Supporting information

Sodium-Iodide-Promoted Nickel-Catalyzed C-N Cross-Coupling of Aryl Chlorides and *N*-nucleophiles under Visible-Light Irradiation

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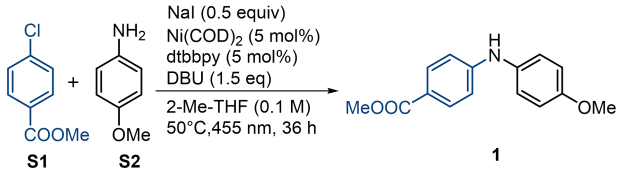
Table of Contents

1. General Information

Unless otherwise noted, all the materials were commercially available and used without further purification. $Ni(COD)_2$ was purchased from Energy Chemical and stored in the glovebox at –20 °C. All solvents were dried before use according to the standard methods. All reactions were performed in an N_2-filled glovebox using standard Schlenk techniques unless otherwise noted. All reactions were monitored by thin-layer chromatography (TLC), visualized by UV. Chromatographic purification of products was accomplished by silica gel chromatography. ^1H NMR, ^{13}C NMR and ^{19}F NMR spectra were recorded on a Bruker Avance II 400. NMR data is reported relative to internal $CHCl_3$ (^1H, δ = 7.26), $CDCl_3$ (^{13}C, δ = 77.0), DMSO (^1H, δ = 2.50), DMSO-d_6 (^{13}C, δ = 39.5). Data for ^1H NMR spectra are reported as follows: chemical shift (δ) in ppm; multiplicities are indicated s (singlet), brs (broad singlet), d (doublet), t (triplet), m (multiplet); coupling constants (J) are in Hertz (Hz) ^{13}C NMR spectra were reported as chemical shifts in ppm. The eight-position parallel light reaction system (RLH-18) were purchased from Beijing Roger Technologies. GC analysis was performed on a SHIMADZU GCMS-TQ8050 instrument equipped with an MS/GC detector using hydrogen/Helium as the carrier gas.

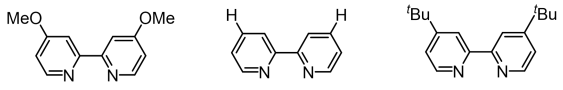
2. Optimization Procedure

Table S1. Optimization of C-N coupling reaction



S1 **S2** **1**

Entry	Variants from standard condition[a]	Yield(%)[b]
1	None	93(88)[c]
2	No Blue LEDs	ND
3	No $Ni(COD)_2$ or dtbbpy	ND
4	$NiCl_2$•DME instead of $Ni(COD)_2$	ND
5	$NiBr_2$•DME instead of $Ni(COD)_2$	ND
6	$Ni(OAc)_2$ instead of $Ni(COD)_2$	ND
7	DMF instead of 2-Me-THF	ND
8	CH_3CN instead of 2-Me-THF	ND
9	CPME instead of 2-Me-THF	18
10	Dioxane instead of 2-Me-THF	7
11	NaI (1.0 eq)	15
12	NaI (0.2 eq)	56
13	No NaI	10
14	Bu_4NI instead of NaI	49
15	KI instead of NaI	17
16	Pyridine instead of DBU	0
17	Et_3N instead of DBU	10
18	MeO-bpy instead of dtbbpy	65
19	bpy instead of dtbbpy	12



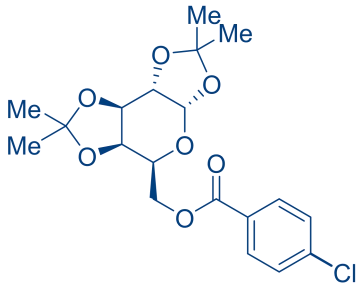
MeO-bpy **bpy** **dtbbpy**

[a]Reactions were run using S1 (0.24 mmol), S2 (0.20 mmol), and NaI (0.1 mmol) unless otherwise noted. [b]NMR yield using 1,2,3-Trimethoxybenzene as the internal standard. [c]Isolated yields. dtbbpy:4,4'-di-tert-butyl-2,2'-bypyridine; COD： 1,5-cyclooctadiene; CPME: cyclopentyl methyl ether; DMF: N,N-dimethylformamide; 2-Me-THF: 2-methyltetrahydrofuran. ND: Not detected

3. Experimental Procedures

3.1 Synthesis of substrates

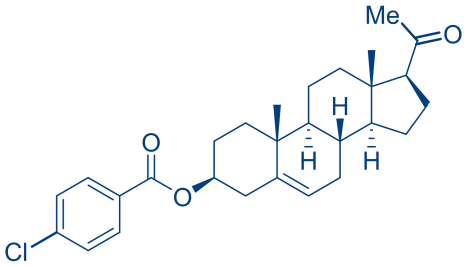
((3aS,5S,5aR,8aR,8bS)-2,2,7,7-tetramethyltetrahydro-5H-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran-5-yl)methyl 4-chlorobenzoate



Prepare from 1,2:3,4-Di-O-isopropylidene-D-galactopyranose, according to the literature.[1]

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98 (d, *J* = 8.0 Hz, 2H), 7.40 (d, *J* = 7.8 Hz, 2H), 5.56 (d, *J* = 4.9 Hz, 1H), 4.65 (d, *J* = 7.7 Hz, 1H), 4.52 (dd, *J* = 11.5, 4.6 Hz, 1H), 4.42 (dd, *J* = 11.5, 7.7 Hz, 1H), 4.36 – 4.28 (m, 2H), 4.19 – 4.13 (m, 1H), 1.49 (d, *J* = 13.4 Hz, 6H), 1.34 (d, *J* = 8.2 Hz, 6H).

^{13}C NMR (101 MHz, CDCl3): δ 165.59, 139.45, 131.10, 128.71, 128.53, 109.75, 108.82, 96.33, 71.14, 70.75, 70.51, 66.14, 64.16, 26.01, 25.97, 24.96, 24.49.

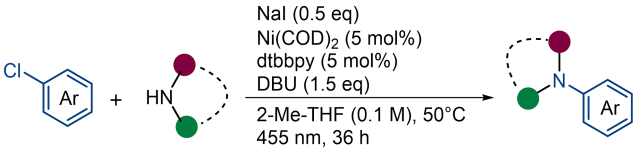


Prepare from 5-Pregnen-3β-ol-20-one, according to the literature.[2]

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97 (d, *J* = 8.4 Hz, 2H), 7.40 (d, *J* = 8.4 Hz, 2H), 5.42 (d, *J* = 4.0 Hz, 1H), 4.90 – 4.79 (m, 1H), 2.54 (t, *J* = 8.8 Hz, 1H), 2.46 (d, *J* = 7.7 Hz, 2H), 2.24 – 2.16 (m, 1H), 2.13 (s, 3H), 2.09 – 1.89 (m, 4H), 1.70 (ddd, *J* = 31.9, 20.0, 6.2 Hz, 6H), 1.51 (dt, *J* = 36.3, 11.2 Hz, 2H), 1.30 – 1.12 (m, 4H), 1.06 (s, 3H), 0.64 (s, 3H).

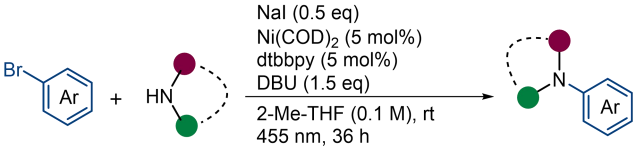
^{13}C NMR (101 MHz, CDCl3): δ 209.57, 165.15, 139.54, 139.23, 131.02, 129.24, 128.62, 122.60, 74.78, 63.69, 56.85, 49.91, 43.99, 38.81, 38.14, 37.02, 36.67, 31.84, 31.80, 31.55, 27.83, 24.49, 22.86, 21.06, 19.36, 13.23.

3.2 C-N coupling of the *N*-nucleophile with aryl chloride



General Procedure A (GPA): In an argon-filled glovebox, a flame-dried 10 mL sealing tube equipped with a Teflon septum and magnetic stir bar was charged with Ni $(COD)_2$ (0.01 mmol, 2.75 mg, 5 mol%), 4,4'-di-tert-butyl-2,2'-bipyridyl (0.01 mmol, 2.35 mg, 5 mol%), and 1 mL 2-Me-THF. The resulting mixture was stirred for 10 min at room temperature, followed by adding nucleophile (0.2 mmol), NaI (0.1 mmol, 15 mg), DBU (0.3 mmol, 45.7 mg), aryl chloride (0.24 mmol) and 1 mL 2-Me-THF in sequence, and sealed with a screwed cap. The sealed tube was taken out of the glove box. It was placed in a photo-reactor under irradiation of blue LEDs (455 nm, 10 W) and kept stirring at 50 °C for 36 h. The mixture was quenched with H_2O (2 mL) and extracted with ethyl acetate (2 mL × 3). The combined organic layers were dried over anhydrous Na_2SO_4, concentrated in vacuo to give crude. The crude product was purified by silica gel column chromatography (PE/EA = 2:1~10:1, Ca. 50~100 mL) to afford the corresponding product**.**

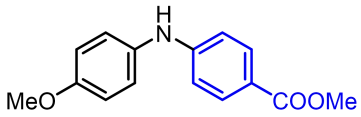
3.3 C-N coupling of the *N*-nucleophile with aryl bromine



General Procedure B (GPB): In an argon-filled glovebox, a flame-dried 10 mL sealing tube equipped with a Teflon septum and magnetic stir bar was charged with Ni $(COD)_2$ (0.01 mmol, 2.75 mg, 5 mol%), 4,4'-di-tert-butyl-2,2'-bipyridyl (0.01 mmol, 2.35 mg, 5 mol%), and 1 mL 2-Me-THF. The resulting mixture was stirred for 10 min at room temperature, followed by adding aryl bromines (0.24 mmol), NaI (0.1 mmol, 15 mg), DBU (0.3 mmol, 45.7 mg), nucleophile (0.2 mmol) and 1 mL 2-Me-THF in sequence, and sealed with a screwed cap. The sealed tube was taken out of the glove box. It was placed in a photo-reactor under irradiation of blue LEDs (455 nm, 10 W) and kept stirring at rt for 36 h. The mixture was quenched with H_2O (3 mL) and extracted with ethyl acetate (2 mL × 3). The combined organic layers were dried over anhydrous Na_2SO_4, concentrated in vacuo to give crude. The crude product was purified by silica gel column chromatography (PE/EA = 5:1~10:1, Ca. 50~100 mL) to afford the corresponding product.

3.4 Characterization of products

methyl 4-((4-methoxyphenyl) amino) benzoate (1)



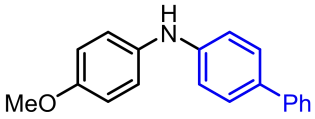
1

According to **GPA**, generated from Methyl 4-chlorobenzoate (40.9 mg, 0.24 mmol) and p-Anisidine (24.6 mg, 0.2 mmol). The crude product was purified with silica gel chromatography (PE/EA = 8:1) to afford **1** (50.9 mg) in 88% yield.[3]

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87 (d, *J* = 8.7 Hz, 2H), 7.13 (d, *J* = 8.7 Hz, 2H), 6.90 (d, *J* = 8.8 Hz, 2H), 6.81 (d, *J* = 8.7 Hz, 2H), 5.92 (s, 1H), 3.86 (s, 3H), 3.81 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 167.14, 156.54, 149.81, 133.39, 131.55, 124.42, 119.91, 114.75, 113.20, 55.56, 51.70.

N-(4-methoxyphenyl)-[1,1'-biphenyl]-4-amine (2)



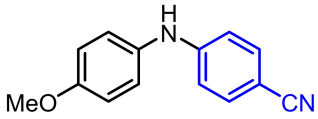
2

According to **GPA**, generated from 4-chloro-1,1'-biphenyl (45.3 mg, 0.24 mmol) and p-Anisidine (24.6 mg, 0.2 mmol). The crude product was purified with silica gel chromatography (PE/EA = 8:1) to afford **2** (40.7 mg) in 74% yield.[4]

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (d, *J* = 8.0 Hz, 2H), 7.48 (d, *J* = 8.6 Hz, 2H), 7.42 (t, *J* = 6.8 Hz, 2H), 7.29 (t, *J* = 8.4 Hz, 1H), 7.13 (d, *J* = 8.9 Hz, 2H), 6.98 (d, 2H), 6.90 (d, *J* = 8.9 Hz, 2H), 5.59 (s, 1H), 3.82 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 155.43, 144.63, 141.01, 135.42, 132.36, 128.75, 128.01, 126.46, 126.41, 122.47, 115.71, 114.73, 55.62.

4-((4-methoxyphenyl) amino) benzonitrile (3)



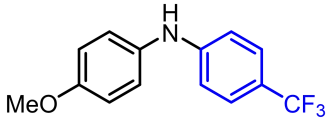
3

According to **GPA**, generated from 4-chlorobenzonitrile (33 mg, 0.24 mmol) and p-Anisidine (24.6 mg, 0.2 mmol). The crude product was purified with silica gel chromatography (PE/EA = 5:1) to afford **3** (44.4 mg) in 99% yield.[5]

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41 (d, *J* = 8.7 Hz, 2H), 7.12 (d, *J* = 8.7 Hz, 2H), 6.91 (d, *J* = 8.8 Hz, 2H), 6.79 (d, *J* = 8.7 Hz, 2H), 6.02 (s, 1H), 3.82 (s,3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 156.99, 149.69, 133.78, 132.52, 125.06, 120.25, 114.88, 113.74, 100.16, 55.57.

4-methoxy-N-(4-(trifluoromethyl) phenyl) aniline (4)



4

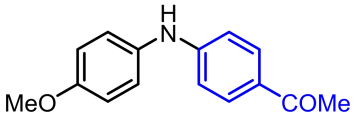
According to **GPA**, generated from 4-chlorobenzotrifluoride (43.3 mg, 0.24 mmol) and p-Anisidine (24.6 mg, 0.2 mmol). The crude product was purified with silica gel chromatography (PE/EA = 10:1) to afford **4** (48.0 mg) in 90% yield. [6]

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41 (d, J = 8.6 Hz, 2H), 7.12 (d, J = 8.8 Hz, 2H), 6.88 (dd, J = 18.6, 8.7 Hz, 4H), 5.73 (s, 1H), 3.82 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 156.53, 148.64, 133.68, 126.68 (q, $^{3}J_{CF}$ = 3.8 Hz), 124.9 (q, $^{1}J_{CF}$ = 270.5 Hz), 124.4, 120.43 (q, $^{2}J_{CF}$ = 32.7 Hz), 114.80, 113.72, 55.82.

^{19}F NMR (377 MHz, $CDCl_3$): δ -61.38.

1-(4-((4-methoxyphenyl) amino) phenyl) ethan-1-one (5)



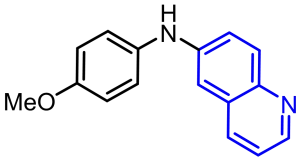
5

According to **GPA**, generated from 4-chloroacetophenone (37 mg, 0.24 mmol) and p-Anisidine (24.6 mg, 0.2 mmol). The crude product was purified with silica gel chromatography (PE/EA = 6:1) to afford **5** (41.5 mg) in 86% yield.[7]

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83 (d, J = 8.8 Hz, 2H), 7.14 (d, J = 8.9 Hz, 2H), 6.91 (d, J = 6.6 Hz, 2H), 6.81 (d, J = 8.8 Hz, 2H), 5.92 (s, 1H), 3.82 (s, 3H), 2.51 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 196.60, 156.65, 150.18, 133.13, 130.79, 127.98, 124.60, 114.78, 113.11, 55.57, 26.16.

N-(4-methoxyphenyl) quinolin-6-amine (6)

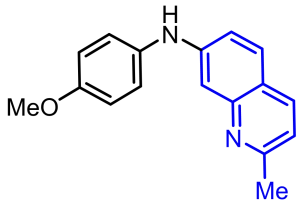


6

According to **GPA**, generated from 6-chloroquinoline (39.3 mg, 0.24 mmol) and p-Anisidine (24.6 mg, 0.2 mmol). The crude product was purified with silica gel chromatography (PE/EA = 8:1) to afford **6** (43.1 mg) in 86% yield.[8]

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.67 (dd, *J* = 4.2, 1.5 Hz, 1H), 7.96 (d, *J* = 9.0 Hz, 1H), 7.89 (d, *J* = 8.1 Hz, 1H), 7.30 (ddd, *J* = 12.5, 8.6, 3.4 Hz, 2H), 7.20 (d, *J* = 8.9 Hz, 2H), 7.11 (d, *J* = 2.5 Hz, 1H), 6.94 (d, *J* = 8.9 Hz, 2H), 6.00 (s, 1H), 3.84 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 155.98, 146.89, 143.75, 143.73, 134.70, 134.24, 130.37, 129.82, 123.40, 122.14, 121.50, 114.81, 106.68, 55.59.

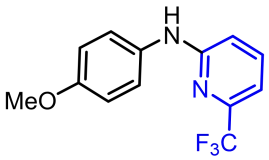
N-(4-methoxyphenyl)-2-methylquinolin-7-amine (7)



7

According to **GPA**, generated from 7-chloro-2-methylquinoline (42.6 mg, 0.24 mmol) and p-Anisidine (24.6 mg, 0.2 mmol). The crude product was purified with silica gel chromatography (PE/EA = 5:1) to afford **7** (33.8 mg) in 64% yield. m.p. 169.5-171.3 ℃.
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86 (d, *J* = 8.2 Hz, 1H), 7.57 (d, *J* = 8.7 Hz, 1H), 7.35 (d, *J* = 2.0 Hz, 1H), 7.18 (d, *J* = 8.6 Hz, 2H), 7.04 (dd, *J* = 13.5, 5.2 Hz, 2H), 6.87 (d, *J* = 8.2 Hz, 2H), 5.95 (s, 1H), 3.80 (s, 3H), 2.65 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 159.28, 156.11, 149.67, 146.88, 135.78, 134.26, 128.54, 123.88, 120.87, 118.72, 117.91, 114.77, 107.94, 55.60, 25.32.
HRMS (ESI) (*m/z*): calcd. for $C_{17}H_{17}N_2O$ $[M+H]^+$: 265.1335, found: 265.1329.

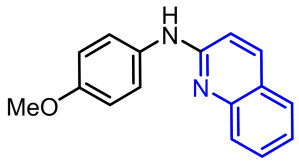
N-(4-methoxyphenyl)-6-(trifluoromethyl) pyridin-2-amine (8)



8

According to **GPA**, generated from 2-chloro-6-(trifluoromethyl) pyridine (43.6 mg, 0.24 mmol) and p-Anisidine (24.6 mg, 0.2 mmol). The crude product was purified with silica gel chromatography (PE/EA = 6:1) to afford **8** (40.7 mg) in 76% yield.
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54 (t, *J* = 7.9 Hz, 1H), 7.25 (d, *J* = 8.9 Hz, 2H), 7.02 (d, *J* = 7.3 Hz, 1H), 6.92 (d, *J* = 8.9 Hz, 2H), 6.79 (d, *J* = 8.5 Hz, 1H), 6.68 (s, 1H), 3.82 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 157.42, 156.87, 146.9 (q, $^2J_{CF}$ = 37.2 Hz), 138.61, 132.08, 124.67, 121.56 (q, $^1J_{CF}$ = 277.8 Hz), 114.74, 110.35 (q, $^3J_{CF}$ = 3.0 Hz), 110.05, 55.54.
^{19}F NMR (377 MHz, $CDCl_3$): δ -68.61.
HRMS (ESI) (*m/z*): calcd. for $C_{13}H_{12}F_3N_2O$ $[M+H]^+$: 269.0896, found: 269.0892

N-(4-methoxyphenyl) quinolin-2-amine (9)



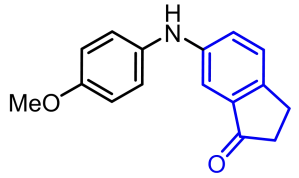
9

According to **GPA**, generated from 2-chloroquinoline (39.3 mg, 0.24 mmol) and p-Anisidine (24.6 mg, 0.2 mmol). Using of Ni $(COD)_2$ (5.5 mg, 0.02 mmol, 10 mol%), 4,4'-Di-*tert*-butyl-2,2'-bipyridyl (5.3 mg, 0.02 mmol, 10 mol%), the crude product was purified with silica gel chromatography (PE/EA = 6:1) to afford **9** (25 mg) in 50% yield.[9]

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87 (d, *J* = 8.9 Hz, 1H), 7.73 (d, *J* = 8.4 Hz, 1H), 7.62 (d, *J* = 7.9 Hz, 1H), 7.57 (t, *J* = 8.2 Hz, 1H), 7.42 (d, *J* = 8.8 Hz, 2H), 7.26 (dd, *J* = 8.5, 6.3 Hz, 1H), 6.93 (d, *J* = 8.8 Hz, 2H), 6.87 (d, *J* = 8.9 Hz, 1H), 3.83 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 156.40, 155.45, 147.71, 137.82, 132.89, 129.83, 127.49, 126.32, 124.03, 123.96, 122.83, 114.58, 110.90, 55.58.

6-((4-methoxyphenyl) amino)-2,3-dihydro-1H-inden-1-one (10)



10

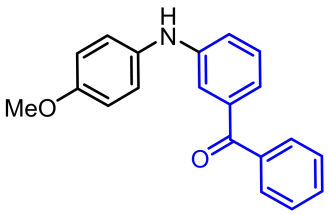
According to **GPA**, generated from 6-chloro-1-indanone (40 mg, 0.24 mmol) and p-Anisidine (24.6 mg, 0.2 mmol). The crude product was purified with silica gel chromatography (PE/EA = 10:1) to afford **10** (33.9 mg) in 67% yield. m.p. 182.9-183.6 ℃.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57 (d, *J* = 8.3 Hz, 1H), 7.16 (d, *J* = 12.1 Hz, 2H), 6.92 (d, *J* = 12.2 Hz, 2H), 6.75 (d, *J* = 13.4 Hz, 2H), 6.25 (s, 1H), 3.82 (s, 3H), 2.99 – 2.93 (m, 2H), 2.63 – 2.59 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 205.04, 158.46, 156.90, 152.17, 132.89, 128.12, 125.60, 125.18, 114.81, 114.52, 108.66, 55.56, 36.43, 25.82.

HRMS (ESI) (*m/z*): calcd. for $C_{16}H_{15}NO_2Na$ $[M+Na]^+$: 276.0995, found: 276.1001

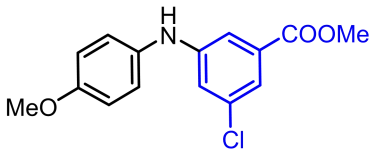
(3-((4-methoxyphenyl) amino) phenyl) (phenyl)methanone (11)



11

According to **GPA**, generated from 3-chlorobenzophenone (52 mg, 0.24 mmol) and p-Anisidine (24.6 mg, 0.2 mmol). The crude product was purified with silica gel chromatography (PE/EA = 10:1) to afford **11** (50.4 mg) in 83% yield.
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82 (d, *J* = 7.1 Hz, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 2H), 7.34 – 7.32 (m, 1H), 7.28 (t, *J* = 7.8 Hz, 1H), 7.17 (d, *J* = 7.6 Hz, 1H), 7.10 (d, *J* = 8.8 Hz, 3H), 6.87 (d, *J* = 8.9 Hz, 2H), 5.76 (s, 1H), 3.80 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 196.99, 155.72, 145.59, 138.73, 137.69, 134.87, 132.42, 130.10, 129.10, 128.23, 122.83, 121.27, 118.88, 116.30, 114.78, 55.58.
HRMS (ESI) (*m/z*): calcd. for $C_{20}H_{18}NO_2$ $[M+H]^+$:304.1332, found: 304.1327

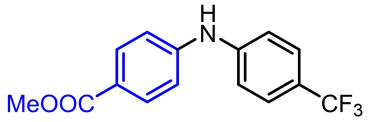
ethyl 3-chloro-5-((4-methoxyphenyl) amino) benzoate (12)



12

According to **GPA**, generated from methyl 3,5-dichlorobenzoate (49.2 mg, 0.24 mmol) and p-Anisidine (24.6 mg, 0.2 mmol). The crude product was purified with silica gel chromatography (PE/EA = 8:1) to afford **12** (29.1 mg) in 50% yield, m.p. 157.1-157.9 ℃.
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41 – 7.39 (m, 1H), 7.38 – 7.36 (m, 1H), 7.10 – 7.07 (m, 2H), 6.98 (t, *J* = 2.1 Hz, 1H), 6.92 – 6.88 (m, 2H), 5.69 (s, 1H), 3.88 (s, 3H), 3.81 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 166.23, 156.44, 147.09, 135.21, 133.68, 132.41, 124.02, 119.72, 118.05, 114.90, 114.13, 55.56, 52.40.
HRMS (ESI) (*m/z*): calcd. for $C_{15}H_{13}ClNO_3$ $[M-H]^-$: 290.0589, found: 290.0589

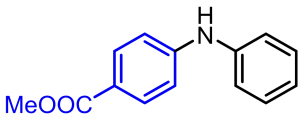
methyl 4-((4-(trifluoromethyl) phenyl) amino) benzoate (13)



13

According to **GPA**, generated from Methyl 4-chlorobenzoate (40.9 mg, 0.24 mmol) and 4-Aminobenzotrifluoride (32.2 mg, 0.2 mmol). The crude product was purified with silica gel chromatography (PE/EA = 10:1) to afford **13** (44.2 mg) in 75% yield.
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97 (d, *J* = 8.6 Hz, 2H), 7.55 (d, *J* = 8.4 Hz, 2H), 7.19 (d, *J* = 8.4 Hz, 2H), 7.10 (d, *J* = 8.6 Hz, 2H), 6.30 (s, 1H), 3.89 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 166.77, 146.15, 144.52, 131.39, 126.82 (q, $^3J_{CF}$ = 12 H), 124.33 (q, $^1J_{CF}$ = 272.7 Hz) 123.70 (q, $^2J_{CF}$ = 32.3 Hz), 122.84, 117.89, 116.47, 52.03.
^{19}F NMR (377 MHz, $CDCl_3$): δ -61.73.
HRMS (ESI) (*m/z*): calcd. for $C_{15}H_{11}F_3NO_2$ $[M-H]^-$: 294.0747, found: 294.0746

methyl 4-(phenylamino)benzoate (14)



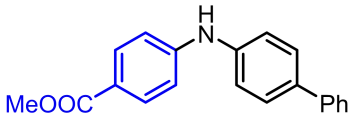
14

According to **GPA**, generated from methyl 4-chlorobenzoate (40.9 mg, 0.24 mmol) and Aniline (18.6 mg, 0.2 mmol). The crude product was purified with silica gel chromatography (PE/EA = 10:1) to afford **14** (35.4 mg) in 78% yield.[10]

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92 (d, *J* = 8.6 Hz, 2H), 7.34 (t, *J* = 7.8 Hz, 2H), 7.17 (d, *J* = 7.8 Hz, 2H), 7.07 (t, *J* = 7.3 Hz, 1H), 6.99 (d, *J* = 8.6 Hz, 2H), 6.11 (s, 1H), 3.88 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 167.12, 148.00, 140.83, 131.60, 129.43, 123.17, 121.21, 120.52, 114.45, 51.80.

methyl 4-([1,1'-biphenyl]-4-ylamino) benzoate (15)



15

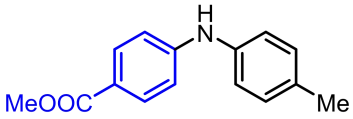
According to **GPA**, generated from methyl 4-chlorobenzoate (40.9 mg, 0.24 mmol) and biphenyl-4-amine (33.8 mg, 0.2 mmol). The crude product was purified with silica gel chromatography (PE/EA = 8:1) to afford **15** (43.6 mg) in 72% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 (d, *J* = 8.7 Hz, 2H), 7.59 (t, *J* = 7.4 Hz, 4H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.34 (t, *J* = 7.3 Hz, 1H), 7.24 (d, *J* = 8.5 Hz, 2H), 7.04 (d, *J* = 8.7 Hz, 2H), 6.16 (s, 1H), 3.89 (s, 3H)

^{13}C NMR (101 MHz, $CDCl_3$): δ 167.10, 147.79, 140.58, 140.27, 135.84, 131.56, 128.86, 128.14, 127.17, 126.72, 121.13, 120.43, 114.81, 51.86.

HRMS (ESI) (*m/z*): calcd. for $C_{20}H_{18}NO_2$ $[M+H]^+$: 304.1332, found: 304.1330

methyl 4-(p-tolylamino) benzoate (16)



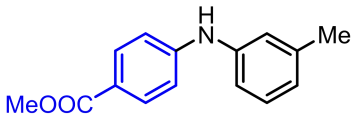
16

According to **GPA**, generated from Methyl 4-chlorobenzoate (40.9 mg, 0.24 mmol) and p-toluidine (21.4 mg, 0.2 mmol). The crude product was purified with silica gel chromatography (PE/EA = 10:1) to afford **16** (35.2 mg) in 73% yield.[11]

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 (d, *J* = 8.7 Hz, 2H), 7.15 (d, *J* = 8.1 Hz, 2H), 7.08 (d, *J* = 8.2 Hz, 2H), 6.92 (d, *J* = 8.7 Hz, 2H), 5.99 (s, 1H), 3.87 (s, 3H), 2.34 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 167.12, 148.83, 138.03, 133.17, 131.52, 130.07, 121.36, 120.43, 113.95, 51.74, 20.88.

methyl 4-(m-tolylamino) benzoate (17)



17

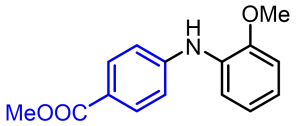
According to **GPA**, generated from methyl 4-chlorobenzoate (40.9 mg, 0.24 mmol) and m-toluidine (21.4 mg, 0.2 mmol). The crude product was purified with silica gel chromatography (PE/EA = 10:1) to afford **17** (42.0 mg) in 87% yield. [12]

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94 (d, *J* = 8.6 Hz, 2H), 7.25 (t, *J* = 8.1 Hz, 1H), 7.01 (d, *J* = 8.4 Hz, 4H), 6.91 (d, *J* = 7.5 Hz, 1H), 6.13 (s, 1H), 3.90 (s, 3H), 2.37 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 167.12, 148.18, 140.76, 139.48, 131.50, 129.28, 123.98, 121.13, 120.86, 117.52, 114.56, 51.78, 21.71.

HRMS (ESI) (*m/z*): calcd. for $C_{15}H_{16}NO_2$ $[M+H]^+$: 242.1175, found: 242.1169

methyl 4-((2-methoxyphenyl) amino) benzoate (18)



18

According to **GPA**, generated from methyl 4-chlorobenzoate (40.9 mg, 0.24 mmol) and o-anisidine (24.6 mg, 0.2 mmol). The crude product was purified with silica gel chromatography (PE/EA = 8:1) to afford **18** (22.6 mg) in 44% yield.[13]

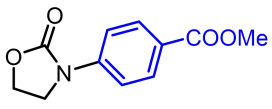
methyl 4-((2-methoxyphenyl) amino) benzoate. According to **GPB**, generated from methyl 4-bromobenzoate (52.3 mg, 0.24 mmol) and o-Anisidine (24.6 mg, 0.2 mmol). The crude product **18** was purified with silica gel chromatography (PE/EA = 8:1) to afford **18** (50.9 mg) in 99% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96 (d, *J* = 8.6 Hz, 2H), 7.43 (d, *J* = 7.7 Hz, 1H), 7.11 (d, *J* = 8.7 Hz, 2H), 6.99 (dt, *J* = 17.4, 7.6 Hz, 3H), 6.43 (s, 1H), 3.90 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 166.95, 149.52, 147.60, 131.25, 130.26, 122.25, 121.14, 120.57, 117.76, 115.04, 110.87, 55.74, 51.77.

HRMS (ESI) (*m/z*): calcd. for $C_{15}H_{16}NO_3$ $[M+H]^+$: 258.1124, found: 258.1120

methyl 4-(2-oxooxazolidin-3-yl) benzoate (19)



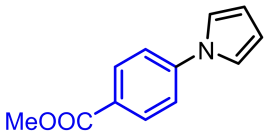
19

According to **GPA,** generated from methyl 4-chlorobenzoate (40.9 mg, 0.24 mmol) and 2-Oxazolidone (17.4 mg, 0.2 mmol). The crude product was purified with silica gel chromatography (PE/EA = 5:1) to afford **19** (14.6 mg) in 33% yield.[14]

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05 (d, *J* = 7.0 Hz, 2H), 7.63 (d, *J* = 11.4 Hz, 2H), 4.51 (dd, *J* = 8.9, 7.1 Hz, 2H), 4.10 (dd, *J* = 8.9, 7.1 Hz, 2H), 3.91 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): 166.54, 154.88, 142.24, 130.72, 125.24, 117.13, 61.38, 52.12, 44.92.

methyl 4-(1H-pyrrol-1-yl) benzoate (20)



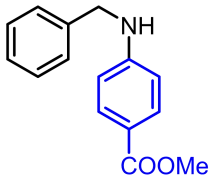
20

According to **GPA**, generated from 4-chlorobenzoic acid methyl (40.9 mg, 0.24 mmol) and pyrrole (13.4 mg, 0.2 mmol). The crude product was purified with silica gel chromatography (PE/EA = 8:1) to afford **20** (18.0 mg) in 45% yield.[15]

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.10 (d, *J* = 8.7 Hz, 2H), 7.45 (d, *J* = 8.7 Hz, 2H), 7.16 (d, *J* = 1.9 Hz, 2H), 6.39 (d, *J* = 1.9 Hz, 2H), 3.93 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 166.47, 143.99, 131.34, 126.88, 119.33, 119.05, 111.50, 52.03.

methyl 4-(benzylamino)benzoate (21)



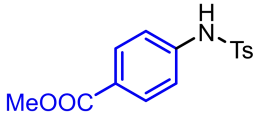
21

According to **GPA**, generated from methyl 4-chlorobenzoate (40.9 mg, 0.24 mmol) and benzylamine (21.4 mg, 0.2 mmol). The crude product was purified with silica gel chromatography (PE/EA = 8:1) to afford **21** (21.7 mg) in 45% yield.[16]

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86 (d, *J* = 8.6 Hz, 2H), 7.35 (s, 4H), 7.30 (dd, *J* = 9.1, 4.5 Hz, 1H), 6.59 (d, *J* = 8.6 Hz, 2H), 4.53 (s, 1H), 4.39 (d, *J* = 5.5 Hz, 2H), 3.84 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 167.33, 151.89, 138.37, 131.59, 128.51, 127.57, 127.44, 118.57, 111.66, 51.73, 47.56.

methyl 4-((4-methylphenyl) sulfonamido) benzoate (22)



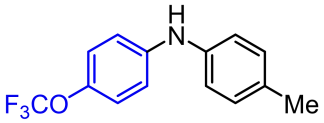
22

According to **GPA**, generated from methyl 4-chlorobenzoate (40.9 mg, 0.24 mmol) and p-Toluenesulfonamide (34.2 mg, 0.2 mmol). The crude product was purified with silica gel chromatography (PE/EA = 8:1) to afford **22** (49.4 mg) in 81% yield.[17]

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93 (d, *J* = 8.5 Hz, 2H), 7.75 (d, *J* = 8.1 Hz, 2H), 7.27 (d, *J* = 8.1 Hz, 2H), 7.16 (d, *J* = 8.5 Hz, 2H), 3.89 (s, 3H), 2.40 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 166.45, 144.48, 140.98, 135.68, 131.16, 129.90, 127.28, 126.21, 118.98, 52.16, 21.60.

4-methyl-N-(4-(trifluoromethoxy) phenyl) aniline (23)



23

According to **GPB**, generated from 1-bromo-4-(trifluoromethoxy) benzene (57.8 mg, 0.24 mmol) and p-toluidine (21.4 mg, 0.2 mmol). The crude product was purified with silica gel chromatography (PE/EA = 8:1) to afford **23** (52.3 mg) in 98% yield. m.p. = 54.1-54.9 ℃.

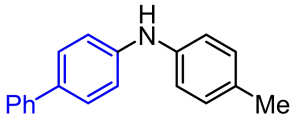
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.22 – 6.93 (m, 8H), 5.63 (s, 1H), 2.34 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 143.01, 142.27, 139.71, 131.70, 130.07, 122.31, 119.44, 117.09, 20.75.

^{19}F NMR (377 MHz, $CDCl_3$): δ -58.10.

HRMS (ESI) (*m/z*): calcd. for $C_{14}H_{13}F_3NO$ $[M+H]^+$: 268.0943, found: 268.0937

N-(p-tolyl)-[1,1'-biphenyl]-4-amine (24)



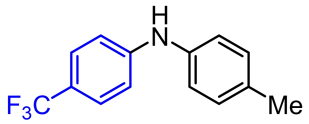
24

According to **GPB**, generated from 4-bromobiphenyl (55.9 mg, 0.24 mmol) and p-toluidine (21.4 mg, 0.2 mmol). The crude product was purified with silica gel chromatography (PE/EA = 8:1) to afford **24** (29.0 mg) in 56% yield. [18]

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62 – 7.57 (m, 2H), 7.53 (dd, *J* = 5.0, 3.4 Hz, 2H), 7.47 – 7.41 (m, 2H), 7.35 – 7.30 (m, 1H), 7.16 – 7.04 (m, 6H), 5.70 (s, 1H), 2.35 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 143.41, 140.96, 140.01, 133.05, 131.23, 129.97, 128.78, 128.01, 126.53, 119.19, 116.88, 20.79.

4-methyl-N-(4-(trifluoromethyl) phenyl) aniline (25)



25

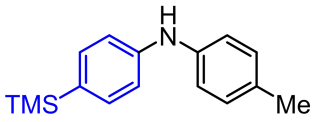
According to **GPB**, generated from 4-bromobenzotrifluoride (54 mg, 0.24 mmol) and p-toluidine (21.4 mg, 0.2 mmol). The crude product was purified with silica gel chromatography (PE/EA = 8:1) to afford **25** (32.6 mg) in 65% yield.[19]

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45 (d, *J* = 8.4 Hz, 2H), 7.16 (d, *J* = 8.1 Hz, 2H), 7.07 (d, *J* = 8.2 Hz, 2H), 6.98 (d, *J* = 8.4 Hz, 2H), 5.84 (s, 1H), 2.35 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 147.52, 138.34, 133.04, 130.11, 126.69 (q, $^3J_{CF}$ = 3.7 Hz), 124.73 (q, $^1J_{CF}$ = 274.7 Hz), 121.06, 121.01 (q, $^2J_{CF}$ = 33.3 Hz), 114.62, 20.83

^{19}F NMR (377 MHz, $CDCl_3$): δ -61.27.

4-methyl-N-(4-(trimethylsilyl) phenyl) aniline (26)



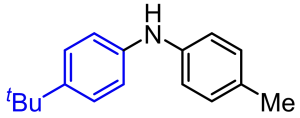
26

According to **GPB**, generated from 1-bromo-4-(trimethylsilyl) benzene (55 mg, 0.24 mmol) and p-toluidine (21.4 mg, 0.2 mmol). The crude product was purified with silica gel chromatography (PE/EA = 10:1) to afford **26** (38.3 mg) in 75% yield. [20]

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43 (d, *J* = 7.8 Hz, 2H), 7.13 (d, *J* = 8.1 Hz, 2H), 7.09 – 7.01 (m, 4H), 5.68 (s, 1H), 2.35 (s, 3H), 0.29 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 144.69, 139.76, 134.59, 131.30, 130.44, 129.92, 119.41, 115.75, 20.80, -0.74.

4-(tert-butyl)-N-(p-tolyl) aniline (27)



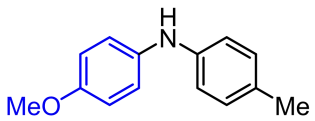
27

According to **GPB**, generated from 1-bromo-4-tert-butylbenzene (52 mg, 0.24 mmol) and p-toluidine (21.4 mg, 0.2 mmol). The crude product was purified with silica gel chromatography (PE/EA = 10:1) to afford **27** (27.8 mg) in 58% yield.[21]

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31 (d, *J* = 8.6 Hz, 2H), 7.11 (d, *J* = 8.0 Hz, 2H), 7.06 – 6.98 (m, 4H), 5.57 (s, 1H), 2.33 (s, 3H), 1.35 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 143.46, 141.18, 140.89, 130.34, 129.86, 126.15, 118.18, 117.13, 34.17, 31.55, 20.73.

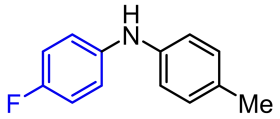
4-methoxy-N-(p-tolyl) aniline (28)



28

According to **GPB**, generated from 1-Bromo-4-tert-butylbenzene (47.3 mg, 0.24 mmol) and p-toluidine (21.4 mg, 0.2 mmol). The crude product was purified with silica gel chromatography (PE/EA = 10:1) to afford **28** (35 mg) in 82% yield.[22]
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.04 (dd, *J* = 7.2, 4.0 Hz, 4H), 6.86 (dd, *J* = 5.3, 2.6 Hz, 4H), 5.41 (s, 1H), 3.79 (s, 3H), 2.28 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 154.78, 142.39, 136.61, 129.79, 129.33, 121.12, 116.54, 114.66, 55.63, 20.62.

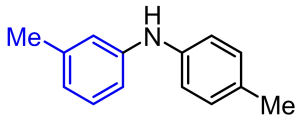
4-fluoro-N-(p-tolyl) aniline (29)



29

According to **GPB**, generated from 4-bromofluorobenzene (42 mg, 0.24 mmol) and p-toluidine (21.4 mg, 0.2 mmol). The crude product was purified with silica gel chromatography (PE/EA = 10:1) to afford **29** (39.4 mg) in 98% yield.[23]
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.09 (d, *J* = 8.1 Hz, 2H), 7.02 – 6.96 (m, 4H), 6.93 (d, *J* = 8.3 Hz, 2H), 5.49 (s, 1H), 2.32 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 157.63 (d, $^1J_{CF}$ = 239.4 Hz), 141.10, 139.8, 130.50, 130.01, 119.38 (d, $^3J_{CF}$ = 7.0 Hz), 117.87, 115.89 (d, $^2J_{CF}$ = 23.2 Hz), 20.87.
^{19}F NMR (377 MHz, $CDCl_3$): δ -123.05.

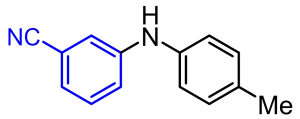
3-methyl-N-(p-tolyl) aniline (30)



30

According to **GPB**, generated from 3-bromotoluene (41 mg, 0.24 mmol) and p-toluidine (21.4 mg, 0.2 mmol). The crude product was purified with silica gel chromatography (PE/EA = 10:1) to afford **30** (32.7 mg) in 83% yield.[24]
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.16 (d, *J* = 5.9 Hz, 1H), 7.11 (dd, *J* = 7.3, 5.2 Hz, 2H), 7.02 (t, *J* = 5.8 Hz, 2H), 6.85 (t, *J* = 5.6 Hz, 2H), 6.77 – 6.71 (m, 1H), 5.58 (s, 1H), 2.32 (d, *J* = 4.5 Hz, 6H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 143.91, 140.38, 139.22, 130.74, 129.88, 129.19, 121.21, 118.94, 117.52, 113.99, 21.60, 20.74.

3-(p-tolylamino) benzonitrile (31)



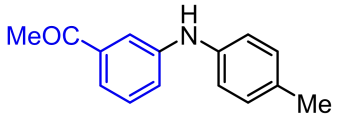
31

According to **GPB**, generated from 3-bromobenzonitrile (43.7 mg, 0.24 mmol) and p-toluidine (21.4 mg, 0.2 mmol). The crude product was purified with silica gel chromatography (PE/EA = 5:1) to afford **31** (39.5 mg) in 95% yield.[25]

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28 (t, *J* = 7.9 Hz, 1H), 7.16 (dd, *J* = 16.0, 8.0 Hz, 4H), 7.08 (d, *J* = 7.5 Hz, 1H), 7.03 (d, *J* = 8.1 Hz, 2H), 5.83 (s, 1H), 2.35 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 145.36, 138.23, 133.10, 130.22, 130.01, 122.89, 120.81, 119.83, 119.20, 117.93, 113.01, 20.87.

1-(3-(p-tolylamino) phenyl) ethan-1-one (32)



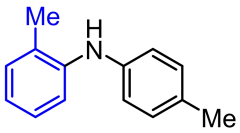
32

According to **GPB**, generated from 3-bromoacetophenones (47.8 mg, 0.24 mmol) and p-toluidine (21.4 mg, 0.2 mmol). The crude product was purified with silica gel chromatography (PE/EA = 5:1) to afford **32** (43.7 mg) in 97% yield.[26]

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58 (s, 1H), 7.43 (d, *J* = 7.6 Hz, 1H), 7.31 (t, *J* = 7.8 Hz, 1H), 7.20 (d, *J* = 9.1 Hz, 1H), 7.12 (d, *J* = 8.1 Hz, 2H), 7.03 (d, *J* = 8.2 Hz, 2H), 5.84 (s, 1H), 2.57 (s, 3H), 2.33 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 198.45, 144.66, 139.47, 138.29, 131.90, 130.06, 129.50, 120.86, 120.11, 119.57, 115.58, 26.70, 21.13.

2-methyl-N-(p-tolyl) aniline (33)



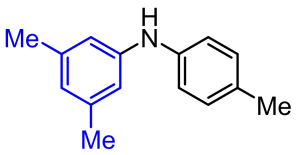
33

According to **GPB**, generated from 2-bromotoluene (41 mg, 0.24 mmol) and p-toluidine (21.4 mg, 0.2 mmol). Prepared at 50 °C, the crude product was purified with silica gel chromatography (PE/EA = 10:1) to afford **33** (22.5 mg) in 57% yield.[27]

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.20 (d, *J* = 8.0 Hz, 2H), 7.13 (dd, *J* = 14.7, 7.6 Hz, 3H), 6.92 (dd, *J* = 20.5, 7.8 Hz, 3H), 5.32 (s, 1H), 2.33 (s, 3H), 2.28 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 142.08, 141.01, 130.88, 130.51, 129.88, 126.97, 126.79, 121.06, 118.70, 117.14, 20.84, 17.89.

3,5-dimethyl-N-(p-tolyl) aniline (34)



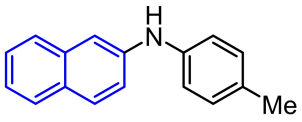
34

According to **GPB**, generated from 5-bromo-m-xylene (45.1 mg, 0.24 mmol) and p-toluidine (21.4 mg, 0.2 mmol). Prepared at 50 °C, the crude product **34** was purified with silica gel chromatography (PE/EA = 10:1) to afford (30 mg) in 71% yield.[28]

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.12 (d, *J* = 7.2 Hz, 2H), 7.02 (d, *J* = 6.8 Hz, 2H), 6.68 (s, 2H), 6.58 (s, 1H), 5.55 (s, 1H), 2.34 (s, 3H), 2.29 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 143.92, 140.46, 139.07, 130.74, 129.87, 122.23, 119.03, 114.65, 21.50, 20.77.

N-(p-tolyl) naphthalen-2-amine (35)



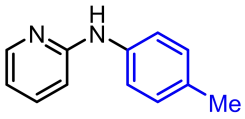
35

According to **GPB**, generated from 1-bromonaphthalene (49.7 mg, 0.24 mmol) and p-toluidine (21.4 mg, 0.2 mmol). The crude product was purified with silica gel chromatography (PE/EA = 8:1) to afford **35** (42.9 mg) in 92% yield.[29]

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79 – 7.73 (m, 2H), 7.65 (d, *J* = 8.2 Hz, 1H), 7.42 (dd, *J* = 15.2, 7.3 Hz, 2H), 7.32 (t, *J* = 7.4 Hz, 1H), 7.22 – 7.10 (m, 5H), 5.78 (s, 1H), 2.38 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 141.77, 140.15, 134.76, 131.42, 130.02, 129.20, 128.89, 127.70, 126.48, 126.42, 123.23, 119.63, 119.37, 110.25, 20.84.

N-(p-tolyl) pyridin-2-amine (36)



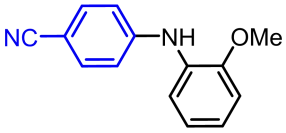
36

According to **GPB**, generated from p-bromotoluene (41 mg, 0.24 mmol) and 2-aminopyridine (18.8 mg, 0.2 mmol). The crude product was purified with silica gel chromatography (PE/EA = 5:1) to afford **36** (33.1 mg) in 90% yield.[20]

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.18 (d, *J* = 4.2 Hz, 1H), 7.46 (t, *J* = 8.5 Hz, 1H), 7.21 (d, *J* = 8.3 Hz, 2H), 7.14 (d, *J* = 8.2 Hz, 2H), 6.82 (d, *J* = 8.4 Hz, 1H), 6.72 – 6.67 (m, 1H), 2.33 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 156.63, 148.39, 137.78, 137.68, 132.81, 129.86, 121.29, 114.60, 107.69, 20.84.

4-((2-methoxyphenyl) amino) benzonitrile (37)



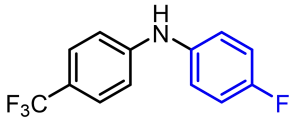
37

According to **GPB**, generated from 4-bromobenzonitrile (43.7 mg, 0.24 mmol) and o-anisidine (24.6 mg, 0.2 mmol). The crude product was purified with silica gel chromatography (PE/EA = 5:1) to afford **37** (40.8 mg) in 91% yield.[30]

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49 (d, *J* = 8.6 Hz, 2H), 7.36 (d, *J* = 7.5 Hz, 1H), 7.05 (dd, *J* = 13.4, 8.2 Hz, 3H), 6.95 (t, *J* = 7.2 Hz, 2H), 6.35 (s, 1H), 3.88 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 150.04, 147.52, 133.69, 129.51, 123.29, 120.75, 120.04, 118.76, 115.48, 111.09, 101.53, 55.65.

4-fluoro-N-(4-(trifluoromethyl) phenyl) aniline (38)



38

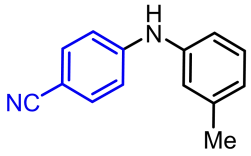
According to **GPB**, generated from 4-bromofluorobenzene (42 mg, 0.24 mmol) and 4-aminobenzotrifluoride (32.2 mg, 0.2 mmol). The crude product was purified with silica gel chromatography (PE/EA = 10:1) to afford **38** (36.7 mg) in 72% yield. [31]

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54 (d, *J* = 8.5 Hz, 2H), 7.42 – 7.36 (m, 2H), 7.35 – 7.31 (m, 1H), 7.26 (d, *J* = 6.1 Hz, 1H), 7.12 (d, *J* = 8.5 Hz, 2H), 6.15 (s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 159.14 (d, *J* = 247.5 Hz), 147.54, 136.98 (d, $^3J_{CF}$ = 2.7 Hz), 126.76 (q, $^3J_{CF}$ = 3.7 Hz), 124.63 (d, $^1J_{CF}$ = 270.6 Hz), 123.11 (d, $^3J_{CF}$ = 8.0 Hz), 121.42 (d, $^2J_{CF}$ = 32.6 Hz), 116.28 (d, $^2J_{CF}$ = 22.6 Hz), 114.57.

^{19}F NMR (377 MHz, $CDCl_3$): δ -61.35, -118.98.

4-(m-tolylamino) benzonitrile (39)



39

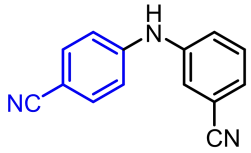
According to **GPB**, generated from 4-bromobenzonitrile (43.7 mg, 0.24 mmol) and m-toluidine (21.4 mg, 0.2 mmol). The crude product was purified with silica gel chromatography (PE/EA = 5:1) to afford **39** (31.2 mg) in 75% yield. m.p. = 90.3-91.5 ℃.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46 (d, *J* = 8.6 Hz, 2H), 7.24 (t, *J* = 8.0 Hz, 1H), 7.00 – 6.91 (m, 5H), 6.17 (s, 1H), 2.35 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 148.16, 139.91, 139.67, 133.79, 129.46, 124.83, 121.91, 120.08, 118.29, 114.90, 101.20, 21.42.

HRMS (ESI) (*m/z*): calcd. for $C_{14}H_{13}N_2$ $[M+H]^+$: 209.1073, found: 209.1066

3-((4-cyanophenyl) amino) benzonitrile (40)



40

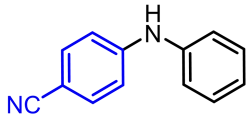
According to **GPB**, generated from 4-bromobenzonitrile (43.7 mg, 0.24 mmol) and 3-aminobenzonitrile (23.6 mg, 0.2 mmol). The crude product was purified with silica gel chromatography (PE/EA = 4:1) to afford **40** (37.2 mg) in 85% yield. m.p. = 332.1-333.4 ℃.

^{1}H NMR (400 MHz, DMSO_D$_6$): δ 9.20 (s, 1H), 7.66 (d, *J* = 8.6 Hz, 2H), 7.51 (dd, *J* = 12.5, 5.5 Hz, 3H), 7.41 (d, *J* = 6.8 Hz, 1H), 7.17 (d, *J* = 8.7 Hz, 2H).

^{13}C NMR (101 MHz, DMSO_D$_6$): δ 147.32, 142.44, 134.27, 131.24, 125.74, 123.98, 121.73, 120.13, 119.17, 116.17, 112.73, 101.27.

HRMS (ESI) (*m/z*): calcd. for $C_{14}H_8N_3$ [M-H]$^-$: 218.0724, found: 218.0720.

4-(phenylamino)benzonitrile (41)



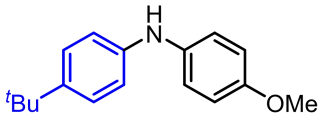
41

According to **GPB**, generated from 4-bromobenzonitrile (43.7 mg, 0.24 mmol) and aniline (18.6 mg, 0.2 mmol). The crude product was purified with silica gel chromatography (PE/EA = 5:1) to afford **41** (31.0 mg) in 80% yield.[32]

^{1}H NMR (400 MHz, CDCl$_3$): δ 7.49 (d, *J* = 8.4 Hz, 2H), 7.38 (t, *J* = 7.6 Hz, 2H), 7.20 (d, *J* = 8.0 Hz, 2H), 7.14 (t, *J* = 7.4 Hz, 1H), 7.01 (d, *J* = 8.5 Hz, 2H), 6.26 (s, 1H).

^{13}C NMR (101 MHz, CDCl$_3$): δ 148.10, 140.03, 133.80, 129.67, 123.95, 121.20, 120.09, 114.91, 101.26.

4-(tert-butyl)-N-(4-methoxyphenyl) aniline (42)



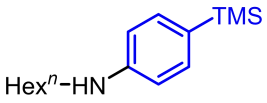
42

According to **GPA**, generated from 4-tert-butyl-1-chlorobenzene (40.5 mg, 0.24 mmol) and p-anisidine (24.6 mg, 0.2 mmol). The crude product **S-3** was purified with silica gel chromatography (PE/EA = 10:1) to afford **S-3** (11.2 mg) in 22% yield.[33]

According to **GPB**, generated from 1-bromo-4-tert-butylbenzene (52.1 mg, 0.24 mmol) and p-anisidine (24.6 mg, 0.2 mmol). The crude product was purified with silica gel chromatography (PE/EA = 10:1) to afford **42** (50.5 mg) in 99% yield.[33]

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29 (d, *J* = 8.7 Hz, 2H), 7.08 (d, *J* = 8.9 Hz, 2H), 6.91 (dd, *J* = 13.9, 8.8 Hz, 4H), 5.48 (s, 1H), 3.83 (s, 3H), 1.35 (s, 9H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 154.88, 142.70, 142.47, 136.41, 126.15, 121.44, 115.86, 114.69, 55.64, 34.11, 31.58.

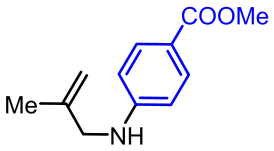
N-hexyl-4-(trimethylsilyl)aniline (43)



43

According to **GPB**, generated from 1-bromo-4-(trimethylsilyl) benzene (55 mg, 0.24 mmol) and 1-hexanamine (20.2 mg, 0.2 mmol). The crude product was purified with silica gel chromatography (PE/EA = 10:1) to afford **43** (47.9 mg) in 96% yield.[34]
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35 (d, *J* = 7.7 Hz, 2H), 6.63 (d, *J* = 7.9 Hz, 2H), 3.69 (s, 1H), 3.13 (t, *J* = 7.1 Hz, 2H), 1.62 (dd, *J* = 14.6, 7.3 Hz, 2H), 1.42 (dd, *J* = 14.0, 7.6 Hz, 2H), 1.37 – 1.31 (m, 4H), 0.92 (t, *J* = 6.4 Hz, 3H), 0.24 (s, 9H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 149.13, 134.55, 126.40, 112.24, 43.71, 31.69, 29.57, 26.88, 22.68, 14.10, -0.78.

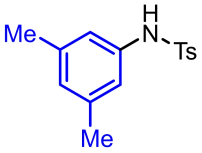
methyl 4-((2-methylallyl) amino) benzoate (44)



44

According to **GPB**, generated from methyl 4-bromobenzoate (52.3 mg, 0.24 mmol) and 2-methylallylamine (14.2 mg, 0.2 mmol). The crude product was purified with silica gel chromatography (PE/EA = 10:1) to afford **44** (28.7 mg) in 70% yield.[35]
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 (d, *J* = 8.7 Hz, 2H), 6.55 (d, *J* = 8.7 Hz, 2H), 4.91 (d, *J* = 15.6 Hz, 2H), 3.84 (s, 3H), 3.73 (s, 2H), 1.78 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 167.33, 152.17, 141.46, 131.49, 118.29, 111.75, 111.31, 51.45, 48.98, 20.37.

N-(3,5-dimethylphenyl)-4-methylbenzenesulfonamide (45)



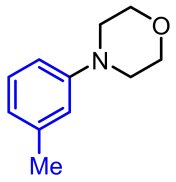
45

According to **GPB**, generated from 5-bromo-m-xylene (45.1 mg, 0.24 mmol) and p-toluenesulfonamide (34.2 mg, 0.2 mmol). The crude product was purified with silica gel chromatography (PE/EA = 8:1) to afford **45** (51.2 mg) in 93% yield.[36]

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72 (d, *J* = 8.3 Hz, 2H), 7.21 (d, *J* = 8.0 Hz, 2H), 6.71 (d, *J* = 8.9 Hz, 3H), 2.36 (s, 3H), 2.20 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 143.71, 138.98, 136.53, 136.27, 129.61, 127.30, 126.79, 118.77, 21.52, 21.23.

4-(m-tolyl) morpholine (46)



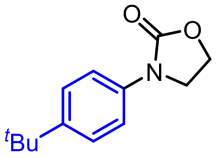
46

According to **GPB**, generated from 3-bromotoluene (41 mg, 0.24 mmol) and morpholine (16.4 mg, 0.2 mmol). The crude product was purified with silica gel chromatography (PE/EA = 10:1) to afford **46** (25.5 mg) in 72% yield.[37]

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.19 (t, *J* = 7.6 Hz, 1H), 6.77 – 6.71 (m, 3H), 3.90 – 3.86 (m, 4H), 3.19 – 3.14 (m, 4H), 2.34 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 151.40, 138.95, 129.07, 121.06, 116.63, 112.94, 67.01, 49.52, 21.82.

3-(4-(tert-butyl) phenyl) oxazolidin-2-one (47)



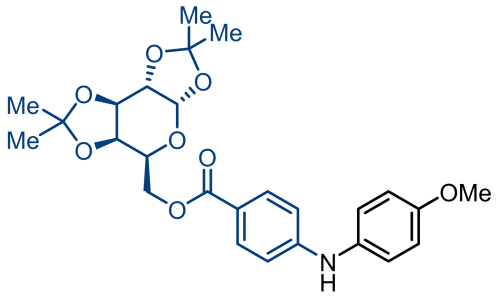
47

According to **GPB**, generated from 1-bromo-4-tert-butylbenzene (52.1 mg, 0.24 mmol) and 2-Oxazolidone (17.4 mg, 0.2 mmol). The crude product was purified with silica gel chromatography (PE/EA = 5:1) to afford **47** (37.3 mg) in 85% yield.[38]

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45 (d, *J* = 8.8 Hz, 2H), 7.39 (d, *J* = 8.8 Hz, 2H), 4.45 (t, *J* = 8.6 Hz, 2H), 4.03 (t, *J* = 8.0 Hz, 2H), 1.31 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 155.48, 147.12, 135.65, 125.94, 118.16, 61.38, 45.33, 34.35, 31.35.

(2,2,7,7-tetramethyltetrahydro-5H-bis ([1,3] dioxolo) [4,5-b:4',5'-d] pyran-5-yl) methyl 4-((4-methoxyphenyl) amino) benzoate (48)



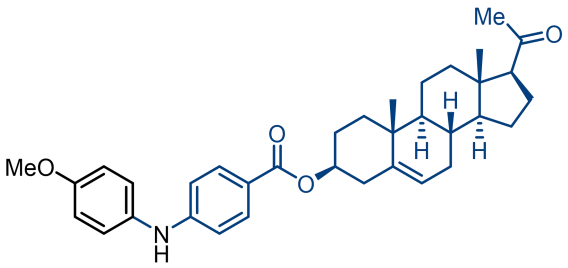
According to **GPA**, generated from (2,2,7,7-tetramethyltetrahydro-5H-bis ([1,3] dioxolo) [4,5-b:4',5'-d] pyran-5-yl) methyl 4-chlorobenzoate (47.9 mg, 0.12 mmol) and p-Anisidine (12.3 mg, 0.1 mmol), stiring at 80 °C for 48h. The crude product was purified with silica gel chromatography (PE/EA = 6:1) to afford **48** (29.6 mg) in 61% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88 (d, *J* = 8.7 Hz, 2H), 7.13 (d, *J* = 8.8 Hz, 2H), 6.90 (d, *J* = 8.8 Hz, 2H), 6.80 (d, *J* = 8.7 Hz, 2H), 5.84 (s, 1H), 5.56 (d, *J* = 4.9 Hz, 1H), 4.64 (dd, *J* = 7.9, 2.3 Hz, 1H), 4.49 (dd, *J* = 11.4, 5.0 Hz, 1H), 4.35 (dt, *J* = 14.1, 8.2 Hz, 2H), 4.16 (t, *J* = 6.0 Hz, 1H), 3.82 (s, 3H), 1.51 (s, 3H), 1.47 (s, 3H), 1.35 (s, 3H), 1.33 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 166.36, 156.58, 149.89, 133.43, 131.70, 124.45, 119.93, 114.79, 113.23, 109.64, 108.79, 96.35, 71.20, 70.75, 70.60, 66.29, 63.30, 55.55, 26.05, 25.99, 25.01, 24.51.

HRMS (ESI) (*m/z*): calcd. for $C_{26}H_{32}NO_8$ $[M+H]^+$: 485.2122, found: 486.2125

(3S,8S,9S,10R,13S,14S,17S)-17-acetyl-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl4-((4-methoxyphenyl)amino)benzoate (49)



According to **GPA**, generated from (3S,8S,9S,10R,13S,14S,17S)-17-acetyl-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl 4-chlorobenzoate (109 mg, 0.24 mmol) and p-Anisidine (24.6 mg, 0.2 mmol)，stiring at 80 °C for 48h. The crude product was purified with silica gel chromatography (PE/EA = 6:1) to afford **49** (96.4 mg) in 89% yield .

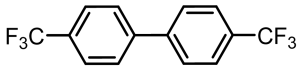
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87 (d, *J* = 8.7 Hz, 2H), 7.12 (d, *J* = 8.8 Hz, 2H), 6.88 (d, *J* = 8.8 Hz, 2H), 6.81 (d, *J* = 8.7 Hz, 2H), 5.98 (s, 1H), 5.39 (d, *J* = 4.3 Hz, 1H), 4.86 – 4.75 (m, 1H), 3.80 (s, 3H), 2.53 (t, *J* = 8.8 Hz, 1H), 2.44 (d, *J* = 6.0 Hz,

2H), 2.23 – 2.09 (m, 4H), 2.07 – 1.86 (m, 4H), 1.73 – 1.57 (m, 5H), 1.53 – 1.40 (m, 3H), 1.29 – 1.13 (m, 4H), 1.05 (d, J = 4.9 Hz, 3H), 0.63 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 209.68, 166.06, 156.43, 149.73, 139.89, 133.60, 131.48, 124.21, 122.25, 120.56, 114.76, 113.25, 73.76, 63.70, 56.85, 55.54, 49.92, 44.01, 38.82, 38.32, 37.09, 36.68, 31.86, 31.80, 31.56, 27.97, 24.50, 22.85, 21.07, 19.39, 13.23.

HRMS (ESI) (*m/z*): calcd. for $C_{35}H_{42}NO_4$ $[M-H]^-$: 540.3119, found: 540.3156

4,4'-bis(trifluoromethyl)-1,1'-biphenyl (S-4)



S-4

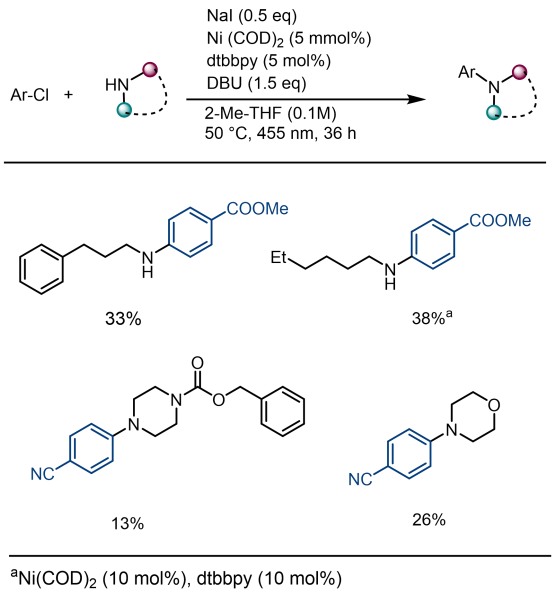
In an argon-filled glovebox, a flame-dried 10 mL sealing tube equipped with a Teflon septum and magnetic stir bar was charged with 4-Iodobenzotrifluoride (0.4 mmol)，$Pd(OAc)_2$ (1 mol%, 0.5 mg) and Cs_2CO_3 (0.4 mmol), indene (0.4 mmol) and DMF (3 mL), and sealed with a screwed cap, the sealed tube was taken out of the glove box. The resulting mixture was stirred for 10 min at room temperature, and then placed in a pre-heated oil bath at 90 °C stirring for 24 h. After the reaction was completed, ethyl acetate and water were added and extracted in a separatory funnel. The combined organic layers were dried over anhydrous Na_2SO_4, concentrated in vacuo to give crude, The crude product was purified by silica gel column chromatography to afford the corresponding product.[39]

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76 – 7.69 (m, 8H).

^{19}F NMR (377 MHz, $CDCl_3$): δ -62.56.

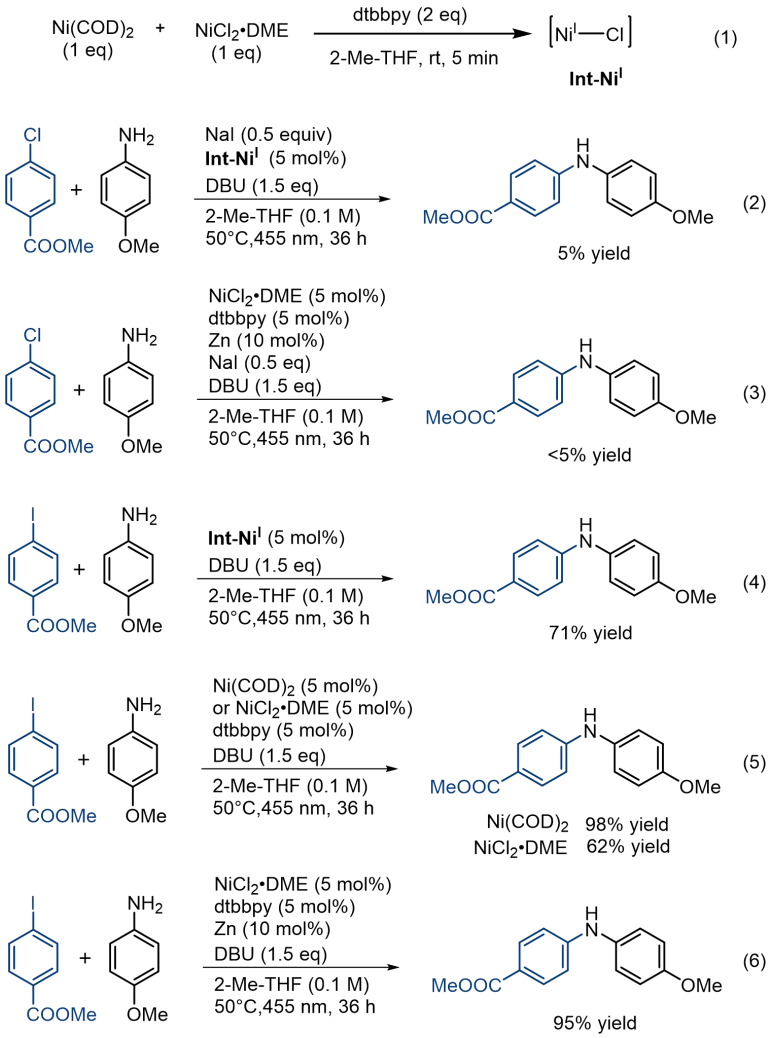
3.5 Extended substrate scope

Table S2. Extended scope of primary and secondary amines



[a]$Ni(COD)_2$ (10 mol%), dtbbpy (10 mol%)

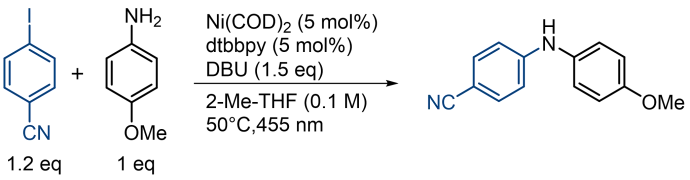
4. Mechanism studies



Scheme S1 C-N cross-couplings with different nickel sources as precatalysts

Results and Comments: Variants of nickel source including Ni(0), Ni(I), and Ni(II) almost did not change the reactivity of the coupling process when using the aryl iodides as coupling partners. However, only Ni(0) species are suitable for achieving C-N coupling using aryl chlorides as coupling partners. Based on these results, Ni(0) species is really important to activate the relative inert aryl chloride, possibly ascribe to Ni(0) favor rapid oxidative addition step to initiate the reaction.(see the part of **Theoretical calculations**) The Ni^{I} complex prepared in-situ or ex-situ was not very efficient.

Uv-vis and NMR spectra analysis



Experimental Procedure C: In an argon-filled glovebox, a flame-dried 10 mL sealing tube equipped with a Teflon septum and magnetic stir bar was charged with Ni $(COD)_2$ (0.005 mmol, 1.4 mg), 4,4'-di-*tert*-butyl-2,2'-bipyridyl (0.005 mmol, 1.8 mg), and 0.5 mL 2-Me-THF was added, the mixture was stirred for 10 min at room temperature, followed by adding *p*-Anisidine (0.1 mmol, 12.3 mg), DBU (0.15 mmol, 22.7 mg), 4-Iodobenzonitrile (0.12 mmol, 27.5 mg) and 0.5 mL 2-Me-THF in sequence, and sealed with a screwed cap. The sealed tube was taken out of the glove box. Then it was placed in a photo-reactor under blue LEDs irradiation (455 nm, 10 W) or in dark at 50 °C for different time to determine the yield and Uv-vis spectra.

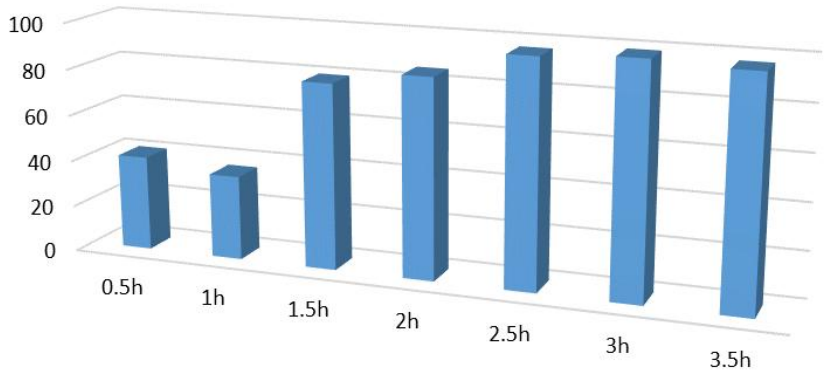


Fig. S1 The yield of coupling products at different stage

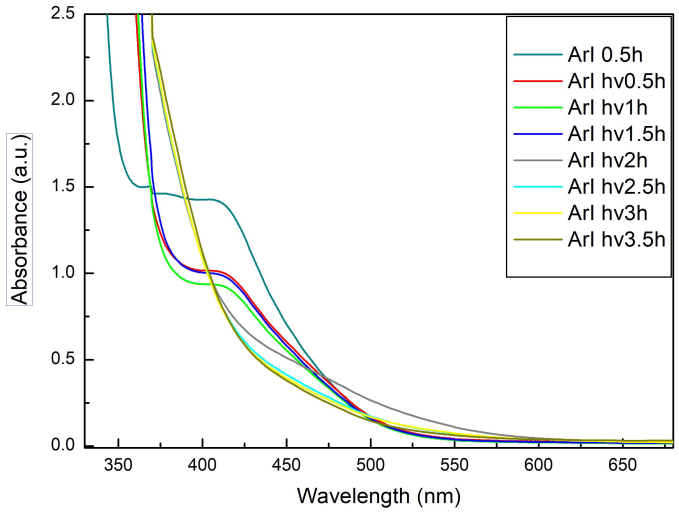
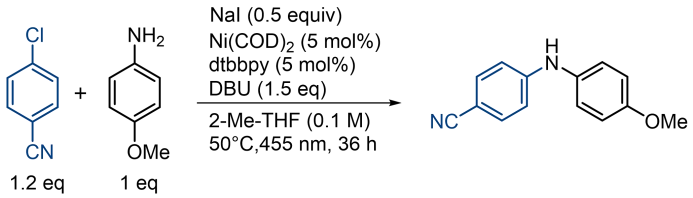


Fig. S2 Uv-vis spectra (3.90×10^{-4} M based on nickel concentration, 1 mm pathlength quartz cuvette) in 2-Me-THF

Results and Comments: The aryl-Ni^{II}-I is always observed by the Uv-vis spectroscopy in 1.5 h and around 80% coupling product was obtained, indicating the *Ni^{II} might be the activated specie for yielding the coupling product via reductive elimination. With the almost consumption of the aniline substrates, the absorption of MLCT excited-state aryl-Ni^{II}-I at 410 nm disappears, which suggests the aryl-Ni^{II}-I is not stable, and start to decompose to generate the possible Ni^{I} specie when the nucleophile was almost consumed.



Experimental Procedure D: In an argon-filled glovebox, a flame-dried 10 mL sealing tube equipped with a Teflon septum and magnetic stir bar was charged with Ni $(COD)_2$ (0.005 mmol, 1.4 mg, 5 mol%), 4,4'-di-tert-butyl-2,2'-bipyridyl (0.005 mmol, 1.8 mg, 5 mol%), and 0.5 mL 2-Me-THF. The resulting mixture was stirred for 10 min at room temperature, followed by adding *p*-anisidine (0.1 mmol, 12.3 mg), NaI (0.05 mmol, 7.5 mg), DBU (0.15 mmol, 22.7 mg), 4-Chlorobenzonitrile (0.12 mmol, 16.5 mg) and 0.5 mL 2-Me-THF in sequence, and sealed with a screwed cap. The sealed tube was taken out of the glove box. It was placed in a photo-reactor under irradiation of blue LEDs (455 nm, 10 W) and kept stirring at 50 °C at different time for Uv-vis analysis or determination of yield by ^{1}H NMR using 1,3,5-methoxy benzene as the internal standard.

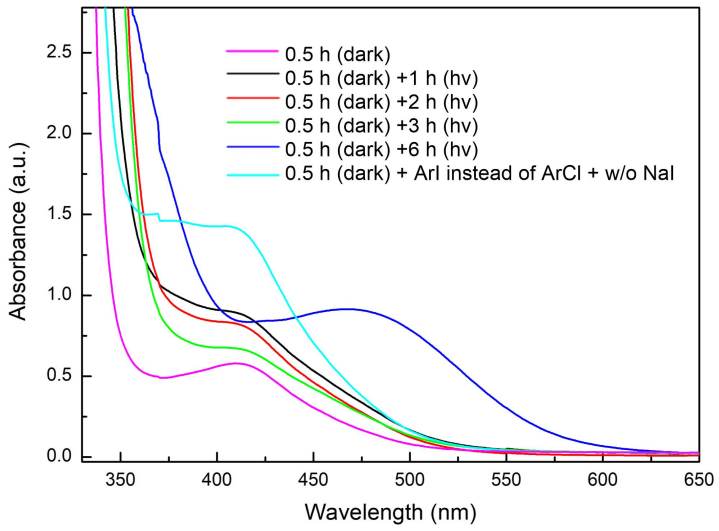


Fig. S3 Uv-vis spectra (3.90×10^{-4} M based on nickel concentration,

1 mm pathlength quartz cuvette) in 2-Me-THF

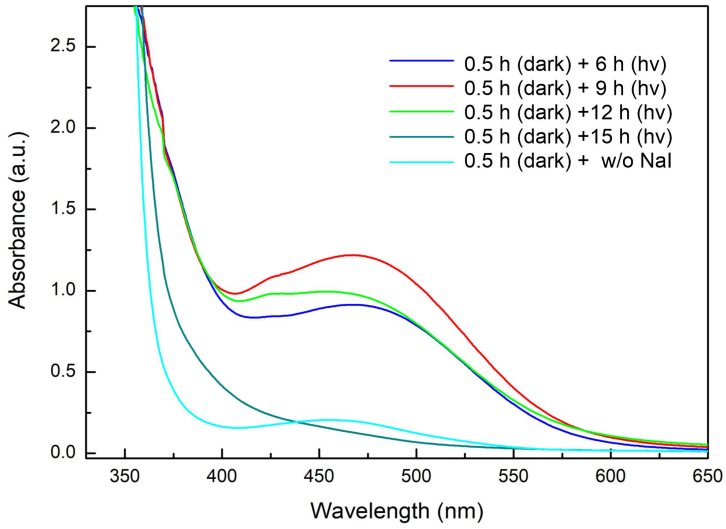


Fig. S4 Uv-vis spectra (3.90 ×10^{-4} M based on nickel concentration, 1 mm pathlength quartz cuvette) in 2-Me-THF

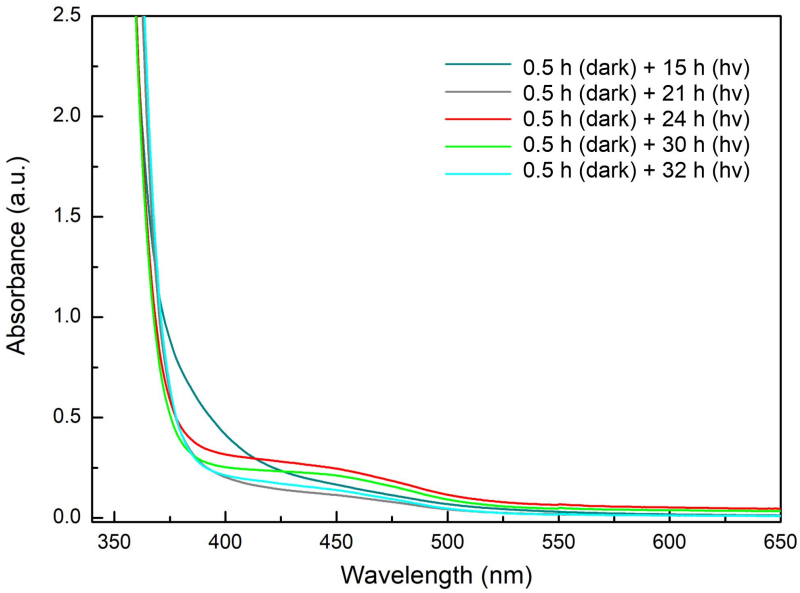


Fig. S5 Uv-vis spectra (3.90 ×10^{-4} M based on nickel concentration, 1 mm pathlength quartz cuvette) in 2-Me-THF

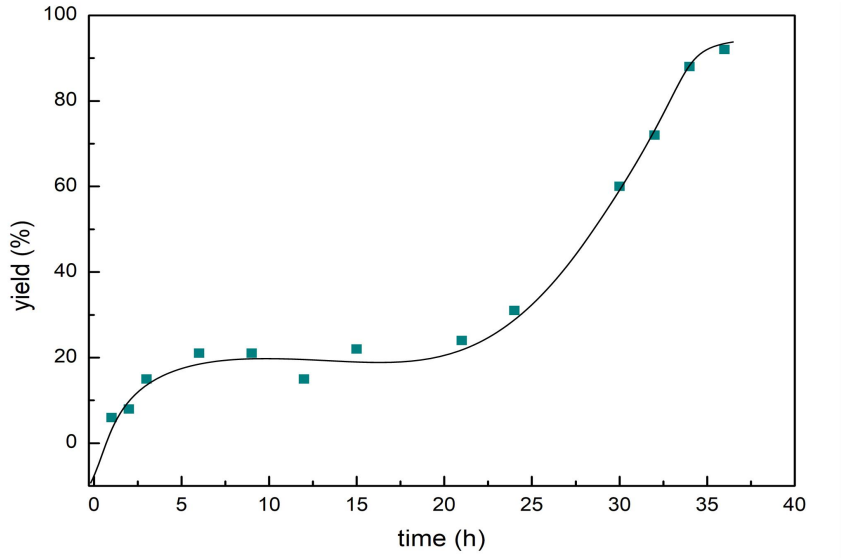
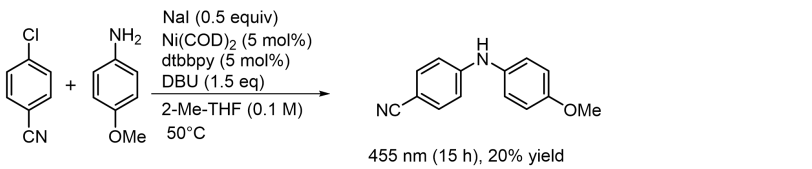


Fig. S6 The relationship of the reaction time and yield

Results and Comments: The absorption at 410 nm was always observed at least last for 3 h (Fig. S3) , which support the formation of aryl-Ni^{II}-I specie via halogen exchange from aryl-Ni^{II}-Cl that showed the absorption at 470 nm (the light blue curve in Fig. S3). At this stage, the aryl-Ni-I might undergo ligand exchange, and reductive elimination to release the Ni(0) and C-N coupling product. With the consumption of sodium iodide, the sodium cation decreased and the chloride anion increased, which lead to slow halogen exchange on the aryl-Ni-Cl complex, and absorption at 470 nm increased. At the period of 6-12 h, might be the formation of the aryl-Ni-amido complex was inhibited too, leading to almost shut down the coupling process via reductive elimination on MLCT excited-state aryl-Ni^{II}-amido complex (Fig. S4). Accumulated the aryl-Ni-Cl was exposed on 455 nm blue LEDs for several hours, resulting in decomposition to form enough active momo-Ni^{I} species. The expected momo-active Ni^{I} specie showed good reactivity for coupling reaction (15-32 h in Fig. S5 & S6), which might need the help of iodide anion for further ligand exchange to from the aryl-Ni^{III}-amido for generation of coupled product because the reaction mixture without sodium iodide did not form product. The calculation also showed the oxidation addition of Ni^{I} species is not thermally stable. (see the part of **Theoretical calculations**)

Light-dark experiments



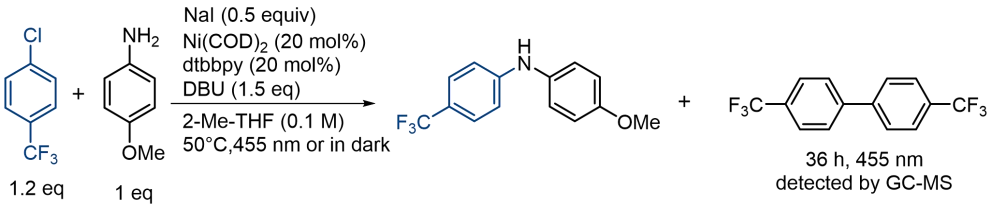
455 nm (15 h), 20% yield
455 nm (15 h) + dark (1 h), 20% yield
455 nm (15 h) + dark (1 h) + 455 nm (21 h), 20% yield

455 nm (15 h), 20% yield
455 nm (15 h) + dark (0.5 h), 20% yield
455 nm (15 h) + dark (0.5 h) + 455 nm (21 h), 20% yield

Experimental Procedure E:
In an argon-filled glovebox, a flame-dried 10 mL sealing tube equipped with a Teflon septum and magnetic stir bar was charged with Ni $(COD)_2$ (0.005 mmol, 1.4 mg, 5 mol%), 4,4'-Di-tert-butyl-2,2'-bipyridyl (0.005 mmol, 1.8 mg, 5 mol%), and 0.5 mL 2-Me-THF was added, the mixture was stirred for 10 min at room temperature, followed by adding *p*-Anisidine (0.1 mmol, 12.3 mg), NaI (0.05 mmol, 7.5 mg), DBU (0.15 mmol, 22.7 mg), 4-Chlorobenzonitrile (0.12 mmol, 16.5 mg) and 0.5 mL 2-Me-THF in sequence, and sealed with a screwed cap. The sealed tube was taken out of the glove box. It was placed in a photo-reactor under irradiation of blue LEDs (455 nm, 10 W) and kept stirring at 50 °C for 15 h. After that, the mixture was stirred in dark for 0.5 h or 1 h, followed by 455 nm blue LEDs irradiation for 21 h. The ^{1}H NMR yield was obtained as showed using 1,3,5-trimethoxy benzene as the internal standard.

Results and Comments: These data showed the active intermediate was not stable in the mixture in absence of light. We anticipated that the ligand exchange of Ni^{III} dihalides complex required visible-light irradiation, otherwise the reversible reductive elimination would occur to form Ni^{I}-complex. The accumulated Ni^{I}-complex would loss the reactivity by dimerization.

^{19}F-NMR analysis



Experimental Procedure F: In an argon-filled glovebox, a flame-dried 10 mL sealing tube equipped with a Teflon septum and magnetic stir bar was charged with Ni $(COD)_2$ (0.02 mmol, 5.5 mg), 4,4'-Di-tert-butyl-2,2'-bipyridyl (0.02 mmol, 7.2 mg), and 0.5 mL 2-Me-THF. The resulting mixture was stirred for 10 min at room temperature, followed by adding p-Anisidine (0.1 mmol, 12.3 mg), DBU (0.15 mmol, 22.7 mg), 4-Chlorobenzotrifluoride (0.12 mmol, 21.7 mg) and 0.5 mL 2-Me-THF in sequence, and sealed with a screwed cap. The sealed tube was taken out of the glove box. It was kept stirring in darkness for 0.5 h. Then it was placed in a photo-reactor under irradiation of blue LEDs (455 nm, 10 W) at 50°C for different time as the spectra showed.

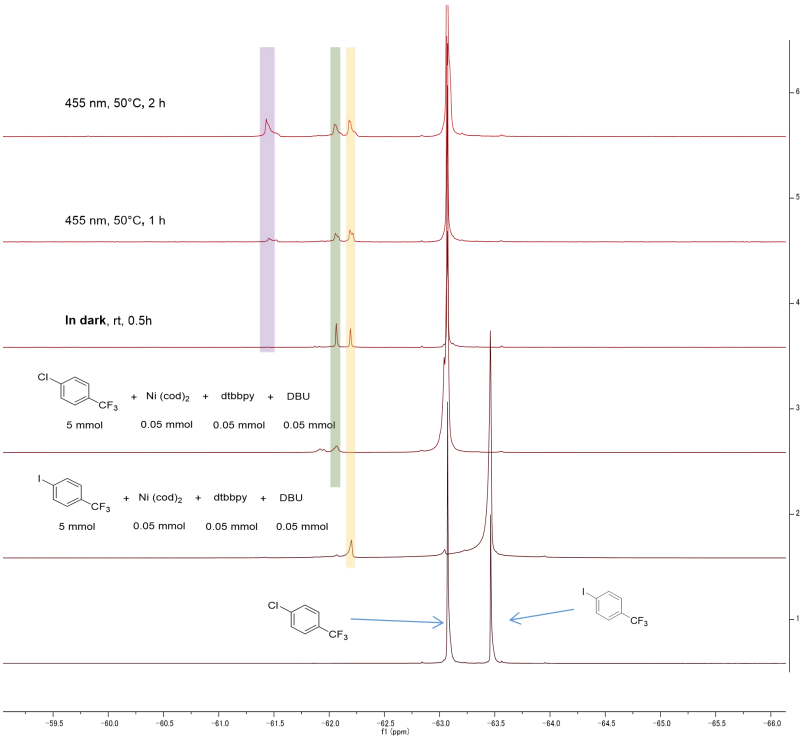


Fig. S7 ^{19}F-NMR spectra of the reaction mixture, 4-chlorobenzotrifluoride, 4-iodobenzotrifluoride and the aryl-Ni^{II}-halide generated in situ

Results and Comments: The reaction mixture showed aryl-Ni^{II}-Cl (green band) and aryl-Ni^{II}-I (yellow band) were formed. The aryl-Ni^{II}-I gradually increased via halogen exchange from aryl-Ni^{II}-Cl, which is accompanied with generation of coupled product.

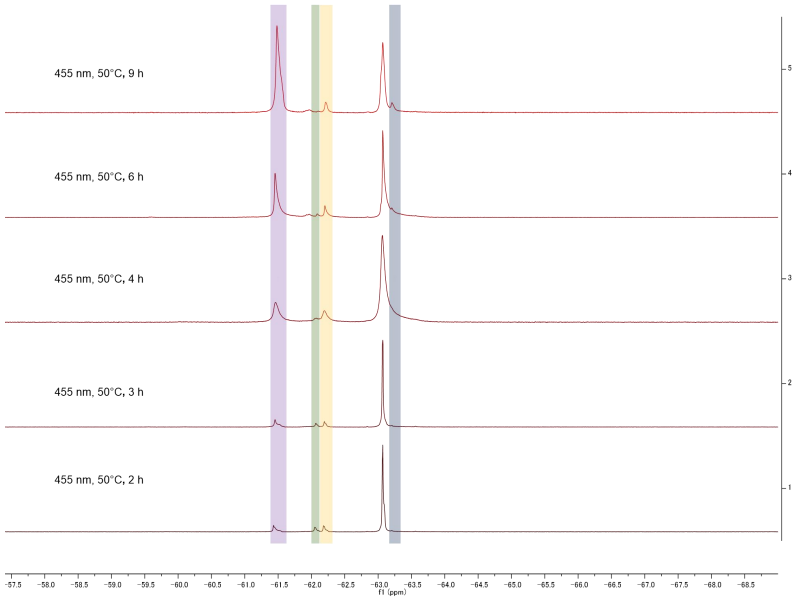


Fig. S8 ^{19}F-NMR spectra of the reaction mixture (2-9 h)

Results and Comments: Aryl-Ni^{II}-I (yellow band) almost did not change, but the

aryl-Ni^{II}-Cl gradually discomposed with a new fluoro-peak (gray band) gradually generated, which was supposed to be a new nickel specie. At this stage, the coupled product generated rapidly when the supposed Ni^{III} specie showed up, indicating that the active mom-nickel specie was generated in this stage for coupling.

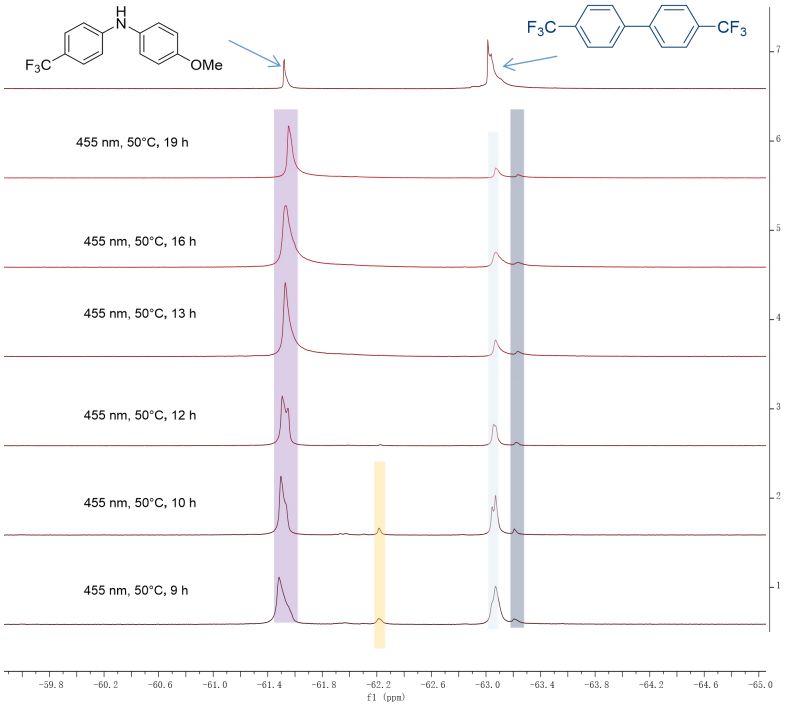


Fig. S9 ^{19}F-NMR spectra of the reaction mixture (9-19 h) and pre-prepared cross-coupling and homo-coupling products

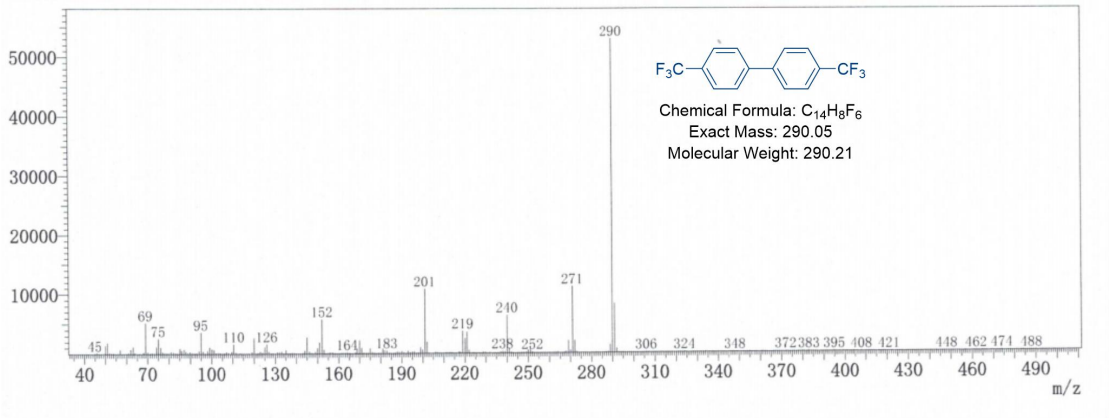


Fig. S10 The homo-coupling product detected by GC-MS

Results and Comments: Even the aryl-Ni^{II}-I (yellow band) disppearred after 12 h, but the product was still growing. The reaction mixture was subjected to GC-MS, the homo-coupling (molecular weight is 290) was detected. Therefore, we postulated the mono-Ni^{I} is one of active species.

Proposed mechanism

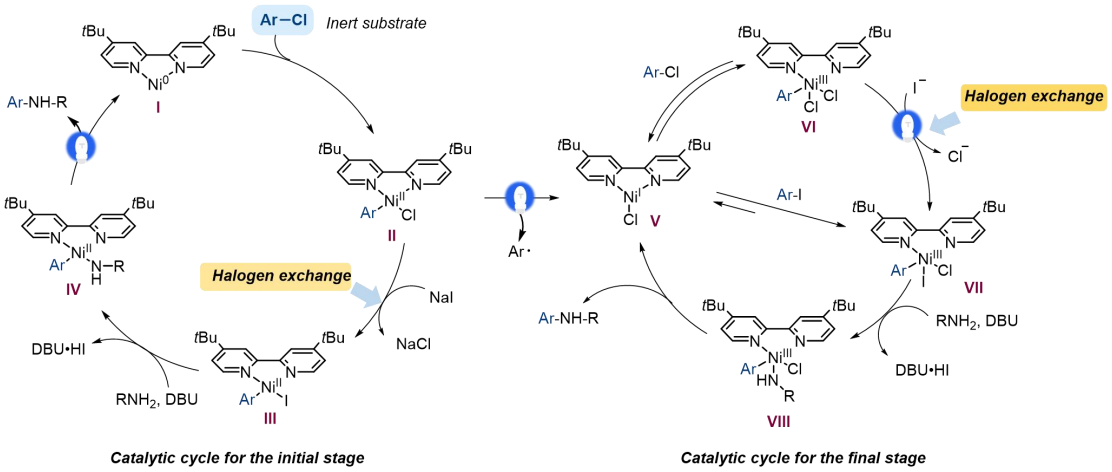


Fig. S11 The proposed catalytic cycle for the whole process

Based on the experimental results and Uv-vis analysis, the mechanism was tentatively proposed in Fig. S11. At the initial stage, the aryl-Ni^{II}-Cl specie **II** can undergo halogen exchange to precipitate the sodium chloride, ligand exchange to form aryl-Ni^{II}-amido complexe **IV**, and reductive elimination via MLCT-excited-state of **IV** to form the final coupling product. With the consumption of sodium iodides, the less reactivity of aryl-Ni^{II}-Cl specie for ligand exchange is gradually accumulated. The aryl-Ni^{II}-Cl might undergo the homolysis of the aryl-Ni^{II} bond to form the active monomer Ni^{I} specie **V**, oxidative addition to ArCl, and halogen exchange to form activated Ni^{III} specie **VII**, followed by ligand exchange and reductive elimination to afford the complex **V** and final coupling product. The light is supposed to be a significant factor for promoting the halogen exchange and ligand exchange.

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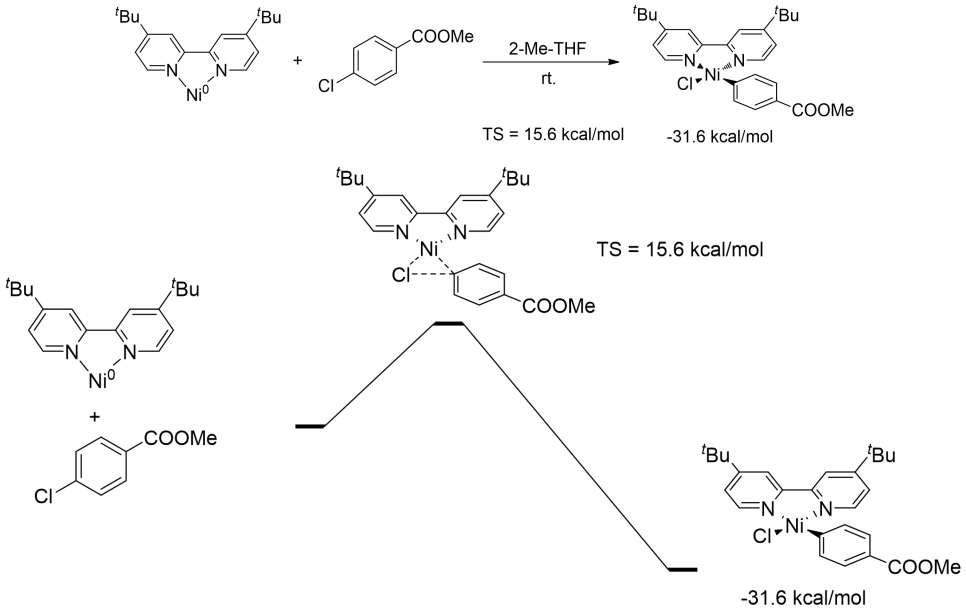
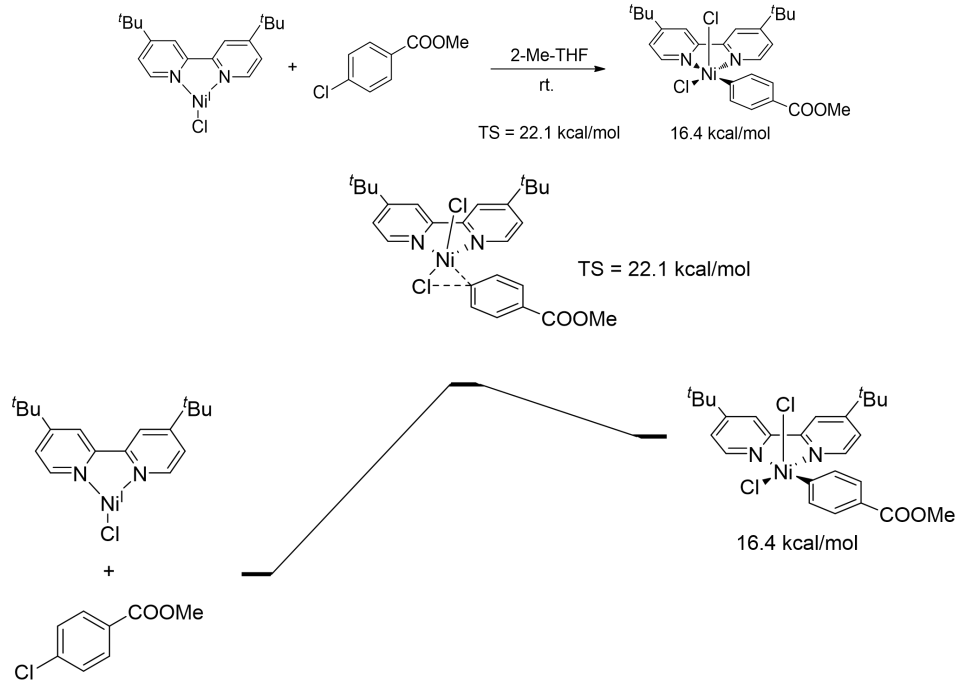
Theoretical calculations

Computational details: Geometry optimizations and frequency analyses were performed in gas phase using Gaussian 16 (Revision A03)[40] with pbe1pbe method. D3(bj) corrections were taken into consideration. The Ni atom was represented by the LANL2TZ(f) basis set. Other atoms were described by 6-31G(d) basis set.





$Ni^{(0)}$_$ClC_6H_4CO_2Me$_Adduct

SCF: -1973.468396 Hartree

Lowest frequency: 10.70 cm^{-1}

Gibbs energy: -1972.994783 Hartree

Charge: 0 Multiplicity: 1

N	-0.49654300	-1.46018400	-0.34830900
N	0.18910300	0.98519400	-0.78957900
C	-0.20790000	3.33932100	-0.81241400
C	-1.52445100	3.22091500	-0.39678400
C	-1.98941900	1.88745300	-0.15538100
C	-1.08958600	0.82043500	-0.36366400
C	0.61112000	2.21982700	-0.99709400
C	-3.30049100	1.51750300	0.28961000
C	-1.47465600	-0.54555000	-0.12418700
C	-2.77318100	-0.87931200	0.31556400
C	-3.66739000	0.22420500	0.50808100
C	-3.07899000	-2.26235100	0.53055600
C	-2.05391700	-3.15816600	0.27282500
C	-0.79205600	-2.73447600	-0.15913000
H	-4.04220100	2.28317900	0.46581400
H	0.22721500	4.31059300	-1.00869600
H	1.64303200	2.32453500	-1.31768900
H	-4.67887800	0.04290400	0.84251200
H	-2.20250100	-4.22212800	0.40404200
H	0.00320100	-3.44458000	-0.36572100
Ni	1.17920800	-0.68649700	-0.92816500
C	-4.44140400	-2.76241900	1.01710300
C	-2.39356000	4.46759100	-0.21272400
C	-4.75033300	-2.18977100	2.41249300
H	-4.77455800	-1.09903700	2.44438400
H	-5.72495000	-2.55731700	2.75362100
H	-3.99380400	-2.52115200	3.13212600

C	-4.46855700	-4.28962300	1.16123300
H	-5.45941400	-4.59462400	1.51375800
H	-4.28887200	-4.79709800	0.20712000
H	-3.73558600	-4.64716500	1.89268300
C	-5.53873900	-2.40346700	-0.00145600
H	-5.63874800	-1.33151500	-0.18086200
H	-5.32867900	-2.87854900	-0.96593800
H	-6.50607000	-2.77578700	0.35473600
C	-2.83567300	4.59814200	1.25648000
H	-3.44951300	5.49827300	1.37577400
H	-3.41596800	3.74762400	1.61897800
H	-1.95993300	4.69818300	1.90690500
C	-3.60132600	4.42287400	-1.16719500
H	-4.24518800	3.55386600	-1.02058500
H	-4.21269100	5.32142300	-1.02623000
H	-3.26032600	4.40643200	-2.20810600
C	-1.62337300	5.75101900	-0.54838400
H	-0.75594800	5.89315200	0.10526600
H	-1.28477200	5.76742500	-1.59013000
H	-2.28636600	6.61062000	-0.40524000
Cl	2.26564600	-3.30386500	-2.17725100
C	2.56581700	-1.91541300	-1.06337200
C	2.98721100	-0.63118000	-1.63296400
C	3.87899600	0.18261200	-0.88271700
C	4.28902000	-0.16201900	0.38581400
C	3.88067800	-1.41749900	0.94101300
C	3.09516500	-2.27677100	0.23099600
H	2.93482700	-0.48356900	-2.71142900
H	4.26841300	1.10198200	-1.31443400
H	4.22673000	-1.68940300	1.93239300
H	2.83956100	-3.25229100	0.63720200
C	5.15823100	0.77702600	1.10297000

O	5.51281000	1.86808400	0.69649500
O	5.54259200	0.30488300	2.31207200
C	6.38523900	1.17953000	3.04439200
H	6.60783900	0.66428100	3.98003400
H	7.30765900	1.38495600	2.49323900
H	5.88271600	2.13101500	3.24307200

TS_Ni$^{(0)}$_ClC$_6$H$_4$CO$_2$Me

SCF: -1973.443071 Hartree

Lowest frequency: -156.35 cm^{-1}

Gibbs energy: -1972.969850 Hartree

Charge: 0 Multiplicity: 1

N	-0.29815400	0.38969400	-0.79238400
N	1.14293200	-1.67308500	-0.18288600
C	3.19892700	-2.72727900	0.43101500
C	3.88186700	-1.52944000	0.58196200
C	3.13001800	-0.34240100	0.31529300
C	1.77744300	-0.47527200	-0.07514000
C	1.85323700	-2.76369000	0.06076500
C	3.61913400	1.00045600	0.41736200
C	0.96540000	0.67162900	-0.37693700
C	1.46791200	1.98524700	-0.23474900
C	2.83817500	2.08781100	0.17144800
C	0.59155900	3.08259800	-0.50709000
C	-0.69579400	2.74371700	-0.89555700
C	-1.10165700	1.41369100	-1.02841500
H	4.64438400	1.17757200	0.70921400
H	3.69126900	-3.67382100	0.61227500
H	1.32883000	-3.70973600	-0.03577600

H	3.29017800	3.06232800	0.28804200
H	-1.42806900	3.50967100	-1.11654100
H	-2.11469800	1.16094700	-1.33085400
Ni	-0.70734000	-1.53586100	-0.77822000
C	1.00339100	4.55195500	-0.38162100
C	5.35148700	-1.52638000	1.01196500
C	1.40872500	4.87348500	1.06858700
H	2.24599600	4.27620100	1.43400100
H	1.69147700	5.92971800	1.14596600
H	0.56367300	4.69937400	1.74351700
C	-0.15615100	5.49648400	-0.72375100
H	0.18565000	6.53151100	-0.61787800
H	-0.50071800	5.36866500	-1.75582100
H	-1.00936400	5.36184000	-0.04995900
C	2.13477000	4.88012600	-1.37325500
H	3.03782500	4.28505500	-1.22463400
H	1.79683700	4.70995300	-2.40135100
H	2.41083000	5.93672900	-1.27893400
C	5.51238100	-0.80087300	2.36069500
H	6.56735300	-0.80796800	2.65791200
H	5.17589100	0.23706900	2.34430400
H	4.93910600	-1.31800600	3.13784300
C	6.22801400	-0.89236900	-0.08360000
H	5.95774700	0.13815600	-0.32084600
H	7.27688100	-0.89987100	0.23455400
H	6.15187700	-1.47201500	-1.01004600
C	5.88497400	-2.94933500	1.22192400
H	5.34118700	-3.48091500	2.01056400
H	5.84210800	-3.54438800	0.30309900
H	6.93485900	-2.89310500	1.52815100
Cl	-1.67999100	-2.97825100	-2.44378700
C	-2.46786700	-1.78819100	-1.16036200

C	-2.56778400	-2.38678500	0.14164100
C	-3.46648100	-1.83248300	1.05037600
C	-4.34695000	-0.81915100	0.66891300
C	-4.36348700	-0.38430200	-0.68145000
C	-3.47129700	-0.87626700	-1.60089900
H	-2.05184800	-3.31435600	0.37112200
H	-3.53659800	-2.21662600	2.06432800
H	-5.09629400	0.35807700	-0.98233100
H	-3.48160700	-0.54638900	-2.63558600
C	-5.27061400	-0.29478000	1.67717800
O	-5.32269900	-0.64861000	2.83999700
O	-6.08957200	0.66531400	1.18194300
C	-7.00352300	1.20017700	2.12567800
H	-7.58351900	1.95051100	1.58601400
H	-7.66203600	0.41934600	2.51754000
H	-6.47397300	1.65867600	2.96617700

Ni(Cl)($C_6H_4CO_2Me$)

SCF: -1973.519457 Hartree

Lowest frequency: 12.39 cm^{-1}

Gibbs energy: -1973.045112 Hartree

Charge: 0 Multiplicity: 1

N	1.42581200	-1.66146300	-0.00621700
N	-0.15043200	0.36956800	0.01821300
C	-0.58349200	2.71922900	0.01143100
C	0.75431300	3.07429000	-0.00185000
C	1.68592100	1.98701400	-0.01068900
C	1.17861400	0.66994300	-0.00101800
C	-1.00080400	1.38519400	0.02089200
C	3.11403900	2.10444000	-0.02894100

C	2.05674100	-0.46497800	-0.01263500
C	3.45974200	-0.32132700	-0.03038300
C	3.94511400	1.02583600	-0.03765300
C	4.25642100	-1.51194900	-0.03980900
C	3.56136200	-2.70996100	-0.03252900
C	2.16180400	-2.75551300	-0.01610700
H	3.56803400	3.08446200	-0.03654400
H	-1.35893200	3.47403500	0.01724800
H	-2.05335000	1.12771100	0.03573100
H	5.00895800	1.21382200	-0.05125600
H	4.08801500	-3.65527400	-0.03898100
H	1.60454300	-3.68907400	-0.00991200
Ni	-0.57644500	-1.50904200	0.03225400
C	5.78687300	-1.50314400	-0.05576500
C	1.16493500	4.54845800	-0.00565500
C	6.30260100	-0.82087500	-1.33616200
H	5.97702700	0.21517100	-1.44617000
H	7.39842700	-0.82972400	-1.33897500
H	5.95884400	-1.36804000	-2.22066800
C	6.36388900	-2.92449200	-0.06042000
H	7.45688300	-2.86152500	-0.07077400
H	6.07605200	-3.48960400	0.83277000
H	6.05921900	-3.49048900	-0.94745000
C	6.32825900	-0.81869600	1.21285300
H	6.00307700	0.21684100	1.32856100
H	6.00394400	-1.36550700	2.10487800
H	7.42391300	-0.82573000	1.19275600
C	1.94843200	4.88097200	-1.28908600
H	2.22943100	5.94014100	-1.28096600
H	2.86051100	4.29444400	-1.41251400
H	1.32286800	4.70470300	-2.17085300
C	1.97939200	4.87777600	1.25937600

H	2.89392800	4.29074100	1.35975600
H	2.26050000	5.93688000	1.24692400
H	1.37512700	4.69976500	2.15552900
C	-0.05675700	5.47570000	0.01095000
H	-0.68978500	5.33786200	-0.87227400
H	-0.66871300	5.33305800	0.90810400
H	0.28680700	6.51521300	0.00954700
Cl	-0.92568800	-3.64548200	0.02649000
C	-2.42211800	-1.22219400	0.09034900
C	-3.06903400	-0.96815100	1.30970700
C	-4.41602600	-0.63007600	1.35228400
C	-5.15813600	-0.54441100	0.17041600
C	-4.53384700	-0.81752500	-1.05126300
C	-3.18519700	-1.15461800	-1.08437400
H	-2.51162400	-1.03454100	2.24176300
H	-4.91843300	-0.42817800	2.29418200
H	-5.11146900	-0.76615900	-1.96906000
H	-2.72014400	-1.37597200	-2.04231700
C	-6.58277900	-0.17018800	0.27061100
O	-7.16290800	0.09746200	1.30278300
O	-7.19872100	-0.14890400	-0.92999000
C	-8.57543900	0.19508000	-0.88094500
H	-8.92589700	0.16412300	-1.91341400
H	-9.13209300	-0.51854300	-0.26678400
H	-8.71207200	1.19557900	-0.46010000

$Ni^{(I)}Cl\_ClC_6H_4CO_2Me\_Adduct$

SCF: -2433.589910 Hartree

Lowest frequency: 6.03 cm^{-1}

Gibbs energy: -2433.118365 Hartree

Charge: 0 Multiplicity: 2

N	1.35157100	-1.00022800	-1.38283700
N	-1.19516000	-0.64823600	-1.49594900
C	-3.17620300	0.66047800	-1.23517300
C	-2.49503000	1.78480600	-0.79272500
C	-1.06917200	1.67961700	-0.76844700
C	-0.48362900	0.44408500	-1.11817700
C	-2.51077500	-0.52028900	-1.57146900
C	-0.15506300	2.72162400	-0.40375700
C	0.93939900	0.24878200	-1.06252800
C	1.81446400	1.28570600	-0.67425600
C	1.19338100	2.53861100	-0.36163200
C	3.21478800	0.99872100	-0.61566100
C	3.59045800	-0.28350200	-0.98557200
C	2.64867900	-1.24879200	-1.35264100
H	-0.53502900	3.70298400	-0.15888000
H	-4.25613800	0.66064400	-1.30143800
H	-3.06152300	-1.40268500	-1.88306400
H	1.80435500	3.38495200	-0.08273400
H	4.62964400	-0.58369600	-0.96820900
H	2.94790600	-2.26181600	-1.60591700
Ni	-0.13320400	-2.28754800	-1.60140200
C	4.26568700	2.00766300	-0.14602000
C	-3.26326100	3.02774200	-0.33816600
C	4.32350100	3.21209800	-1.10248600
H	3.37846300	3.75254100	-1.18655100
H	5.08436300	3.92054500	-0.75538000
H	4.60289300	2.88327900	-2.10938600
C	5.67100100	1.39351700	-0.12954500
H	6.38385700	2.14590900	0.22363300
H	5.73352700	0.53523700	0.54834900
H	5.99530500	1.07821800	-1.12740200

C	3.96907200	2.44370100	1.30111300
H	3.00038500	2.93258700	1.42177800
H	3.98582300	1.57358000	1.96623200
H	4.74129400	3.14475900	1.63780700
C	-2.97883400	4.20864000	-1.28272900
H	-3.53018500	5.09212600	-0.94118100
H	-1.92148600	4.47650200	-1.34063800
H	-3.31310200	3.97352900	-2.29938600
C	-2.91212900	3.36502500	1.12351800
H	-3.15027000	2.51330000	1.76786300
H	-1.86033000	3.61473200	1.27524900
H	-3.50682600	4.22659500	1.44837500
C	-4.77823600	2.78878700	-0.36201300
H	-5.15167700	2.58204700	-1.37131500
H	-5.06190400	1.96524300	0.30243700
H	-5.28552500	3.69191400	-0.00704500
Cl	3.20097400	-1.38509400	2.35721900
C	1.48248200	-1.22490300	2.13877200
C	0.86199600	-0.03001300	2.50476500
C	-0.51337400	0.07940100	2.36749500
C	-1.26193200	-0.99051400	1.86799100
C	-0.61869000	-2.16749100	1.47478000
C	0.76045100	-2.28985200	1.61201200
H	1.45175500	0.79112800	2.89774300
H	-1.02880900	0.99107900	2.65155300
H	-1.18342100	-2.99541400	1.06053100
H	1.25650700	-3.20073800	1.29485100
C	-2.72983900	-0.82597500	1.77368900
O	-3.33969600	0.16549300	2.12363100
O	-3.33314200	-1.90689900	1.25928900
C	-4.74880400	-1.82140700	1.16289000
H	-5.07495200	-2.78319000	0.76757600

H	-5.19182300	-1.63591100	2.14483900
H	-5.03970400	-1.01089300	0.48810400
Cl	-0.08733600	-4.44754300	-1.47340400

TS_Ni$^{(I)}$Cl_ClC$_6$H$_4$CO$_2$Me

SCF: -2433.556763 Hartree

Lowest frequency: -94.27 cm^{-1}

Gibbs energy: -2433.083216 Hartree

Charge: 0 Multiplicity: 2

N	-1.96862200	-1.25111000	0.33148900
N	0.30013000	-0.62012000	1.44010300
C	2.05933400	0.89747500	1.92671800
C	1.36334100	1.99462400	1.44606700
C	0.01613700	1.75365900	1.02170300
C	-0.43901300	0.41902800	1.00441800
C	1.50092900	-0.38601000	1.92570900
C	-0.92568000	2.74101900	0.58576800
C	-1.72750800	0.07360400	0.45834800
C	-2.63769000	1.07006000	0.04353300
C	-2.17649200	2.42323300	0.15071600
C	-3.91007600	0.64825100	-0.46348100
C	-4.11565000	-0.71979700	-0.54596400
C	-3.12738400	-1.63443900	-0.16597700
H	-0.65503000	3.78686600	0.61025300
H	3.07456500	0.99990200	2.28631600
H	2.03804700	-1.25851800	2.28836800
H	-2.82572000	3.23621700	-0.14016100
H	-5.04635100	-1.11944800	-0.92621700
H	-3.26676300	-2.70477200	-0.28574100
Ni	-0.35472700	-2.45939200	0.81481800

C	-5.00624300	1.62034800	-0.90681800
C	2.04936700	3.35790500	1.33821600
C	-5.42458900	2.51883600	0.27146500
H	-4.60834800	3.11430000	0.68357500
H	-6.21096300	3.20807900	-0.05593300
H	-5.82922700	1.90883600	1.08641500
C	-6.27313700	0.88295400	-1.35884700
H	-7.02806500	1.62184900	-1.64669400
H	-6.09188500	0.24484100	-2.23062100
H	-6.70167600	0.27098300	-0.55756000
C	-4.52856700	2.44607100	-2.11582400
H	-3.63170100	3.03671700	-1.92138800
H	-4.30914700	1.78528800	-2.96154300
H	-5.32345100	3.13462300	-2.42367400
C	1.39707400	4.37349800	2.29308700
H	1.90206700	5.34127300	2.19676100
H	0.33339100	4.53438100	2.10597700
H	1.50039600	4.04039500	3.33167500
C	2.01517200	3.84083400	-0.12478900
H	2.51354500	3.12142000	-0.78418500
H	1.00517800	3.99165900	-0.51072200
H	2.54615700	4.79645800	-0.20230700
C	3.53055900	3.27579600	1.72882600
H	3.67052600	2.98128300	2.77485200
H	4.08140500	2.57792000	1.08829300
H	3.98392000	4.26473200	1.60564000
Cl	-0.73639300	-3.99650900	-0.88122700
C	0.74608200	-2.24454400	-0.83089000
C	0.42593800	-1.19501700	-1.69178000
C	1.44486200	-0.34986000	-2.10357100
C	2.77076600	-0.60461600	-1.73221500
C	3.08021200	-1.76621900	-1.01280700

C	2.06781100	-2.61108900	-0.57500300
H	-0.60540500	-0.99668300	-1.96209300
H	1.23080400	0.53776500	-2.69155400
H	4.11342900	-1.98305100	-0.76145800
H	2.28007200	-3.47862300	0.04078100
C	3.78641900	0.40861800	-2.07588200
O	3.54110500	1.49447500	-2.56583400
O	5.03425200	0.02333400	-1.75653700
C	6.04425700	0.98626000	-2.03087000
H	6.98409000	0.52211200	-1.73130400
H	6.06102500	1.23673500	-3.09483400
H	5.86989900	1.90268800	-1.45905100
Cl	0.61385000	-3.65996000	2.46075300

$Ni(Cl)_2(C_6H_4CO_2Me)$

SCF: -2433.565518 Hartree

Lowest frequency: 15.62 cm^{-1}

Gibbs energy: -2433.092284 Hartree

Charge: 0 Multiplicity: 2

N	-1.44809600	-1.58486800	-0.13699300
N	0.14183900	0.47032700	-0.09014100
C	0.57824600	2.80667900	0.02464700
C	-0.76074300	3.15584400	-0.01847400
C	-1.69199200	2.07056200	-0.09651400
C	-1.18310500	0.75383300	-0.11876100
C	0.99435600	1.47288200	-0.01167300
C	-3.11863200	2.19078500	-0.14547900
C	-2.06193000	-0.38331700	-0.15097800
C	-3.46437400	-0.23503900	-0.17681000
C	-3.94863200	1.11256700	-0.18460900

C	-4.26644700	-1.42241100	-0.18303200
C	-3.58071300	-2.62557600	-0.16627500
C	-2.18228000	-2.67645800	-0.14365300
H	-3.57204400	3.17100200	-0.14841900
H	1.34906000	3.56280400	0.09188200
H	2.04600400	1.21193600	0.02798400
H	-5.01190800	1.30063400	-0.21567200
H	-4.11306400	-3.56742600	-0.16637800
H	-1.63434200	-3.61433300	-0.13275300
Ni	0.55553900	-1.48373500	0.07677200
C	-5.79699300	-1.40611400	-0.19841800
C	-1.17536900	4.62822100	0.03080600
C	-6.33285200	-0.71355700	1.06828000
H	-6.00633600	0.32215500	1.17721400
H	-7.42856100	-0.72006200	1.05170000
H	-6.00490700	-1.25501500	1.96204300
C	-6.38108900	-2.82468000	-0.19508500
H	-7.47367200	-2.75569200	-0.20609400
H	-6.07965500	-3.39756900	-1.07889500
H	-6.09686200	-3.38570000	0.70176400
C	-6.31091100	-0.72893500	-1.48233000
H	-5.97953000	0.30431300	-1.60088900
H	-5.97324800	-1.28450500	-2.36402300
H	-7.40672700	-0.73087500	-1.48226800
C	-2.02956300	4.89798200	1.28377100
H	-2.30963400	5.95706200	1.31199900
H	-2.94684200	4.30859700	1.32950000
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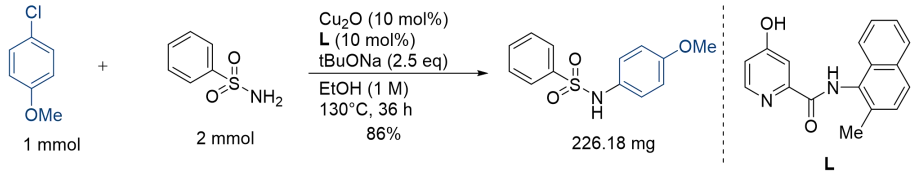
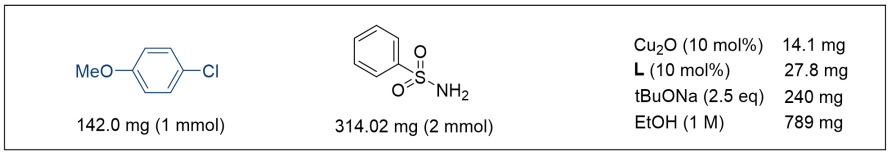
C	-1.91558500	5.01839400	-1.26155200
H	-2.82252300	4.43881200	-1.44333000
H	-2.19796200	6.07607900	-1.21432200
H	-1.26032900	4.88315400	-2.12893900

C	0.04200500	5.55636300	0.13130900
H	0.62346100	5.37471900	1.04164400
H	0.70598000	5.46306400	-0.73515200
H	-0.30618400	6.59373000	0.16658100
Cl	0.96258200	-3.51091600	-0.68251800
C	2.45344000	-1.23951300	-0.02338700
C	2.92581200	-0.92637200	-1.29633100
C	4.24708100	-0.52070100	-1.44571200
C	5.09164200	-0.46207300	-0.33375200
C	4.60725100	-0.82049200	0.92712100
C	3.28107500	-1.21633100	1.08985800
H	2.27880800	-0.99982200	-2.16643900
H	4.64660800	-0.25818800	-2.42070700
H	5.26968400	-0.78434500	1.78589400
H	2.88937800	-1.47824000	2.06588200
C	6.48844900	-0.02133200	-0.55371200
O	6.94166000	0.32380000	-1.62439700
O	7.21762900	-0.03878800	0.57623000
C	8.57039700	0.36945700	0.41610300
H	9.01814500	0.30393900	1.40807000
H	9.09158700	-0.28909000	-0.28416500
H	8.62282400	1.39410300	0.03762100
Cl	0.29503600	-1.34904200	2.36214000

5. The evaluation of quantitative green metrics

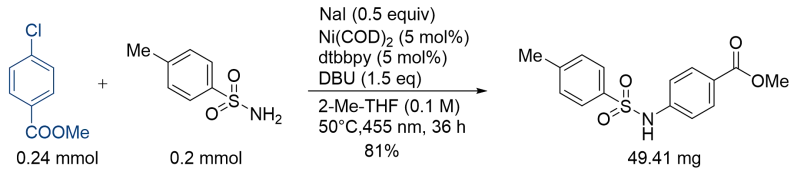


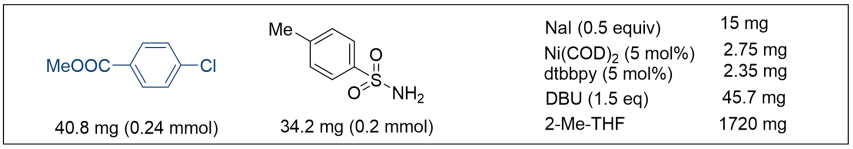


atom economy (AE)	reaction mass efficiency (RME)	optimum efficiency (OE)
75.6 %	49.6 %	65.6 %

Q. Li, L. Xu, D. Ma, *Angew. Chem. Int. Ed*. 2022, **61**, e202210483

Fig. S12 The quantitative green metrics of reported method





atom economy (AE)	reaction mass efficency (RME)	optimum efficiency (OE)
89.5%	65.9%	73%

Fig. S13 The quantitative green metrics of method decribled in the manuscript

Results and Comments: Based on the quantitative green metrics of the method compared with data in the reported literature with the similar reaction (Fig. S12 & S13). The ratio of aryl chloride/sulfonamide is 1.2/1 for our method, while the ratio of aryl chloride/sulfonamide: 2/1 is required for the literature, thus, the reaction mass efficency(RME) is really better than the data in reported literature as well as optimu efficency. However, the process mass intensity is not well comparable with the literature, because we can not find the amount of work up solvent used by the reported literature. According to the data of RME and OE, the coupling reaction described in the manuscript is highly efficient. The lower temperature and weaker organic base made the method useful.

6. Reference

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7. NMR spectra

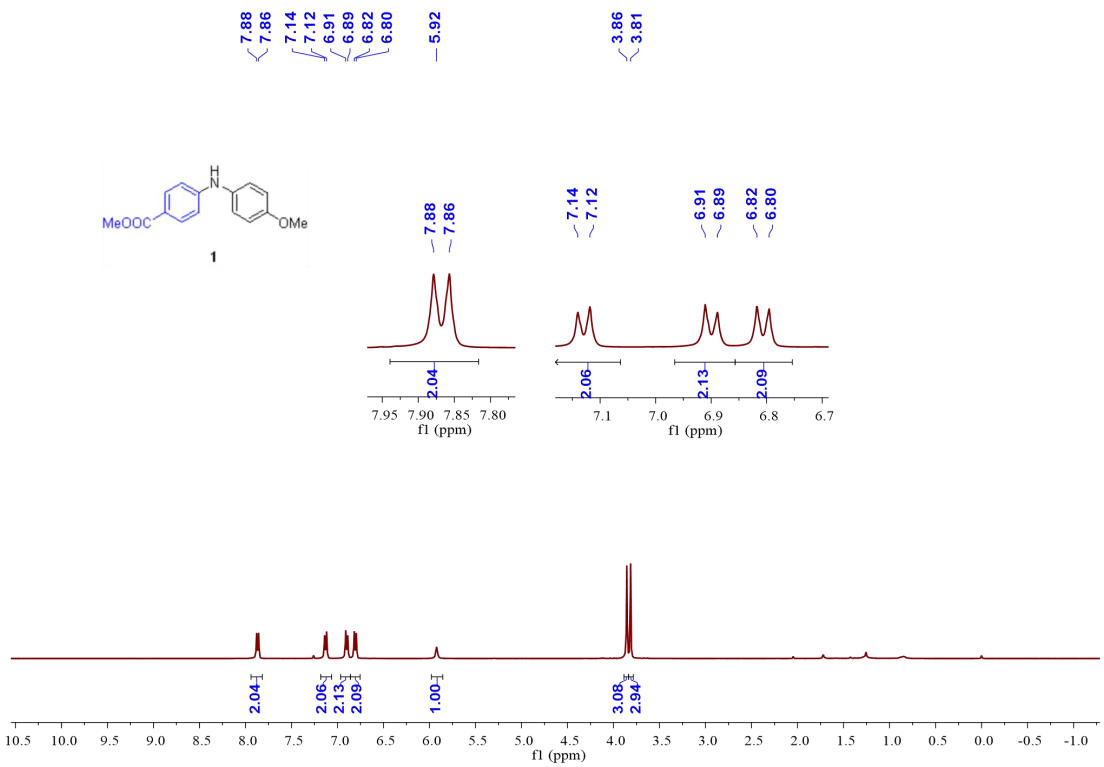

Fig. S14 ^{1}H NMR spectrum of **1** in $CDCl_3$ (400 MHz)

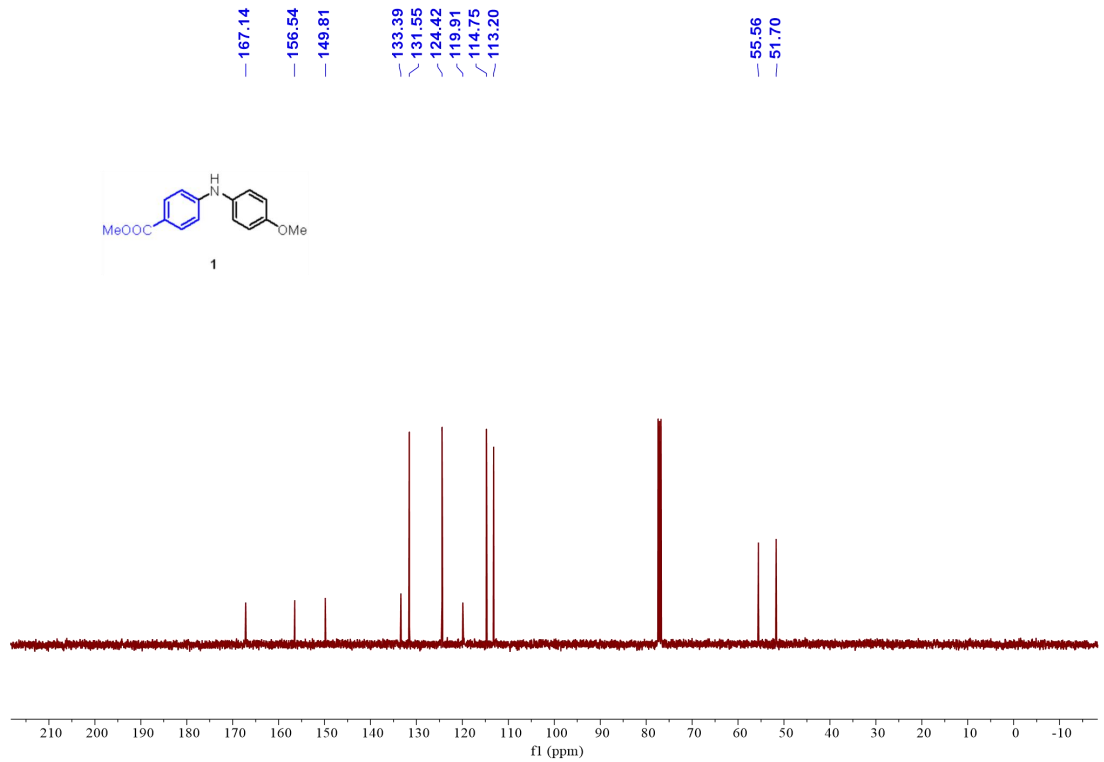

Fig. S15 ^{13}C NMR spectrum of **1** in $CDCl_3$ (101 MHz)

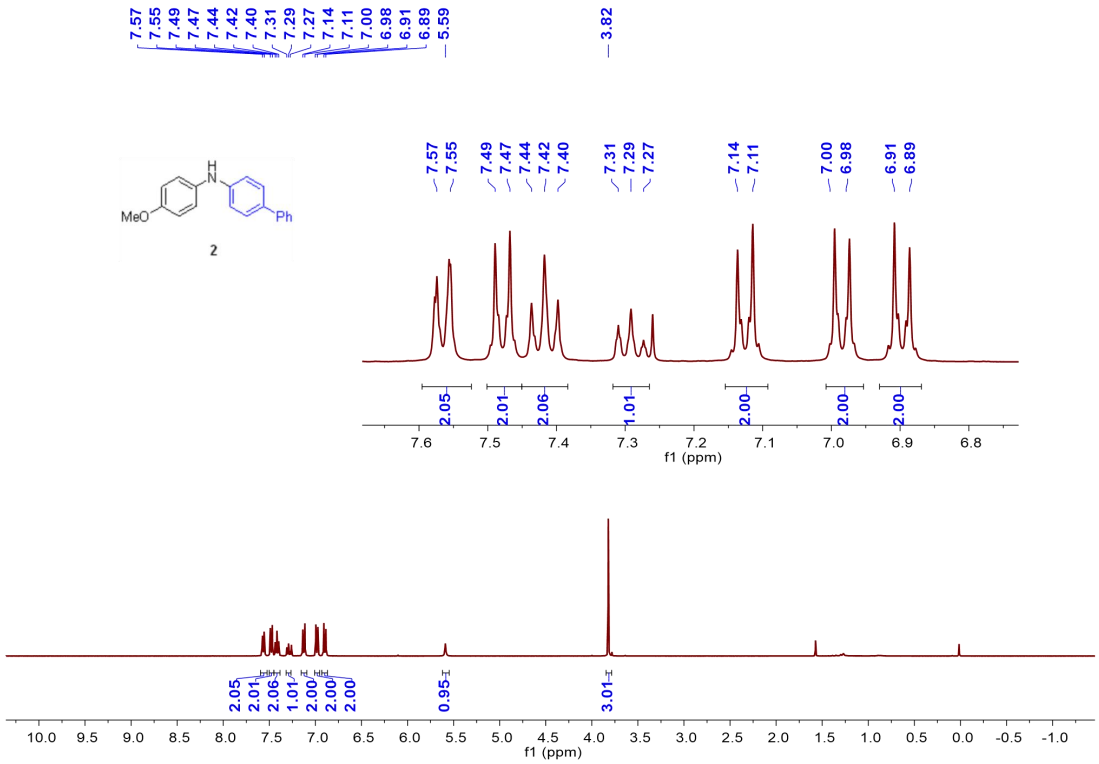

Fig. S16 ^{1}H NMR spectrum of **2** in $CDCl_3$ (400 MHz)

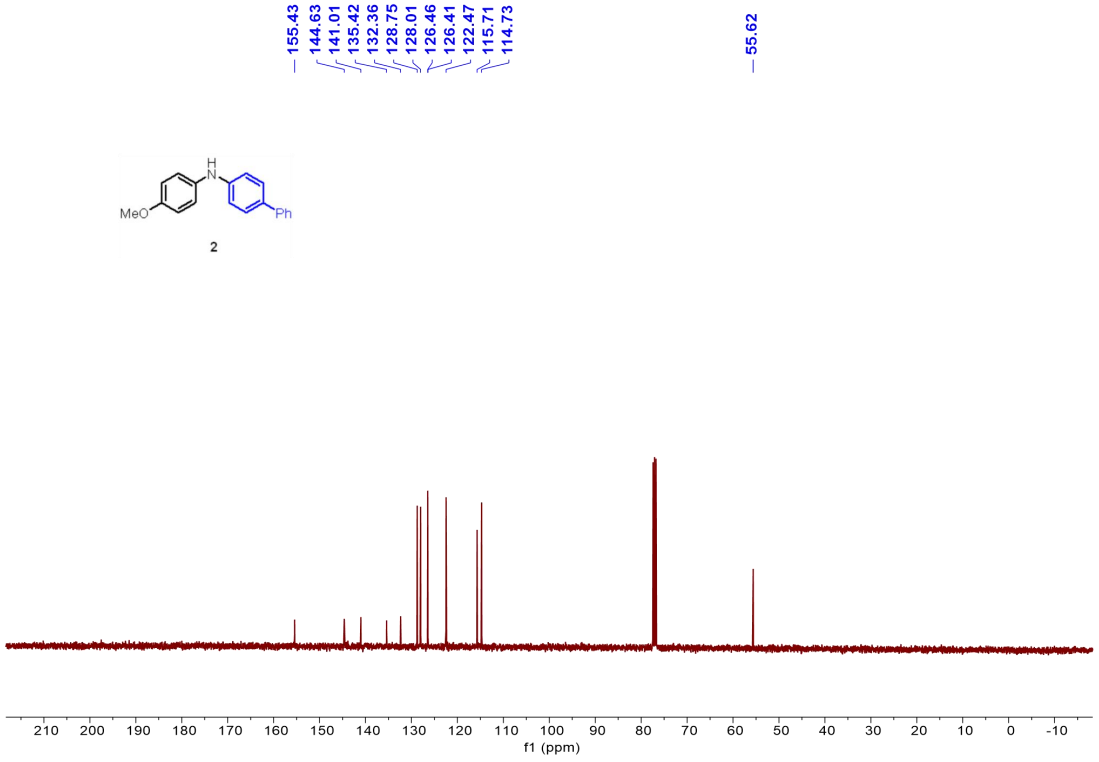

Fig. S17 ^{13}C NMR spectrum of **2** in $CDCl_3$ (101 MHz)

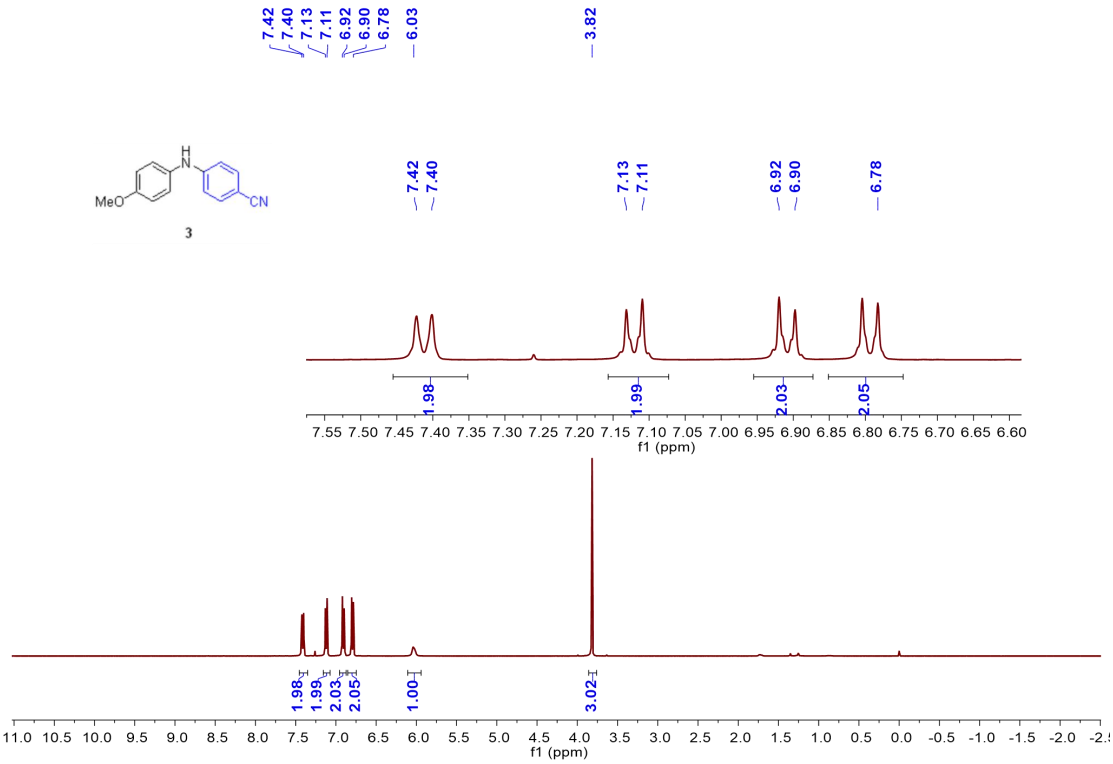

Fig. S18 ^{1}H NMR spectrum of **3** in $CDCl_3$ (400 MHz)

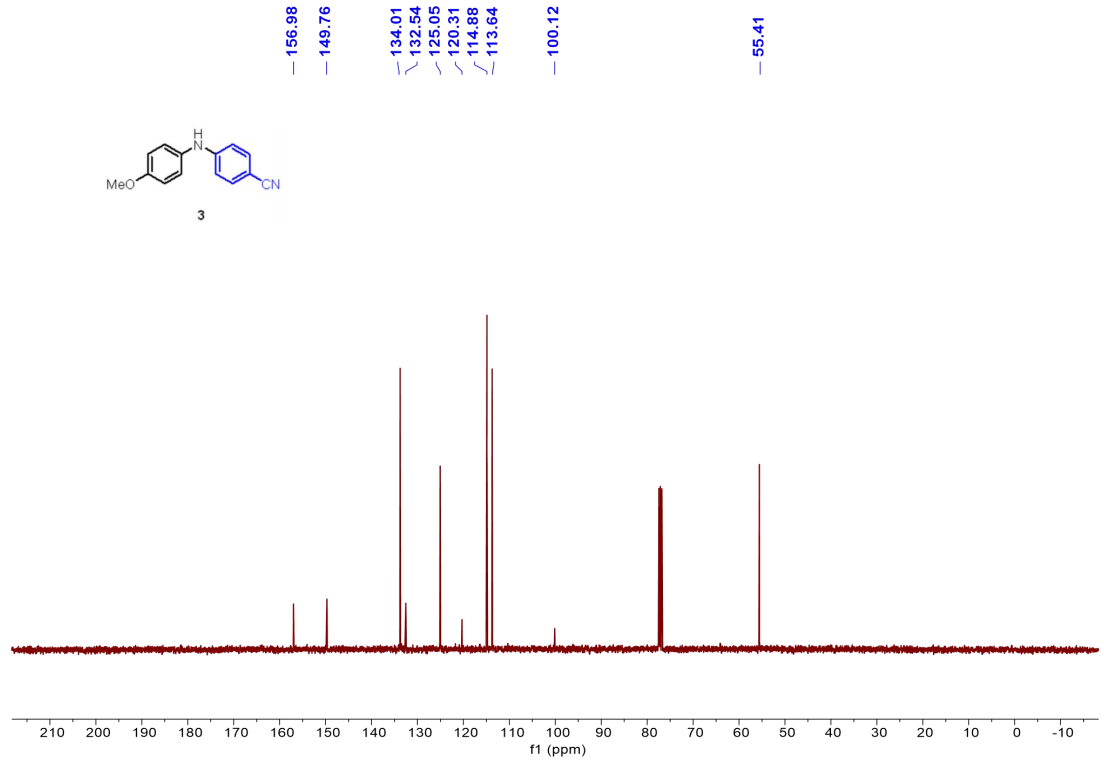

Fig. S19 ^{13}C NMR spectrum of **3** in $CDCl_3$ (101 MHz)

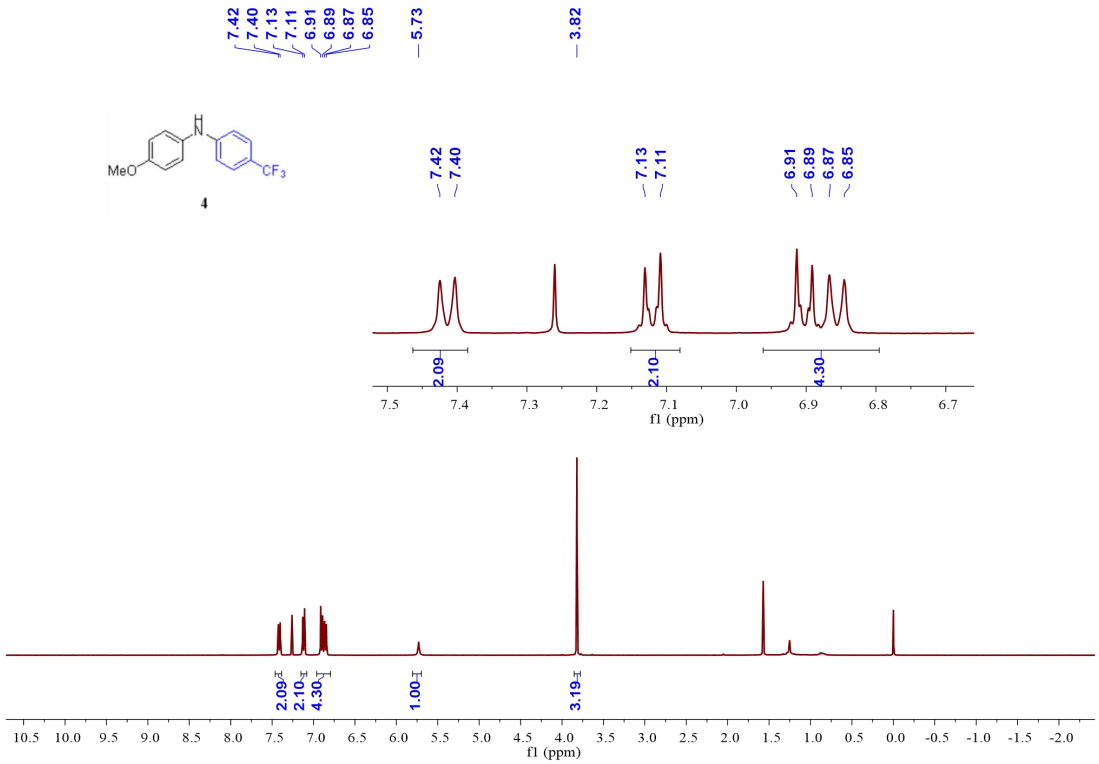

Fig. S20 ^{1}H NMR spectrum of **4** in $CDCl_3$ (400 MHz)

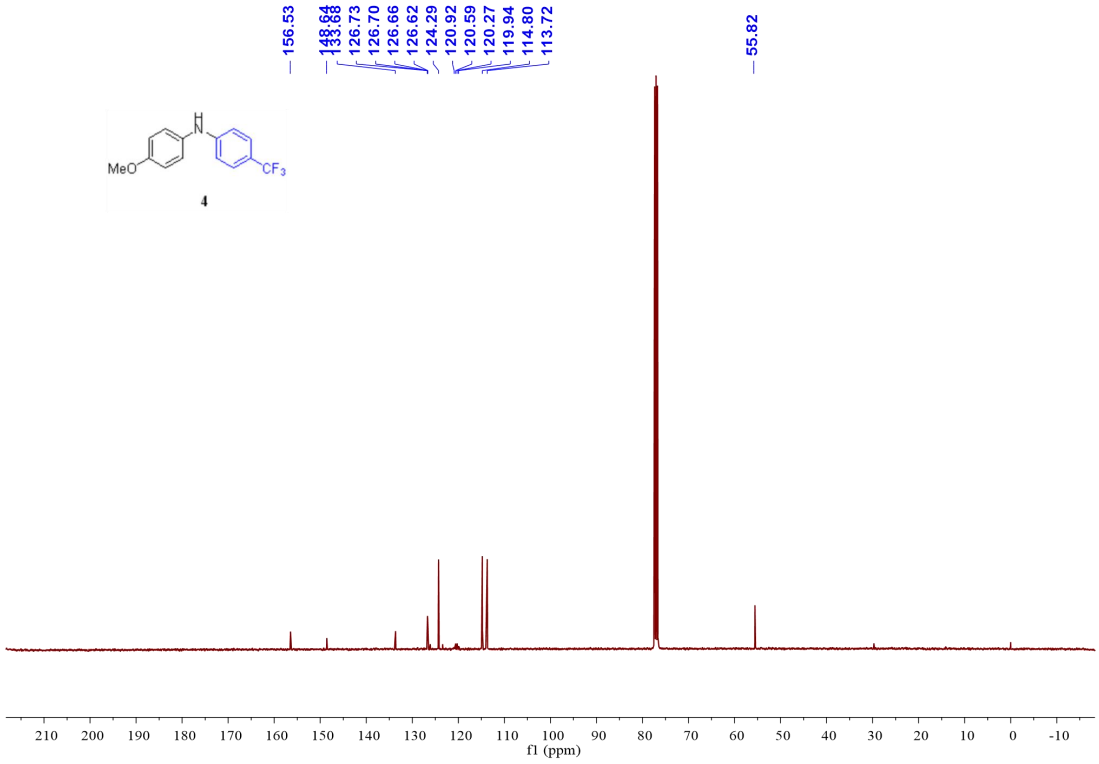

Fig. S21 ^{13}C NMR spectrum of **4** in $CDCl_3$ (101 MHz)

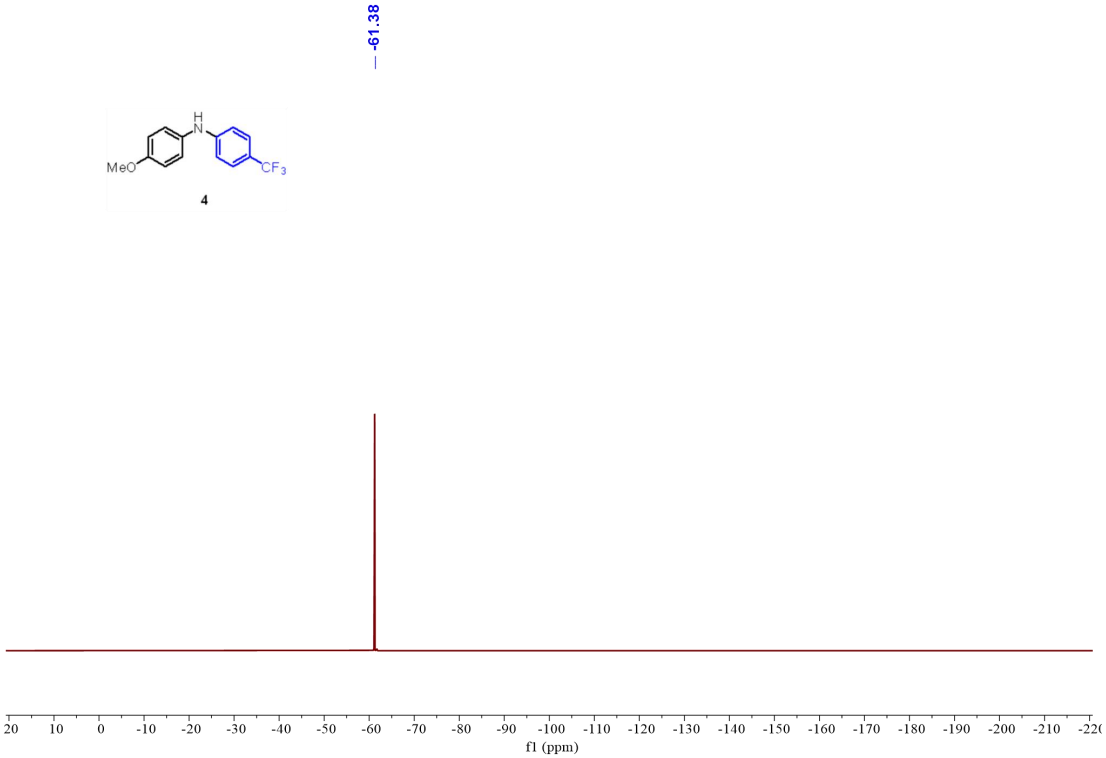

Fig. S22 ^{19}F NMR spectrum of **4** in $CDCl_3$ (377 MHz)

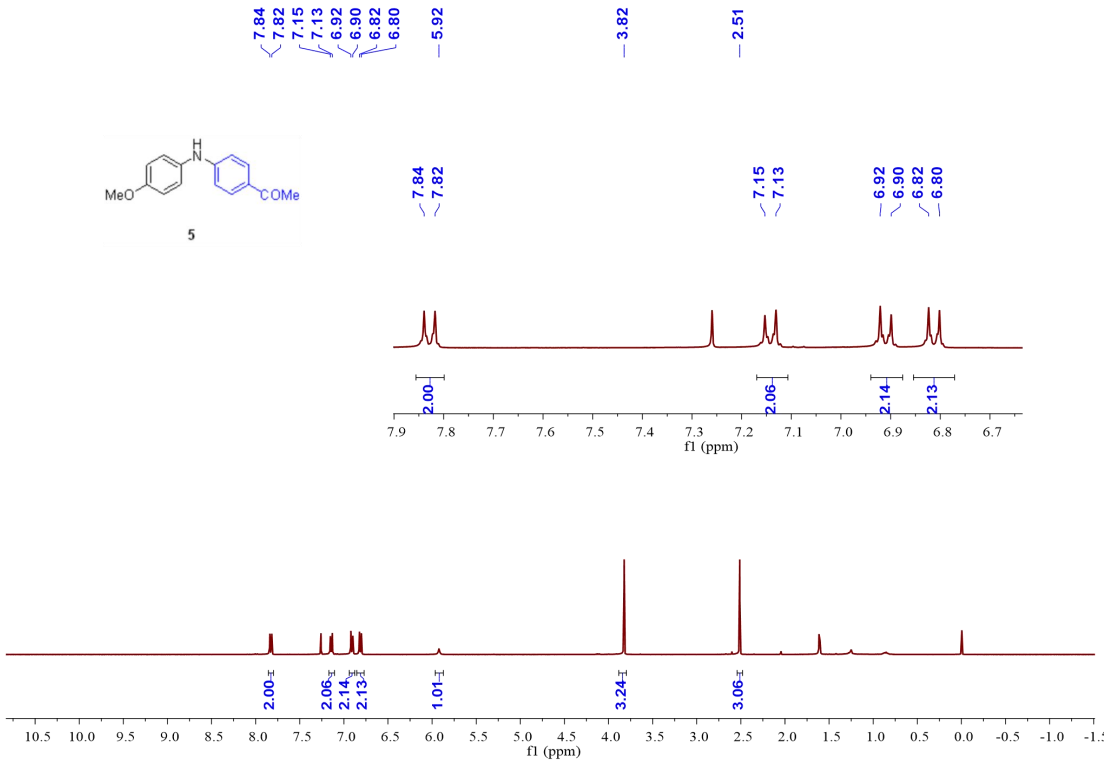

Fig. S23 ^{1}H NMR spectrum of **5** in $CDCl_3$ (400 MHz)

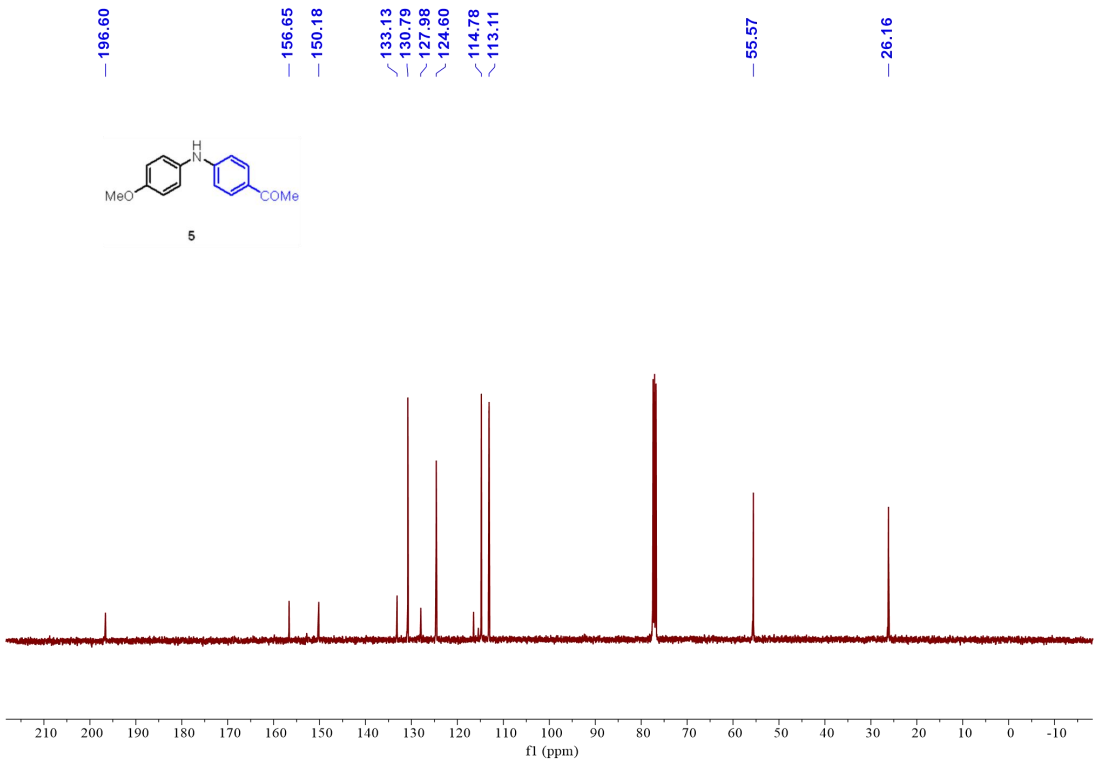

Fig. S24 ^{13}C NMR spectrum of **5** in $CDCl_3$ (101 MHz)

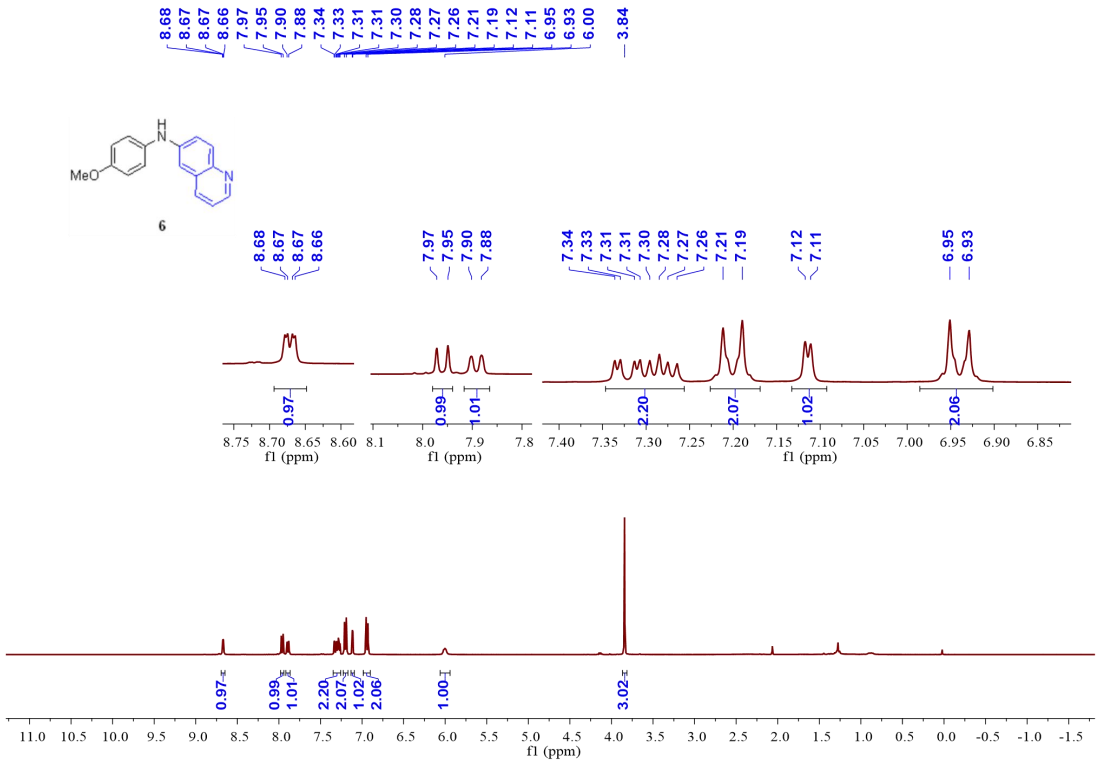

Fig. S25 ^{1}H NMR spectrum of **6** in $CDCl_3$ (400 MHz)

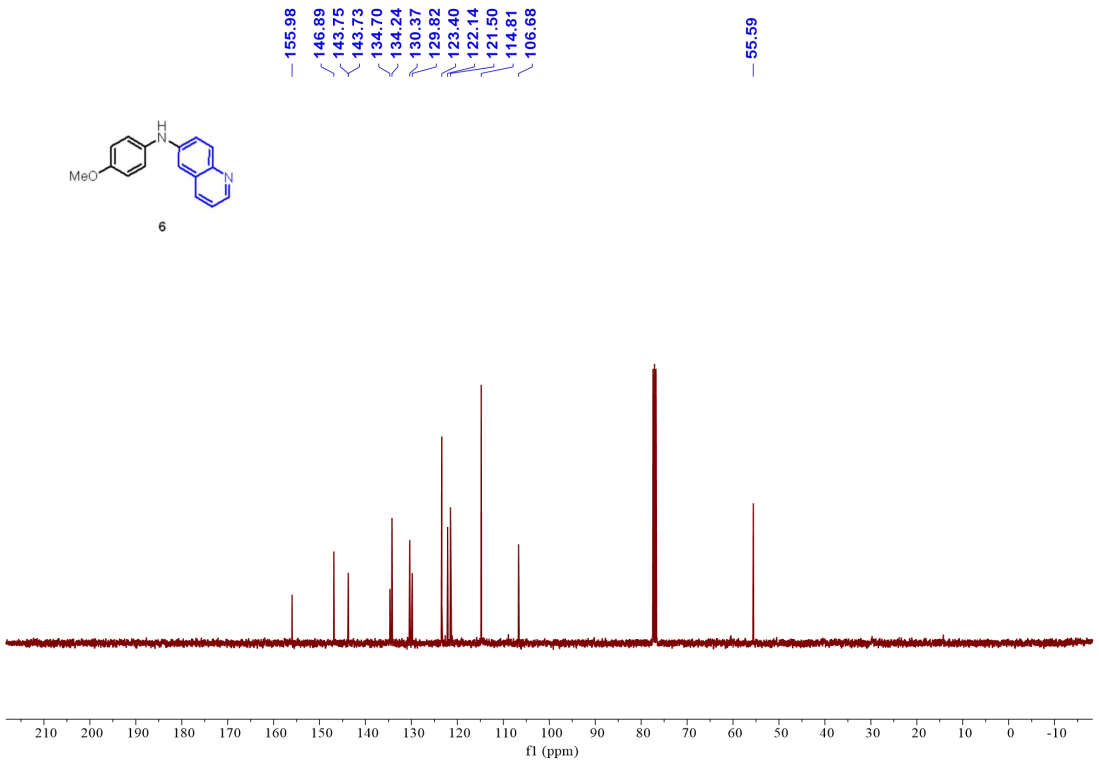

Fig. S26 ^{13}C NMR spectrum of **6** in $CDCl_3$ (101 MHz)

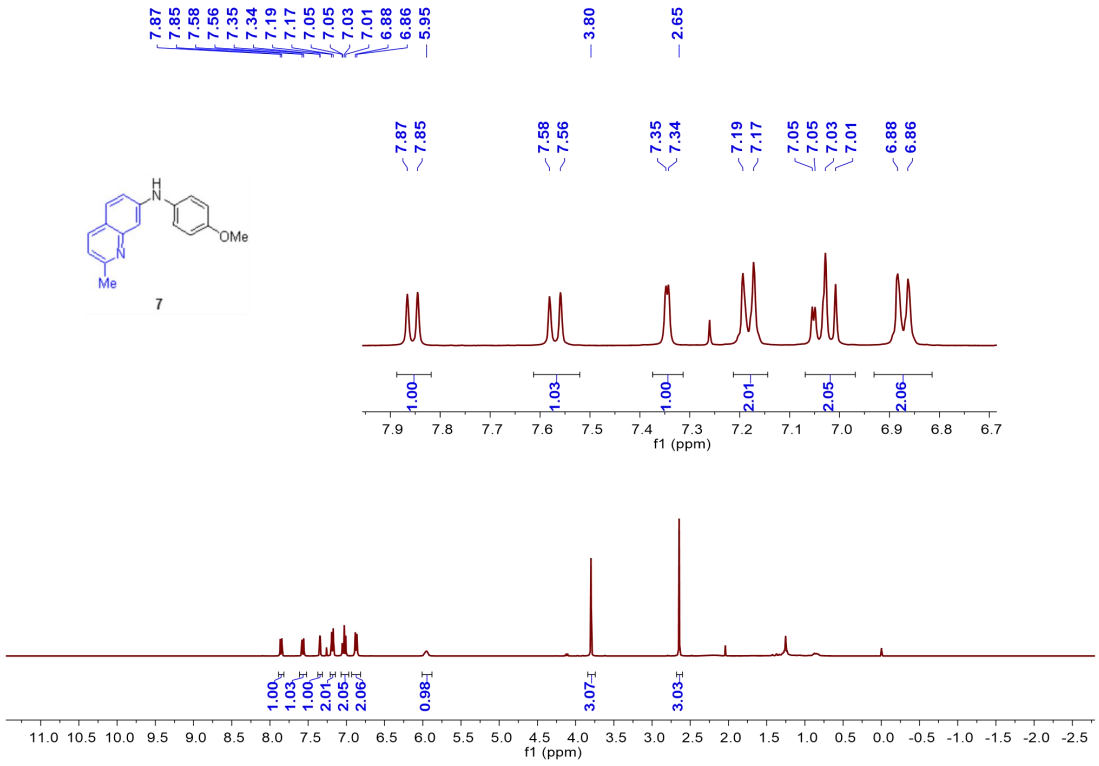

Fig. S27 ^{1}H NMR spectrum of **7** in $CDCl_3$ (400 MHz)

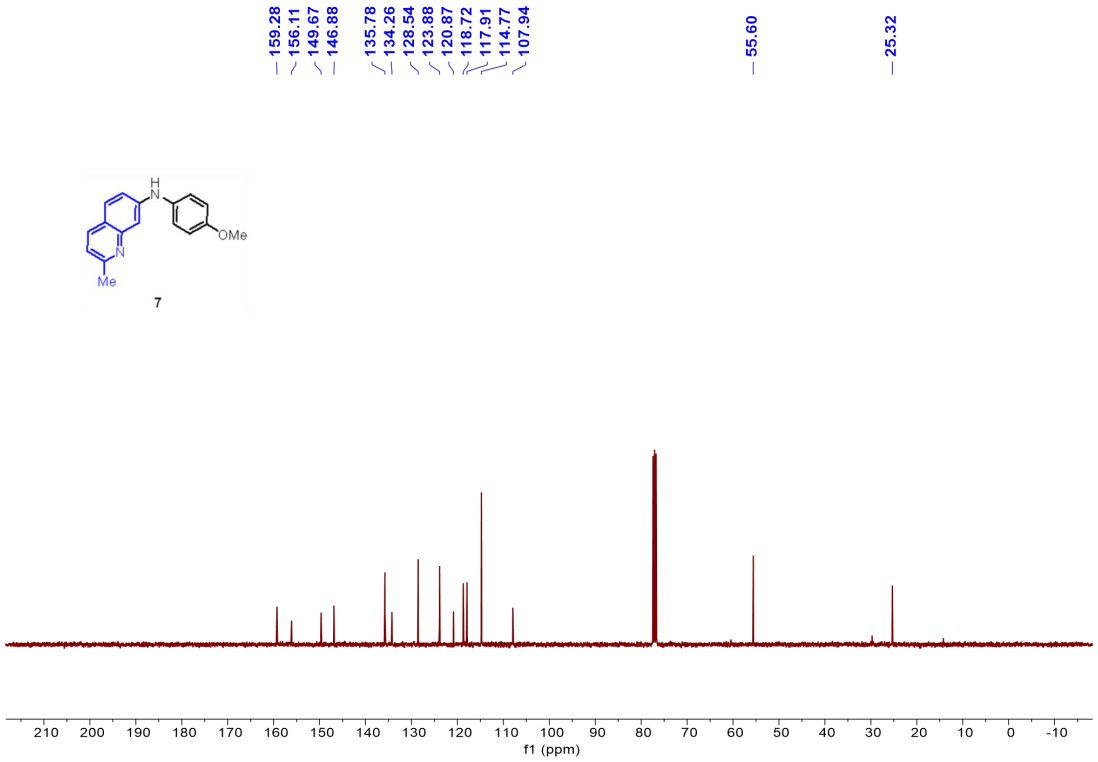

Fig. S28 ^{13}C NMR spectrum of **7** in $CDCl_3$ (101 MHz)

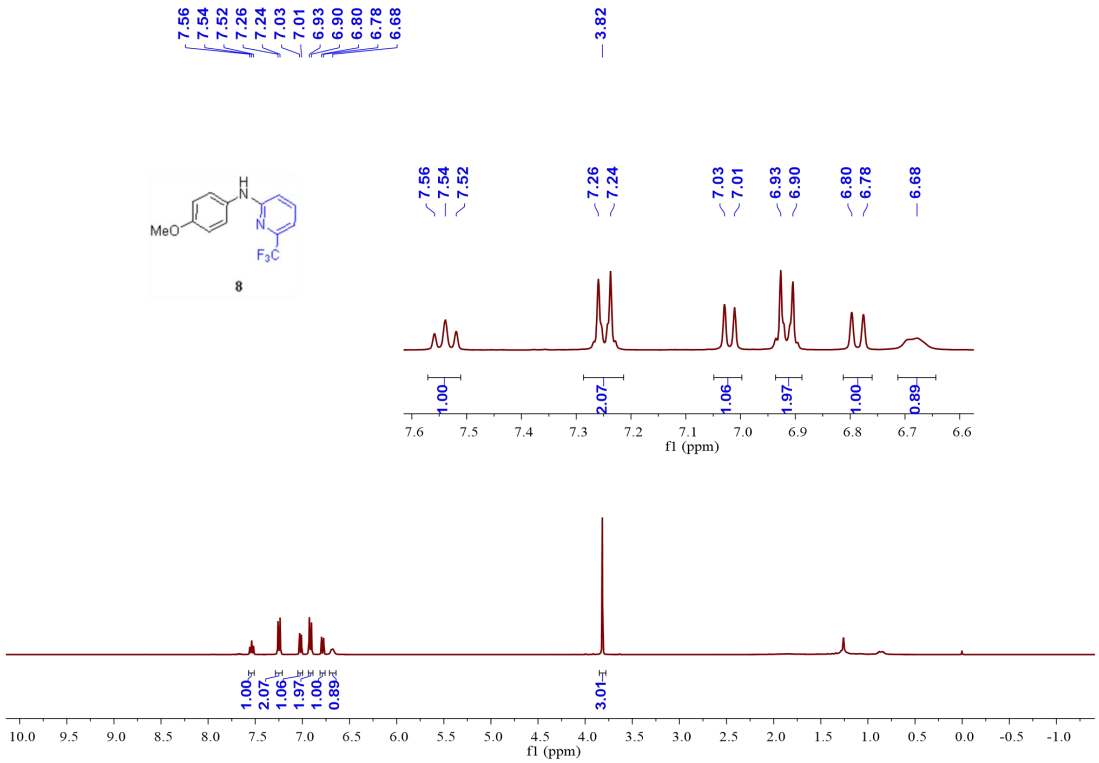

Fig. S29 ^{1}H NMR spectrum of **8** in $CDCl_3$ (400 MHz)

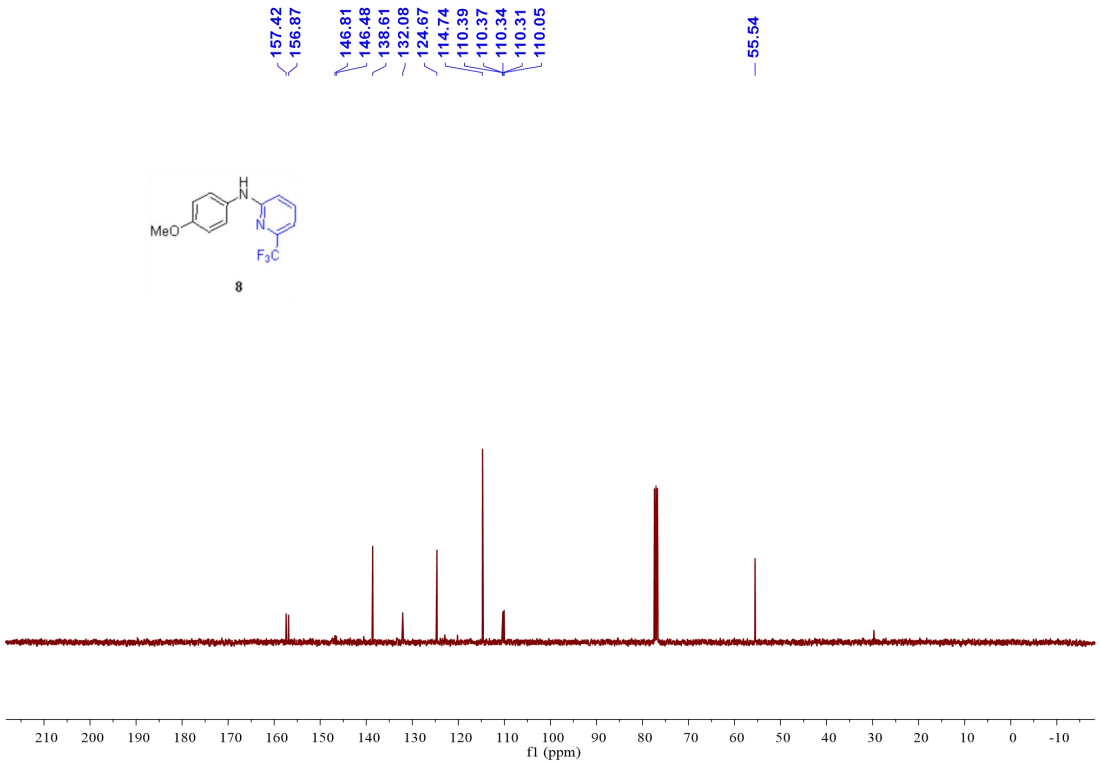

Fig. S30 ^{13}C NMR spectrum of **8** in $CDCl_3$ (101 MHz)

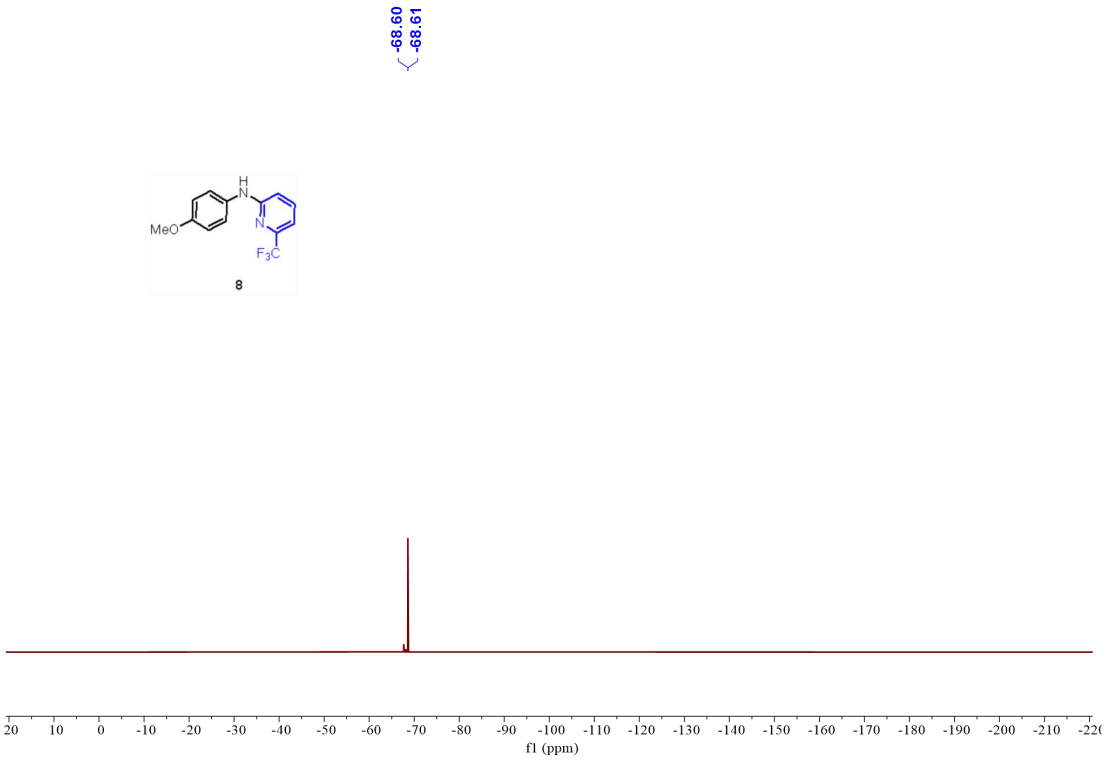

Fig. S31 ^{19}F NMR spectrum of **8** in $CDCl_3$ (377 MHz)

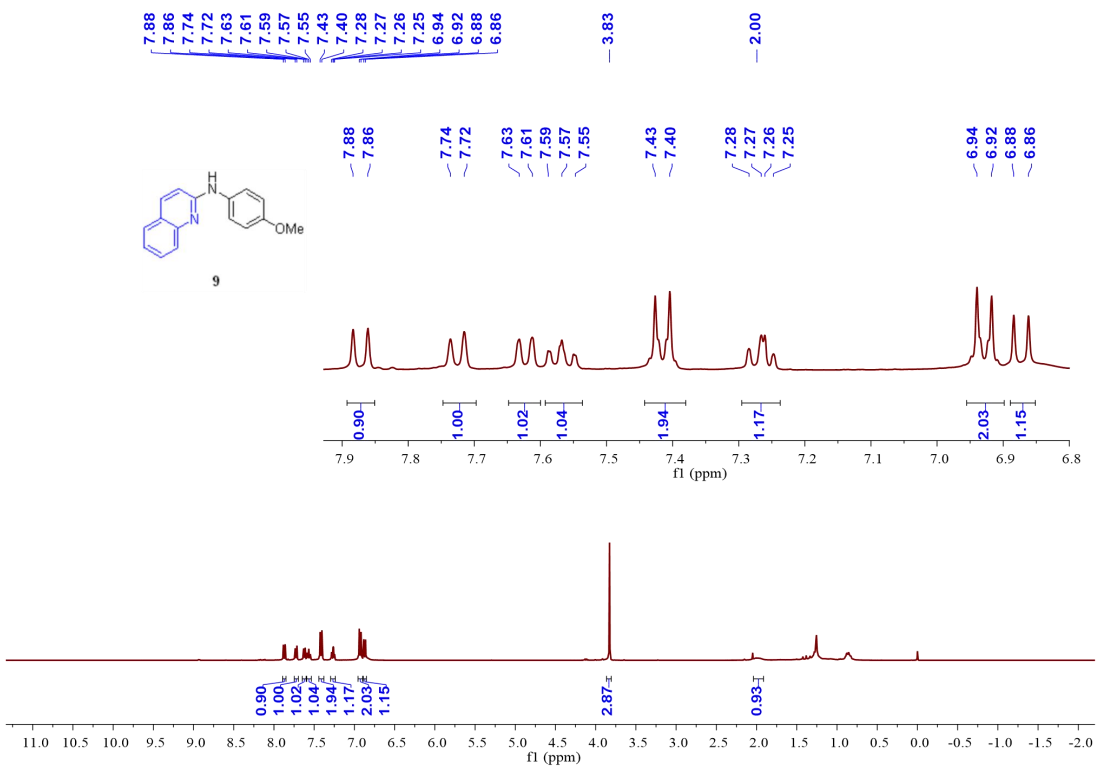

Fig. S32 ^{1}H NMR spectrum of **9** in $CDCl_3$ (400 MHz)

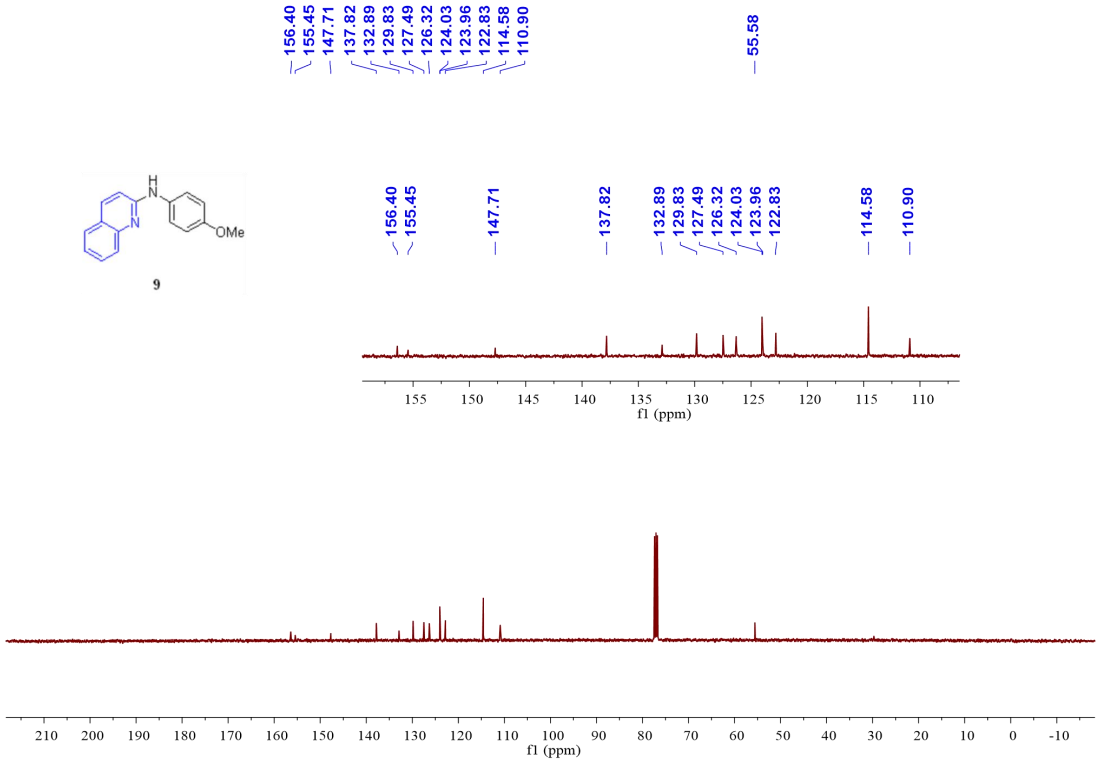

Fig. S33 ^{13}C NMR spectrum of **9** in $CDCl_3$ (101 MHz)

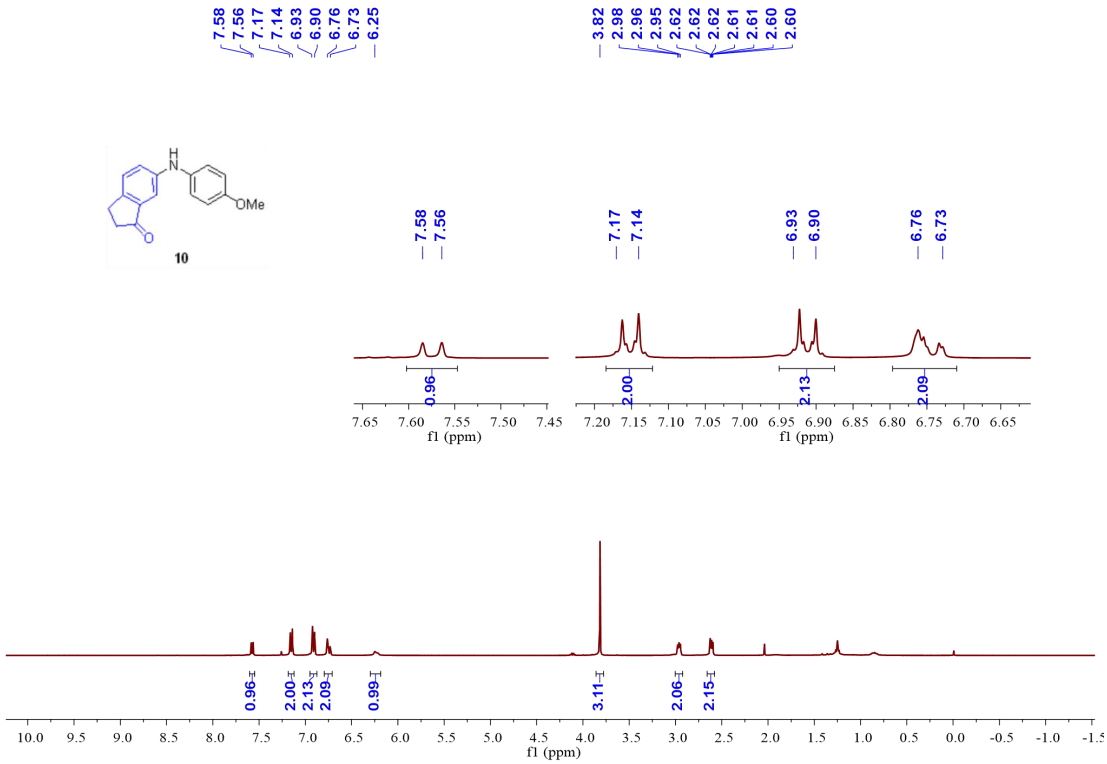

Fig. S34 ^{1}H NMR spectrum of **10** in $CDCl_3$ (400 MHz)

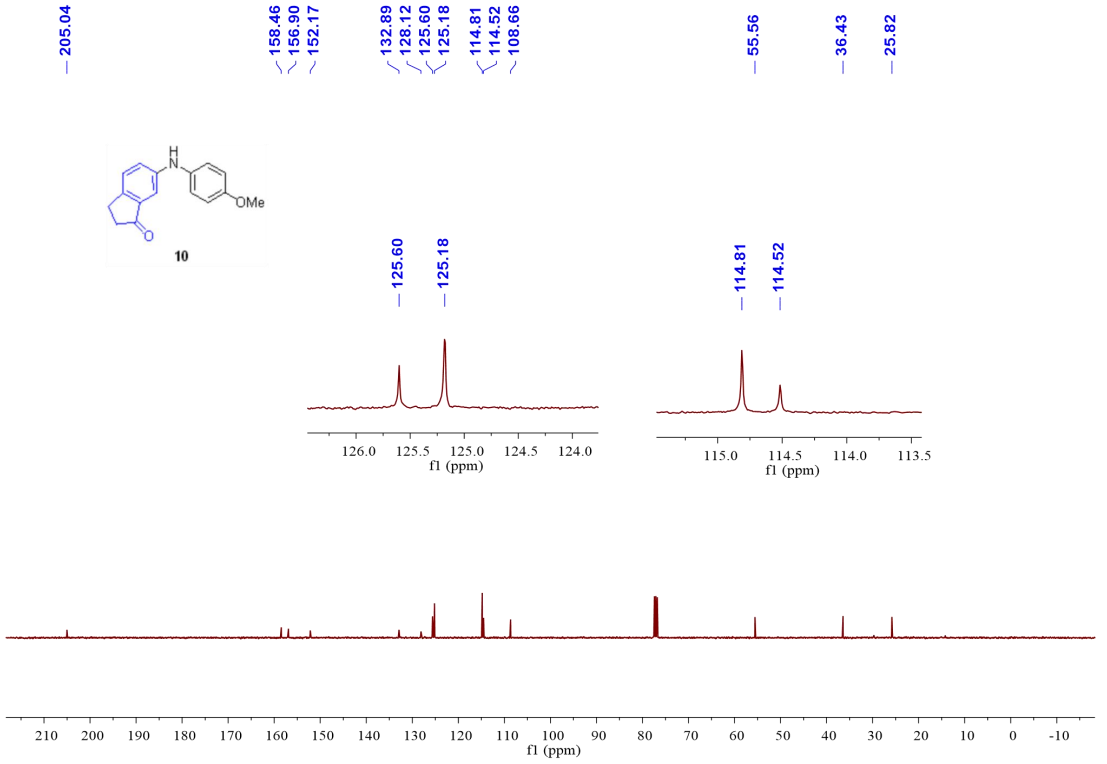

Fig. S35 ^{13}C NMR spectrum of **10** in $CDCl_3$ (101 MHz)

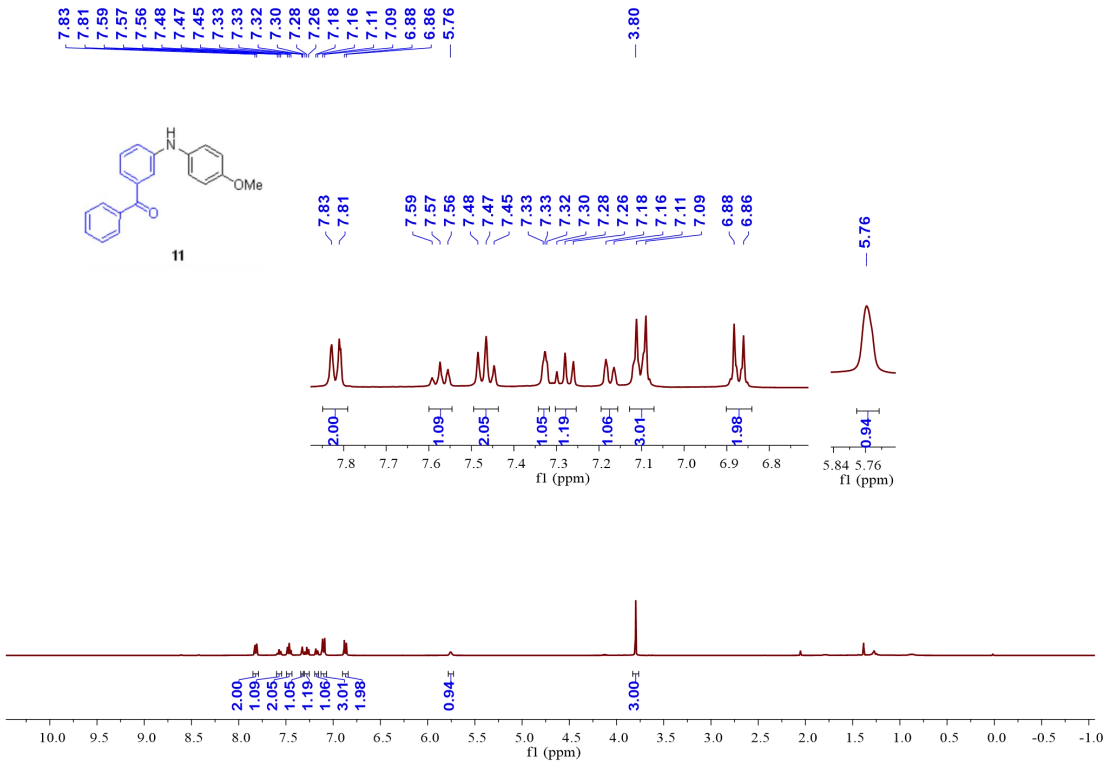

Fig. S36 ^{1}H NMR spectrum of **11** in $CDCl_3$ (400 MHz)

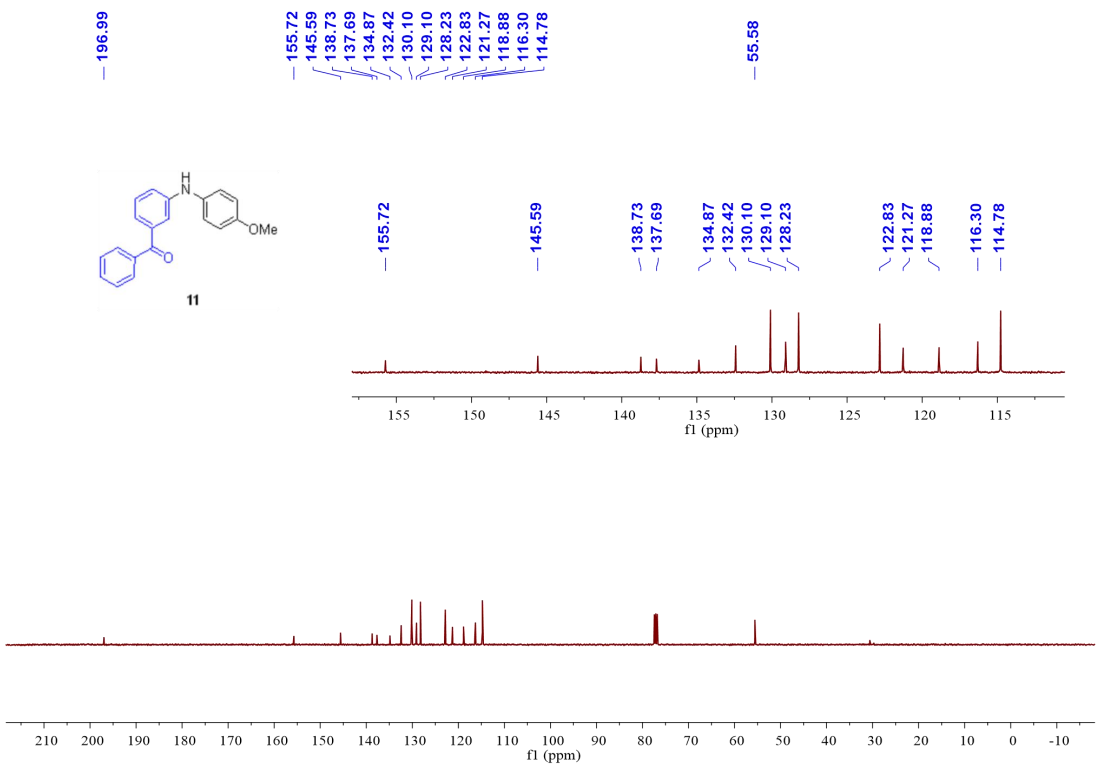

Fig. S37 ^{13}C NMR spectrum of **11** in $CDCl_3$ (101 MHz)

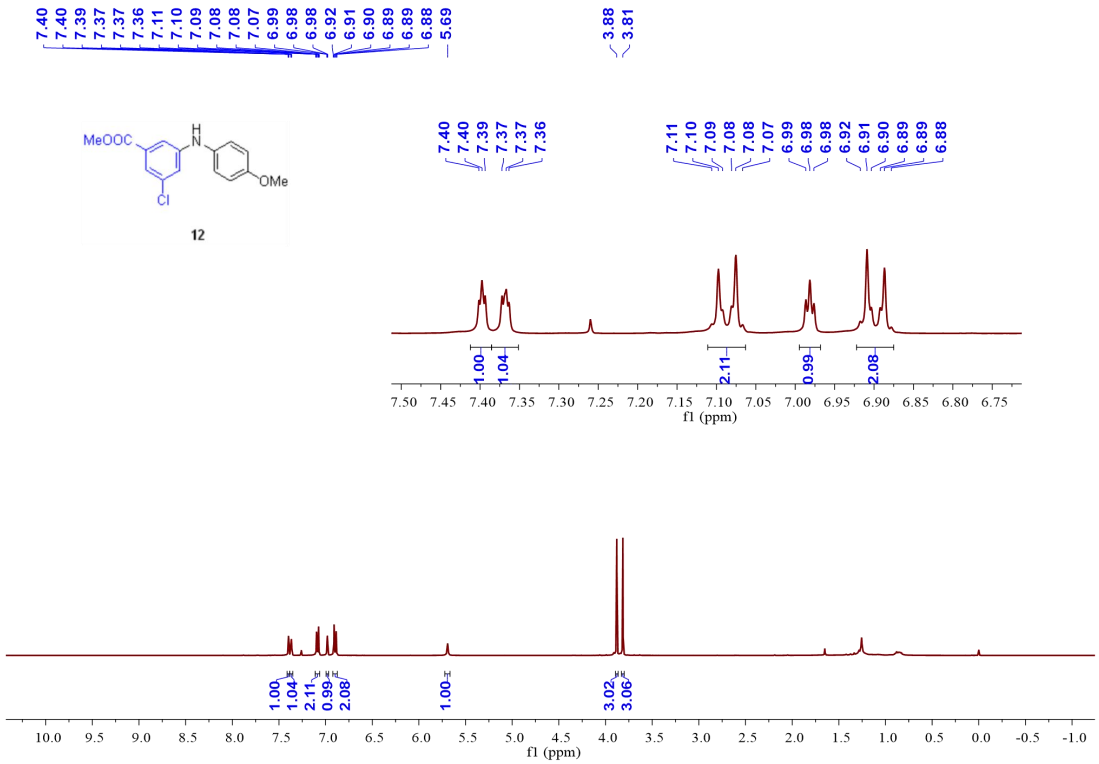

Fig. S38 ^{1}H NMR spectrum of **12** in $CDCl_3$ (400 MHz)

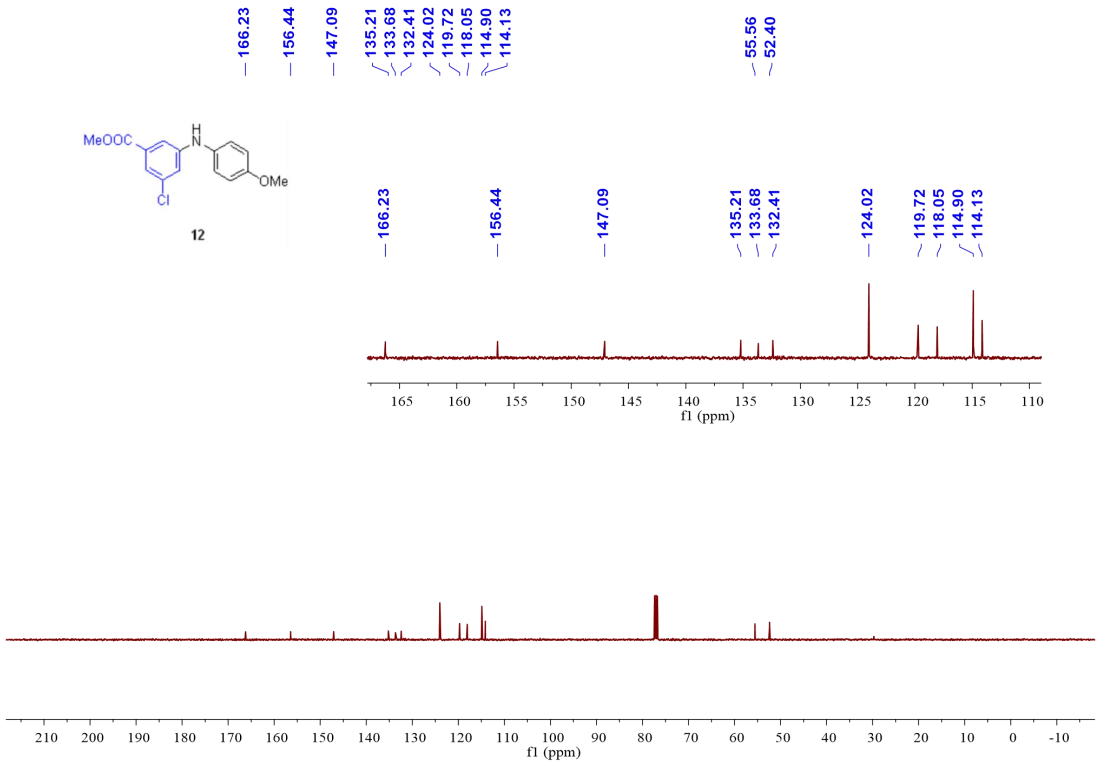

Fig. S39 ^{13}C NMR spectrum of **12** in $CDCl_3$ (101 MHz)

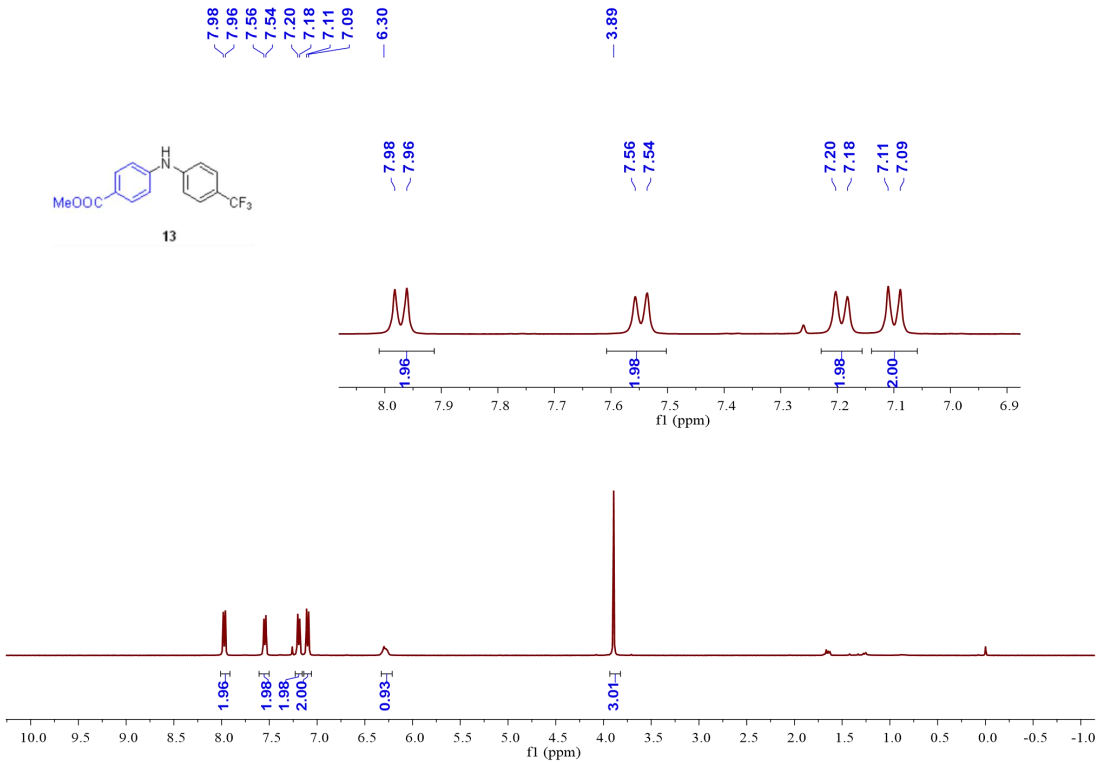

Fig. S40 ^{1}H NMR spectrum of **13** in $CDCl_3$ (400 MHz)

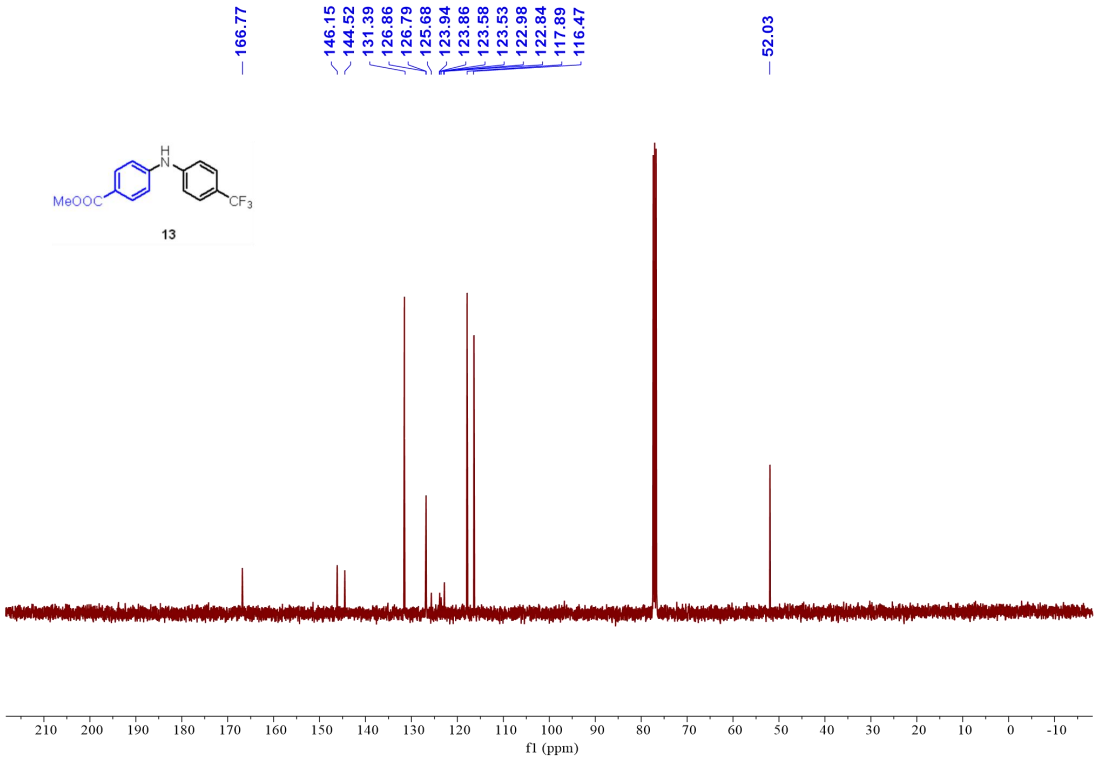

Fig. S41 ^{13}C NMR spectrum of **13** in $CDCl_3$ (101 MHz)

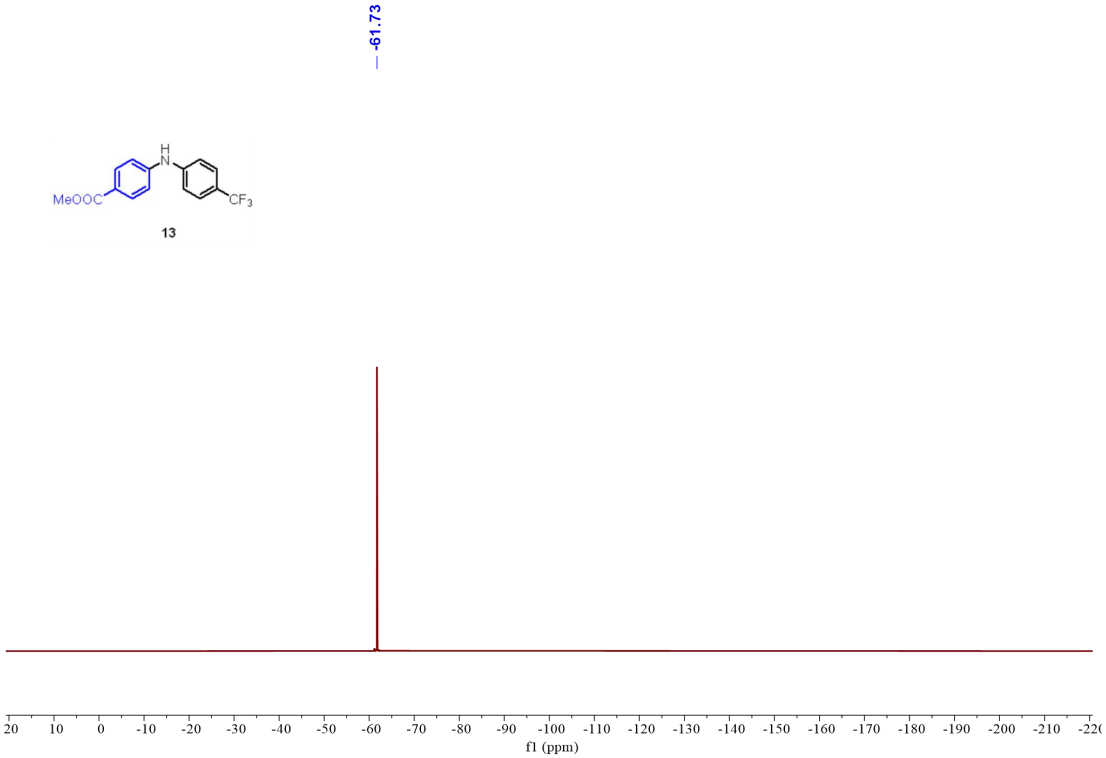

Fig. S42 ^{19}F NMR spectrum of **13** in $CDCl_3$ (377 MHz)

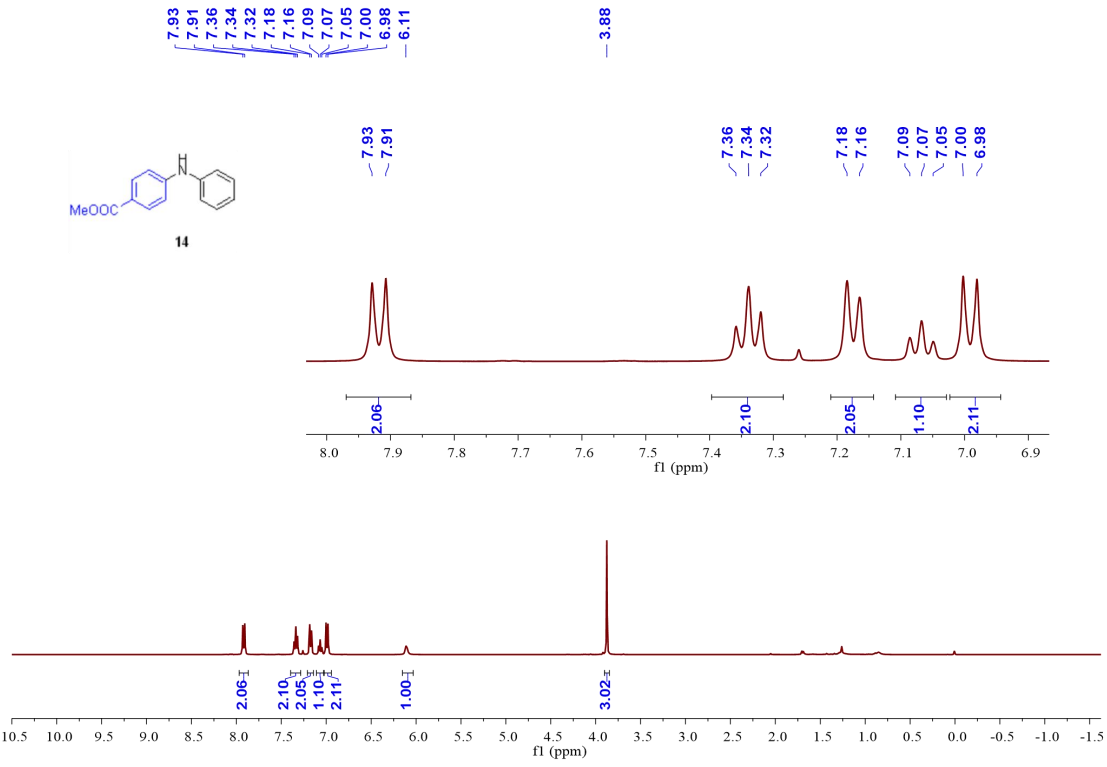

Fig. S43 ^{1}H NMR spectrum of **14** in $CDCl_3$ (400 MHz)

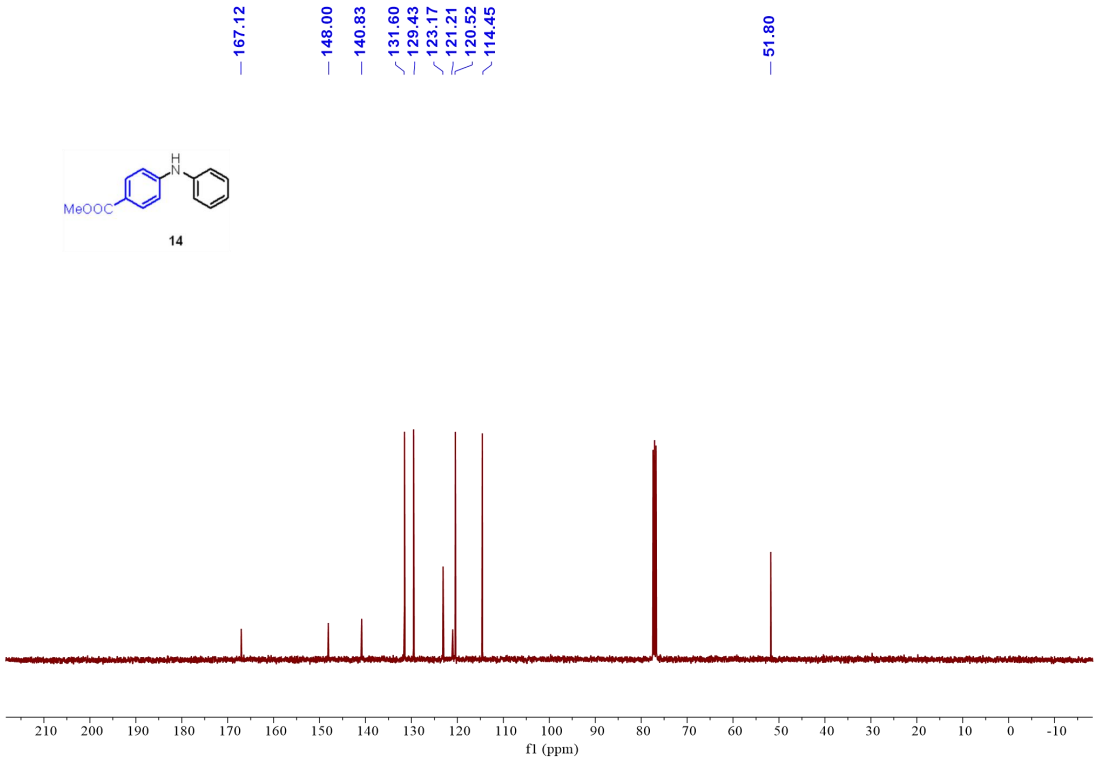

Fig. S44 ^{13}C NMR spectrum of **14** in $CDCl_3$ (101 MHz)

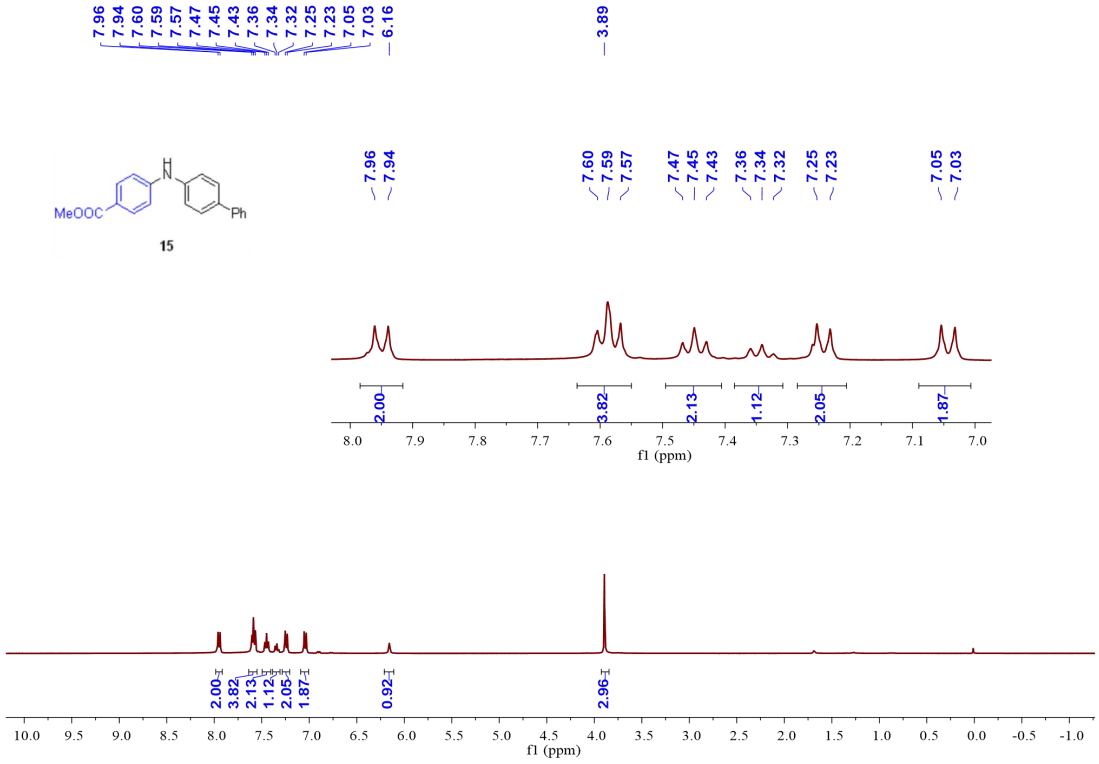

Fig. S45 ^{1}H NMR spectrum of **15** in $CDCl_3$ (400 MHz)

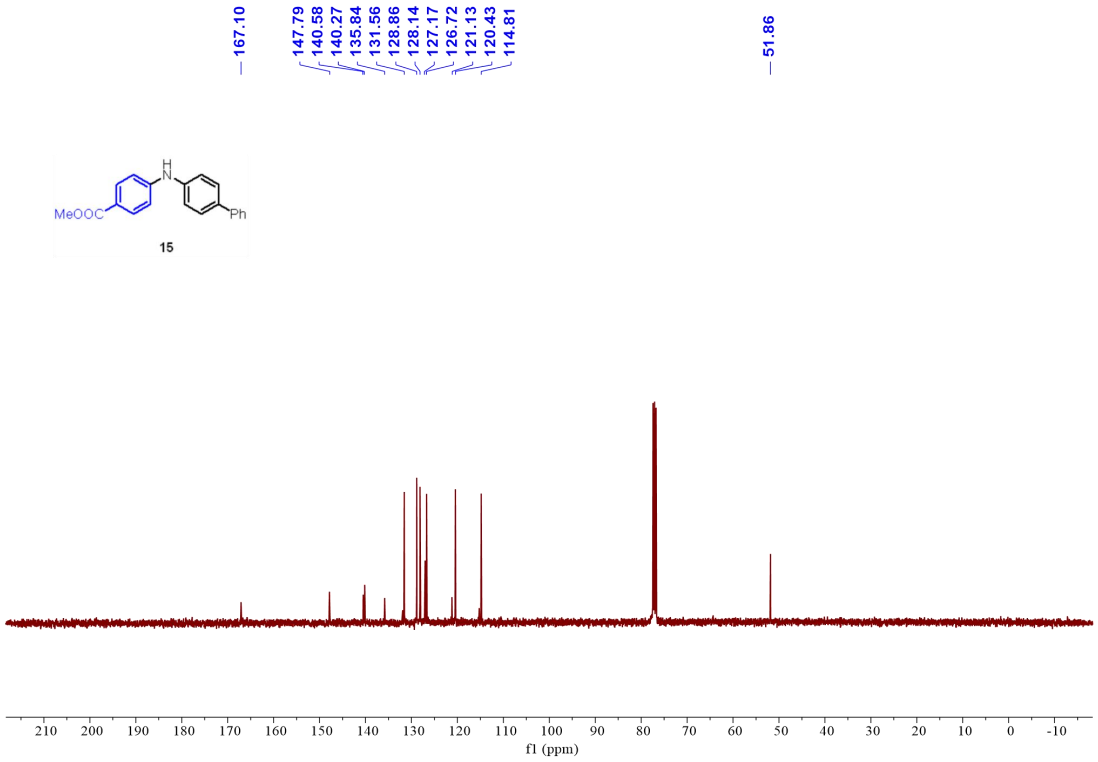

Fig. S46 ^{13}C NMR spectrum of **15** in $CDCl_3$ (101 MHz)

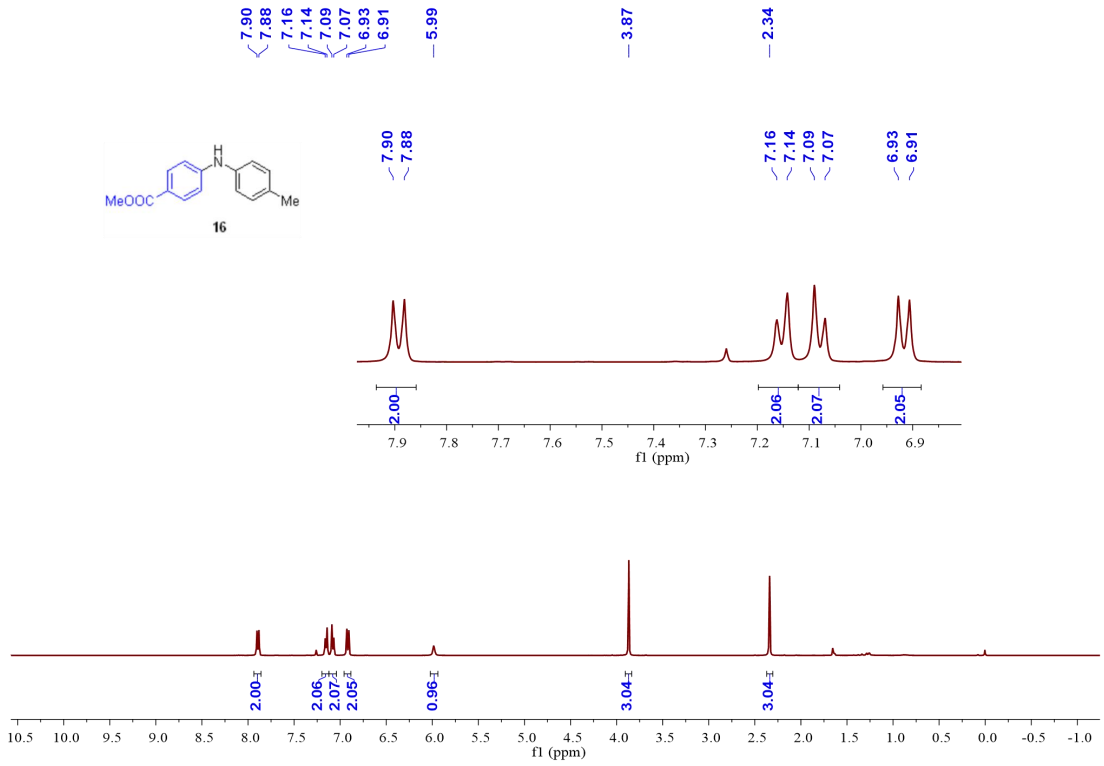

Fig. S47 ^{1}H NMR spectrum of **16** in $CDCl_3$ (400 MHz)

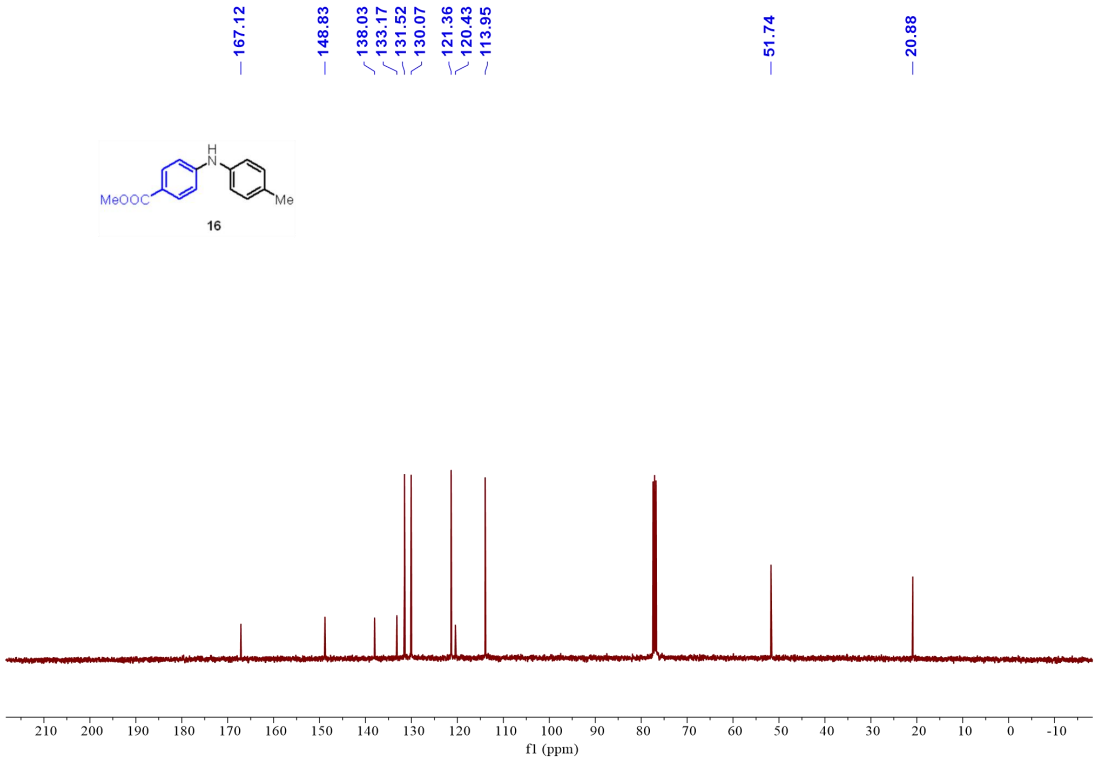

Fig. S48 ^{13}C NMR spectrum of **16** in $CDCl_3$ (101 MHz)

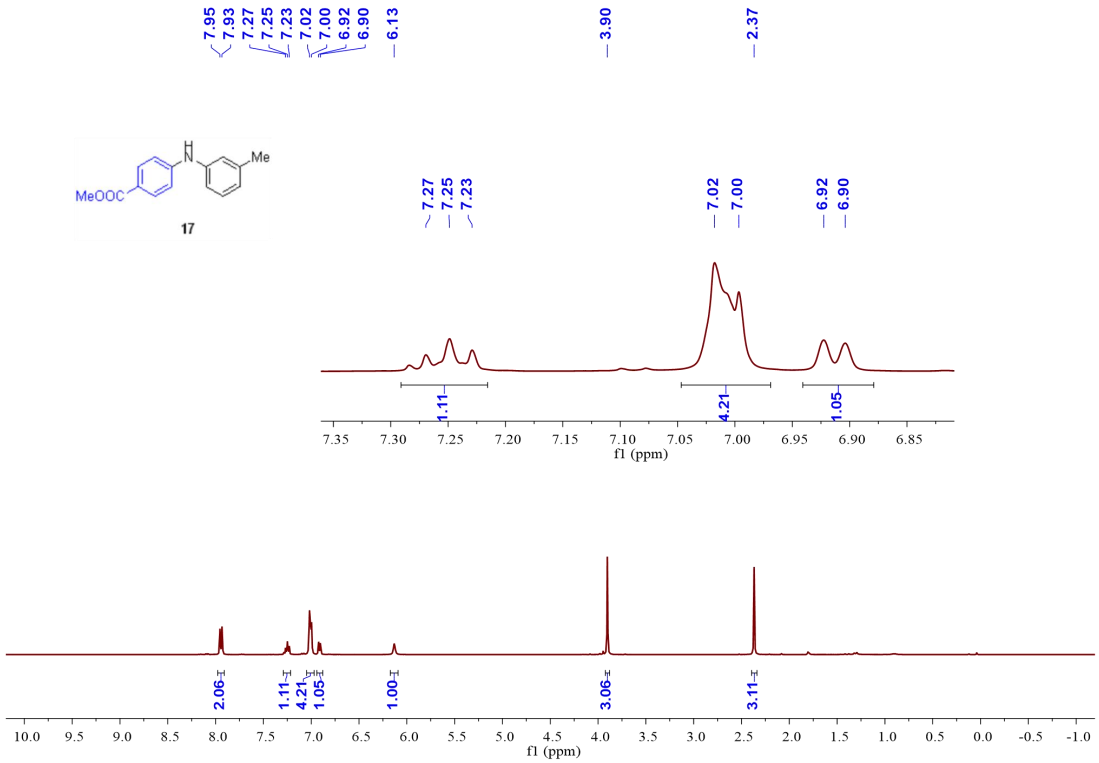

Fig. S49 ^{1}H NMR spectrum of **17** in $CDCl_3$ (400 MHz)

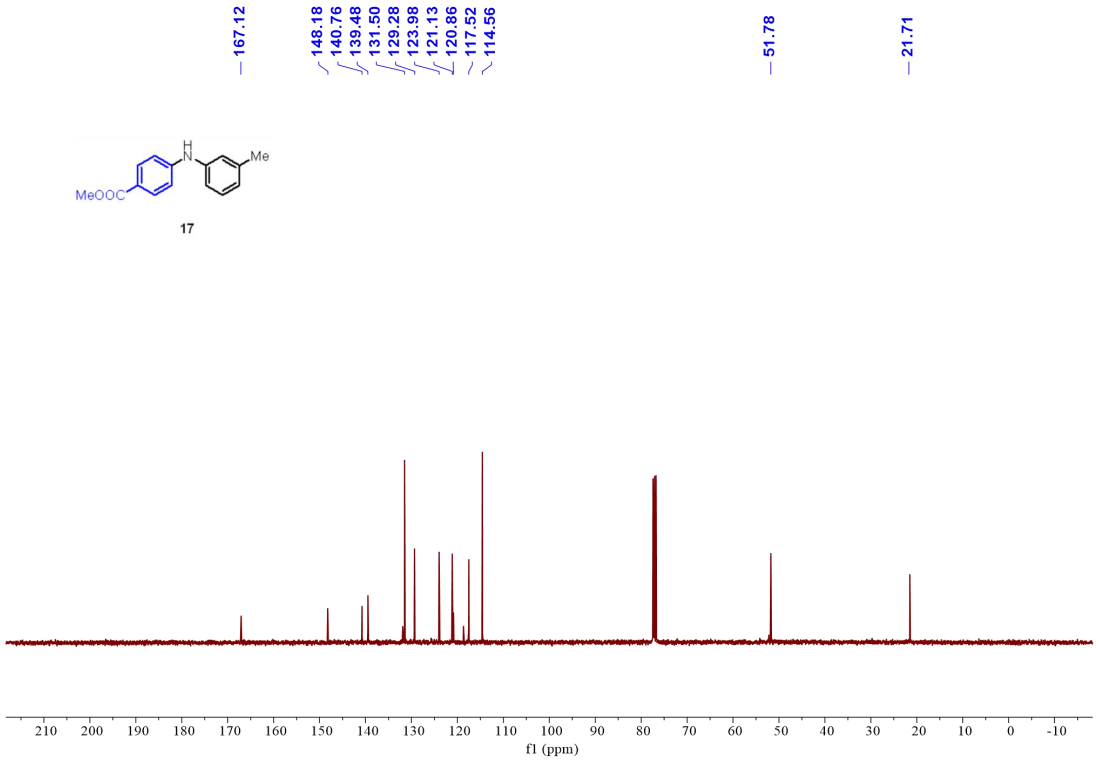

Fig. S50 ^{13}C NMR spectrum of **17** in $CDCl_3$ (101 MHz)

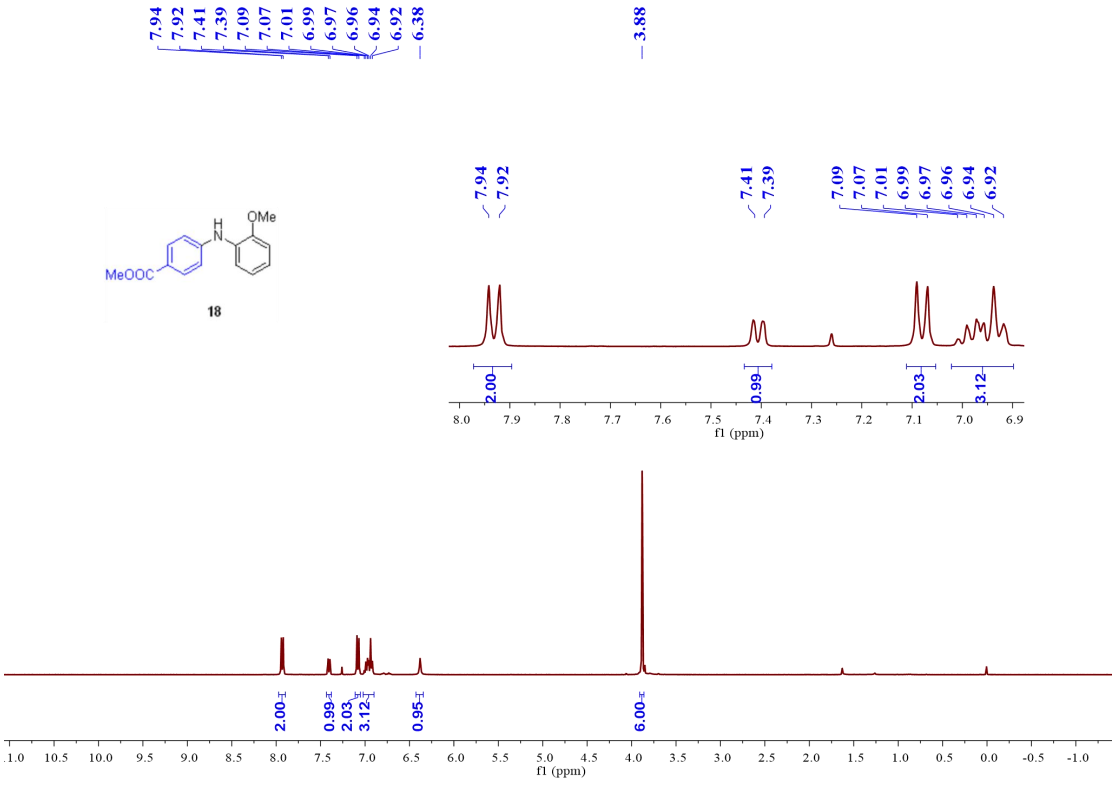

Fig. S51 ^{1}H NMR spectrum of **18** in $CDCl_3$ (400 MHz)

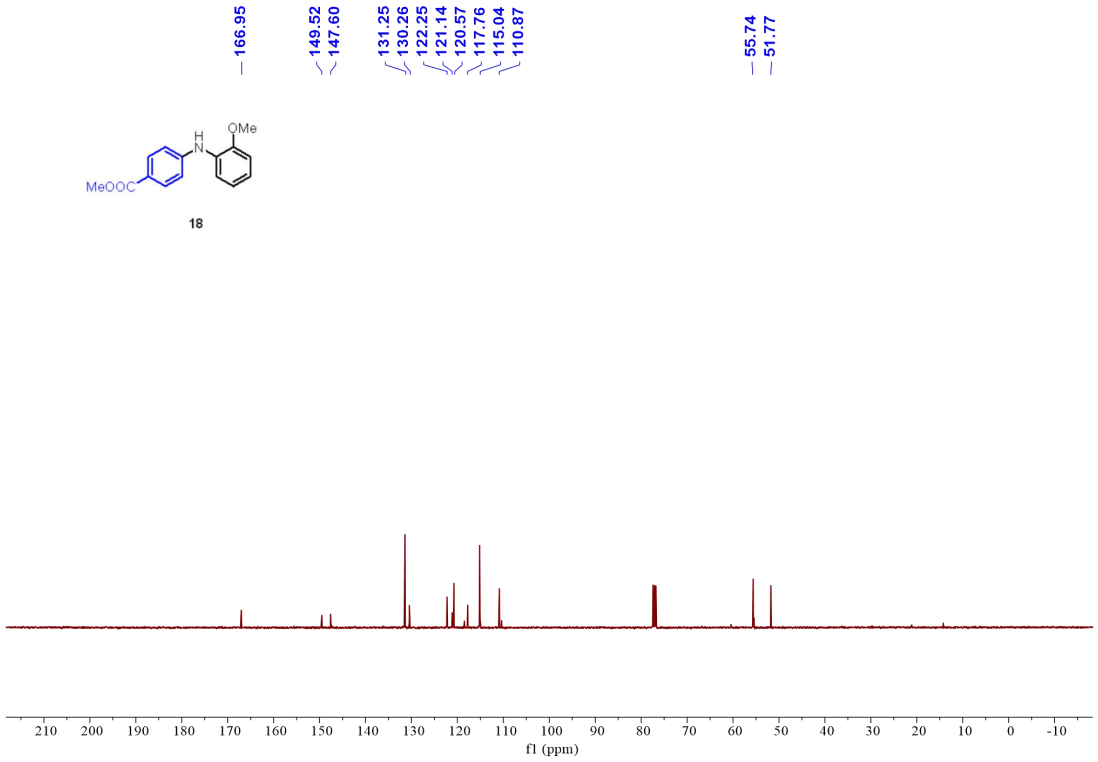

Fig. S52 ^{13}C NMR spectrum of **18** in $CDCl_3$ (101 MHz)

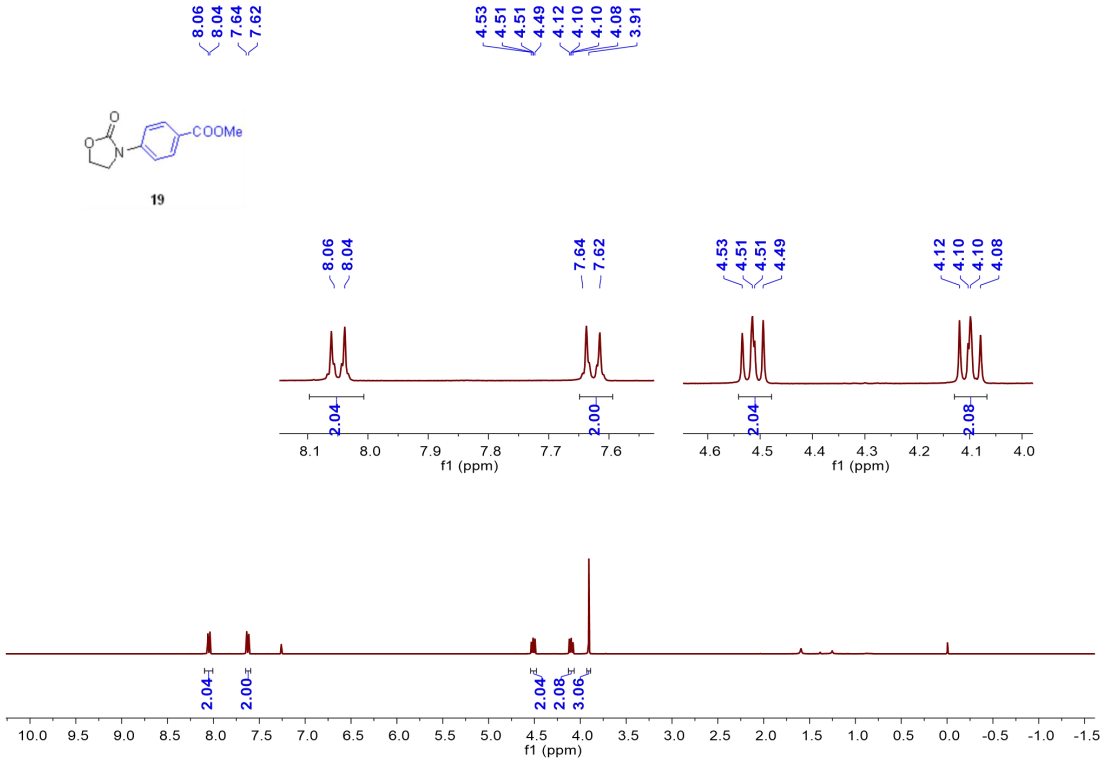

Fig. S53 ^{1}H NMR spectrum of **19** in $CDCl_3$ (400 MHz)

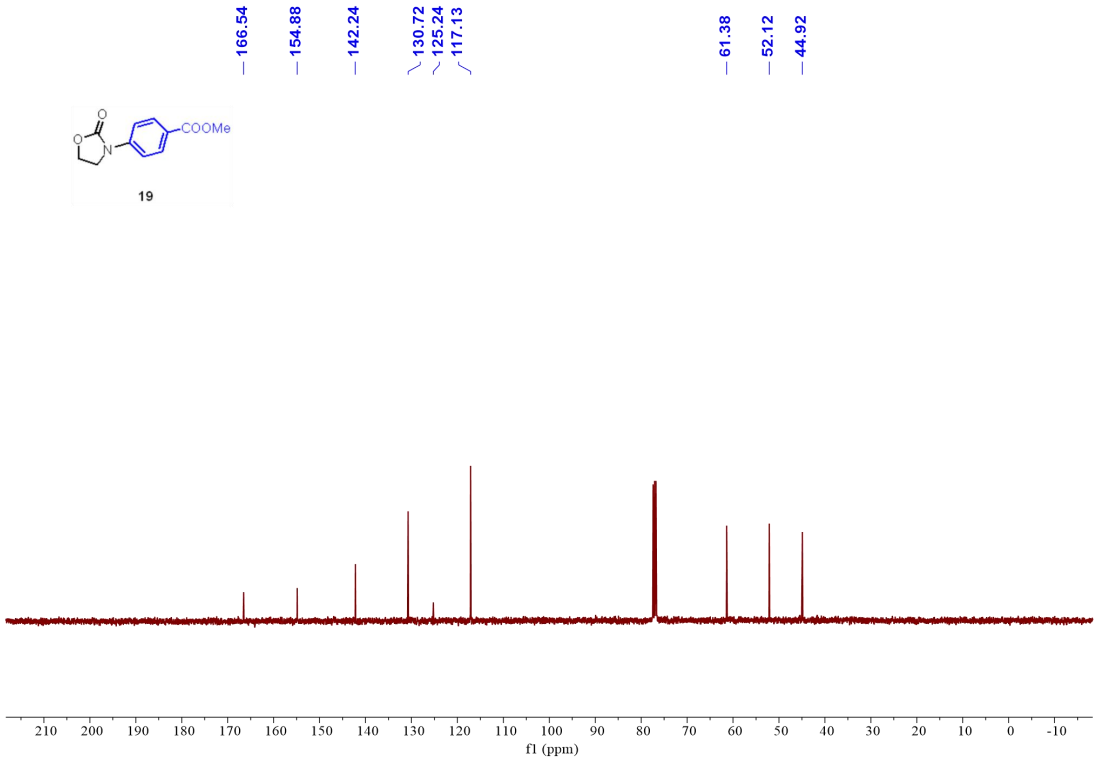

Fig. S54 ^{13}C NMR spectrum of **19** in $CDCl_3$ (101 MHz)

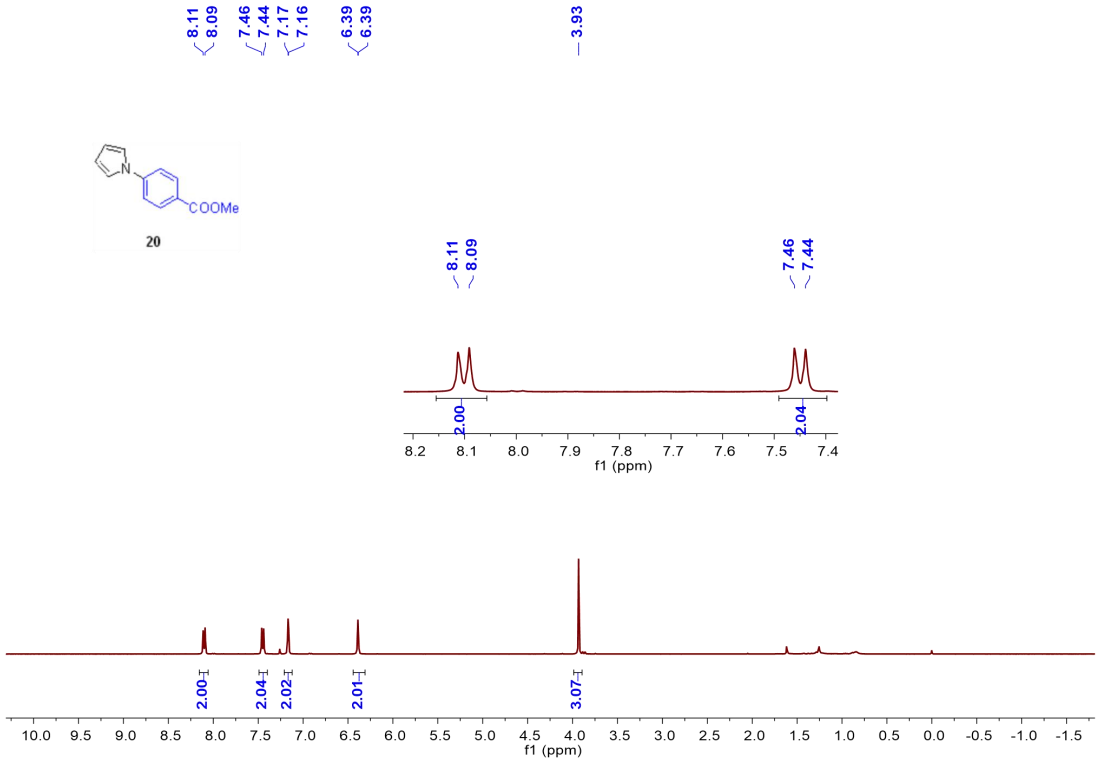

Fig. S55 ^{1}H NMR spectrum of **20** in $CDCl_3$ (400 MHz)

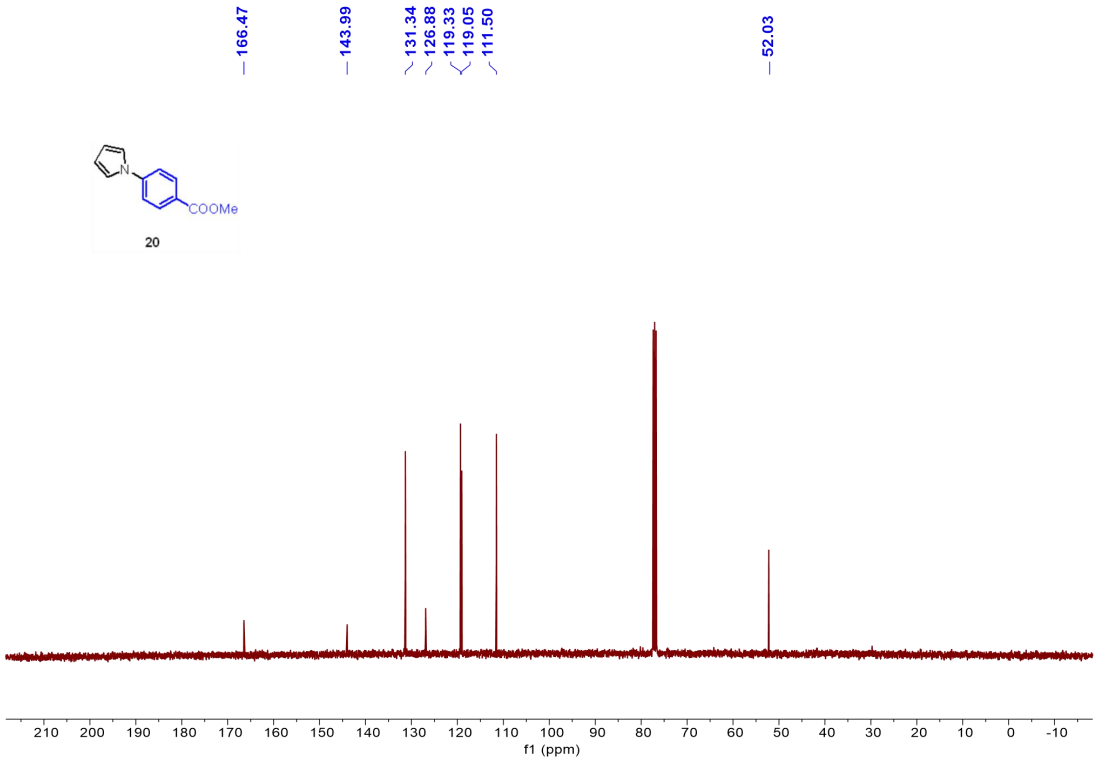

Fig. S56 ^{13}C NMR spectrum of **20** in $CDCl_3$ (101 MHz)

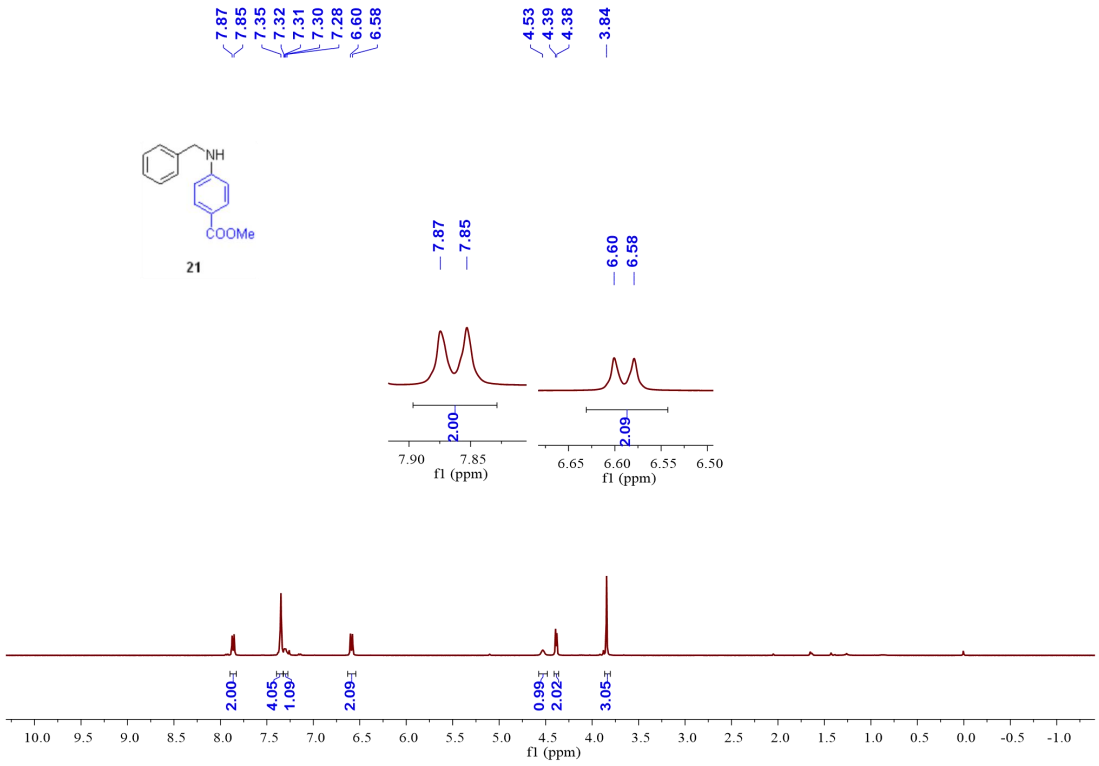

Fig. S57 ^{1}H NMR spectrum of **21** in $CDCl_3$ (400 MHz)

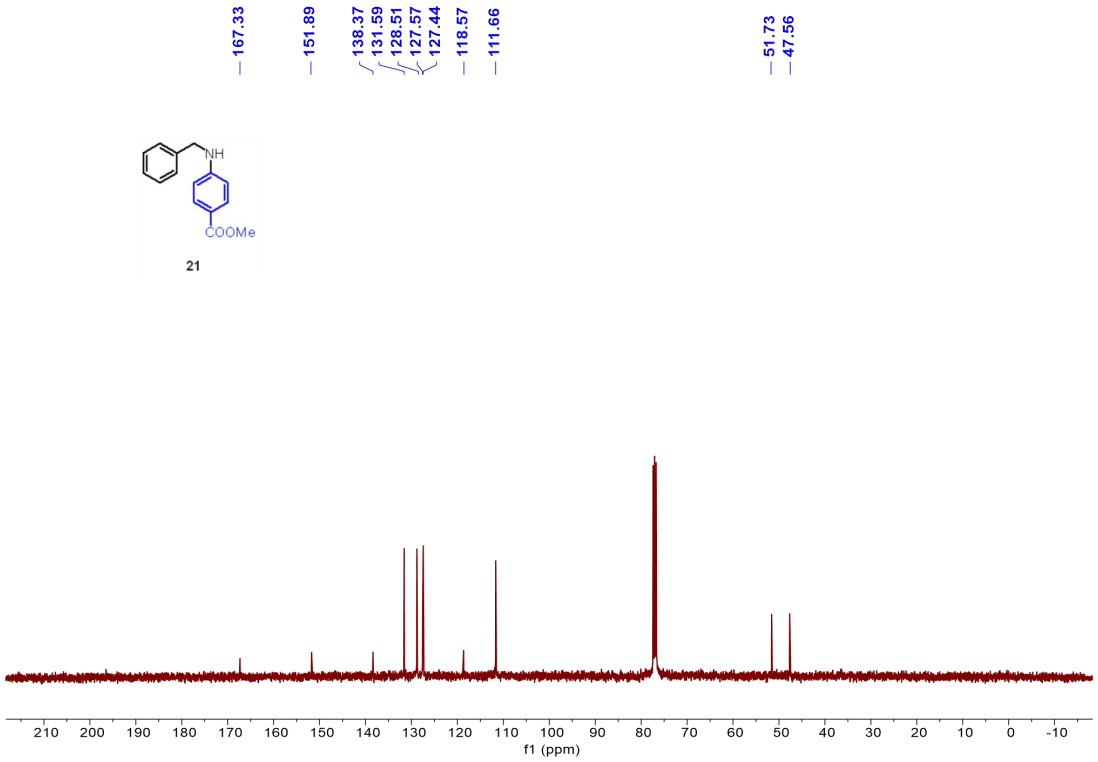

Fig. S58 ^{13}C NMR spectrum of **21** in $CDCl_3$ (101 MHz)

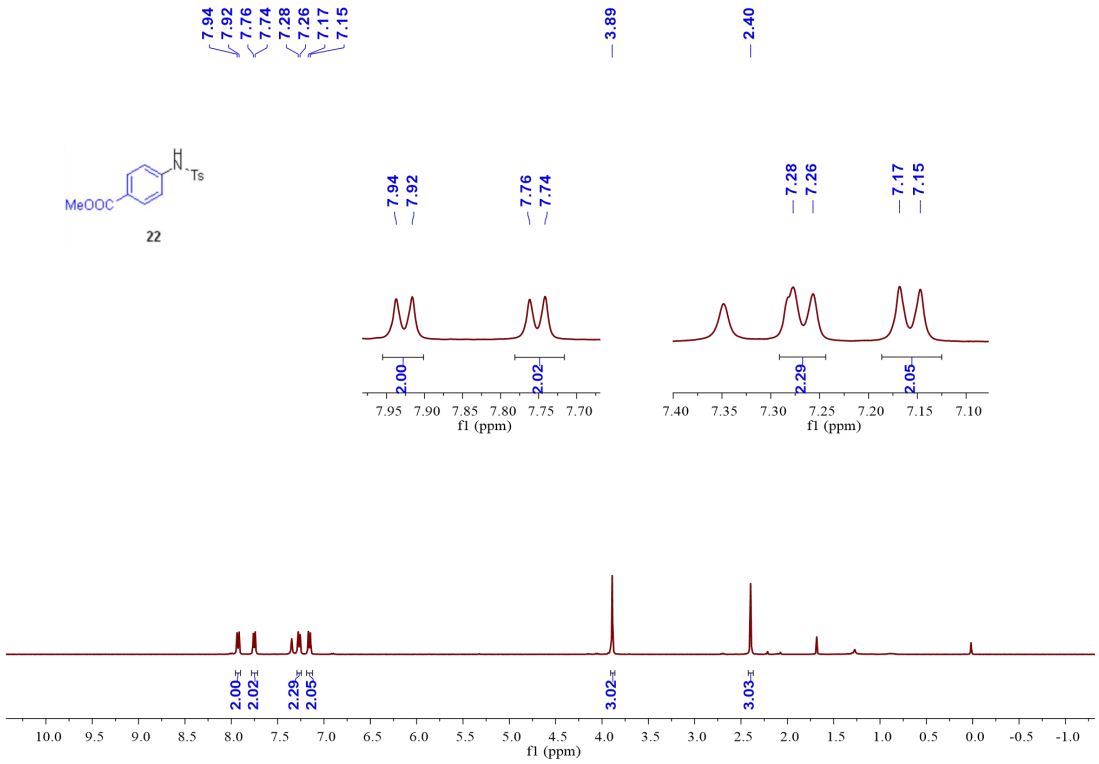

Fig. S59 ^{1}H NMR spectrum of **22** in $CDCl_3$ (400 MHz)

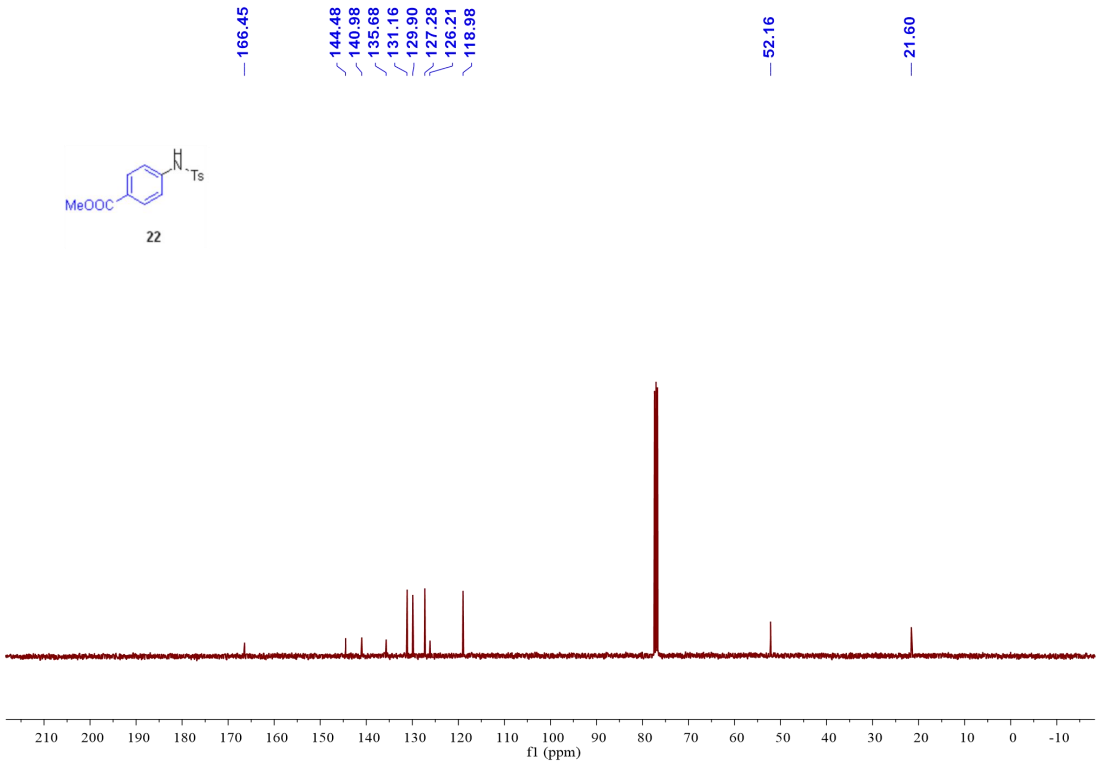

Fig. S60 ^{13}C NMR spectrum of **22** in $CDCl_3$ (101 MHz)

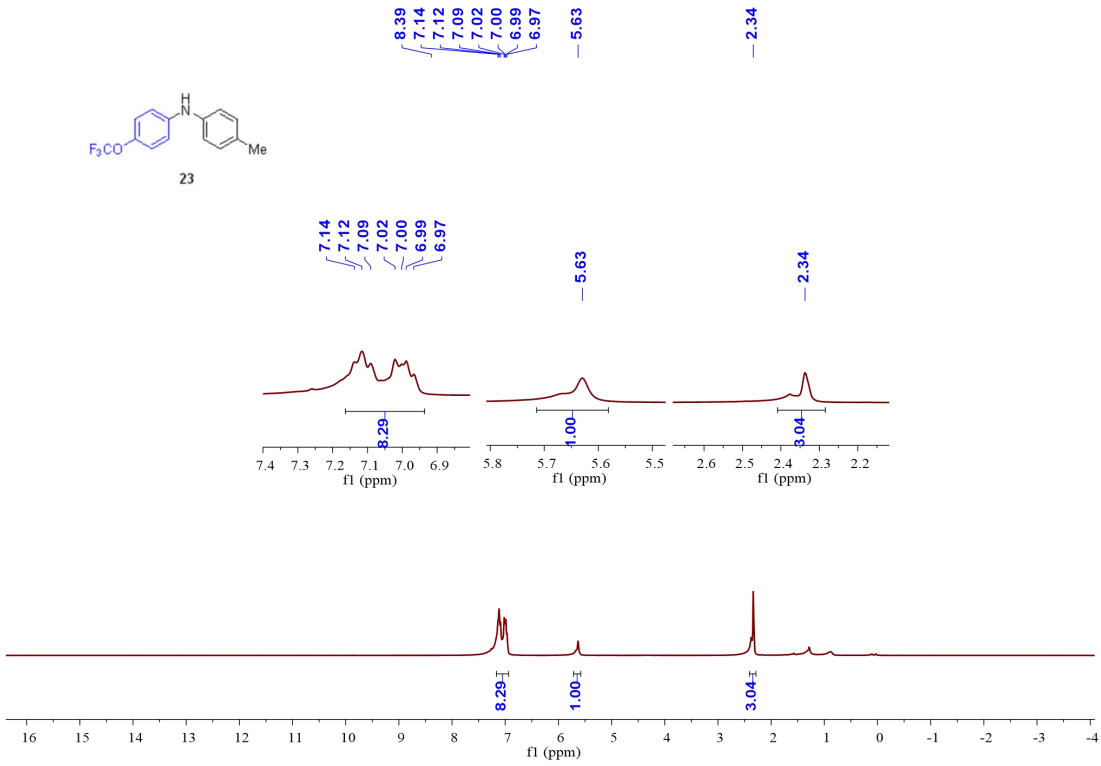

Fig. S61 ^{1}H NMR spectrum of **23** in $CDCl_3$ (400 MHz)

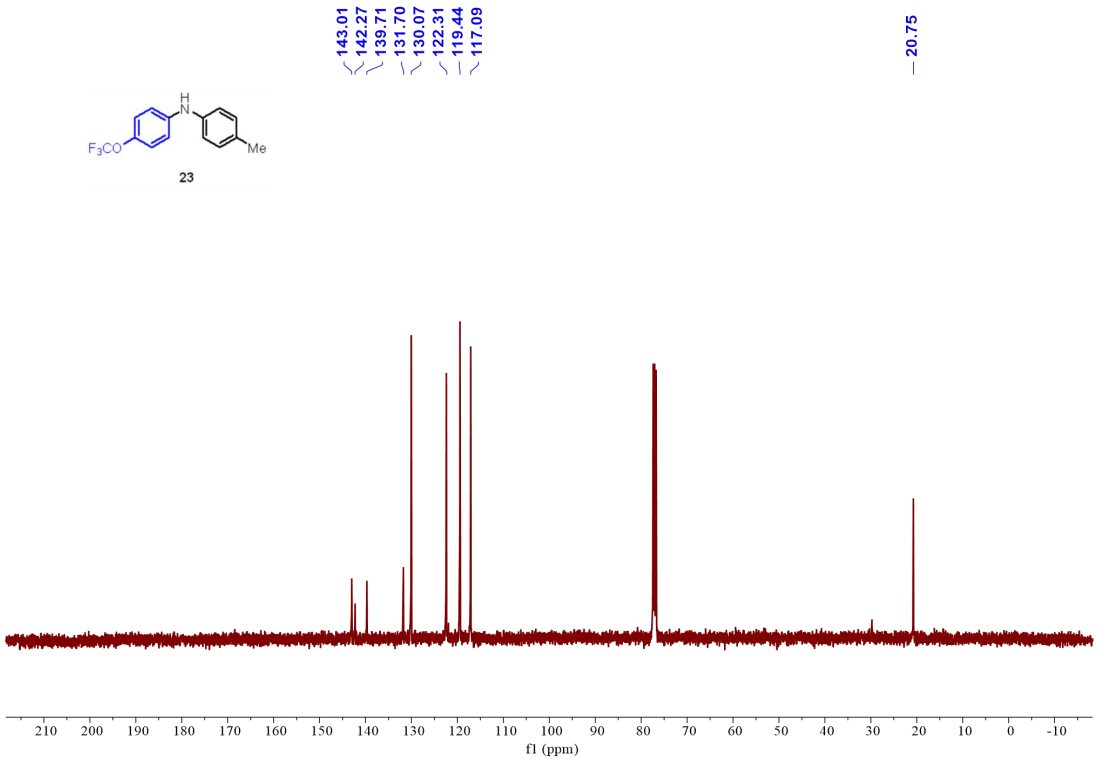

Fig. S62 ^{13}C NMR spectrum of **23** in $CDCl_3$ (101 MHz)

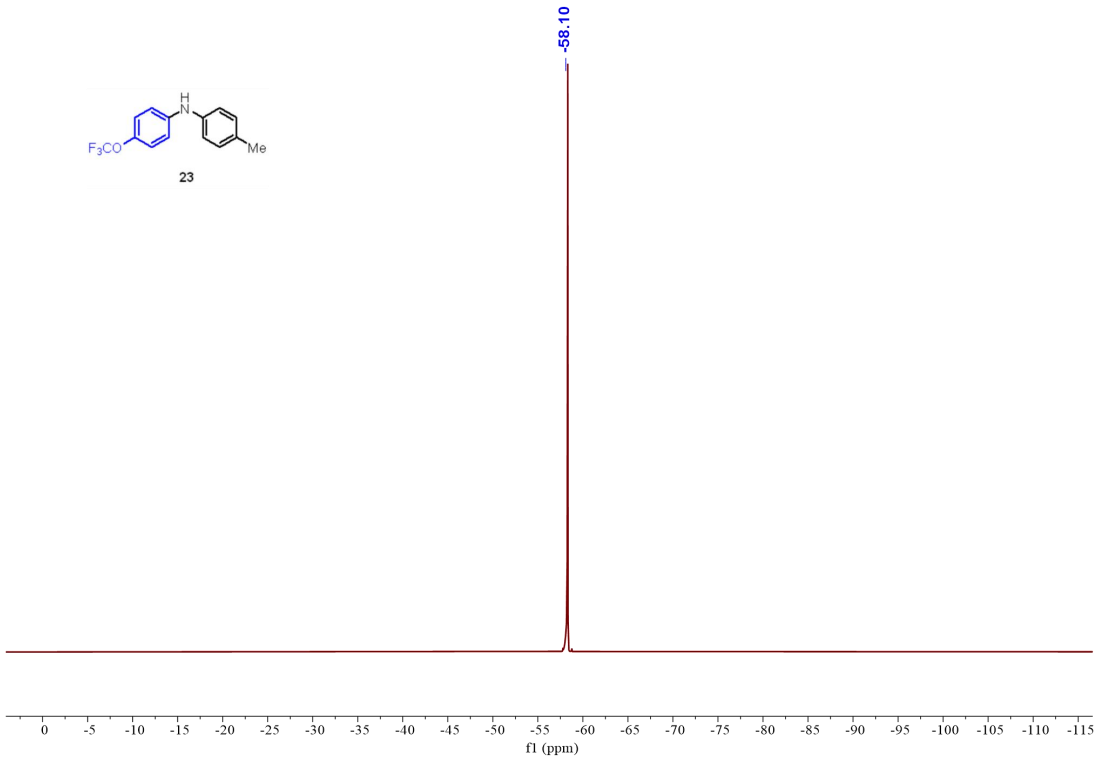

Fig. S63 ^{19}F NMR spectrum of **23** in $CDCl_3$ (377 MHz)

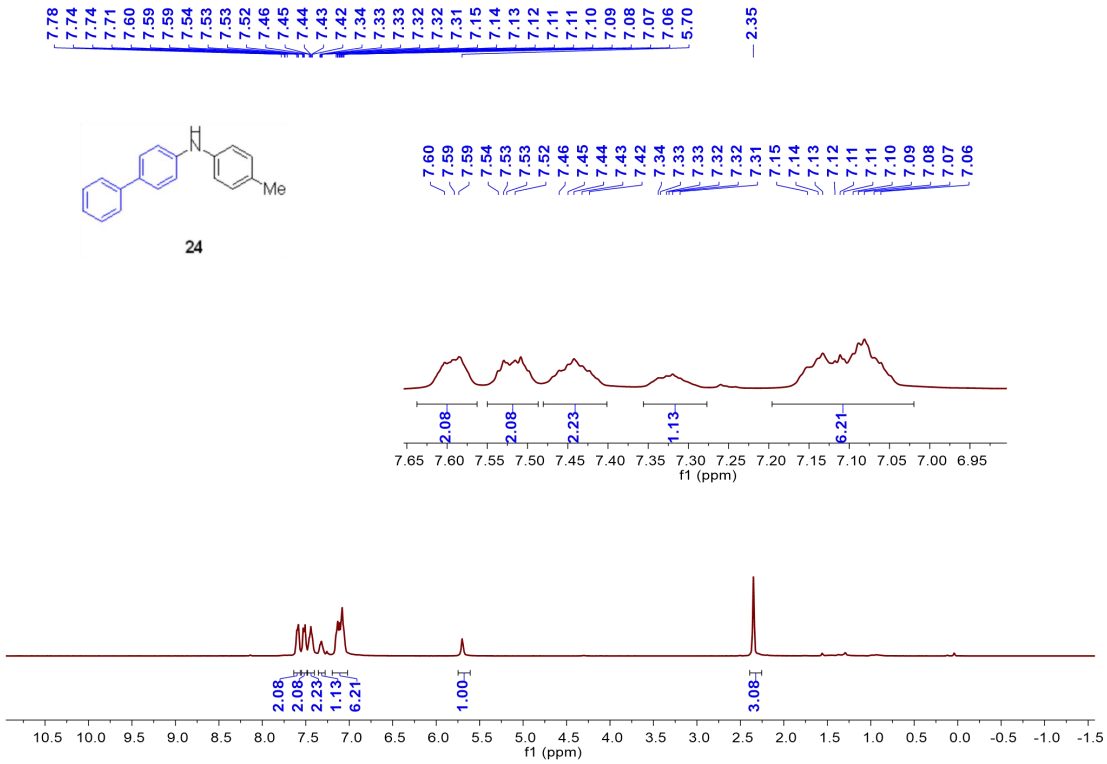

Fig. S64 ^{1}H NMR spectrum of **24** in $CDCl_3$ (400 MHz)

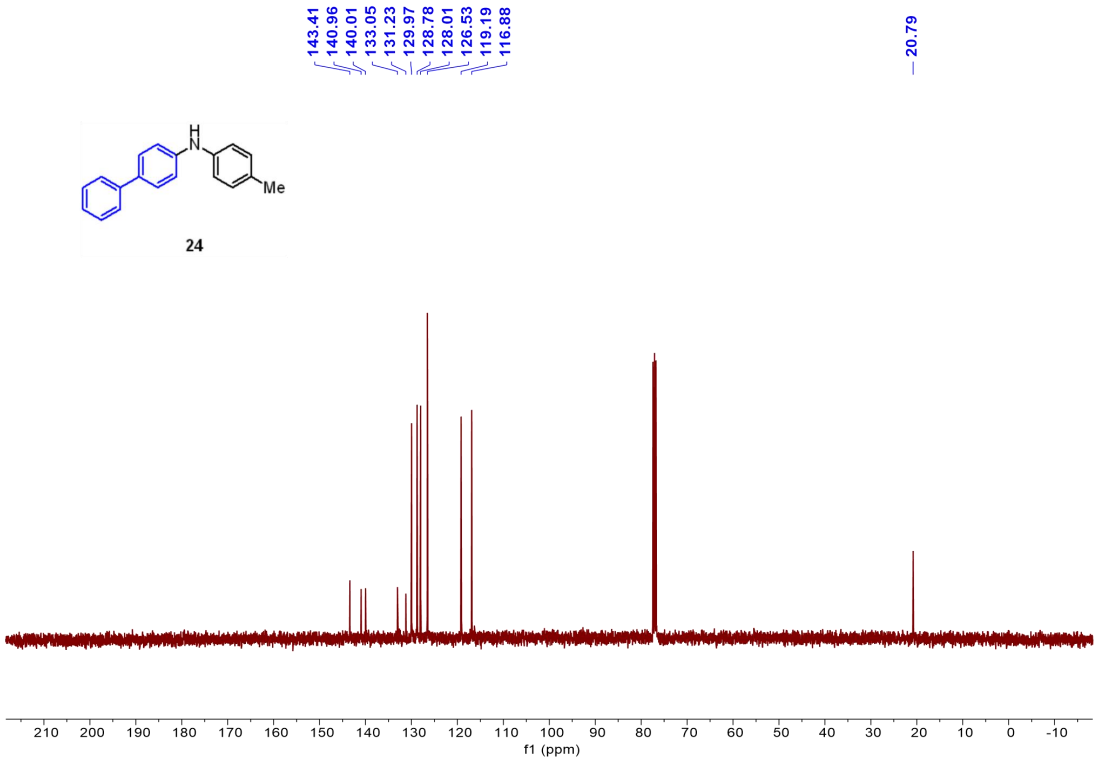

Fig. S65 ^{13}C NMR spectrum of **24** in $CDCl_3$ (101 MHz)

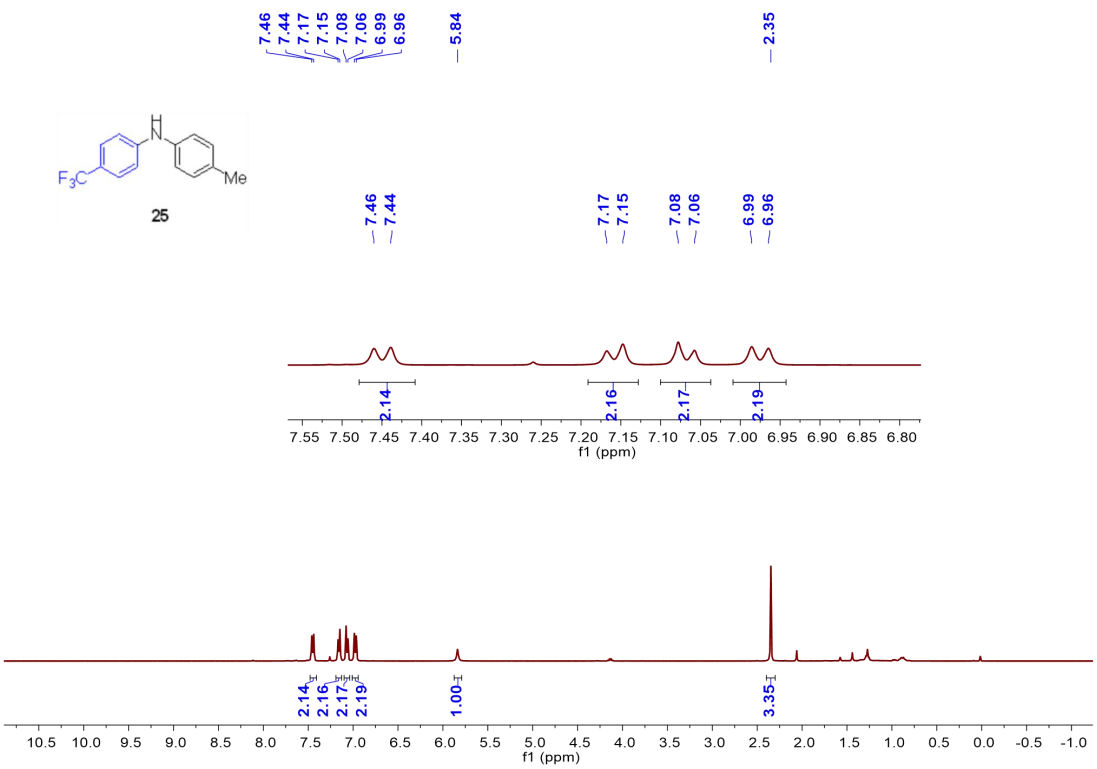

Fig. S66 ^{1}H NMR spectrum of **25** in $CDCl_3$ (400 MHz)

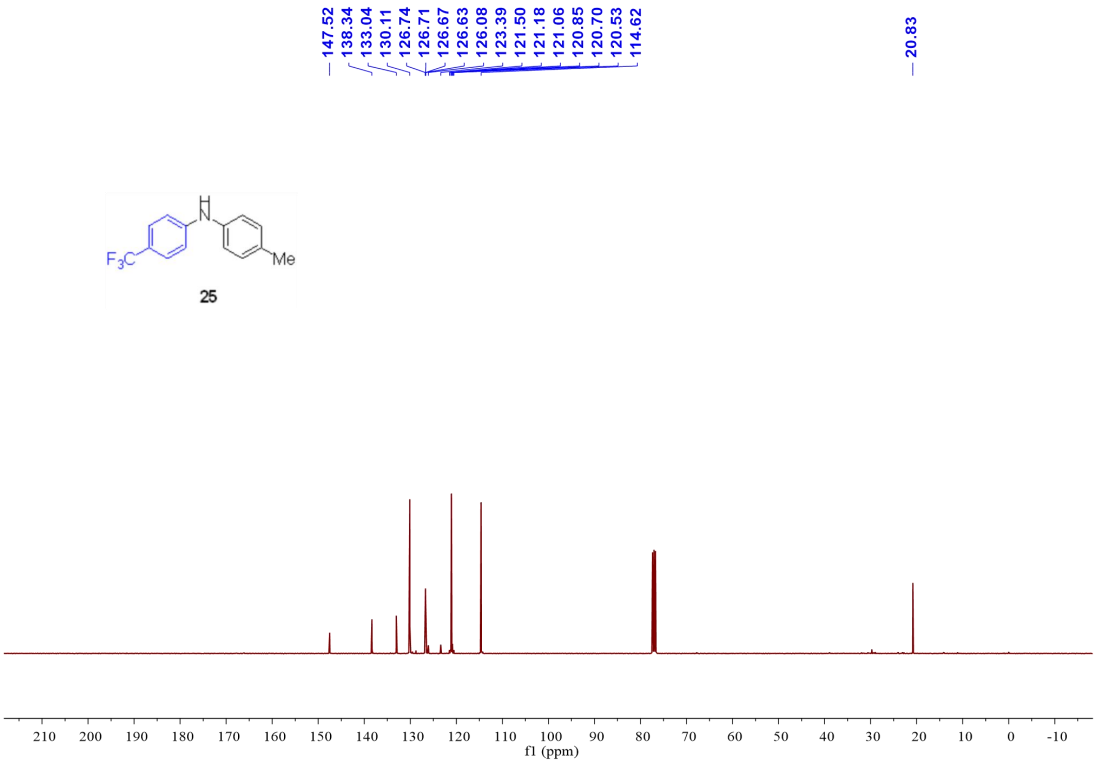

Fig. S67 ^{13}C NMR spectrum of **25** in $CDCl_3$ (101 MHz)

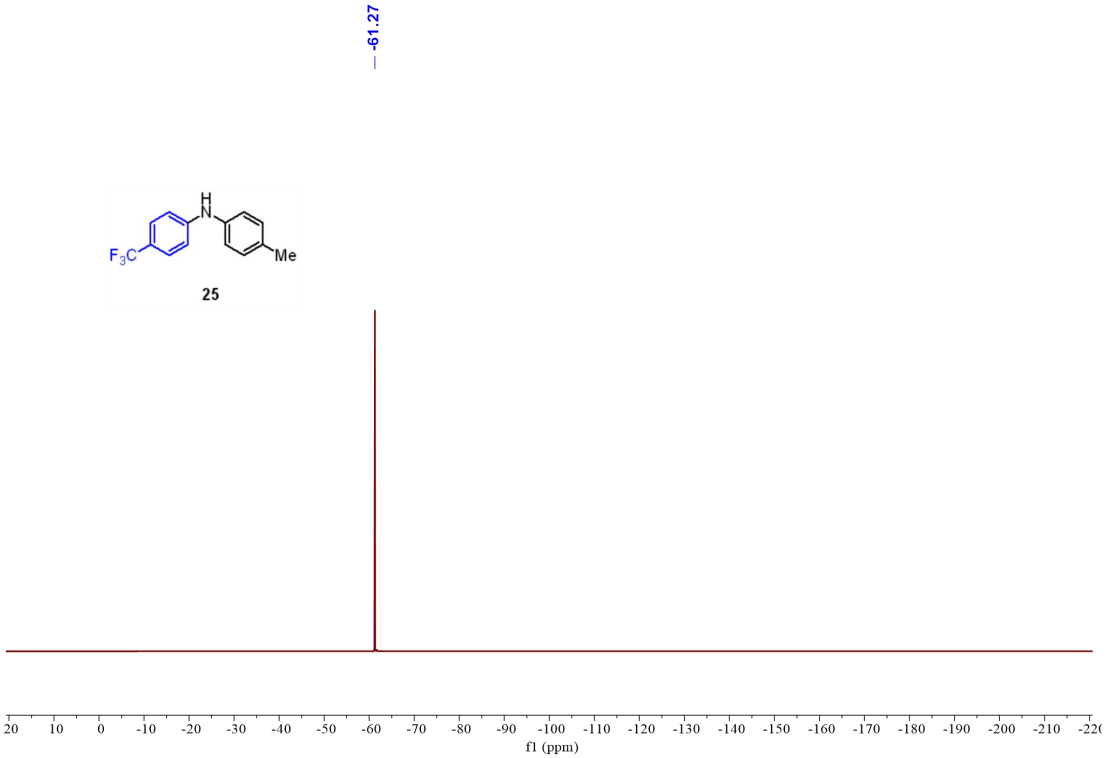

Fig. S68 ^{19}F NMR spectrum of **25** in $CDCl_3$ (377 MHz)

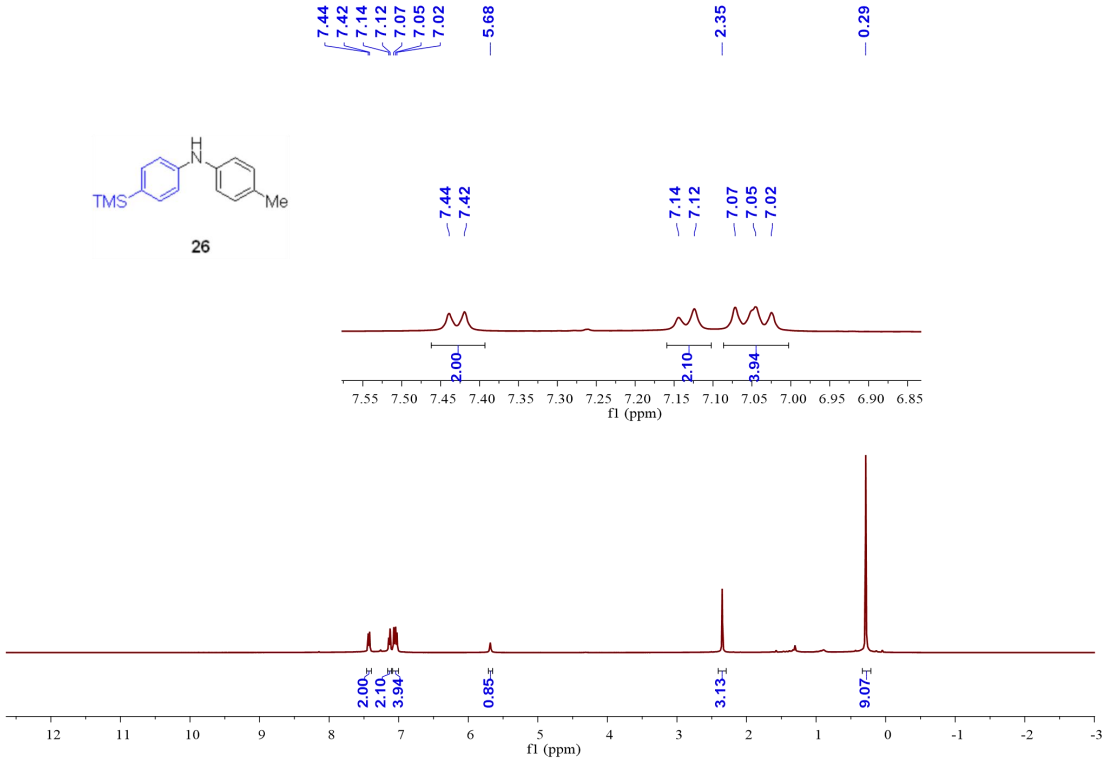

Fig. S69 ^{1}H NMR spectrum of **26** in $CDCl_3$ (400 MHz)

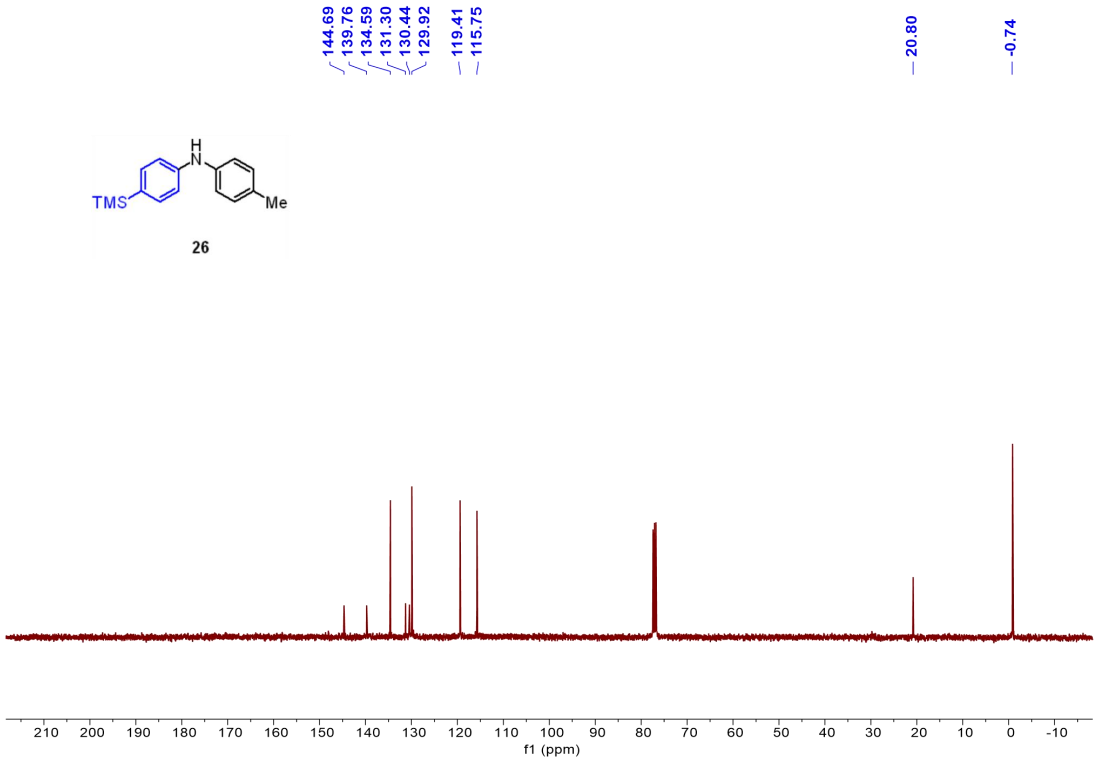

Fig. S70 ^{13}C NMR spectrum of **26** in $CDCl_3$ (101 MHz)

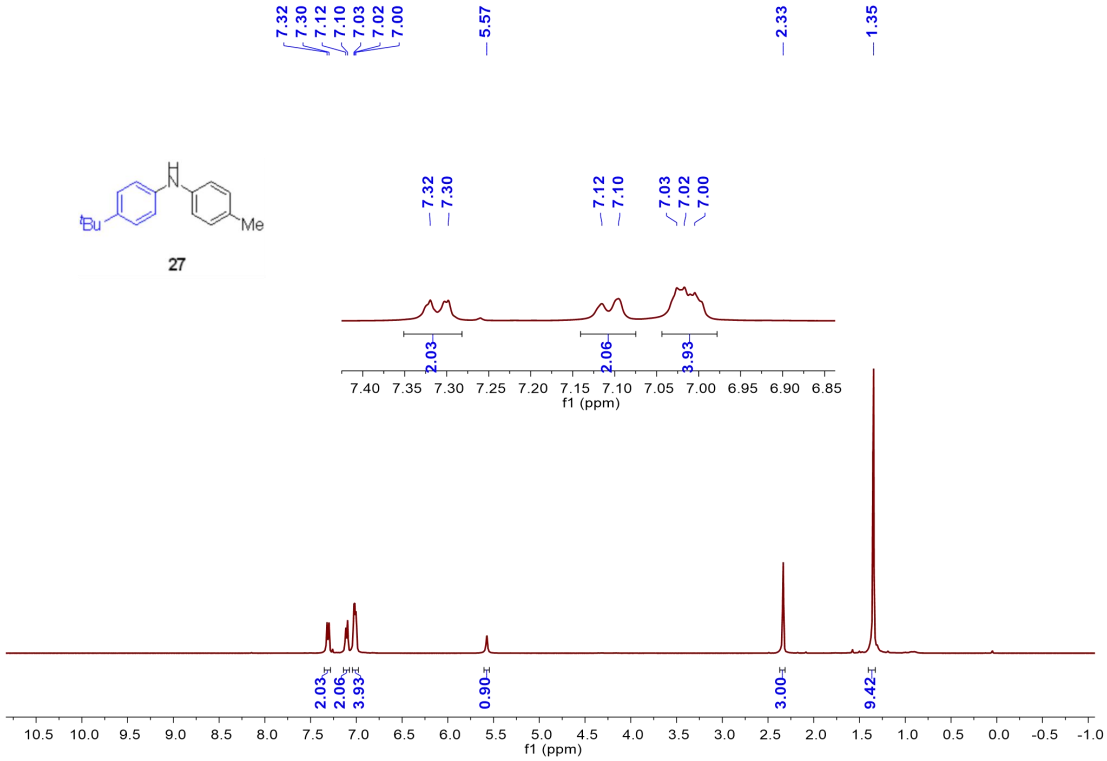

Fig. S71 ^{1}H NMR spectrum of **27** in $CDCl_3$ (400 MHz)

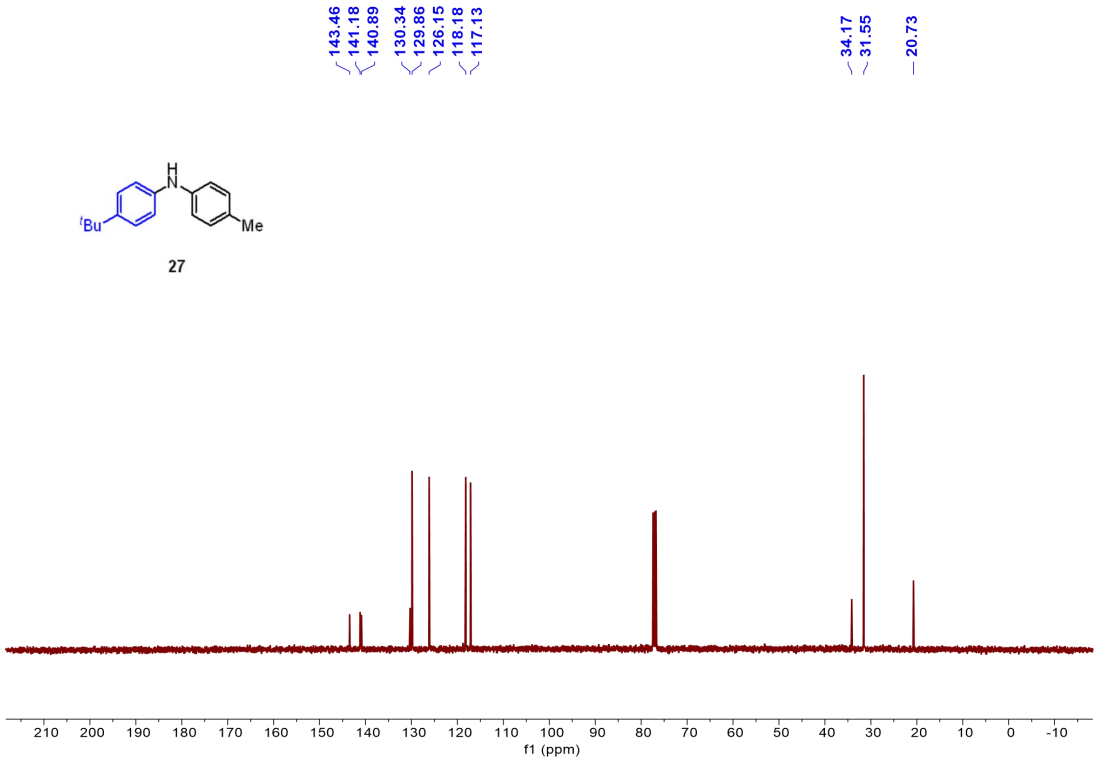

Fig. S72 ^{13}C NMR spectrum of **27** in $CDCl_3$ (101 MHz)

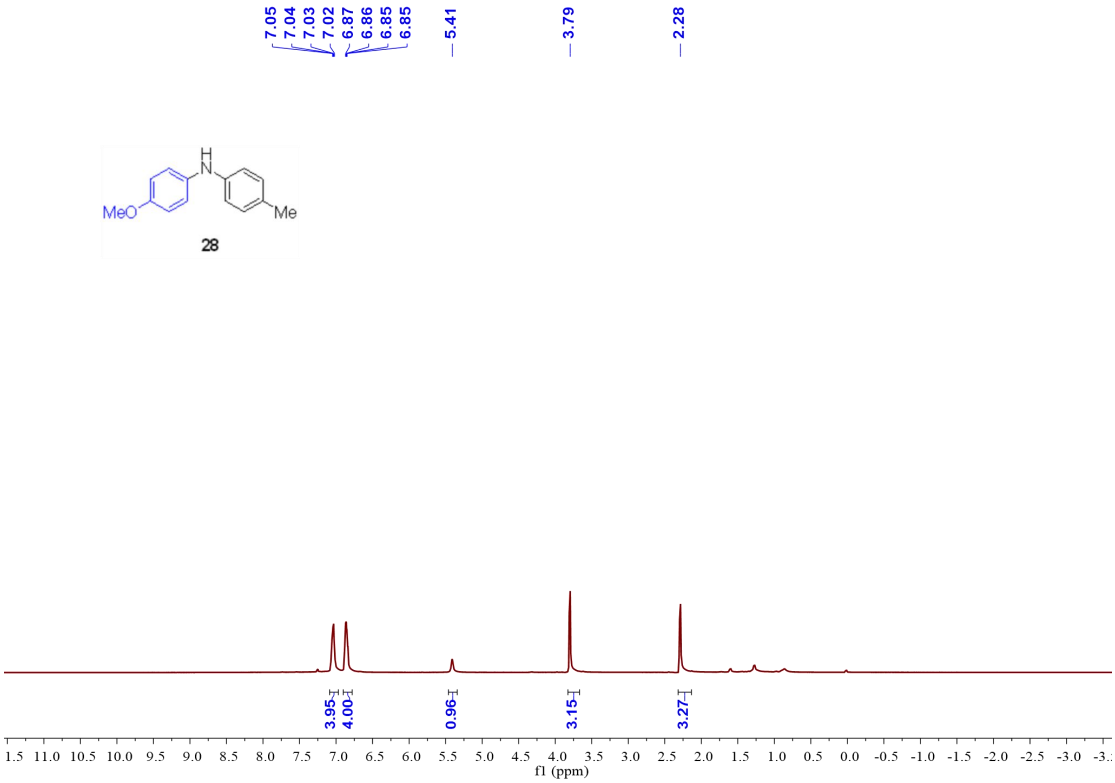

Fig. S73 ^{1}H NMR spectrum of **28** in $CDCl_3$ (400 MHz)

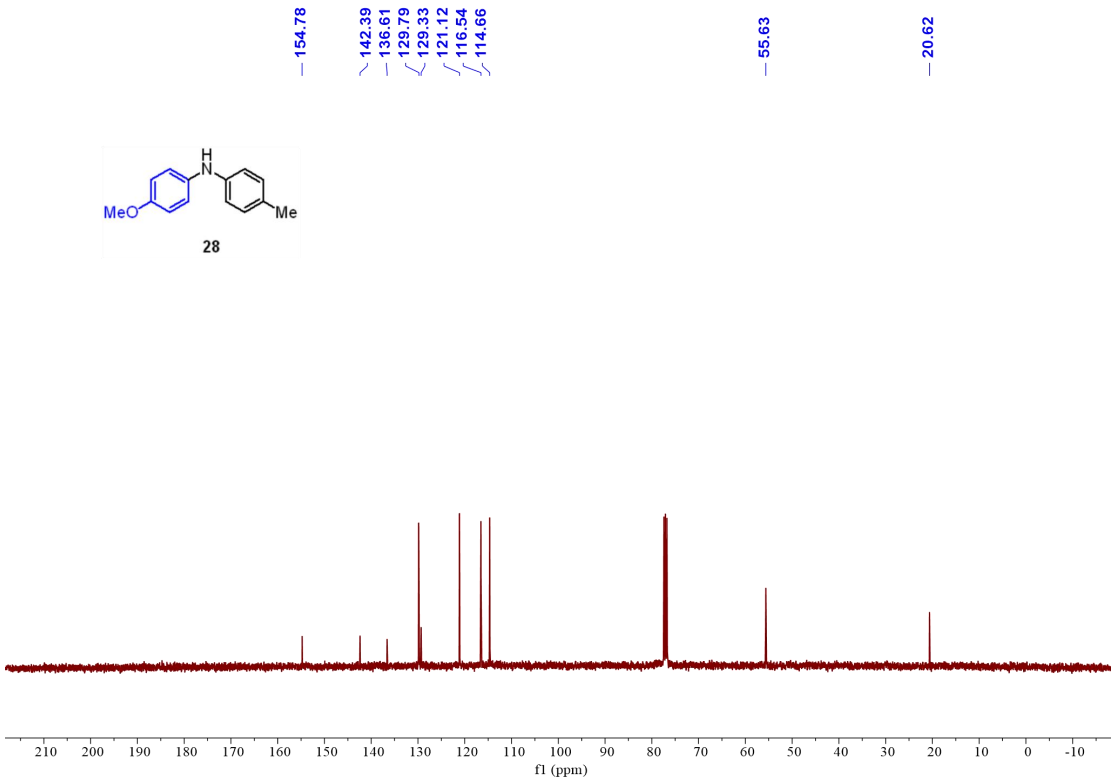

Fig. S74 ^{13}C NMR spectrum of **28** in $CDCl_3$ (101 MHz)

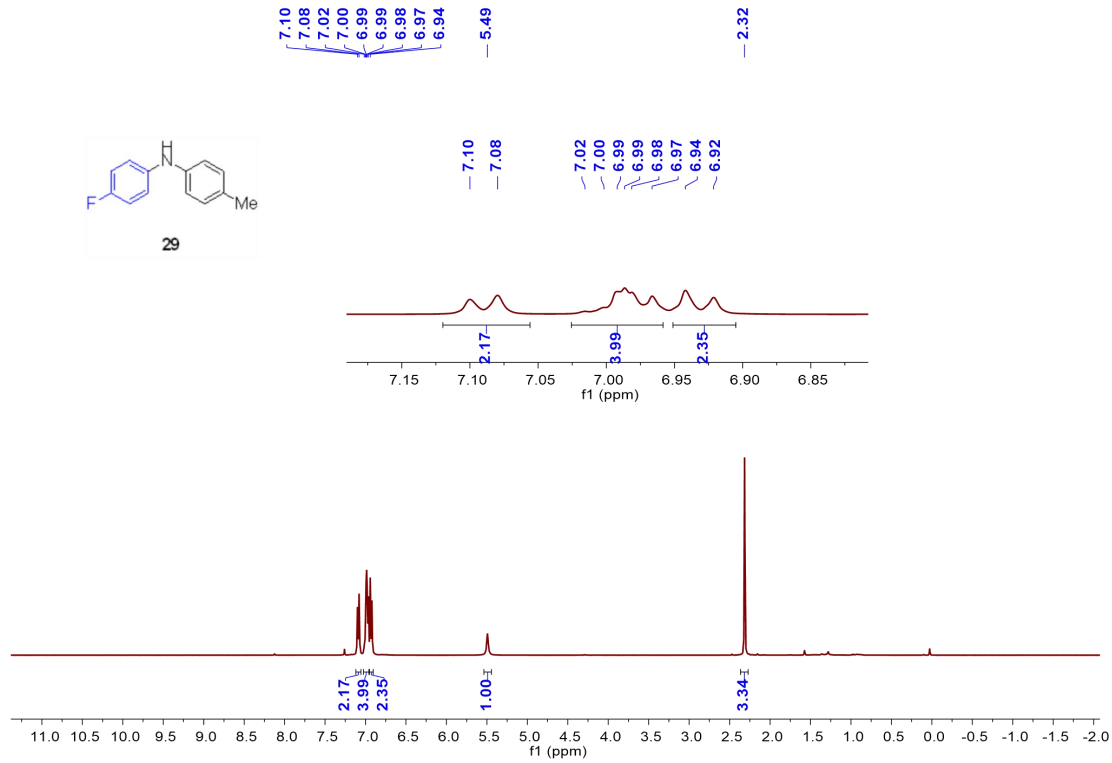

Fig. S75 ^{1}H NMR spectrum of **29** in $CDCl_3$ (400 MHz)

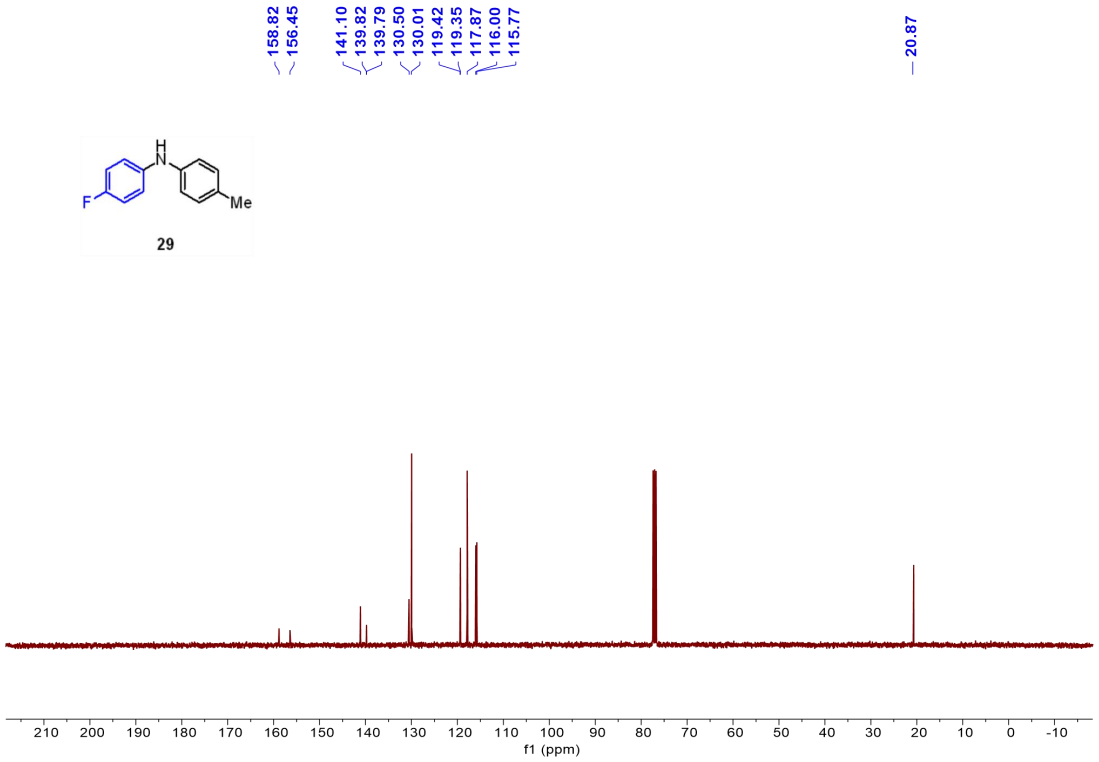

Fig. S76 ^{13}C NMR spectrum of **29** in $CDCl_3$ (101 MHz)

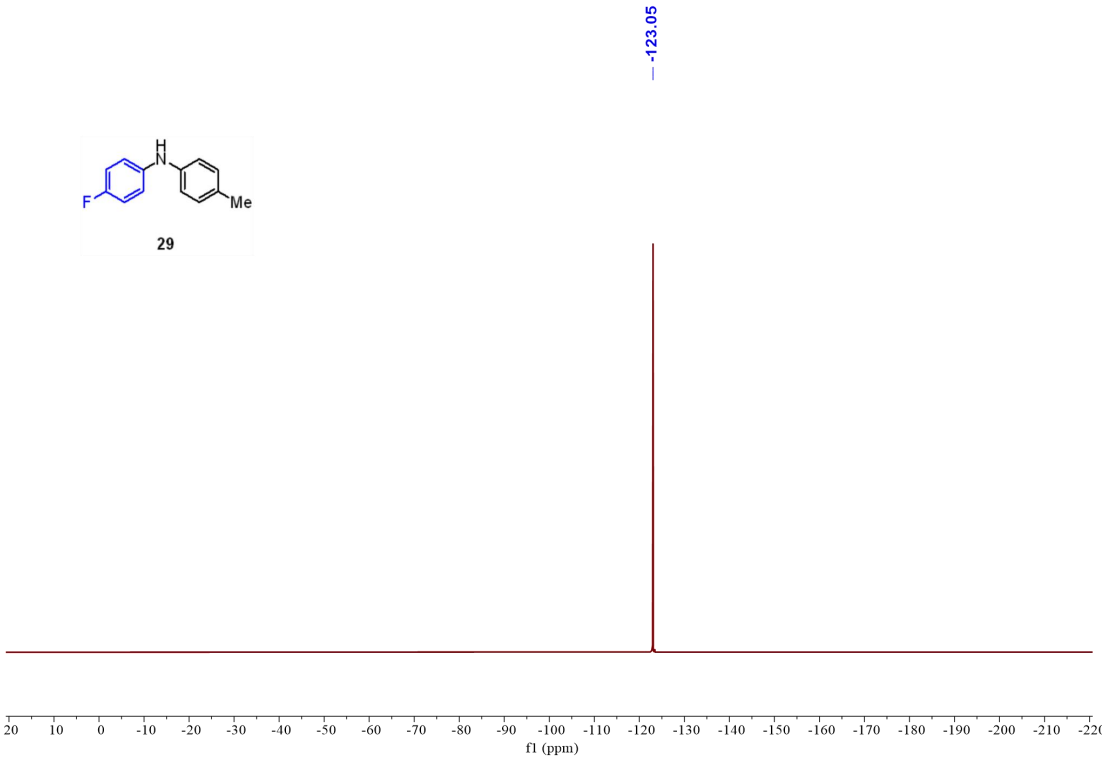

Fig. S77 ^{19}F NMR spectrum of **29** in $CDCl_3$ (377 MHz)

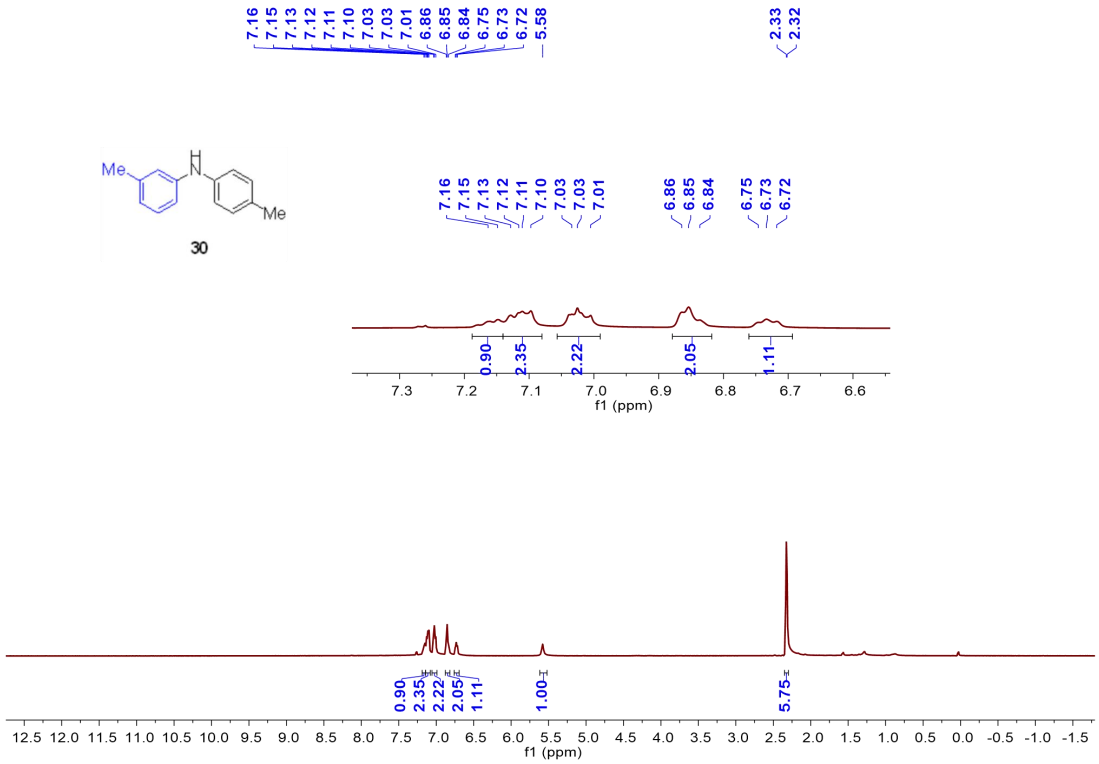

Fig. S78 ^{1}H NMR spectrum of **30** in $CDCl_3$ (400 MHz)

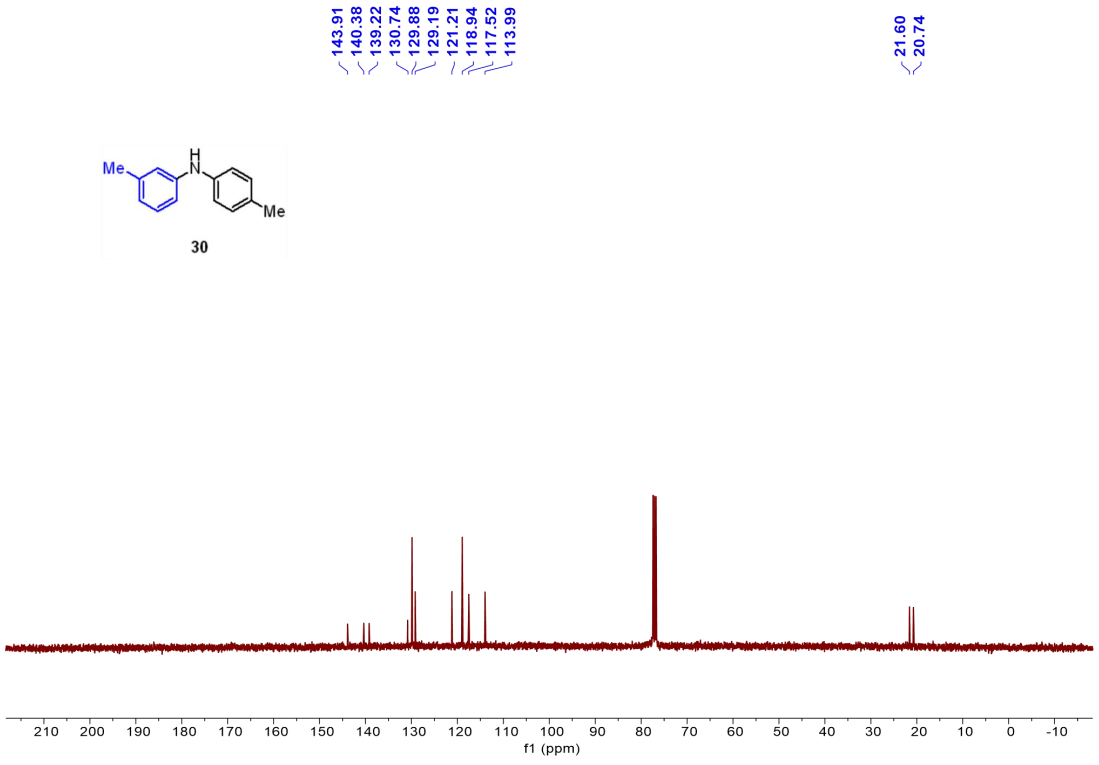

Fig. S79 ^{13}C NMR spectrum of **30** in $CDCl_3$ (101 MHz)

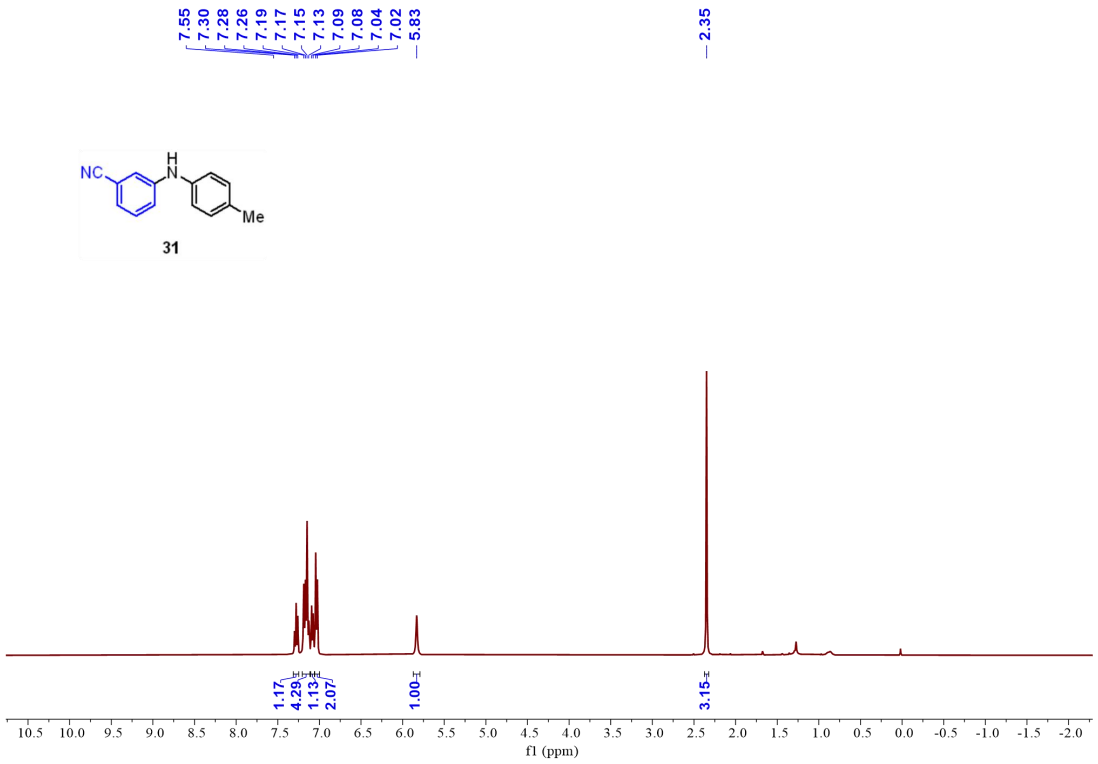

Fig. S80 ^{1}H NMR spectrum of **31** in $CDCl_3$ (400 MHz)

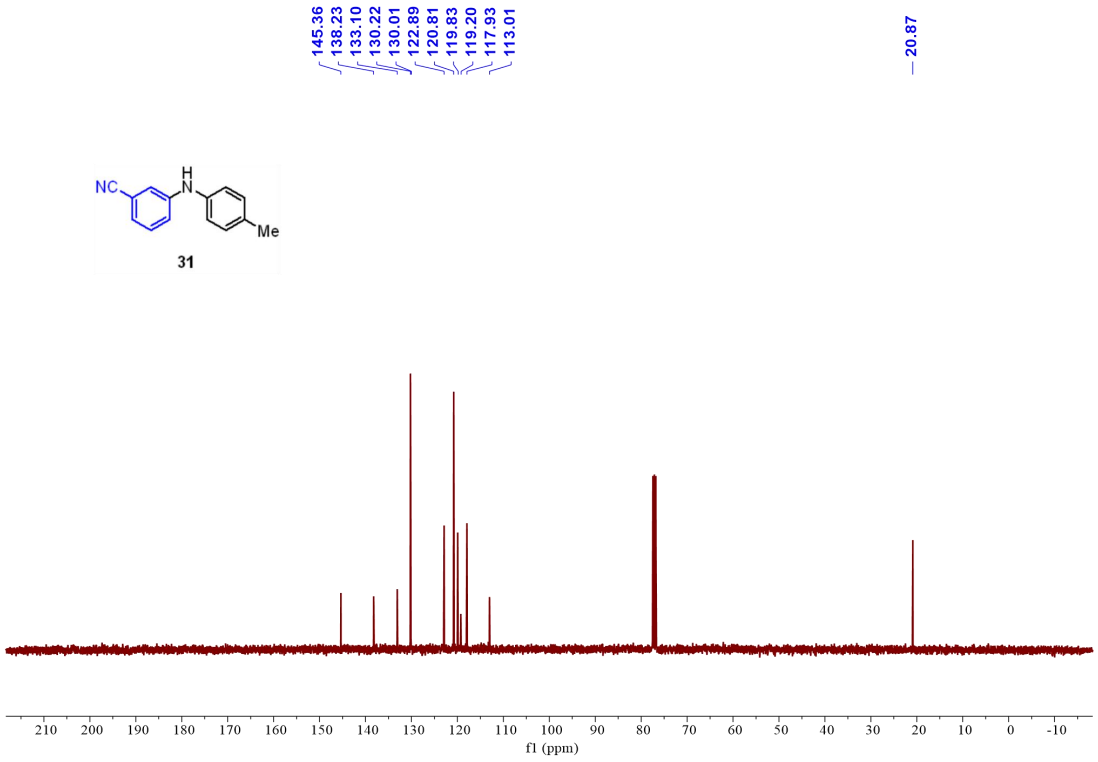

Fig. S81 ^{13}C NMR spectrum of **31** in $CDCl_3$ (101 MHz)

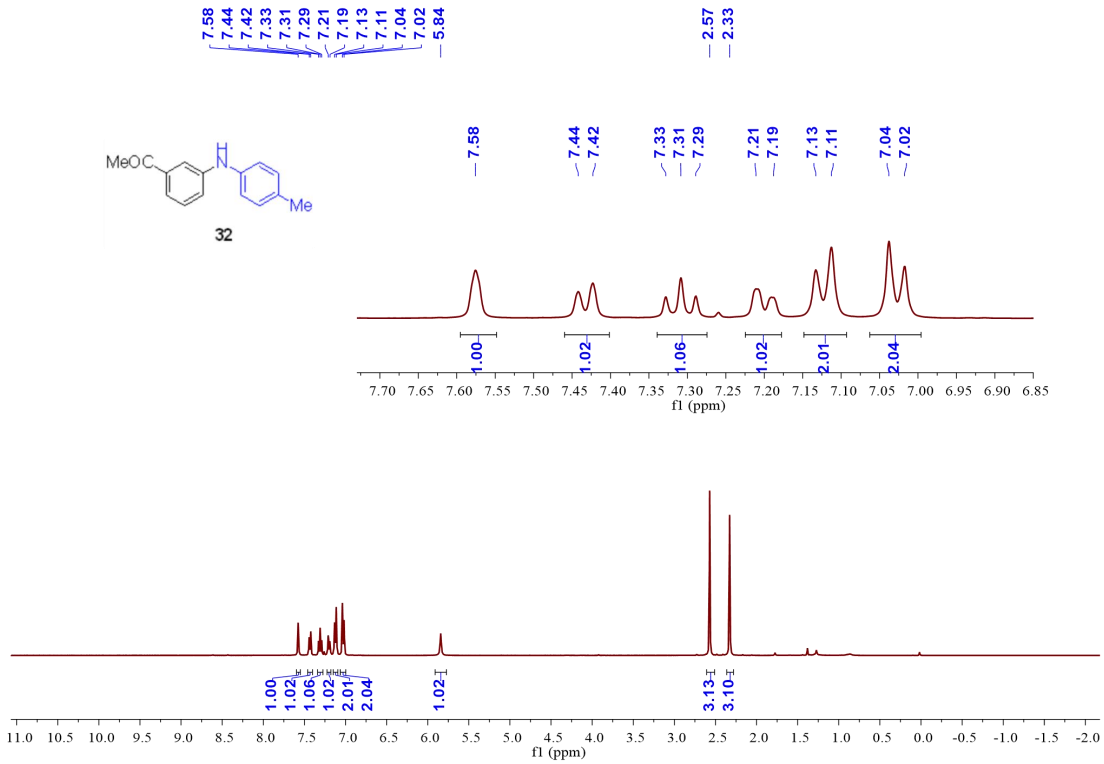

Fig. S82 ^{1}H NMR spectrum of **32** in $CDCl_3$ (400 MHz)

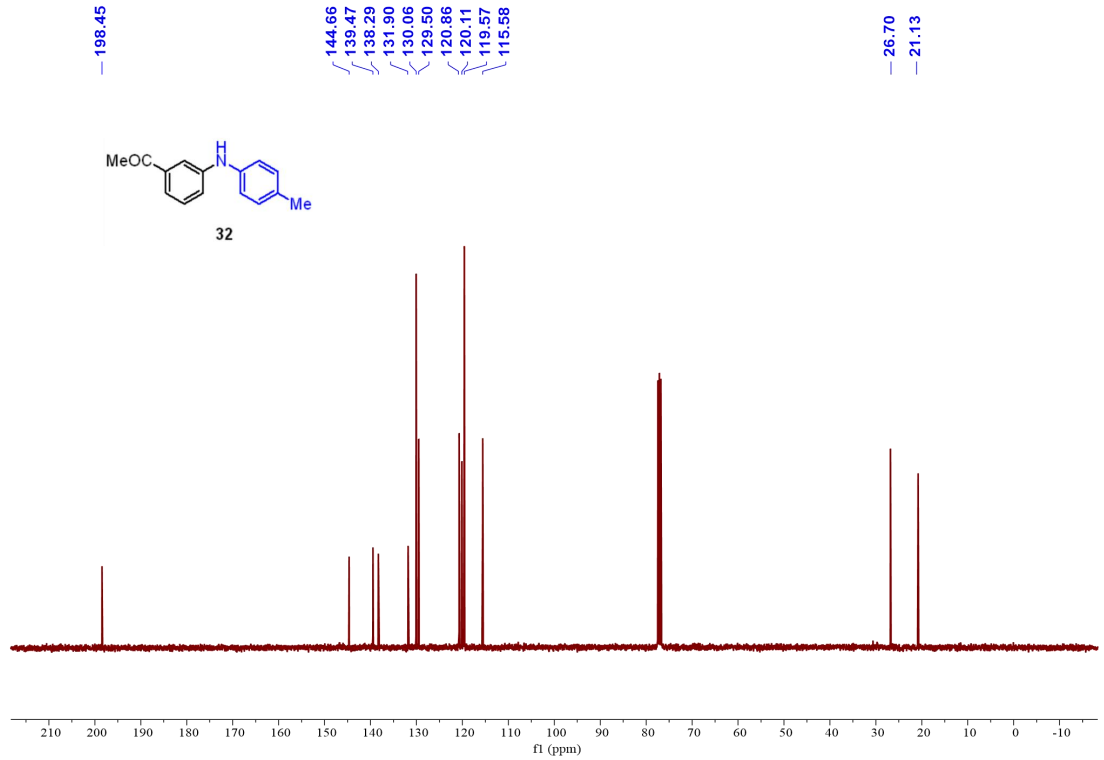

Fig. S83 ^{13}C NMR spectrum of **32** in $CDCl_3$ (101 MHz)

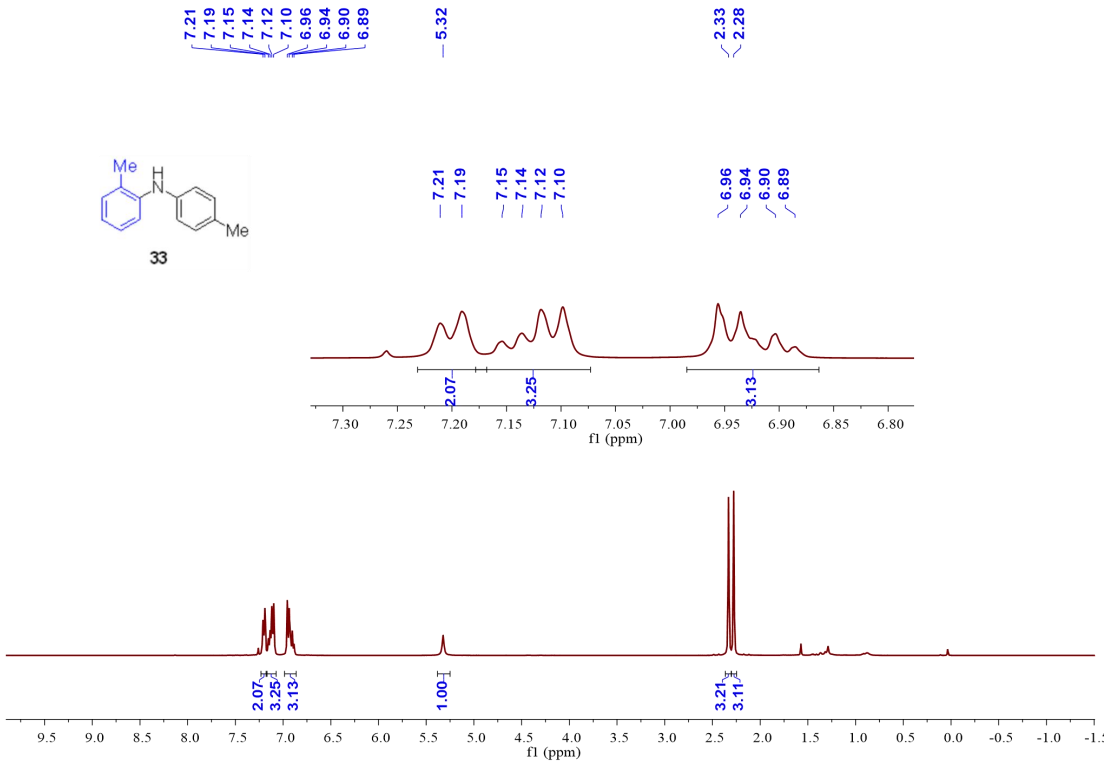

Fig. S84 ^{1}H NMR spectrum of **33** in $CDCl_3$ (400 MHz)

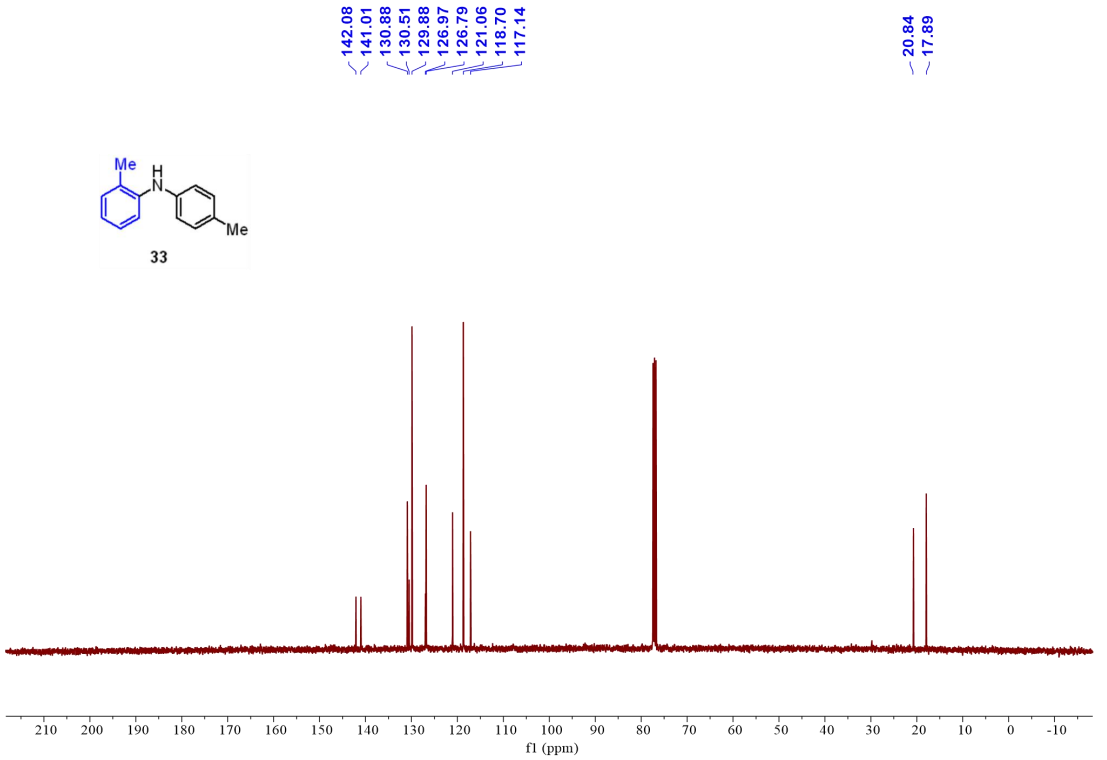

Fig. S85 ^{13}C NMR spectrum of **33** in $CDCl_3$ (101 MHz)

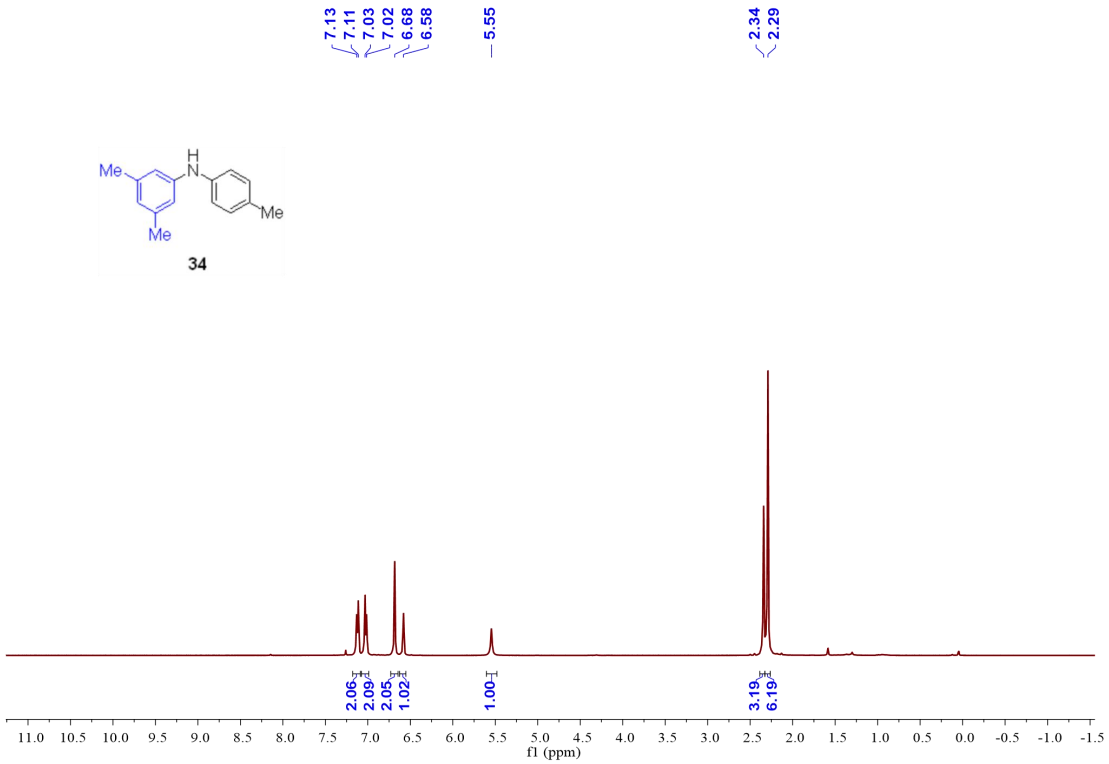

Fig. S86 ^{1}H NMR spectrum of **34** in $CDCl_3$ (400 MHz)

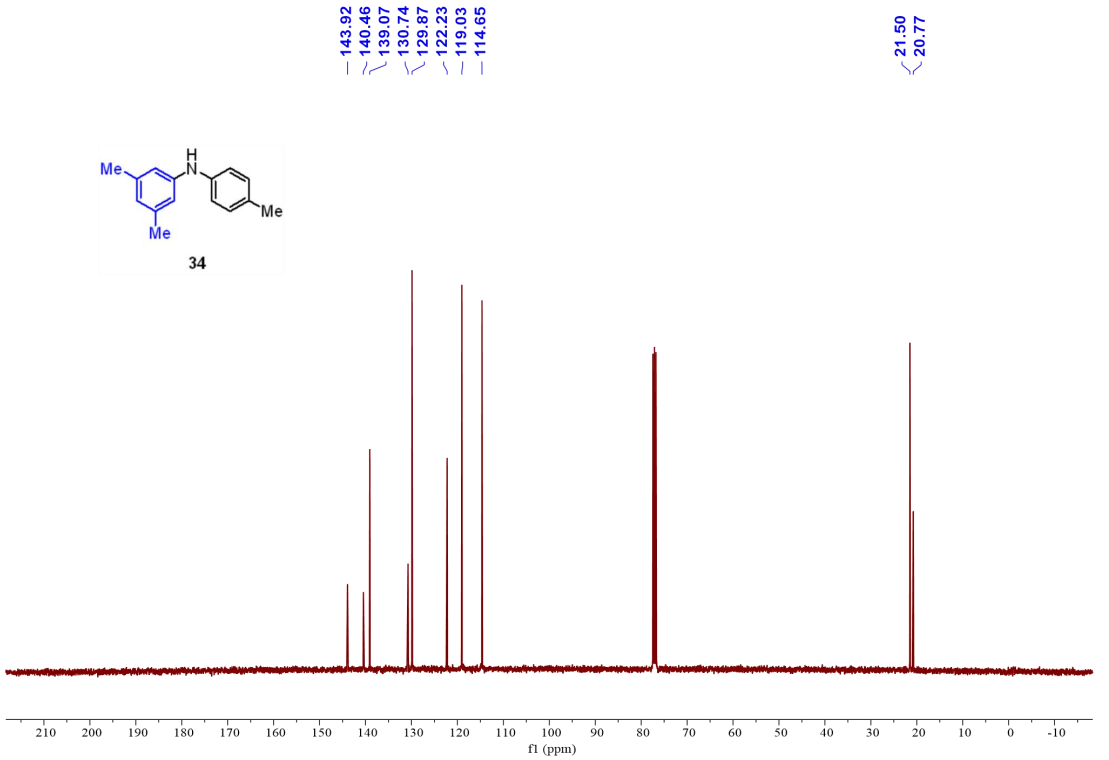

Fig. S87 ^{13}C NMR spectrum of **34** in $CDCl_3$ (101 MHz)

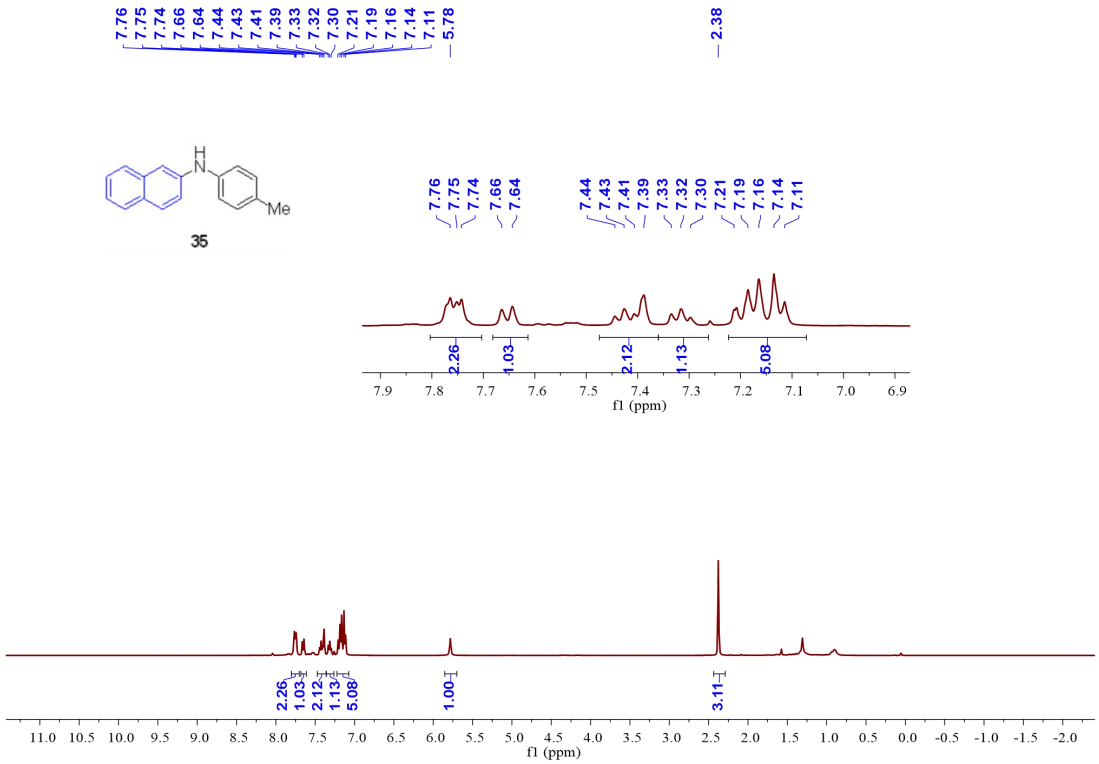

Fig. S88 ^{1}H NMR spectrum of **35** in $CDCl_3$ (400 MHz)

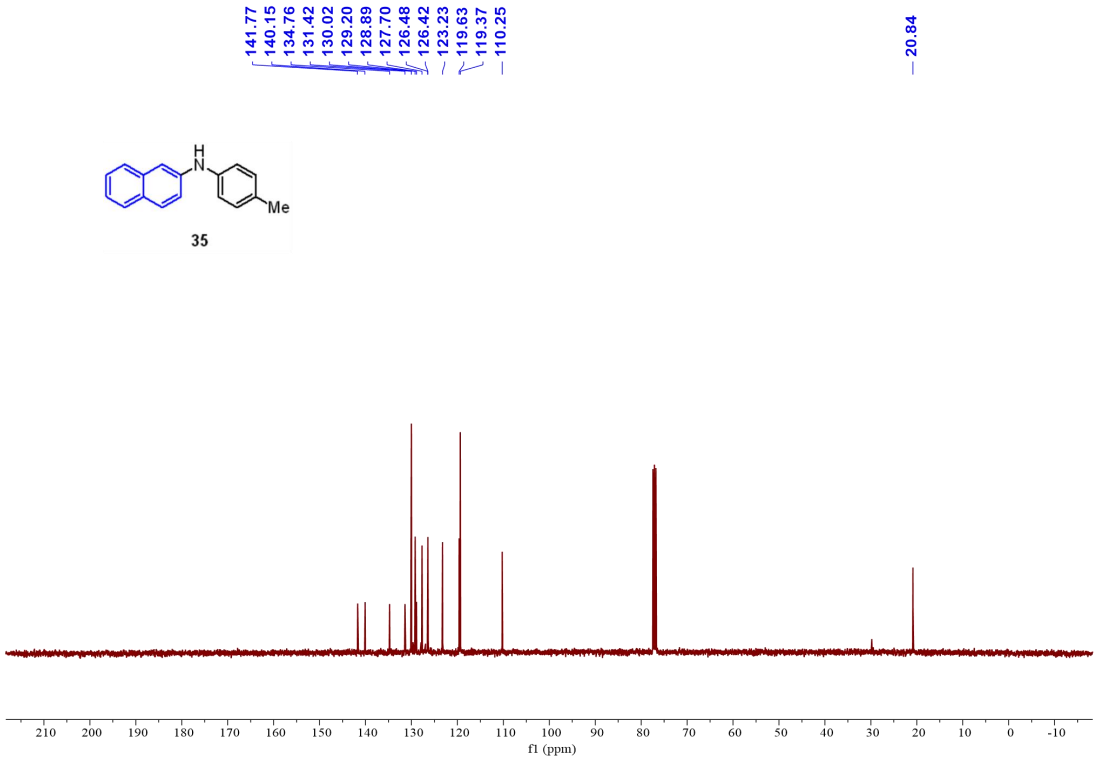

Fig. S89 ^{13}C NMR spectrum of **35** in $CDCl_3$ (101 MHz)

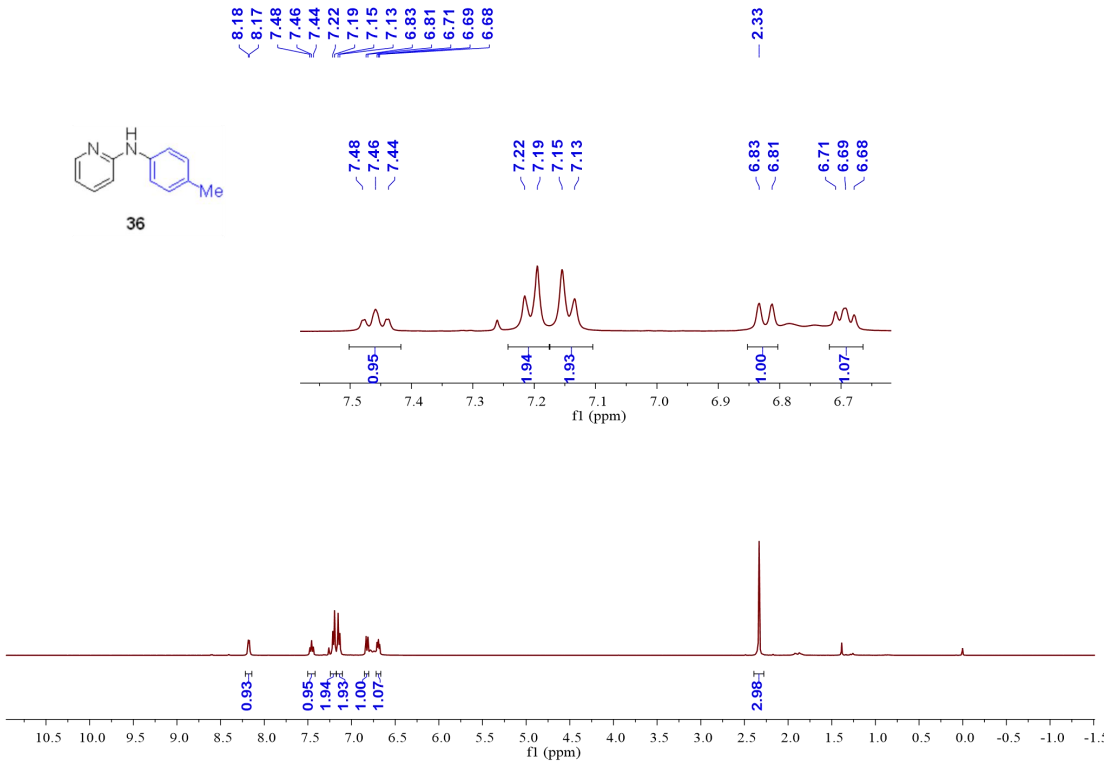

Fig. S90 ^{1}H NMR spectrum of **36** in $CDCl_3$ (400 MHz)

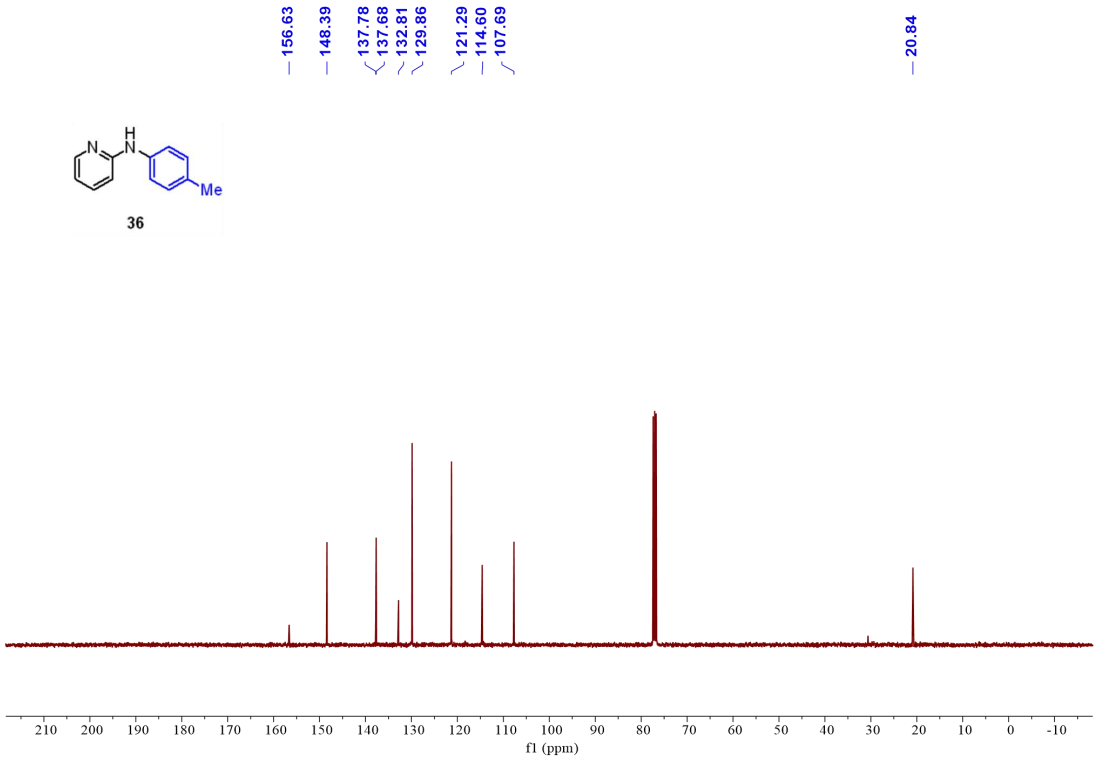

Fig. S91 ^{13}C NMR spectrum of **36** in $CDCl_3$ (101 MHz)

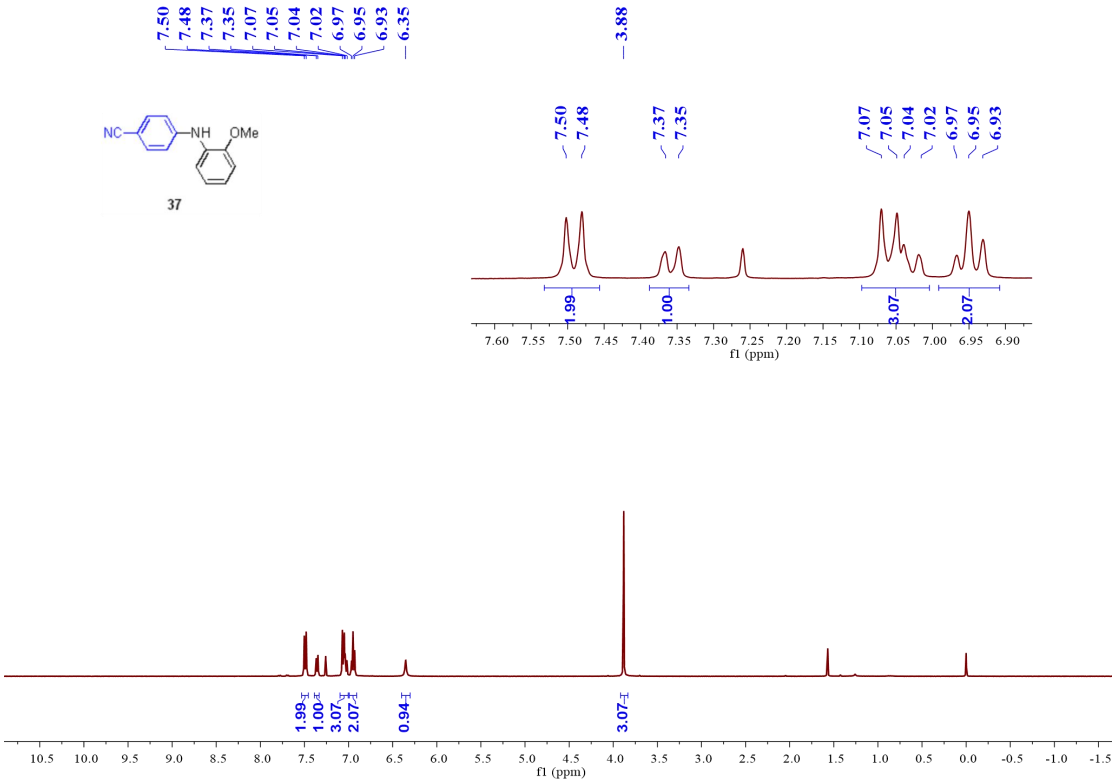

Fig. S92 ^{1}H NMR spectrum of **37** in $CDCl_3$ (400 MHz)

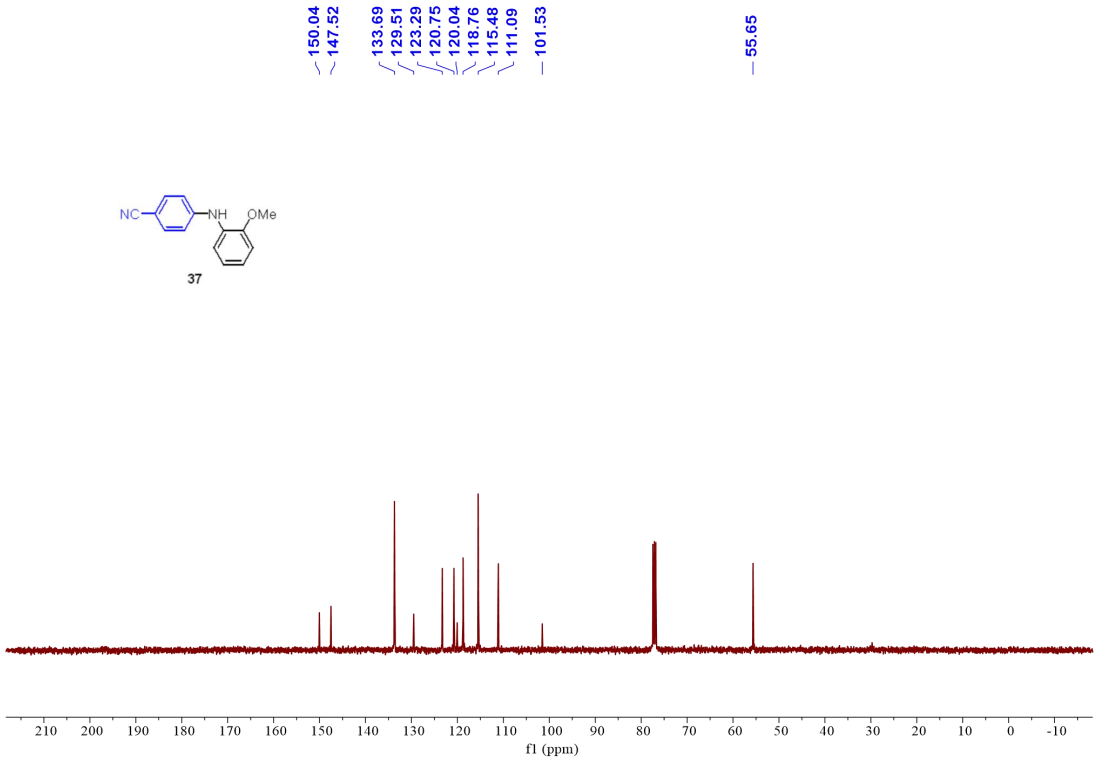

Fig. S93 ^{13}C NMR spectrum of **37** in $CDCl_3$ (101 MHz)

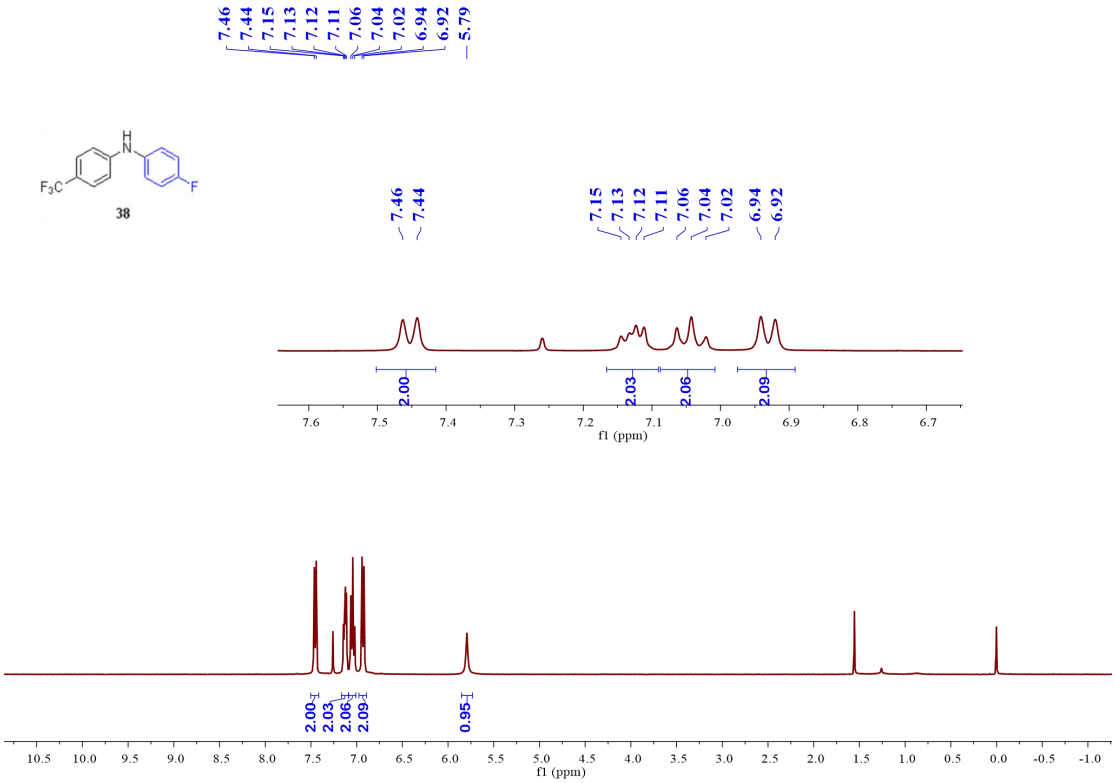

Fig. S94 ^{1}H NMR spectrum of **38** in $CDCl_3$ (400 MHz)

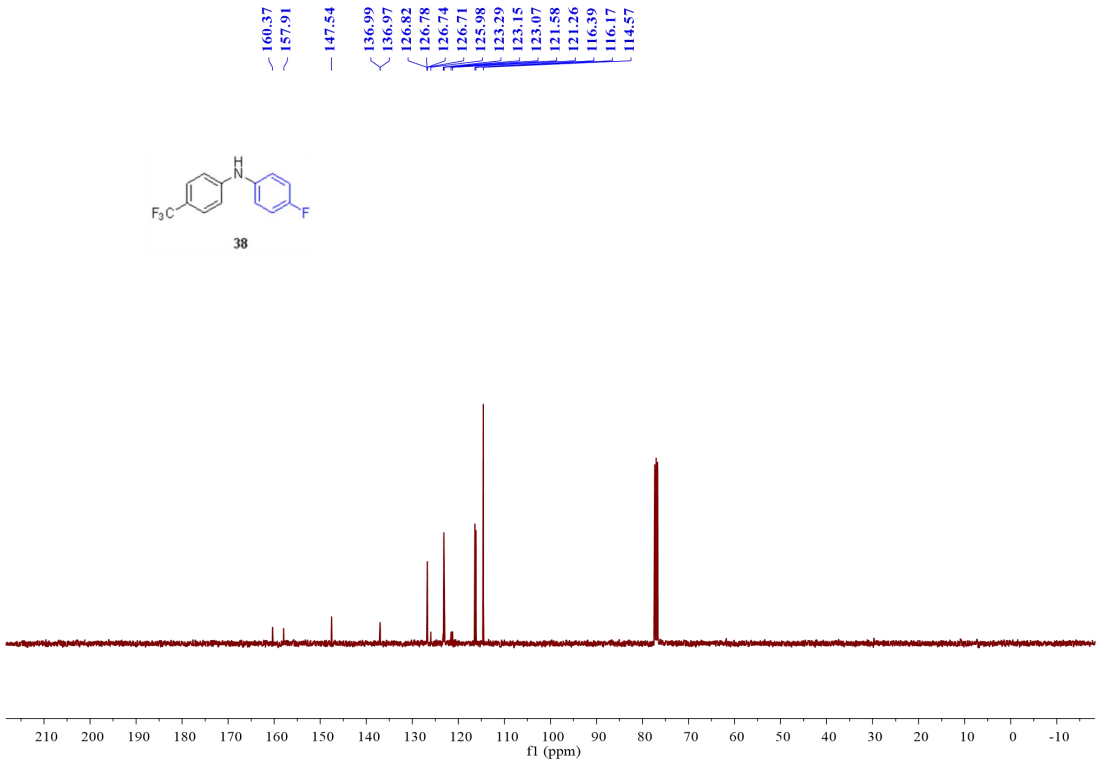

Fig. S95 ^{13}C NMR spectrum of **38** in $CDCl_3$ (101 MHz)

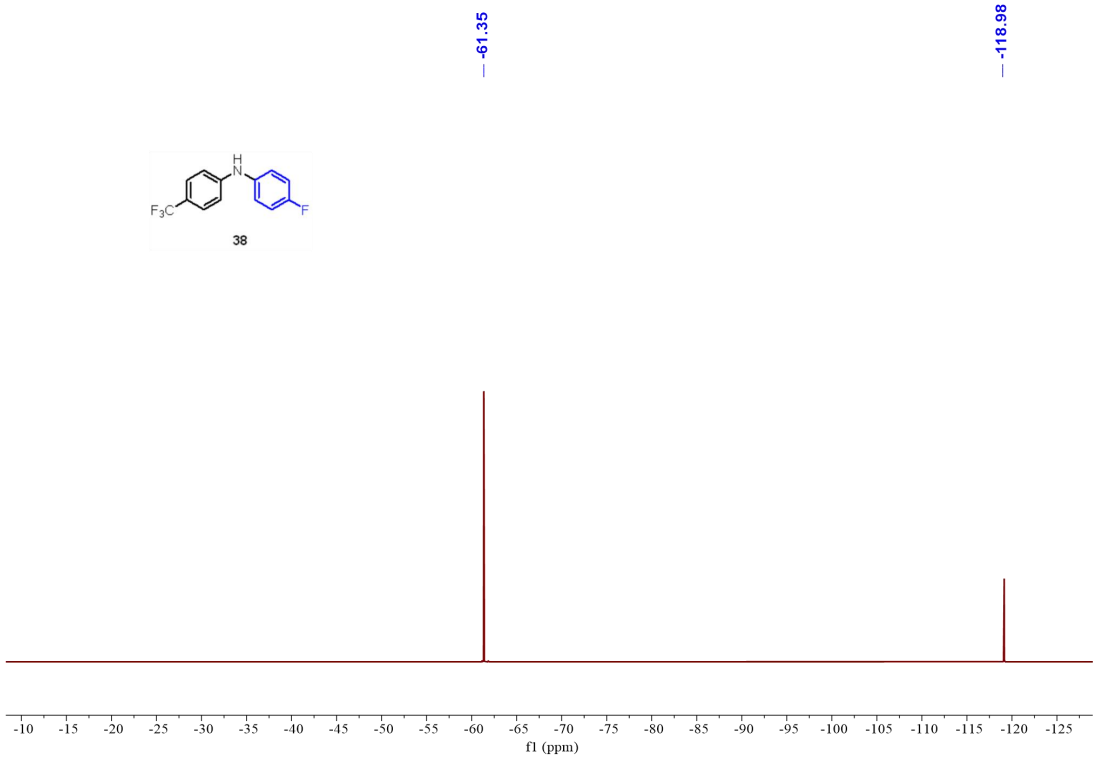

Fig. S96 ^{19}F NMR spectrum of **38** in $CDCl_3$ (377 MHz)

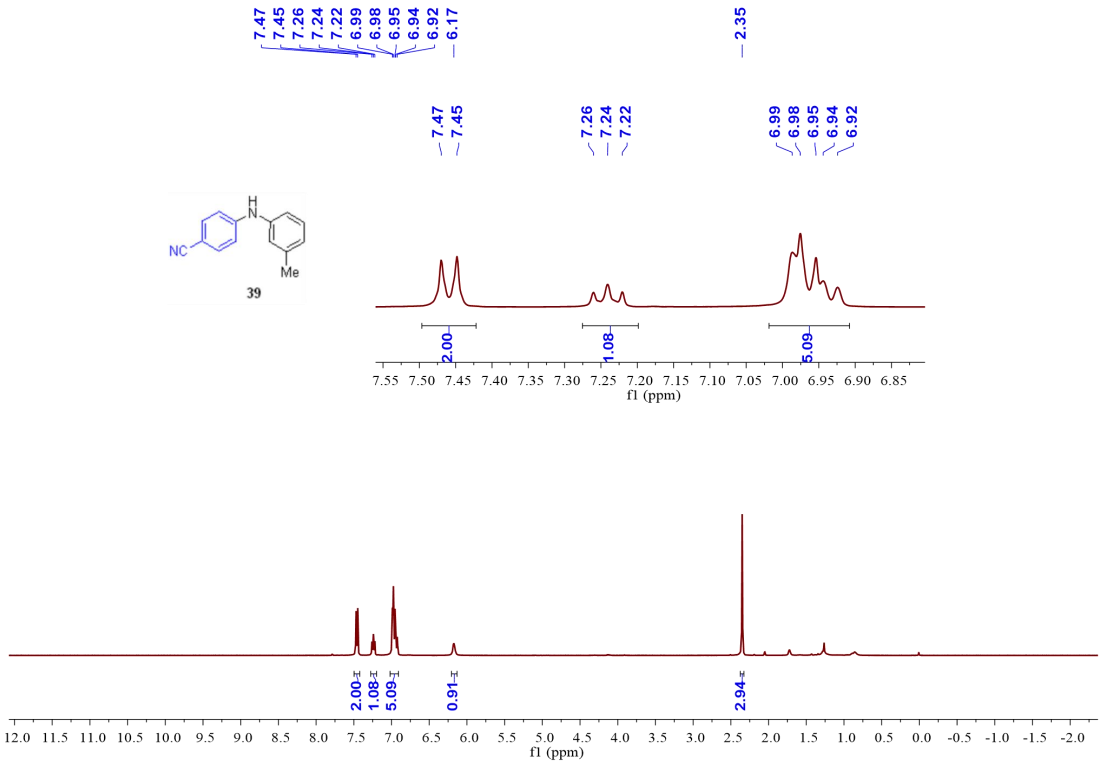

Fig. S97 ^{1}H NMR spectrum of **39** in $CDCl_3$ (400 MHz)

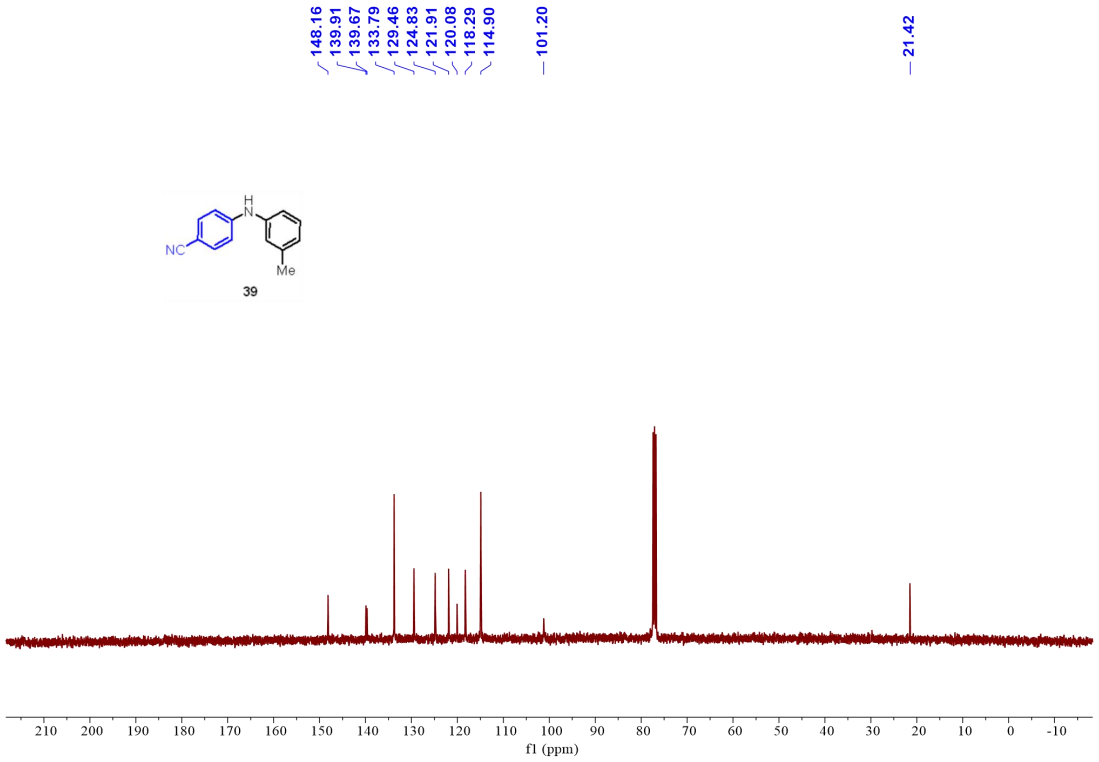

Fig. S98 ^{13}C NMR spectrum of **39** in $CDCl_3$ (101 MHz)

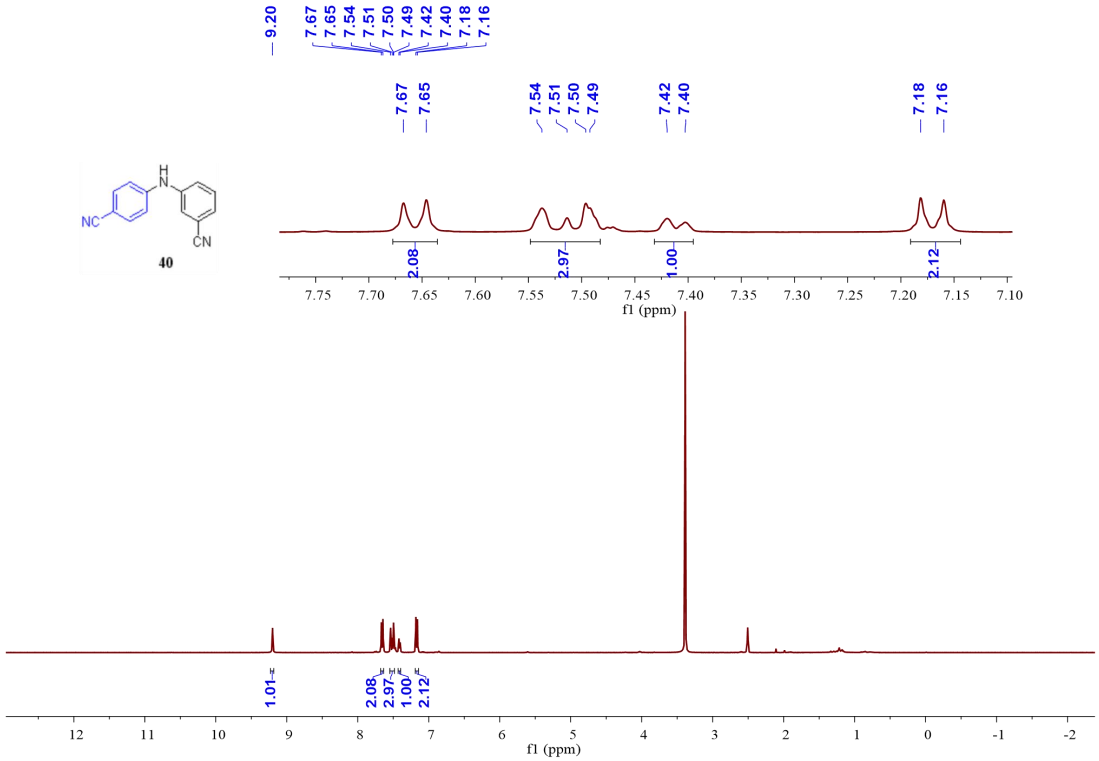

Fig. S99 ^{1}H NMR spectrum of **40** in DMSO-d^6 (400 MHz)

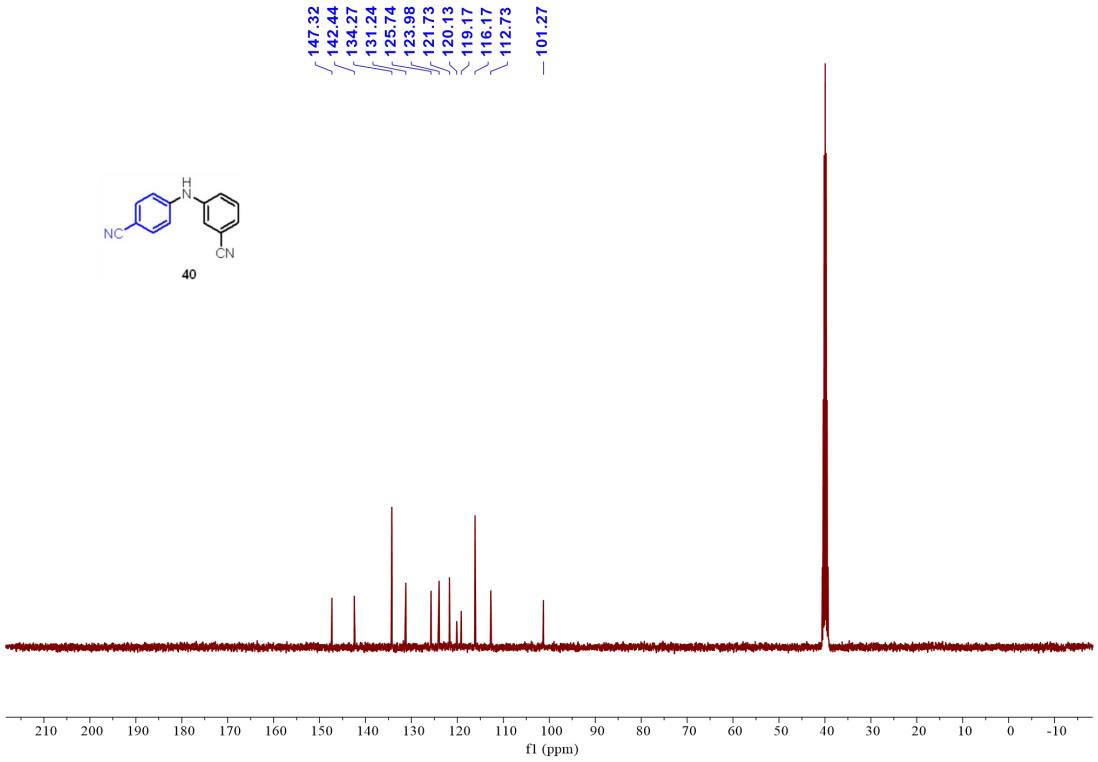

Fig. S100 ^{13}C NMR spectrum of **40** in DMSO-d^{6} (101 MHz)

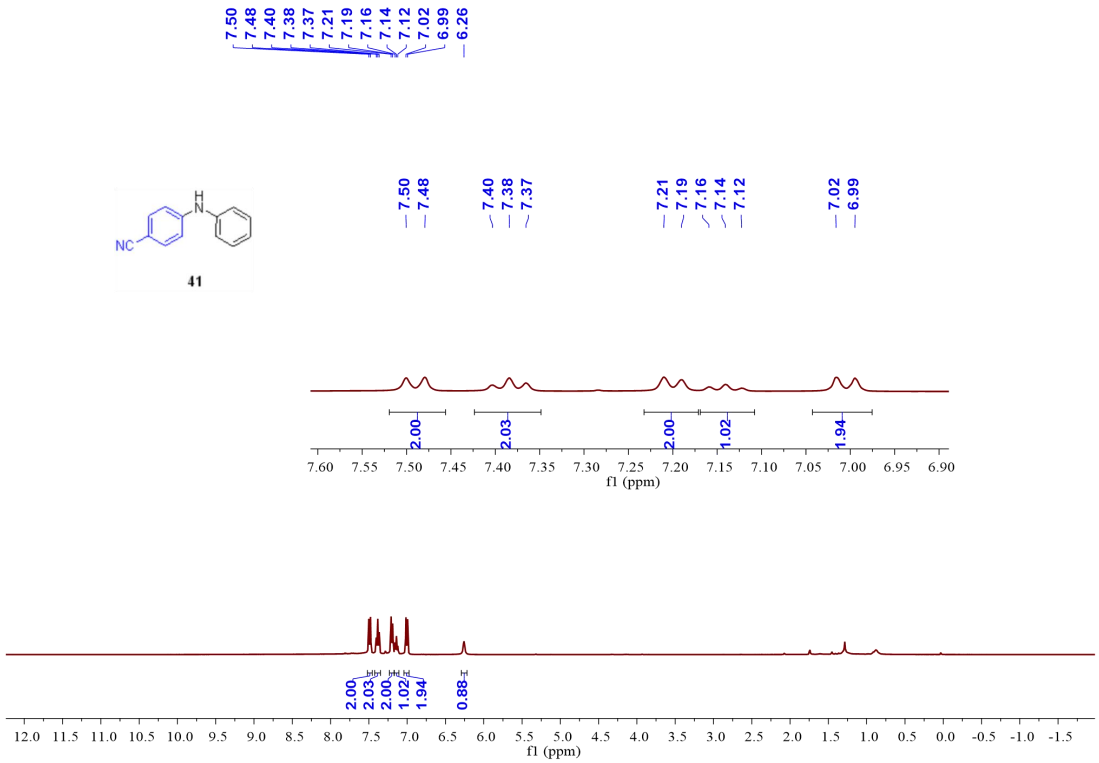

Fig. S101 ^{1}H NMR spectrum of **41** in $CDCl_3$ (400 MHz)

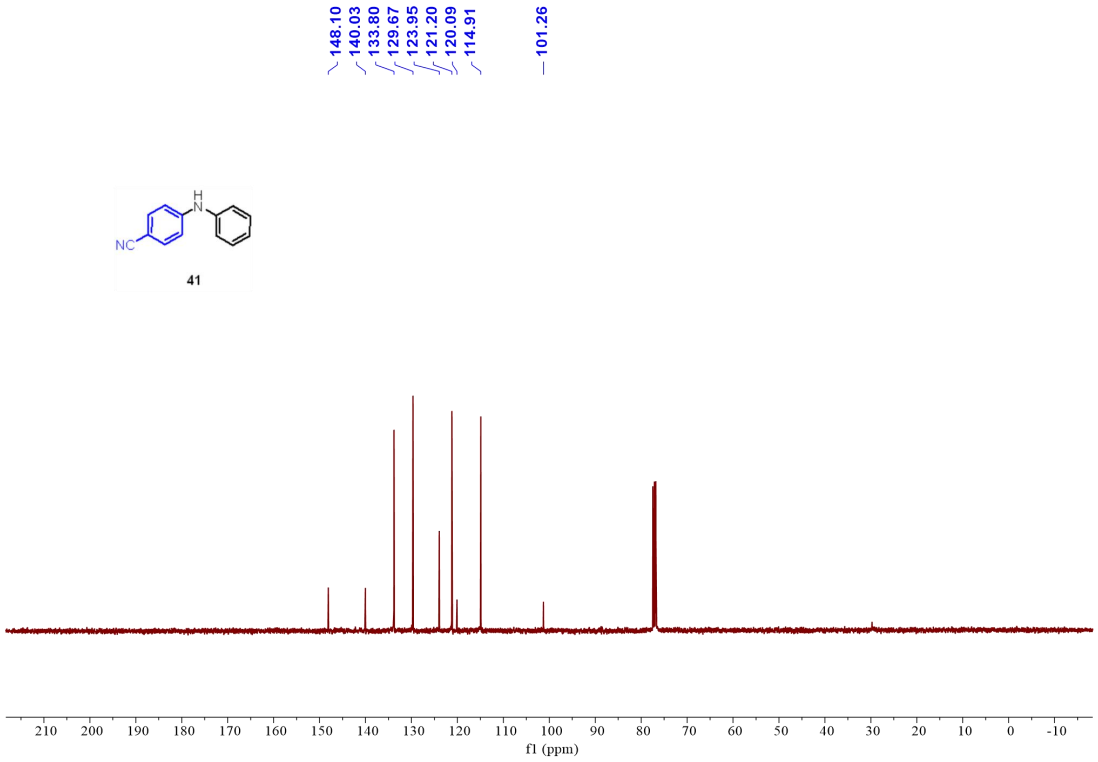

Fig. S102 ^{13}C NMR spectrum of **41** in $CDCl_3$ (101 MHz)

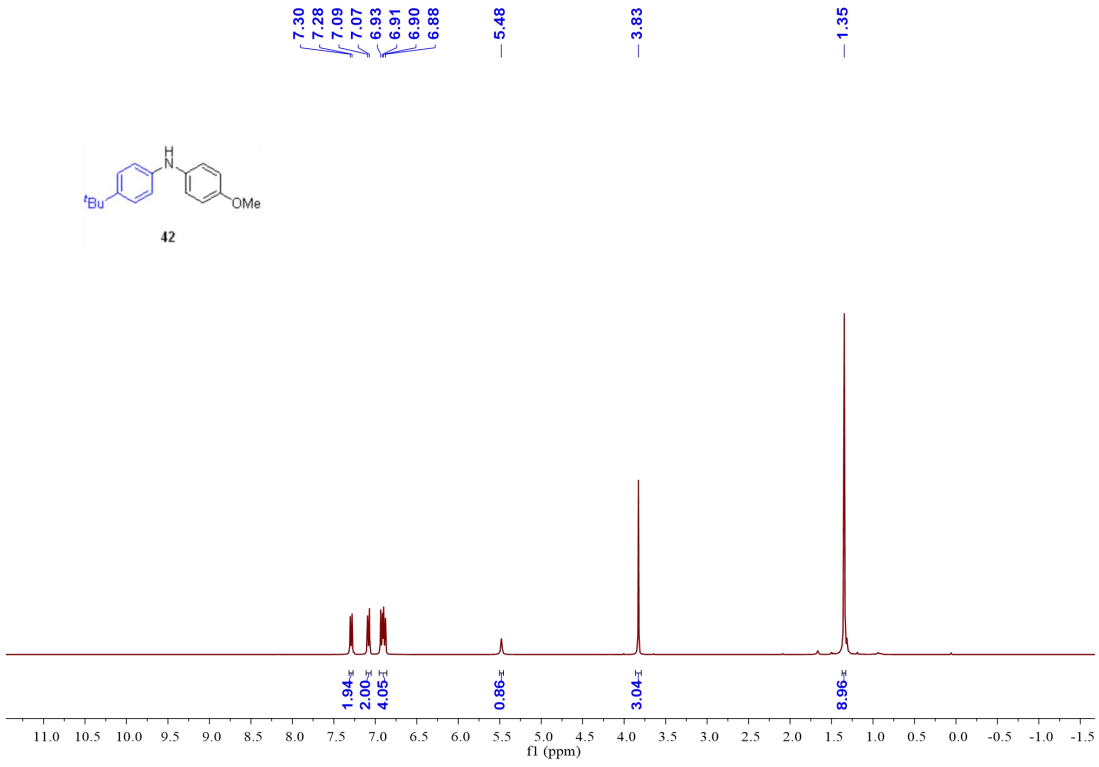

Fig. S103 ^{1}H NMR spectrum of **42** in $CDCl_3$ (400 MHz)

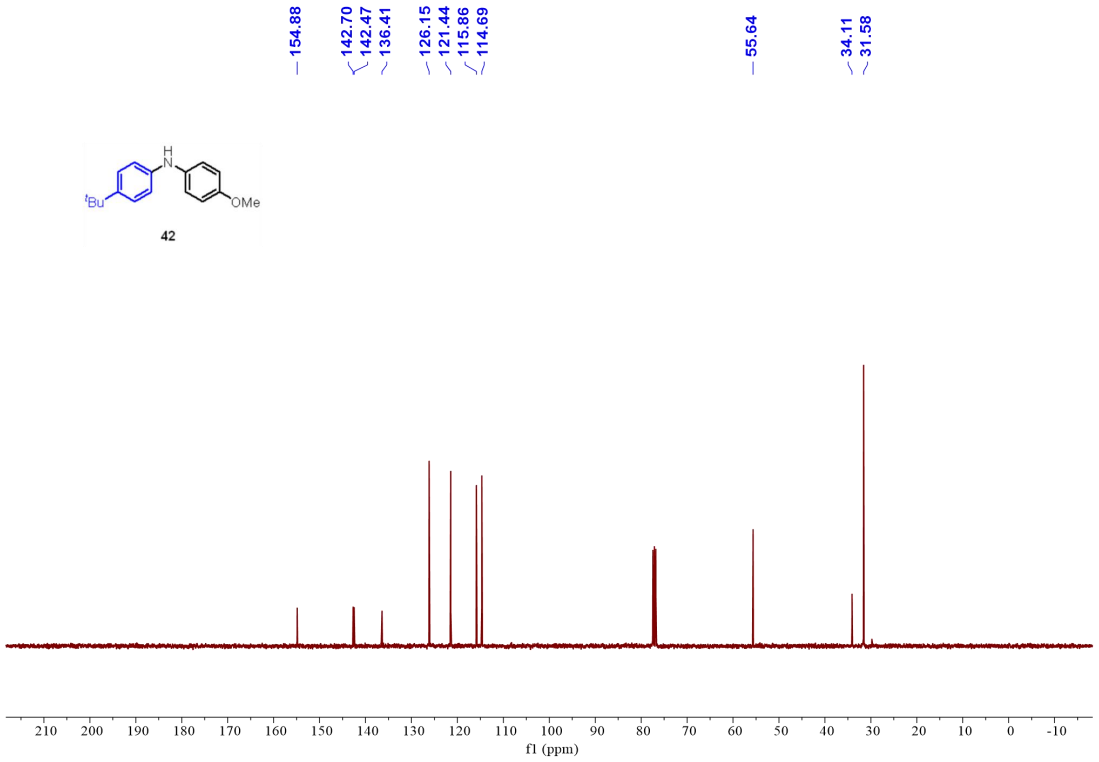

Fig. S104 ^{13}C NMR spectrum of **42** in $CDCl_3$ (101 MHz)

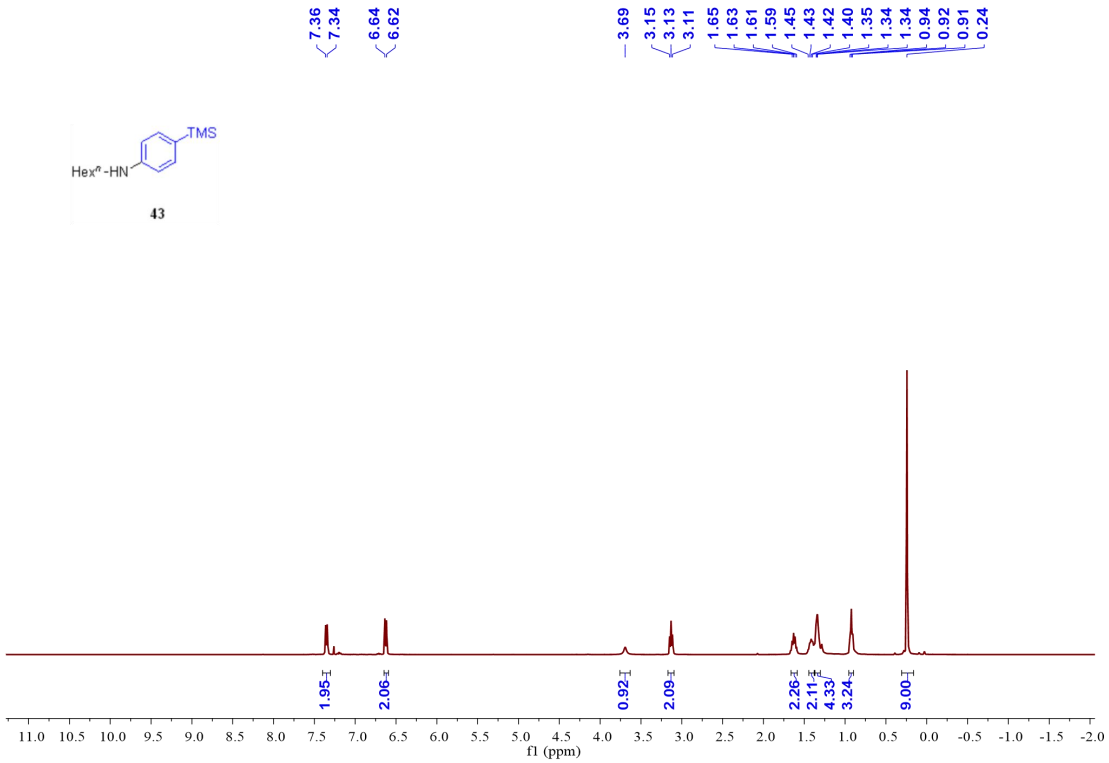

Fig. S105 ^{1}H NMR spectrum of **43** in $CDCl_3$ (400 MHz)

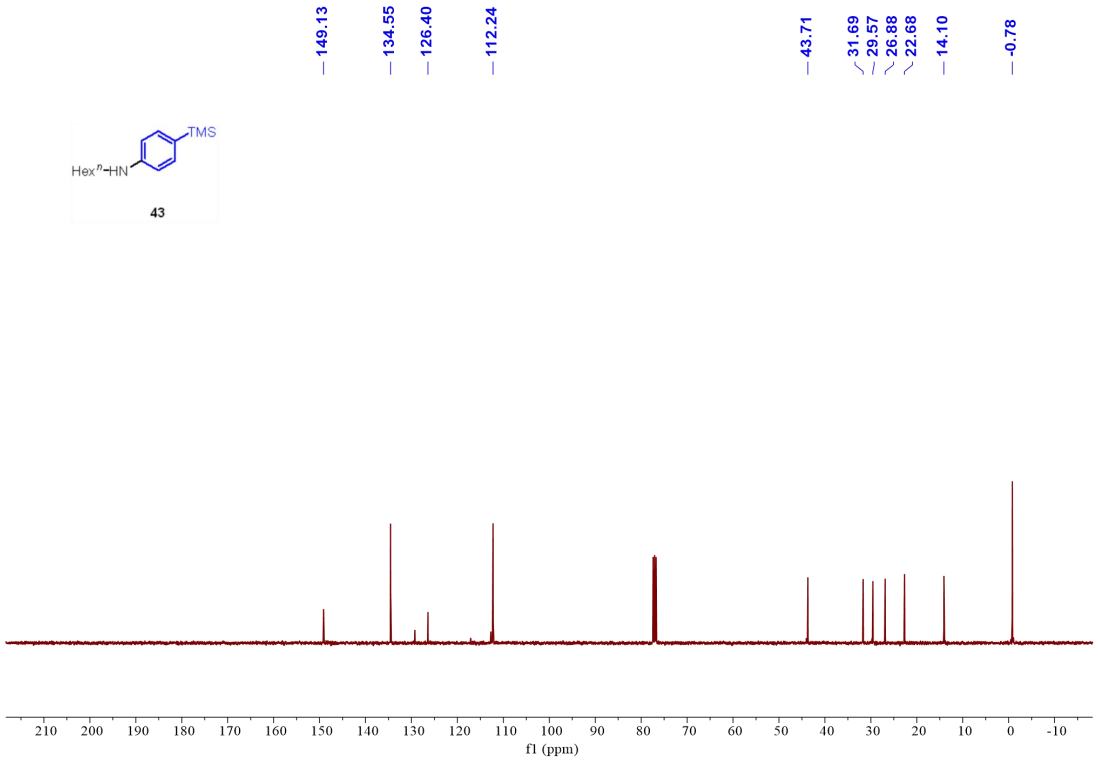

Fig. S106 ^{13}C NMR spectrum of **43** in $CDCl_3$ (101 MHz)

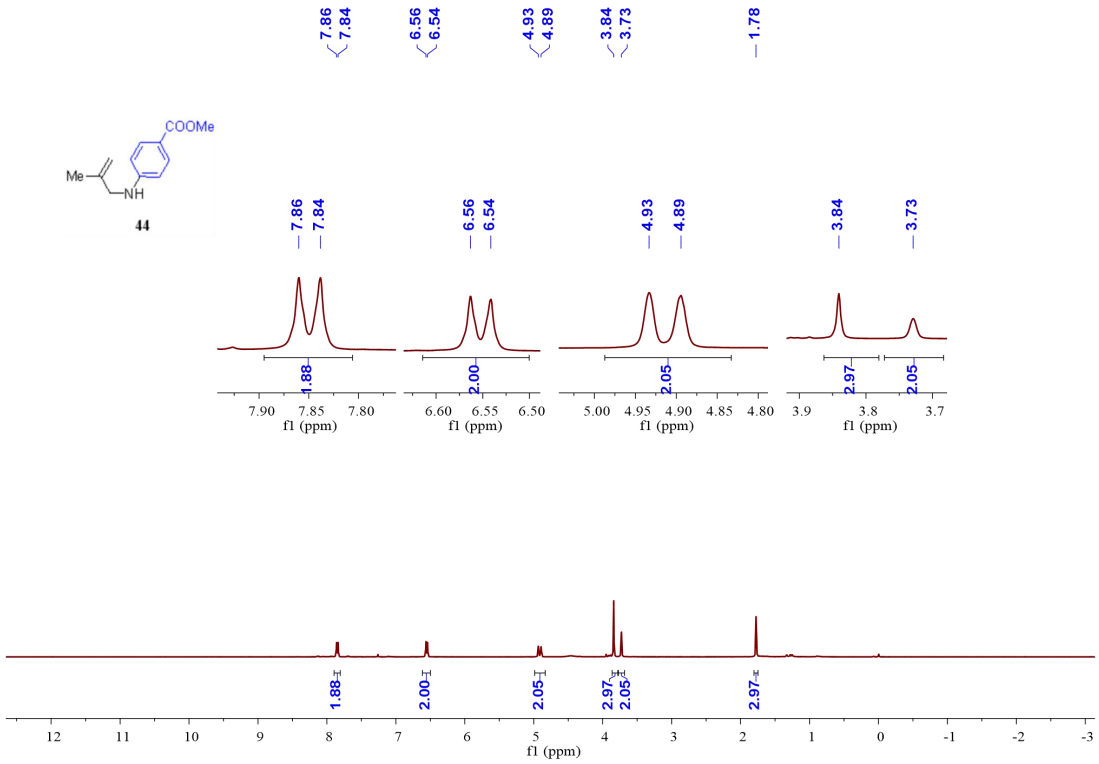

Fig. S107 ^{1}H NMR spectrum of **44** in $CDCl_3$ (400 MHz)

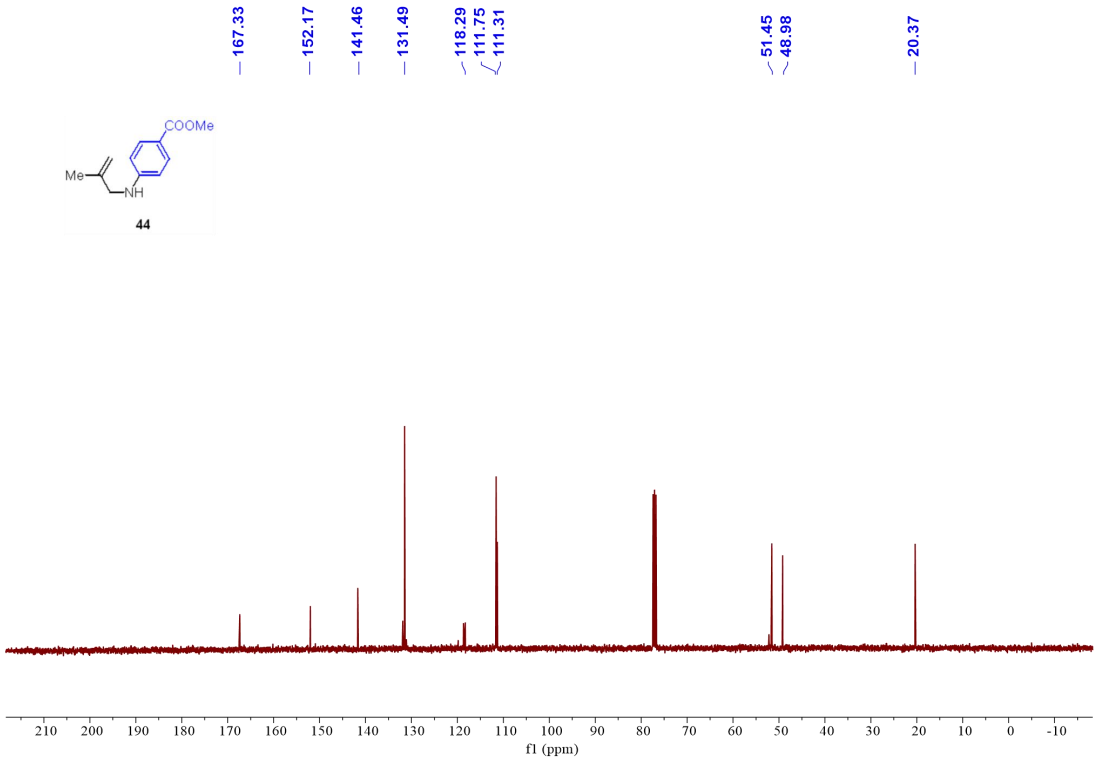

Fig. S108 ^{13}C NMR spectrum of **44** in $CDCl_3$ (101 MHz)

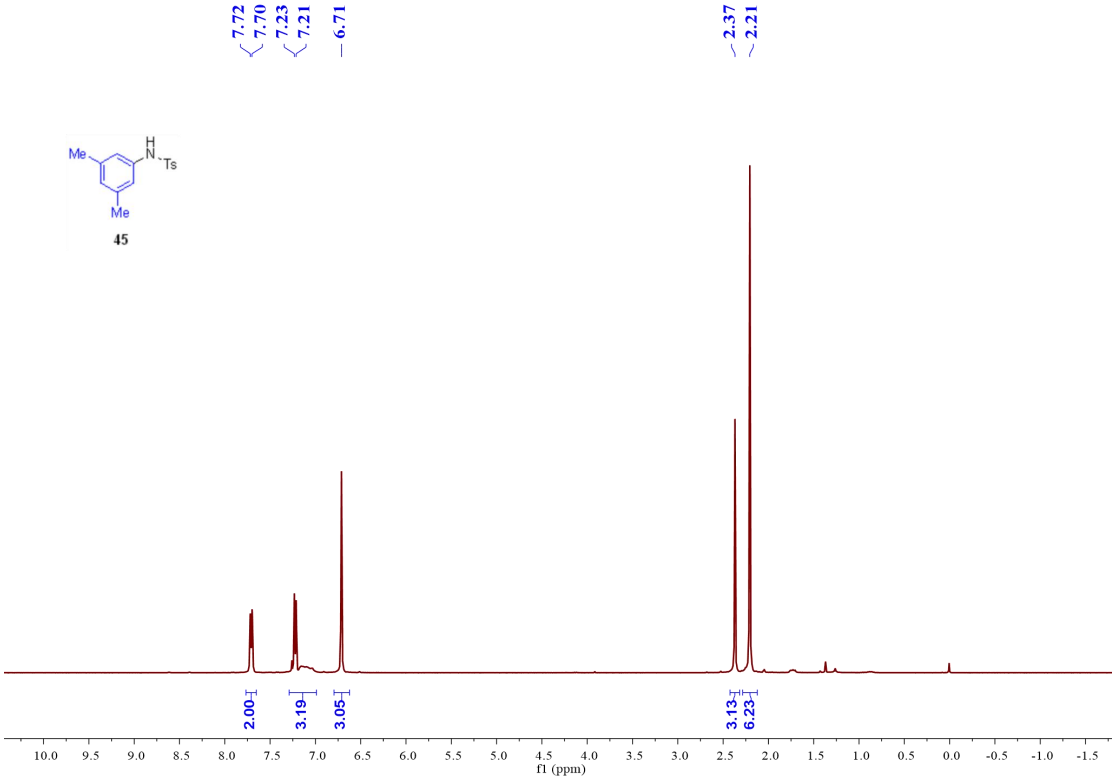

Fig. S109 ^{1}H NMR spectrum of **45** in $CDCl_3$ (400 MHz)

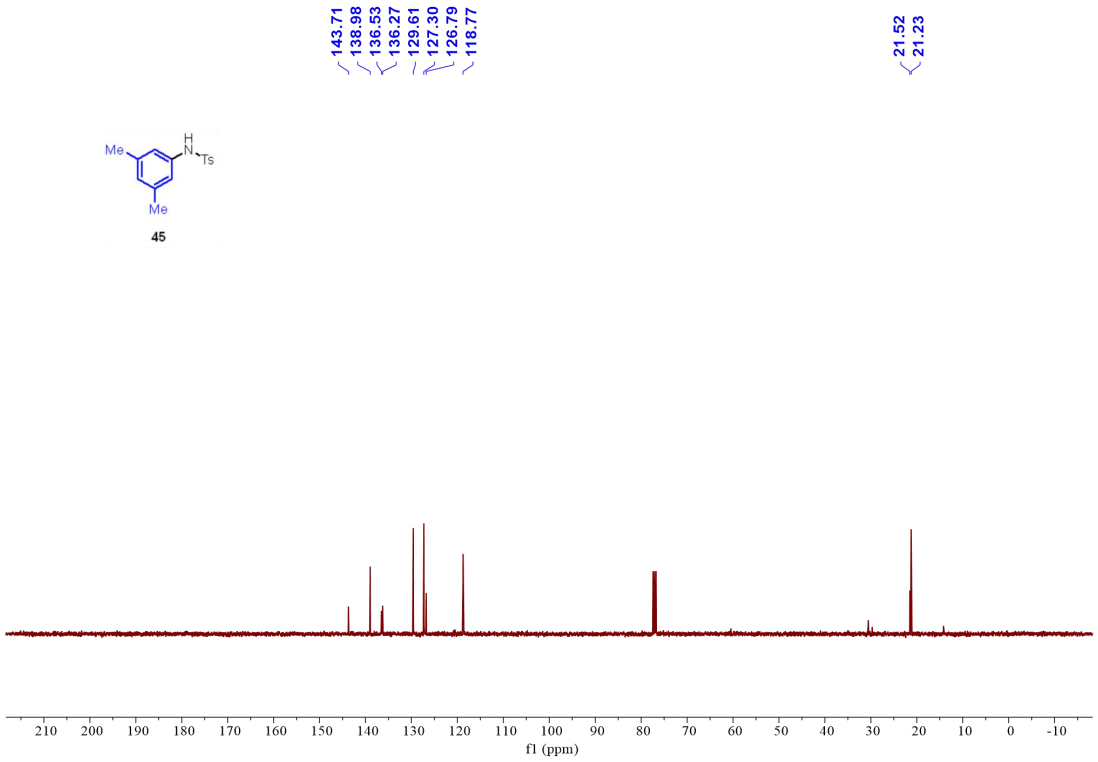

Fig. S110 ^{13}C NMR spectrum of **45** in $CDCl_3$ (101 MHz)

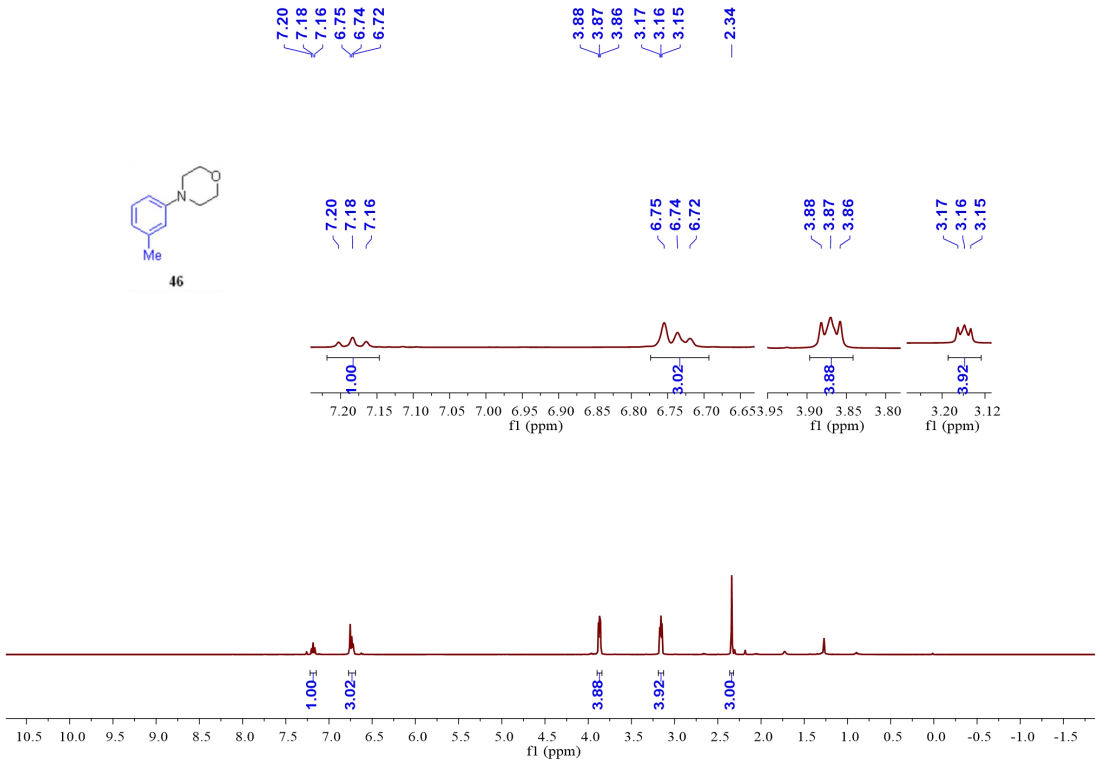

Fig. S111 ^{1}H NMR spectrum of **46** in $CDCl_3$ (400 MHz)

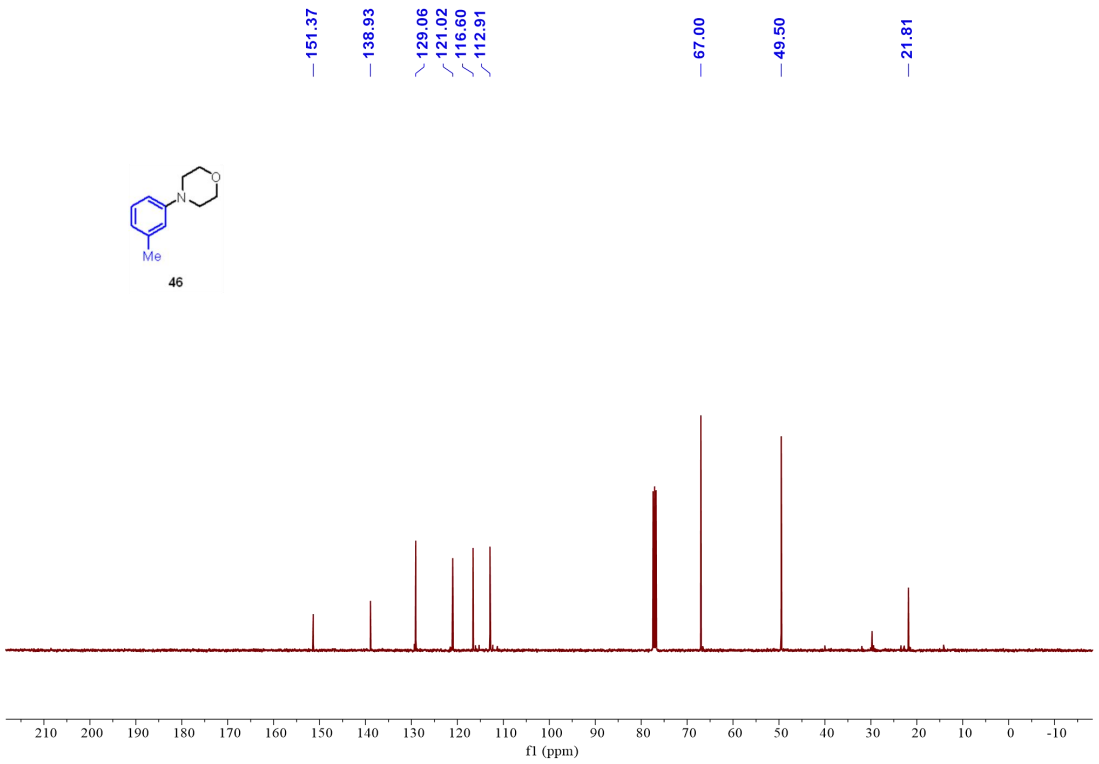

Fig. S112 ^{13}C NMR spectrum of **46** in $CDCl_3$ (101 MHz)

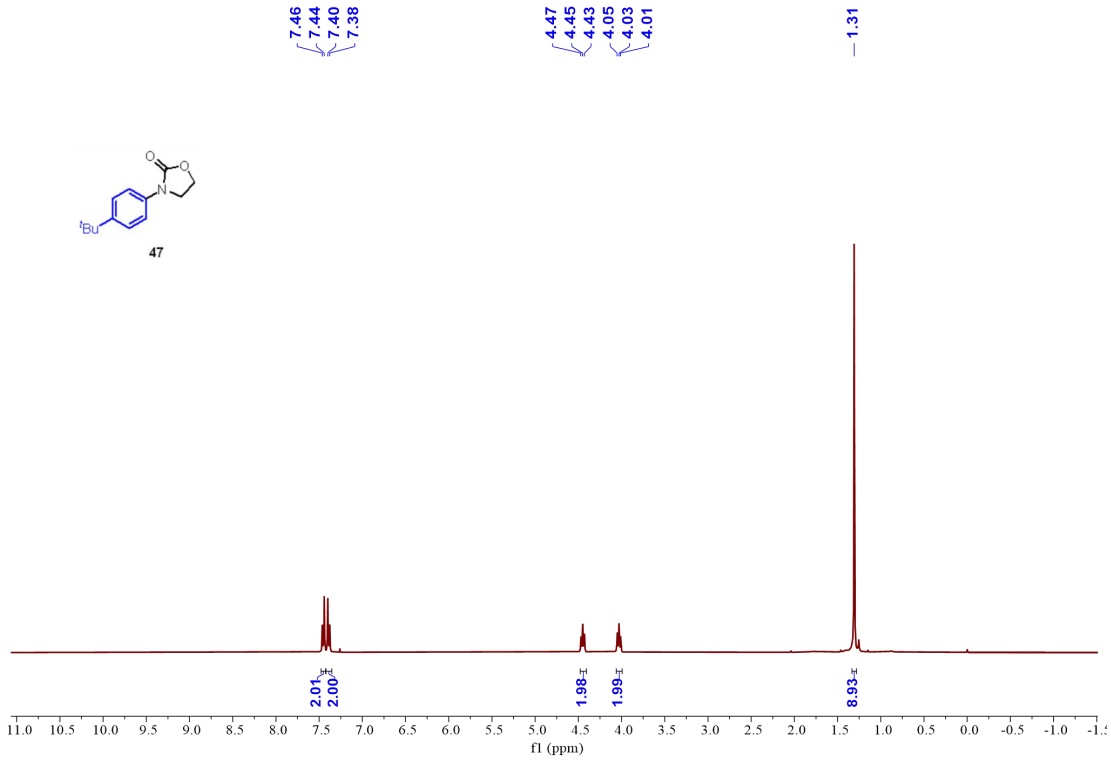

Fig. S113 ^{1}H NMR spectrum of **47** in $CDCl_3$ (400 MHz)

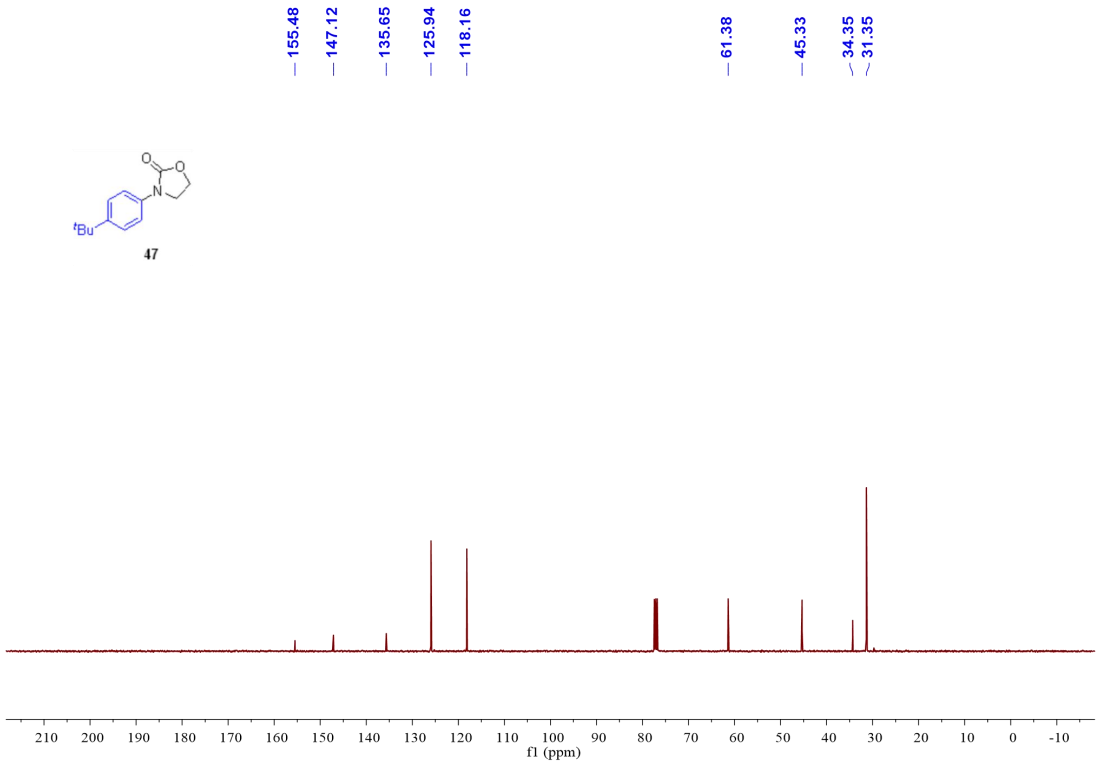

Fig. S114 ^{13}C NMR spectrum of **47** in $CDCl_3$ (101 MHz)

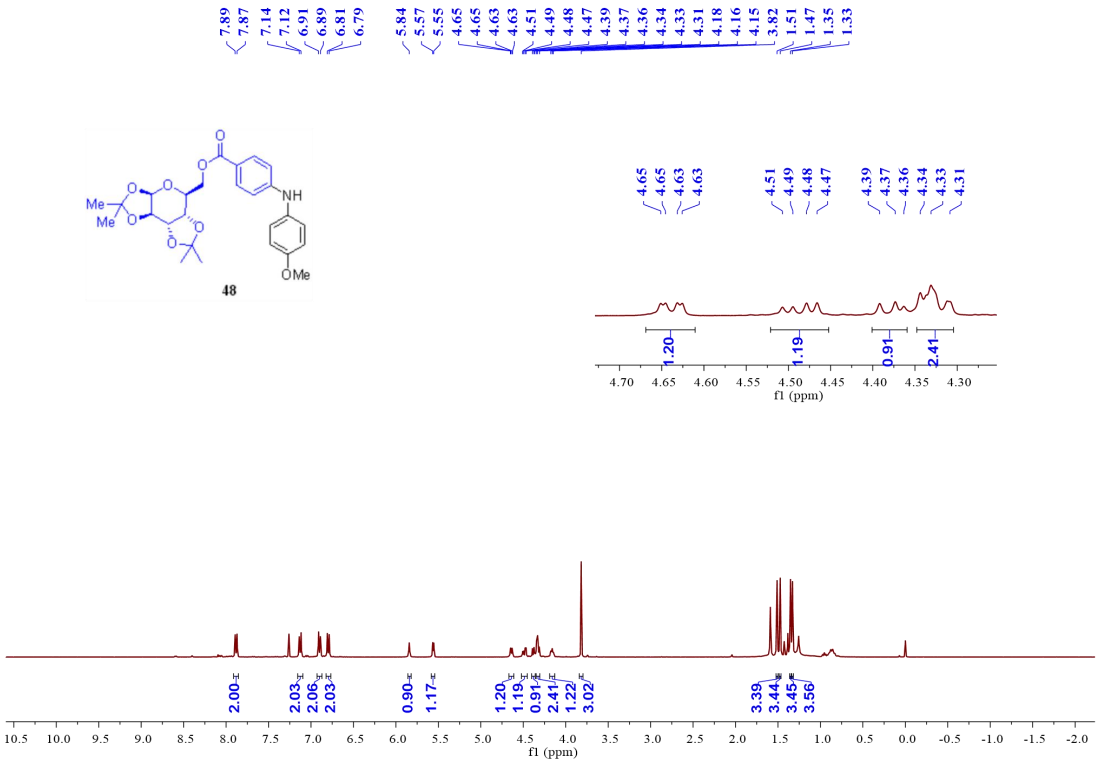

Fig. S115 ^{1}H NMR spectrum of **48** in $CDCl_3$ (400 MHz)

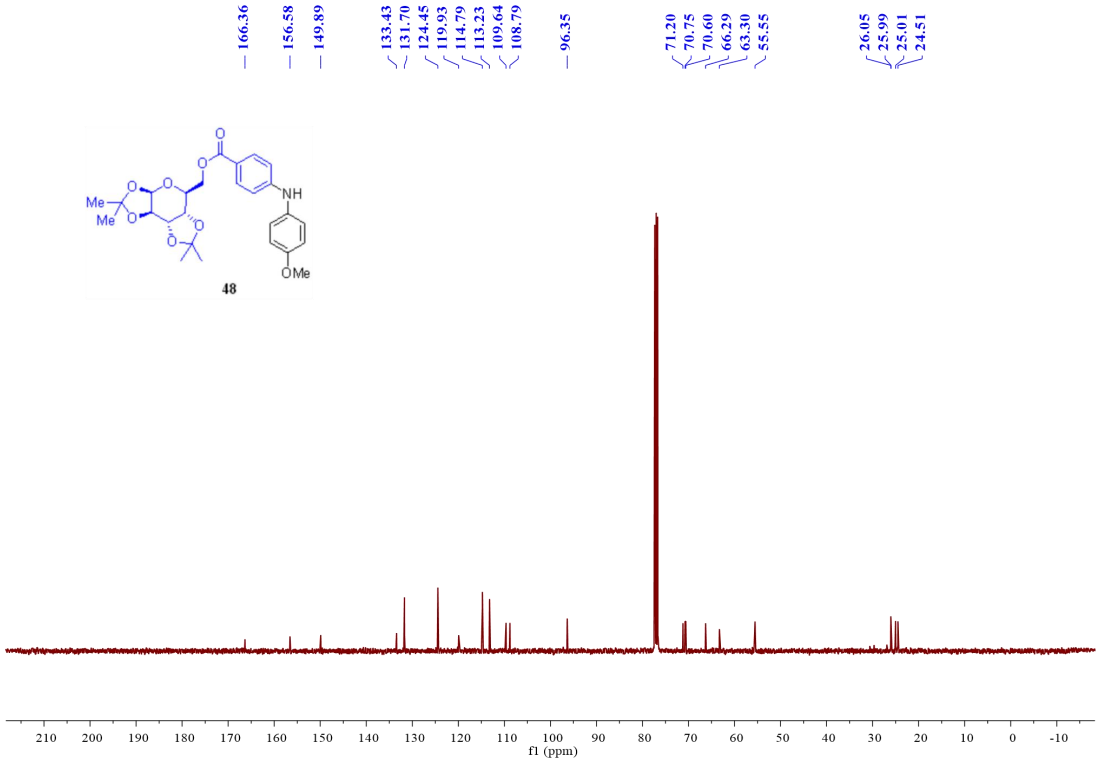

Fig. S116 ^{13}C NMR spectrum of **48** in $CDCl_3$ (101 MHz)

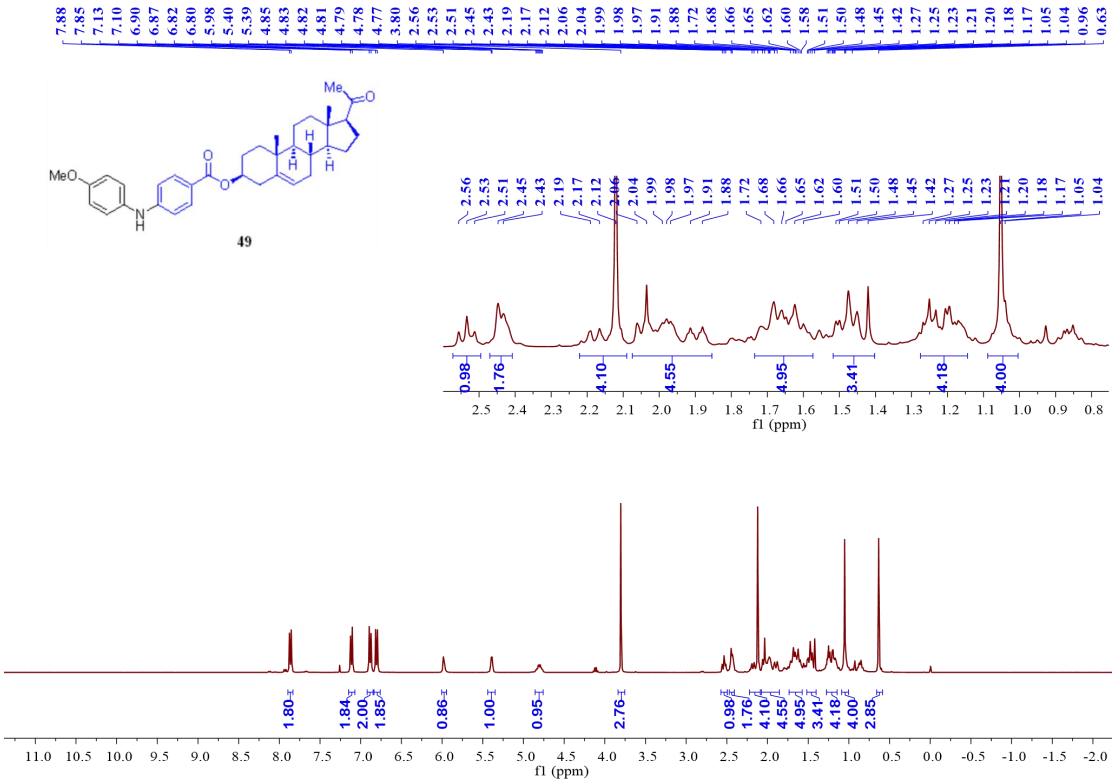

Fig. S117 ^{1}H NMR spectrum of **49** in $CDCl_3$ (400 MHz)

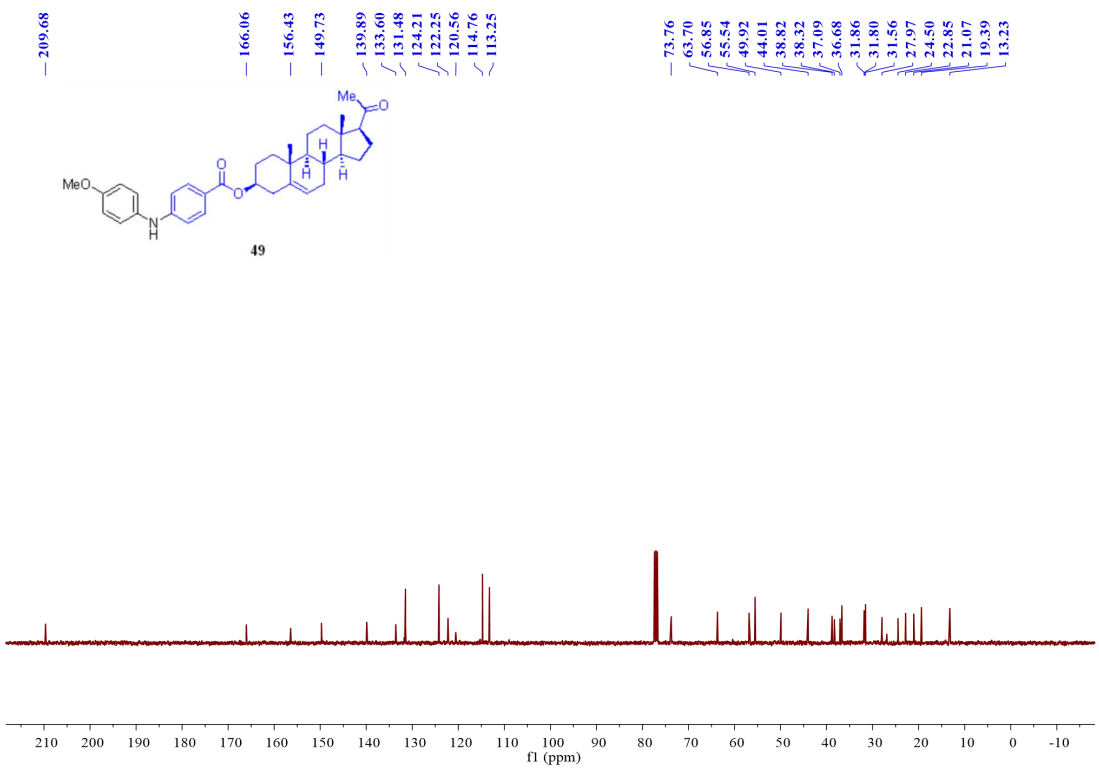

Fig. S118 ^{13}C NMR spectrum of **49** in $CDCl_3$ (101 MHz)