Supporting Information

Electrochemical Assembly of Isoxazoles *via* Four-Components Domino Reaction

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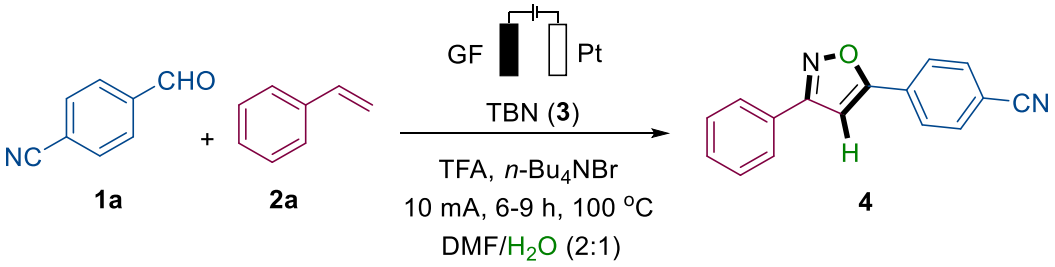
1. General Remarks

Catalytic reactions were performed under natural ambient conditions. Dimethylformamide and water were distilled prior to use. The substrates were purchased directly from commercial suppliers, and were used without further purification. The yields were determined based on aldehydes. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Mercury VX 300 or Bruker Avance III 400 or Bruker- Avance 500 or Agilent VNMRS-600 with tetramethylsilane as an internal reference. Chemical shifts (δ) and coupling constants (*J*) were expressed in ppm and Hz, respectively. IR spectra were recorded on a PerkinElmer Spectrum 100 Optica FT-IR. EI-MS was recorded on AB SCIEX Triple Quad^{TM} 3500. HR-MS was recorded on a Xevo G2-XS QTOF/MS detector. GC-MS data were measured by Bruker GC-MS 456-Scion. Note: for the CF_3COOH/Electro-Mediated multicomponent reaction, the byproduct benzonitrile cannot be well avoided, the yield is less than 20% under optimal conditions.

2. Optimization of the reaction conditions

Table S1. Preliminary Optimization of Three-components Reaction



1a 2a 4

Entry	Deviation from standard conditions	Yield[%][b]
1	none	62
2	CH_3CN/*tert*-Butanol/HFIP/dioxane instead of DMF	21/0/0/0
3	$TBAPF_6$/$TBAClO_4$/TBAOAc/LiBr instead of TBABr	25/38/37/61
4	AcOH/1-AdOH/MesCOOH/TsOH instead of TFA	40/42/55/52
5	no current/8 mA/5 mA	8/56/35
6	0.1 mol/L of **1a**/0.5 mol/L of **1a**	58/56
7	2.0 equiv **2a**/5.0 equiv **2a**	43/59
8	DMF:H_2O (v/v=1:1)/(v/v=4:1)	55/25
9	t = 4 h/10 h	38/61
10	$FeCl_3$/$Co(OAc)_2$/$MnBr(Co)_5$	56/18/24
11	Pt(+) I Pt(-) / Pt(+) I GF(-)	62/54

[a] Reaction conditions: **1** (0.75 mmol), **2** (2.25 mmol), **3** (2.25 mmol), *n*-Bu_4NBr (0.75 mmol), TFA (1.50 mmol), solvent (3.0 mL), 100 °C, 6-9 h, constant current electrolysis (CCE) at 10 mA, GF electrodes (10 mm ×10 mm × 6 mm) , Pt electrodes (10 mm ×10 mm × 0.25 mm).
[b] Yield of isolated product. TFA = trifluoroacetic acid. by-product **5**, benzonitrile.

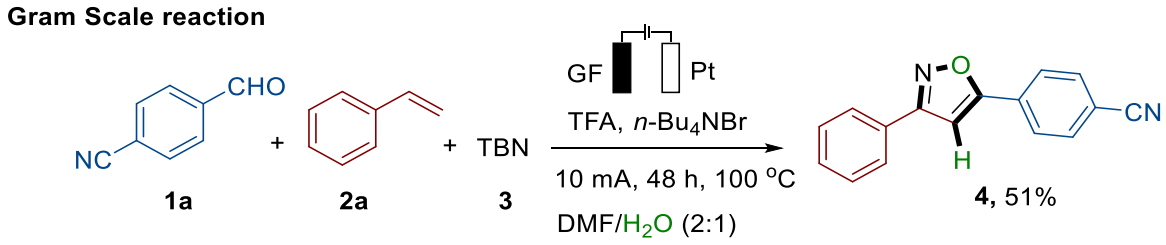
3. General Procedure for the Synthesis of Substituted Isoxazoles

3.1 Standard reaction

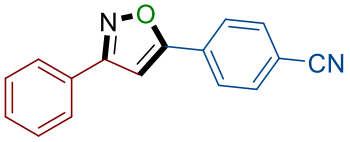
In an undivided cell setup using a graphite felt (GF) anode and a platinum plate (Pt) cathode, aldehyde **1** (0.75 mmol), alkene **2** (2.25 mmol, 3.0 equiv), TBN **3** (2.25 mmol, 3.0 equiv), TFA (1.5 mmol, 2.0 equiv), and *n*-Bu_4NBr (0.75 mmol, 1.0 equiv) were added in DMF/H_2O (2:1, 3.0 mL). Electrocatalysis was performed at 100 °C with a constant current of 10 mA maintained for 9 h. After cooling to ambient temperature, a saturated aqueous $NaHCO_3$ (25 mL) was added and the reaction mixture was extracted with EtOAc (3 × 15 mL). The combined organic layers were washed with brine (25 mL), dried over Na_2SO_4, filtered and concentrated *in vacuo*. Purification by column chromatography on silica gel (*n*-hexane/Dichloromethane: 1/1→1/4) yielded the corresponding products.

3.2 Gram Scale reaction

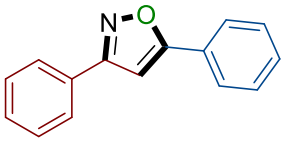
To an undivided two-necked flask equipped with a teflon-coated magnetic stirring bar and teflon cap, platinum electrodes (25 mm x 50 mm x 0.25 mm), **1a** (3.0 mmol, 396 mg), **2a** (9.0 mmol, 3.0 equiv), **3** (9.0 mmol, 3.0 equiv), TFA (6.0 mmol, 2.0 equiv), and *n*-Bu_4NBr (3 mmol, 1.0 equiv) were added in DMF/H_2O (2:1, 12 mL). Electrocatalysis was performed at 100 °C with a constant current of 10 mA maintained for 48 h. After cooling to ambient temperature, a saturated aqueous $NaHCO_3$ (25 mL) was added and the reaction mixture was extracted with EtOAc (3 × 15 mL). The combined organic layers were washed with brine (25 mL), dried over Na_2SO_4, filtered and concentrated in vacuo. The crude product was purified by column chromatography on silica gel (*n*-hexane/Dichloromethane: 1/2) and yielded **4** (398 mg, 51%).



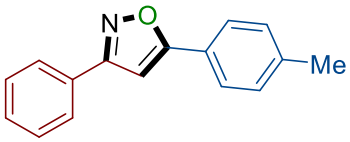
4. Product Characterization



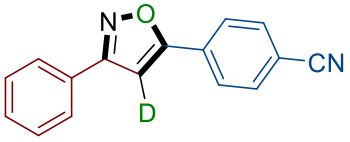
4-(3-phenylisoxazol-5-yl)benzonitrile (**4**) was prepared according to the general procedure and purified by column chromatography on silica gel (*n*-hexane/dichloromethane, 1:2) to yield the product **4** (114 mg, 62%) as a light purple solid. **M.p.** = 196 – 197 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.0 Hz, 2H), 7.90 – 7.83 (m, 2H), 7.78 (d, *J* = 8.0 Hz, 2H), 7.49 (s, 3H), 6.96 (s, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 168.3 (C_q), 163.4 (C_q), 133.0 (CH), 131.3 (C_q), 130.5 (CH), 129.2 (CH), 128.6 (C_q), 126.9 (CH), 126.4 (CH), 118.3 (C_q), 113.8 (C_q), 99.8 (CH). **IR** (ATR): $\tilde{\nu}$ = 2230, 1696, 1558, 1542, 1414, 930, 688 cm^{-1}. **MS** (ESI) m/z (relative intensity): 247 (100) $[M+H]^+$. **HR-MS** (ESI) calcd for $C_{16}H_{11}N_2O^+$ $[M+H]^+$: 247.0866, found: 247.0863.



3, 5-diphenylisoxazole (**7**) was prepared according to the general procedure and purified by column chromatography on silica gel (*n*-hexane/dichloromethane, 2:1) to yield the product **7** (85 mg, 51%) as a white solid. **M.p.** = 133 – 134 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.89 – 7.84 (m, 4H), 7.44 – 7.55 (m, 7.0 Hz, 6H), 6.84 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.5 (C_q), 163.1 (C_q), 130.4 (CH), 130.2 (CH), 129.3 (C_q), 129.2 (CH), 129.1 (CH), 127.6 (C_q), 127.0 (CH), 126.0 (CH), 97.6 (CH). **IR** (ATR): $\tilde{\nu}$ = 2224, 1060, 910, 762, 670 cm^{-1}. **MS** (ESI) m/z (relative intensity): 222 (100) $[M+H]^+$. **HR-MS** (ESI) calcd for $C_{15}H_{12}NO^+$ $[M+H]^+$: 222.0913, found 222.0909.

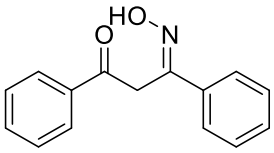


3-phenyl-5-(p-tolyl)isoxazole (**8**) was prepared according to the general procedure and purified by column chromatography on silica gel (*n*-hexane/dichloromethane, 1:1) to yield the product **8** (80 mg, 45%) as a light yellow solid. **M.p.** = 126 – 128 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.88 – 7.86 (m, 2H), 7.73 (d, *J* = 8.1 Hz, 2H), 7.50 – 7.46 (m, 3H), 7.29 (d, *J* = 7.9 Hz, 2H), 6.78 (s, 1H), 2.42 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 170.7 (C_q), 163.1 (C_q), 140.7 (C_q), 130.1 (CH), 129.8 (CH), 129.3 (C_q), 129.0 (CH), 126.9 (CH), 125.9 (CH), 124.9 (C_q), 97.0 (CH), 21.6 (CH_3). **IR** (ATR): $\tilde{\nu}$ = 2934, 2245, 1910, 1442, 1270, 922, 804, 680 cm^{-1}. **MS** (ESI) m/z (relative intensity): 236 (100) $[M+H]^+$. **HR-MS** (ESI) calcd for $C_{16}H_{14}NO^+$ $[M+H]^+$: 236.1070, found 236.1075.

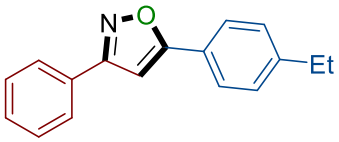


4-(3-phenylisoxazol-5-yl-4-D)benzonitrile (**9**) was prepared according to the general procedure and purified by column chromatography on silica gel (*n*-hexane/dichloromethane, 1:2) to yield the product **9** (119 mg, 64%) as a pink solid. **M.p.** = 202 – 203 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.0 Hz, 2H), 7.86 (d, *J* = 3.6 Hz, 2H), 7.78 (d, *J* = 8.0 Hz, 2H), 7.49 (t, *J* = 2.6 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.2 (C_q), 163.4 (C_q), 133.0

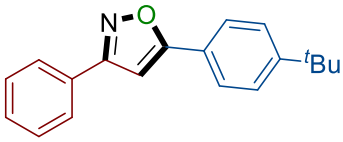
(CH), 131.3 (C_q), 130.5 (CH), 129.2 (CH), 128.6 (C_q), 127.0 (CH), 126.4 (CH), 118.3 (C_q), 113.8 (C_q), 99.8 (CH). **IR** (ATR): $\tilde{\nu}$ = 2231, 1485, 1452, 1419, 1080, 843, 741,716, 696, 553 cm^{-1}. **MS** (ESI) m/z (relative intensity): 248 (100) $[M+H]^+$. **HR-MS** (ESI) calcd for $C_{16}H_{10}DN_2O^+$ $[M+H]^+$: 248.0929, found 248.0920.



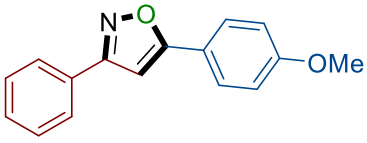
(*E*)-3-(hydroxyimino)-1,3-diphenylpropan-1-one (**11**) was prepared according to the reference [1] and purified by column chromatography on silica gel (*n*-hexane/dichloromethane, 1:4) to yield the compound **11** (72 mg, 60%) as a white solid. **M.p.** = 146 – 148 °C. **^{1}H NMR** (600 MHz, DMSO-d_6) δ 7.72 (dtd, *J* = 6.5, 4.6, 3.9, 2.7 Hz, 2H), 7.60 – 7.55 (m, 2H), 7.47 (dq, *J* = 6.9, 3.8, 2.8 Hz, 4H), 7.43 – 7.39 (m, 2H), 7.38 – 7.34 (m, 1H), 3.57 (s, 2H). Analytical data are consistent with reported literature.[1]



5-(4-ethylphenyl)-3-phenylisoxazole (**12**) was prepared according to the general procedure and purified by column chromatography on silica gel (*n*-hexane/dichloromethane, 1:4) to yield the product **12** (75 mg, 40%) as a white solid. **M.p.** = 82 – 83 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.87 (dd, *J* = 7.7, 1.4 Hz, 2H), 7.77 (d, J = 8.1 Hz, 2H), 7.50 – 7.46 (m, 3H), 7.32 (d, *J* = 8.1 Hz, 2H), 6.79 (s, 1H), 2.72 (q, *J* = 7.6 Hz, 2H), 1.28 (t, *J* = 7.6 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 170.7 (C_q), 163.1 (C_q), 146.9 (C_q), 130.1 (CH), 129.4 (C_q), 129.0 (CH), 128.6 (CH), 126.9 (CH), 126.0 (CH), 125.1 (C_q), 97.0 (CH), 29.0 (CH_2), 15.5(CH_3). **IR** (ATR): $\tilde{\nu}$ = 2934, 2234, 1904, 1806, 1280, 936, 816, 688 cm^{-1}. **MS** (ESI) m/z (relative intensity): 250 (100) $[M+H]^+$. **HR-MS** (ESI) calcd for $C_{17}H_{16}NO^+$ $[M+H]^+$: 250.1226, found 250.1224.

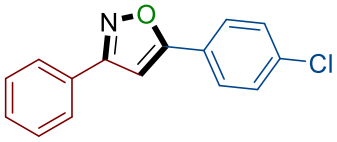


5-(4-(*tert*-butyl)phenyl)-3-phenylisoxazole (**13**) was prepared according to the general procedure and purified by column chromatography on silica gel (*n*-hexane/dichloromethane, 1:4) to yield the product **13** (75 mg, 36%) as a white solid. **M.p.** = 88 – 89 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.89 – 7.85 (m, 2H), 7.81 – 7.75 (m, 2H), 7.52 – 7.43 (m, 5H), 6.80 (s, 1H), 1.37 (s, 9H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 170.7 (C_q), 163.1 (C_q), 153.8 (C_q), 130.1 (CH), 129.4 (C_q), 129.0 (CH), 127.0 (CH), 126.1 (CH), 125.8 (CH), 124.9 (C_q), 97.1 (CH), 35.1 (C_q), 31.3 (CH_3). **IR** (ATR): $\tilde{\nu}$ = 2838, 2235, 1472, 1390, 1274, 1106, 924, 812, 688 cm^{-1}. **MS** (ESI) m/z (relative intensity): 278 (100) $[M+H]^+$. **HR-MS** (ESI) calcd for $C_{19}H_{20}NO^+$ $[M+H]^+$: 278.1539, found 278.1548.

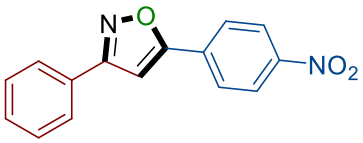


5-(4-methoxyphenyl)-3-phenylisoxazole (**14**) was prepared according to the general procedure and purified by column chromatography on silica gel (*n*-hexane/dichloromethane, 1:4) to yield the product **14** (66 mg, 35%) as a white solid. **M.p.** = 119 – 121 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.86 (dd, *J* = 7.8, 1.5 Hz, 2H), 7.78 (d, *J* = 8.8 Hz,

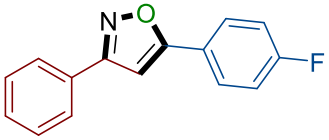
2H), 7.50 – 7.43 (m, 3H), 7.00 (d, J = 8.8 Hz, 2H), 6.71 (s, 1H), 3.87 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 170.5 (C_q), 163.1 (C_q), 161.3 (C_q), 130.1 (CH), 129.4 (C_q), 129.0 (CH), 127.6 (CH), 126.9 (CH), 120.5 (C_q), 114.6 (CH), 96.3 (CH), 55.6 (CH_3). **IR** (ATR): $\tilde{\nu}$ = 3006, 2258, 1884, 1684, 1456, 1056, 912, 796, 684 cm^{-1}. **MS** (ESI) m/z (relative intensity): 252 (100) $[M+H]^+$. **HR-MS** (ESI) calcd for $C_{16}H_{14}NO_2^+$ $[M+H]^+$: 252.1019, found 252.1030.



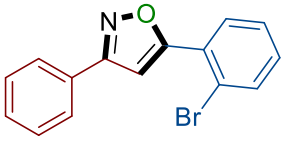
5-(4-chlorophenyl)-3-phenylisoxazole (**15**) was prepared according to the general procedure and purified by column chromatography on silica gel (*n*-hexane/dichloromethane, 1:4) to yield the product **15** (111 mg, 58%) as a white solid. **M.p.** = 166 – 168 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.89 – 7.82 (m, 2H), 7.81 – 7.74 (m, 2H), 7.50 – 7.43 (m, 5H), 6.82 (s, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 169.4 (C_q), 163.2 (C_q), 136.4 (C_q), 130.2 (CH), 129.5 (CH), 129.1 (CH), 129.1 (C_q), 127.2 (CH), 127.0 (CH), 126.1 (C_q), 98.0 (CH). **IR** (ATR): $\tilde{\nu}$ = 2296, 1930, 1408, 1074, 924, 816, 680 cm^{-1}. **MS** (ESI) m/z (relative intensity): 256 (100) $[M+H]^+$. **HR-MS** (ESI) calcd for $C_{15}H_{11}ClNO^+$ $[M+H]^+$: 256.0529, found 256.0536.



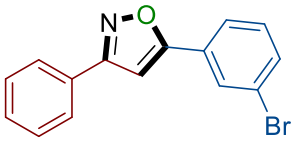
5-(4-nitrophenyl)-3-phenylisoxazole (**16**) was prepared according to the general procedure and purified by column chromatography on silica gel (*n*-hexane/dichloromethane, 1:4) to yield the product **16** (112 mg, 56%) as a yellow solid. **M.p.** = 198 – 200 °C. **^{1}H NMR** (600 MHz, DMSO-d_6) δ 8.43 – 8.41 (m, 2H), 8.20 – 8.18 (m, 2H), 7.94 (dd, J = 7.7, 1.8 Hz, 2H), 7.92 (s, 1H), 7.57 – 7.53 (m, 3H). **^{13}C NMR** (151 MHz, DMSO-d_6) δ 167.6 (C_q), 163.0 (C_q), 148.2 (C_q), 132.3 (C_q), 130.6 (CH), 129.3 (CH), 128.1 (C_q), 126.8 (CH), 126.7 (CH), 124.7 (CH), 101.6 (CH). **IR** (ATR): $\tilde{\nu}$ = 2928, 2326, 1402, 1088, 768, 690 cm^{-1}. **MS** (ESI) m/z (relative intensity): 267 (100) $[M+H]^+$. **HR-MS** (ESI) calcd for $C_{15}H_{11}N_2O_3^+$ $[M+H]^+$: 267.0764, found 267.0765.



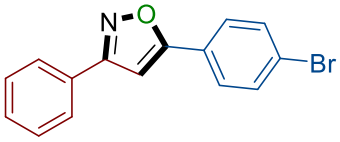
5-(4-fluorophenyl)-3-phenylisoxazole (**17**) was prepared according to the general procedure and purified by column chromatography on silica gel (*n*-hexane/dichloromethane, 1:4) to yield the product **17** (111 mg, 62%) as a white solid. **M.p.** = 163 – 164 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.97 – 7.74 (m, 4H),7.48 (d, J = 7.1 Hz, 3H), 7.19 (t, J = 8.6 Hz, 2H), 6.78 (s, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 169.6 (C_q), 164.0 (d, $^1J_{CF}$ = 256.7 Hz), 163.2 (C_q), 130.1 (CH), 129.1 (C_q), 129.1 (CH), 128.1 (d, $^3J_{CF}$ = 8.6 Hz), 126.9 (CH), 124.0 (d, $^4J_{CF}$ = 3.4 Hz), 116.4 (d, $^2J_{CF}$ = 22.0 Hz), 97.4 (CH). **^{19}F NMR** (564 MHz, $CDCl_3$) δ -109.5 (tt, J = 9.1, 5.1 Hz). **IR** (ATR): $\tilde{\nu}$ = 2924, 2356, 1908, 1082, 912, 828, 690 cm^{-1}. **MS** (ESI) m/z (relative intensity): 240 (100) $[M+H]^+$. **HR-MS** (ESI) calcd for $C_{15}H_{11}FNO^+$ $[M+H]^+$: 240.0819, found 240.0828.



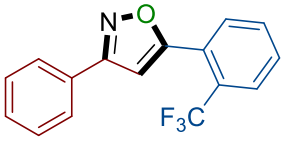
5-(2-bromophenyl)-3-phenylisoxazole (**18**) was prepared according to the general procedure and purified by column chromatography on silica gel (*n*-hexane/dichloromethane, 1:4) to yield the product **18** (63 mg, 28%) as a light yellow solid. **M.p.** = 107 – 108 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.93 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.91 – 7.88 (m, 2H), 7.74 (dd, *J* = 8.1, 1.1 Hz, 1H), 7.51 – 7.42 (m, 4H), 7.31 (td, *J* = 7.8, 1.7 Hz, 1H), 7.29 (s, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 168.1 (C_q), 162.9 (C_q), 134.4 (CH), 131.2 (CH), 130.3 (CH), 130.2 (CH), 129.2 (C_q), 129.1 (CH), 128.5 (C_q), 127.9 (CH), 127.0 (CH), 121.3 (C_q), 102.4 (CH). **IR** (ATR): $\tilde{\nu}$ = 2245, 1926, 1434, 1274, 1008, 934, 732, 520 cm^{-1}. **MS** (ESI) m/z (relative intensity): 300 (100) $[M+H]^+$. **HR-MS** (ESI) calcd for $C_{15}H_{11}BrNO^+$ $[M+H]^+$: 300.0019, found 300.0024.



5-(3-bromophenyl)-3-phenylisoxazole (**19**) was prepared according to the general procedure and purified by column chromatography on silica gel (*n*-hexane/dichloromethane, 1:4) to yield the product **19** (99 mg, 44%) as a light blue solid. **M.p.** = 124 – 126 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.98 (s, 1H), 7.86 (dd, *J* = 7.4, 2.1 Hz, 2H), 7.77 (d, *J* = 7.8 Hz, 1H), 7.58 (dd, *J* = 8.0, 0.7 Hz, 1H), 7.51 – 7.41 (m, 3H), 7.36 (t, *J* = 7.9 Hz, 1H), 6.85 (s, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 168.9 (C_q), 163.2 (C_q), 133.2 (CH), 130.7 (CH), 130.3 (CH), 129.4 (C_q), 129.1 (CH), 129.0 (C_q), 128.9 (CH), 126.9 (CH), 124.5 (CH), 123.2 (C_q), 98.4 (CH). **IR** (ATR): $\tilde{\nu}$ = 2249, 1840, 1412, 1320, 1060, 910, 774, 684, 516 cm^{-1}. **MS** (ESI) m/z (relative intensity): 300 (100) $[M+H]^+$. **HR-MS** (ESI) calcd for $C_{15}H_{11}BrNO^+$ $[M+H]^+$: 300.0019, found 300.0024.

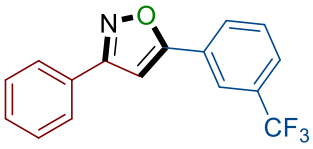


5-(4-bromophenyl)-3-phenylisoxazole (**20**) was prepared according to the general procedure and purified by column chromatography on silica gel (*n*-hexane/dichloromethane, 1:4) to yield the product **20** (121 mg, 54%) as a white solid. **M.p.** = 177 – 179 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.87 – 7.85 (m, 2H), 7.67 (dd, *J* = 40.6, 8.4 Hz, 4H), 7.48 (d, *J* = 5.5 Hz, 3H), 6.84 (s, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 169.5 (C_q), 163.2 (C_q), 132.4 (CH), 130.3 (CH), 129.1 (CH), 129.0 (C_q), 127.4 (CH), 127.0 (CH), 126.5 (C_q), 124.7 (C_q), 98.0 (CH). **IR** (ATR): $\tilde{\nu}$ = 2222, 1932, 1418, 1268, 1104, 934, 822, 544 cm^{-1}. **MS** (ESI) m/z (relative intensity): 300 (100) $[M+H]^+$. **HR-MS** (ESI) calcd for $C_{15}H_{11}BrNO^+$ $[M+H]^+$: 300.0019, found 300.0024.

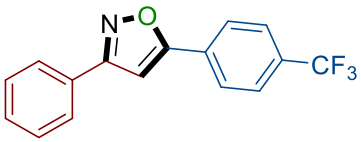


3-phenyl-5-(2-(trifluoromethyl)phenyl)isoxazole (**21**) was prepared according to the general procedure and purified by column chromatography on silica gel (*n*-hexane/dichloromethane, 1:4) to yield the product **21** (69 mg, 32%) as a yellow oil substance. **M.p.** = 194 – 196 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.90 – 7.83 (m, 4H), 7.69 (t, *J* = 7.4 Hz, 1H), 7.61 (t, *J* = 7.7 Hz, 1H), 7.52-7.47 (m, *J* = 9.2, 4.5, 1.8 Hz, 1H), 6.88 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.6 (C_q), 163.0 (C_q), 132.2 (CH), 131.1 (CH), 130.3 (CH), 130.3 (CH), 129.1 (CH), 129.0 (C_q), 128.1 (q, *J* = 31.2 Hz), 127.0 (CH), 126.9 (q, *J* = 5.8 Hz), 126.5 (d, *J* = 2.1 Hz), 123.7 (d, *J* = 273.4 Hz), 102.6 (CH). **^{19}F**

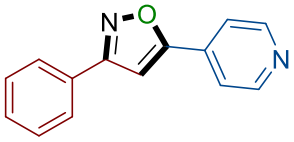
NMR (564 MHz, $CDCl_3$) δ -59.2. **IR** (ATR): $\tilde{\nu}$ = 2218, 1424, 1320, 1108, 920, 796, 672 cm^{-1}. **MS** (ESI) m/z (relative intensity): 290 (100) $[M+H]^+$. **HR-MS** (ESI) calcd for $C_{16}H_{11}F_3NO^+$ $[M+H]^+$: 290.0787, found 290.0779.



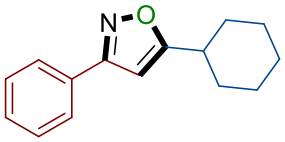
3-phenyl-5-(3-(trifluoromethyl)phenyl)isoxazole (**22**) was prepared according to the general procedure and purified by column chromatography on silica gel (*n*-hexane/dichloromethane, 1:4) to yield the product **22** (137 mg, 63%) as a blue solid. **M.p.** = 128 – 130 ˚C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.09 (s, 1H), 8.04 (d, *J* = 7.8 Hz, 1H), 7.92 – 7.84 (m, 2H), 7.72 (d, *J* = 7.8 Hz, 1H), 7.64 (t, *J* = 7.8 Hz, 1H), 7.54 – 7.45 (m, 3H), 6.93 (s, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 168.9 (C_q), 163.3 (C_q), 131.8 (*J* = 32.8 Hz), 130.4 (CH), 129.8 (CH), 129.2 (CH), 129.0 (C_q), 128.9 (CH), 128.3 (CH), 127.0 (CH), 126.9 (q, *J* = 3.8 Hz), 123.8 (d, *J* = 272.4 Hz), 122.9 (q, *J* = 3.9 Hz), 98.7 (CH). **^{19}F NMR** (564 MHz, $CDCl_3$) δ -62.9 (s). **IR** (ATR): $\tilde{\nu}$ = 2215, 1424, 1320, 1108, 920, 796, 672 cm^{-1}. **MS** (ESI) m/z (relative intensity): 290 (100) $[M+H]^+$. **HR-MS** (ESI) calcd for $C_{16}H_{11}F_3NO^+$ $[M+H]^+$: 290.0787, found 290.0779.



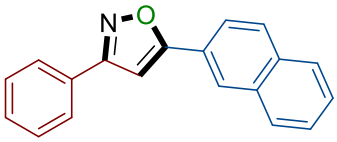
3-phenyl-5-(4-(trifluoromethyl)phenyl)isoxazole (**23**) was prepared according to the general procedure and purified by column chromatography on silica gel (*n*-hexane/dichloromethane, 1:4) to yield the product **23** (156 mg, 72%) as a green solid. **M.p.** = 185 – 187 ˚C. **^{1}H NMR** (600 MHz, DMSO-d_6) δ 8.15 (d, *J* = 8.2 Hz, 2H), 8.01 – 7.91 (m, 4H), 7.84 (s, 1H), 7.61 – 7.52 (m, 3H). **^{13}C NMR** (151 MHz, DMSO-d_6) δ 168.7 (C_q), 163.3 (C_q), 131.0 (CH), 130.9 (C_q), 130.6 (C_q), 129.7 (CH), 128.7 (CH), 127.1 (CH), 126.8 (CH), 126.8 (C_q), 125.3($^1J_{CF}$ = 271.8 Hz), 101.0 (CH). **^{19}F NMR** (564 MHz, $CDCl_3$) δ -62.9 (s). **IR** (ATR): $\tilde{\nu}$ = 2257, 1936, 1674, 1420, 1112, 930, 678 cm^{-1}. **MS** (ESI) m/z (relative intensity): 290 (100) $[M+H]^+$. **HR-MS** (ESI) calcd for $C_{16}H_{11}F_3NO^+$ $[M+H]^+$: 290.0787, found 290.0779.



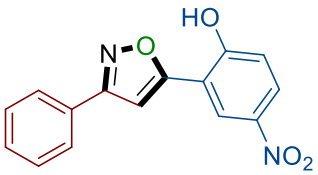
3-phenyl-5-(pyridin-4-yl)isoxazole (**24**) was prepared according to the general procedure and purified by column chromatography on silica gel (*n*-hexane/dichloromethane, 1:4) to yield the product **24** (75 mg, 45%) as a white solid. **M.p.** = 165 – 166 ˚C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.77 (d, *J* = 6.1 Hz, 2H), 7.89 – 7.84 (m, 2H), 7.70 – 7.68 (m, 2H), 7.49 (m, 3H), 7.02 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.9 (C_q), 163.4 (C_q), 150.9 (CH), 134.3 (C_q), 130.5 (CH), 129.2 (CH), 128.6 (C_q), 127.0 (CH), 119.7 (CH), 100.3 (CH). **IR** (ATR): $\tilde{\nu}$ = 2234, 1474, 1272, 1210, 1086, 926, 808, 524 cm^{-1}. **MS** (ESI) m/z (relative intensity): 223 (100) $[M+H]^+$. **HR-MS** (ESI) calcd for $C_{15}H_{11}N_2O^+$ $[M+H]^+$: 223.0866, found 223.0865.



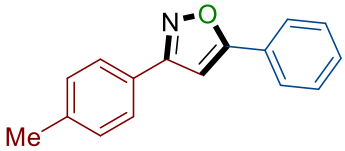
5-cyclohexyl-3-phenylisoxazole (**25**) was prepared according to the general procedure and purified by column chromatography on silica gel (*n*-hexane/dichloromethane, 1:4) to yield the product **25** (61 mg, 36%) as a white solid. **M.p.** = 79 – 80 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.69 (dd, *J* = 8.0, 1.8 Hz, 2H), 7.42 (m, *J* = 6.8, 6.2 Hz, 3H), 6.01 (d, *J* = 4.5 Hz, 1H), 4.93 (dd, *J* = 6.8, 4.4 Hz, 1H), 1.81 (q, *J* = 14.0 Hz, 4H), 1.40 – 0.97 (m, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 150.7 (C_q), 131.1 (CH), 129.3 (CH), 127.0 (C_q), 126.6 (CH), 92.9 (C_q), 91.7 (CH), 41.3 (CH), 28.0 (CH_2), 27.9 (CH_2), 26.1 (CH_2), 25.7 (CH_2), 25.5 (CH_2). **IR** (ATR): $\tilde{\nu}$ = 2132, 1752, 1348, 1066, 918, 784, 688, 544 cm^{-1}. **MS** (ESI) m/z (relative intensity): 228 (100) $[M+H]^+$. **HR-MS** (ESI) calcd for $C_{15}H_{18}NO^+$ $[M+H]^+$: 228.1383, found 228.1388.



5-(naphthalen-2-yl)-3-phenylisoxazole (**26**) was prepared according to the general procedure and purified by column chromatography on silica gel (*n*-hexane/dichloromethane, 1:3) to yield the product **26** (98 mg, 48%) as a white solid. **M.p.** = 160 – 161 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.37 (s, 1H), 7.98 – 7.85 (m, 6H), 7.56 (dq, *J* = 6.6, 3.5 Hz, 2H), 7.50 (q, *J* = 6.1 Hz, 3H), 6.95 (s, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 170.6 (C_q), 163.2 (C_q), 134.1 (C_q), 133.2 (C_q), 130.2 (CH), 129.3 (CH), 129.1 (CH), 129.0 (CH), 128.8 (C_q), 128.0 (CH), 127.5 (CH), 127.1 (CH), 127.0 (CH), 125.7 (C_q), 124.8 (CH), 123.1 (CH), 98.0 (CH). **IR** (ATR): $\tilde{\nu}$ = 2256, 1748, 1470, 1376, 912, 760 cm^{-1}. **MS** (ESI) m/z (relative intensity): 272 (100) $[M+H]^+$. **HR-MS** (ESI) calcd for $C_{19}H_{14}NO^+$ $[M+H]^+$: 272.1070, found 272.1064.

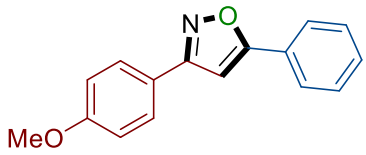


4-nitro-2-(3-phenylisoxazol-5-yl)phenol (**27**) was prepared according to the general procedure and purified by column chromatography on silica gel (*n*-hexane/dichloromethane, 1:3) to yield the product **27** (104 mg, 49%) as a white solid. **M.p.** = 171 – 172 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.47 (d, *J* = 2.4 Hz, 1H), 8.28 (dd, *J* = 9.0, 2.4 Hz, 1H), 7.98 – 7.81 (m, 2H), 7.57 – 7.42 (m, 3H), 7.01 (d, *J* = 9.0 Hz, 1H), 6.62 (d, *J* = 8.3 Hz, 1H), 6.36 (d, *J* = 8.3 Hz, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 163.2 (C_q), 154.1 (C_q), 143.1 (C_q), 131.0 (CH), 129.2 (CH), 128.4 (C_q), 127.5 (C_q), 127.3 (CH), 126.2 (C_q), 123.3 (CH), 111.4 (CH), 92.6 (CH), 84.2 (CH). IR (ATR): $\tilde{\nu}$ = 3466, 2230, 1634, 1330, 1242, 1064, 902, 826, 752, 672 cm^{-1}. **MS** (ESI) m/z (relative intensity): 283 (100) $[M+H]^+$. **HR-MS** (ESI) calcd for $C_{15}H_{11}N_2O_4^+$ $[M+H]^+$: 283.0713, found 283.0709.

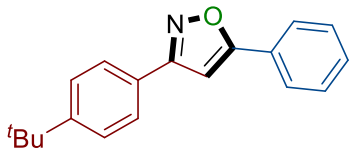


5-phenyl-3-(p-tolyl)isoxazole (**28**) was prepared according to the general procedure and purified by column chromatography on silica gel (*n*-hexane/dichloromethane, 1:2) to yield the product **28** (99 mg, 56%) as a white solid. **M.p.** = 128 – 129 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.87 – 7.80 (m, 2H), 7.76 (d, *J* = 8.1 Hz, 2H), 7.50 – 7.44 (m, 3H), 7.29 (d, *J* = 8.0 Hz, 2H), 6.81 (s, 1H), 2.42 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 170.3 (C_q), 163.1 (C_q),

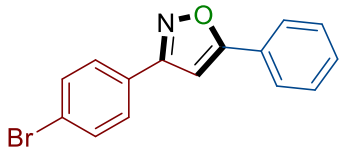
140.3 (C_q), 130.3 (CH), 129.8 (CH), 129.1 (CH), 127.7 (C_q), 126.8 (CH), 126.4 (C_q), 126.0 (CH), 97.6 (CH), 21.6 (CH_3). **IR** (ATR): $\tilde{\nu}$ = 2936, 2234, 1680, 908, 796, 502 cm^{-1}. **MS** (ESI) m/z (relative intensity): 236 (100) $[M+H]^+$. **HR-MS** (ESI) calcd for $C_{16}H_{14}NO^+$ $[M+H]^+$: 236.1070, found 236.1075.



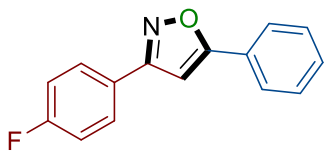
3-(4-methoxyphenyl)-5-phenylisoxazole (**29**) was prepared according to the general procedure and purified by column chromatography on silica gel (*n*-hexane/dichloromethane, 1:2) to yield the product **29** (94 mg, 50%) as a white solid. **M.p.** = 114 – 115 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.85 – 7.79 (m, 4H), 7.52 – 7.43 (m, 3H), 7.01 – 6.99 (m, 2H), 6.78 (s, 1H), 3.87 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.3 (C_q), 162.7 (C_q), 161.1 (C_q), 130.3 (CH), 129.1 (CH), 128.3 (CH), 127.7 (C_q), 125.9 (CH), 121.8 (C_q), 114.4 (CH), 97.4 (CH), 55.5 (CH_3). **IR** (ATR): $\tilde{\nu}$ = 3006, 2222, 1884, 1684, 1456, 1056, 912, 796, 684 cm^{-1}. **MS** (ESI) m/z (relative intensity): 252 (100) $[M+H]^+$. **HR-MS** (ESI) calcd for $C_{16}H_{14}NO_2^+$ $[M+H]^+$: 252.1019, found 252.1020.



3-(4-(tert-butyl)phenyl)-5-phenylisoxazole (**30**) was prepared according to the general procedure and purified by column chromatography on silica gel (*n*-hexane/dichloromethane, 1:2) to yield the product **30** (125 mg, 60%) as a white solid. **M.p.** = 111 – 113 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.85 (dd, *J* = 8.2, 1.2 Hz, 2H), 7.86 – 7.78 (m, 2H), 7.54 – 7.41 (m, 5H), 6.82 (s, 1H), 1.37 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 170.3 (C_q), 163.0 (C_q), 153.4 (C_q), 130.3 (CH), 129.1 (CH), 127.7 (C_q), 126.7 (CH), 126.4 (C_q), 126.0 (CH), 126.0 (CH), 97.6, (CH) 35.0 (C_q), 31.4 (CH_3). **IR** (ATR): $\tilde{\nu}$ = 2944, 2268, 1424, 1266, 1104, 922, 812, 750, 672 cm^{-1}. **MS** (ESI) m/z (relative intensity): 278 (100) $[M+H]^+$. **HR-MS** (ESI) calcd for $C_{19}H_{20}NO^+$ $[M+H]^+$: 278.1545, found 278.1535.

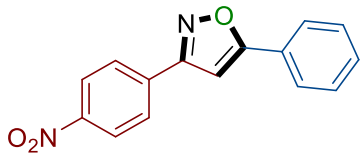


3-(4-bromophenyl)-5-phenylisoxazole (**31**) was prepared according to the general procedure and purified by column chromatography on silica gel (*n*-hexane/dichloromethane, 1:2) to yield the product **31** (101 mg, 45%) as a white solid. **M.p.** = 175 – 177 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.87 – 7.79 (m, 2H), 7.74 (d, *J* = 8.5 Hz, 2H), 7.62 (d, *J* = 8.5 Hz, 2H), 7.55 – 7.43 (m, 3H), 6.80 (s, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 170.8 (C_q), 162.2 (C_q), 132.3 (CH), 130.5 (CH), 129.2 (CH), 128.5 (CH), 128.2 (C_q), 127.4 (C_q), 126.0 (CH), 124.5 (C_q), 97.4 (CH). **IR** (ATR): $\tilde{\nu}$ = 2230, 1914, 1420, 1070, 922, 810, 682 cm^{-1}. **MS** (ESI) m/z (relative intensity): 300 (100) $[M+H]^+$. **HR-MS** (ESI) calcd for $C_{15}H_{11}BrNO^+$ $[M+H]^+$: 300.0024, found 300.0022.

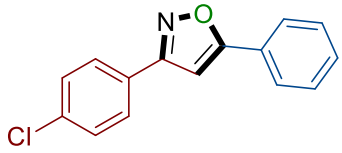


3-(4-fluorophenyl)-5-phenylisoxazole (**32**) was prepared according to the general procedure and purified by column chromatography on silica gel (*n*-hexane/dichloromethane, 1:2) to yield the product **32** (75 mg, 42%) as a

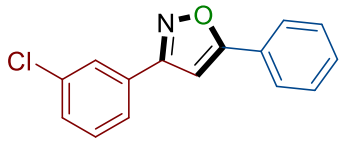
white solid. **M.p.** = 166 – 167 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.87 – 7.83 (m, 4H), 7.51 – 7.46 (m, 3H), 7.18 (t, J = 8.6 Hz, 2H), 6.80 (s, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 170.7 (C_q), 164.0 (d, $^1J_{CF}$ = 256.7 Hz), 162.2 (C_q), 130.5 (CH), 129.2 (CH), 128.9 (d, $^3J_{CF}$ = 8.3 Hz), 127.5 (C_q), 126.0 (CH), 125.5 (d, $^4J_{CF}$ = 3.4 Hz), 116.2 (d, $^2J_{CF}$ = 21.9 Hz), 97.5 (CH). **^{19}F NMR** (564 MHz, $CDCl_3$) δ -110.6 (tt, J = 8.4, 5.3 Hz). **IR** (ATR): $\tilde{\nu}$ = 2225, 1908, 1082, 912, 828, 690 cm^{-1}. **MS** (ESI) m/z (relative intensity): 240 (100) $[M+H]^+$. **HR-MS** (ESI) calcd for $C_{15}H_{11}FNO^+$ $[M+H]^+$: 240.0819, found 240.0828.



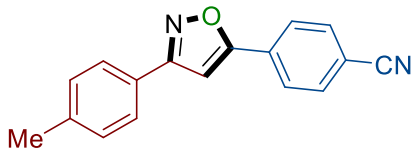
3-(4-nitrophenyl)-5-phenylisoxazole (**33**) was prepared according to the general procedure and purified by column chromatography on silica gel (*n*-hexane/dichloromethane, 1:2) to yield the product **33** (76 mg, 38%) as a yellow solid. **M.p.** = 186 – 188 °C. **^{1}H NMR** (600 MHz, DMSO-d_6) δ 8.41 (d, J = 8.8 Hz, 2H), 8.21 (d, J = 8.8 Hz, 2H), 7.96 – 7.92 (m, 2H), 7.79 (s, 1H), 7.58 (dt, J = 23.4, 7.1 Hz, 3H). **^{13}C NMR** (151 MHz, DMSO-d_6) δ 170.6 (C_q), 161.2 (C_q), 148.5 (C_q), 134.6 (C_q), 130.8 (CH), 129.4 (CH), 127.9 (CH), 126.5 (C_q), 125.7 (CH), 124.4 (CH), 99.1 (CH). **IR** (ATR): $\tilde{\nu}$ = 2240, 1362, 1152, 836, 696 cm^{-1}. **MS** (ESI) m/z (relative intensity): 267 (100) $[M+H]^+$. **HR-MS** (ESI) calcd for $C_{15}H_{11}N_2O_3^+$ $[M+H]^+$: 267.0764, found 267.0765.



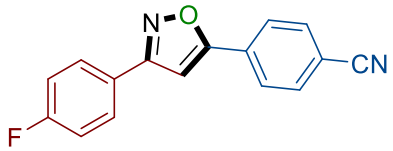
3-(4-chlorophenyl)-5-phenylisoxazole (**34**) was prepared according to the general procedure and purified by column chromatography on silica gel (*n*-hexane/dichloromethane, 1:2) to yield the product **34** (99 mg, 52%) as a white solid. **M.p.** = 173 – 174 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.84 – 7.80 (m, 4H), 7.51 – 7.45 (m, 5H), 6.80 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.8 (C_q), 162.1 (C_q), 136.2 (C_q), 130.5 (CH), 129.4 (CH), 129.2 (CH), 128.2 (CH), 127.7 (C_q), 127.4 (C_q), 126.0 (CH), 97.4 (CH). **IR** (ATR): $\tilde{\nu}$ = 2215, 1552, 1272, 912, 770, 684 cm^{-1}. **MS** (ESI) m/z (relative intensity): 256 (100) $[M+H]^+$. **HR-MS** (ESI) calcd for $C_{15}H_{11}ClNO^+$ $[M+H]^+$: 256.0529, found 256.0536.



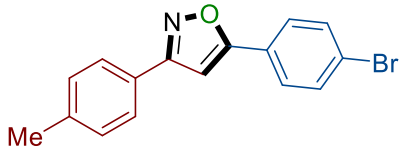
3-(3-chlorophenyl)-5-phenylisoxazole (**35**) was prepared according to the general procedure and purified by column chromatography on silica gel (*n*-hexane/dichloromethane, 1:2) to yield the product **35** (88 mg, 46%) as a white solid. **M.p.** = 168 – 170 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.87 (t, J = 1.5 Hz, 1H), 7.85 – 7.82 (m, 2H), 7.76 (dt, J = 7.0, 1.6 Hz, 1H), 7.52 – 7.40 (m, 5H), 6.81 (s, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 170.9 (C_q), 162.0 (C_q), 135.1 (C_q), 131.0 (C_q), 130.5 (CH), 130.4 (CH), 130.2 (CH), 129.2 (CH), 127.4 (C_q), 127.1 (CH), 126.0 (CH), 125.0 (CH), 97.5 (CH). **IR** (ATR): $\tilde{\nu}$ = 2216, 1562, 1272, 913, 771, 695 cm^{-1}. **MS** (ESI) m/z (relative intensity): 256 (100) $[M+H]^+$. **HR-MS** (ESI) calcd for $C_{15}H_{11}ClNO^+$ $[M+H]^+$: 256.0529, found 256.0536.



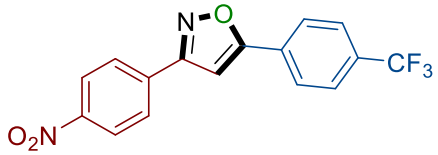
4-(3-(*p*-tolyl)isoxazol-5-yl)benzonitrile (**36**) was prepared according to the general procedure and purified by column chromatography on silica gel (*n*-hexane/dichloromethane, 1:2) to yield the product **36** (148 mg, 76%) as a pink solid. **M.p.** = 196 – 197 °C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.2 Hz, 2H), 7.85 – 7.70 (m, 4H), 7.30 (d, *J* = 7.8 Hz, 2H), 6.94 (s, 1H), 2.42 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 168.1 (C_q), 163.4 (C_q), 140.8 (C_q), 133.0 (CH), 131.4 (C_q), 129.9 (CH), 126.9 (CH), 126.4 (CH), 125.8 (C_q), 118.3 (C_q), 113.7 (C_q), 99.7 (CH), 21.6 (CH_3). **IR** (ATR): $\tilde{\nu}$ = 2357, 1419, 1264, 842, 733, 701 cm^{-1}. **MS** (ESI) m/z (relative intensity): 261 (100) $[M+H]^+$. **HR-MS** (ESI) calcd for $C_{17}H_{13}N_2O^+$ $[M+H]^+$: 261.1022, found 261.1025.



4-(3-(4-fluorophenyl)isoxazol-5-yl)benzonitrile (**37**) was prepared according to the general procedure and purified by column chromatography on silica gel (*n*-hexane/dichloromethane, 1:2) to yield the product **37** (109 mg, 55%) as a pink solid: 55% yield. **M.p.** = 162 – 163 °C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.2 Hz, 2H), 7.86 (dd, *J* = 8.6, 5.4 Hz, 2H), 7.80 (d, *J* = 8.2 Hz, 2H), 7.25 – 7.13 (m, 3H), 6.93 (s, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 168.5 (C_q), 164.2 (d, $^1J_{CF}$ = 251.2 Hz), 133.0 (CH), 131.2 (C_q), 129.0 (d, $^3J_{CF}$ = 8.5 Hz), 126.4 (C_q), 124.9 (d, $^4J_{CF}$ = 3.3 Hz), 118.3 (C_q), 116.4 (d, $^2J_{CF}$ = 21.9 Hz), 113.9 (C_q), 99.6 (CH). **^{19}F NMR** (282 MHz, $CDCl_3$) δ -109.8 (s). **IR** (ATR): $\tilde{\nu}$ = 2245, 1632, 1558, 1541, 1457, 1264, 736, 702 cm^{-1}. **MS** (ESI) m/z (relative intensity): 265 (100) $[M+H]^+$. **HR-MS** (ESI) calcd for $C_{16}H_{10}FN_2O^+$ $[M+H]^+$: 265.0772, found 265.0772.

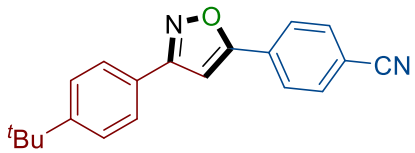


5-(4-bromophenyl)-3-(p-tolyl)isoxazole (**38**) was prepared according to the general procedure and purified by column chromatography on silica gel (*n*-hexane/dichloromethane, 1:2) to yield the product **38** (146 mg, 62%) as a pink solid. **M.p.** = 202 – 203 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.74 (dd, *J* = 8.0, 2.9 Hz, 2H), 7.69 (dd, *J* = 8.5, 3.0 Hz, 2H), 7.62 (dd, *J* = 8.5, 3.0 Hz, 2H), 7.28 (d, *J* = 5.8 Hz, 2H), 6.80 (s, 1H), 2.41 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 169.3 (C_q), 163.2 (C_q), 140.5 (C_q), 132.4 (CH), 129.8 (CH), 127.4 (CH), 126.8 (CH), 126.6 (C_q), 126.2 (C_q), 124.7 (C_q), 98.0 (CH), 21.6 (CH_3). **IR** (ATR): $\tilde{\nu}$ = 2924, 2218, 1538, 1276, 932, 812, 515 cm^{-1}. **MS** (ESI) m/z (relative intensity): 314 (100) $[M+H]^+$. **HR-MS** (ESI) calcd for $C_{16}H_{13}BrNO^+$ $[M+H]^+$: 314.0175, found 314.0182.

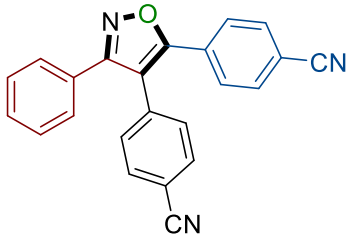


3-(4-nitrophenyl)-5-(4-(trifluoromethyl)phenyl)isoxazole (**39**) was prepared according to the general procedure and purified by column chromatography on silica gel (*n*-hexane/dichloromethane, 1:2) to yield the product **39** (150 mg, 60%) as a yellow solid. **M.p.** = 194 – 196 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.39 – 8.34 (m, 2H), 8.08 – 8.04 (m, 2H), 7.98 (d, *J* = 8.1 Hz, 2H), 7.79 (d, *J* = 8.2 Hz, 2H), 7.01 (s, 1H). **^{13}C NMR** (151 MHz, DMSO-d_6) δ 168.9

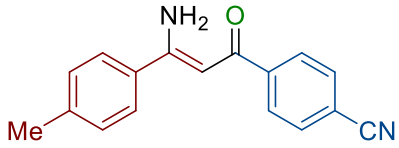
(C_q), 161.4 (C_q), 148.5 (C_q), 134.3 (CH), 130.5 ($^2J_{CF}$ = 30.2 Hz) 130.1 (CH), 127.9 (CH), 126.4 (CH), 126.3 (CH), 124.8 ($^1J_{CF}$ = 271.8 Hz), 124.4 (C_q), 100.9 (CH). **^{19}F NMR** (564 MHz, $CDCl_3$) δ -63.0 (s). **IR** (ATR): $\tilde{\nu}$ = 2235, 1946, 1568, 1330, 1140, 938, 836, 598 cm^{-1}. **MS** (ESI) m/z (relative intensity): 335 (100) $[M+H]^+$. **HR-MS** (ESI) calcd for $C_{16}H_{10}F_3N_2O_3^+$ $[M+H]^+$: 335.0638, found 335.0647.



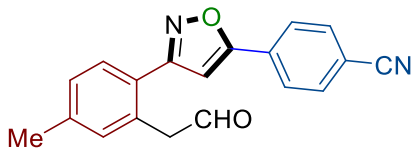
4-(3-(4-(*tert*-butyl)phenyl)isoxazol-5-yl)benzonitrile (**40**) was prepared according to the general procedure and purified by column chromatography on silica gel (*n*-hexane/dichloromethane, 1:2) to yield the product **40** (190 mg, 78%) as a white solid. **M.p.** = 183 – 185 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.0 Hz, 2H), 7.82 – 7.76 (m, 4H), 7.52 (d, *J* = 8.5 Hz, 2H), 6.95 (s, 1H), 1.37 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.1 (C_q), 163.3 (C_q), 153.9 (C_q), 133.0 (CH), 131.4 (C_q), 126.7 (CH), 126.4 (CH), 126.2 (CH), 125.8 (C_q), 118.3 (C_q), 113.7 (C_q), 99.8 (CH), 35.0 (C_q), 31.3 (CH_3). **IR** (ATR): $\tilde{\nu}$ = 2940, 2222, 1928, 1414, 1104, 934, 822, 708 cm^{-1}. **MS** (ESI) m/z (relative intensity): 325 (100) $[M+Na]^+$. **HR-MS** (ESI) calcd for $C_{20}H_{18}N_2NaO^+$ $[M+Na]^+$: 325.1311, found 325.1314.



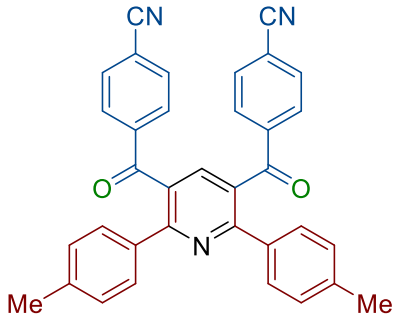
4, 4'-(3-phenylisoxazole-4, 5-diyl)dibenzonitrile (**41**) was purified by column chromatography on silica gel (*n*-hexane/dichloromethane, 1:2) to yield the product **41** (46 mg, 66%) as a white solid. **M.p.** = 220 – 221 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.71 (dd, *J* = 8.2, 1.6 Hz, 2H), 7.69 – 7.59 (m, 4H), 7.43 (dp, *J* = 7.4, 2.5 Hz, 1H), 7.37 (d, *J* = 1.6 Hz, 1H), 7.37 – 7.31 (m, 5H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 164.1 (C_q), 162.5 (C_q), 134.9(C_q), 133.2 (CH), 132.9 (CH), 131.2 (CH), 130.3 (CH), 129.0 (CH), 128.6 (CH), 127.8 (C_q), 127.6 (CH), 118.3 (C_q), 118.0 (C_q), 115.7 (C_q), 114.1 (C_q), 113.0 (C_q). **IR** (ATR): $\tilde{\nu}$ = 2229, 1588, 1474, 1398, 976, 851, 698, 554 cm^{-1}. **MS** (ESI) m/z (relative intensity): 348 (100) $[M+H]^+$. **HR-MS** (ESI) calcd for $C_{23}H_{14}N_3O^+$ $[M+H]^+$: 348.1131, found 348.1133.



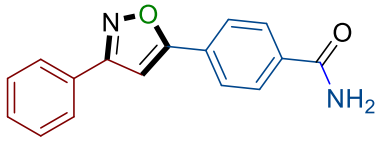
(Z)-4-(3-amino-3-(p-tolyl)acryloyl)benzonitrile (**42**) was purified by column chromatography on silica gel (*n*-hexane/dichloromethane, 1:1) to yield the product **42** (28 mg, 54%) as a white solid. **M.p.** = 182 – 183 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.51 (s, 1H), 8.00 (d, *J* = 8.1 Hz, 2H), 7.71 (d, *J* = 8.2 Hz, 2H), 7.53 (d, *J* = 8.1 Hz, 2H), 7.28 (d, *J* = 7.8 Hz, 2H), 6.08 (s, 1H), 5.73 (s, 1H), 2.42 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 187.6 (C_q), 164.5 (C_q), 144.3 (C_q), 141.9 (C_q), 134.1 (C_q), 132.3 (CH), 123.0 (CH), 127.8 (C_q), 126.3 (CH), 118.7 (C_q), 114.2 (C_q), 91.4 (CH), 21.5 (CH_3). **IR** (ATR): $\tilde{\nu}$ = 2228, 1591, 1558, 1544, 1506, 1491, 1329, 777 cm^{-1}. **MS** (ESI) m/z (relative intensity): 263 (100) $[M+H]^+$. **HR-MS** (ESI) calcd for $C_{17}H_{15}N_2O^+$ $[M+H]^+$: 263.1179, found 263.1180.



4-(3-(4-methyl-2-(2-oxoethyl)phenyl)isoxazol-5-yl)benzonitrile (43) was purified by column chromatography on silica gel (dichloromethane) to yield the product **43** (40 mg, 67%) as a green solid. **M.p.** = 175 – 176 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.81 (t, *J* = 1.5 Hz, 1H), 8.01 – 7.86 (m, 2H), 7.84 – 7.75 (m, 2H), 7.51 (d, *J* = 7.9 Hz, 1H), 7.26 – 7.22 (m, 2H), 7.15 (s, 1H), 6.85 (s, 1H), 4.05 (d, *J* = 1.6 Hz, 2H), 2.42 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 199.6 (CH), 167.6 (C_q), 163.3 (C_q), 140.6 (C_q), 133.1 (CH), 132.9 (CH), 131.5 (C_q), 131.0 (C_q), 129.8 (CH), 128.7 (CH), 126.4 (CH), 125.8 (C_q), 118.2 (C_q), 113.8 (C_q), 101.8 (CH), 49.3 (CH_2), 21.3 (CH_3). **IR** (ATR): $\tilde{\nu}$ = 2246, 1717, 1653, 1507, 1457, 1419, 1264, 735, 702 cm^{-1}. **MS** (ESI) m/z (relative intensity): 303 (100) $[M+H]^+$. **HR-MS** (ESI) calcd for $C_{19}H_{15}N_2O_2^+$ $[M+H]^+$: 303.1128, found 303.1123.



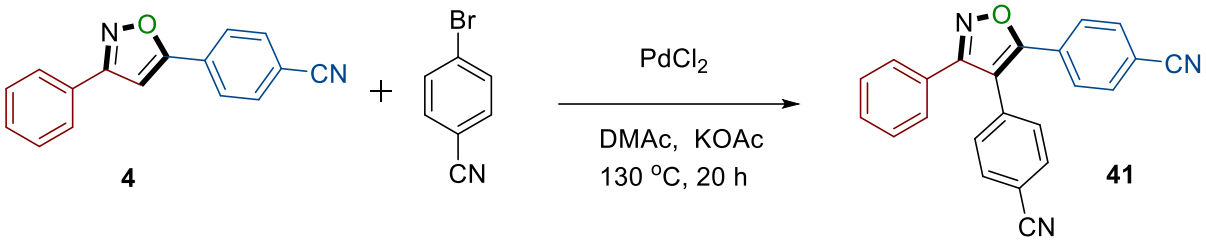
4-(4-bromo-3-(4-(bromomethyl)phenyl)isoxazol-5-yl)benzonitrile (44) was purified by column chromatography on silica gel (dichloromethane) to yield the product **44** (74 mg, 72%) as a white solid. **M.p.** = 223 – 224 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.21 (s, 1H), 7.73 (d, *J* = 8.4 Hz, 4H), 7.53 (dd, *J* = 13.8, 8.3 Hz, 8H), 7.07 (d, *J* = 8.4 Hz, 4H), 2.29 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 195.5 (CH), 158.8 (C_q), 140.7 (C_q), 140.4 (C_q), 139.6 (C_q), 135.5 (C_q), 132.3 (CH), 130.6 (C_q), 130.0 (CH), 129.8 (CH), 129.6 (CH), 117.9 (C_q), 116.5 (C_q), 21.4 (CH_3). **IR** (ATR): $\tilde{\nu}$ = 2240, 1652, 1558, 1457, 1318, 1255, 1011, 854, 736 cm^{-1}. **MS** (ESI) m/z (relative intensity): 518 (100) $[M+H]^+$. **HR-MS** (ESI) calcd for $C_{35}H_{24}N_3O_2^+$ $[M+H]^+$: 518.1863, found 518.1861.



4-(3-phenylisoxazol-5-yl)benzamide (45) was purified by recrystallization with ethanol to yield the product **45** (43 mg, 81%) as a white solid. **M.p.** = 210 – 211 °C. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 8.13 (s, 1H), 8.09 – 7.97 (m, 4H), 7.93 (d, *J* = 7.0 Hz, 2H), 7.74 (s, 1H), 7.59 – 7.50 (m, 4H). **^{13}C NMR** (101 MHz, DMSO-d_6) δ 169.0 (C_q), 167.0 (C_q), 162.8 (C_q), 135.7 (C_q), 130.4 (CH), 129.2 (CH), 129.0 (C_q), 128.5 (CH), 128.4 (C_q), 126.6 (CH), 125.5 (CH), 99.8 (CH). **IR** (ATR): $\tilde{\nu}$ = 2239, 1653, 1457, 772, 698, 406 cm^{-1}. **MS** (ESI) m/z (relative intensity): 265 (100) $[M+H]^+$. **HR-MS** (ESI) calcd for $C_{16}H_{13}N_2O_2^+$ $[M+H]^+$: 265.0972, found 265.0975.

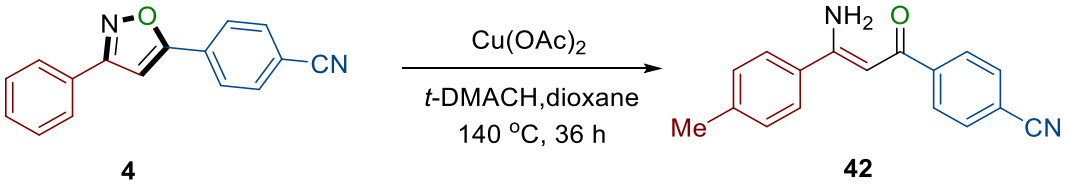
5. Late-Stage-Diversification

(a) Late-Stage-Diversification of product 4



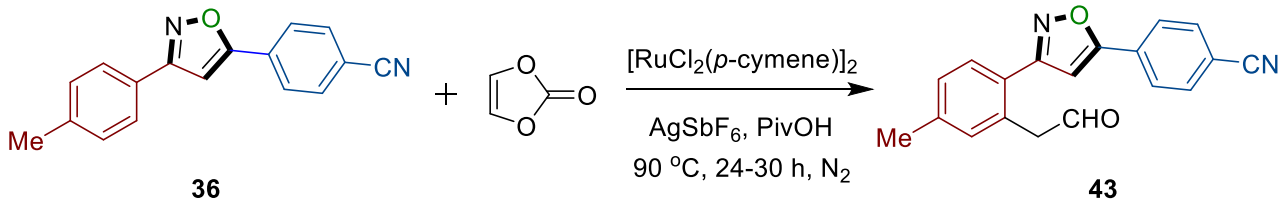
The Late-Stage-Diversification of product **4** was performed based on the previously reported procedure with light adjustment.[2] A sealed tube was loaded with **4** (0.2 mmol, 49.6 mg, 1.0 equiv), 4-bromobenzonitrile (5.0 equiv), $PdCl_2$ (0.1 equiv), and KOAc (2.0 equiv) in DMAc (1 mL) at 130 °C for 20 hours. The mixture was cooled to room temperature and subsequently extracted with EtOAc three times. The organic layer was dried with anhydrous Na_2SO_4. The solvent was concentrated, and the residue was purified by column chromatography on silica gel (*n*-hexane/dichloromethane, 1:2) to give **41** (46 mg, 66%).

(b) Late-Stage-Diversification of product 4



The Late-Stage-Diversification of product **4** was performed based on the previously reported procedure.[3] A sealed tube was loaded with **4** (0.2 mmol, 49.2 mg, 1.0 equiv), $Cu(OAc)_2$ (0.2 equiv), and *t*-DMACH (2.0 equiv) in dioxane (3 mL) at 140 °C for 36 hours. The mixture was cooled to room temperature and subsequently extracted with EtOAc three times. The organic layer was dried with anhydrous Na_2SO_4. The solvent was concentrated, and the residue was purified by column chromatography on silica gel (*n*-hexane/dichloromethane, 1:1) to give **42** (28 mg, 54%).

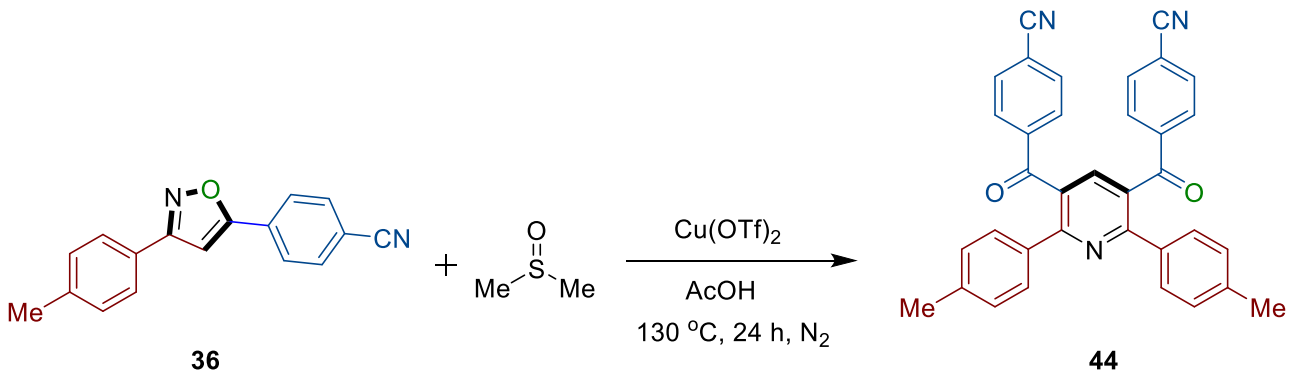
(c) Late-Stage-Diversification of product 36



The Late-Stage-Diversification of product **36** was performed based on the previously reported procedure.[4] In a pressure tube equipped with a stir bar, **36** (0.2 mmol, 52.2 mg, 1.0 equiv) was dissolved in HFIP (1.0 mL). The reaction mixture was degassed with nitrogen for 10 min followed by the addition of the vinylene carbonate (2.0 equiv), $[RuCl_2(p\text{-cymene})]_2$ (0.05 equiv), $AgSbF_6$ (0.5 equiv), and PivOH (0.50 equiv). The tube was fitted with a Teflon screw cap under a nitrogen flow, and the reaction mixture was heated to 90 °C and allowed to stir for 24-30 h. Upon cooling to room temperature, the reaction mixture was diluted with ethyl acetate and filtered through a pad of Celite. The filtrate was washed with a saturated solution of $NaHCO_3$ and brine. The organic extract was dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by

column chromatography on silica gel (dichloromethane) to give **43** (40 mg, 67%).

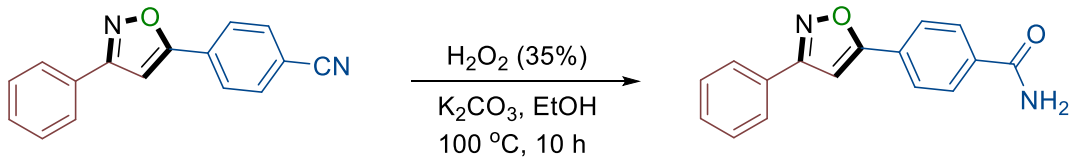
(d) Late-Stage-Diversification of product 36



36 **44**

The Late-Stage-Diversification of product **36** was performed based on the previously reported procedure.[5] In a pressure tube equipped with a stir bar, **36** (0.2 mmol, 52.2 mg, 1.0 equiv) was dissolved in dry DMSO (1.0 mL). The reaction mixture was stirred for 10-15 min followed by the addition of AcOH (2.0 equiv) and $Cu(OTf)_2$ (2.0 equiv). The tube was fitted with a Teflon screw cap under an N_2, and the reaction mixture was heated to 130 °C (oil bath) and allowed to stir for 24 h. Upon cooling to room temperature, the reaction mixture was diluted with ethyl acetate and filtered through a pad of Celite. The filtrate was washed with saturated solution of $NaHCO_3$ and brine. The organic extract was dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (dichloromethane) to give **44** (74 mg, 72%).

(e) Late-Stage-Diversification of product 4

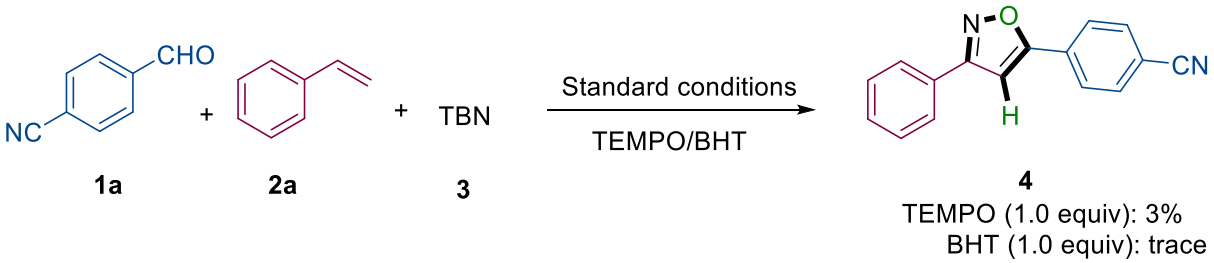


4 **45**

A sealed tube was loaded with **4** (0.2 mmol, 49.2 mg, 1.0 equiv), H_2O_2 (35%, 10.0 equiv), K_2CO_3 (2.0 equiv) and EtOH (1.0 mL). Under nitrogen atmosphere, the reaction mixture was stirred at 100 °C for 10 h. The mixture was cooled to room temperature and subsequently extracted with EtOAc three times. The organic layer was dried with anhydrous Na_2SO_4. The solvent was concentrated, and the residue was purified by recrystallization with ethanol to give **45** (43 mg, 81%).

6. Mechanistic Studies

6.1 Radical experiment



According to the established method, the TEMPO (0, and 1.0 equiv) was added into the reaction system under the standard conditions, respectively. After the reaction being completed, the peak area of **4** was determined by GC-MS using benzophenone as the internal standard (IS) as shown in **Fig. S1.**

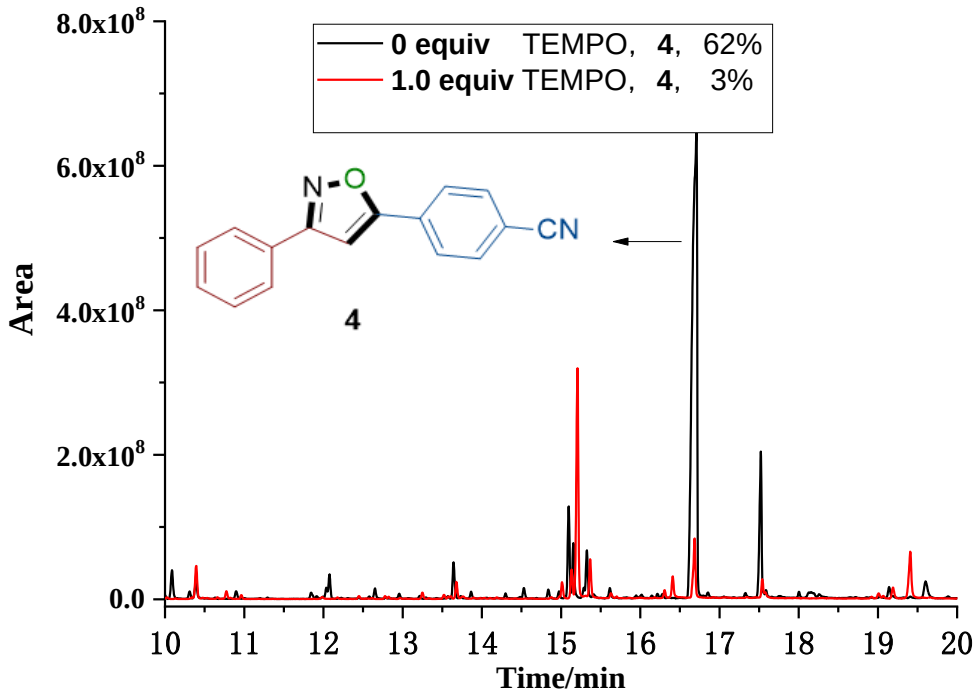


Fig. S1 The GC-MS profile of TEMPO experiments

According to the established method, BHT (0, and 1.0 equiv) was added into the reaction system under the standard conditions, respectively. After the reaction being completed, the peak area of **4** was determined by GC-MS using benzophenone as the internal standard (IS) as shown in **Fig. S2** and one adduct containing radical N=O was successfully captured by HR-MS technique and showed in **Fig. S3.**

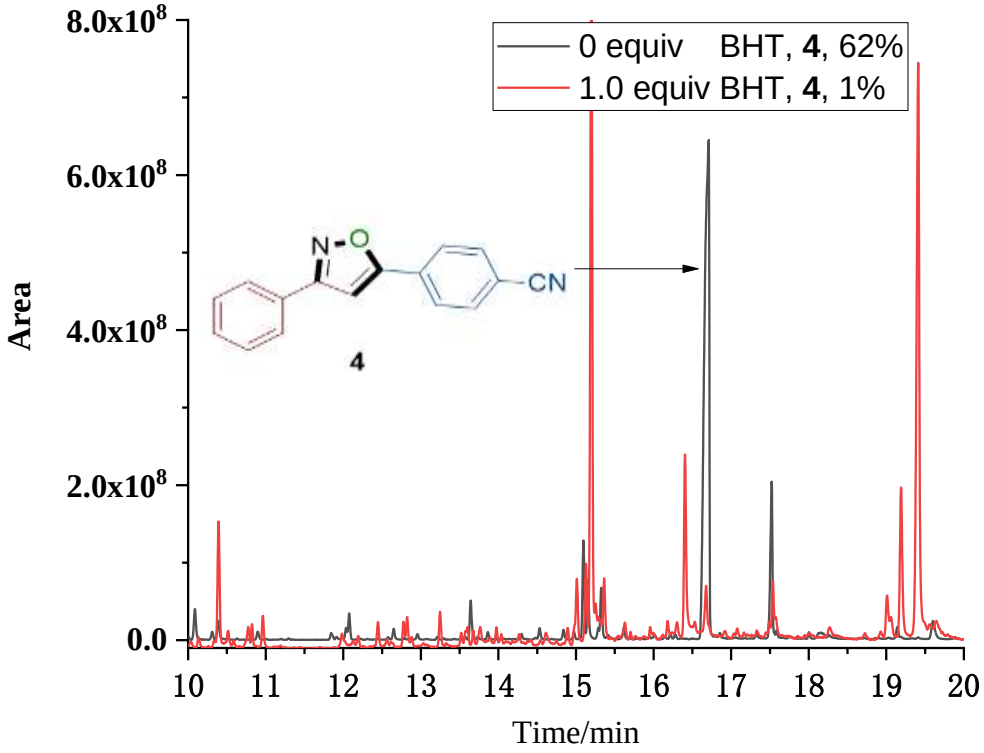


Fig. S2 The GC-MS profile of BHT experiments

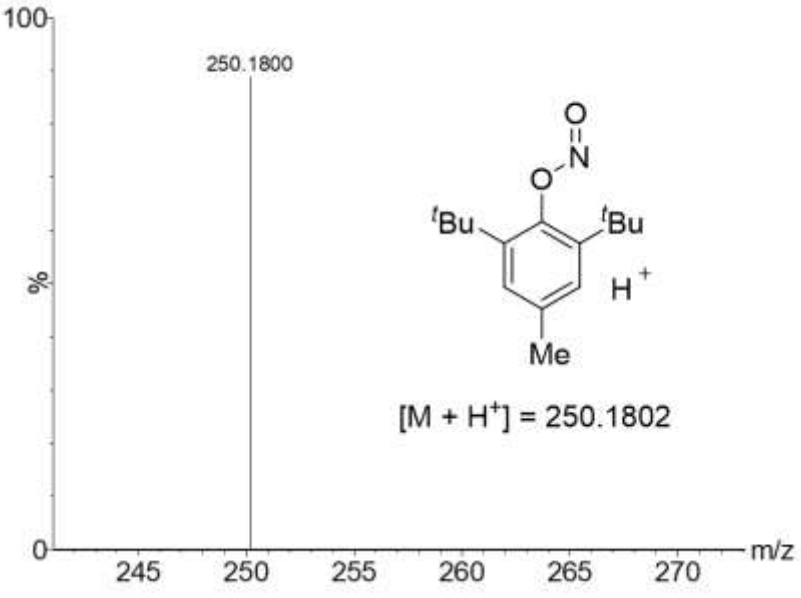
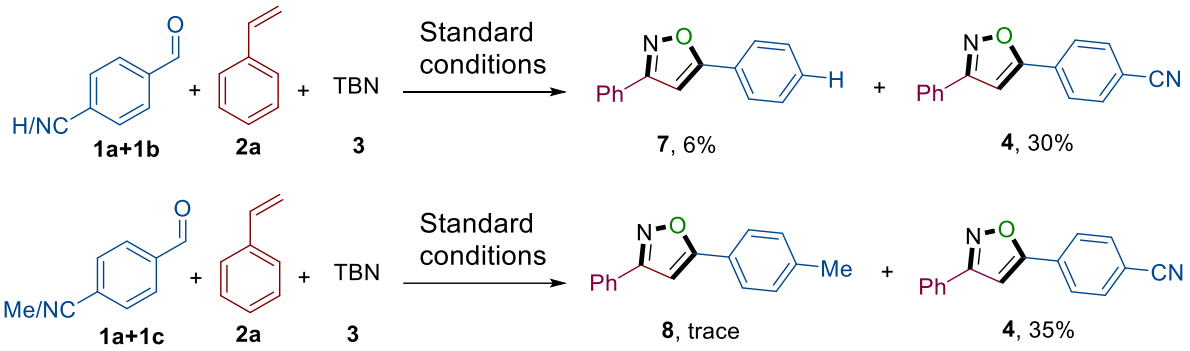


Fig. S3 The HR-MS data of BHT adducts **6**

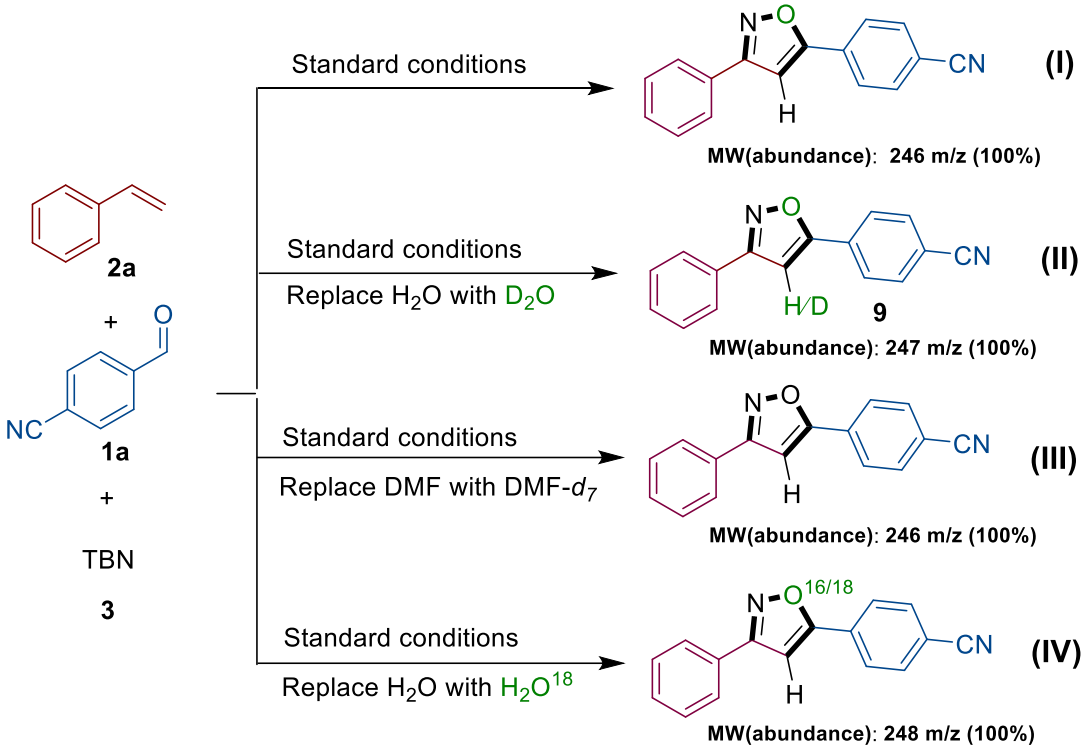
6.2 Intermolecular Competition Experiments



In an undivided cell with GF electrodes (10 mm x 15 mm x 6 mm) and Pt electrodes (10 mm x 15 mm x 0.25 mm), a mixture of aldehyde **1a** and **1b** (1:1, 0.75 mmol), **2a** (3.0 equiv), TBN (3.0 equiv), TFA (2.0 equiv), and *n*-Bu_4NBr (1.0 equiv) were added in DMF/H_2O (2:1, 3.0 mL). Electrocatalysis was performed at 100 °C with a constant current of 10 mA maintained for 9 h. After cooling to ambient temperature, a saturated aqueous $NaHCO_3$ (25 mL) was added and the reaction mixture was extracted with EtOAc (3 × 15 mL). The combined organic layers were washed with brine (25 mL), dried over Na_2SO_4, filtered and concentrated *in vacuo*. Purification by column chromatography on silica gel (*n*-hexane/Dichloromethane: 1/1→1/4) yielded the corresponding products **7** (5 mg, 6%) and **4** (28 mg, 30%).

In an undivided cell with GF electrodes (10 mm x 15 mm x 6 mm) and Pt electrodes (10 mm x 15 mm x 0.25 mm), a mixture of aldehyde **1a** and **1c** (1:1, 0.75 mmol), **2a** (3.0 equiv), TBN (3.0 equiv), TFA (2.0 equiv), and *n*-Bu_4NBr (1.0 equiv) were added in DMF/H_2O (2:1, 3.0 mL). Electrocatalysis was performed at 100 °C with a constant current of 10 mA maintained for 9 h. After cooling to ambient temperature, a saturated aqueous $NaHCO_3$ (25 mL) was added and the reaction mixture was extracted with EtOAc (3 × 15 mL). The combined organic layers were washed with brine (25 mL), dried over Na_2SO_4, filtered and concentrated *in vacuo*. Purification by column chromatography on silica gel (*n*-hexane/Dichloromethane: 1/1→1/4) yielded the corresponding products **8** (trace) and **4** (32 mg, 35%).

6.3 Isotope experiments



Scheme S1 Isotope labeling experiments

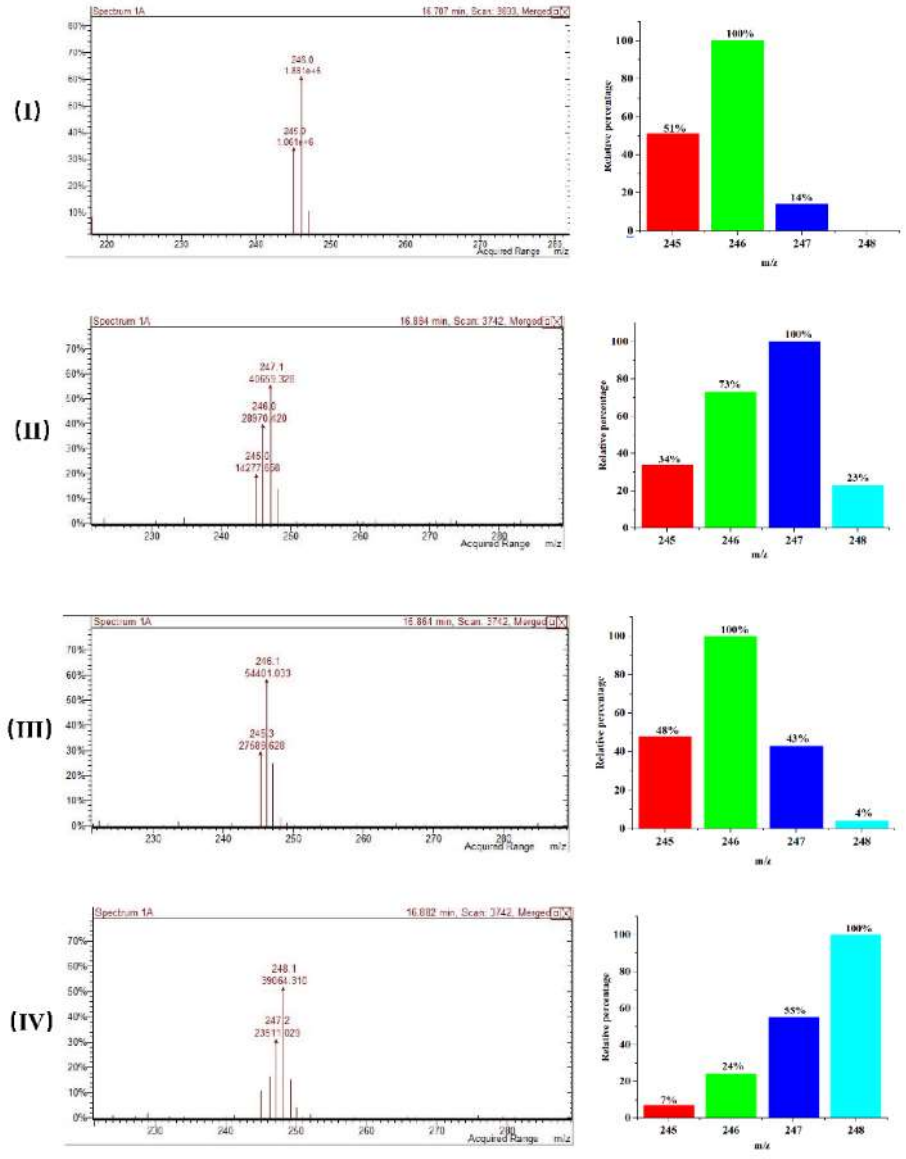
(I) In an undivided cell with GF electrodes (10 mm x 15 mm x 6 mm) and Pt electrodes (10 mm x 15 mm x 0.25 mm), aldehyde **1a** (0.75 mmol), **2a** (3.0 equiv), TBN (3.0 equiv), TFA (2.0 equiv), and *n*-Bu_4NBr (1.0 equiv) were added in DMF/H_2O (2:1, 3.0 mL). Electrocatalysis was performed at 100 °C with a constant current of 10 mA maintained for 9 h. After cooling to ambient temperature, a saturated aqueous $NaHCO_3$ (25 mL) was added and the reaction mixture was extracted with EtOAc (3 × 15 mL). The combined organic layers were washed with brine (25 mL), dried over Na_2SO_4, filtered and concentrated *in vacuo*. Subsequently, the reaction solution including product **4** was diluted with EtOAc to desired concentrations and passed through a 0.22 μm Millipore membrane filter prior to GC-MS analysis.

(II) In an undivided cell with GF electrodes (10 mm x 15 mm x 6 mm) and Pt electrodes (10 mm x 15 mm x 0.25 mm), aldehyde **1a** (0.75 mmol), **2a** (3.0 equiv), TBN (3.0 equiv), TFA (2.0 equiv), and *n*-Bu_4NBr (1.0 equiv) were added in DMF/D_2O (2:1, 3.0 mL). Electrocatalysis was performed at 100 °C with a constant current of 10 mA maintained for 9 h. After cooling to ambient temperature, a saturated aqueous $NaHCO_3$ (25 mL) was added and the reaction mixture was extracted with EtOAc (3 × 15 mL). The combined organic layers were washed with brine (25 mL), dried over Na_2SO_4, filtered and concentrated *in vacuo*. Subsequently, the reaction solution was diluted with EtOAc to desired concentrations and passed through a 0.22 μm Millipore membrane filter prior to GC-MS analysis. Additionally, the crude product was purified by column chromatography on silica gel (*n*-hexane/ Dichloromethane, 1/2) to yield the product **9** (119mg, 64%).

(III) In an undivided cell with GF electrodes (10 mm x 15 mm x 6 mm) and Pt electrodes (10 mm x 15 mm x 0.25 mm), aldehyde **1a** (0.75 mmol), **2a** (3.0 equiv), TBN (3.0 equiv), TFA (2.0 equiv), and nBu_4NBr (1.0 equiv) were

added in DMF-d_7/H_2O (2:1, 3.0 mL). Electrocatalysis was performed at 100 °C with a constant current of 10 mA maintained for 9 h. After cooling to ambient temperature, a saturated aqueous $NaHCO_3$ (25 mL) was added and the reaction mixture was extracted with EtOAc (3 × 15 mL). The combined organic layers were washed with brine (25 mL), dried over Na_2SO_4, filtered and concentrated *in vacuo*. Subsequently, the reaction solution including product **4** was diluted with EtOAc to desired concentrations and passed through a 0.22 μm Millipore membrane filter prior to GC-MS analysis.

(IV) In an undivided cell with GF electrodes (10 mm x 15 mm x 6 mm) and Pt electrodes (10 mm x 15 mm x 0.25 mm), aldehyde **1a** (0.75 mmol), **2a** (3.0 equiv), TBN (3.0 equiv), TFA (2.0 equiv), and nBu_4NBr (1.0 equiv) were added in DMF-d_7/H_2O[18] (2:1, 3.0 mL). Electrocatalysis was performed at 100 °C with a constant current of 10 mA maintained for 9 h. After cooling to ambient temperature, a saturated aqueous $NaHCO_3$ (25 mL) was added and the reaction mixture was extracted with EtOAc (3 × 15 mL). The combined organic layers were washed with brine (25 mL), dried over Na_2SO_4, filtered and concentrated *in vacuo*. Subsequently, the reaction solution including product **4** was diluted with EtOAc to desired concentrations and passed through a 0.22 μm Millipore membrane filter prior to GC-MS analysis.



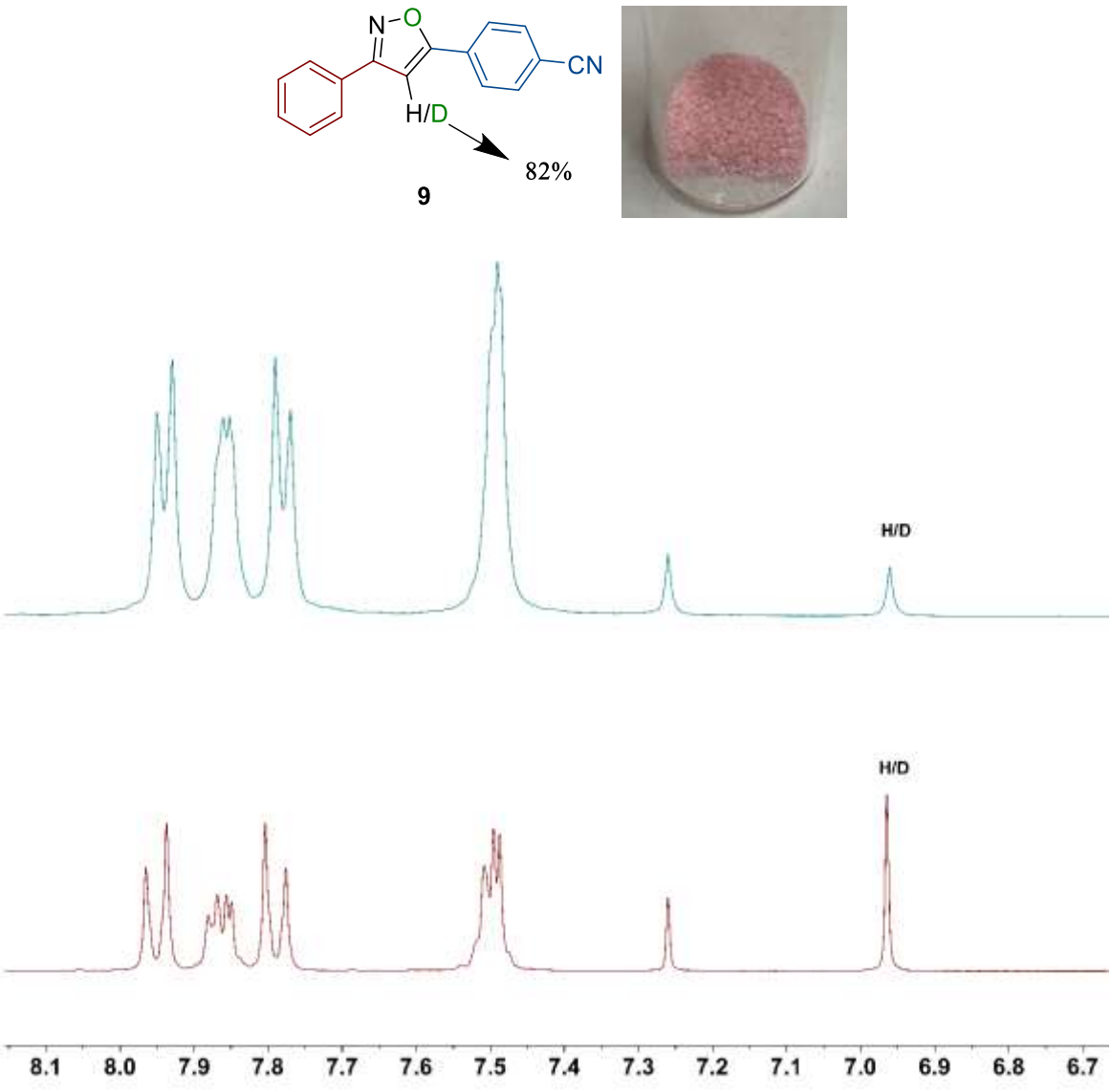
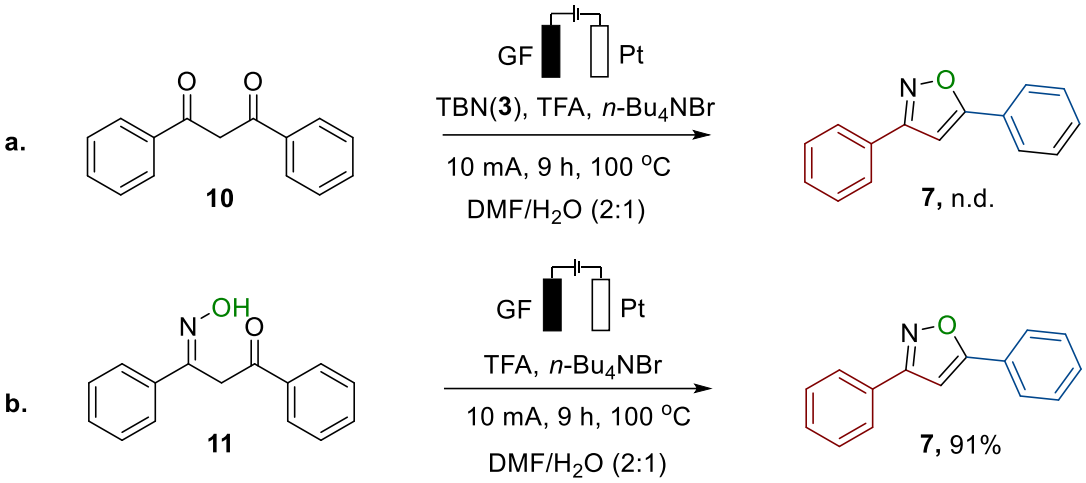


Fig. S4 NMR analysis for Deuterated product **9**

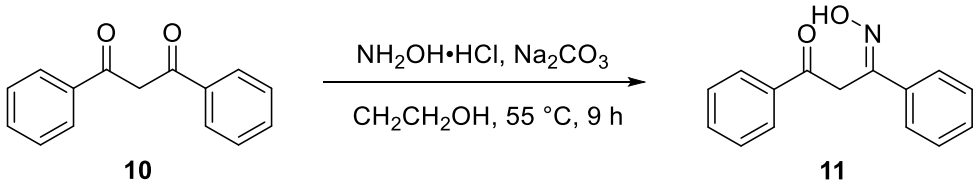
6.4 Intermediate experiments



Reaction **a**: To an undivided two-necked flask equipped with a teflon-coated magnetic stirring bar and teflon cap, GF electrodes (10 mm x 10 mm x 6 mm) and Pt electrodes (10 mm x 10 mm x 0.25 mm), **10** (0.75 mmol, 0.168 g), TBN (2.25 mmol, 3.0 equiv), TFA (1.5 mmol, 2.0 equiv), and *n*-Bu_4NBr (243 mg, 1.0 equiv) were added in DMF/H_2O (2:1, 3.0 mL). Electrocatalysis was performed at 100 °C with a constant current of 10 mA maintained for 48 h. After cooling to ambient temperature, a saturated aqueous $NaHCO_3$ (25 mL) was added and the reaction mixture was extracted with EtOAc (3 × 15 mL). The combined organic layers were washed with brine (25 mL), dried over Na_2SO_4, filtered and concentrated in vacuo. The crude product was purified by column chromatography on silica gel (*n*-hexane/Dichloromethane, 1/1) to yield the product **7** (0 mg, 0%).

Reaction **b**: To an undivided two-necked flask equipped with a teflon-coated magnetic stirring bar and teflon cap, GF electrodes (10 mm x 10 mm x 6 mm) and Pt electrodes (10 mm x 10 mm x 0.25 mm), **11** (0.75 mmol, 0.179 g), TFA (1.5 mmol, 2.0 equiv), and *n*-Bu_4NBr (243 mg, 1.0 equiv) were added in DMF/H_2O (2:1, 3.0 mL). Electrocatalysis was performed at 100 °C with a constant current of 10 mA maintained for 48 h. After cooling to ambient temperature, a saturated aqueous $NaHCO_3$ (25 mL) was added and the reaction mixture was extracted with EtOAc (3 × 15 mL). The combined organic layers were washed with brine (25 mL), dried over Na_2SO_4, filtered and concentrated in vacuo. The crude product was purified by column chromatography on silica gel (*n*-hexane/ Dichloromethane, 1/1) to yield the product **7** (151 mg, 91%).

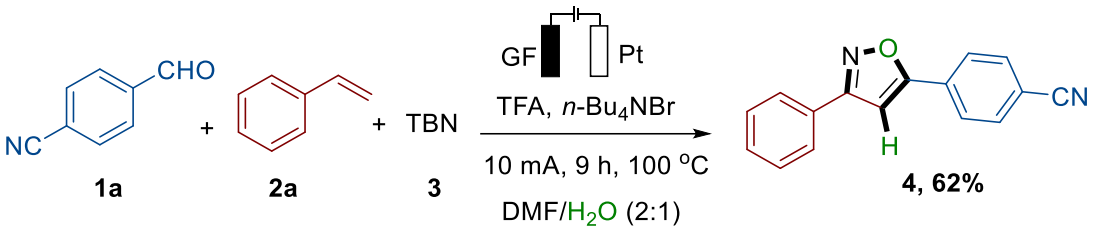
Synthetic Procedure for Intermediate 11:



To an oven-dried Schlenk bottle (10 mL) with a magnetic bar was added dibenzoylmethane (1.5 mmol, 243 mg, 1.0 equiv), $NH_2OH{\cdot}HCl$ (1.0 equiv), Na_2CO_3 (2.0 equiv) and ethanol (2 mL). The mixture was stirred at 55 °C for 9 h. After cooling to room temperature, the mixture was extracted with EtOAc. The organic phase dried over Na_2SO_4. The solvent was evaporated, and the residue was purified by flash chromatography on silica gel (Dichloromethane /ethyl acetate, 25:1) to afford the product **11** (215 mg, 60%).

6.5 Kinetic studies

Time course experiment



In an undivided cell with GF electrodes (10 mm x 15 mm x 6 mm) and Pt electrodes (10 mm x 15 mm x 0.25 mm), the mixture containing aldehyde **1a** (0.75 mmol, 99 mg), alkene **2a** (2.25 mmol, 3.0 equiv), TBN (2.25 mmol, 3.0 equiv), TFA (1.5 mmol, 2.0 equiv), and *n*-Bu_4NBr (1.5 mmol, 1.0 equiv) was diluted with DMF/H_2O (2:1) to 3.0 mL. Electrocatalysis was performed at 100 °C with a constant current of 10 mA. The reaction tube was taking out oil bath at 0.5 h, 1.0 h, 2.0 h, 4.0 h, 5 h, 6 h, 7.5 h, and 9 h. The reaction mixture was filtered with EA *via* a small section silica gel (200-300 mesh), and a small amount of solution was syringed out for analysis.

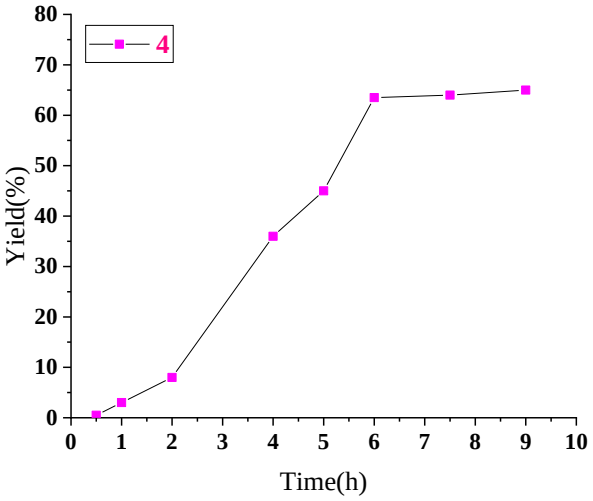


Fig. S5 Line chart of reaction monitoring

Table S2. The concentration of product **4** in different concentration of styrene (**2a**) at different time interval.

Time (min)	0.25 M [PhCH=CH_2]	0.50 M [PhCH=CH_2]	0.75 M [PhCH=CH_2]	1.0 M [PhCH=CH_2]
1500	0.00912	0.01140	0.01503	0.01603
2100	0.01862	0.02115	0.02584	0.03284
2700	0.02539	0.03248	0.03761	0.04761
3300	0.03416	0.04084	0.04784	0.06084

Table S3. The k_{in} value of product **4** in different concentration of styrene (**2a**).

3 (M)	k_{in} (10^{-5} Ms^{-1})	R^2	b
0.25 M	1.36477	0.99439	-0.01093
0.50 M	1.66067	0.99538	-0.01339
0.75 M	1.83687	0.99902	-0.01250
1.00 M	2.48688	0.99567	-0.02035

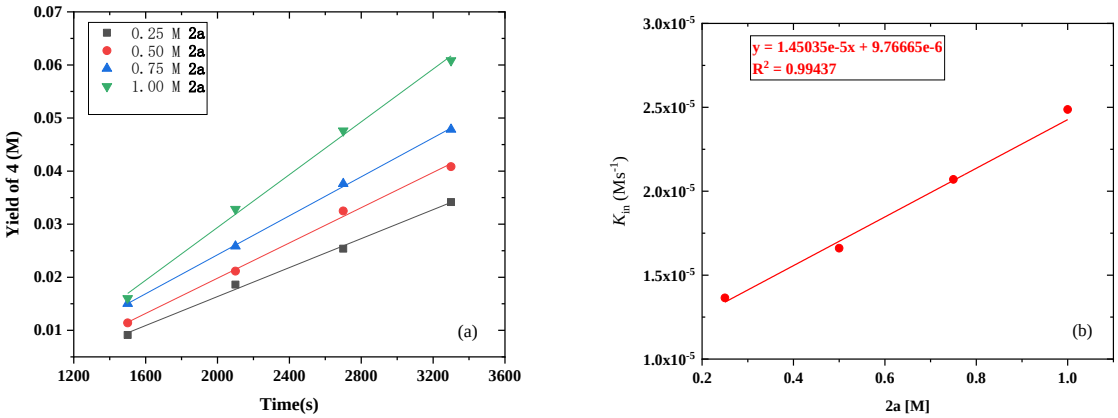


Fig. S6 Kinetic investigation 1**:** (a) Plot of the rise of product **4** from the reaction of **1a** (0.0833 M), **TBN** (0.25 M), **TFA** (0.1667 M) with 0.25 M, 0.50 M, 0.75 M, 1.00 M of **2a** in different time interval. The curve depicts the results of an unweighted least-square fit to y = k*x + b. (b) Plot of k_{in} versus **2a** from the reaction of **1a** (0.0833 M), **TBN** (0.25 M), **TFA** (0.1667 M) with 0.25 M, 0.50 M, 0.75 M, 1.00 M of **2a**. The curve depicts the results of an unweighted least-square fit to y = k*x + b.

Table S4. The concentration of product **4** in different concentration of **4-CNPhCHO** (**1a**) at different time interval.

Time (min)	0.25 M [4-CNPhCHO]	0.50 M [4-CNPhCHO]	0.75M [4-CNPhCHO]
1500	0.00912	0.01140	0.01503
2100	0.01862	0.02115	0.02584
2700	0.02539	0.03248	0.03761
3300	0.03416	0.04084	0.04784

Table S5. The k_{in} value of product **4** in different concentration of styrene (**2a**).

3 (M)	k_{in} (10^{-5} Ms^{-1})	R^2	b
0.25 M	0.54282	0.98408	-0.00254
0.50 M	1.32273	0.99460	-0.00905
0.75 M	1.93545	0.99921	-0.01529
1.00 M	2.42608	0.99798	-0.01859

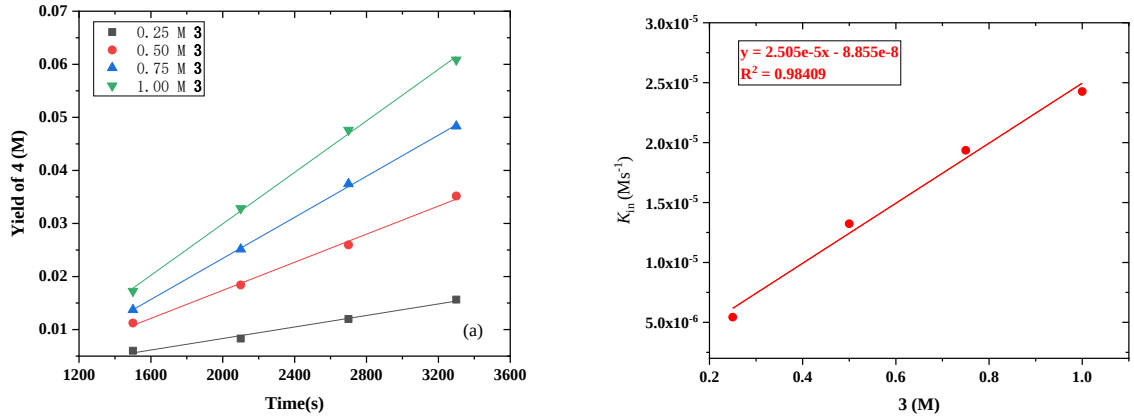


Fig. S7 Kinetic investigation 2: (a) Plot of the rise of product **4** from the reaction of **1a** (0.0833 M), **2a** (0.25 M), **TFA** (0.1667 M) with 0.25 M, 0.50 M, 0.75 M, 1.00 M of **TBN** in different time interval. The curve depicts the results of an unweighted least-square fit to y = k*x + b. (b) Plot of k_{in} versus **3** from the reaction of **1a** (0.0833 M),

2a (0.25 M), **TFA** (0.1667 M) with 0.25 M, 0.50 M, 0.75 M, 1.00 M of **3**. The curve depicts the results of an unweighted least-square fit to y = k*x + b.

Table S6. The concentration of product **4** in different concentration of **4-CNPhCHO** (**1a**) at different time interval.

Time (min)	0.0833 M [1a]	0.1666 M [1a]	0.2499 M [1a]	0.3332 M [1a]
1500	0.01584	0.01512	0.01569	0.01334
2100	0.02679	0.02704	0.02686	0.02432
2700	0.03965	0.04001	0.0391	0.0361
3300	0.04981	0.0504	0.04912	0.04718

Table S7. The k_{in} value of product **4** in different concentration of **4-CNPhCHO** (**1a**).

3 (M)	k_{in} (10^{-5} Ms^{-1})	R^2	b
0.0833 M	1.91283	0.99723	-0.01289
0.1666 M	1.88996	0.9973	-0.01405
0.2499 M	1.87575	0.99793	-0.01232
0.3332 M	1.88803	0.99604	-0.01318

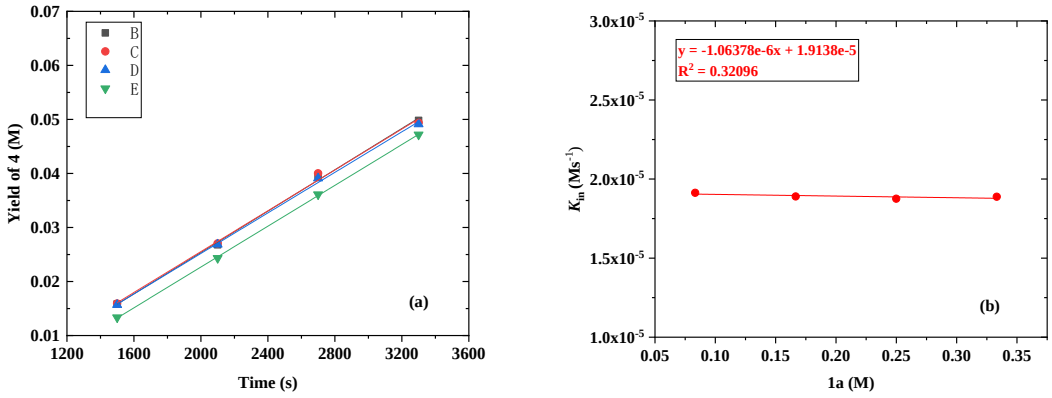


Fig. S8 Kinetic investigation 3: (a) Plot of the rise of product **4** from the reaction of **2a** (0.25 M), **TBN** (0.25 M), **TFA** (0.1667 M) with 0.0833 M, 0.1666 M, 0.2499 M, 0.3332 M of **1a** in different time interval. The curve depicts the results of an unweighted least-square fit to y = k*x + b. (b) Plot of k_{in} versus **3** from the reaction of **2a** (0.25 M), **TBN** (0.25 M), **TFA** (0.1667 M) with 0.0833 M, 0.1666 M, 0.2499 M, 0.3332 M of **1a**. The curve depicts the results of an unweighted least-square fit to y = k*x + b.

6.6 Cyclic Voltammetry

The cyclic voltammetry was performed with a Metrohm Autolab PGSTAT204 workstation and the analysis was conducted with a Nova 2.0 software. A glassy-carbon electrode (3 mm-diameter, disc-electrode) was used as the working electrode, a Pt wire as the auxiliary electrode and a saturated calomel electrode (SCE) was employed as the reference. The measurements were carried out at a scan rate of 100 mVs^{-1}. The operating temperature was at 298 K under inert conditions with **1a** as the model substrate.

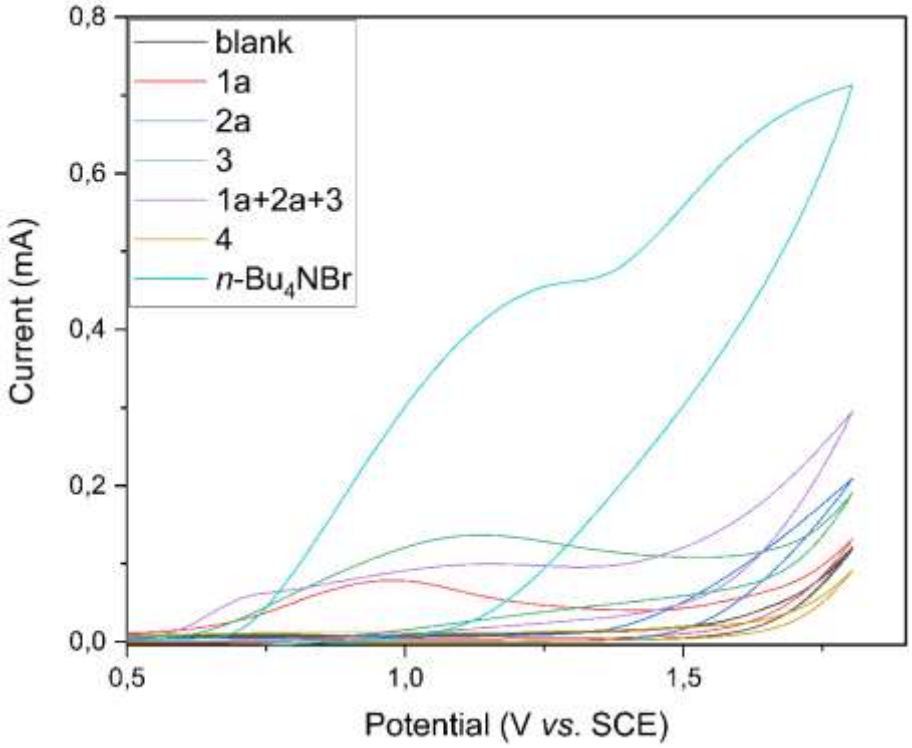


Fig. S9 Cyclic voltammetry at 100 mVs^{-1} in DMF/H_2O (2:1) using tetrabutylammonium hexafluorophosphate ($TBAPF_6$, 100 mM) as electrolyte: effect of reaction components and product. Concentrations of **1a**, **2a**, **3,** and **4** are 25 μM.

6.7 Control experiments

6.7.1 Control experiments without acid

In an undivided cell with GF electrodes (10 mm x 15 mm x 6 mm) and Pt electrodes (10 mm x 15 mm x 0.25 mm), the mixture containing aldehyde **1a** (0.75 mmol, 99 mg), alkene **2a** (2.25 mmol, 3.0 equiv), TBN (2.25 mmol, 3.0 equiv), and *n*-Bu_4NBr (0.75 mmol, 1.0 equiv) was diluted with DMF/H_2O (2:1) to 3.0 mL. Electrocatalysis was performed at 100 °C with a constant current of 10 mA maintained for 9 h. After cooling to ambient temperature, a saturated aqueous $NaHCO_3$ (25 mL) was added and the reaction mixture was extracted with EtOAc (3 × 15 mL). The combined organic layers were washed with brine (25 mL), dried over Na_2SO_4, filtered and concentrated *in vacuo*. The crude product was purified by column chromatography on silica gel (*n*-hexane/ Dichloromethane, 1/2) to yield the product **4** (103 mg, 42%).

6.7.2 Control experiments without H_2O

In an undivided cell with GF electrodes (10 mm x 15 mm x 6 mm) and Pt electrodes (10 mm x 15 mm x 0.25 mm), the mixture containing aldehyde **1a** (0.75 mmol, 99 mg), alkene **2a** (2.25 mmol, 3.0 equiv), TBN (2.25 mmol, 3.0 equiv), TFA (1.5 mmol, 2.0 equiv), and *n*-Bu_4NBr (0.75 mmol, 1.0 equiv) was diluted with DMF to 3.0 mL. Electrocatalysis was performed at 100 °C with a constant current of 10 mA maintained for 9 h. After cooling to ambient temperature, a saturated aqueous $NaHCO_3$ (25 mL) was added and the reaction mixture was extracted with EtOAc (3 × 15 mL). The combined organic layers were washed with brine (25 mL), dried over Na_2SO_4, filtered and concentrated *in vacuo*. The crude product was purified by column chromatography on silica gel (*n*-hexane/ Dichloromethane, 1/2) to yield **4** (15 mg, 8%).

6.7.3 Control experiments with D_2O

In an undivided cell with GF electrodes (10 mm x 15 mm x 6 mm) and Pt electrodes (10 mm x 15 mm x 0.25 mm), the mixture containing product **4** (0.75 mmol), TFA (1.5 mmol, 2.0 equiv), and *n*-Bu_4NBr (0.75 mmol, 1.0 equiv) was diluted with DMF/D_2O to 3.0 mL. Electrocatalysis was performed at 100 °C with a constant current of 10 mA for 3 h. After cooling to ambient temperature, a saturated aqueous $NaHCO_3$ (25 mL) was added, and the reaction mixture was extracted with EtOAc (3 × 15 mL). The combined organic layers were washed with brine (25 mL), dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude product was purified by column chromatography on silica gel (*n*-hexane/ Dichloromethane, 1/2) to yield the product **9** (132 mg, 71%).

6.8 By-product

Following the completion of the reaction under standard conditions, the reaction mixture underwent filtration using EA through a small-section silica gel (200-300 mesh). A small aliquot of the solution was then extracted for analysis. The GC-MS analysis, depicted in **Fig. S10**, revealed the composition of the reaction system. Notably, **Fig. S11** exhibits the successful detection of an adduct containing the radical Br.

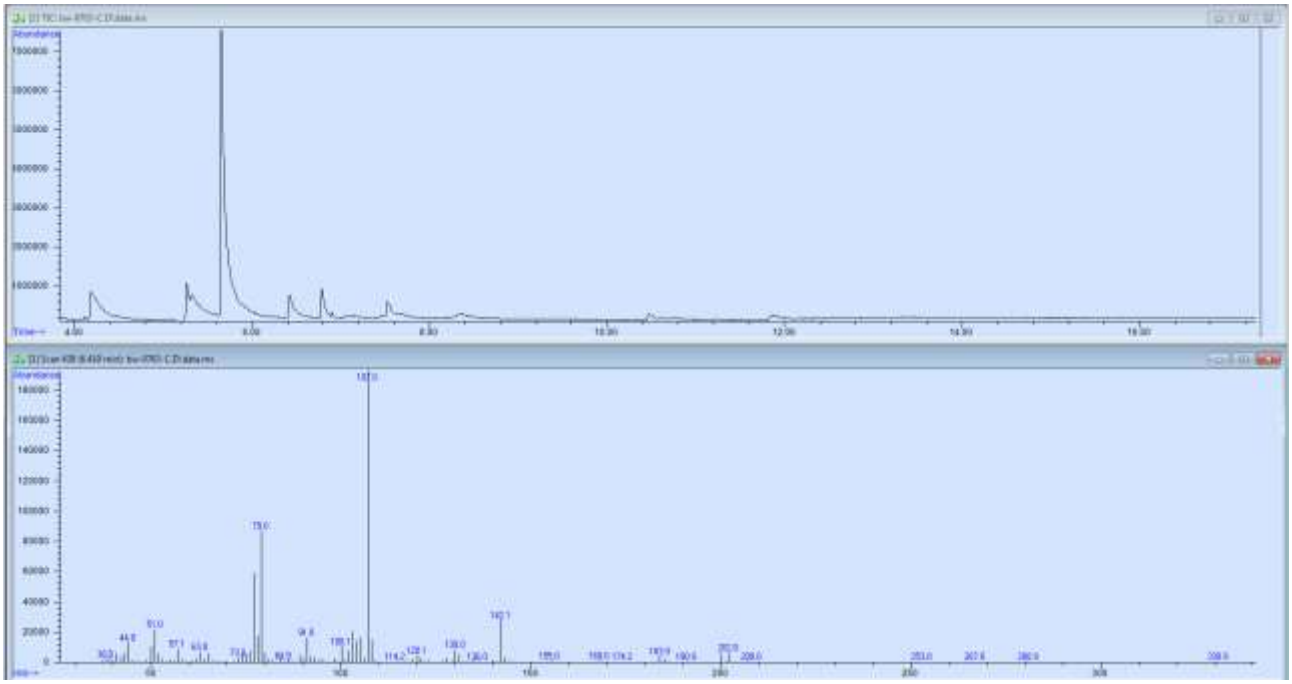


Fig. S10 GC-MS analysis for the by-product under standard conditions

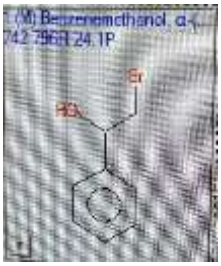


Fig. S11 The structure of the by-product 2-bromo-1-phenylethan-1-ol at 6.42 min

6.9 The plots of concentration versus time of product 4

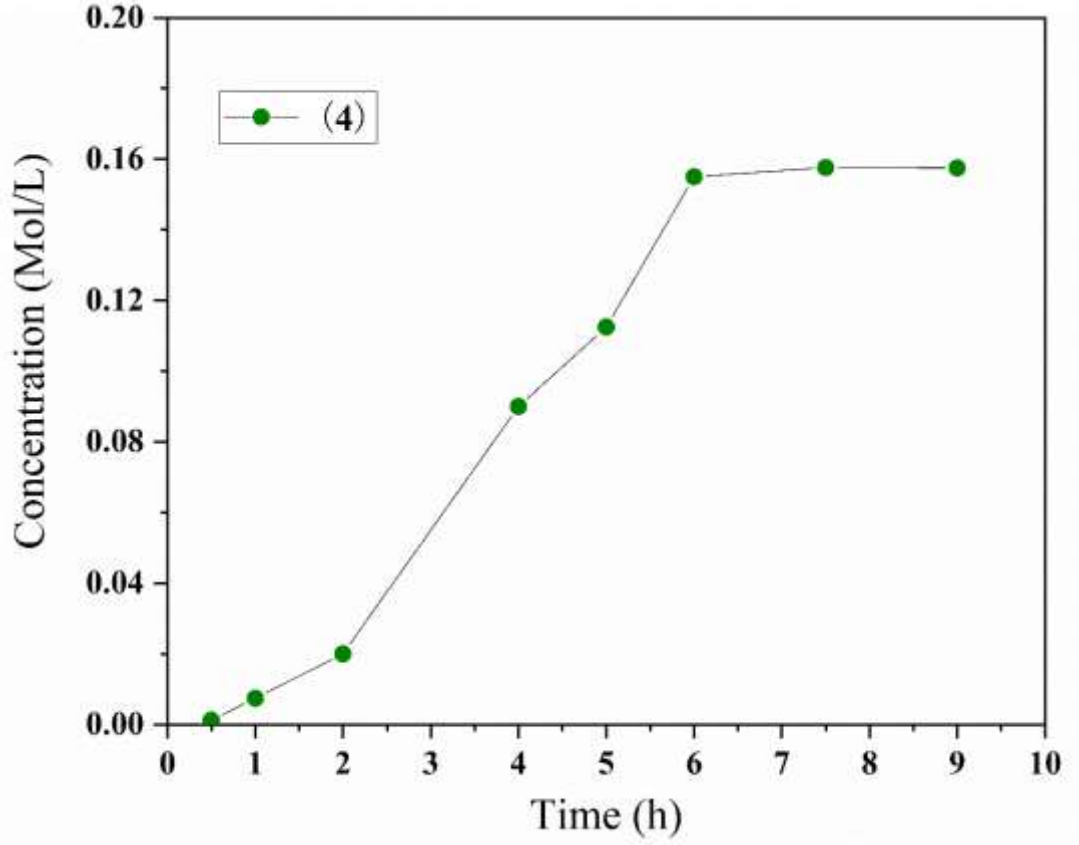
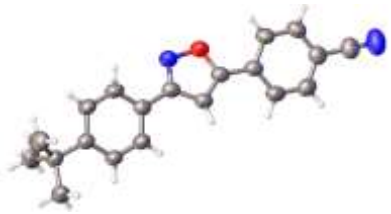


Fig. S12 Formation of **4** dependent on time and concentration.

7. X-ray Crystal data

Crystallographic data for compound **40** (CCDC-2267215) has been deposited with the Cambridge Crystallographic Data Centre, Copies of the data can be obtained, free of charge, on application to CCDC (Email:deposit@ccdc.cam.ac.uk).



Bond precision:	C-C = 0.0017 A	Wavelength=1.54184	
Cell:	a=6.00486(6)	b=7.13118(10)	c=37.8376(4)
	alpha=90	beta=91.6595(9)	gamma=90
Temperature:	293 K		
	Calculated		Reported
Volume	1619.58(3)		1619.58(3)
Space group	P 21/n		P 1 21/n 1
Hall group	-P 2yn		-P 2yn
Moiety formula	C20 H18 N2 O		C20 H18 N2 O
Sum formula	C20 H18 N2 O		C20 H18 N2 O
Mr	302.36		302.36
Dx, g cm-3	1.240		1.240
Z	4		4
Mu (mm-1)	0.608		0.608
F000	640.0		640.0
F000’	641.78		
h,k,lmax	7,8,46		7,8,46
Nref	3251		3111
Tmin,Tmax	0.875,0.896		0.689,1.000
Tmin’	0.875		

Correction method= # Reported T Limits: Tmin=0.689 Tmax=1.000

AbsCorr = MULTI-SCAN

Data completeness= 0.975	Theta(max)= 72.976
R(reflections)= 0.0430(2907)	wR2(reflections)= 0.1241(3111)
S = 1.040	Npar = 212

8. References

[1] L. Chen, Z. Wang, H. Liu, X. Li and B. Wang, *Chem. Commun.*, 2022, **58**, 9152.

[2] Y. Fall, C. Reynaud, H. Doucet, and M. Santelli. *Eur. J. Org. Chem.* 2009, **2009**, 4041.

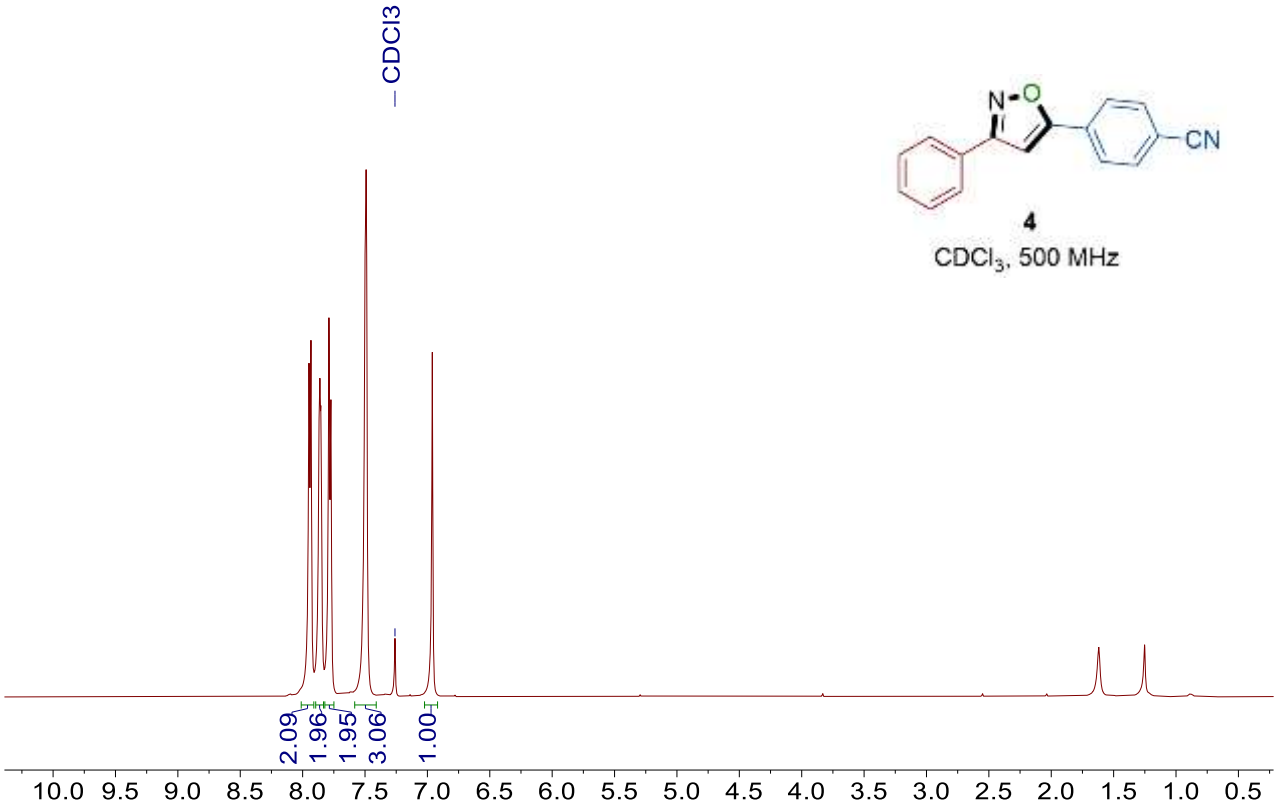
[3] C. Wan, J. Y. Pang, W. Jiang, X. W. Zhang, and X. G. Hu. *J. Org. Chem.* 2021, **86**, 4557.

[4] P. Kumar and M. Kapur, *Chem. Commun.*, 2022, **58**, 4476.

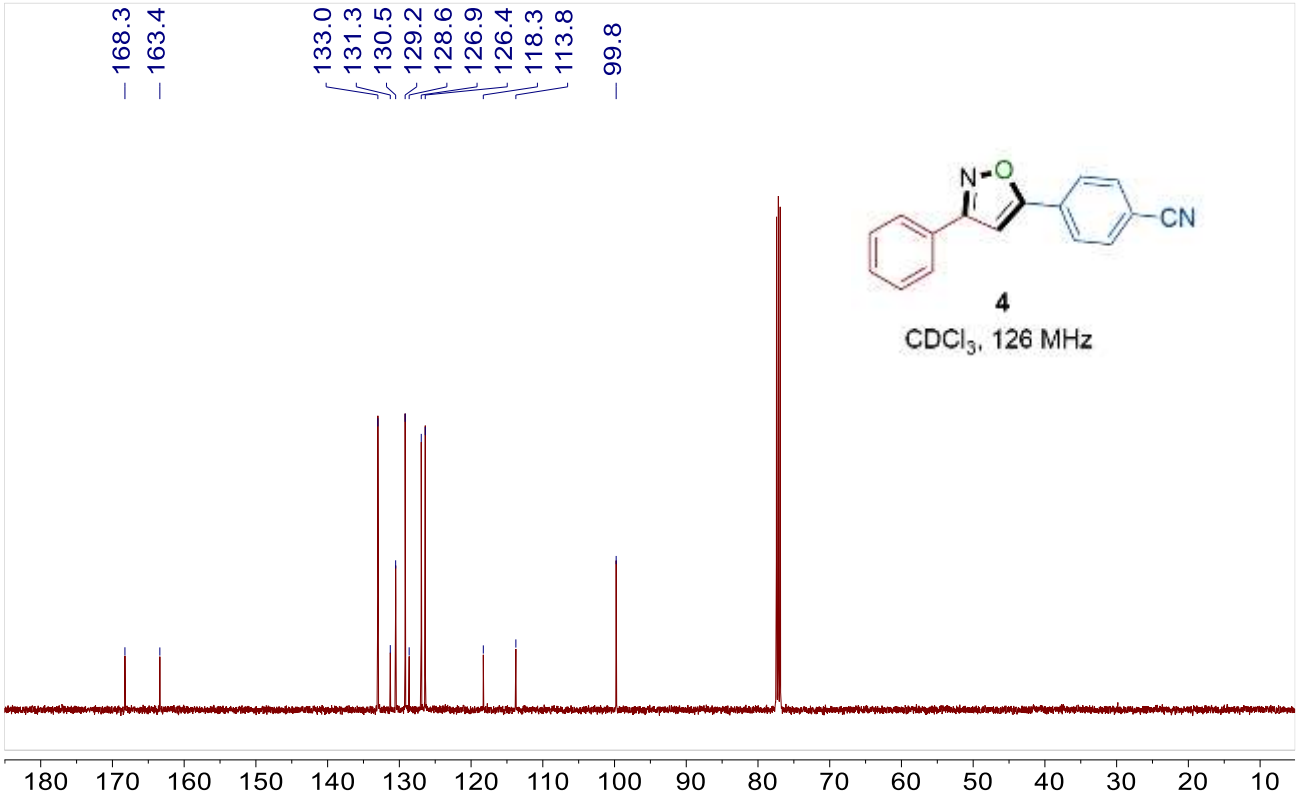
[5] P. Kumar and M. Kapur, Org. Lett., 2020, **22**, 5855.

9. The ^{1}H NMR and ^{13}C NMR Spectra of products

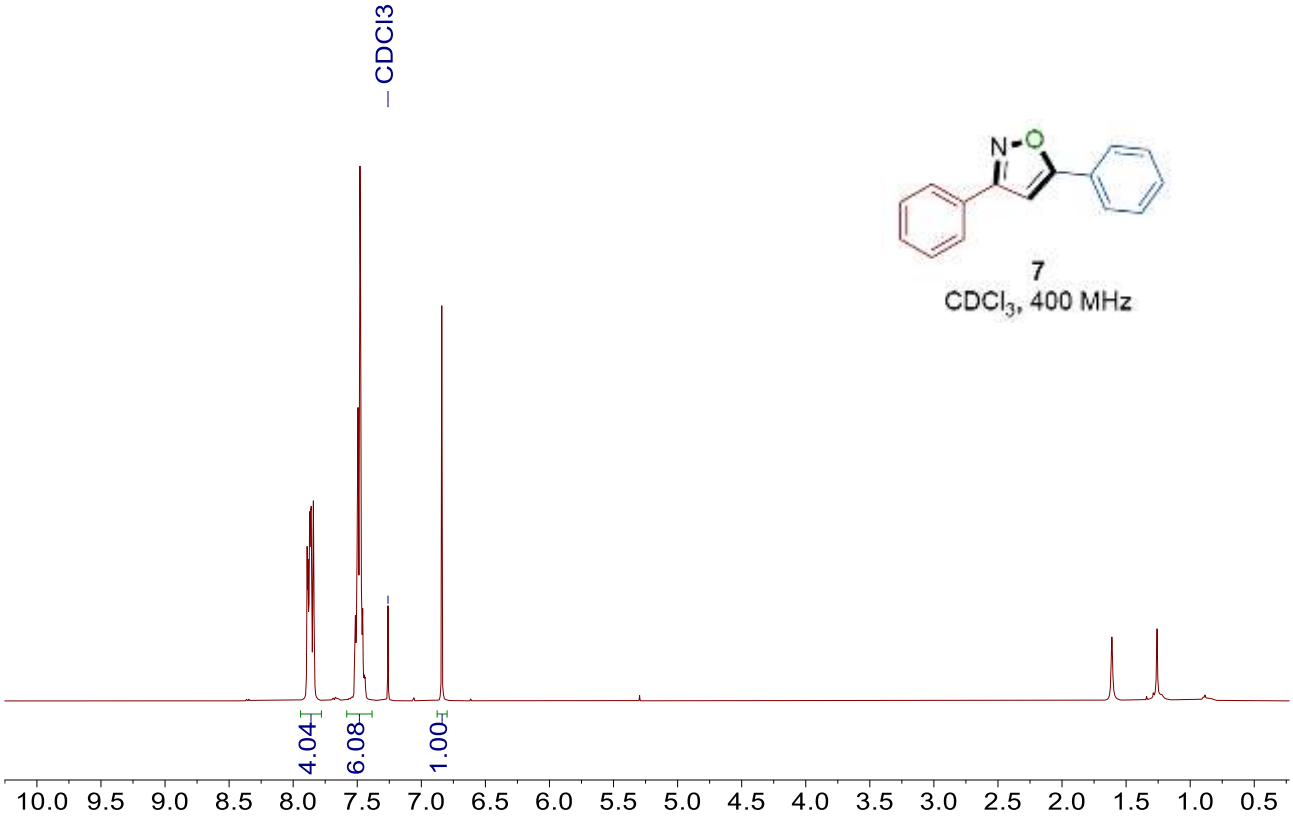
^{1}H NMR spectrum of **4**



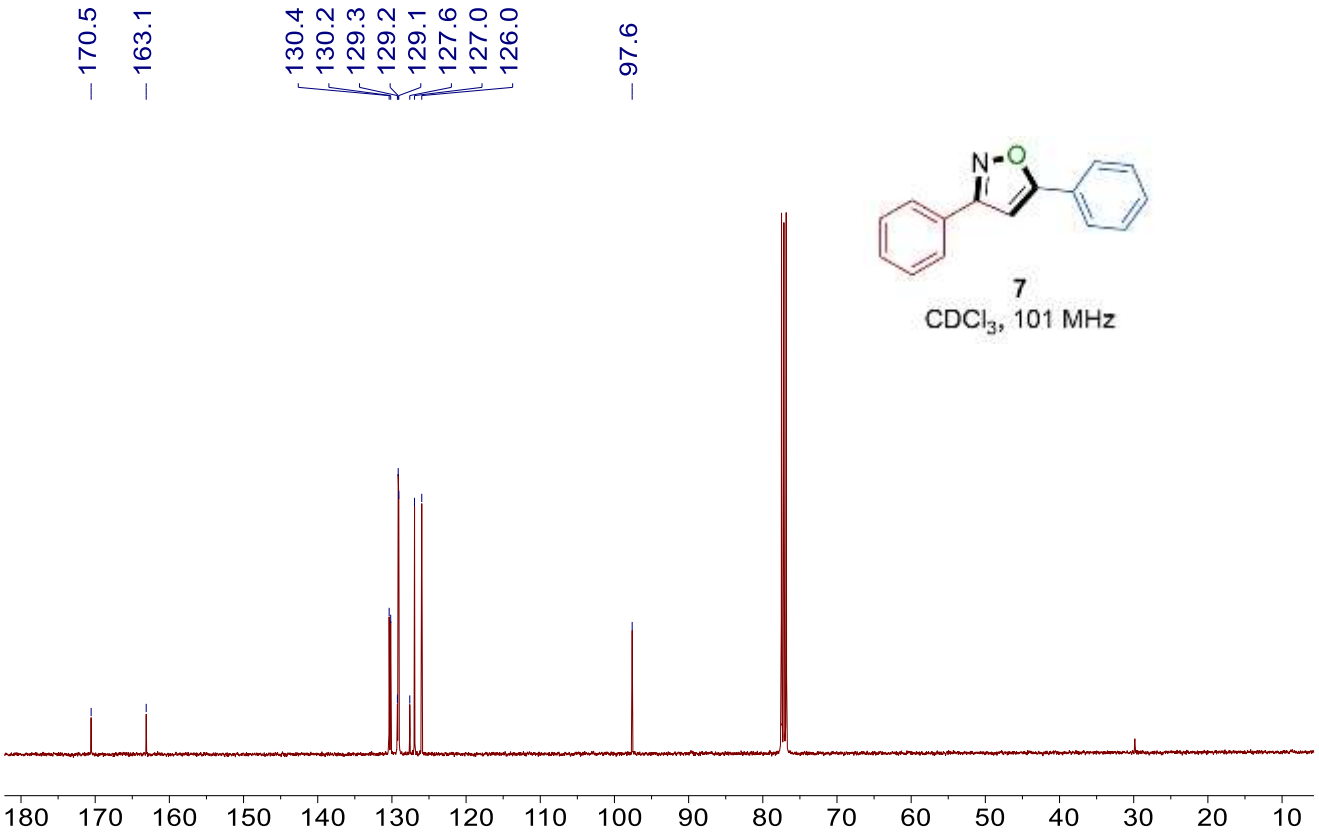
^{13}C NMR spectrum of **4**



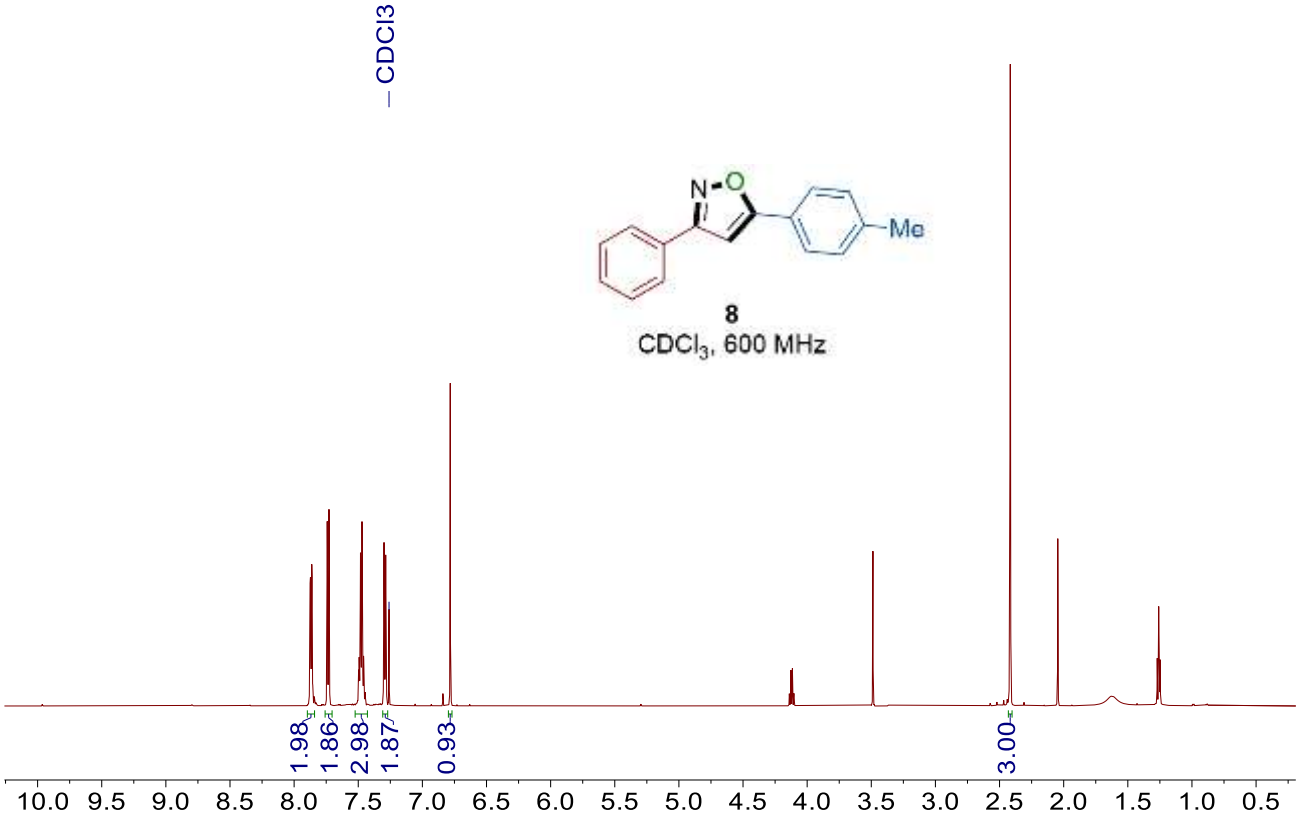
^{1}H NMR spectrum of **7**



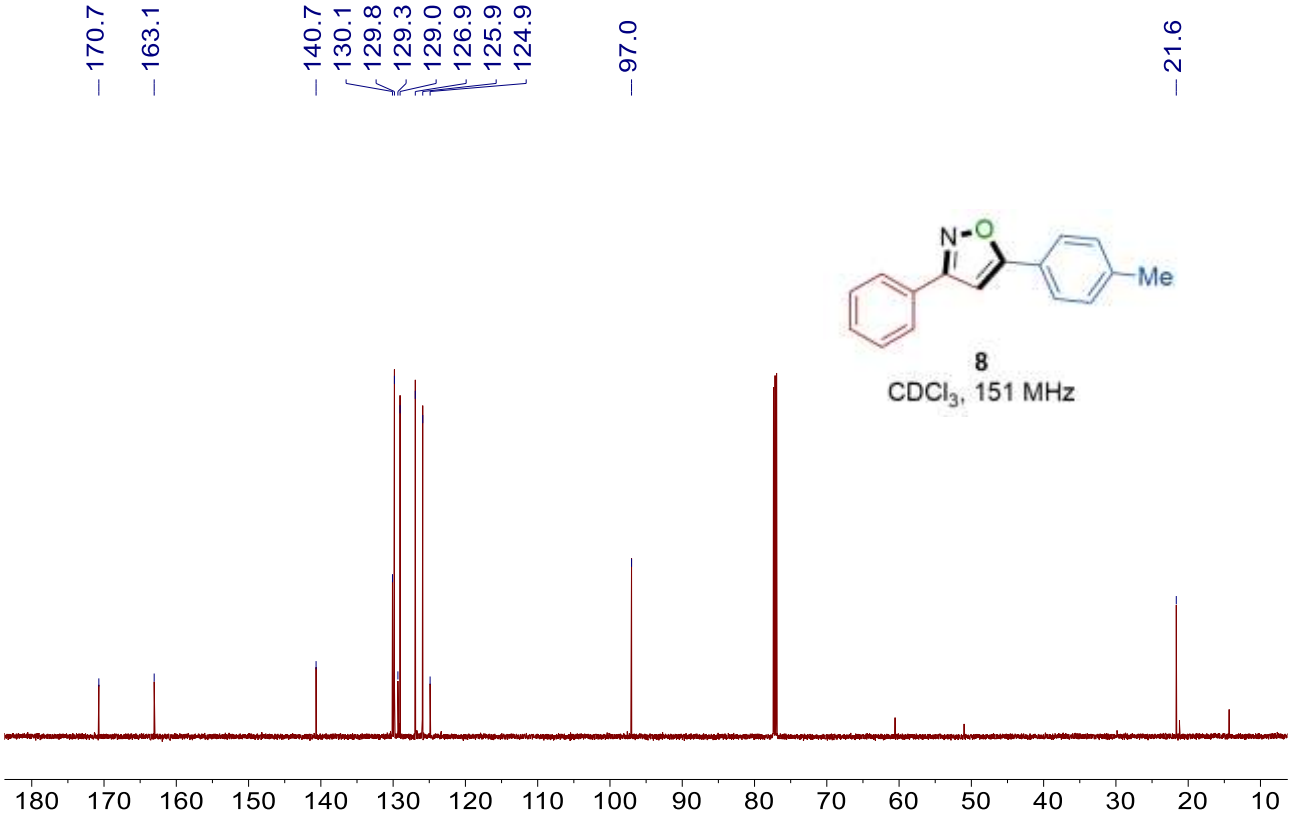
^{13}C NMR spectrum of **7**



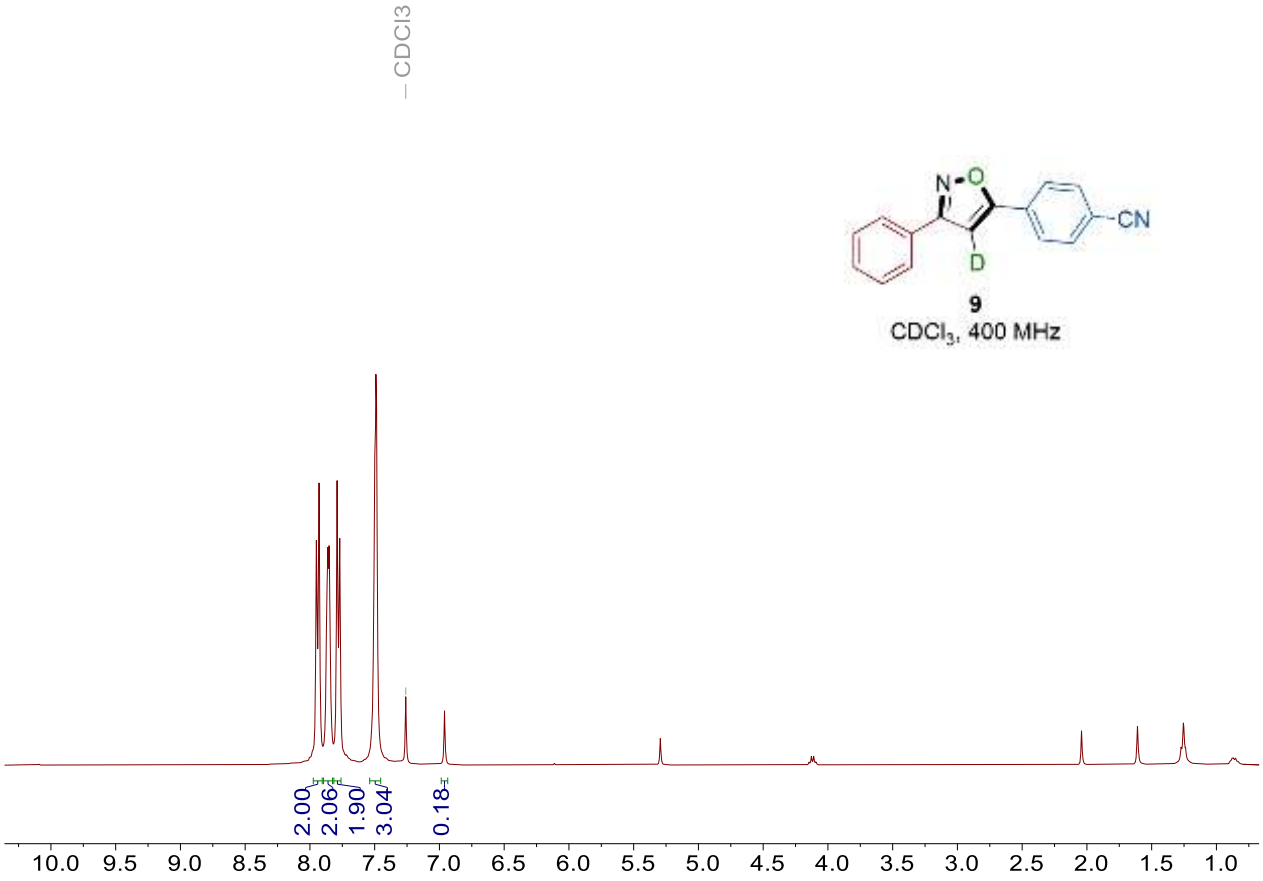
^{1}H NMR spectrum of **8**



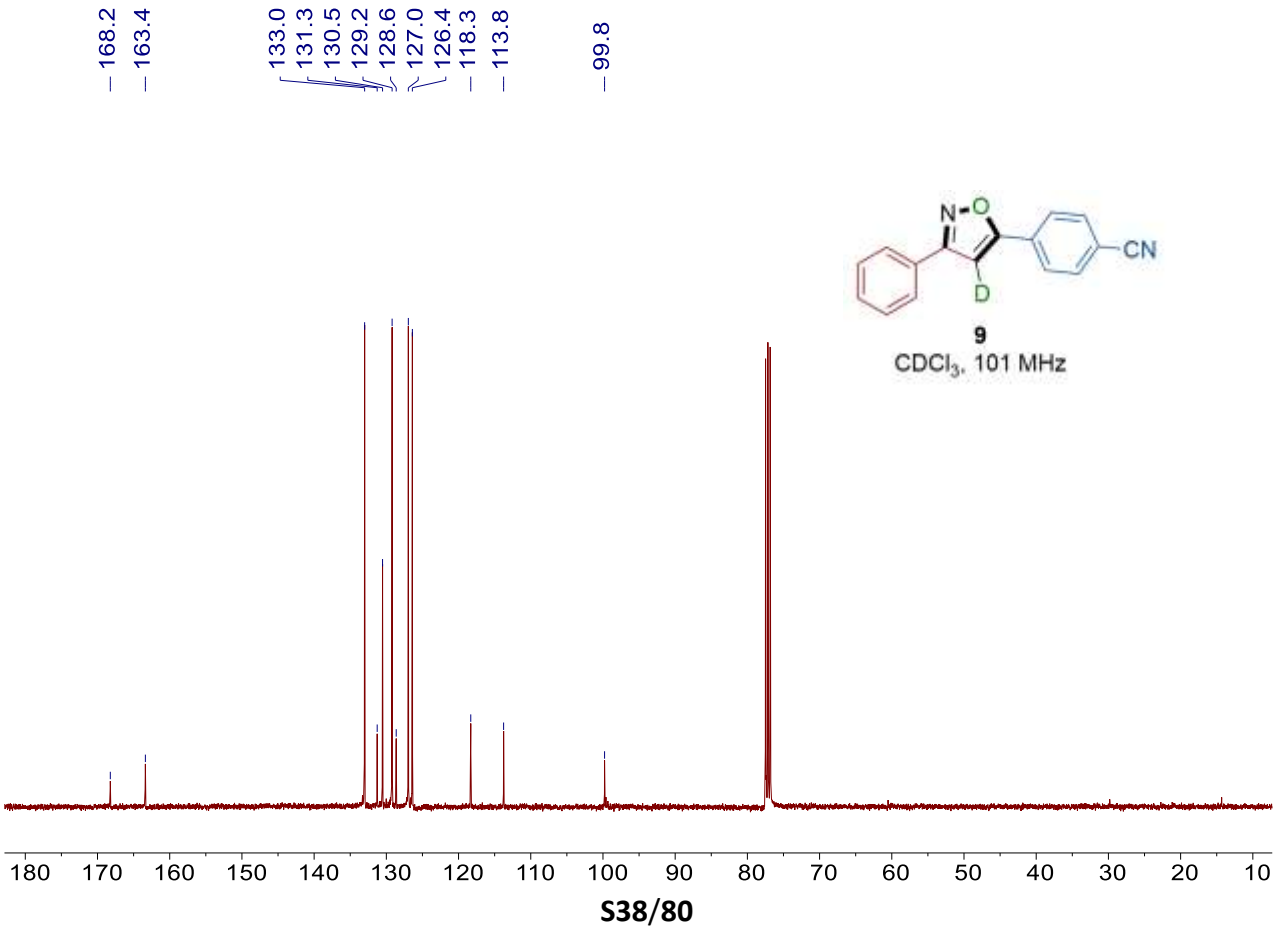
^{13}C NMR spectrum of **8**



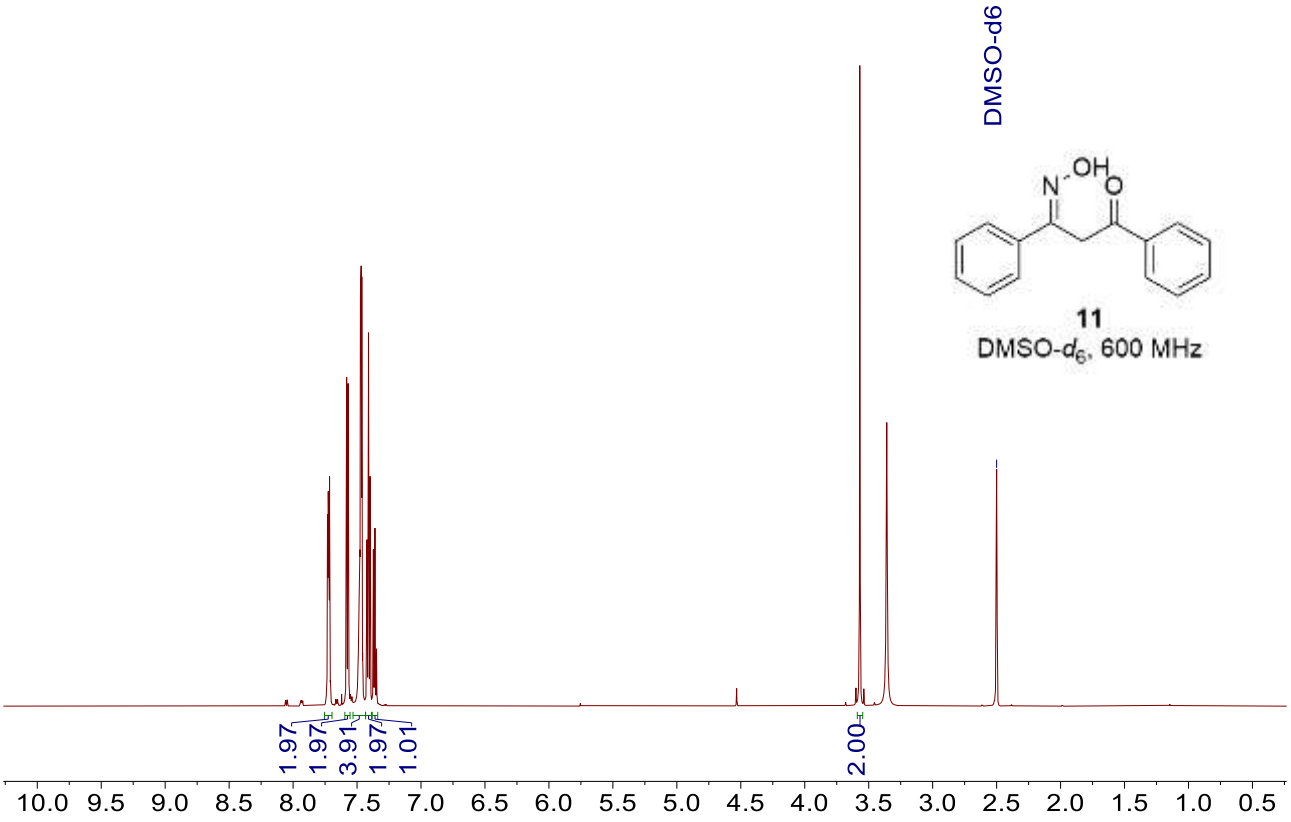
^{1}H NMR spectrum of **9**



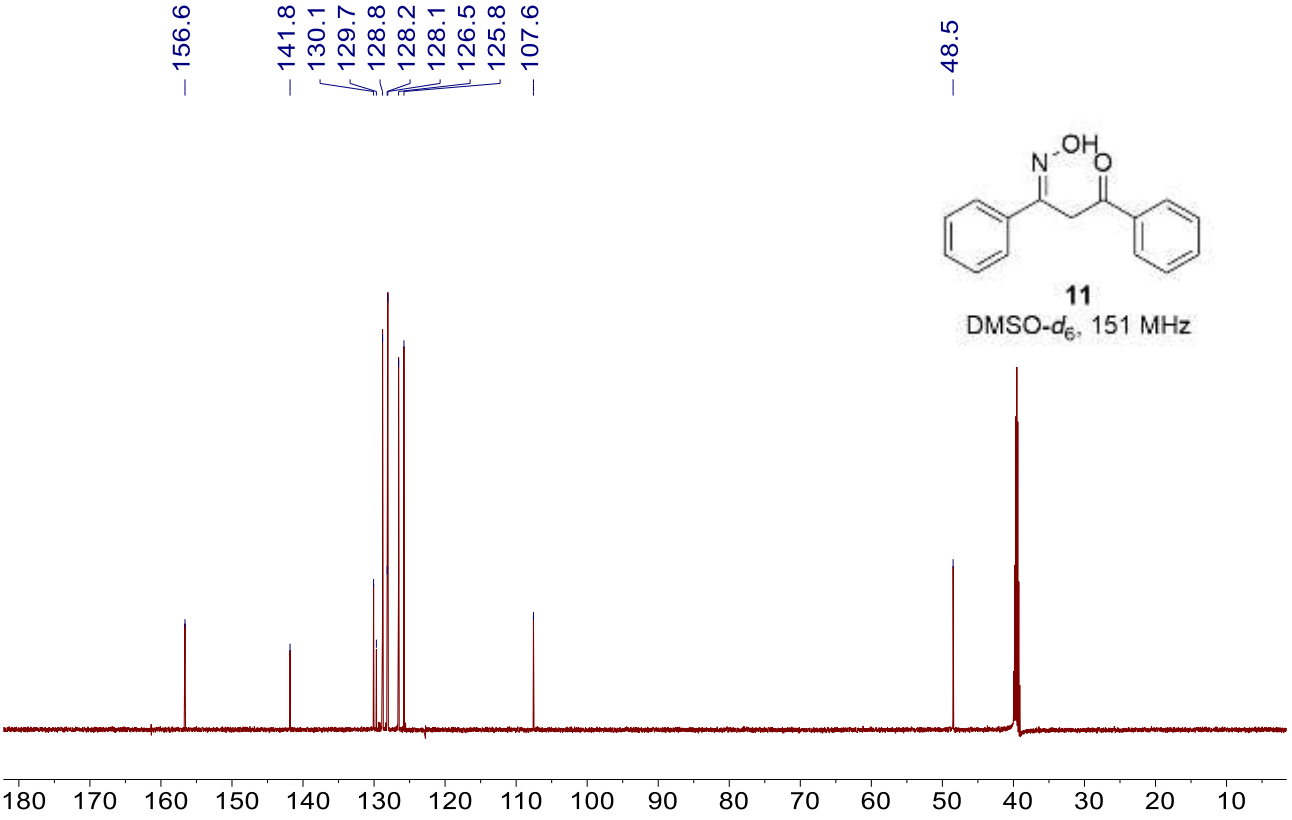
^{13}C NMR spectrum of **9**



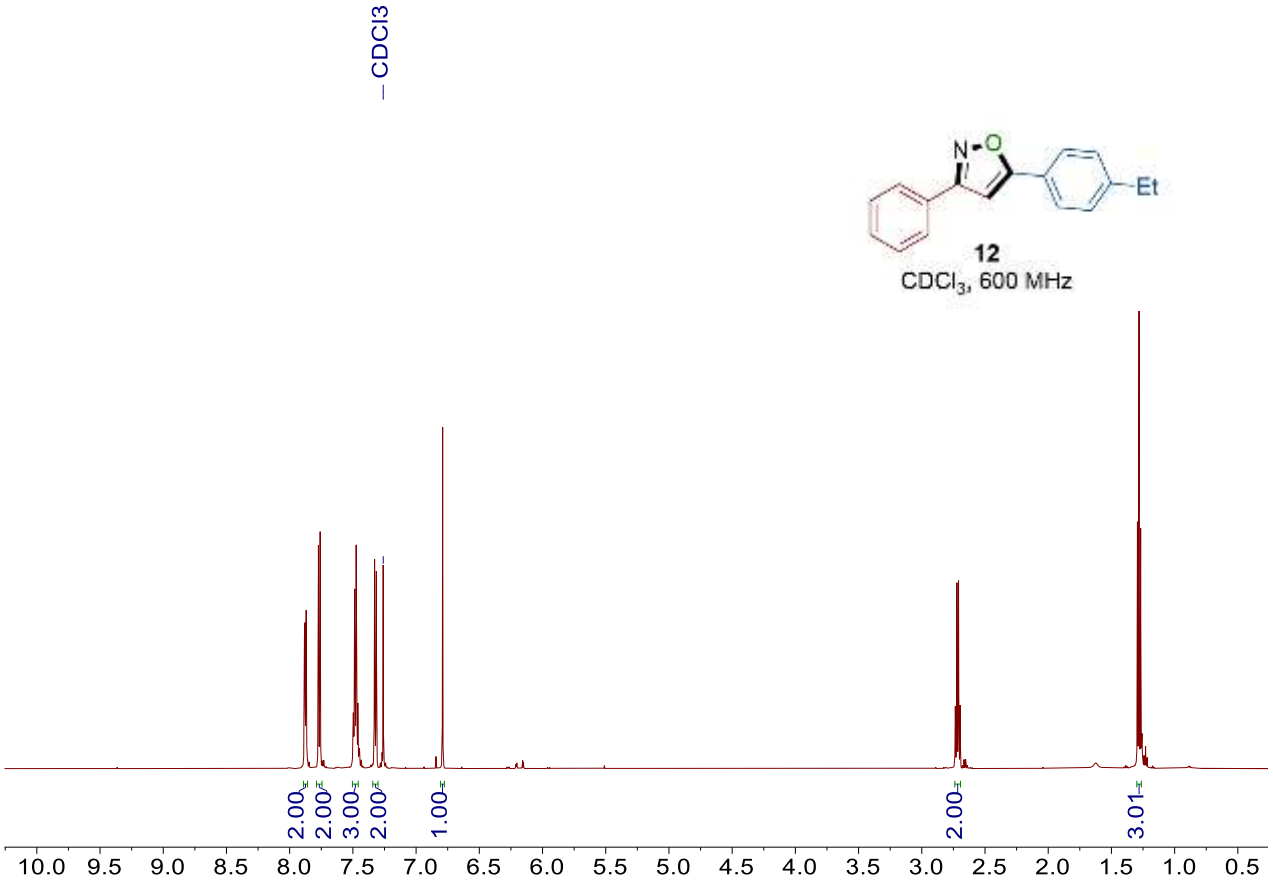
^{1}H NMR spectrum of **11**



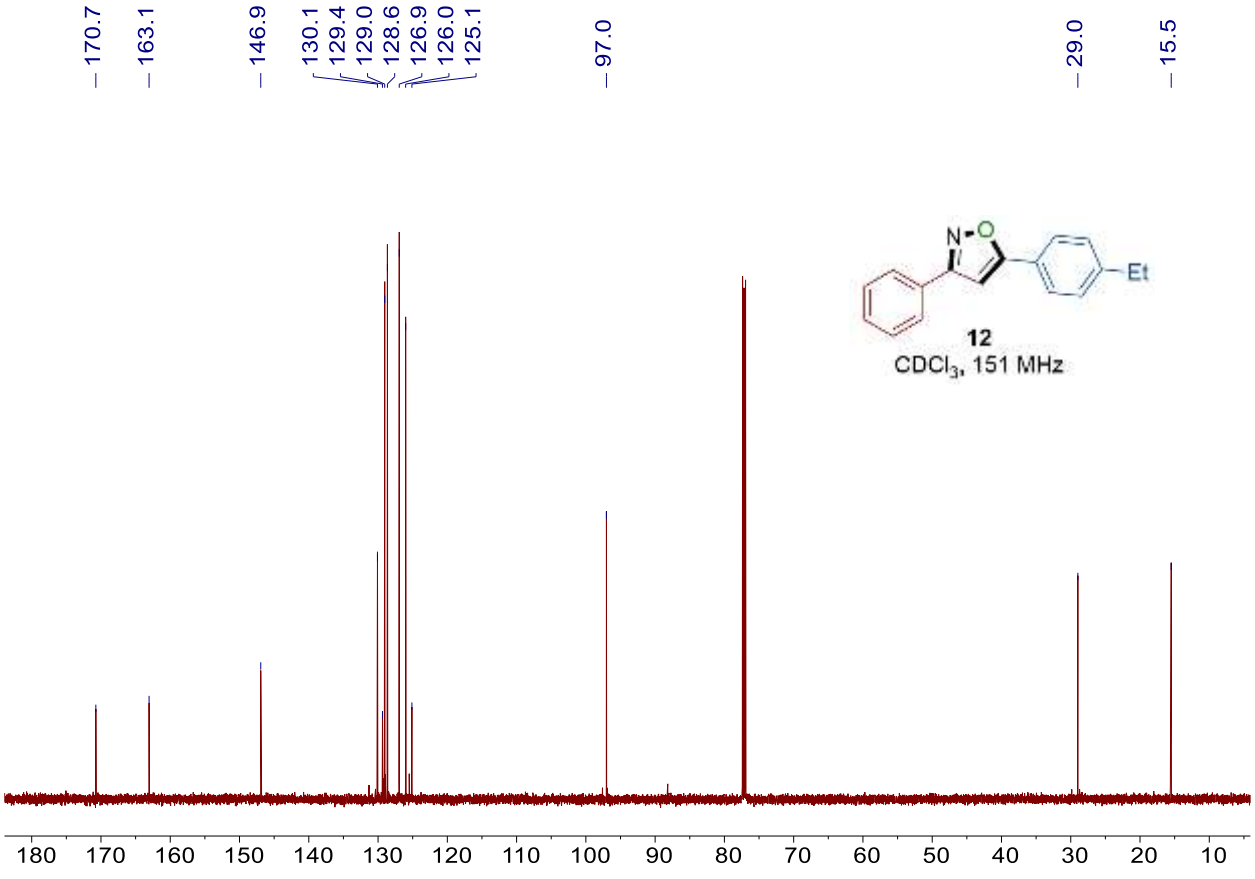
^{13}C NMR spectrum of **11**



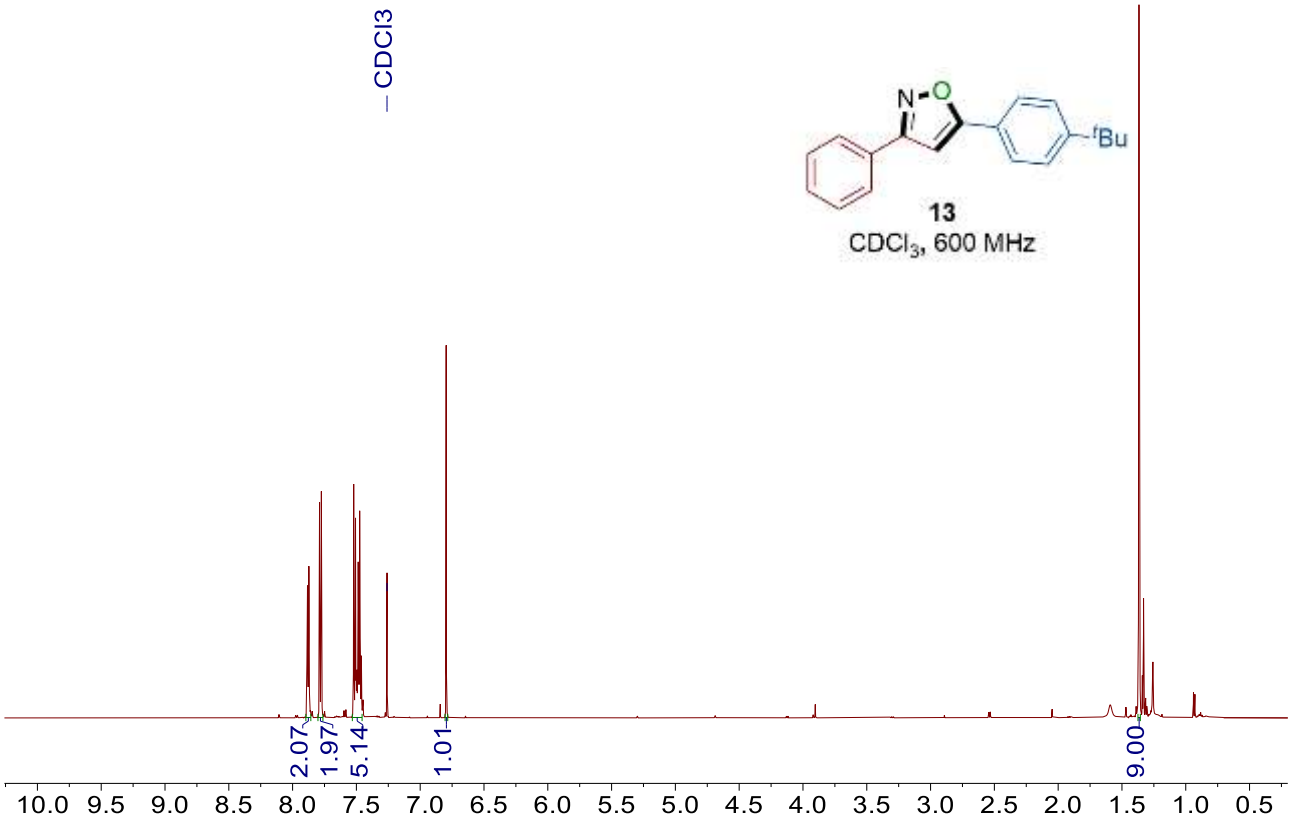
^{1}H NMR spectrum of **12**



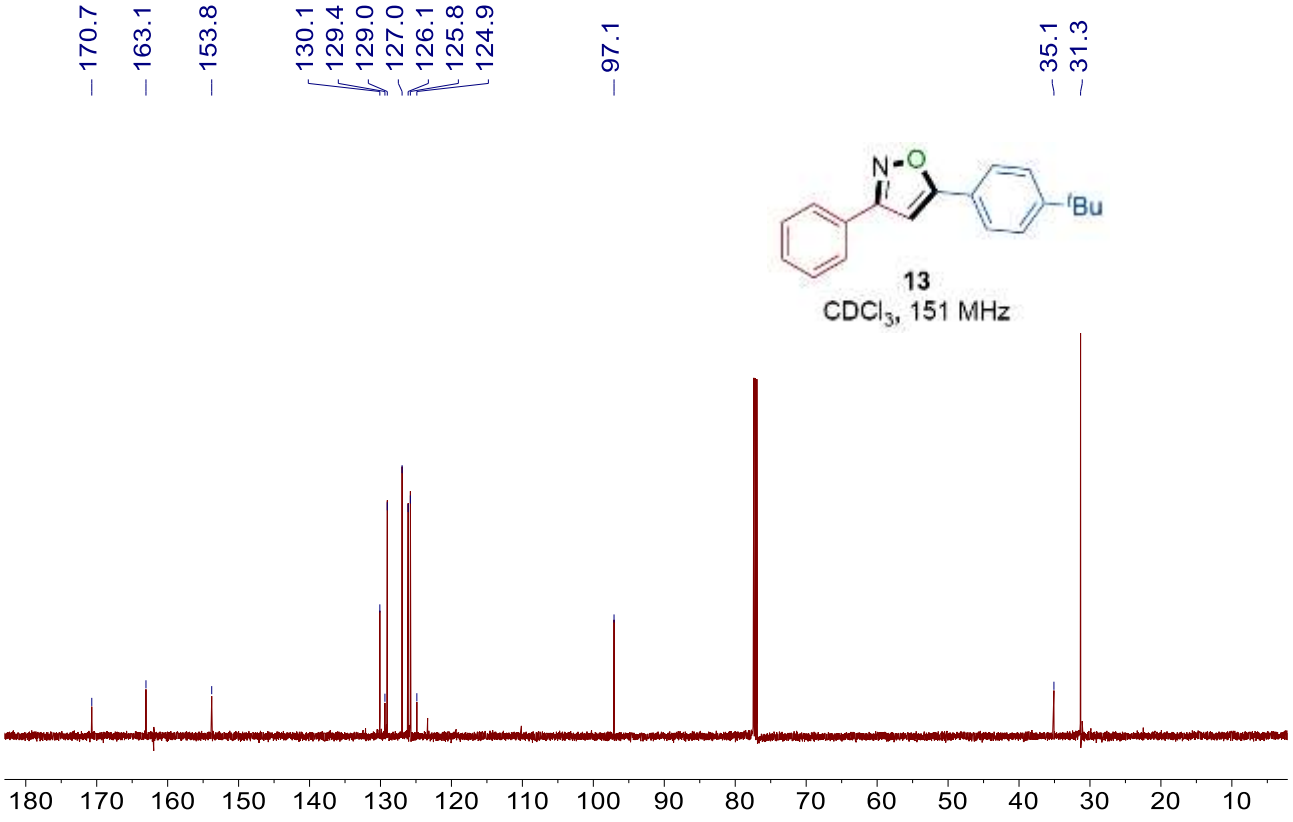
^{13}C NMR spectrum of **12**



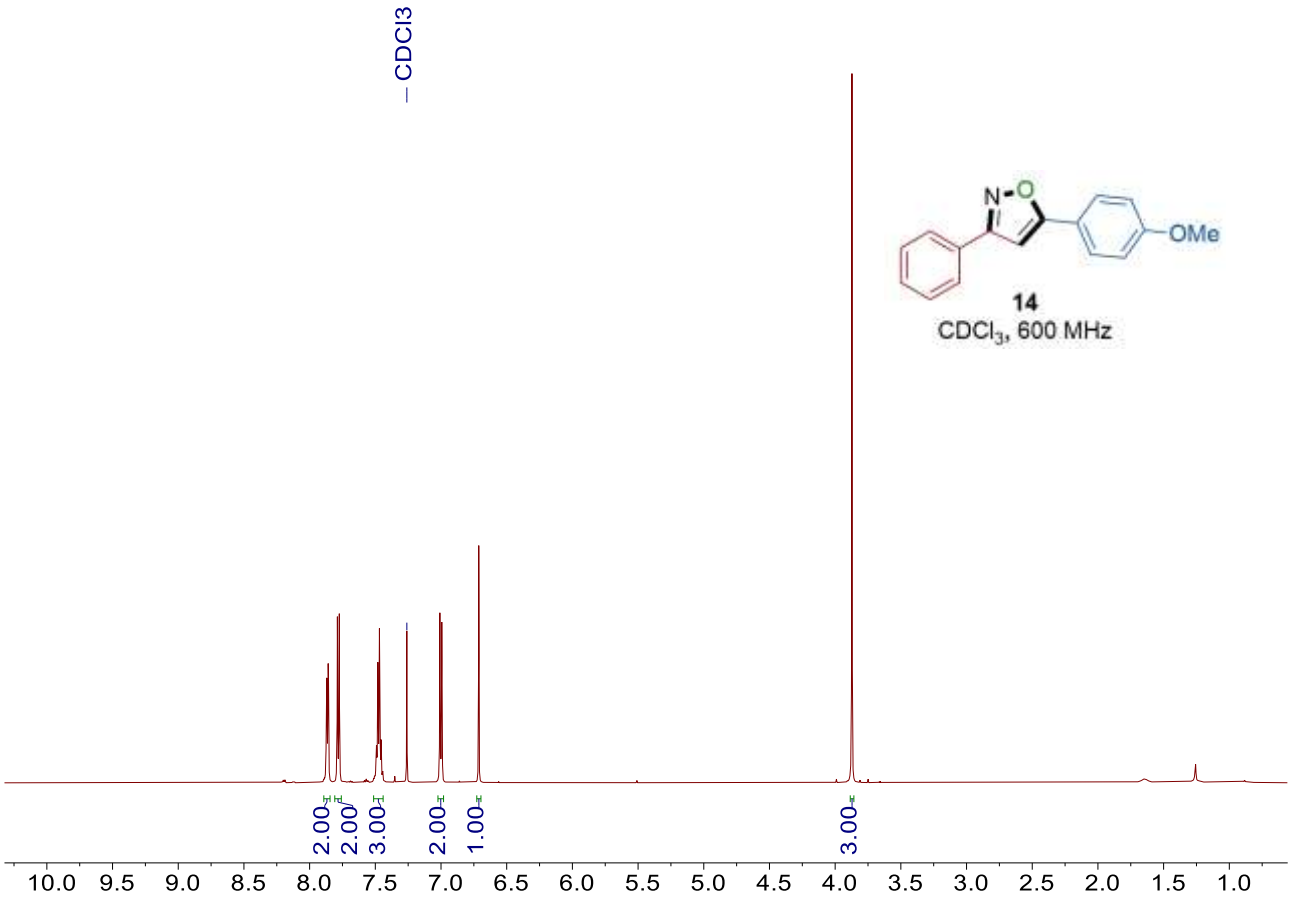
^{1}H NMR spectrum of **13**



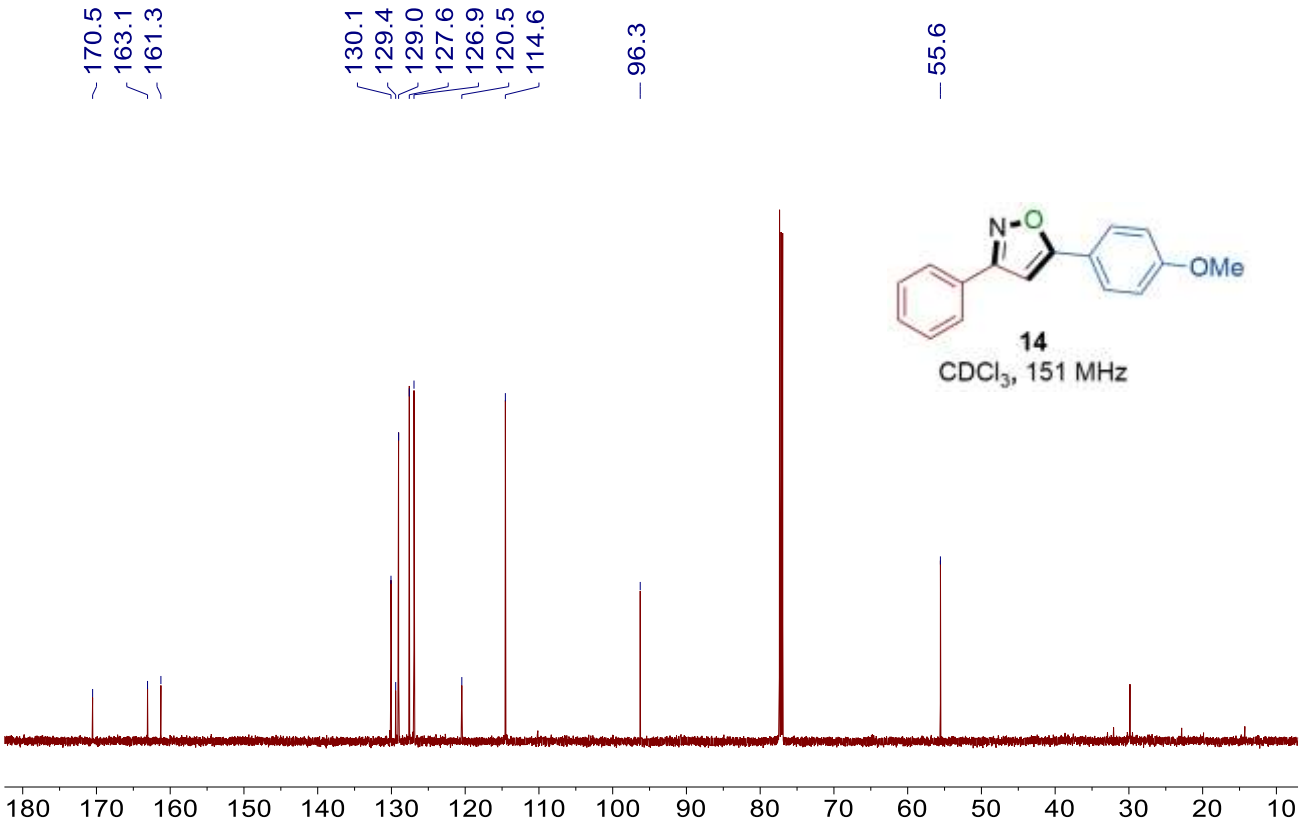
^{13}C NMR spectrum of **13**



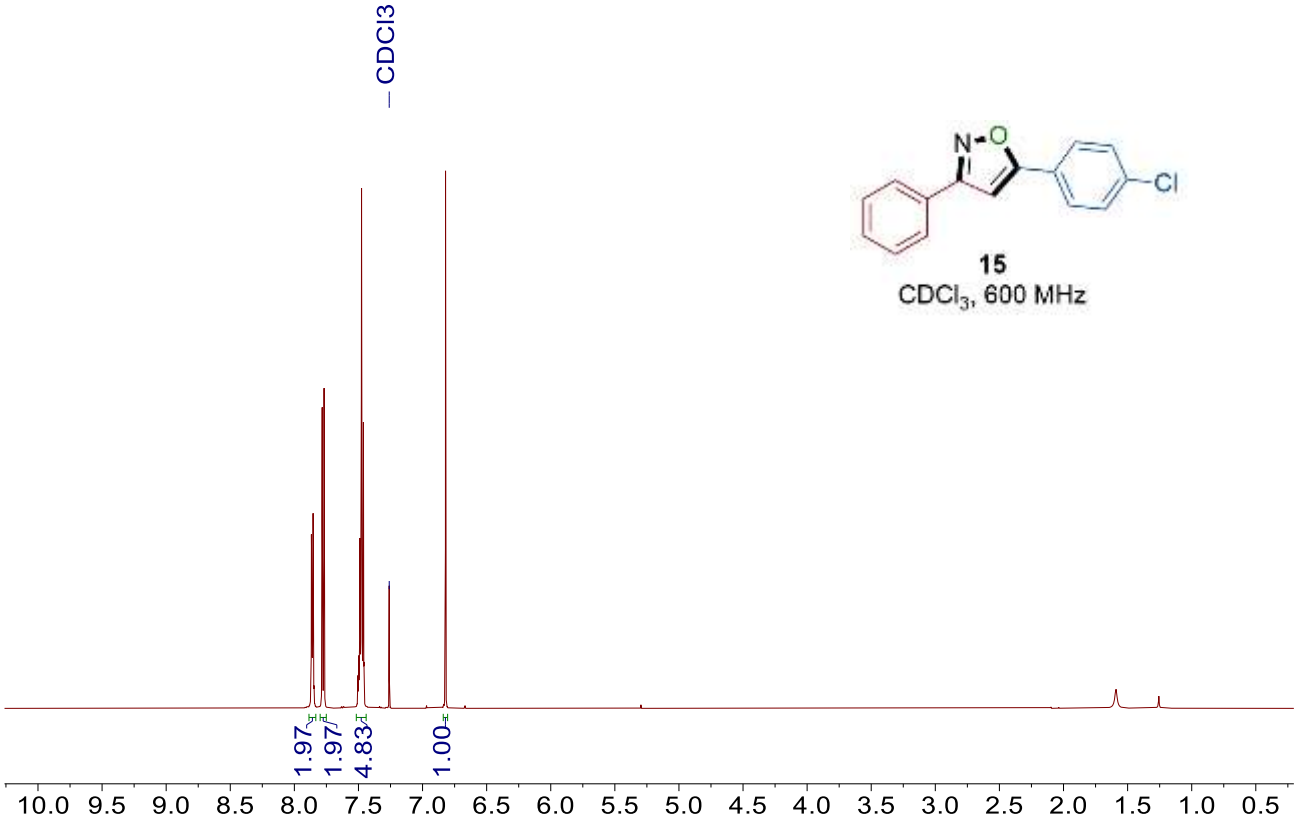
^{1}H NMR spectrum of **14**



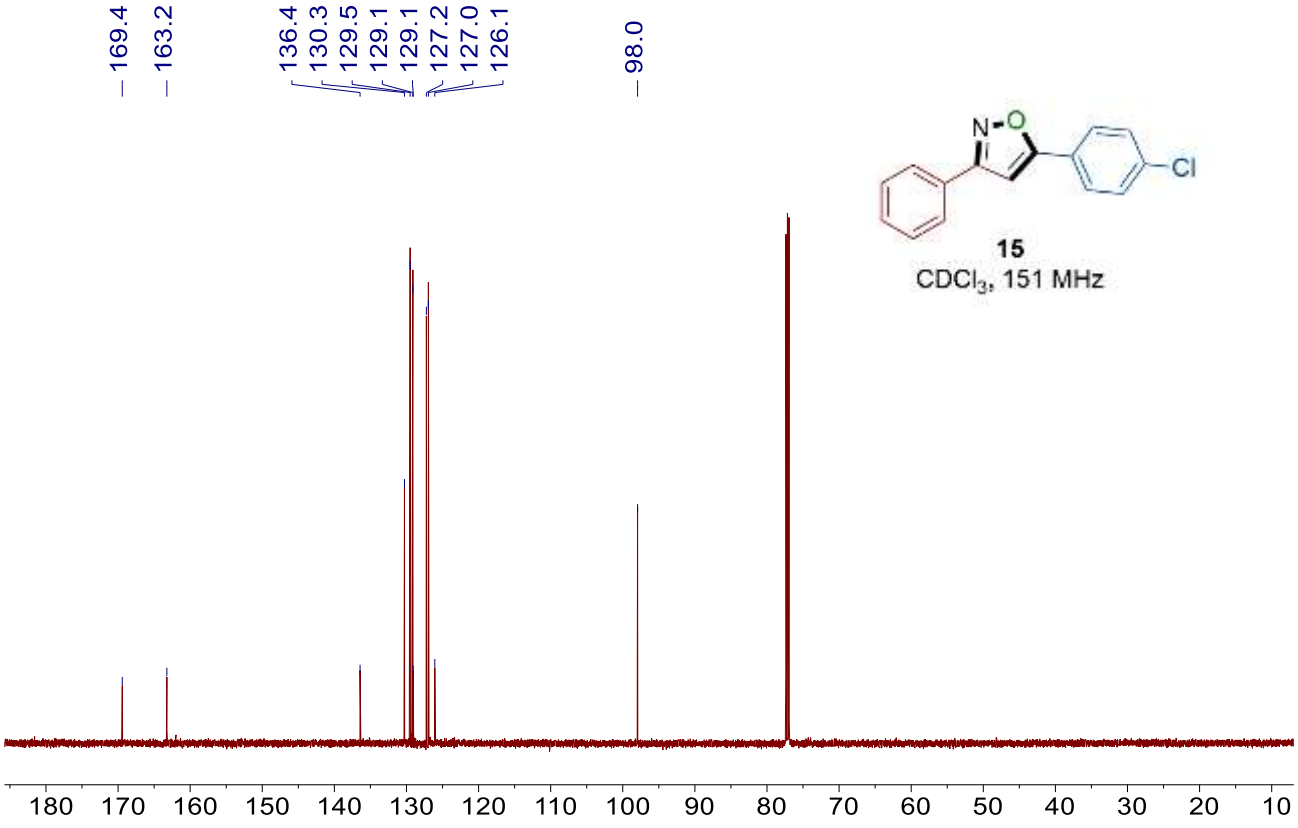
^{13}C NMR spectrum of **14**



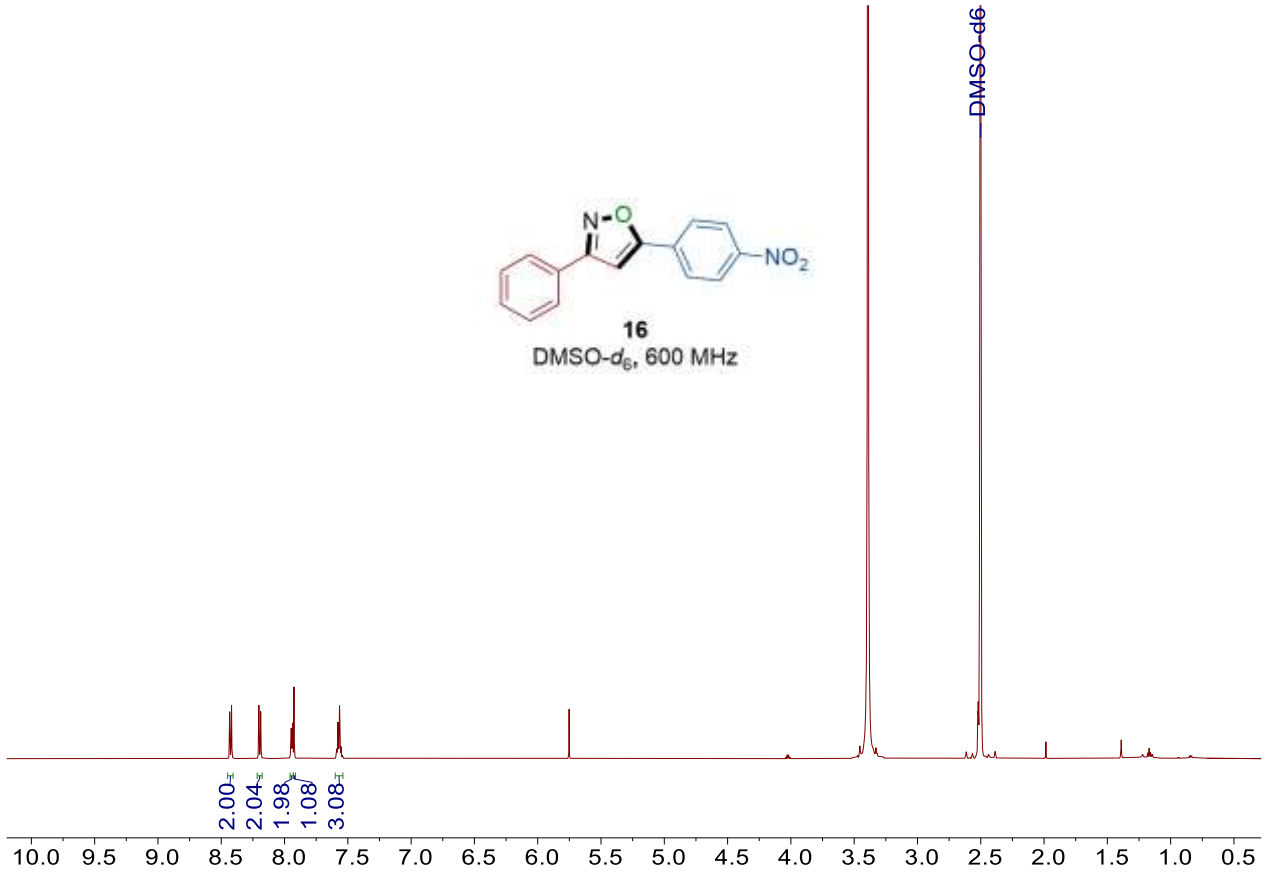
^{1}H NMR spectrum of **15**



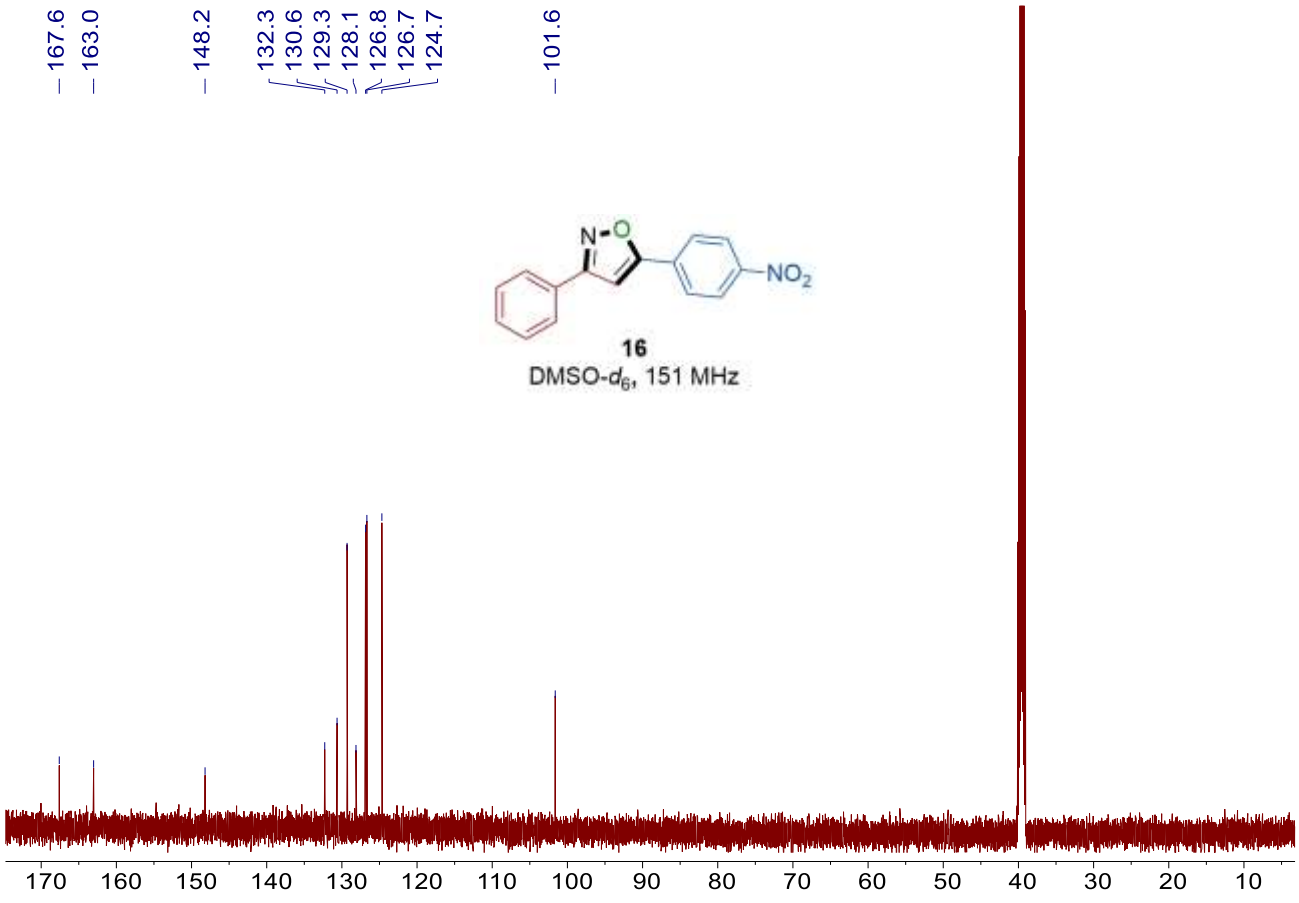
^{13}C NMR spectrum of **15**



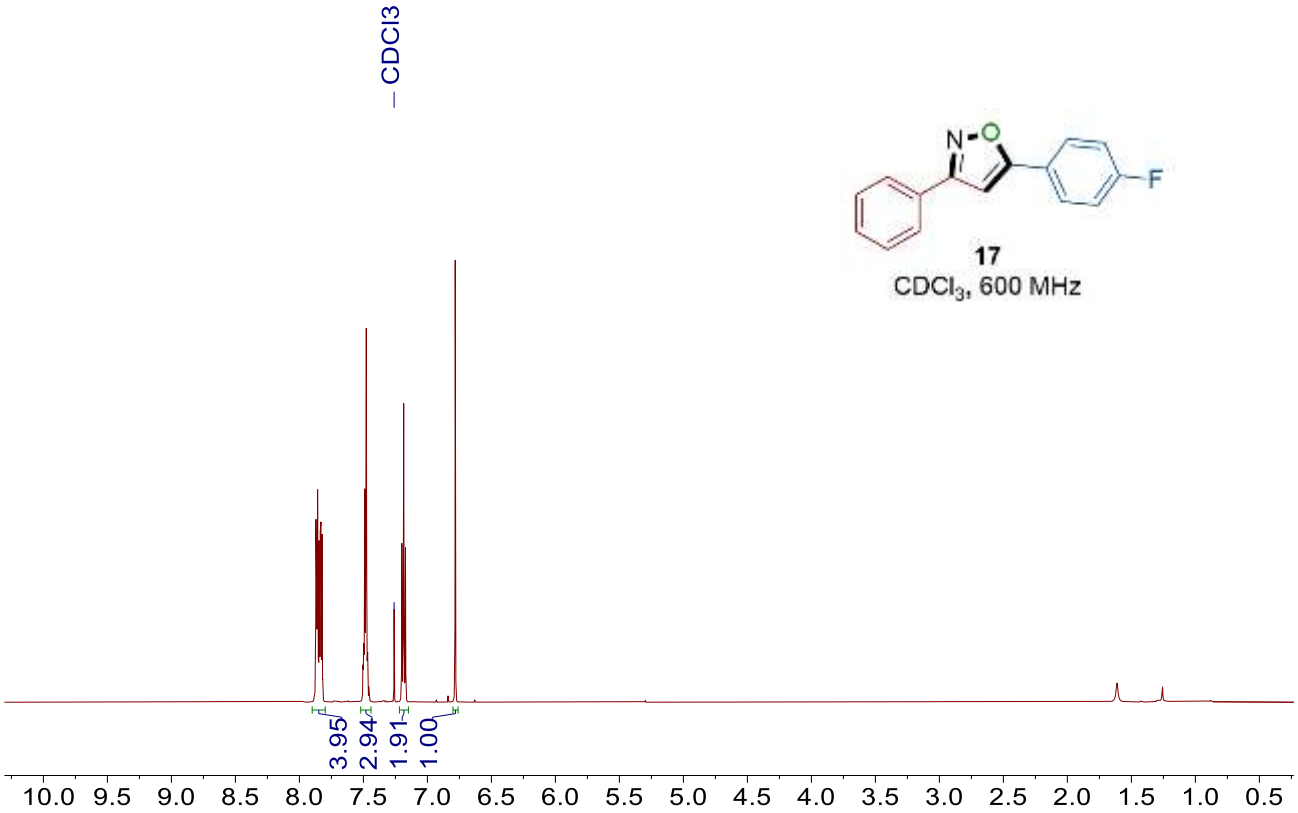
^{1}H NMR spectrum of **16**



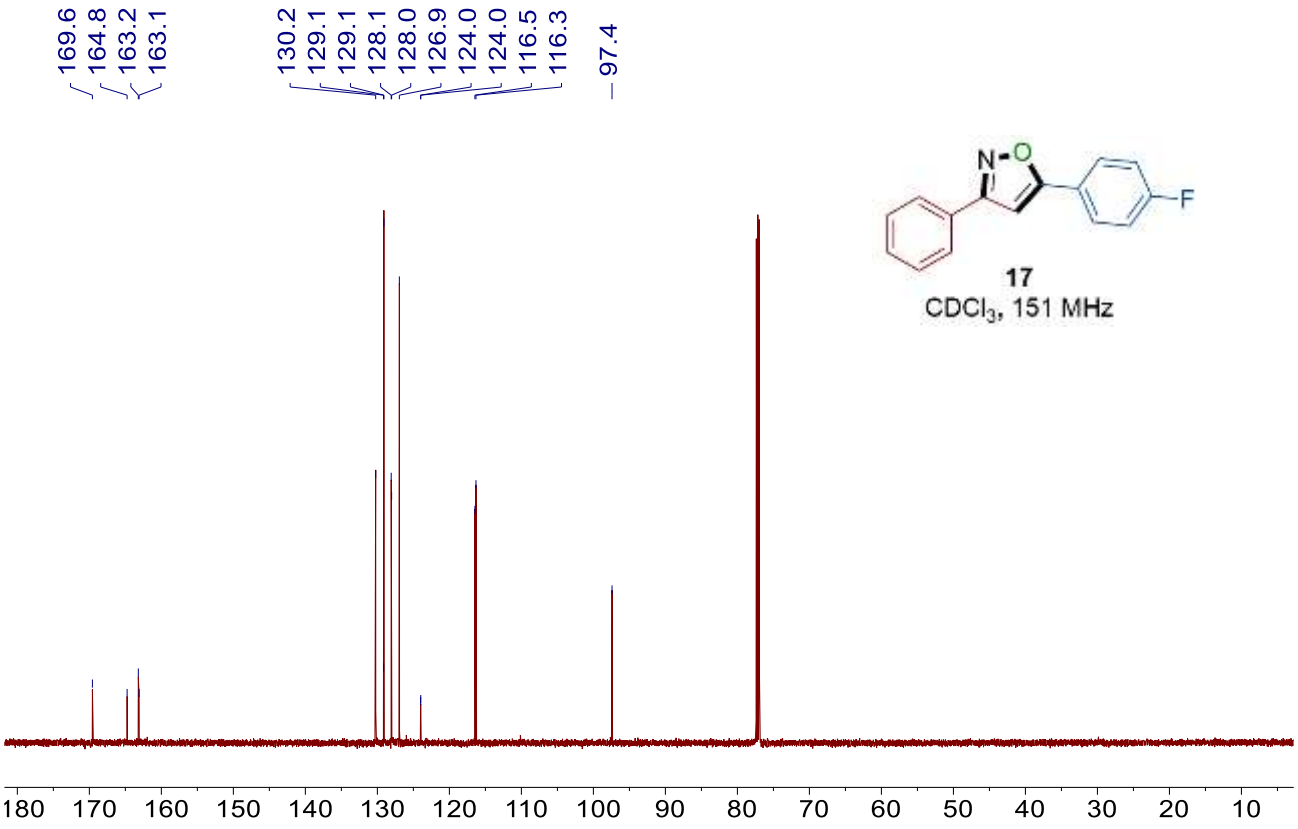
^{13}C NMR spectrum of **16**



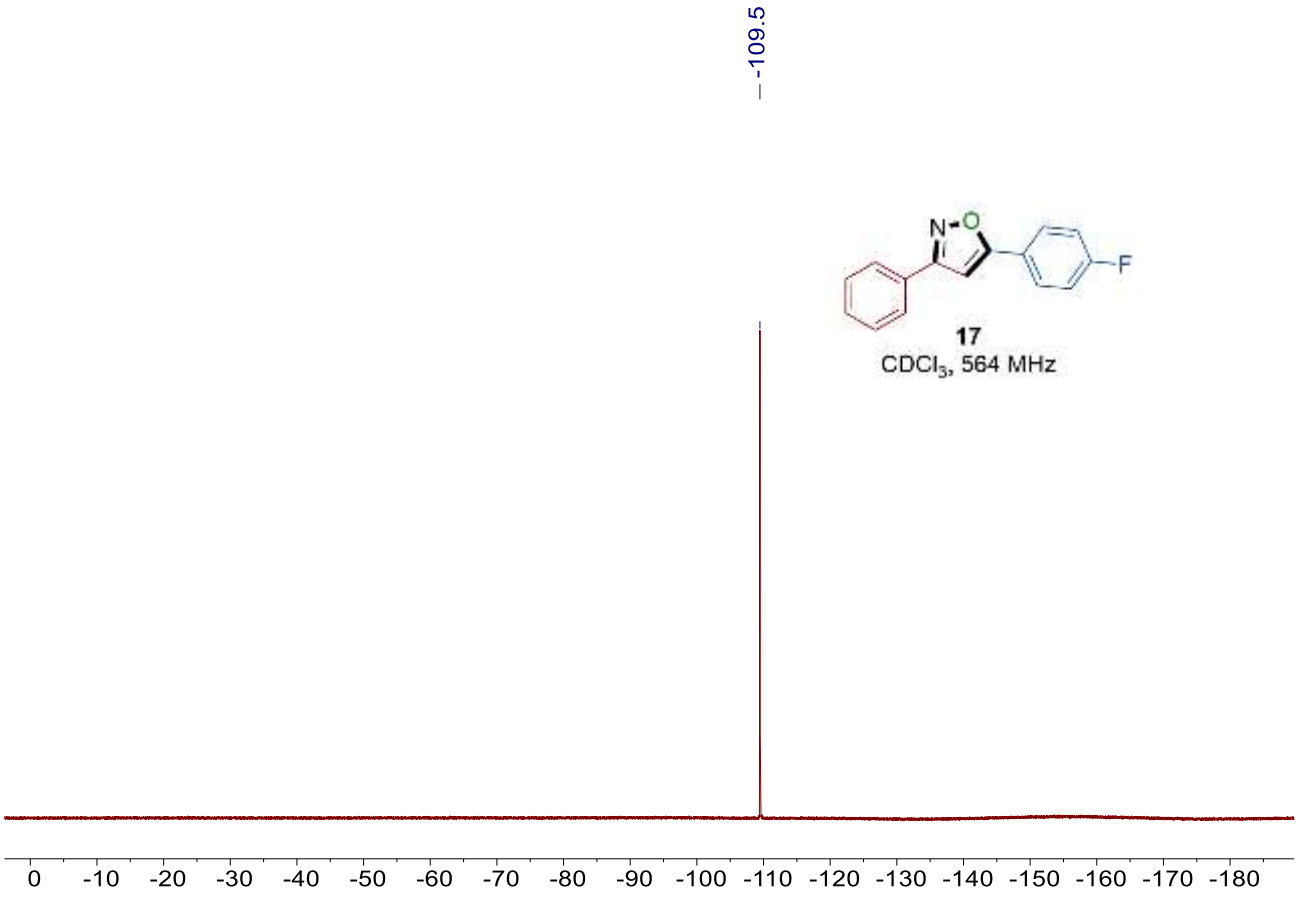
^{1}H NMR spectrum of **17**



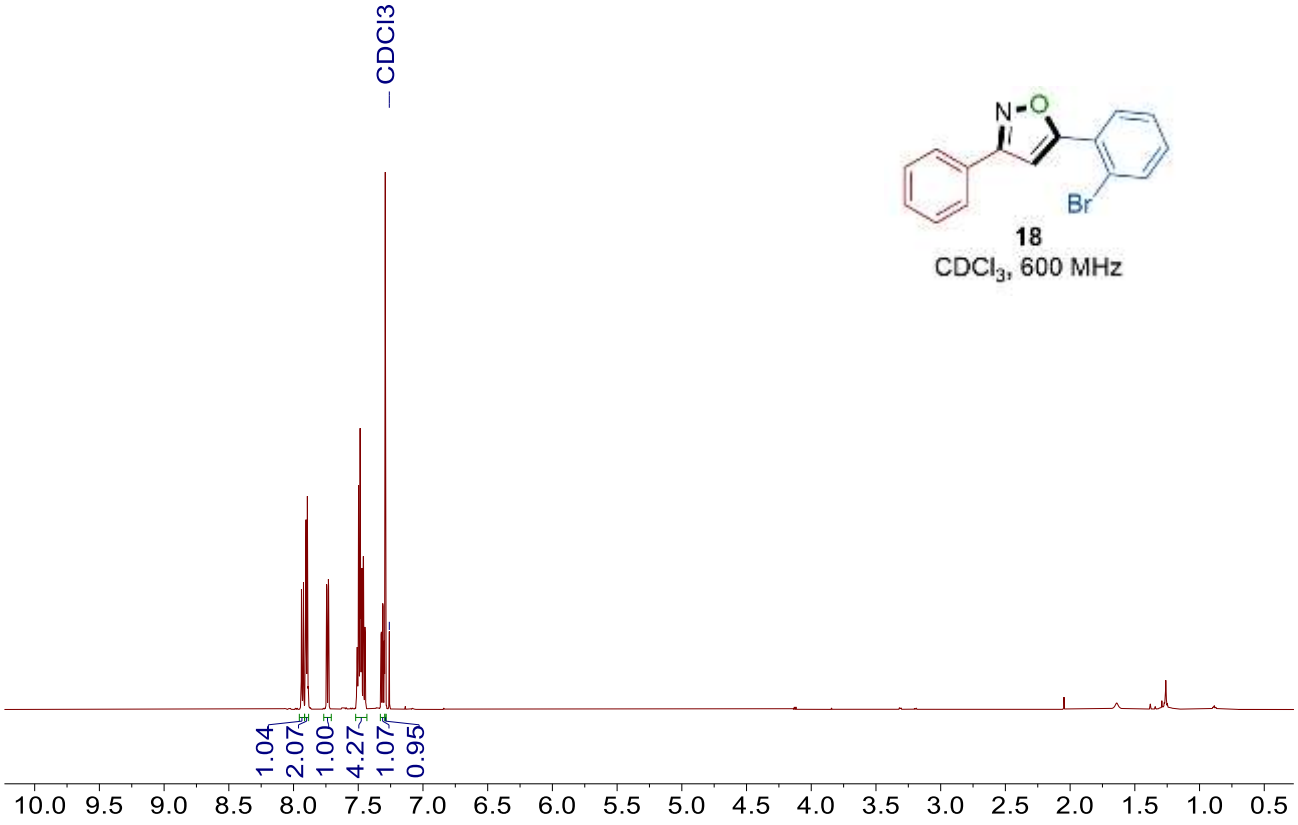
^{13}C NMR spectrum of **17**



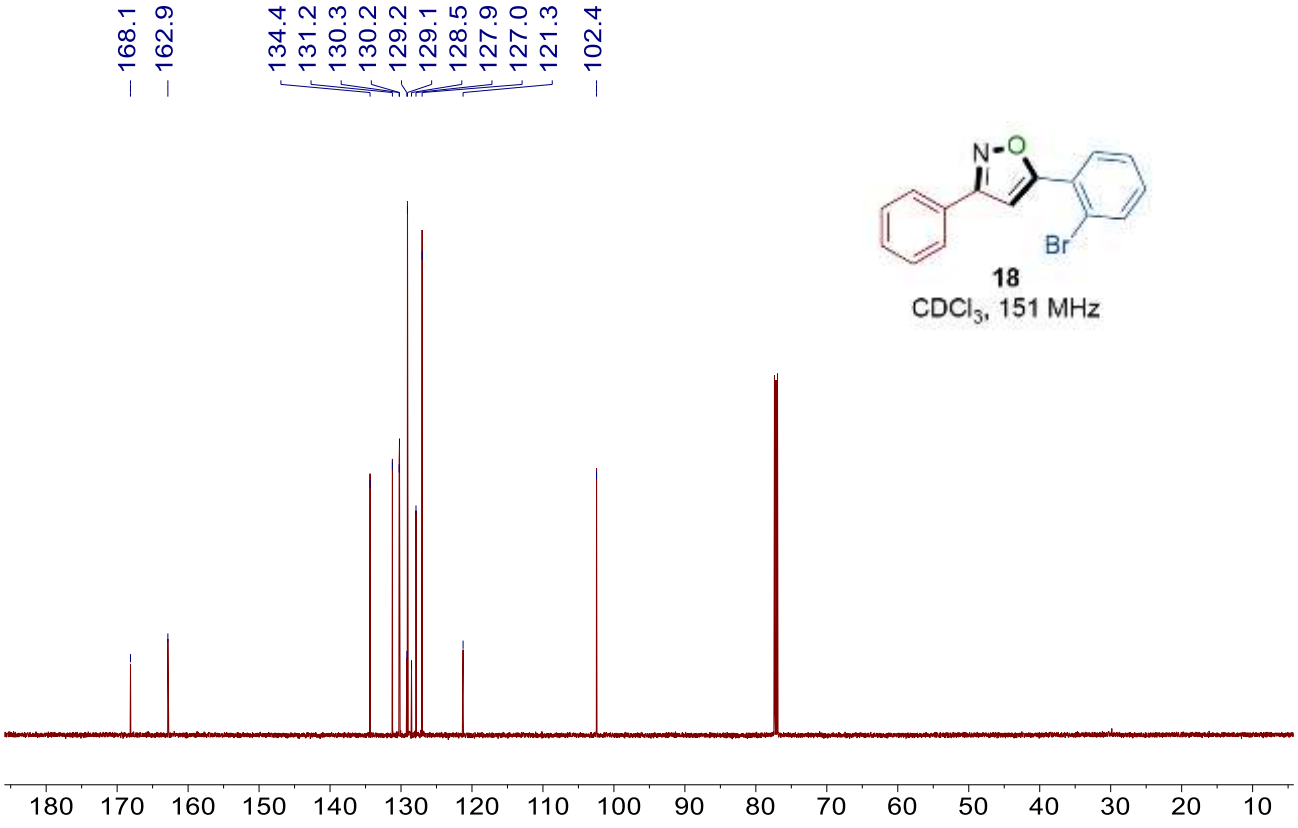
^{19}F NMR spectrum of **17**



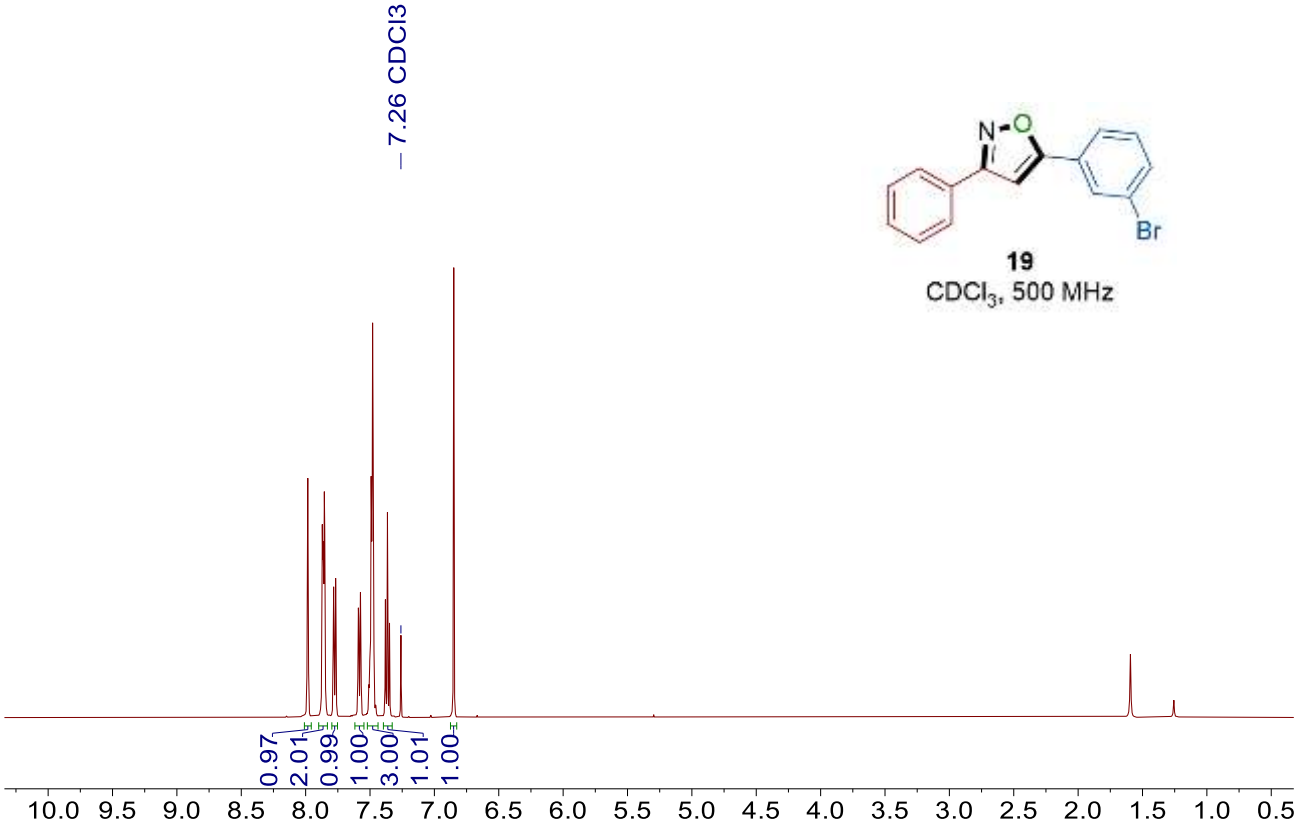
^{1}H NMR spectrum of **18**



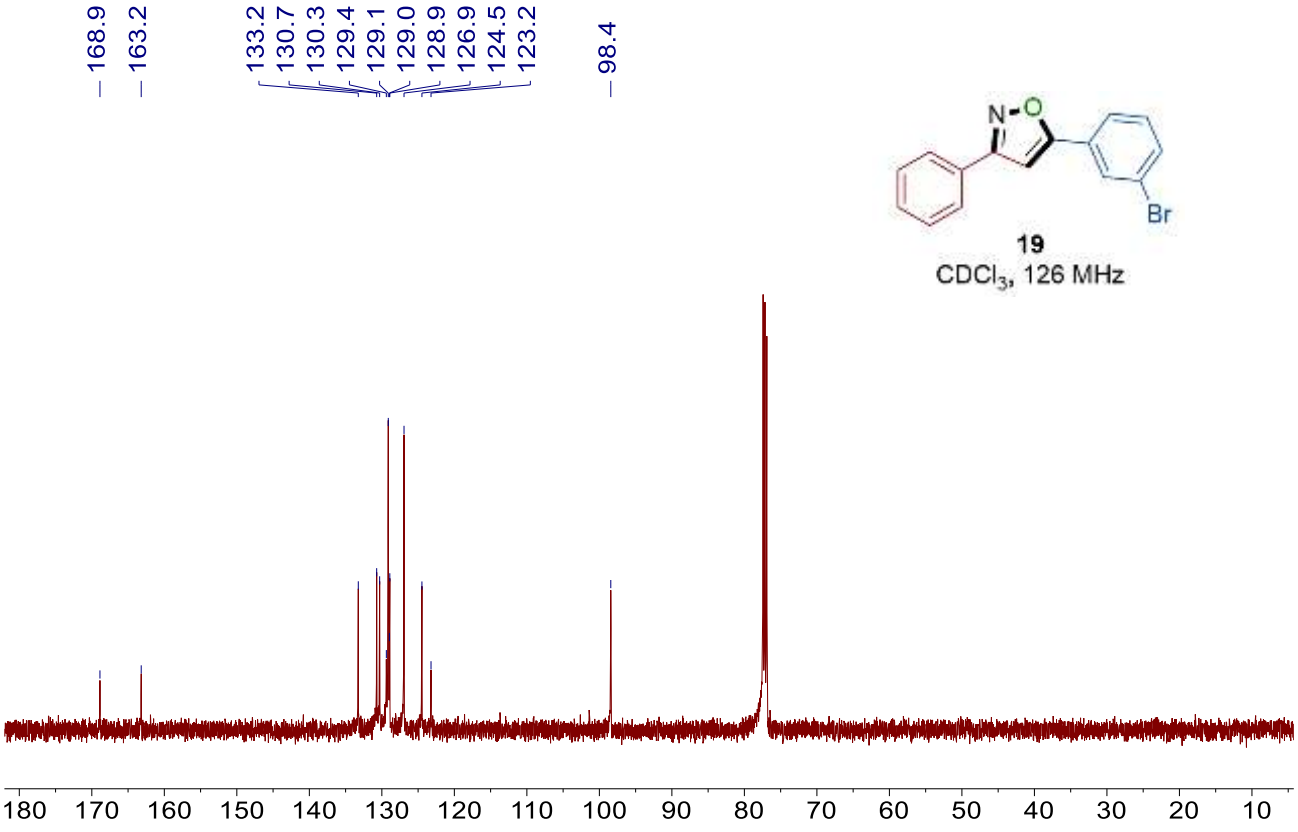
^{13}C NMR spectrum of **18**



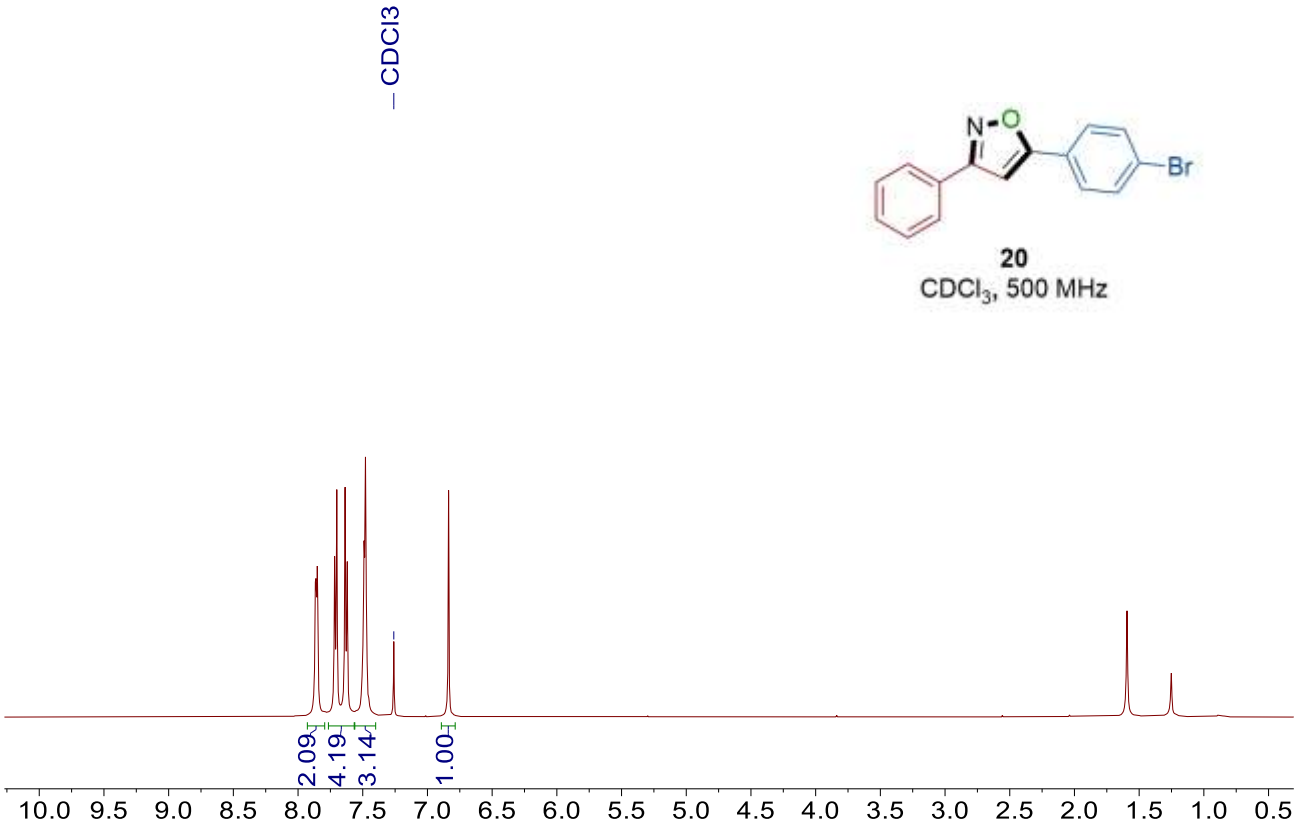
^{1}H NMR spectrum of **19**



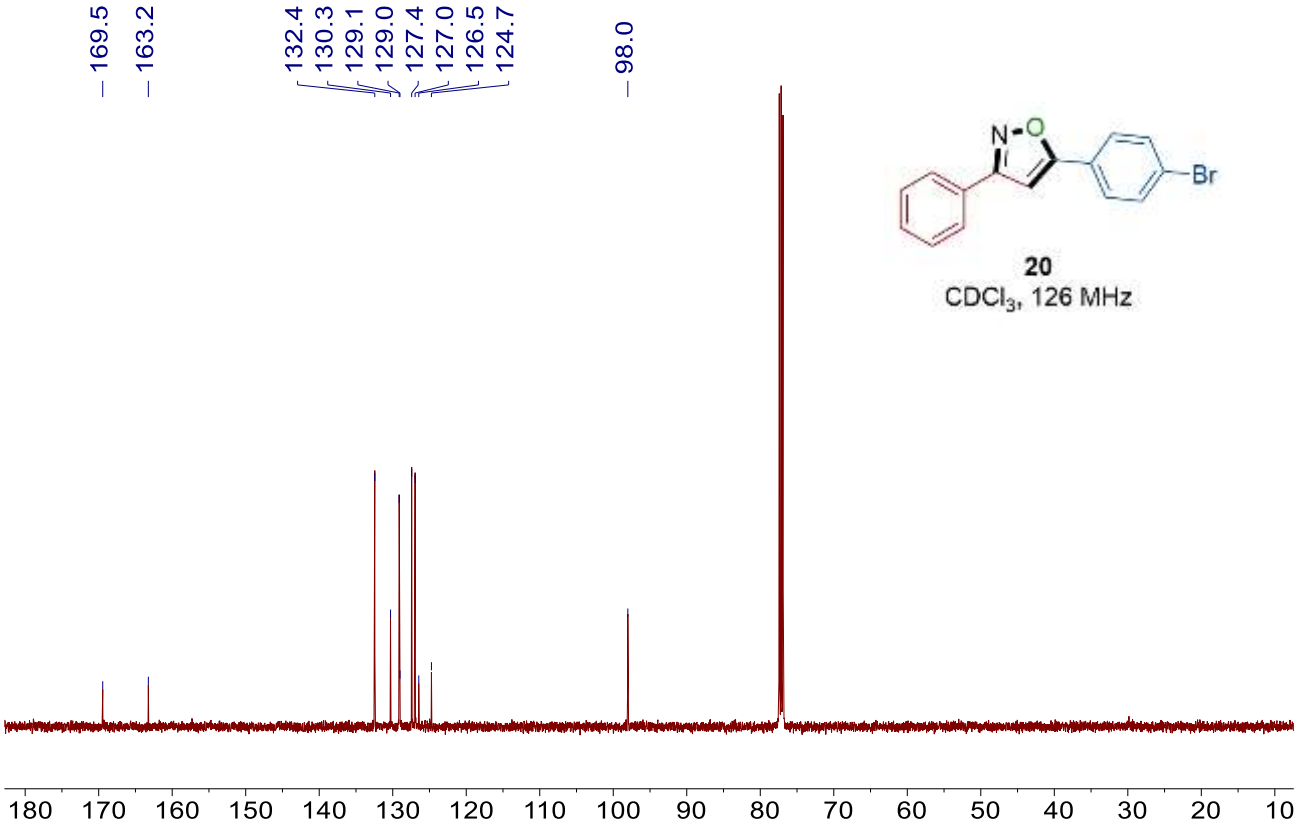
^{13}C NMR spectrum of **19**



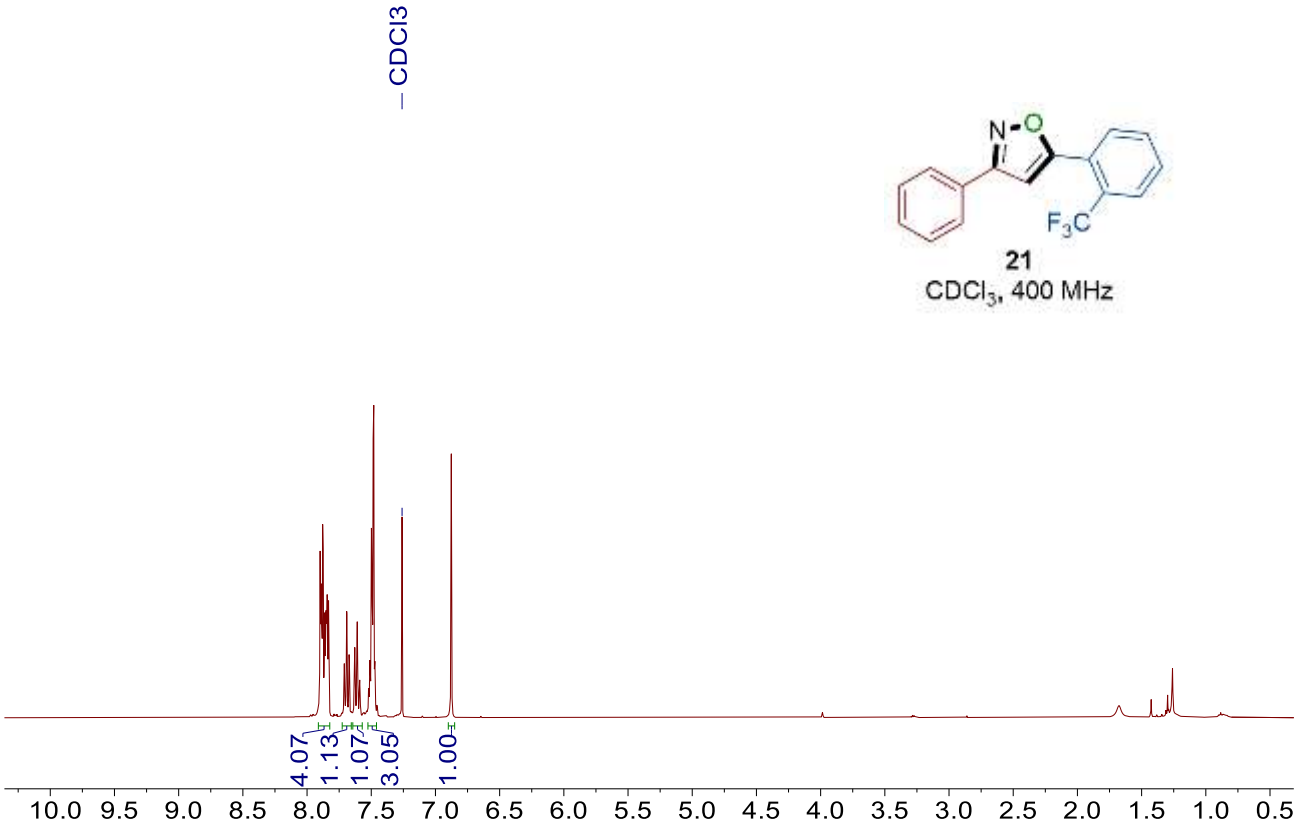
^{1}H NMR spectrum of **20**



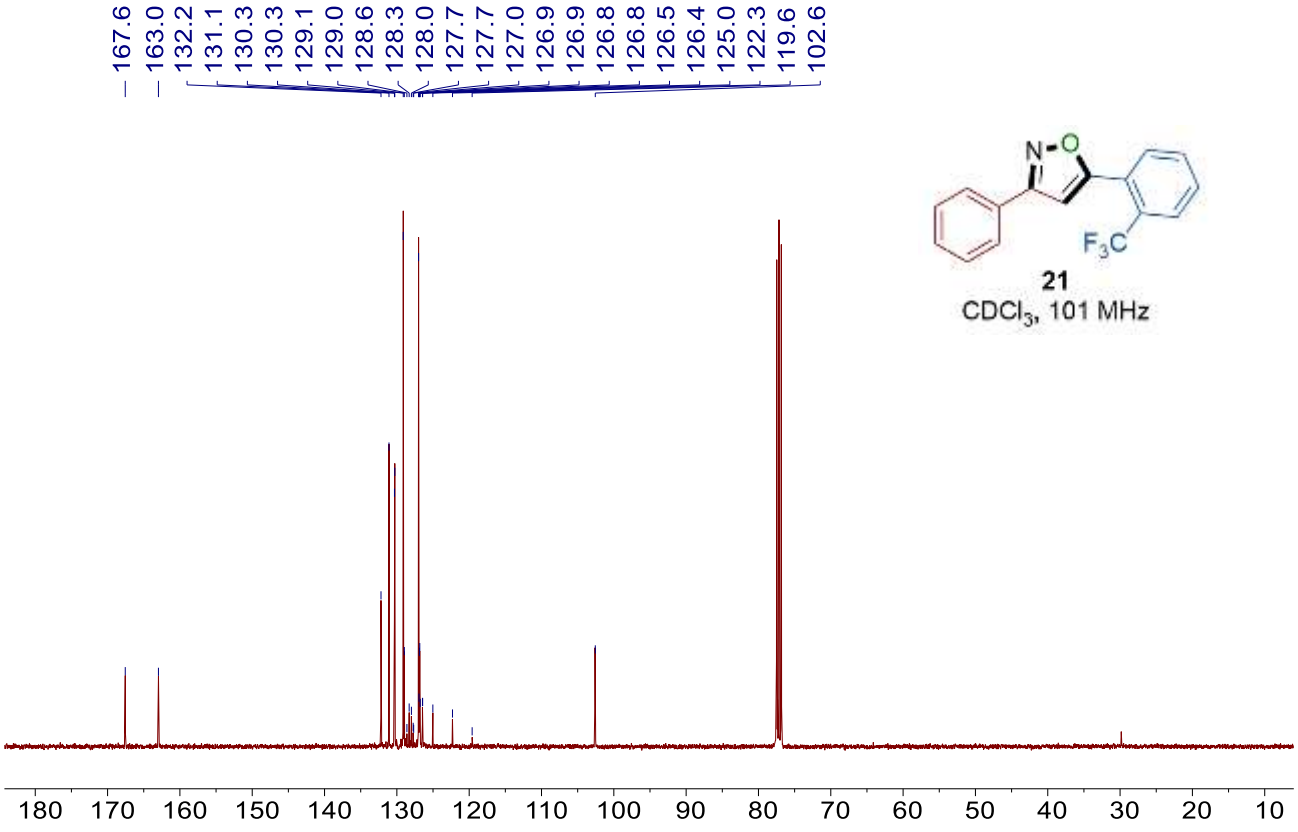
^{13}C NMR spectrum of **20**



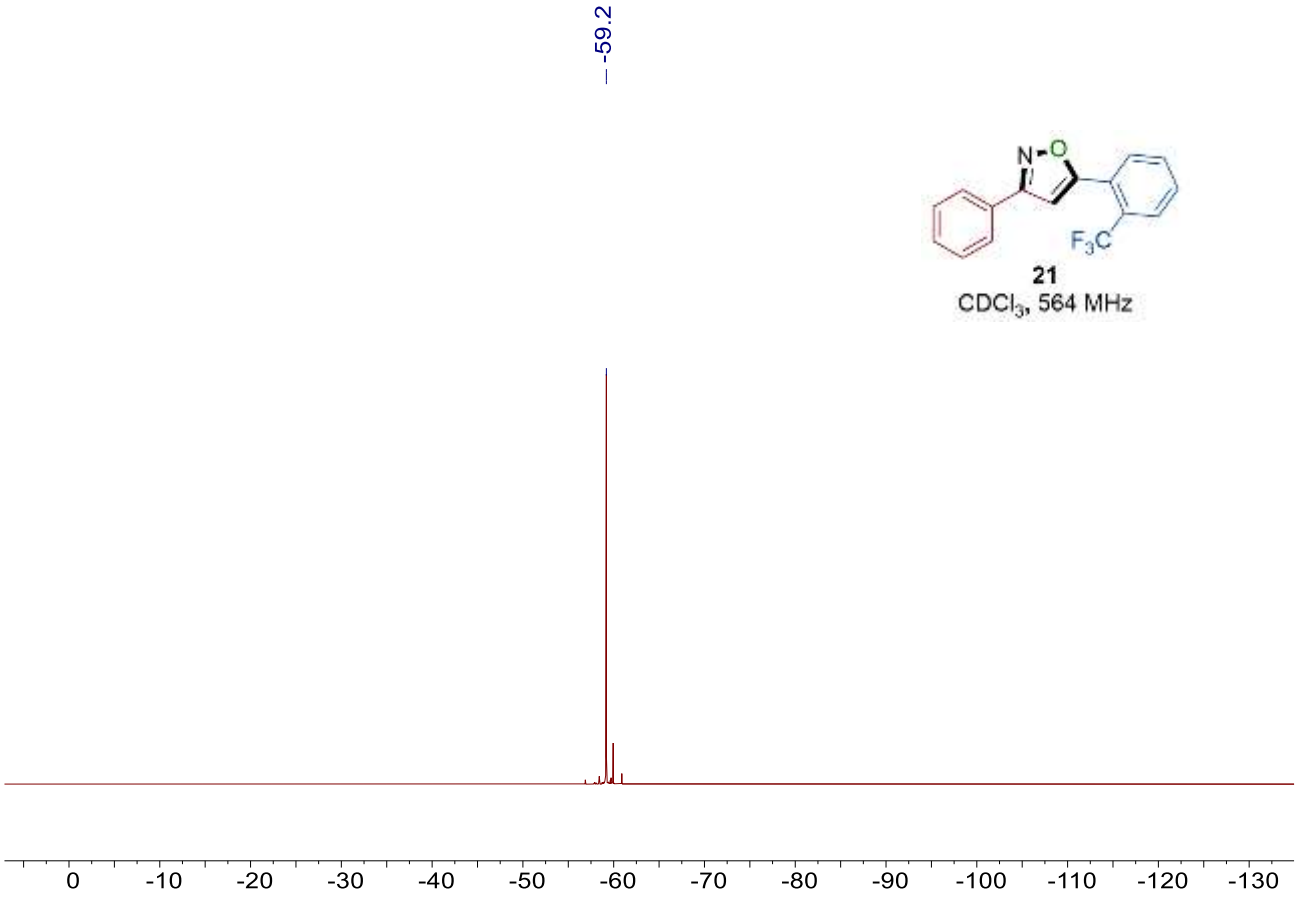
^{1}H NMR spectrum of **21**



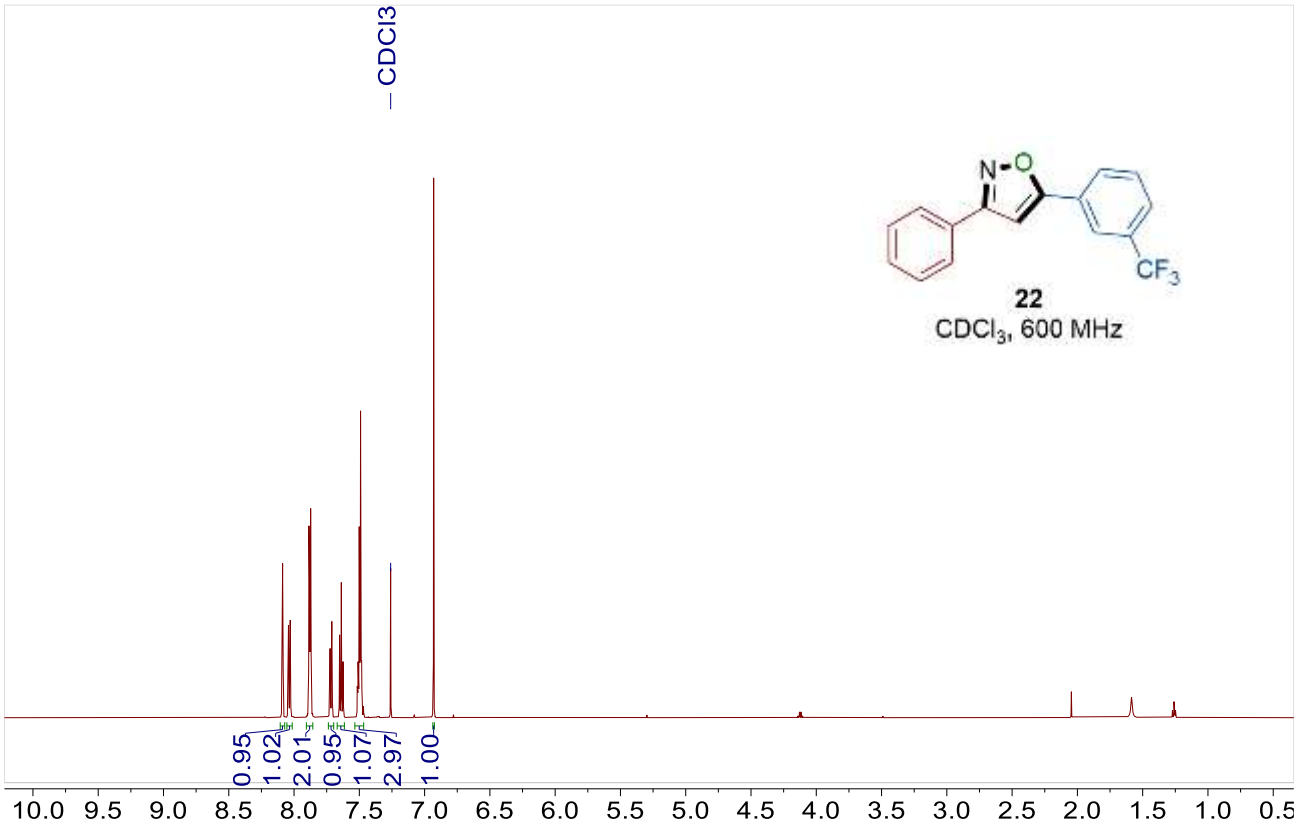
^{13}C NMR spectrum of **21**



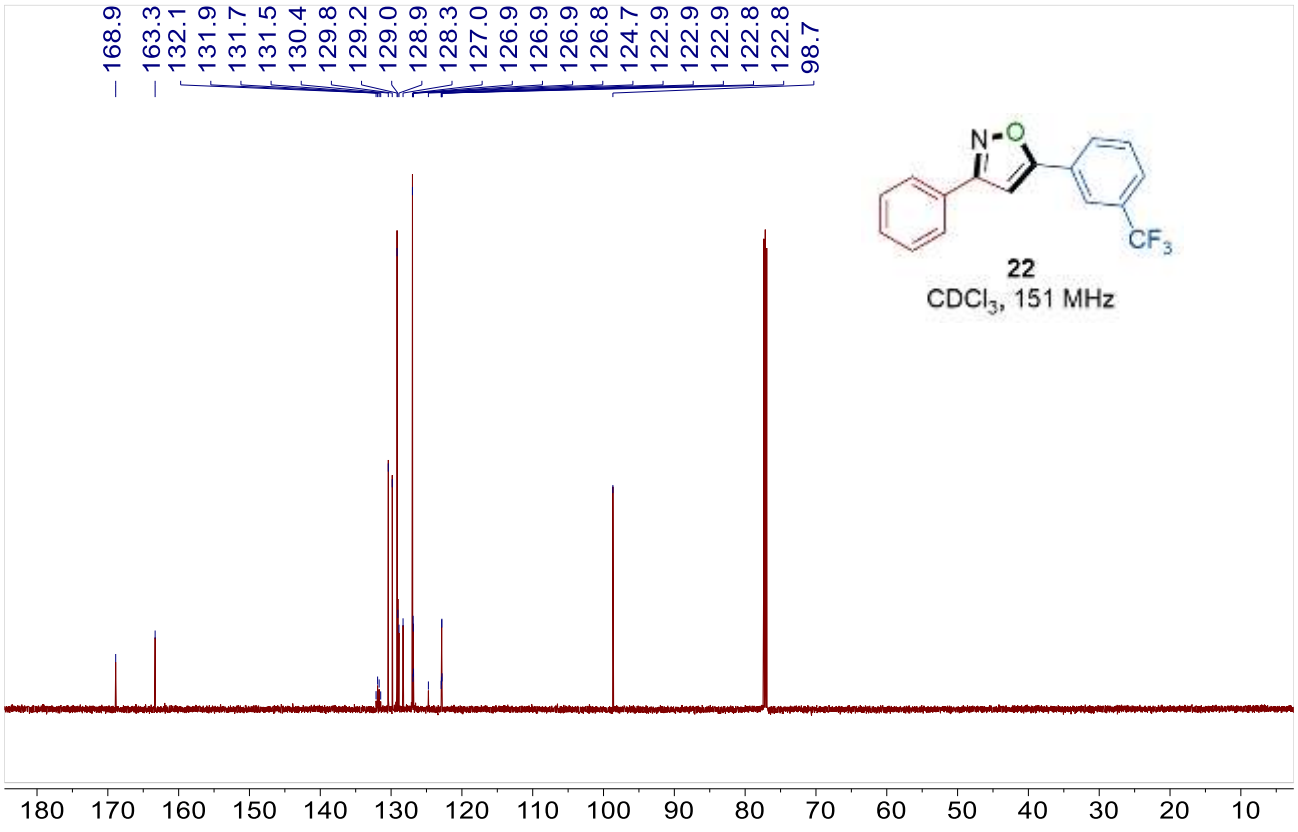
^{19}F NMR spectrum of **21**



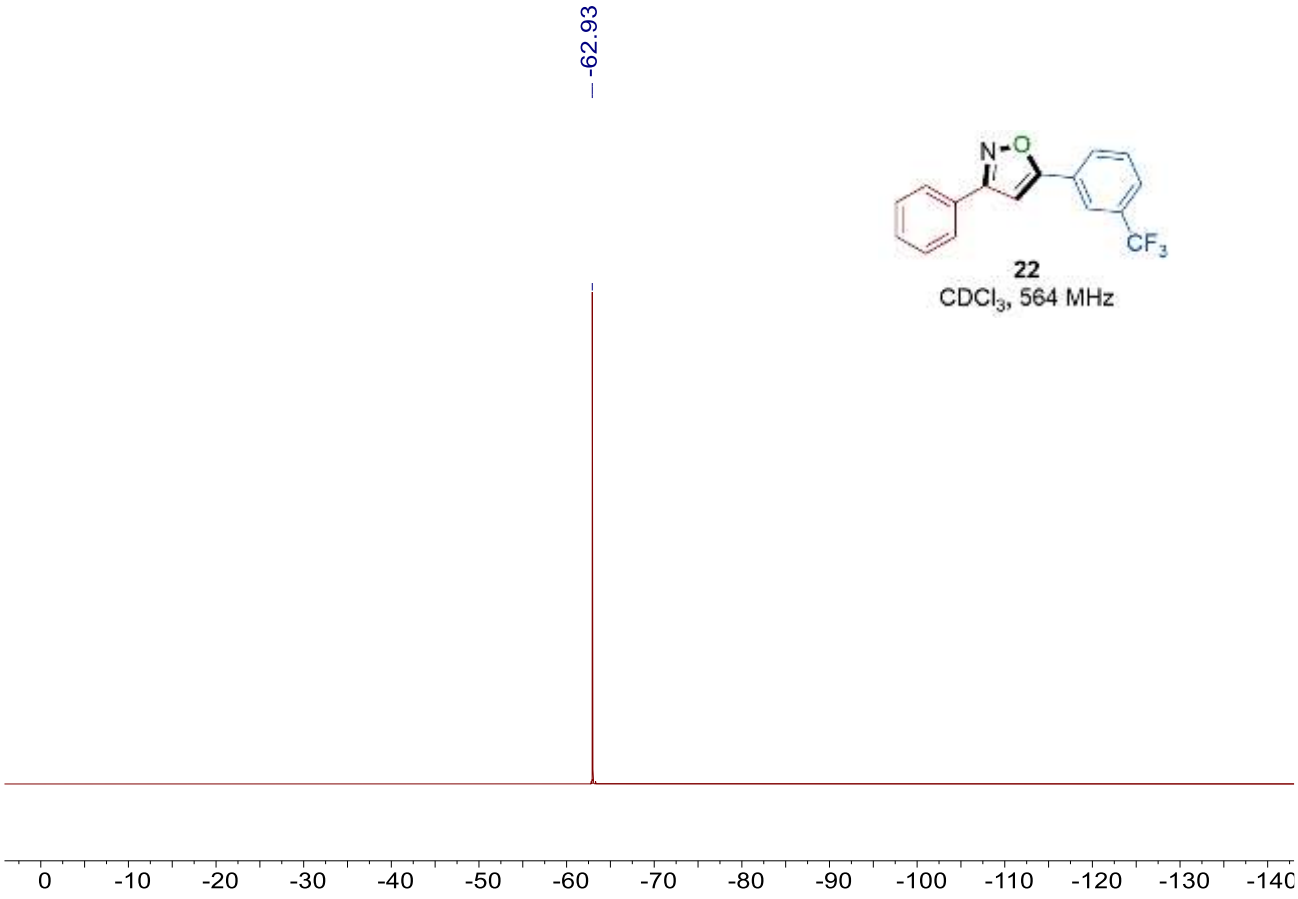
^{1}H NMR spectrum of **22**



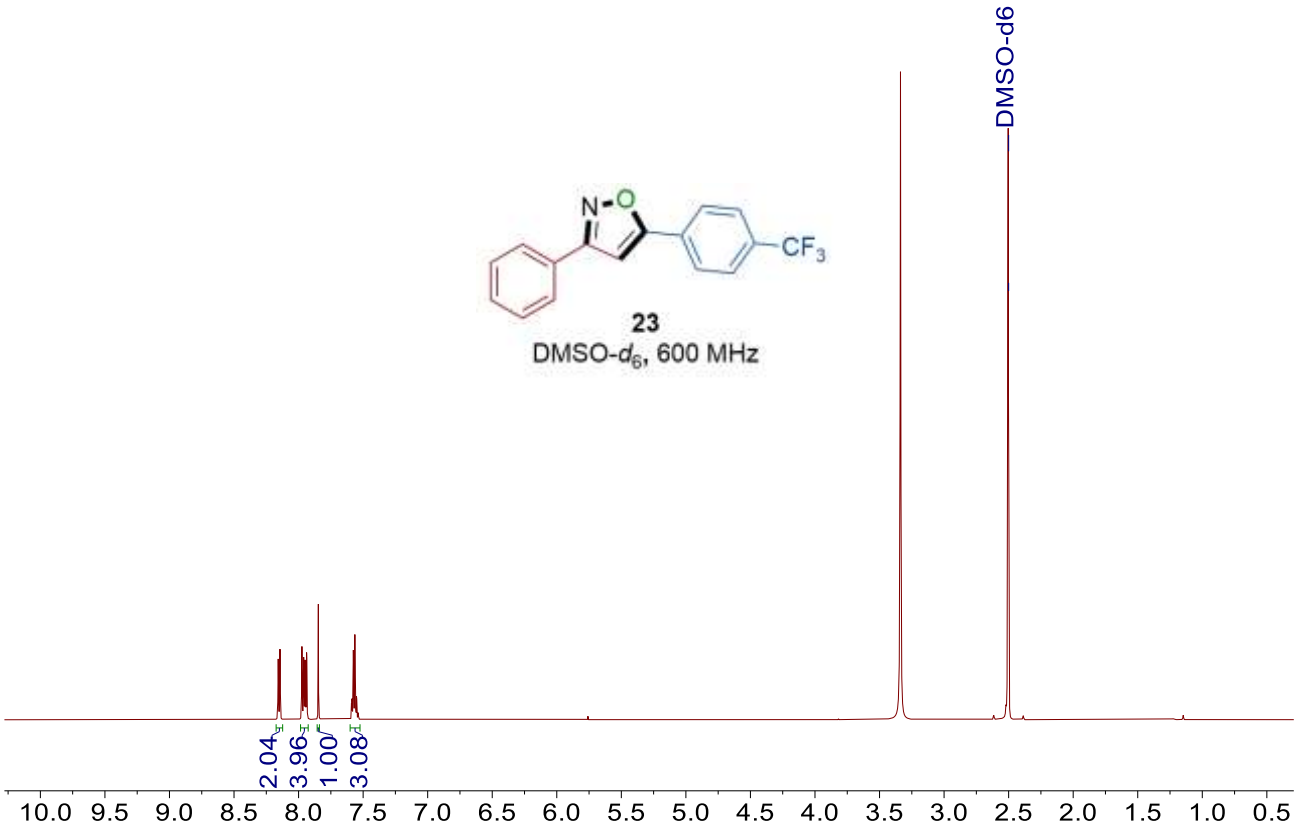
^{13}C NMR spectrum of **22**



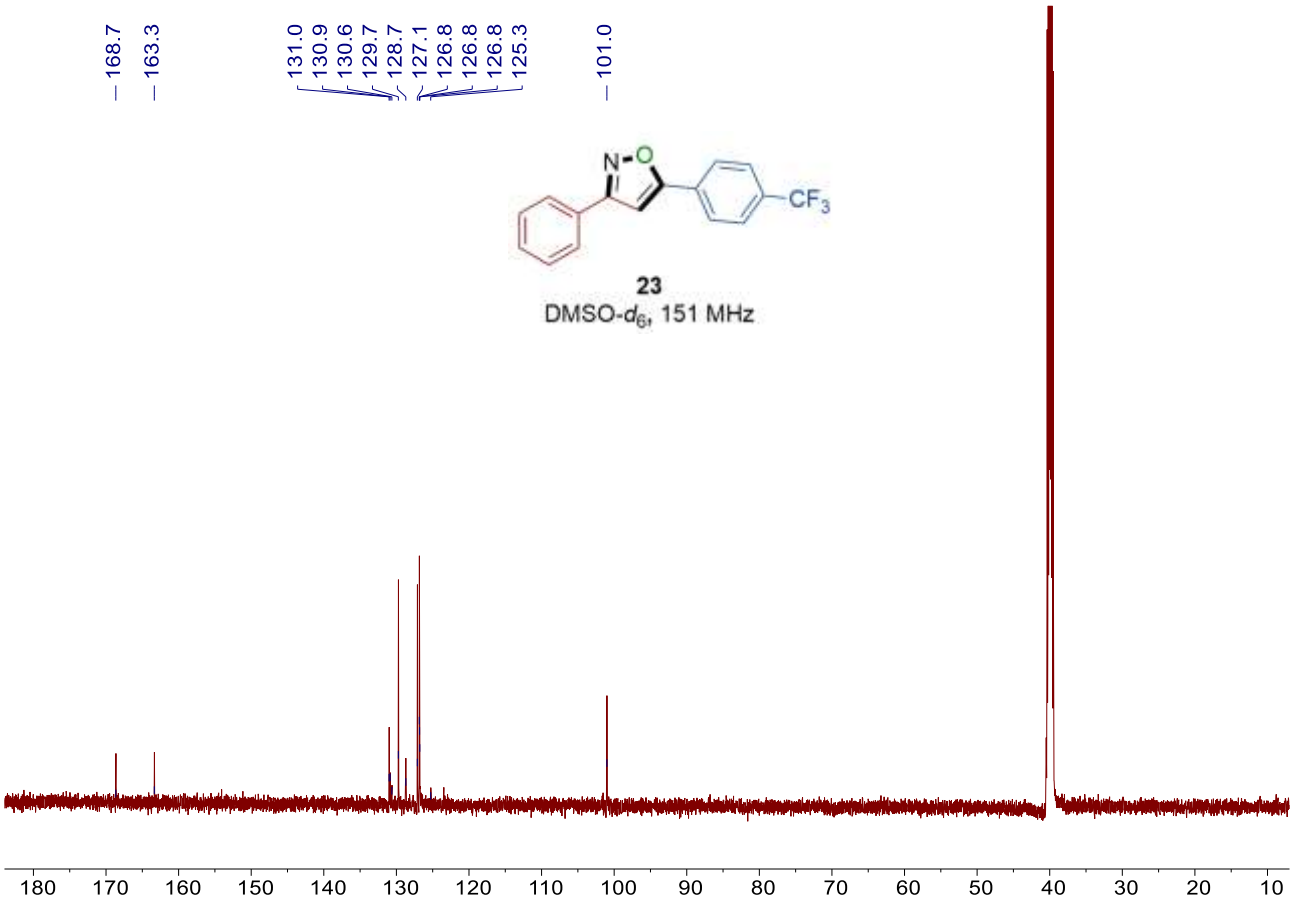
^{19}F NMR spectrum of **22**



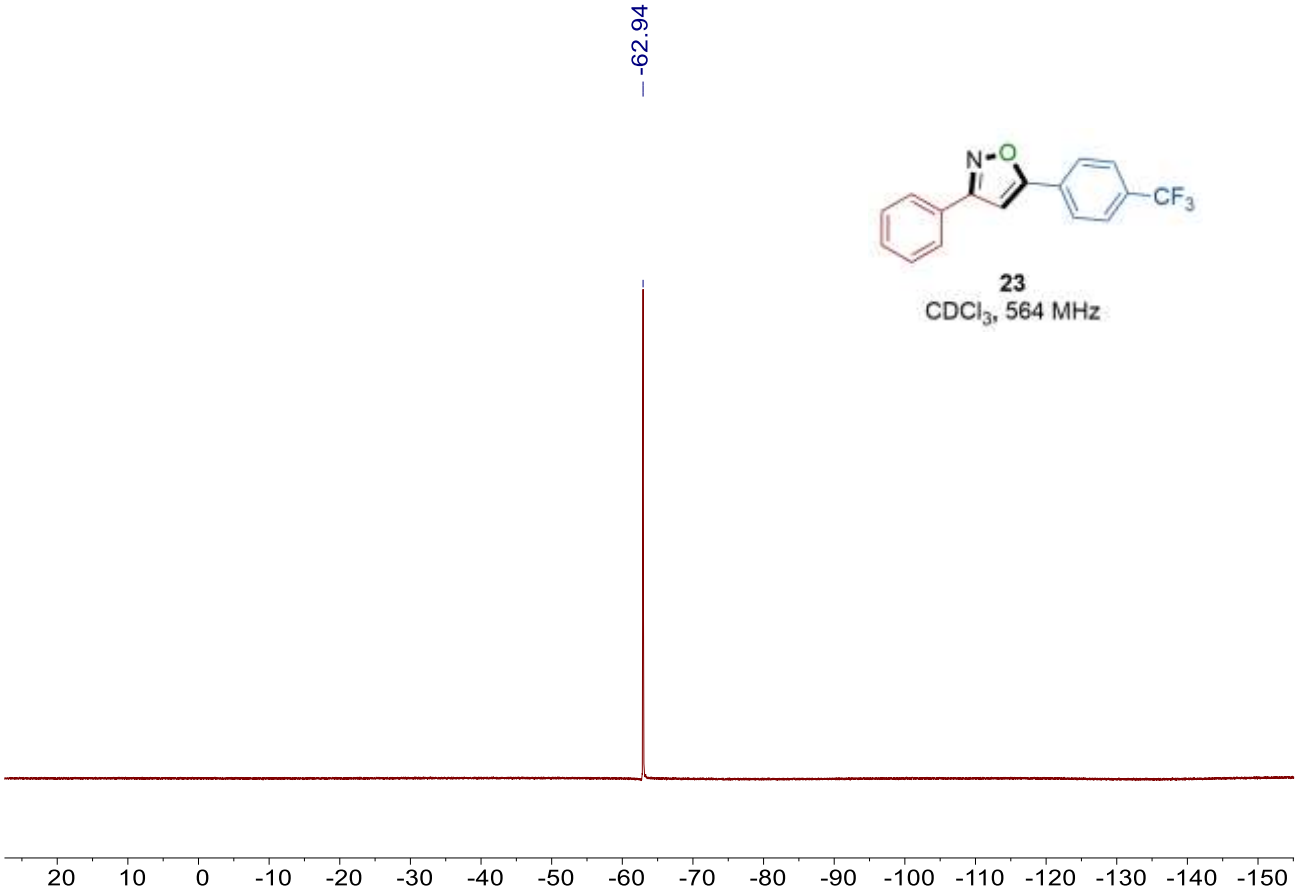
^{1}H NMR spectrum of **23**



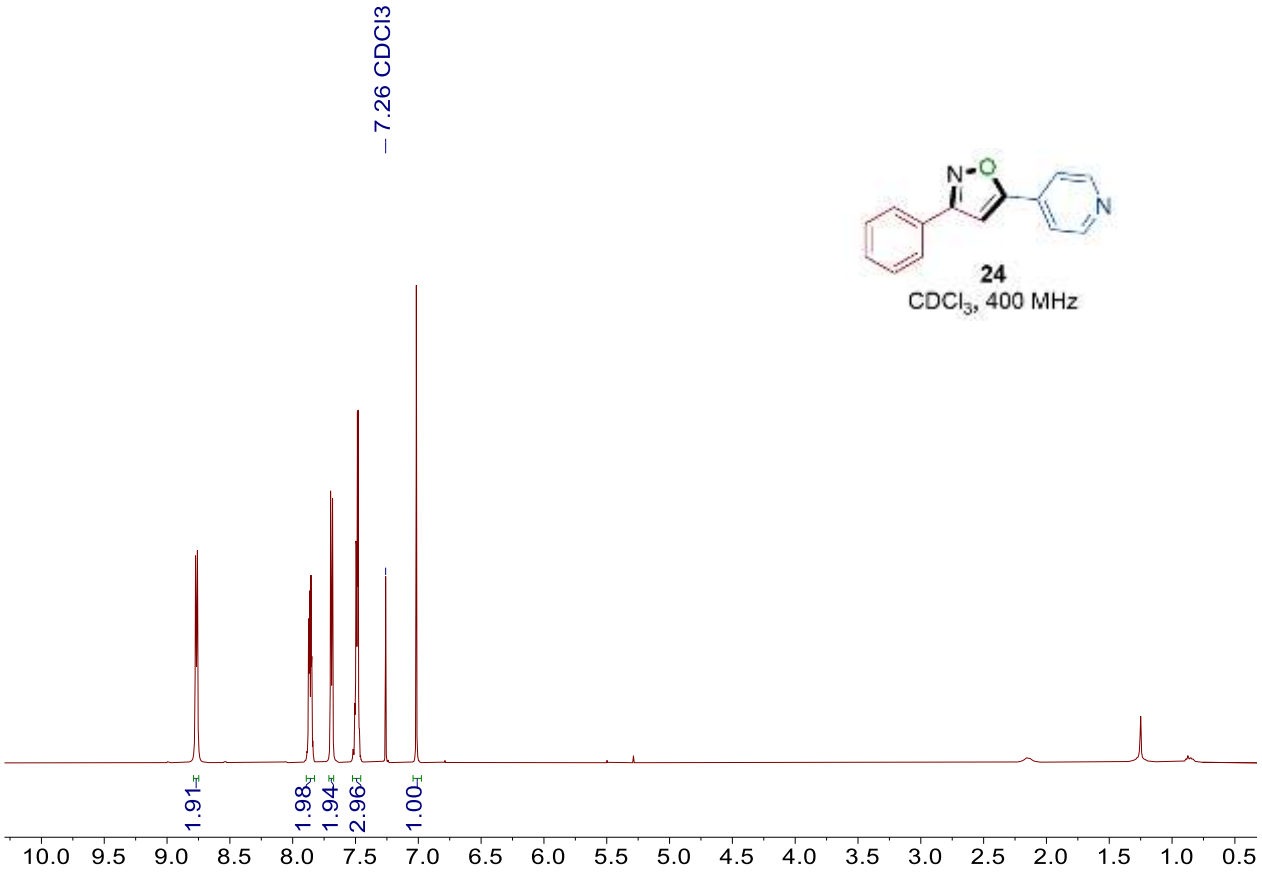
^{13}C NMR spectrum of **23**



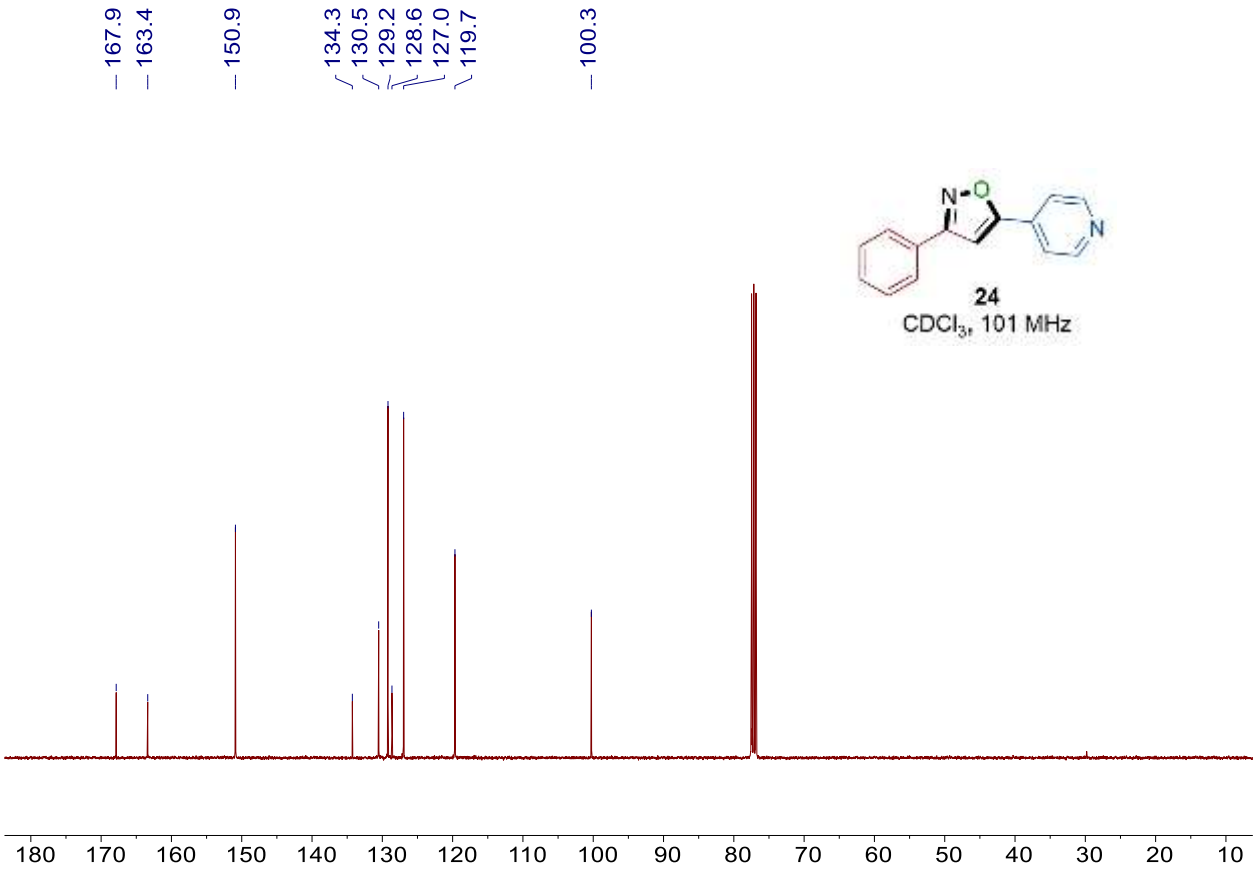
^{19}F NMR spectrum of **23**



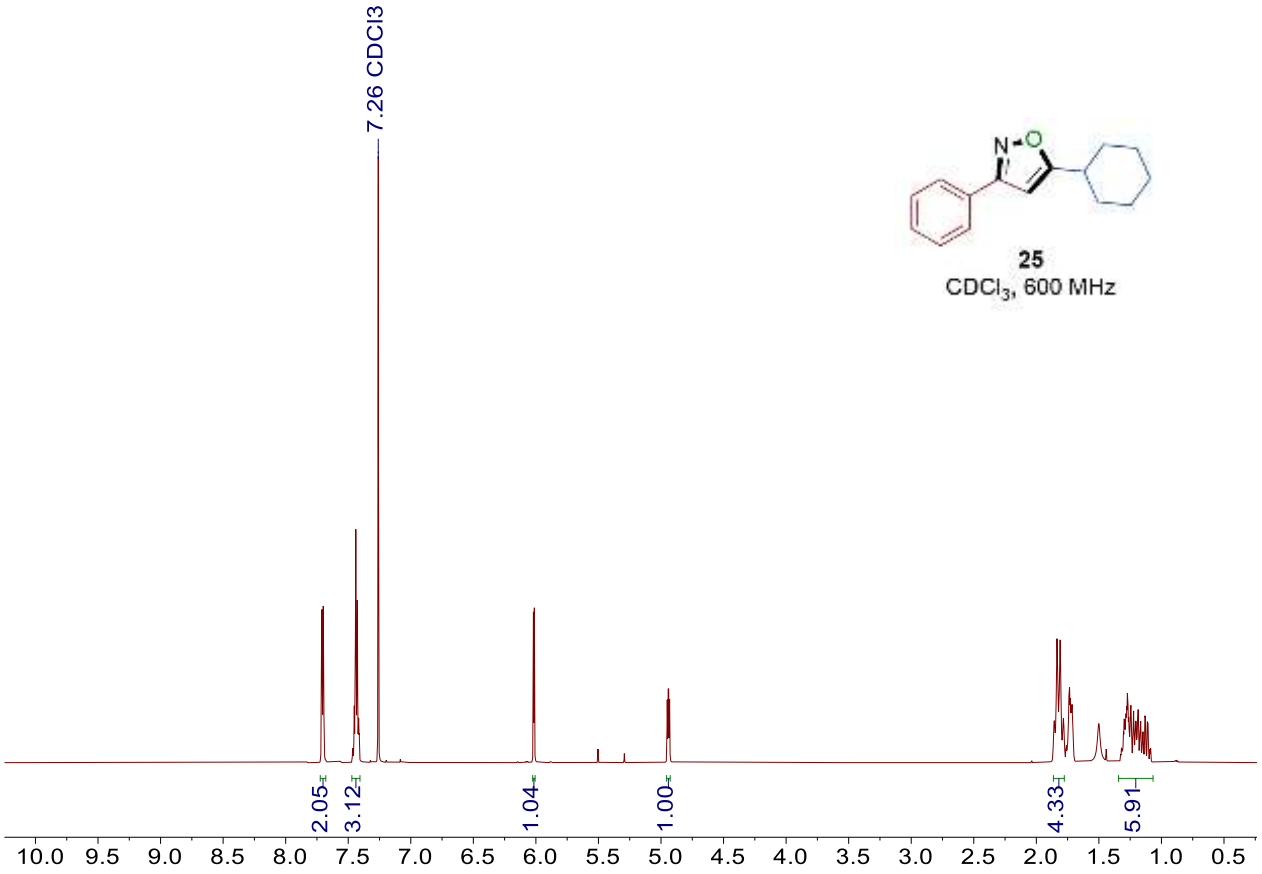
^{1}H NMR spectrum of **24**



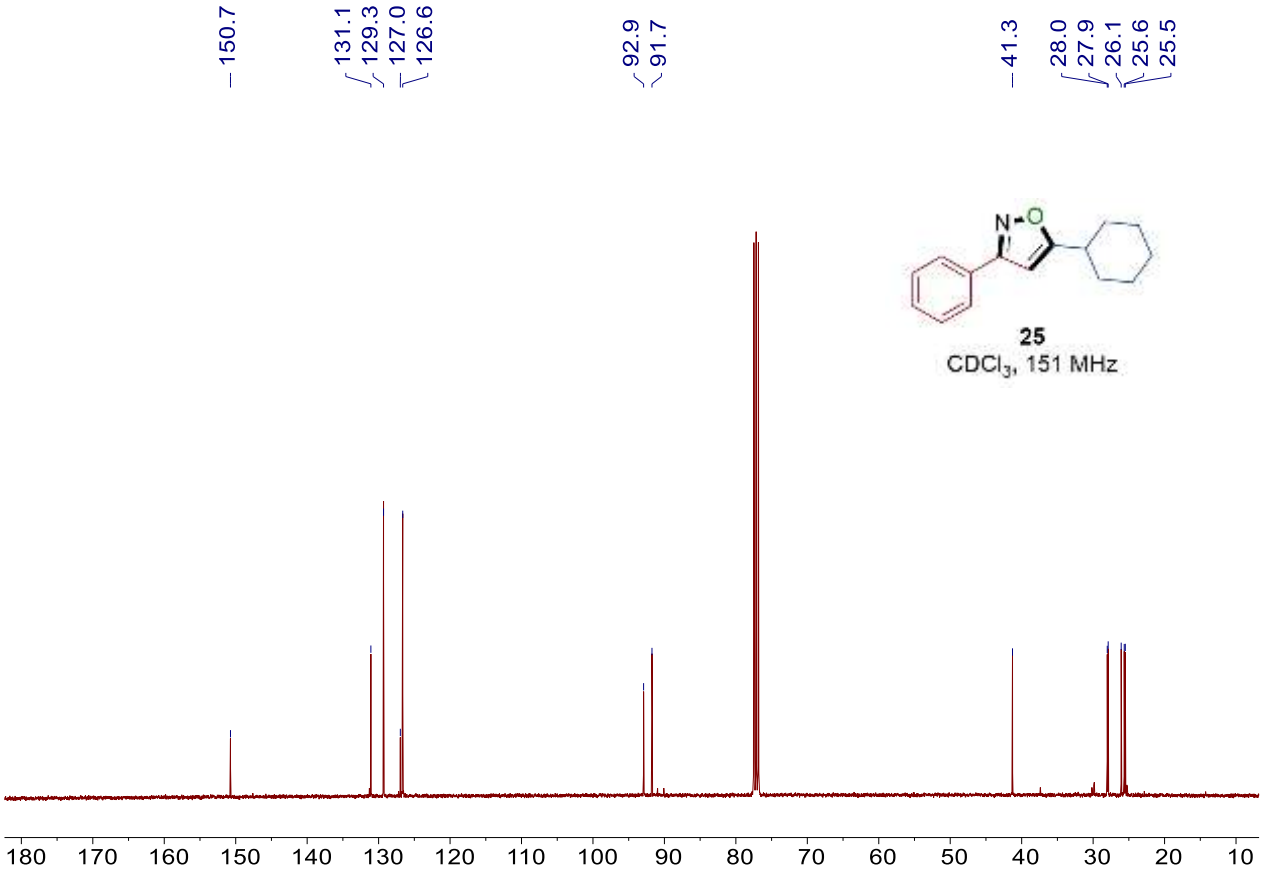
^{13}C NMR spectrum of **24**



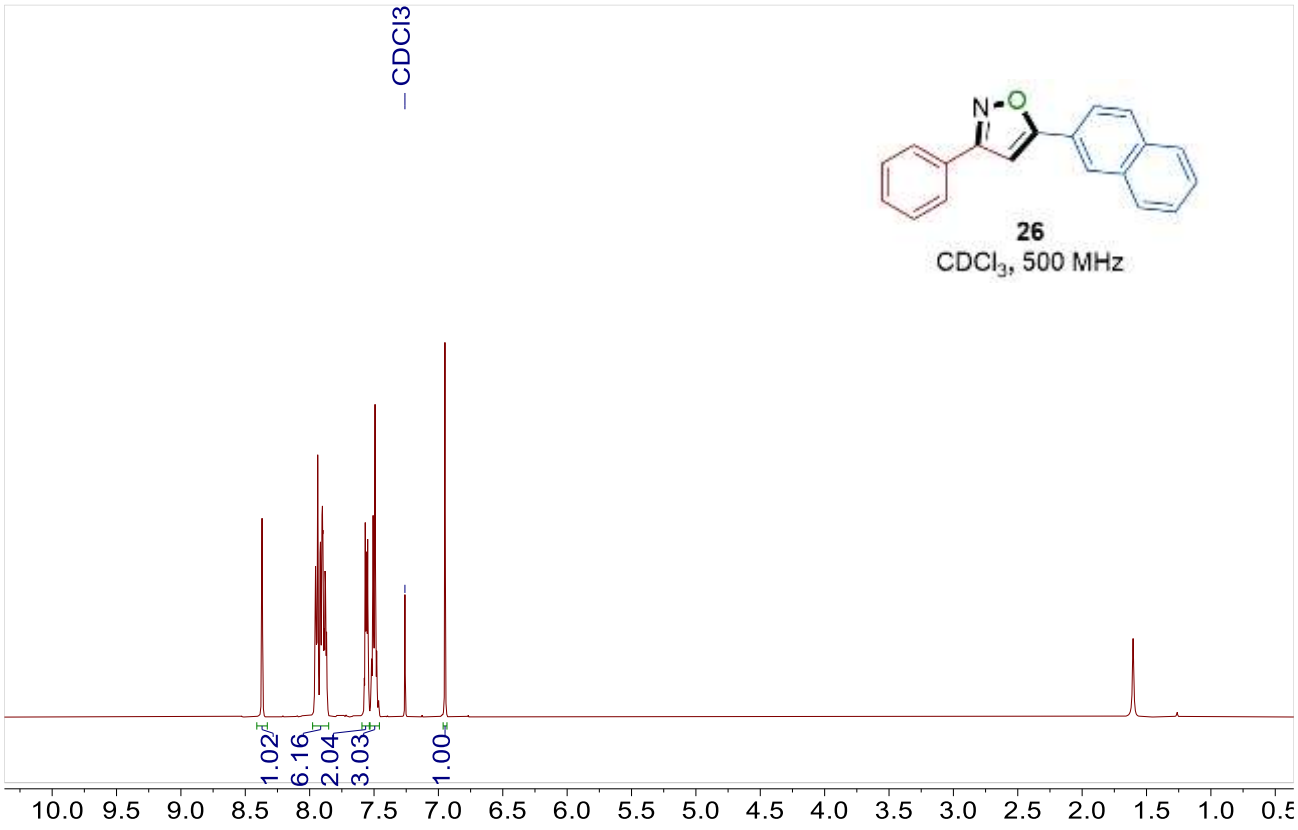
^{1}H NMR spectrum of **25**



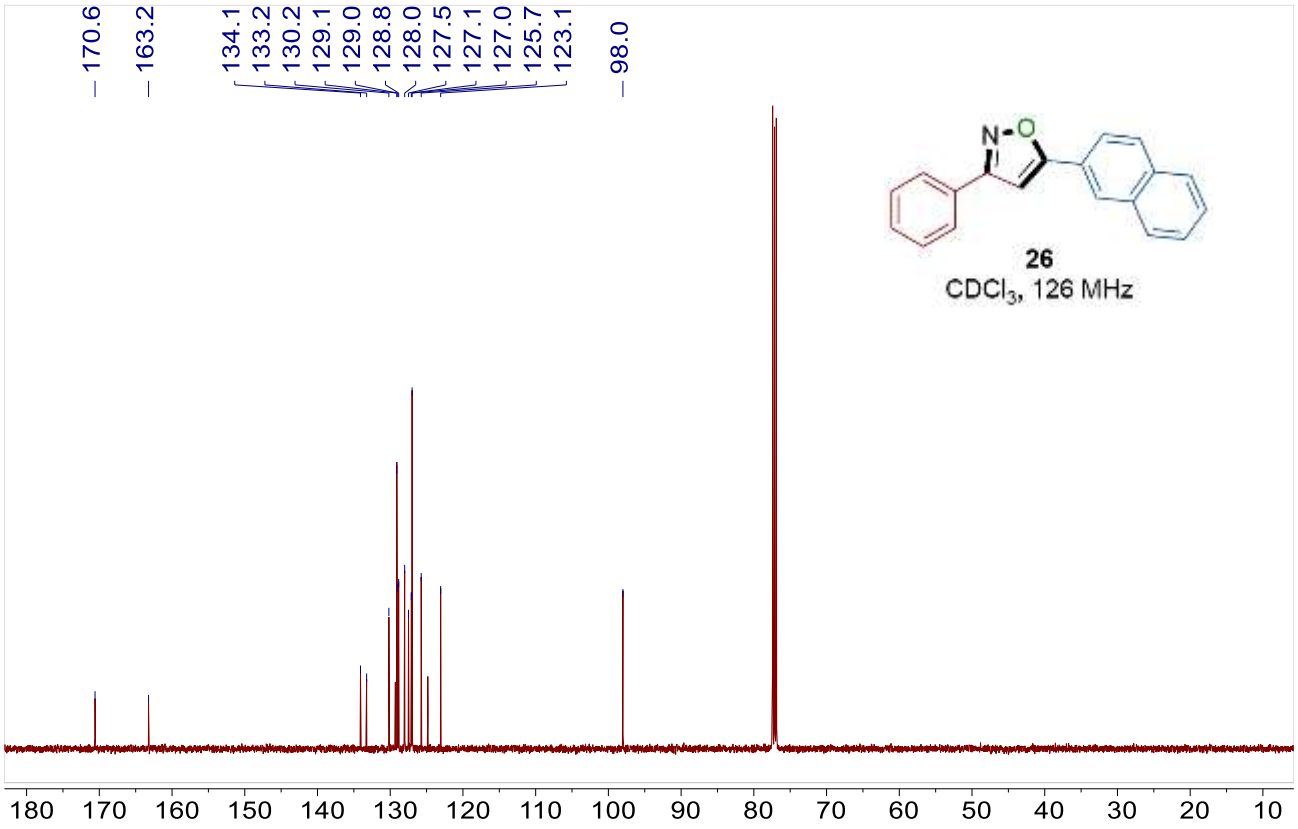
^{13}C NMR spectrum of **25**



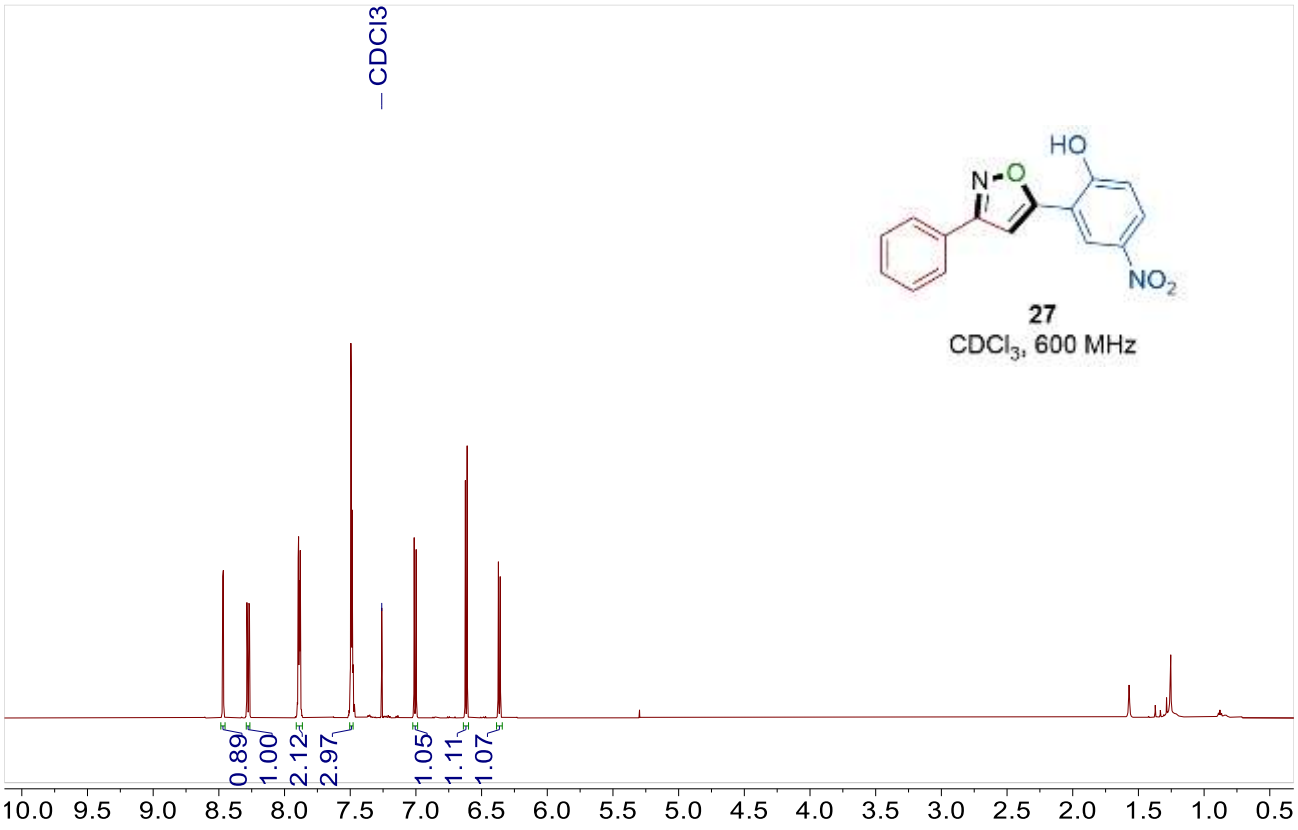
^{1}H NMR spectrum of **26**



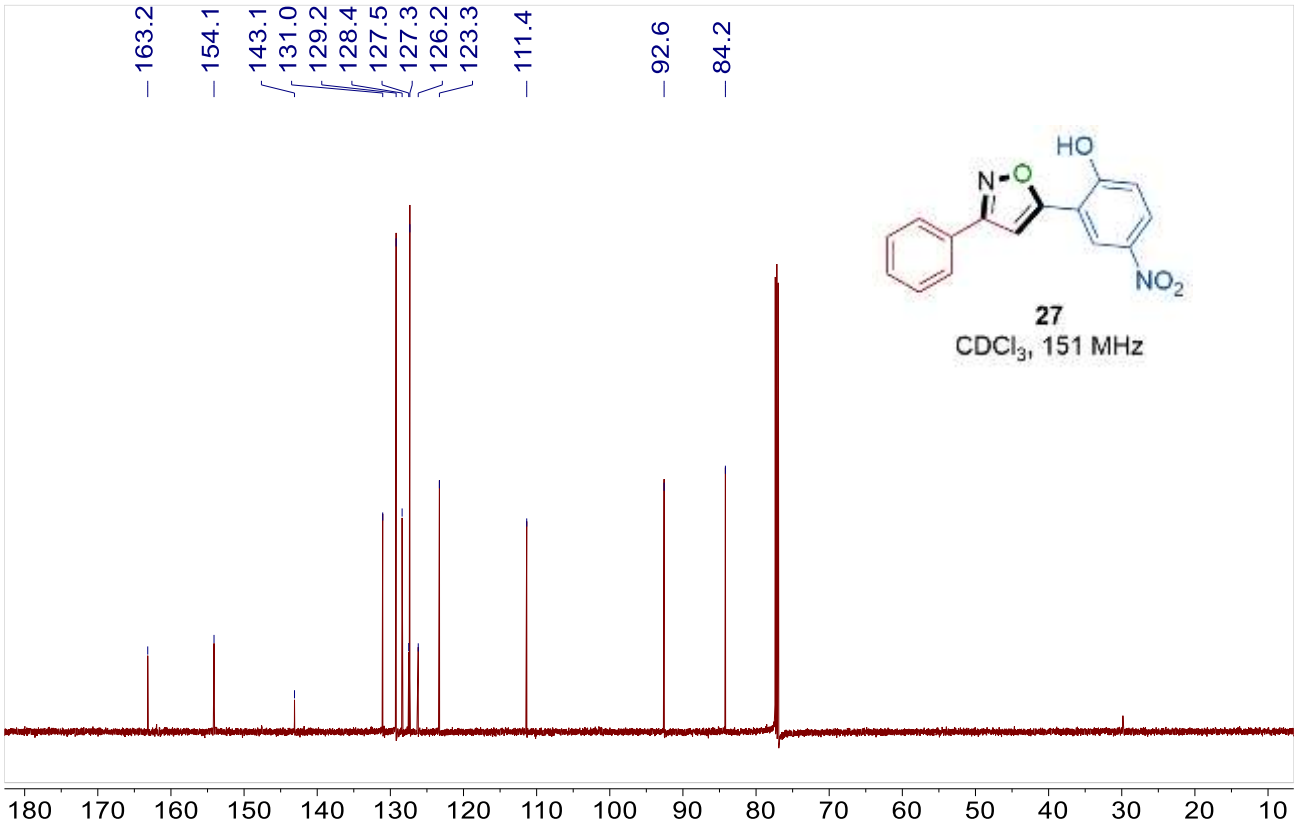
^{13}C NMR spectrum of **26**



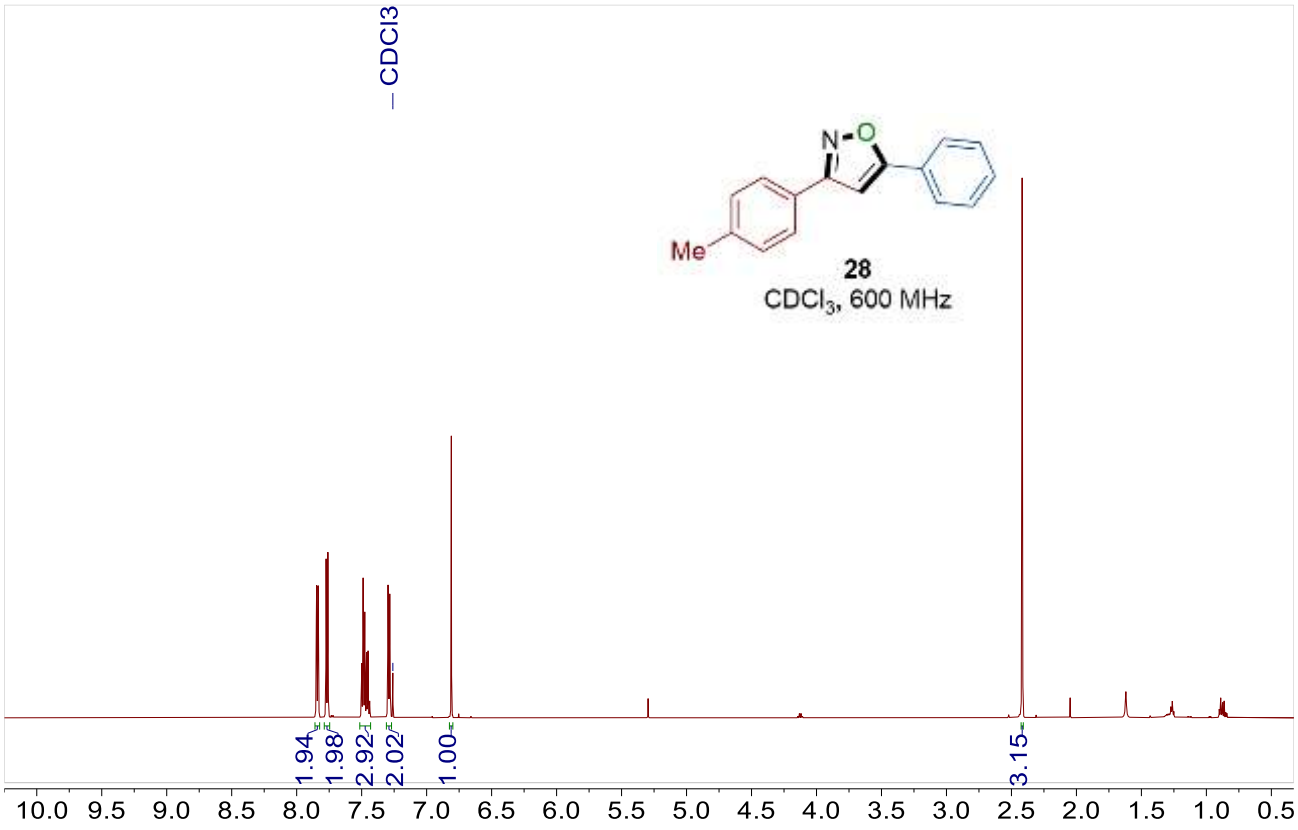
^{1}H NMR spectrum of **27**



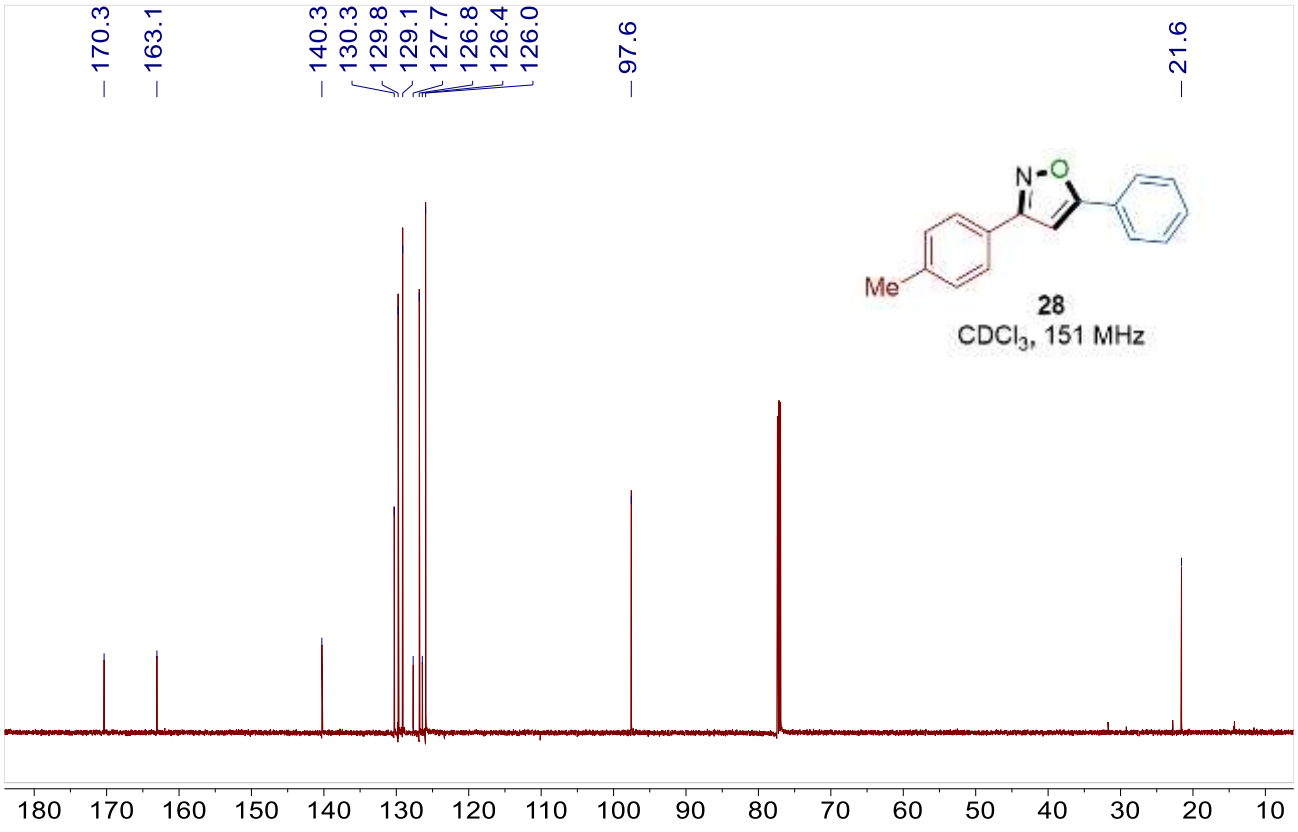
^{13}C NMR spectrum of **27**



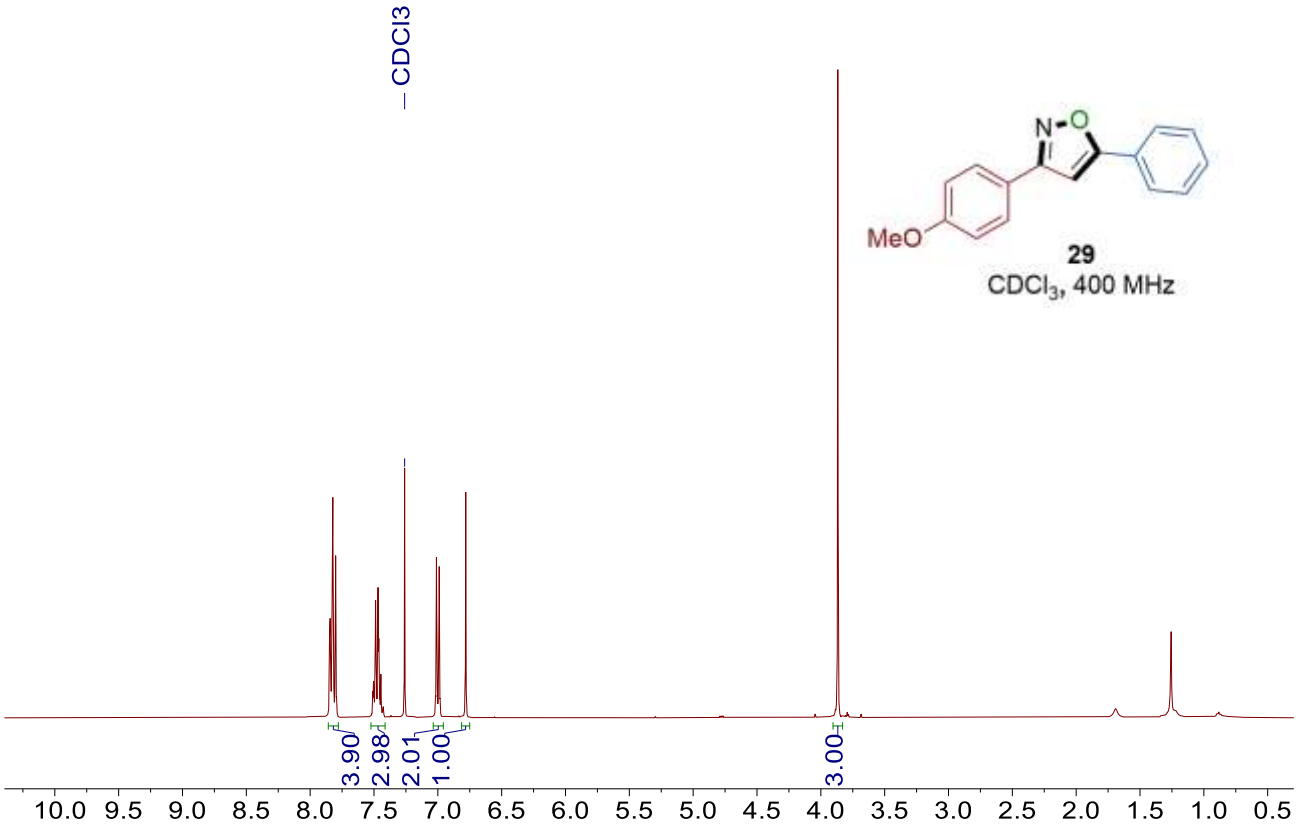
^{1}H NMR spectrum of **28**



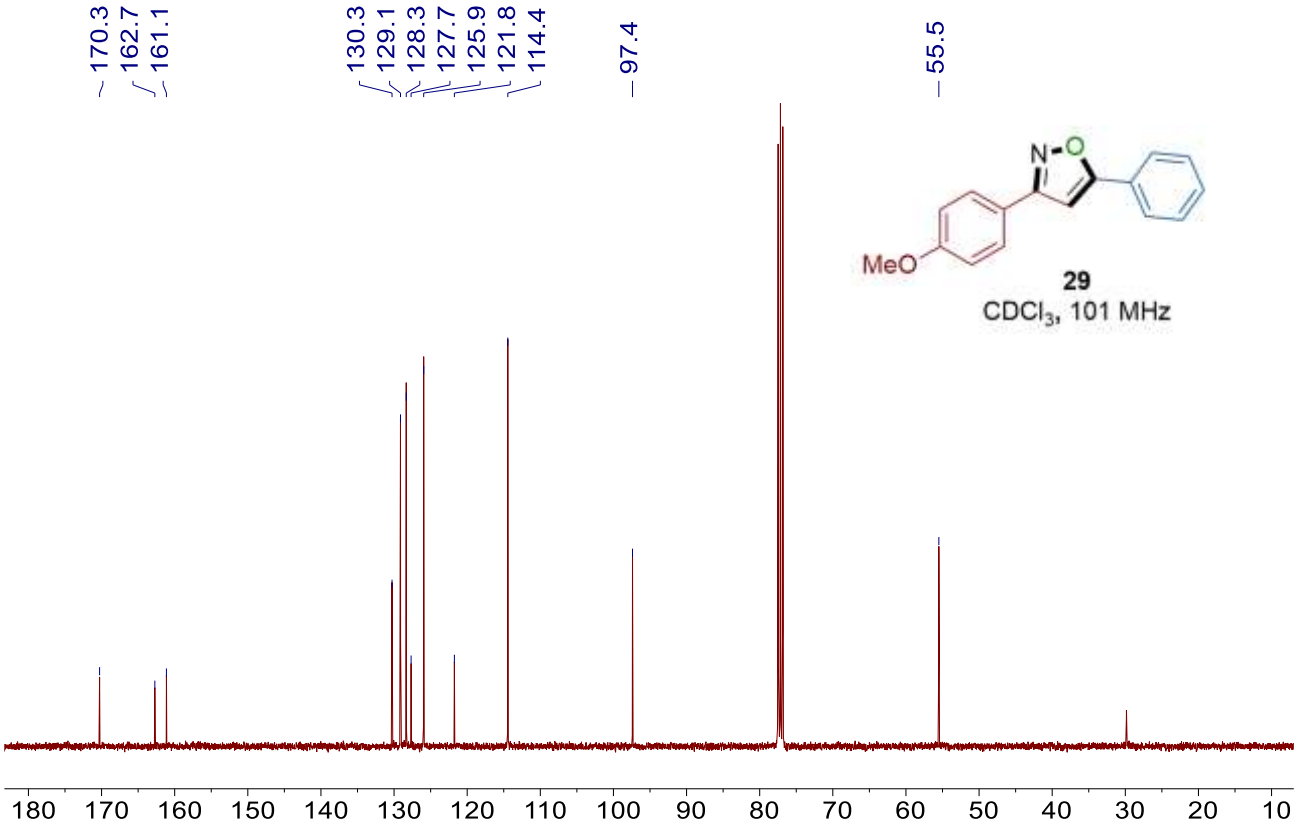
^{13}C NMR spectrum of **28**



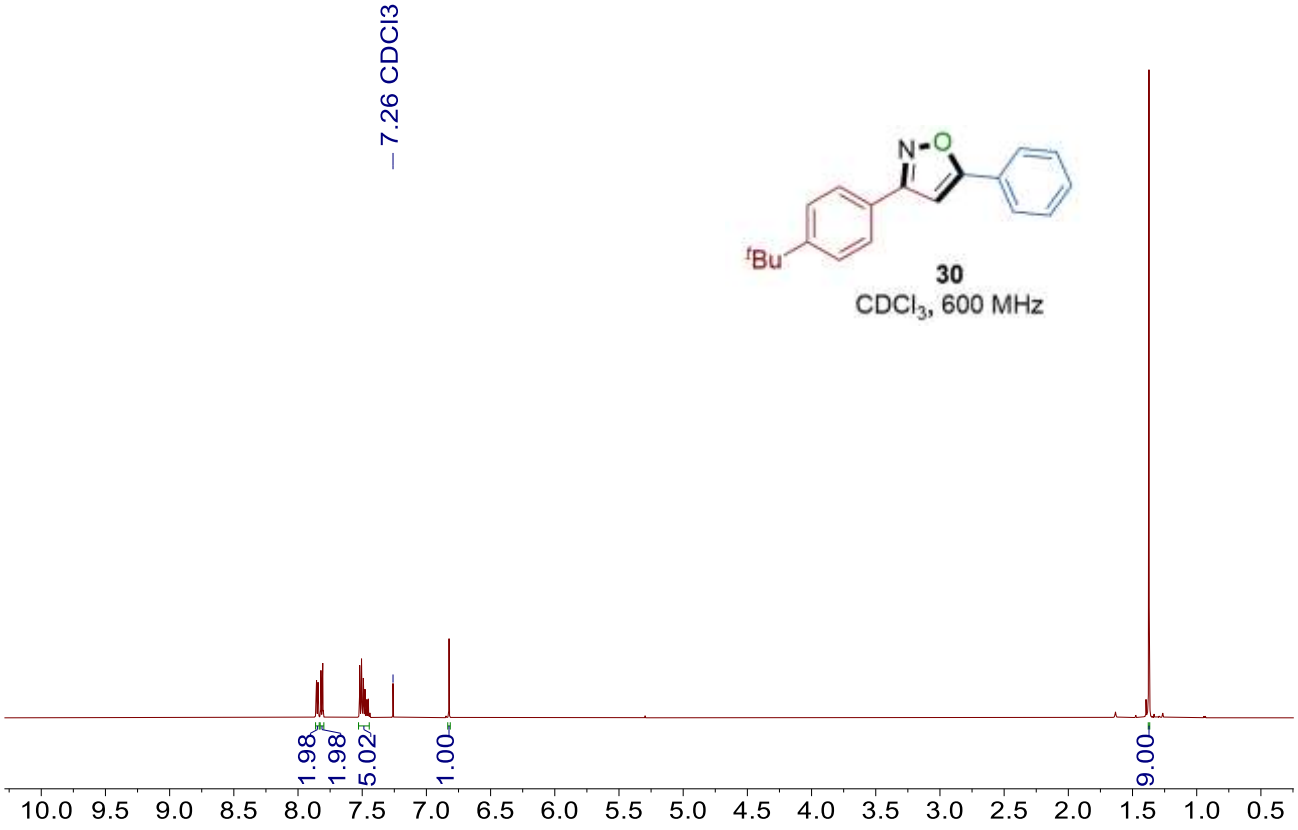
^{1}H NMR spectrum of **29**



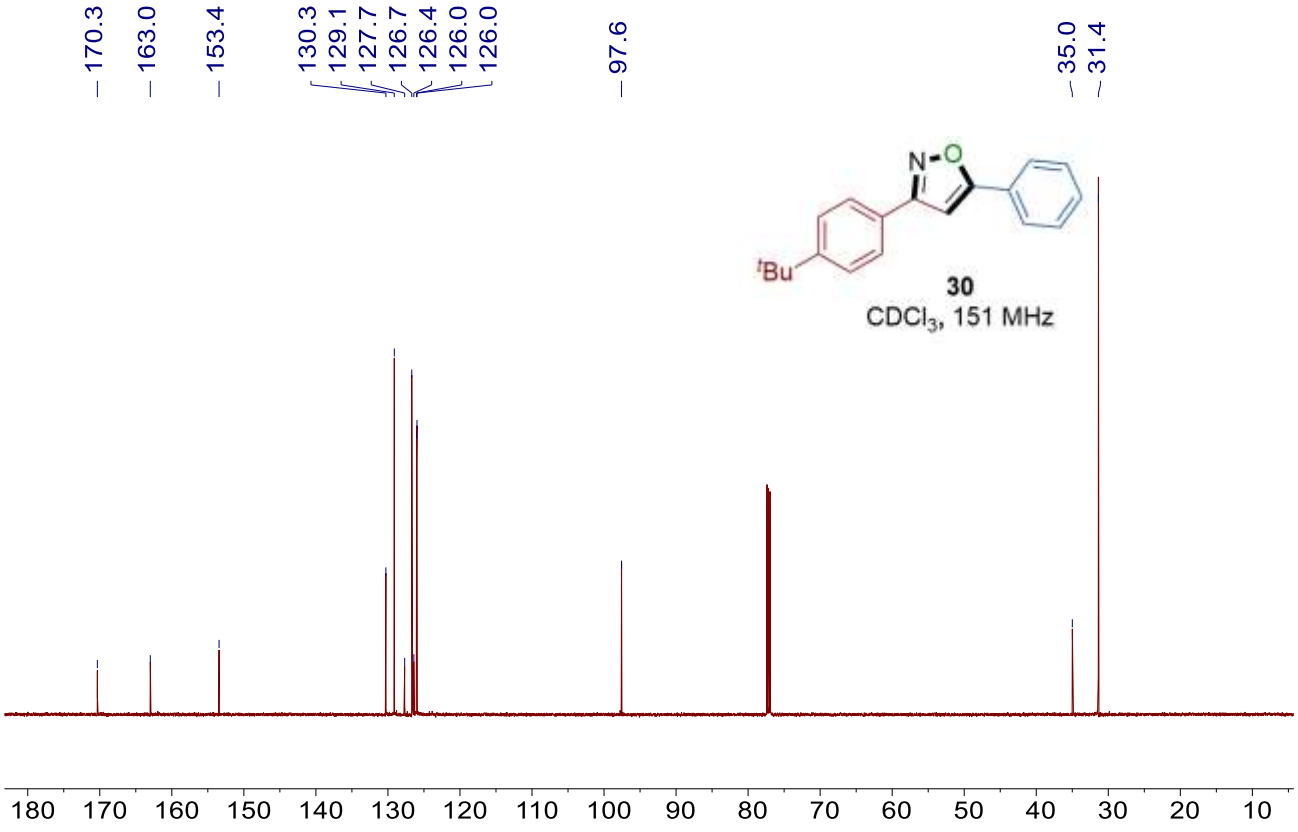
^{13}C NMR spectrum of **29**



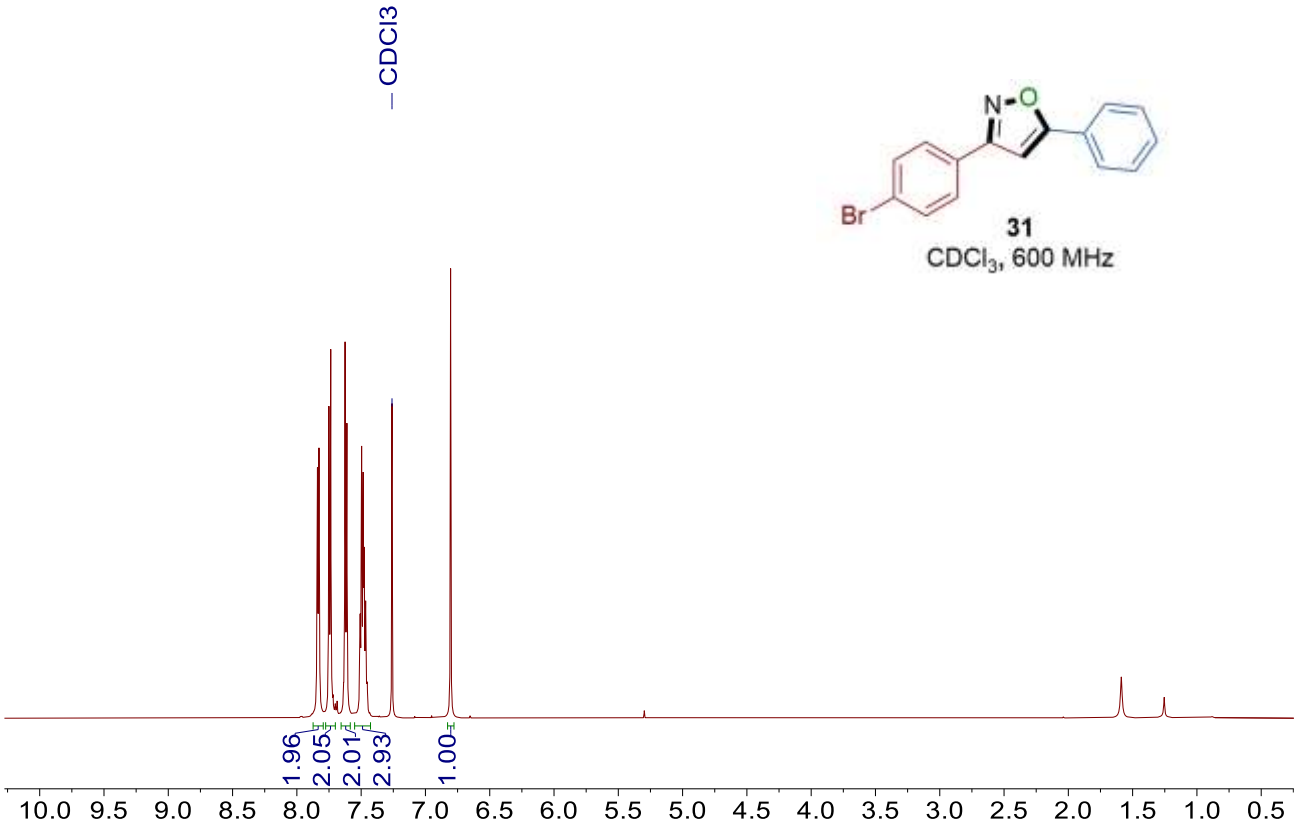
^{1}H NMR spectrum of **30**



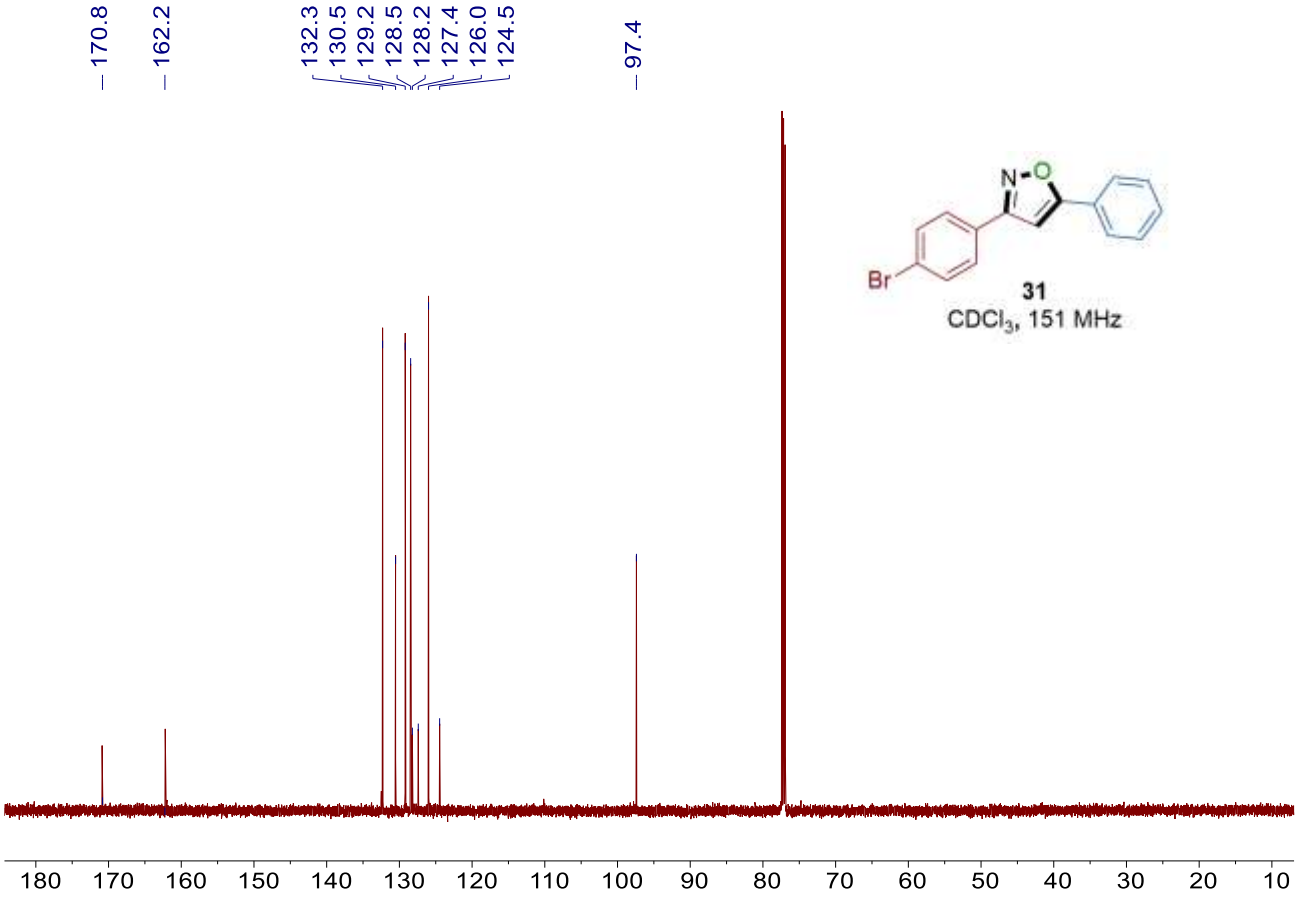
^{13}C NMR spectrum of **30**



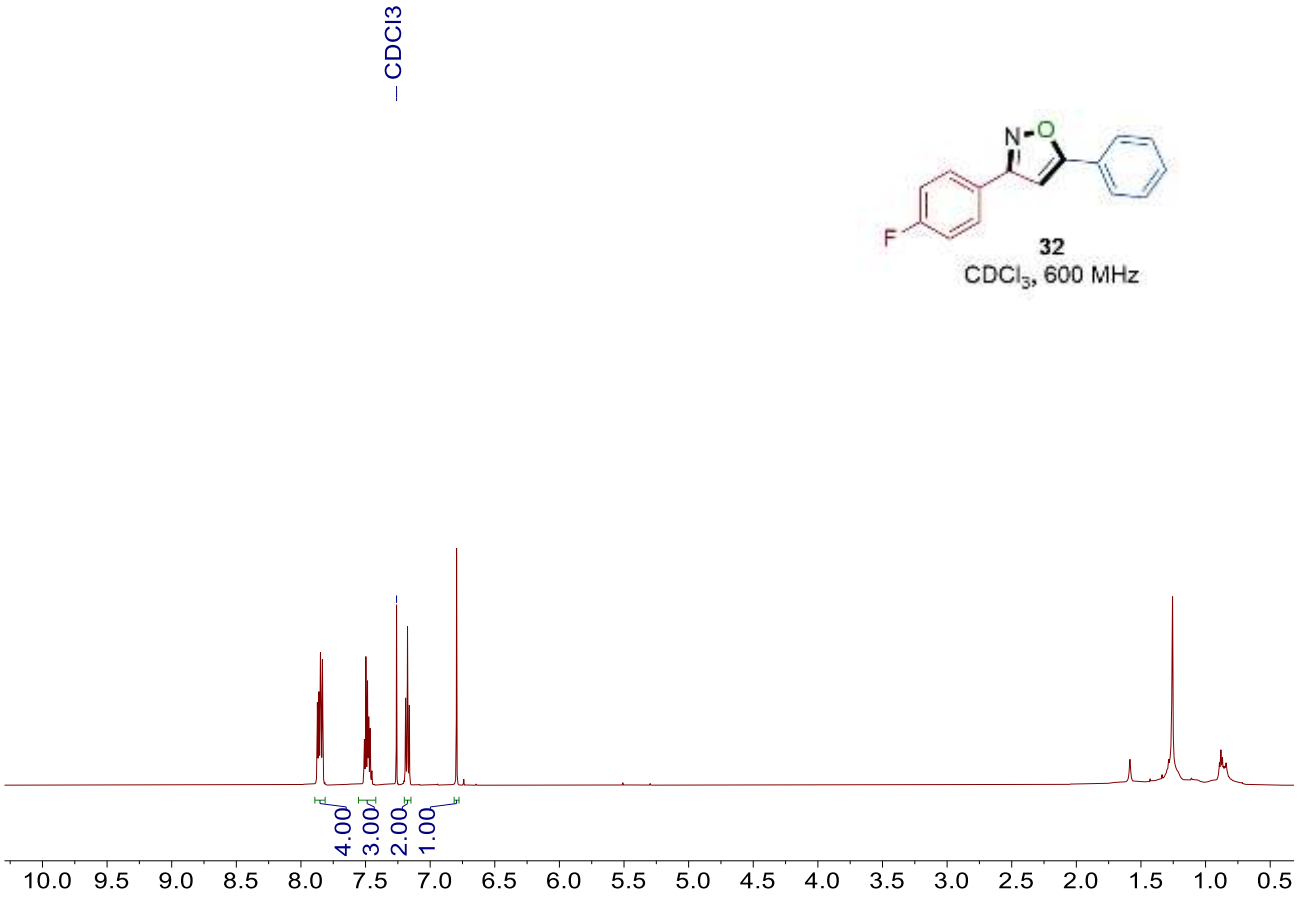
^{1}H NMR spectrum of **31**



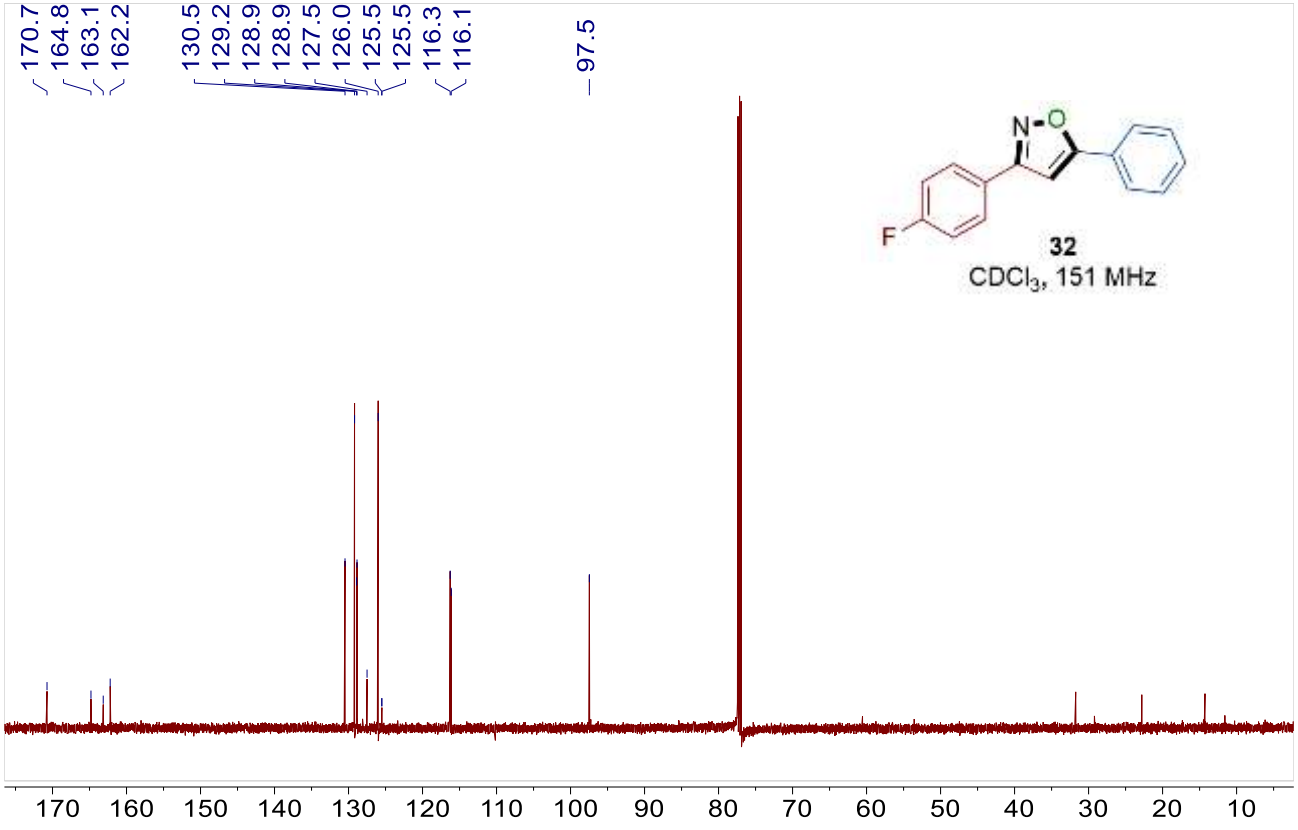
^{13}C NMR spectrum of **31**



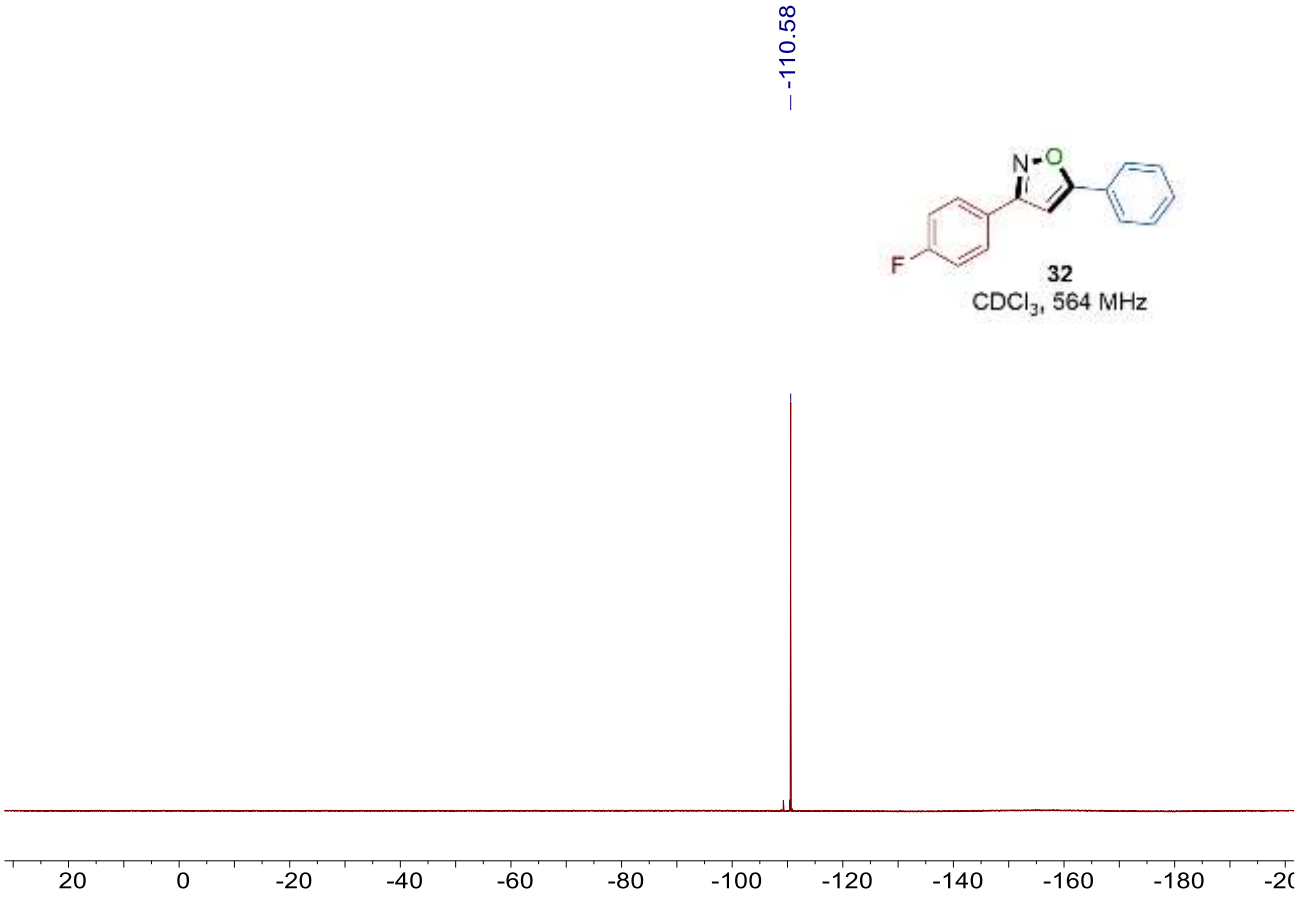
^{1}H NMR spectrum of **32**



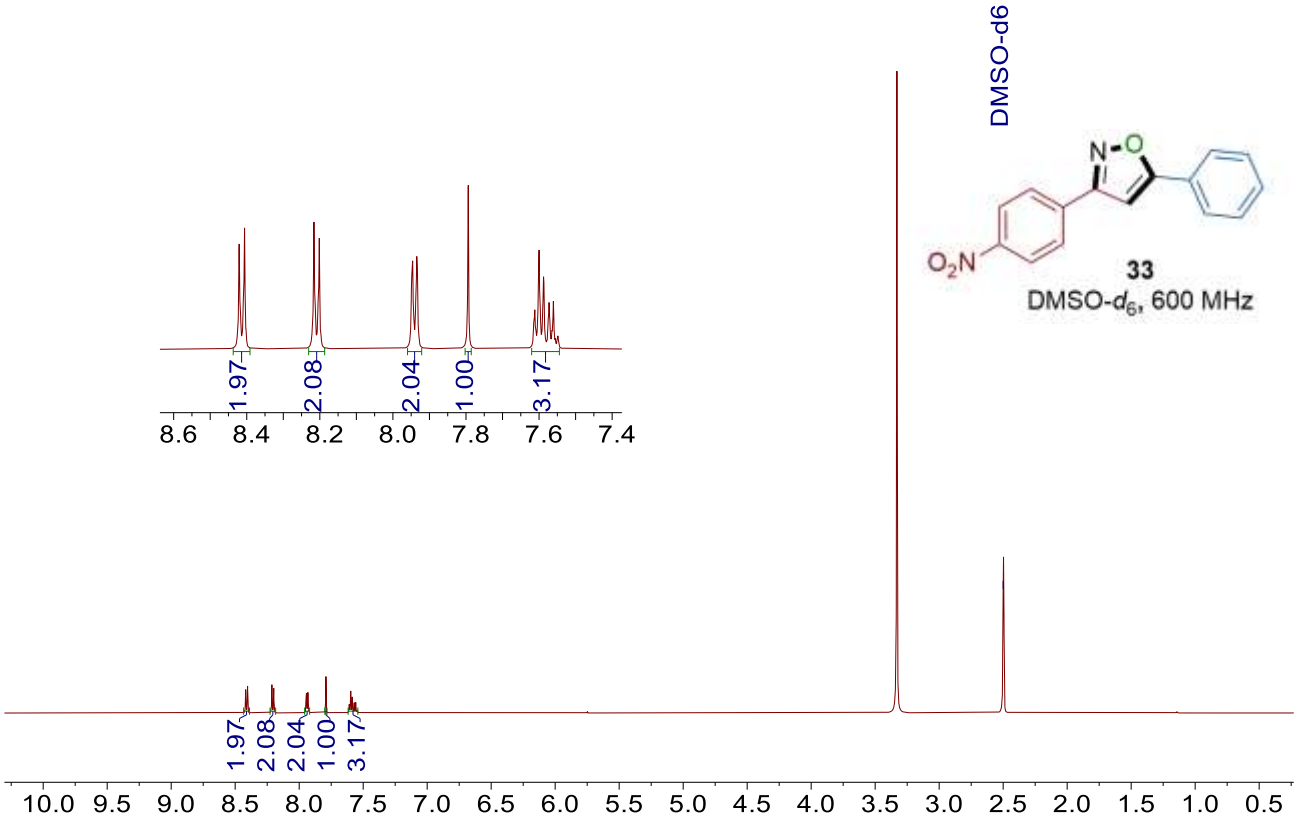
^{13}C NMR spectrum of **32**



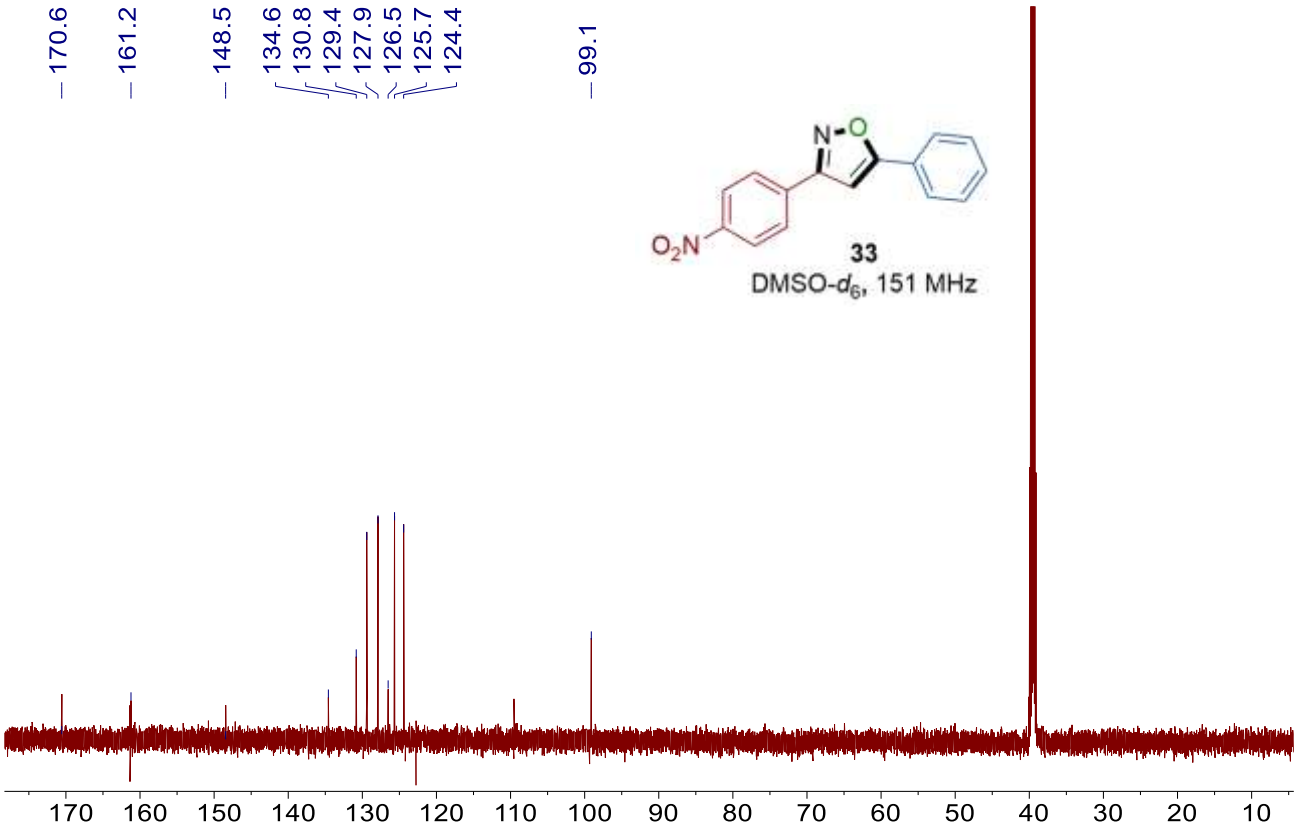
^{19}F NMR spectrum of **32**



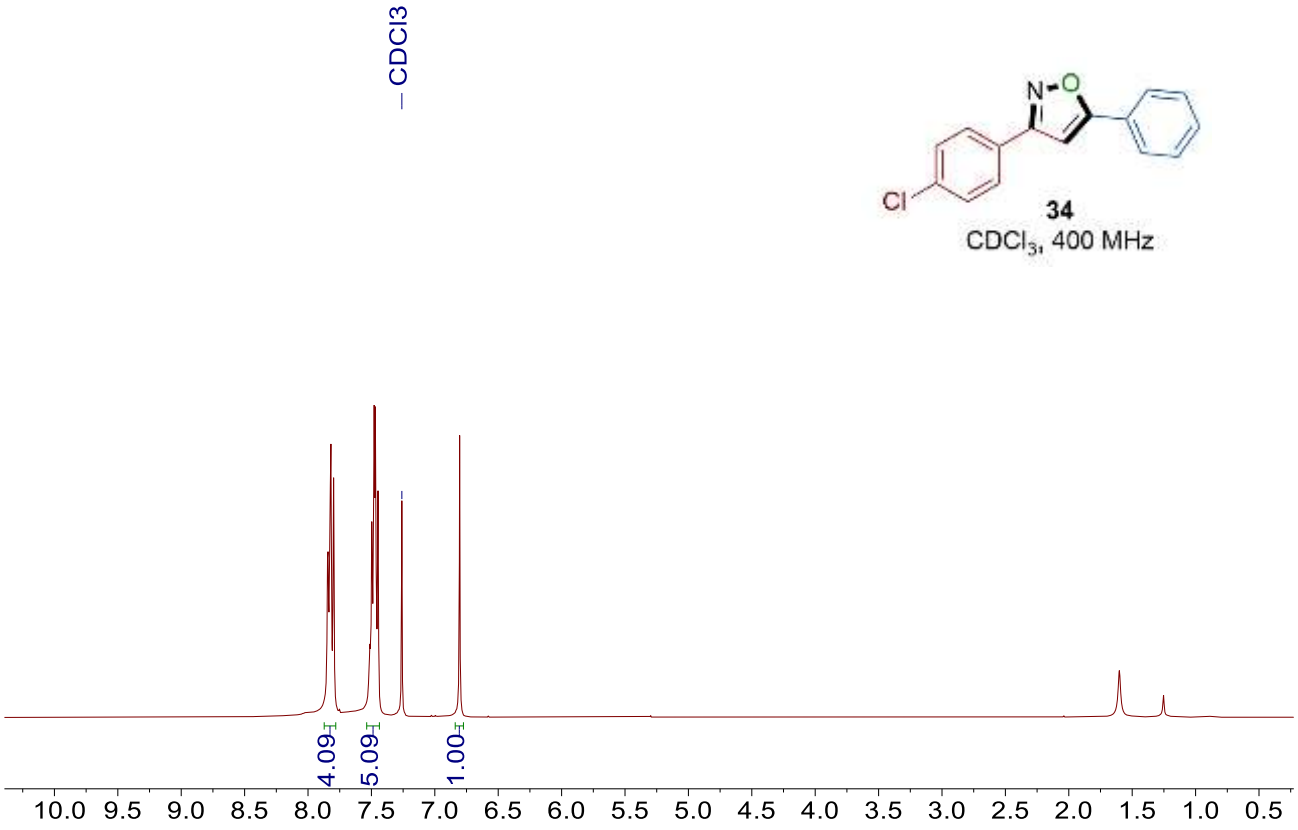
^{1}H NMR spectrum of **33**



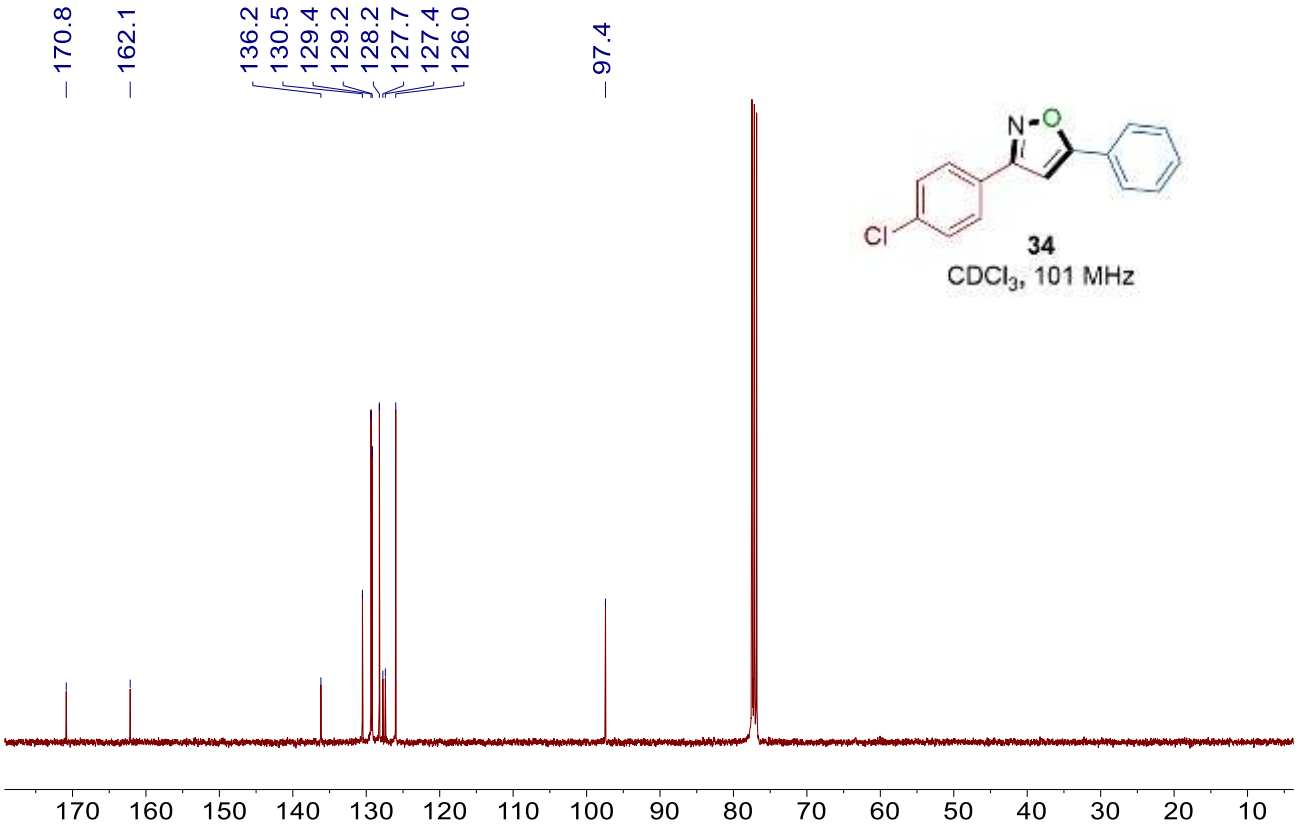
^{13}C NMR spectrum of **33**



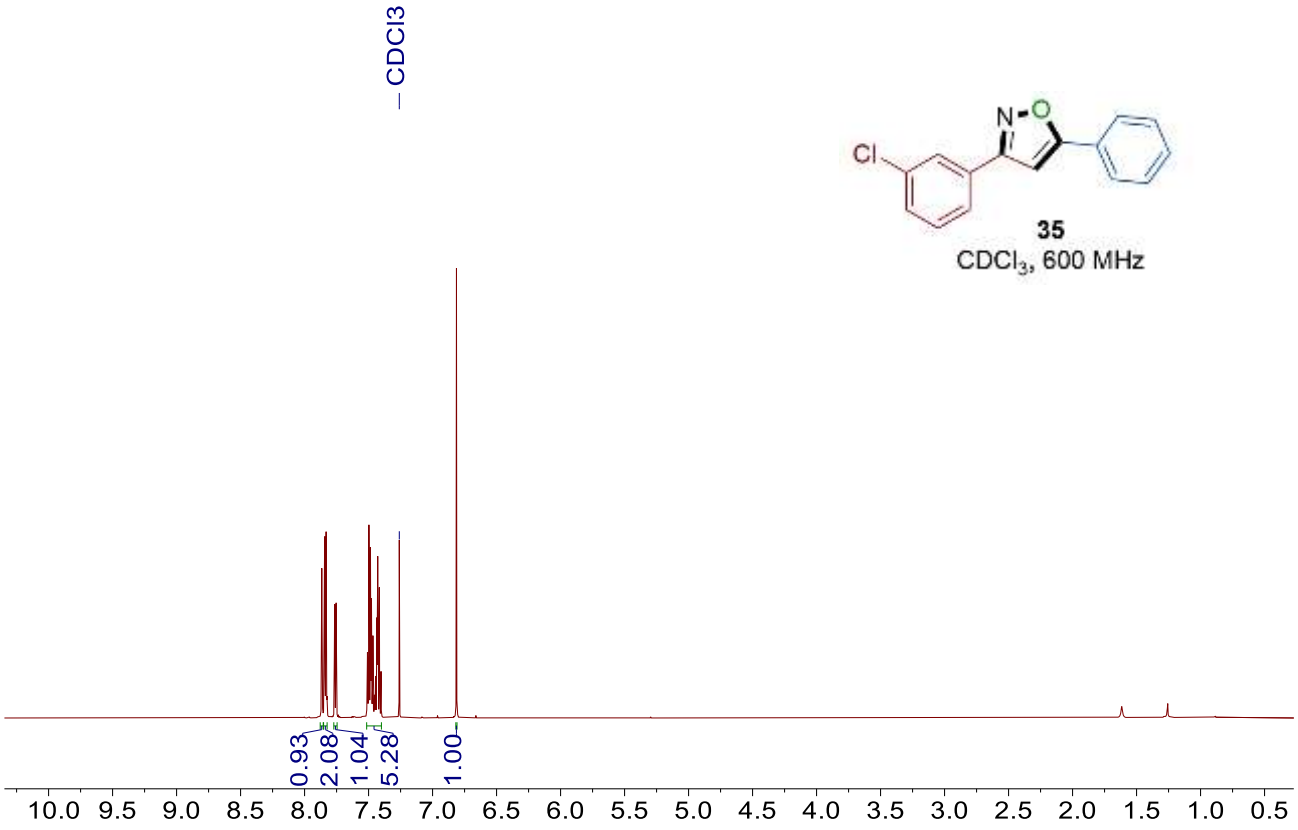
^{1}H NMR spectrum of **34**



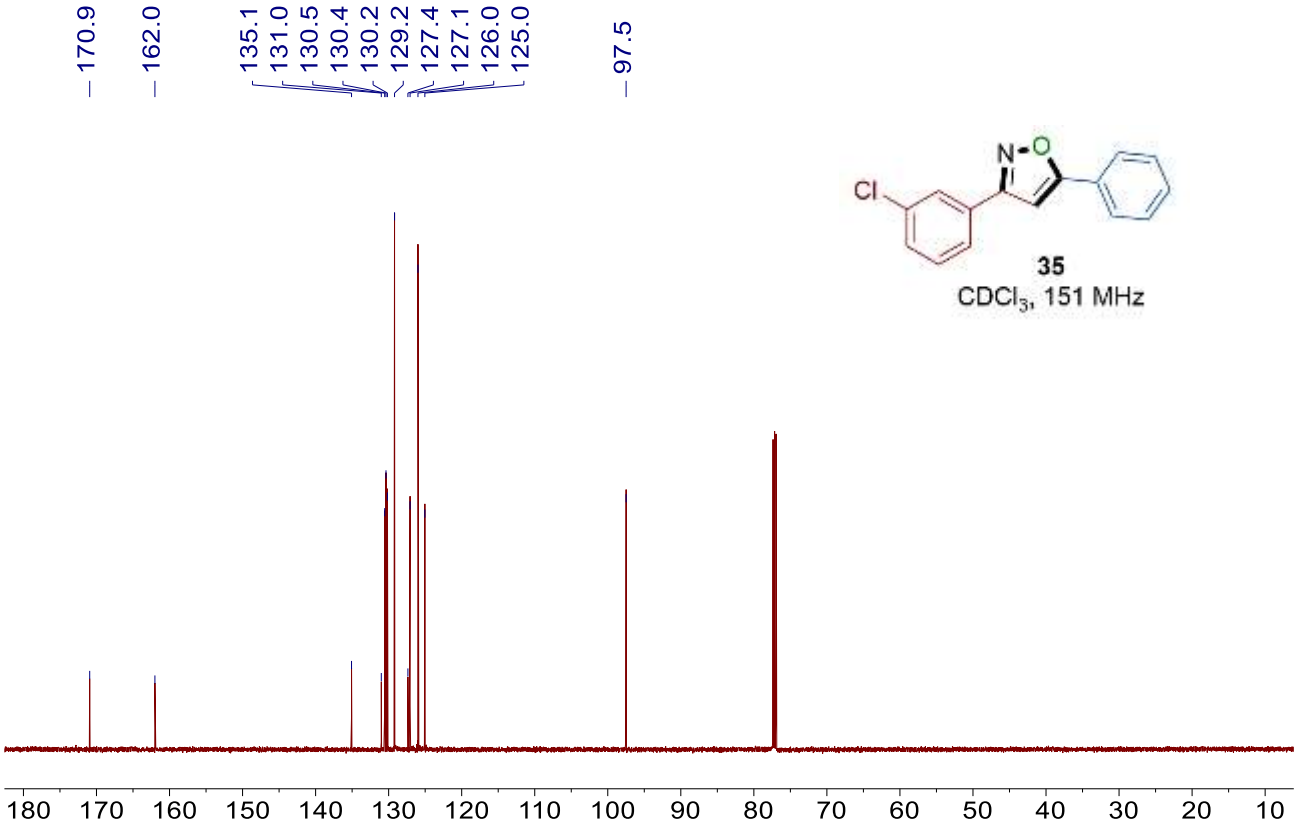
^{13}C NMR spectrum of **34**



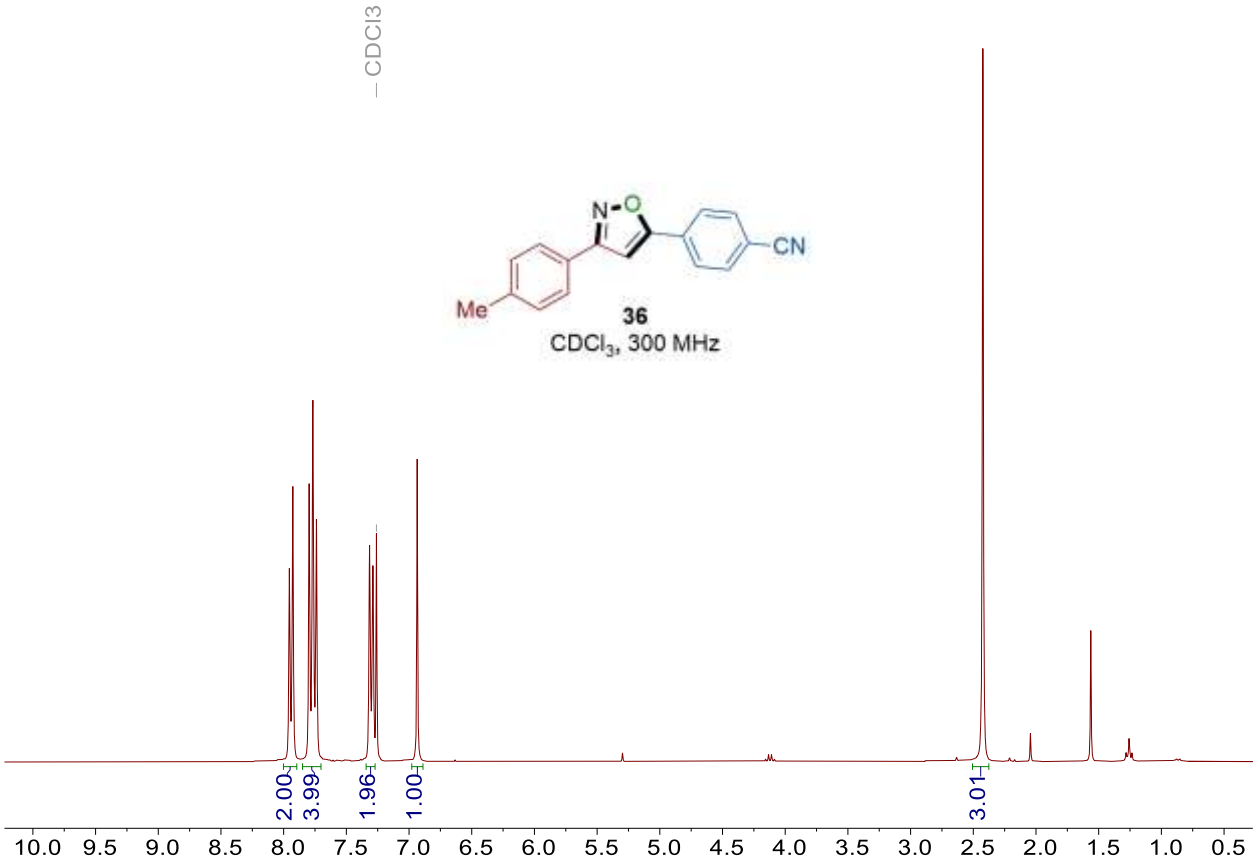
^{1}H NMR spectrum of **35**



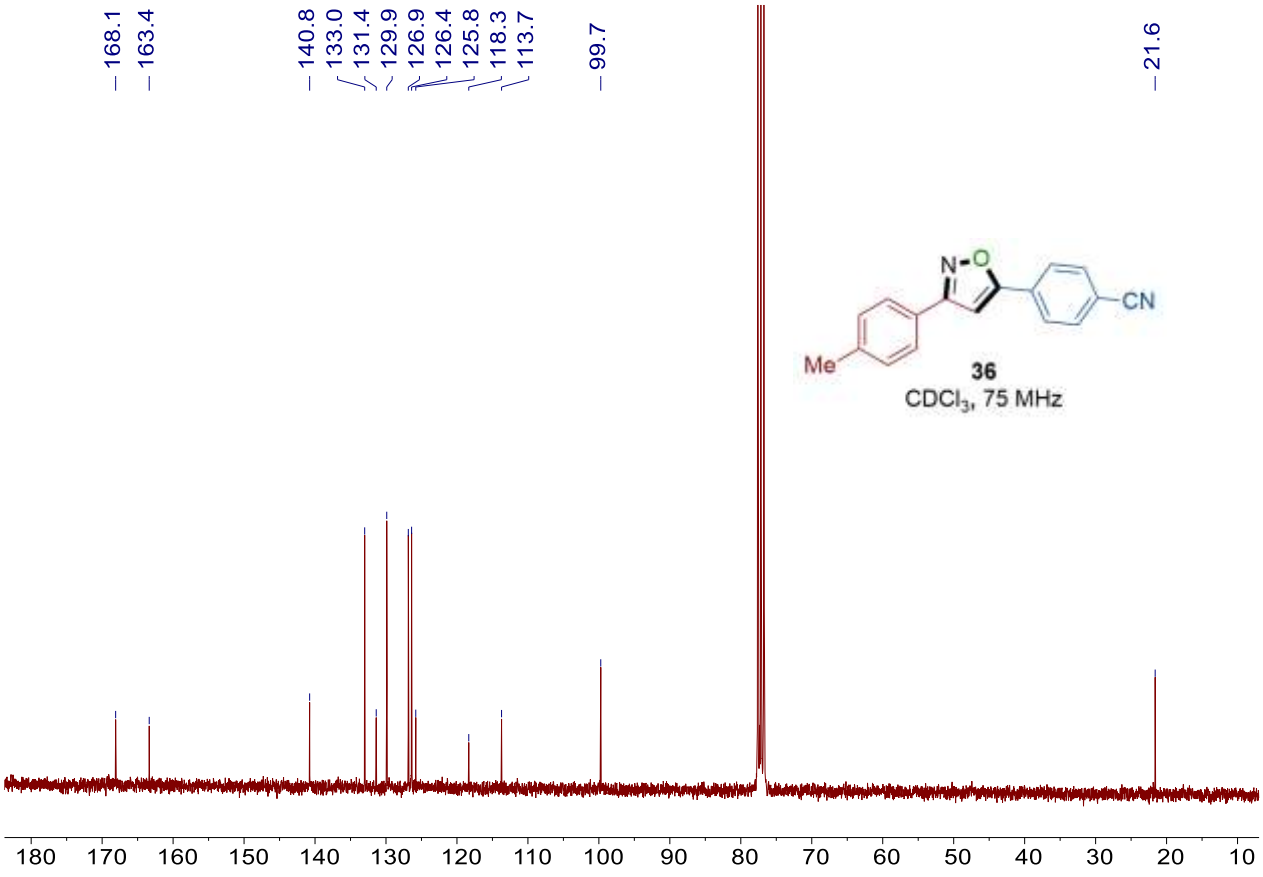
^{13}C NMR spectrum of **35**



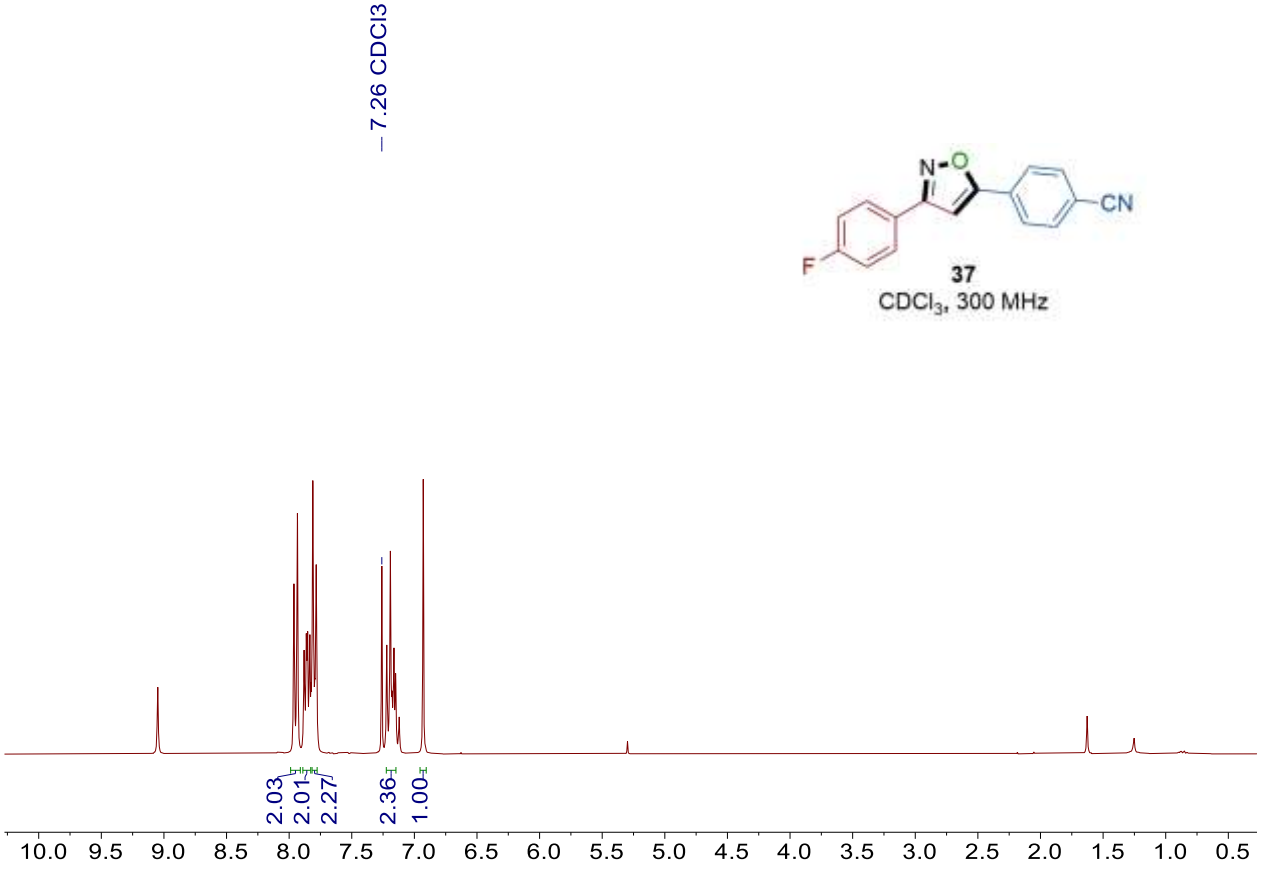
^{1}H NMR spectrum of **36**



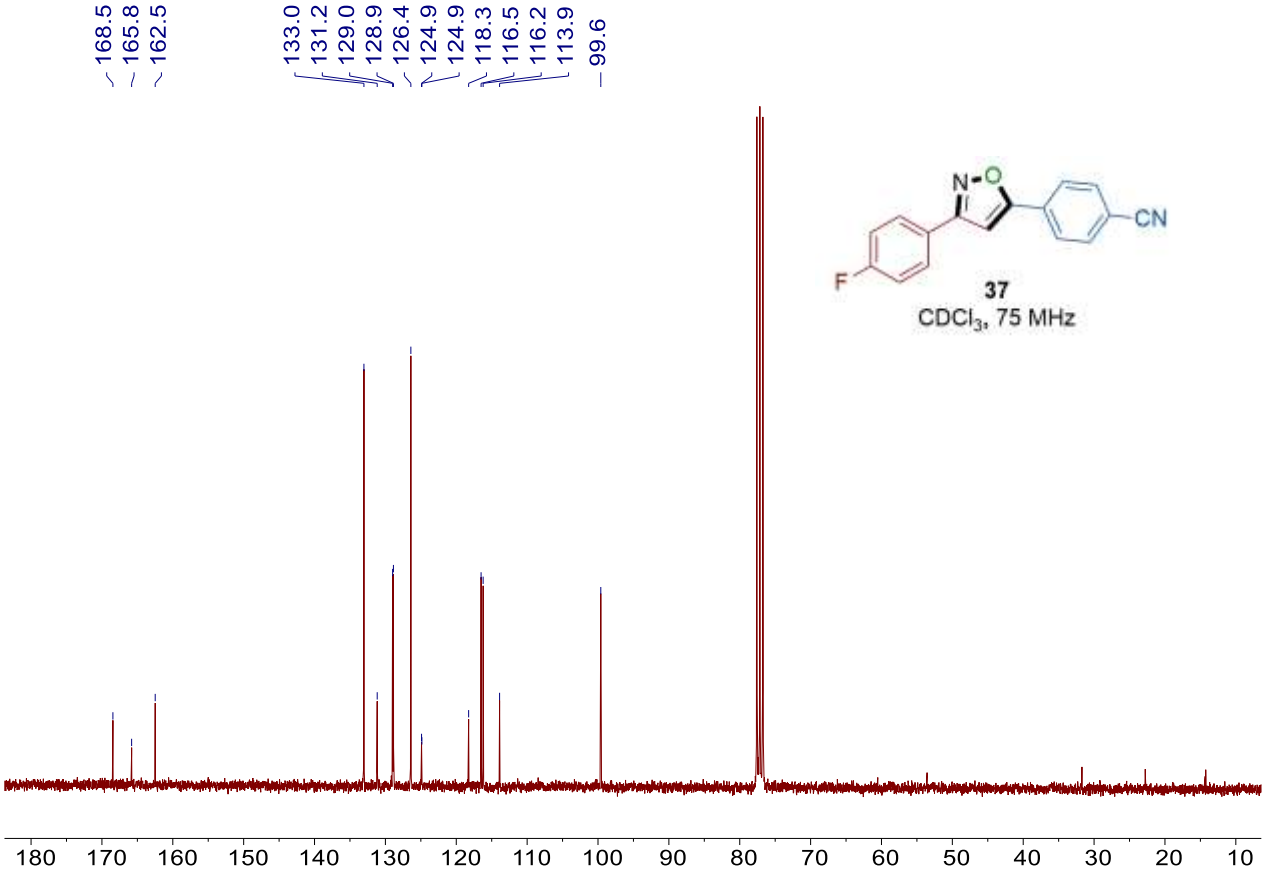
^{13}C NMR spectrum of **36**



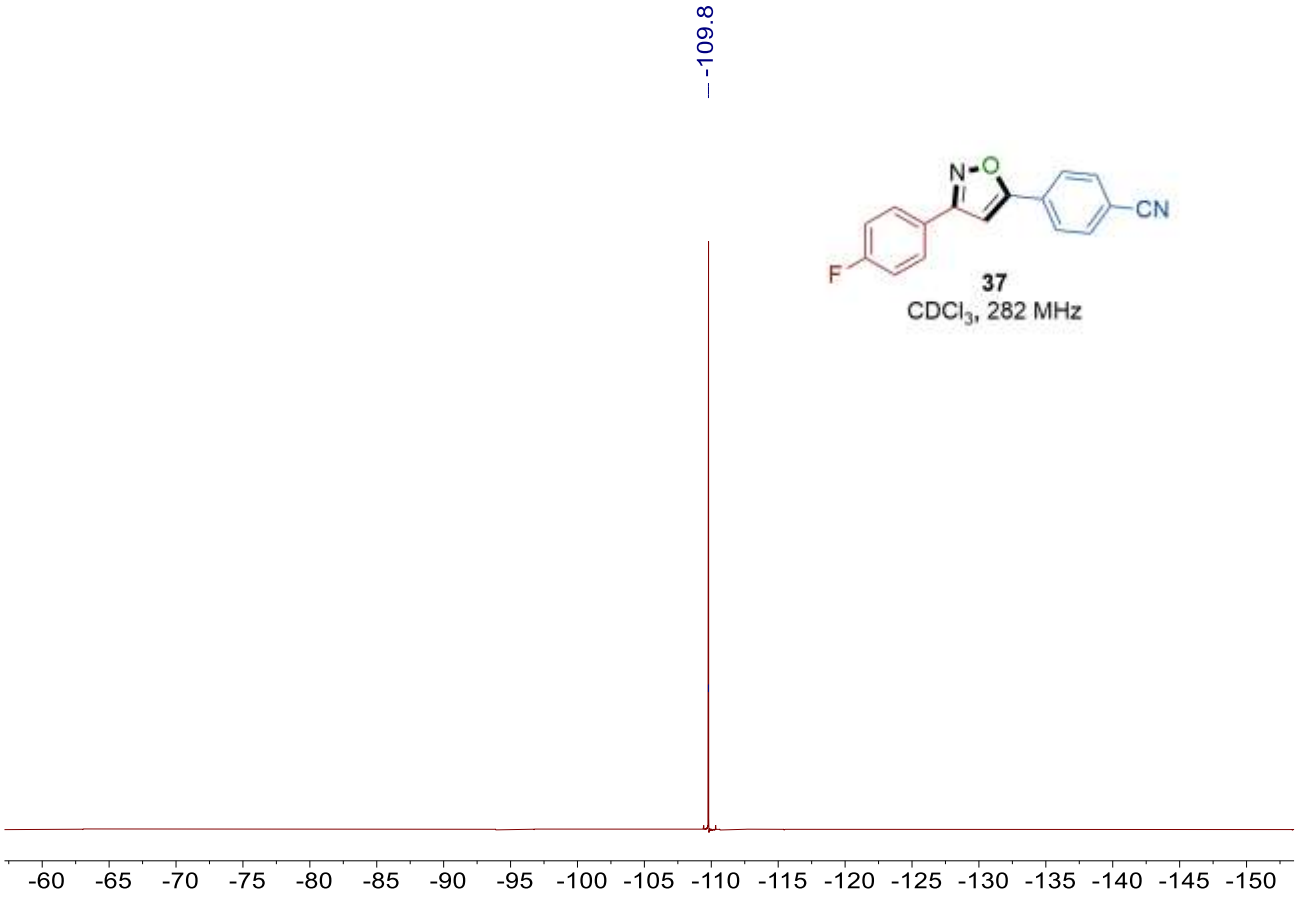
^{1}H NMR spectrum of **37**



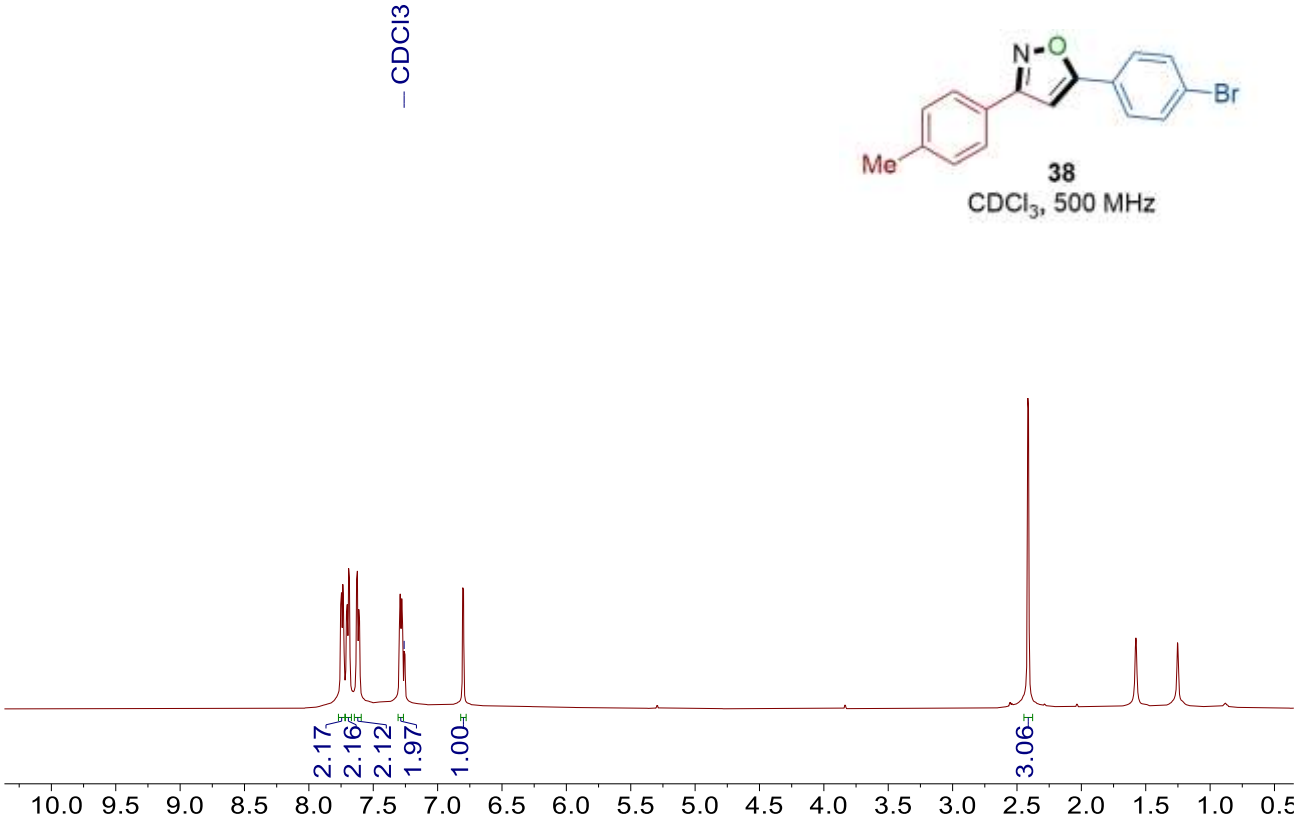
^{13}C NMR spectrum of **37**



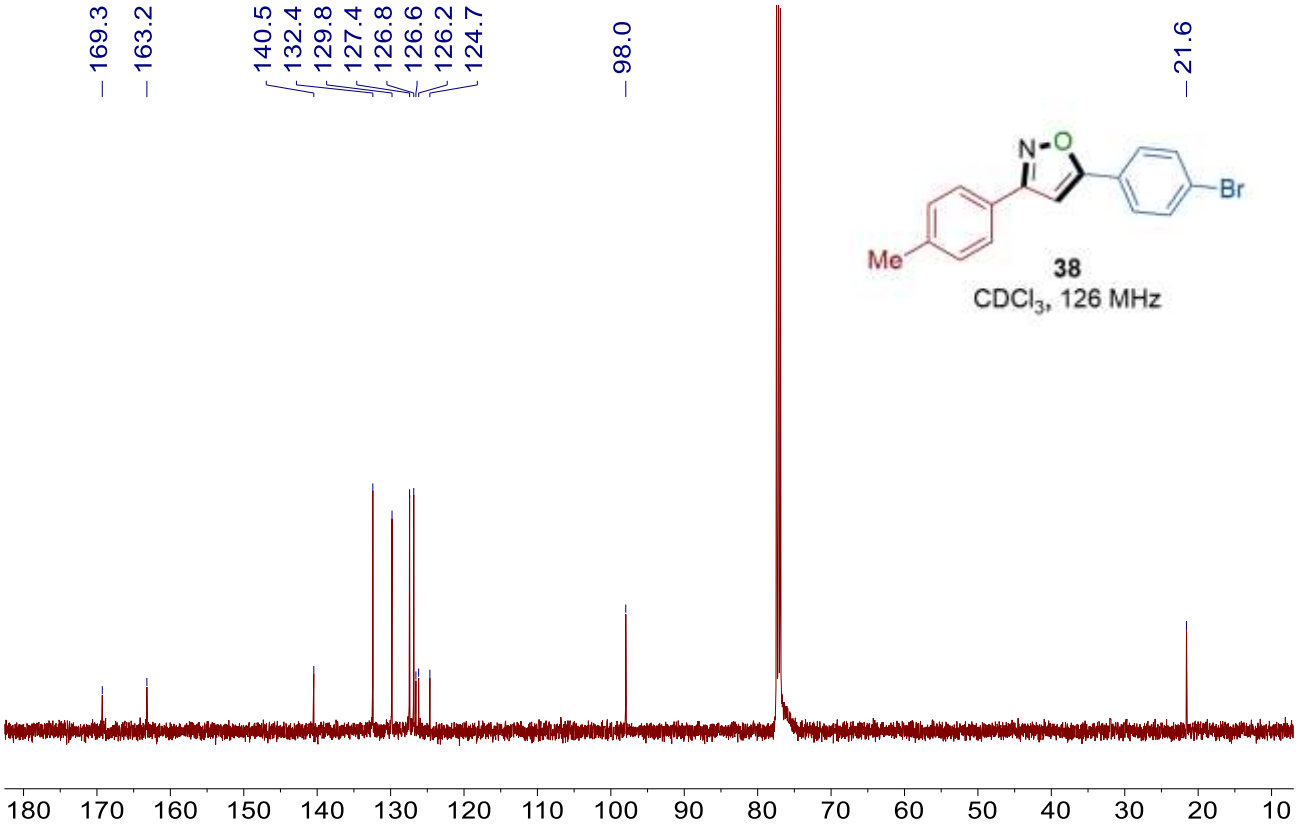
^{19}F NMR spectrum of **37**



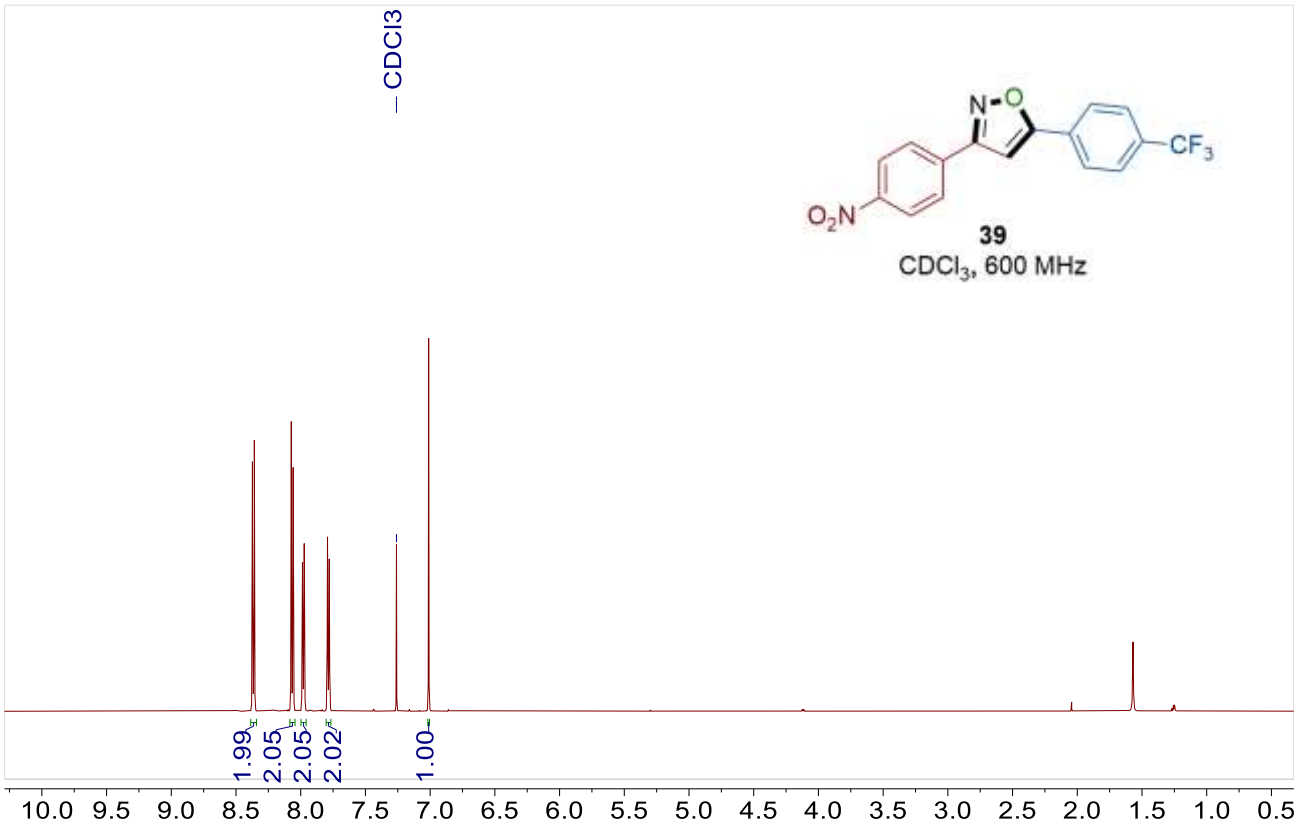
^{1}H NMR spectrum of **38**



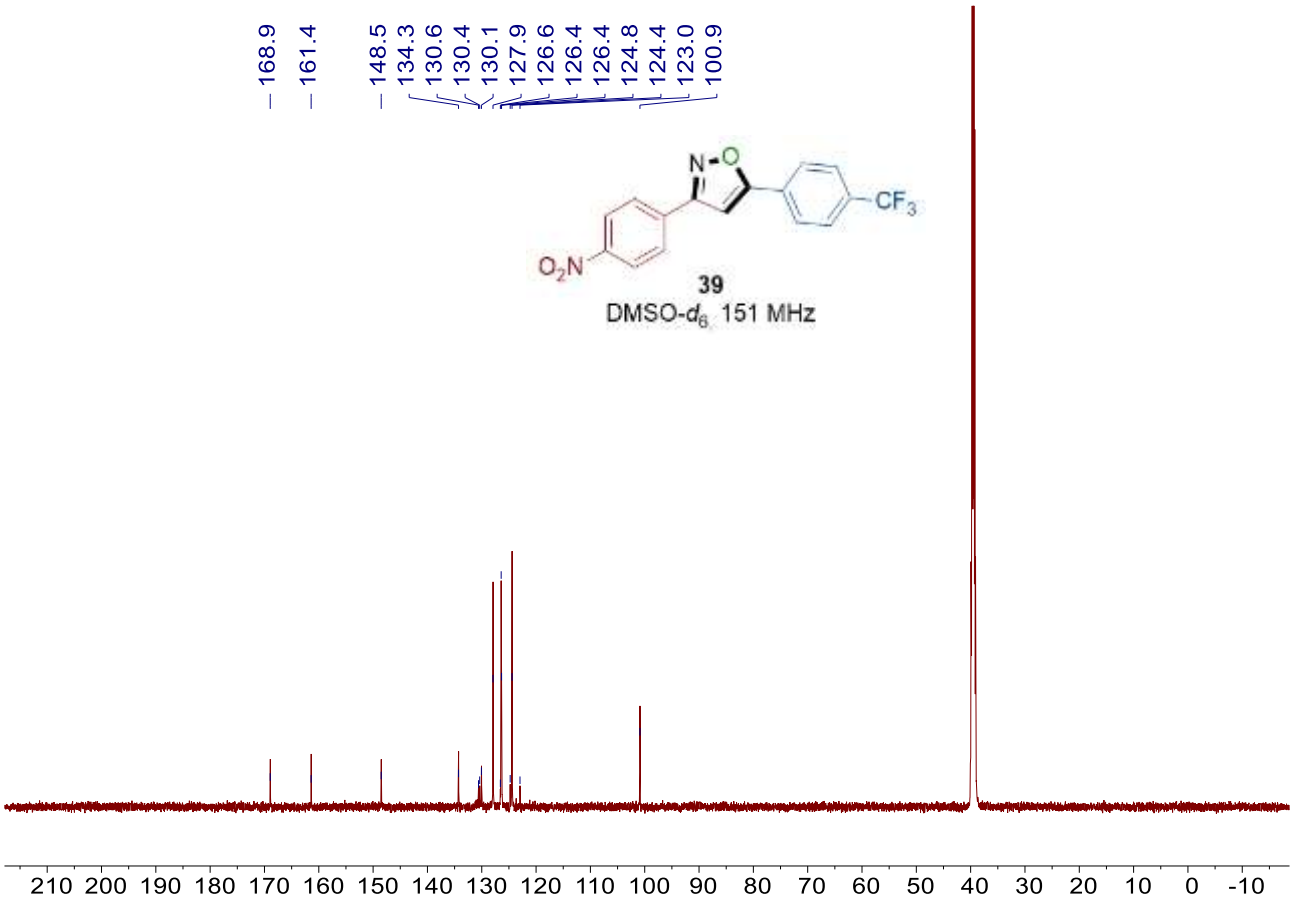
^{13}C NMR spectrum of **38**



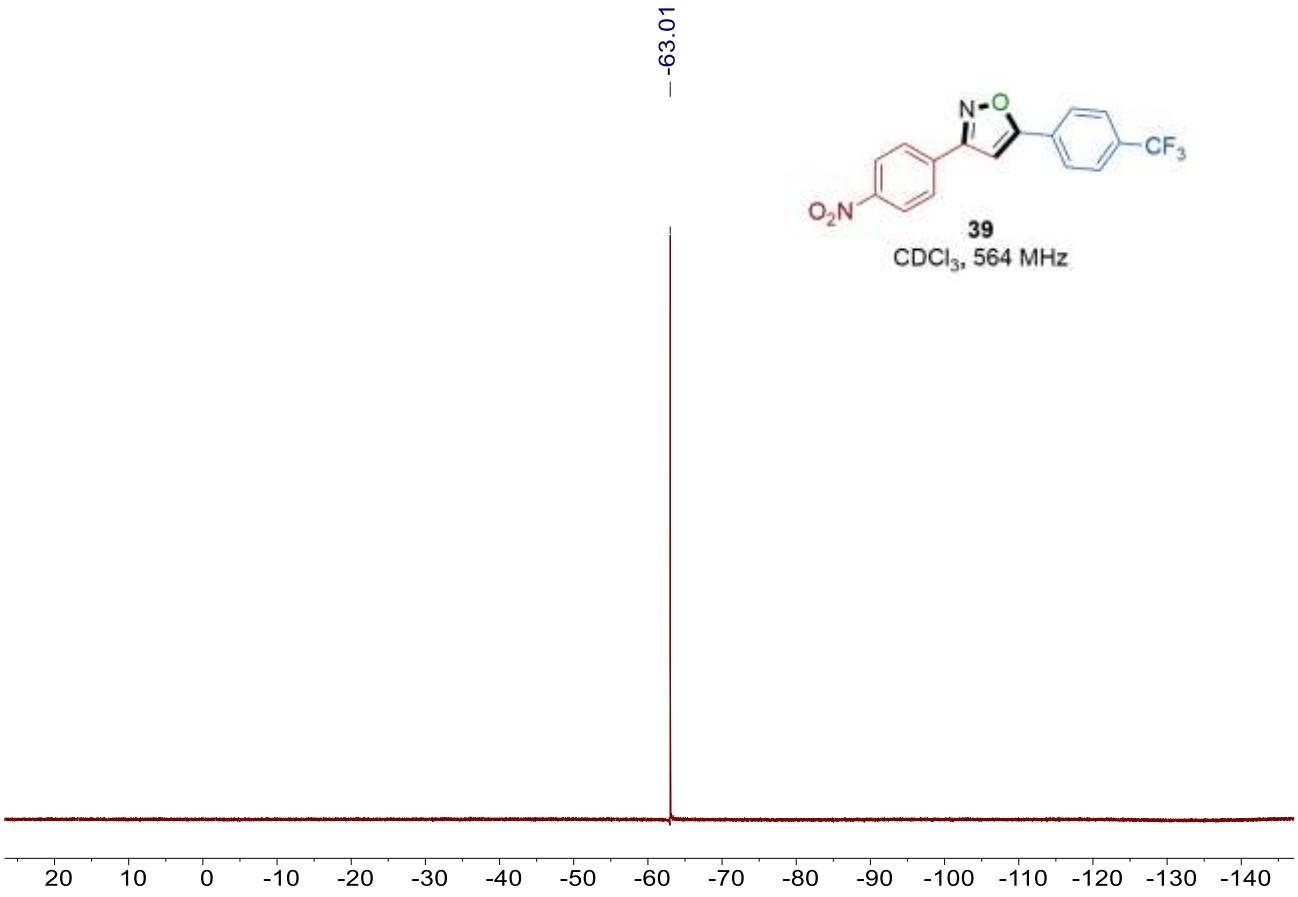
^{1}H NMR spectrum of **39**



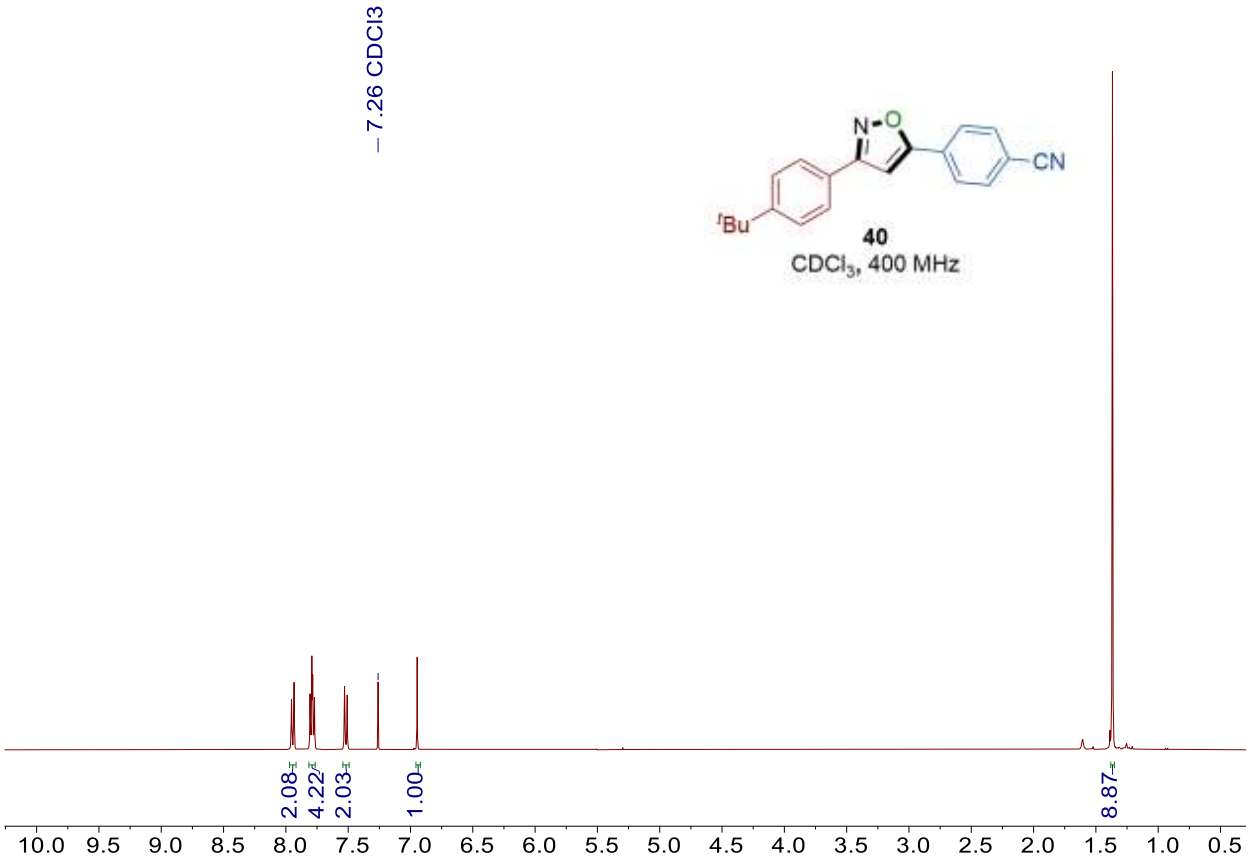
^{13}C NMR spectrum of **39**



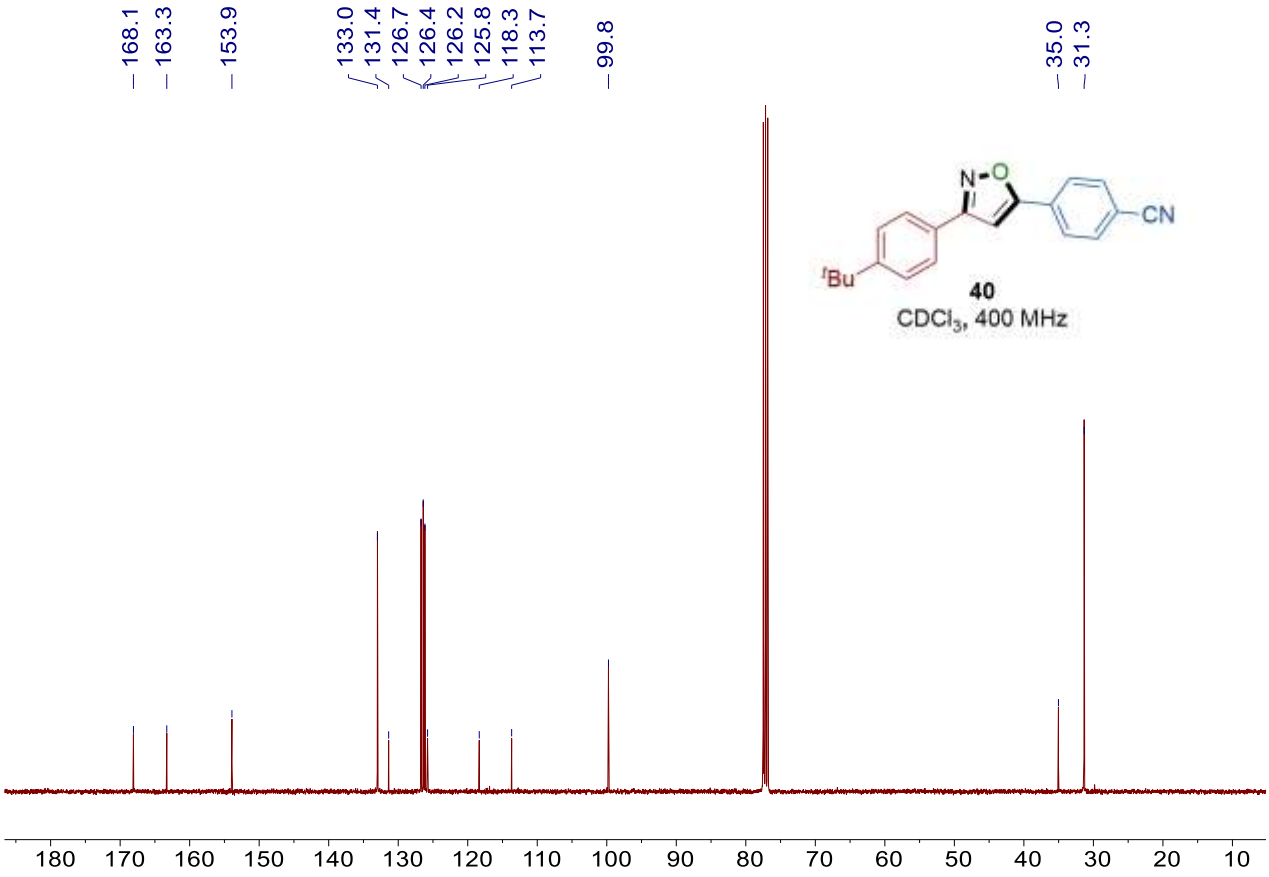
^{19}F NMR spectrum of **39**



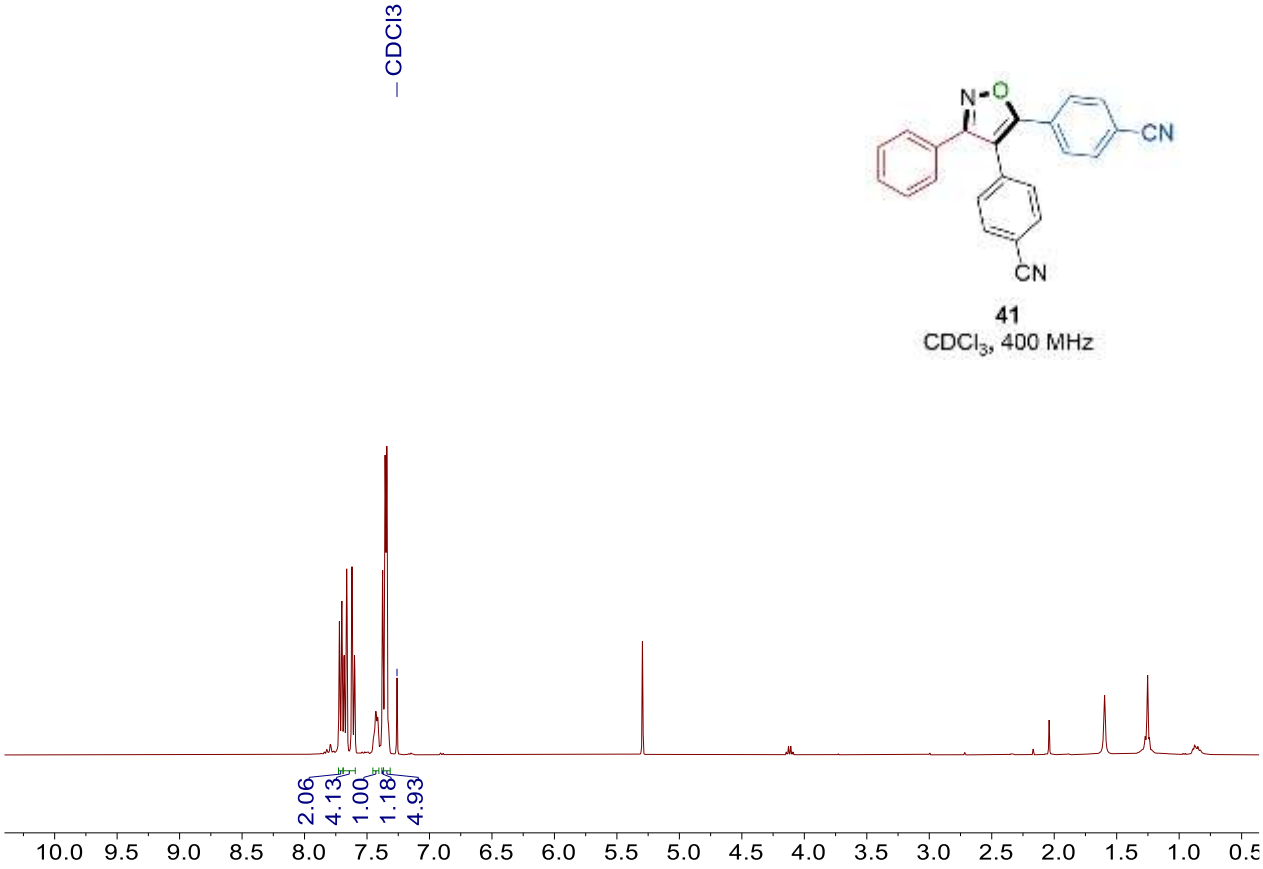
^{1}H NMR spectrum of **40**



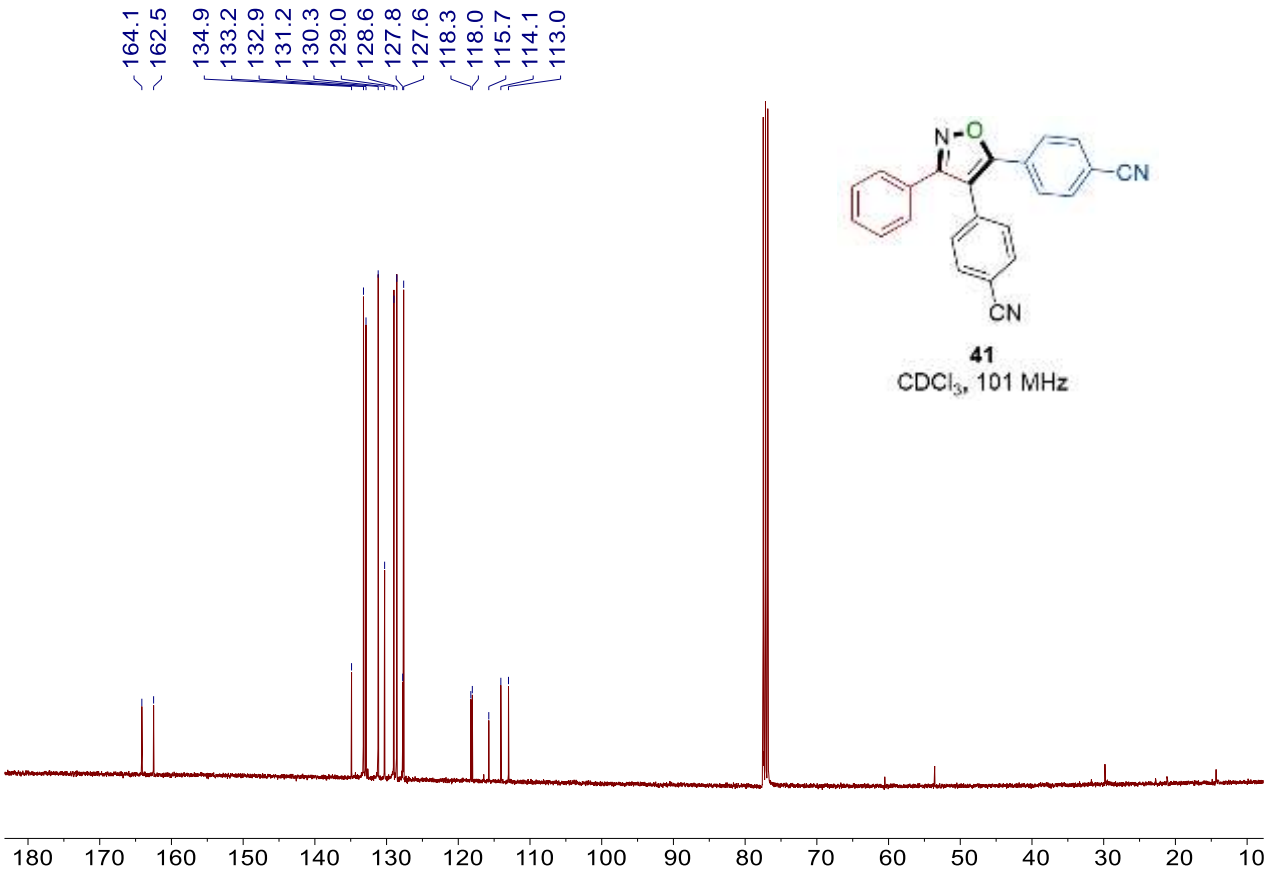
^{13}C NMR spectrum of **40**



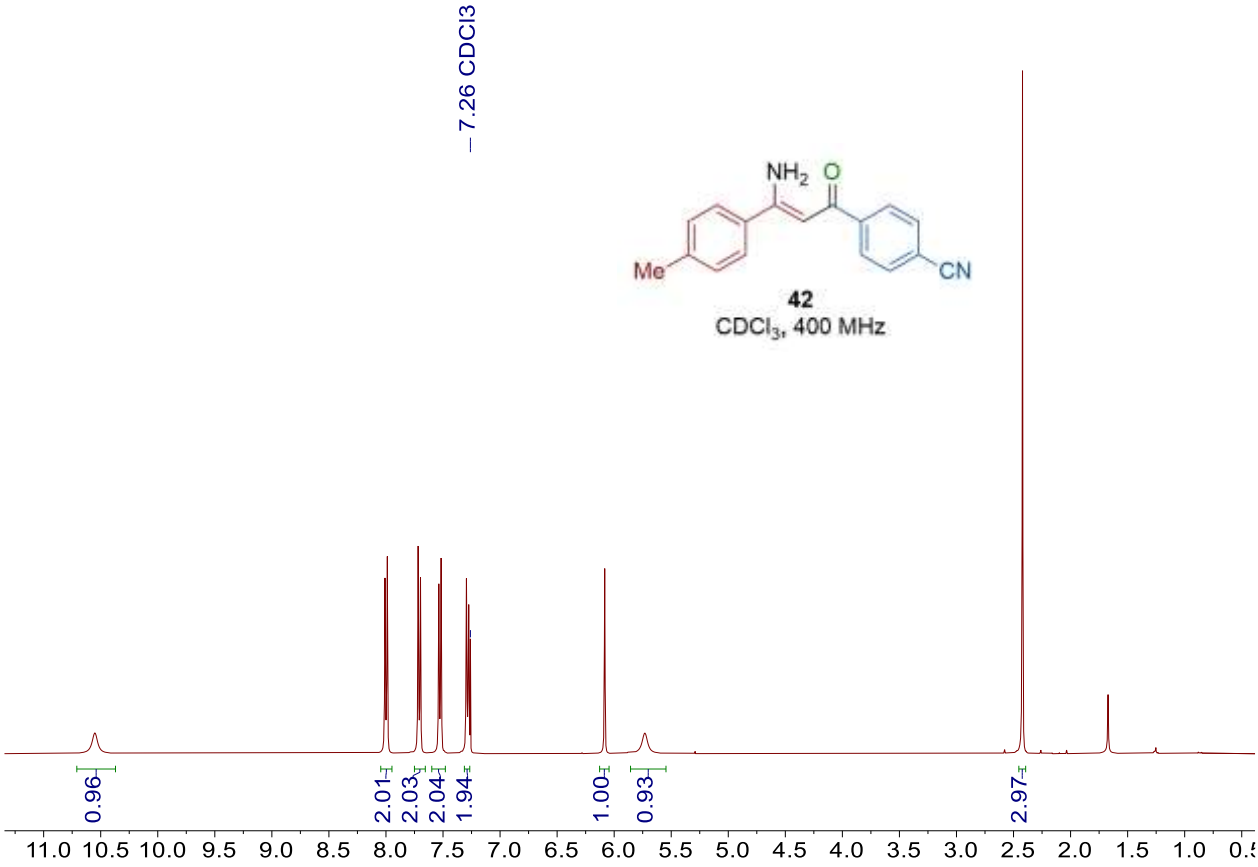
^{1}H NMR spectrum of **41**



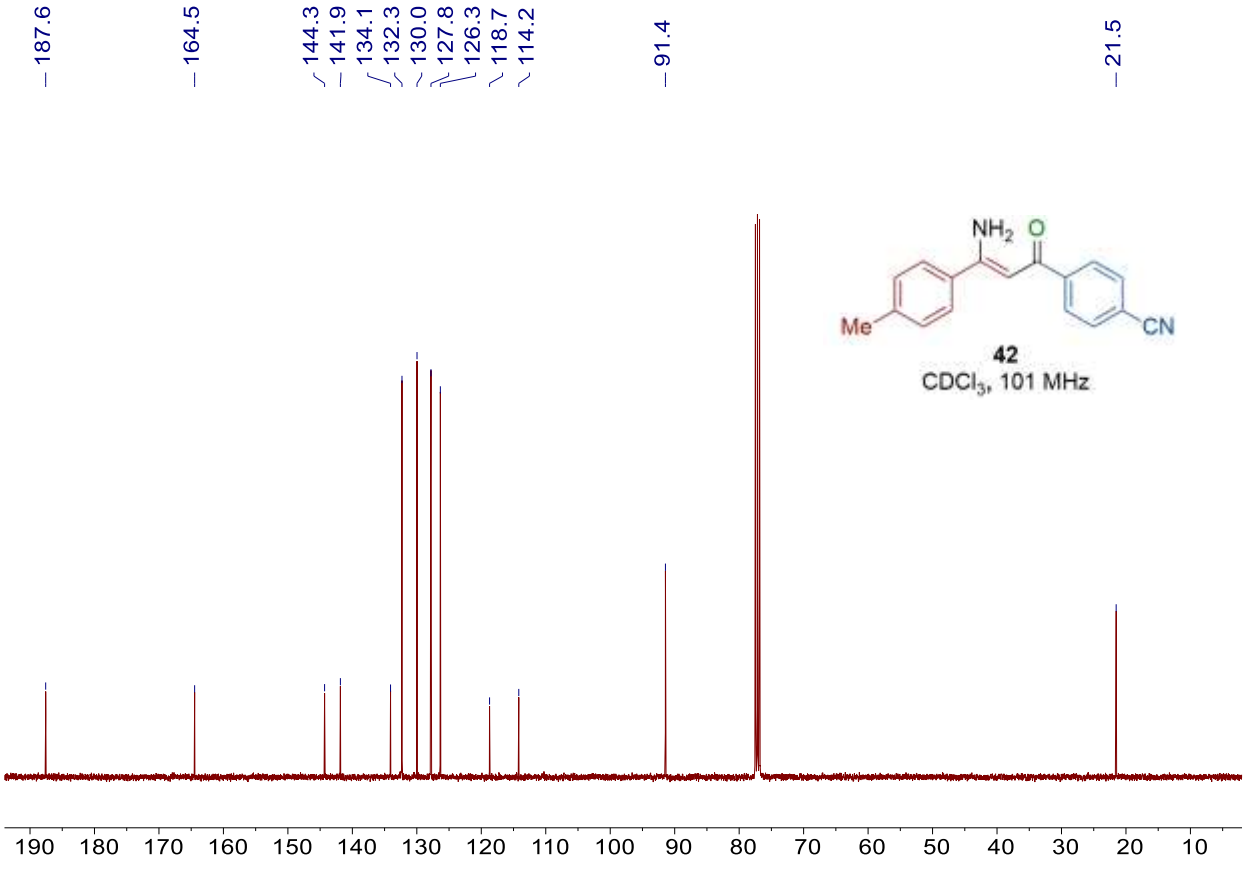
^{13}C NMR spectrum of **41**



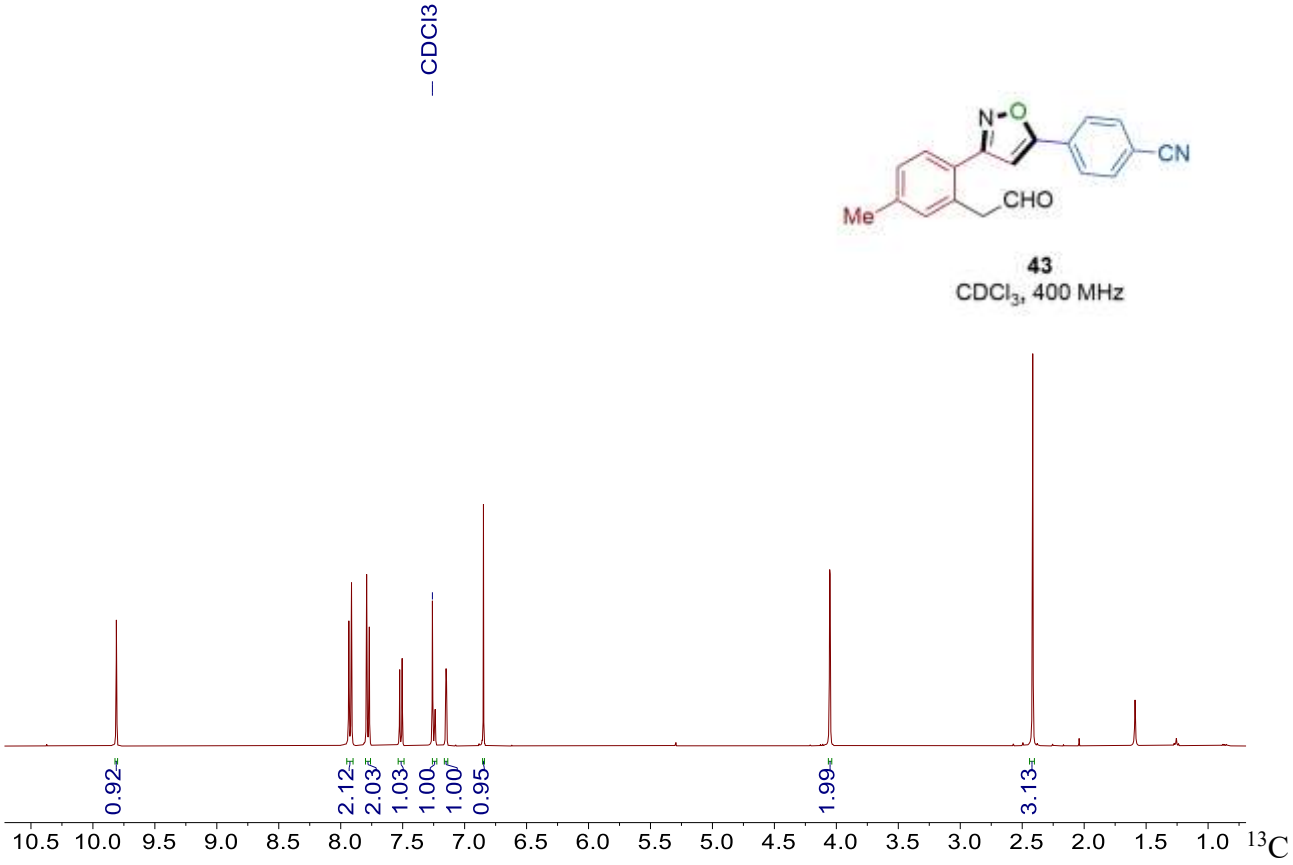
^{1}H NMR spectrum of **42**



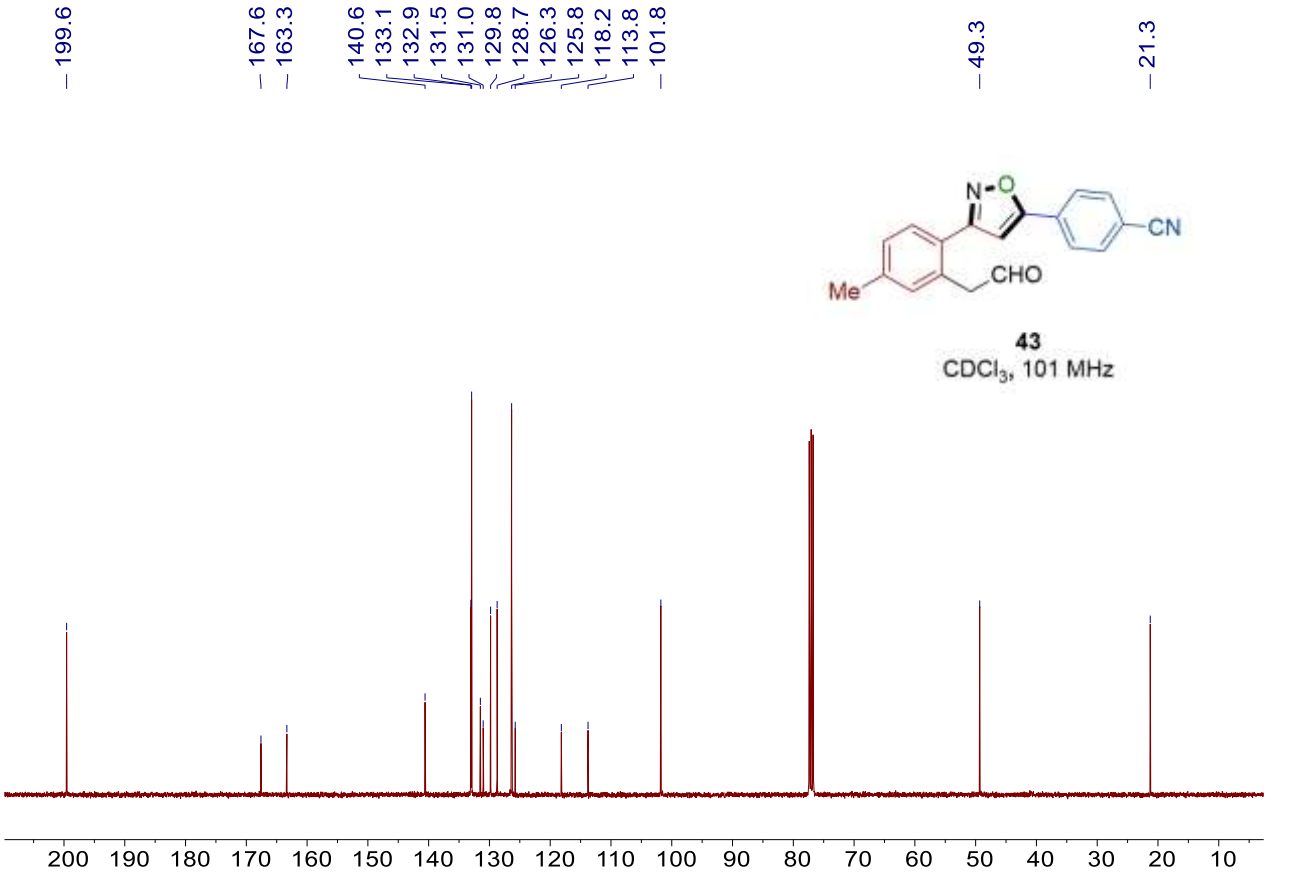
^{13}C NMR spectrum of **42**



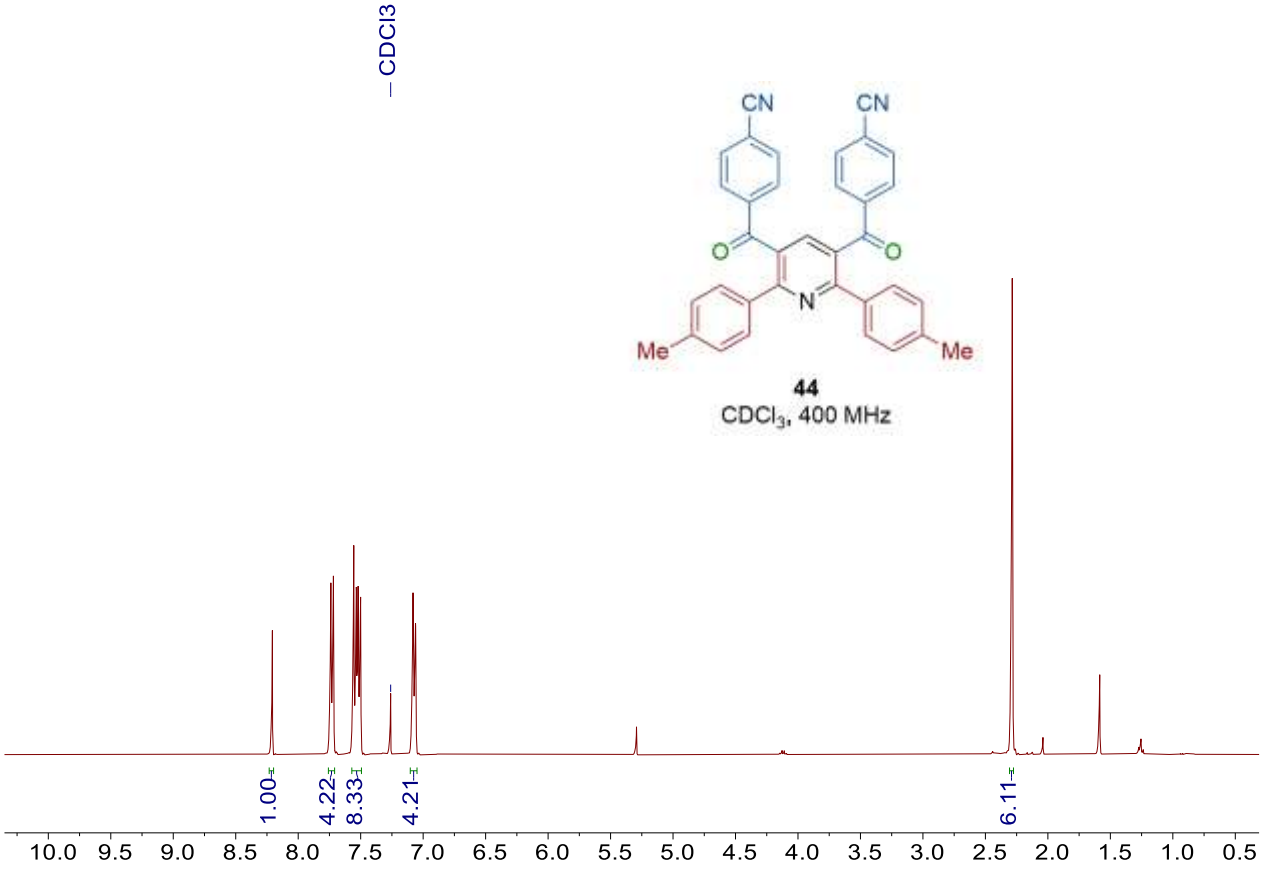
^{1}H NMR spectrum of **43**



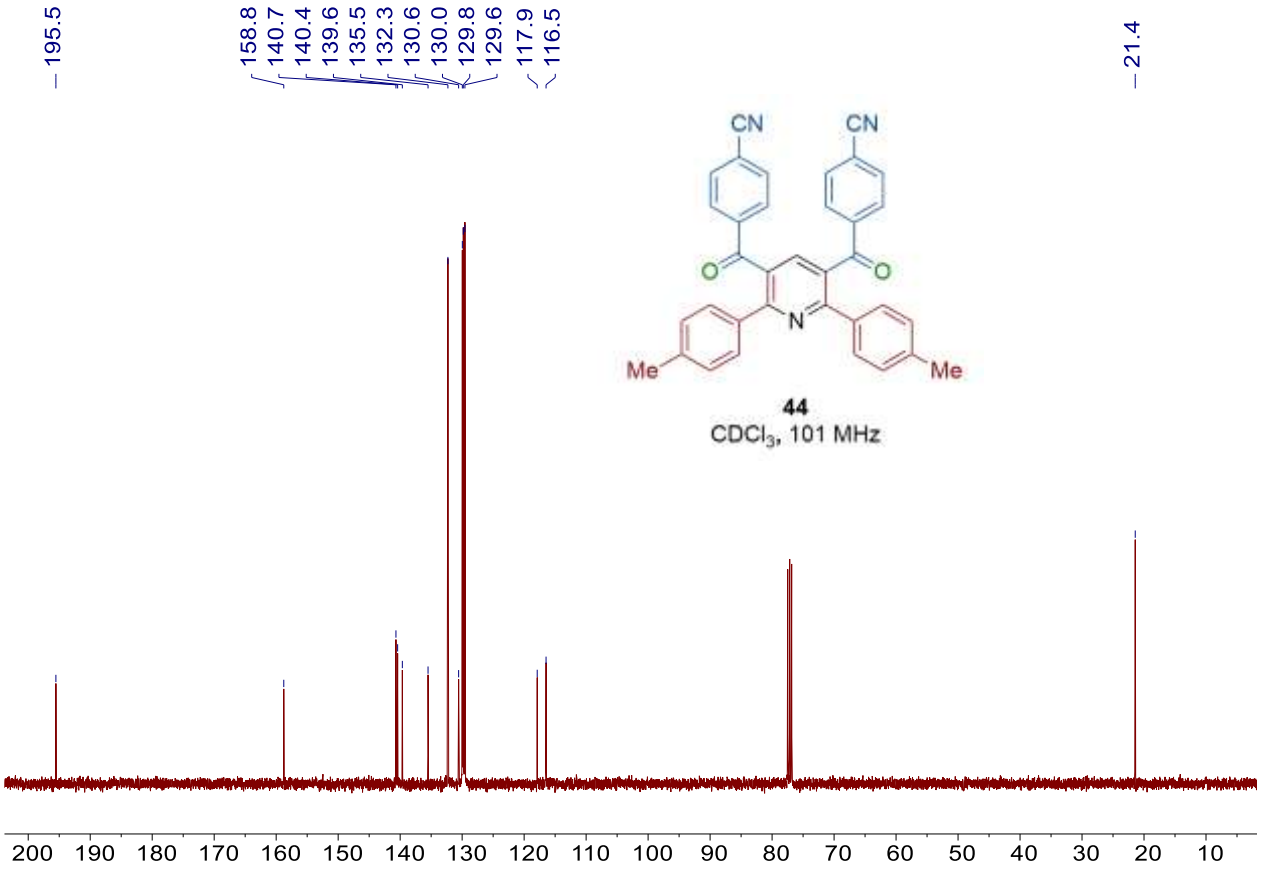
^{13}C NMR spectrum of **43** ($CDCl_3$, 101 MHz)



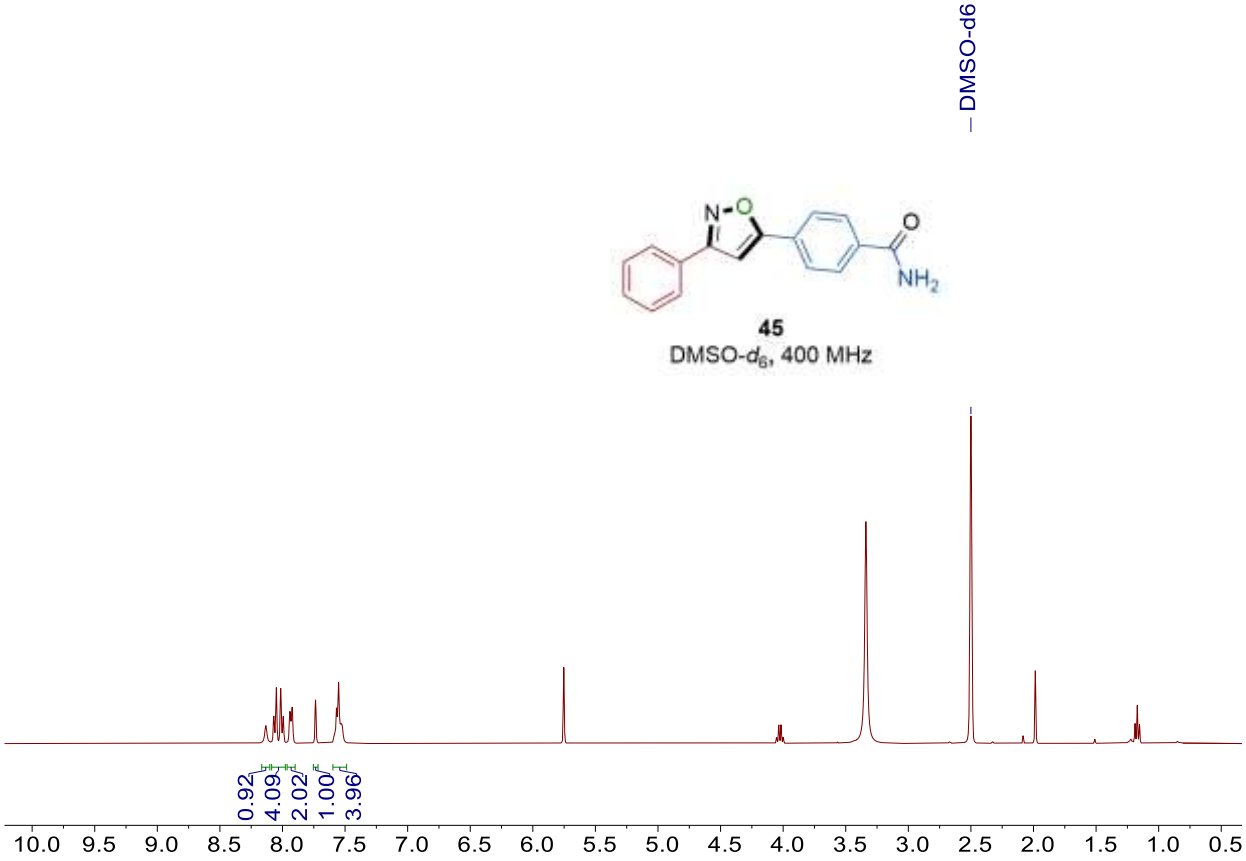
^{1}H NMR spectrum of **44**



^{13}C NMR spectrum of **44**



^{1}H NMR spectrum of **45**



^{13}C NMR spectrum of **45** (DMSO-d_6, 101 MHz)