Electronic Supplementary Information for:

Structures of nickel chloride and thiolate complexes supported by PCN and POCOP pincer ligands and catalytic reactivity of the chloride complexes

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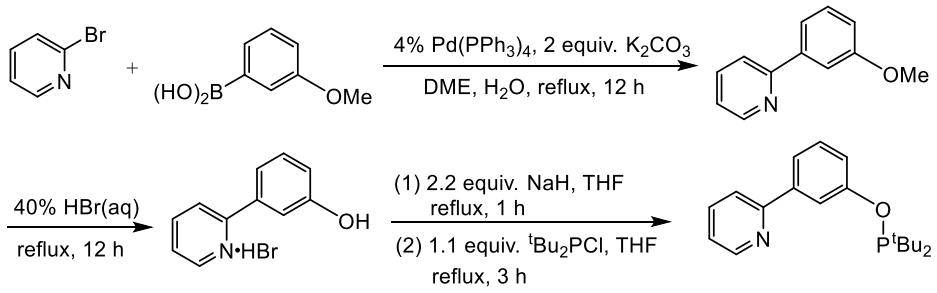
Contents

Synthesis of 2-(3-((di-tert-butylphosphino)oxy)phenyl)pyridine

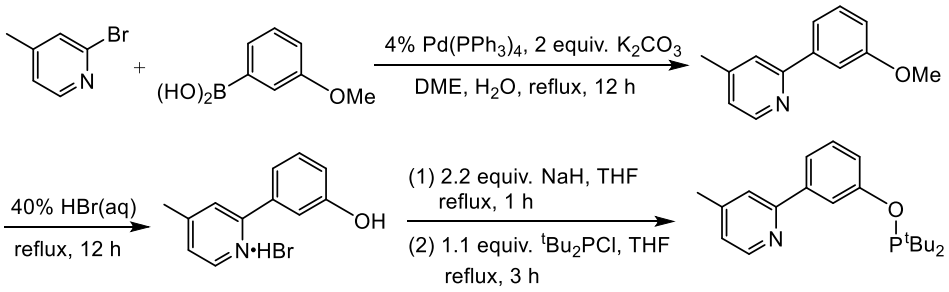


Under nitrogen atmosphere, 2-bromopyridine (1.58 g, 10 mmol), 3-methoxyphenylboronic acid (1.79 g, 11.8 mmol), K_2CO_3 (3.38 g, 24.5 mmol), $Pd(PPh_3)_4$ (0.46 g, 0.4 mmol), DME (17 mL) and distilled water (11 mL) were added to a 100 mL Schlenk flask. The reaction mixture was refluxed for 12 h and cooled to room temperature. The solution was then filtered. The filtrate was extracted with ethyl acetate (30 mL × 3). The combined organic layer was washed with brine and dried over anhydrous Na_2SO_4. After the removal of the solvent, the crude product was purified with silica gel column chromatography (ethyl acetate/petroleum ether, v/v = 1/10) affording 1.65 g of colorless oil, which was used directly in the next step.

The colorless oil obtained in the above step (1.65 g) was added to a 100 mL Schlenk flask. Then, an aqueous solution of HBr (40%, 32 mL) was added. The reaction mixture was heated at 120 ℃ for 12 h. Then, water was removed under vacuum at 80°C. The resulting crude product was recrystallized in ethanol to afford a beige white solid (1.94 g), which was used directly in the next step.

0.5 g of the beige white solid prepared in the above step was charged to a 50 mL Schlenk flask. Then NaH (0.11 mg, 4.4 mmol) and THF (25 mL) were added. The reaction mixture was heated to reflux for 1 h. Di-*tert*-butylchlorophosphine (0.42 mL, 2.2 mmol) was then added to a solution and the resulting solution was heated to reflux for 3 h. After evaporation of the solvent under vacuum, the residue was extracted with 30 mL of hexane, and the extract was cannula transferred and filtered through a pad of Celite. After removal of hexane under vacuum, the flask was heated at 70 ℃ for 1 h under vacuum to remove the remaining di-*tert*-butylchlorophosphine. 2-(3-((di-tert-butylphosphino)oxy)phenyl)pyridine was obtained as colorless viscous oil (0.55g). NMR characterization of the obtained product is in good agreement with the literature report.[S1]

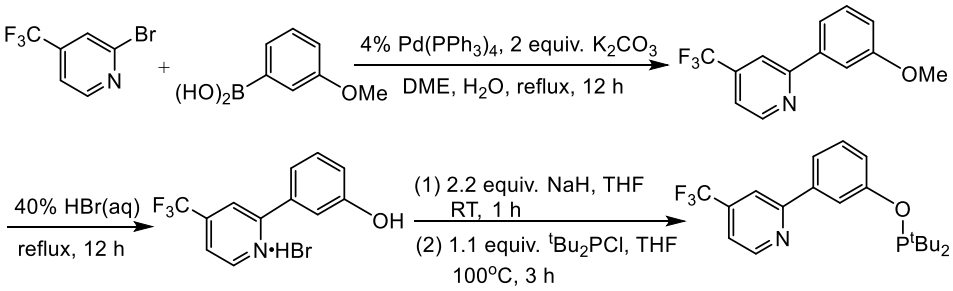
Synthesis of 2-(3-((di-tert-butylphosphino)oxy)phenyl)-4-methylpyridine



2-(3-((di-*tert*-butylphosphino)oxy)phenyl)-4-methylpyridine was prepared similarly in 84% yield from 2-bromo-4-methylpyridine by following the same procedure as described above. ^{1}H NMR (600 MHz, C_6D_6, δ): 8.51 (d, 1H, $J_{H\text{-}H}$ = 5.1 Hz), 8.43–8.44 (m, 1H), 7.79 (d, 1H, $J_{H\text{-}H}$ = 8.0 Hz), 7.38–7.40 (m, 1H), 7.32 (s, 1H), 7.22–7.25 (m, 1H), 6.52 (d, 1H, $J_{H\text{-}H}$ = 5.1 Hz), 1.82 (s, 3H, CH_3), 1.15 (d, 18H, $J_{H\text{-}P}$ = 11.7 Hz, C(CH_3)$_3$). ^{13}C{^{1}H} NMR (151 MHz, C_6D_6, δ): 160.81 (d, $J_{C\text{-}P}$ = 9.7 Hz), 157.01 (s), 149.71 (s), 147.37 (s), 141.56 (s), 129.85 (s), 123.36 (s), 121.24 (s), 120.40 (s), 118.92 (d, $J_{C\text{-}P}$ = 11.6 Hz), 117.45 (d, $J_{C\text{-}P}$ = 10.7 Hz), 35.78 (d, $J_{C\text{-}P}$ = 25.9 Hz, *C*(CH$_3$)$_3$), 27.60 (d,

$J_{C\text{-}P}$ = 15.8 Hz, C(*C*H$_3$)$_3$), 20.91 (s, *C*H$_3$). $^{31}P\{^1H\}$ NMR (243 MHz, C_6D_6, δ): 152.20 (s). HRMS (ESI): *m/z* calculated for $C_{20}H_{28}NOP$ $[M + H]^+$ 330.1981; Found 330.1982.

Synthesis of 2-(3-((di-tert-butylphosphino)oxy)phenyl)-4-trifluoromethylpyridine



2-(3-((di-tert-butylphosphino)oxy)phenyl)-4-trifluoromethylpyridine was prepared similarly in 71% yield from 2-bromo-4-(trifluoromethyl)pyridine by following the same procedure as described above. ^1H NMR (600 MHz, C_6D_6, δ): 8.36 (s, br, 2H), 7.66 (s, 1H), 7.38–7.39 (m, 2H), 7.12–7.15 (m, 1H), 6.73 (s, br, 1H), 1.13 (d, 18H, $J_{H\text{-}P}$ = 11.7 Hz, C(C*H*$_3$)$_3$). $^{13}C\{^1H\}$ NMR (151 MHz, C_6D_6, δ): 161.07 (d, $J_{C\text{-}P}$ = 9.7 Hz), 158.56 (s), 150.86 (s), 139.97 (s), 138.68 (q, $J_{C\text{-}F}$ = 33.8 Hz), 130.15 (s), 123.66 (q, $J_{C\text{-}F}$ = 273.9 Hz, *C*F$_3$), 120.36 (s), 119.97 (d, $J_{C\text{-}P}$ = 11.8 Hz), 117.62 (d, $J_{C\text{-}P}$ = 10.7 Hz), 117.52 (q, $J_{C\text{-}F}$ = 3.5 Hz), 115.71 (q, $J_{C\text{-}F}$ = 3.8 Hz), 35.78 (d, $J_{C\text{-}P}$ = 25.9 Hz, *C*(CH$_3$)$_3$), 27.50 (d, $J_{C\text{-}P}$ = 15.8 Hz, C(*C*H$_3$)$_3$). $^{31}P\{^1H\}$ NMR (243 MHz, C_6D_6, δ): 153.29 (s). $^{19}F\{^1H\}$ NMR (565 MHz, C_6D_6, δ): -64.69 (s). HRMS (ESI): *m/z* calculated for $C_{20}H_{25}F_3NOP$ $[M + H]^+$ 384.1699; Found 384.1696.

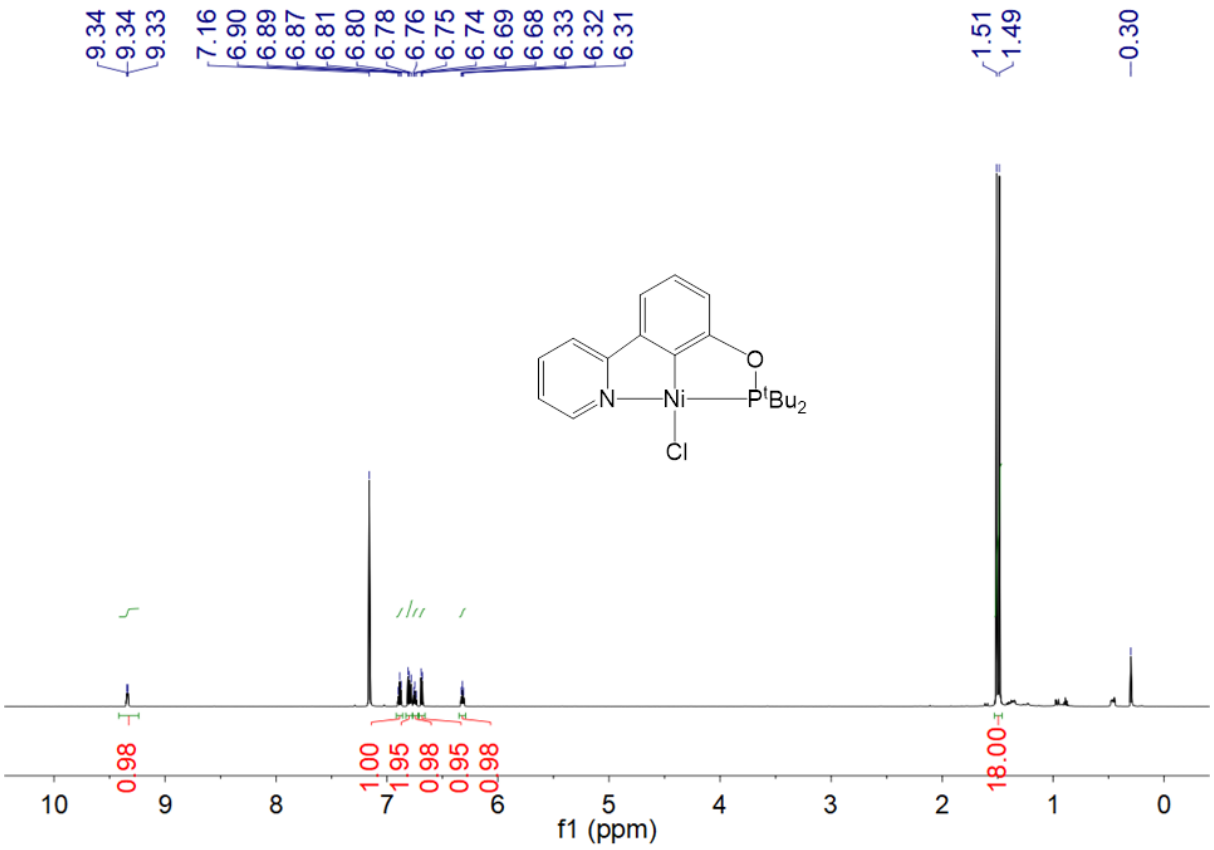


Fig. S1 ^{1}H NMR spectrum of complex **1** (600 MHz, C_6D_6)

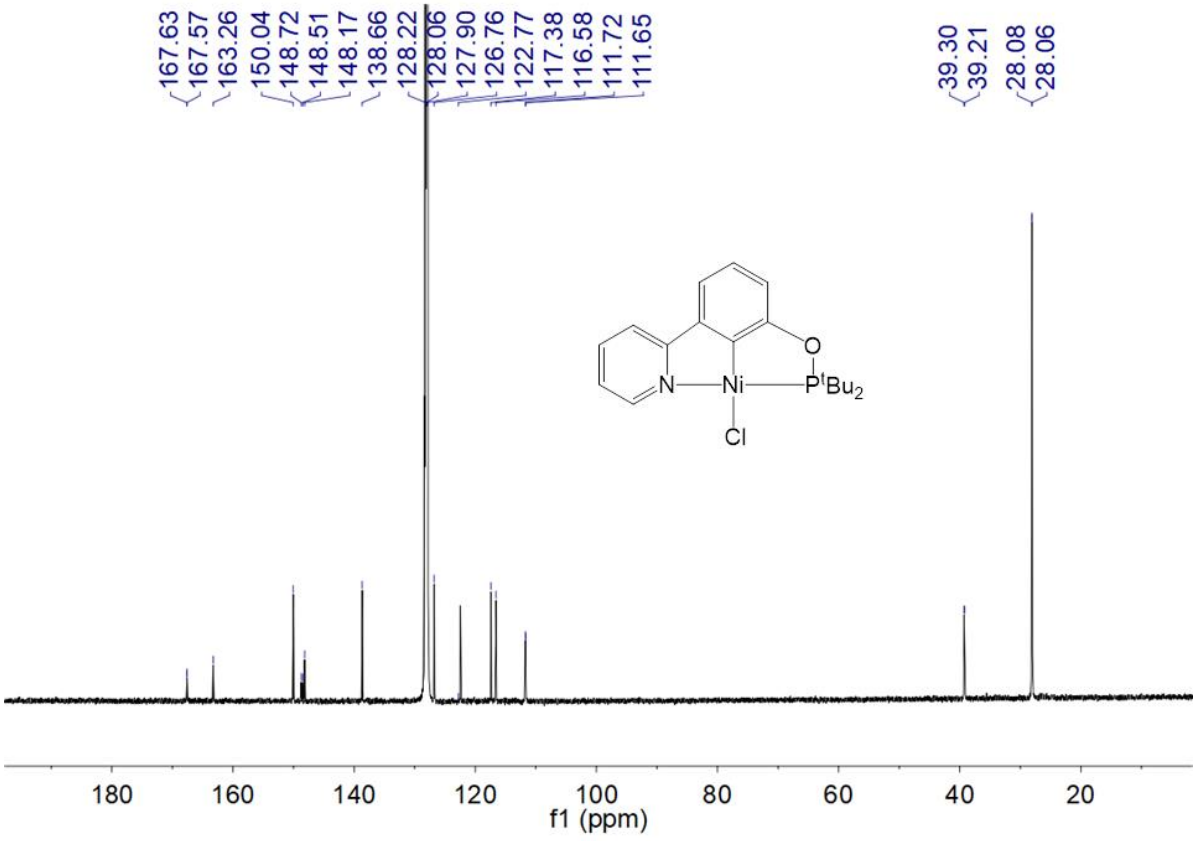


Fig. S2 ^{13}C{^{1}H} NMR spectrum of complex **1** (151 MHz, C_6D_6)

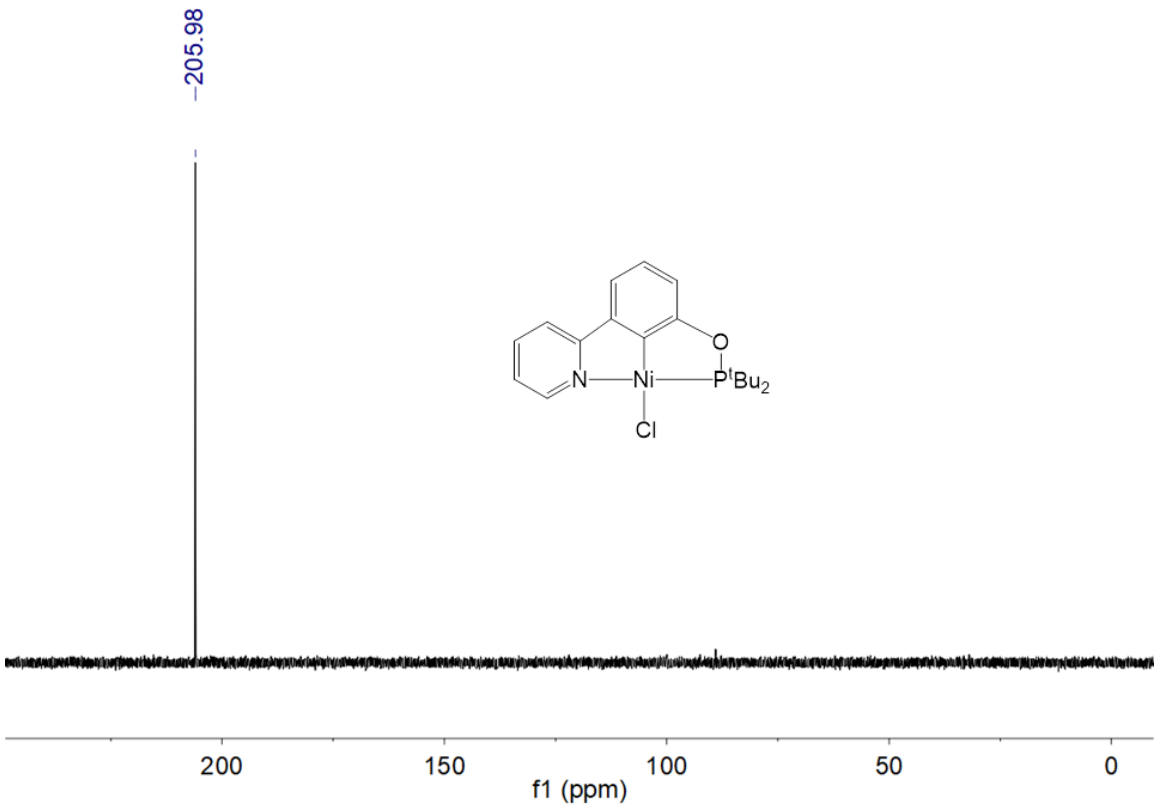


Fig. S3 $^{31}P\{^1H\}$ NMR spectrum of complex **1** (243 MHz, C_6D_6)

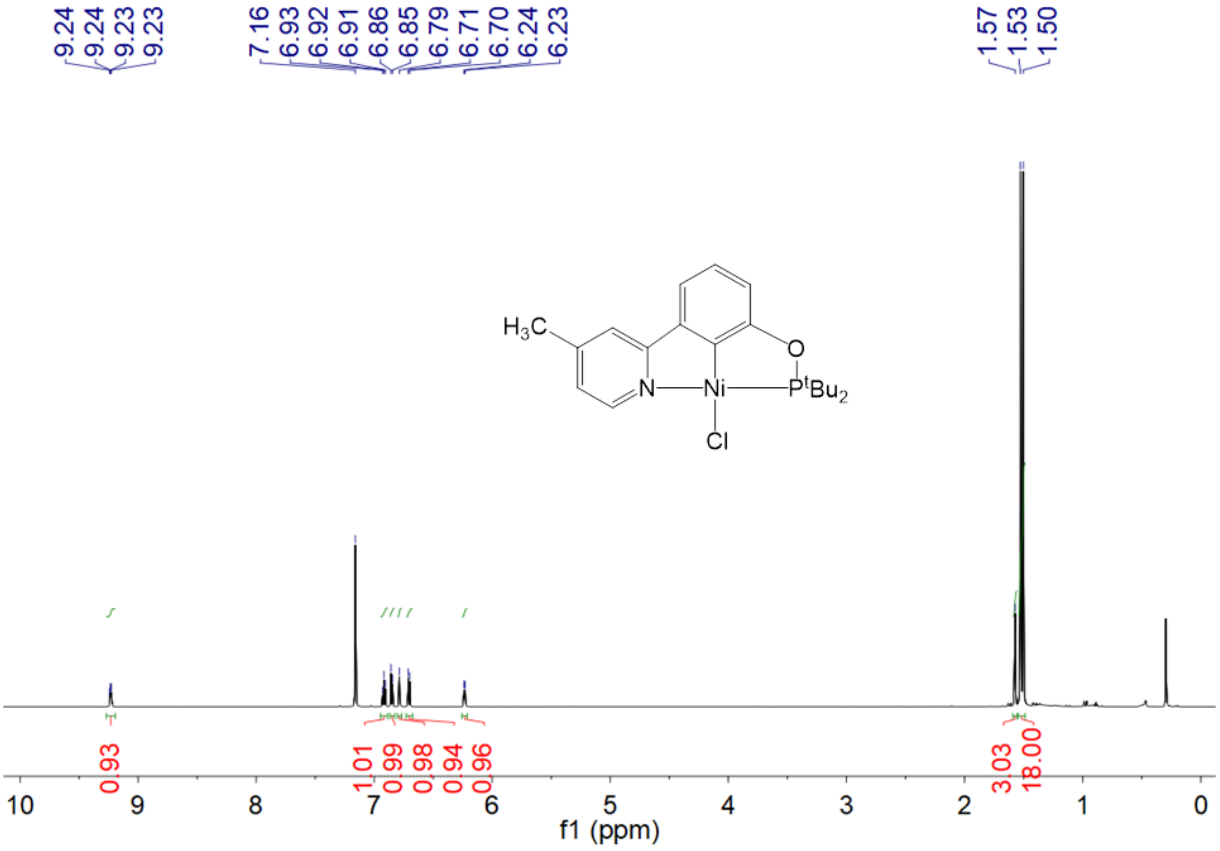


Fig. S4 ^1H NMR spectrum of complex **2** (600 MHz, C_6D_6)

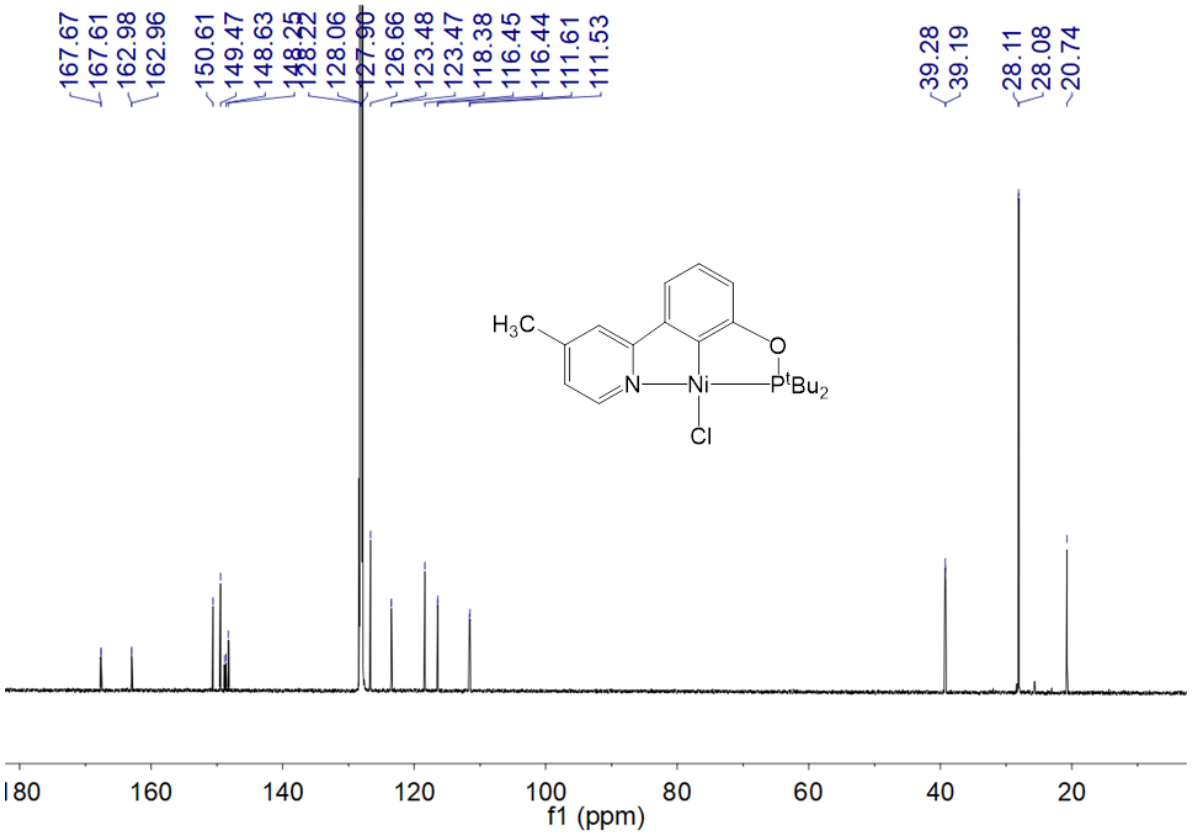


Fig. S5 $^{13}C\{^{1}H\}$ NMR spectrum of complex **2** (151 MHz, C_6D_6)

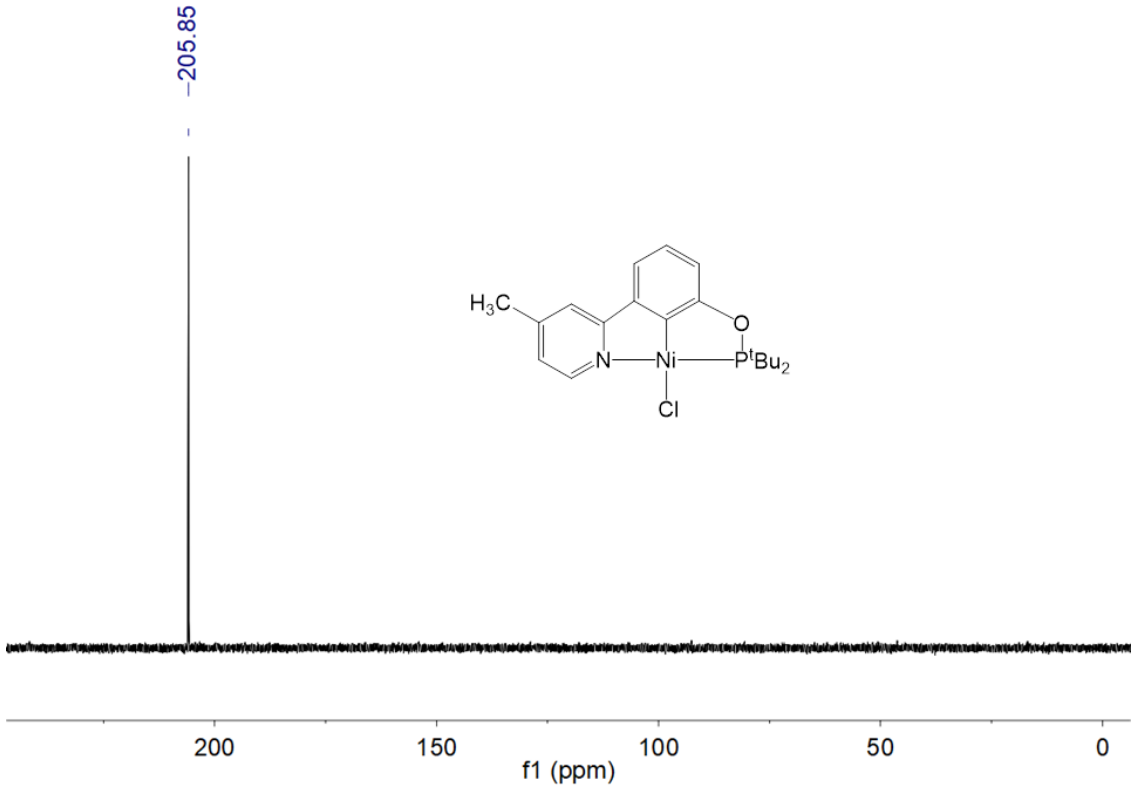


Fig. S6 $^{31}P\{^{1}H\}$ NMR spectrum of complex **2** (243 MHz, C_6D_6)

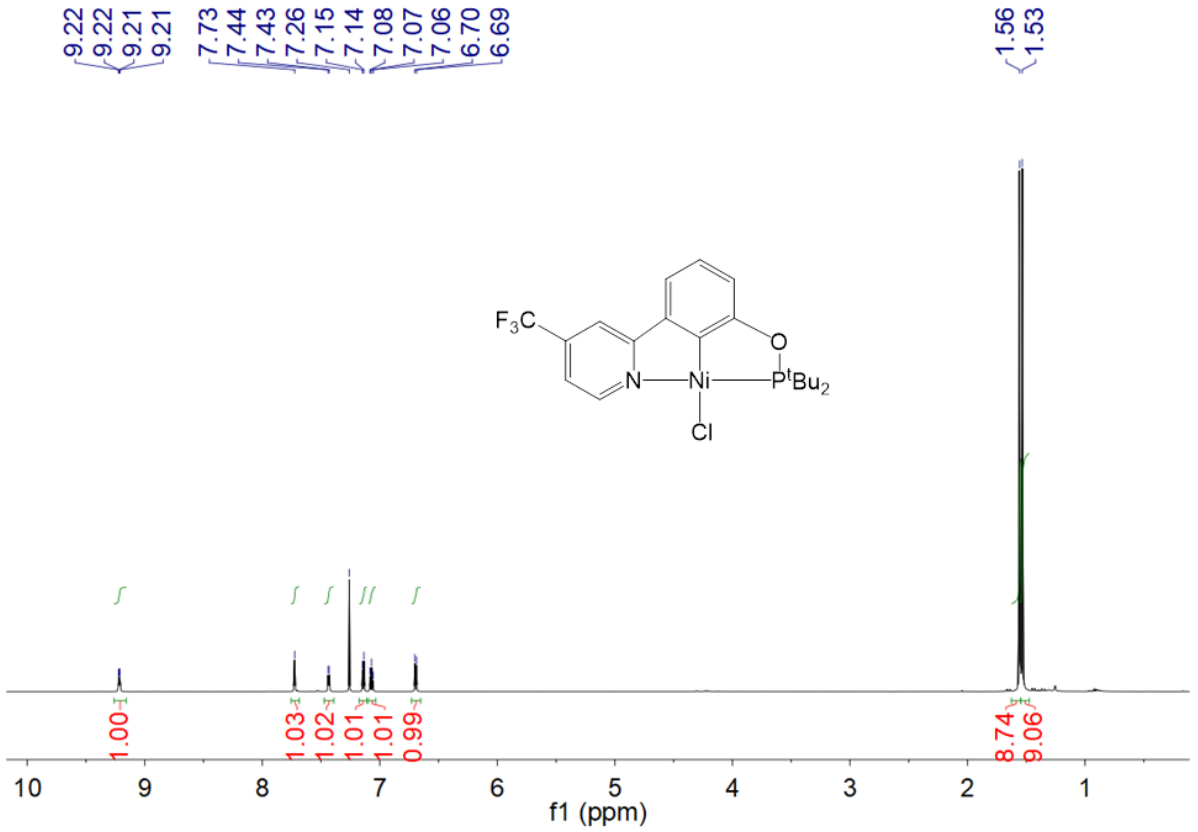


Fig. S7 ^{1}H NMR spectrum of complex **3** (600 MHz, $CDCl_3$)

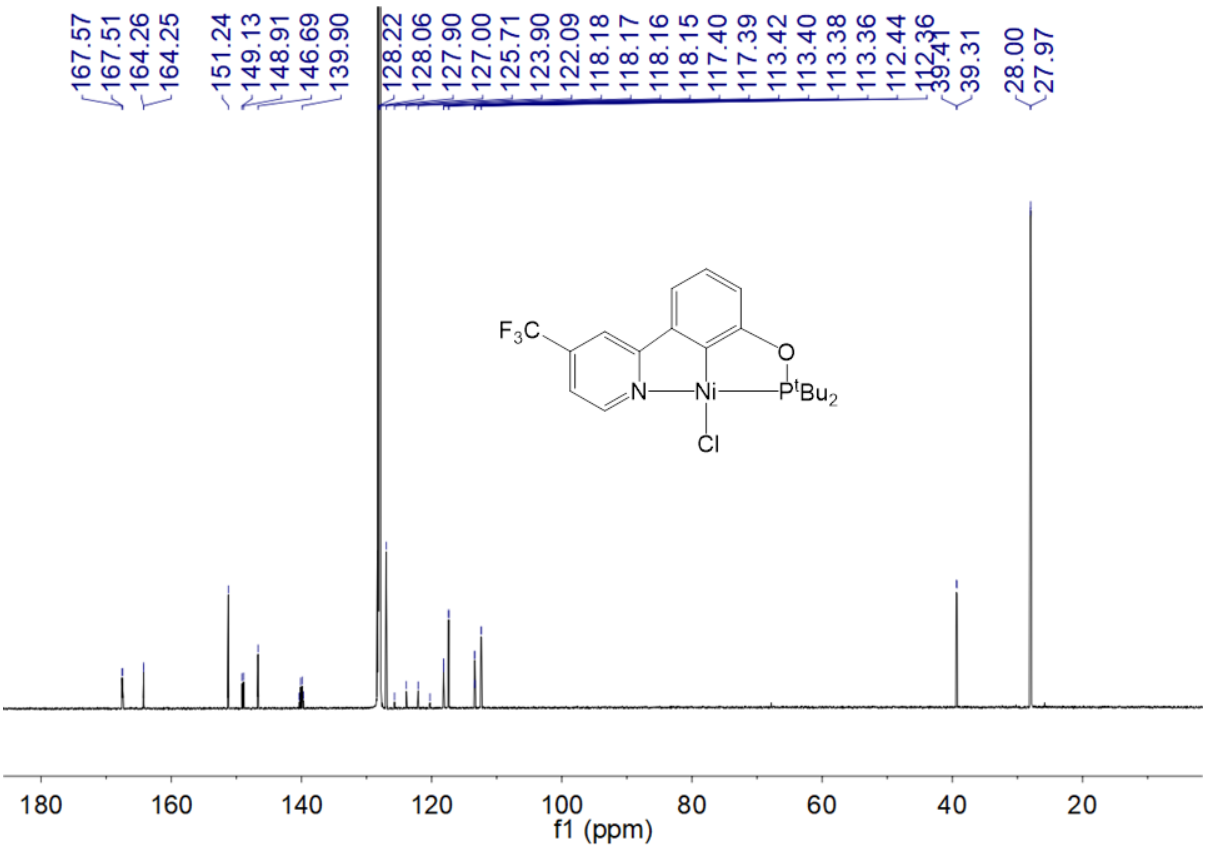


Fig. S8 $^{13}C\{^{1}H\}$ NMR spectrum of complex **3** (151 MHz, C_6D_6)

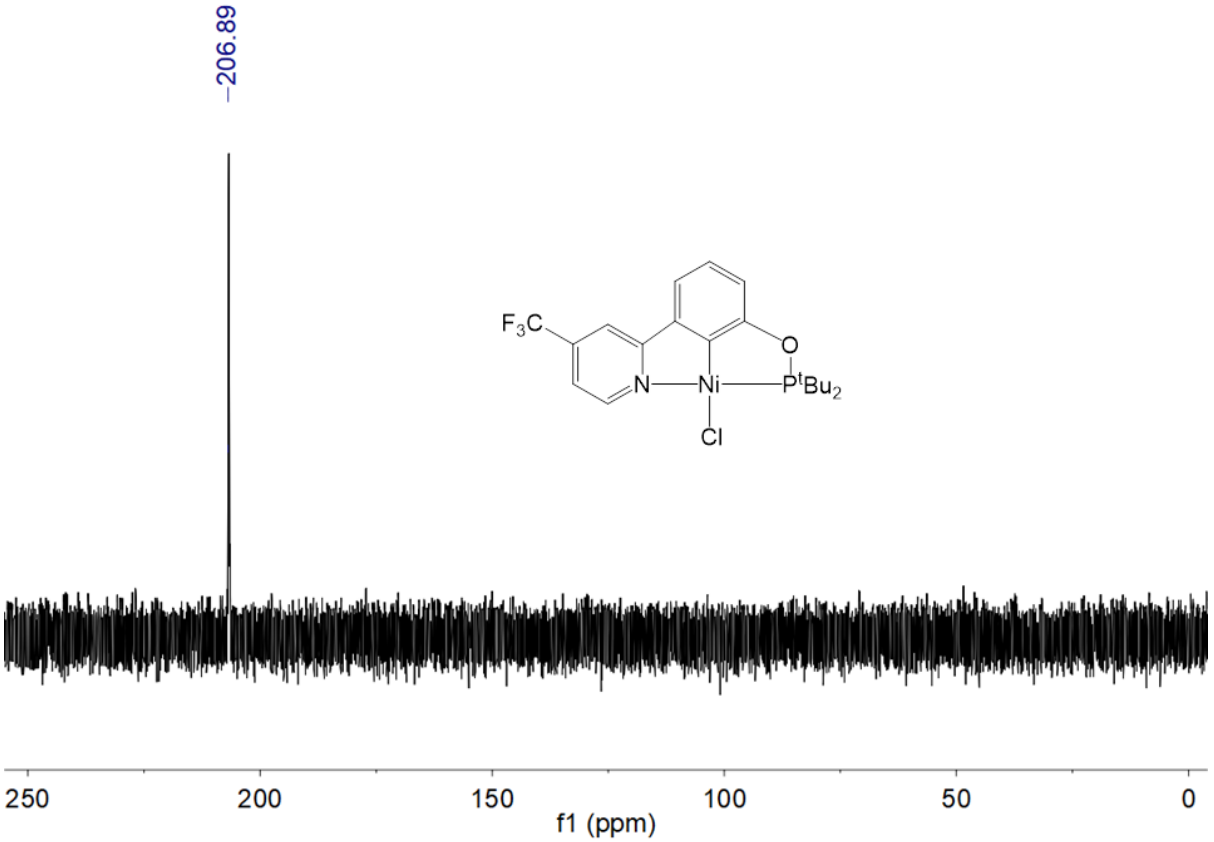


Fig. S9 $^{31}P\{^{1}H\}$ NMR spectrum of complex **3** (243 MHz, C_6D_6)

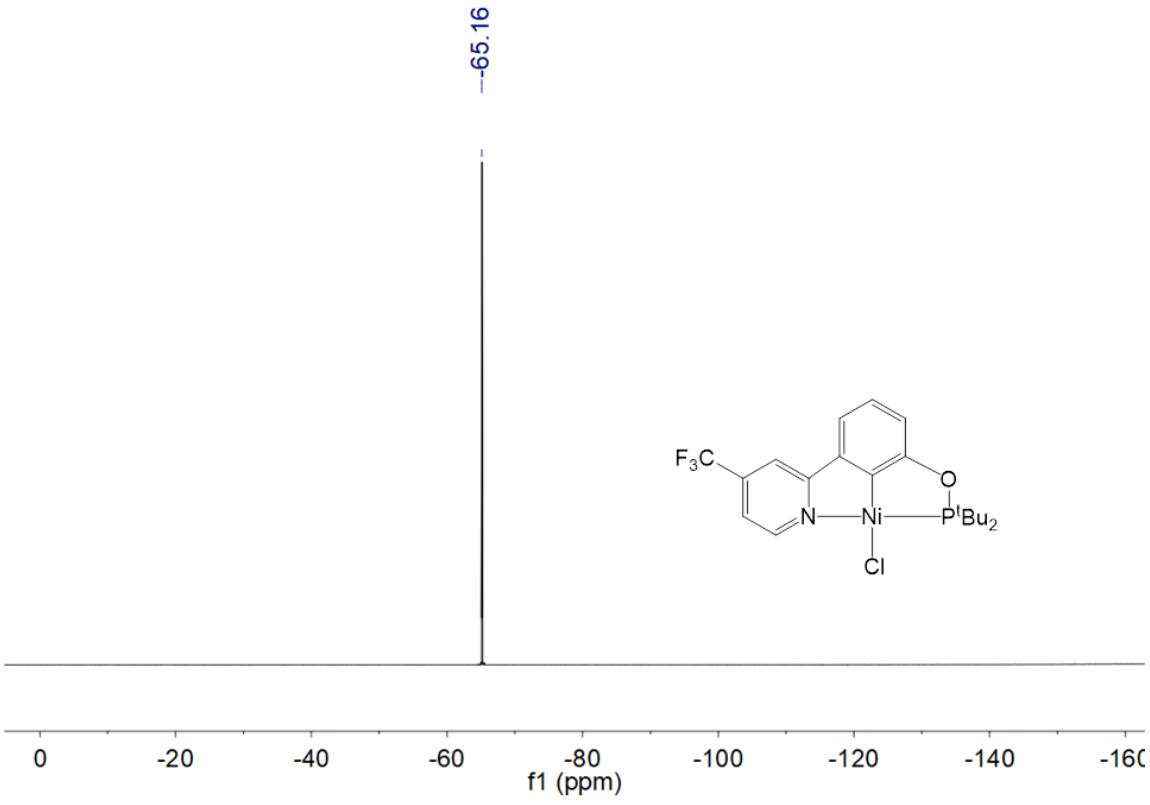


Fig. S10 ^{19}F NMR spectrum of complex **3** (565 MHz, C_6D_6).

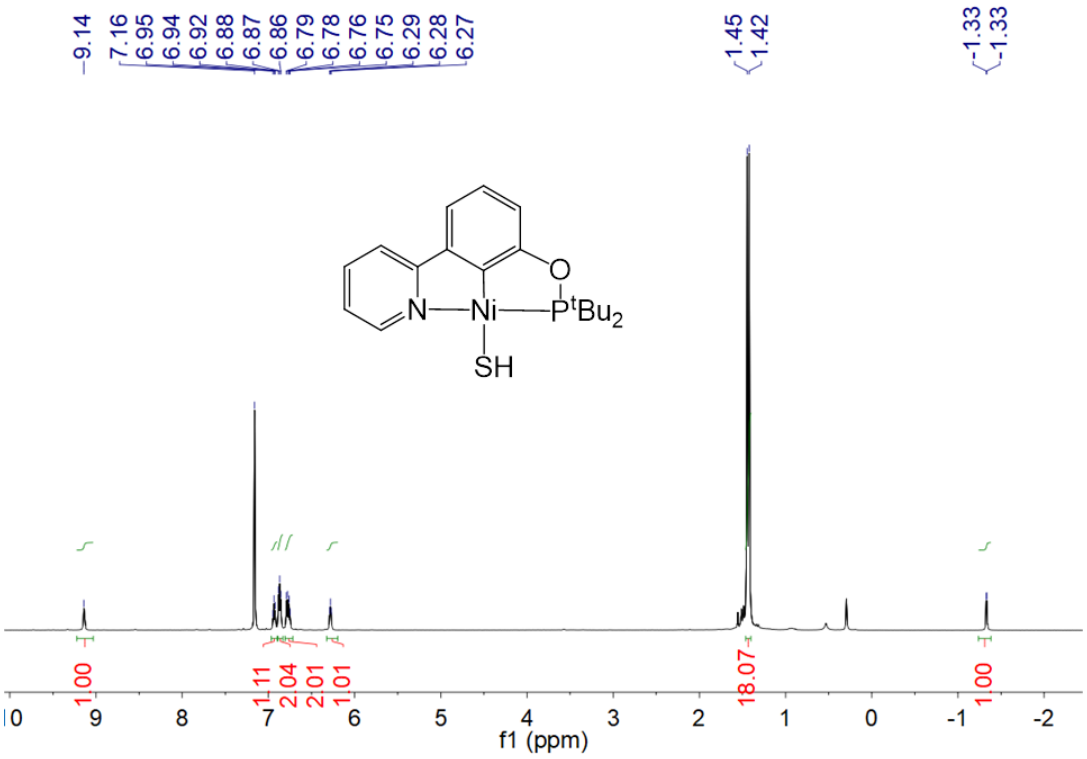


Fig. S11 ^{1}H NMR spectrum of complex **4** (600 MHz, C_6D_6)

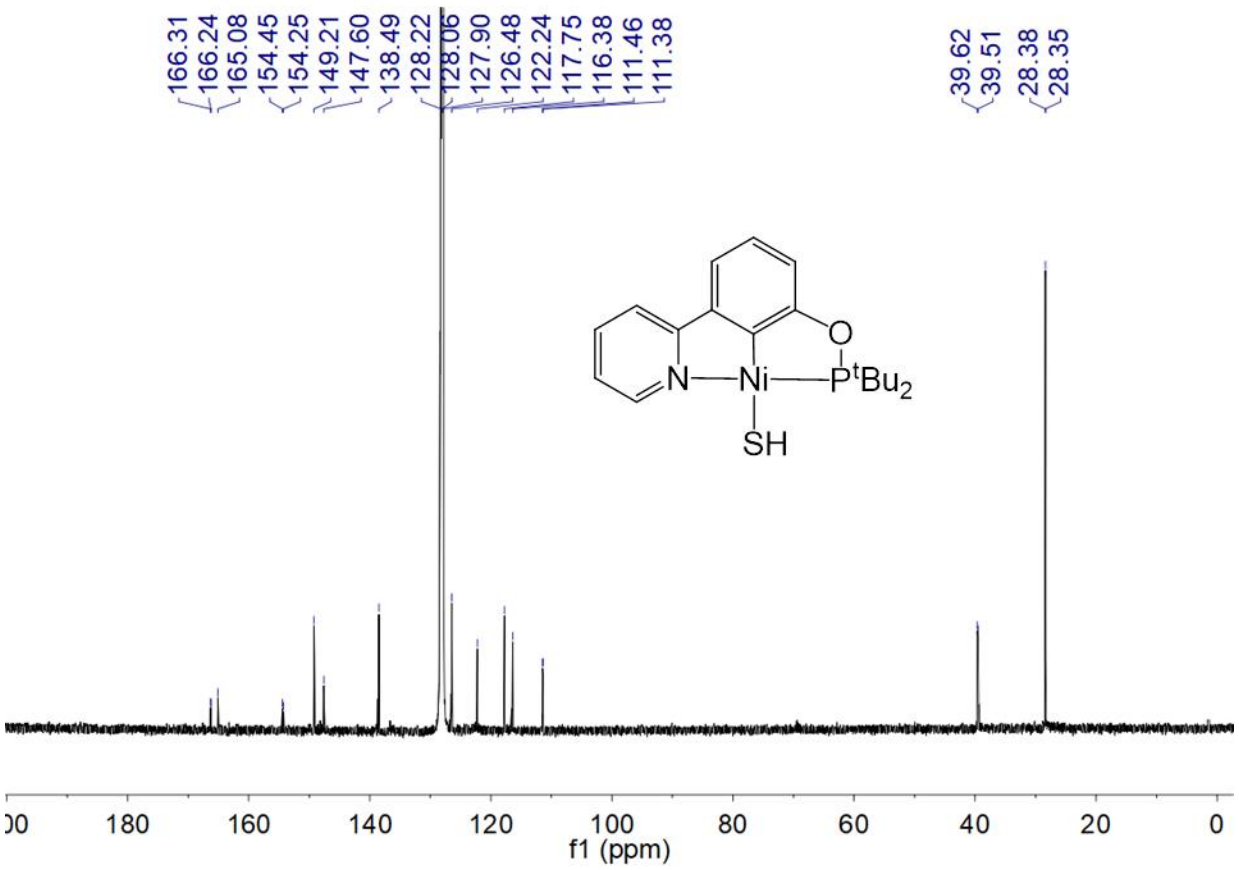


Fig. S12 ^{13}C{^{1}H} NMR spectrum of complex **4** (151 MHz, C_6D_6)

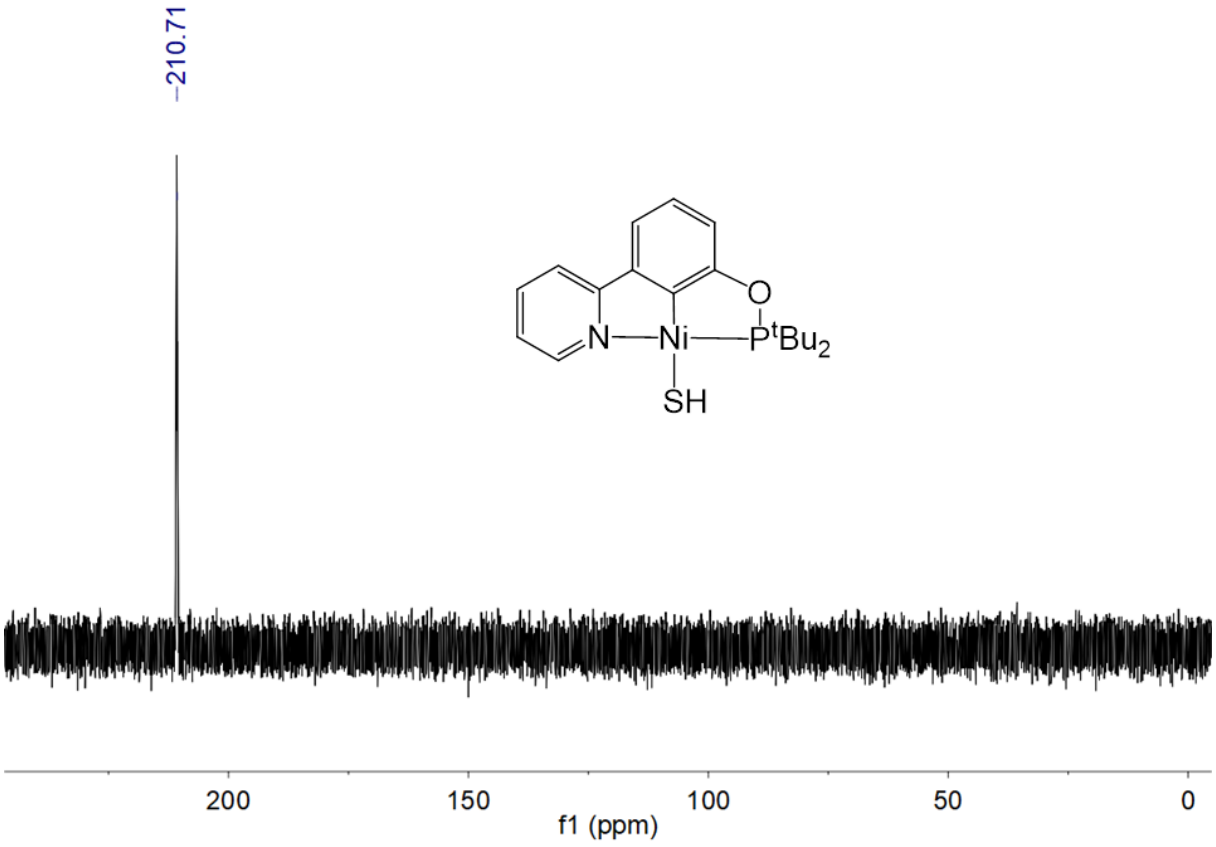


Fig. S13 $^{31}P\{^{1}H\}$ NMR spectrum of complex **4** (243 MHz, C_6D_6)

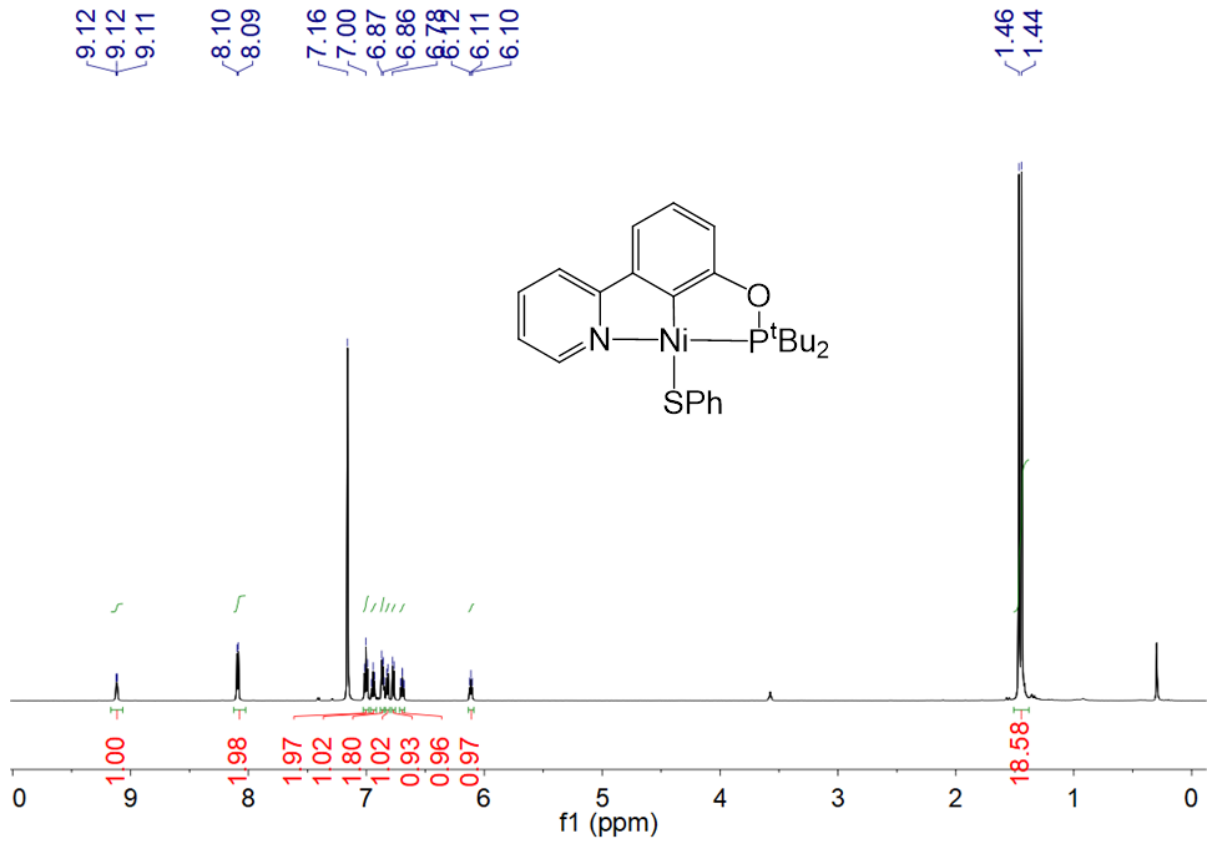


Fig. S14 ^{1}H NMR spectrum of complex **5** (600 MHz, C_6D_6)

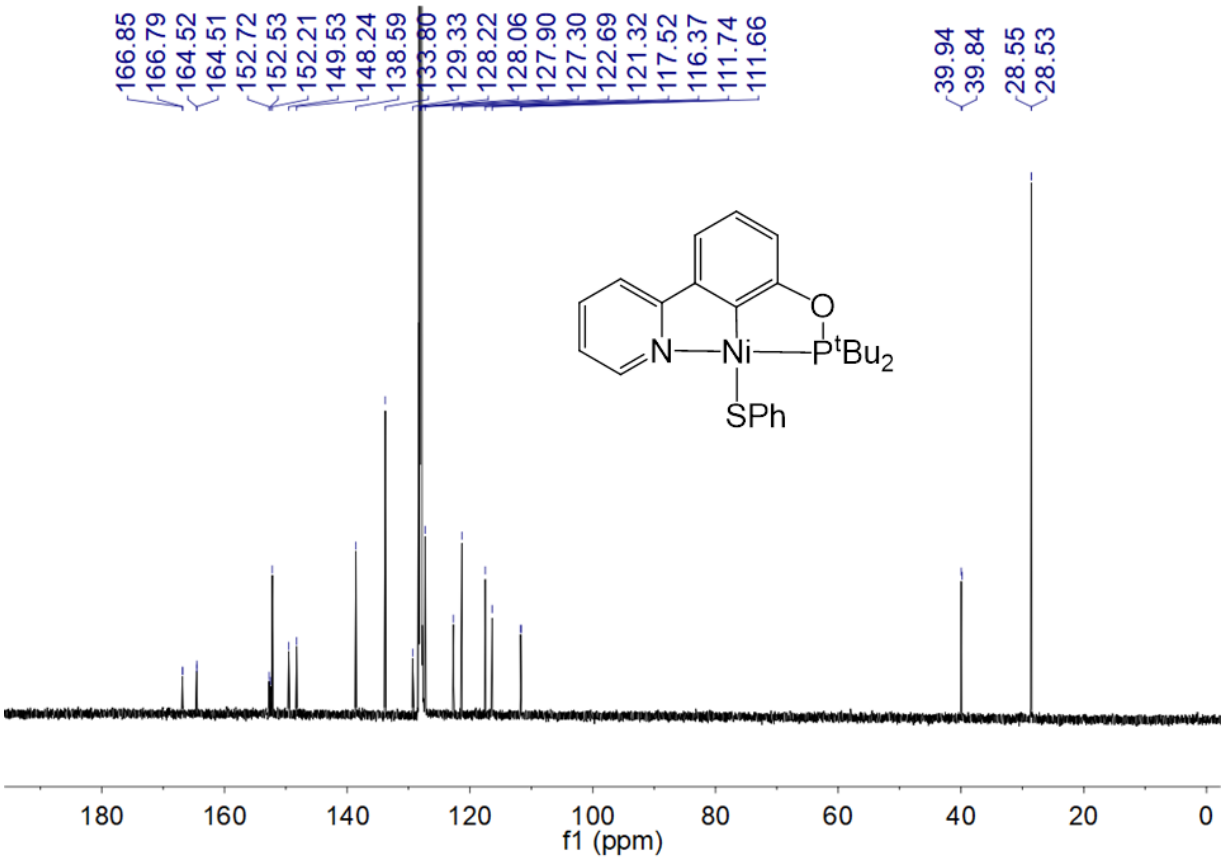


Fig. S15 $^{13}C\{^1H\}$ NMR spectrum of complex **5** (151 MHz, C_6D_6)

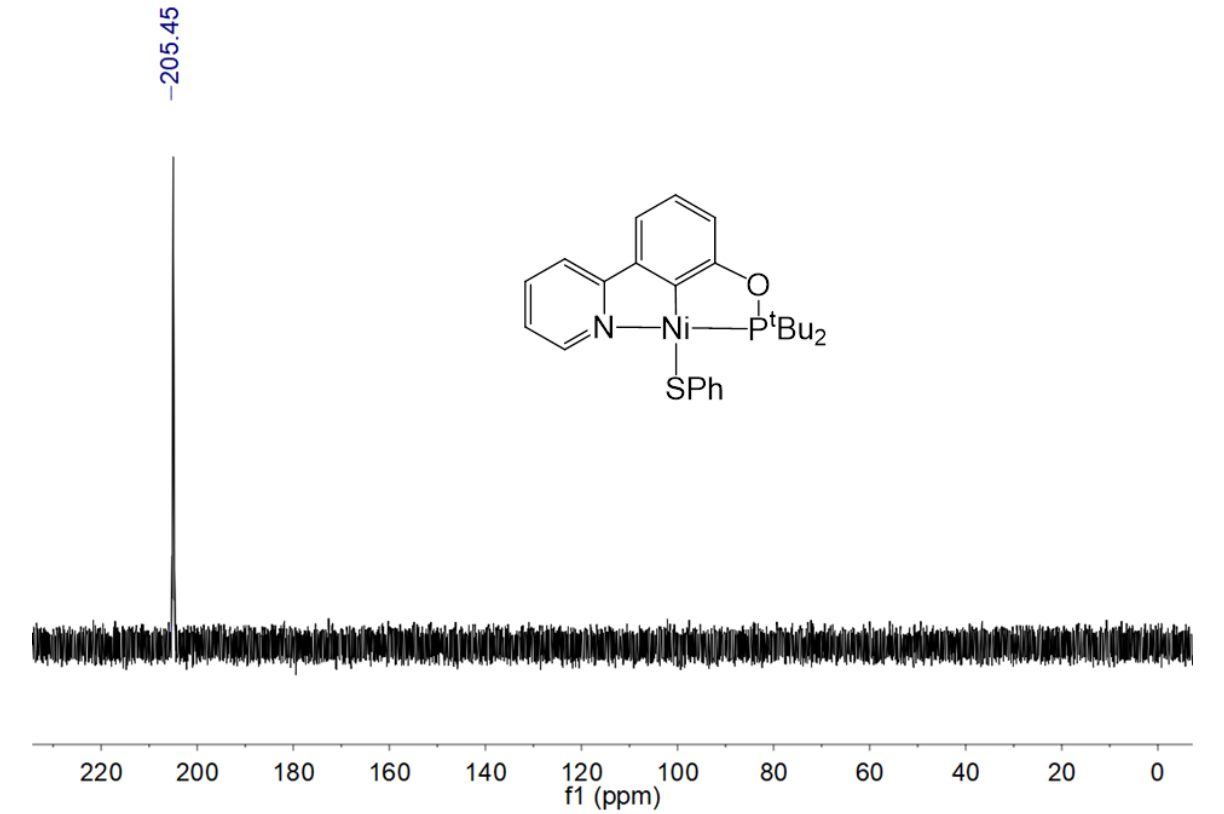
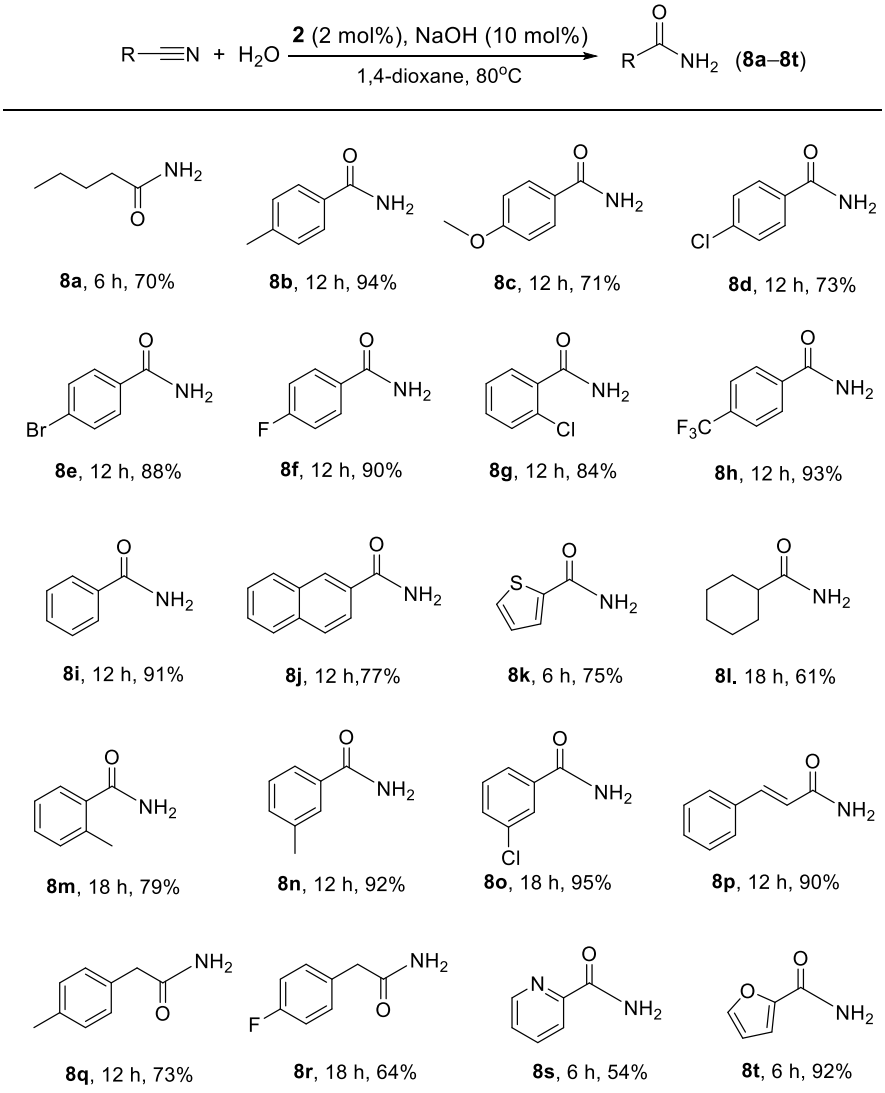


Fig. S16 $^{31}P\{^1H\}$ NMR spectrum of complex **5** (243 MHz, C_6D_6)

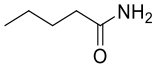
General procedure for the catalytic reactions

Nitrile (1.0 mmol), 1,4-dioxane (1.0 mL), water (1.0 mL), and complex **2** (8.5 mg, 0.02 mmol) were mixed in a reaction tube. The tube was then sealed. The reaction mixture was stirred at 80 ℃ and monitored by GC-MS. The reaction was stopped at certain time or until the nitrile substrate was consumed completely. Solvents were removed under reduced pressure. The resulting residue was extracted with dichloromethane (3 × 10 mL) and filtered. Crude amide products were obtained after dichloromethane was removal from the combined extraction solutions. The products were further purified by washing with cold diethyl ether or *n*-hexane and dried in vacuo. The isolated amide products were characterized by ^{1}H and $^{13}C\{^{1}H\}$ NMR spectroscopy. Scope of the substrates is presented in Scheme S1 and the NMR spectra are presented in the Fig. S19–S58.



Scheme S1 Catalytic hydration of different nitriles catalysed by complex **2**. Reaction conditions: nitrile (0.5 mmol), 1,4-dioxane (1.0 mL), water (1.0 mL). Yields were based on the isolated products.

Characterization of the isolated amide products



(**8a**)

White solid (35 mg, 70% yield), M.P. 104–105 ℃. ^{1}H NMR (600 MHz, CD_3OD, δ): 2.22 (t, J = 7.2 Hz, 2H, CH_2), 1.58–1.63 (m, 2H, CH_2), 1.37–1.40 (m, 2H, CH_2), 0.96 (t, J = 7.2 Hz, 3H, CH_3). ^{13}C{^{1}H} NMR (151 MHz, CD_3OD, δ): 179.24 (*C*O), 36.21 (*C*H_2), 28.95 (*C*H_2), 23.36 (*C*H_2), 14.01 (*C*H_3). These data are in good agreement with literature report.[S2]

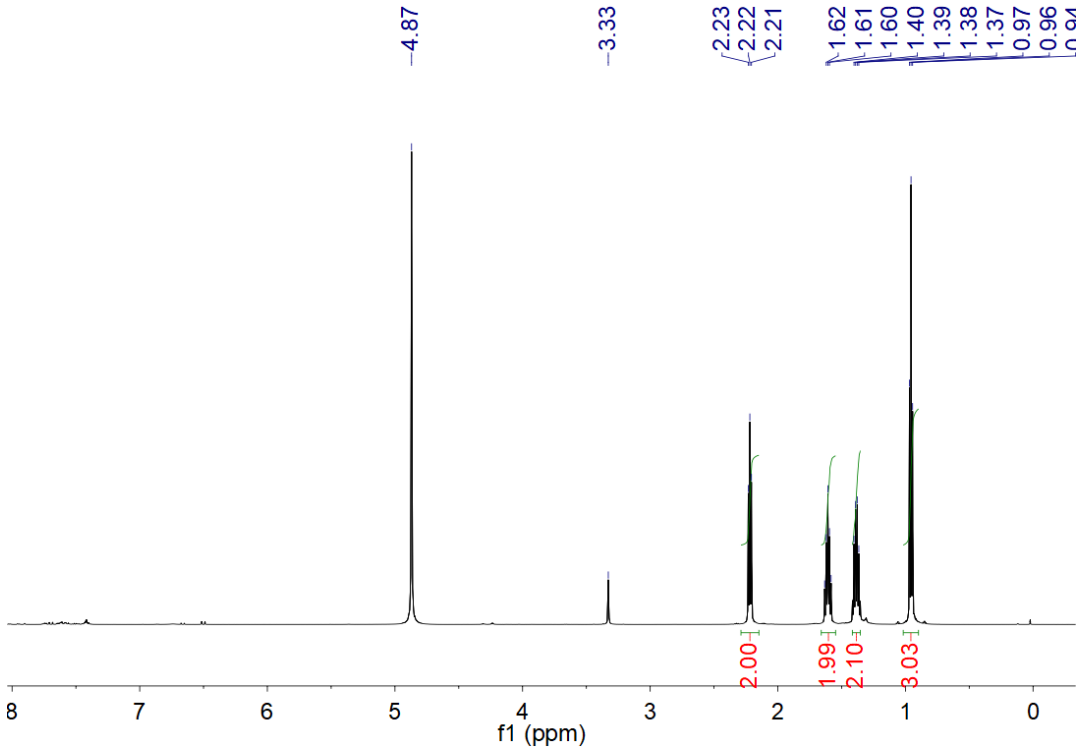


Fig. S17 ^{1}H NMR spectrum of the isolated **8a** (600 MHz, CD_3OD)

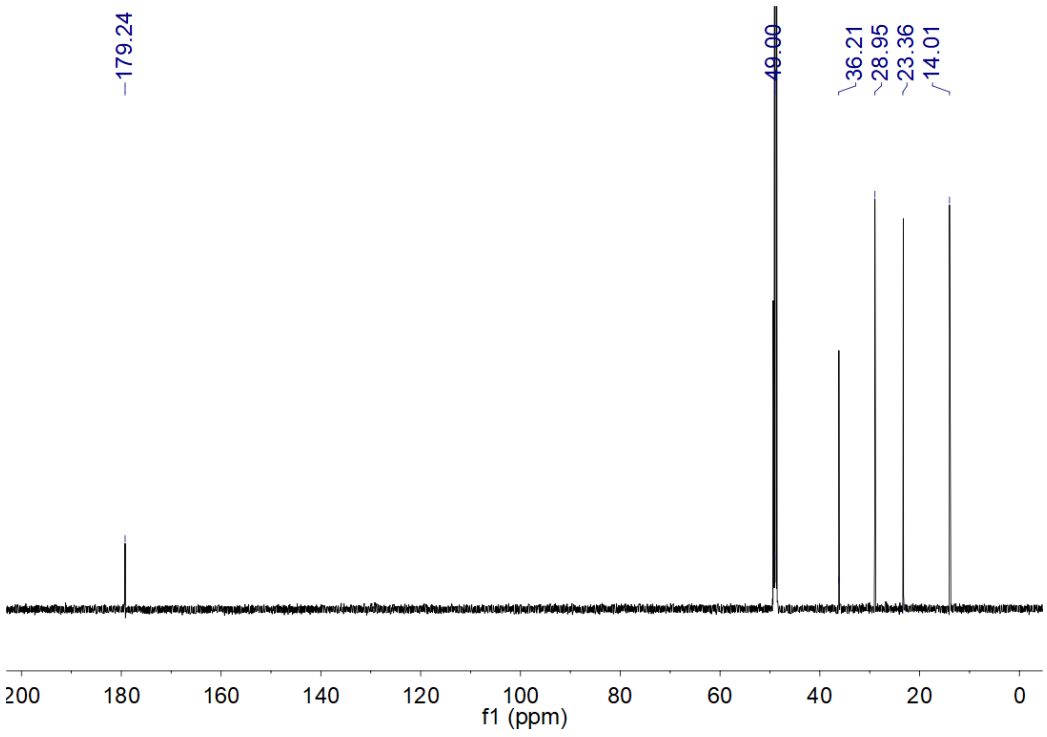
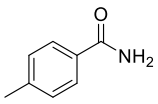


Fig. S18 ^{13}C{^{1}H} NMR spectrum of the isolated **8a** (151 MHz, CD_3OD)



(**8b**)

White solid (64 mg, 94% yield), M.P. 162–164 ℃. ^{1}H NMR (600 MHz, CD_3OD, δ): 7.78 (d, J = 8.4 Hz, 2H, Ar*H*), 7.28 (d, J = 8.4 Hz, 2H, Ar*H*), 2.40 (s, 3H, CH_3). ^{13}C{^{1}H} NMR (151 MHz, CD_3OD, δ): 172.43 (*C*O), 143.66 (Ar*C*), 132.07 (Ar*C*), 130.11 (Ar*C*), 128.71 (Ar*C*), 21.42 (*C*H_3). These data are in good agreement with literature report.[S3]

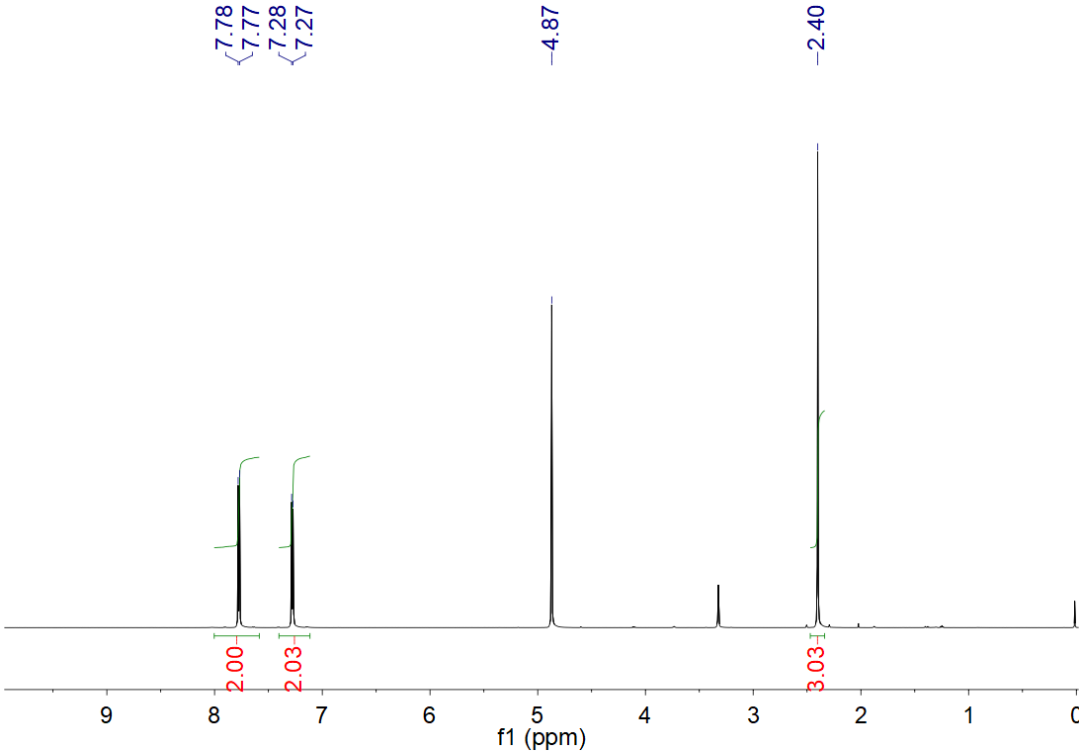


Fig. S19 ^{1}H NMR spectrum of the isolated **8b** (600 MHz, CD_3OD)

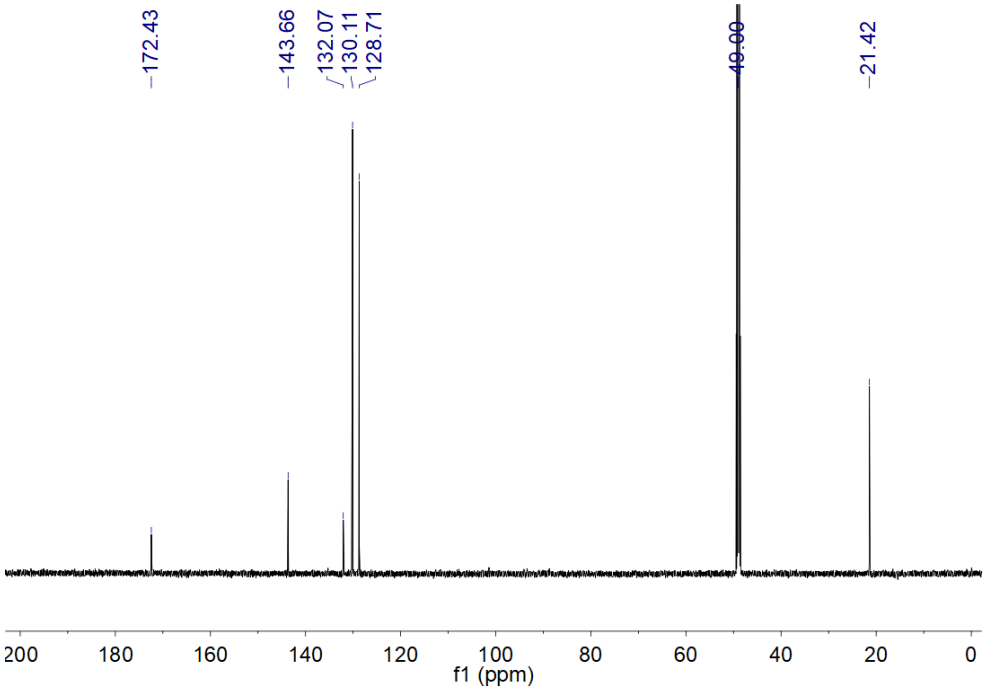
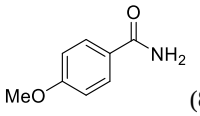


Fig. S20 ^{13}C{^{1}H} NMR spectrum of the isolated **8b** (151 MHz, CD_3OD)



(**8c**)

White solid (54 mg, 71% yield), M.P. 164–166 ℃. ^{1}H NMR (600 MHz, CD_3OD, δ): 7.85 (d, J = 9 Hz, 2H, Ar*H*), 6.98 (d, J = 7.8 Hz, 2H, Ar*H*), 3.86 (s, 3H, CH_3). ^{13}C{^{1}H} NMR (151 MHz, CD_3OD, δ): 172.05 (*C*O), 164.16 (Ar*C*), 130.61 (Ar*C*), 126.93 (Ar*C*), 114.67 (Ar*C*), 55.91 (*C*H_3). These data are in good agreement with literature report.[S3]

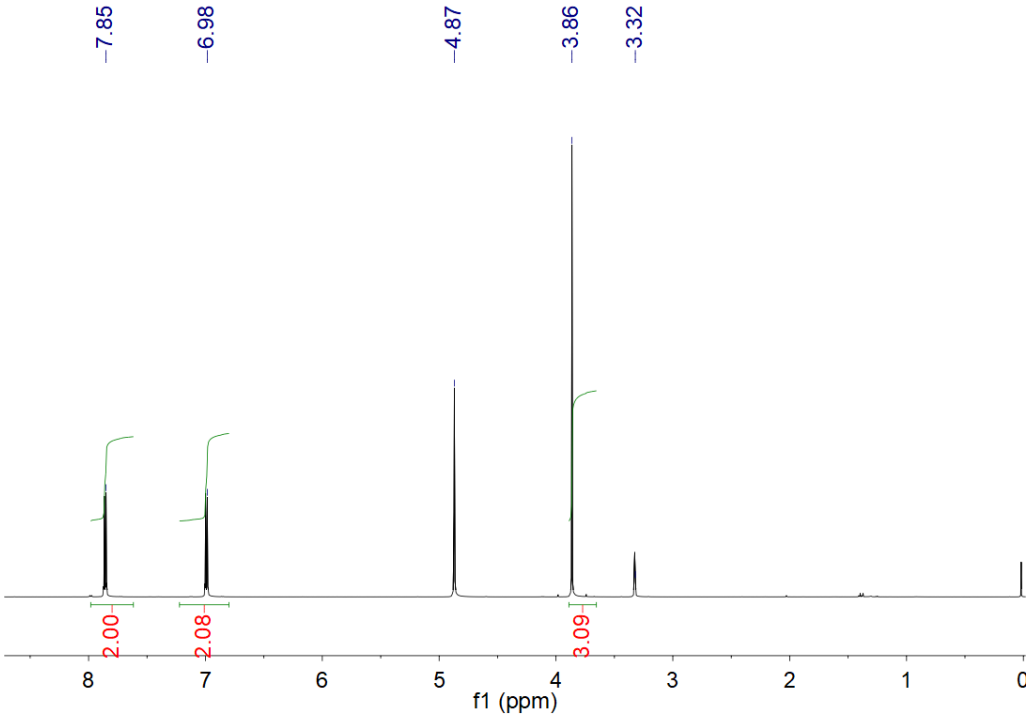


Fig. S21 ^{1}H NMR spectrum of the isolated **8c** (600 MHz, CD_3OD)

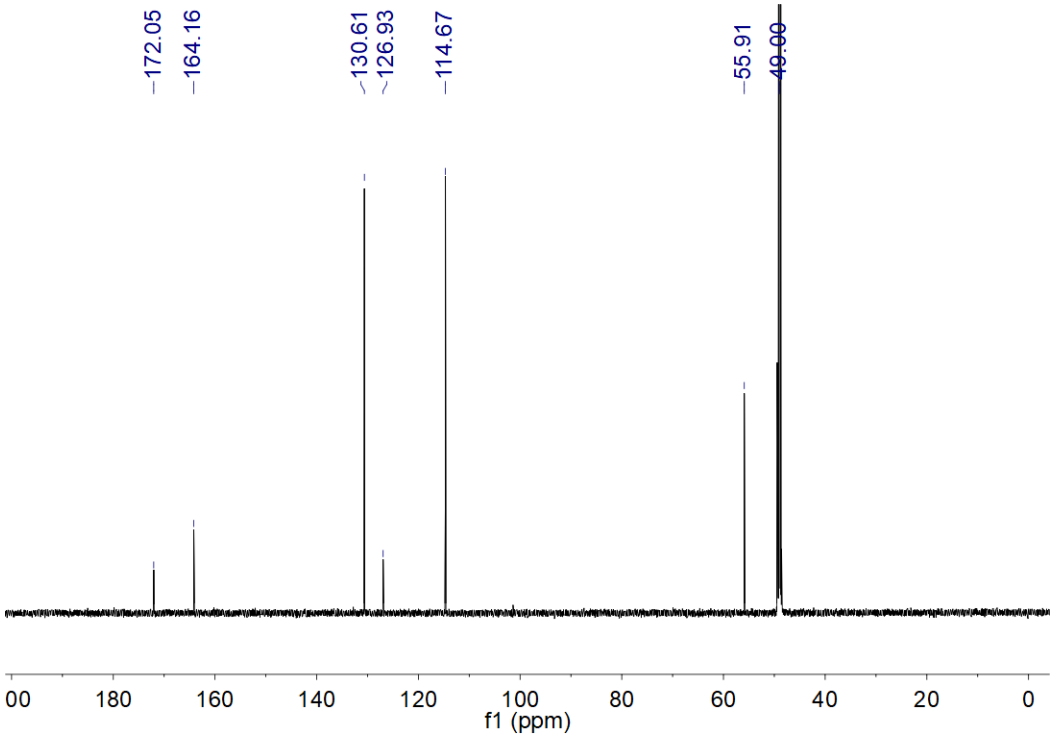
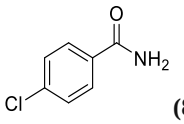


Fig. S22 ^{13}C{^{1}H} NMR spectrum of the isolated **8c** (151 MHz, CD_3OD)



(8d)

White solid (57 mg, 73% yield), M.P. 173–174 ℃. ^{1}H NMR (600 MHz, CD_3OD, δ): 7.86 (d, J = 8.4 Hz, 2H, Ar*H*), 7.47 (d, J = 9 Hz, 2H, Ar*H*). ^{13}C{^{1}H} NMR (151 MHz, CD_3OD, δ): 171.12 (*C*O), 139.00 (Ar*C*), 133.68 (Ar*C*), 130.36 (Ar*C*), 129.69 (Ar*C*). These data are in good agreement with literature report.[S4]

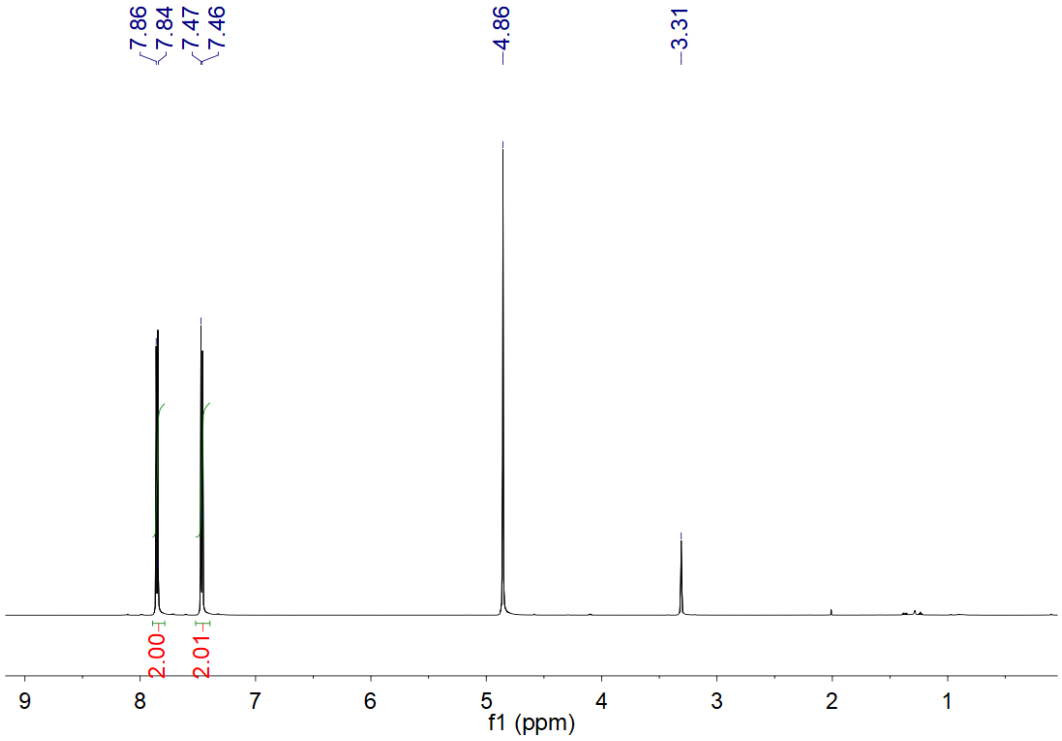


Fig. S23 ^{1}H NMR spectrum of the isolated **8d** (600 MHz, CD_3OD)

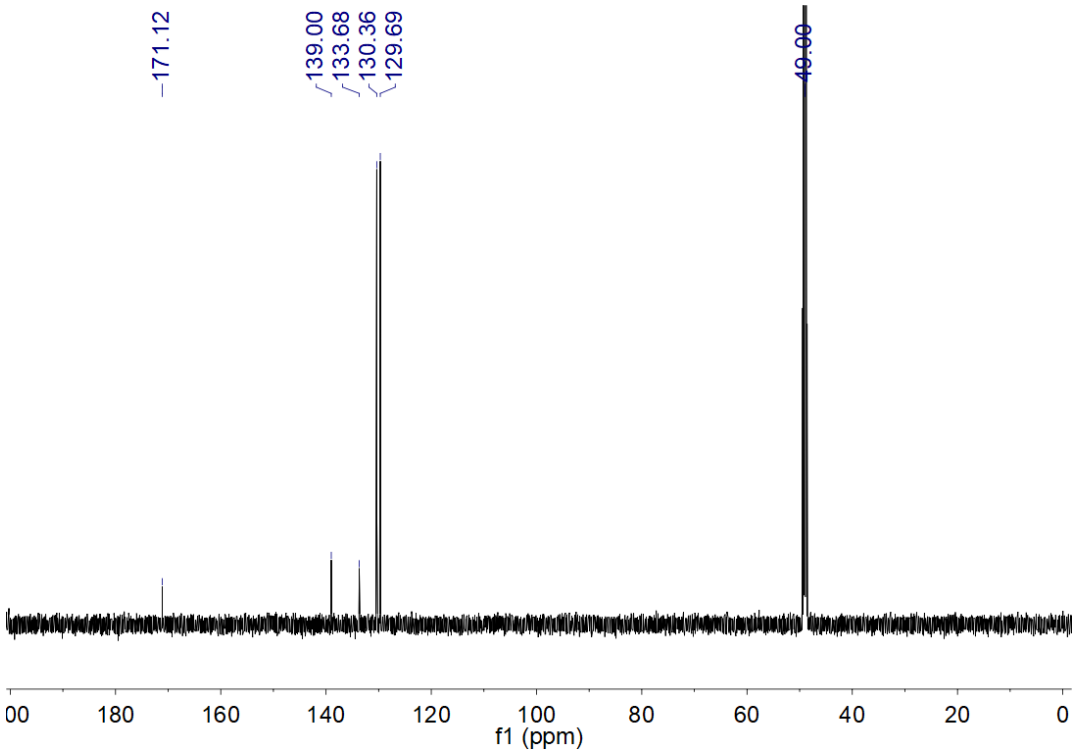
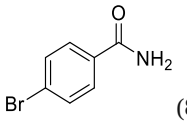


Fig. S24 ^{13}C{^{1}H} NMR spectrum of the isolated **8d** (151 MHz, CD_3OD)



(**8e**)

White solid (88 mg, 88% yield), M.P. 191–193 ℃. ^{1}H NMR (600 MHz, CD_3OD, δ): 7.80 (d, J = 7.8 Hz, 2H, Ar*H*), 7.64 (d, J = 7.8 Hz, 2H, Ar*H*). $^{13}C\{^{1}H\}$ NMR (151 MHz, CD_3OD, δ): 171.21 (*C*O), 134.09 (Ar*C*), 132.73 (Ar*C*), 130.50 (Ar*C*), 127.35 (Ar*C*). These data are in good agreement with literature report.[S3]

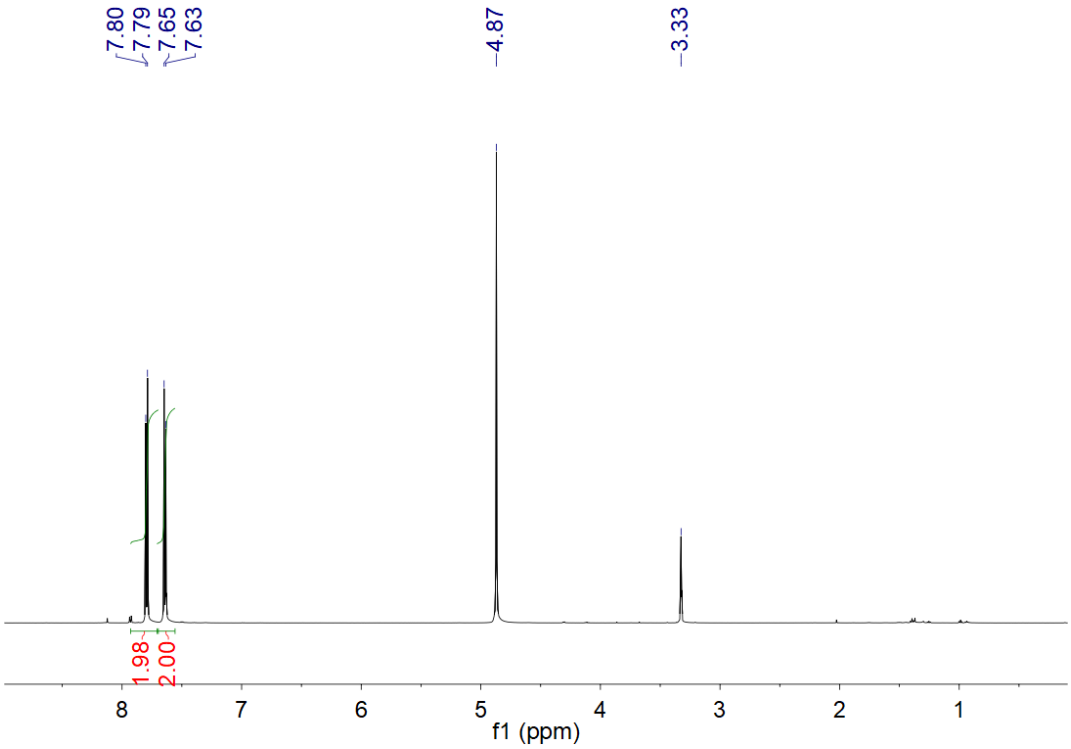


Fig. S25 ^{1}H NMR spectrum of the isolated **8e** (600 MHz, CD_3OD)

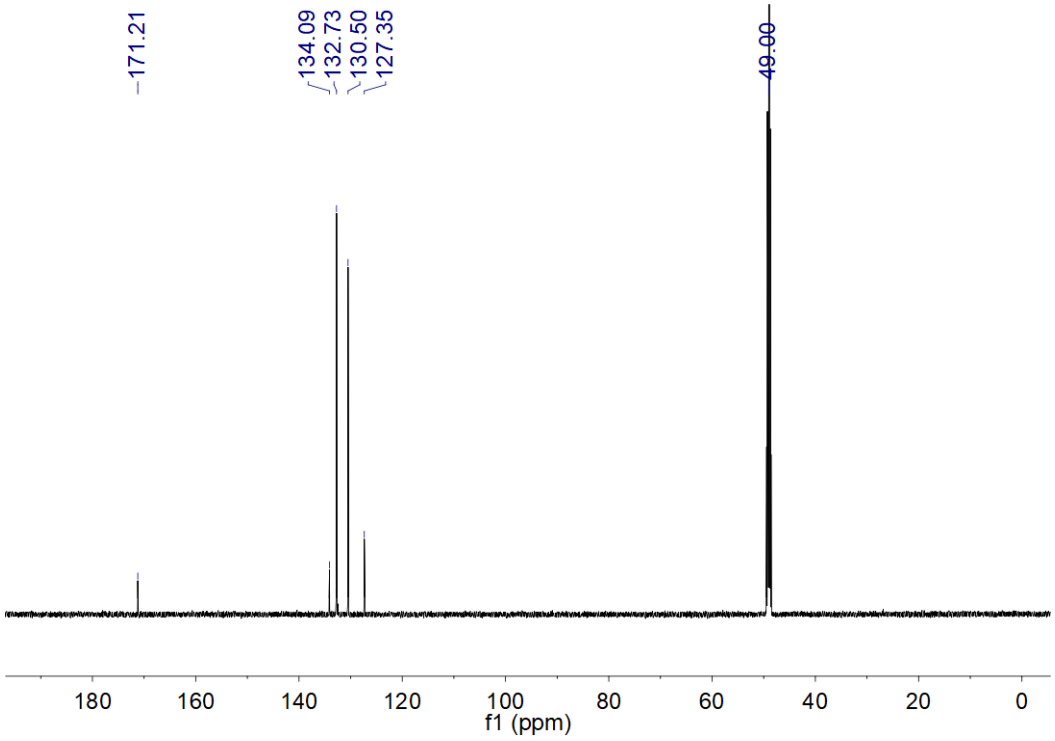
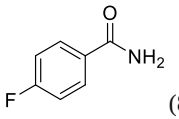


Fig. S26 $^{13}C\{^{1}H\}$ NMR spectrum of the isolated **8e** (151 MHz, CD_3OD)



(**8f**)

White solid (63 mg, 90% yield), M.P. 154–156 ℃. ^{1}H NMR (600 MHz, CD_3OD, δ): 7.92–7.94 (m, 2H, Ar*H*), 7.16–7.20 (m, 2H, Ar*H*). $^{13}C\{^{1}H\}$ NMR (151 MHz, CD_3OD, δ): 171.15 (*C*O), 166.37 (d, $^{1}J_{C\text{-}F}$ = 252 Hz, Ar*C*), 131.30 (d, $^{3}J_{C\text{-}F}$ = 9.1 Hz, Ar*C*), 116.32 (d, $^{2}J_{C\text{-}F}$ = 22 Hz, Ar*C*). $^{19}F\{^{1}H\}$ NMR (565 MHz, CD_3OD, δ): -106.29. These data are in good agreement with literature report.[S5]

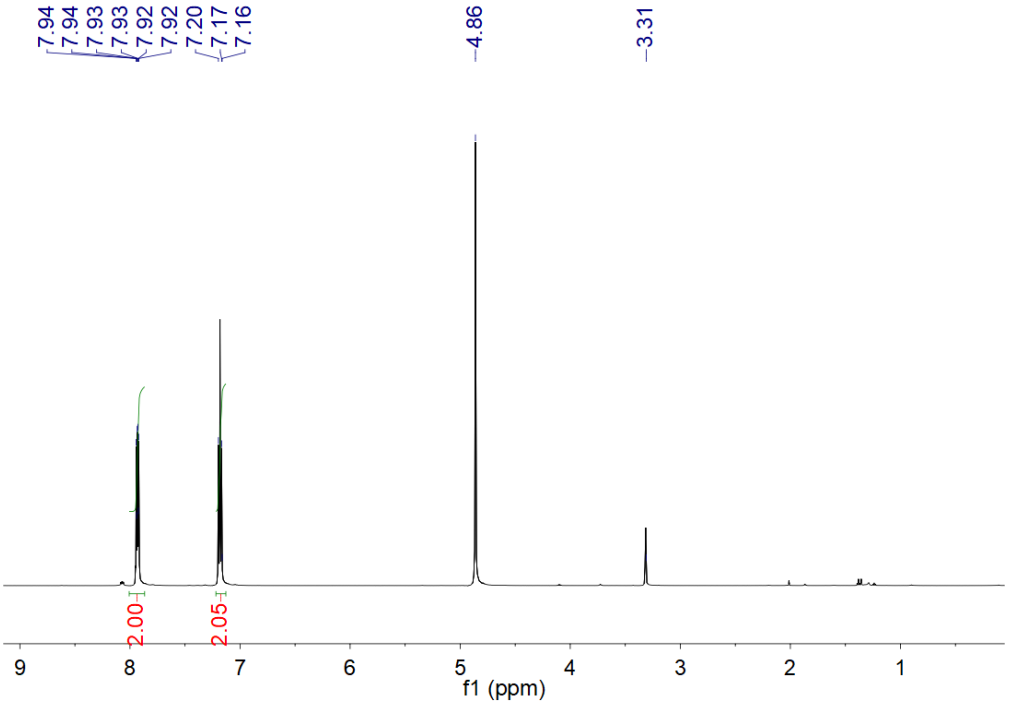


Fig. S27 ^{1}H NMR spectrum of the isolated **8f** (600 MHz, CD_3OD)

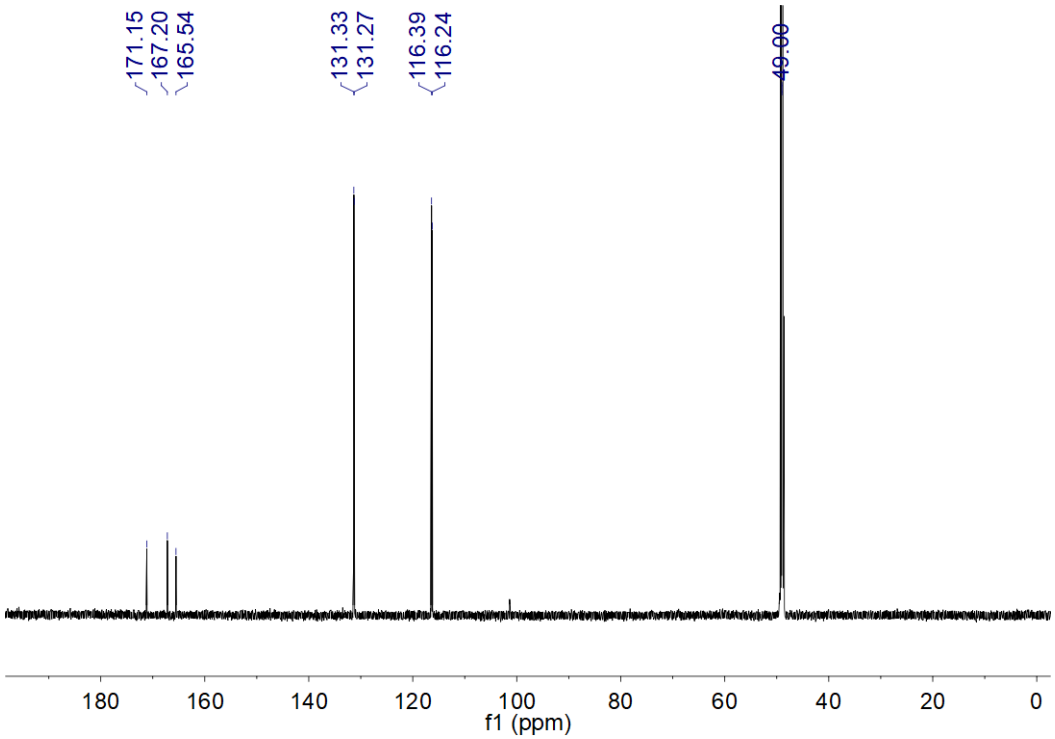
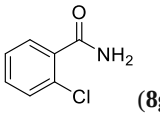


Fig. S28 $^{13}C\{^{1}H\}$ NMR spectrum of the isolated **8f** (151 MHz, CD_3OD)



(**8g**)

White solid (65 mg, 84% yield), M.P. 142–144 ℃. ^{1}H NMR (600 MHz, CD_3OD, δ): 7.52 (d, J = 7.2 Hz, 1H, Ar*H*), 7.48 (d, J = 7.8 Hz, 1H, Ar*H*), 7.38 (t, J = 7.8 Hz, 1H, Ar*H*), 7.45 (t, J = 7.8 Hz, 1H, Ar*H*). ^{13}C{^{1}H} NMR (151 MHz, CD_3OD, δ): 172.34 (*C*O), 137.32 (Ar*C*), 132.17 (Ar*C*), 131.76 (Ar*C*), 131.09 (Ar*C*), 129.92 (Ar*C*), 128.05 (Ar*C*). These data are in good agreement with literature report.[S3]

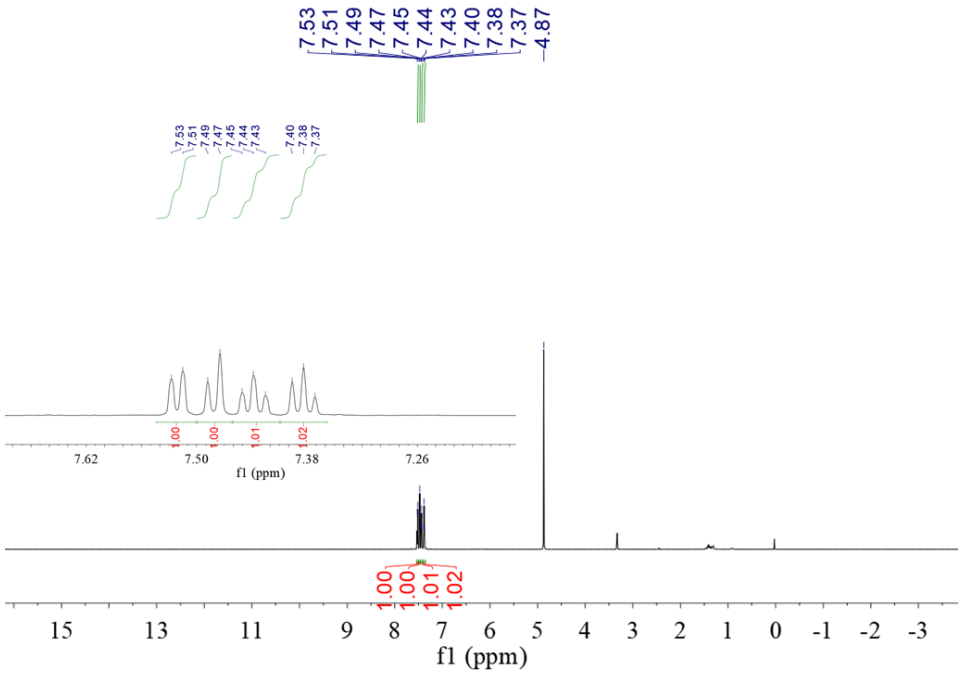


Fig. S29 ^{1}H NMR spectrum of the isolated **8g** (600 MHz, CD_3OD)

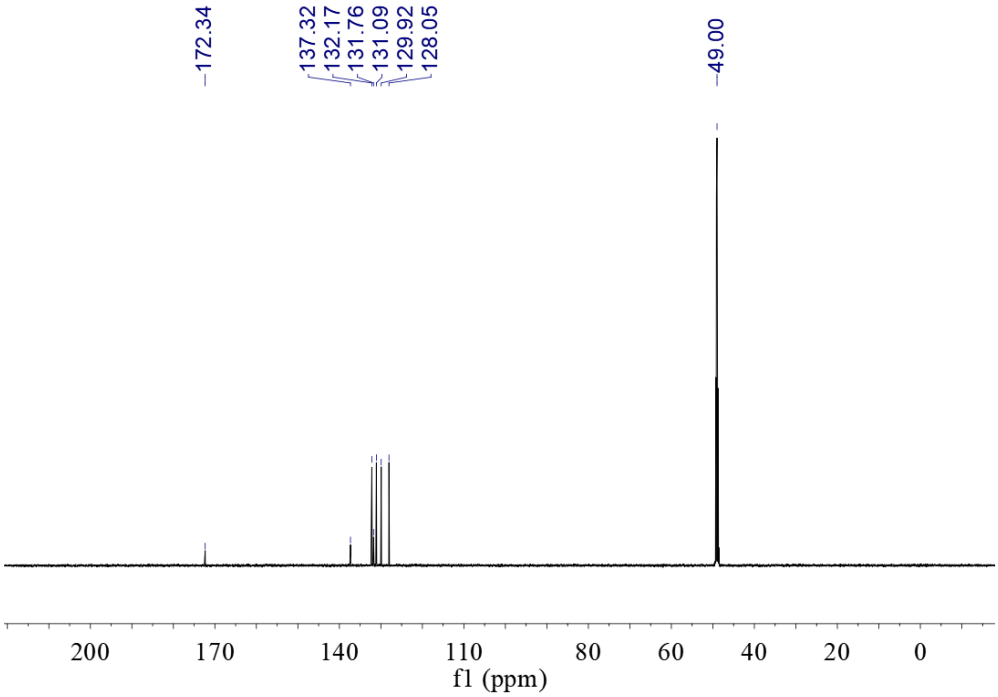
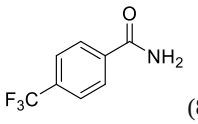


Fig. S30 ^{13}C{^{1}H} NMR spectrum of the isolated **8g** (151 MHz, CD_3OD)



(**8h**)

White solid (87 mg, 93% yield), M.P. 183–185 ℃. ^{1}H NMR (600 MHz, CD_3OD, δ): 8.05 (d, J = 8.4 Hz, 2H, Ar*H*), 7.77 (d, J = 8.4 Hz, 2H, Ar*H*). $^{13}C\{^{1}H\}$ NMR (151 MHz, CD_3OD, δ): 170.82 (*C*O), 138.79 (Ar*C*), 134.26 (q, $^{2}J_{C\text{-}F}$= 33 Hz, ArC), 129.38 (Ar*C*), 126.46 (q, $^{3}J_{C\text{-}F}$= 4 Hz, Ar*C*), 125.27 (q, $^{1}J_{C\text{-}F}$= 272 Hz, *C*F_3). $^{19}F\{^{1}H\}$ NMR (565 MHz, CD_3OD, δ): -64.50. These data are in good agreement with literature report.[S4]

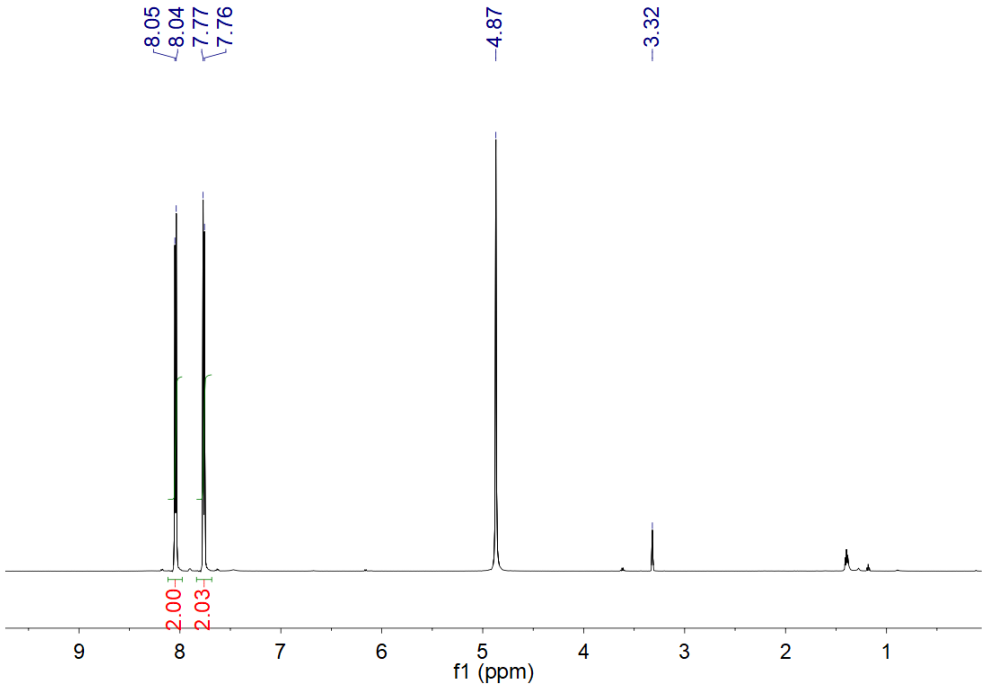


Fig. S31 ^{1}H NMR spectrum of the isolated **8h** (600 MHz, CD_3OD)

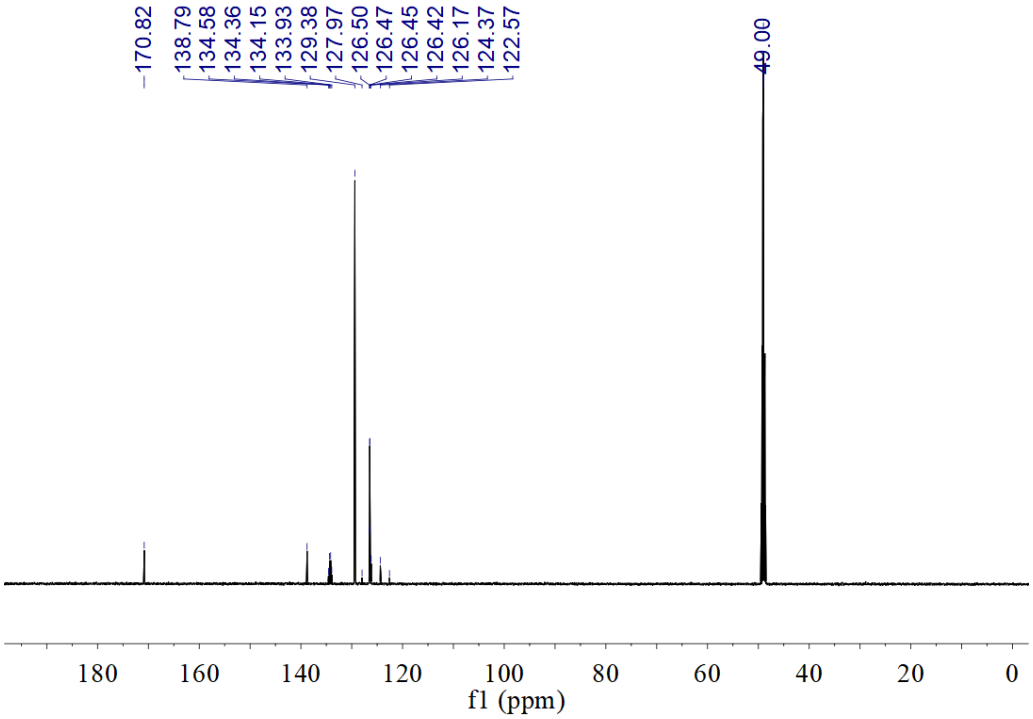
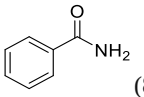


Fig. S32 $^{13}C\{^{1}H\}$ NMR spectrum of the isolated **8h** (151 MHz, CD_3OD)



(**8i**)

White solid (55 mg, 91% yield), M.P. 128–131 ℃. ^{1}H NMR (600 MHz, CD_3OD, δ): 7.87 (d, J = 7.8 Hz, 2H, Ar*H*), 7.54 (t, J = 7.8 Hz, 1H, Ar*H*), 7.45 (t, J = 7.8 Hz, 2H, Ar*H*). ^{13}C{^{1}H} NMR (151 MHz, CD_3OD, δ): 172.52 (*C*O), 134.97 (Ar*C*), 132.92 (Ar*C*), 129.51 (Ar*C*), 128.63 (Ar*C*). These data are in good agreement with literature report.[S3]

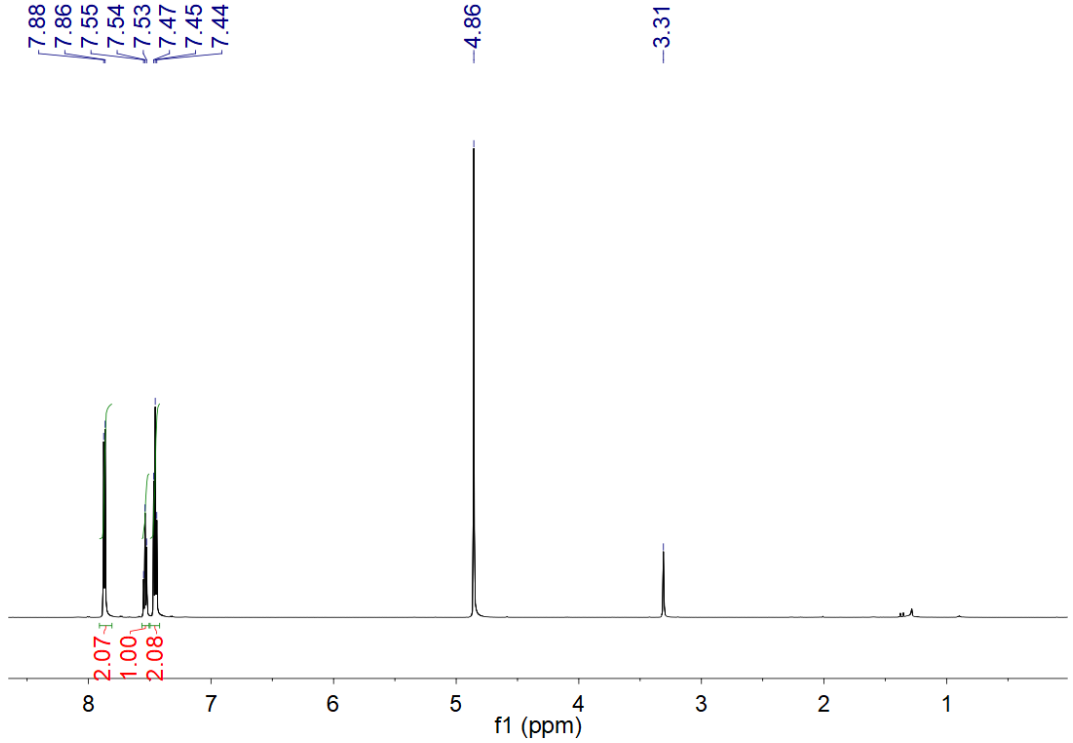


Fig. S33 ^{1}H NMR spectrum of the isolated **8i** (600 MHz, CD_3OD)

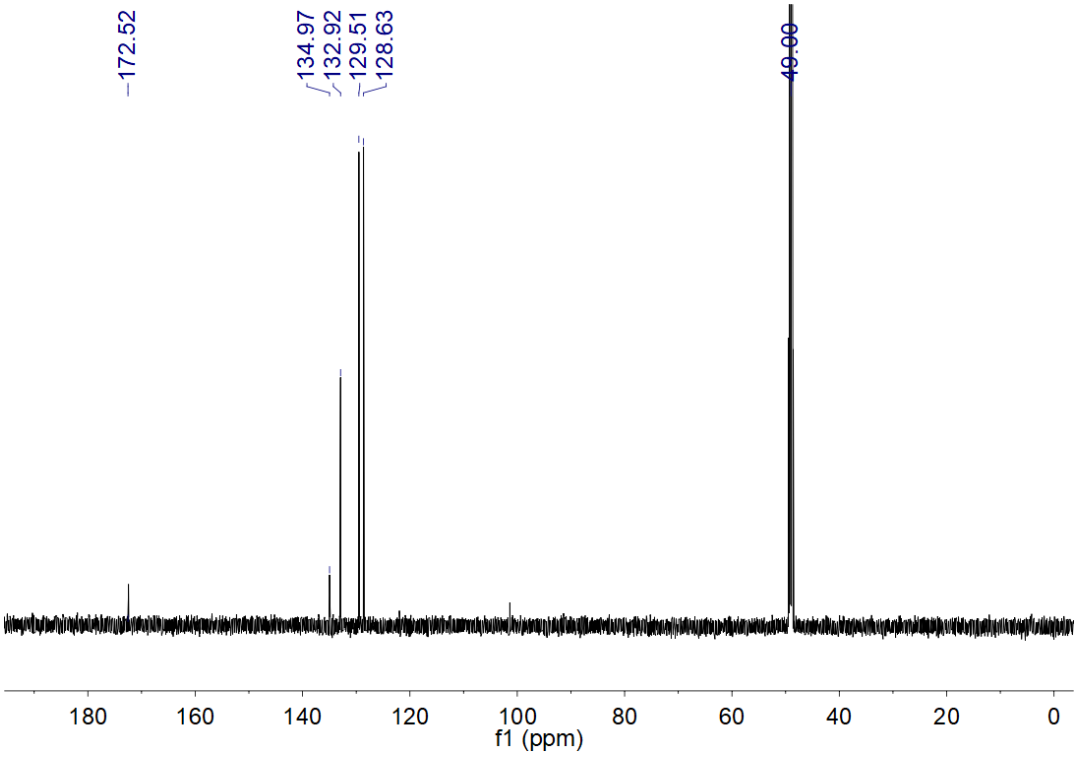
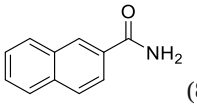


Fig. S34 ^{13}C{^{1}H} NMR spectrum of the isolated **8i** (151 MHz, CD_3OD)



(**8j**)

White solid (66 mg, 77% yield), M.P. 190–192 ℃. ^{1}H NMR (600 MHz, CD_3OD, δ): 8.43 (s, 1H, Ar*H*), 7.97 (d, 1H, $J_{H\text{-}H}$ = 8.2 Hz, Ar*H*), 7.90–7.93 (m, 3H, Ar*H*), 7.54–7.60 (m, 2H, Ar*H*). ^{13}C{^{1}H} NMR (151 MHz, CD_3OD, δ): 172.45 (*C*O), 136.41 (Ar*C*), 134.04 (Ar*C*), 132.18 (Ar*C*), 130.08 (Ar*C*), 129.32 (Ar*C*), 129.27 (Ar*C*), 128.92 (Ar*C*), 128.75 (Ar*C*), 127.81 (Ar*C*), 125.08 (Ar*C*). These data are in good agreement with literature report.[S4]

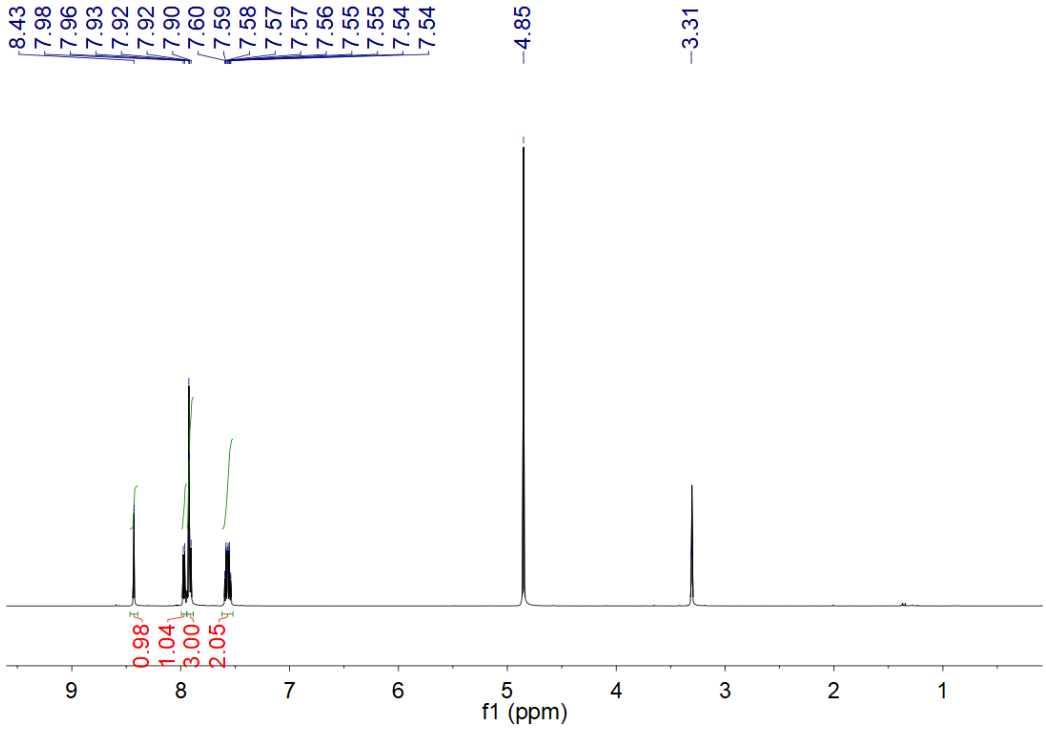


Fig. S35 ^{1}H NMR spectrum of the isolated **8j** (600 MHz, CD_3OD)

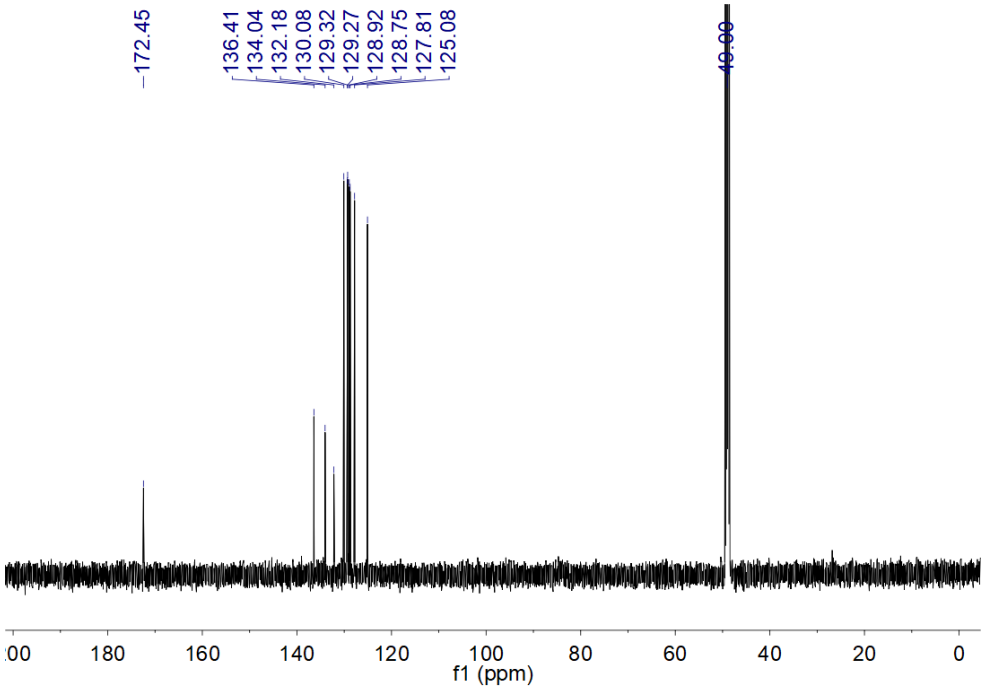
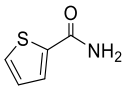


Fig. S36 ^{13}C{^{1}H} NMR spectrum of the isolated **8j** (151 MHz, CD_3OD)



(**8k**)

White solid (48 mg, 75% yield), M.P. 180–183 ℃. ^{1}H NMR (600 MHz, CD_3OD, δ): 7.71 (d, J = 3.7 Hz, 1H), 7.65 (d, J = 5.0 Hz, 1H), 7.11 (t, J = 4.3 Hz, 1H). $^{13}C\{^{1}H\}$ NMR (151 MHz, CD_3OD, δ): 166.81 (*C*O), 139.88 (Ar*C*), 132.40 (Ar*C*), 130.49 (Ar*C*), 128.95 (Ar*C*). These data are in good agreement with literature report.[S4]

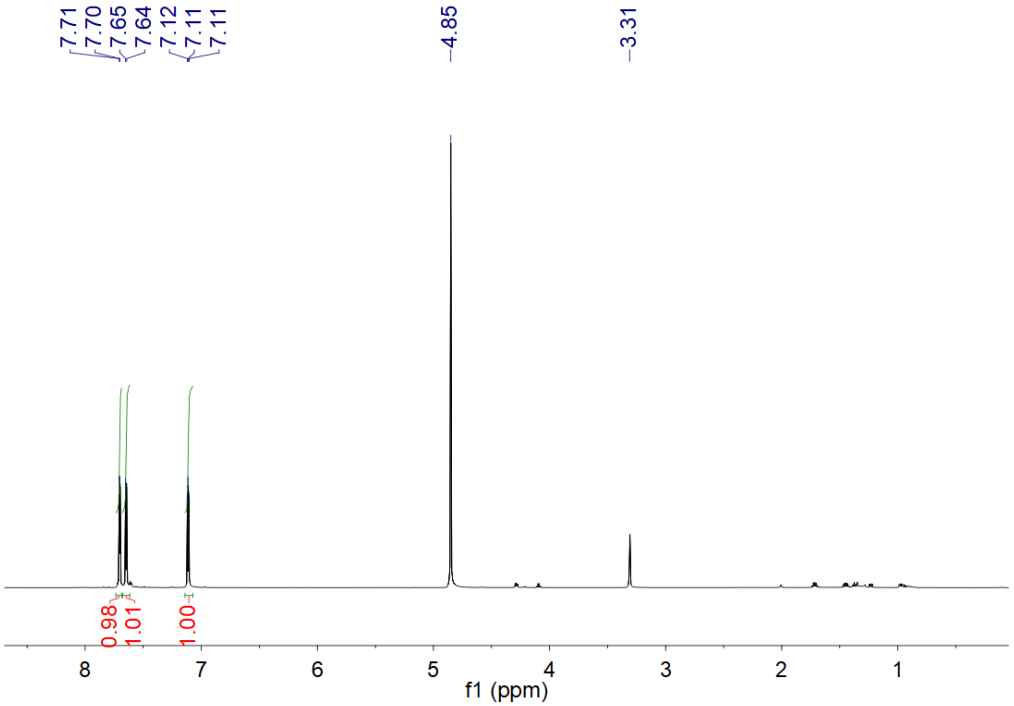


Fig. S37 ^{1}H NMR spectrum of the isolated **8k** (600 MHz, CD_3OD)

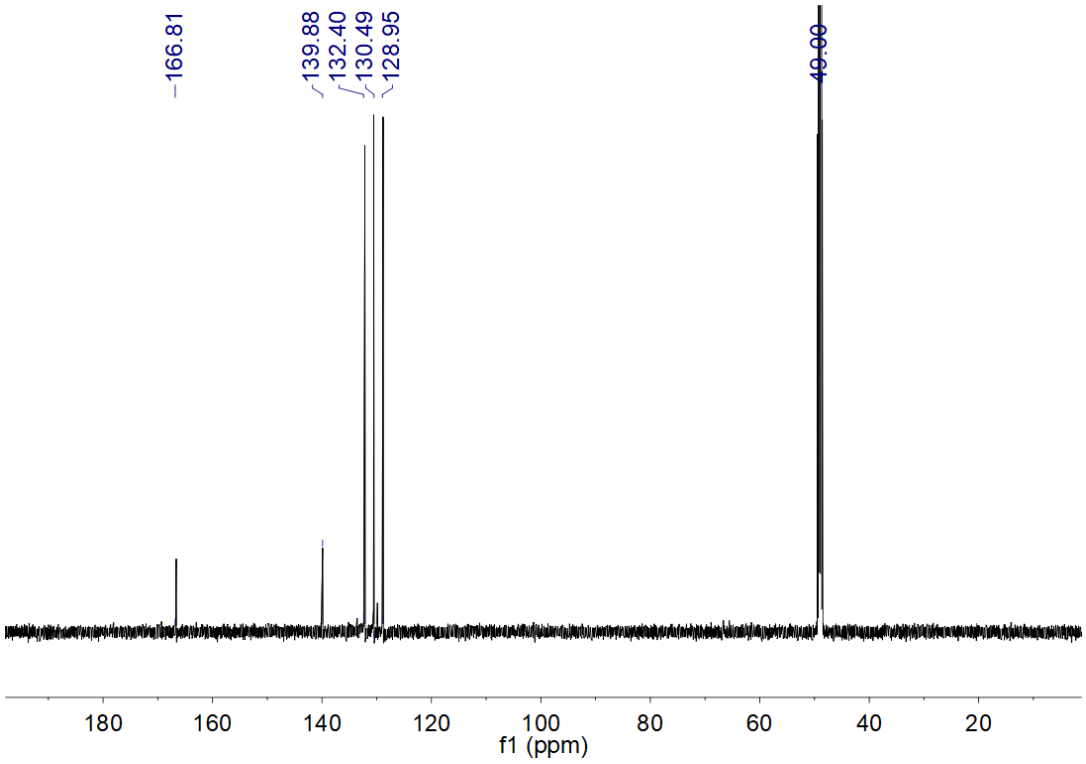
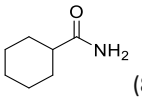


Fig. S38 $^{13}C\{^{1}H\}$ NMR spectrum of the isolated **8k** (151 MHz, CD_3OD)



(**8l**)

White solid (39 mg, 61% yield), M.P. 183–185 ℃. ^{1}H NMR (600 MHz, CD_3OD, δ): 2.22 (tt, J = 12.0, 3.4 Hz, 1H, CH), 1.79–1.84 (m, 4H, CH_2), 1.70 (d, J = 7.6 Hz, 1H, CH_2), 1.41–1.47 (m, 2H, CH_2), 1.24–1.36 (m, 3H, CH_2). ^{13}C{^{1}H} NMR (151 MHz, CD_3OD, δ): 182.13 (*C*O), 45.96 (*C*H), 30.74 (*C*H_2), 26.91 (*C*H_2), 26.81 (*C*H_2). These data are in good agreement with literature report.[S4]

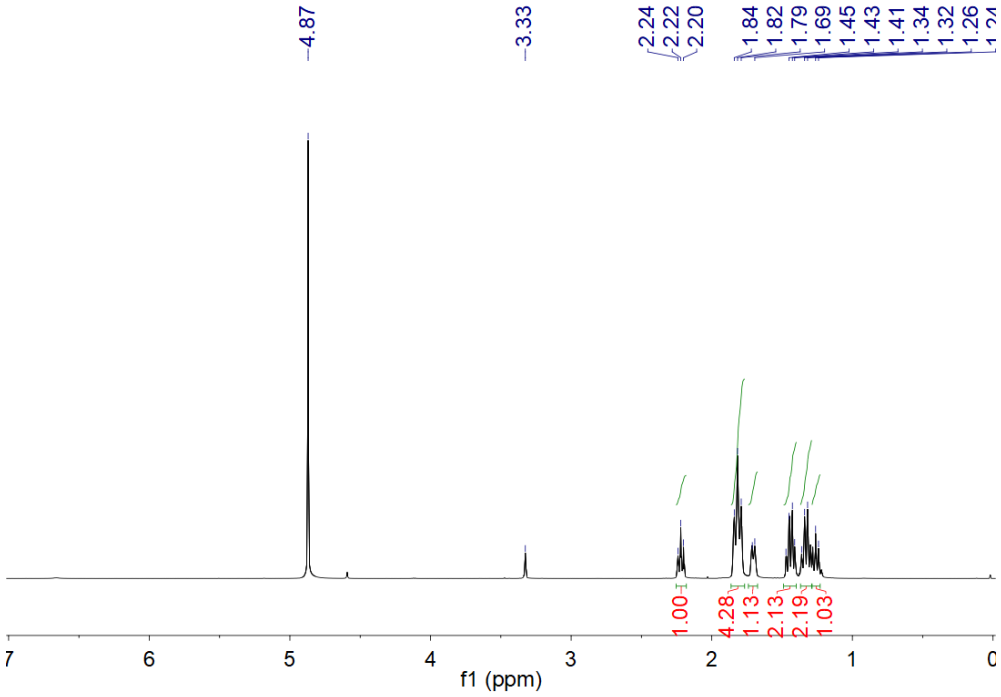


Fig. S39 ^{1}H NMR spectrum of the isolated **8l** (600 MHz, CD_3OD)

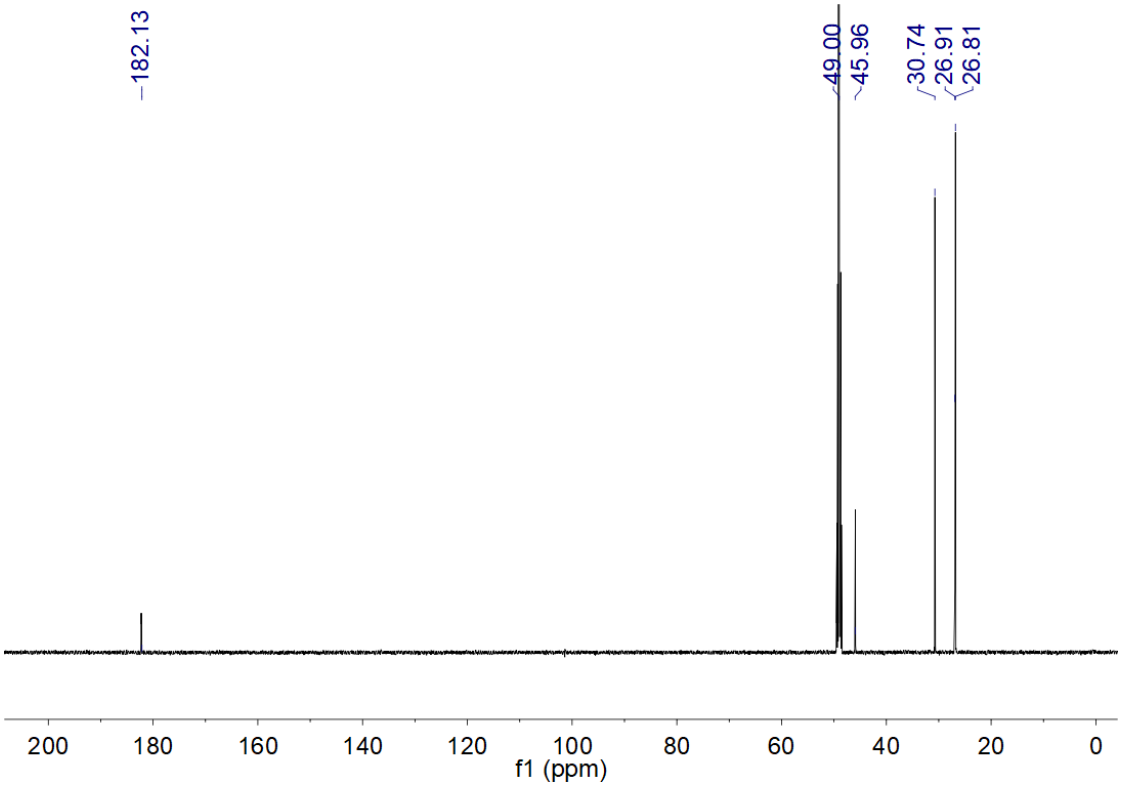
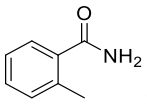


Fig. S40 ^{13}C{^{1}H} NMR spectrum of the isolated **8l** (151 MHz, CD_3OD)



(**8m**)

White solid (53 mg, 79% yield), M.P. 146–148 ℃. ^{1}H NMR (600 MHz, CD_3OD, δ): 7.69 (s, 1H, Ar*H*), 7.65 (d, *J* = 7.1 Hz, 1H, Ar*H*), 7.31–7.36 (m, 2H, Ar*H*), 2.38 (s, 3H, CH_3). ^{13}C{^{1}H} NMR (151 MHz, CD_3OD, δ): 172.63 (*C*O), 139.49 (Ar*C*), 134.91 (Ar*C*), 133.56 (Ar*C*), 129.42 (Ar*C*), 129.18 (Ar*C*), 125.76 (Ar*C*), 21.34 (*C*H_3). These data are in good agreement with literature report.[S3]

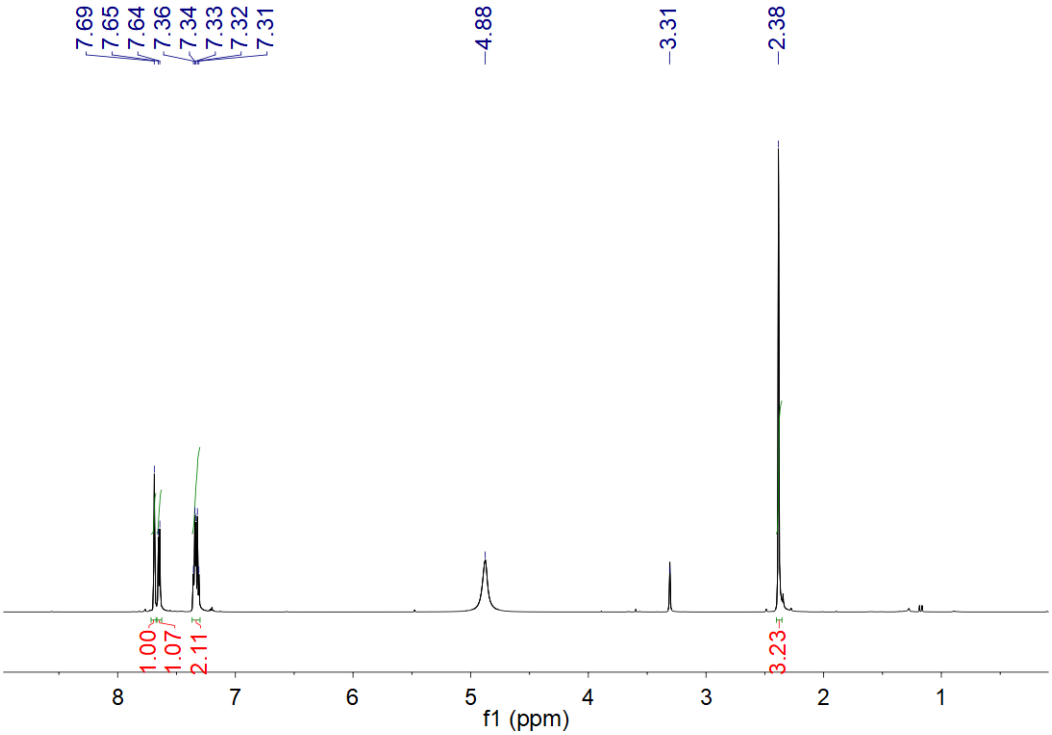


Fig. S41 ^{1}H NMR spectrum of the isolated **8m** (600 MHz, CD_3OD)

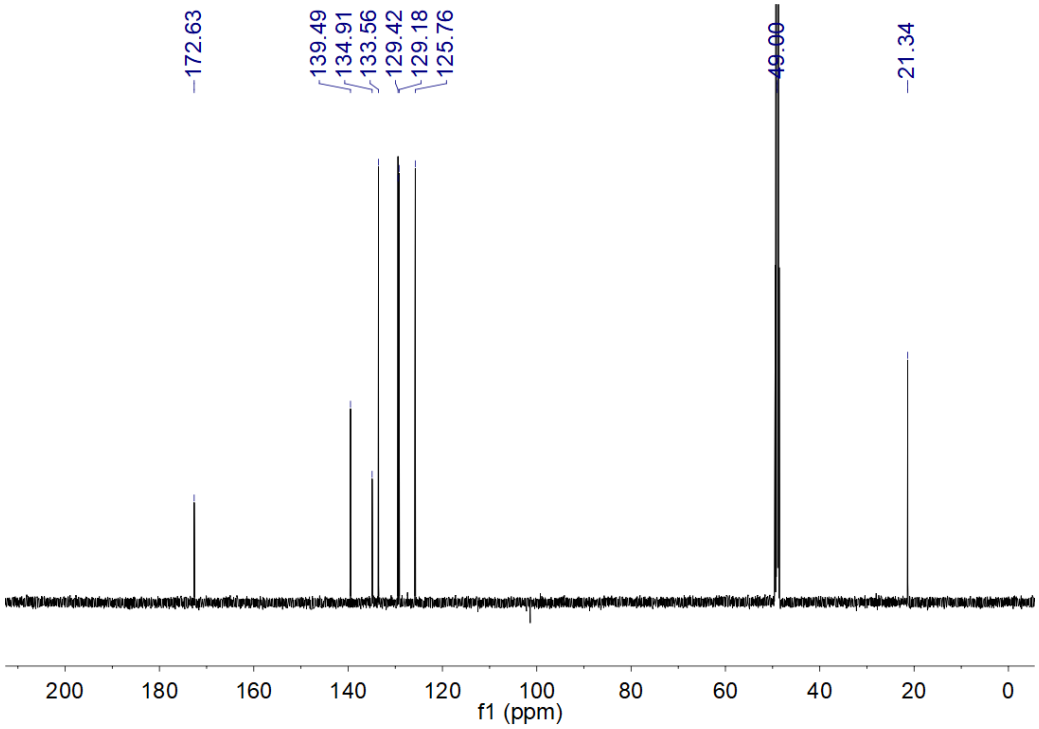
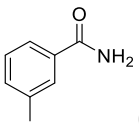


Fig. S42 ^{13}C{^{1}H} NMR spectrum of the isolated **8m** (151 MHz, CD_3OD)



(**8n**)

White solid (62 mg, 92% yield), M.P. 94–97 ℃. ^{1}H NMR (600 MHz, CD_3OD, δ): 7.64–7.69 (m, 2H, Ar*H*), 7.31–7.36 (m, 2H, Ar*H*), 2.39 (s, 3H, CH_3). ^{13}C{^{1}H} NMR (151 MHz, CD_3OD, δ): 172.49 (*C*O), 139.35 (Ar*C*), 134.77 (Ar*C*), 133.42 (Ar*C*), 129.28 (Ar*C*), 129.04 (Ar*C*), 125.62 (Ar*C*), 21.20 (*C*H_3). These data are in good agreement with literature report.[S2]

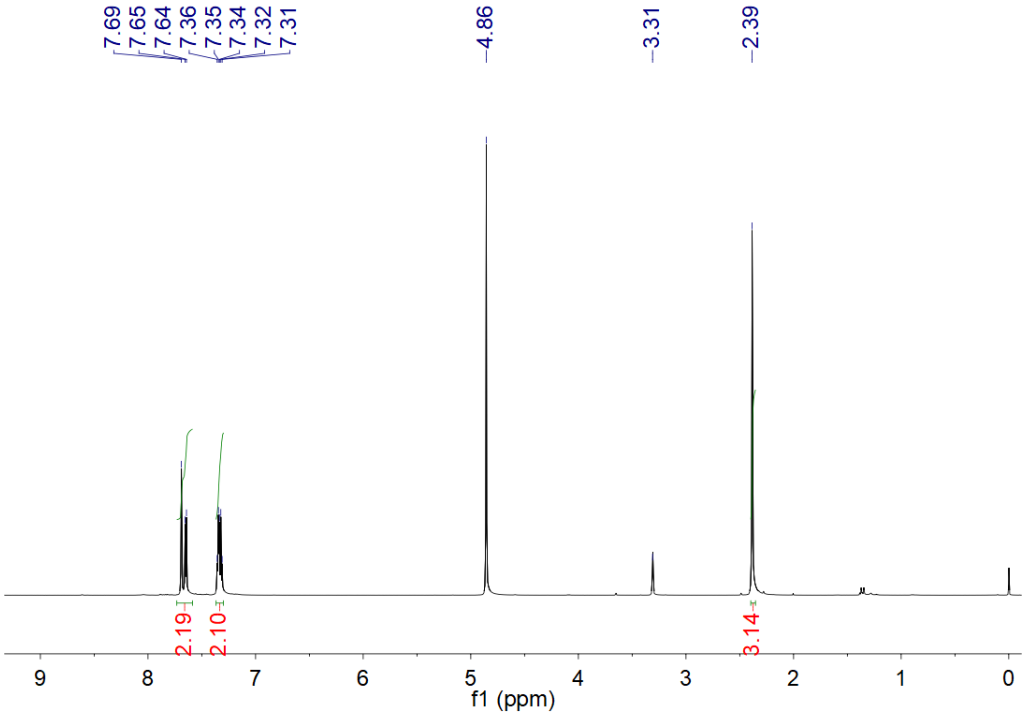


Fig. S43 ^{1}H NMR spectrum of the isolated **8n** (600 MHz, CD_3OD)

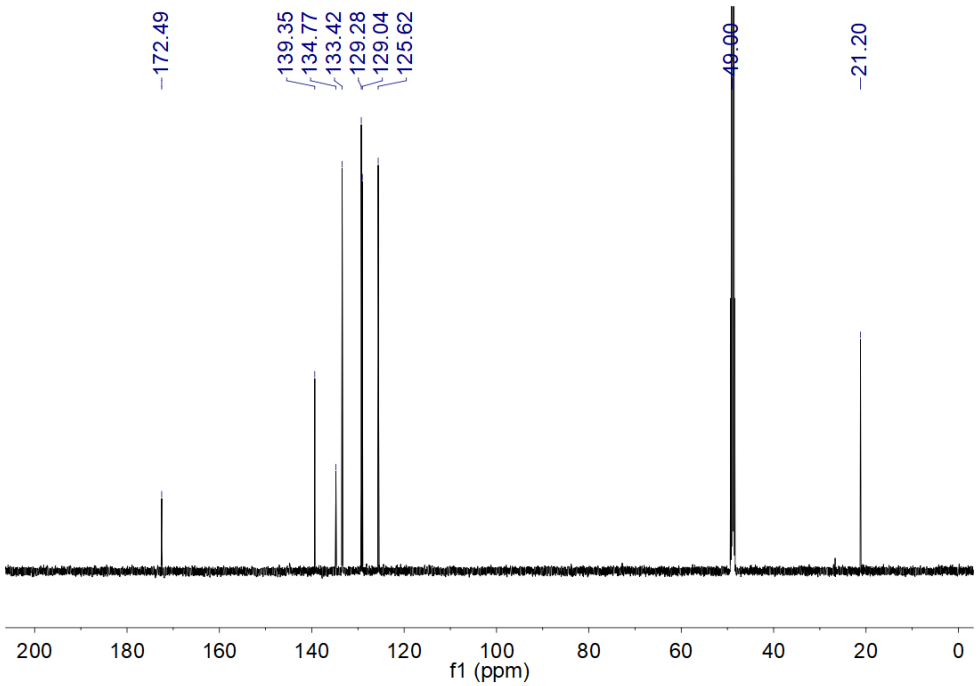
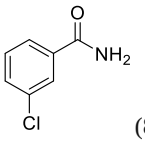


Fig. S44 ^{13}C{^{1}H} NMR spectrum of the isolated **8n** (151 MHz, CD_3OD)



(**8o**)

White solid (74 mg, 95% yield), M.P. 131–133 ℃. ^{1}H NMR (600 MHz, CD_3OD, δ): 7.88 (s, 1H, Ar*H*), 7.79 (d, J = 7.8 Hz, 1H, Ar*H*), 7.54 (d, J = 7.8 Hz, 1H, Ar*H*), 7.44 (t, J = 7.8 Hz, 1H, Ar*H*). ^{13}C{^{1}H} NMR (151 MHz, CD_3OD, δ): 170.71 (*C*O), 136.99 (Ar*C*), 135.57 (Ar*C*), 132.74 (Ar*C*), 131.11 (Ar*C*), 128.79 (Ar*C*), 126.97 (Ar*C*). These data are in good agreement with literature report.[S3]

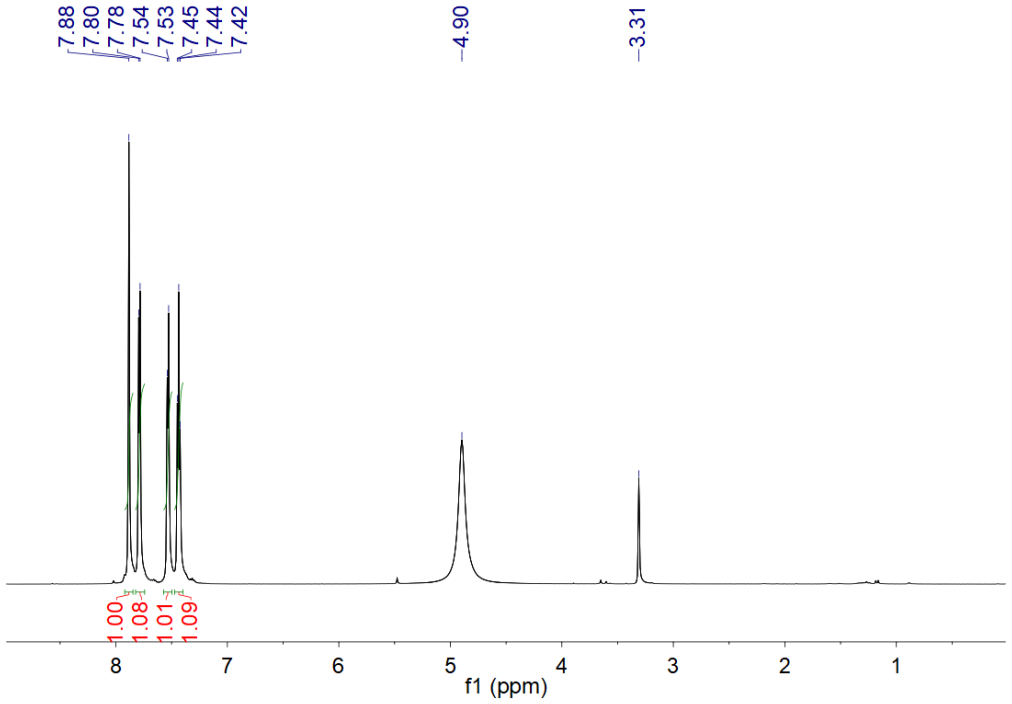


Fig. S45 ^{1}H NMR spectrum of the isolated **8o** (600 MHz, CD_3OD)

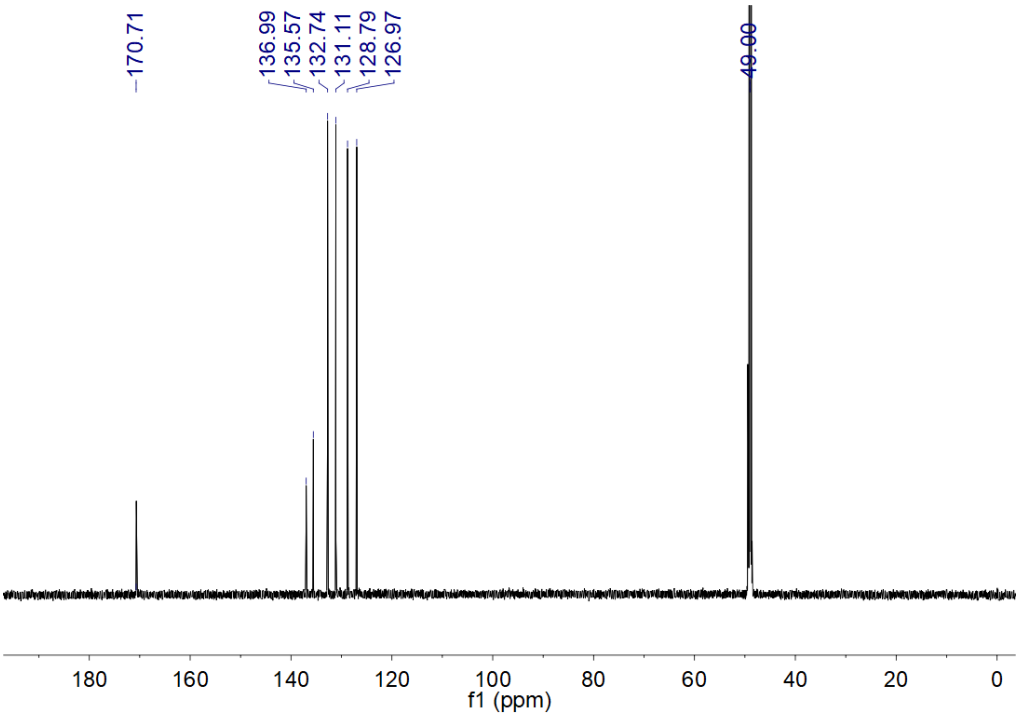
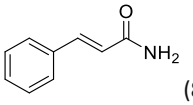


Fig. S46 ^{13}C{^{1}H} NMR spectrum of the isolated **8o** (151 MHz, CD_3OD)



(**8p**)

White solid (66 mg, 90% yield), M.P. 148–151 ℃. ^{1}H NMR (600 MHz, CD_3OD, δ): 7.54–7.57 (m, 3H), 7.34–7.39 (m, 3H), 6.65 (d, J = 15.9 Hz, 1H). $^{13}C\{^{1}H\}$ NMR (151 MHz, CD_3OD, δ): 170.882 (*C*O), 142.70, 136.13, 130.92, 129.93, 128.85, 121.39. These data are in good agreement with literature report.[S4]

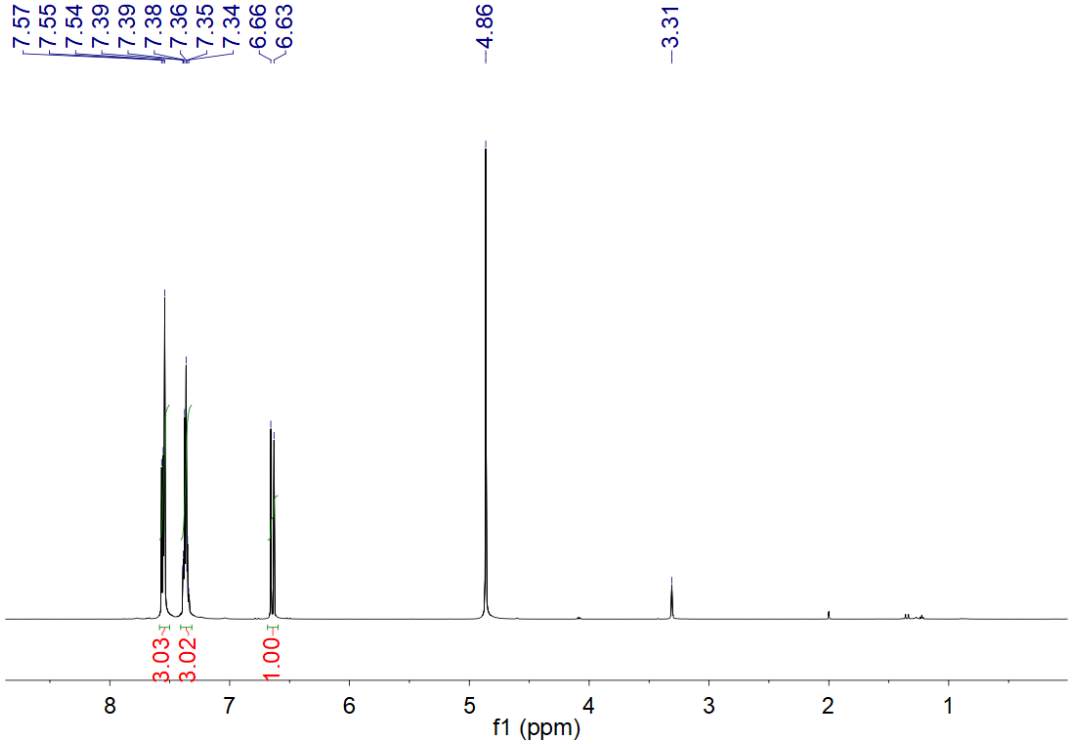


Fig. S47 ^{1}H NMR spectrum of the isolated **8p** (600 MHz, CD_3OD)

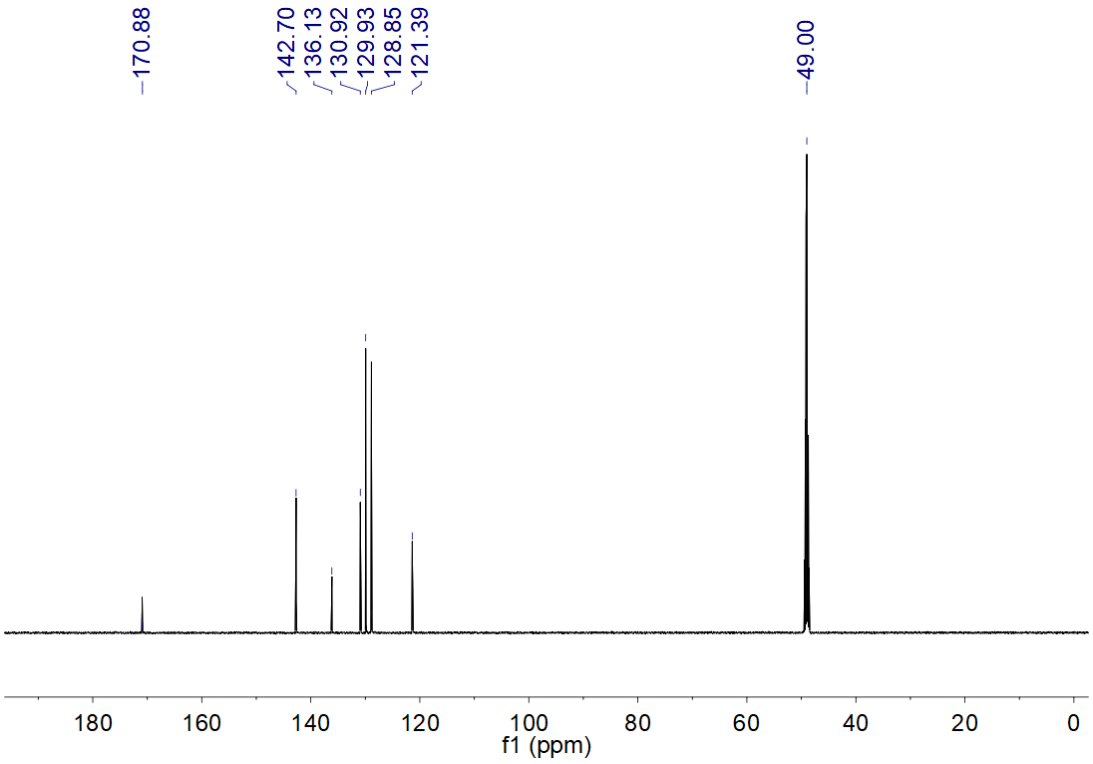
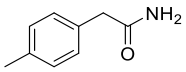


Fig. S48 $^{13}C\{^{1}H\}$ NMR spectrum of the isolated **8p** (151 MHz, CD_3OD)



(**8q**)

White solid (54 mg, 73% yield), M.P. 183–186 ℃. ^{1}H NMR (600 MHz, CD_3OD, δ): 7.17 (d, J = 7.8 Hz, 2H, Ar*H*), 7.11 (d, J = 7.8 Hz, 2H, Ar*H*), 3.45 (s, 2H, CH_2), 2.30 (s, 3H, CH_3). ^{13}C{^{1}H} NMR (151 MHz, CD_3OD, δ): 177.14 (*C*O), 137.67 (Ar*C*), 133.59 (Ar*C*), 130.18 (Ar*C*), 130.03 (Ar*C*), 43.18 (*C*H_2), 20.98 (*C*H_3). These data are in good agreement with literature report.[S6]

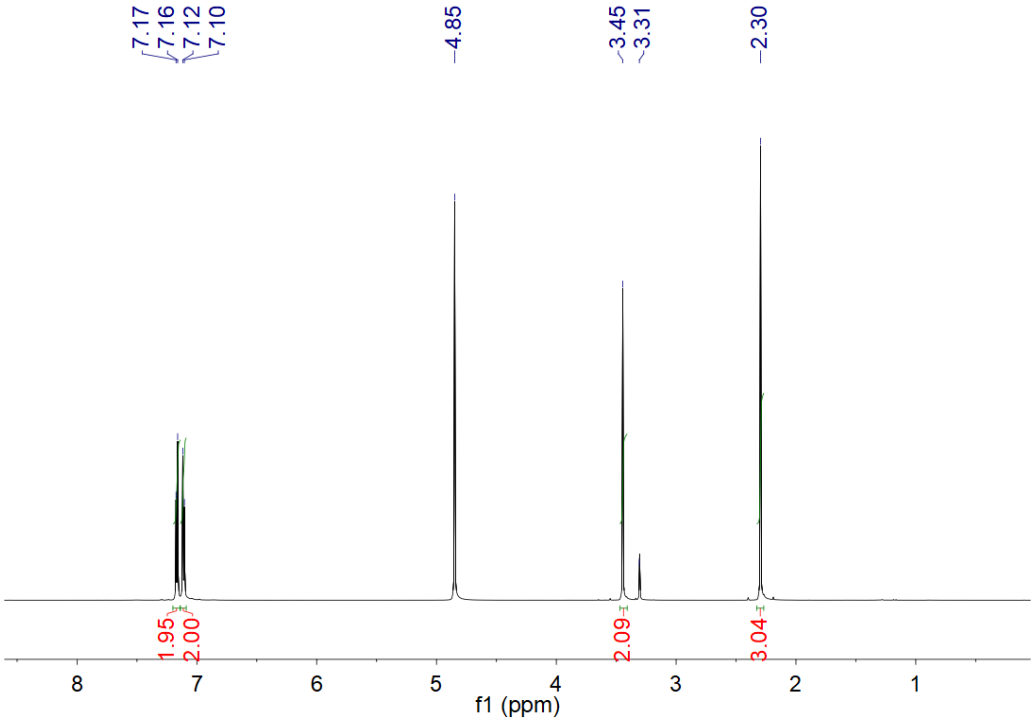


Fig. S49 ^{1}H NMR spectrum of the isolated **8q** (600 MHz, CD_3OD)

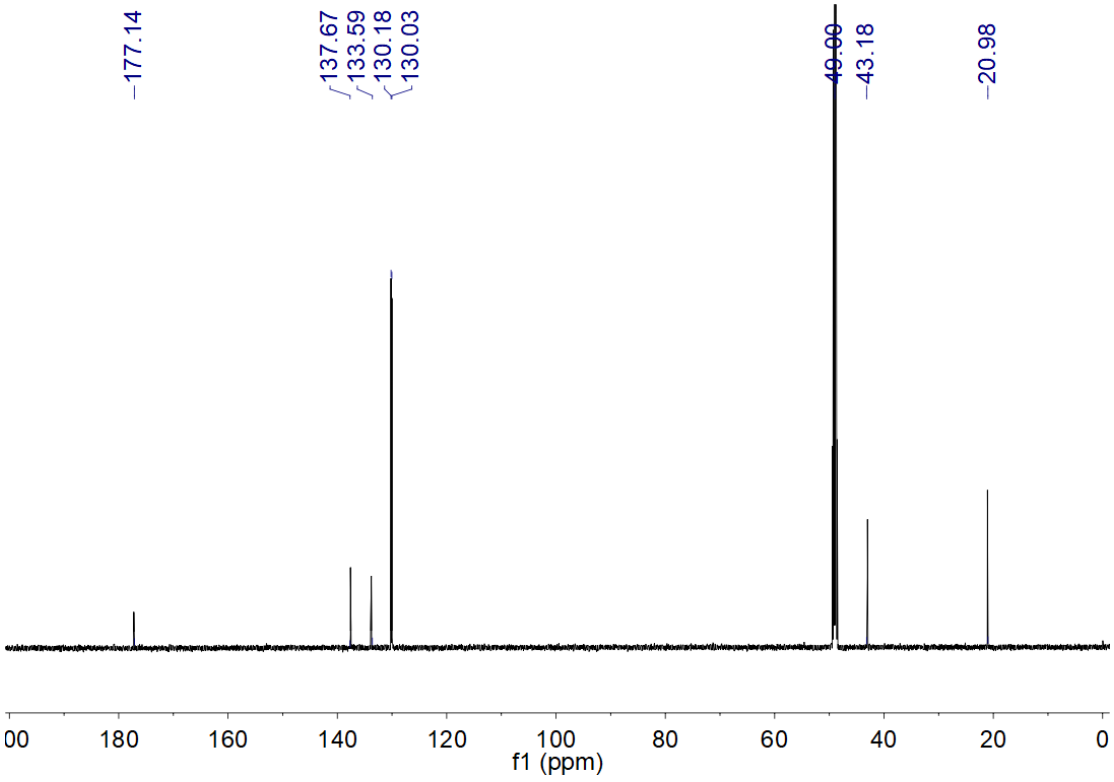
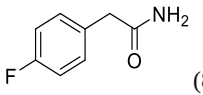


Fig. S50 ^{13}C{^{1}H} NMR spectrum of the isolated **8q** (151 MHz, CD_3OD)



(**8r**)

White solid (49 mg, 64% yield), M.P. 158–159 ℃. ^{1}H NMR (600 MHz, CD_3OD, δ): 7.28–7.30 (m, 2H, Ar*H*), 7.00–7.03 (m, 2H, Ar*H*), 3.48 (s, 2H, CH_2). ^{13}C{^{1}H} NMR (151 MHz, CD_3OD, δ): 176.70 (*C*O), 163.30 (d, $^{1}J_{C\text{-}F}$ = 244.3 Hz, Ar*C*), 132.87 (d, $^{3}J_{C\text{-}F}$ = 3.3 Hz, Ar*C*), 131.91 (d, $^{4}J_{C\text{-}F}$ = 3.1 Hz, Ar*C*), 116.12 (d, $^{2}J_{C\text{-}F}$ = 21.8 Hz, Ar*C*), 42.39 (*C*H_2). ^{19}F{^{1}H} NMR (565 MHz, CD_3OD, δ): -118.37. These data are in good agreement with literature report.[S2]

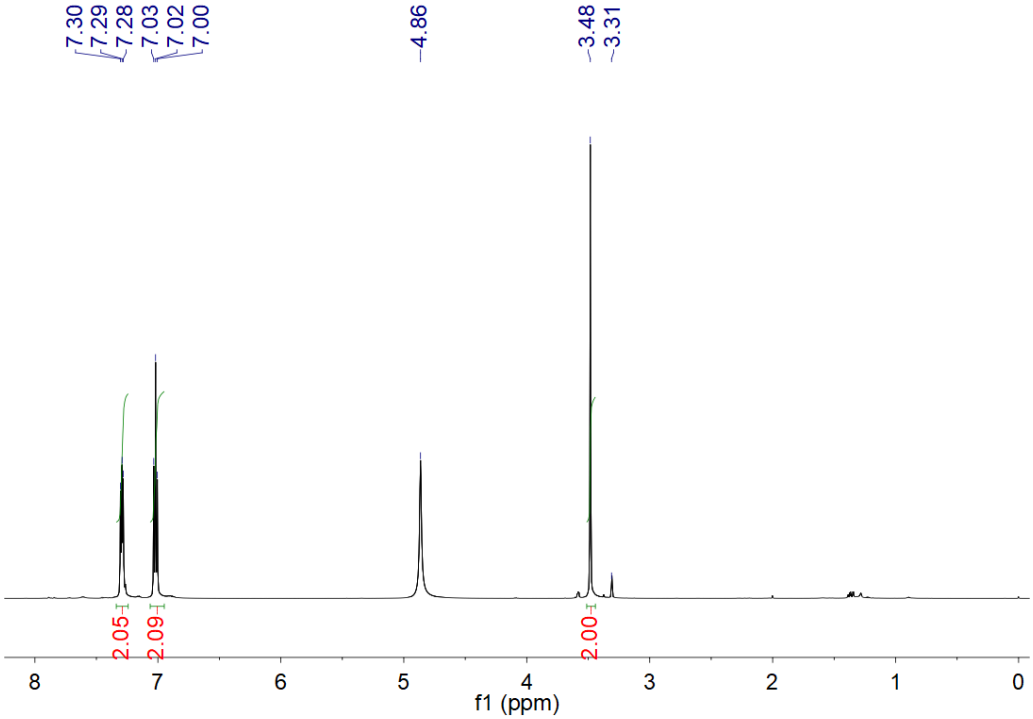


Fig. S51 ^{1}H NMR spectrum of the isolated **8r** (600 MHz, CD_3OD)

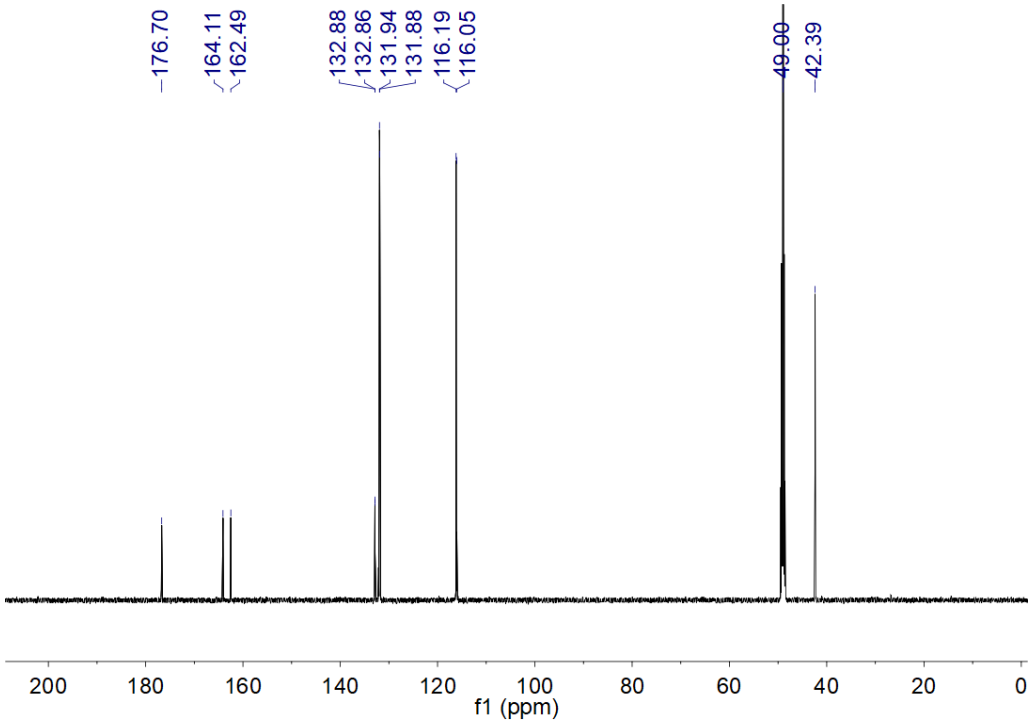
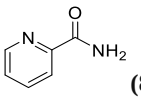


Fig. S52 ^{13}C{^{1}H} NMR spectrum of the isolated **8r** (151 MHz, CD_3OD)



(8s)

White solid (33 mg, 54% yield), M.P. 109–110 ℃. ^{1}H NMR (600 MHz, CD_3OD, δ): 8.61 (d, J = 4.7 Hz, 1H), 8.11 (d, J = 7.8 Hz, 1H), 7.92 (t, J = 7.7 Hz, 1H), 7.51–7.53 (m, 1H). ^{13}C{^{1}H} NMR (151 MHz, CD_3OD, δ): 169.37 (*C*O), 151.09 (Ar*C*), 149.80 (Ar*C*), 138.71 (Ar*C*), 127.82 (Ar*C*), 123.24 (Ar*C*). These data are in good agreement with literature report.[S3]

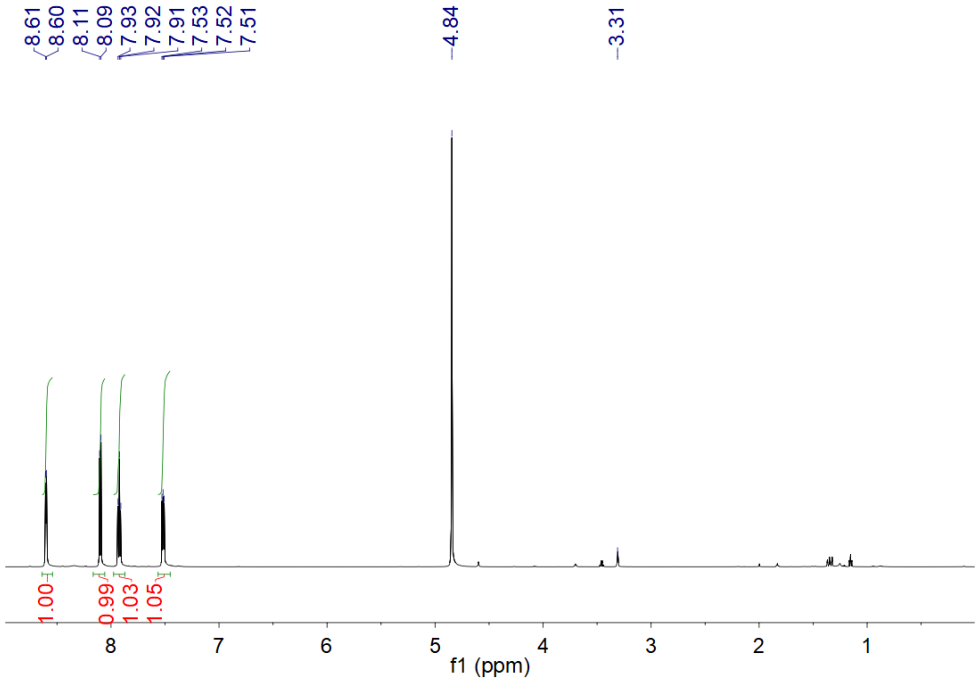


Fig. S53 ^{1}H NMR spectrum of the isolated **8s** (600 MHz, CD_3OD)

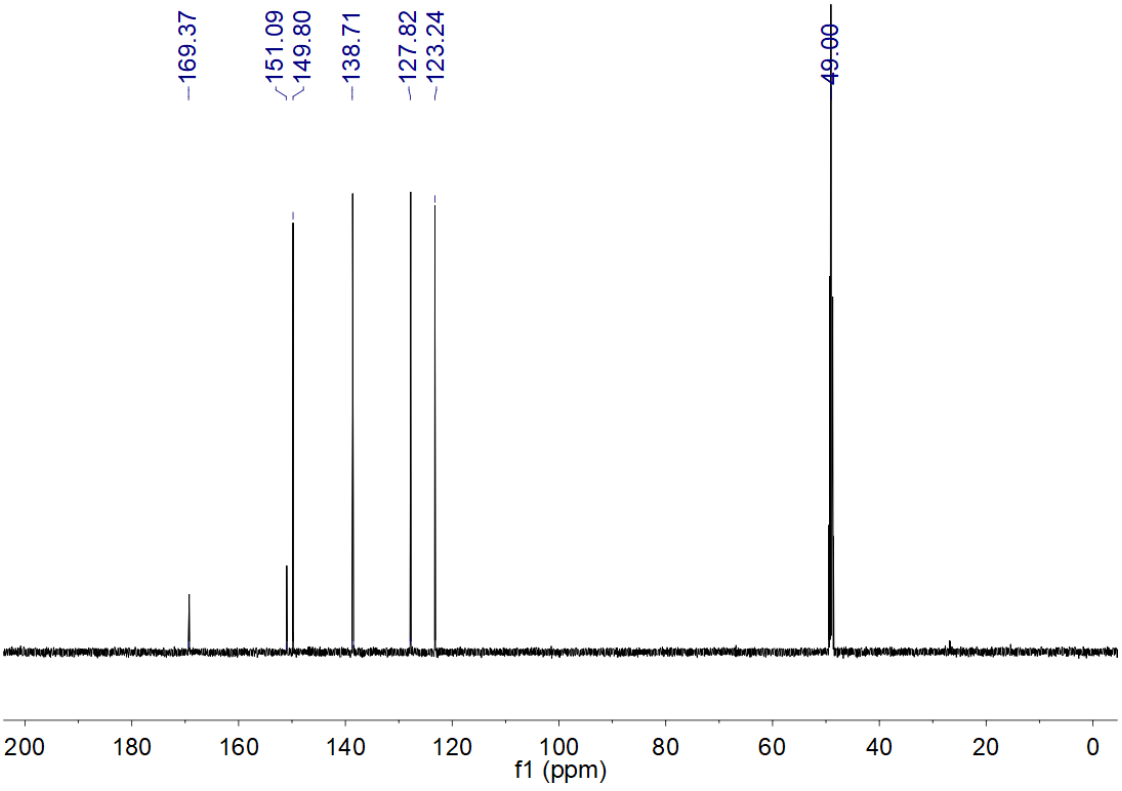
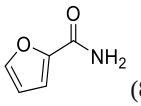


Fig. S54 ^{13}C{^{1}H} NMR spectrum of the isolated **8s** (151 MHz, CD_3OD)



(**8t**)

White solid (51 mg, 92% yield), M.P. 140–142 ℃. ^{1}H NMR (600 MHz, CD_3OD, δ): 7.64 (d, J = 1.6 Hz, 1H), 7.16 (d, J = 3.5 Hz, 1H), 6.57 (dd, J = 3.3, 1.6 Hz, 1H). ^{13}C{^{1}H} NMR (151 MHz, CD_3OD, δ): 163.00 (*C*O), 148.95 (Ar*C*), 146.42 (Ar*C*), 115.72 (Ar*C*), 113.26 (Ar*C*). These data are in good agreement with literature report.[S4]

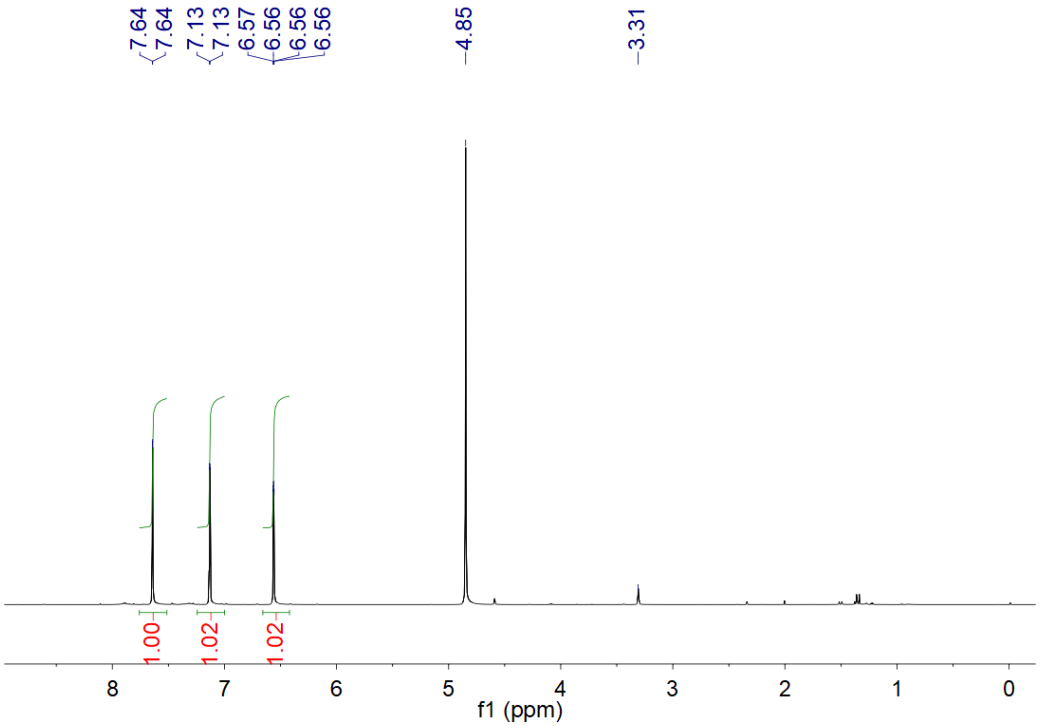


Fig. S55 ^{1}H NMR spectrum of the isolated **8t** (600 MHz, CD_3OD)

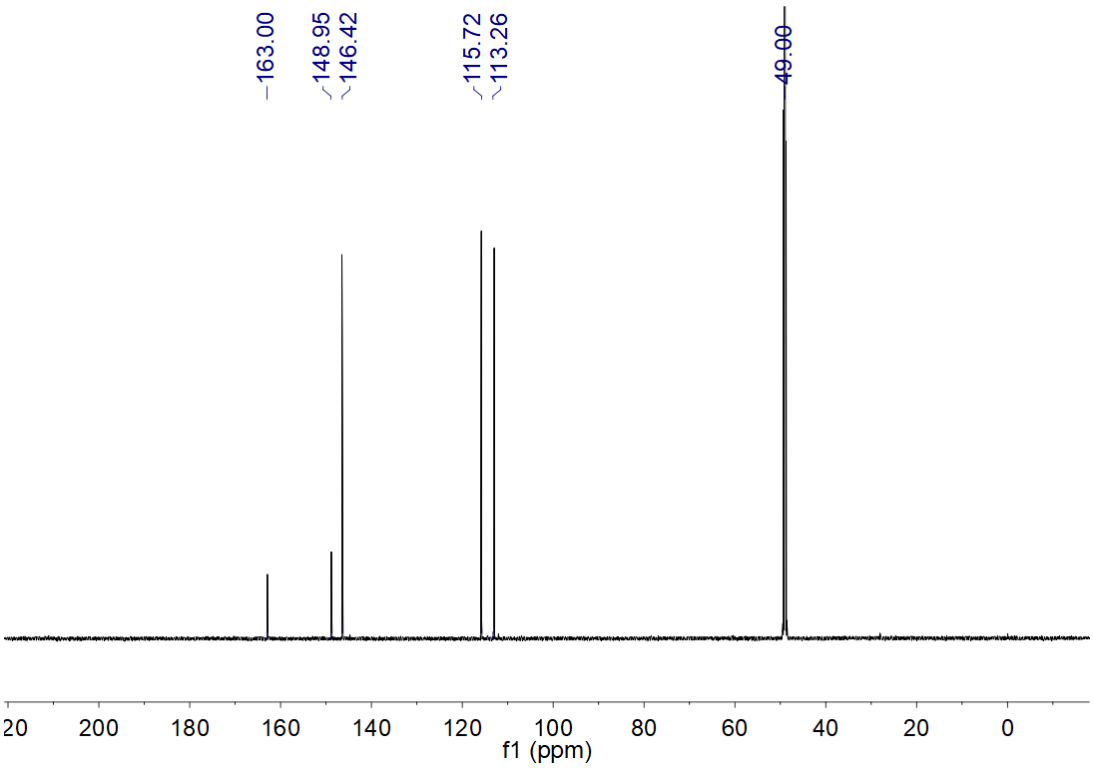


Fig. S56 ^{13}C{^{1}H} NMR spectrum of the isolated **8t** (151 MHz, CD_3OD)

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