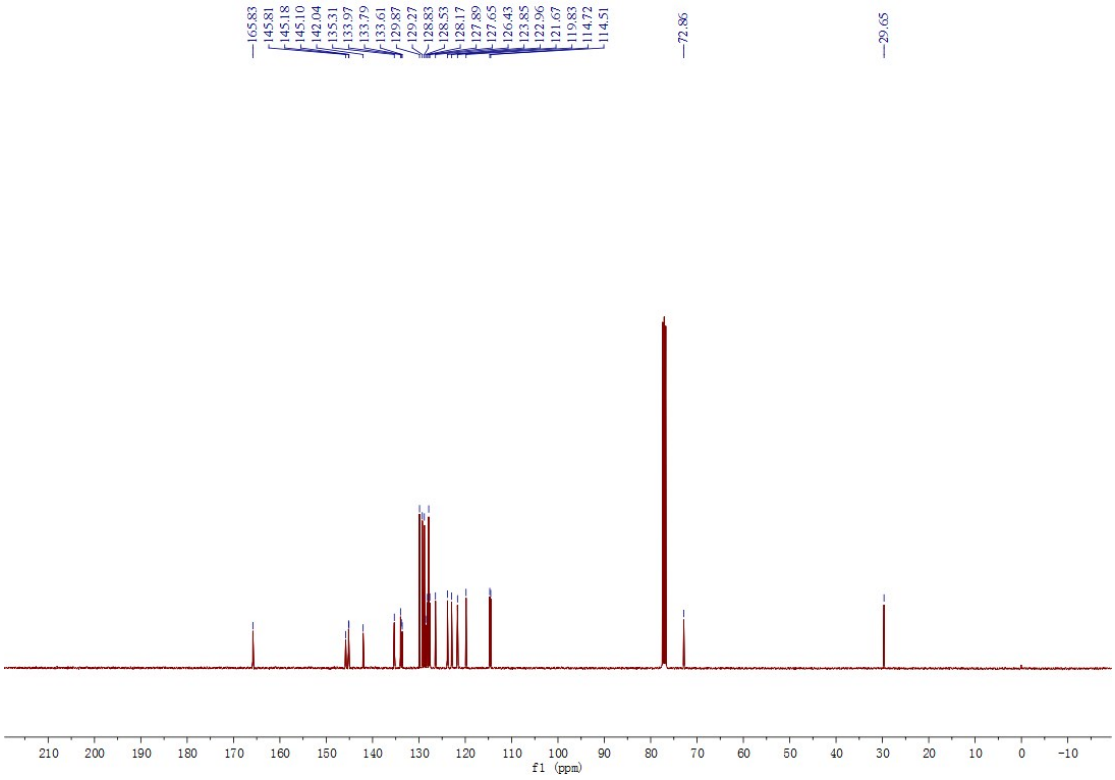
^{1}H NMR spectra of 3f ($CDCl_3$)



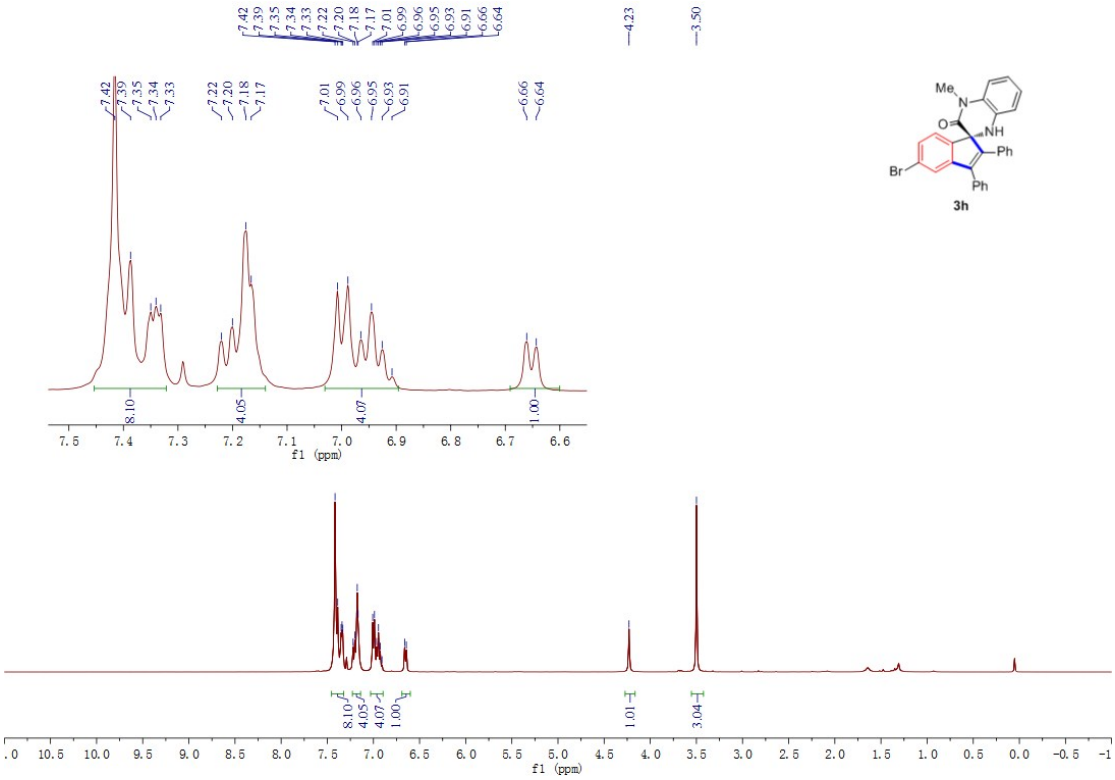
^{13}C NMR spectra of 3f ($CDCl_3$)



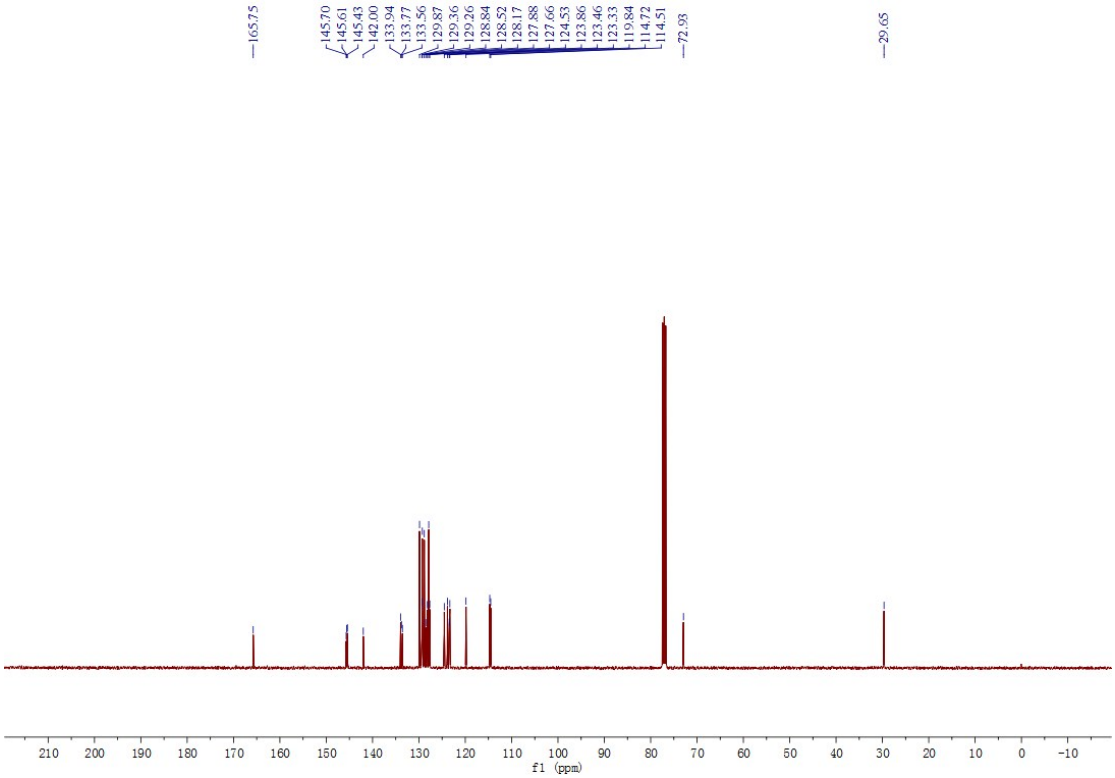
^{1}H NMR spectra of 3g ($CDCl_3$)



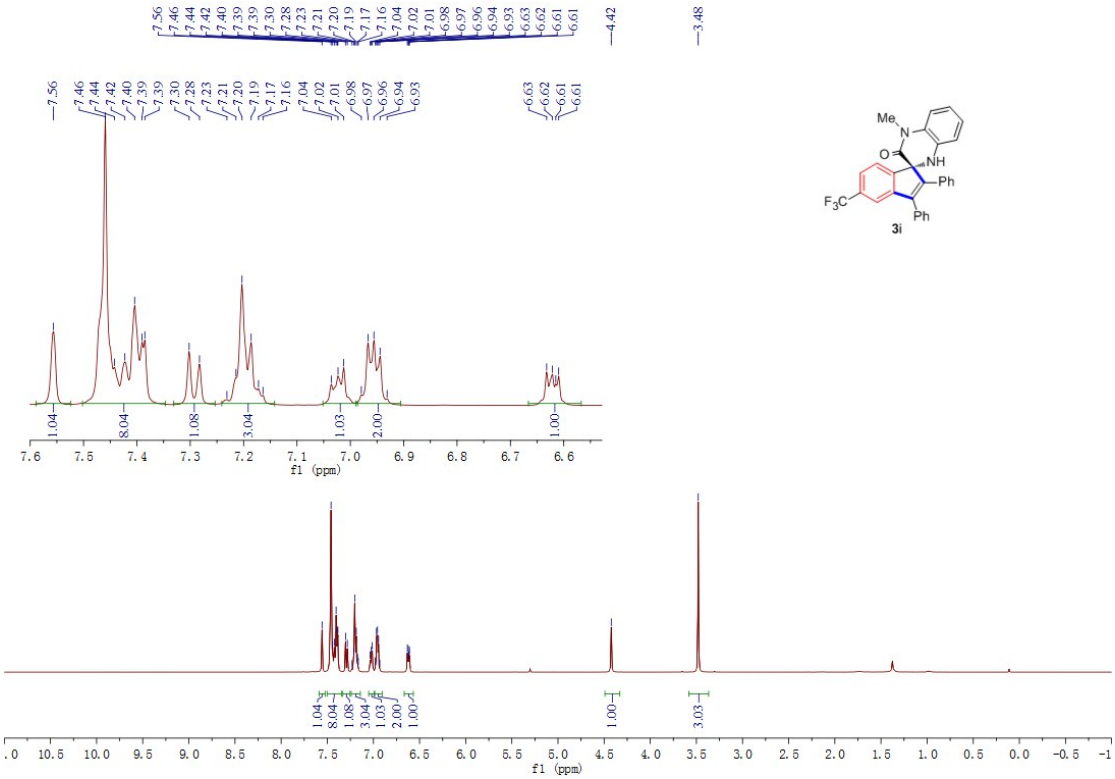
^{13}C NMR spectra of 3g ($CDCl_3$)



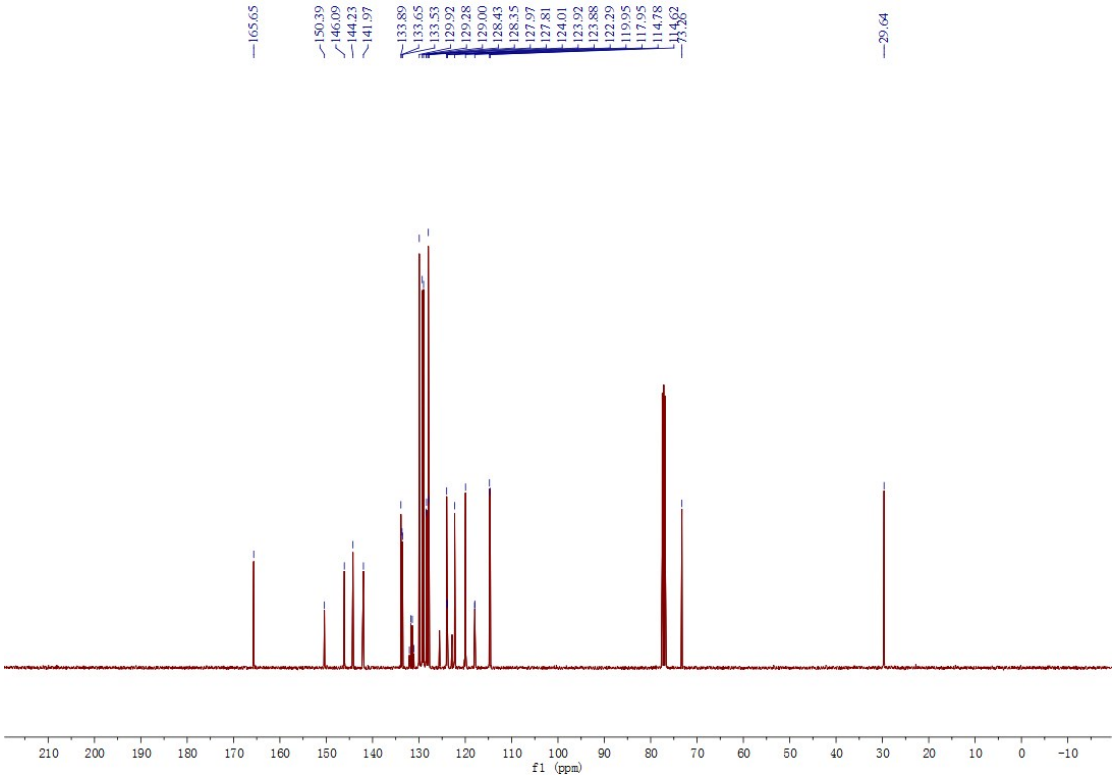
^{1}H NMR spectra of 3h ($CDCl_3$)



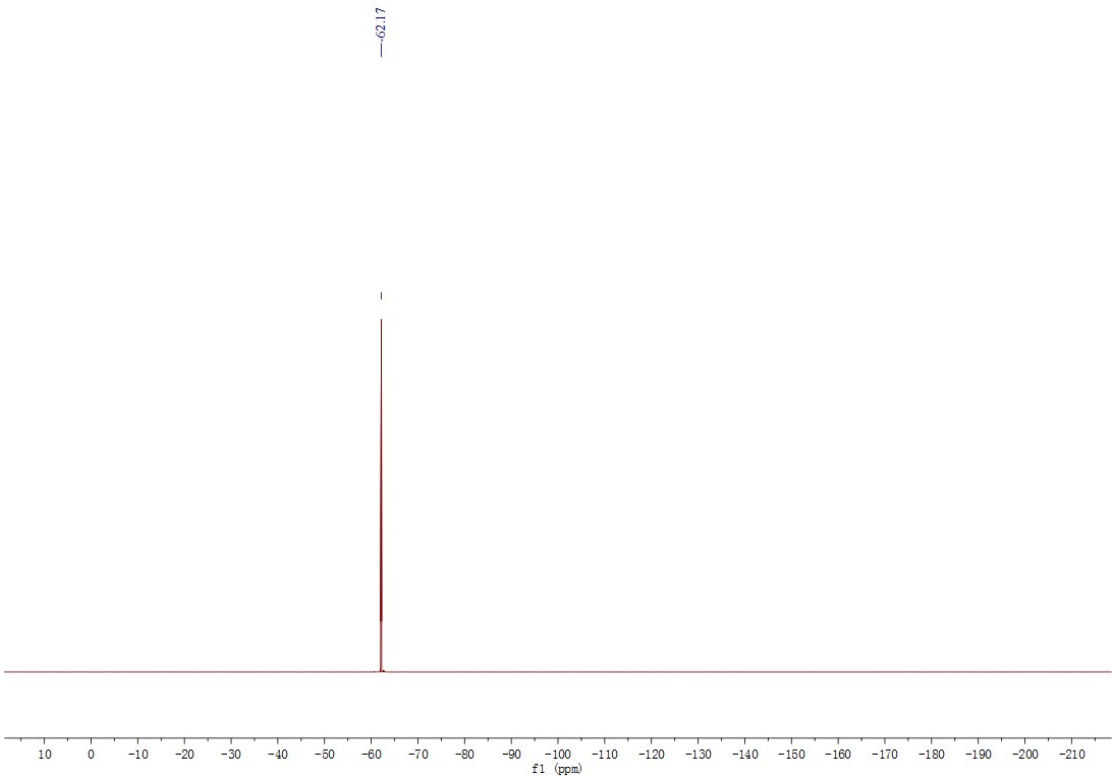
^{13}C NMR spectra of 3h ($CDCl_3$)



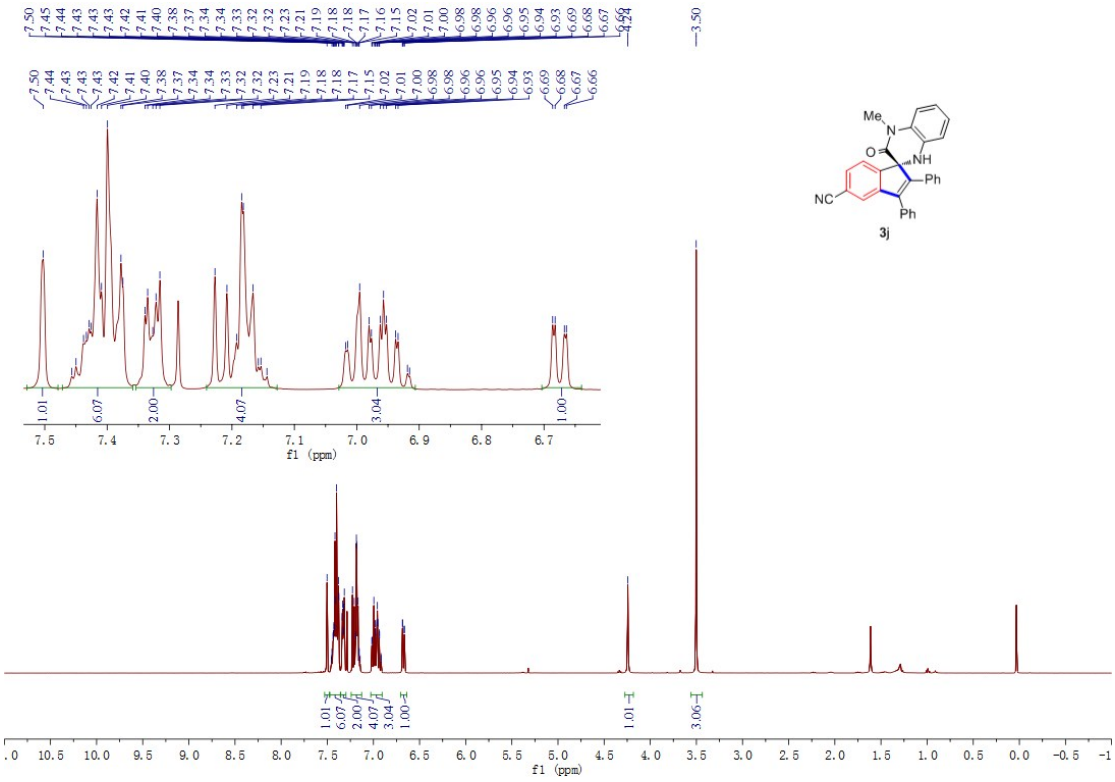
^{1}H NMR spectra of 3i ($CDCl_3$)



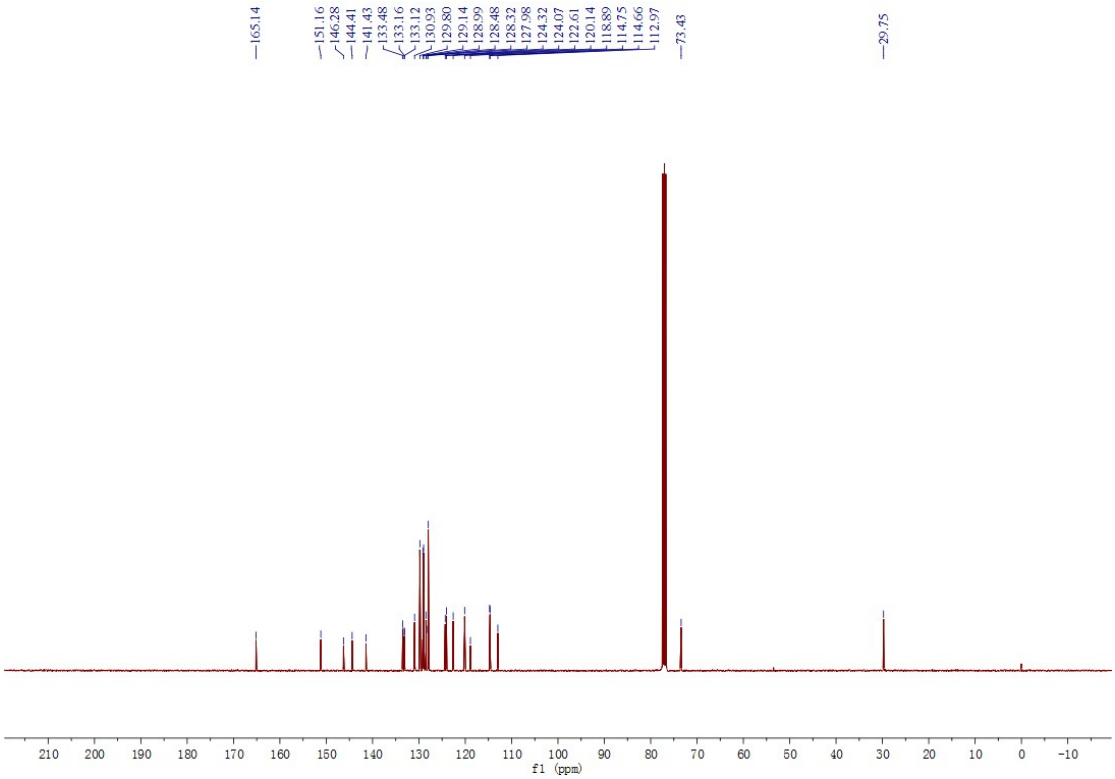
^{13}C NMR spectra of 3i ($CDCl_3$)



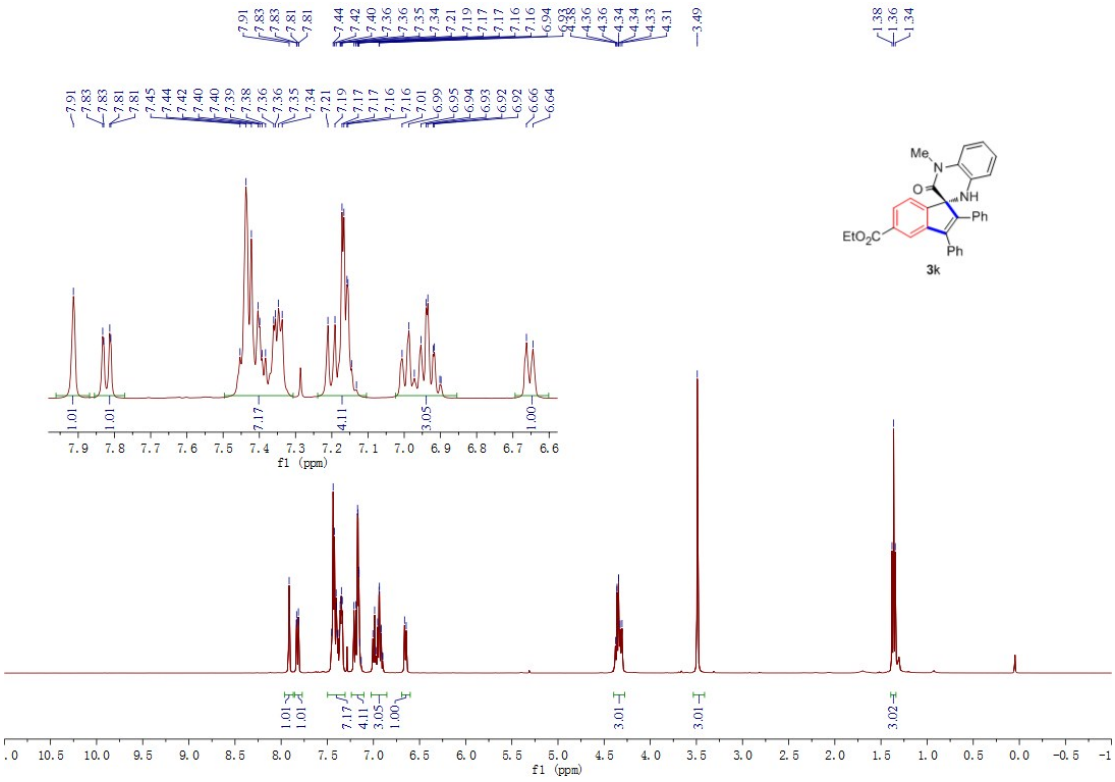
^{19}F NMR spectra of 3i ($CDCl_3$)



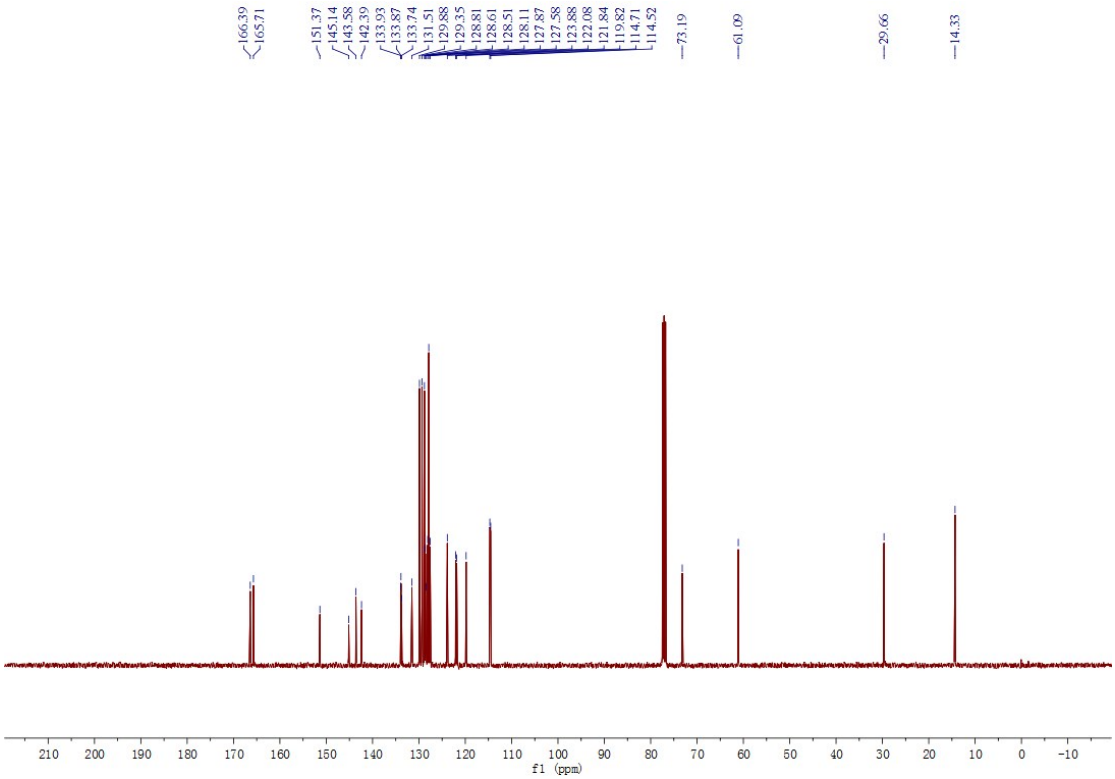
^{1}H NMR spectra of 3j ($CDCl_3$)



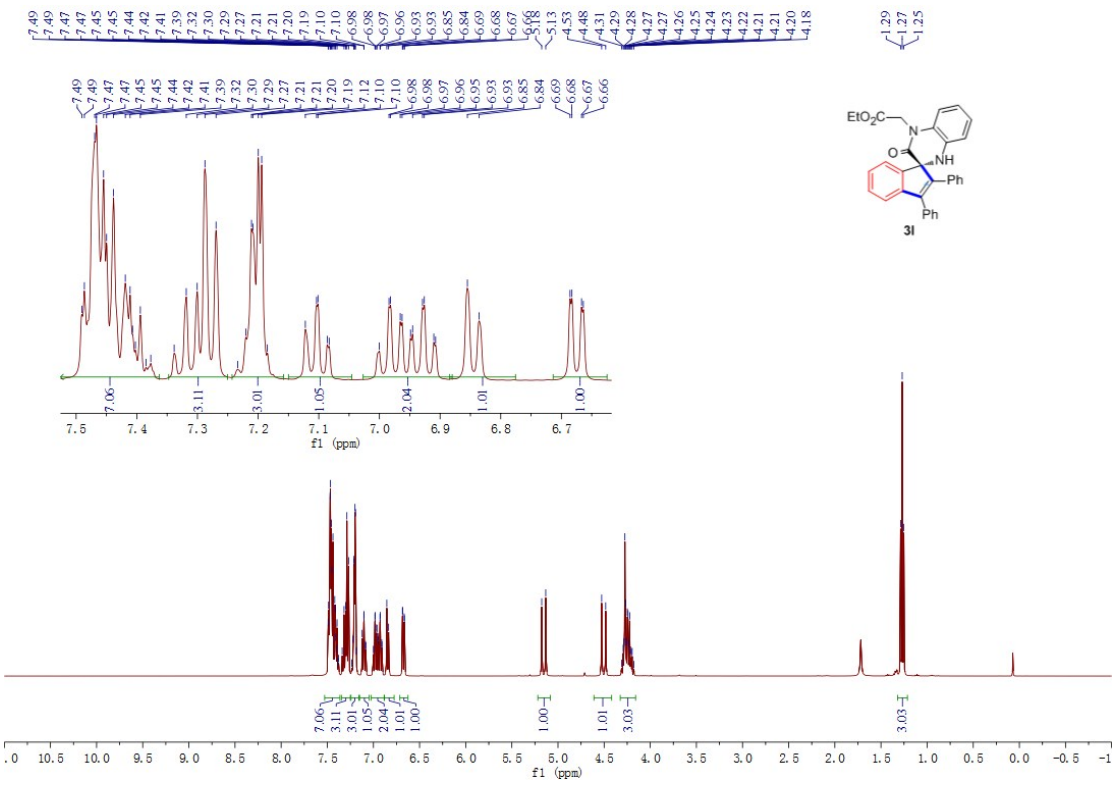
^{13}C NMR spectra of 3j ($CDCl_3$)



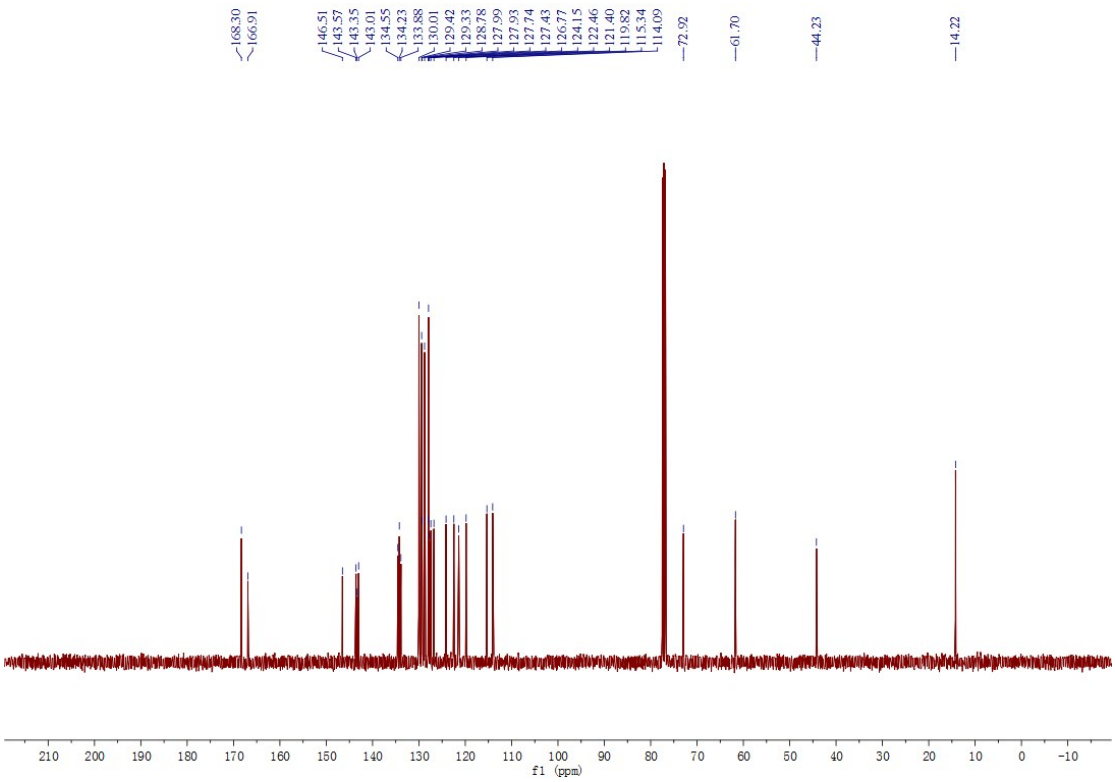
^{1}H NMR spectra of 3k ($CDCl_3$)



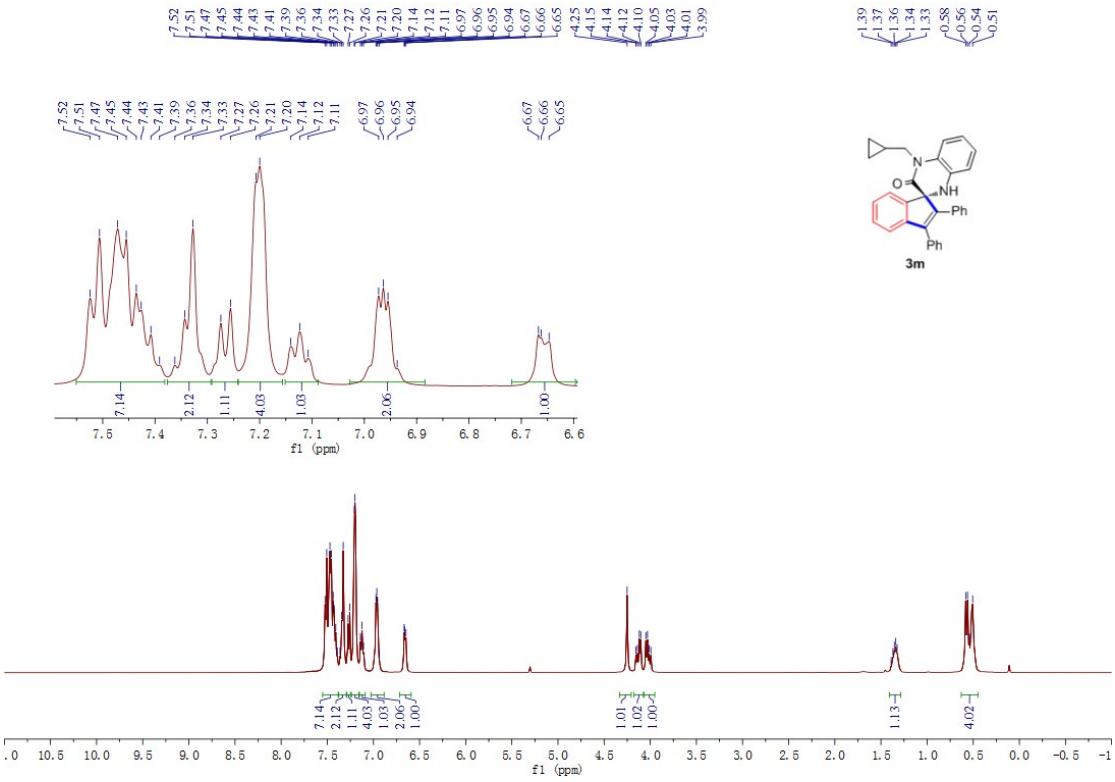
^{13}C NMR spectra of 3k ($CDCl_3$)



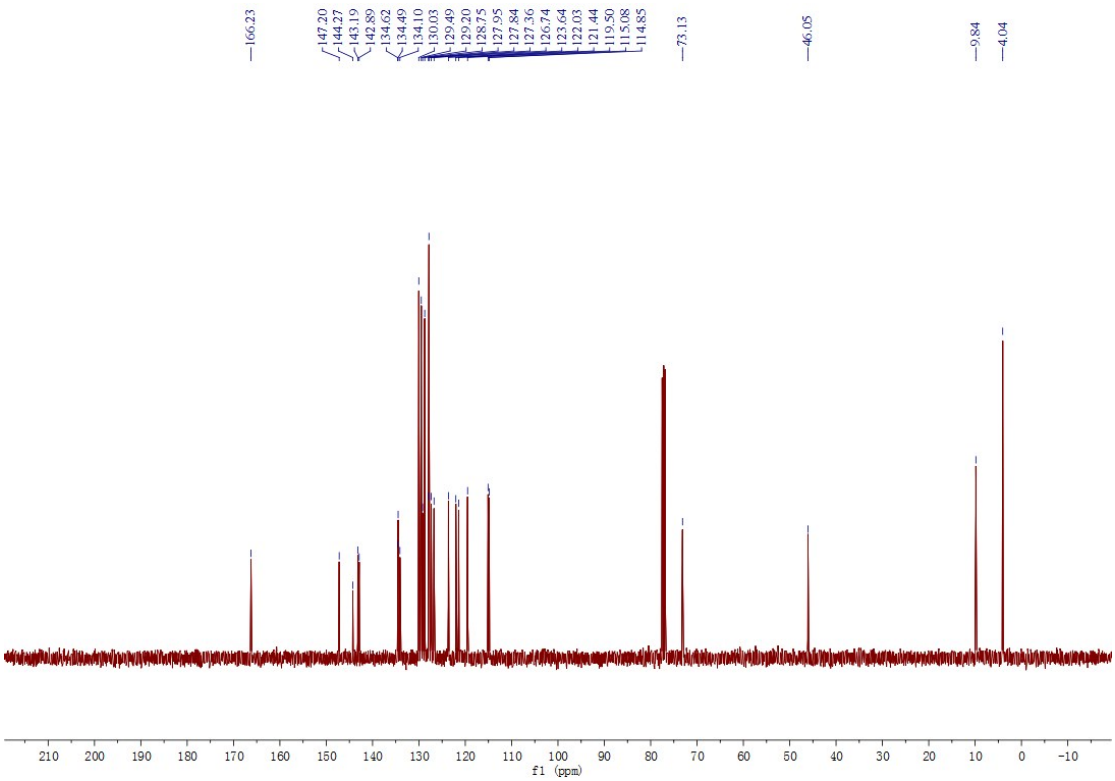
^{1}H NMR spectra of 3l ($CDCl_3$)



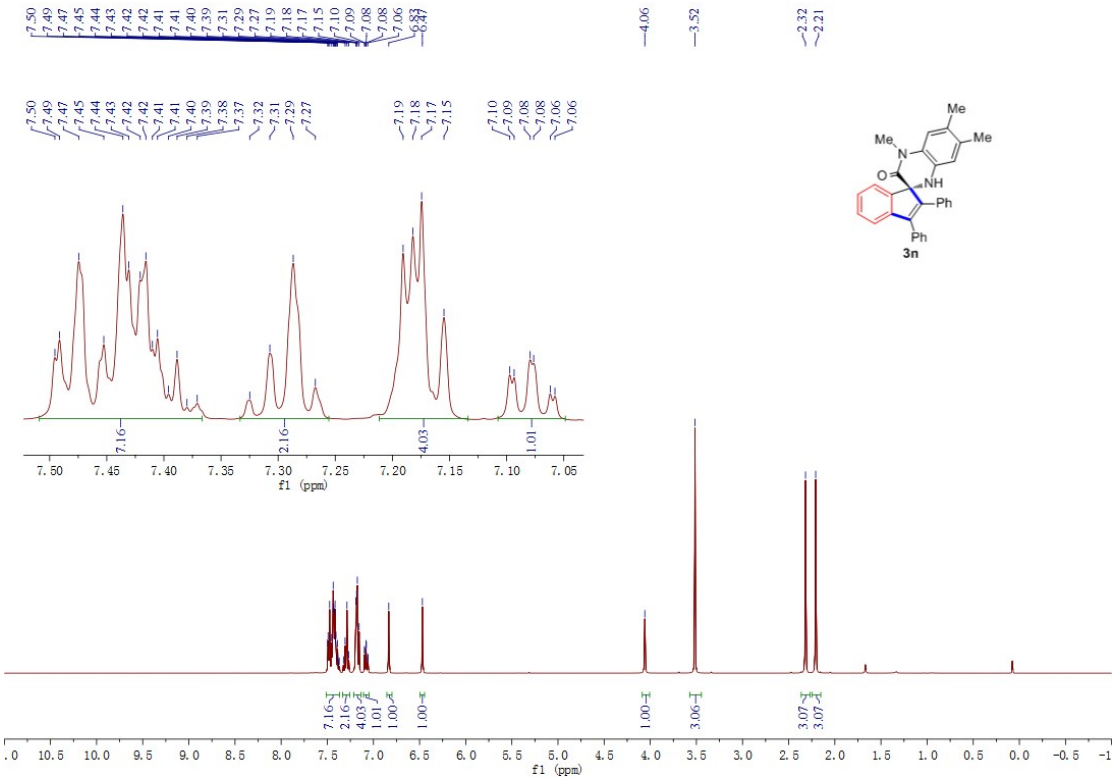
^{13}C NMR spectra of 3l ($CDCl_3$)



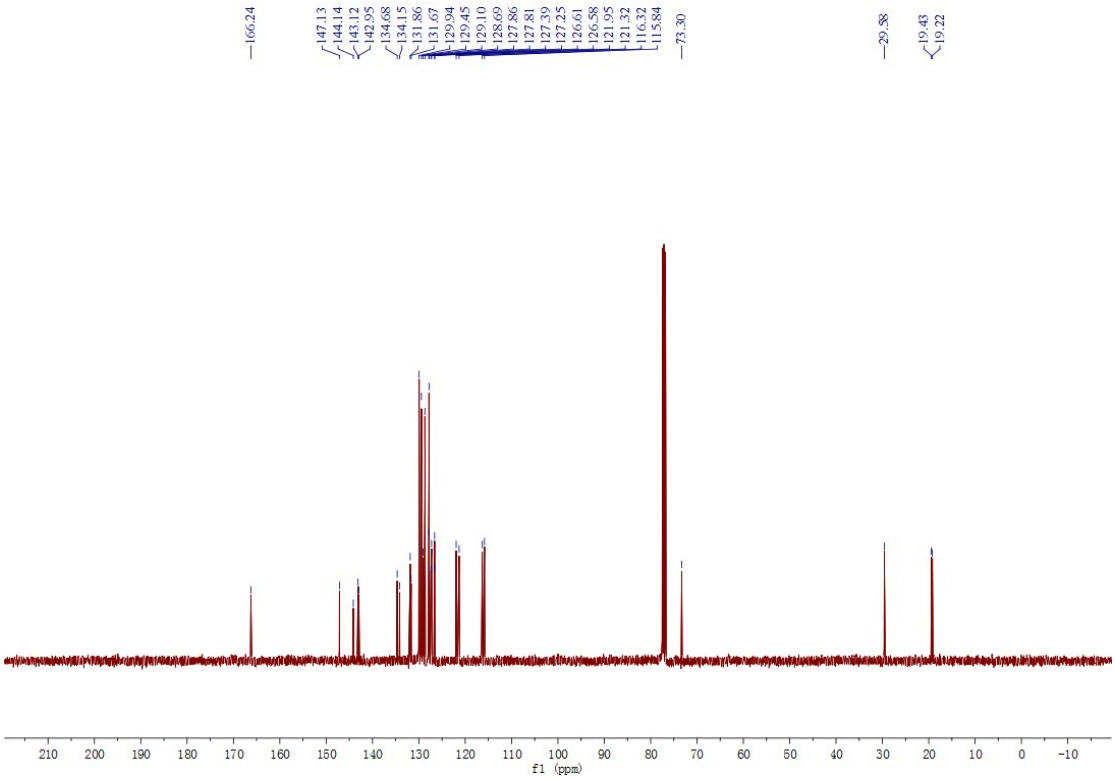
^{1}H NMR spectra of 3m ($CDCl_3$)



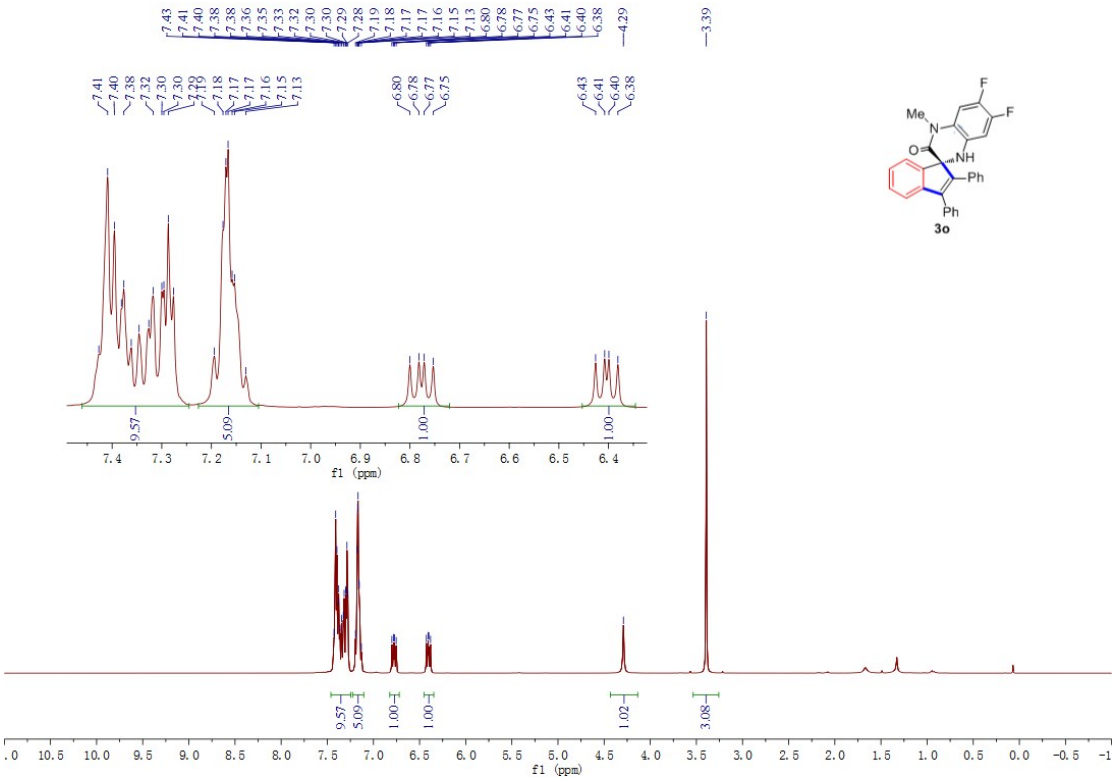
^{13}C NMR spectra of 3m ($CDCl_3$)



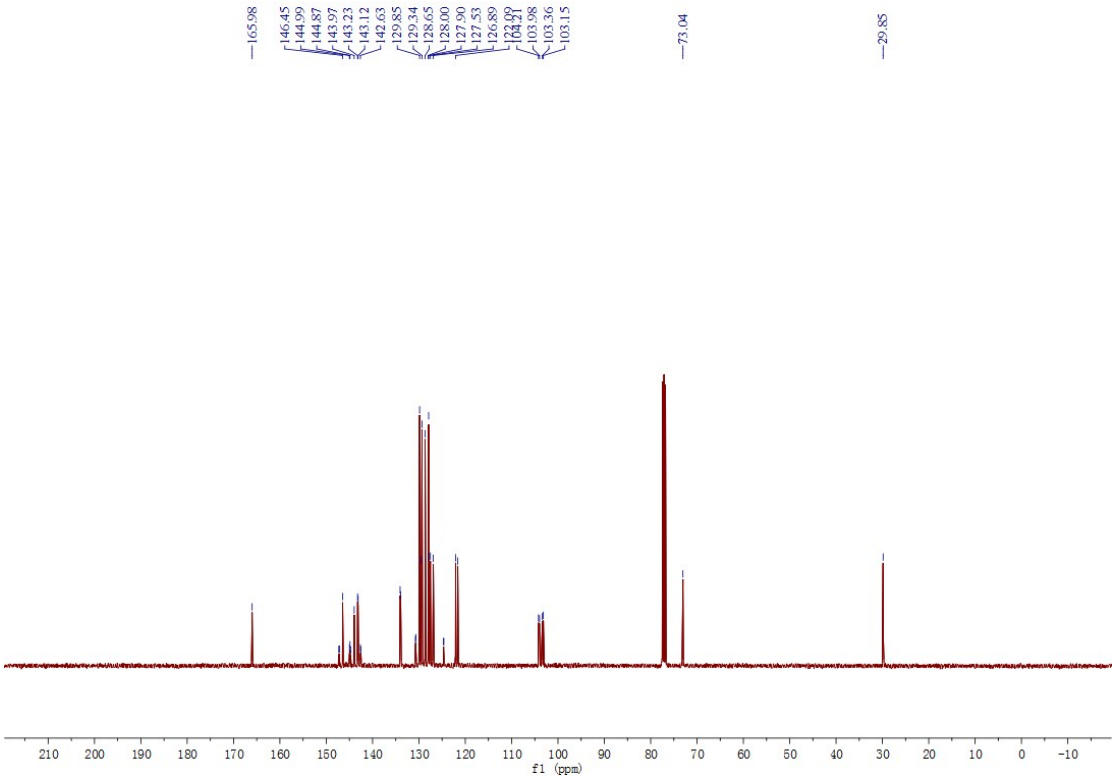
^{1}H NMR spectra of 3n ($CDCl_3$)



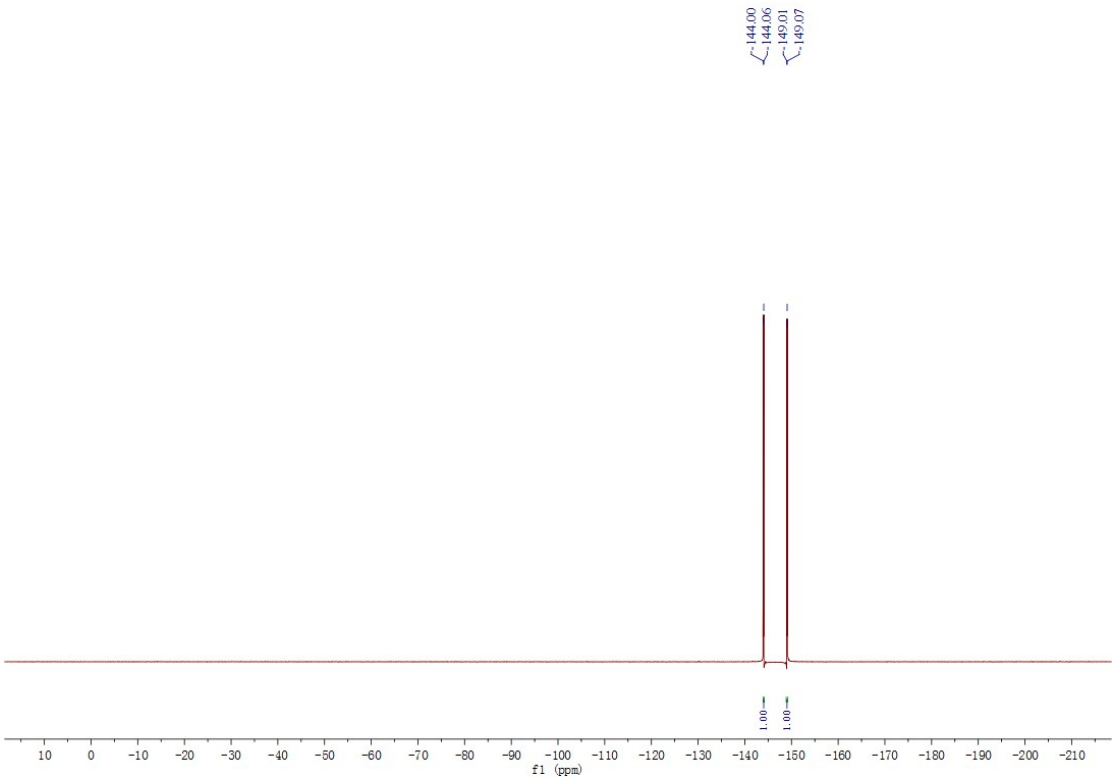
^{13}C NMR spectra of 3n ($CDCl_3$)



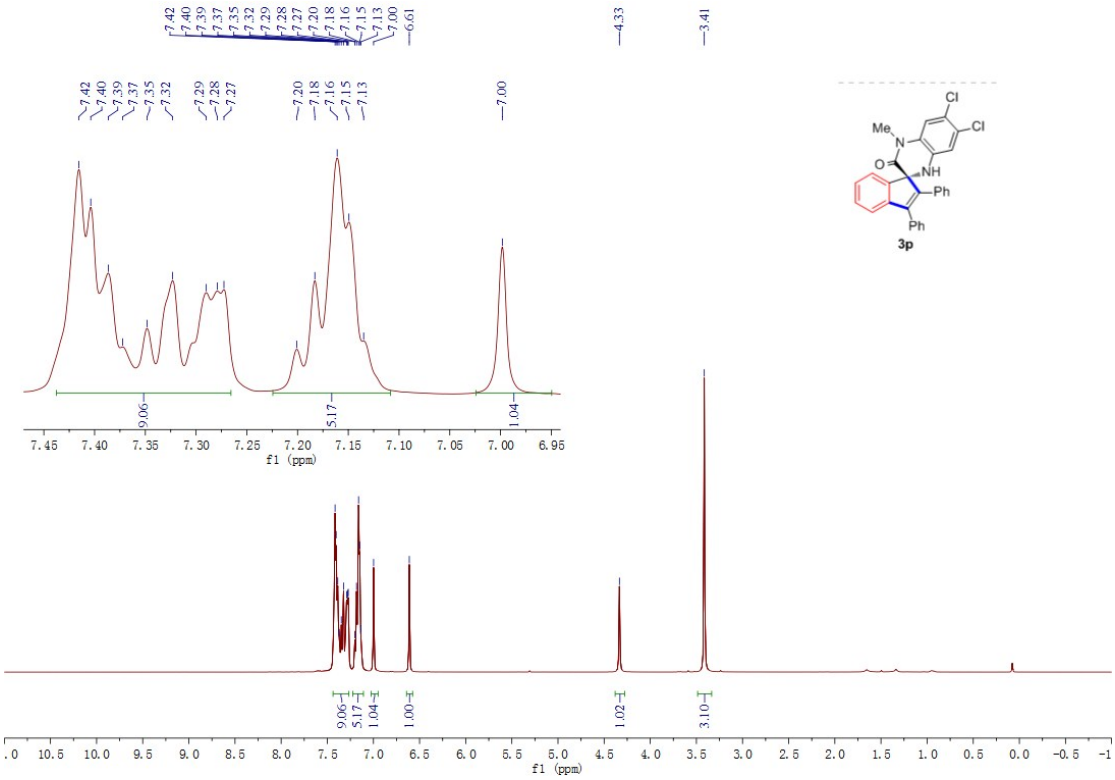
^{1}H NMR spectra of 3o ($CDCl_3$)



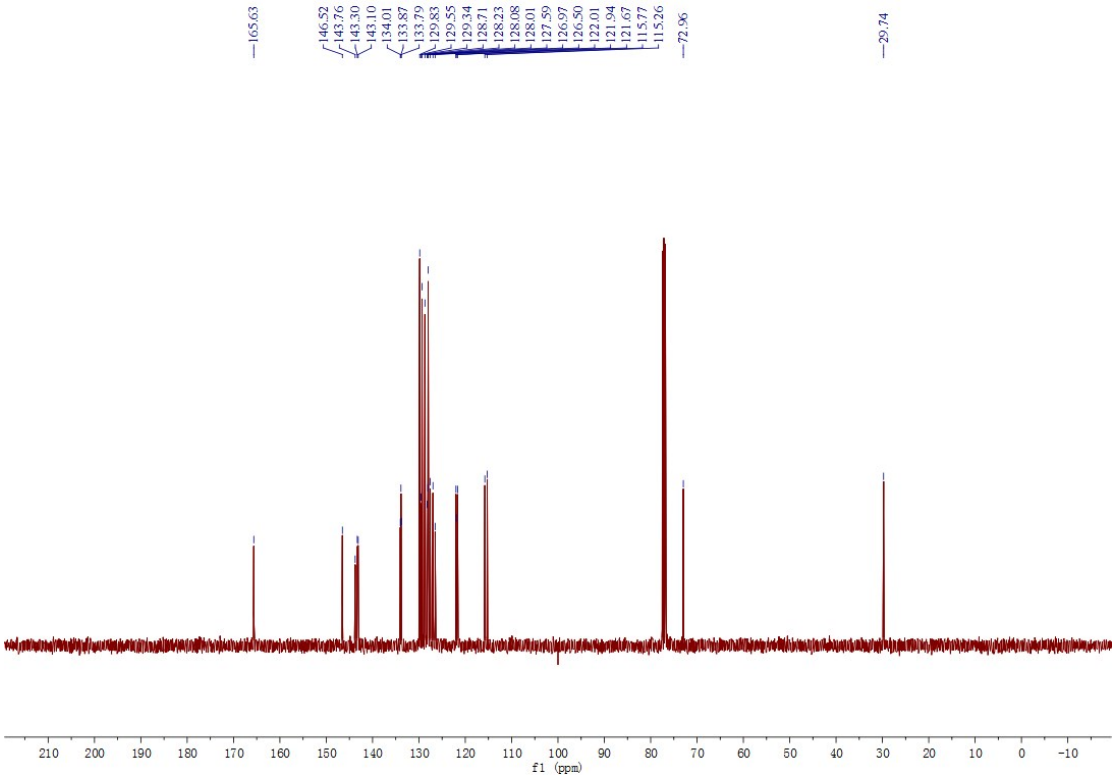
^{13}C NMR spectra of 3o ($CDCl_3$)



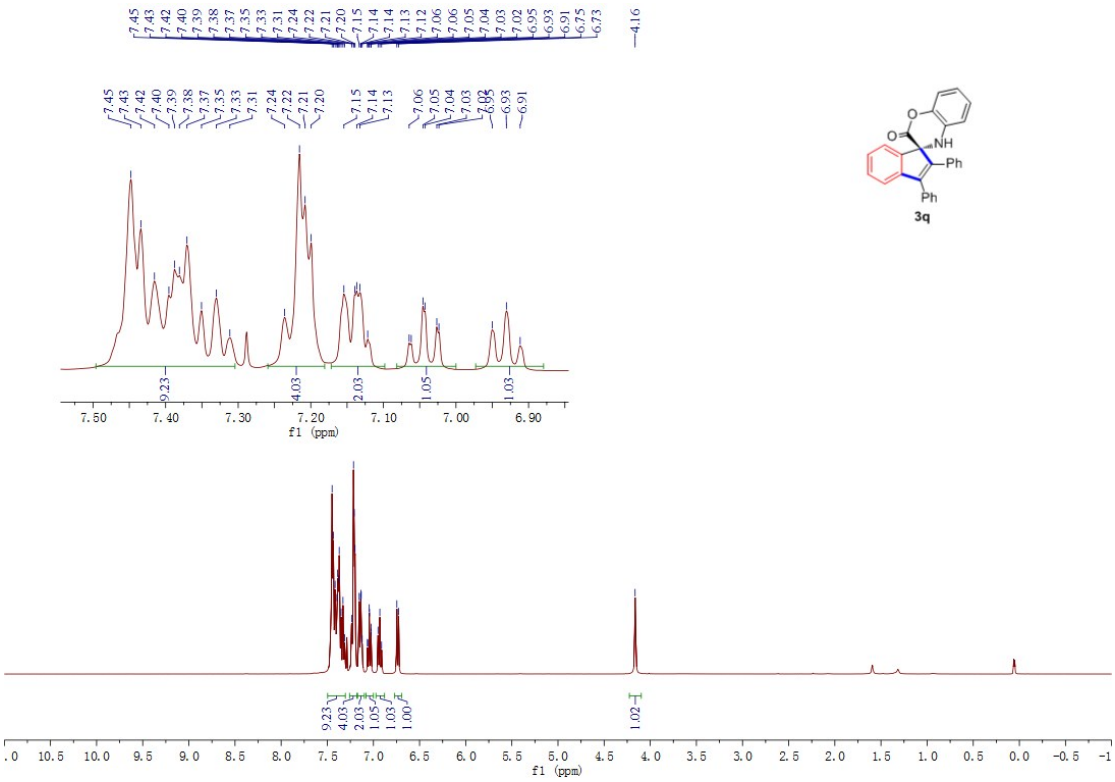
^{19}F NMR spectra of 3o ($CDCl_3$)



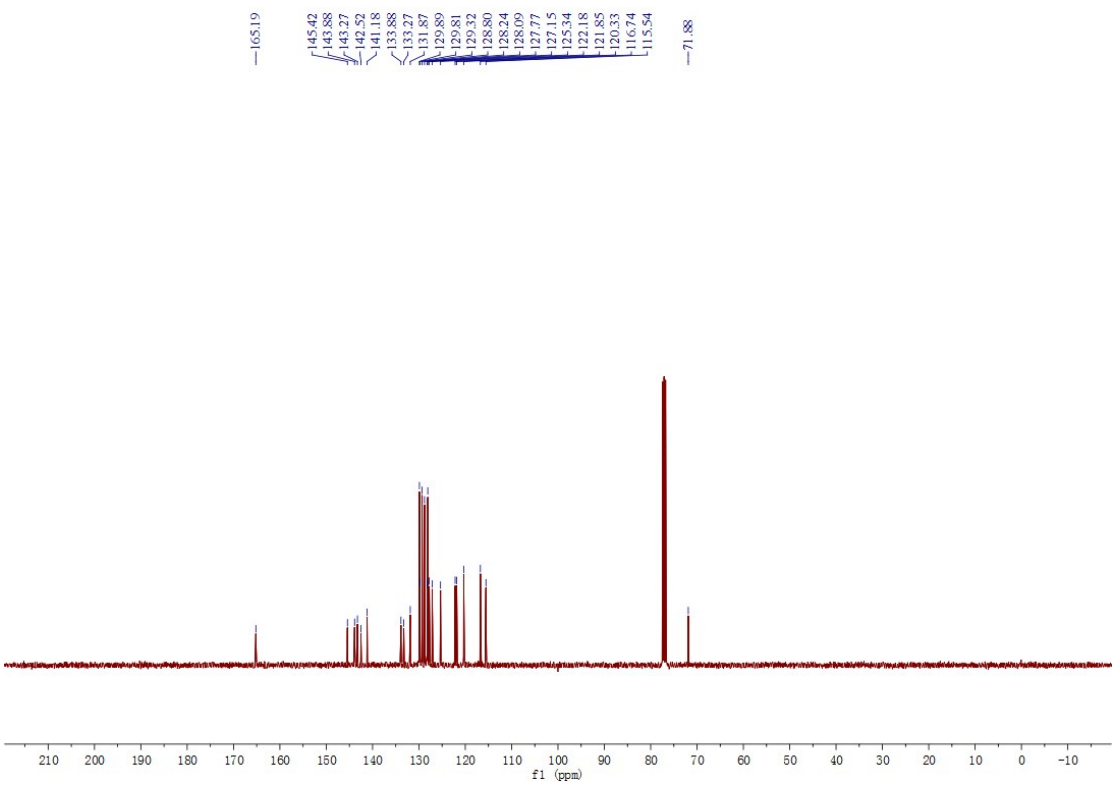
^{1}H NMR spectra of 3p ($CDCl_3$)



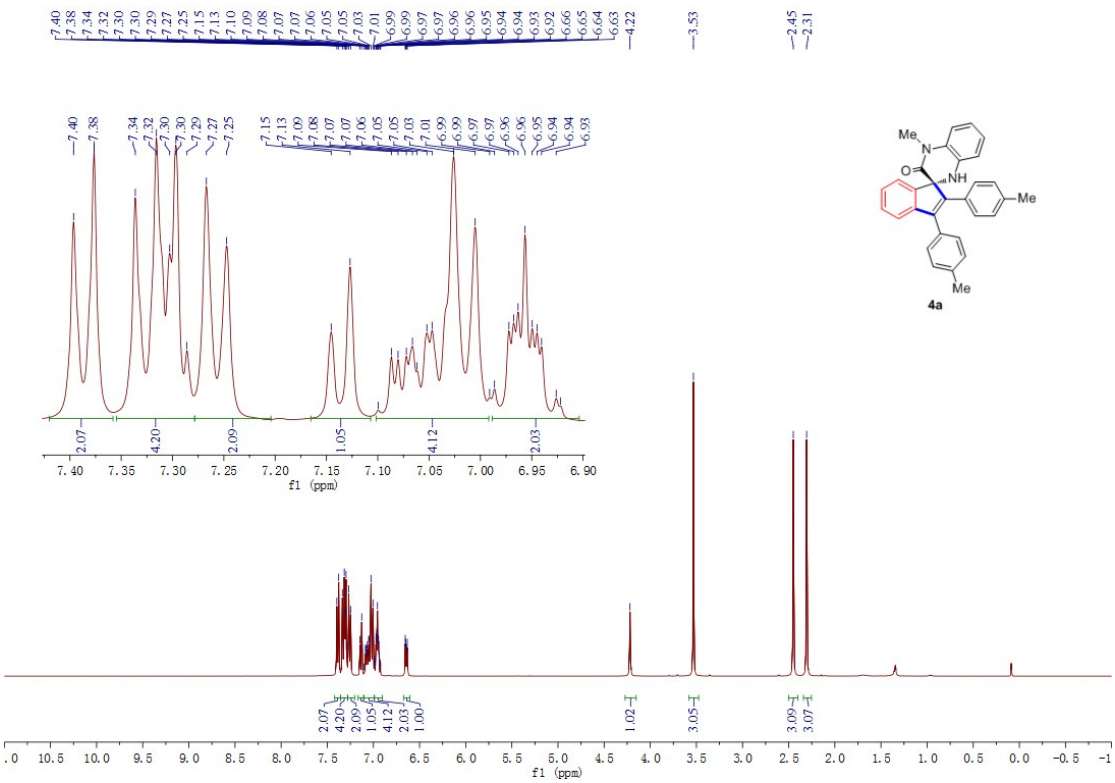
^{13}C NMR spectra of 3p ($CDCl_3$)



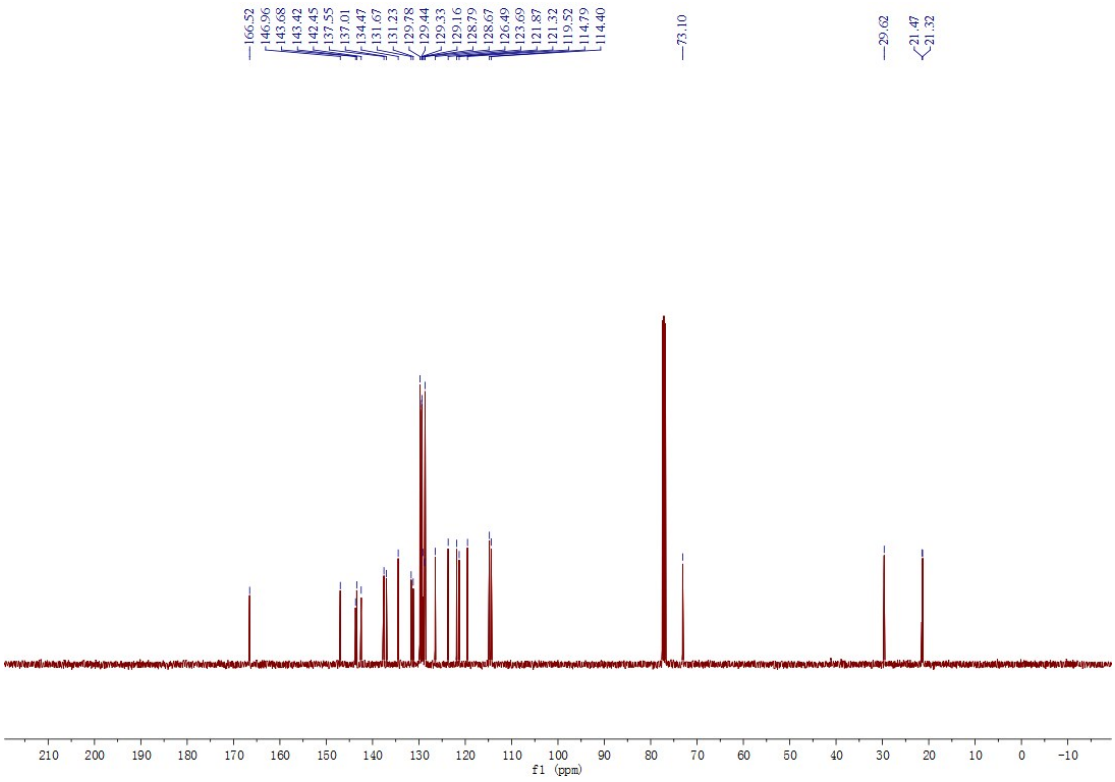
^{1}H NMR spectra of 3q ($CDCl_3$)



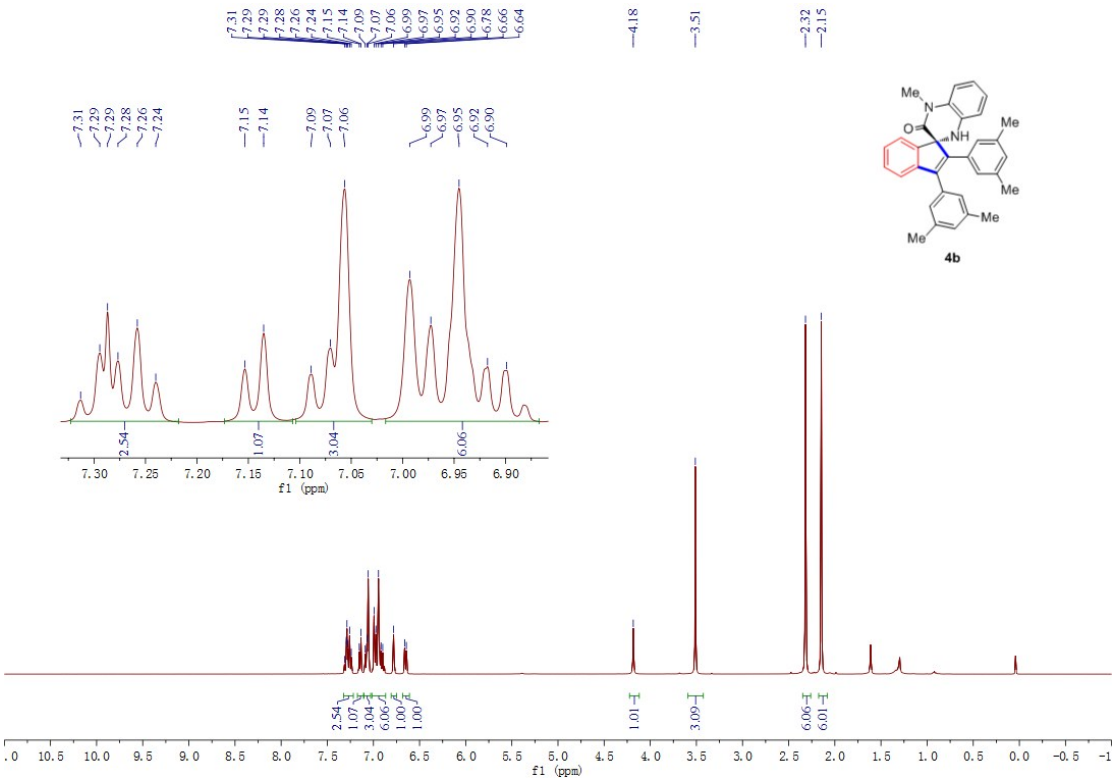
^{13}C NMR spectra of 3q ($CDCl_3$)



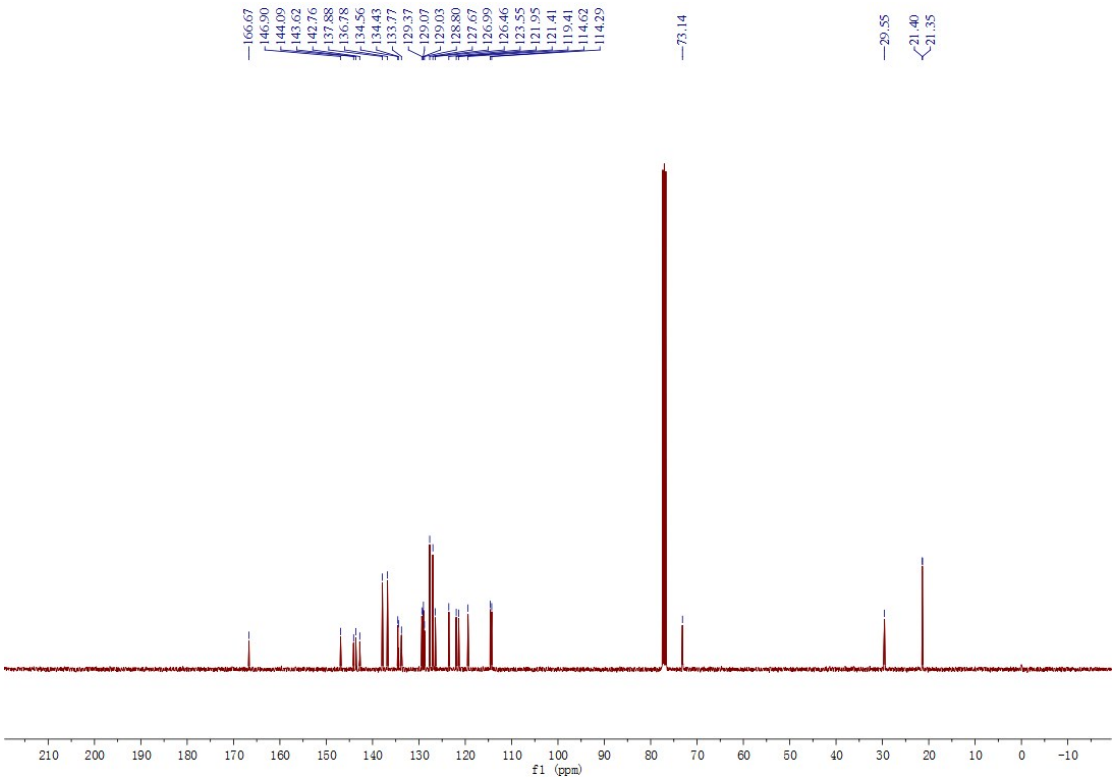
^{1}H NMR spectra of 4a ($CDCl_3$)



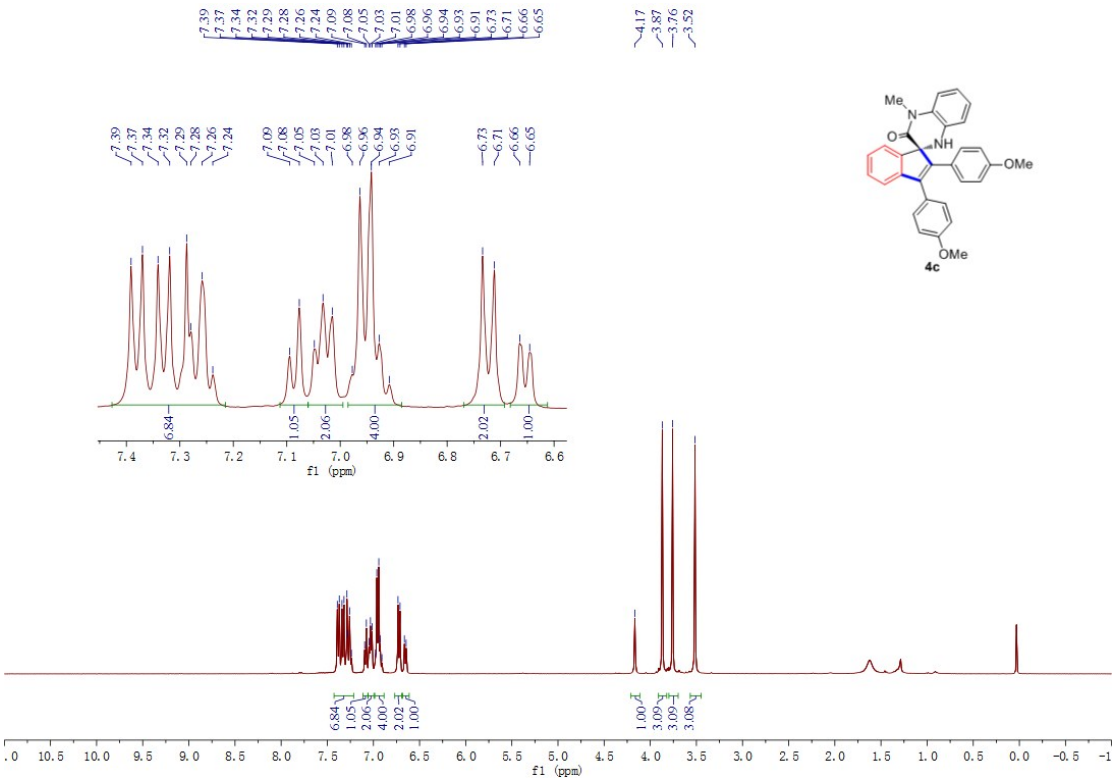
^{13}C NMR spectra of 4a ($CDCl_3$)



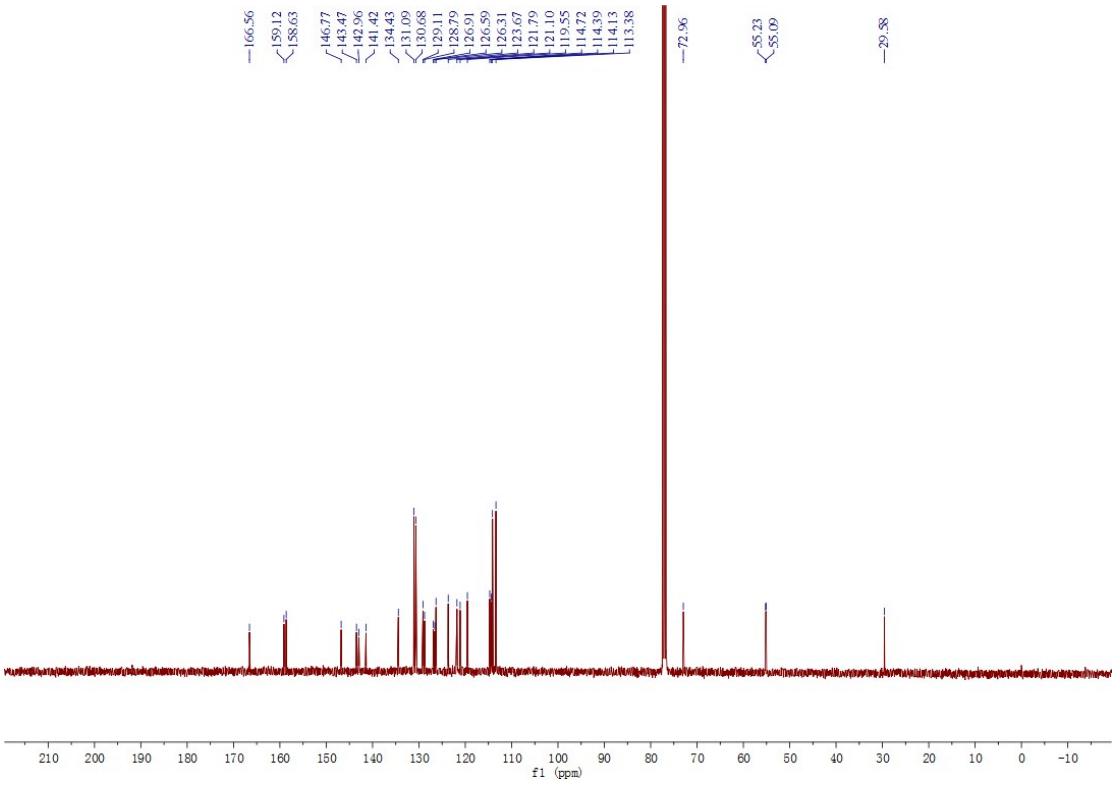
^{1}H NMR spectra of 4b ($CDCl_3$)



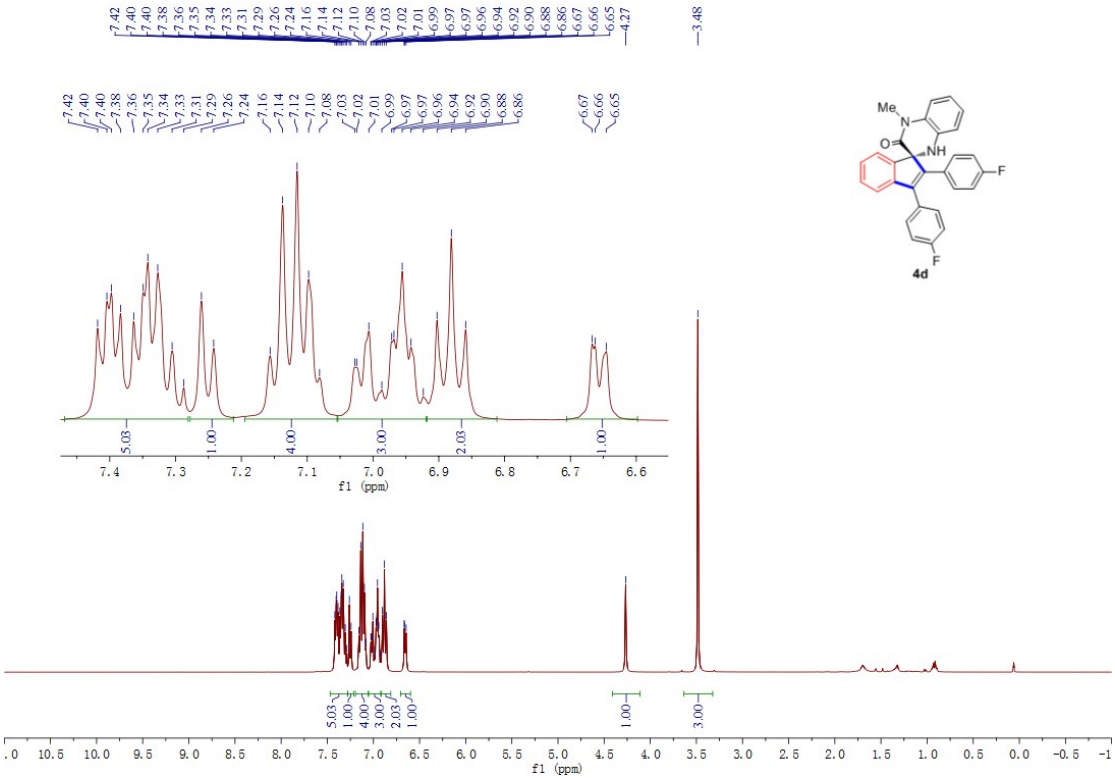
^{13}C NMR spectra of 4b ($CDCl_3$)



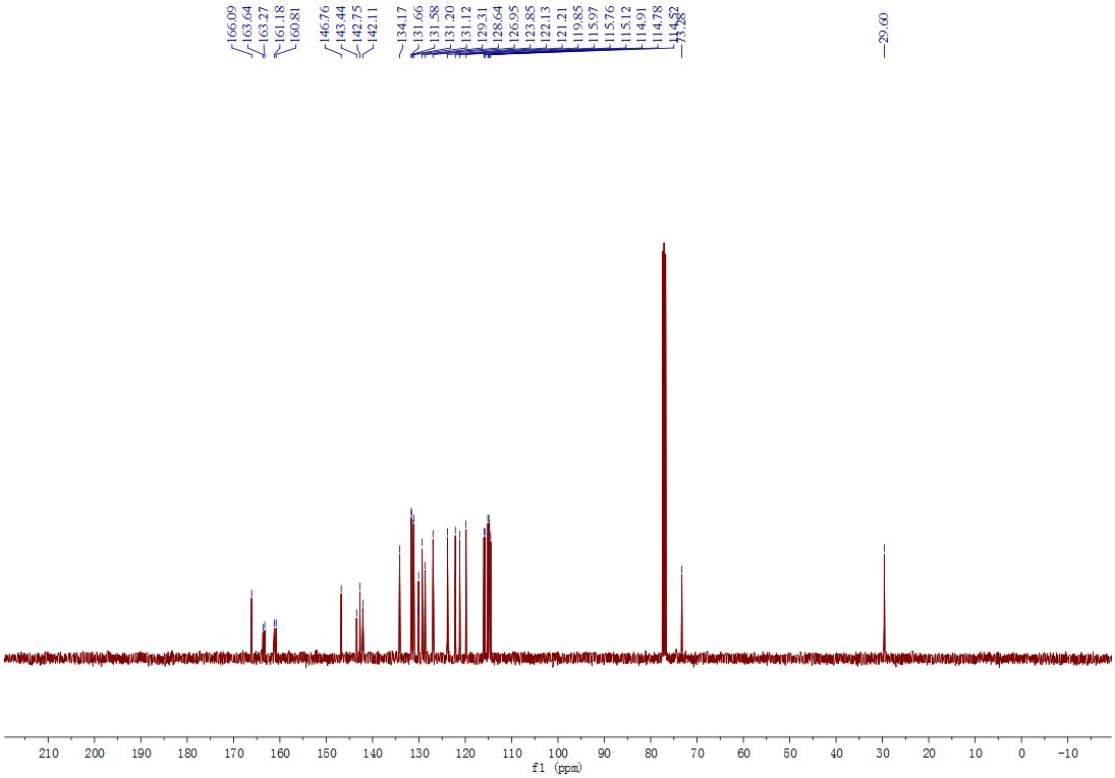
^{1}H NMR spectra of 4c ($CDCl_3$)



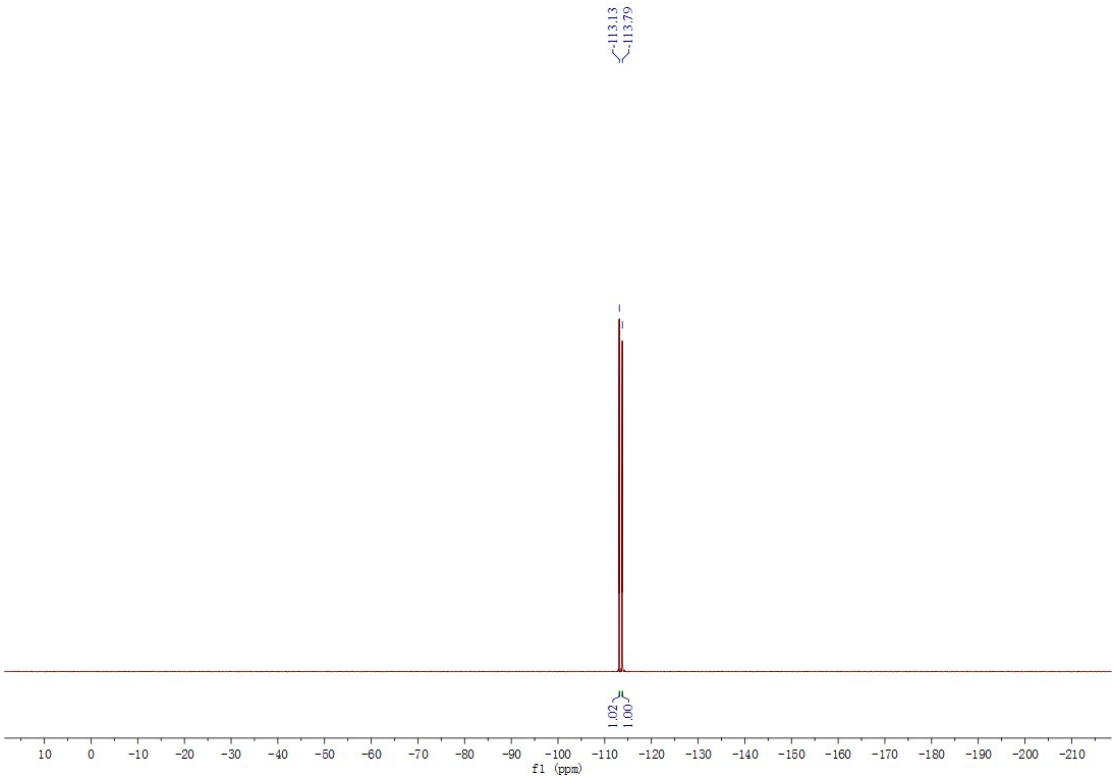
^{13}C NMR spectra of 4c ($CDCl_3$)



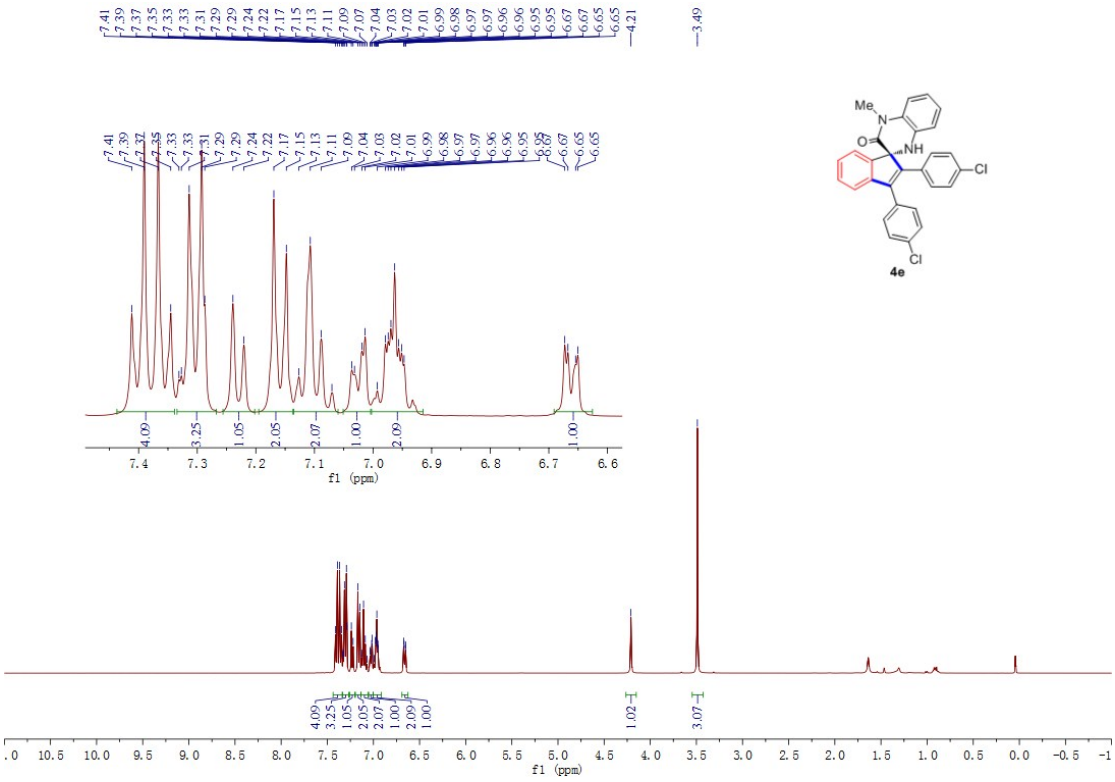
^{1}H NMR spectra of 4d ($CDCl_3$)



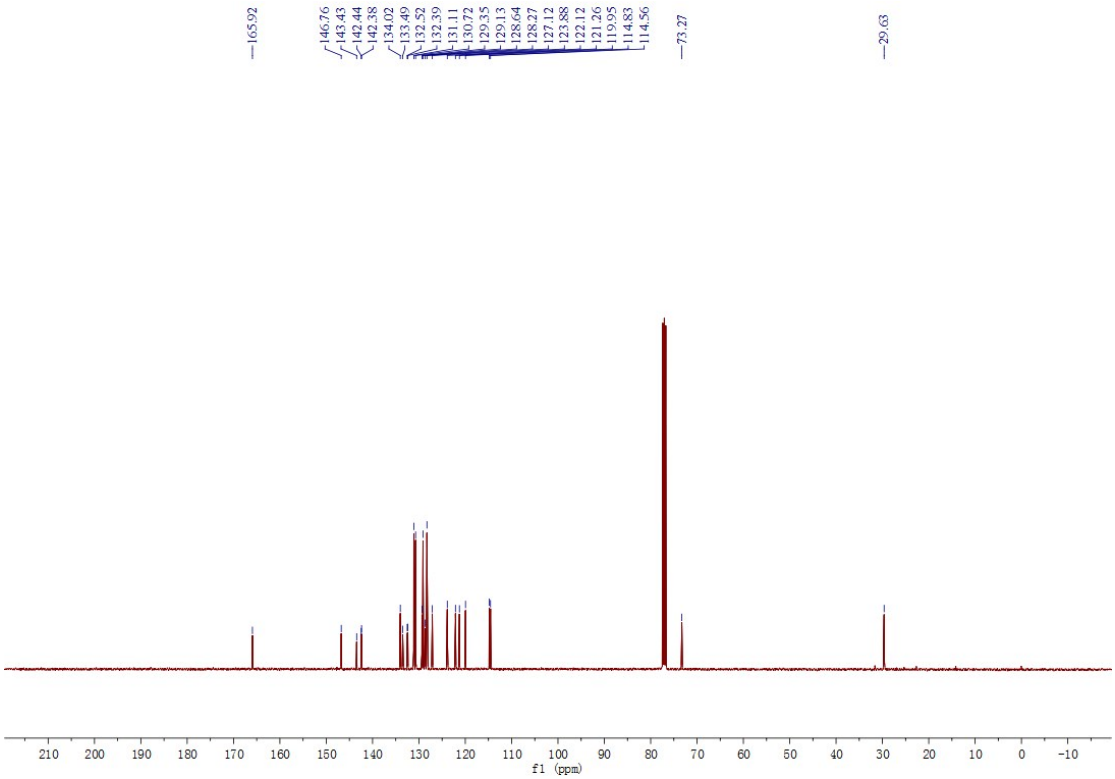
^{13}C NMR spectra of 4d ($CDCl_3$)



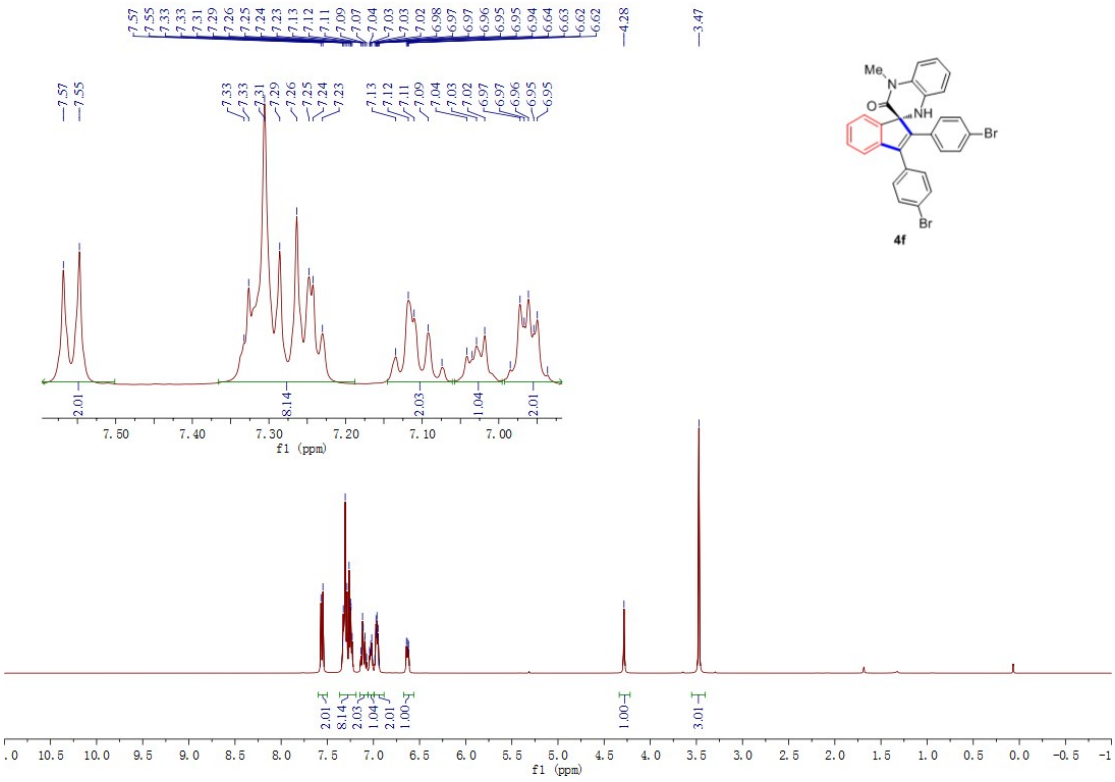
^{19}F NMR spectra of 3d ($CDCl_3$)



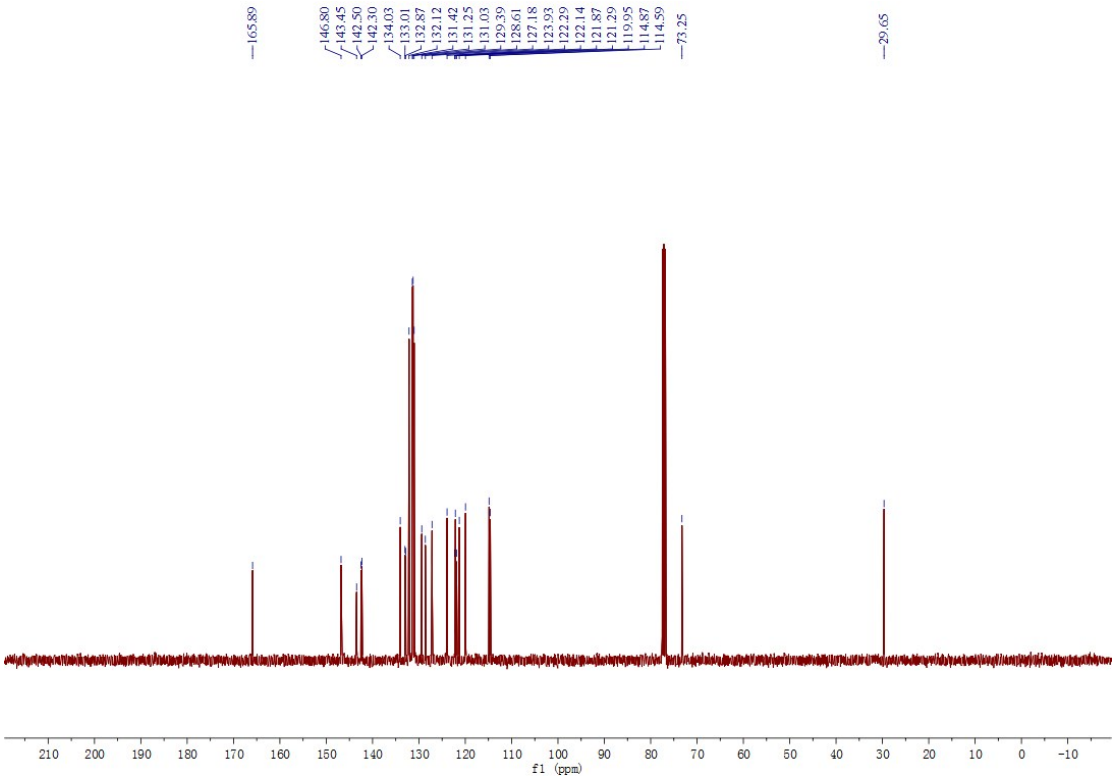
^{1}H NMR spectra of 4e ($CDCl_3$)



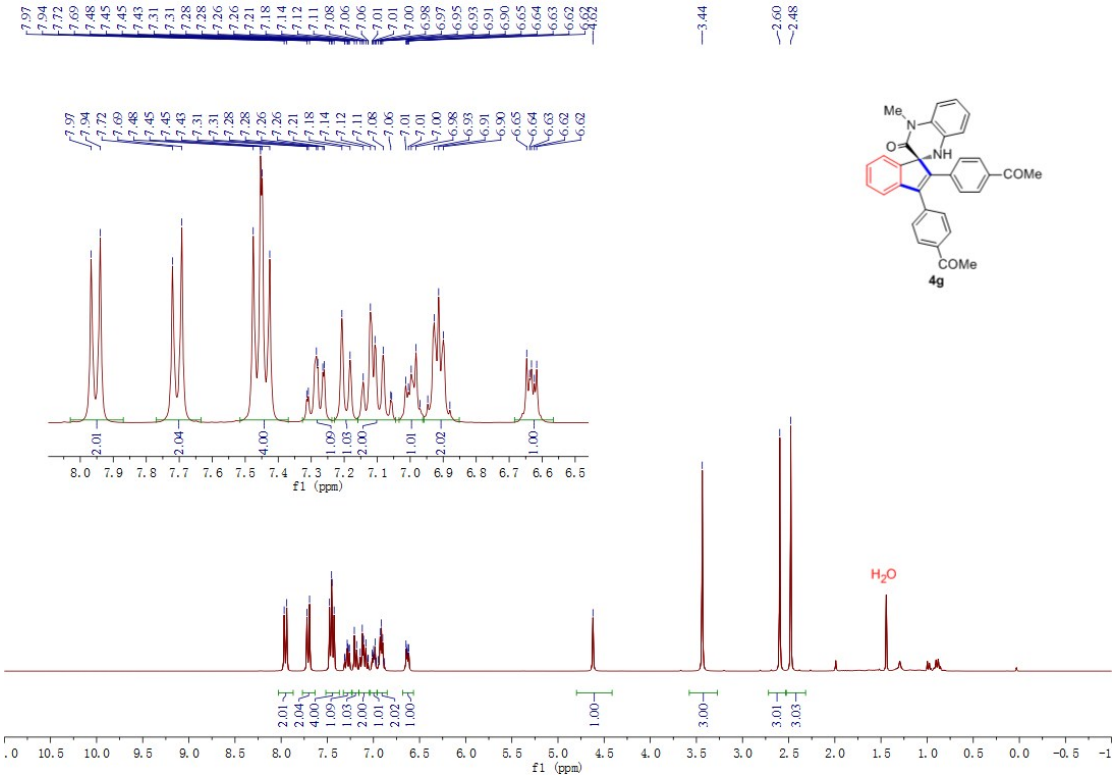
^{13}C NMR spectra of 4e ($CDCl_3$)



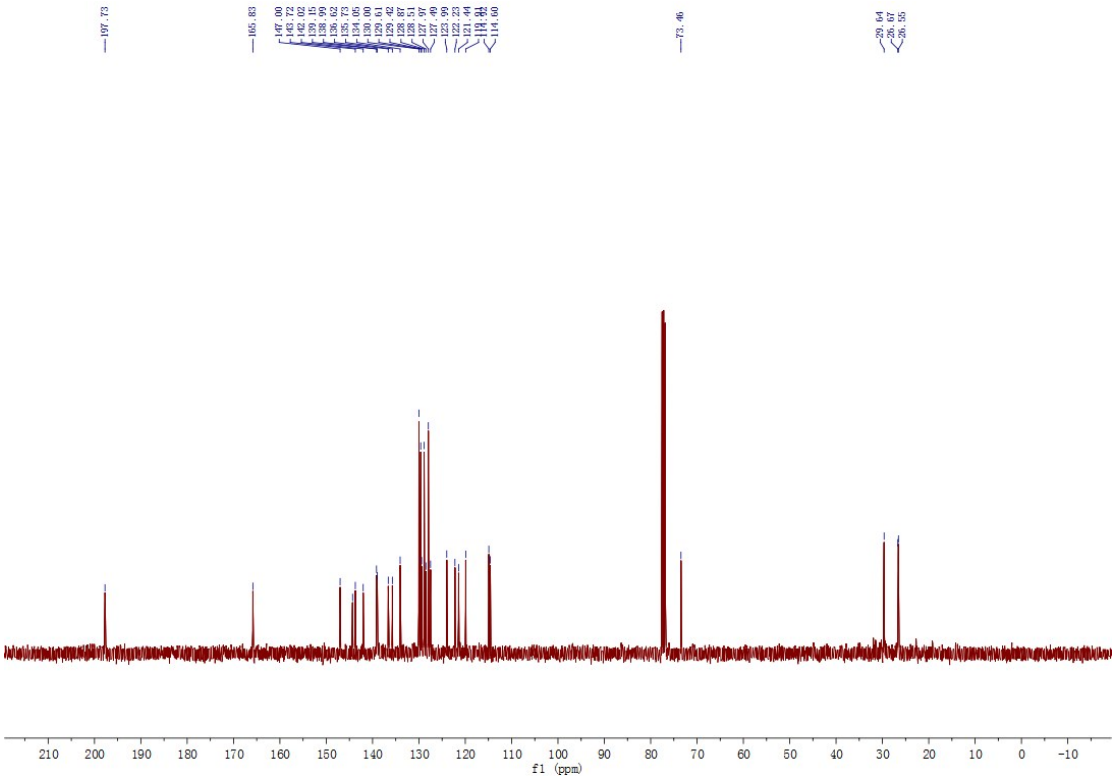
^{1}H NMR spectra of 4f ($CDCl_3$)



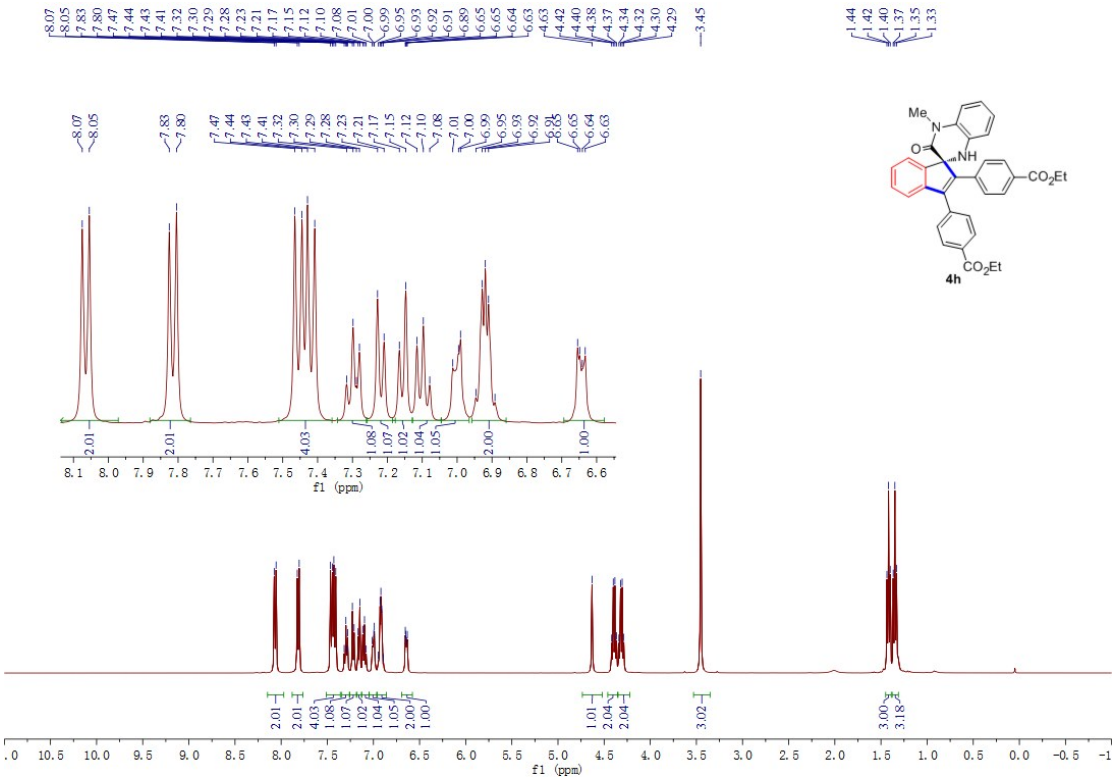
^{13}C NMR spectra of 4f ($CDCl_3$)



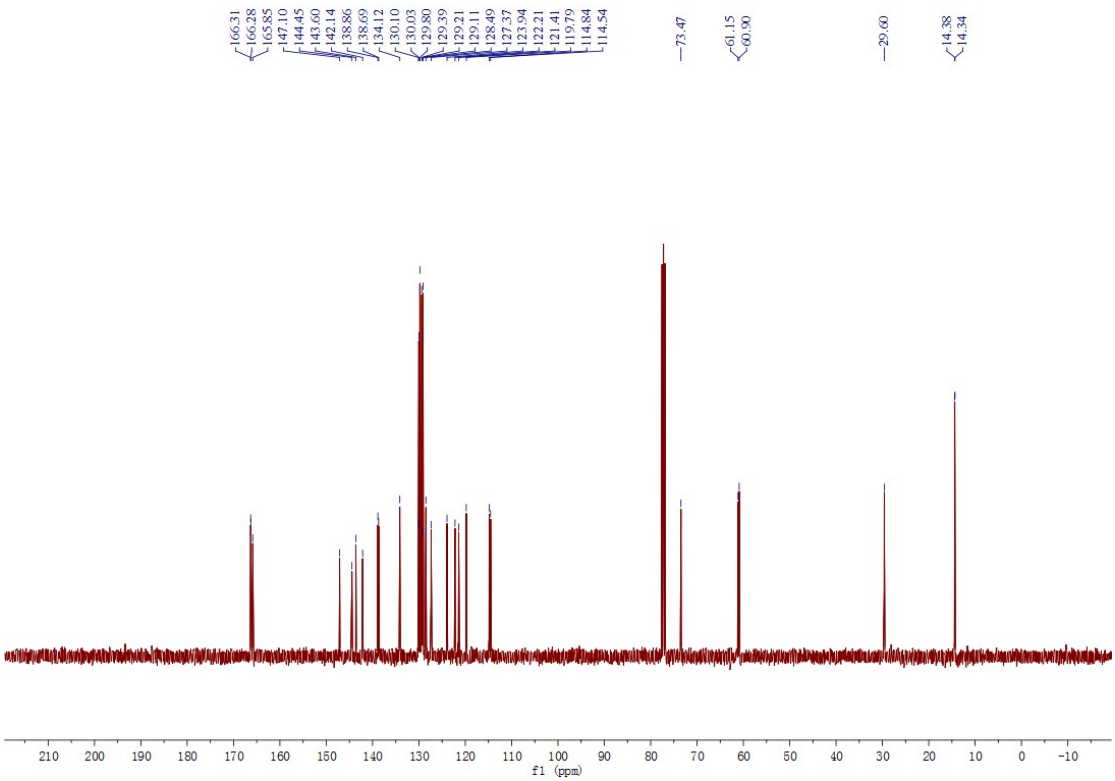
^{1}H NMR spectra of 4g ($CDCl_3$)



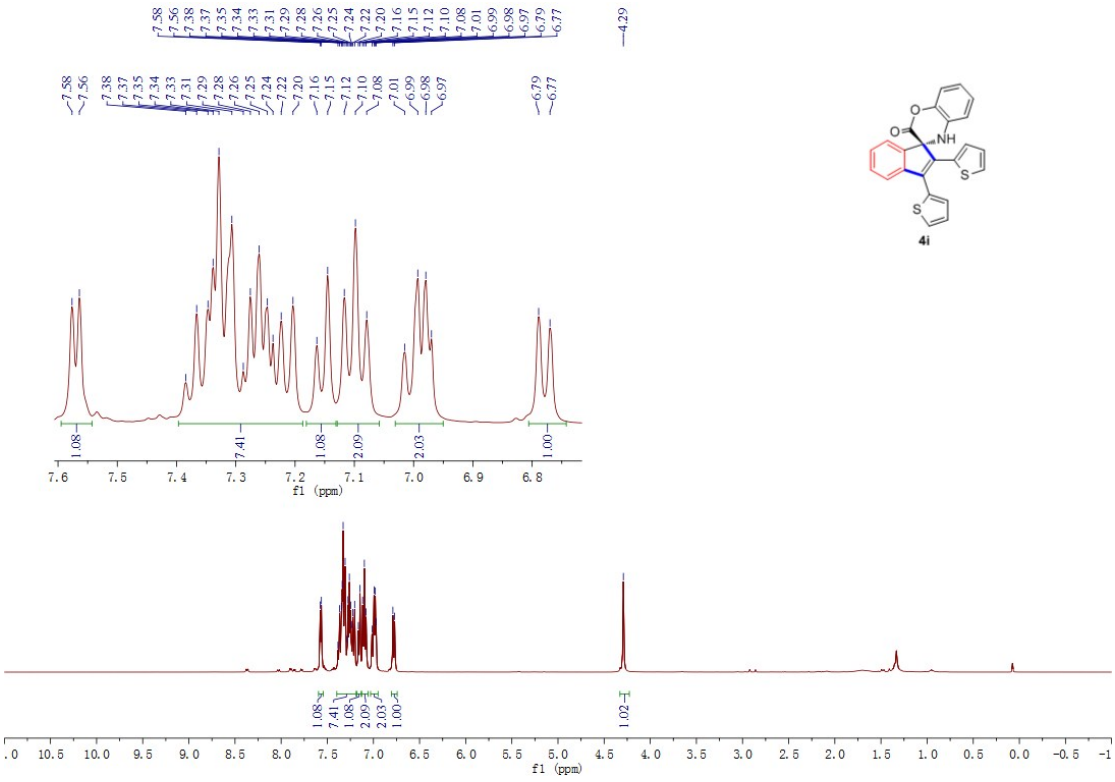
^{13}C NMR spectra of 4g ($CDCl_3$)



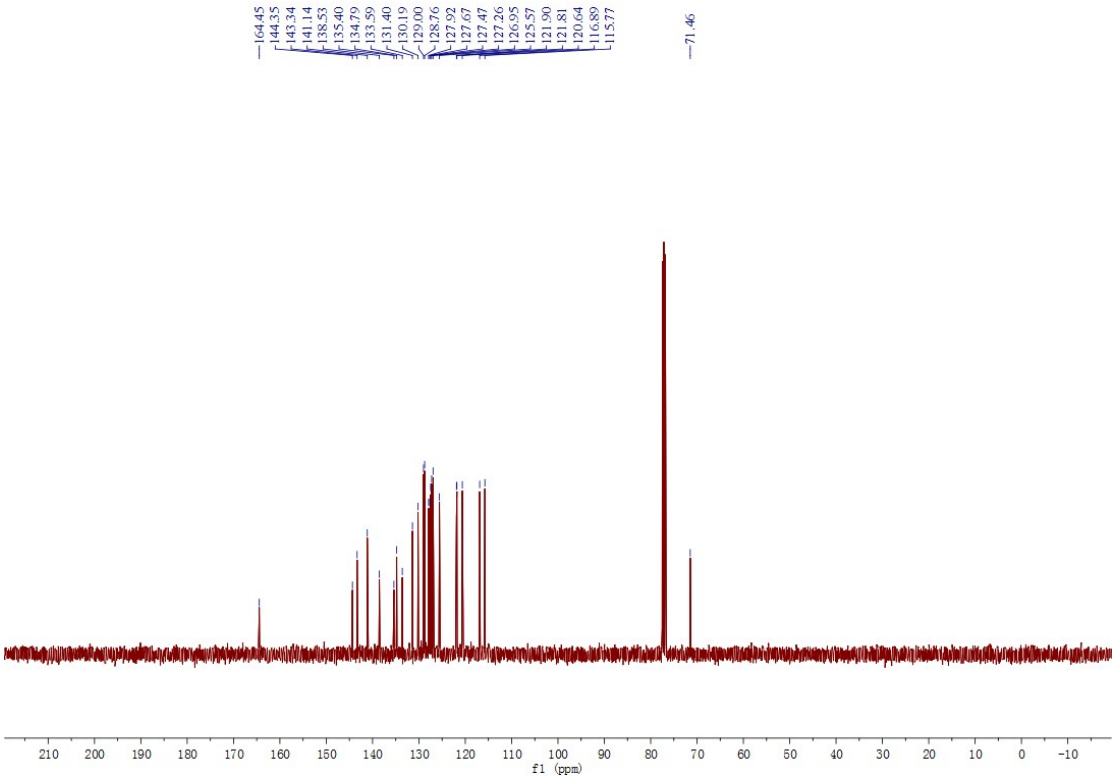
^{1}H NMR spectra of 4h ($CDCl_3$)



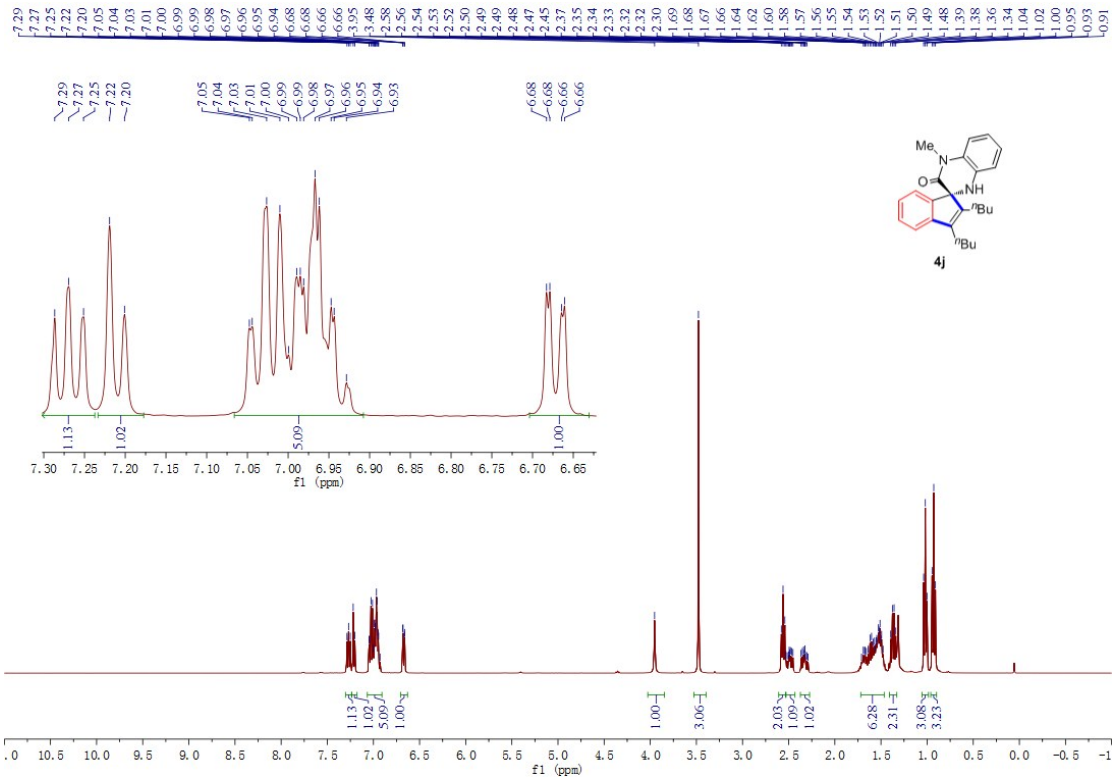
^{13}C NMR spectra of 4h ($CDCl_3$)



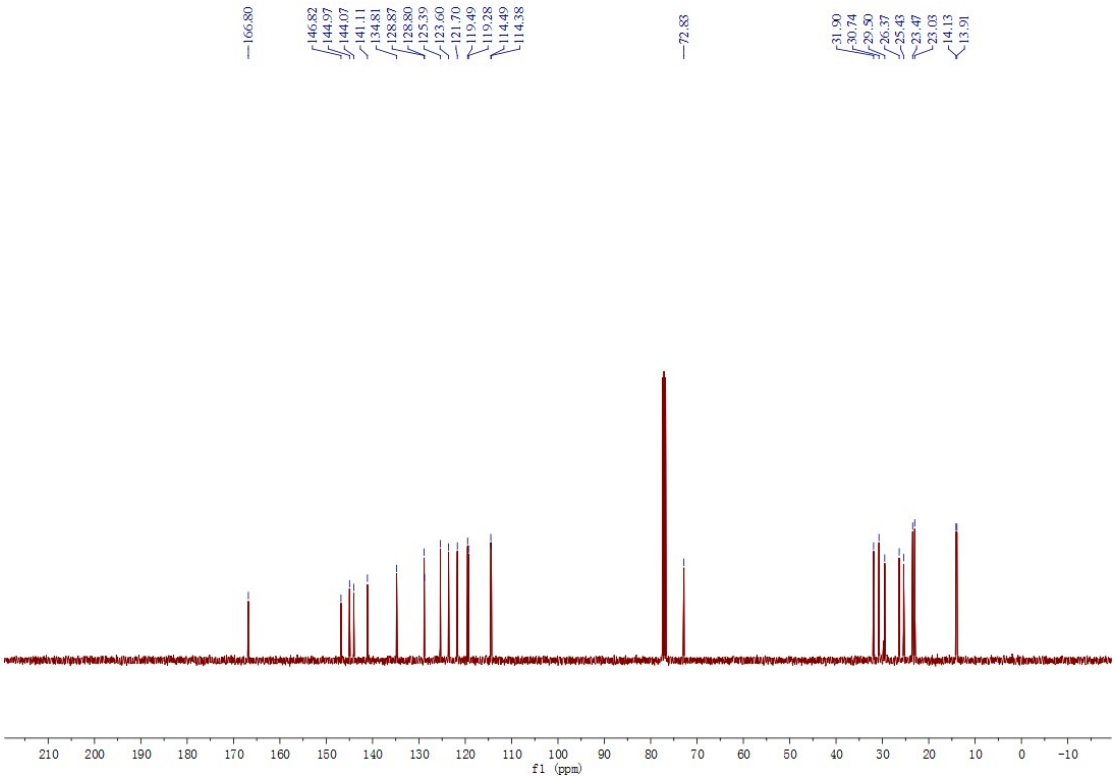
^{1}H NMR spectra of 4i ($CDCl_3$)



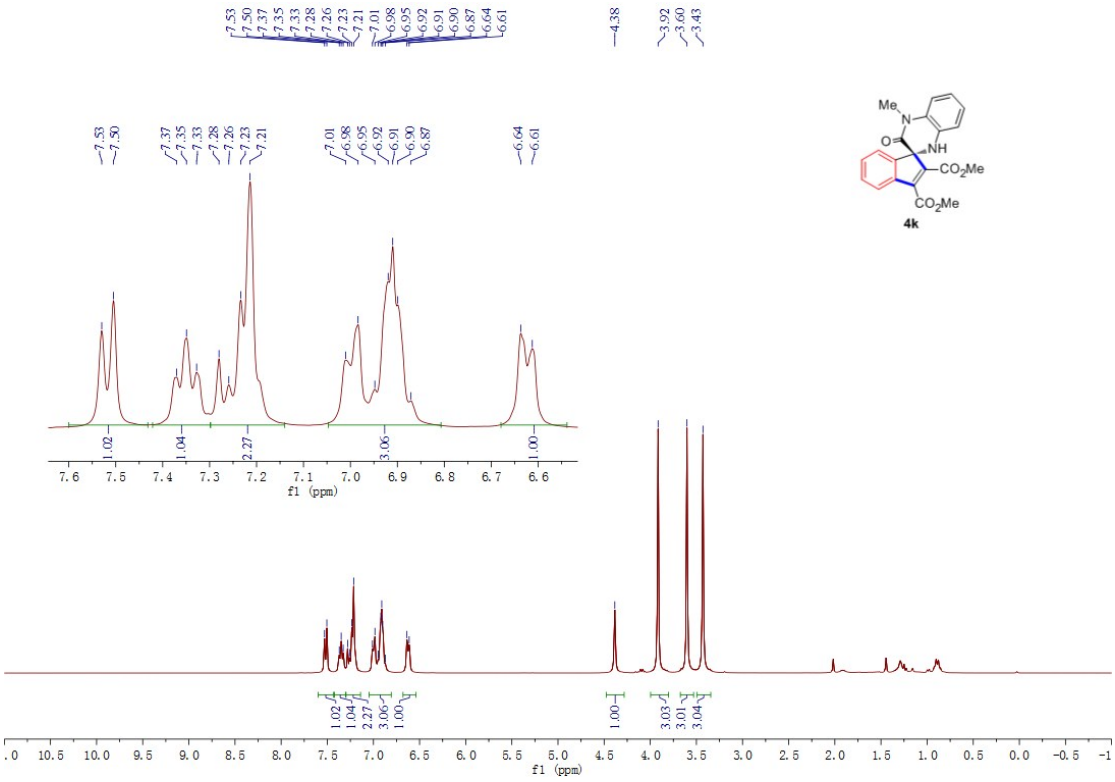
^{13}C NMR spectra of 4i ($CDCl_3$)



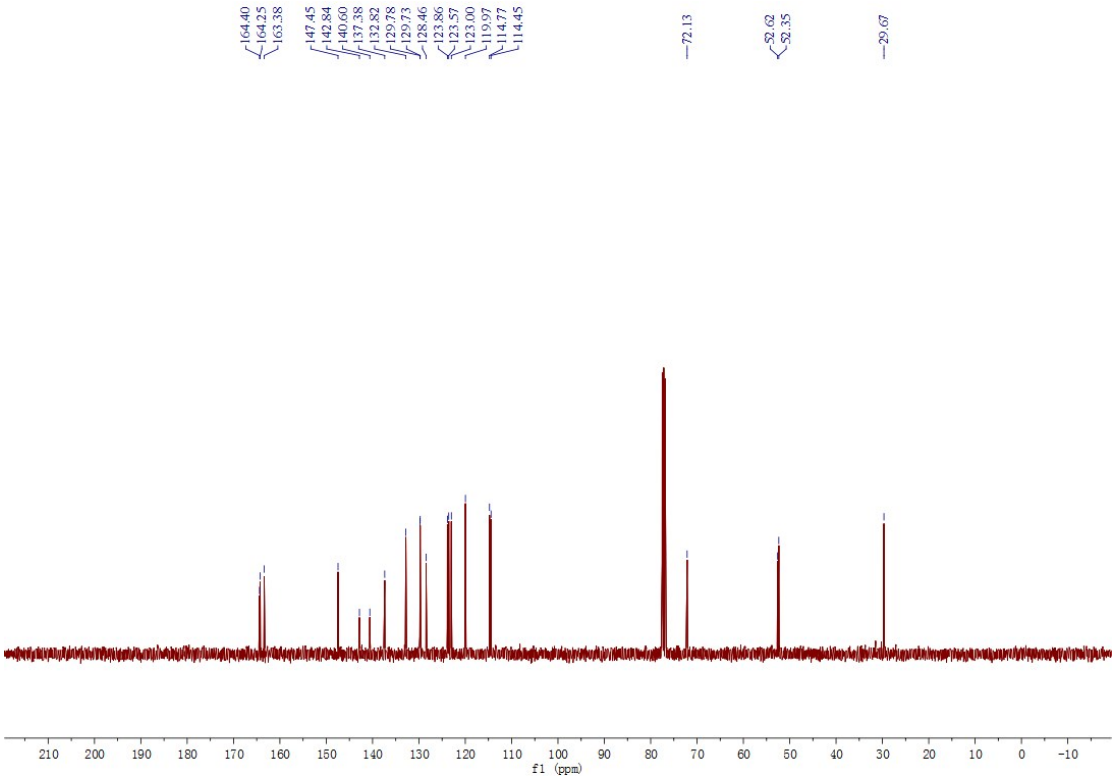
^{1}H NMR spectra of 4j ($CDCl_3$)



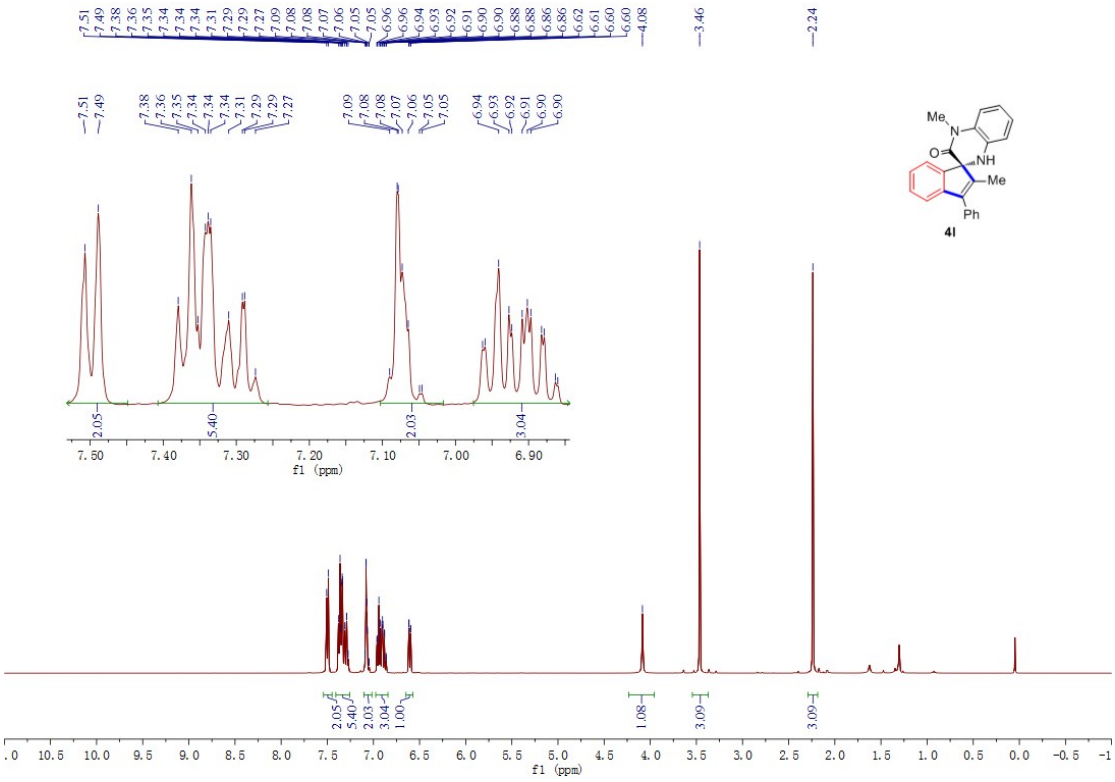
^{13}C NMR spectra of 4j ($CDCl_3$)



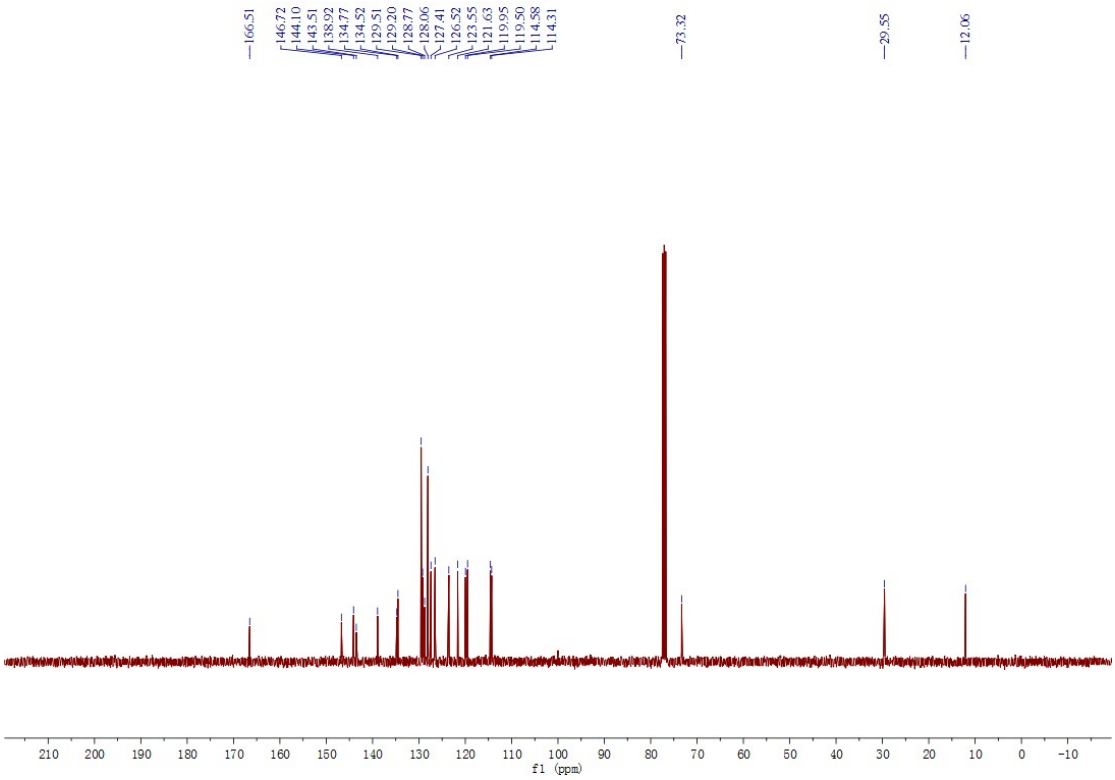
^{1}H NMR spectra of 4k ($CDCl_3$)



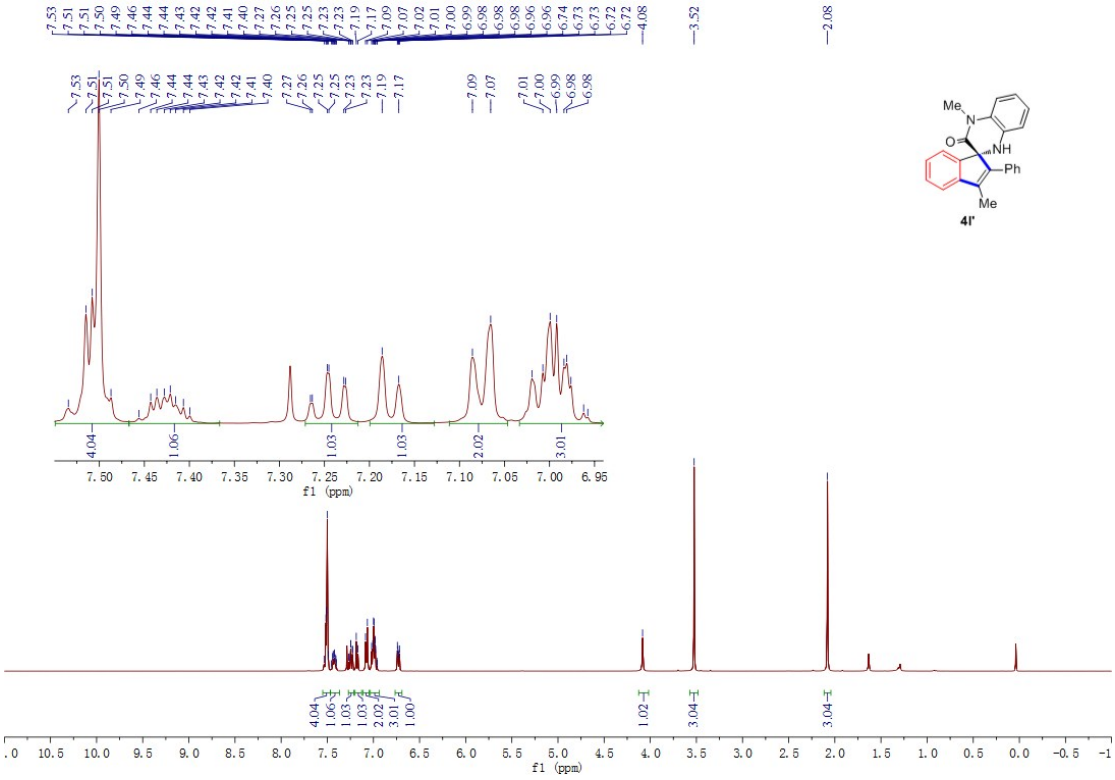
^{13}C NMR spectra of 4k ($CDCl_3$)



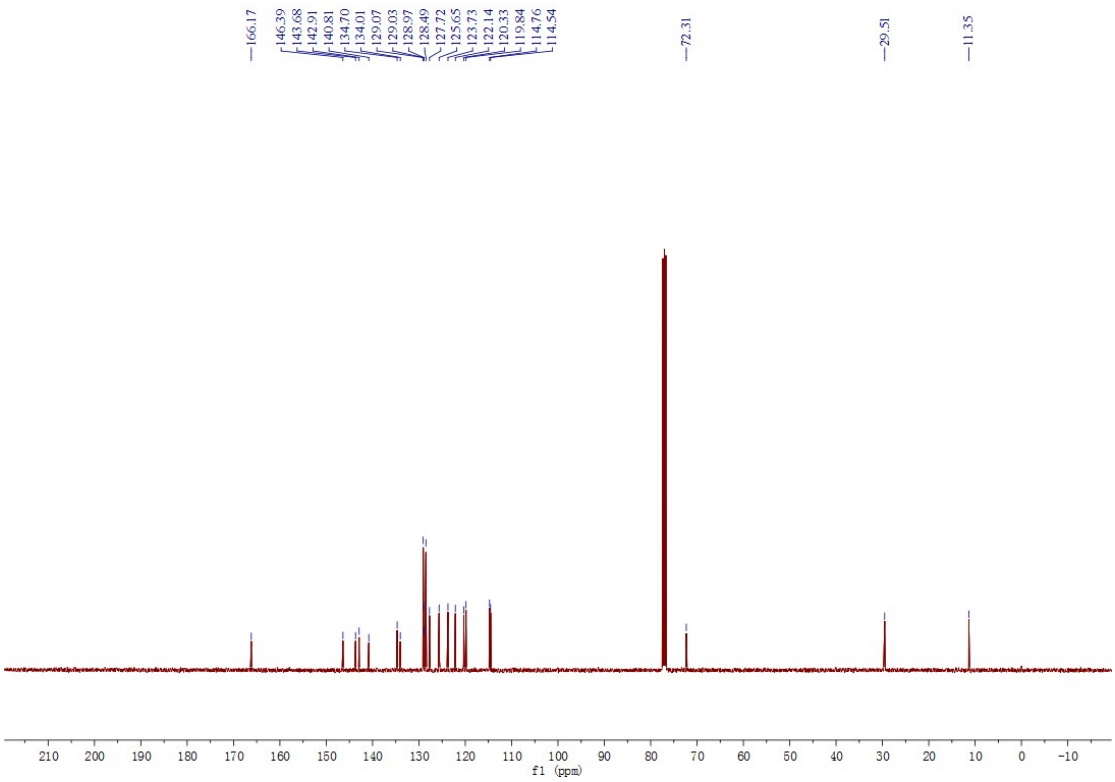
^{1}H NMR spectra of 4l ($CDCl_3$)



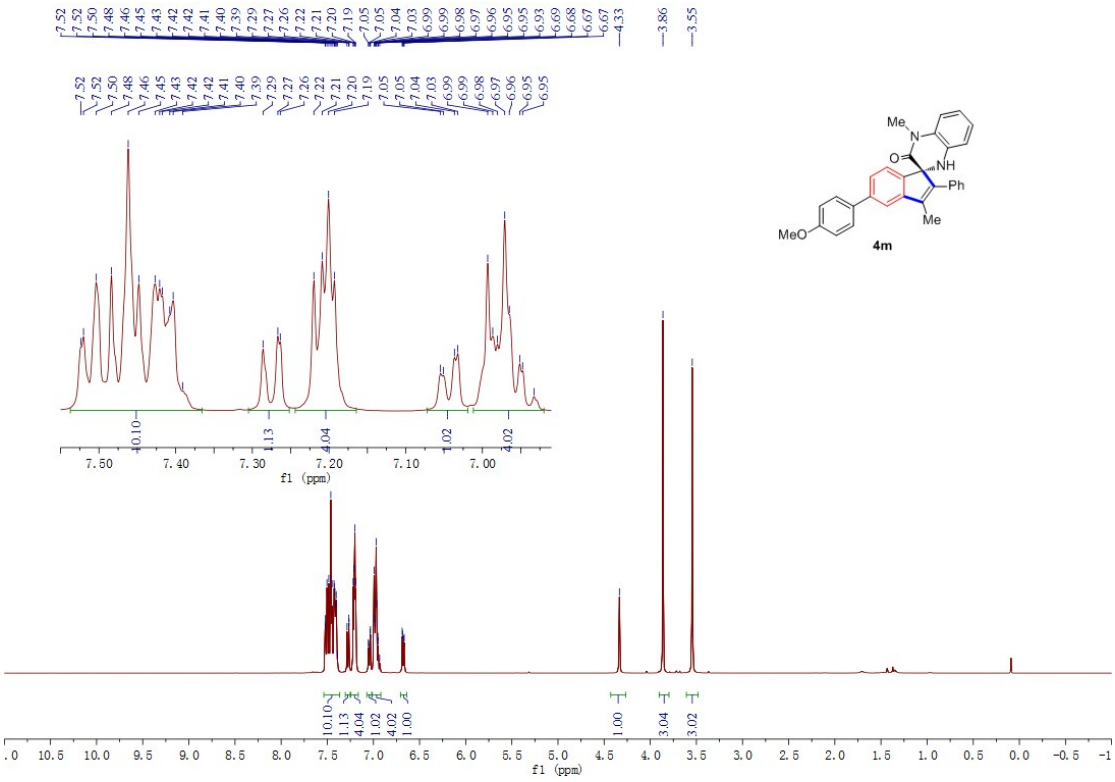
^{13}C NMR spectra of 4l ($CDCl_3$)



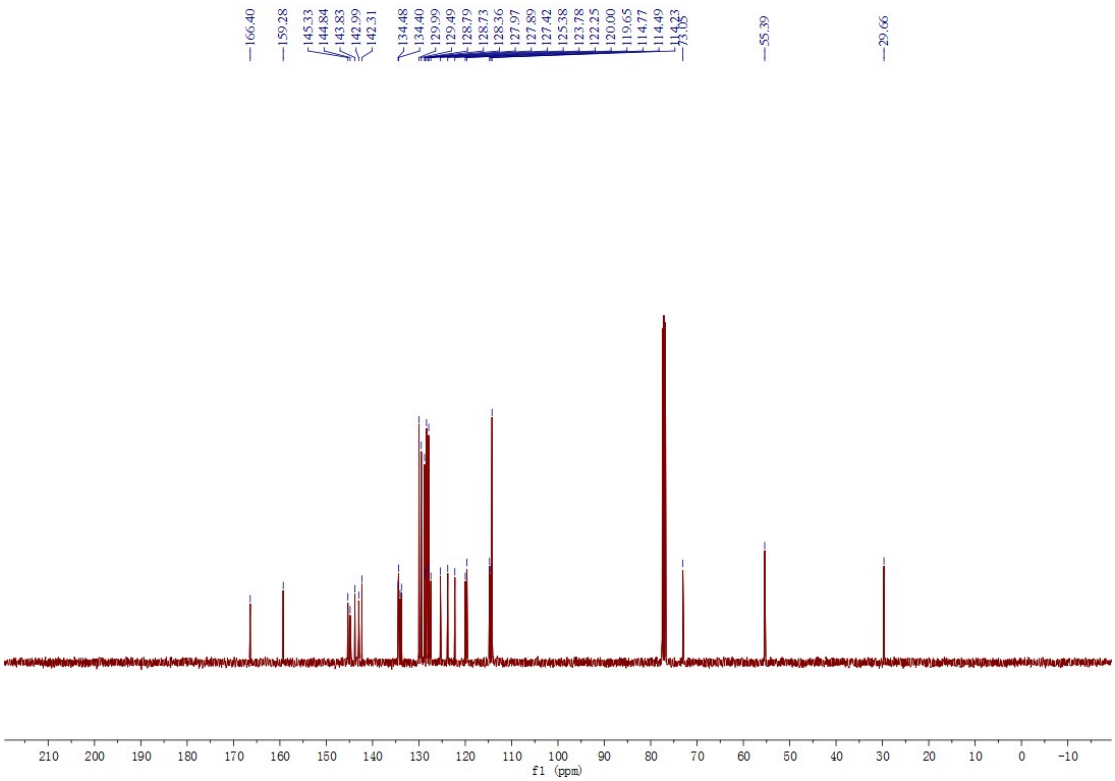
^{1}H NMR spectra of 4l' ($CDCl_3$)



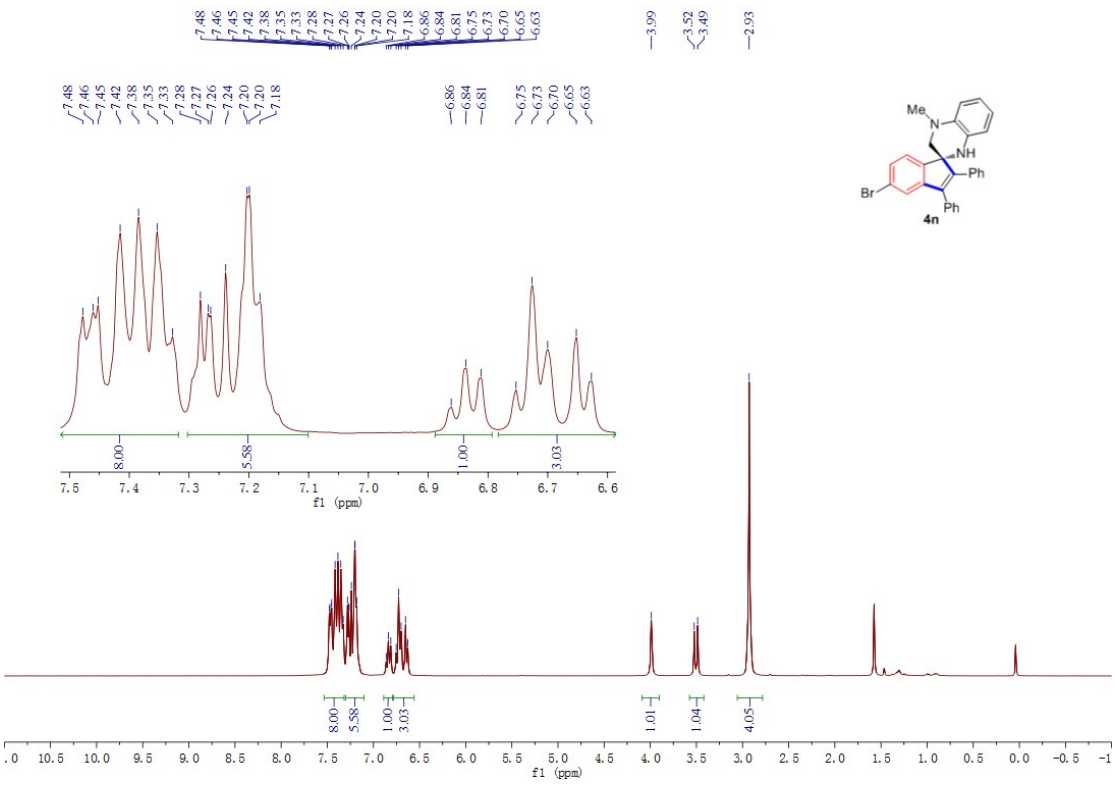
^{13}C NMR spectra of 4l' ($CDCl_3$)



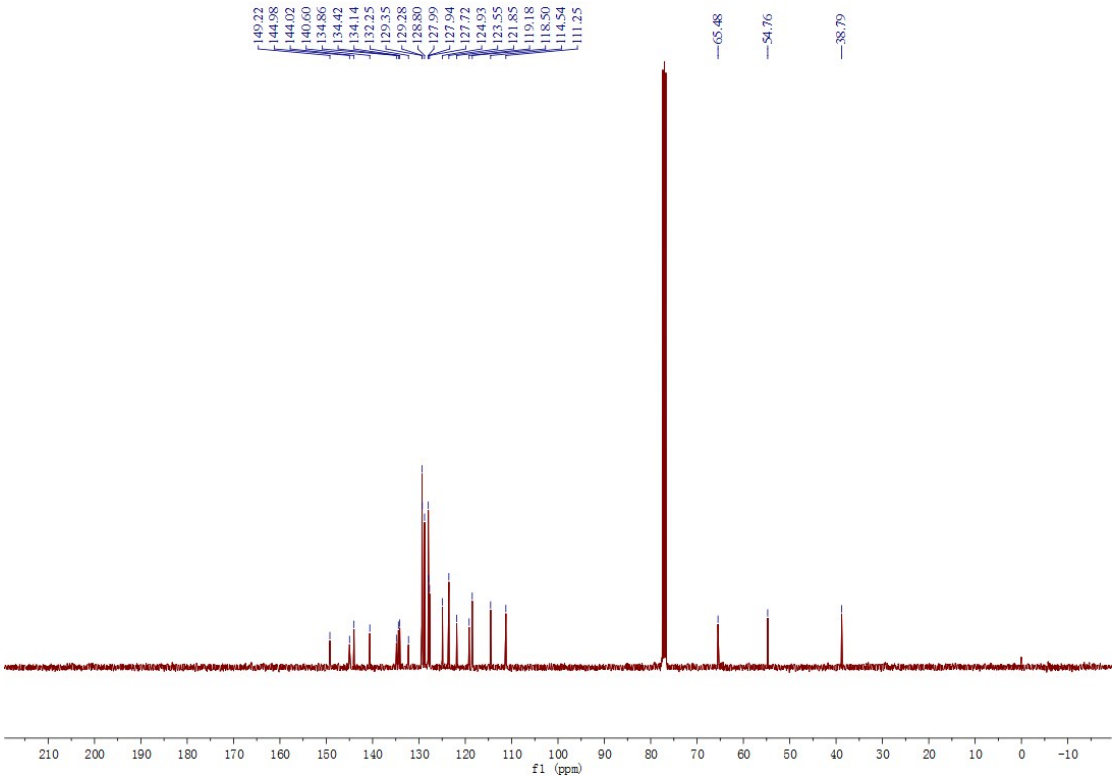
^{1}H NMR spectra of 4m ($CDCl_3$)



^{13}C NMR spectra of 4m ($CDCl_3$)



^{1}H NMR spectra of 4n ($CDCl_3$)



^{13}C NMR spectra of 4n ($CDCl_3$)