

Supporting Information

Synthesis of fluorene-indole/benzofuran bicyclic molecules through palladium-catalyzed carboheterofunctionalization of alkynes

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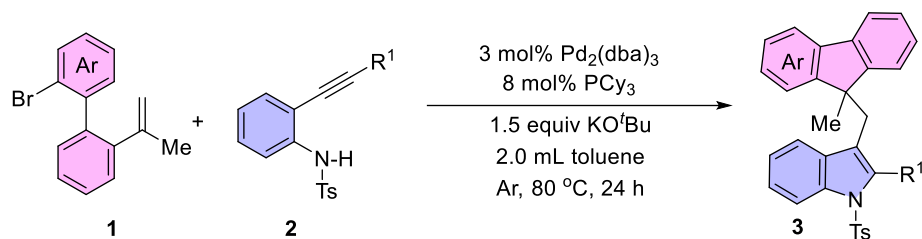
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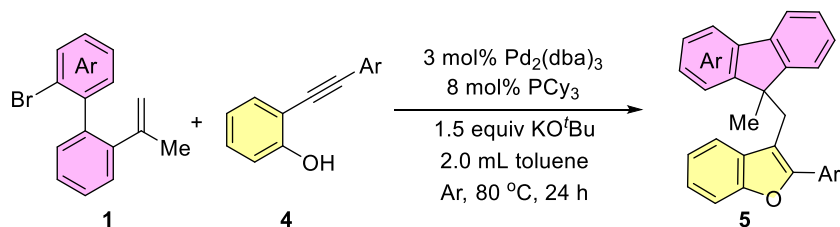
1. General information

Unless otherwise noted, all reactions were carried out under Argon atmosphere; materials obtained from commercial suppliers were used directly without further purification. ^1H NMR spectra, ^{13}C NMR spectra, and ^{19}F NMR spectra were recorded on Agilent 400, Bruker 400 MHz, 600 MHz spectrometer in CDCl_3 . NMR experiments are reported in δ units, parts per million (ppm), and were referenced to CDCl_3 (δ 7.26 or 77.0 ppm) as the internal standard. The data is being reported as (s = singlet, d = doublet, dd = doublet of doublet, t = triplet, m = multiplet or unresolved, br = broad signal, coupling constant(s) in Hz, integration). All the solvents were used directly without further purification. Reactions were monitored by TLC. Flash column chromatography was performed on silica (particle size 300-400 mesh ASTM, purchased from Yantai, China) and eluted with petroleum ether/ethyl acetate/acetone. Copies of NMR were processed with MestReNova Software. Single-crystal X-ray data were collected with a Bruker Smart APEX-2 CCD diffractometer. All the 2-(phenylethynyl)anilines substrates were synthesized according to the literature^[1].

2. General procedure



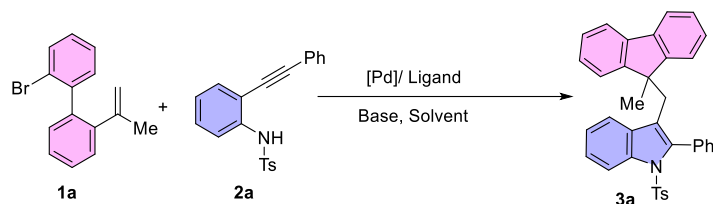
A sealed tube (10 mL) equipped with a magnetic stir bar was charged with Pd₂(dba)₃ (5.5 mg, 0.006 mmol, 0.03 equiv), PCy₃ (4.5 mg, 0.016 mmol, 0.08 equiv), KO^tBu (33.7 mg, 0.30 mmol, 1.5 equiv), aryl halide **1** (0.20 mmol, 1.0 equiv), *ortho*-ethynylaniline **2** (0.26 mmol, 1.3 equiv), and 2.0 mL toluene were added sequentially. Degassed toluene and backfilled with argon for 3 times (3× 1 min) at -78 °C. The reaction mixture was kept stirring at 80 °C for 24 h by use of module heating. After completion of the reaction (monitored by TLC), the mixture was concentrated in vacuum and the residue was purified by flash column chromatography on silica gel with petroleum ether-acetone or petroleum ether- ethyl acetate as eluent to give the desired product **3**.



A sealed tube (10 mL) equipped with a magnetic stir bar was charged with Pd₂(dba)₃ (5.5 mg, 0.006 mmol, 0.03 equiv), PCy₃ (4.5 mg, 0.016 mmol, 0.08 equiv), KO^tBu (33.7 mg, 0.30 mmol, 1.5 equiv), aryl halide **1** (0.20 mmol, 1.0 equiv), *ortho*-ethynylphenols **4** (0.26 mmol, 1.3 equiv) and 2.0 mL toluene were added sequentially. Degassed toluene and backfilled with argon for 3 times (3× 1 min) at -78 °C. The reaction mixture was kept stirring at 80 °C for 24 h by use of module heating. After completion of the reaction (monitored by TLC), the mixture was concentrated in vacuum and the residue was purified by flash column chromatography on silica gel with petroleum ether-acetone or petroleum ether- ethyl acetate as eluent to give the desired product **5**.

3. Screening of reaction conditions

Table S1 Optimization of reaction conditions conditions of 3-((9-methyl-9H-fluoren-9-yl)methyl)-2-phenyl-1-tosyl-1H-indole^a

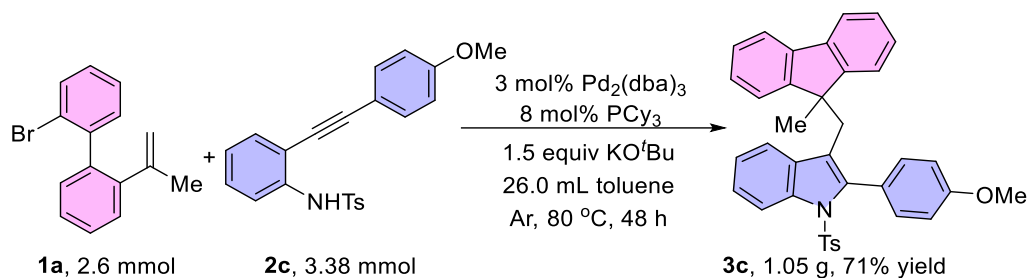


Entry	Pd sources	Ligand	Base	Solvent	Yield(%) ^b
1	Pd ₂ (dba) ₃	RuPhos	NaO ^t Bu	Toluene	19
2	Pd ₂ (dba) ₃	XPhos	NaO ^t Bu	Toluene	8
3	Pd ₂ (dba) ₃	PCy ₃	NaO ^t Bu	Toluene	60
4	Pd ₂ (dba) ₃	SPhos	NaO ^t Bu	Toluene	11
5	Pd ₂ (dba) ₃	/	NaO ^t Bu	Toluene	NR
6 ^c	Pd(OAc) ₂	PCy ₃	NaO ^t Bu	Toluene	43
7	[Pd(allyl)Cl] ₂	PCy ₃	NaO ^t Bu	Toluene	57
8 ^c	Pd(cod)Cl ₂	PCy ₃	NaO ^t Bu	Toluene	31
9 ^c	Pd(TFA) ₂	PCy ₃	NaO ^t Bu	Toluene	35
10	/	PCy ₃	NaO ^t Bu	Toluene	NR
11	Pd ₂ (dba) ₃	PCy ₃	KO ^t Bu	Toluene	97
12	Pd ₂ (dba) ₃	PCy ₃	LiO ^t Bu	Toluene	11
13	Pd ₂ (dba) ₃	PCy ₃	K ₂ CO ₃	Toluene	88
14	Pd ₂ (dba) ₃	PCy ₃	KOAc	Toluene	12
15	Pd ₂ (dba) ₃	PCy ₃	DABCO	Toluene	58
16	Pd ₂ (dba) ₃	PCy ₃	Et ₃ N	Toluene	trace
17	Pd ₂ (dba) ₃	PCy ₃	/	Toluene	NR
18	Pd ₂ (dba) ₃	PCy ₃	KO ^t Bu	Mesitylene	77
19	Pd ₂ (dba) ₃	PCy ₃	KO ^t Bu	THF	89
20	Pd ₂ (dba) ₃	PCy ₃	KO ^t Bu	1,4-dioxane	NR
21	Pd ₂ (dba) ₃	PCy ₃	KO ^t Bu	DCE	45
22	Pd ₂ (dba) ₃	PCy ₃	KO ^t Bu	DMSO	NR
23	Pd ₂ (dba) ₃	PCy ₃	KO ^t Bu	DMF	NR
24	Pd ₂ (dba) ₃	PCy ₃	KO ^t Bu	DMA	NR
25 ^d	Pd ₂ (dba) ₃	PCy ₃	KO ^t Bu	Toluene	50

^aReaction conditions: ^aReaction conditions: **1a** (0.2 mmol), **2a** (0.26 mmol), 3 mol% of Pd catalyst, ligands (8 mol%), base (1.5 equiv) in 2.0 mL toluene under argon at 80 °C for 24 h. ^bIsolated yields.

^cPd catalyst (6 mol%) were used. ^dUnder air for 24 h.

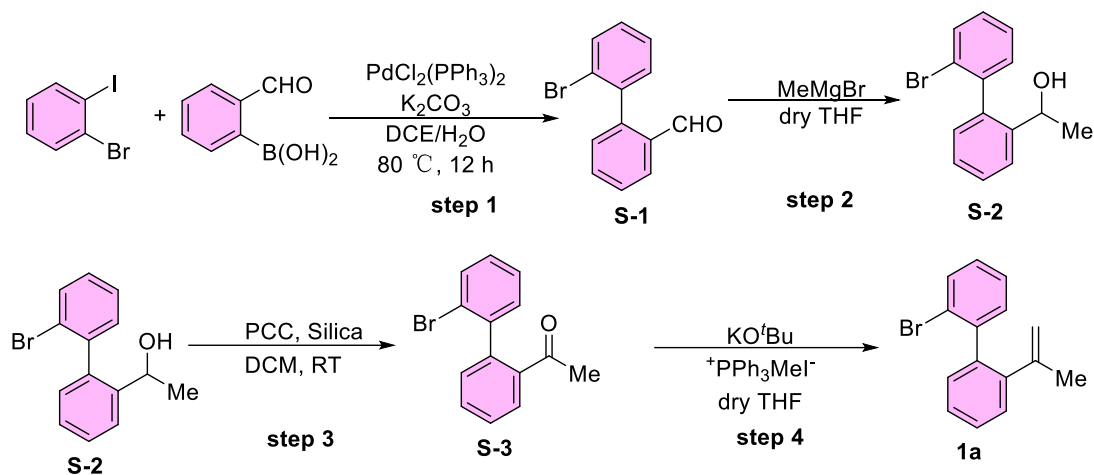
4. Gram-scale synthesis of 3c



A sealed tube (100 mL) equipped with a magnetic stir bar was charged with Pd₂(dba)₃ (71.4 mg, 0.078 mmol, 0.03 equiv), PCy₃ (58.3 mg, 0.208 mmol, 0.08 equiv), 2-bromo-2'-(prop-1-en-2-yl)-1,1'-biphenyl **1a** (0.710 g, 2.6 mmol, 1.0 equiv), *N*-(2-((4-methoxyphenyl)ethynyl)phenyl)-4-methylbenzenesulfonamide **2c** (1.275 g, 3.38 mmol, 1.3 equiv), KO^tBu (437.6 mg, 3.9 mmol, 1.5 equiv) and 26 mL toluene were added sequentially. Degassed toluene and backfilled with argon for 3 times (3 × 1 min) at -78 °C. The reaction mixture was kept stirring at 80 °C for 24 h by use of oil bath heating. After completion of the reaction (monitored by TLC), the mixture was concentrated in vacuum and the residue was purified by flash column chromatography on silica gel with petroleum ether-ethyl acetate as eluent to give the desired product **3c** (71% yield, 1.05 g).

5. General procedure for preparation of substrates

5.1 General procedure for the synthesis Biphenyl-Alkene substrates 1a.



Step 1. 2'-bromo-1,1'-biphenyl-2-carbaldehyde (**S-1**) was synthesized according to the literature^[2].

Step 2. Under argon atmosphere, an oven-dried Schlenk tube equipped with a magnetic stir bar was charged with 2'-bromo-1,1'-biphenyl-2-carbaldehyde (**S-1**) (4.78 g, 18.3 mmol). Dry THF (35 mL) was then added. A solution of and the mixture was stirred at 0°C, MeMgBr (25.6 mL, 25.6 mmol) was added dropwise at 0 °C. Then, the solution was stirred at 0 °C and allowing to naturally warm up to room temperature. After the reaction was complete, the reaction was quenched with saturated aqueous NH₄Cl (2 × 15 mL), extracted with ethyl acetate (2 × 20 mL), and concentrated to give the products **S-2** for the next step.

Step 3. Under argon atmosphere, an oven-dried Schlenk tube equipped with a magnetic stir bar was charged with PCC (11.38 g, 52.8 mmol) and silica (11.38 g) gel in 60 mL dichloromethane. **S-2** (4.88 g, 17.6 mmol) was then added and stirred at room temperature overnight. After the reaction is complete. The reaction solution is filtered through a diatomaceous earth pad, concentration in vacuo followed by silica gel column purification gave the desired product **S-3** (4.32 g, 90%, petroleum ether: ethyl acetate, 20:1).

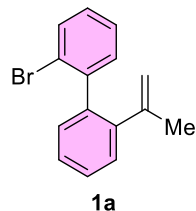
Step 4. An oven-dried round-bottom flask was charged with CH₃PPh₃I (12.69 g, 31.4 mmol) and Dry THF (100 mL). KO^tBu (5.29 g, 47.1 mmol) was added to the suspension at 0 °C. The resulting mixture was allowed to warm up to room temperature and stirred for 1 h. The yellow suspension was cooled to 0 °C again followed by portion-wise addition of the carbonyl substrate **S-3** (4.32 g, 15.7 mmol). Subsequently, the mixture was further stirred at room temperature for 12 hours. After the completion of the reaction, the solvent was removed by evaporation, the resulting mixture was diluted with saturated aqueous NH₄Cl (30 mL) and extract with ethyl acetate (3 × 20 mL), and the combined organic layer was dried with anhydrous Na₂SO₄. Concentration in vacuo followed by silica gel column purification with petroleum ether/ethyl acetate eluent gave the desired product **1a** (3.60 g, 84%, petroleum ether: ethyl acetate, 100:1).

5.2. Synthesis the substrates **1b-1d** method follows the method of synthesis **1a**.

6. Characterization data

6.1 Characterization data for the substrates.

2-bromo-2'-(prop-1-en-2-yl)-1,1'-biphenyl (**1a**)

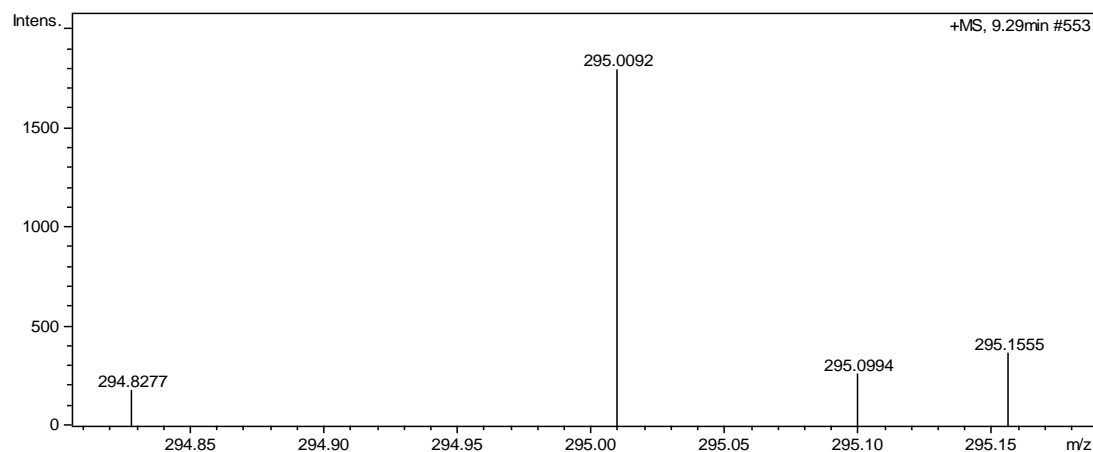


Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 100:1) give the product **1a** (3.60 g, 84% yield) as a white solid from the corresponding ketone **S-3** (4.32 g, 15.7 mmol). Mp: 51-53 °C.

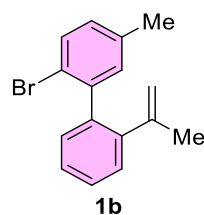
$^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ 7.63 (d, $J=8.0$ Hz, 1H), 7.39-7.32 (m, 3H), 7.30-7.28 (m, 1H), 7.26-7.16 (m, 3H), 4.98 (s, 1H), 4.83 (s, 1H), 1.78 (s, 3H);

$^{13}\text{C NMR}$ (CDCl_3 , 100 MHz) δ 144.8, 142.7, 142.6, 138.8, 132.5, 131.5, 130.4, 128.5, 128.3, 127.8, 126.8, 126.5, 123.7, 116.3, 23.5;

HRMS Calcd (ESI) m/z for $\text{C}_{15}\text{H}_{13}\text{Br Na}$ $[\text{M} + \text{Na}]^+$: 295.0093, found: 295.0092.



2-bromo-5-methyl-2'-(prop-1-en-2-yl)-1,1'-biphenyl (**1b**)



Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 100:1) give the product **1b** (3.78 g, 84% yield) as a white solid from the corresponding ketone

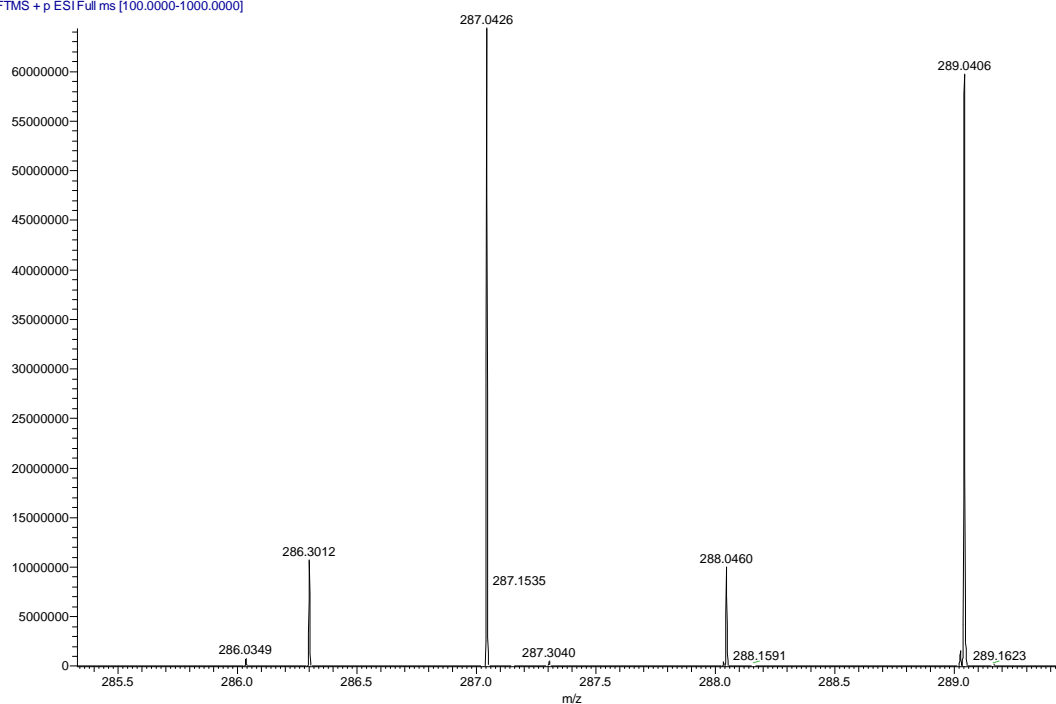
(4.54 g, 15.7 mmol). Mp: 50-52 °C.

$^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ 7.50 (d, $J=8.0$ Hz, 1H), 7.38-7.29 (m, 3H), 7.21-7.19 (m, 1H), 7.07 (s, 1H), 7.01-6.99 (m, 1H), 4.99 (s, 1H), 4.85 (s, 1H), 2.31 (s, 3H), 1.80 (s, 3H);

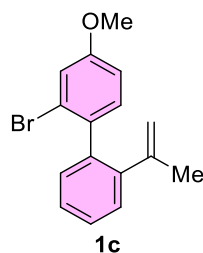
$^{13}\text{C NMR}$ (CDCl_3 , 100 MHz) δ 144.9, 142.7, 142.3, 138.9, 136.6, 132.2 (2C), 130.4, 129.4, 128.2, 127.6, 126.5, 120.2, 116.1, 23.5, 20.9;

HRMS Calcd (ESI) m/z for $\text{C}_{16}\text{H}_{16}\text{Br}$ $[\text{M} + \text{H}]^+$: 287.0430, found: 287.0426.

LHR-1-12 #1549 RT: 6.91 AV: 1 NL: 6.44E7
T: FTMS + p ESI Full ms [100.0000-1000.0000]



2-bromo-4-methoxy-2'-(prop-1-en-2-yl)-1,1'-biphenyl (**1c**)



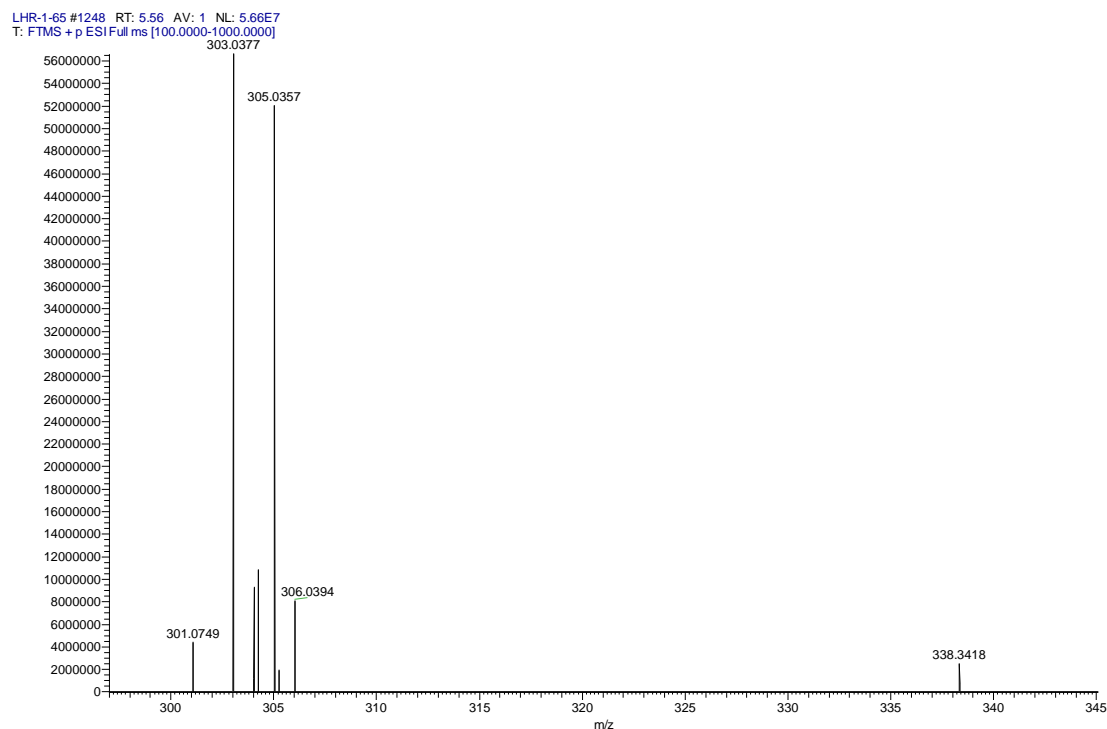
Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 90:1) give the product **1c** (0.74 g, 76% yield) as a white oil from the corresponding ketone (0.96 g, 3.2 mmol).

$^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ 7.36-7.33 (m, 2H), 7.32-7.29 (m, 1H), 7.22-7.19 (m, 2H), 7.15 (d, $J=8.4$ Hz, 1H), 6.88-6.85 (m, 1H), 4.99 (s, 1H), 4.85 (s, 1H), 3.84 (s, 3H),

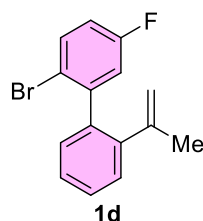
1.77 (s, 3H);

^{13}C NMR (CDCl_3 , 100 MHz) δ 159.0, 145.2, 143.1, 138.4, 134.8, 131.9, 130.9, 128.3, 127.6, 126.5, 123.8, 117.5, 116.1, 113.1, 55.5, 23.4;

HRMS Calcd (ESI) m/z for $\text{C}_{16}\text{H}_{16}\text{BrO}$ $[\text{M} + \text{H}]^+$: 303.0379, found: 303.0377.



2-bromo-5-fluoro-2'-(prop-1-en-2-yl)-1,1'-biphenyl (**1d**)



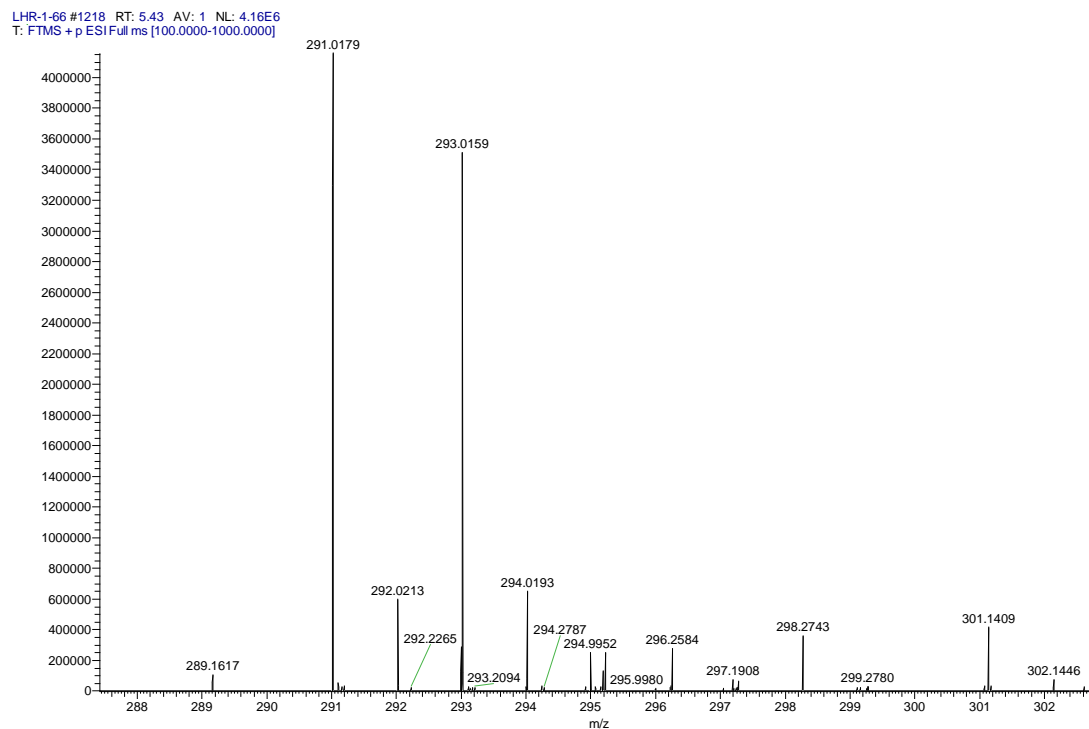
Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 100:1) give the product **1d** (0.80 g, 86% yield) as a white solid from the corresponding ketone (0.95 g, 3.2 mmol). Mp: 36-38 °C.

^1H NMR (CDCl_3 , 400 MHz) δ 7.58 (dd, $J_1 = 8.8$ Hz, $J_2 = 5.6$ Hz, 1H), 7.41-7.35 (m, 2H), 7.33-7.31 (m, 1H), 7.20-7.18 (m, 1H), 6.99 (dd, $J_1 = 9.2$ Hz, $J_2 = 3.2$ Hz, 1H), 6.95-6.90 (m, 1H), 5.01 (s, 1H), 4.83 (s, 1H), 1.82 (s, 3H);

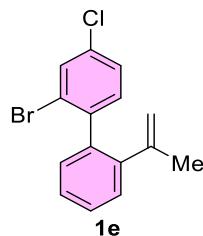
^{13}C NMR (CDCl_3 , 100 MHz) δ 161.4 (d, $J = 246.1$ Hz), 144.5 (d, $J = 7.9$ Hz), 144.4, 142.6, 137.8, 133.7 (d, $J = 8.2$ Hz), 130.2, 128.3, 128.2, 126.6, 118.5 (d, $J = 22.4$ Hz), 118.0 (d, $J = 3.1$ Hz), 116.6, 115.7 (d, $J = 22.3$ Hz), 23.5;

^{19}F NMR (CDCl_3 , 376 MHz) δ -115.7;

HRMS Calcd (ESI) m/z for $\text{C}_{15}\text{H}_{13}\text{BrF}$ $[\text{M} + \text{H}]^+$: 291.0179, found: 291.0179.



2-bromo-4-chloro-2'-(prop-1-en-2-yl)-1,1'-biphenyl (**1e**)



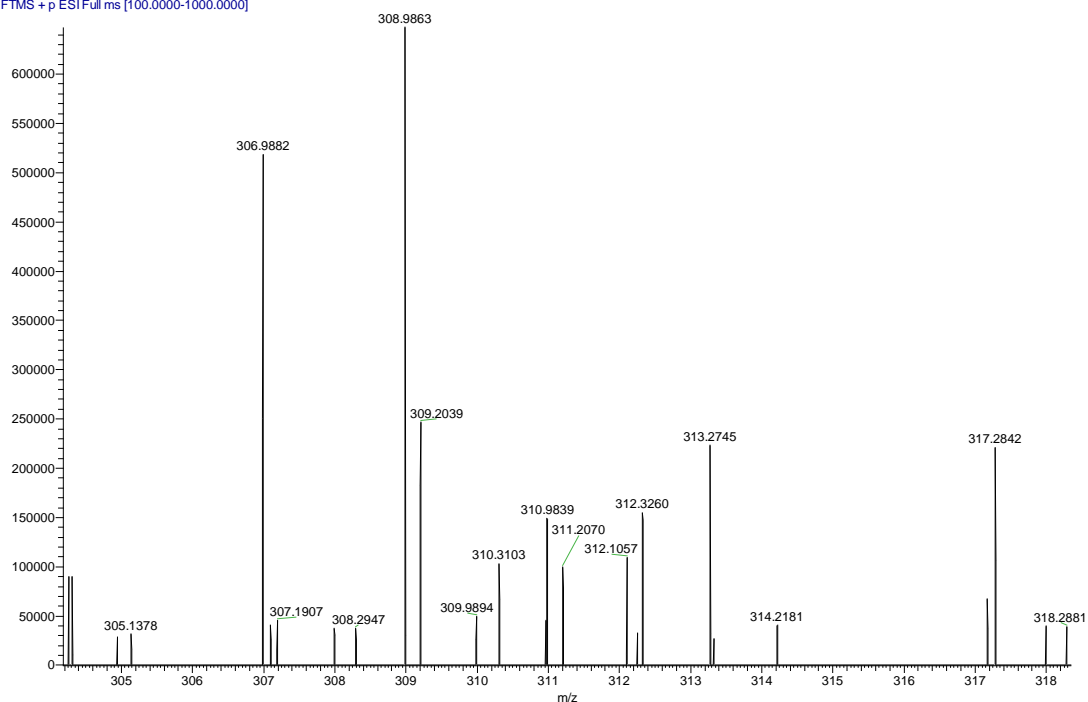
Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 100:1) give the product **1e** (0.74 g, 75% yield) as a white oil from the corresponding ketone (0.97 g, 3.2 mmol).

^1H NMR (CDCl_3 , 400 MHz) δ 7.66-7.65 (m, 1H), 7.40-7.32 (m, 3H), 7.29 (dd, $J_1 = 8.4$ Hz, $J_2 = 2.0$ Hz, 1H), 7.19-7.17 (m, 2H), 5.00 (s, 1H), 4.81 (s, 1H), 1.80 (s, 3H);

^{13}C NMR (CDCl_3 , 100 MHz) δ 144.5, 142.8, 141.2, 137.6, 133.4, 132.2 (2C), 130.4, 128.3, 128.1, 127.1, 126.6, 124.0, 116.6, 23.6;

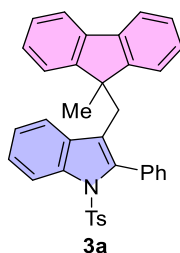
HRMS Calcd (ESI) m/z for $\text{C}_{15}\text{H}_{13}\text{BrCl}$ $[\text{M} + \text{H}]^+$: 306.9884, found: 306.9882.

LHR-1-67 #1903 RT: 8.49 AV: 1 NL: 6.47E5
T: FTMS + p ESIFull ms [100.0000-1000.0000]



6.2. Characterization data for the product.

3-((9-methyl-9H-fluoren-9-yl)methyl)-2-phenyl-1-tosyl-1H-indole (**3a**)

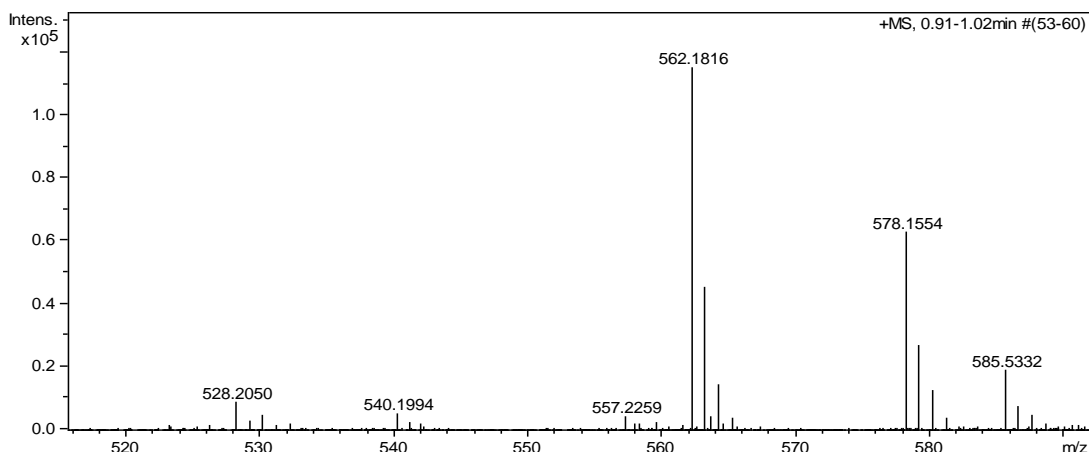


Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 18: 1) give the product **3a** (104.7 mg, 97% yield) as a yellow solid. Mp: 152-153 °C.

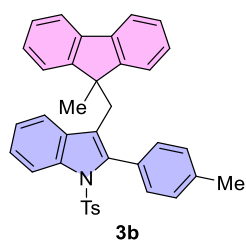
$^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ 8.34 (d, $J = 8.4$ Hz, 1H), 7.65 (d, $J = 7.6$ Hz, 2H), 7.40-7.36 (m, 1H), 7.33-7.28 (m, 6H), 7.26-7.25 (m, 1H), 7.10-7.03 (m, 7H), 6.92 (d, $J = 7.6$ Hz, 1H), 6.88 (d, $J = 7.2$ Hz, 2H), 2.95 (s, 2H), 2.32 (s, 3H), 1.32 (s, 3H);

$^{13}\text{C NMR}$ (CDCl_3 , 100 MHz) δ 151.7, 144.4, 139.3, 138.7, 136.7, 135.5, 131.9, 131.1 (2C), 129.2, 128.4, 127.1, 127.0, 126.8 (2C), 124.5, 123.8, 123.0, 120.9, 120.8, 119.8, 115.4, 51.2, 35.1, 25.0, 21.5;

HRMS Calcd (ESI) m/z for $\text{C}_{36}\text{H}_{29}\text{NNaO}_2\text{S}$ [$\text{M} + \text{Na}$] $^+$: 562.1811, found: 562.1816.



3-((9-methyl-9H-fluoren-9-yl)methyl)-2-(p-tolyl)-1-tosyl-1H-indole (**3b**)



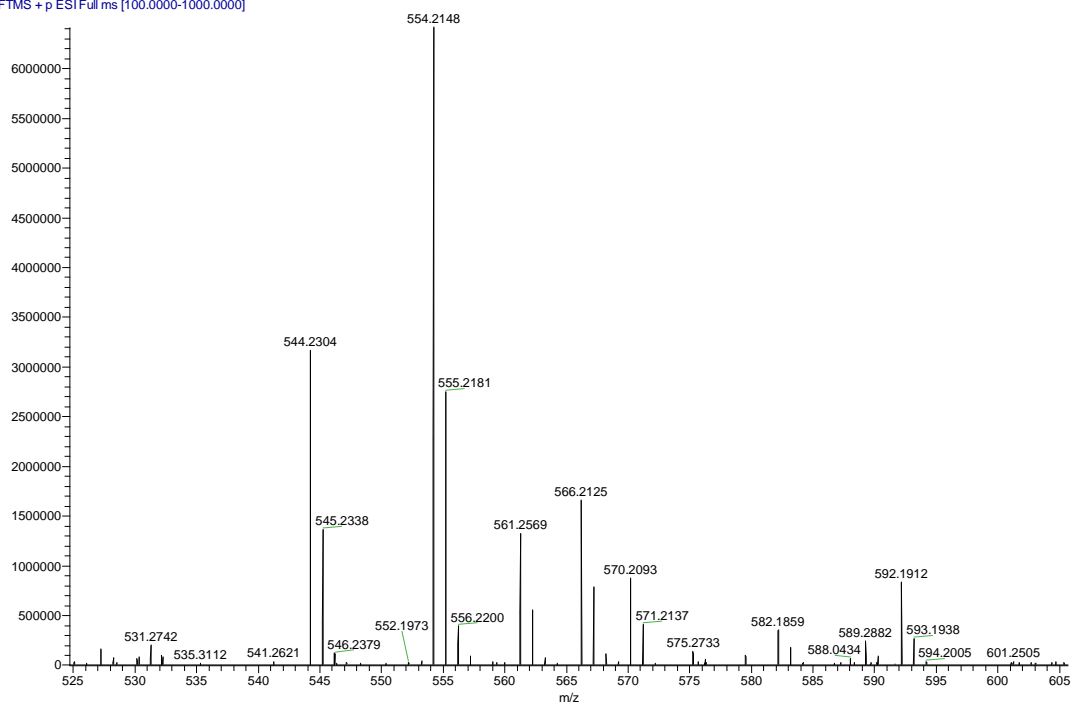
Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 18: 1) give the product **3b** (61.3 mg, 55% yield) as a yellow solid. Mp: 150-151 °C.

¹H NMR (CDCl₃, 400 MHz) δ 8.32 (d, *J* = 8.4 Hz, 1H), 7.65 (d, *J* = 7.6 Hz, 2H), 7.34-7.27 (m, 5H), 7.13-7.09 (m, 4H), 7.07-7.02 (m, 3H), 6.93-6.87 (m, 5H), 2.94 (s, 2H), 2.42 (s, 3H), 2.33 (s, 3H), 1.33 (s, 3H);

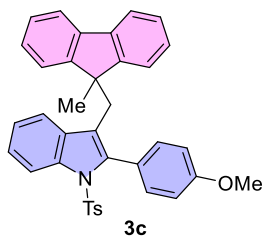
¹³C NMR (CDCl₃, 100 MHz) δ 151.8, 144.3, 139.3, 138.9, 138.2, 136.7, 135.6, 131.7, 131.3, 129.2, 128.2, 127.9, 127.0, 126.8, 126.7, 124.4, 123.9, 123.0, 120.9, 120.7, 119.8, 115.5, 51.2, 35.1, 25.1, 21.5 (2C);

HRMS Calcd (ESI) m/z for C₃₇H₃₂NO₂S [M + H]⁺: 554.2148, found: 554.2148.

LHR-1-54-5 #1869 RT: 8.34 AV: 1 NL: 6.41E6
T: FTMS + p ESI Full ms [100.0000-1000.0000]



2-(4-methoxyphenyl)-3-((9-methyl-9H-fluoren-9-yl)methyl)-1-tosyl-1H-indole (**3c**)

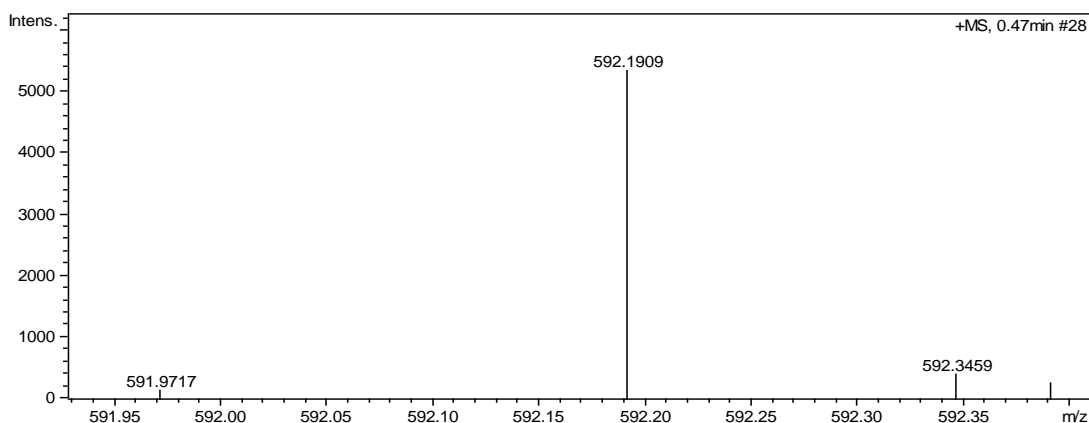


Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 10: 1) give the product **3c** (109.3 mg, 96% yield) as a yellow solid. Mp: 105-107 °C.

¹H NMR (CDCl₃, 400 MHz) δ 8.31 (d, *J* = 8.4 Hz, 1H), 7.62 (d, *J* = 7.6 Hz, 2H), 7.29-7.24 (m, 5H), 7.07 (d, *J* = 8.4 Hz, 2H), 7.04-7.00 (m, 3H), 7.91-6.86 (m, 5H), 6.81-6.79 (m, 2H), 3.85 (s, 3H), 2.91 (s, 2H), 2.31 (s, 3H), 1.32 (s, 3H);

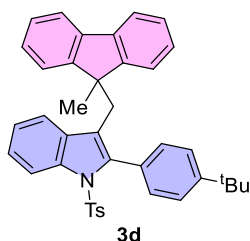
¹³C NMR (CDCl₃, 100 MHz) δ 159.5, 151.8, 144.3, 139.3, 138.6, 136.6, 135.7, 133.2, 131.2, 129.2, 127.0, 126.8, 126.7, 124.3, 123.9, 123.2, 122.9, 120.8, 120.6, 119.8, 115.4, 112.6, 55.2, 51.2, 35.1, 25.1, 21.5;

HRMS Calcd (ESI) m/z for C₃₇H₃₁NNaO₃S [M + Na]⁺: 592.1917, found: 592.1909.



2-(4-(tert-butyl)phenyl)-3-((9-methyl-9H-fluoren-9-yl)methyl)-1-tosyl-1H-indole

(3d)



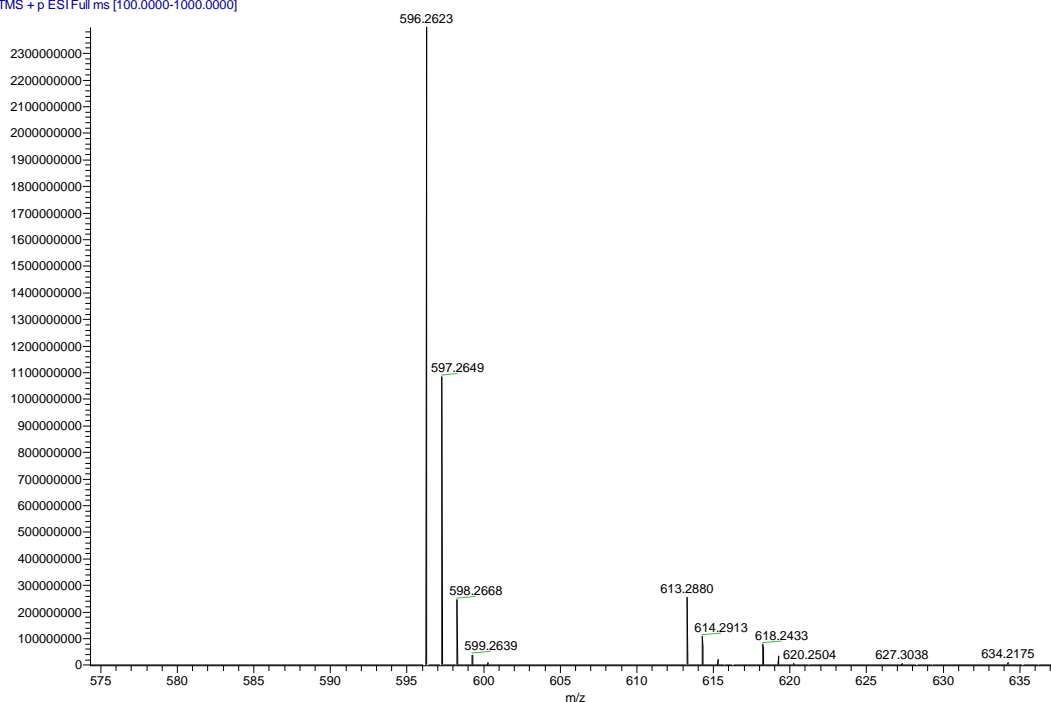
Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 18: 1) give the product **3d** (101.3 mg, 85% yield) as a yellow solid. Mp: 139-140 °C.

$^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ 8.29 (d, $J = 8.4$ Hz, 1H), 7.61 (d, $J = 7.6$ Hz, 2H), 7.28-7.23 (m, 7H), 7.05-7.00 (m, 5H), 6.94-6.92 (m, 2H), 6.88-6.84 (m, 3H), 2.93 (s, 2H), 2.29 (s, 3H), 1.36 (s, 9H), 1.28 (s, 3H);

$^{13}\text{C NMR}$ (CDCl_3 , 100 MHz) δ 151.8, 151.3, 144.2, 139.3, 138.9, 136.7, 135.5, 131.6, 131.2, 129.2, 128.0, 126.9 (2C), 126.8, 124.3, 124.0, 123.8, 122.9, 120.8, 120.6, 119.7, 115.4, 51.2, 35.0, 34.6, 31.3, 25.0, 21.5;

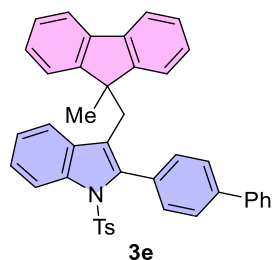
HRMS Calcd (ESI) m/z for $\text{C}_{40}\text{H}_{38}\text{NO}_2\text{S}$ $[\text{M} + \text{H}]^+$: 596.2618, found: 596.2623.

LHR-1-52-1 #713 RT: 3.18 AV: 1 NL: 2.40E9
T: FTMS + p ESI Full ms [100.0000-1000.0000]



2-([1,1'-biphenyl]-4-yl)-3-((9-methyl-9H-fluoren-9-yl)methyl)-1-tosyl-1H-indole

(3e)

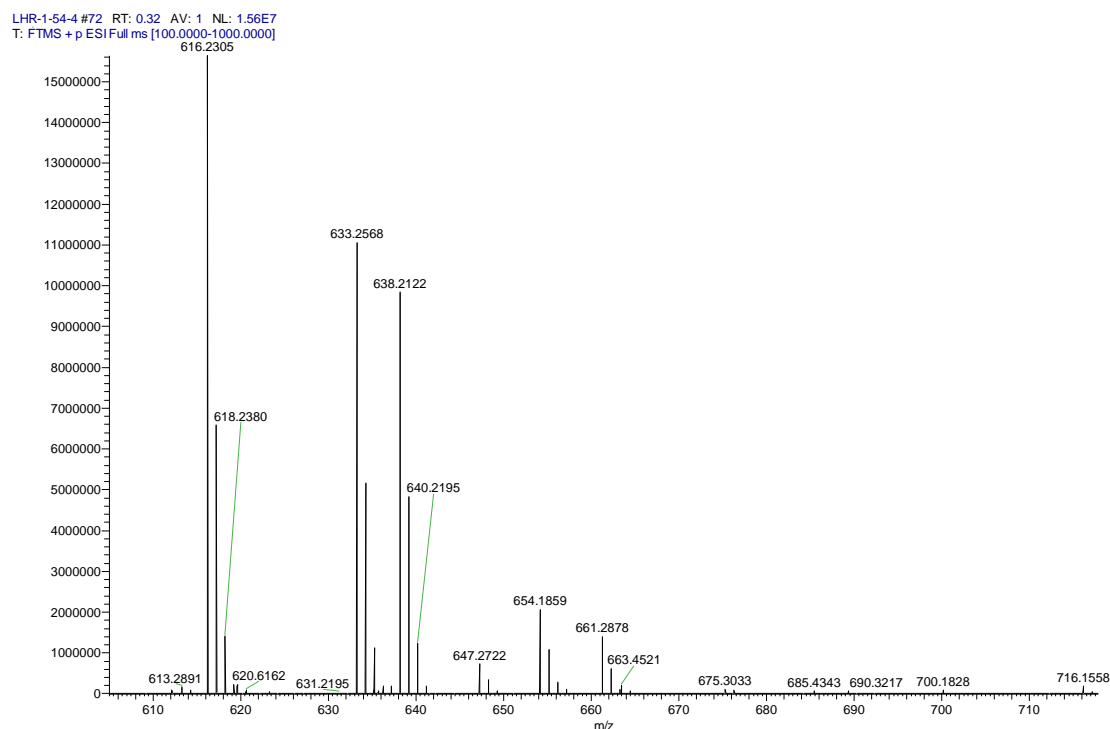


Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 18: 1) give the product **3e** (106.9 mg, 87% yield) as a yellow solid. Mp: 206-208 °C.

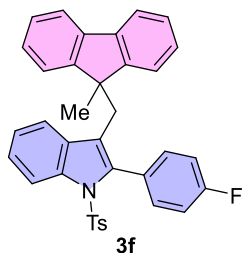
$^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ 8.40 (d, $J = 8.4$ Hz, 1H), 7.72 (d, $J = 7.2$ Hz, 2H), 7.67 (d, $J = 7.6$ Hz, 2H), 7.57 (d, $J = 8.4$ Hz, 2H), 7.52 (t, $J = 7.6$ Hz, 2H), 7.46-7.36 (m, 4H), 7.34-7.29 (m, 2H), 7.17-7.06 (m, 7H), 7.03 (d, $J = 7.6$ Hz, 1H), 6.94 (d, $J = 7.6$ Hz, 2H), 3.03 (s, 2H), 2.35 (s, 3H), 1.41 (s, 3H);

$^{13}\text{C NMR}$ (CDCl_3 , 100 MHz) δ 151.7, 144.4, 140.7, 140.4, 139.3, 138.4, 136.8, 135.4, 132.2, 131.2, 130.1, 129.2, 128.7, 127.5, 127.0 (2C), 126.8 (2C), 125.7, 124.5, 123.8, 123.1, 121.1, 120.9, 119.8, 115.5, 51.2, 35.2, 25.2, 21.5;

HRMS Calcd (ESI) m/z for $C_{42}H_{34}NO_2S$ $[M + H]^+$: 616.2305, found: 616.2305.



2-(4-fluorophenyl)-3-((9-methyl-9H-fluoren-9-yl)methyl)-1-tosyl-1H-indole (3f)



Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 18: 1) give the product **3f** (109.1 mg, 98% yield) as a yellow solid. Mp: 153-154 °C.

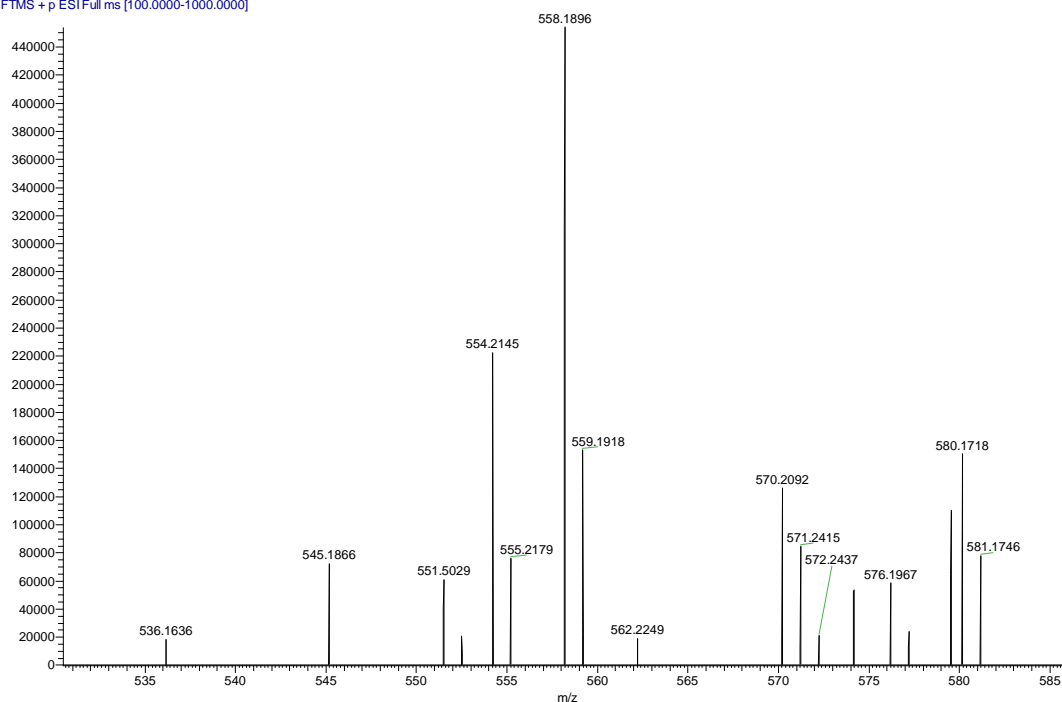
1H NMR ($CDCl_3$, 400 MHz) δ 8.35 (d, $J = 8.4$ Hz, 1H), 7.65 (d, $J = 7.6$ Hz, 2H), 7.36-7.32 (m, 1H), 7.31-7.26 (m, 4H), 7.15-7.04 (m, 6H), 6.97-6.85 (m, 6H), 2.92 (s, 2H), 2.35 (s, 3H), 1.40 (s, 3H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 162.6 (d, $J = 247.3$ Hz), 151.6, 144.5, 139.3, 137.5, 136.7, 135.6, 133.6 (d, $J = 8.2$ Hz), 130.9, 129.3, 127.1, 126.9 (d, $J = 3.5$ Hz), 126.8, 126.7, 124.7, 123.7, 123.1, 121.0 (2C), 119.9, 115.4, 114.2 (d, $J = 21.4$ Hz), 51.2, 35.2, 25.3, 21.5;

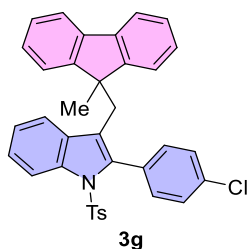
^{19}F NMR ($CDCl_3$, 376 MHz) δ -112.7;

HRMS Calcd (ESI) m/z for $C_{36}H_{29}FNO_2S$ $[M + H]^+$: 558.1898, found: 558.1896.

LHR-1-52-4 #1218 RT: 5.43 AV: 1 NL: 4.54E5
T: FTMS + p ESI Full ms [100.0000-1000.0000]



2-(4-chlorophenyl)-3-((9-methyl-9H-fluoren-9-yl)methyl)-1-tosyl-1H-indole (**3g**)



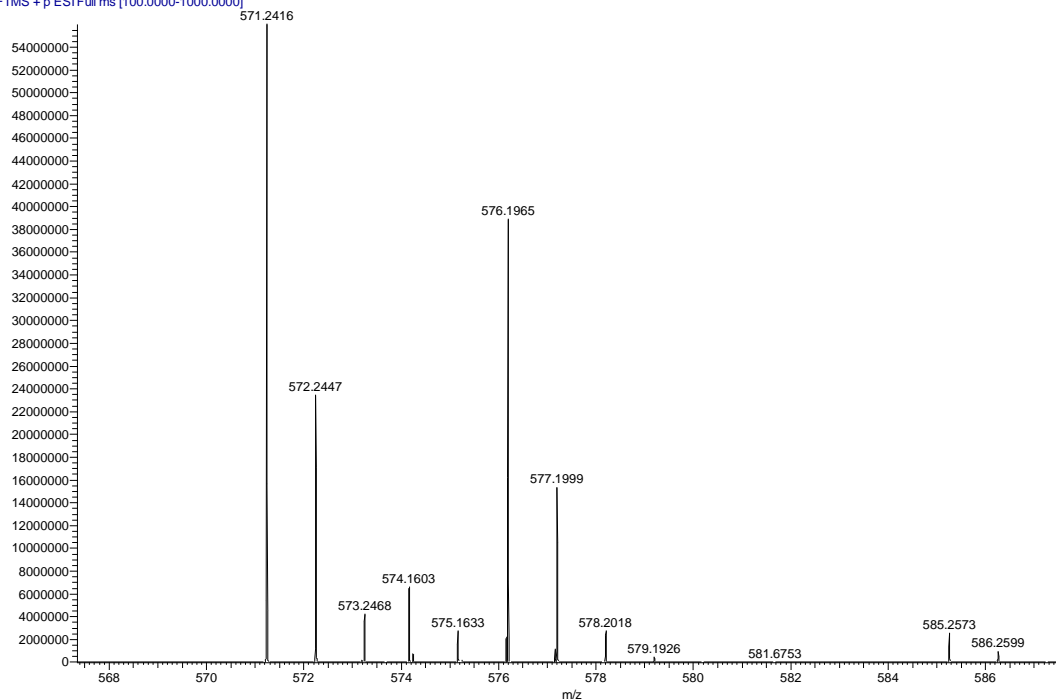
Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 18: 1) give the product **3g** (100.1 mg, 87% yield) as a yellow solid. Mp: 138-139 °C.

¹H NMR (CDCl₃, 400 MHz) δ 8.31 (d, *J* = 8.4 Hz, 1H), 7.63 (d, *J* = 7.6 Hz, 2H), 7.34-7.30 (m, 1H), 7.29-7.25 (m, 4H), 7.20 (d, *J* = 8.4 Hz, 2H), 7.13-7.07 (m, 4H), 7.03 (t, *J* = 7.6 Hz, 2H), 6.86 (d, *J* = 7.6 Hz, 2H), 6.80 (d, *J* = 8.4 Hz, 2H), 2.89 (s, 2H), 2.34 (s, 3H), 1.38 (s, 3H);

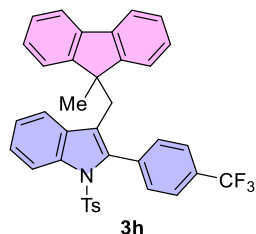
¹³C NMR (CDCl₃, 100 MHz) δ 151.5, 144.6, 139.3, 137.3, 136.8, 135.5, 134.5, 133.0, 131.0, 129.5, 129.4, 127.4, 127.1, 126.8 (2C), 124.8, 123.7, 123.2, 121.3, 121.0, 119.9, 115.5, 51.2, 35.2, 25.4, 21.6;

HRMS Calcd (ESI) m/z for C₃₆H₂₉ClNO₂S [M + H]⁺: 574.1602, found: 574.1603.

LHR-1-52-5 #1522 RT: 6.79 AV: 1 NL: 5.60E7
T: FTMS + p ESI Full ms [100.0000-1000.0000]



3-((9-methyl-9H-fluoren-9-yl)methyl)-1-tosyl-2-(4-(trifluoromethyl)phenyl)-1H-indole (**3h**)



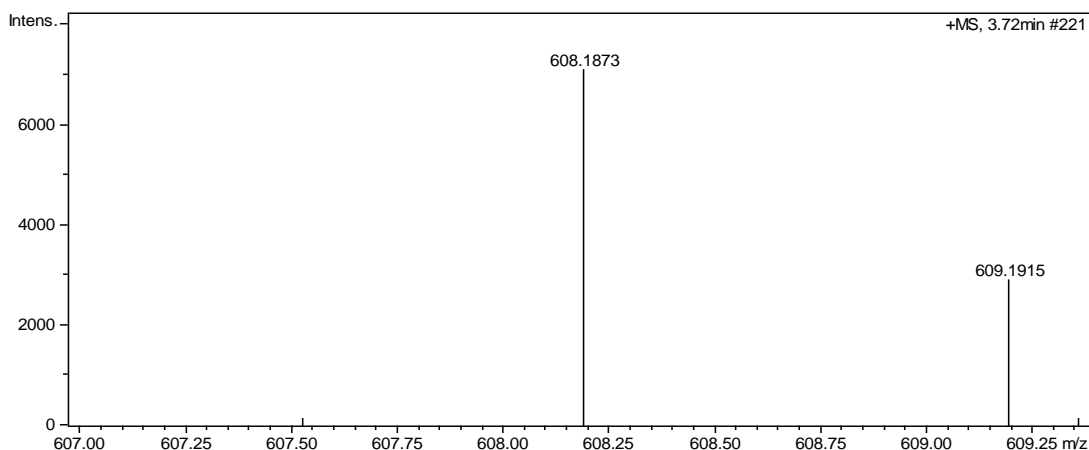
Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 18: 1) give the product **3h** (110.6 mg, 91% yield) as a yellow soild. Mp: 176-177 °C.

¹H NMR (CDCl₃, 400 MHz) δ 8.36 (d, *J* = 8.8 Hz, 1H), 7.65 (d, *J* = 7.6 Hz, 2H), 7.51 (d, *J* = 8.0 Hz, 2H), 7.40-7.36 (m, 1H), 7.32-7.28 (m, 4H), 7.22-7.16 (m, 2H), 7.12 (d, *J* = 7.6 Hz, 2H), 7.07 (t, *J* = 7.6 Hz, 2H), 7.02 (d, *J* = 8.0 Hz, 2H), 6.91 (d, *J* = 7.2 Hz, 2H), 2.97 (s, 2H), 2.35 (s, 3H), 1.44 (s, 3H);

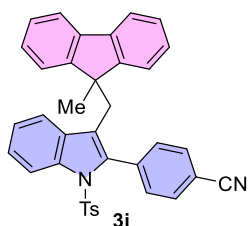
¹³C NMR (CDCl₃, 100 MHz) δ 151.4, 144.7, 139.3, 136.9 (2C), 135.2, 134.9, 131.9, 131.0, 130.0 (q, *J* = 32.2 Hz), 129.4, 127.1, 126.8, 126.7, 125.0, 124.1 (q, *J* = 270.7 Hz), 124.0 (q, *J* = 3.6 Hz), 123.6, 123.4, 122.0, 121.1, 119.9, 115.6, 51.2, 35.2, 25.4, 21.5;

¹⁹F NMR (CDCl₃, 376 MHz) δ -62.5;

HRMS Calcd (ESI) m/z for C₃₇H₂₉F₃NO₂S [M + H]⁺: 608.1866, found: 608.1873.



3-((9-methyl-9H-fluoren-9-yl)methyl)-2-(p-tolyl)-1-tosyl-1H-indole (**3i**)

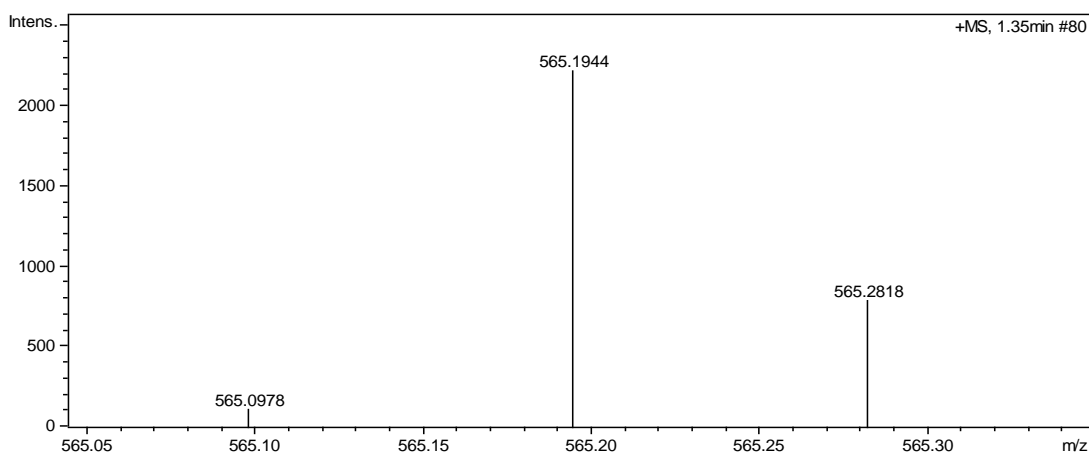


Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 18: 1) give the product **3i** (70.1 mg, 62% yield) as a white soild. Mp: 198-199 °C.

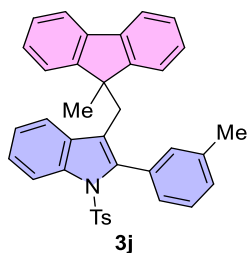
¹H NMR (CDCl₃, 400 MHz) δ 8.33 (d, *J* = 8.4 Hz, 1H), 7.65 (d, *J* = 7.6 Hz, 2H), 7.50 (d, *J* = 8.0 Hz, 2H), 7.40 (t, *J* = 7.2 Hz, 1H), 7.32-7.28 (m, 5H), 7.23-7.19 (m, 1H), 7.14 (d, *J* = 8.4 Hz, 2H), 7.06 (t, *J* = 7.6 Hz, 2H), 6.95 (d, *J* = 8.0 Hz, 2H), 6.88 (d, *J* = 7.6 Hz, 2H), 2.93 (s, 2H), 2.37 (s, 3H), 1.46 (s, 3H);

¹³C NMR (CDCl₃, 100 MHz) δ 151.3, 144.9, 139.3, 137.0, 136.4, 136.0, 135.0, 132.1, 130.9, 130.8, 129.5, 127.2, 126.9, 126.7, 125.3, 123.6 (2C), 122.5, 121.2, 120.0, 118.7, 115.6, 111.8, 51.2, 35.2, 25.5, 21.6;

HRMS Calcd (ESI) *m/z* for C₃₇H₂₉N₂O₂S [M + H]⁺: 556.1944, found: 556.1944.



3-((9-methyl-9H-fluoren-9-yl)methyl)-2-(m-tolyl)-1-tosyl-1H-indole (3j)



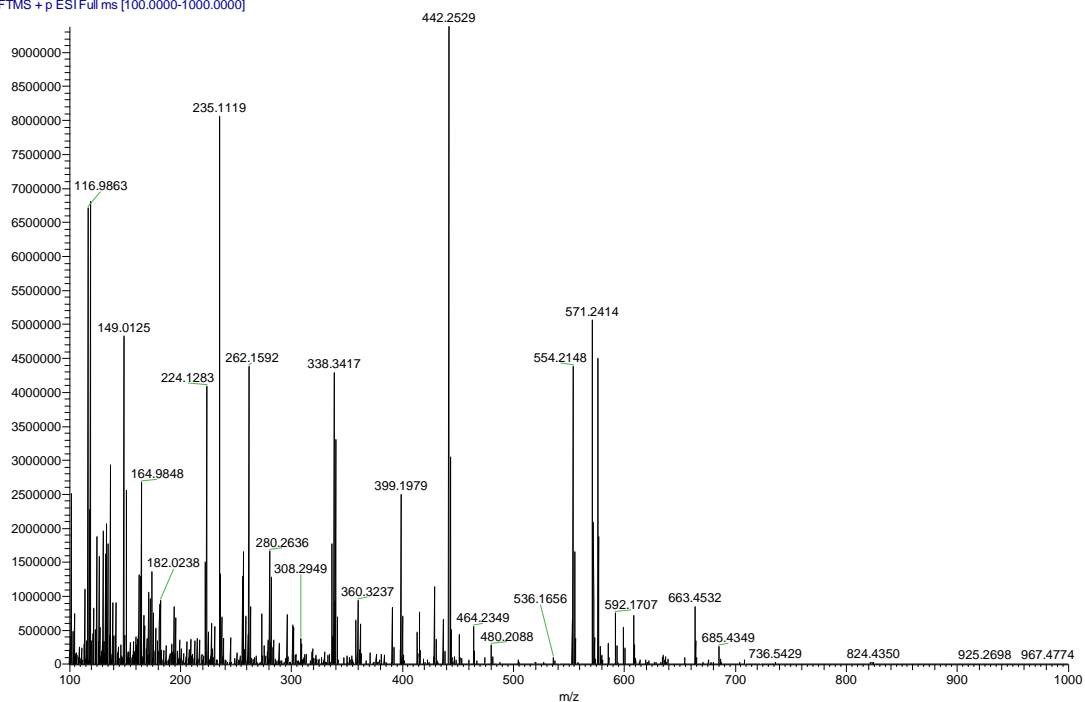
Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 18: 1) give the product **3j** (107.4 mg, 97% yield) as a yellow solid. Mp: 167-168 °C.

¹H NMR (CDCl₃, 400 MHz) δ 8.36 (d, *J* = 8.4 Hz, 1H), 7.66 (d, *J* = 7.2 Hz, 2H), 7.35-7.28 (m, 5H), 7.20-7.15 (m, 2H), 7.13-7.07 (m, 5H), 7.03 (t, *J* = 7.6 Hz, 1H), 6.97 (d, *J* = 7.6 Hz, 1H), 6.84 (d, *J* = 7.2 Hz, 2H), 6.57 (s, 1H), 2.99 (d, *J* = 14.4 Hz, 1H), 2.86 (d, *J* = 14.4 Hz, 1H), 2.36 (s, 3H), 2.27 (s, 3H), 1.41 (s, 3H);

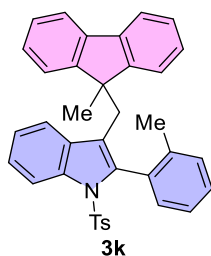
¹³C NMR (CDCl₃, 100 MHz) δ 152.1, 151.6, 144.3, 139.4, 139.2, 138.9, 136.7, 136.4, 135.7, 132.4, 131.1, 130.8, 129.2, 129.1, 128.9, 127.0, 126.9, 126.8, 126.7, 124.4, 124.1, 123.6, 123.0, 120.9, 120.7, 119.8, 115.4, 51.2, 35.2, 25.4, 21.5, 21.3;

HRMS Calcd (ESI) *m/z* for C₃₇H₃₂NO₂S [M + H]⁺: 554.2148, found: 554.2148.

LHR-1-52-3 #525 RT: 2.34 AV: 1 NL: 9.38E6
T: FTMS + p ESI Full ms [100.0000-1000.0000]



3-((9-methyl-9H-fluoren-9-yl)methyl)-2-(o-tolyl)-1-tosyl-1H-indole (3k)



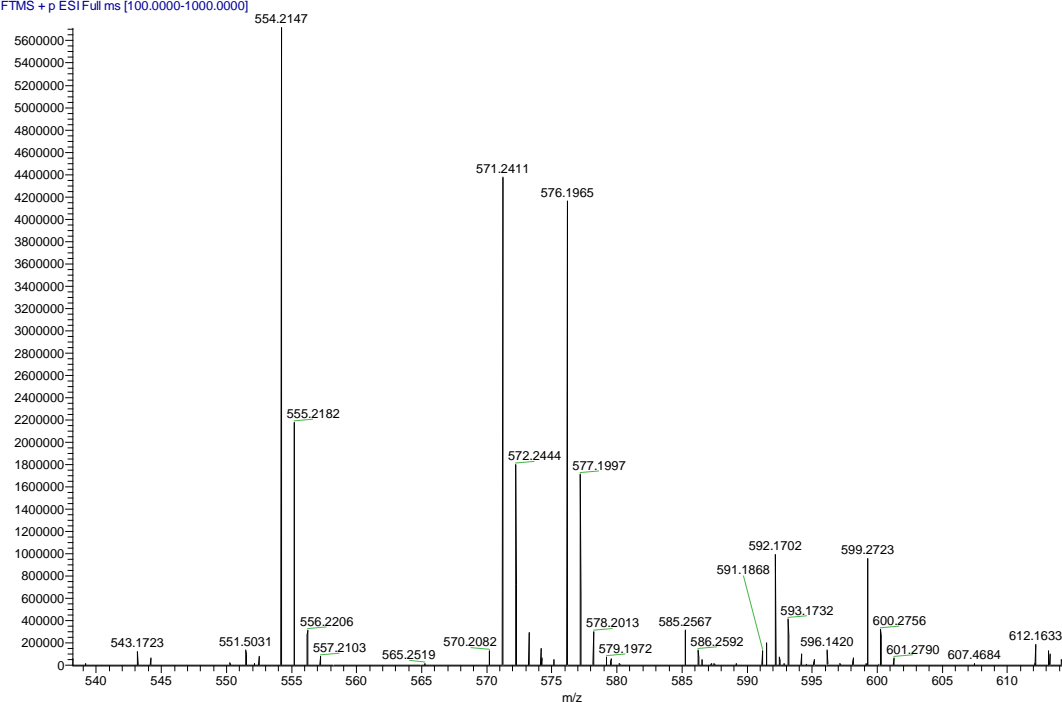
Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 18: 1) give the product **3k** (106.9 mg, 96% yield) as a yellow solid. Mp: 178-179 °C.

¹H NMR (CDCl₃, 400 MHz) δ 8.32 (d, *J* = 8.4 Hz, 1H), 7.65-7.61 (m, 2H), 7.33-7.29 (m, 3H), 7.27-7.22 (m, 3H), 7.19 (d, *J* = 7.6 Hz, 1H), 7.14-7.11 (m, 3H), 7.08 (d, *J* = 8.0 Hz, 2H), 7.03-6.99 (m, 1H), 6.90-6.86 (m, 1H), 6.81 (d, *J* = 7.6 Hz, 1H), 6.69 (d, *J* = 7.2 Hz, 1H), 6.65 (d, *J* = 7.6 Hz, 1H), 3.18 (d, *J* = 14.0 Hz, 1H), 2.51 (d, *J* = 14.0 Hz, 1H), 2.32 (s, 3H), 1.97 (s, 3H), 1.26 (s, 3H);

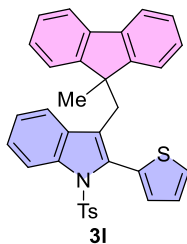
¹³C NMR (CDCl₃, 100 MHz) δ 152.5, 151.0, 144.4, 140.0, 139.6, 139.1, 137.7, 136.4, 135.9, 131.7, 131.0, 130.6, 129.6, 129.3, 129.0, 127.0 (2C), 126.9, 126.8, 126.7, 124.5, 124.3 (2C), 123.4, 122.7, 121.0, 120.2, 119.8 (2C), 115.0, 51.1, 35.2, 24.9, 21.5, 20.3;

HRMS Calcd (ESI) *m/z* for C₃₇H₃₂NO₂S [M + H]⁺: 554.2148, found: 554.2147.

LHR-1-52-2 #1597 RT: 7.13 AV: 1 NL: 5.71E6
T: FTMS + p ESIFull ms [100.0000-1000.0000]



3-((9-methyl-9H-fluoren-9-yl)methyl)-2-(thiophen-2-yl)-1-tosyl-1H-indole (3l)



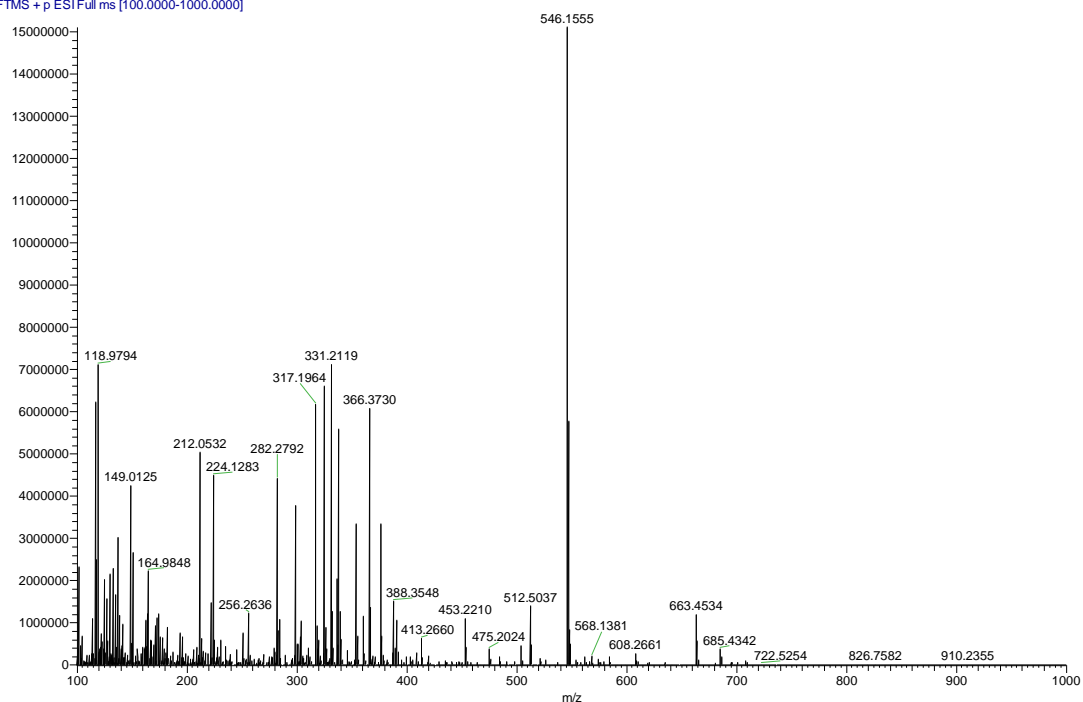
Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 18: 1) give the product **3I** (102.4 mg, 94% yield) as a brown solid. Mp: 132-133 °C.

¹H NMR (CDCl₃, 400 MHz) δ 8.36 (d, *J* = 8.4 Hz, 1H), 7.68 (d, *J* = 7.6 Hz, 2H), 7.44 (d, *J* = 8.4 Hz, 2H), 7.39-7.38 (m, 1H), 7.37-7.33 (m, 1H), 7.32-7.28 (m, 2H), 7.16 (d, *J* = 8.0 Hz, 2H), 7.12 (t, *J* = 8.0 Hz, 1H), 7.07-7.02 (m, 3H), 6.98-6.96 (m, 1H), 6.89 (d, *J* = 7.6 Hz, 2H), 6.61 (d, *J* = 2.8 Hz, 1H), 2.99 (s, 2H), 2.36 (s, 3H), 1.46 (s, 3H);

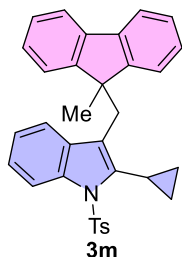
¹³C NMR (CDCl₃, 100 MHz) δ 151.7, 144.5, 139.3, 137.2, 135.5, 131.7, 131.0 (2C), 130.8, 129.3, 128.0, 127.1, 126.9, 126.8, 126.2, 125.1, 123.8, 123.7, 123.2, 121.1, 119.9, 115.5, 51.0, 35.5, 25.2, 21.6;

HRMS Calcd (ESI) *m/z* for C₃₄H₂₈NO₂S₂ [M + H]⁺: 546.1556, found: 546.1555.

LHR-1-54-2 #1254 RT: 5.60 AV: 1 NL: 1.51E7
T: FTMS + p ESI Full ms [100.0000-1000.0000]



2-cyclopropyl-3-((9-methyl-9H-fluoren-9-yl)methyl)-1-tosyl-1H-indole (3m)



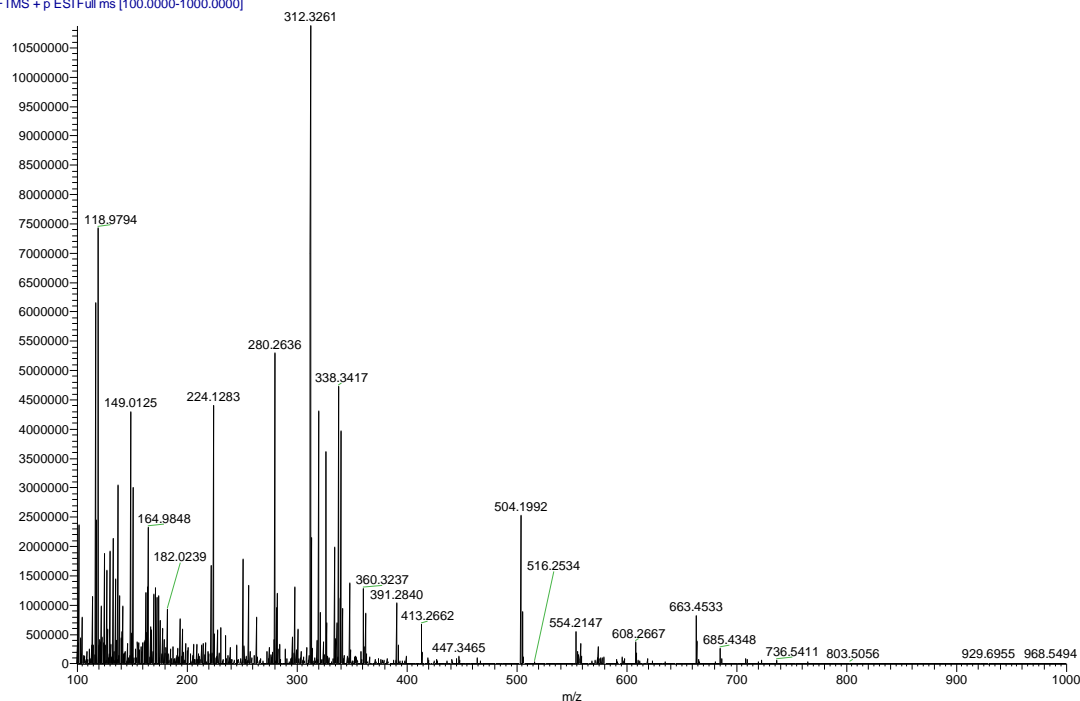
Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 18: 1) give the product **3m** (90.8 mg, 90% yield) as a yellow solid. Mp: 150-151 °C.

¹H NMR (CDCl₃, 400 MHz) δ 8.15 (d, *J* = 8.4 Hz, 1H), 7.64-7.61 (m, 4H), 7.26-7.18 (m, 5H), 6.98-6.93 (m, 3H), 6.73 (d, *J* = 6.4 Hz, 2H), 6.67 (d, *J* = 8.0 Hz, 1H), 3.04 (s, 2H), 2.32 (s, 3H), 1.80-1.73 (m, 1H), 1.48 (s, 3H), 1.05-1.01 (m, 2H), 0.68-0.64 (m, 2H);

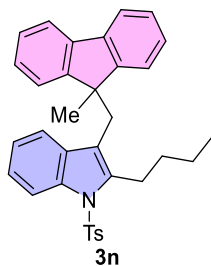
¹³C NMR (CDCl₃, 100 MHz) δ 151.5, 144.5, 139.6, 139.3, 136.7, 135.7, 132.2, 129.4, 127.0, 126.6 (2C), 124.3, 123.8, 123.1, 122.5, 119.8, 119.7, 115.5, 51.4, 35.0, 23.8, 21.6, 9.8, 9.3;

HRMS Calcd (ESI) *m/z* for C₃₃H₃₀NO₂S [M + H]⁺: 504.1992, found: 504.1992.

LHR-1-52-7 #1018 RT: 4.54 AV: 1 NL: 1.09E7
T: FTMS + p ESIFull ms [100.0000-1000.0000]



2-butyl-3-((9-methyl-9H-fluoren-9-yl)methyl)-1-tosyl-1H-indole (3n)



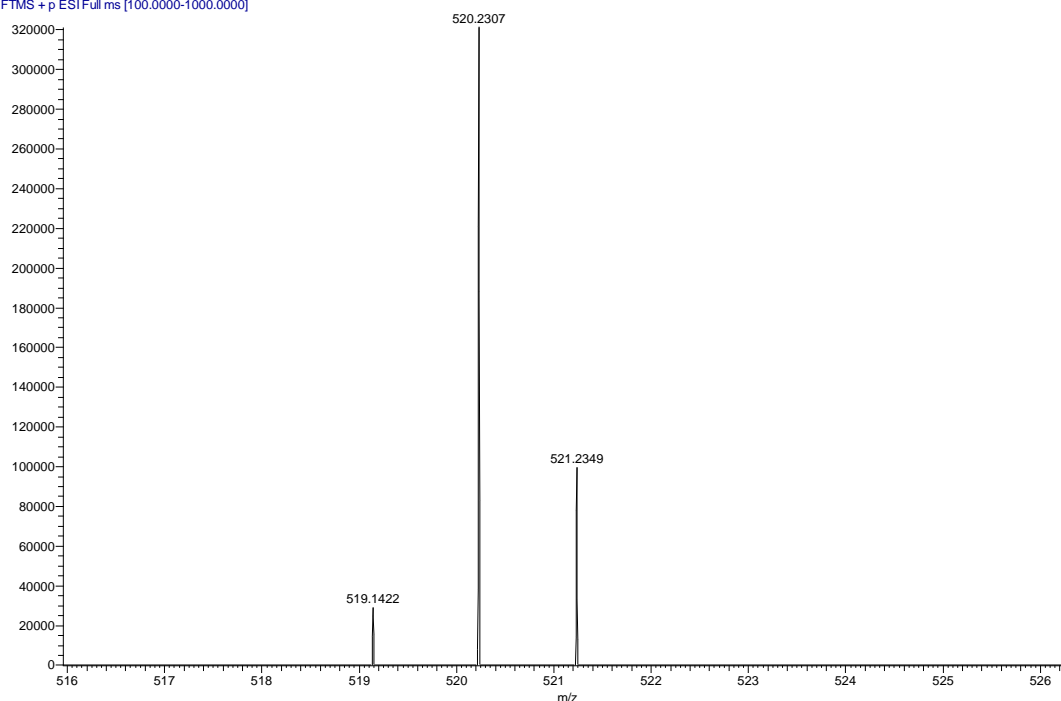
Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 18: 1) give the product **3n** (76.4 mg, 74% yield) as a yellow solid. Mp: 162-163 °C.

¹H NMR (CDCl₃, 400 MHz) δ 8.23 (d, *J* = 8.4 Hz, 1H), 7.68 (d, *J* = 7.6 Hz, 2H), 7.63 (d, *J* = 8.0 Hz, 2H), 7.28 (t, *J* = 7.6 Hz, 2H), 7.25-7.21 (m, 3H), 7.08 (t, *J* = 7.6 Hz, 1H), 7.00-6.96 (m, 3H), 6.75 (d, *J* = 7.6 Hz, 2H), 2.88 (s, 2H), 2.56 (t, *J* = 7.6 Hz, 2H), 2.35 (s, 3H), 1.54-1.50 (m, 2H), 1.43 (s, 3H), 1.22-1.13 (m, 2H), 0.79 (t, *J* = 7.2 Hz, 3H);

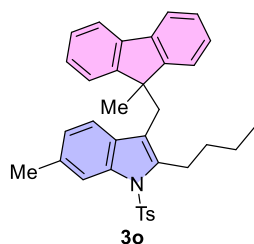
¹³C NMR (CDCl₃, 100 MHz) δ 151.5, 144.7, 140.3, 139.2, 137.0, 135.7, 132.3, 129.6, 127.1, 126.7, 126.4, 123.8, 123.6, 123.3, 119.9, 119.8, 119.1, 115.6, 50.9, 35.0, 32.5, 27.2, 23.8, 22.4, 21.6, 13.8;

HRMS Calcd (ESI) *m/z* for C₃₄H₃₄NO₂S [M + H]⁺: 520.2305, found: 520.2307.

LHR-1-54-1 #1550 RT: 6.91 AV: 1 NL: 3.21E5
T: FTMS + p ESI Full ms [100.0000-1000.0000]



2-butyl-6-methyl-3-((9-methyl-9H-fluoren-9-yl)methyl)-1-tosyl-1H-indole (3o)

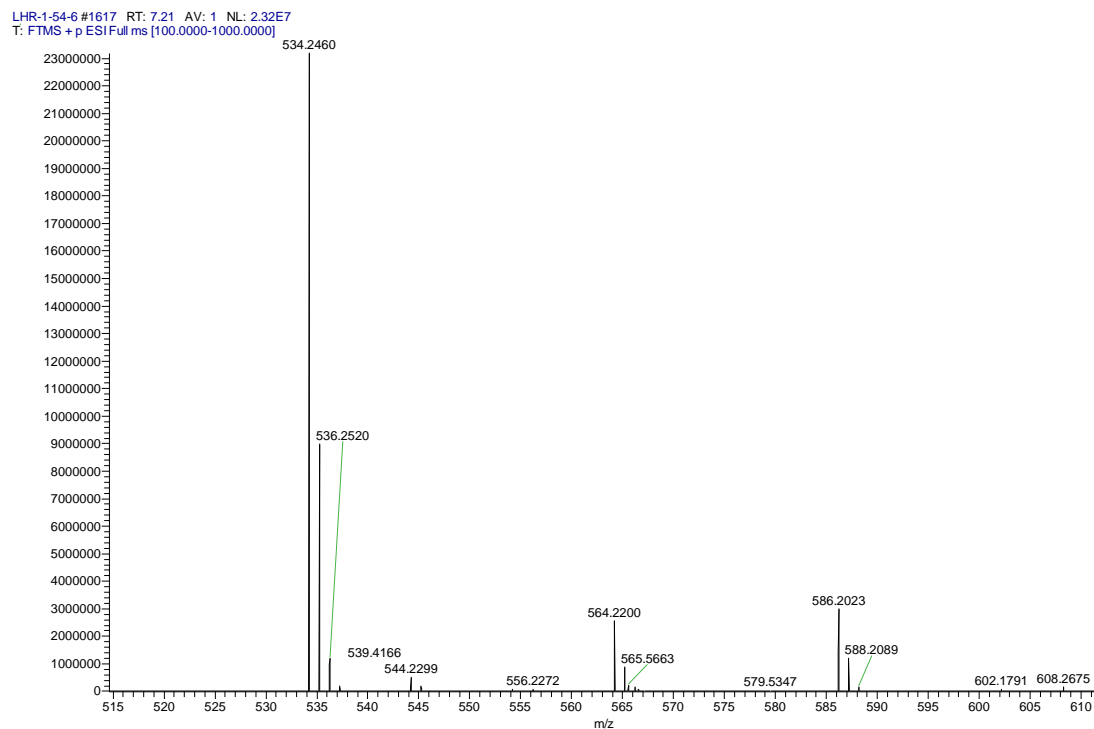


Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 18: 1) give the product **3o** (88.8 mg, 83% yield) as a yellow solid. Mp: 138-139 °C.

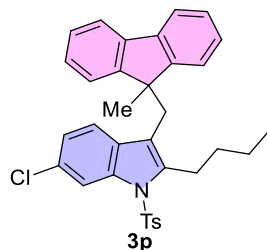
¹H NMR (CDCl₃, 400 MHz) δ 8.08 (d, *J* = 8.4 Hz, 1H), 7.67 (d, *J* = 7.2 Hz, 2H), 7.61 (d, *J* = 8.4 Hz, 2H), 7.30-7.26 (m, 2H), 7.23-7.21 (m, 2H), 7.04-7.02 (m, 1H), 7.00-6.96 (m, 2H), 6.76 (d, *J* = 7.6 Hz, 2H), 6.69 (s, 1H), 2.85 (s, 2H), 2.56 (t, *J* = 7.2 Hz, 2H), 2.34 (s, 3H), 2.27 (s, 3H), 1.56-1.48 (m, 2H), 1.43 (s, 3H), 1.22-1.12 (m, 2H), 0.79 (t, *J* = 7.2 Hz, 3H);

¹³C NMR (CDCl₃, 100 MHz) δ 151.5, 144.5, 140.3, 139.3, 135.6, 135.2, 132.8, 132.5, 129.5, 127.1, 126.6, 126.4, 125.1, 123.6, 120.0, 119.8, 119.1, 115.2, 50.9, 35.2, 32.5, 27.2, 23.7, 22.4, 21.6, 21.2, 13.8;

HRMS Calcd (ESI) *m/z* for C₃₅H₃₆NO₂S [M + H]⁺: 534.2461, found: 534.2460.



2-butyl-6-chloro-3-((9-methyl-9H-fluoren-9-yl)methyl)-1-tosyl-1H-indole (3p)



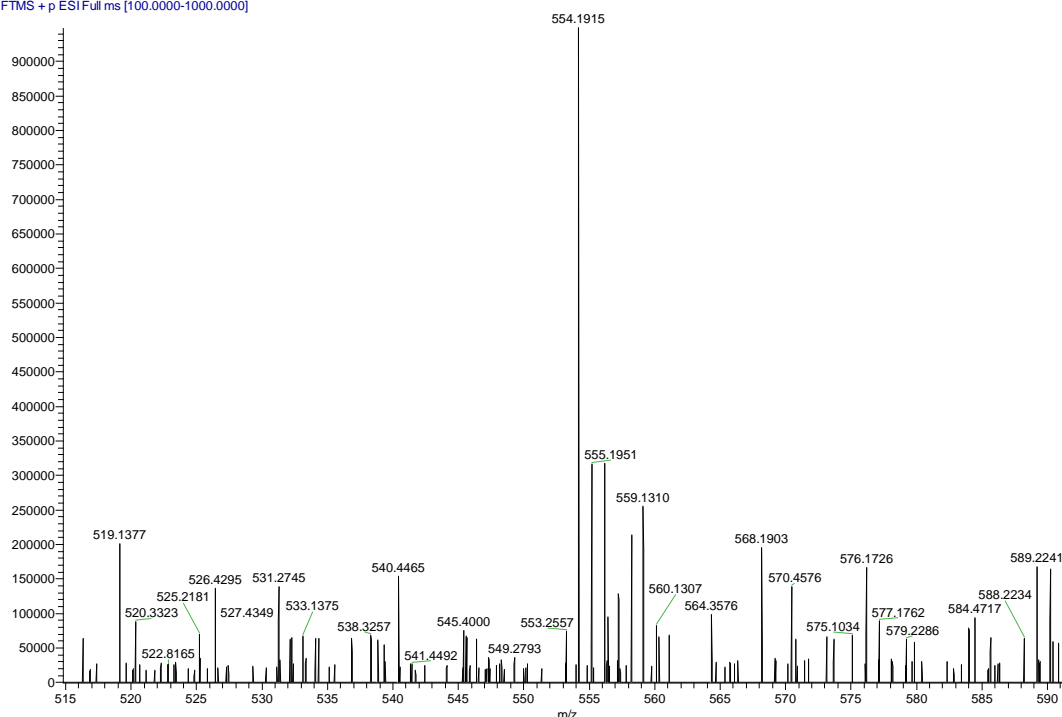
Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 18: 1) give the product **3p** (88.7 mg, 80 % yield) as a yellow solid. Mp: 141-142 °C.

¹H NMR (CDCl₃, 400 MHz) δ 8.10 (d, *J* = 8.8 Hz, 1H), 7.65 (d, *J* = 7.6 Hz, 2H), 7.56 (d, *J* = 8.0 Hz, 2H), 7.30-7.27 (m, 2H), 7.26-7.24 (m, 2H), 7.15 (dd, *J*₁ = 8.8 Hz, *J*₂ = 2.0 Hz, 1H), 7.03-6.99 (m, 2H), 6.86 (s, 1H), 6.81 (d, *J* = 7.6 Hz, 2H), 2.87 (s, 2H), 2.54 (t, *J* = 7.6 Hz, 2H), 2.38 (s, 3H), 1.52-1.49 (m, 2H), 1.46 (s, 3H), 1.21-1.16 (m, 2H), 0.80 (t, *J* = 7.2 Hz, 3H);

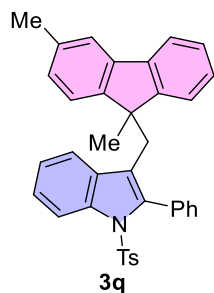
¹³C NMR (CDCl₃, 100 MHz) δ 151.2, 144.9, 141.8, 139.3, 135.5, 135.2, 133.5, 129.7, 129.1, 127.3, 126.7, 126.4, 123.8, 123.5, 112.0, 119.5, 118.3, 116.4, 50.9, 35.3, 32.5, 27.2, 23.9, 22.4, 21.6, 13.7;

HRMS Calcd (ESI) *m/z* for C₃₄H₃₃ClNO₂S [M + H]⁺: 554.1915, found: 554.1915.

LHR-1-153-1 #1508 RT: 6.73 AV: 1 NL: 9.48E5
T: FTMS + p ESI Full ms [100.0000-1000.0000]



3-((3,9-dimethyl-9H-fluoren-9-yl)methyl)-2-phenyl-1-tosyl-1H-indole (3q)

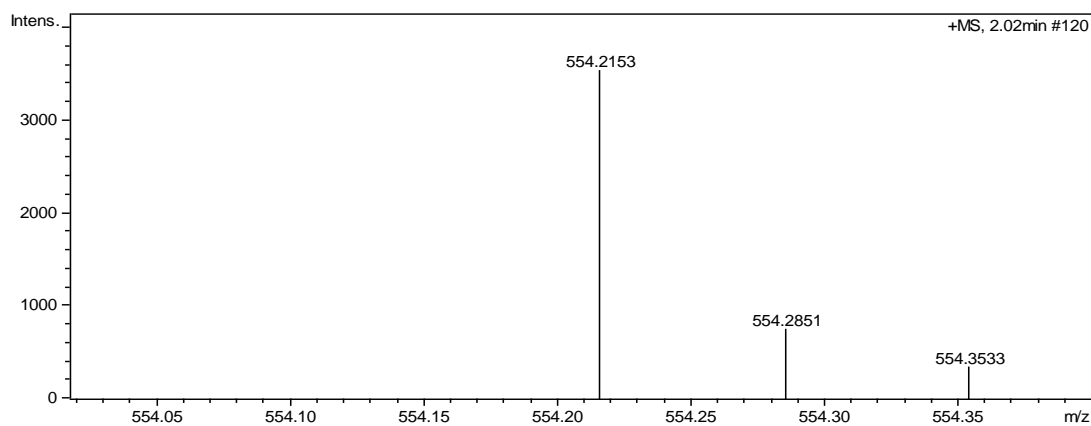


Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 18: 1) give the product **3q** (77.6 mg, 70 % yield) as a yellow solid. Mp: 171-172 °C.

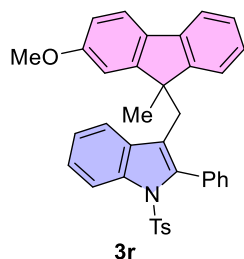
$^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ 8.31 (d, $J = 8.4$ Hz, 1H), 7.59 (d, $J = 7.6$ Hz, 1H), 7.44 (s, 1H), 7.35-7.27 (m, 5H), 7.25-7.22 (m, 2H), 7.08-6.98 (m, 6H), 6.92 (d, $J = 8.0$ Hz, 1H), 6.84-6.82 (m, 2H), 6.75-6.73 (m, 1H), 2.89 (s, 2H), 2.38 (s, 3H), 2.32 (s, 3H), 1.27 (s, 3H);

$^{13}\text{C NMR}$ (CDCl_3 , 100 MHz) δ 152.1, 149.1, 144.4, 139.4, 139.3, 138.6, 136.7, 136.6, 135.6, 131.9, 131.2, 131.1, 129.2, 128.4, 127.6, 127.1, 126.9, 126.8, 126.6, 124.5, 123.9, 123.50, 123.0, 121.0, 120.9, 120.4, 119.7, 115.4, 50.9, 35.2, 25.2, 21.6, 21.5;

HRMS Calcd (ESI) m/z for $\text{C}_{37}\text{H}_{32}\text{NO}_2\text{S}$ $[\text{M} + \text{H}]^+$: 554.2148, found: 554.2153.



3-((2-methoxy-9-methyl-9H-fluoren-9-yl)methyl)-2-phenyl-1-tosyl-1H-indole (**3r**)

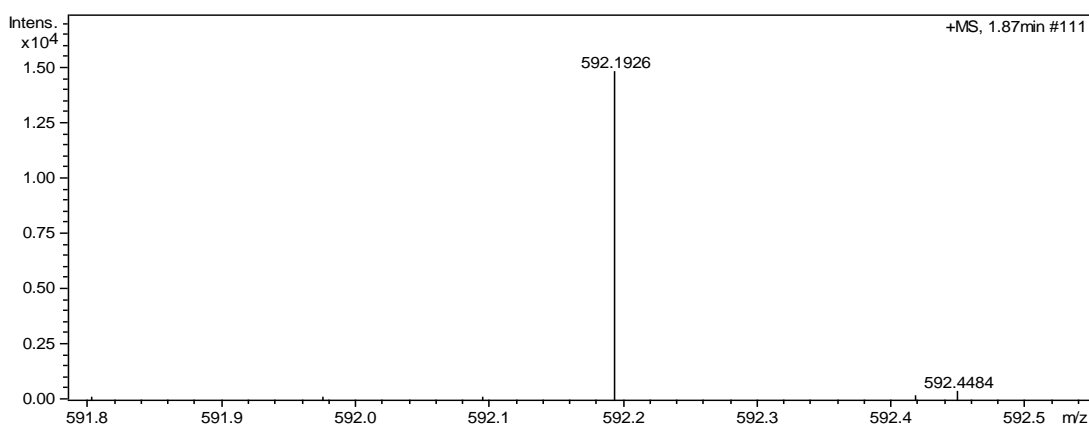


Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 10: 1) give the product **3r** (110.5 mg, 97% yield) as a yellow solid. Mp: 110-111 °C.

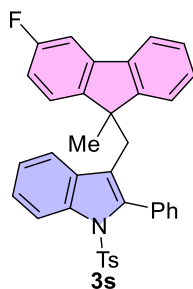
$^1\text{H NMR}$ (CDCl_3 , 600 MHz) δ 8.31 (d, $J = 8.4$ Hz, 1H), 7.55-7.52 (m, 2H), 7.42-7.33 (m, 3H), 7.30-7.28 (m, 3H), 7.25 -7.23 (m, 1H), 7.17-7.11 (m, 2H), 7.08-7.03 (m, 3H), 6.98 (t, $J = 7.8$ Hz 1H), 6.84-6.79 (m, 3H), 6.36 (s, 3H), 3.52 (s, 3H), 2.96 (d, $J = 14.4$ Hz, 1H), 2.87 (d, $J = 14.4$ Hz, 1H), 2.31 (s, 3H), 1.20 (s, 3H);

$^{13}\text{C NMR}$ (CDCl_3 , 150 MHz) δ 159.0, 153.4, 151.4, 144.4, 139.3, 138.8, 136.5, 135.5, 132.2, 132.0, 131.9, 131.3, 131.2, 129.3, 128.5, 127.3, 127.0, 126.8, 125.6, 124.5, 123.6, 123.0, 121.0, 120.5, 119.0, 115.4, 113.3, 109.6, 55.1, 51.2, 35.1, 24.7, 21.5;

HRMS Calcd (ESI) m/z for $\text{C}_{37}\text{H}_{31}\text{NNaO}_3\text{S}$ $[\text{M} + \text{Na}]^+$: 592.1917, found: 592.1926.



3-((3-fluoro-9-methyl-9H-fluoren-9-yl)methyl)-2-phenyl-1-tosyl-1H-indole (**3s**)



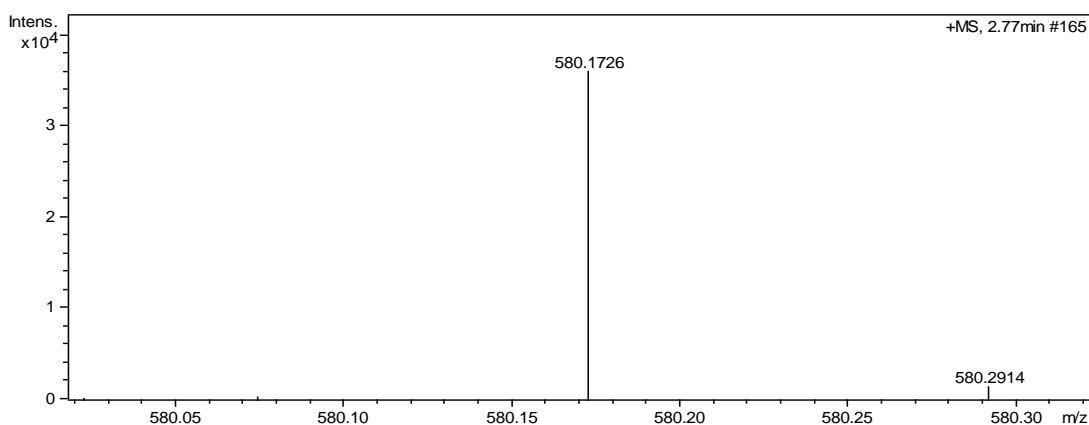
Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 18: 1) give the product **3s** (105.3 mg, 94% yield) as a yellow solid. Mp: 119-120 °C.

$^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ 8.31 (d, $J = 8.4$ Hz, 1H), 7.56 (d, $J = 7.2$ Hz, 1H), 7.39-7.35 (m, 1H), 7.32-7.24 (m, 1H), 7.30-7.29 (m, 1H), 7.28-7.24 (m, 5H), 7.09-7.04 (m, 5H), 7.00-6.98 (m, 1H), 6.92-6.87 (m, 2H), 6.72-6.63 (m, 2H), 2.92 (q, $J = 14.0$ Hz, 2H), 2.31 (s, 3H), 1.27 (s, 3H);

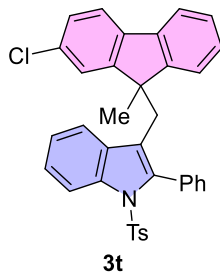
^{13}C NMR (CDCl_3 , 100 MHz) δ 162.6 (d, $J = 242.3$ Hz), 152.7, 146.9, 144.4, 141.3 (d, $J = 8.8$ Hz), 138.7, 138.3 (d, $J = 3.1$ Hz), 136.7, 135.5, 132.1, 131.8, 131.0 (d, $J = 2.9$ Hz), 129.3, 128.5, 127.4, 127.2, 127.1, 126.8, 124.9 (d, $J = 8.8$ Hz), 124.6, 123.8, 123.1, 120.8, 120.5, 120.0, 115.5, 113.4 (d, $J = 22.6$ Hz), 106.7 (d, $J = 22.8$ Hz), 50.8, 35.0, 25.2, 21.5;

^{19}F NMR (CDCl_3 , 376 MHz) δ -116.0;

HRMS Calcd (ESI) m/z for $\text{C}_{36}\text{H}_{28}\text{FNNaO}_2\text{S}$ $[\text{M} + \text{Na}]^+$: 580.1717, found: 580.1726.



3-((2-chloro-9-methyl-9H-fluoren-9-yl)methyl)-2-phenyl-1-tosyl-1H-indole (3t)

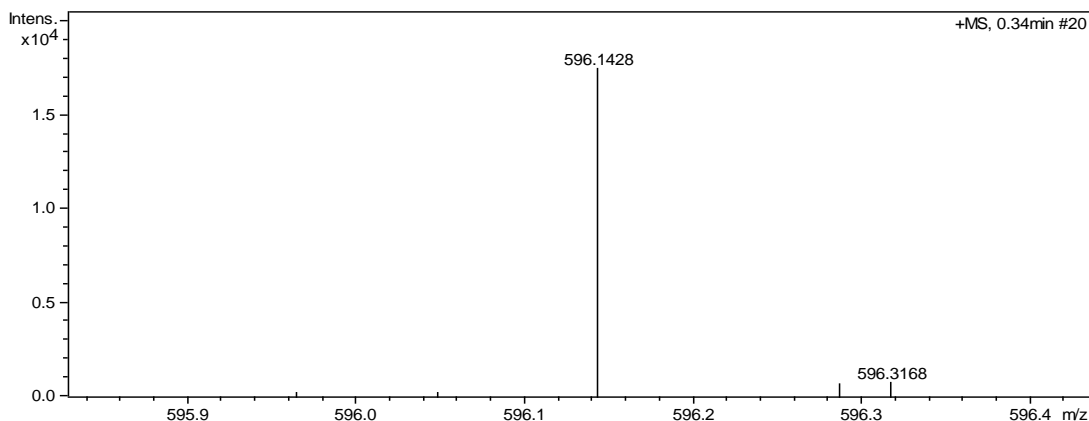


Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 18: 1) give the product **3t** (79.8 mg, 70% yield) as a yellow solid. Mp: 120-121 °C.

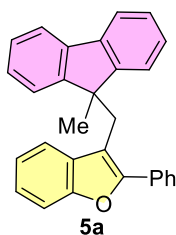
^1H NMR (CDCl_3 , 400 MHz) δ 8.29 (d, $J = 8.4$ Hz, 1H), 7.55 (d, $J = 7.6$ Hz, 1H), 7.48 (d, $J = 8.0$ Hz, 1H), 7.41-7.37 (m, 1H), 7.34 (t, $J = 6.4$ Hz, 2H), 7.29-7.24 (m, 4H), 7.21-7.16 (m, 2H), 7.06-7.00 (m, 5H), 6.88 (d, $J = 7.6$ Hz, 1H), 6.84 (s, 1H), 6.77 (d, $J = 8.0$ Hz, 1H), 2.97 (q, $J = 12.0$ Hz, 2H), 2.30 (s, 3H), 1.26 (s, 3H);

^{13}C NMR (CDCl_3 , 100 MHz) δ 153.4, 151.4, 144.4, 138.8, 138.4, 137.8, 136.6, 135.5, 132.4, 132.1, 132.0, 131.0, 130.9, 129.3, 128.5, 127.3, 127.2, 127.1, 126.8, 124.6, 124.4, 123.9, 123.0, 120.7 (2C), 120.0, 119.8, 115.5, 51.4, 35.0, 24.9, 21.5;

HRMS Calcd (ESI) m/z for $\text{C}_{36}\text{H}_{28}\text{ClNNaO}_2\text{S}$ $[\text{M} + \text{Na}]^+$: 596.1421, found: 596.1428.



3-((9-methyl-9H-fluoren-9-yl)methyl)-2-phenylbenzofuran (**5a**)

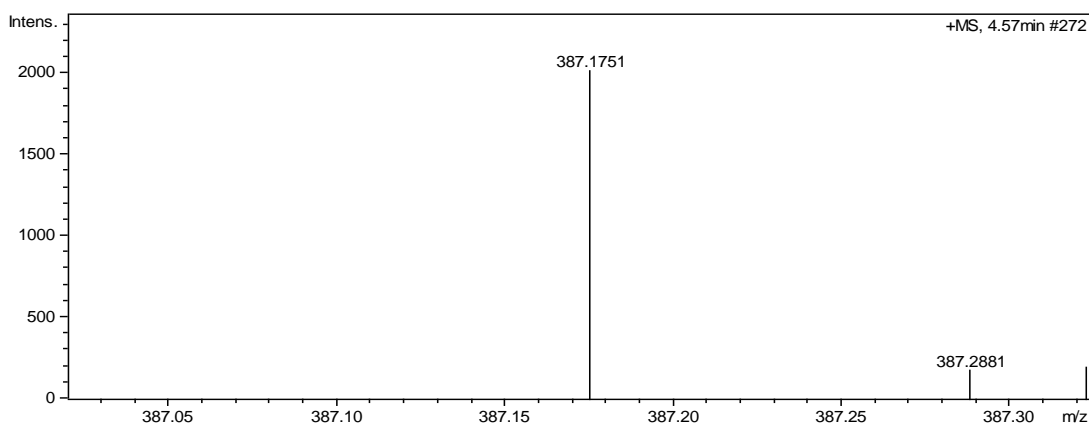


Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 100: 1) give the product **5a** (60.6 mg, 78% yield) as a yellow solid. Mp: 104-105 °C.

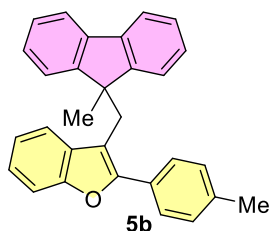
¹H NMR (CDCl₃, 400 MHz) δ 7.67 (d, *J* = 7.6 Hz, 2H), 7.46 (d, *J* = 8.4 Hz, 1H), 7.34 (d, *J* = 7.6 Hz, 1H), 7.27-7.23 (m, 8H), 7.18-7.12 (m, 3H), 7.08 (t, *J* = 7.6 Hz, 2H), 3.35 (s, 2H), 1.61 (s, 3H);

¹³C NMR (CDCl₃, 100 MHz) δ 153.7, 152.9, 151.4, 139.4, 131.2, 130.8, 128.2, 127.9, 127.2 (2C), 127.0, 124.0, 123.8, 122.0, 121.0, 119.8, 113.3, 110.8, 51.5, 35.0, 25.1;

HRMS Calcd (ESI) m/z for C₂₉H₂₃O [M + H]⁺: 387.1743, found: 387.1751.



3-((9-methyl-9H-fluoren-9-yl)methyl)-2-(p-tolyl)benzofuran (**5b**)

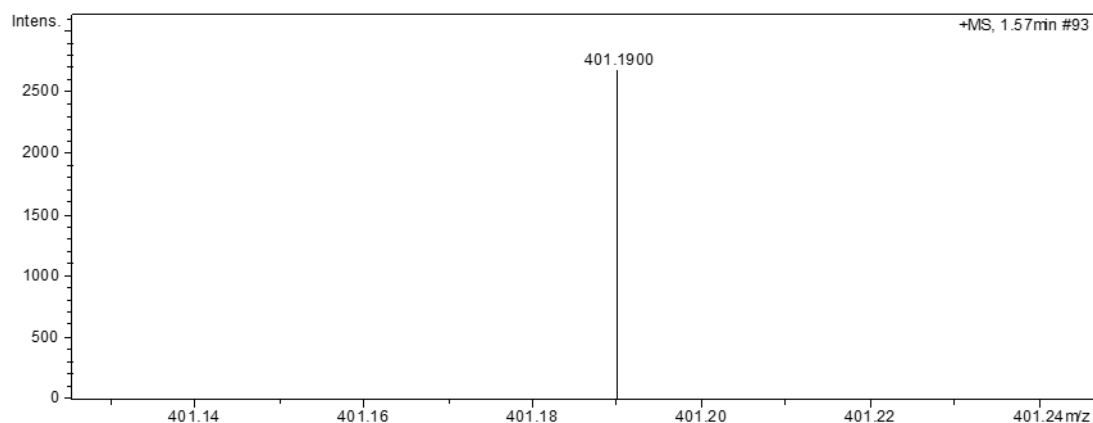


Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 100: 1) give the product **5b** (71.2 mg, 89% yield) as a yellow solid. Mp: 106-107 °C.

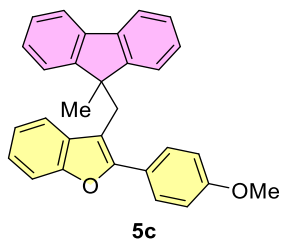
¹H NMR (CDCl₃, 400 MHz) δ 7.68 (d, *J* = 7.6 Hz, 2H), 7.45 (d, *J* = 8.0 Hz, 1H), 7.31 (d, *J* = 8.0 Hz, 1H), 7.28-7.24 (m, 2H), 7.23-7.21 (m, 1H), 7.17-7.14 (m, 4H), 7.12-7.06 (m, 3H), 7.03 (d, *J* = 8.0 Hz, 2H), 3.32 (s, 2H), 2.31 (s, 3H), 1.61 (s, 3H);

¹³C NMR (CDCl₃, 100 MHz) δ 153.7, 153.3, 151.5, 139.4, 137.8, 130.9, 128.9, 128.4, 127.1 (2C), 127.0, 123.9, 123.8, 122.0, 120.9, 119.8, 112.7, 110.7, 51.5, 35.0, 25.1, 21.2;

HRMS Calcd (ESI) *m/z* for C₃₀H₂₅O [M + H]⁺: 401.1900, found: 401.1900.



2-(4-methoxyphenyl)-3-((9-methyl-9H-fluoren-9-yl)methyl)benzofuran (**5c**)

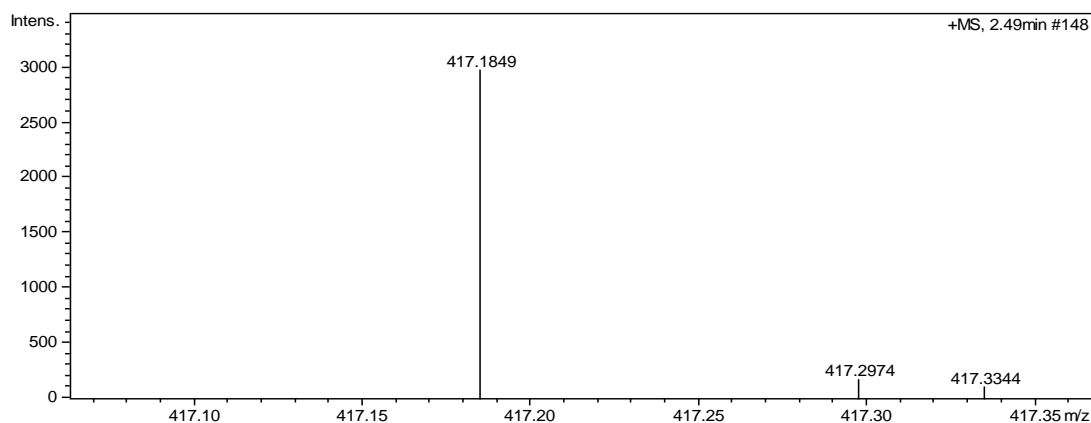


Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 50: 1) give the product **5c** (58.5 mg, 70% yield) as a yellow solid. Mp: 76-77 °C.

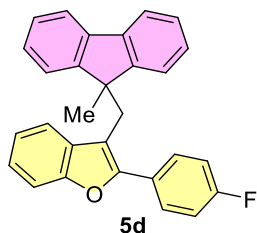
¹H NMR (CDCl₃, 400 MHz) δ 7.68 (d, *J* = 7.2 Hz, 2H), 7.44 (d, *J* = 8.0 Hz, 1H), 7.33 (d, *J* = 7.6 Hz, 1H), 7.28-7.22 (m, 3H), 7.19-7.17 (m, 4H), 7.14-7.07 (m, 3H), 6.75-6.73 (m, 2H), 3.78 (s, 3H), 3.30 (s, 2H), 1.62 (s, 3H);

^{13}C NMR (CDCl_3 , 100 MHz) δ 159.3, 153.6, 153.1, 151.6, 139.4, 131.0, 128.6, 127.2, 127.0, 123.9, 123.6, 122.0, 120.8, 119.8, 113.6, 112.0, 110.7, 110.0, 55.2, 51.5, 35.1, 25.1;

HRMS Calcd (ESI) m/z for $\text{C}_{30}\text{H}_{25}\text{O}_2$ $[\text{M} + \text{H}]^+$: 417.1849, found: 417.1849.



2-(4-fluorophenyl)-3-((9-methyl-9H-fluoren-9-yl)methyl)benzofuran (5d)



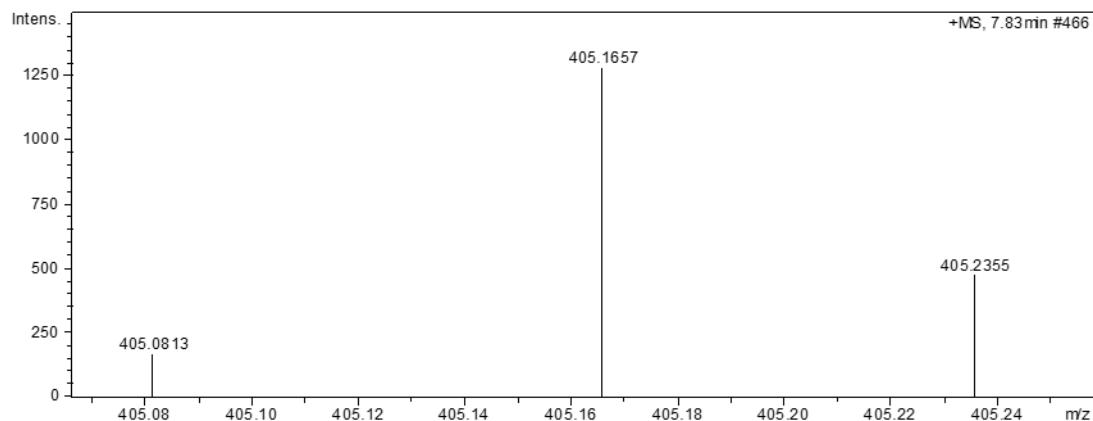
Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 100: 1) give the product **5d** (71.1 mg, 88% yield) as a yellow solid. Mp: 99-100 °C.

^1H NMR (CDCl_3 , 400 MHz) δ 7.66 (d, $J = 7.6$ Hz, 2H), 7.46-7.40 (m, 2H), 7.27-7.24 (m, 3H), 7.20-7.16 (m, 5H), 7.08 (t, $J = 7.6$ Hz, 2H), 6.88 (t, $J = 8.4$ Hz, 2H), 3.30 (s, 2H), 1.63 (s, 3H);

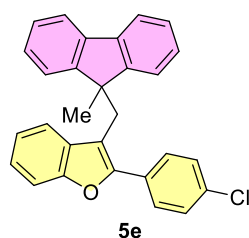
^{13}C NMR (CDCl_3 , 100 MHz) δ 162.3 (d, $J = 247.4$ Hz), 153.6, 152.1 151.3, 139.4, 130.8, 129.0 (d, $J = 8.1$ Hz), 127.4 (d, $J = 3.2$ Hz), 127.3, 127.0, 124.1, 123.8, 122.2, 121.0, 119.8, 115.2 (d, $J = 21.5$ Hz), 113.1, 110.8, 51.5, 35.1, 25.0;

^{19}F NMR (CDCl_3 , 376 MHz) δ -113.1;

HRMS Calcd (ESI) m/z for $\text{C}_{29}\text{H}_{22}\text{FO}$ $[\text{M} + \text{H}]^+$: 405.1649, found: 405.1657.



2-(4-chlorophenyl)-3-((9-methyl-9H-fluoren-9-yl)methyl)benzofuran (5e)

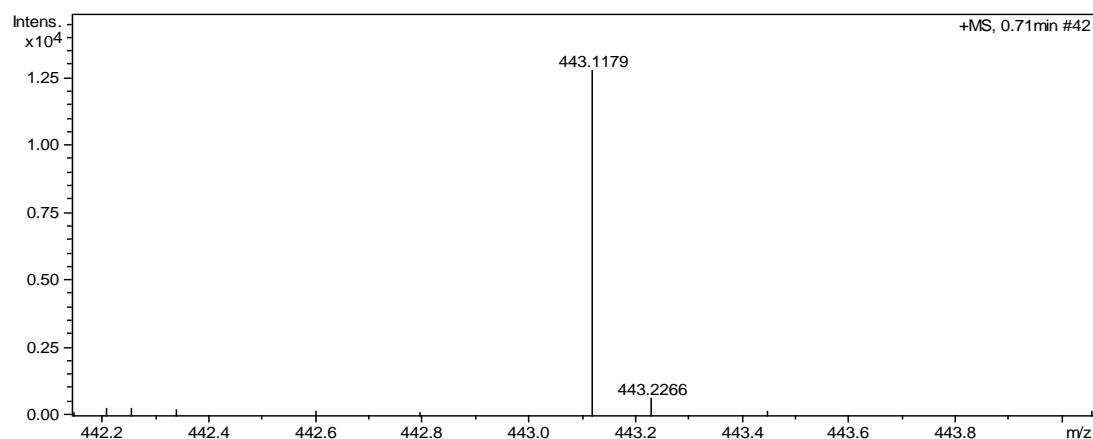


Flash column chromatography on a silica gel (petroleum ether: ethyl acetate:, 100: 1) give the product **5e** (62.3 mg, 74% yield) as a yellow solid. Mp: 95-96 °C.

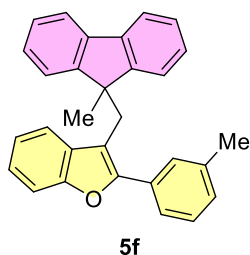
$^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ 7.70 (d, $J = 7.6$ Hz, 2H), 7.48 (t, $J = 8.0$ Hz, 2H), 7.32-7.27 (m, 3H), 7.22-7.15 (m, 7H), 7.13-7.09 (m, 2H), 3.33 (s, 2H), 1.67 (s, 3H);

$^{13}\text{C NMR}$ (CDCl_3 , 100 MHz) δ 153.7, 151.8, 151.3, 139.4, 133.7, 130.8, 129.6, 128.3, 128.2, 127.3, 127.1, 124.3, 123.8, 122.3, 121.0, 119.9, 113.8, 110.9, 51.5, 35.2, 25.0;

HRMS Calcd (ESI) m/z for $\text{C}_{29}\text{H}_{21}\text{ClO}_2\text{Na}$ $[\text{M} + \text{Na}]^+$: 443.1173, found: 443.1179.



3-((9-methyl-9H-fluoren-9-yl)methyl)-2-(m-tolyl)benzofuran (5f)

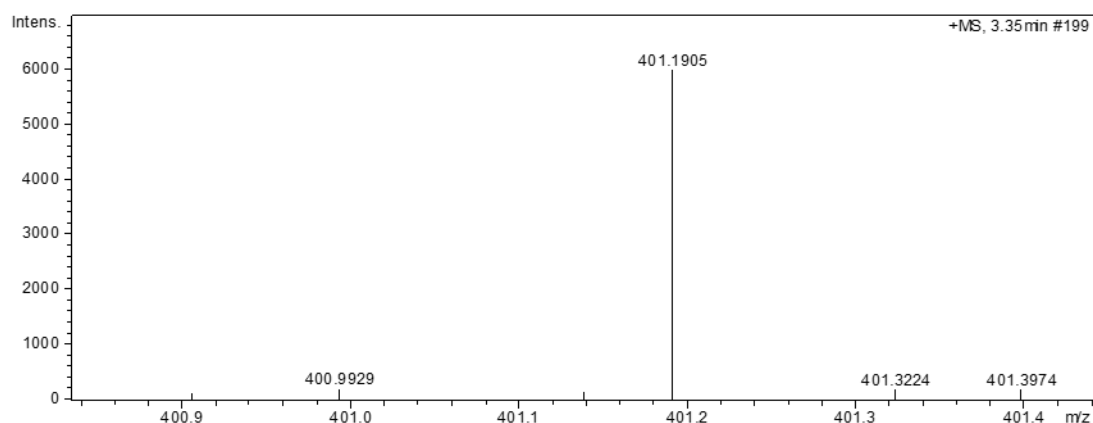


Flash column chromatography on a silica gel (petroleum ether: ethyl acetate:, 100: 1) give the product **5f** (62,4 mg, 78% yield) as a yellow solid. Mp: 103-104 °C.

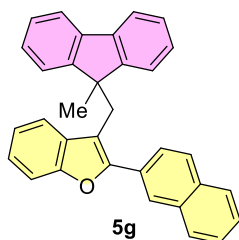
$^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ 7.69 (d, $J = 7.2$ Hz, 2H), 7.47 (d, $J = 8.0$ Hz, 1H), 7.42 (d, $J = 7.6$ Hz, 1H), 7.29-7.23 (m, 3H), 7.18-7.07 (m, 7H), 7.01 (d, $J = 6.8$ Hz, 1H), 6.88 (s, 1H), 3.32 (s, 2H), 2.19 (s, 3H), 1.65 (s, 3H);

$^{13}\text{C NMR}$ (CDCl_3 , 100 MHz) δ 153.7, 153.2, 151.6, 139.5, 137.7, 130.9 (2C), 128.7, 128.0, 127.8, 127.2, 127.0, 124.3, 124.0, 123.9, 122.1, 121.0, 119.8, 113.2, 110.8, 51.5, 35.1, 25.2, 21.4;

HRMS Calcd (ESI) m/z for $\text{C}_{30}\text{H}_{25}\text{O}$ $[\text{M} + \text{H}]^+$: 401.1900, found: 401.1905.



3-((9-methyl-9H-fluoren-9-yl)methyl)-2-(naphthalen-2-yl)benzofuran (**5g**)

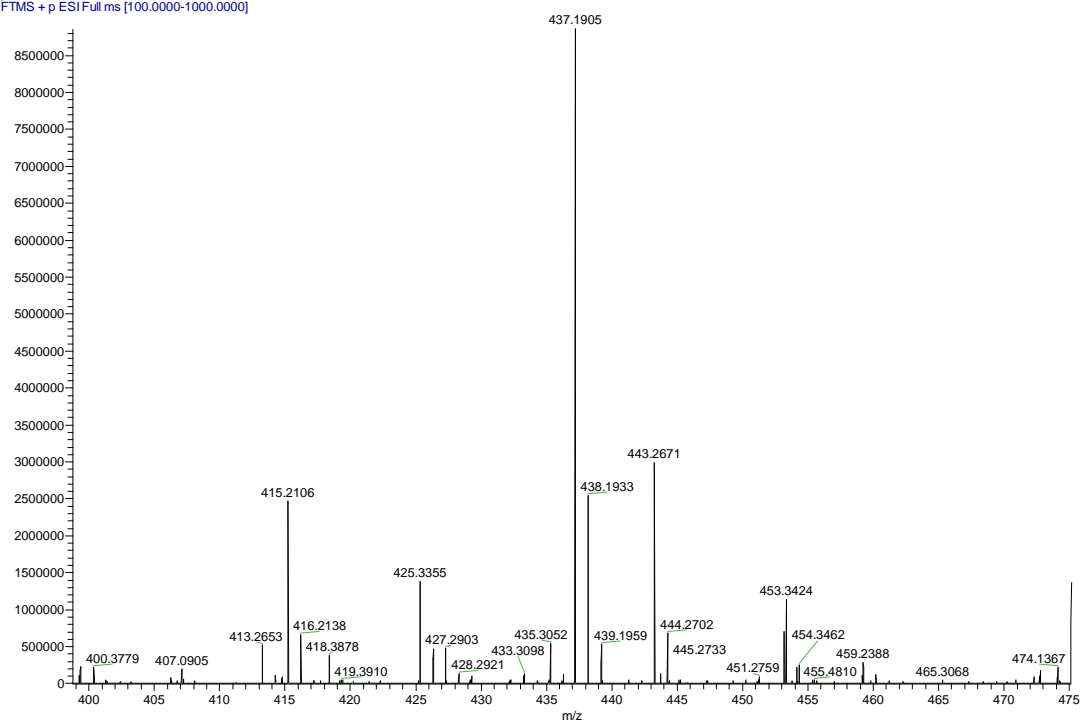


Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 100: 1) give the product **5g** (78.2 mg, 90% yield) as a yellow solid. Mp: 122-123 °C.

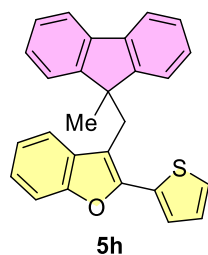
$^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ 7.75-7.73 (m, 3H), 7.68 (d, $J = 8.4$ Hz, 1H), 7.57-7.55 (m, 1H), 7.53-7.48 (m, 3H), 7.44-7.40 (m, 3H), 7.31-7.27 (m, 1H), 7.27-7.24 (m, 1H), 7.23-7.21 (m, 2H), 7.19-7.17 (m, 2H), 7.06-7.02 (m, 2H), 3.40 (s, 2H), 1.68 (s, 3H);
 $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz) δ 154.0, 153.1, 151.6, 139.5, 133.0, 132.7, 131.0, 128.4 (2C), 127.7, 127.4, 127.3, 127.1, 126.5, 126.3, 126.1, 124.8, 124.2, 123.9, 122.2, 121.1, 119.9, 113.9, 110.9, 51.6, 35.4, 25.3;

HRMS Calcd (ESI) m/z for $\text{C}_{33}\text{H}_{25}\text{O}$ [$\text{M} + \text{H}$] $^+$: 437.1900, found: 437.1905.

LHR-1-153-4 #772 RT: 3.45 AV: 1 NL: 8.86E6
T: FTMS + p ESI Full ms [100.0000-1000.0000]



3-((9-methyl-9H-fluoren-9-yl)methyl)-2-(thiophen-2-yl)benzofuran (**5h**)

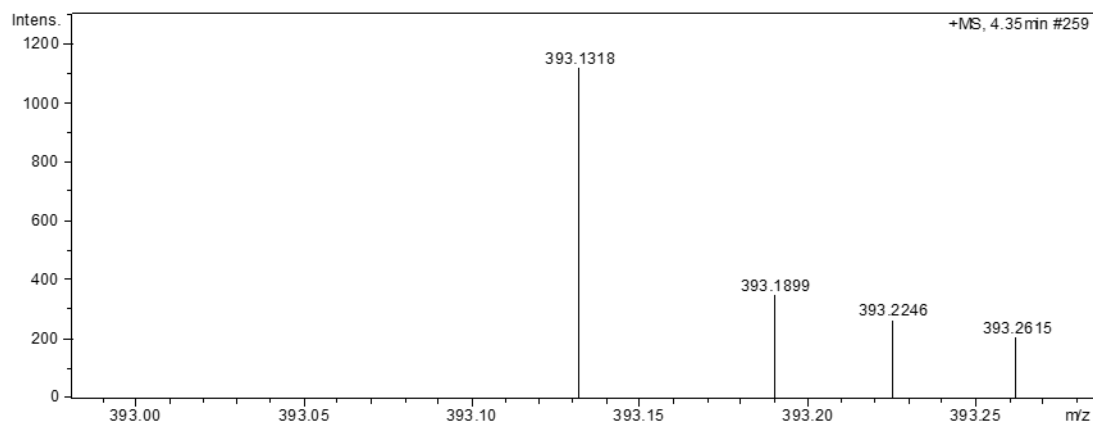


Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 100: 1) give the product **5h** (14.2 mg, 18% yield) as a brown solid. Mp: 117-119 °C.

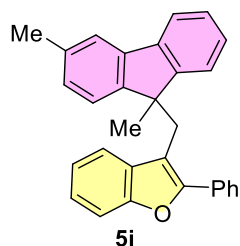
$^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ 7.73-7.70 (m, 2H), 7.49-7.46 (m, 1H), 7.41-7.38 (m, 1H), 7.31-7.26 (m, 3H), 7.24-7.22 (m, 2H), 7.18-7.16 (m, 2H), 7.14-7.09 (m, 2H), 6.86-6.83 (m, 1H), 6.78-6.76 (m, 1H), 3.28 (s, 2H), 1.68 (s, 3H);

^{13}C NMR (CDCl_3 , 100 MHz) δ 153.7, 151.5, 148.9, 139.4, 132.9, 130.8, 127.3, 127.1, 125.8, 125.4, 124.3, 123.8, 122.4, 120.9, 119.9, 112.8, 110.8, 51.4, 35.4, 24.9;

HRMS Calcd (ESI) m/z for $\text{C}_{27}\text{H}_{21}\text{OS}$ $[\text{M} + \text{H}]^+$: 393.1308, found: 393.1318.



3-((3,9-dimethyl-9H-fluoren-9-yl)methyl)-2-phenylbenzofuran (**5i**)

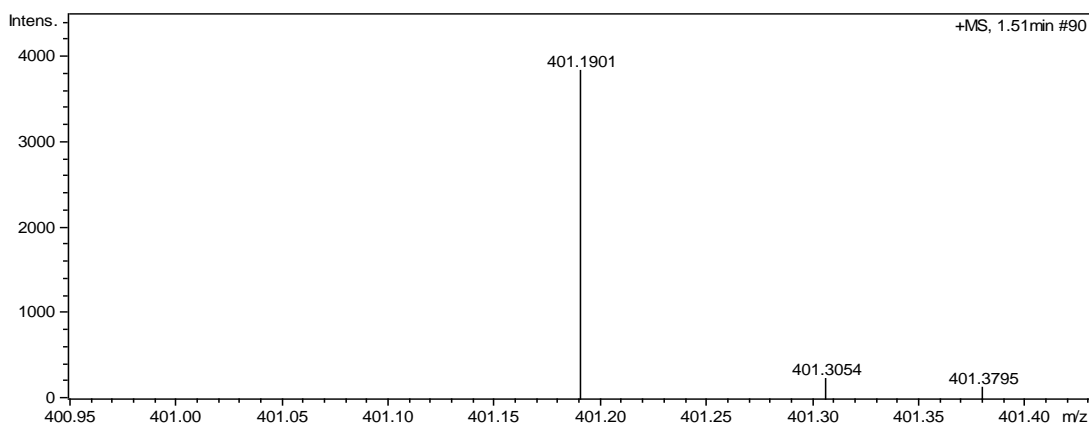


Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 100: 1) give the product **5i** (66.8 mg, 83% yield) as a yellow solid. Mp: 111-112 °C.

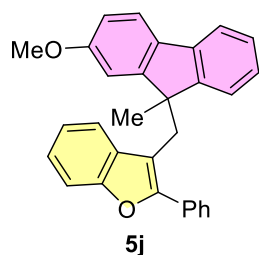
^1H NMR (CDCl_3 , 400 MHz) δ 7.63 (d, $J = 7.6$ Hz, 1H), 7.48-7.45 (m, 2H), 7.36 (d, $J = 8.0$ Hz, 1H), 7.26-7.24 (m, 3H), 7.22-7.20 (m, 4H), 7.15-7.13 (m, 2H), 7.06-7.03 (m, 2H), 6.88 (d, $J = 7.2$ Hz, 1H), 3.31 (s, 2H), 2.36 (s, 3H) 1.58 (s, 3H);

^{13}C NMR (CDCl_3 , 100 MHz) δ 153.7, 152.9, 151.7, 148.7, 139.5 (2C), 136.8, 131.2, 130.9, 128.1, 127.9, 127.8, 127.2, 127.1, 126.8, 124.0, 123.8, 123.5, 122.0, 121.0, 120.4, 119.6, 113.4, 110.8, 51.1, 35.1, 25.1, 21.4;

HRMS Calcd (ESI) m/z for $\text{C}_{30}\text{H}_{25}\text{O}$ $[\text{M} + \text{H}]^+$: 401.1900, found: 401.1901.



3-((2-methoxy-9-methyl-9H-fluoren-9-yl)methyl)-2-phenylbenzofuran (**5j**)

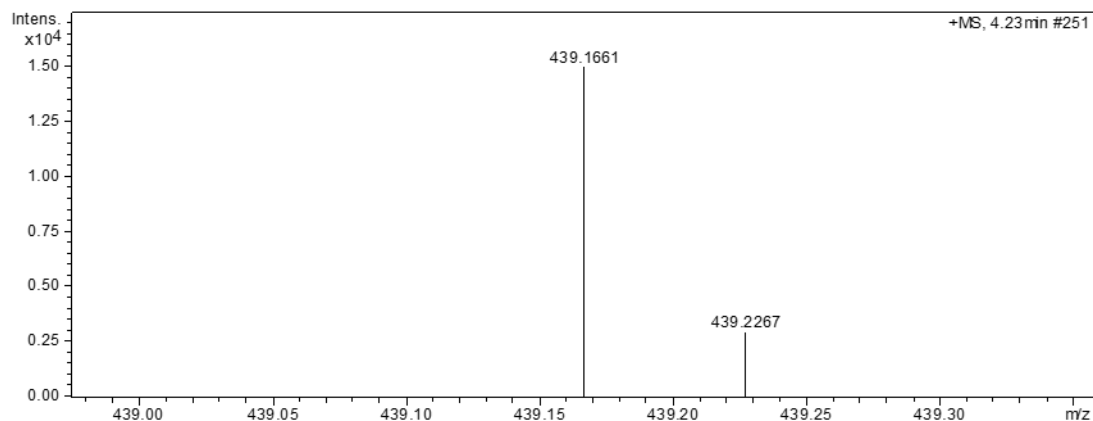


Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 50: 1) give the product **5j** (60.9 mg, 73% yield) as a yellow solid. Mp: 66-67 °C.

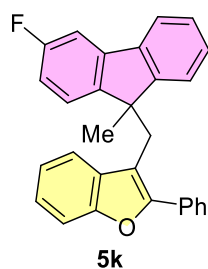
$^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ 7.56 (t, $J = 8.8$ Hz, 2H), 7.46 (d, $J = 8.4$ Hz, 1H), 7.37-7.35 (m, 2H), 7.30 (d, $J = 7.2$ Hz, 1H), 7.25-7.22 (m, 5H), 7.19 (d, $J = 7.6$ Hz, 1H), 7.13 (t, $J = 7.6$ Hz, 1H), 7.04 (t, $J = 7.2$ Hz, 1H), 6.79-6.76 (m, 1H), 6.62-6.61 (m, 1H), 3.56 (s, 3H), 3.40 (d, $J = 14.4$ Hz, 1H), 3.28 (d, $J = 14.4$ Hz, 1H), 1.57 (s, 3H);

$^{13}\text{C NMR}$ (CDCl_3 , 100 MHz) δ 159.2, 153.7, 153.1, 152.9, 151.2, 139.4, 132.3, 131.3, 131.0, 128.2, 127.9, 127.2, 127.1, 125.9, 124.0, 123.5, 122.1, 121.0, 120.5, 119.0, 113.4, 113.1, 110.8, 109.7, 55.3, 51.5, 35.1, 24.9;

HRMS Calcd (ESI) m/z for $\text{C}_{30}\text{H}_{24}\text{NaO}_2$ $[\text{M} + \text{Na}]^+$: 439.1669, found:439.1661.



3-((3-fluoro-9-methyl-9H-fluoren-9-yl)methyl)-2-phenylbenzofuran (**5k**)



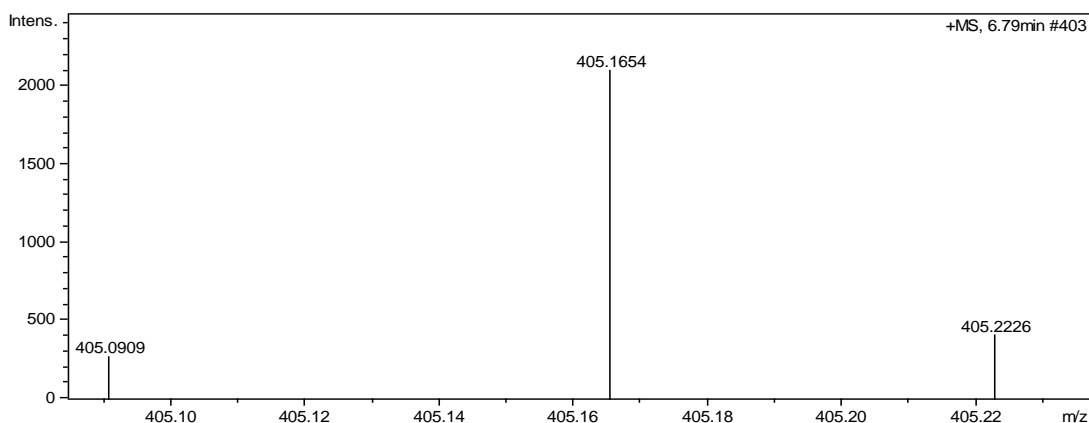
Flash column chromatography on a silica gel (petroleum ether: acetone, 100: 1) give the product **5k** (67.5 mg, 83% yield) as a yellow solid. Mp: 117-118 °C.

¹H NMR (CDCl₃, 400 MHz) δ 7.59 (d, *J* = 7.6 Hz, 1H), 7.44 (d, *J* = 8.0 Hz, 1H), 7.30-7.21 (m, 10H), 7.14-7.10 (m, 2H), 7.01-6.98 (m, 1H), 6.70-6.66 (m, 1H), 3.36 (q, *J* = 13.2 Hz, 2H), 1.58 (s, 3H);

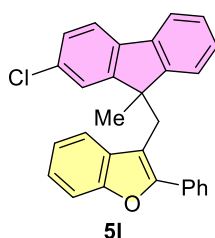
¹³C NMR (CDCl₃, 100 MHz) δ 162.7 (d, *J* = 242.4 Hz), 153.7, 152.9, 152.3, 146.5, 141.4 (d, *J* = 8.6 Hz), 138.5 (d, *J* = 3.0 Hz), 131.2, 130.7, 128.2, 128.0, 127.6, 127.3, 127.2, 124.9 (d, *J* = 9.0 Hz), 124.0, 123.8, 122.1, 120.8, 120.0, 113.5 (d, *J* = 22.7 Hz), 113.0, 110.8, 106.7 (d, *J* = 22.8 Hz), 51.1, 34.9, 25.1;

¹⁹F NMR (CDCl₃, 376 MHz) δ -116.0;

HRMS Calcd (ESI) *m/z* for C₂₉H₂₂FO [M + H]⁺: 405.1649, found: 405.1654.



3-((2-chloro-9-methyl-9H-fluoren-9-yl)methyl)-2-phenylbenzofuran (**5I**)

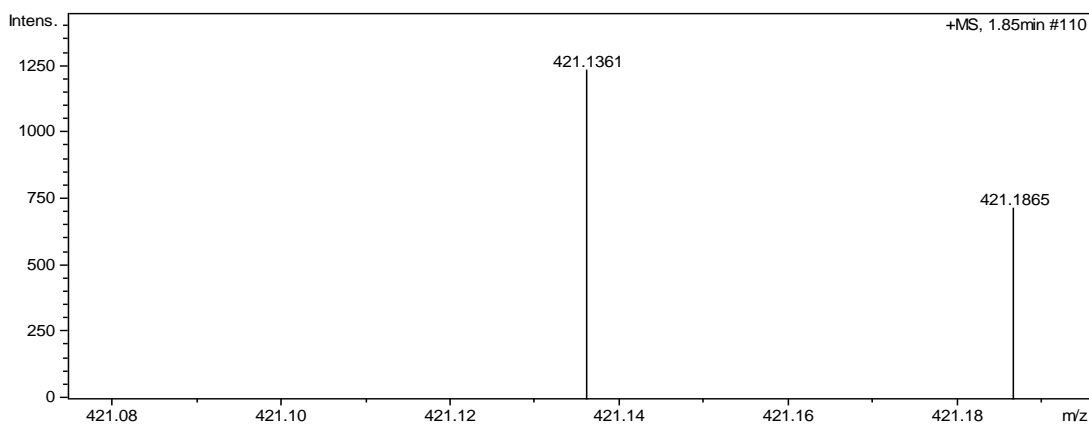


Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 100:1) give the product **5I** (63.5 mg, 75% yield) as a yellow solid. Mp: 101-102 °C.

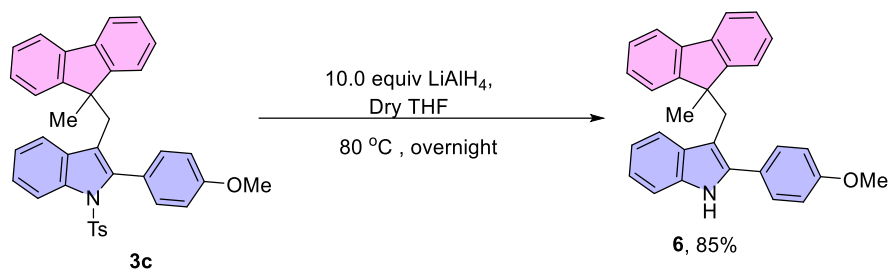
$^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ 7.50 (d, $J = 7.6$ Hz, 1H), 7.42 (d, $J = 8.4$ Hz, 1H), 7.36 (d, $J = 8.4$ Hz, 1H), 7.28-7.26 (m, 2H), 7.20-7.13 (m, 6H), 7.11-7.08 (m, 2H), 7.06-6.99 (m, 3H), 3.30 (s, 2H), 1.48 (s, 3H);

$^{13}\text{C NMR}$ (CDCl_3 , 100 MHz) δ 153.6, 153.1, 153.0, 151.2, 138.5, 138.0, 132.5, 131.2, 130.6, 128.3, 128.1, 127.4, 127.3 (2C), 127.2, 124.5, 124.0, 123.8, 122.1, 120.7 (2C), 119.8, 112.5, 110.8, 51.7, 34.8, 24.8;

HRMS Calcd (ESI) m/z for $\text{C}_{29}\text{H}_{22}\text{ClO}$ $[\text{M} + \text{H}]^+$: 421.1354, found: 421.1361.

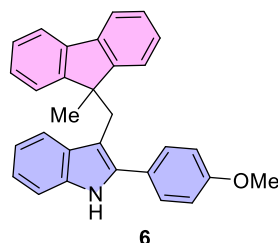


7. Synthetic transformations.



Under argon atmosphere, an oven-drying round-bottom flask (50 mL) equipped with a magnetic stir bar was charged with **3c** (569.2 mg, 1.0 mmol, 1.0 equiv), LiAlH₄ (379.5 mg, 10.0 mmol, 10.0 equiv) and 10 mL Dry THF were added sequentially. Degassed solvent and backfilled with argon for 3 times. Then, the tube was sealed with a rubber stopper at r.t., and the reaction mixture was stirred at 80 °C for 9 h. After completion of the reaction (monitored by TLC), the mixture was diluted with water and extracted with EA (3 × 20 mL). The combined organic layers were dried over anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure and the residue was purified by flash column chromatography on silica gel with petroleum ether-ethyl acetate (10:1) as eluent to give the desired product **6** (352.0 mg, 85% yield) as a yellow oil.

2-(4-methoxyphenyl)-3-((9-methyl-9H-fluoren-9-yl)methyl)-1H-indole (**6**)

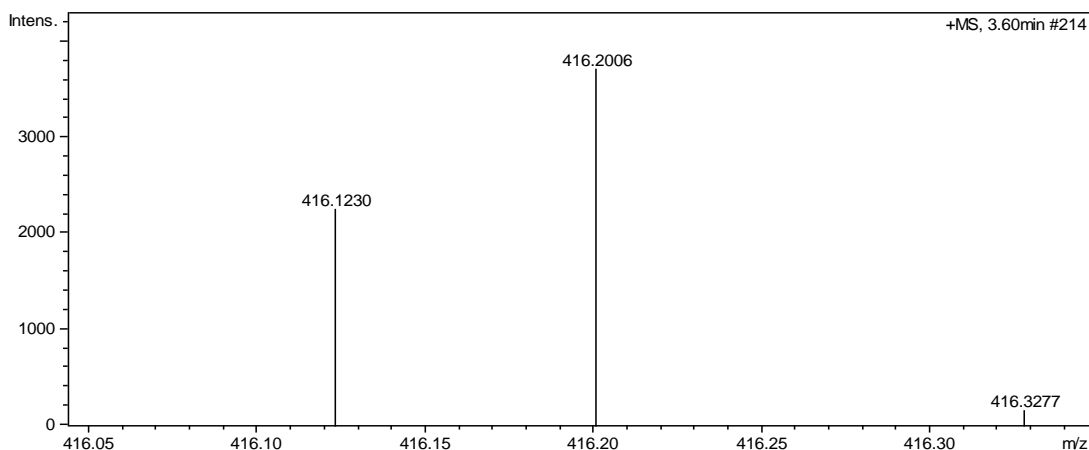


Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 10:1) give the product **6** (352.0 mg, 85% yield) as a yellow oil.

¹H NMR (CDCl₃, 400 MHz) δ 7.93 (s, 1H), 7.70 (d, *J* = 7.6 Hz, 2H), 7.41 (d, *J* = 8.0 Hz, 1H), 7.34-7.29 (m, 3H), 7.21-7.17 (m, 1H), 7.15-7.13 (m, 4H), 7.09-7.05 (m, 3H), 6.86-6.84 (m, 2H), 3.84 (s, 3H), 3.39 (s, 2H), 1.58 (s, 3H);

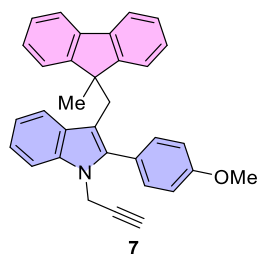
¹³C NMR (CDCl₃, 100 MHz) δ 158.9, 152.2, 139.4, 136.4, 135.3, 129.9, 129.6, 126.8, 126.7, 126.1, 124.0, 121.5, 120.5, 119.6, 119.1, 113.9, 110.3, 109.8, 55.2, 52.1, 35.2, 25.1;

HRMS Calcd (ESI) *m/z* for C₃₀H₂₆NO [M + H]⁺: 416.2009, found: 416.2006.



A round bottle flask equipped with a magnetic stir bar was charged with product **6** (352.0 mg, 0.85 mmol, 1.0 equiv) and DMF (10 mL). After cooling to 0 °C, NaH (32.0 mg 60% NaH, 1.3 mmol, 1.5 equiv) was added slowly and stirred 5 min. Then, propargyl bromide (154.6 mg, 1.3 mmol, 1.5 equiv) was added at 0 °C. The reaction mixture was stirred 2 h at room temperature. Upon the completion of the reaction (monitored by TLC), the reaction mixture was quenched with H₂O and extracted with ethyl acetate (3×15 mL) Then, the mixture was concentrated in vacuum and the residue was purified by flash column chromatography on silica gel with petroleum ether-ethyl acetate as eluent to give the desired product **7** (270.1 mg, 70% yield) as a white solid.

2-(4-methoxyphenyl)-3-((9-methyl-9H-fluoren-9-yl)methyl)-1-(prop-2-yn-1-yl)-1H-indole (7)



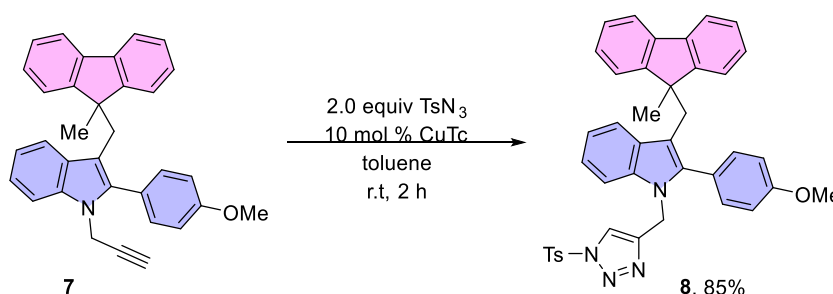
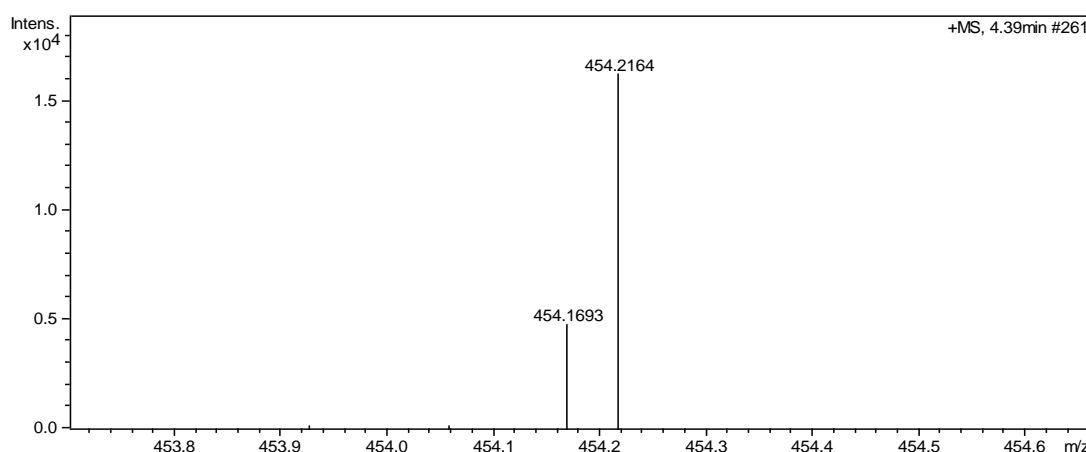
Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 10: 1) give the product **7** (270.1 mg, 70% yield) as a white soild. Mp: 110-112 °C.

¹H NMR (CDCl₃, 400 MHz) δ 7.70 (d, *J* = 7.6 Hz, 2H), 7.50 (d, *J* = 8.4 Hz, 1H), 7.34-

7.27 (m, 4H), 7.19-7.15 (m, 2H), 7.12-7.05 (m, 5H), 6.95-6.91 (m, 2H), 4.67 (s, 2H), 3.88 (s, 3H), 3.24 (s, 2H), 2.30 (t, $J = 2.4$ Hz, 1H), 1.50 (s, 3H);

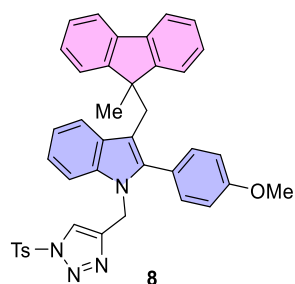
^{13}C NMR (CDCl_3 , 100 MHz) δ 159.3, 152.3, 139.4, 139.1, 135.9, 132.1, 129.0, 126.7 (2C), 124.1, 123.6, 121.6, 120.8, 119.6, 119.4, 113.7, 111.2, 109.4, 79.1, 72.0, 55.2, 51.8, 35.5, 33.6, 25.0;

HRMS Calcd (ESI) m/z for $\text{C}_{33}\text{H}_{28}\text{NO}$ $[\text{M} + \text{H}]^+$: 454.2165, found: 454.2164.



A sealed tube (10 mL) equipped with a magnetic stir bar was charged with product **7** (90.7 mg, 0.2 mmol, 1.0 equiv), CuTc (3.8 mg, 0.02 mmol, 0.1 equiv), TsN₃ (78.9 mg, 0.4 mmol, 2.0 equiv) and 2.0 mL toluene. Degassed toluene and backfilled with argon for 3 times (3 × 1min) at -78 °C. The reaction mixture was kept stirring at room temperature for 2 h. After completion of the reaction (monitored by TLC), the mixture was concentrated in vacuum and the residue was purified by flash column chromatography on silica gel with petroleum ether-ethyl acetate as eluent to give the desired product **8** (111.1 mg, 85% yield) as a white solid.

2-(4-methoxyphenyl)-3-((9-methyl-9H-fluoren-9-yl)methyl)-1-((1-tosyl-1H-1,2,3-triazol-4-yl)methyl)-1H-indole (8**)**

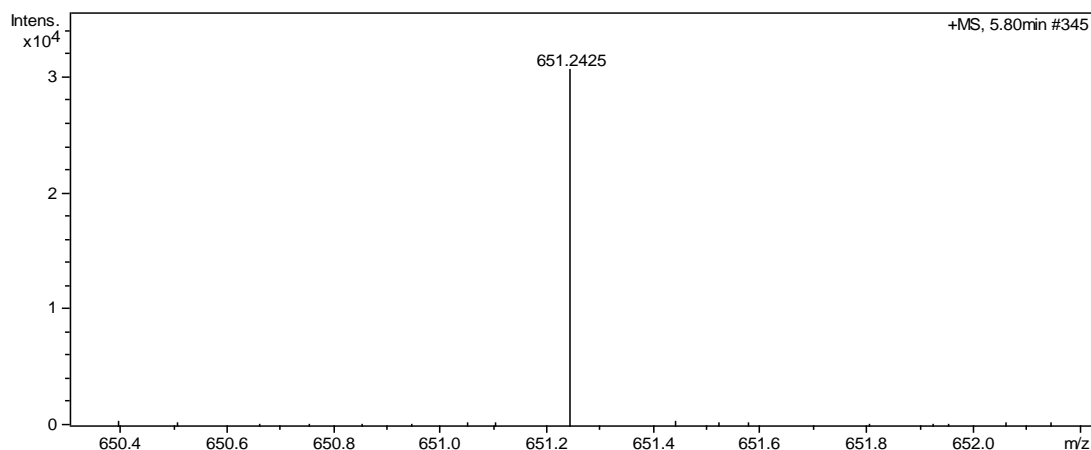


Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 5: 1) give the product **8** (111.1 mg, 85% yield) as a white soild. Mp: 87-89 °C.

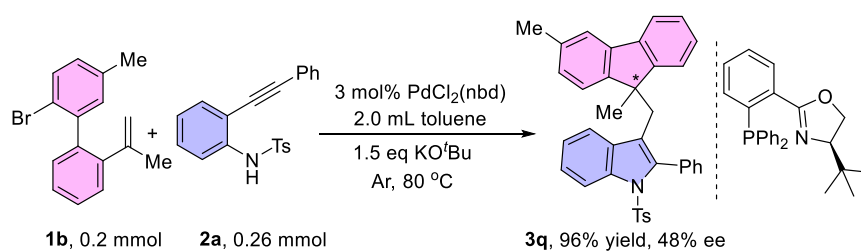
¹H NMR (CDCl₃, 400 MHz) δ 7.89 (d, *J* = 8.4 Hz, 2H), 7.61 (d, *J* = 7.6 Hz, 2H), 7.35-7.32 (m, 3H), 7.28-7.24 (m, 2H), 7.23-7.22 (m, 1H), 7.16 (d, *J* = 8.4 Hz, 1H), 7.13-7.06 (m, 3H), 7.02 (d, *J* = 7.6 Hz, 2H), 6.99-6.95 (m, 1H), 6.79-6.73 (m, 4H), 5.18 (s, 2H), 3.80 (s, 3H), 3.18 (s, 2H), 2.42 (s, 3H), 1.49 (s, 3H);

¹³C NMR (CDCl₃, 100 MHz) δ 159.3, 152.2, 147.3, 145.1, 139.5, 138.8, 135.6, 132.7, 132.0, 130.4, 128.7, 128.6, 126.8, 126.6, 123.9, 123.3, 121.6, 121.2, 120.8, 119.6, 119.3, 113.8, 111.5, 109.1, 55.2, 51.9, 39.2, 35.7, 25.4, 21.8;

HRMS Calcd (ESI) *m/z* for C₄₀H₃₅N₄O₃S [M + H]⁺: 651.2424, found: 654.2425.



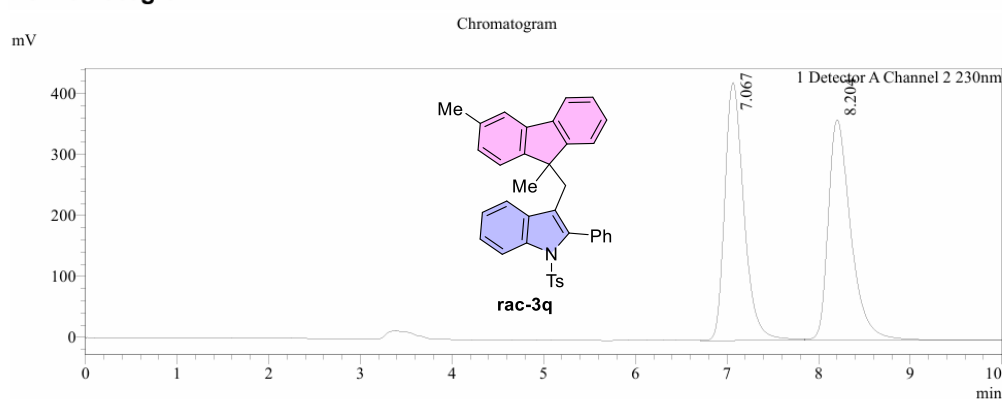
8. Enantioselective synthesis of **3q**.



A sealed tube (10 mL) equipped with a magnetic stir bar was charged with Dichloro(norbornadiene)palladium(II) (3.2 mg, 0.012 mmol, 0.06 equiv), (*R*)-*t*Bu-Phox

(6.2 mg, 0.016 mmol, 0.08 equiv) in 2.0 mL toluene. After the catalyst/ligand was stirred for 30 min at 30 °C. 2-bromo-5-methyl-2'-(prop-1-en-2-yl)-1,1'-biphenyl **1b** (57.4 mg, 0.2 mmol, 1.0 equiv), 4-methyl-*N*-(2-(phenylethynyl)phenyl) benzenesulfonamide **2a** (90.3 mg, 0.26 mmol, 1.3 equiv), and KO^tBu (33.7 mg, 0.3 mmol, 1.5 equiv) were added sequentially. Degassed toluene and backfilled with argon for 3 times (3× 1 min) at -78 °C. The reaction mixture was kept stirring at 80 °C for 24 h by use of module heating. After completion of the reaction (monitored by TLC), the mixture was concentrated in vacuum and the residue was purified by flash column chromatography on silica gel with petroleum ether-acetone or petroleum ether- ethyl acetate as eluent to give the desired product chiral **3q** 106.8 mg in 96% yield with 48% *ee*.

<Chromatogram>

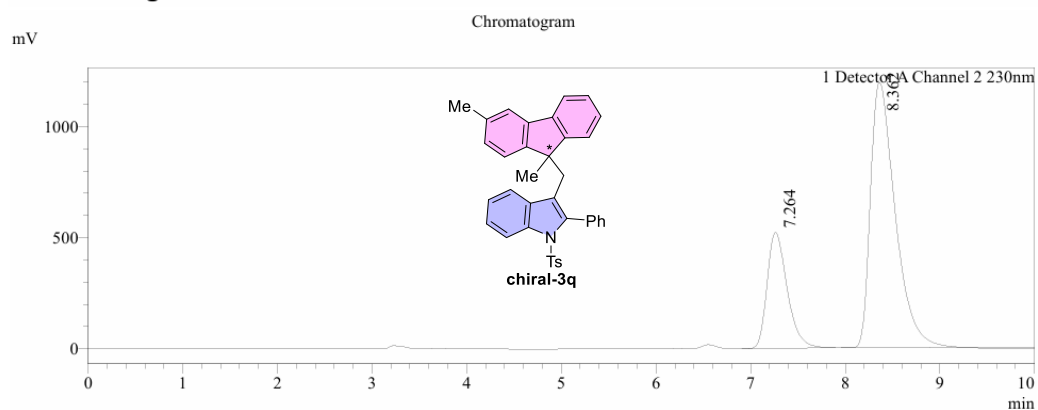


<Peak Table>

Peak Table

Detector A Channel 2 230nm				
Peak#	Ret. Time	Area	Height	Area%
1	7.067	6146155	422715	49.665
2	8.204	6229081	361504	50.335
Total		12375236	784219	100.000

<Chromatogram>



<Peak Table>

Peak Table

Detector A Channel 2 230nm

Peak#	Ret. Time	Area	Height	Area%
1	7.264	7661666	521426	26.236
2	8.362	21540936	1193376	73.764
Total		29202602	1714802	100.000

Chiral 3q HPLC conditions: Daicel Chiralpak IB column (1.0 mL/min, hexane/2-propanol = 95/5), 230 nm; tr (minor) = 7.26 min, tr (major) = 8.36 min, 48% *ee*.

$[\alpha]_{\text{D}}^{20} = 2.725$ (c = 0.2, CHCl₃).

9. Single Crystal X-Ray Diffraction

Crystals of **3f** were obtained by slow diffusion from a solution of the compounds in ethyl acetate layered with petroleum ether at room temperature for several days (Figures 1). Crystal data and details of the structure determination are presented in Table S2.

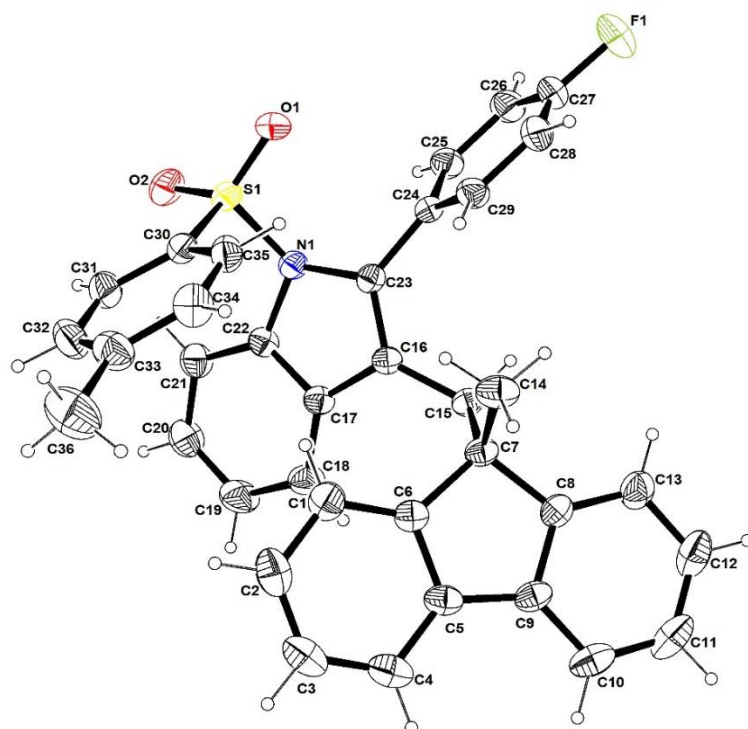


Figure 1. ORTEP drawing (30%) of the Crystal structure of **3f**

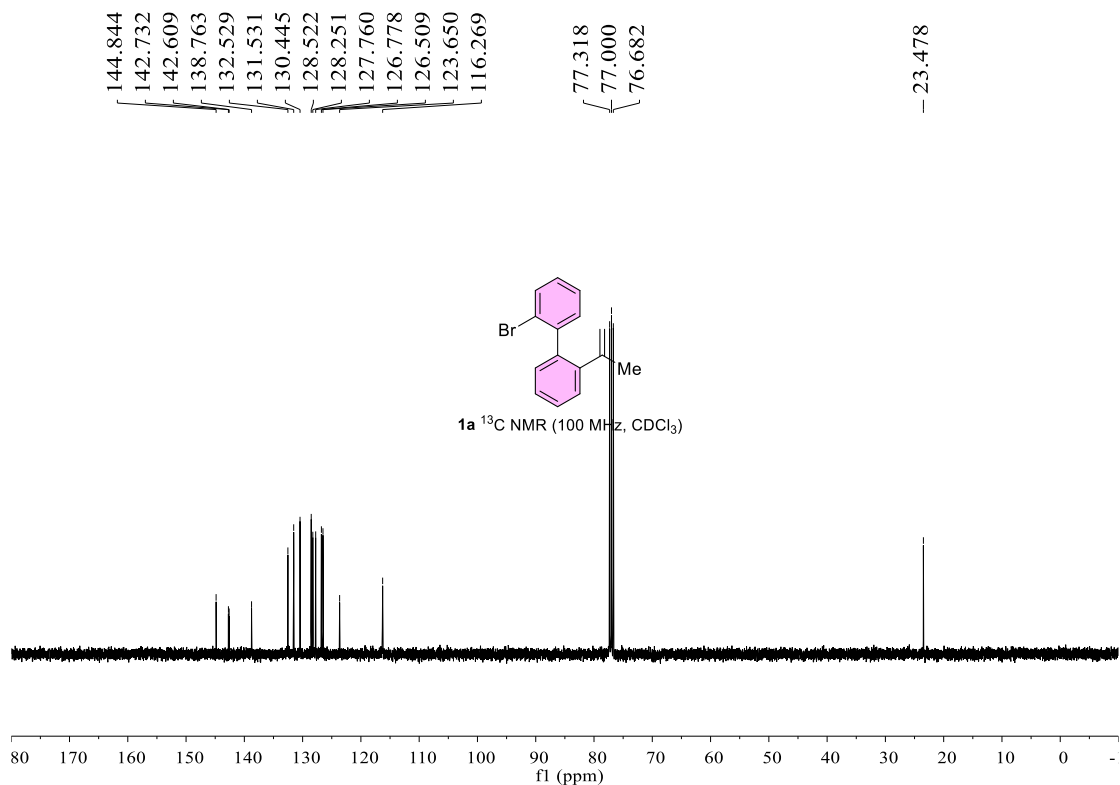
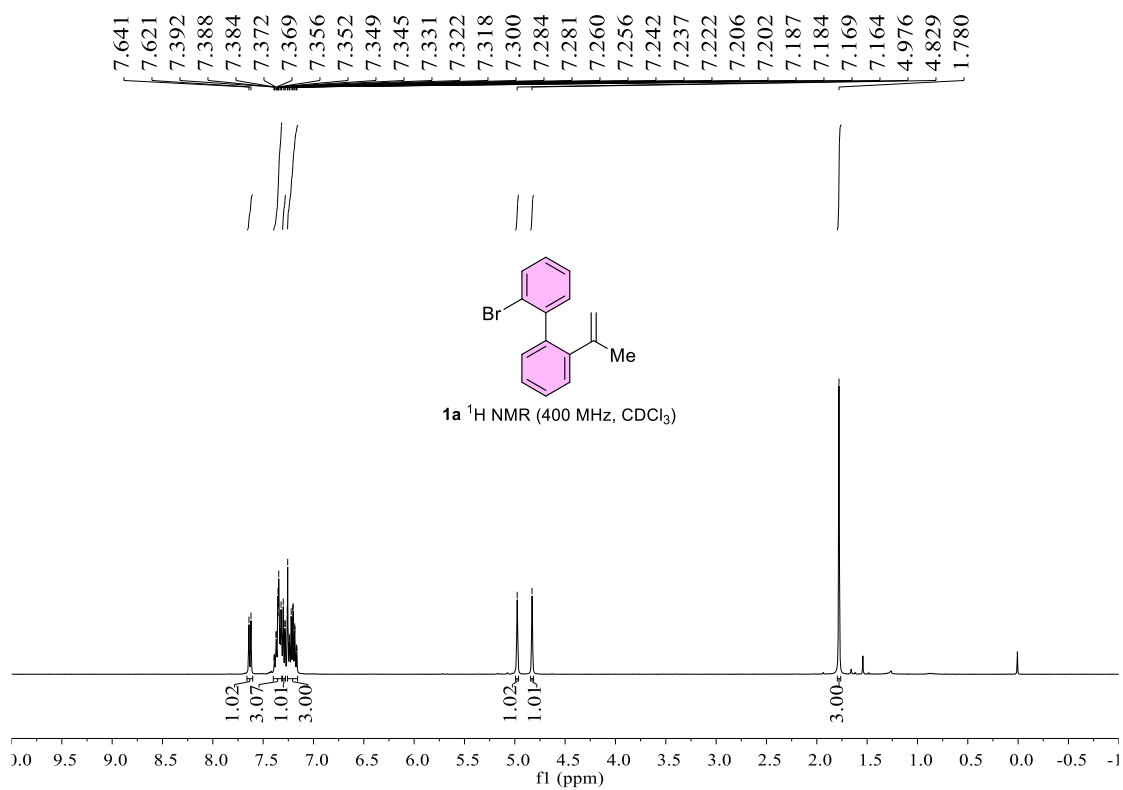
Table S2 The single crystal data of compounds **3f**

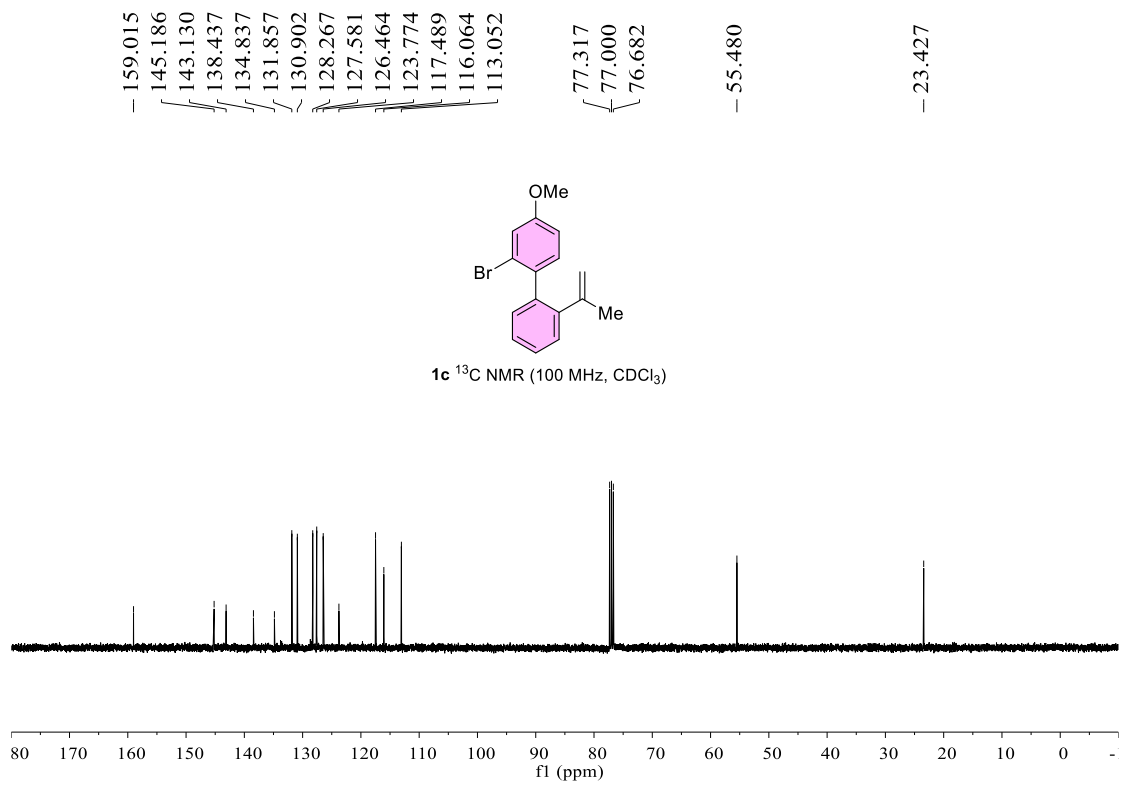
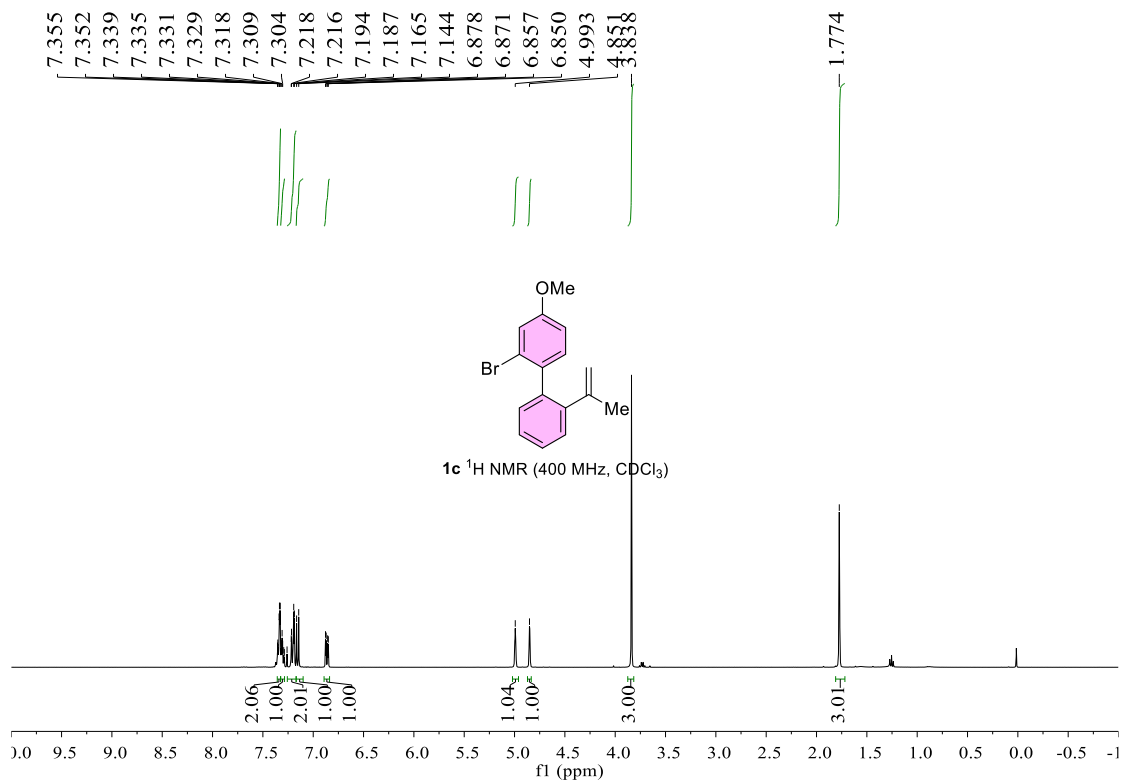
Phase	3f
Identification code	123
Empirical formula	C ₃₆ H ₂₈ FNO ₂ S
Formula weight	557.65
Temperature/K	273.15
Crystal system	triclinic
Space group	P-1
a/Å	10.8464(6)
b/Å	12.0177(6)
c/Å	12.8579(9)
α/°	62.168(2)
β/°	85.094(2)
γ/°	74.649(2)
Volume/Å ³	1427.83(15)
Z	2
ρ _{calc} /cm ³	1.297
μ /mm ⁻¹	0.154
F(000)	584.0
Crystal size/mm ³	0.31 × 0.26 × 0.17
Radiation	MoK α (λ = 0.71073)
2θ range for data collection/°	4.798 to 55.058
Index ranges	-14 ≤ h ≤ 12, -15 ≤ k ≤ 15, -16 ≤ l ≤ 16
Reflections collected	22418
Independent reflections	6552 [R _{int} = 0.0411, R _{sigma} = 0.0554]
Data/restraints/parameters	6552/0/372
Goodness-of-fit on F ²	1.015
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0519, wR ₂ = 0.1089
Final R indexes [all data]	R ₁ = 0.1058, wR ₂ = 0.1287
Largest diff. peak/hole / e Å ⁻³	0.17/-0.33

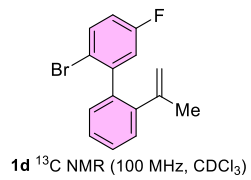
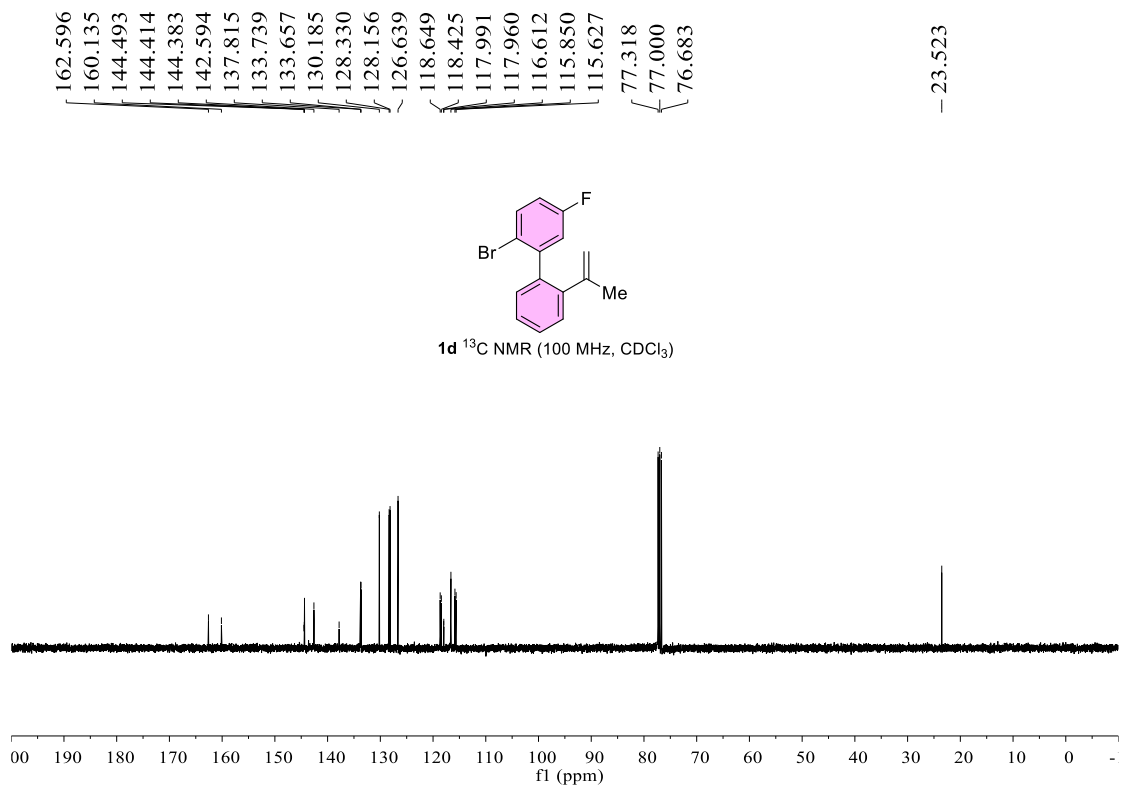
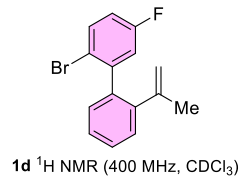
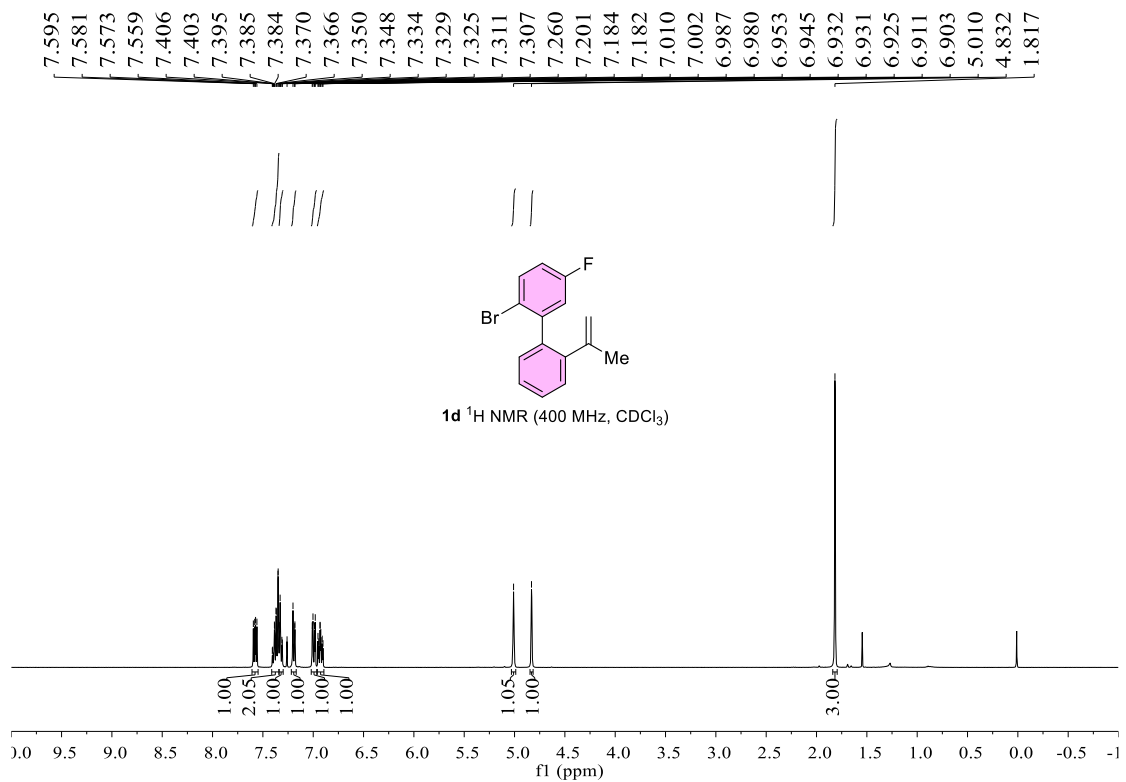
10. References

- [1]. Z. Shen, X. Lu, *Adv. Synth. Catal.* 2009, 351, 3107-3112.
- [2]. Y. Horino, M. Ishibashi, J. Sakamoto, M. Murakami, T. Korenaga, *Adv. Synth. Catal.* 2021, 363, 3592-3599

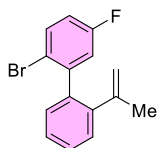
11. Copies of NMR spectra for new compounds



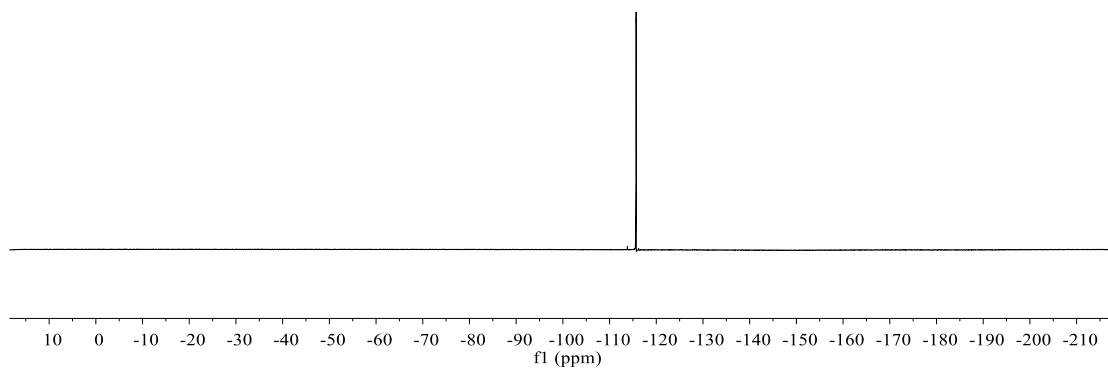


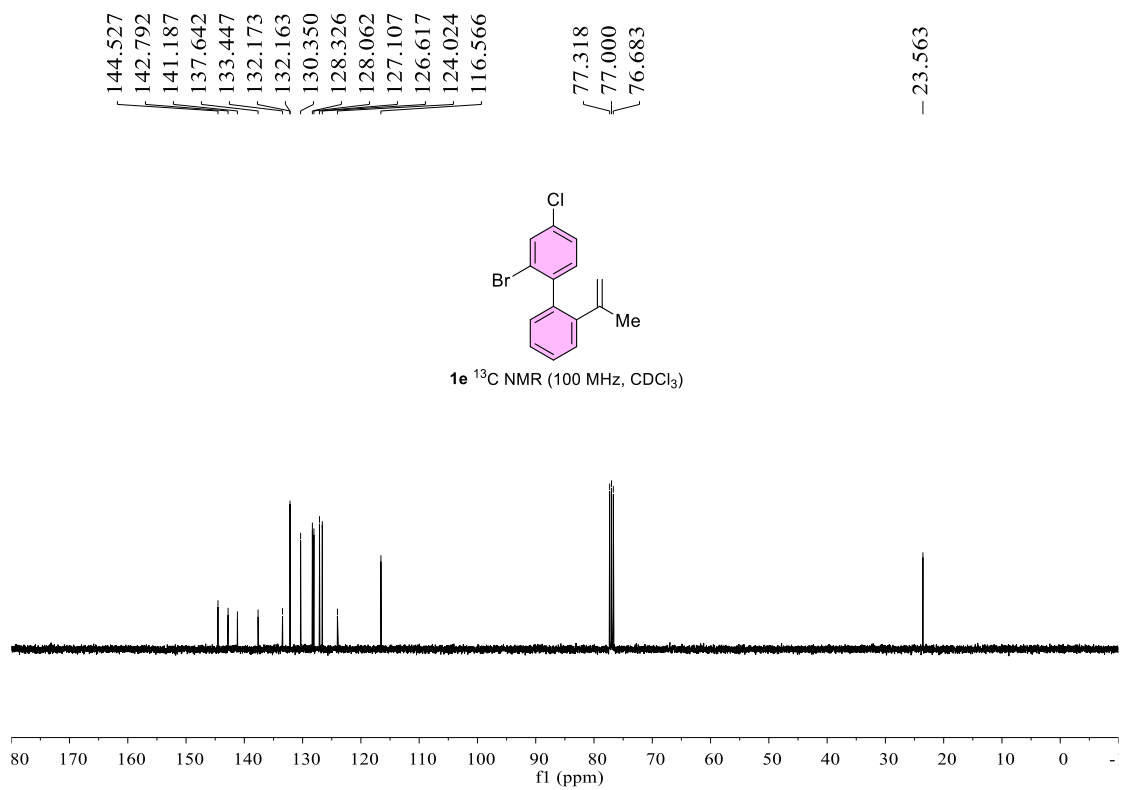
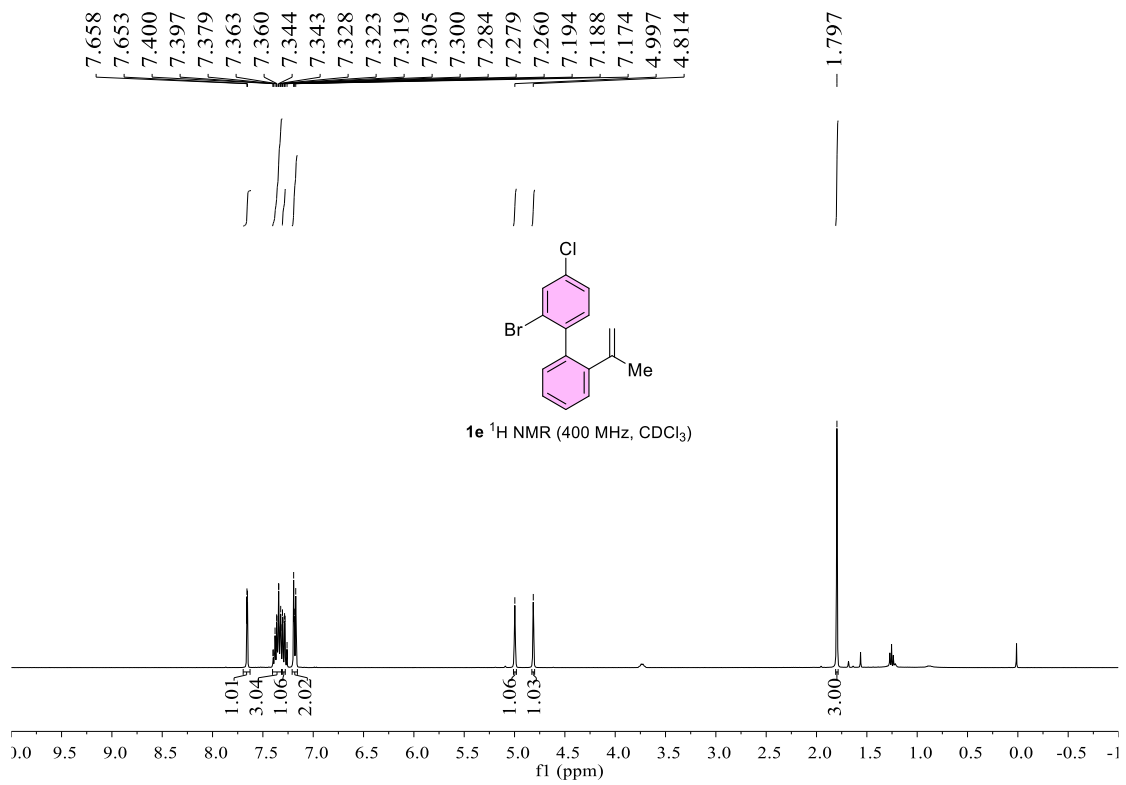


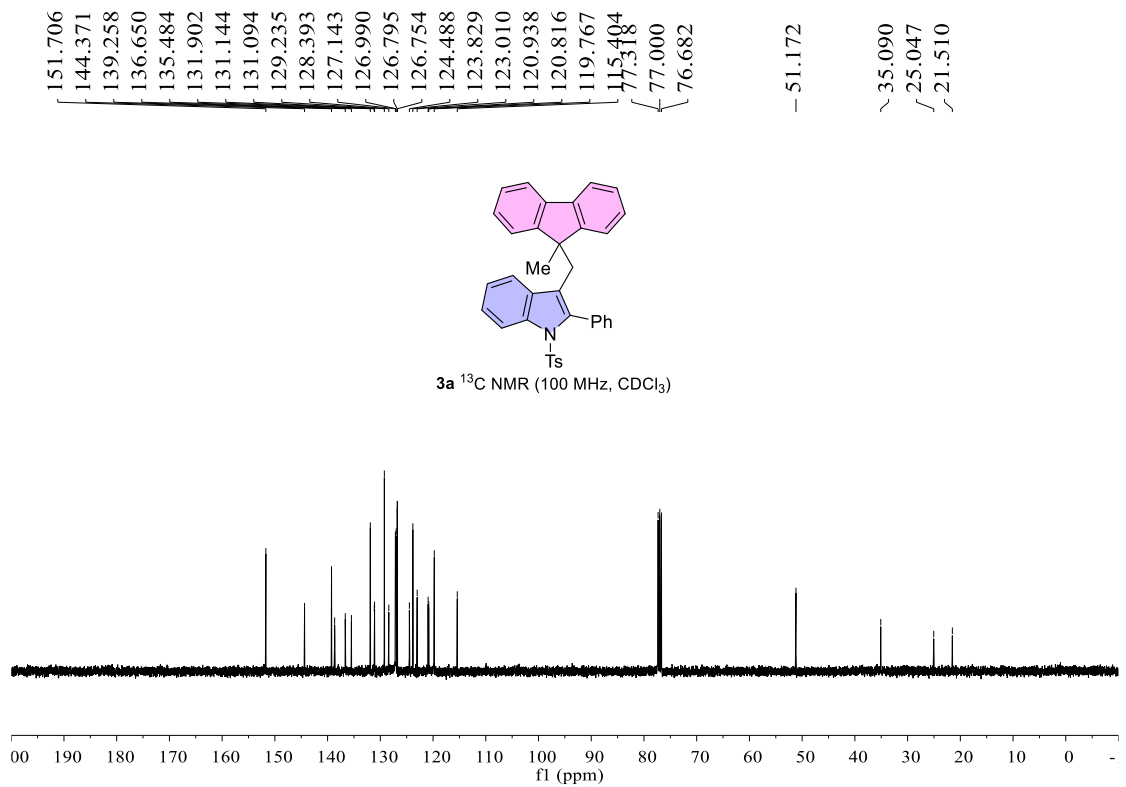
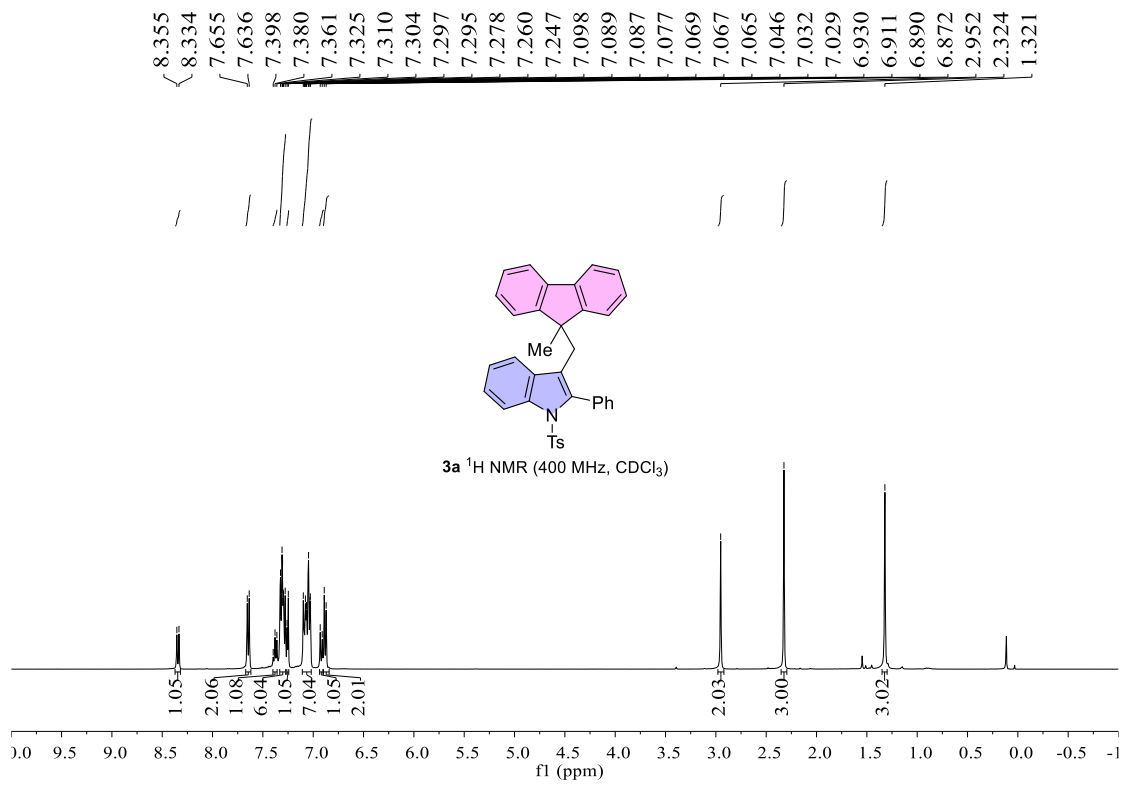
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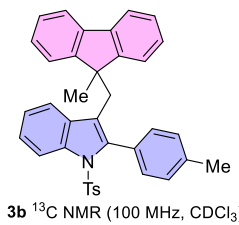
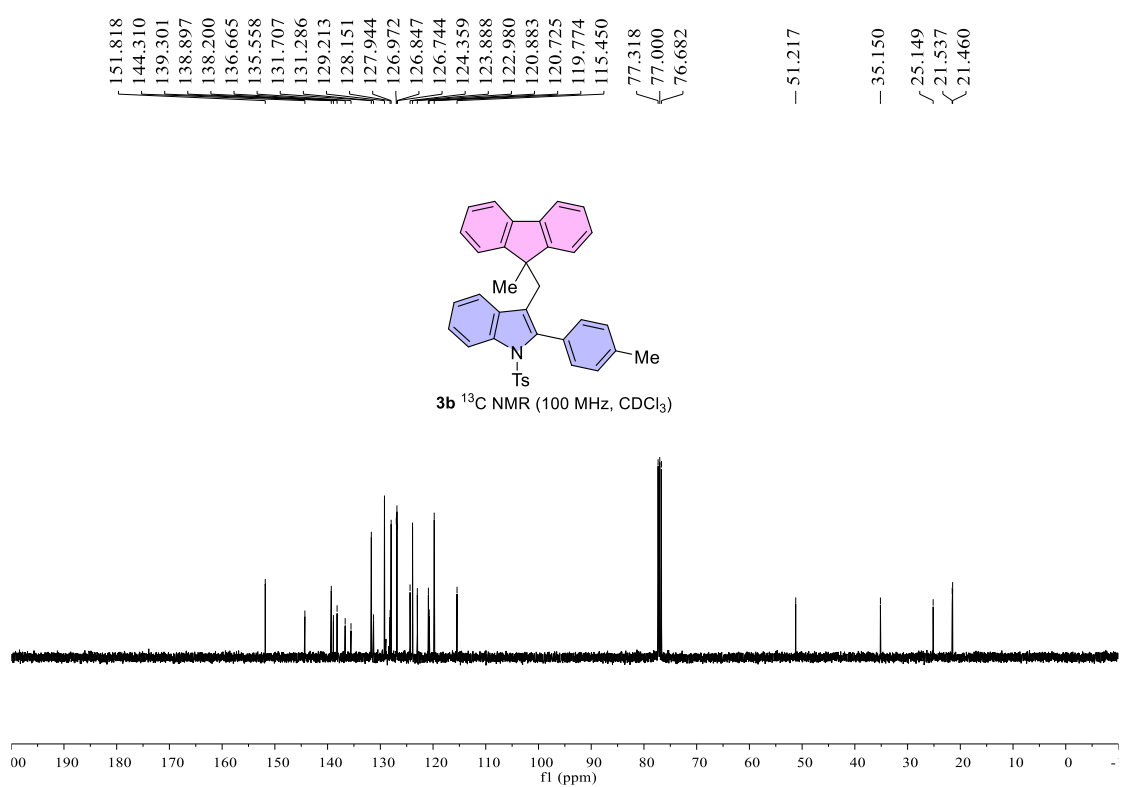
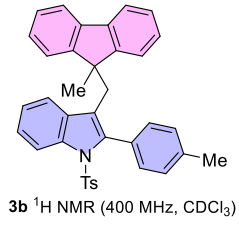
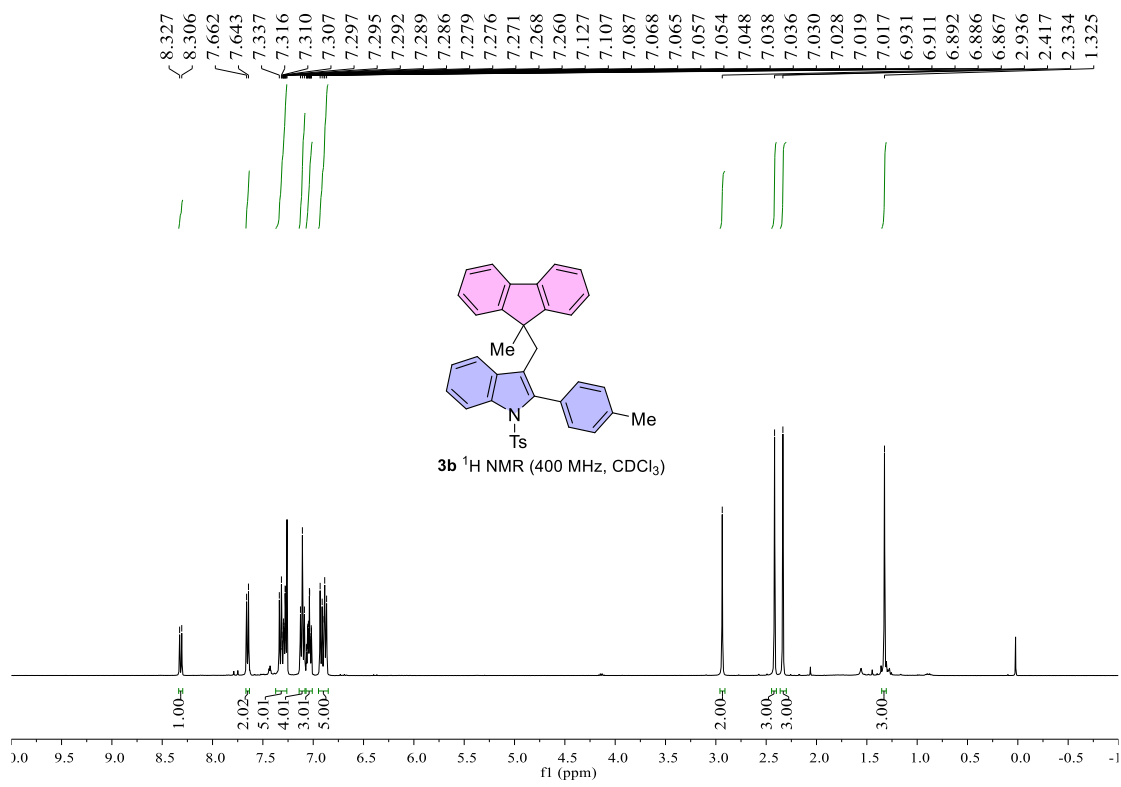


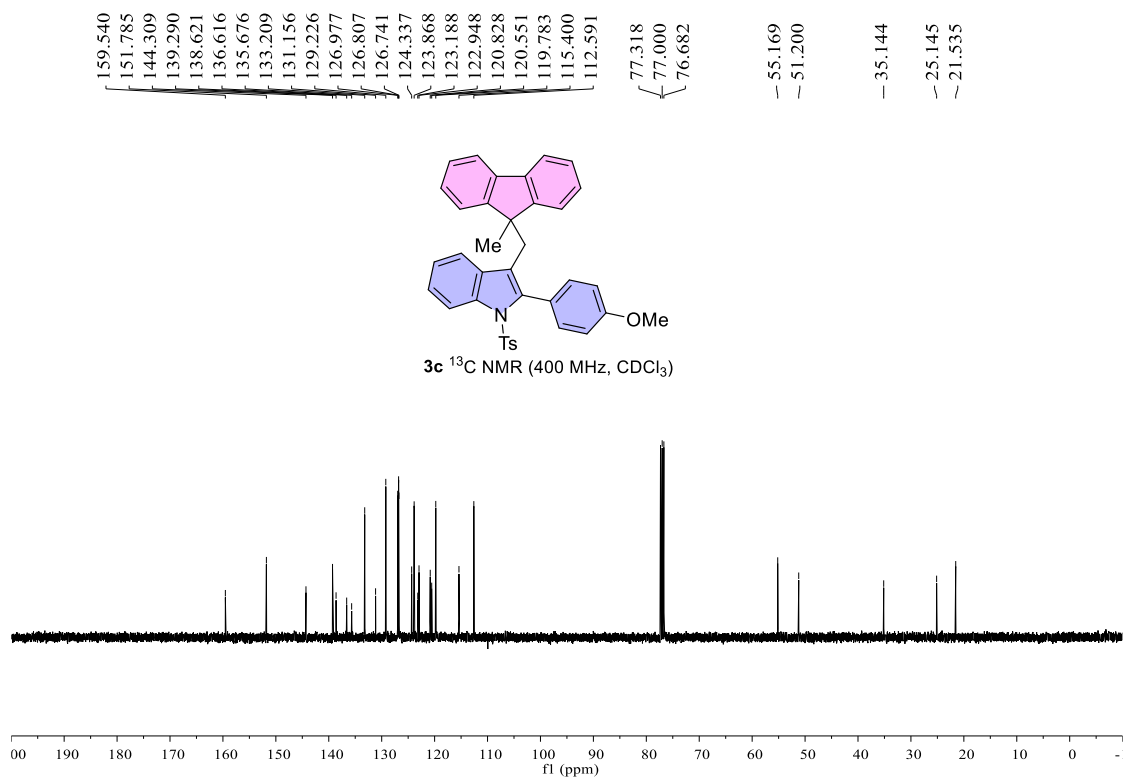
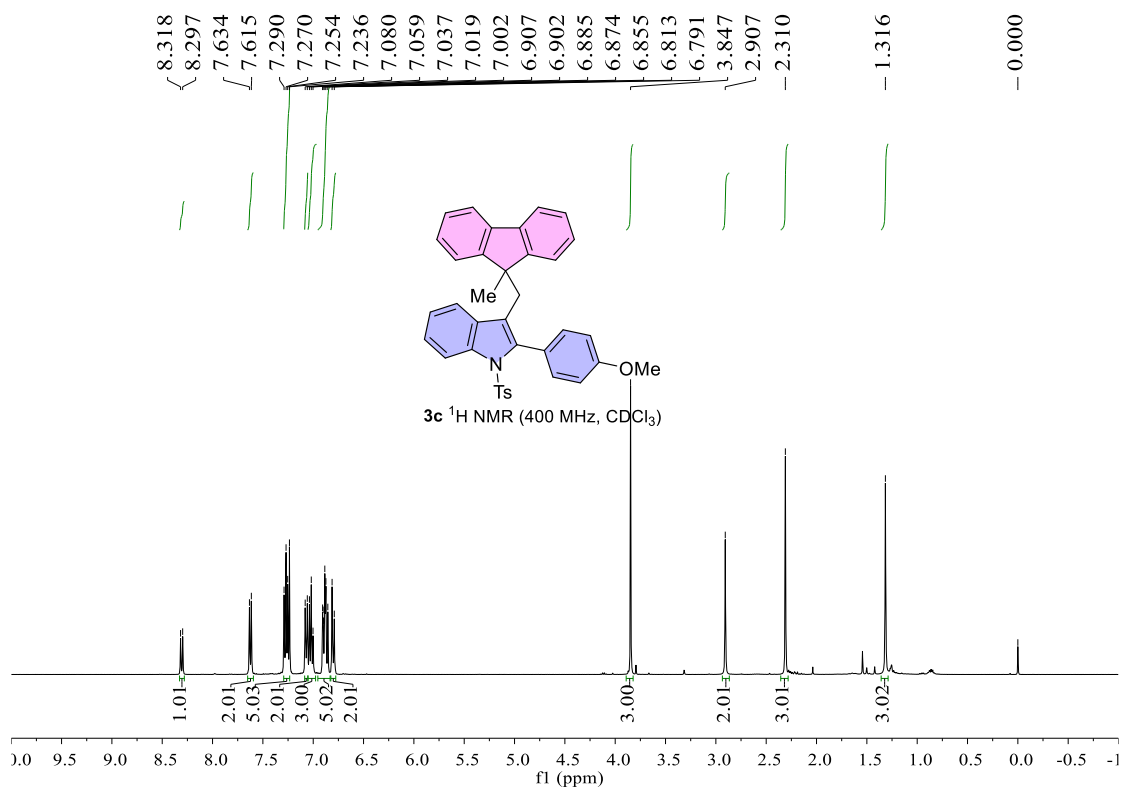
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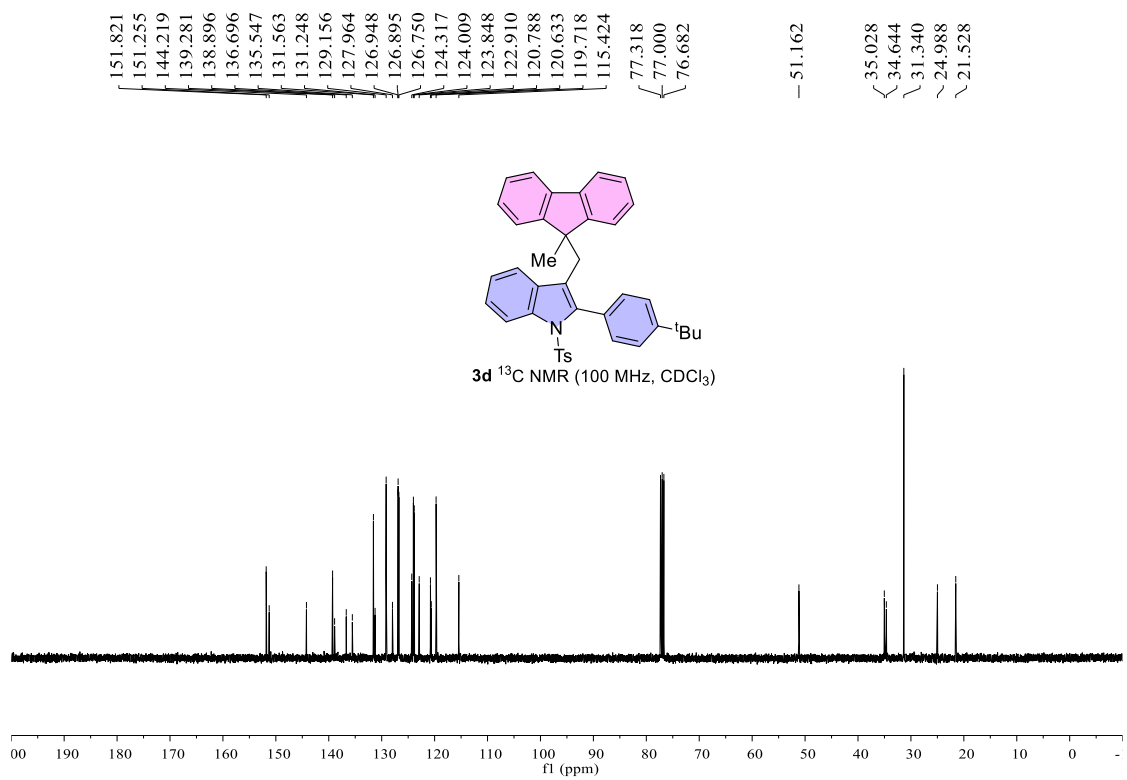
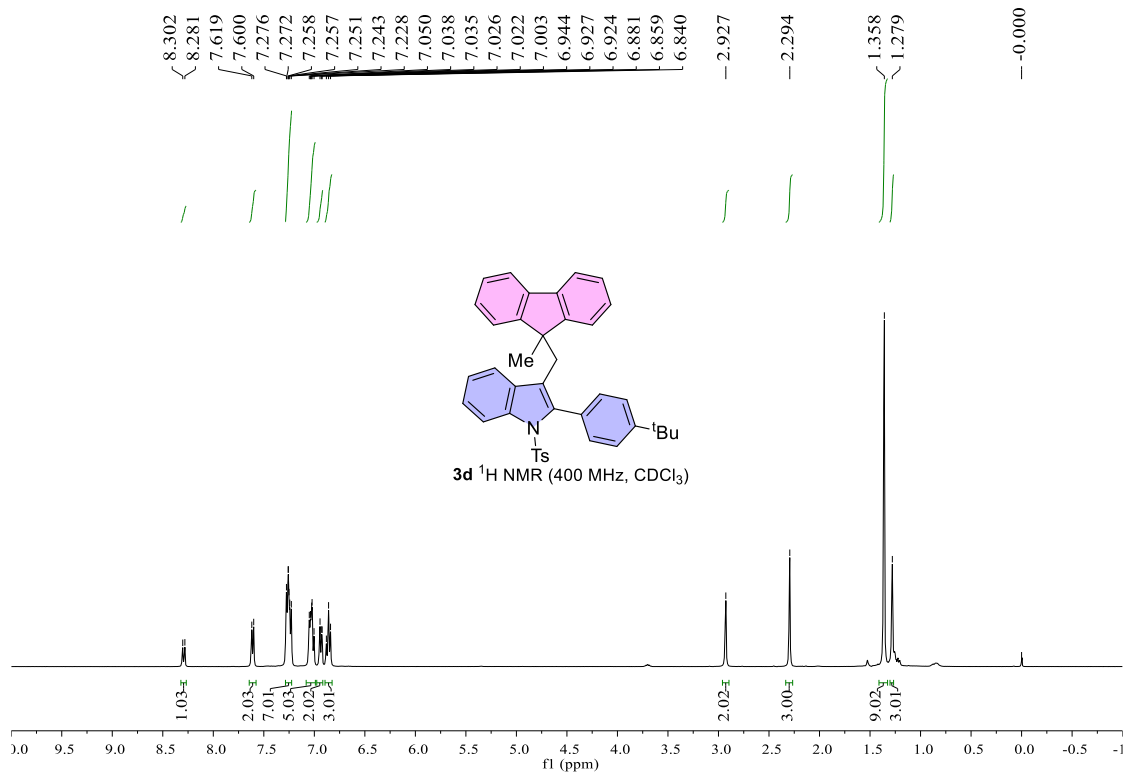


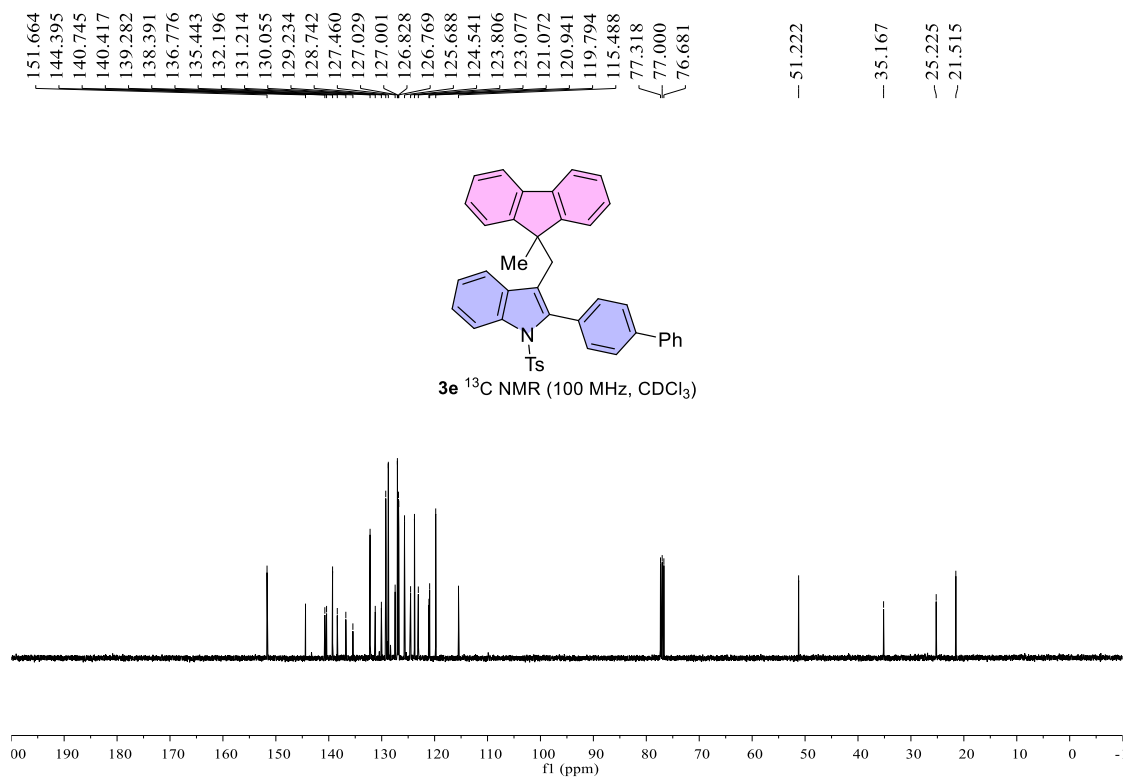
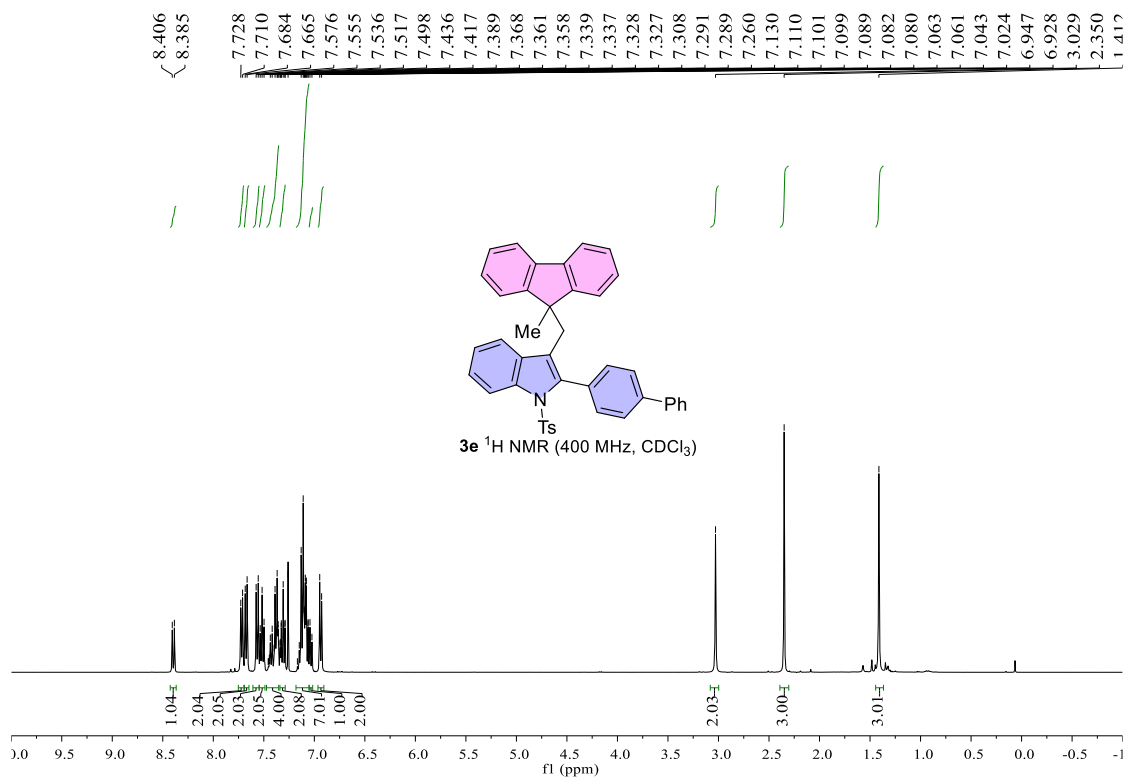


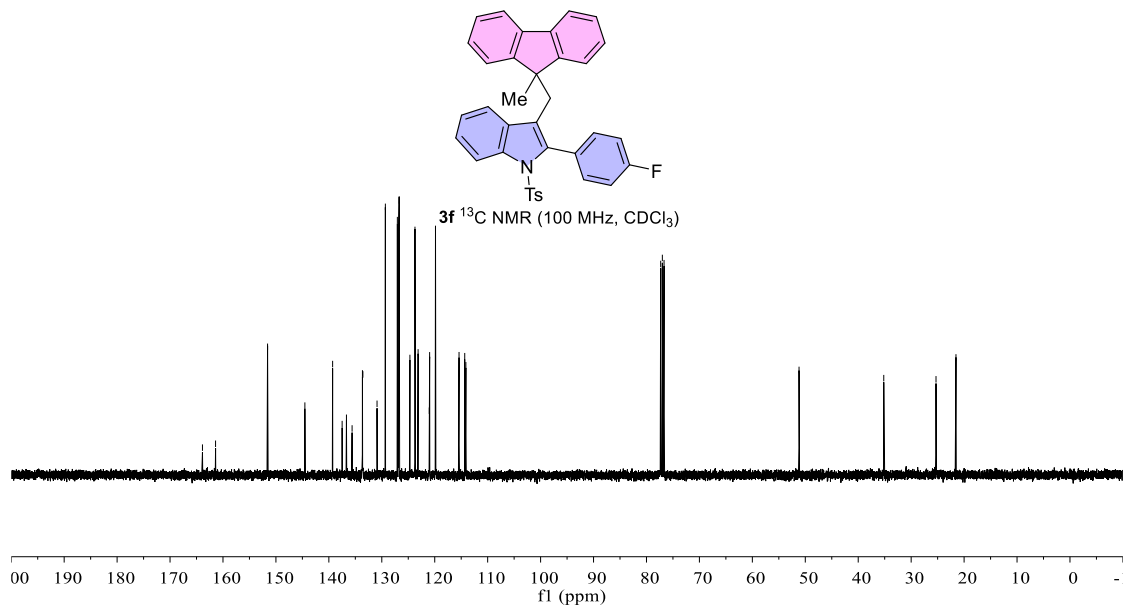
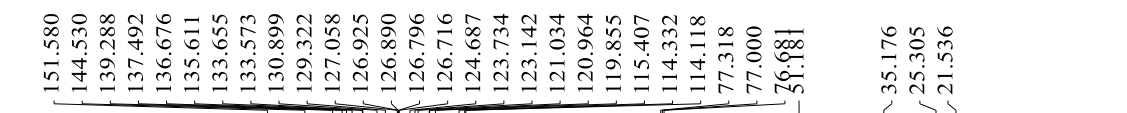
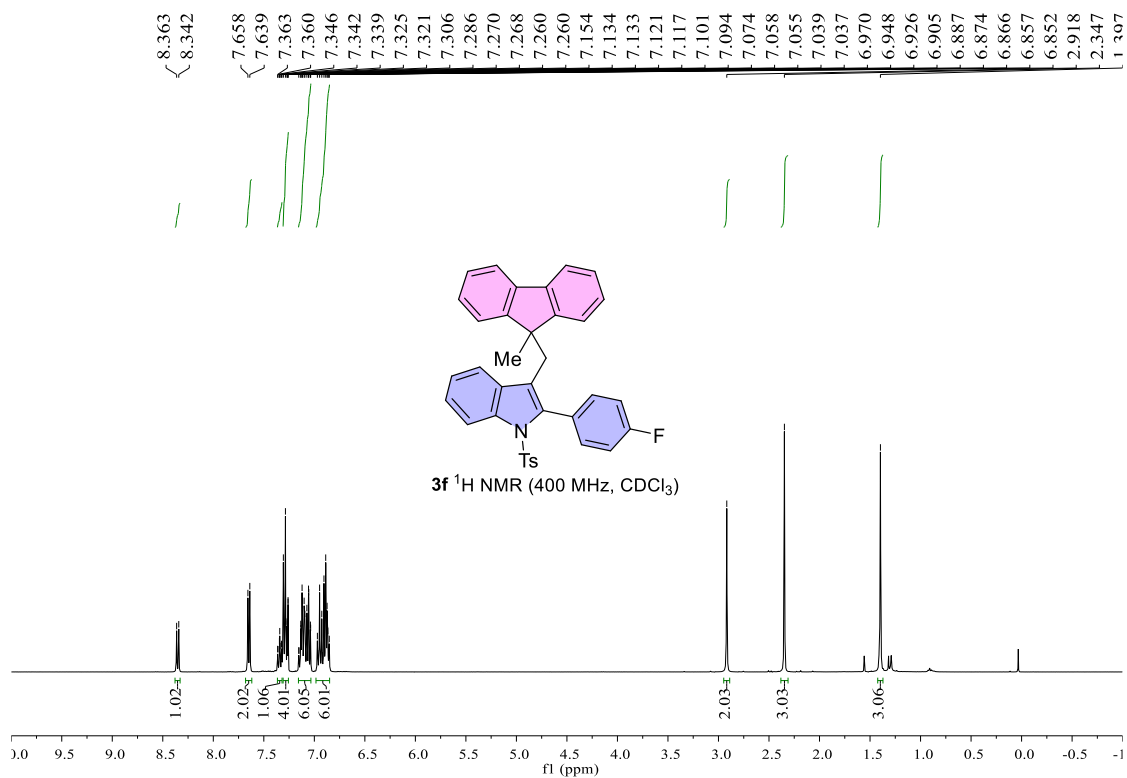


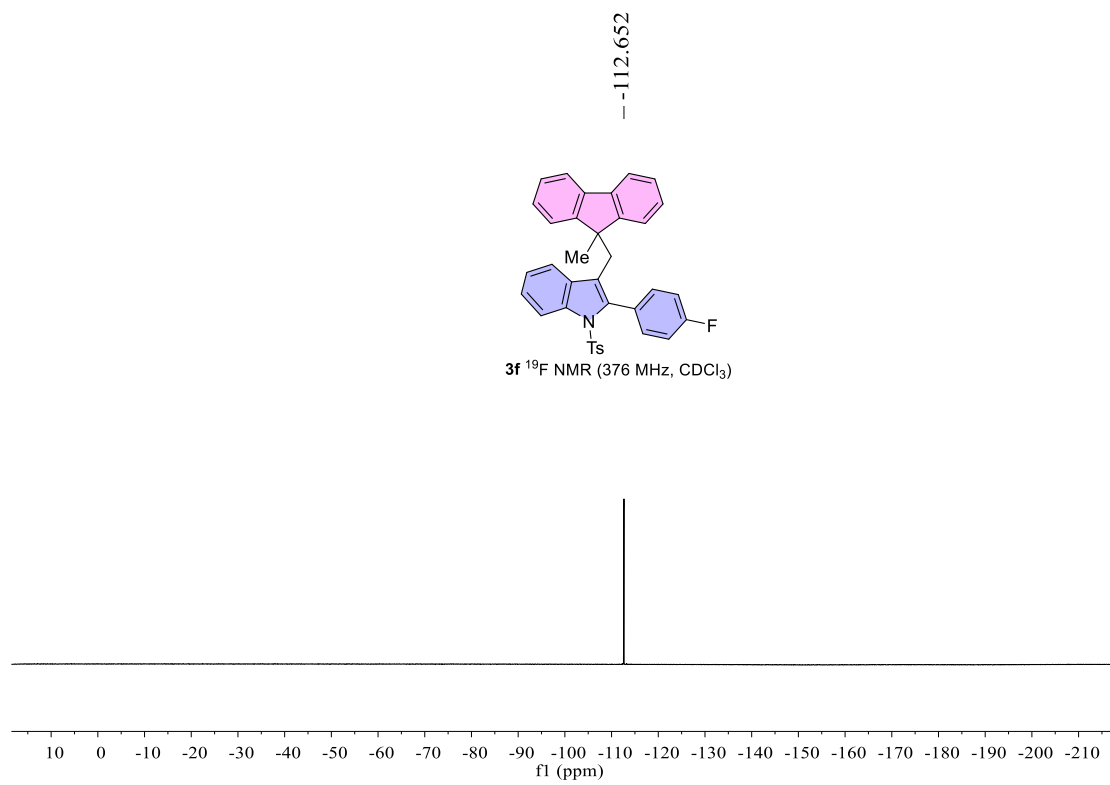




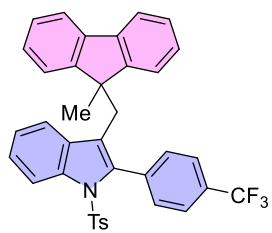




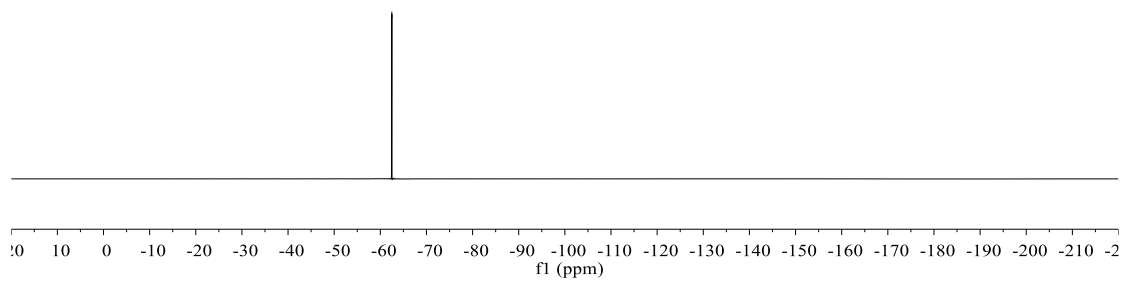


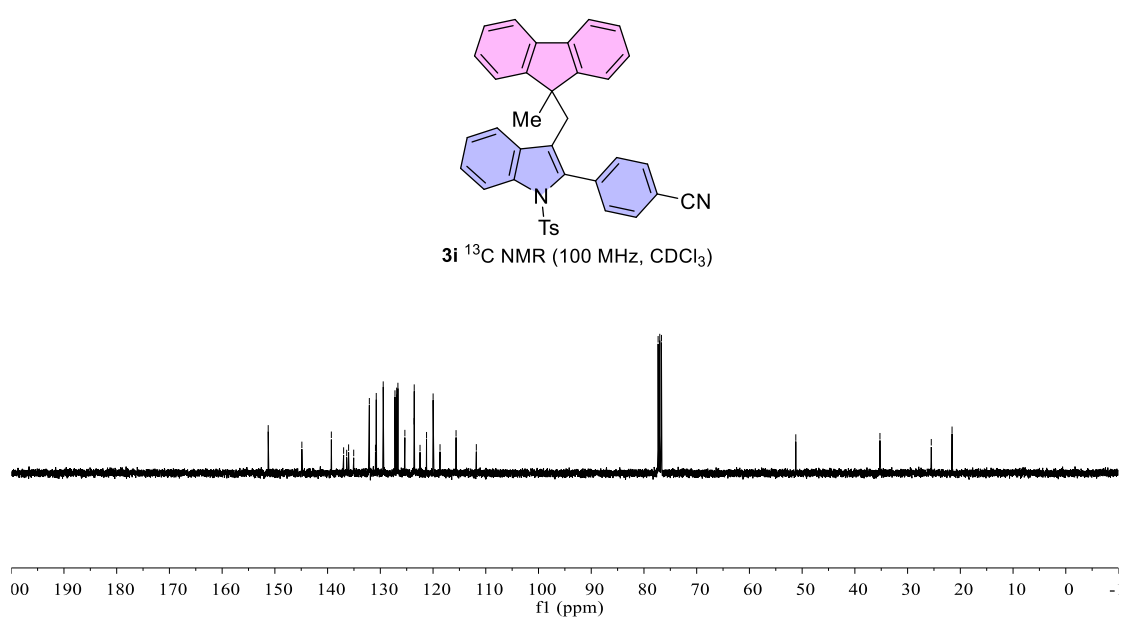
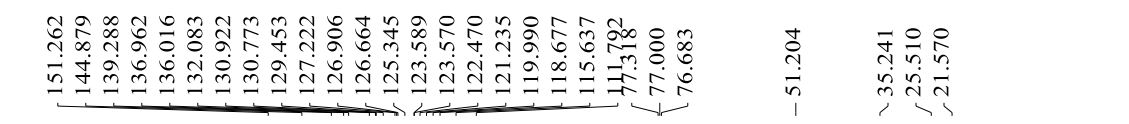
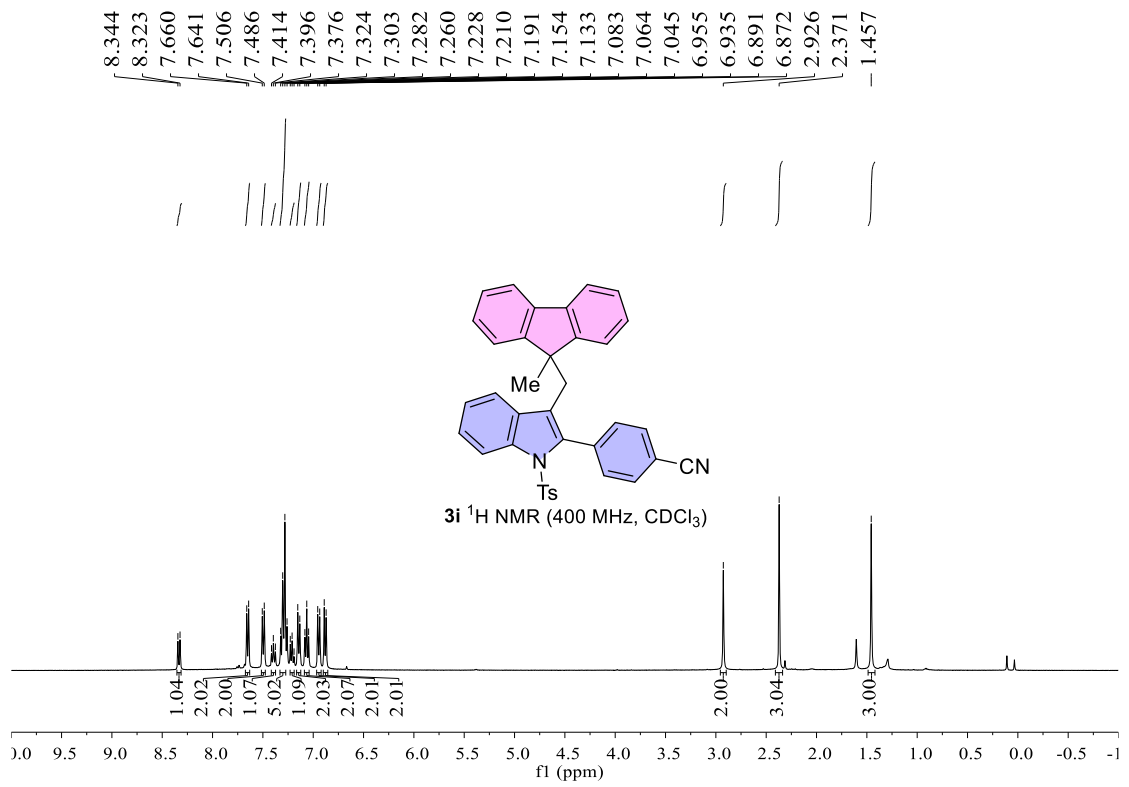


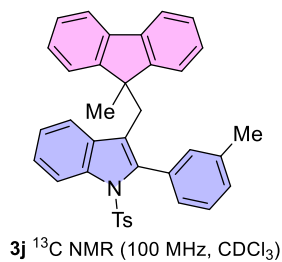
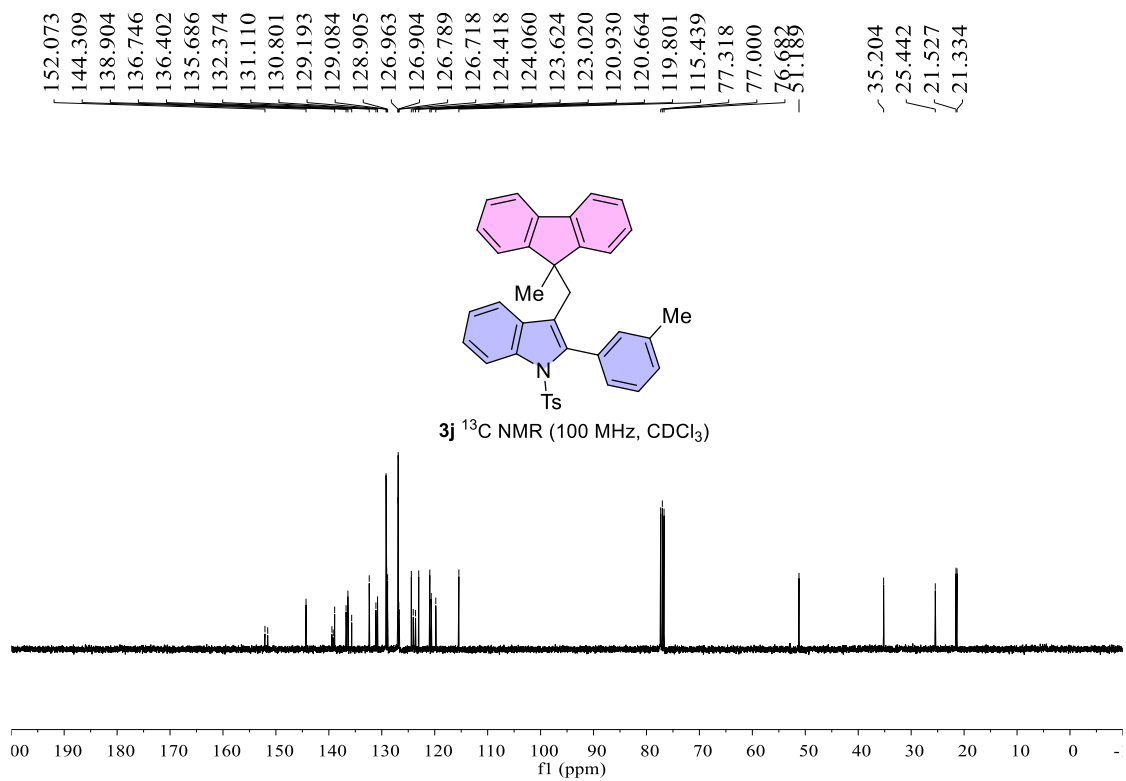
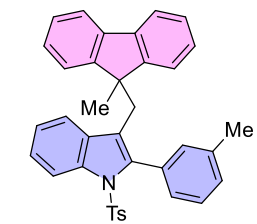
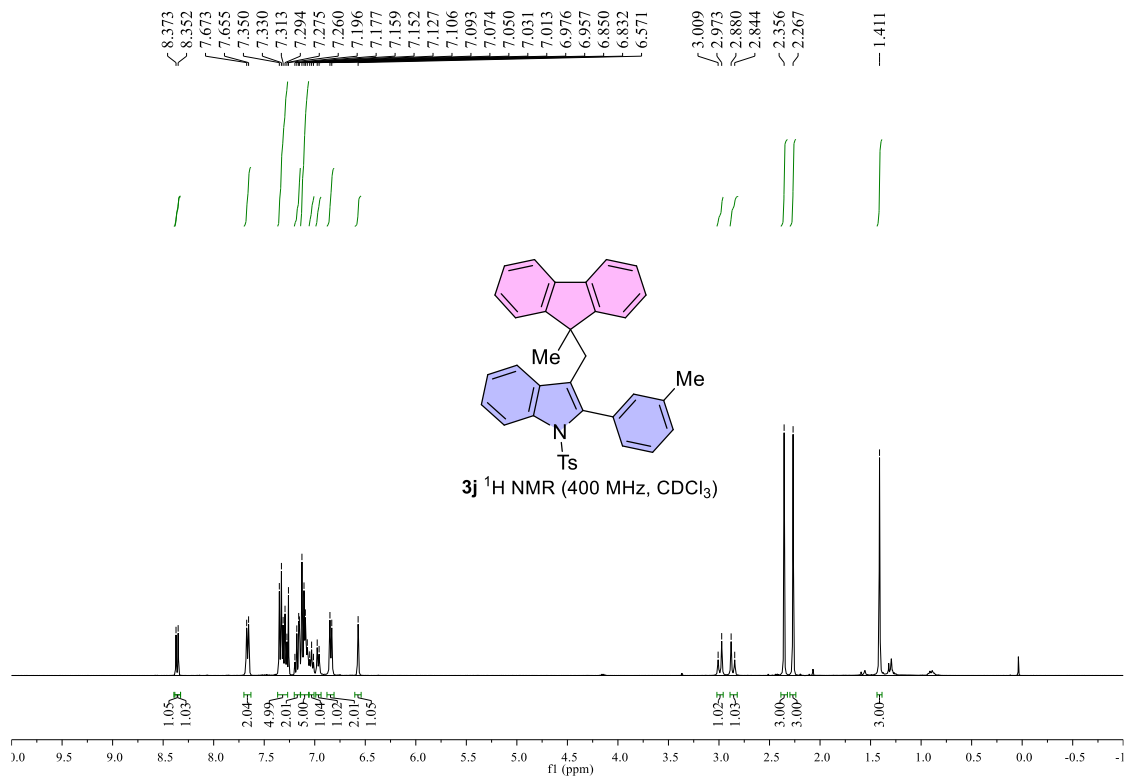
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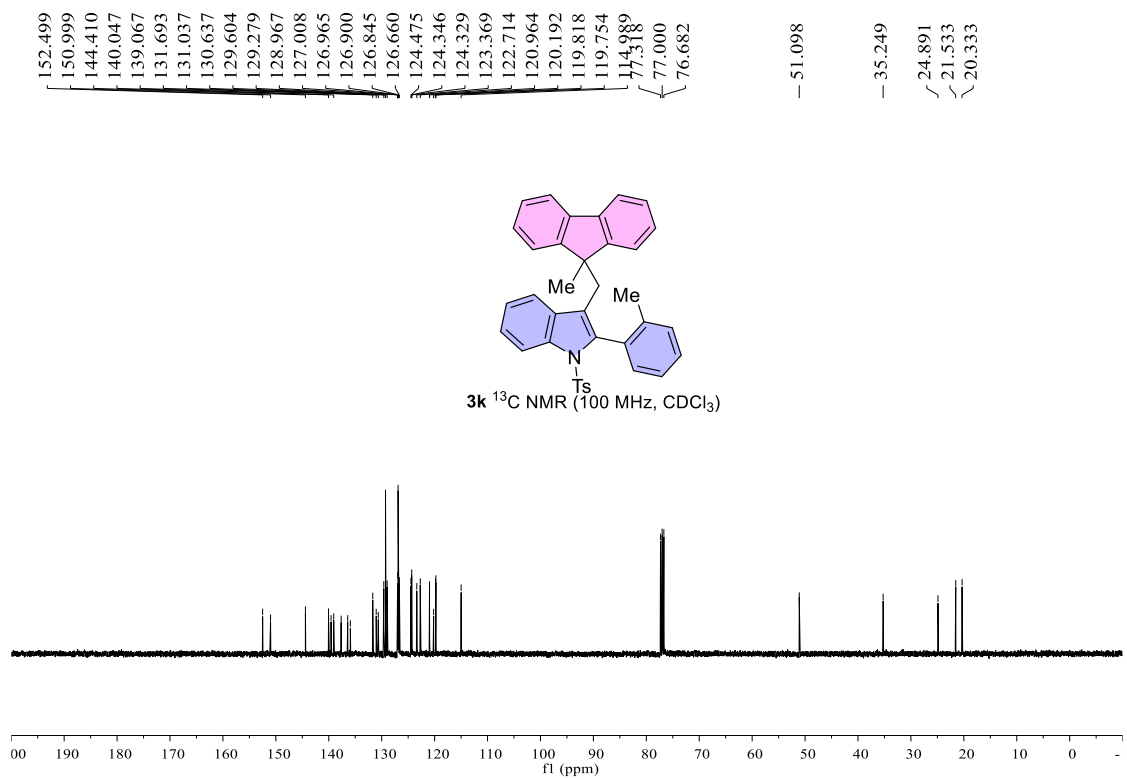
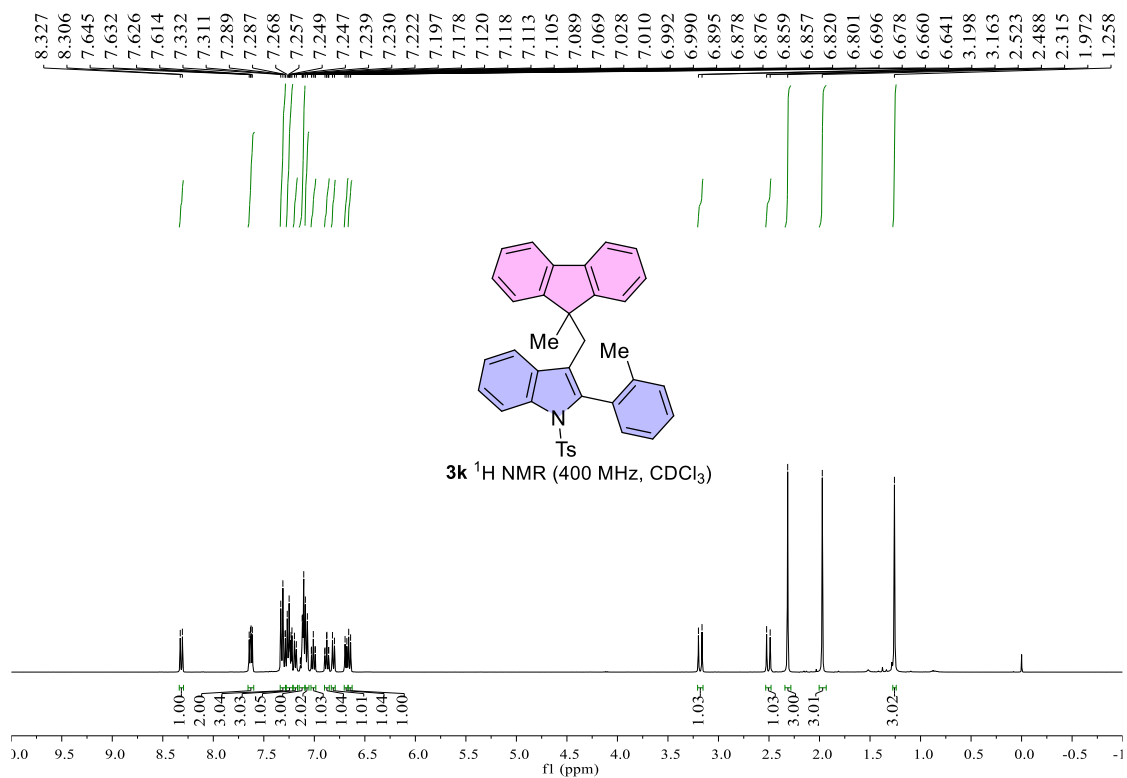


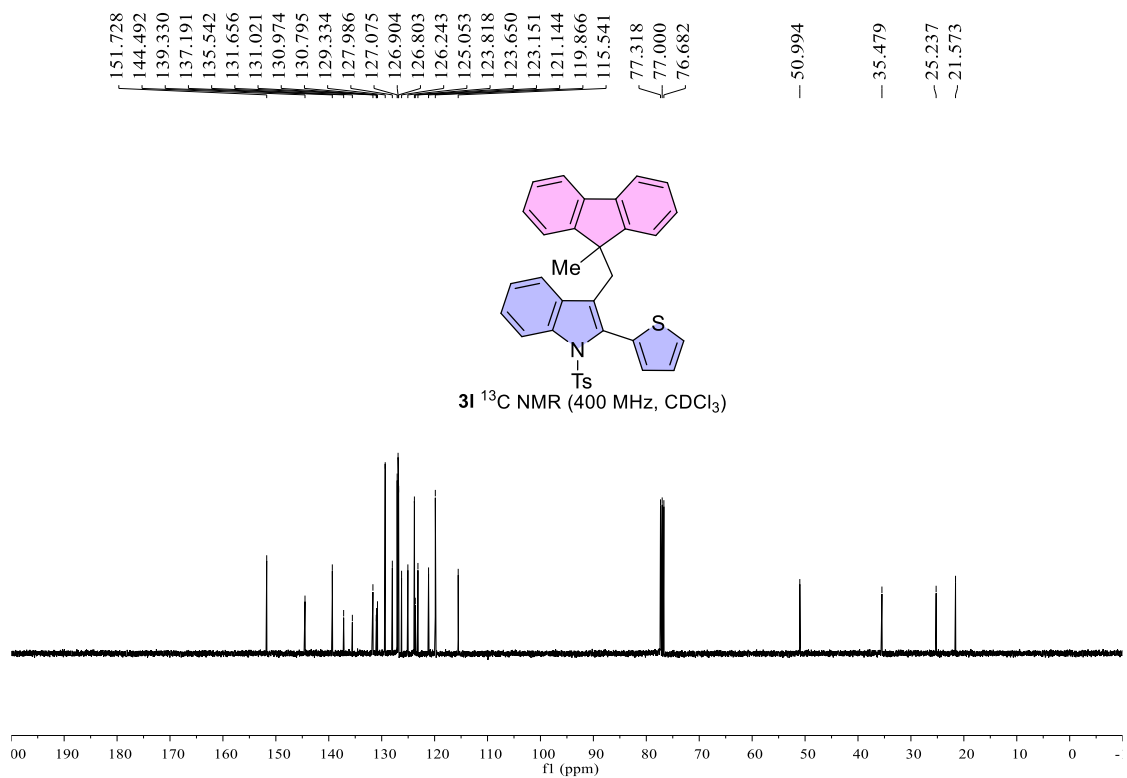
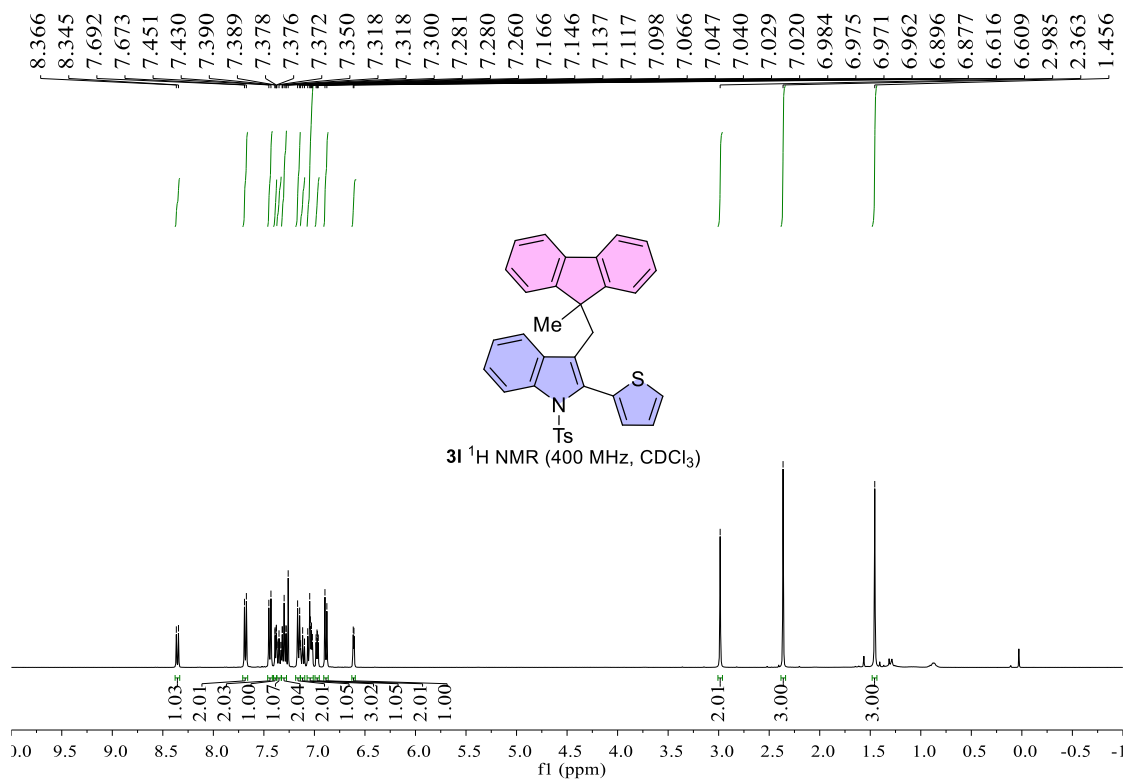
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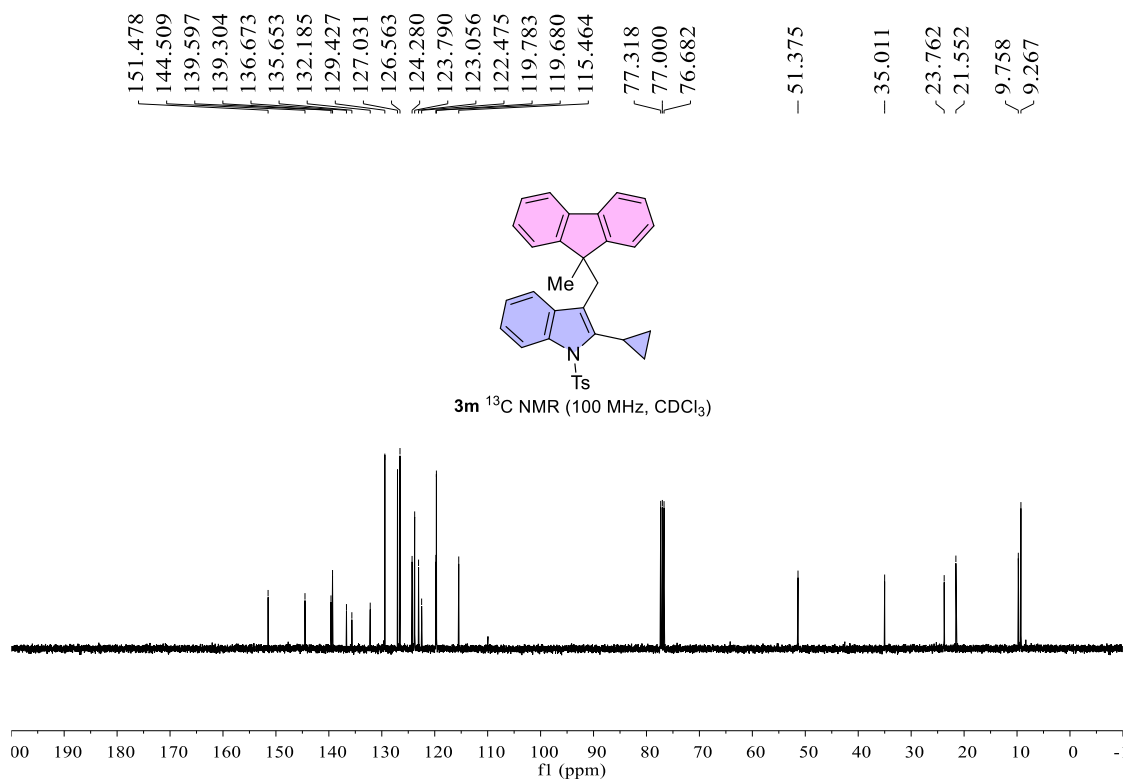
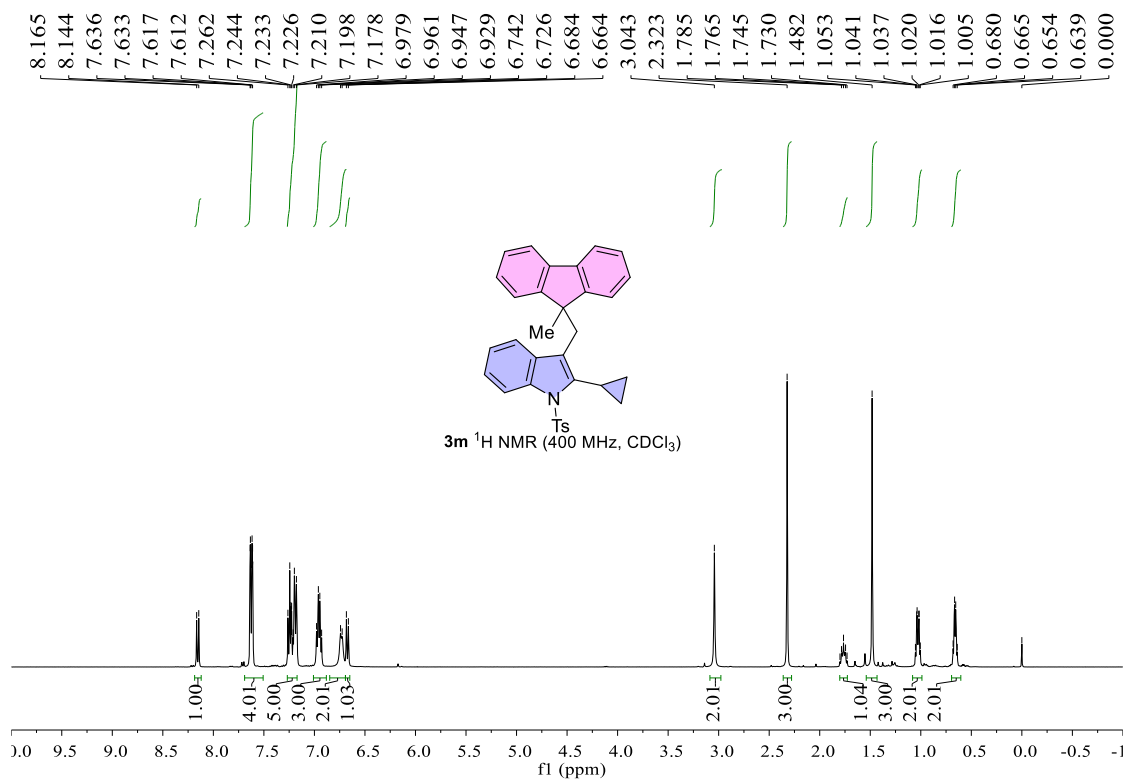


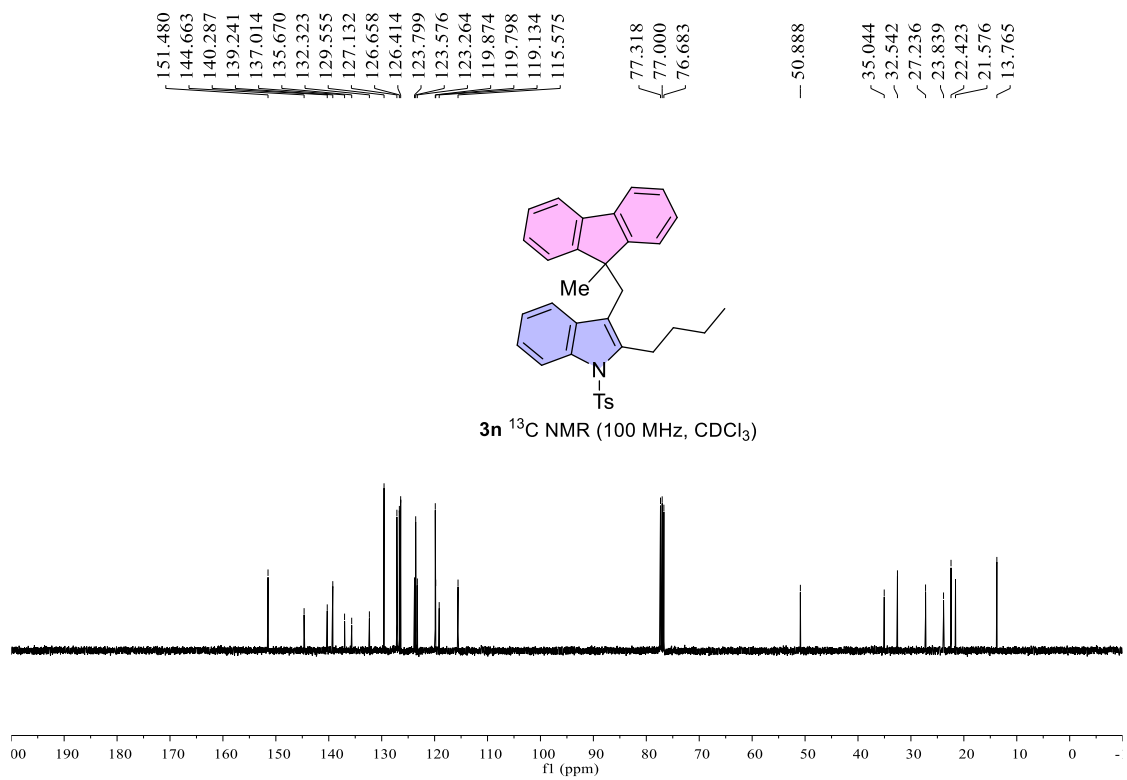
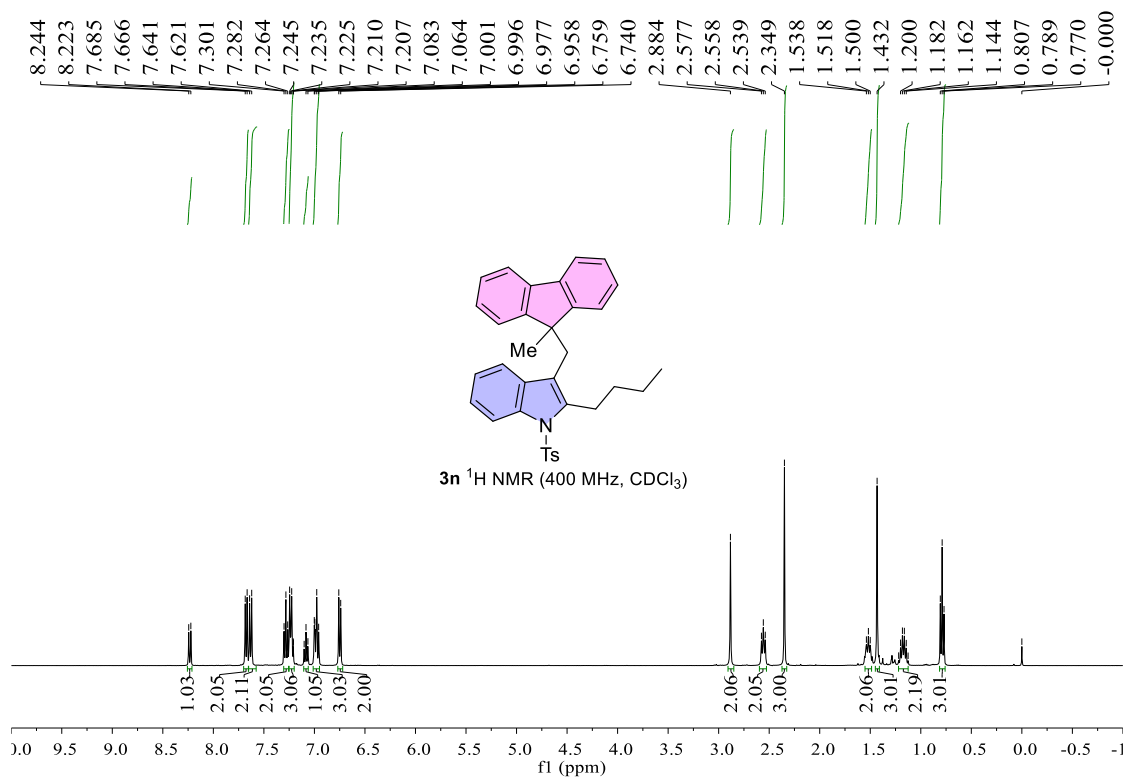


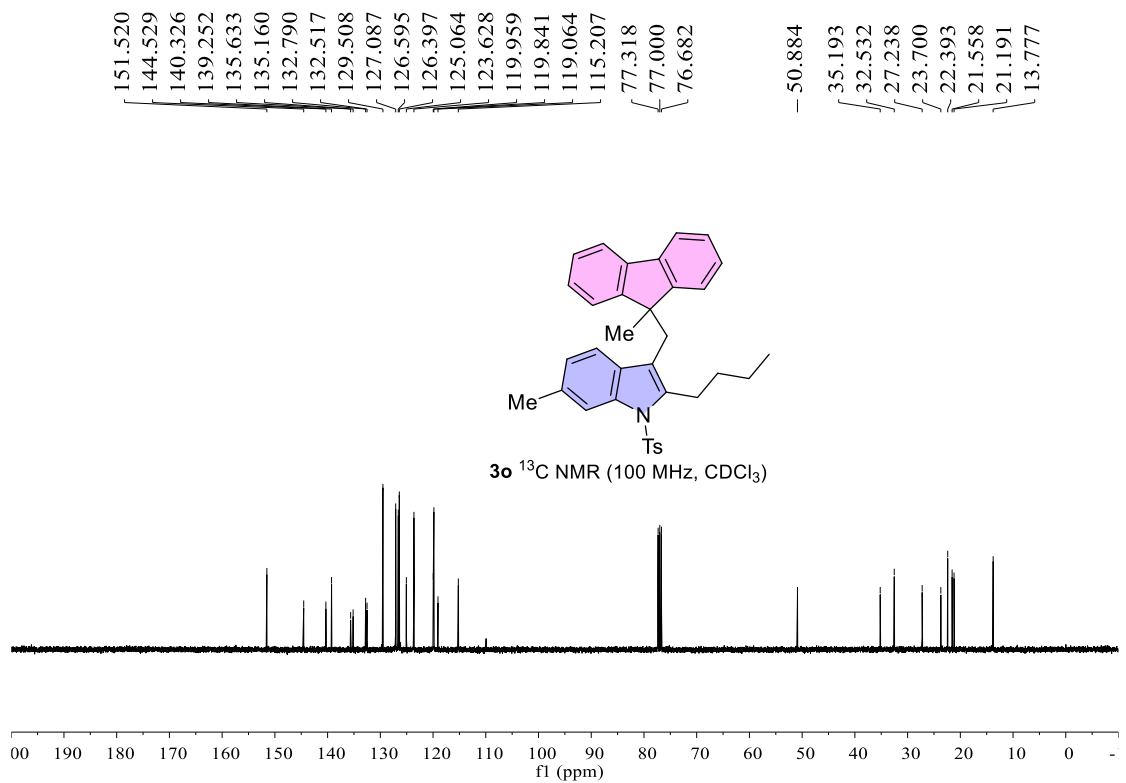
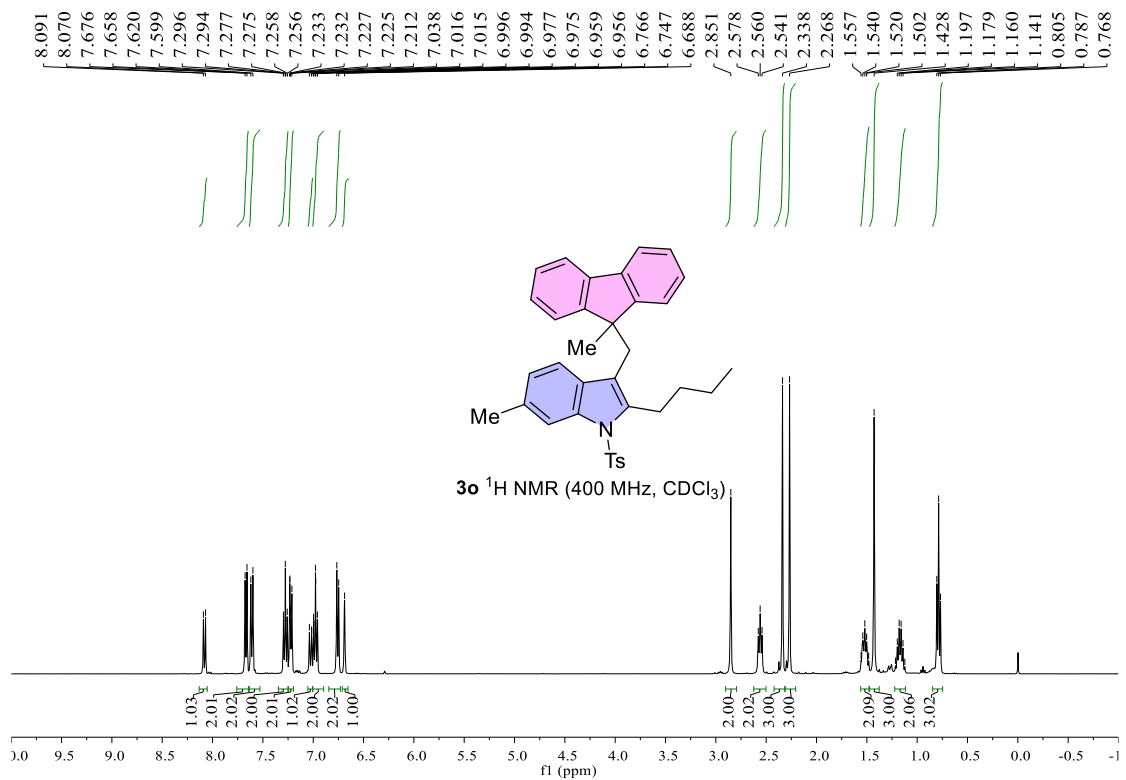


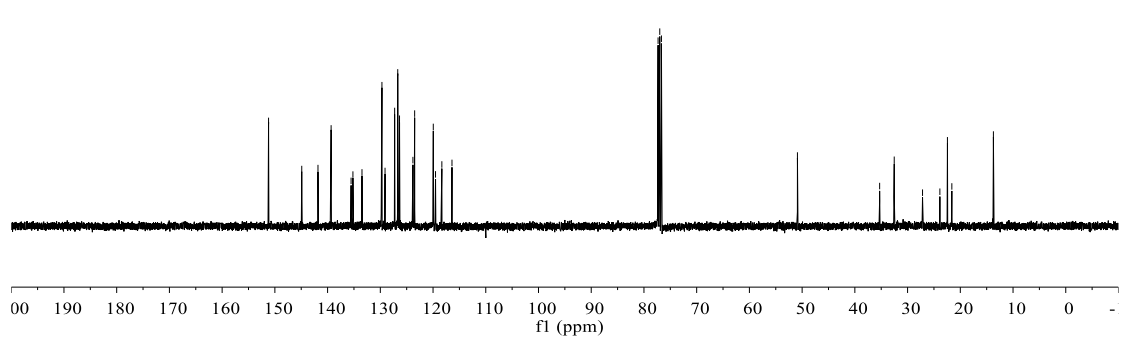
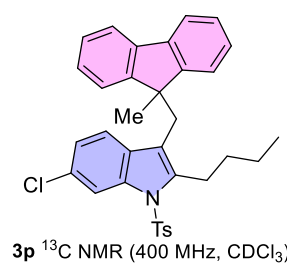
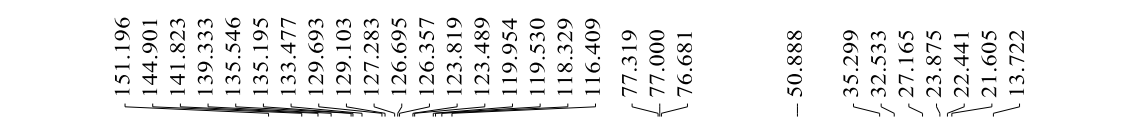
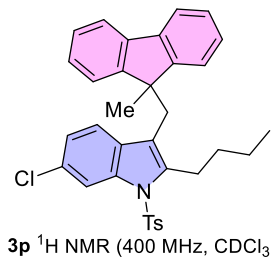
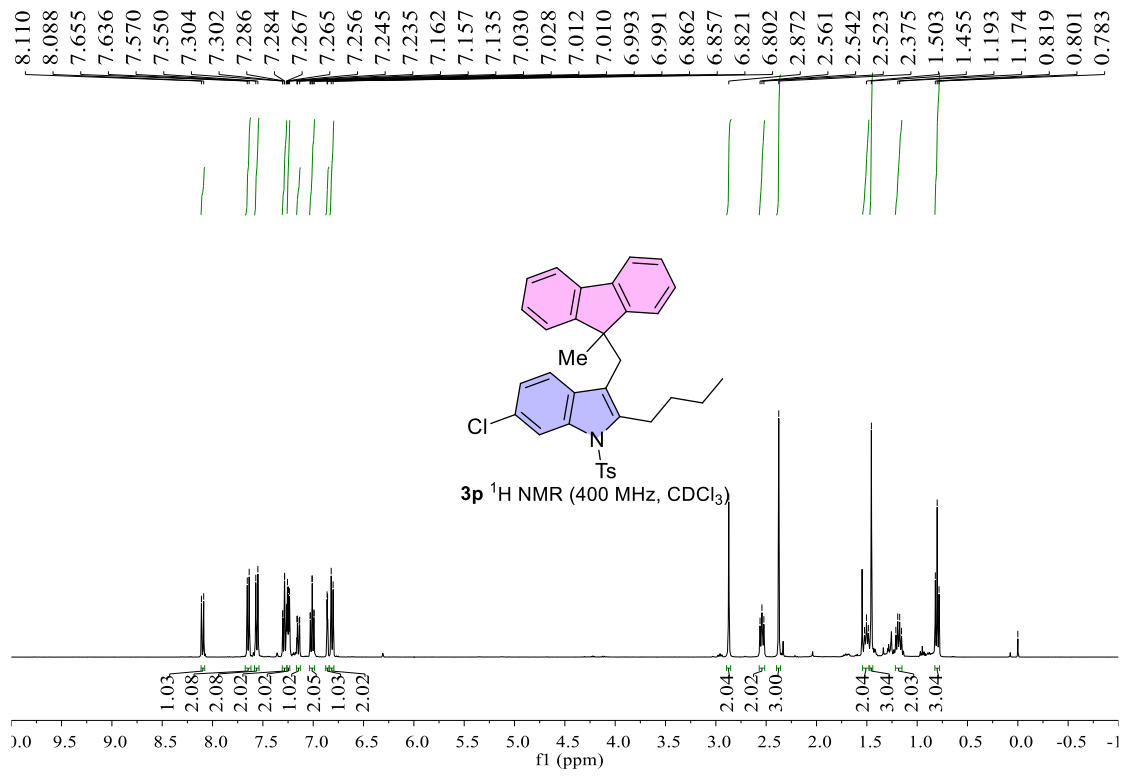


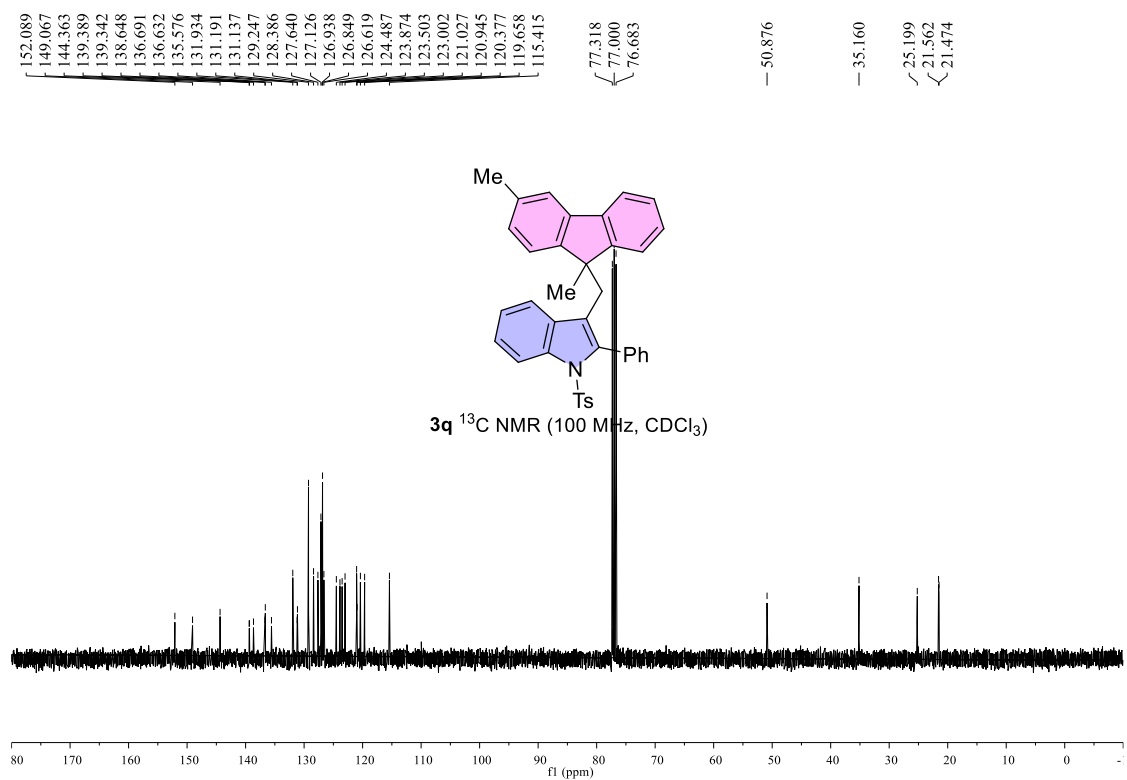
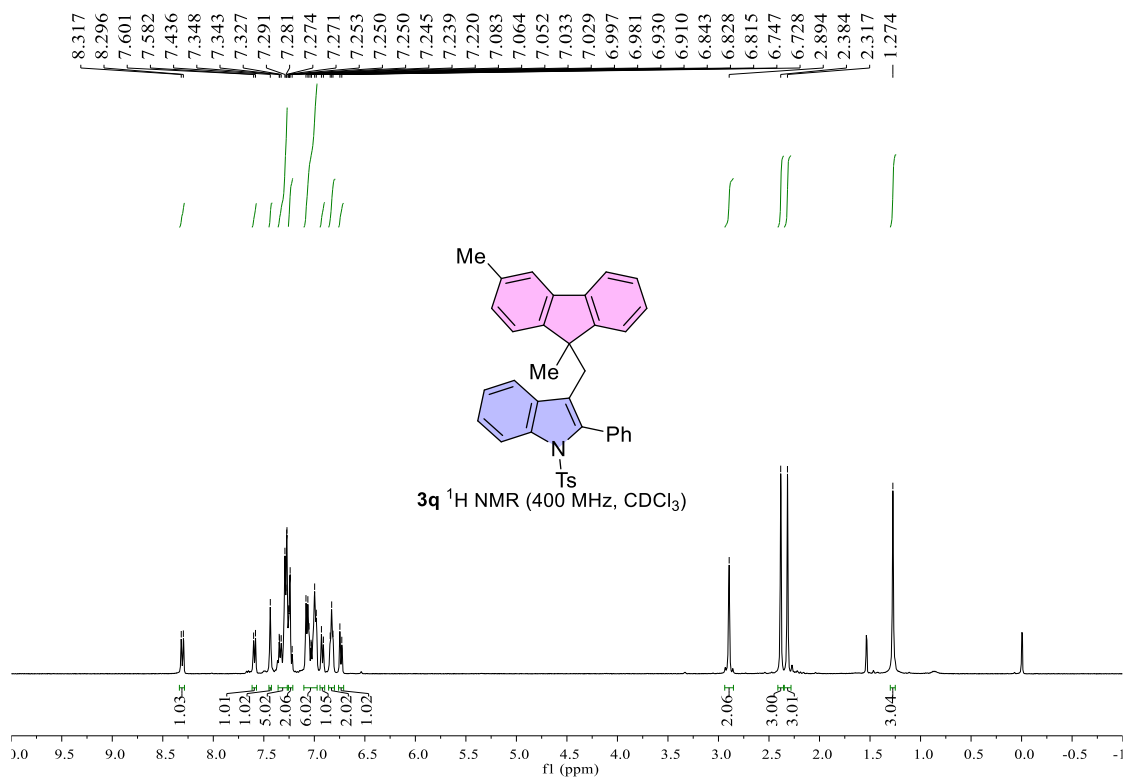


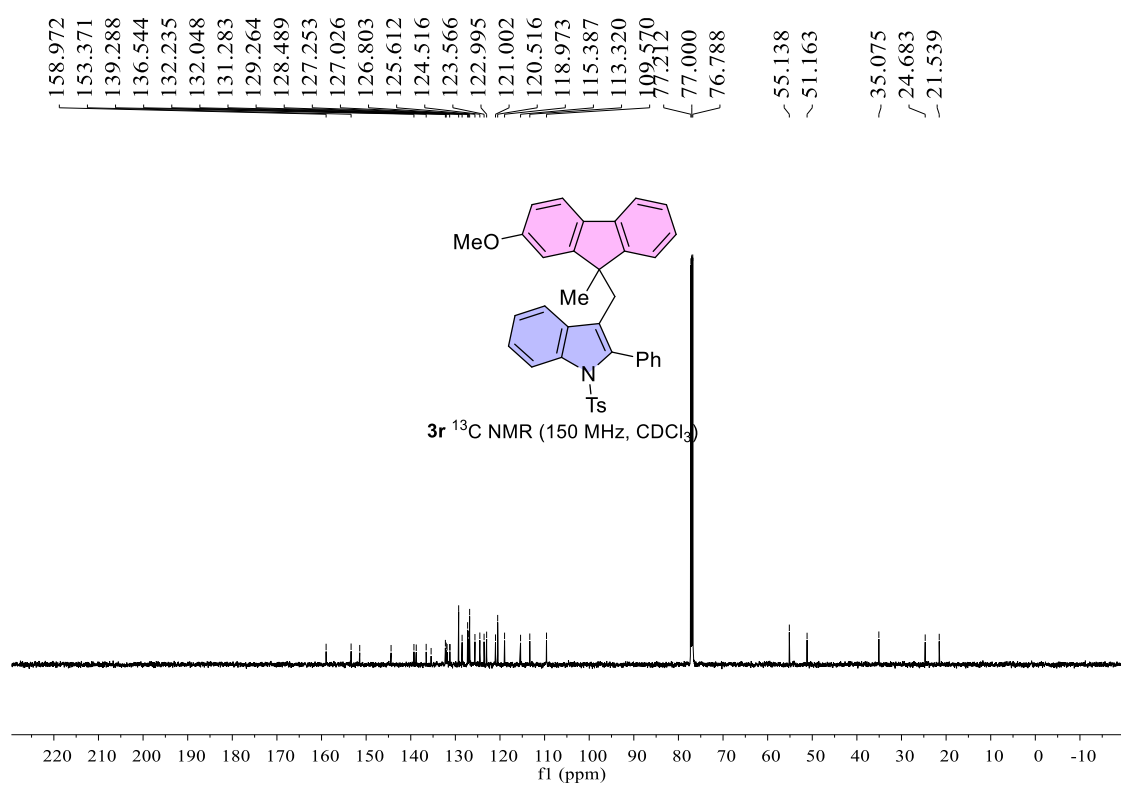
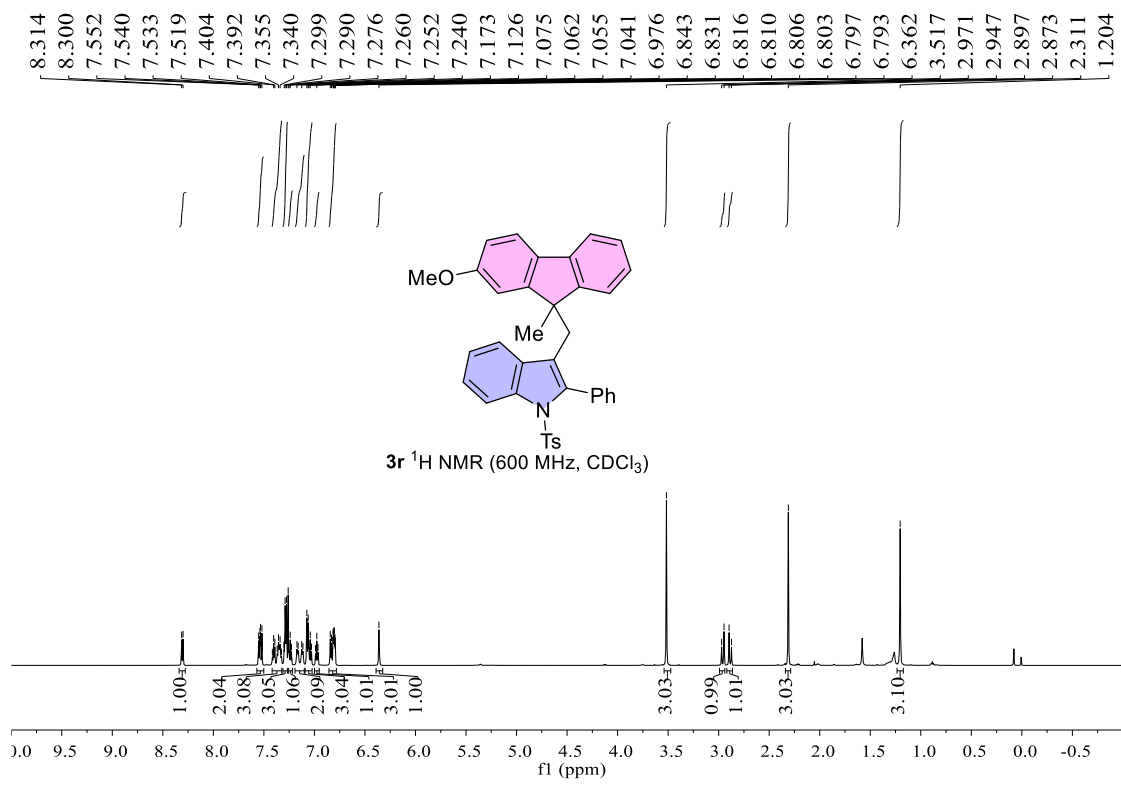


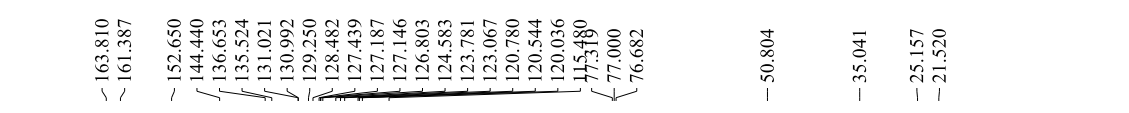
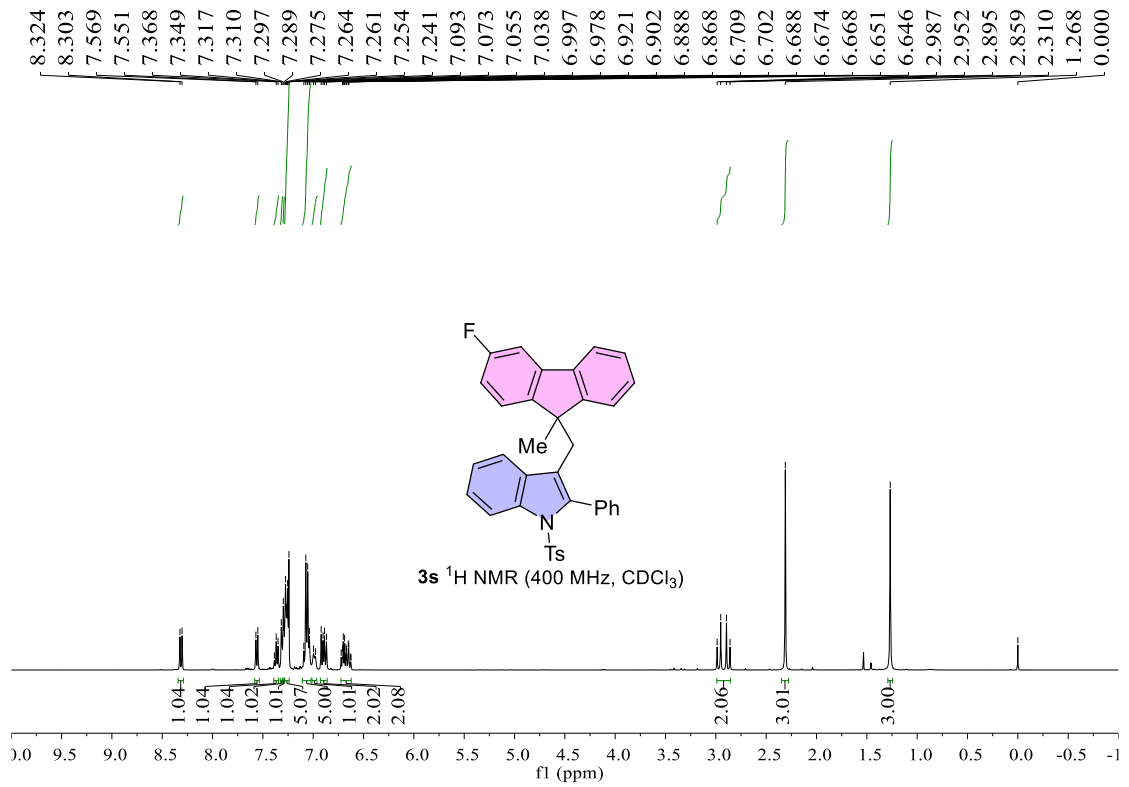




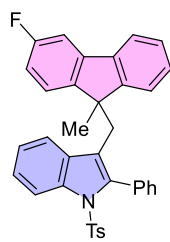




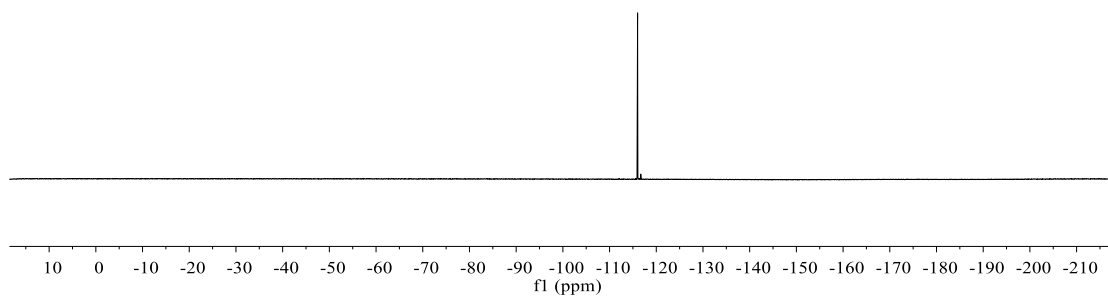


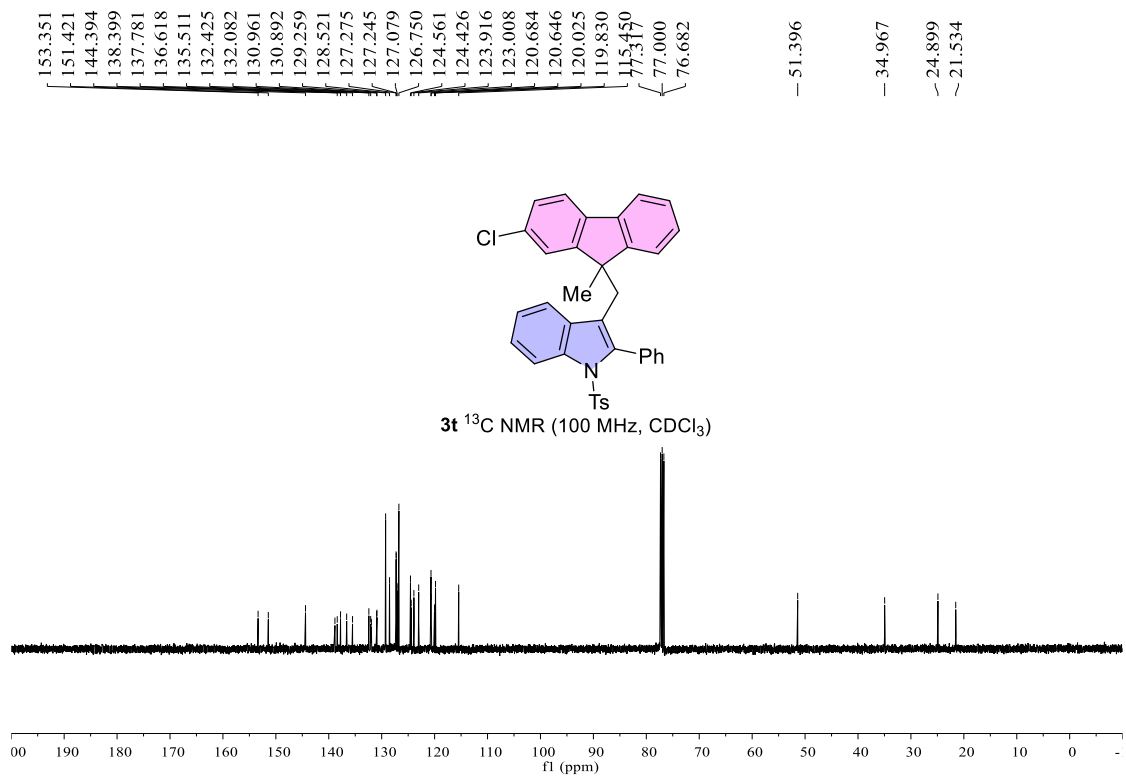
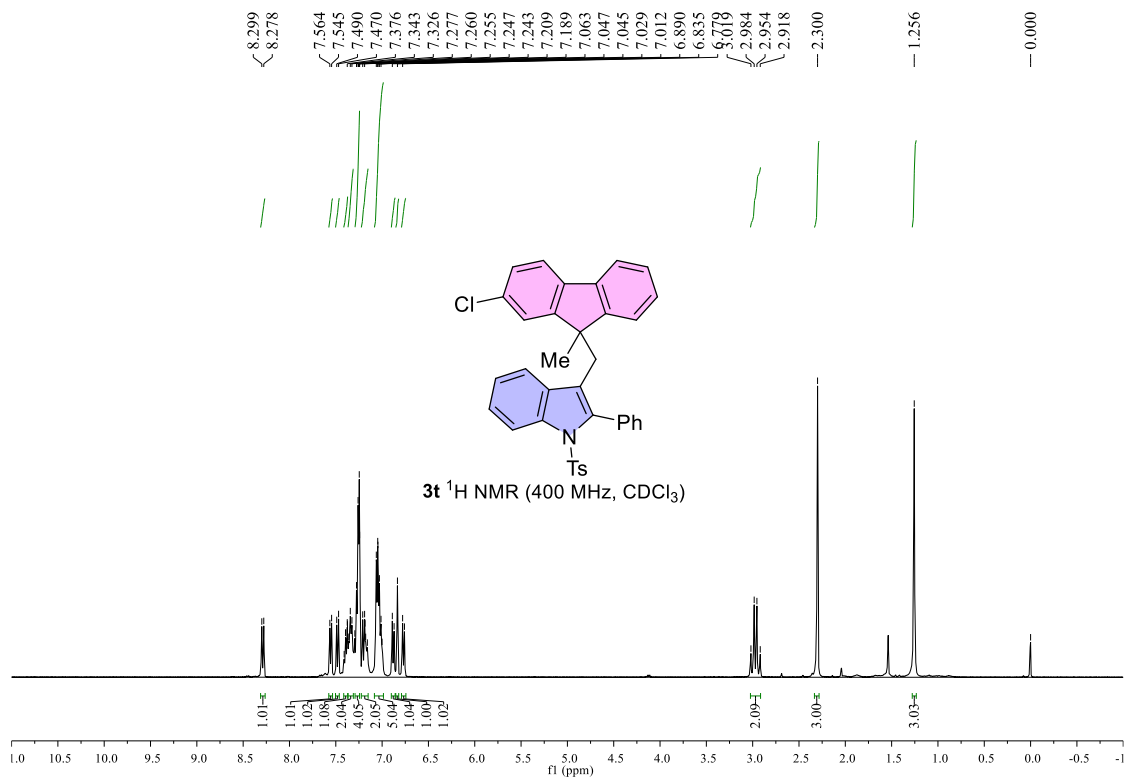


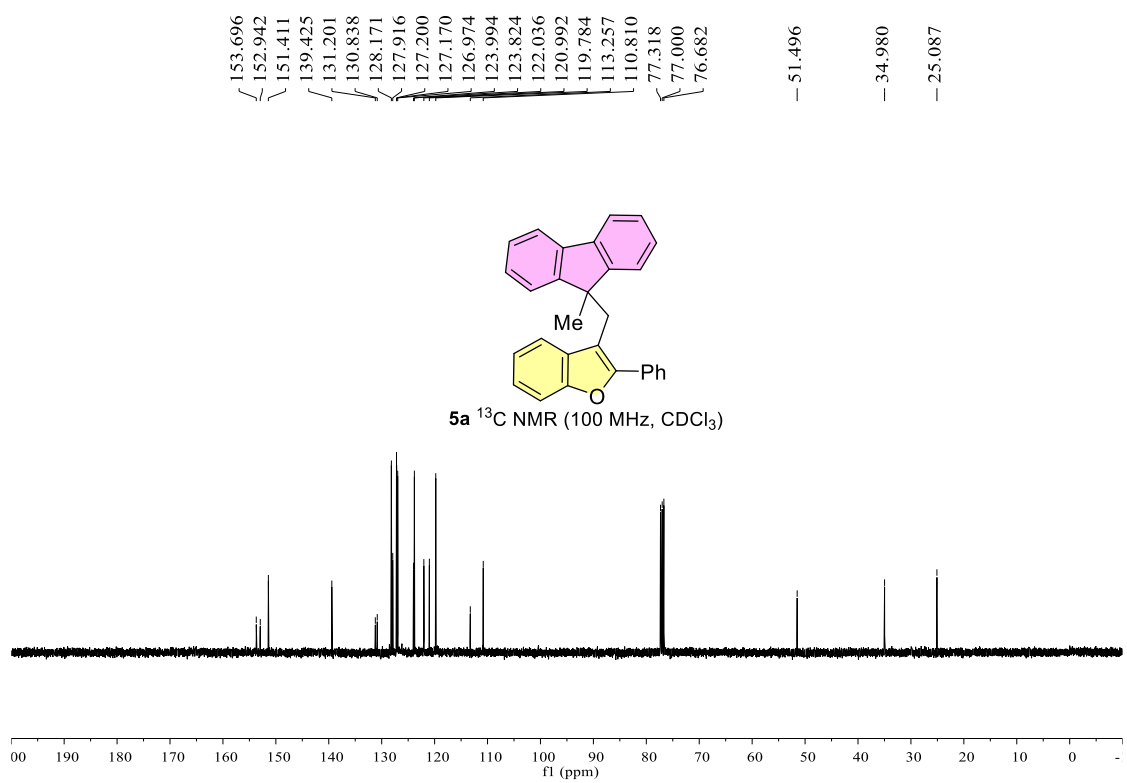
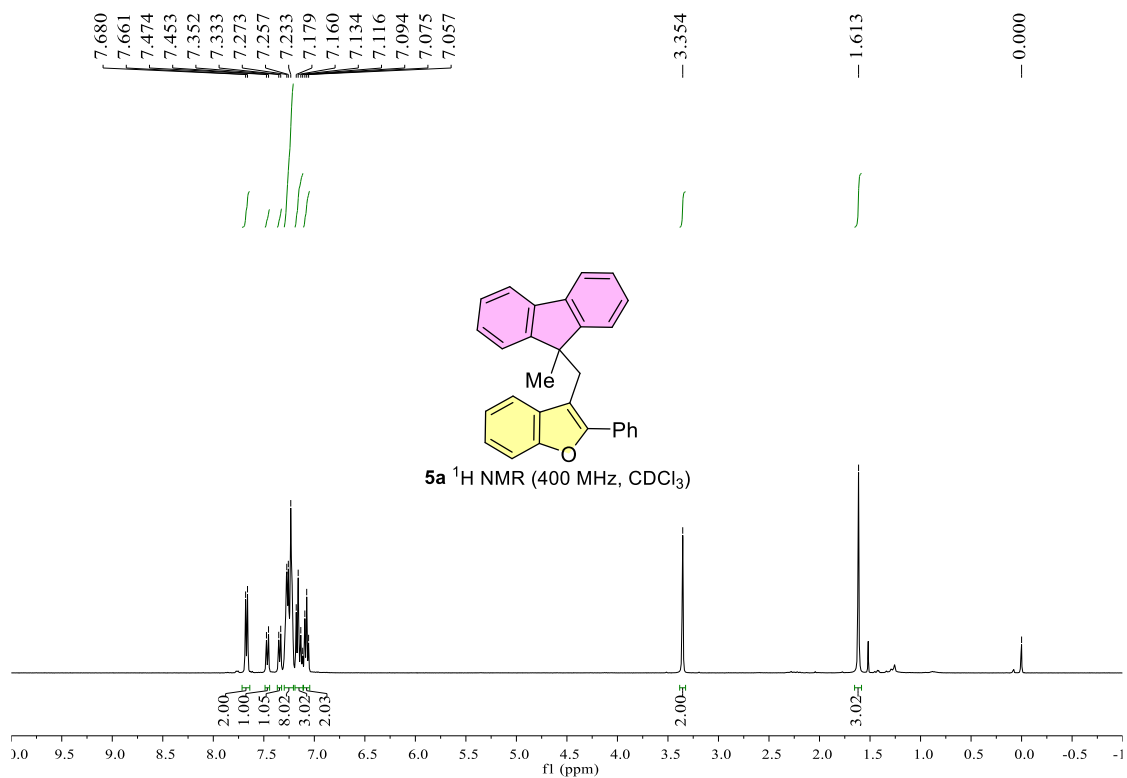
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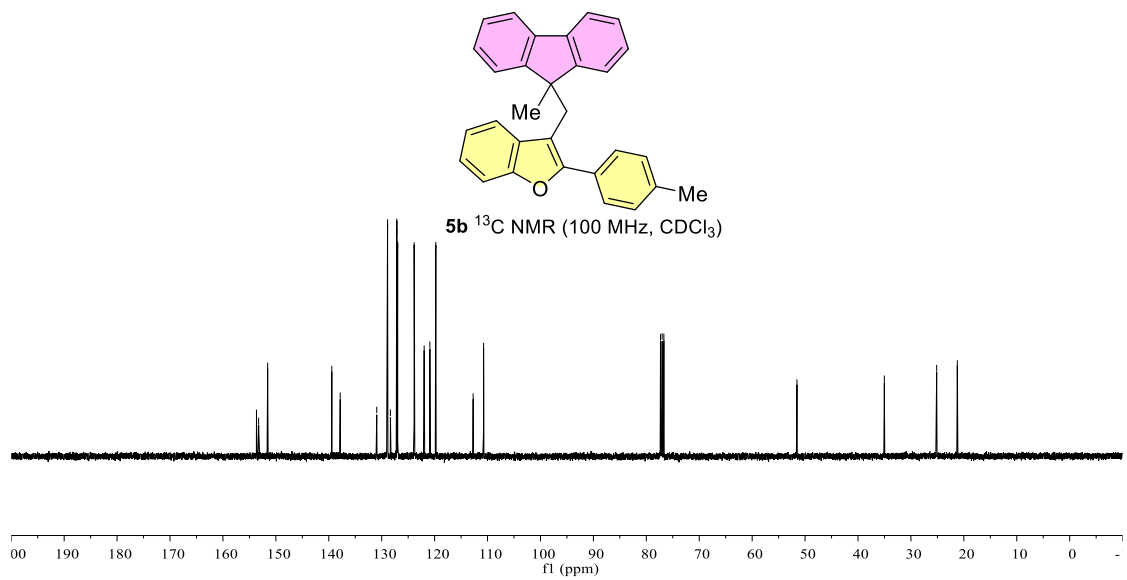
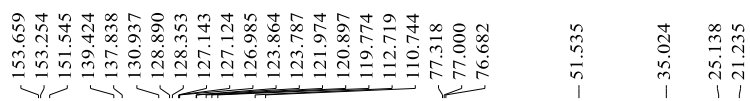
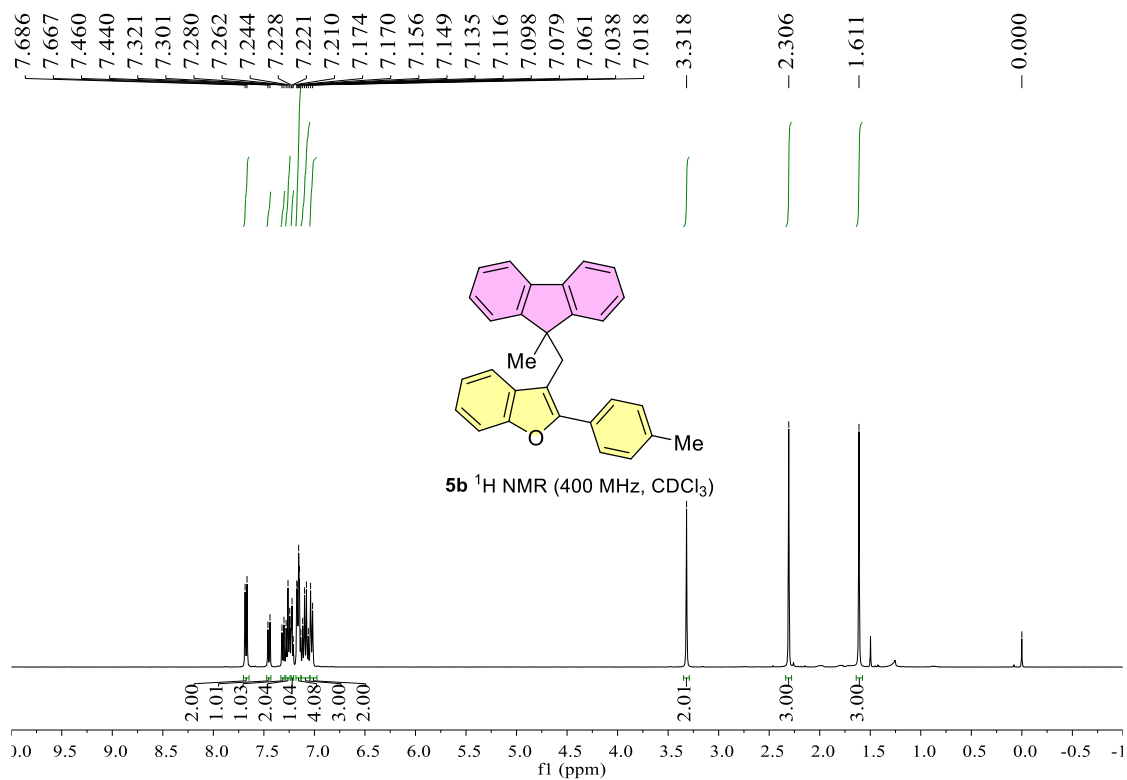


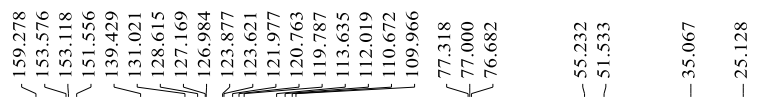
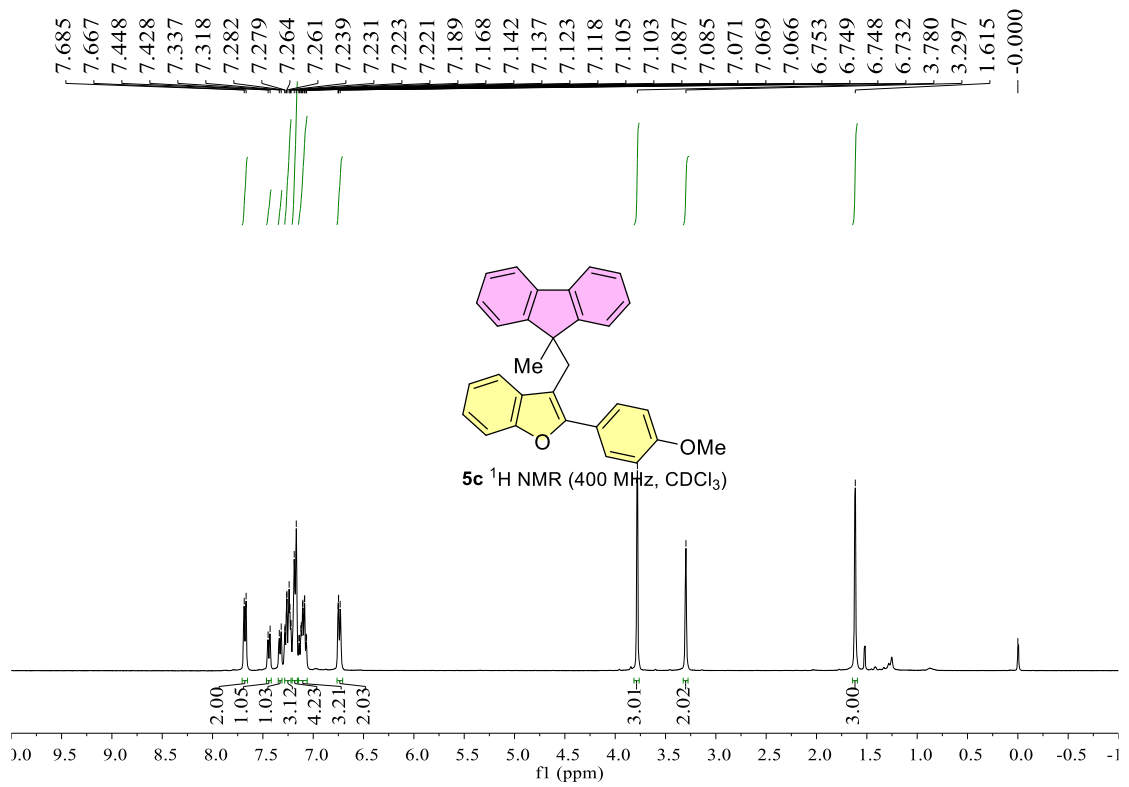
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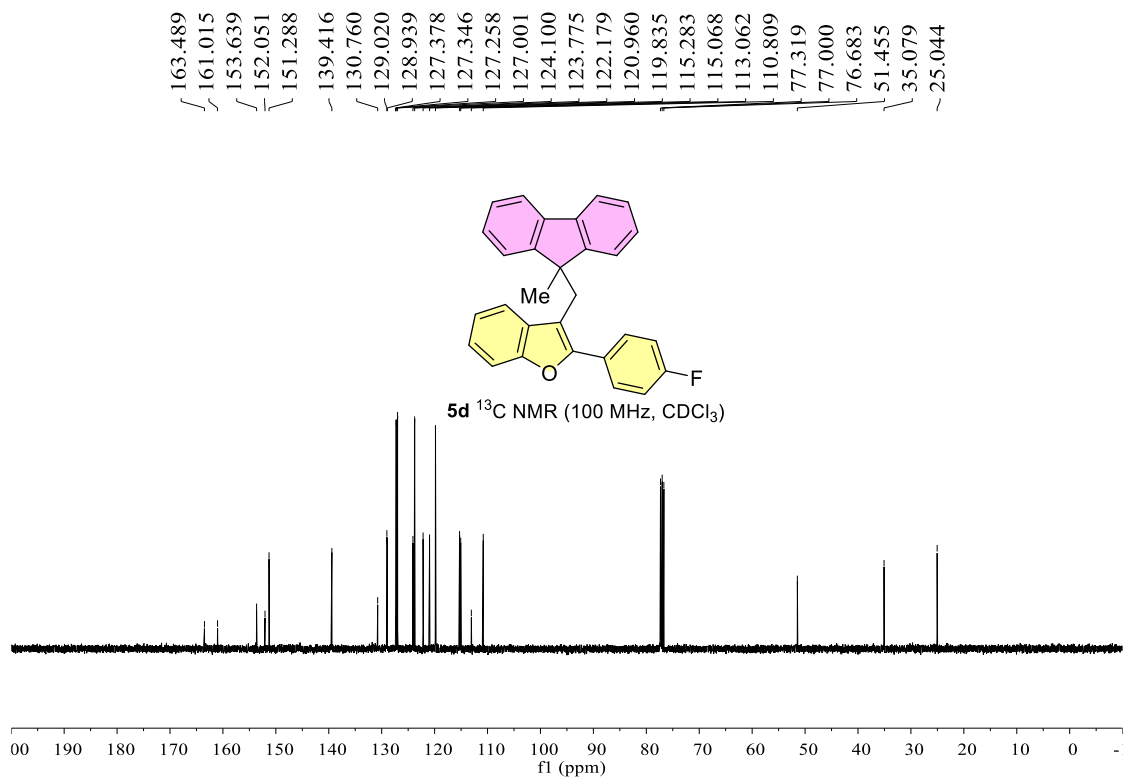
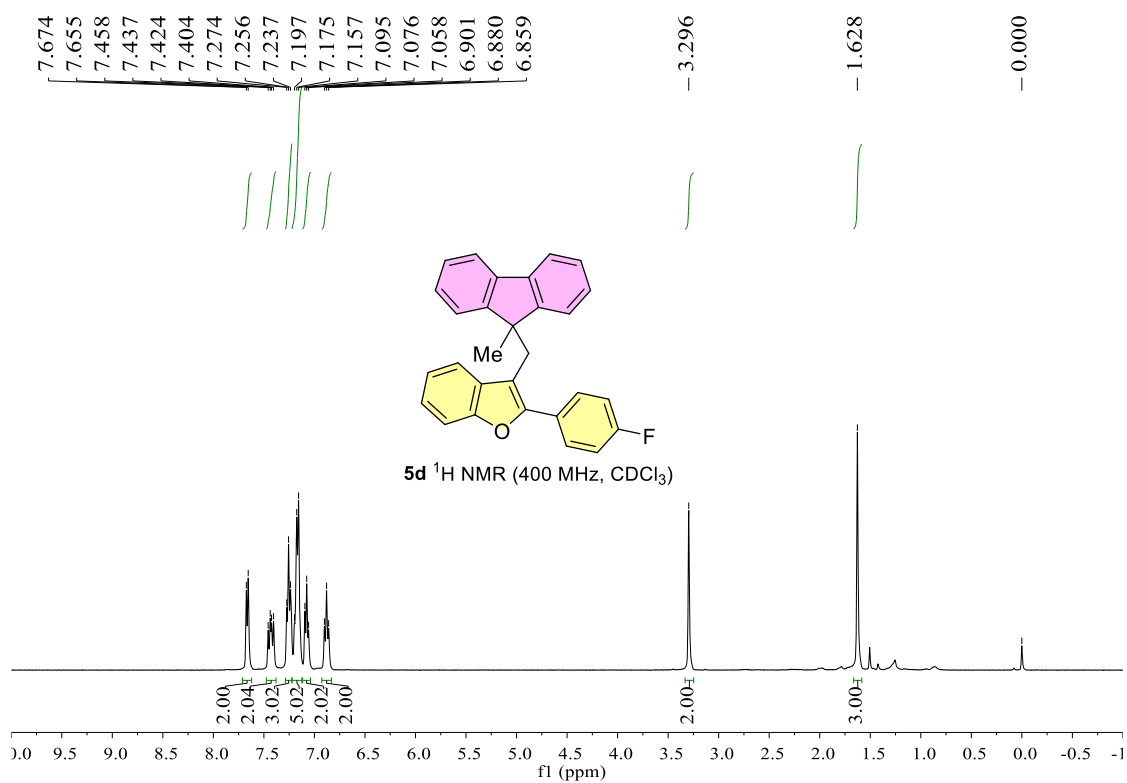




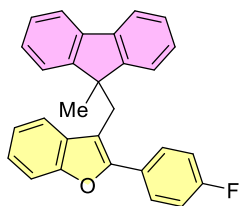




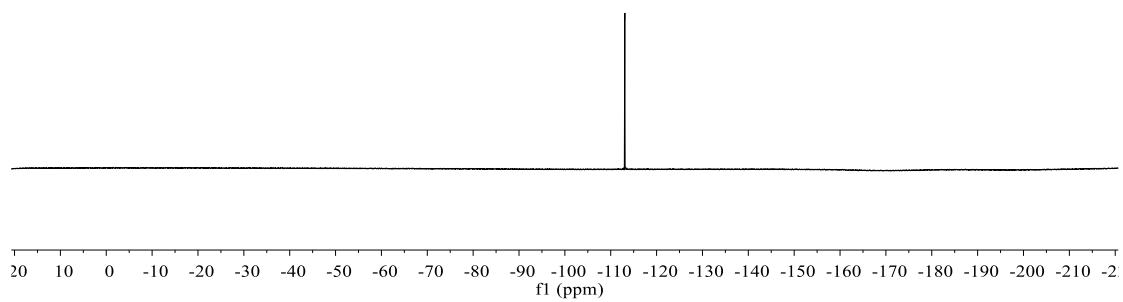


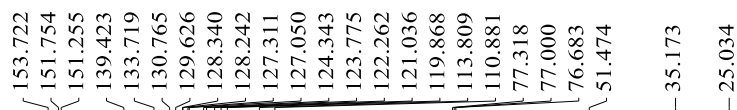
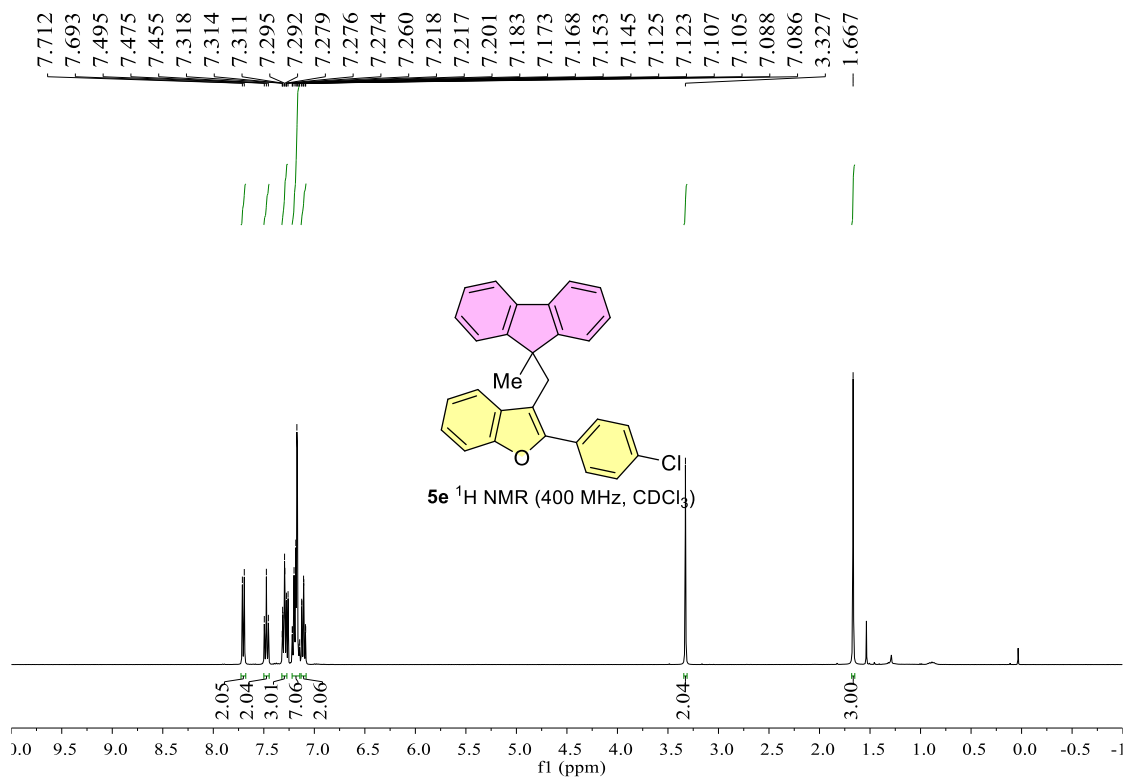


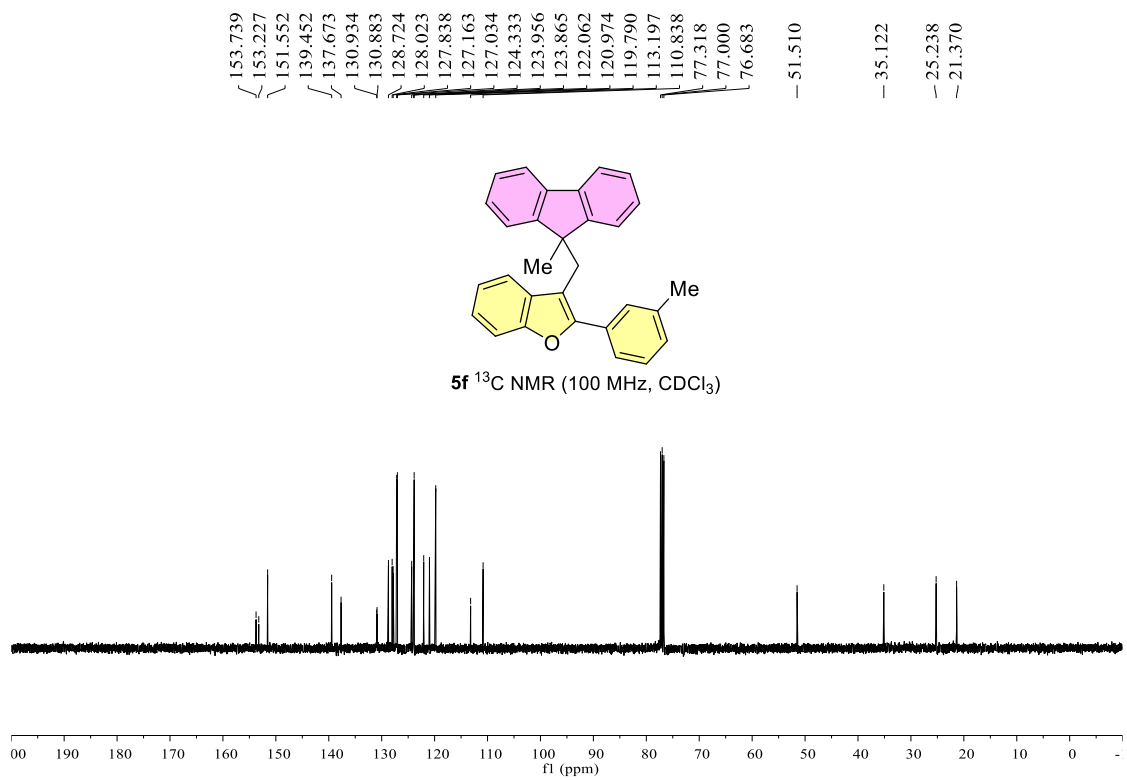
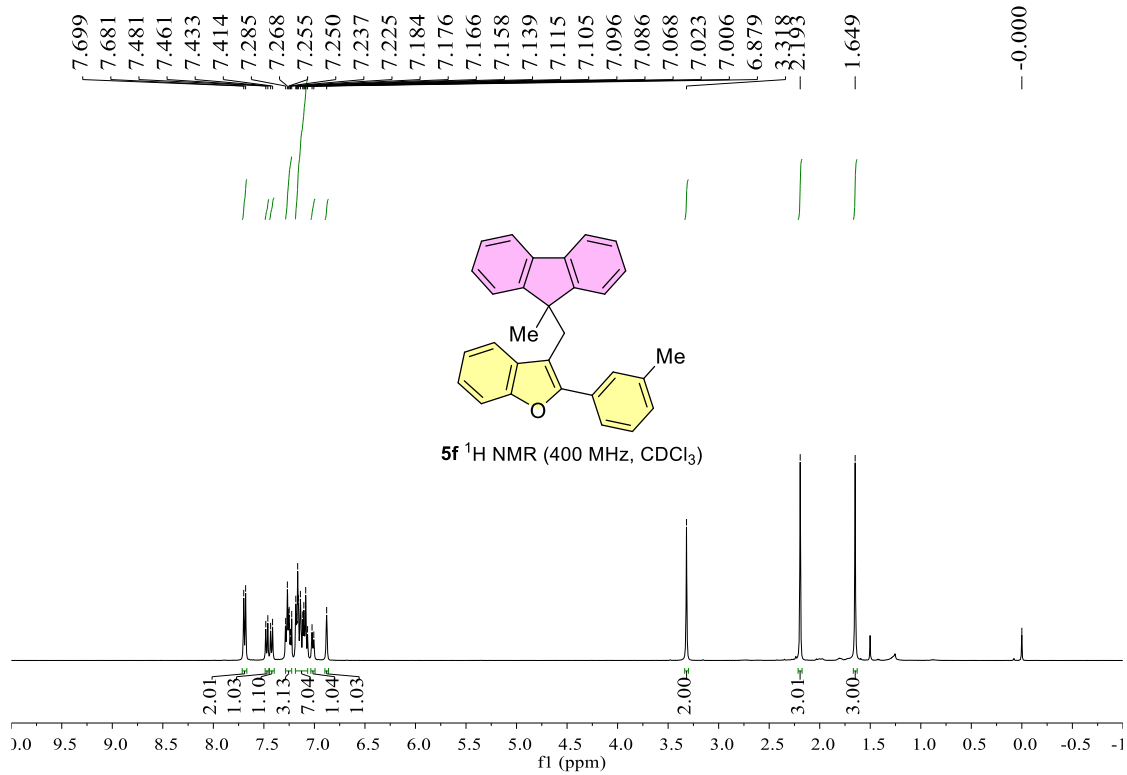
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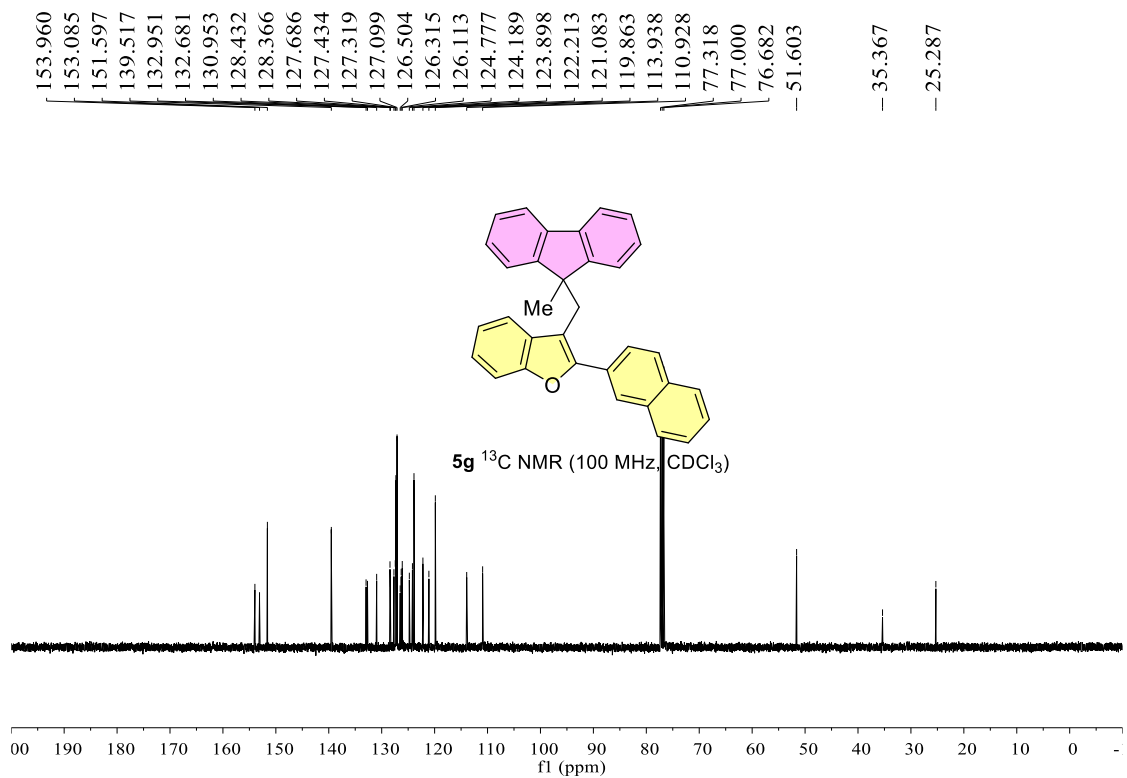
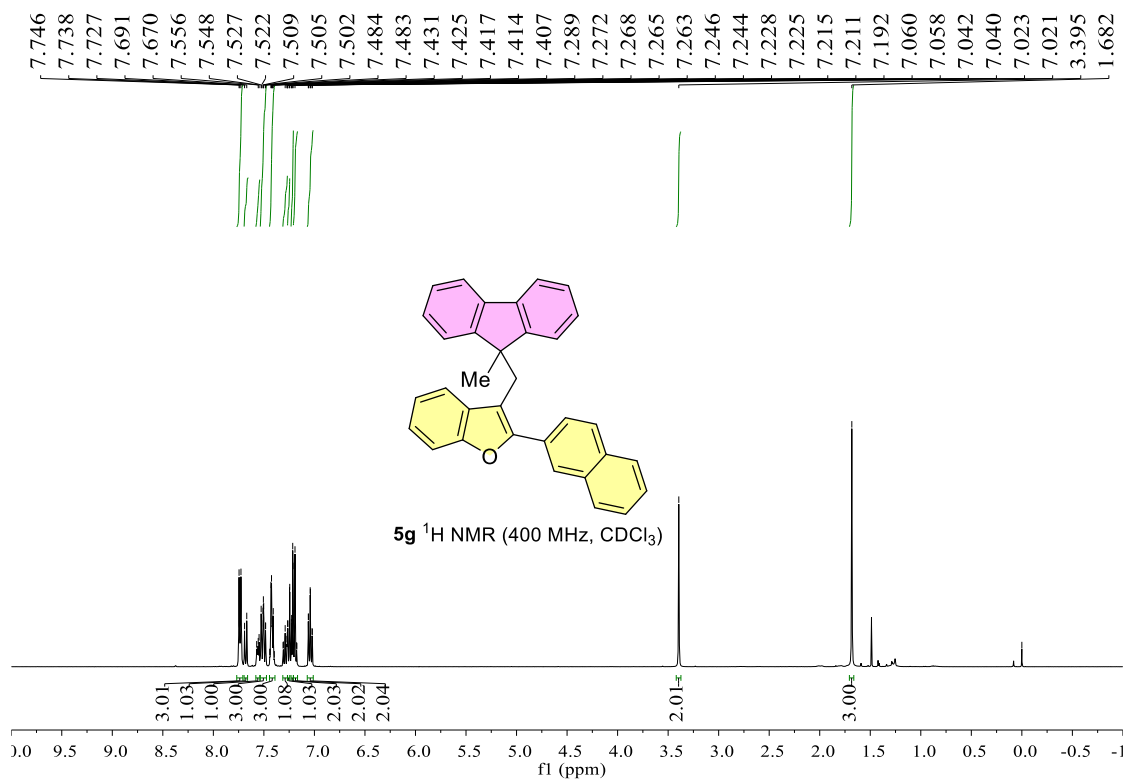


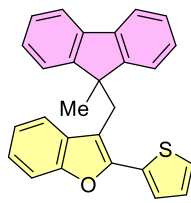
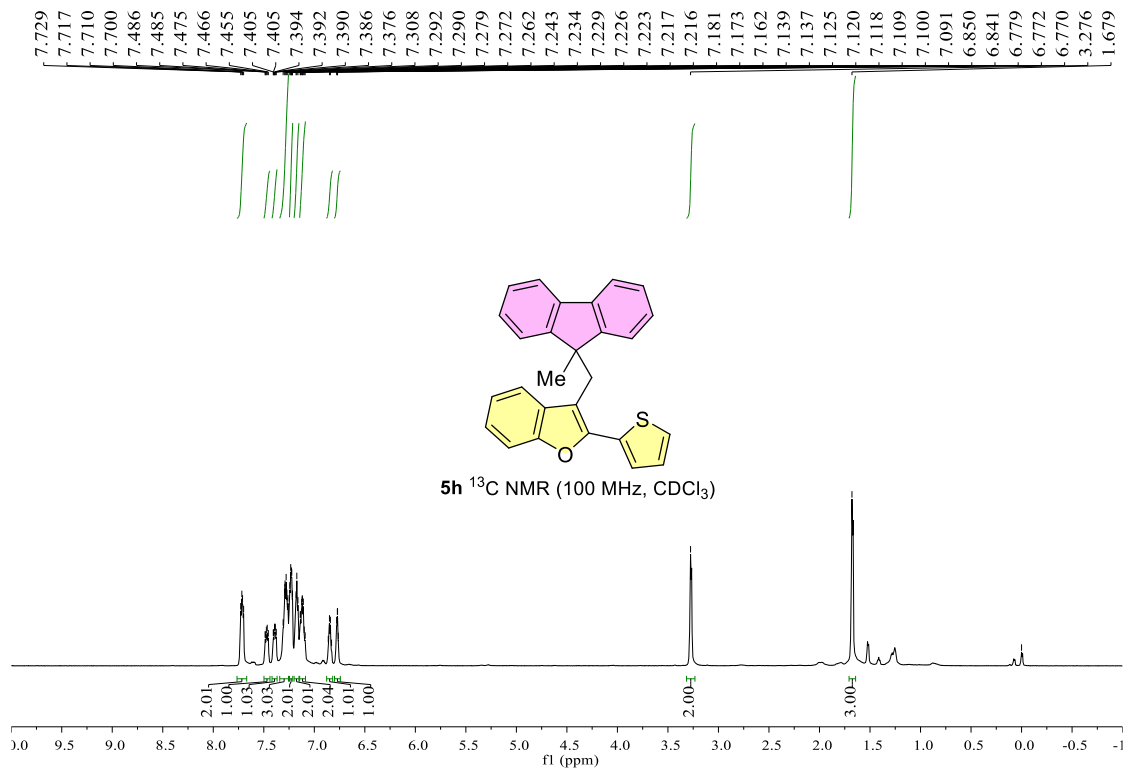
5d ^{19}F NMR (376 MHz, CDCl_3)



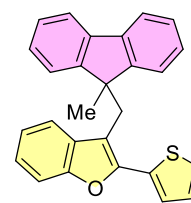
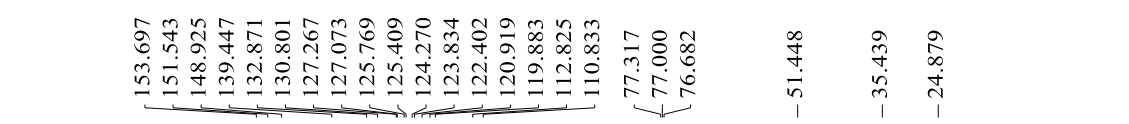




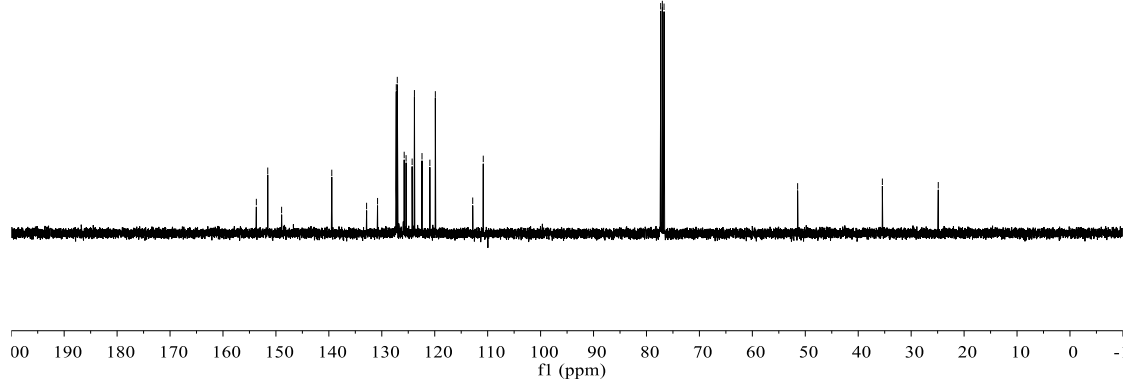


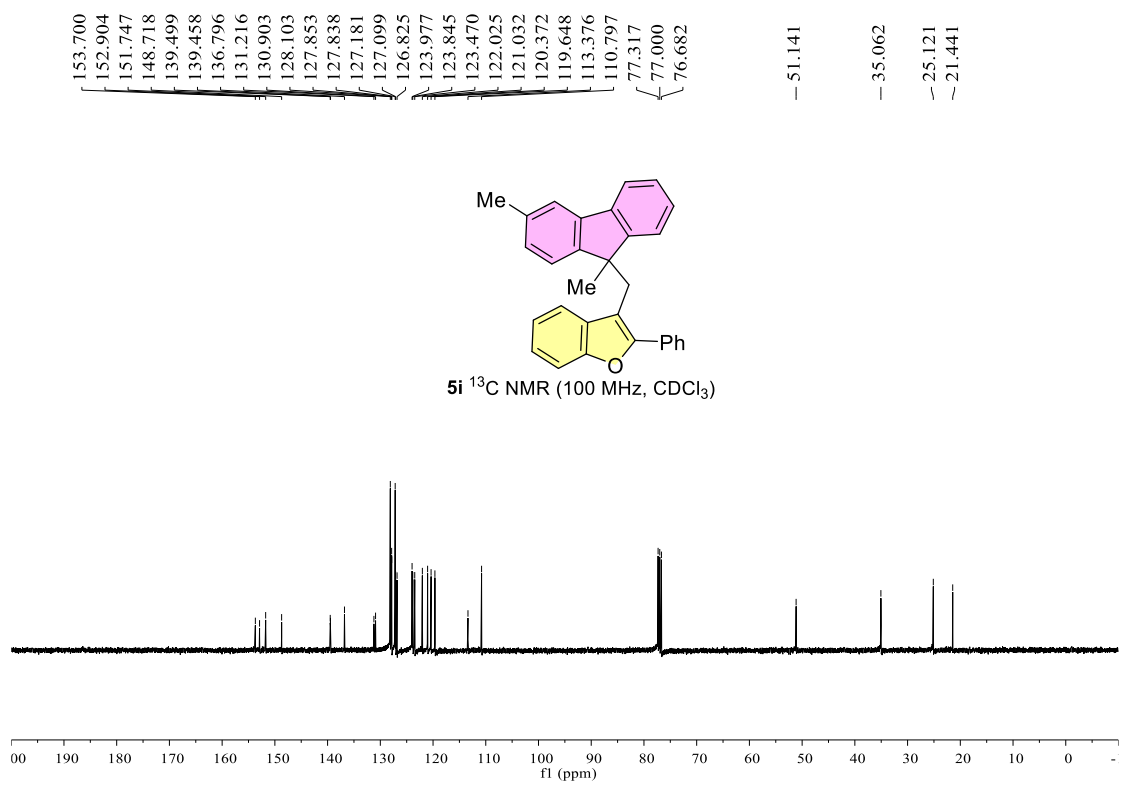
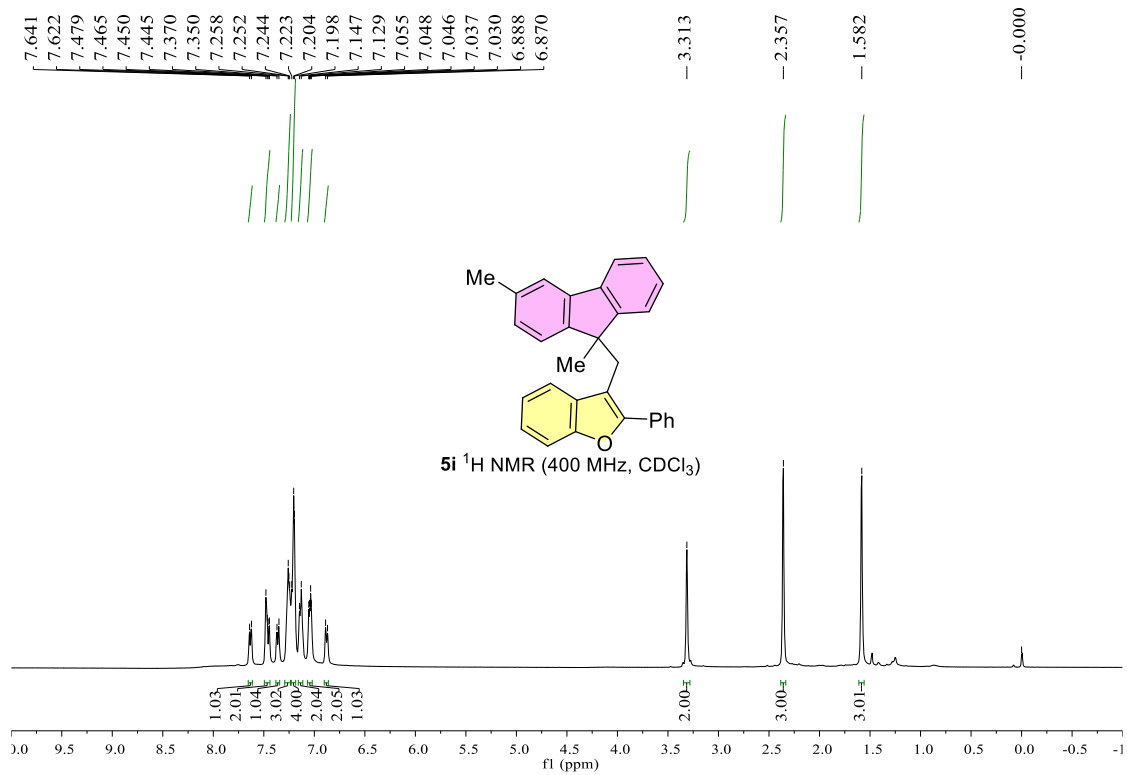


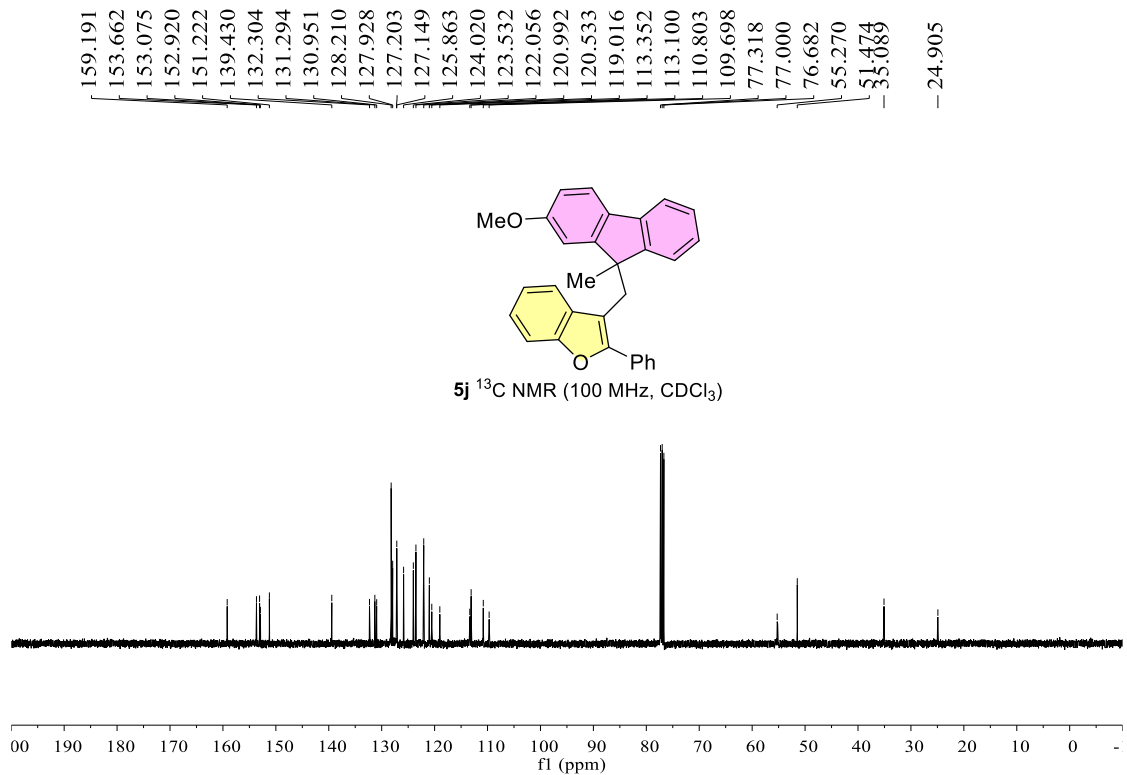
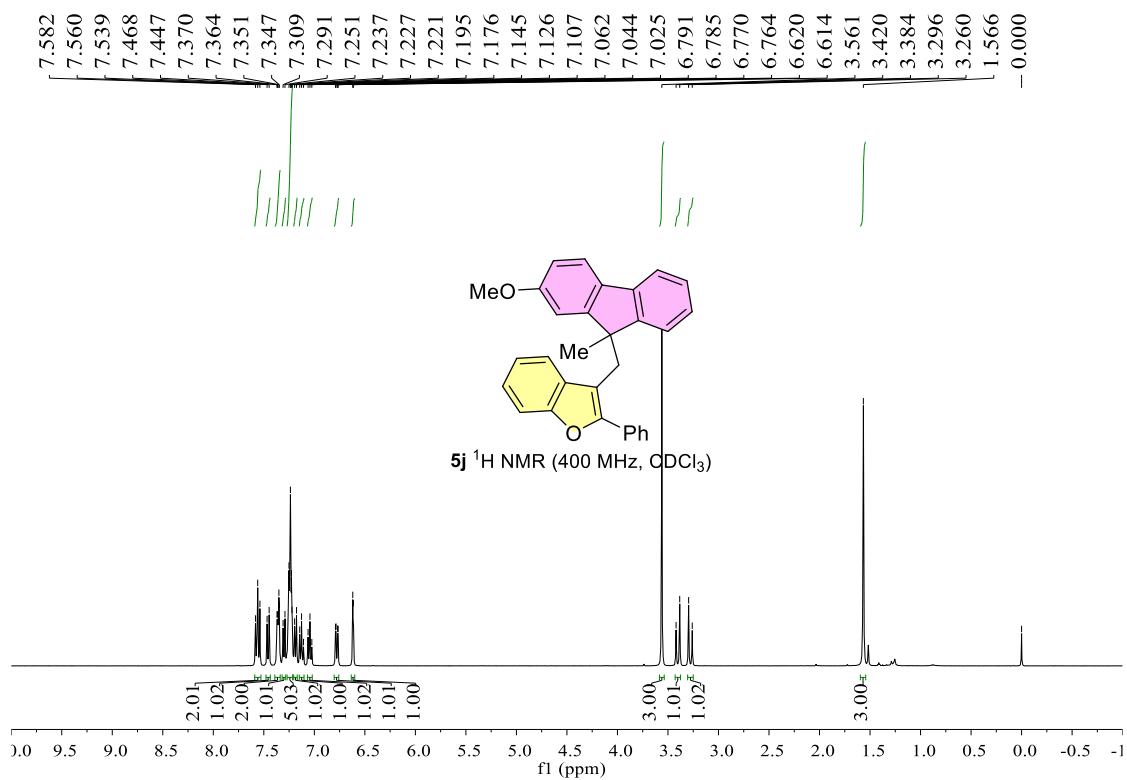
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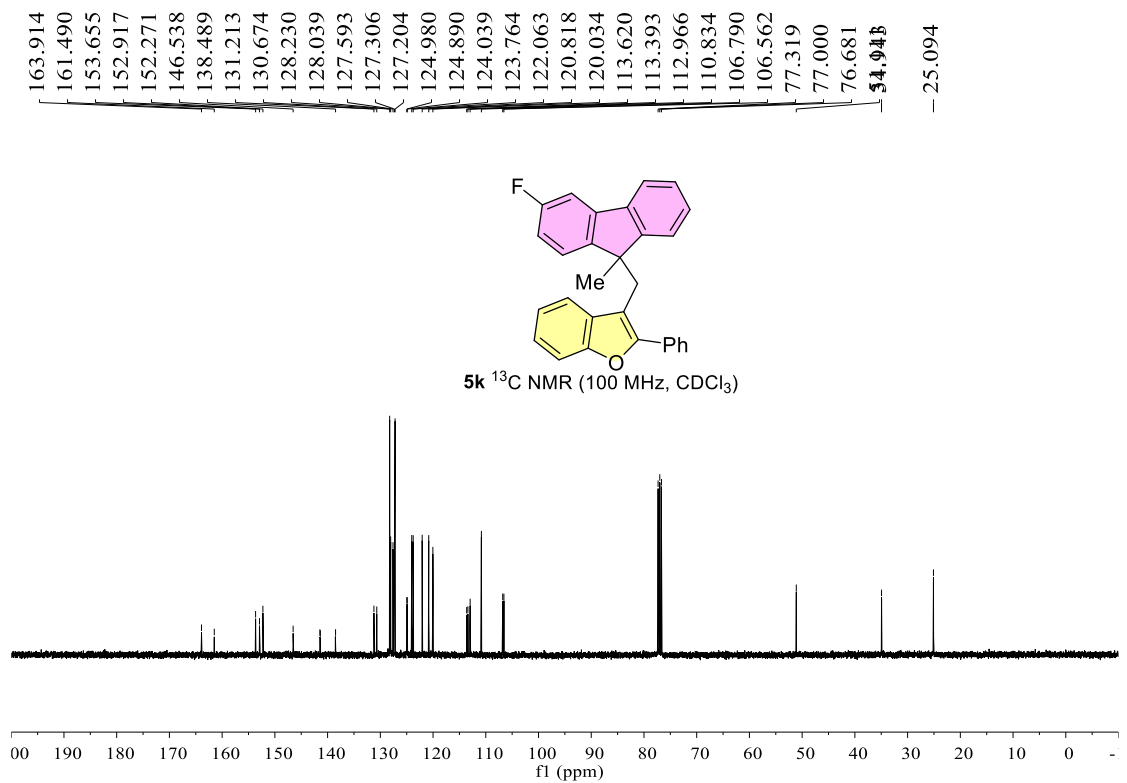
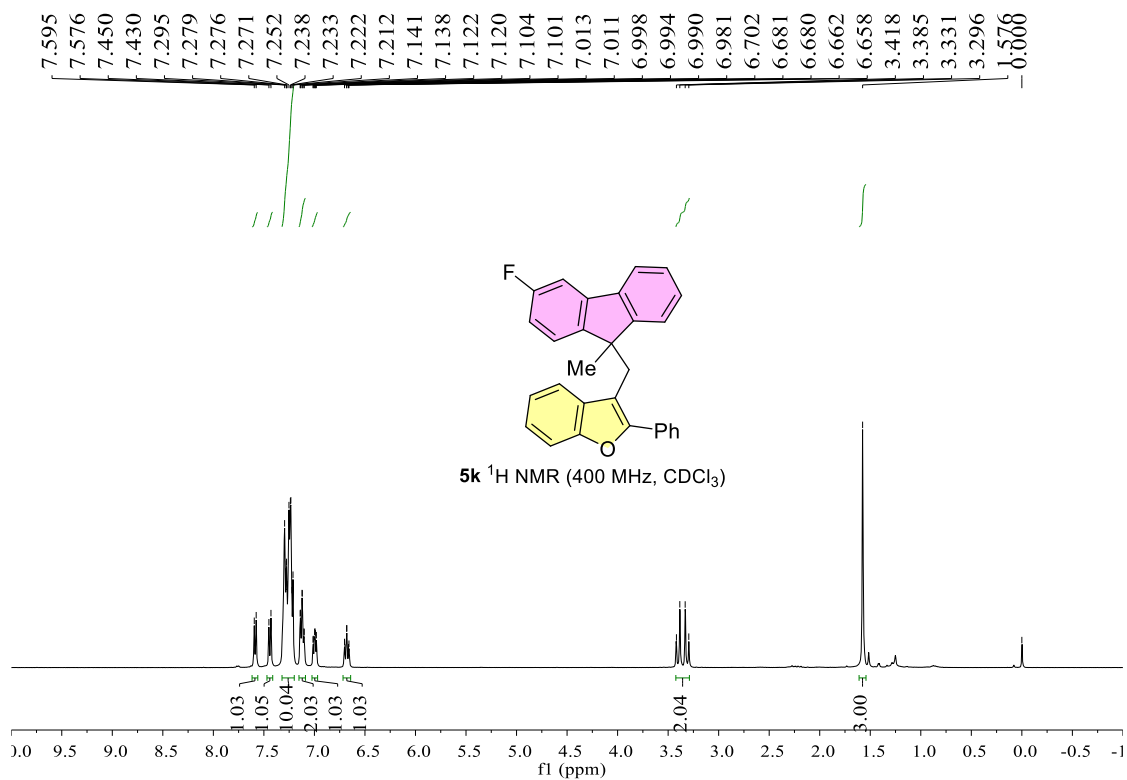


5h ¹³C NMR (100 MHz, CDCl₃)

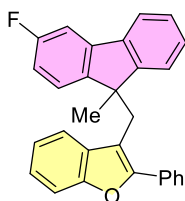








-116.015



5k ^{19}F NMR (376 MHz, CDCl_3)

