

Electronic Supplementary Information (ESI) for

Single Electron Transfer Catalysis by Diphenylthiourea Under Visible Light Photoredox Conditions

Dhananjay Dey[§], Abhishek Kundu[§], Monojit Roy, Vikramjeet Singh, Shyamali Maji, and
Debashis Adhikari*

*Department of Chemical Sciences, Indian Institute of Science Education and Research Mohali, SAS Nagar-
140306, India.*

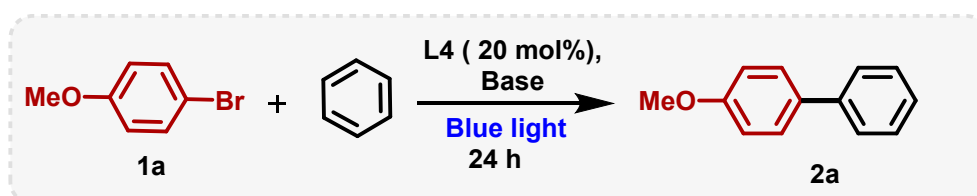
E-mail: adhikari@iisermohali.ac.in

Serial No	Table of Content
1.	General consideration
2.	Screening with different bases
3.	General procedure for the synthesis of cross-coupled products
4.	Mechanistic investigations
5.	Spectroscopic experiments
6.	Cyclic voltammetry experiment for deprotonated DPTU, 7
7.	$E_{o,o}$ calculation for 7
8.	Analytical data of compounds
9.	^1H and ^{13}C NMR spectra of compounds
10.	Crystallographic information
11.	References

1. General Consideration:

All starting compounds employed in this study were procured from commercial suppliers and were used without further purification. All chemicals were purchased from Sigma Aldrich, Avra, TCI, Alfa Aeser, GLR Innovations. Glassware was dried overnight at 160 °C. Benzene was dried by heating over sodium with benzophenone as an indicator. Solvents such as ether, and acetone were used as received from the commercial suppliers. For thin layer chromatography (TLC), silica aluminium foils with fluorescent indicator 254 nm (from Merck) were used. Column chromatography was performed using SD Fine silica gel 60-120 mesh using a gradient of ethyl acetate and hexane as mobile phase. High-resolution mass spectra were recorded on a Waters QTOF mass spectrometer. ¹H NMR and ¹³C NMR spectra were recorded on a 400 MHz Bruker Biospin Advance III FT-NMR spectrometer. Fluorescence quenching experiments were carried out in a Cary Eclipse Fluorescence Spectrofluorometer. UV-Vis was recorded using Varian Cary 60 (Agilent Technologies) spectrophotometer. NMR shifts are reported as delta (δ) units in parts per million (ppm) and coupling constants (J) are reported in Hertz (Hz). The following abbreviations are utilized to describe peak patterns when appropriate: s=singlet, d=doublet, t=triplet, q=quartet, and m=multiplet. Chemical shifts (δ) are quoted to the nearest 0.01 ppm relative to tetramethylsilane (δ 0.00 ppm) in CDCl₃(δ 7.26 ppm). Carbon chemical shifts are internally referenced to the deuterated solvent signals in CDCl₃ (δ 77.1 ppm).

2. Screening with different bases.



Entry	L (mol %)	Base (equiv)	Yield (%)
1	L4 (20)	NaO ^t Bu (3 eq.)	trace
2	L4 (20)	KOH (3 eq.)	-
3	L4 (20)	NaOH (3 eq.)	-
4	L4 (20)	TEA (3 eq.)	-
5	L4 (20)	DIPEA (3 eq.)	-
6	L4 (20)	Et ₃ N (3 eq.)	-

3. General procedure for the synthesis of cross-coupled products.

3.1. Synthesis of biaryls taking aryl halide as substrates.

In an oven-dried pressure tube aryl bromide (0.5 mmol), KO^tBu (1.5 mmol) and diphenylthiourea, **L4** (20 mol%) were added inside a glove box. After that dry benzene (2 mL) was added to the reaction mixture. The reaction mixture was stirred for 24 h under visible light irradiation in an inert atmosphere at room temperature. The reaction flask was placed 7-8 cm away from the LED source. Purification by column chromatography with EtOAc/hexane afforded the corresponding product. The biaryl products were fully characterized by ¹H and ¹³C NMR spectroscopies.

3.2. Synthesis of cyclic amide taking amido-halides as substrates

An oven-dried Schlenk flask with a magnetic stirring bar was charged with 2-Bromo-N,N-dialkylbenzamide (0.5 mmol), catalyst **L4** (20 mol%) and KO^tBu (1.5 mmol) under N₂ atmosphere. 1 ml of dry and degassed THF was added to above reaction mixture. The reaction mixture was stirred under blue light at room temperature for 24 hours. Solvent was removed under rotary evaporator. The desired product was isolated by column chromatography using hexane/ethyl acetate mixture. The pure product was analyzed by NMR spectroscopy.

4. Mechanistic investigations

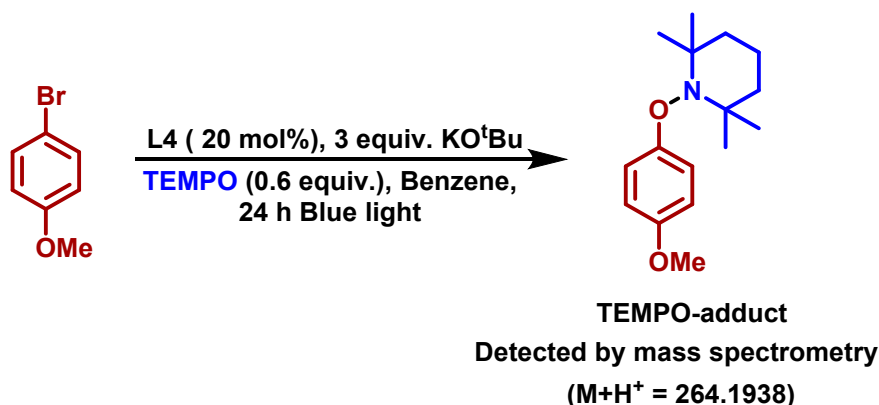
4.1. Radical quenching experiment

In an oven-dried pressure tube 4-bromoanisole (1 mmol), KO^tBu (3 mmol), **L4** (20 mol%), and TEMPO (2 mmol) were added inside a glove box. After that dry benzene (2 mL) was added to the reaction mixture under an argon atmosphere. The reaction mixture was stirred for 24 h under visible light irradiation in an argon atmosphere at room temperature. The reaction was fully quenched and no desired product was isolated from the reaction mixture.

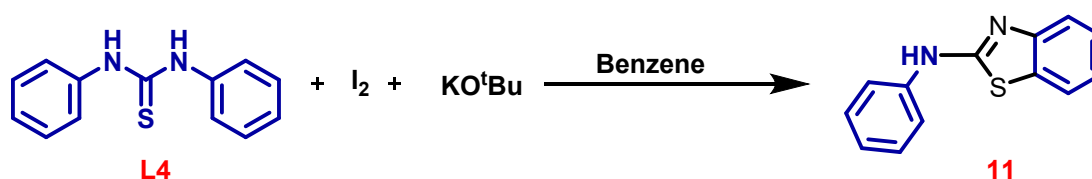
Entry	TEMPO (equiv)	Yield (%)
1.	0.5	5%
2.	2.0	-

4.2. Trapping the radical intermediate:

In an oven-dried pressure tube 4-bromoanisole (1 mmol), KO^tBu (3 mmol), **L4** (20 mol%) and TEMPO (0.6 mmol) were added inside a glove box. After that dry benzene (2 mL) was added to the reaction mixture under an inert atmosphere. The reaction mixture was stirred for 24 h under visible light irradiation in an inert atmosphere at room temperature. Then the crude reaction mixture was subjected to HRMS. The desired intermediate was characterised by high-resolution ESI-MS. (M+H⁺ = 264.1938).



4.3. Reaction of diphenylthiourea with I_2 in the presence of KO^tBu .



In an oven-dried Schlenk flask, **L4** (1 mmol), KO^tBu (2.2 mmol), and I_2 (2 mmol) were mixed under an inert atmosphere. After that dry benzene (2 mL) was added to the reaction mixture. The reaction mixture was stirred under visible light irradiation for 24 h under an inert atmosphere at room temperature. After the completion of the reaction, excess I_2 was quenched with saturated sodium thiosulfate solution and the mixture was extracted with EtOAc. Then the resulting solution was dried over Na_2SO_4 , filtered, and concentrated under reduced pressure. Purification by column chromatography with EtOAc/hexane afforded **11** (58%).

1H NMR (400 MHz, $CDCl_3$) δ 9.34 (s, 1H), 7.63 (dd, $J = 8.0, 1.2$ Hz, 1H), 7.58 – 7.55 (m, 1H), 7.53 – 7.49 (m, 2H), 7.42 (dd, $J = 8.5, 7.3$ Hz, 2H), 7.35 – 7.30 (m, 1H), 7.21 – 7.13 (m, 2H)

^{13}C NMR (100 MHz, $CDCl_3$) δ 165.4, 151.4, 140.1, 129.7, 126.3, 124.6, 122.4, 121.0, 120.7, 119.3.

Spectroscopic data matched with the literature.¹²

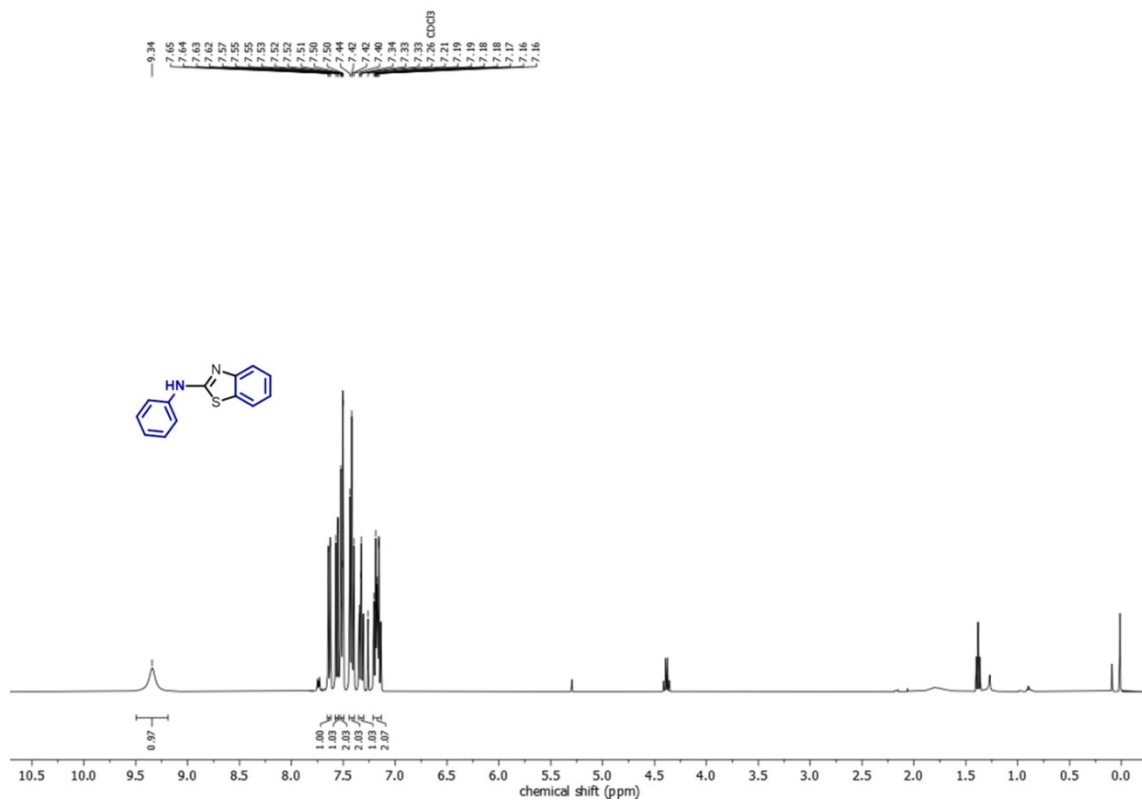


Figure S1. ¹H NMR spectrum (400 MHz) of 11 in CDCl₃.

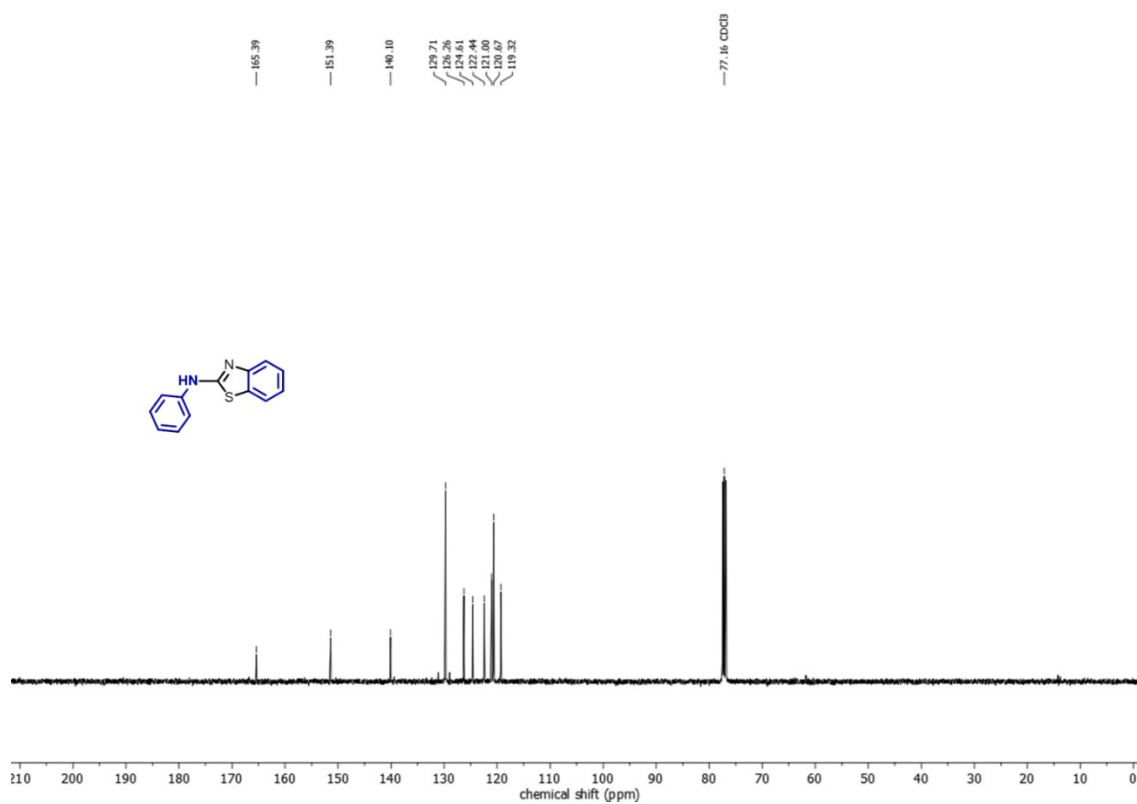
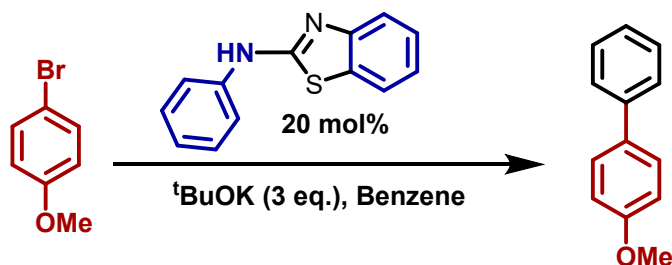


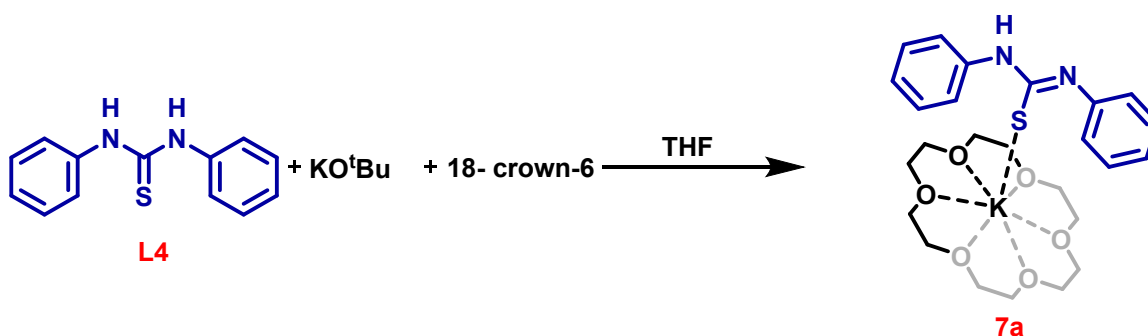
Figure S2. ¹³C NMR spectrum (100 MHz) of 11 in CDCl₃.

4.4. Catalysis with isolated **11**.



To confirm that **11** is an intermediate species in this electron transfer catalysis, 4-bromoanisole (0.5 mmol), KO^tBu (1.5 mmol), and **11** (20 mol%) were added to an oven-dried pressure tube along with 2 mL of dry benzene. The reaction mixture was stirred at room temperature for 24 h under visible light irradiation. Column chromatographic purification by EtOAc/hexane mixture afforded the corresponding product in 11% yield.

4.5. Detection of the potential single electron donor species.



In a 10 ml reaction vial **L4** (1 mmol), KO^tBu (1.1 mmol), and 18-crown-6 (1.1 mmol) were charged under the inert atmosphere of a glove box. 5 ml THF was added to the mixture and stirred for 20 mins. The stir bar was removed and the solution was kept at room temperature. After four days the solution afforded pale yellowish needle-shaped crystals.

5. Spectroscopic experiments:

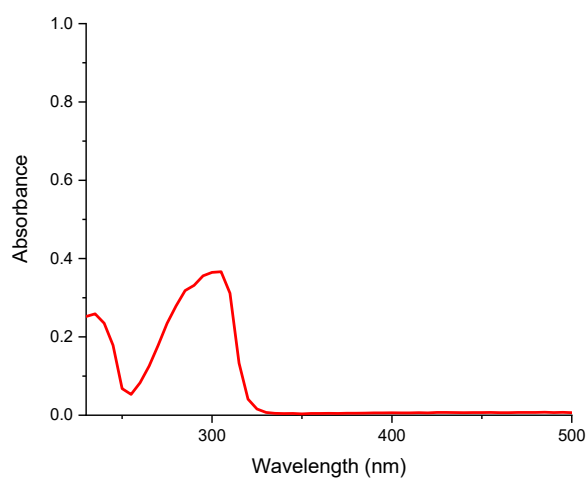


Figure S3. UV-visible spectra of **L4** (10^{-4} M) in MeCN.

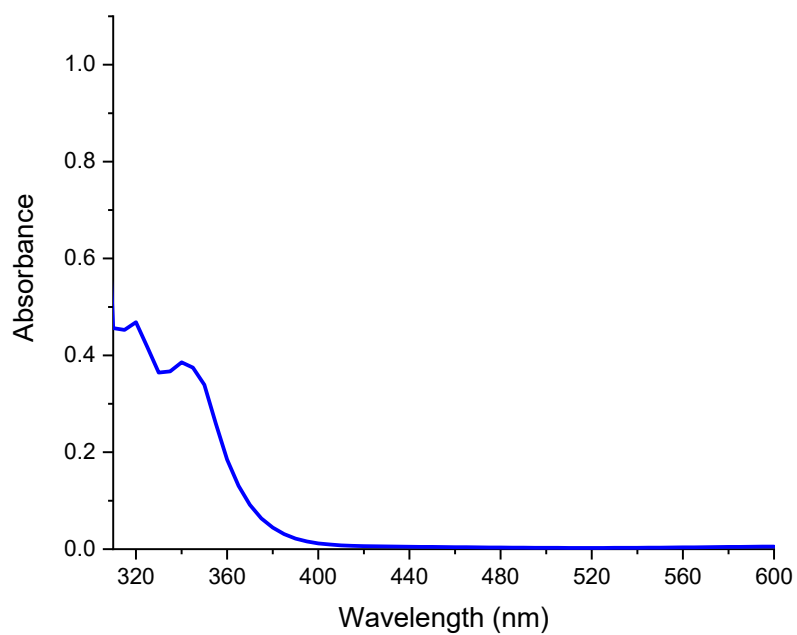


Figure S4. UV-visible spectra of deprotonated DPTU, **7** (10^{-4} M) in MeCN.

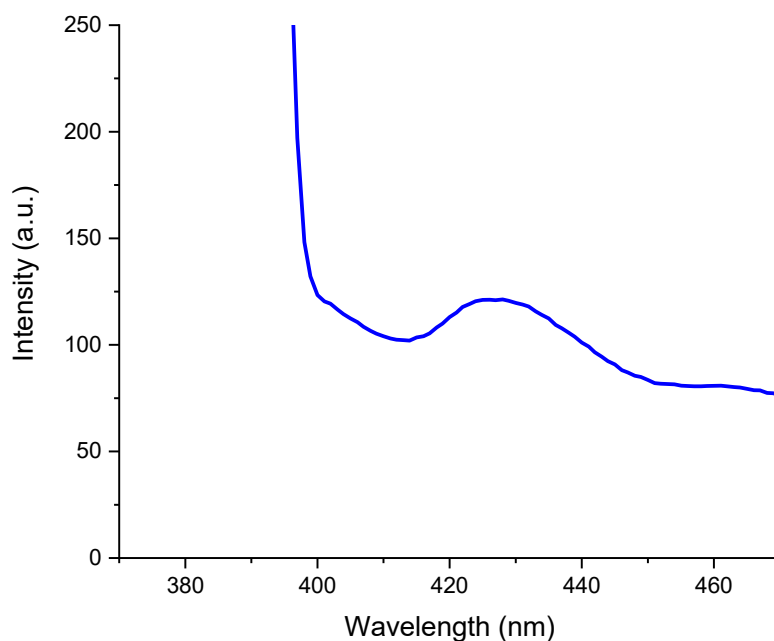


Figure S5. Emission spectra of deprotonated DPTU, **7** (10^{-4} M) in MeCN (excitation wavelength = 380 nm).

The Stern-Volmer experiment was not successful for the overlapping emission band of L4 anion with 11 anion.

6. Cyclic voltammetry experiment for deprotonated DPTU, **7**

We attempted to determine the oxidation potential of deprotonated DPTU (**7**) by cyclic voltammetry. To prepare deprotonated L4, 2.28 mg of N,N'-Diphenylthiourea and 3 mg of KH (30 % w/w in mineral oil) were taken in 1 mL of dry MeCN and stirred for 10 min. Then the solution was filtered through PTFE filter. Then 19 mL MeCN solution of 0.1 M (nBu₄N)PF₆ was added to the filtrate as the supporting electrolyte. To evaluate the ground-state oxidation, a three-electrode set-up was used where glassy carbon was the working electrode, a Pt wire as the counter and Ag/AgCl containing 2 M KCl solution as the reference electrode, respectively. The shown voltammogram (Figure S4) was collected with a scan rate of 100 mV sec⁻¹. The peak positions for the anodic and cathodic waves were internally referenced with respect to Fc⁺/Fc couple.

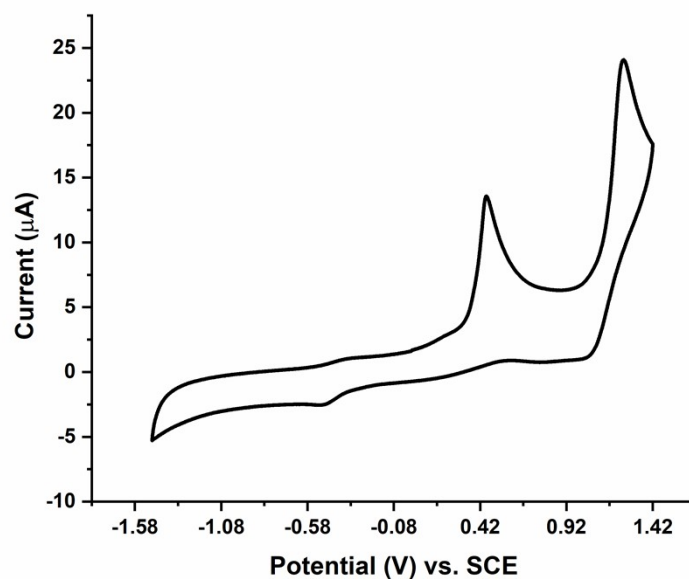


Figure S6. CV of 1 mM of **7** dissolved in acetonitrile along with 0.1 M solution of tetrabutylammonium hexafluorophosphate salt as an electrolyte.

7. $E_{0,0}$ calculation for **7**.

Excitation wavelength = 380 nm

Emission max = 428 nm

Average wavelength = 404 nm

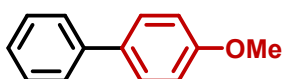
$$E_{0,0} = 1240/404 \text{ eV} = 3.07 \text{ eV}$$

$$E^*_{\text{ox}} = E_{\text{ox}} - E_{0,0}$$

$$E^*_{\text{ox}} = 0.53 - 3.07 = -2.54 \text{ V vs SCE}$$

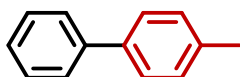
8. Analytical data

4-methoxy-1,1'-biphenyl (**2a**):



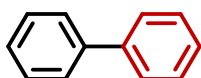
The compound was purified by column chromatography (silica gel 60–120 mesh) with hexane to give the product as a colourless solid (yield: 82 mg, 89%). ^1H NMR (400 MHz, CDCl_3) δ 7.55 (t, $J = 8.2$ Hz, 4H), 7.43 (t, $J = 7.7$ Hz, 2H), 7.31 (t, $J = 7.4$ Hz, 1H), 6.99 (d, $J = 8.7$ Hz, 2H), 3.86 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 159.2, 141.0, 133.9, 128.9, 128.3, 126.9, 126.8, 114.3, 55.5. Spectroscopic data matched with the literature.¹

4-methyl-1,1'-biphenyl (2b):



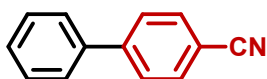
The compound was purified by column chromatography (silica gel 60–120 mesh) with hexane to give the product as a colourless solid (yield: 71 mg, 85%). ¹H NMR (400 MHz, CDCl₃) δ 7.59 (d, *J* = 8.1 Hz, 2H), 7.50 (d, *J* = 8.1 Hz, 2H), 7.43 (t, *J* = 7.6 Hz, 2H), 7.33 (t, *J* = 7.3 Hz, 1H), 7.26 (d, *J* = 8.1 Hz, 2H), 2.40 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 141.3, 138.5, 137.2, 129.6, 128.8, 127.1, 127.1, 21.2. Spectroscopic data matched with the literature.²

biphenyl (2c):



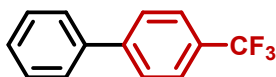
The compound was purified by column chromatography (silica gel 60–120 mesh) with hexane to give the product as a colourless solid (yield: 66 mg, 86 %). ¹H NMR (400 MHz, CDCl₃) δ 7.71 – 7.63 (m, 2H), 7.51 (q, *J* = 7.6 Hz, 2H), 7.42 (d, *J* = 5.7 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 141.4, 128.9, 128.9, 127.4, 127.3, 127.3. Spectroscopic data matched with the literature¹.

[1,1'-biphenyl]-4-carbonitrile (2d) :



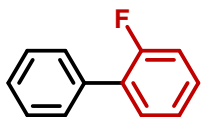
The compound was purified by column chromatography (silica gel 60–120 mesh) with hexane to give the product as a colourless solid (yield: 79 mg, 88%). ¹H NMR (400 MHz, CDCl₃) δ 7.75 – 7.67 (m, 4H), 7.61 – 7.57 (m, 2H), 7.51 – 7.46 (m, 2H), 7.46 – 7.41 (m, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 145.8, 139.3, 132.7, 128.8, 127.8, 127.3, 119.1, 111.0. Spectroscopic data matched with the literature.³

4-(trifluoromethyl)-1,1'-biphenyl (2e) :



The compound was purified by column chromatography (silica gel 60–120 mesh) with hexane to give the product as a colourless solid (yield: 87 mg, 78 %). ¹H NMR (400 MHz, CDCl₃) δ 7.71 (s, 4H), 7.64 – 7.59 (m, 2H), 7.49 (t, *J* = 7.4 Hz, 2H), 7.42 (t, *J* = 7.3 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 144.9, 139.9, 129.1, 128.3, 127.6, 127.4, 125.9, 125.9, 125.8, 125.8. ¹⁹F NMR (376 MHz, CDCl₃): δ -62.3. Spectroscopic data matched with the literature.⁴

2-fluoroy-1,1'-biphenyl (2f):



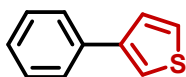
The compound was purified by column chromatography (silica gel 60–120 mesh) with hexane to give the product as a colourless solid (yield: 65 mg, 75%). ^1H NMR (400 MHz, CDCl_3) δ 7.57 (d, $J = 7.6$ Hz, 2H), 7.47 (t, $J = 7.6$ Hz, 3H), 7.36 (dt, $J = 24.6, 6.4$ Hz, 2H), 7.25 – 7.12 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 158.7, 136.0, 130.9, 130.9, 129.3, 129.2, 129.2, 129.1, 129.0, 128.6, 127.8, 124.5, 124.5, 116.3, 116.1. ^{19}F NMR (376 MHz, CDCl_3): δ -115.9. Spectroscopic data matched with the literature.⁵

2-methoxy-3-phenylpyridine (2g):



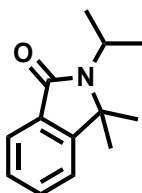
The compound was purified by column chromatography (silica gel 60–120 mesh) with hexane to give the product as a colourless solid (yield: 66 mg, 71%). ^1H NMR (400 MHz, CDCl_3) δ 8.21 (dd, $J = 5.0, 2.0$ Hz, 1H), 7.65 – 7.58 (m, 3H), 7.46 (t, $J = 7.5$ Hz, 2H), 7.39 (t, $J = 7.3$ Hz, 1H), 6.99 (dd, $J = 7.3, 5.0$ Hz, 1H), 4.02 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 160.9, 145.8, 138.6, 136.8, 129.2, 128.3, 127.6, 124.7, 117.1, 53.6, 53.5. Spectroscopic data matched with the literature.⁶

3-phenylthiophene (2h):



The compound was purified by column chromatography (silica gel 60–120 mesh) with hexane to give the product as a colourless solid (yield: 58 mg, 72%). ^1H NMR (400 MHz, CDCl_3) δ 7.72 – 7.63 (m, 2H), 7.52 – 7.50 (m, 1H), 7.49 – 7.41 (m, 4H), 7.40 – 7.33 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 142.4, 135.9, 128.9, 127.2, 126.6, 126.4, 126.3, 120.4. Spectroscopic data matched with the literature.⁷

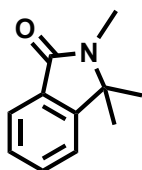
2-isopropyl-3,3-dimethylisoindolin-1-one (4a)



The compound was purified by column chromatography (silica gel) with 10 % mixture of ethyl acetate in hexane to give the product as a white solid (68 mg, 65%). ^1H NMR (400 MHz, CDCl_3) δ 7.74 (d, $J = 7.5$ Hz, 1H), 7.47 (t, $J = 7.5$ Hz, 1H), 7.37 (t, $J = 7.4$ Hz, 1H), 7.31 (d, $J = 7.6$ Hz, 1H), 3.62 (hept, $J = 6.8$ Hz, 1H), 1.53 (d, $J = 6.9$ Hz, 6H), 1.44 (s, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 167.25, 151.32,

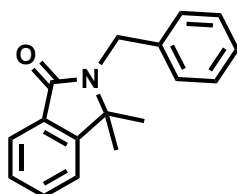
132.04, 131.29, 127.88, 123.17, 120.67, 63.32, 44.56, 25.49, 20.54. Spectroscopic data matched with the literature.⁸

2,3,3-trimethylisoindolin-1-one (4b)



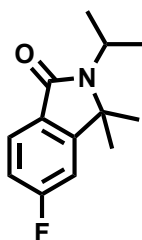
The compound was purified by column chromatography (silica gel) with 10 % mixture of ethyl acetate in hexane to give the product as a white solid (55 mg, 63%). ¹H NMR (400 MHz, CDCl₃) δ 7.79 (d, *J* = 7.2 Hz, 1H), 7.50 (t, *J* = 6.8 Hz, 1H), 7.39 (t, *J* = 7.3 Hz, 2H), 3.00 (s, 3H), 1.42 (s, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 167.25, 151.56, 131.50, 130.93, 127.99, 123.55, 120.72, 62.10, 24.96, 23.88. Spectroscopic data matched with the literature.⁹

2-benzyl-3,3-dimethylisoindolin-1-one (4c)



The compound was purified by column chromatography (silica gel) with 10 % mixture of ethyl acetate in hexane to give the product as a white solid (67 mg, 55%). ¹H NMR (400 MHz, CDCl₃) δ 7.89 (d, *J* = 8.6 Hz, 1H), 7.56 – 7.50 (m, 1H), 7.44 (t, *J* = 6.9 Hz, 1H), 7.36 (d, *J* = 7.5 Hz, 3H), 7.28 (t, *J* = 7.3 Hz, 2H), 7.22 (d, *J* = 7.2 Hz, 1H), 4.75 (s, 2H), 1.35 (s, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 167.90, 151.95, 138.68, 131.79, 130.40, 128.46, 128.02, 127.75, 127.17, 123.80, 120.68, 63.18, 42.63, 26.33. Spectroscopic data matched with the literature.⁸

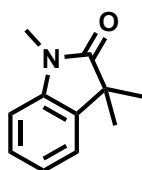
5-fluoro-2-isopropyl-3,3-dimethylisoindolin-1-one (4d)



The compound was purified by column chromatography (silica gel) with 10 % mixture of ethyl acetate in hexane to give the product as a white solid (79 mg, 72%). ¹H NMR (400 MHz, CDCl₃) δ 7.74 (dd, *J* = 8.3, 5.1 Hz, 1H), 7.12 – 7.06 (m, 1H), 7.01 (dd, *J* = 8.2, 2.2 Hz, 1H), 3.62 (hept, *J* = 6.8 Hz, 1H), 1.54 (d, *J* = 6.9 Hz, 6H), 1.47 (s, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 166.37, 163.81 (¹J_{C-F} = 251 Hz), 153.73 (³J_{C-F} = 9 Hz), 128.09 (⁴J_{C-F} = 2 Hz), 125.35 (³J_{C-F} = 9 Hz), 115.54 (²J_{C-F} = 24 Hz), 108.29 (²J_{C-F} = 23 Hz), 63.08, 44.83, 25.52, 20.63. ¹⁹F NMR (376 MHz, CDCl₃): δ -108.1

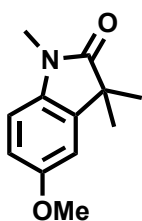
Spectroscopic data matched with the literature.¹⁰

1,3,3-trimethylindolin-2-one (6a)



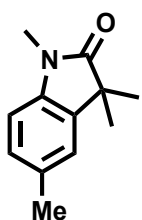
The compound was purified by column chromatography (silica gel) with 5 % mixture of ethyl acetate in hexane to give the product as a colorless oil (63 mg, 73%). ¹H NMR (400 MHz, CDCl₃) δ 7.29 – 7.23 (m, 1H), 7.20 (d, *J* = 6.1 Hz, 1H), 7.06 (t, *J* = 7.5 Hz, 1H), 6.84 (d, *J* = 7.7 Hz, 1H), 3.22 (s, 3H), 1.37 (s, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 181.50, 142.75, 135.95, 127.77, 122.59, 122.37, 108.12, 44.29, 26.32, 24.49. Spectroscopic data matched with the literature.¹¹

5-methoxy-1,3,3-trimethylindolin-2-one (6b)



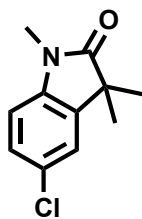
The compound was purified by column chromatography (silica gel) with 10 % mixture of ethyl acetate in hexane to give the product as a colorless oil (72 mg, 70%). ¹H NMR (400 MHz, CDCl₃) δ 6.81 (d, *J* = 2.3 Hz, 1H), 6.77 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.73 (d, *J* = 8.4 Hz, 1H), 3.79 (s, 3H), 3.17 (s, 3H), 1.34 (s, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 181.10, 156.15, 137.32, 136.23, 111.63, 110.14, 108.31, 55.87, 44.69, 26.35, 24.49. Spectroscopic data matched with the literature.¹¹

1,3,3,5-tetramethylindolin-2-one (6c)



The compound was purified by column chromatography (silica gel) with 5 % mixture of ethyl acetate in hexane to give the product as a yellow oil (63 mg, 68%). ¹H NMR (400 MHz, CDCl₃) δ 7.06 (d, *J* = 7.8 Hz, 1H), 7.03 (s, 1H), 6.73 (d, *J* = 7.8 Hz, 1H), 3.19 (s, 3H), 2.35 (s, 3H), 1.36 (s, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 181.47, 140.38, 136.02, 132.11, 127.95, 123.29, 107.85, 44.35, 26.35, 24.54. Spectroscopic data matched with the literature.¹¹

5-chloro-1,3,3-trimethylindolin-2-one (6d)



The compound was purified by column chromatography (silica gel) with 5 % mixture of ethyl acetate in hexane to give the product as a yellow solid (75 mg, 72%). ¹H NMR (400 MHz, CDCl₃) δ 7.22 (dd, *J* = 8.3, 2.1 Hz, 1H), 7.17 (d, *J* = 2.1 Hz, 1H), 6.75 (d, *J* = 8.2 Hz, 1H), 3.19 (s, 3H), 1.35 (s, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 180.91, 141.31, 137.58, 127.97, 127.67, 123.04, 109.05, 44.57, 26.44, 24.38. Spectroscopic data matched with the literature.¹¹

9. ^1H and ^{13}C NMR spectra of compounds

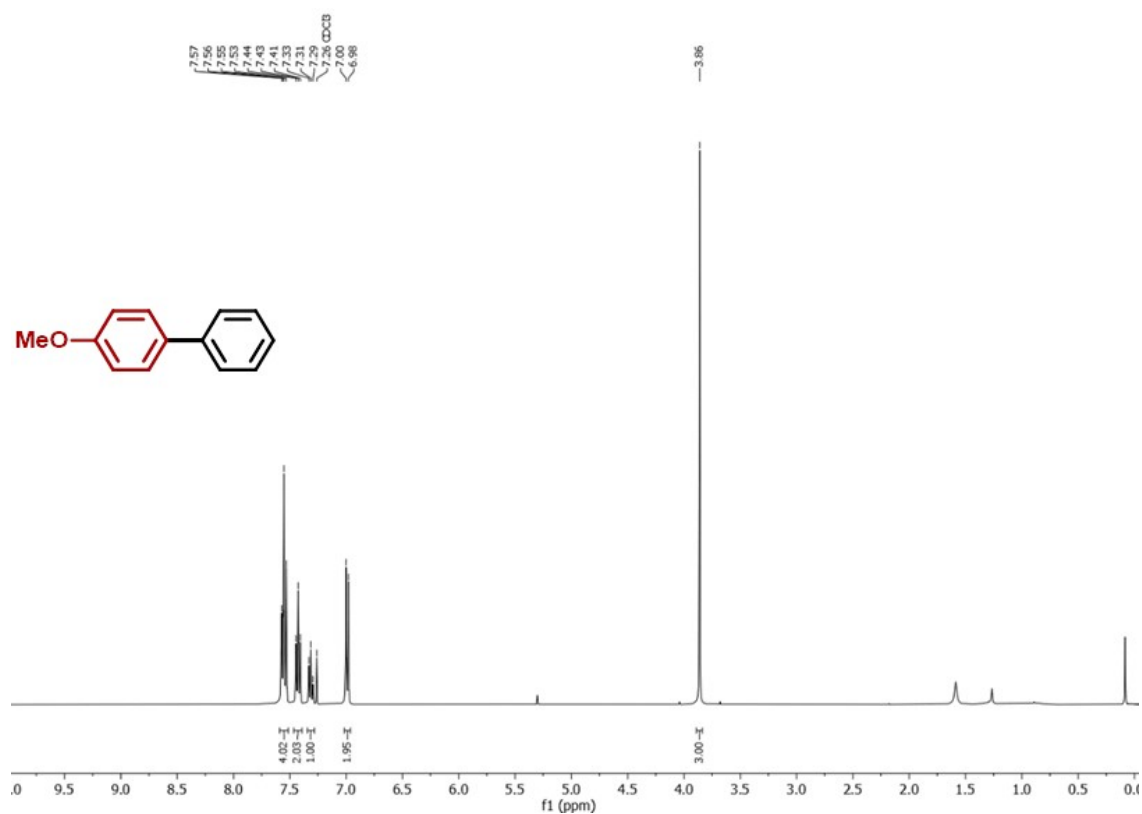


Figure S7. ^1H NMR spectrum (400 MHz) of 2a in CDCl_3 .

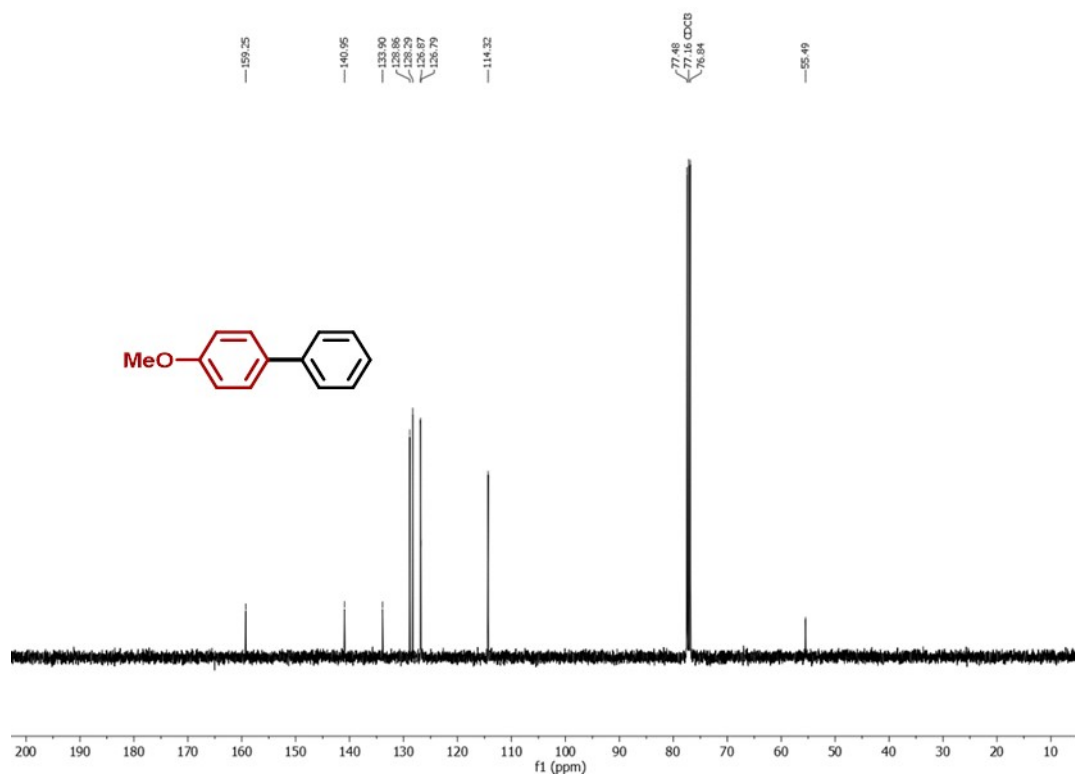


Figure S8. ^{13}C NMR spectrum (100 MHz) of 2a in CDCl_3 .

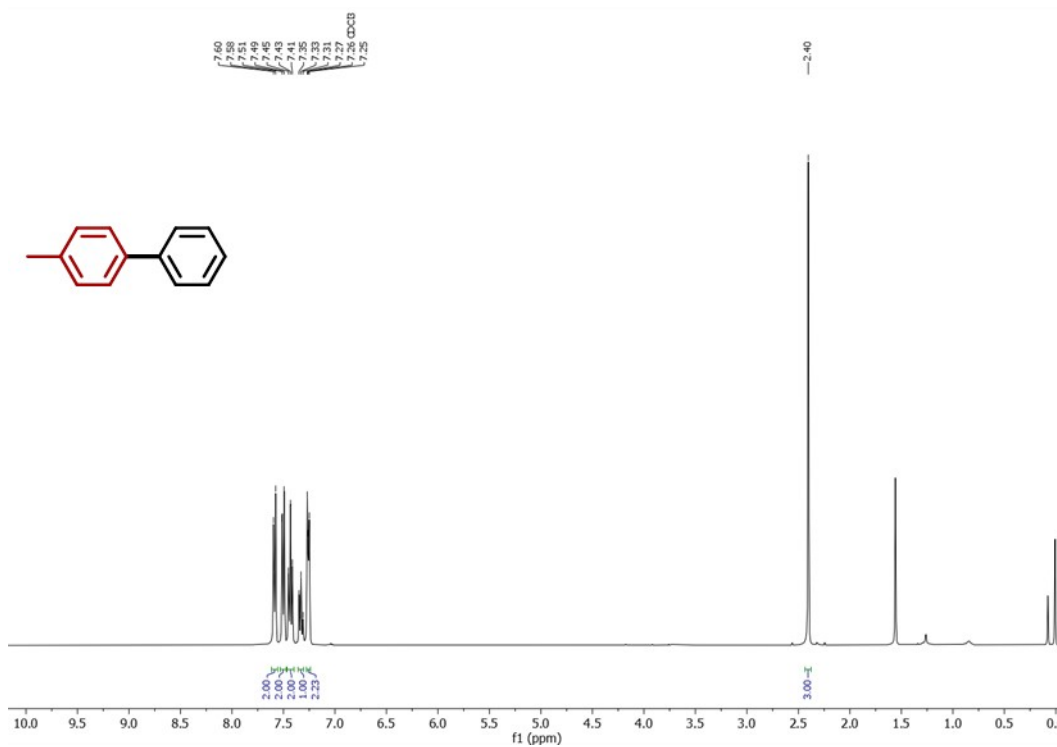


Figure S9. ¹H NMR spectrum (400 MHz) of **2b** in CDCl₃.

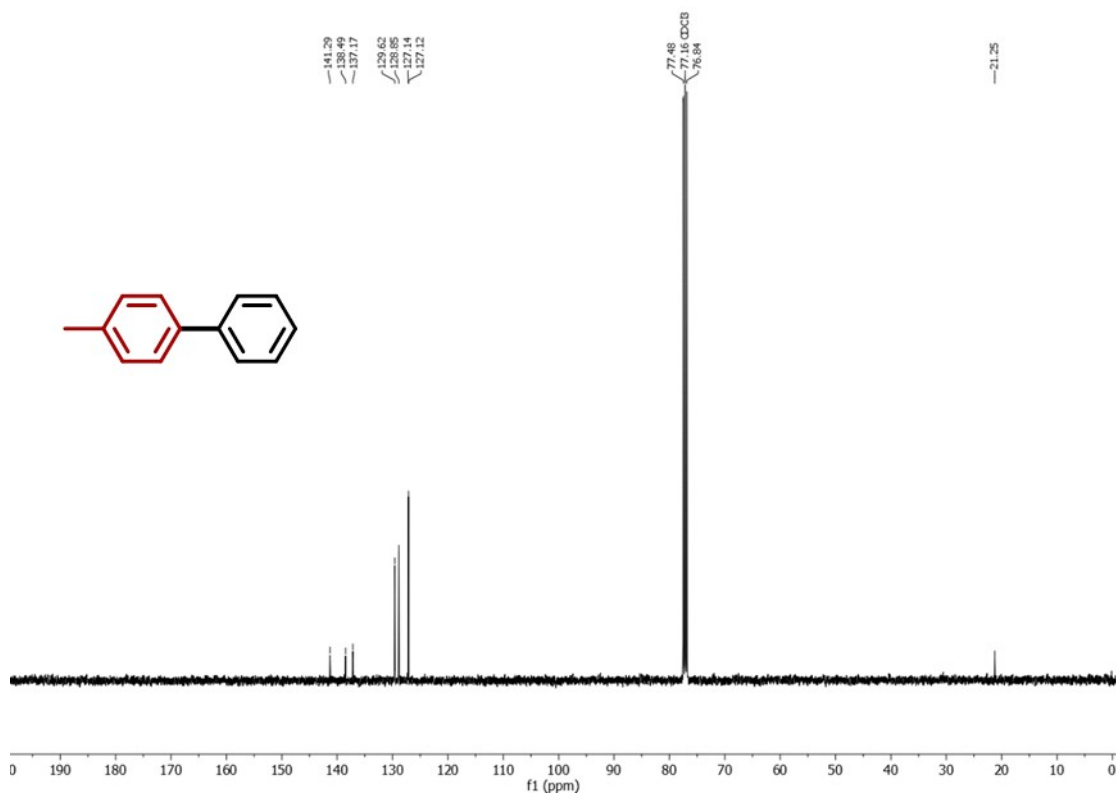


Figure S10. ¹³C NMR spectrum (100 MHz) of **2b** in CDCl₃.

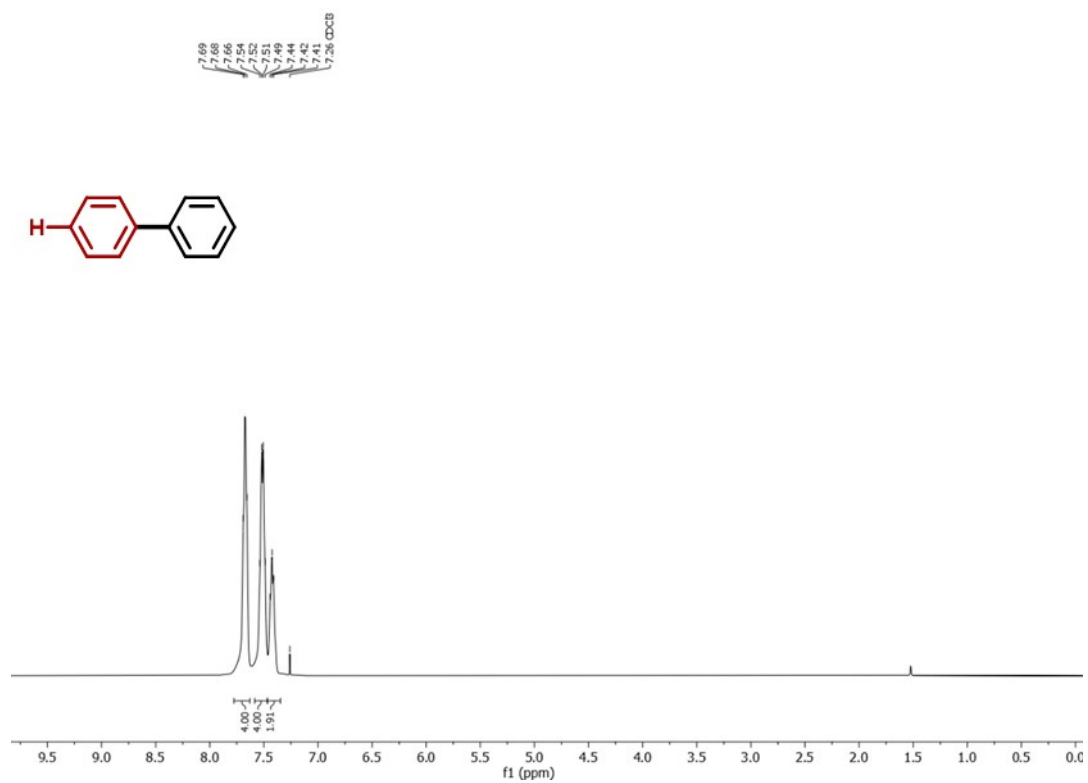


Figure S11. ^1H NMR spectrum (400 MHz) of 2c in CDCl_3 .

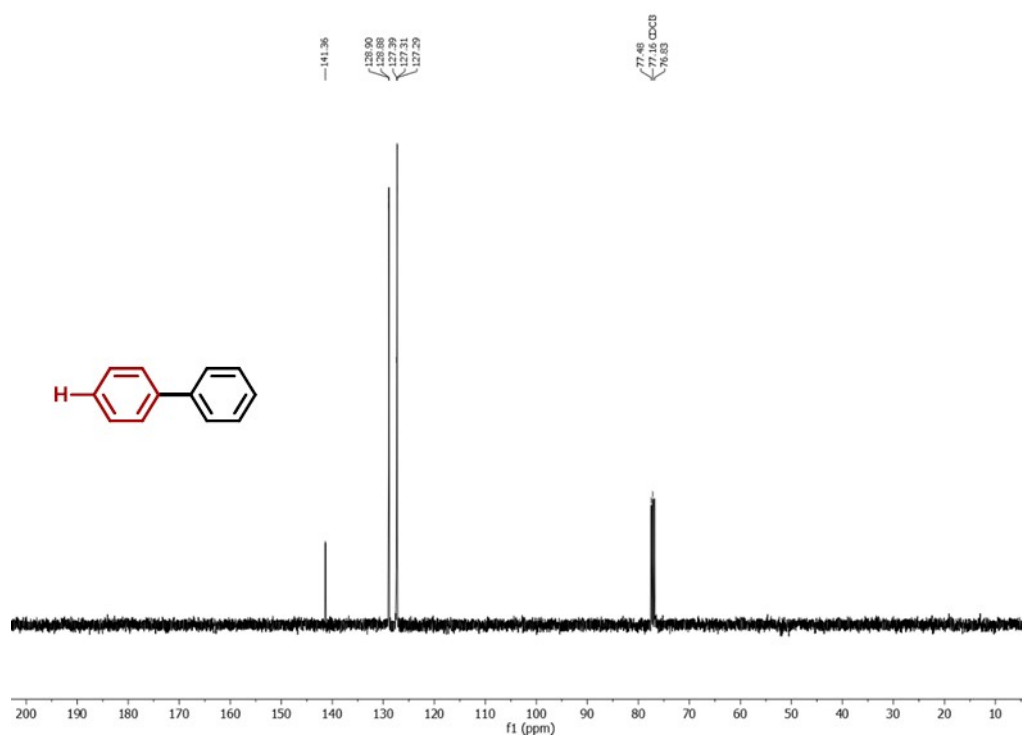


Figure S12. ^{13}C NMR spectrum (100 MHz) of 2c in CDCl_3 .

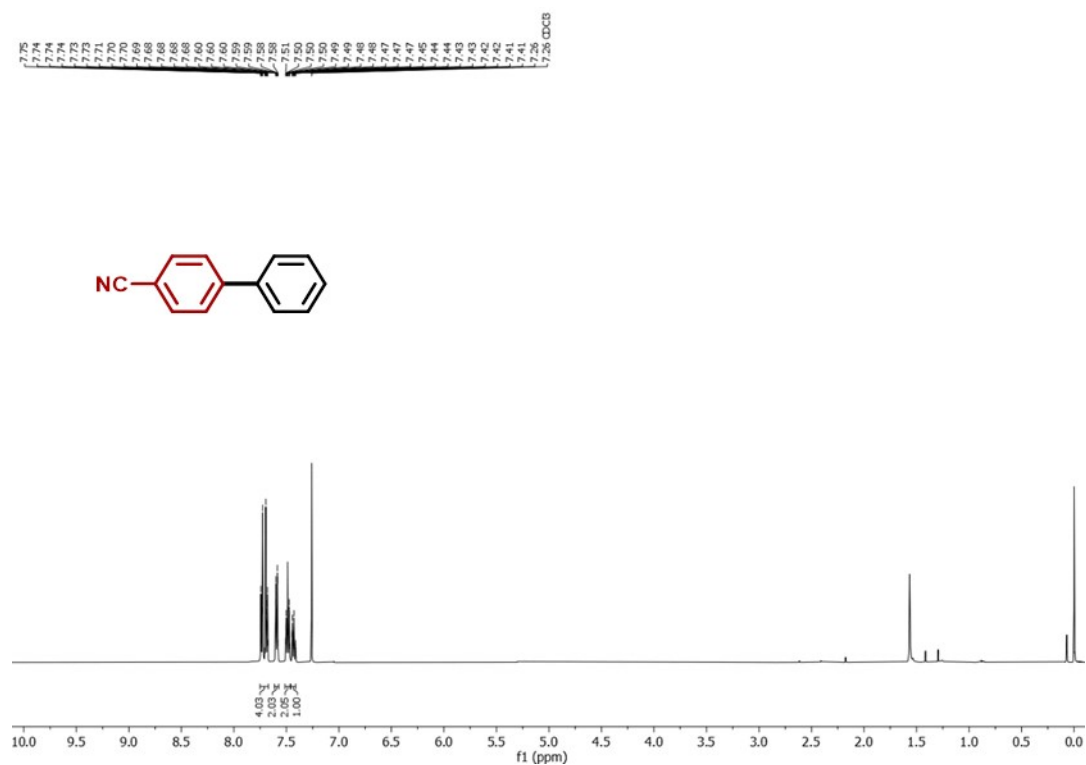


Figure S13. ¹H NMR spectrum (400 MHz) of 2d in CDCl₃.

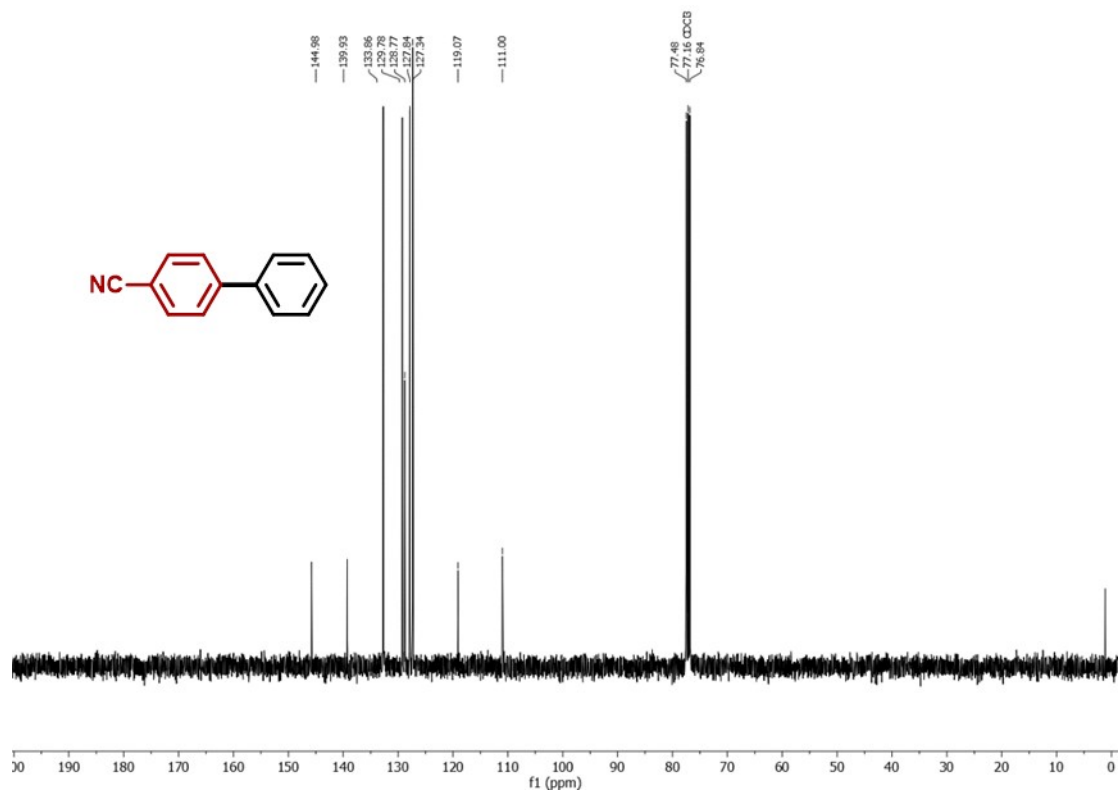


Figure S14. ¹³C NMR spectrum (100 MHz) of 2d in CDCl₃.

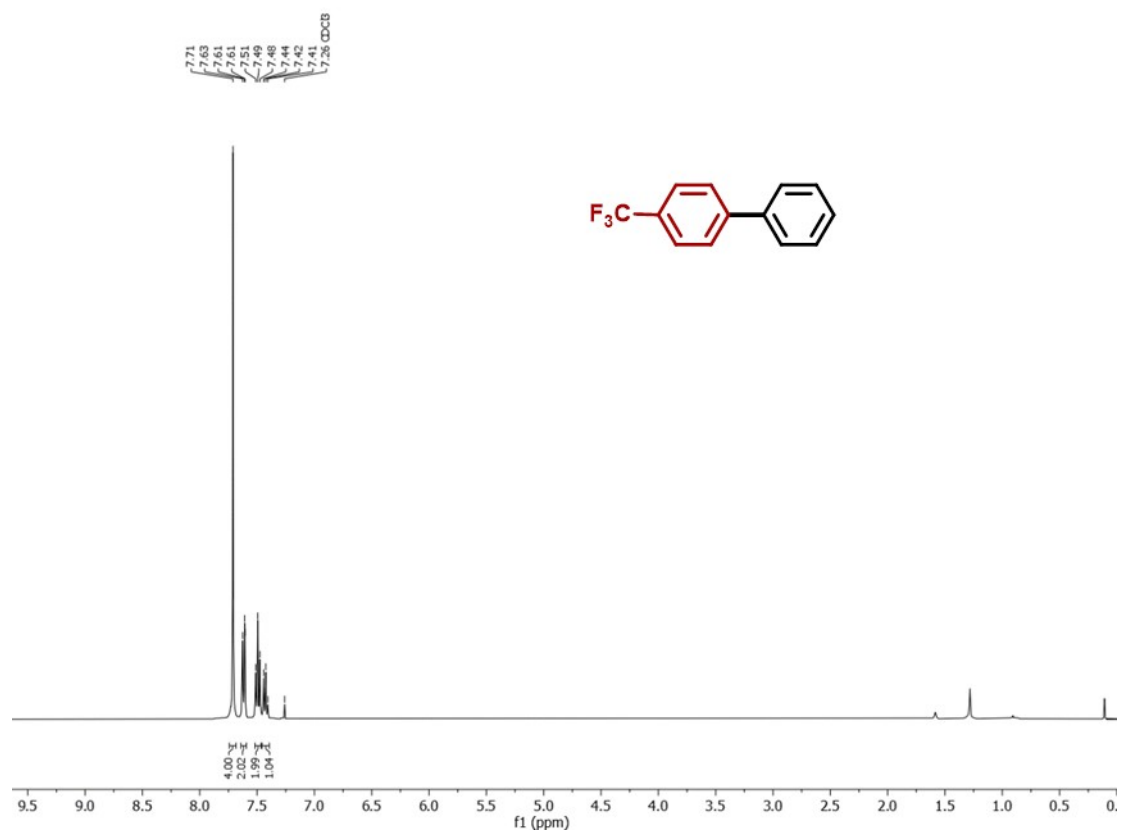


Figure S15. ¹H NMR spectrum (400 MHz) of 2e in CDCl₃.

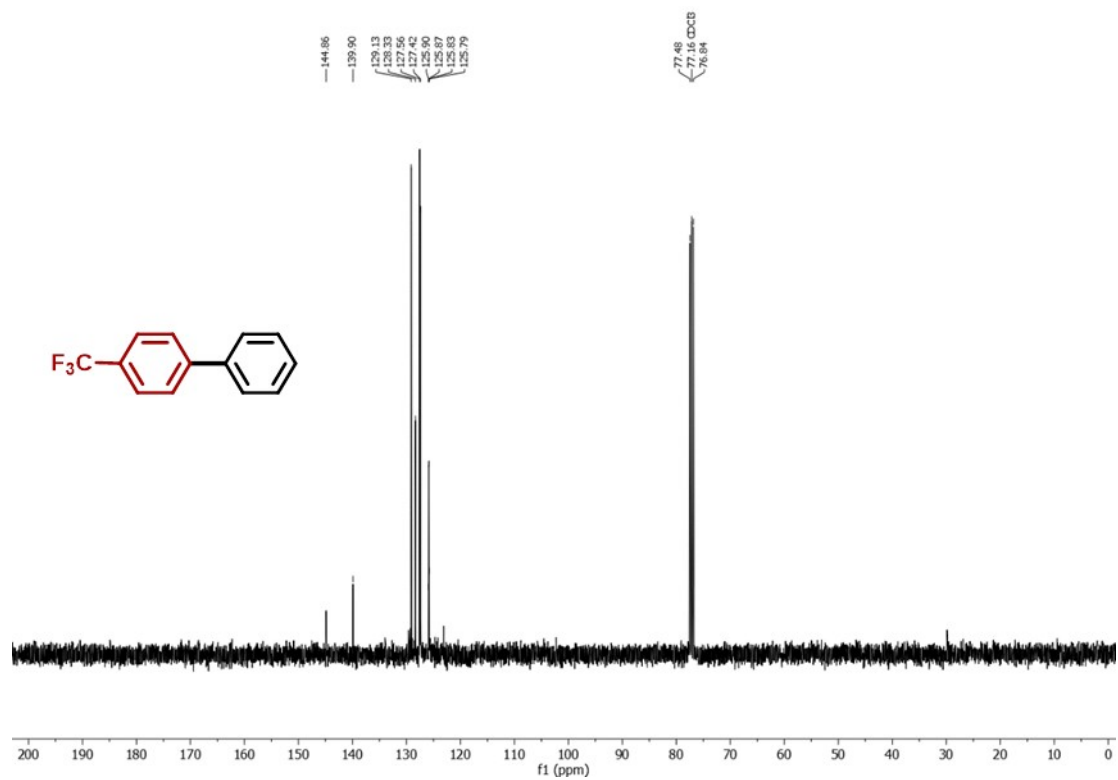


Figure S16. ¹³C NMR spectrum (100 MHz) of 2e in CDCl₃.

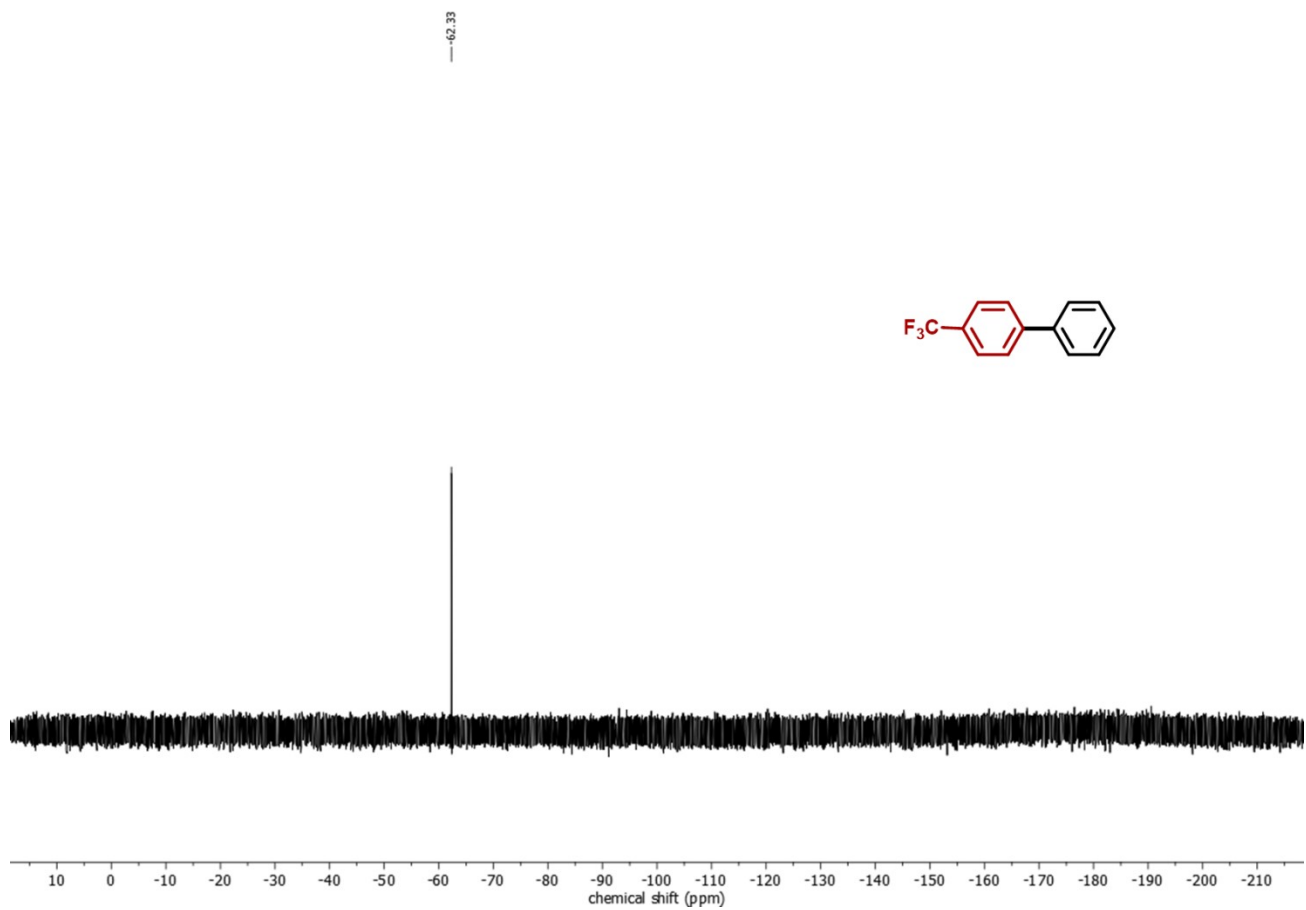


Figure S17. ^{19}F NMR spectrum (376 MHz) of **2e** in CDCl_3 .

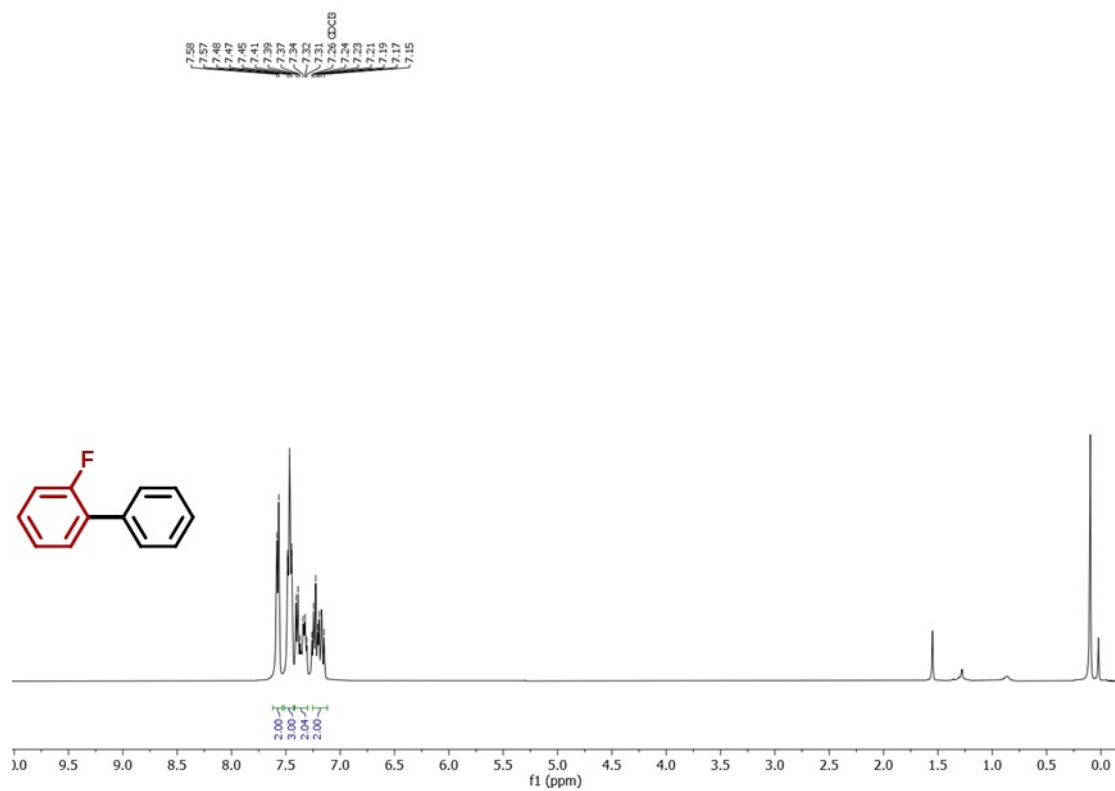


Figure S18. ^1H NMR spectrum (400 MHz) of **2f** in CDCl_3 .

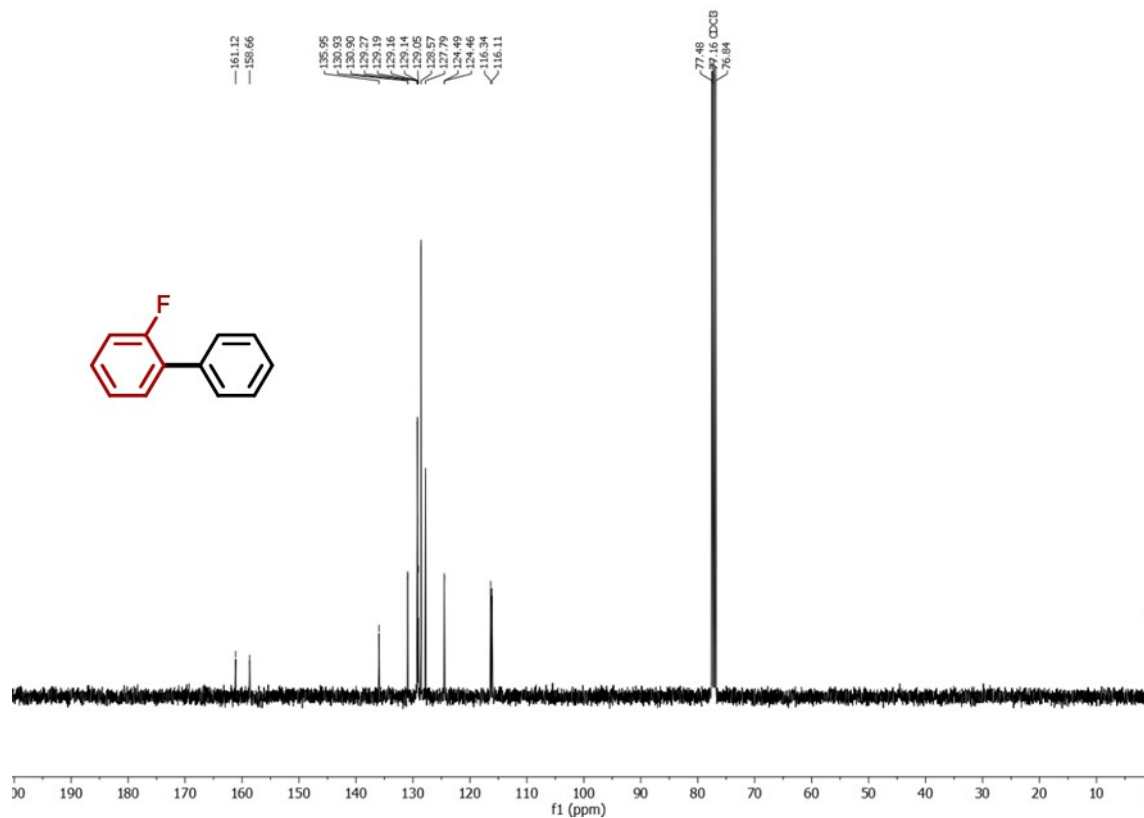


Figure S19. ^{13}C NMR spectrum (100 MHz) of **2f** in CDCl_3 .

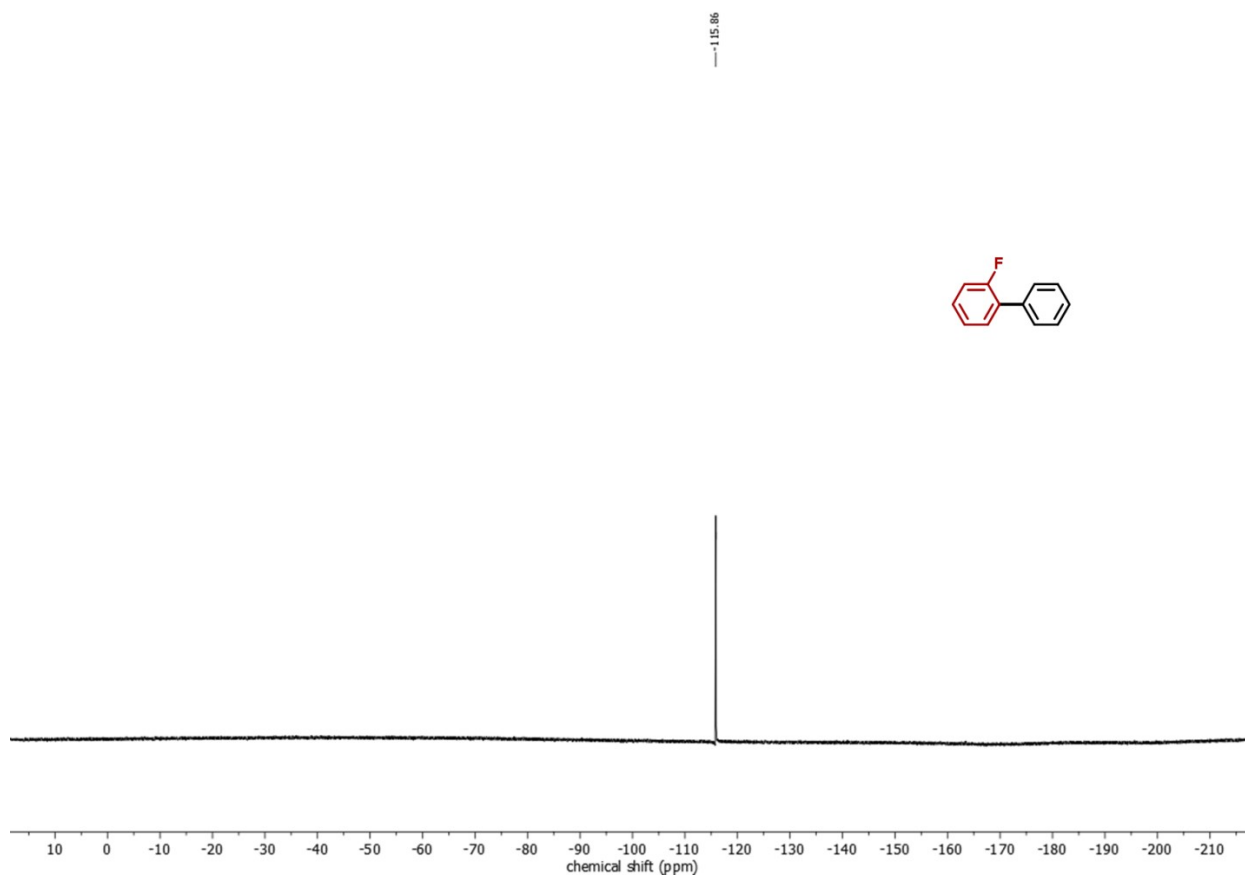
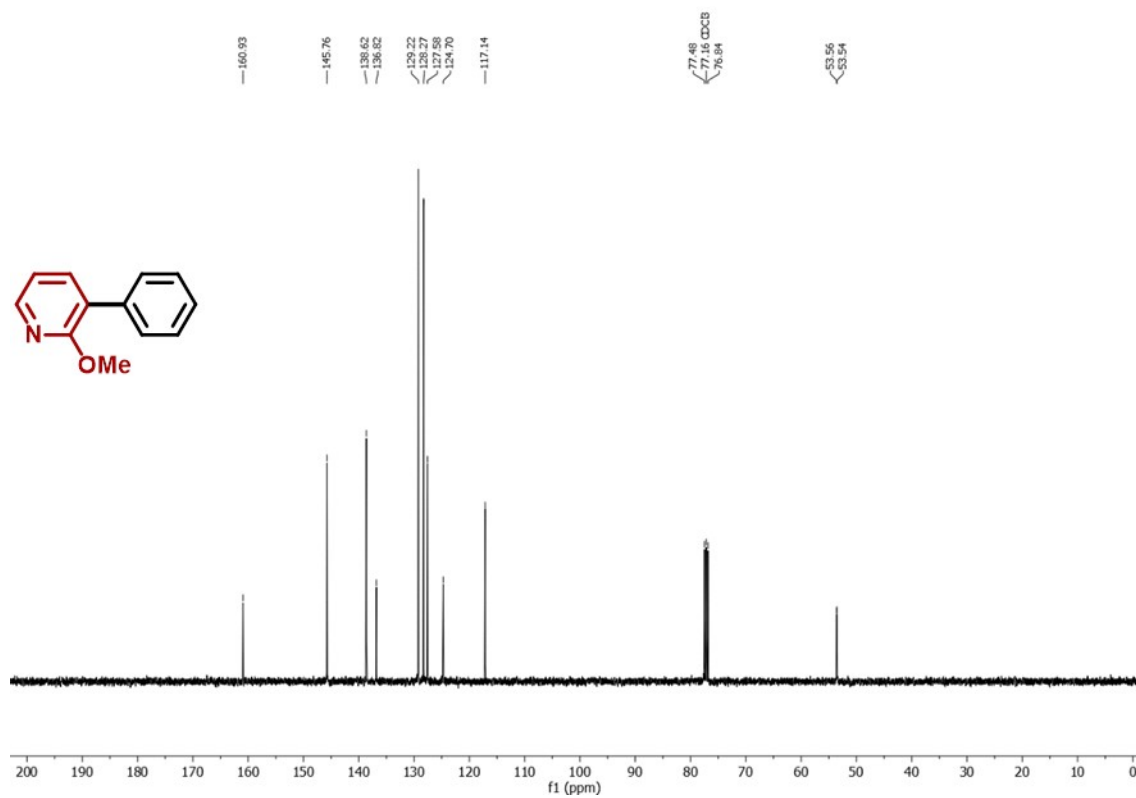
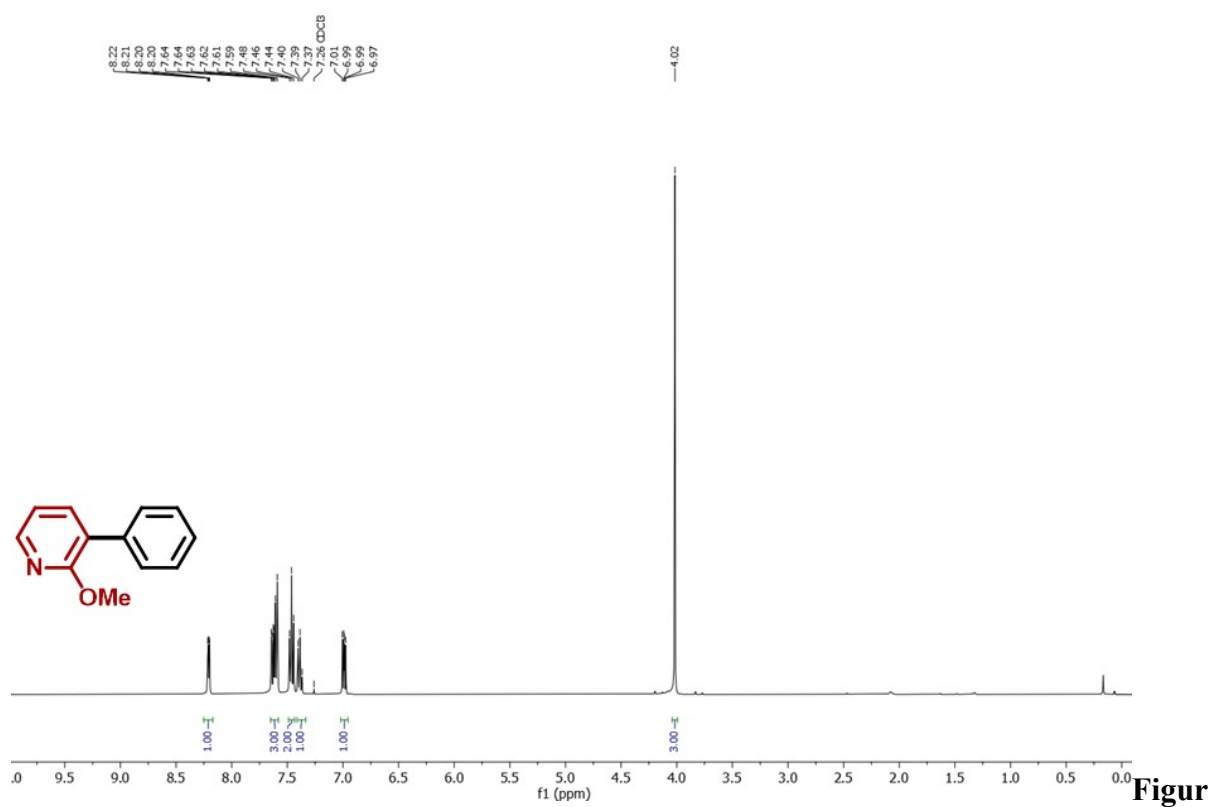


Figure S20. ^{19}F NMR spectrum (376 MHz) of **2f** in CDCl_3 .



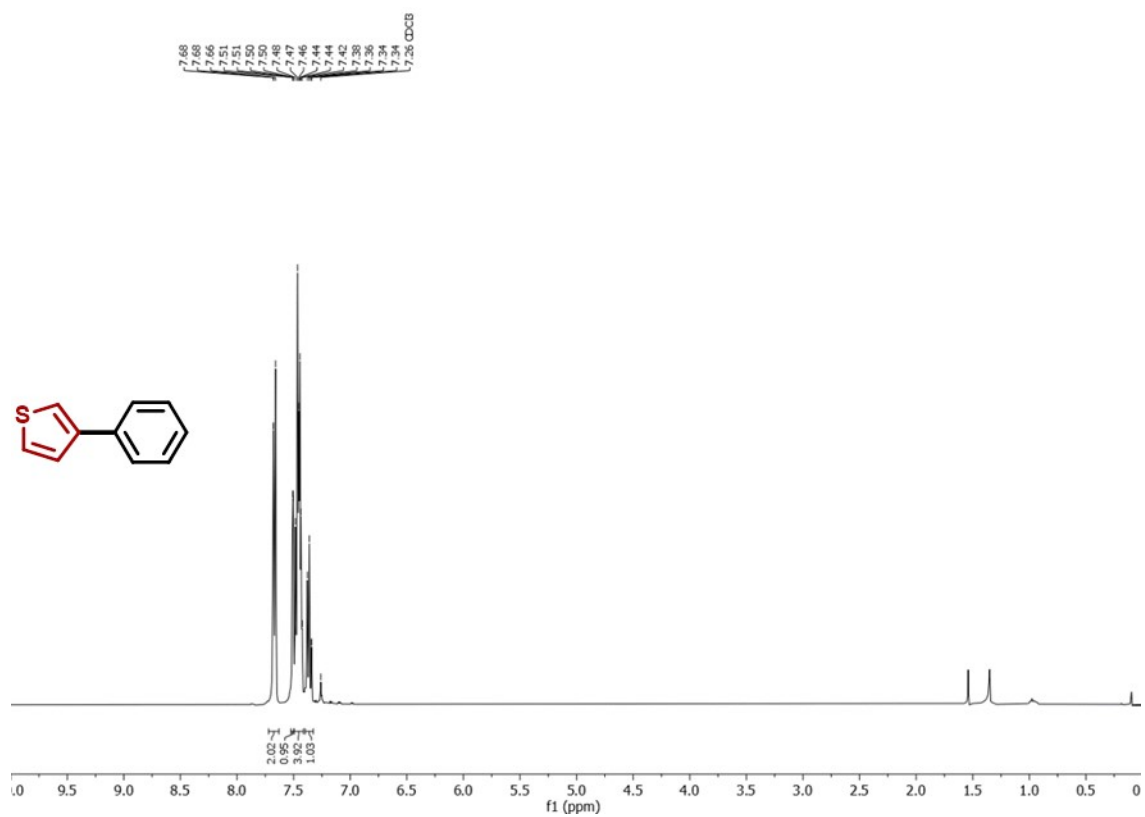


Figure S23. ¹H NMR spectrum (400 MHz) of 2h in CDCl₃.

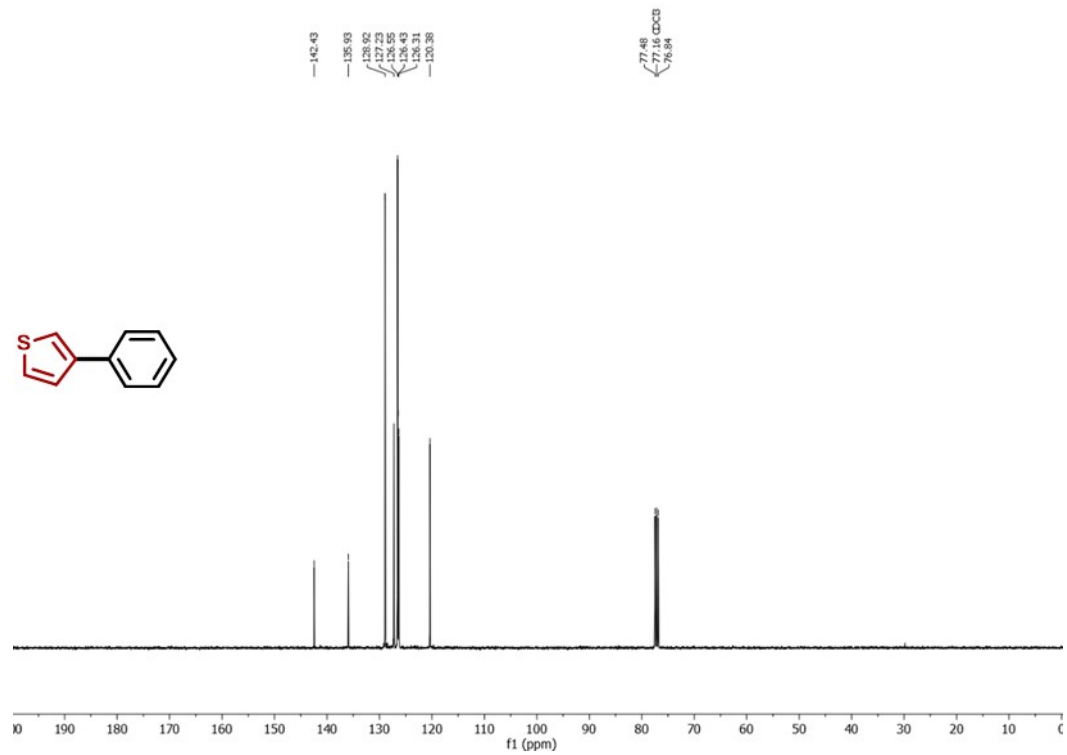


Figure S24. ¹³C NMR spectrum (100 MHz) of 2h in CDCl₃.

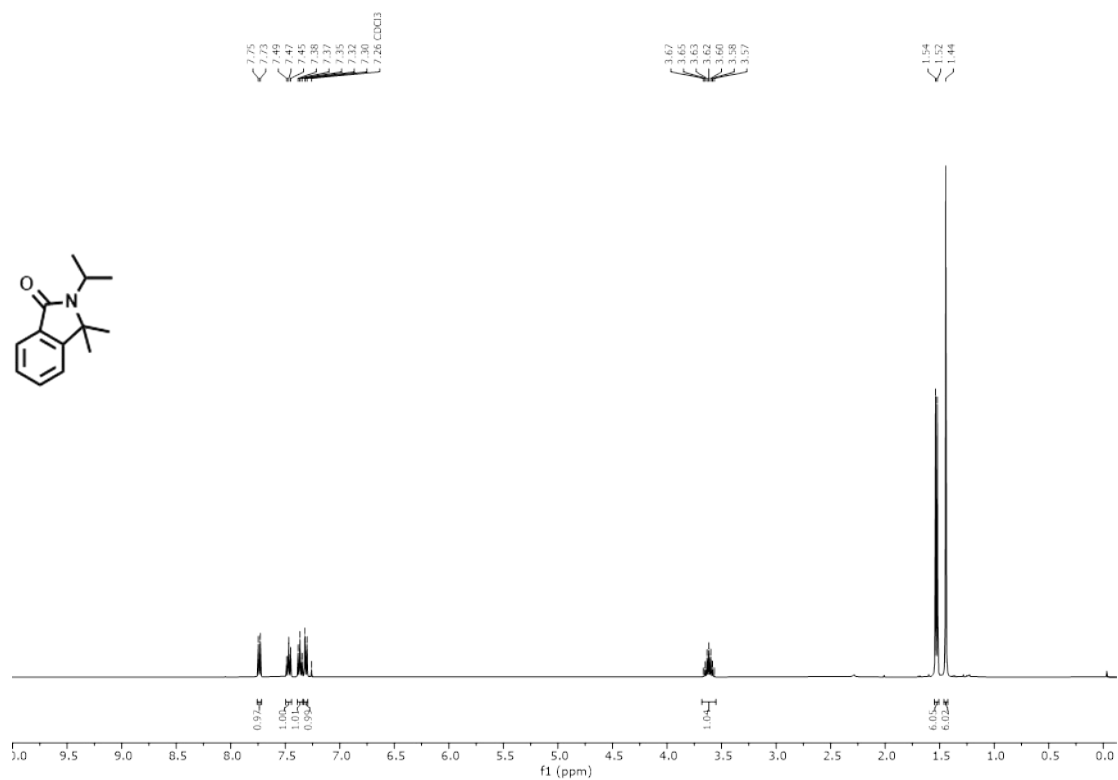


Figure S25. ¹H NMR spectrum (400 MHz) of 4a in CDCl₃.

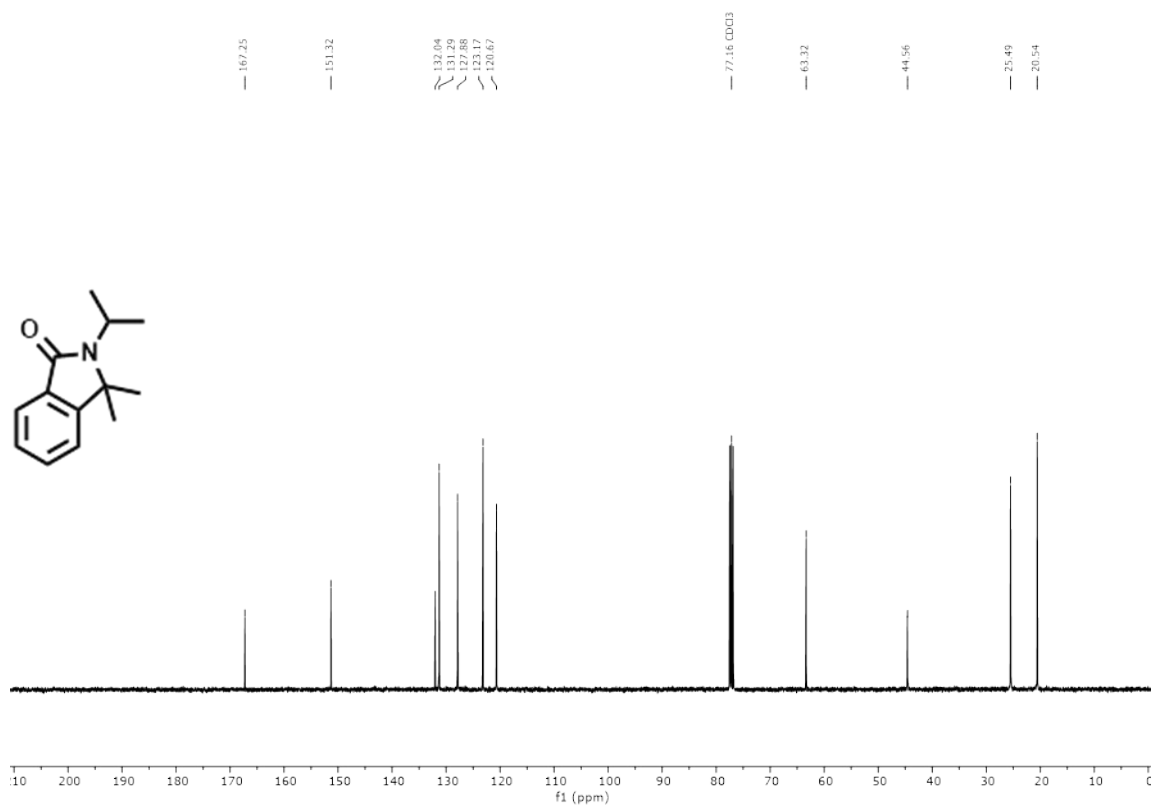


Figure S26. ¹³C NMR spectrum (100 MHz) of 4a in CDCl₃.

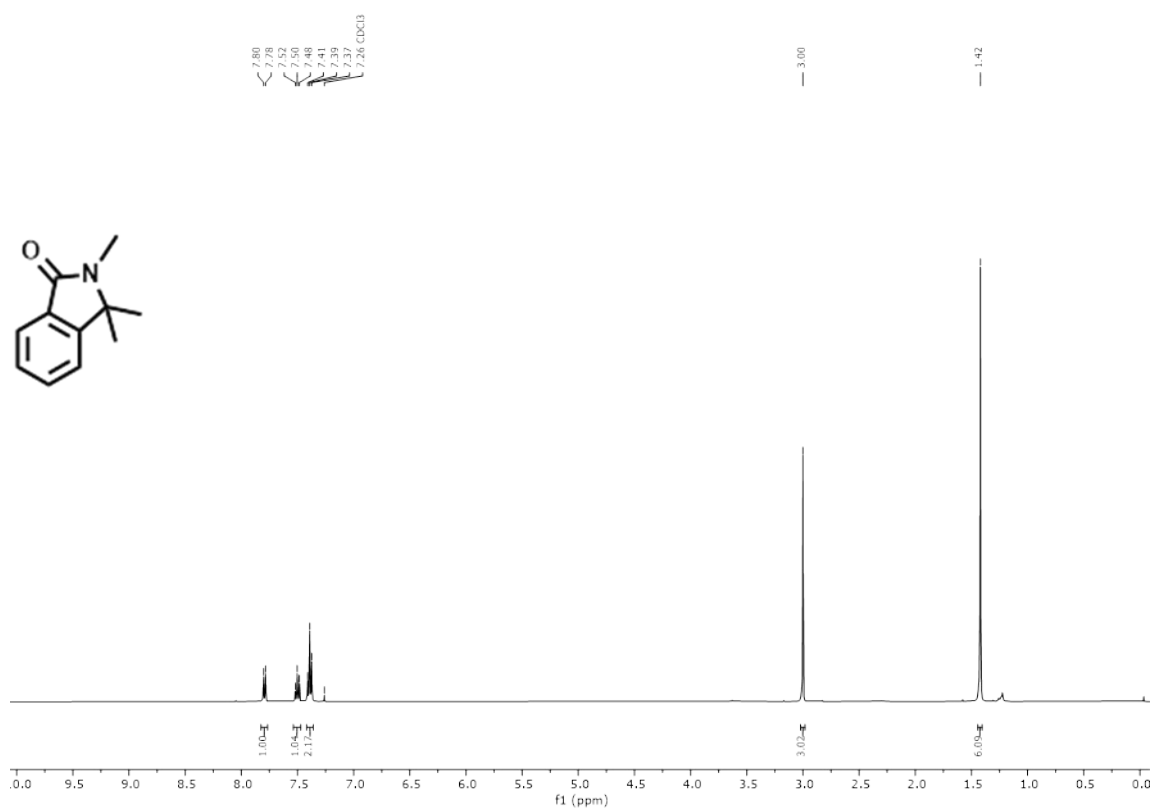


Figure S27. ¹H NMR spectrum (400 MHz) of **4b** in CDCl₃.

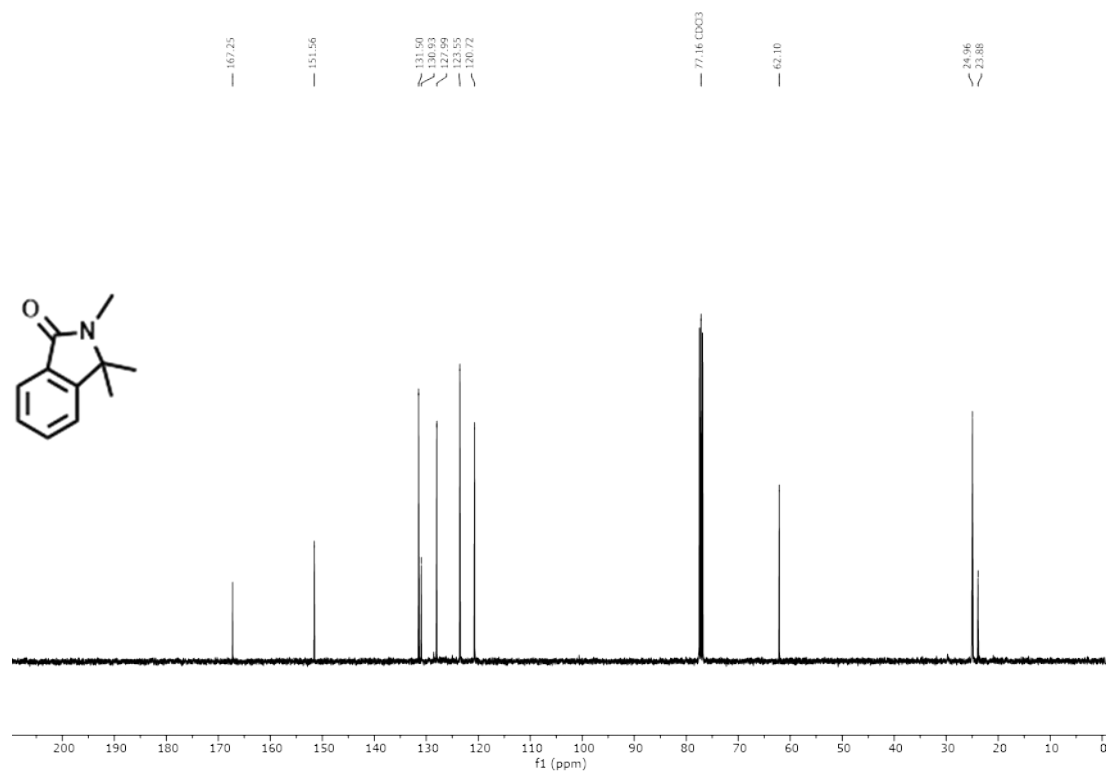


Figure S28. ¹³C NMR spectrum (100 MHz) of **4b** in CDCl₃.

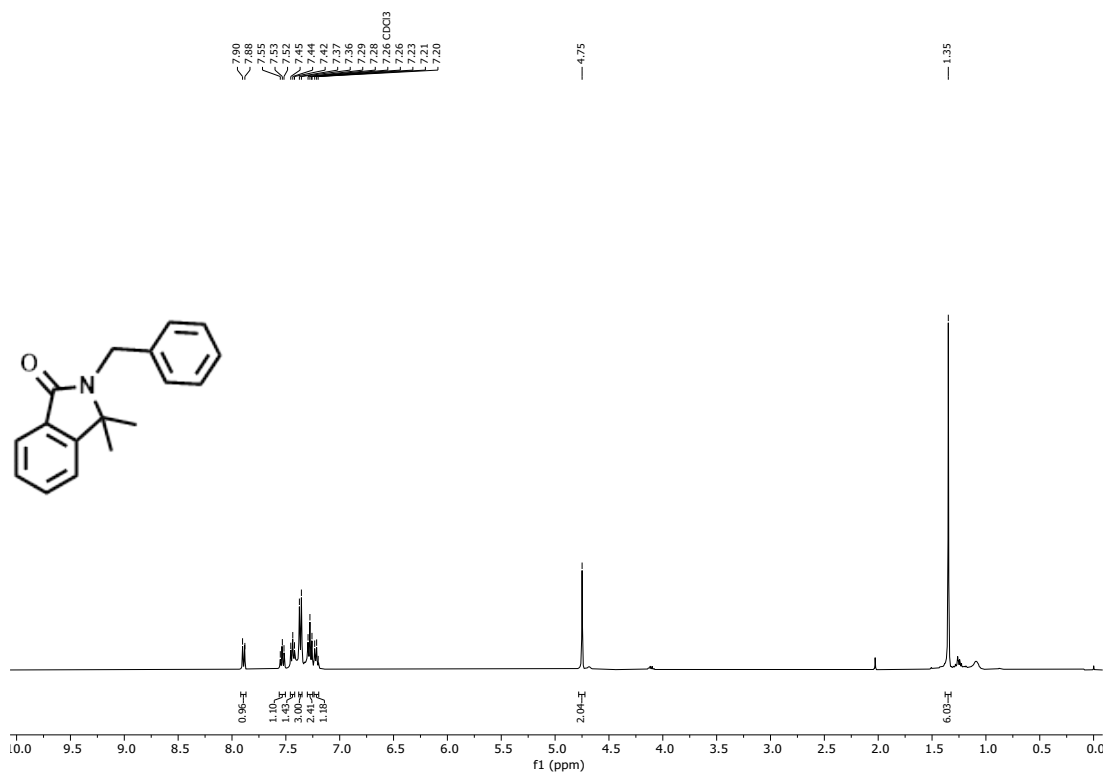


Figure S29. ¹H NMR spectrum (400 MHz) of 4c in CDCl₃.

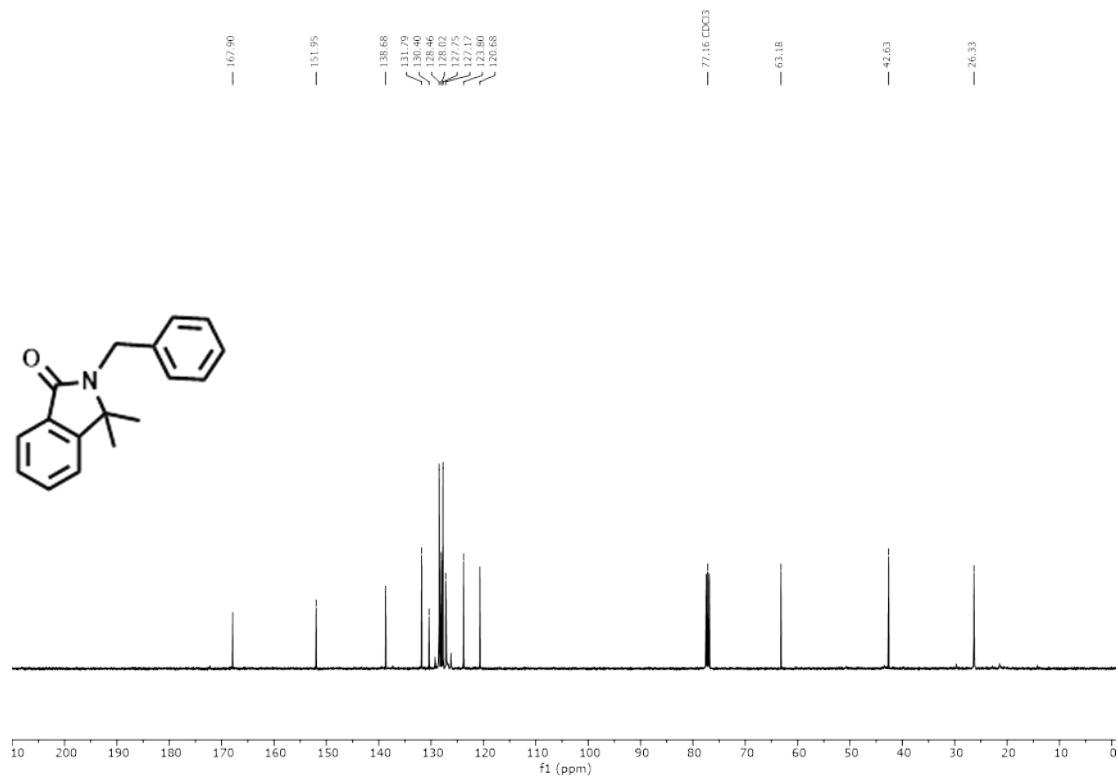


Figure S30. ¹³C NMR spectrum (100 MHz) of 4c in CDCl₃.

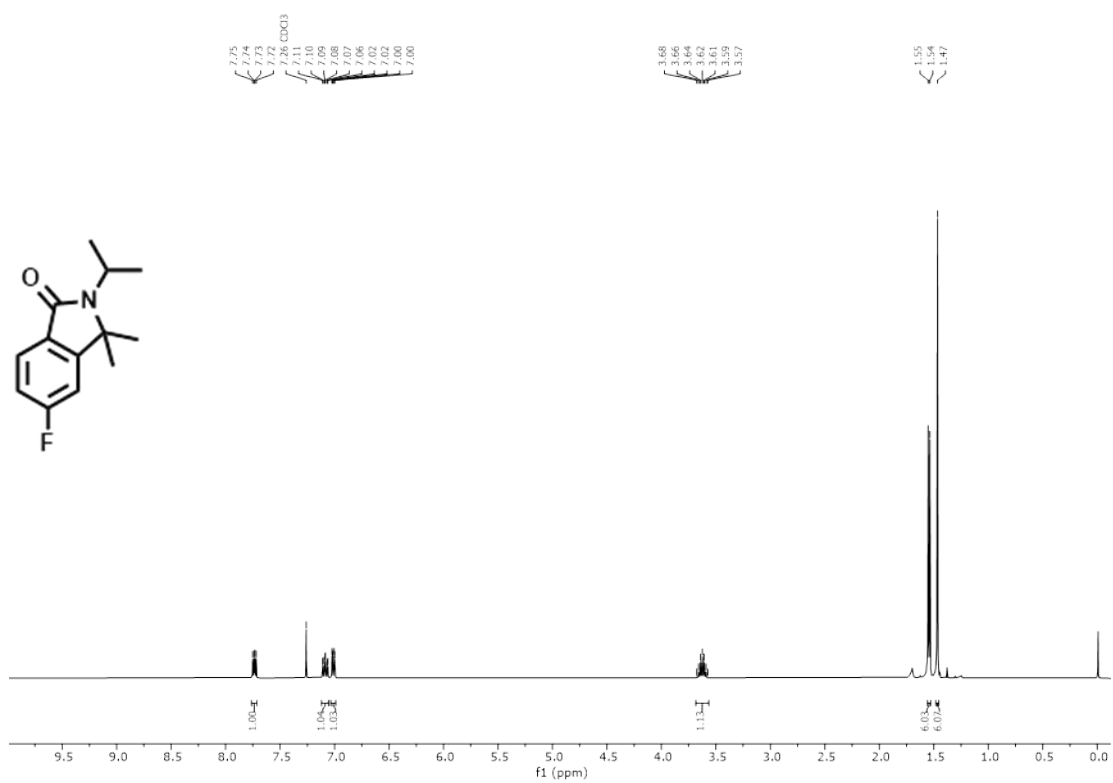


Figure S31. ¹H NMR spectrum (400 MHz) of 4d in CDCl₃

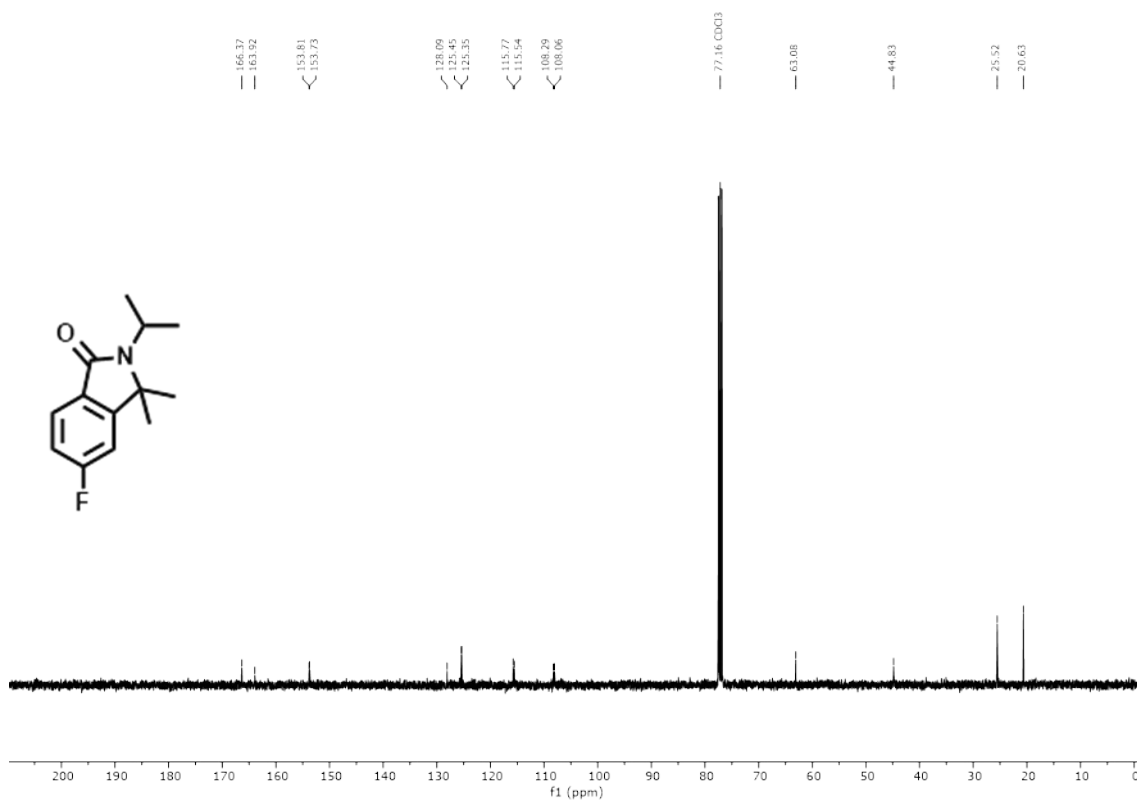


Figure S32. ¹³C NMR spectrum (100 MHz) of 4d in CDCl₃.



Figure S33. ^{19}F NMR spectrum (376 MHz) of **4d** in CDCl_3 .

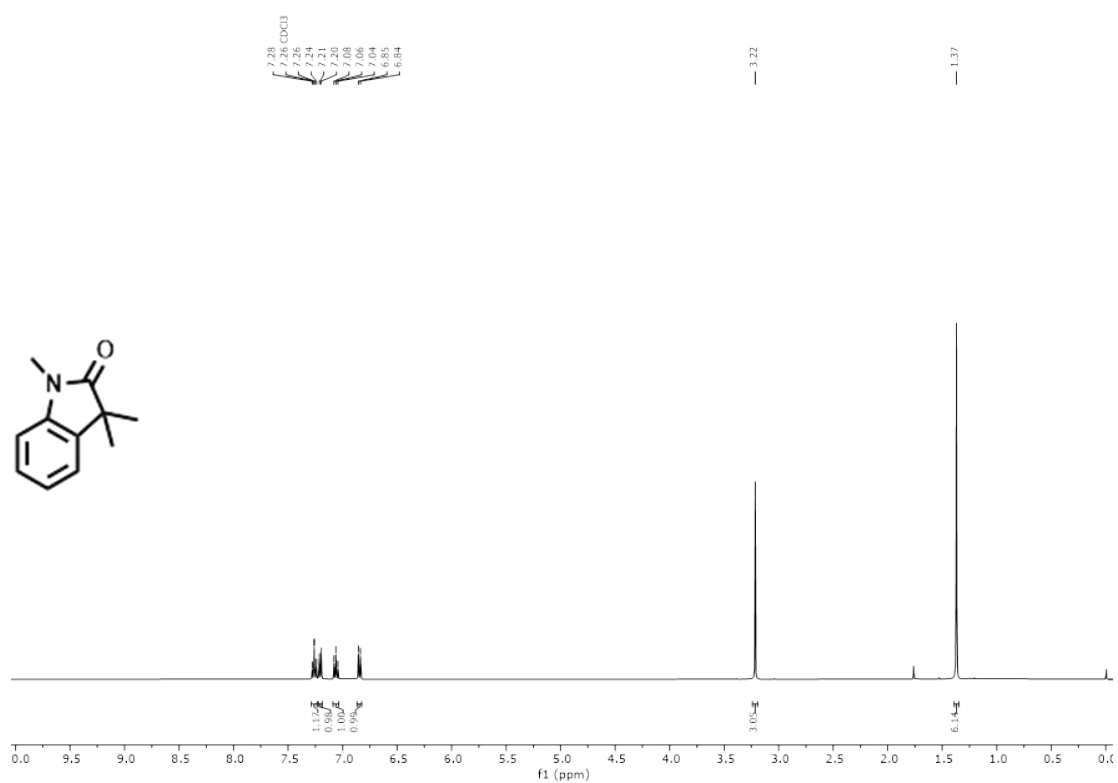


Figure S34. ^1H NMR spectrum (400 MHz) of **6a** in CDCl_3 .

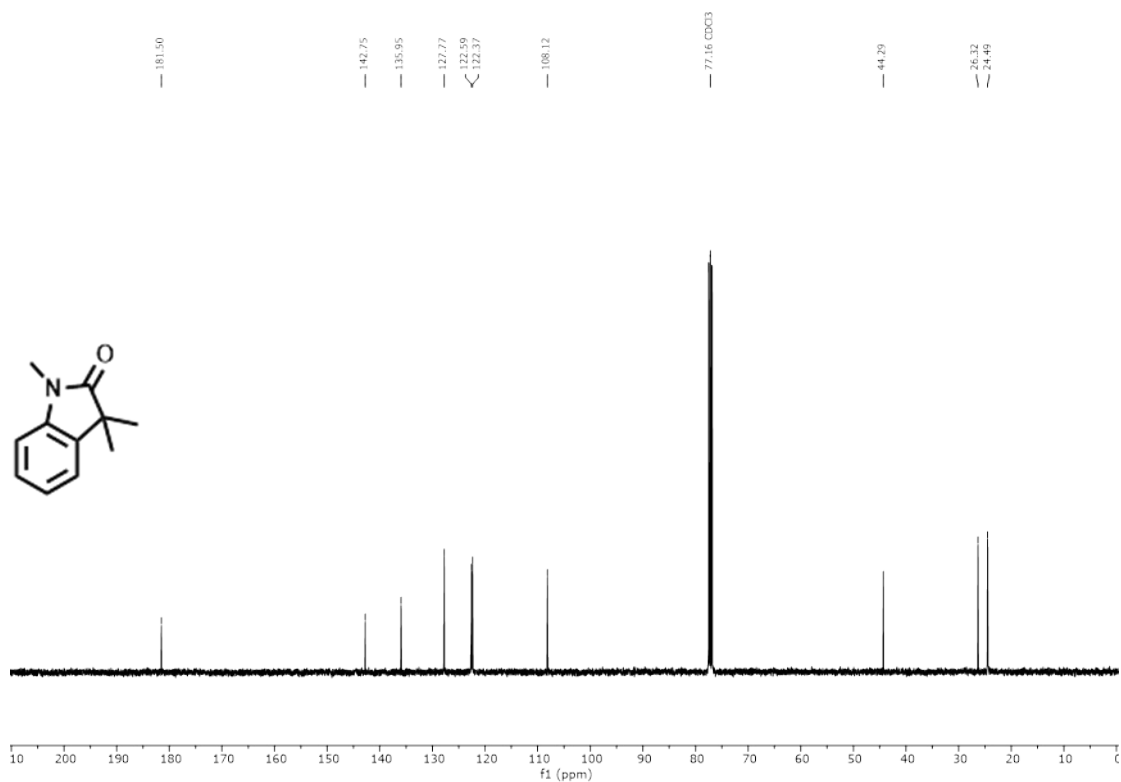


Figure S35. ^{13}C NMR spectrum (100 MHz) of **6a** in CDCl_3 .

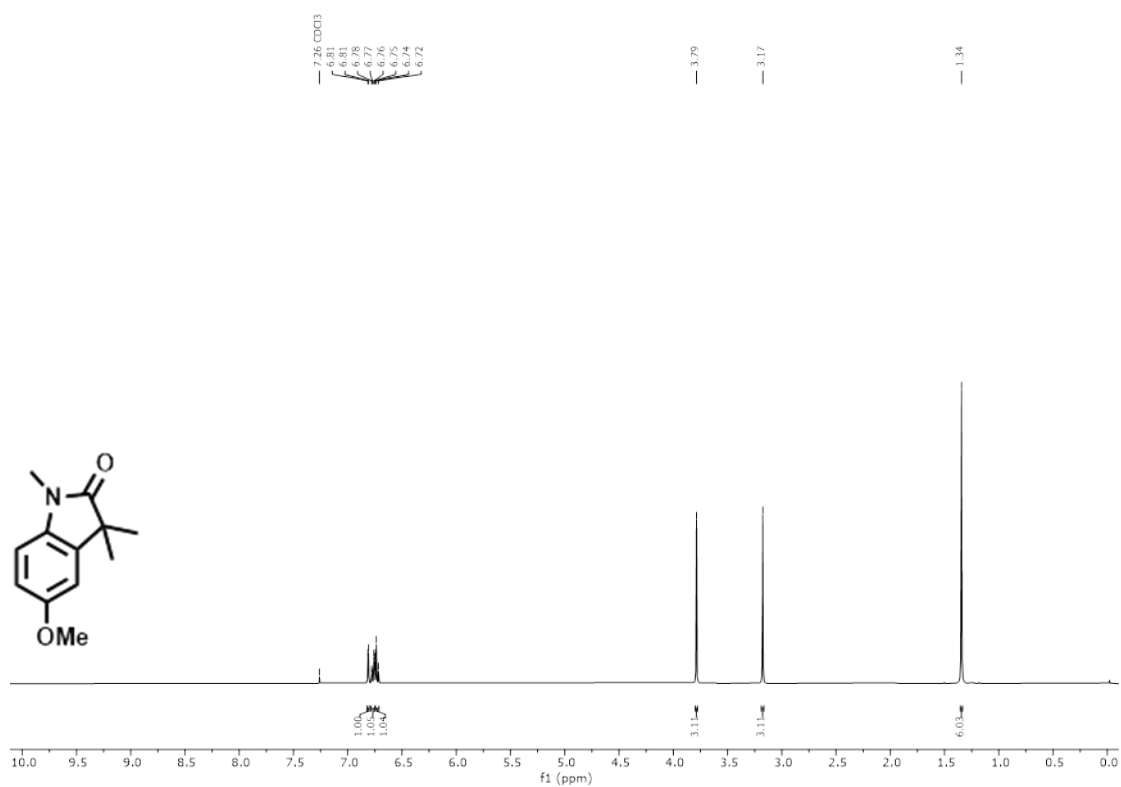


Figure S36. ^1H NMR spectrum (400 MHz) of **6b** in CDCl_3 .

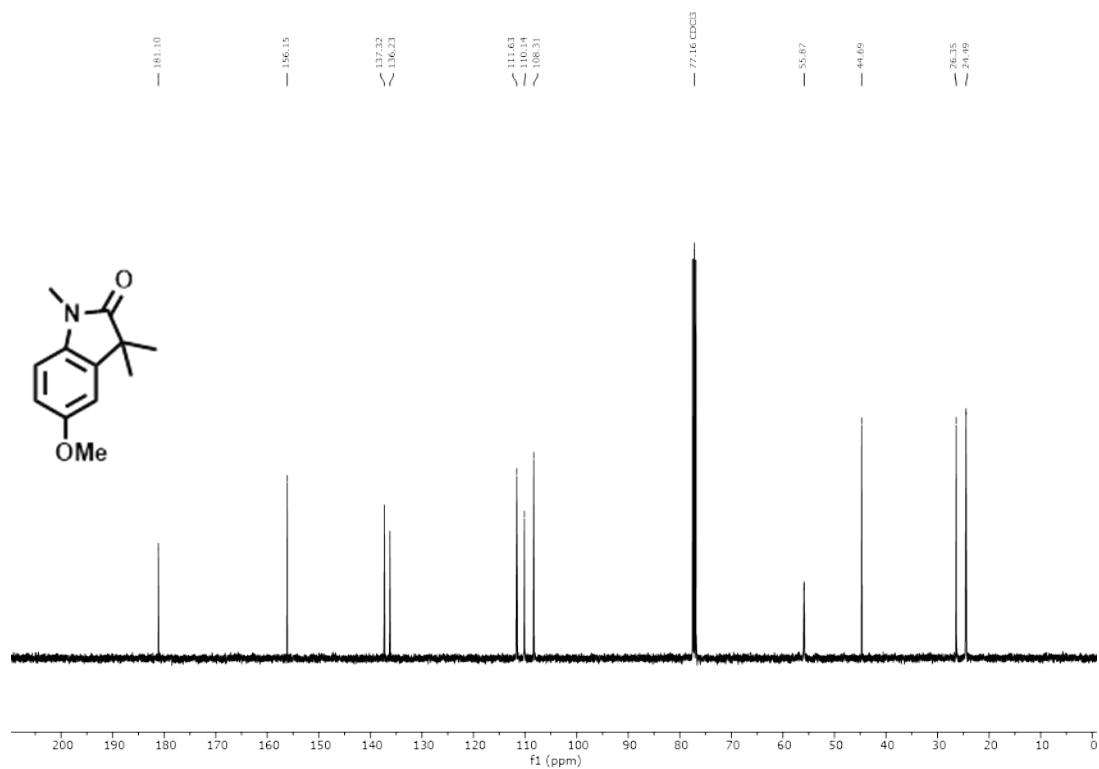


Figure S37. ^{13}C NMR spectrum (100 MHz) of **6b** in CDCl_3 .

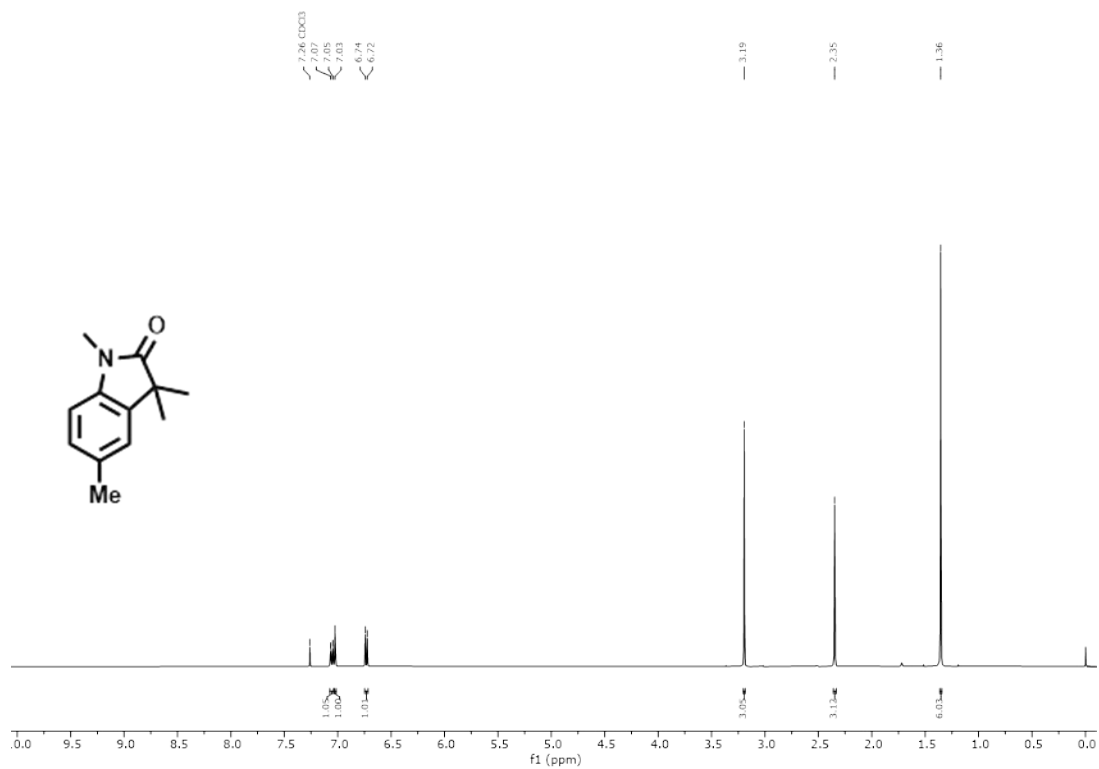


Figure S38. ^1H NMR spectrum (400 MHz) of **6c** in CDCl_3 .

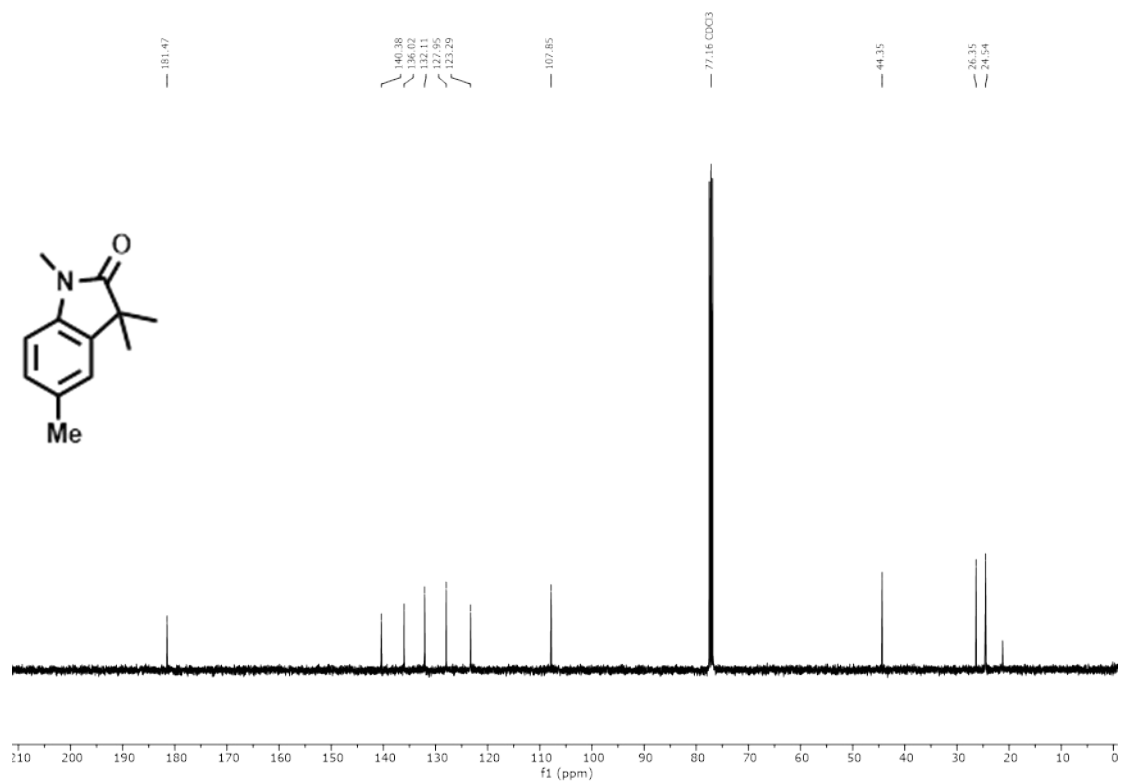


Figure S39. ^{13}C NMR spectrum (100 MHz) of **6c** in CDCl_3 .

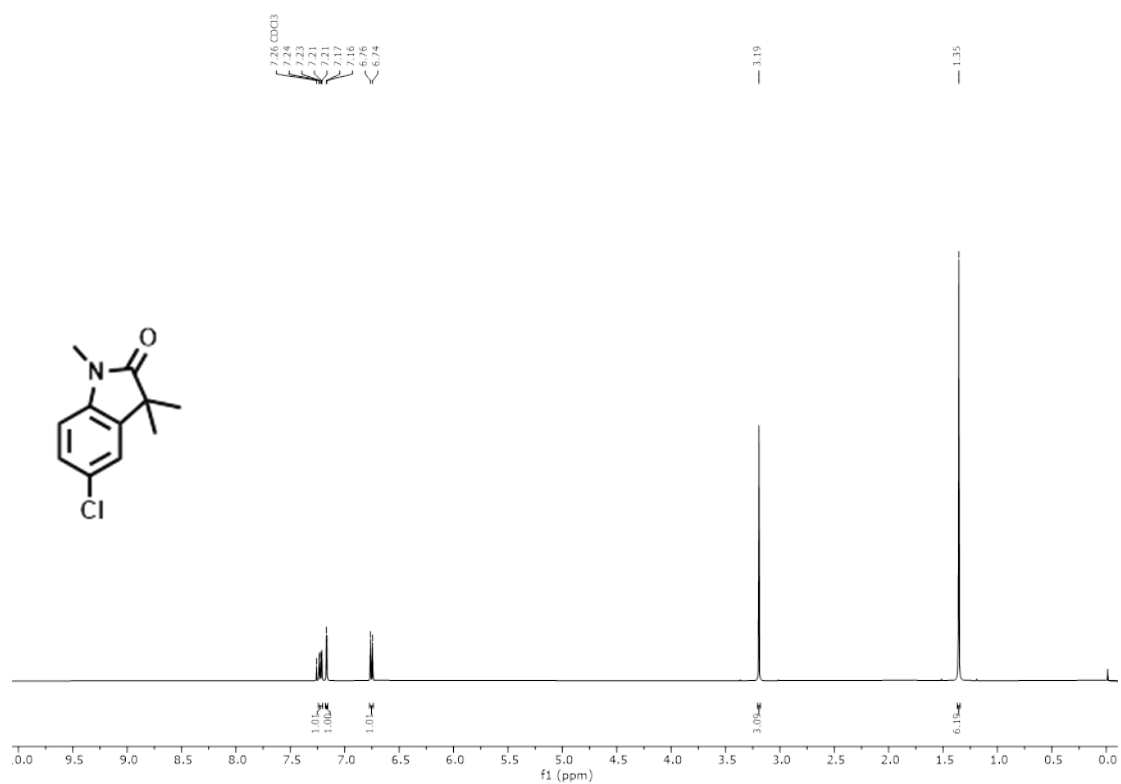


Figure S40. ^1H NMR spectrum (400 MHz) of **6d** in CDCl_3 .

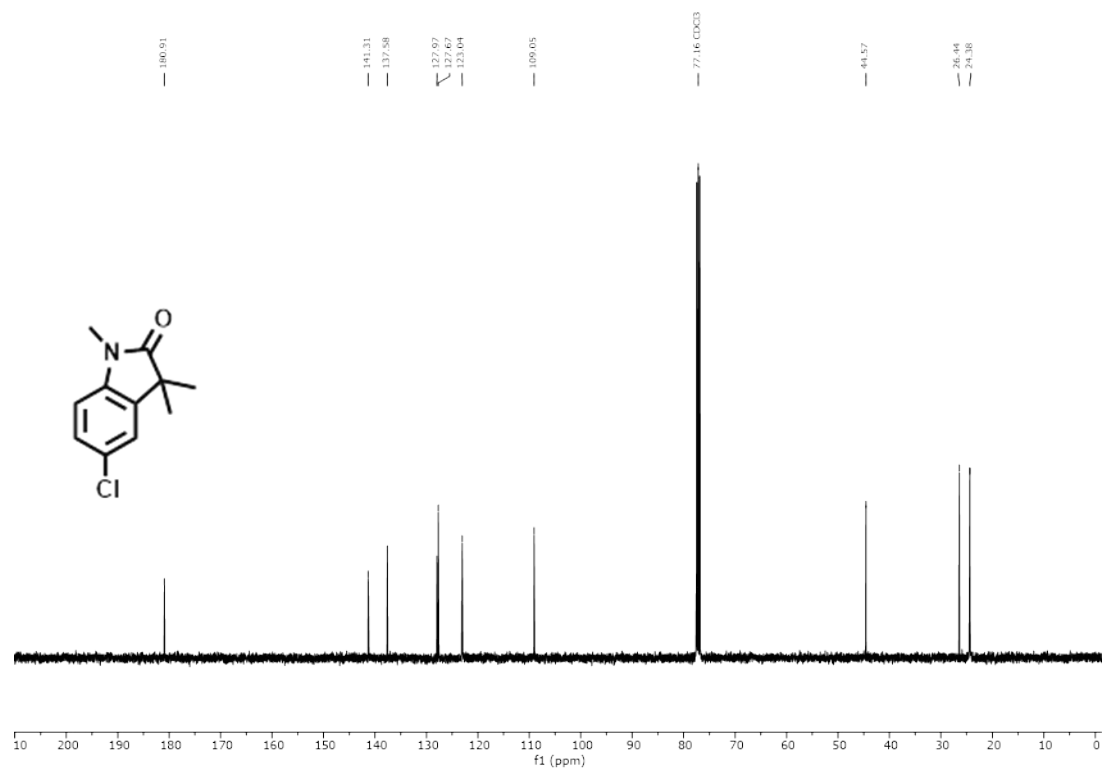


Figure S41. ^{13}C NMR spectrum (100 MHz) of **6d** in CDCl_3 .

10. Crystallographic data, bond length and bond angles of **7a** (CCDC no. 2285425).

Empirical formula	$\text{C}_{29}\text{H}_{43}\text{KN}_2\text{O}_7\text{S}$
Formula weight	602.84
Temperature/K	150.0(1)
Crystal system	Monoclinic
Space group	P 1 21/c 1
a/Å	10.8580(3)
b/Å	21.3088(6)
c/Å	13.4896(4)
$\alpha/^\circ$	90
$\beta/^\circ$	92.703(2)

$\gamma/^\circ$	90
Volume/ \AA^3	3117.63(15)
Z	4
$\rho_{\text{calc}}/\text{g/cm}^3$	1.284
μ/mm^{-1}	0.283
F(000)	1290.1
Crystal size/ mm^3	0.2 x 0.2 x 0.2
Radiation	Mo K α ($\lambda = 0.71073$)
2 Θ range for data collection/ $^\circ$	5.28 to 50
Index ranges	$-12 \leq h \leq 12, -25 \leq k \leq 25, -16 \leq l \leq 16$
Reflections collected	27651
Independent reflections	5474 [$R_{\text{int}} = 0.0371, R_{\text{sigma}} = 0.0575$]
Data/restraints/parameters	2854/0/203
Goodness-of-fit on F^2	1.050
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0459, wR_2 = 0.1307$

Table 4: Bond Distances (\AA) for **7a**

Atom	Atom	Length/ \AA	Atom	Atom	Length/ \AA
K1	S1	3.2310(8)	N1	C7	1.301(3)
K1	O1	2.7991(17)	N1	C8	1.396(3)
K1	O2	2.7804(17)	N2	C6	1.402(3)
K1	O3	2.9022(16)	N2	C7	1.392(3)
K1	O4	2.7382(17)	C1	C2	1.380(3)
K1	O5	2.8792(16)	C1	C6	1.400(3)
K1	O6	2.7214(16)	C2	C3	1.387(4)
K1	O7	2.8923(18)	C3	C4	1.373(4)
K1	C19	3.499(3)	C4	C5	1.391(3)
K1	C23	3.495(3)	C5	C6	1.402(3)
K1	C24	3.492(3)	C8	C9	1.398(4)
S1	C7	1.747(2)	C8	C13	1.393(3)
O1	C23	1.427(3)	C9	C10	1.389(4)

O1	C24	1.431(3)	C10	C11	1.377(4)
O2	C21	1.426(3)	C11	C12	1.391(4)
O2	C22	1.422(3)	C12	C13	1.381(4)
O3	C19	1.424(3)	C14	C15	1.497(4)
O3	C20	1.430(3)	C16	C17	1.504(4)
O4	C17	1.420(3)	C18	C19	1.495(4)
O4	C18	1.420(3)	C20	C21	1.495(3)
O5	C15	1.434(3)	C22	C23	1.499(4)
O5	C16	1.427(3)	C24	C25	1.501(4)
O6	C14	1.422(3)	C26	C27	1.481(4)
O6	C25	1.423(3)	C27	C28	1.461(5)
O7	C26	1.416(3)	C28	C29	1.496(5)
O7	C29	1.430(3)			

Table 5: Bond Angles (Degrees) for **7a**

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O1	K1	S1	87.18(4)	C22	O2	K1	115.44(13)
O2	K1	S1	95.39(4)	C22	O2	C21	112.13(19)
O2	K1	O1	61.51(5)	C19	O3	K1	102.52(13)
O3	K1	S1	111.62(3)	C20	O3	K1	113.46(13)
O3	K1	O1	119.24(5)	C20	O3	C19	112.65(18)
O3	K1	O2	59.62(5)	C17	O4	K1	119.47(14)
O4	K1	S1	97.74(4)	C18	O4	K1	120.42(14)
O4	K1	O1	175.06(5)	C18	O4	C17	112.69(19)
O4	K1	O2	118.13(5)	C15	O5	K1	110.88(13)
O4	K1	O3	59.31(5)	C16	O5	K1	110.61(14)
O5	K1	S1	103.34(3)	C16	O5	C15	110.20(18)
O5	K1	O1	118.22(5)	C14	O6	K1	120.55(13)
O5	K1	O2	161.26(5)	C25	O6	K1	118.76(14)
O5	K1	O3	112.57(5)	C25	O6	C14	113.08(18)
O5	K1	O4	60.32(5)	C26	O7	K1	108.77(15)
O6	K1	S1	83.56(4)	C29	O7	K1	116.67(16)

O6	K1	O1	61.01(5)	C29	O7	C26	108.4(2)
O6	K1	O2	122.50(5)	C8	N1	C7	121.35(19)
O6	K1	O3	164.74(5)	C7	N2	C6	130.49(18)
O6	K1	O4	118.95(5)	C6	C1	C2	121.4(2)
O6	K1	O5	60.15(5)	C3	C2	C1	120.4(2)
O7	K1	S1	164.50(4)	C4	C3	C2	118.9(2)
O7	K1	O1	77.37(5)	C5	C4	C3	121.8(2)
O7	K1	O2	76.30(5)	C6	C5	C4	119.8(2)
O7	K1	O3	75.75(5)	C1	C6	N2	117.42(19)
O7	K1	O4	97.72(5)	C5	C6	N2	124.7(2)
O7	K1	O5	85.31(5)	C5	C6	C1	117.8(2)
O7	K1	O6	89.90(5)	N1	C7	S1	127.69(18)
C19	K1	S1	94.99(5)	N2	C7	S1	113.89(15)
C19	K1	O1	137.48(6)	N2	C7	N1	118.39(19)
C19	K1	O2	76.03(6)	C9	C8	N1	119.0(2)
C19	K1	O3	23.41(5)	C13	C8	N1	122.8(2)
C19	K1	O4	42.79(6)	C13	C8	C9	117.8(2)
C19	K1	O5	102.59(6)	C10	C9	C8	120.6(3)
C19	K1	O6	161.47(6)	C11	C10	C9	121.1(3)
C19	K1	O7	95.61(6)	C12	C11	C10	118.6(2)
C23	K1	S1	79.18(6)	C13	C12	C11	120.7(3)
C23	K1	O1	22.97(6)	C12	C13	C8	121.2(2)
C23	K1	O2	42.37(6)	C15	C14	O6	108.32(19)
C23	K1	O3	101.99(6)	C14	C15	O5	110.43(19)
C23	K1	O4	158.78(6)	C17	C16	O5	109.9(2)
C23	K1	O5	140.90(6)	C16	C17	O4	109.0(2)
C23	K1	O6	81.79(6)	C19	C18	O4	109.7(2)
C23	K1	O7	86.01(7)	O3	C19	K1	54.07(11)
C23	K1	C19	116.18(7)	C18	C19	K1	84.38(14)
C24	K1	S1	73.35(5)	C18	C19	O3	108.6(2)
C24	K1	O1	23.11(6)	C21	C20	O3	109.29(18)
C24	K1	O2	81.90(6)	C20	C21	O2	107.1(2)
C24	K1	O3	141.30(6)	C23	C22	O2	108.0(2)
C24	K1	O4	159.20(6)	O1	C23	K1	49.96(11)

C24	K1	O5	102.73(6)	C22	C23	K1	82.80(14)
C24	K1	O6	42.59(6)	C22	C23	O1	108.5(2)
C24	K1	O7	92.35(6)	O1	C24	K1	50.15(11)
C24	K1	C19	153.98(7)	C25	C24	K1	82.96(14)
C24	K1	C23	39.74(6)	C25	C24	O1	108.2(2)
C7	S1	K1	90.42(7)	C24	C25	O6	108.1(2)
C23	O1	K1	107.08(14)	C27	C26	O7	107.5(3)
C24	O1	K1	106.75(14)	C28	C27	C26	107.0(3)
C24	O1	C23	112.38(19)	C29	C28	C27	105.9(3)
C21	O2	K1	113.58(12)	C28	C29	O7	106.2(2)

11. References

1. J. Ahmed, S. Chakraborty, S. P. Jose, and S. K. Mandal, Integrating Organic Lewis Acid and Redox Catalysis: The Phenalenyl Cation in Dual Role, *J. Am. Chem. Soc.* 2018, **140**, 8330–8339.
2. I. Fujii, K. Semba and Y. Nakao, The Kumada–Tamao–Corriu Coupling Reaction Catalyzed by Rhodium–Aluminum Bimetallic Complexes, *Org. Lett.* 2022, **24**, 3075-3079.
3. M. J. West and A. J. B. Watson, Ni vs. Pd in Suzuki–Miyaura sp^2 – sp^2 cross-coupling: a head-to-head study in a comparable precatalyst/ligand system, *Org. Biomol. Chem.*, 2019, **17**, 5055-5059.
4. W. Liu, H. Cao, H. Zhang, H. Zhang, K. H. Chung, C. He, H. Wang, F. Y. Kwong, and A. Lei, Organocatalysis in Cross-Coupling: DMEDA-Catalyzed Direct C–H Arylation of Unactivated Benzene, *J. Am. Chem. Soc.* 2010, **132**, 16737-16740.
5. C. Dunst, and P. Knochel, Selective Mg Insertion into Substituted Mono- and Dichloro Arenes in the Presence of LiCl: A New Preparation of Boscalid, *Synlett*, 2011, **14**, 2064-2068.
6. K. Chen, W. Chen, X. Yi, W. Chen, M. Liu and H. Wu, Sterically hindered N-heterocyclic carbene/palladium(II) catalyzed Suzuki–Miyaura coupling of nitrobenzenes, *Chem. Commun.*, 2019, **55**, 9287-9290.

7. L. Liu, K. Zhao, W. Li, M. Liu, Y. Chen, Y. Dong, Synthesis of heterobiaryls via Suzuki-Miyaura coupling reaction of potassium aryltrifluoroborates with heteroaryl halides in aqueous systems, *Appl. Organometal Chem.* 2019, **33**, e4831.
8. M. C. Cecotka, J. Predygier, S. Crespi, J. Szczepanik, M. Giedyk, Photocatalysis in Aqueous Micellar Media Enables Divergent C–H Arylation and N-Dealkylation of Benzamides, *ACS Catal.* 2022, **12**, 3543–3549.
9. B. S. Bhakuni, A. Yadav, S. Kumar, S. Patel, S. Sharma, S. Kumar, KO(t)Bu-mediated synthesis of dimethylisoindolin-1-ones and dimethyl-5-phenylisoindolin-1-ones: selective C–C coupling of an unreactive tertiary sp³ C–H bond, *J. Org. Chem.* 2014, **79**, 2944–2954.
10. W. C. Wertjes, L. C. Wolfe, P. J. Waller, D. Kalyani, Nickel or Phenanthroline Mediated Intramolecular Arylation of sp³ C–H Bonds Using Aryl Halides, *Org. Lett.* 2013, **15**, 5986–5989.
11. S. Wu, Q. Zhao, C. Wu, C. Wang, H. Lei, Transition-metal-free oxindole synthesis: quinone–K₂CO₃ catalyzed intramolecular radical cyclization, *Org. Chem. Front.*, 2022, **9**, 2593–2599.
12. W. Zhang, Y. Yue, D. Yu, L. Song, Y. Y. Xu, Y. J. Tian, Y. J. Guo, 1,10-phenanthroline-catalyzed tandem reaction of 2-iodoanilines with isothiocyanates in water, *Adv. Synth. Catal.* 2012, **354**, 2283 – 2287