Electronic Supplementary Information for:

# Reactions and catalytic applications of a PNCNP pincer palladium hydride complex

Jiarui Chang,[a] Man Ding,[a] Jia-Xue Mao,[a] Jie Zhang,*[,a] and Xuenian Chen*[a,b]

[a] Henan Key Laboratory of Boron Chemistry and Advanced Energy Materials, Key Laboratory of Green Chemical Media and Reactions, Ministry of Education, Collaborative Innovation Centre of Henan Province for Green Manufacturing of Fine Chemicals, School of Chemistry and Chemical Engineering, Henan Normal University, Xinxiang, Henan 453007, China, E-mail: jie.zhang@htu.edu.cn

[b] College of Chemistry and Molecular Engineering, Zhengzhou University zhengzhou, Henan 450001, China, E-mail: xuenian_chen@zzu.edu.cn

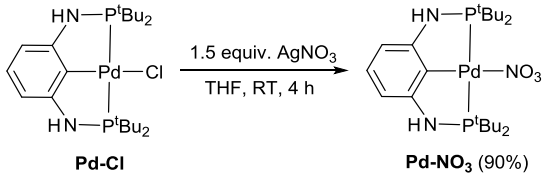
## Contents

**Experimental general information**

The reactions were carried out under a nitrogen atmosphere. The solvents were dried using standard procedures and degassed before use. NMR spectra were recorded on a 600 MHz Bruker Advance spectrometer at room temperature. The chemical shifts were either referenced internally to the residual solvent peaks or standardized by outside samples. High resolution mass spectrometry (HRMS) was performed in the ESI mode by using a MicrOTOF mass spectrometer. GC-MS analyses were performed by using a SHIMADZU-(GCMS-QP2020) instrument. Elemental analysis was performed on an Elementar Vario-III analyzer. FTIR spectra were recorded on a VECTOR 22 Bruker spectrophotometer. The starting palladium pincer chloride complex [2,6-($^t$Bu$_2$PNH)$_2$C$_6$H$_3$]PdCl (**Pd-Cl**) was prepared according to the literature method.[S1]

**Synthesis and characterization of [2,6-($^t$Bu$_2$PNH)$_2$C$_6$H$_3$]PdNO$_3$ (Pd-NO$_3$)**

A mixture of complex **Pd-Cl** (537 mg, 1.0 mmol), $AgNO_3$ (255 mg, 1.5 mmol) and THF (30 mL) was stirred at room temperature for 4 h. Solvent was evaporated under vacuum and the residue was extracted with $CH_2Cl_2$ (15 mL × 3). $CH_2Cl_2$ was removed from the combined extraction and a light grey crystalline solid of complex **Pd-NO$_3$** was obtained (509 mg, 90% yield). $^1$H NMR (600 MHz, $CDCl_3$, $\delta$): 6.75 (t, 1H, $J_{H\text{-}H}$ = 7.8 Hz, Ar*H*), 6.10 (d, 2H, $J_{H\text{-}H}$ = 7.8 Hz, Ar*H*), 4.15 (s, 2H, N*H*), 1.37–1.39 (m, 36H, C(C*H*$_3$)$_3$). $^{13}$C{$^1$H} NMR (151 MHz, $CDCl_3$, $\delta$): 158.28 (t, $J_{C\text{-}P}$ = 11.1 Hz, Ar*C*), 127.48 (s, Ar*C*), 116.74 (s, Ar*C*), 102.10 (t, $J_{C\text{-}P}$ = 7.8 Hz, Ar*C*), 38.13 (t, $J_{C\text{-}P}$ = 8.7 Hz, *C*(CH$_3$)$_3$), 28.11 (t, $J_{C\text{-}P}$ = 3.8 Hz, C(*C*H$_3$)$_3$). $^{31}$P{$^1$H} NMR (243 MHz, $CDCl_3$, $\delta$): 119.48 (s). Anal. calcd for $C_{22}H_{41}N_3O_3P_2Pd$: C, 46.86; H, 7.33. Found: C, 47.01; H, 7.40. HRMS (ESI): *m/z* calculated for $C_{22}H_{41}N_3O_3P_2Pd + H^+$ $[M + H]^+$ 564.1737, found 564.1739.




**Scheme S1** Synthesis of complex **Pd-NO$_3$**

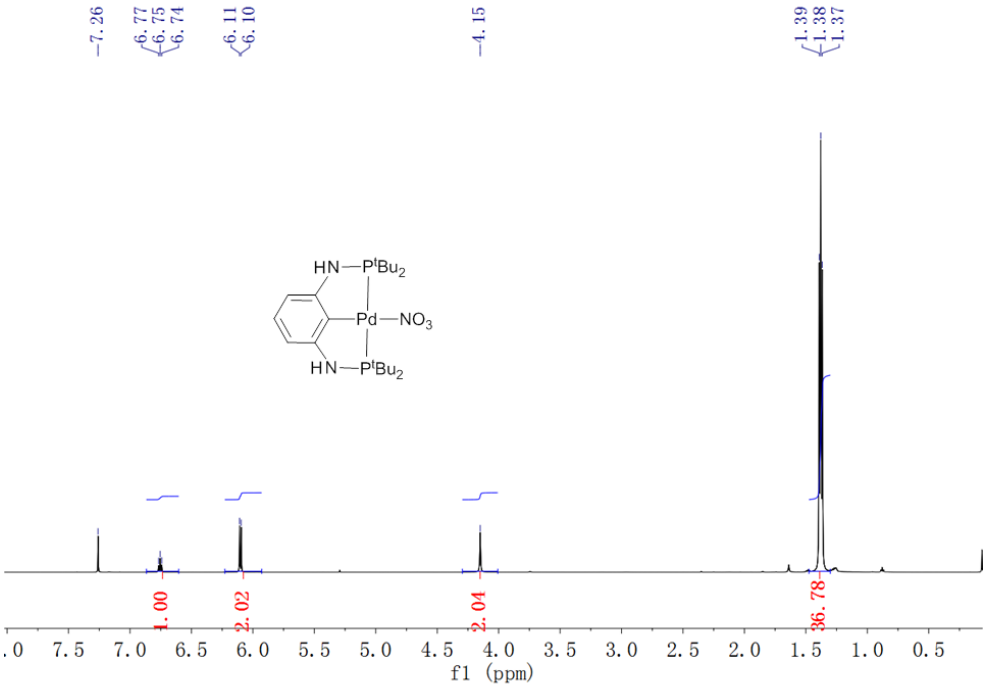



**Fig. S1** $^1$H NMR spectrum of complex **Pd-NO$_3$** (600 MHz, $CDCl_3$)

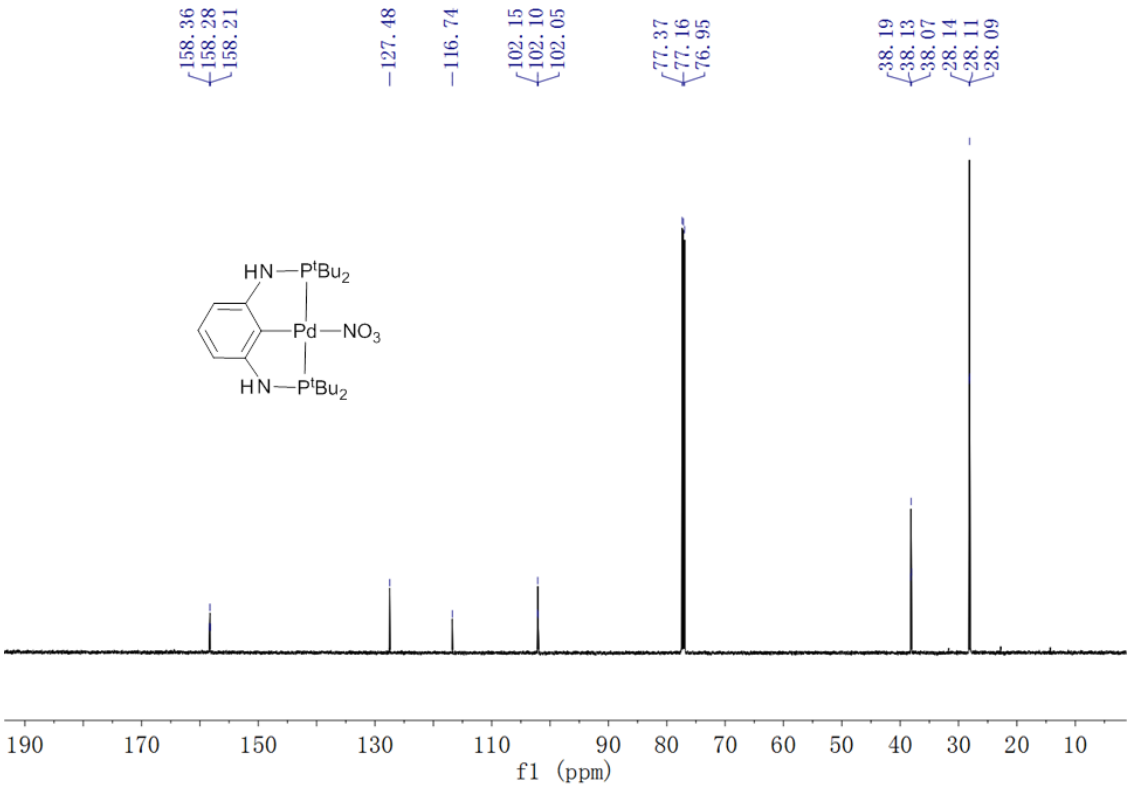



**Fig. S2** $^{13}C\{^{1}H\}$ NMR spectrum of complex **Pd-NO$_3$** (151 MHz, $CDCl_3$)

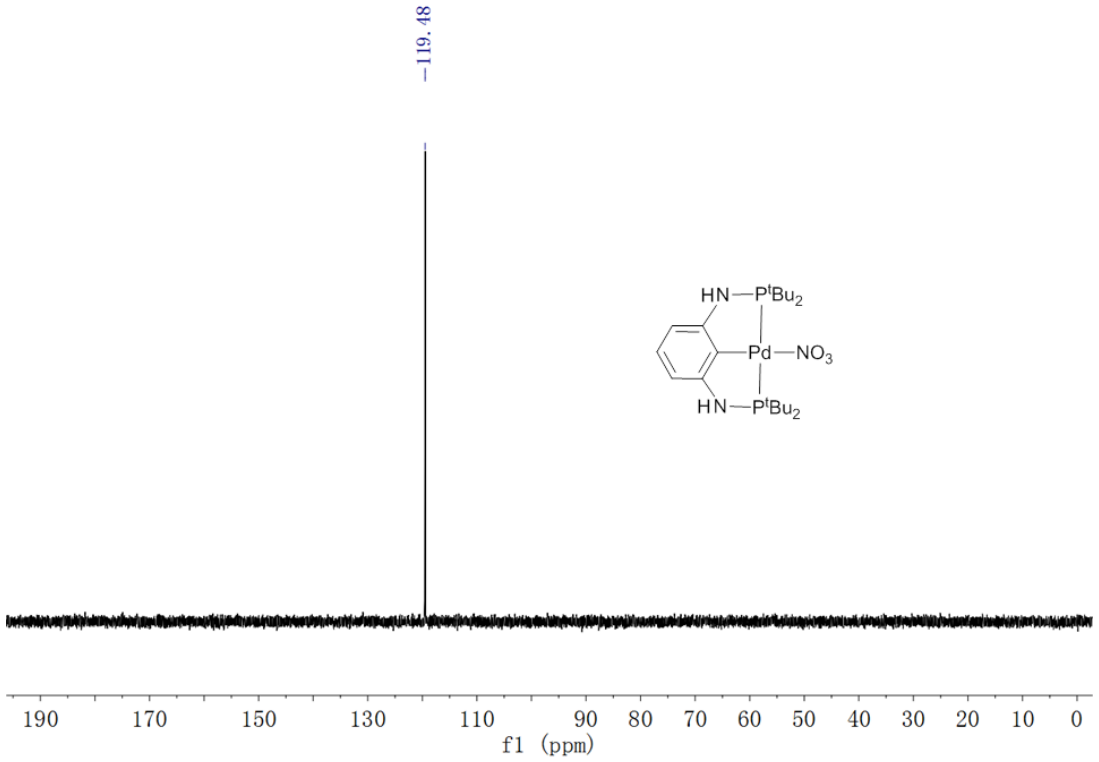



**Fig. S3** $^{31}P\{^{1}H\}$ NMR spectrum of complex **Pd-NO$_3$** (243 MHz, $CDCl_3$)

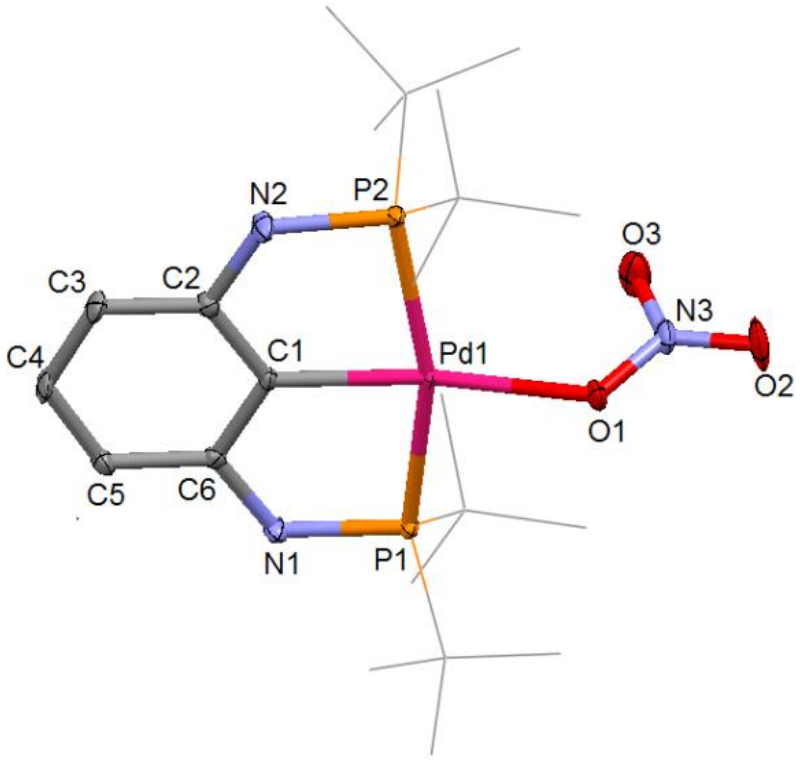



**Fig. S4** Thermal ellipsoid plots of complex **Pd-NO$_3$** at the 50% probability level (for clarity, hydrogen atoms and the co-crystallized THF molecule have been omitted and the *tert*-butyl groups have been simplified). Selected bond lengths (Å) and angles (˚): Pd1-C1, 1.996(3); Pd1-P1, 2.3084(6); Pd1-P2, 2.3296(6); Pd1-O1, 2.1415(18); Pd1 ··O3, 3.122(2); N3-O1, 1.279(3); N3-O3, 1.247(3); N3-O2, 1.224(3); P1-Pd1-P2, 162.70(2); C1-Pd1-O1, 170.32(9); O3-N3-O1, 119.2(2); O2-N3-O1, 118.1(2); O2-N3-O3, 122.7(2).

**Synthesis and characterization of [2,6-($^t$Bu$_2$PNH)$_2$C$_6$H$_3$]PdH (1)**

*Route (I)*: A suspension of complex **Pd-Cl** (537 mg, 1.0 mmol) and $LiAlH_4$ (76 mg, 2.0 mmol) in THF (30 mL) was stirred at room temperature for 1 h. Solvent was evaporated under vacuum and the residue was extracted with toluene (15 mL ×3). Toluene was then removed from the combined extraction solutions and a white crystalline solid of [2,6-($^t$Bu$_2$PNH)$_2$C$_6$H$_3$]PdH (**1**) was obtained (407 mg, 81% yield).

*Route (II)*: A mixture of complex **Pd-NO$_3$** (282 mg, 0.5 mmol), $KOCH_3$ (700 mg, 10 mmol) and THF (20 mL) was sonicated at room temperature for 5 h. The resulting suspension was centrifuged and the solvent was evaporated under reduced pressure. The solid residue was extracted with *n*-hexane (15 mL × 3). The combined extraction solution was concentrated and recrystallized. Complex [2,6-($^t$Bu$_2$PNH)$_2$C$_6$H$_3$]PdH (**1**) was obtained in 85% yield.

$^1$H NMR (600 MHz, benzene-$d_6$, $\delta$): 7.10 (t, 1H, $J_{H\text{-}H}$ = 7.7 Hz, Ar*H*), 6.40 (dd, 2H, $J_{H\text{-}H}$ = 7.7, 0.9 Hz, Ar*H*), 3.94 (s, 2H, N*H*), 1.19–1.22 (m, 36H, C(C*H*$_3$)$_3$), -2.84 (t, 1H, $J_{H\text{-}P}$ = 19.6 Hz, Pd*H*). $^{13}$C{$^1$H} NMR (151 MHz, benzene-$d_6$, $\delta$): 157.72 (t, $J_{C\text{-}P}$ = 11.7 Hz, Ar*C*), 140.47 (t, $J_{C\text{-}P}$ = 3.8 Hz, Ar*C*), 126.85 (s, Ar*C*), 101.23 (t, $J_{C\text{-}P}$ = 7.4 Hz, Ar*C*), 36.76 (t, $J_{C\text{-}P}$ = 9.5 Hz, *C*(CH$_3$)$_3$), 28.86 (t, $J_{C\text{-}P}$ = 4.5 Hz, C(*C*H$_3$)$_3$). $^{31}$P{$^1$H} NMR (243 MHz, benzene-$d_6$, $\delta$): 141.37 (s). Anal. calcd for $C_{22}H_{42}N_2P_2Pd$: C, 52.54; H, 8.42. Found: C, 52.67; H, 8.55. HRMS (ESI): *m/z* calculated for $C_{22}H_{42}N_2P_2Pd$ [M] 502.1853, found 502.1811. Selected FTIR absorptions (KBr disc, cm$^{-1}$): 3367 (m), 1718 (s).

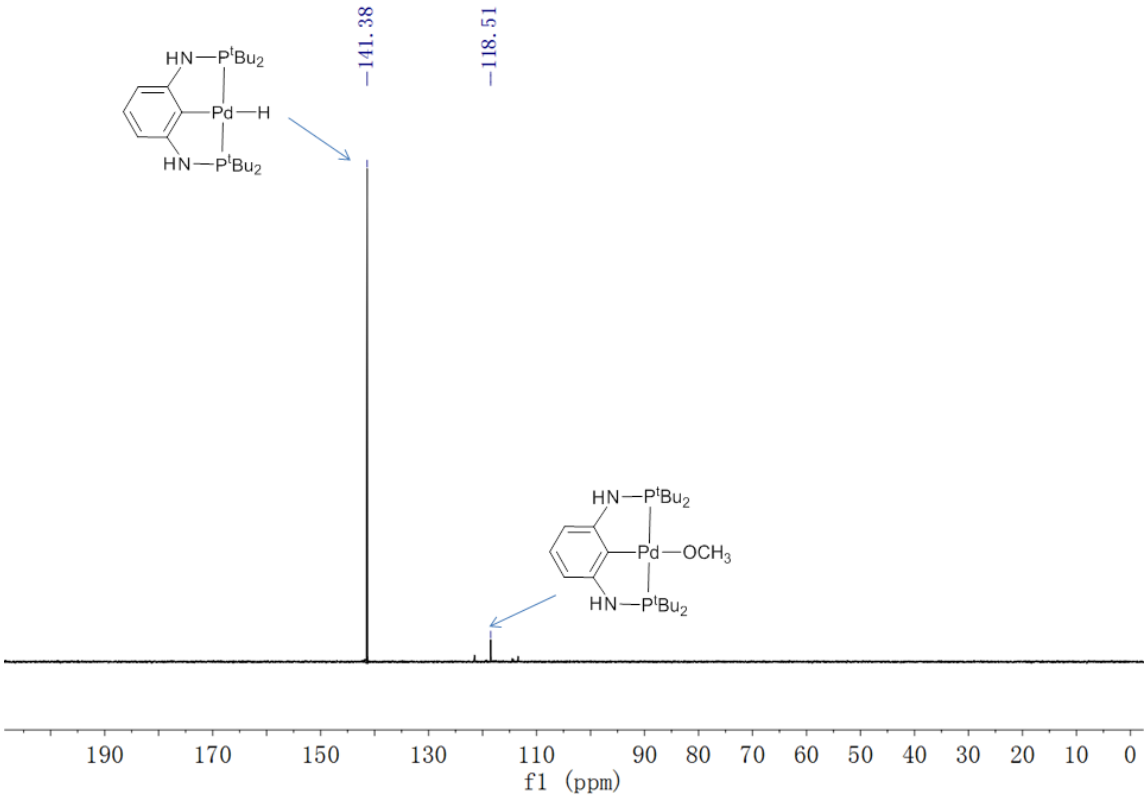



**Fig. S5** $^{31}P\{^1H\}$ NMR spectrum the reaction mixture of complex **Pd-NO$_3$**, $KOCH_3$ and THF recorded 3 h after mixing the reactants (Route II).

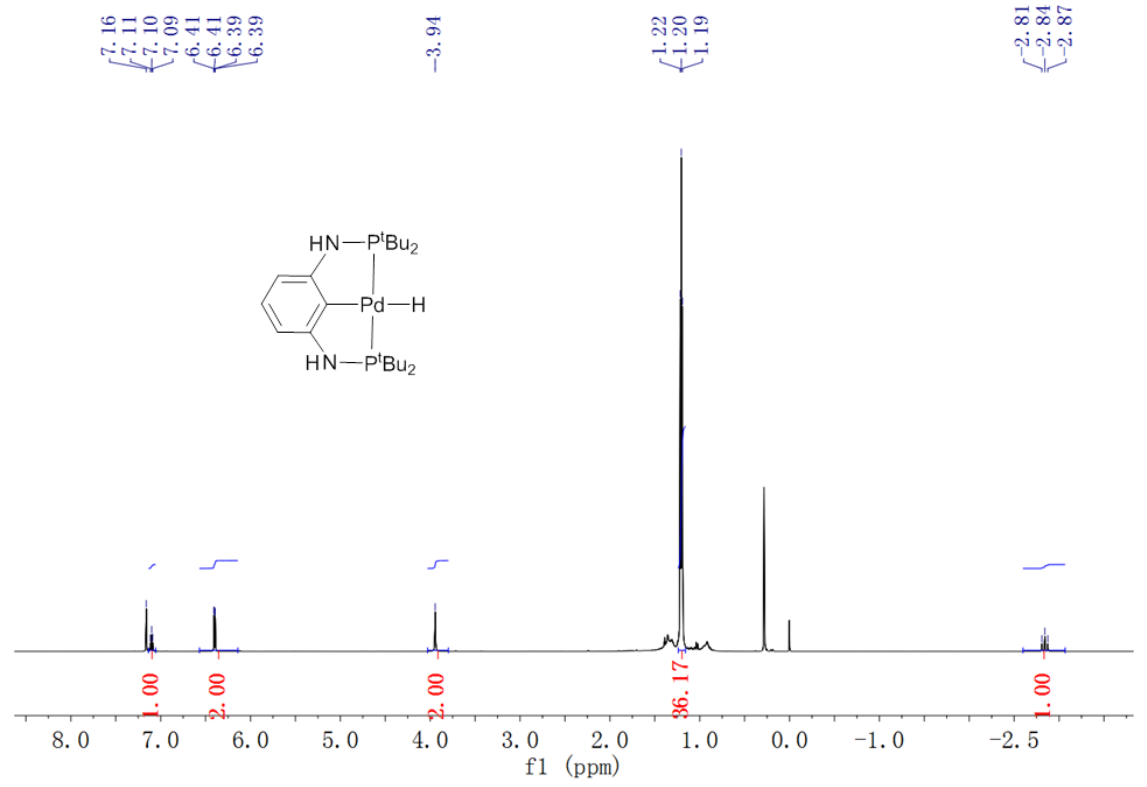



**Fig. S6** $^1H$ NMR spectrum of complex **1** (600 MHz, $C_6D_6$)

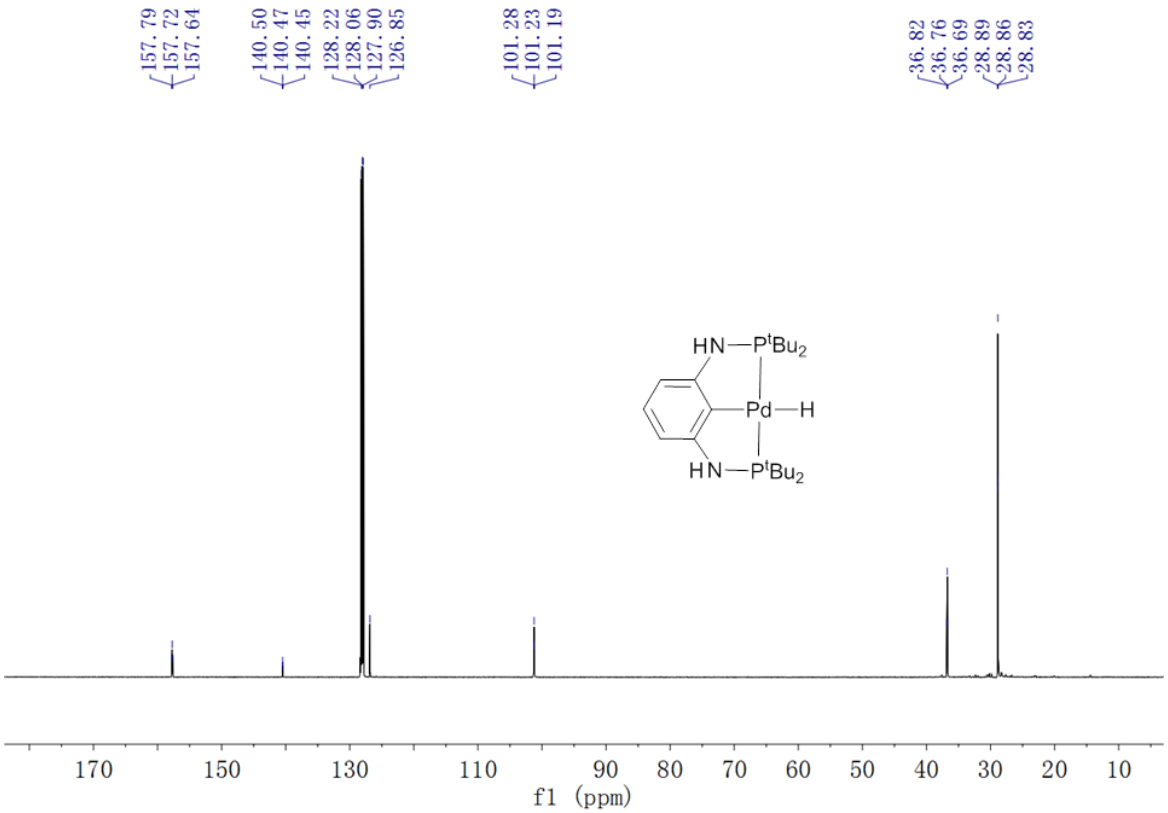



**Fig. S7** $^{13}C\{^{1}H\}$ NMR spectrum of complex **1** (151 MHz, $C_6D_6$)

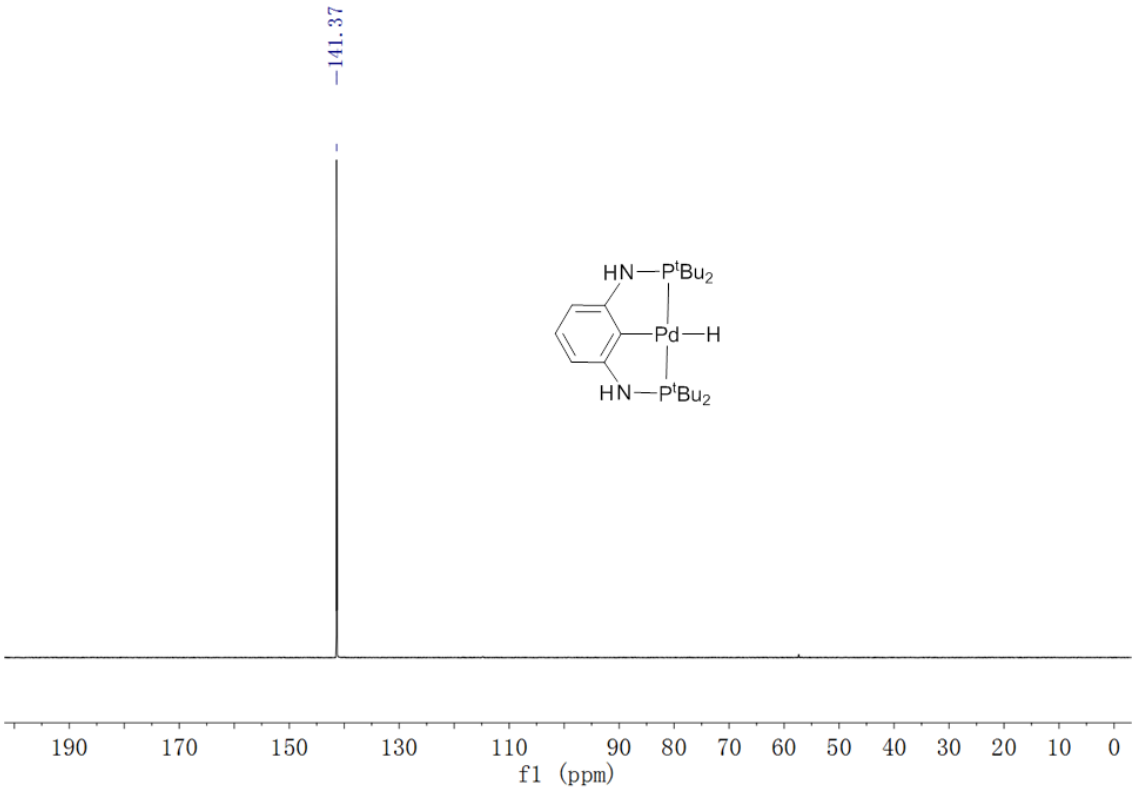



**Fig. S8** $^{31}P\{^{1}H\}$ NMR spectrum of complex **1** (243 MHz, $C_6D_6$)

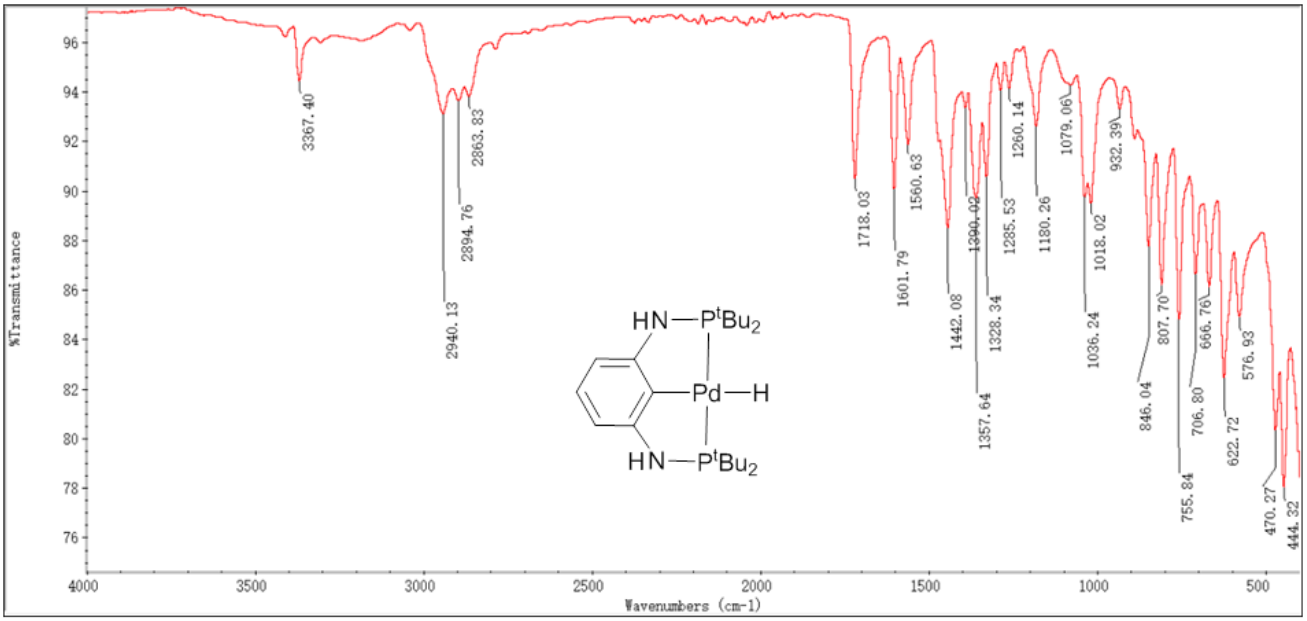



**Fig. S9** FTIR spectrum of complex **1** (KBr disc)

**Reaction of [2,6-($^t$Bu$_2$PNH)$_2$C$_6$H$_3$]PdH (1) with methanol**

*EXP (I):* Complex **1** (0.01 mmol) was dissolved in 0.5 mL of benzene-$d_6$ in a NMR tube, and then 50 equiv. of methanol was added. The NMR tube was sealed and the reaction was monitored by $^1$H and $^{31}$P{$^1$H} NMR spectra at room temperature.

*EXP (II):* Complex **1** (0.01 mmol) was dissolved in 0.5 mL of methanol/methanol-$d_4$ (1:4) in a NMR tube. The NMR tube was sealed and the reaction was monitored by $^1$H NMR spectra at room temperature.

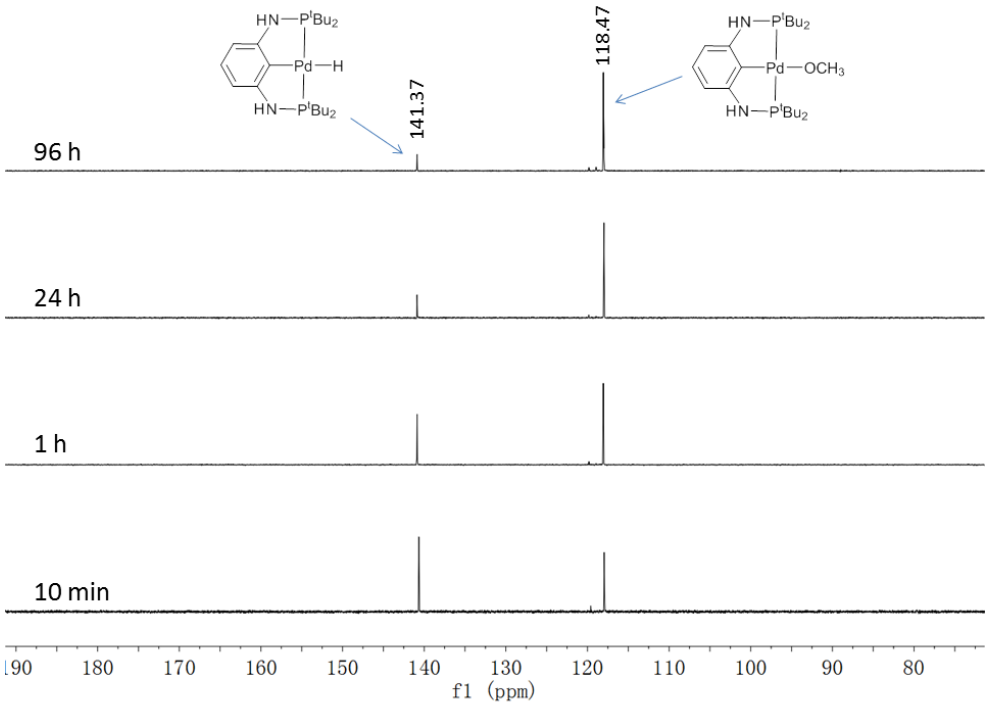



**Fig. S10** $^{31}$P{$^1$H} NMR spectra of the reaction of complex **1** with methanol (243 MHz, $C_6D_6$, EXP I).

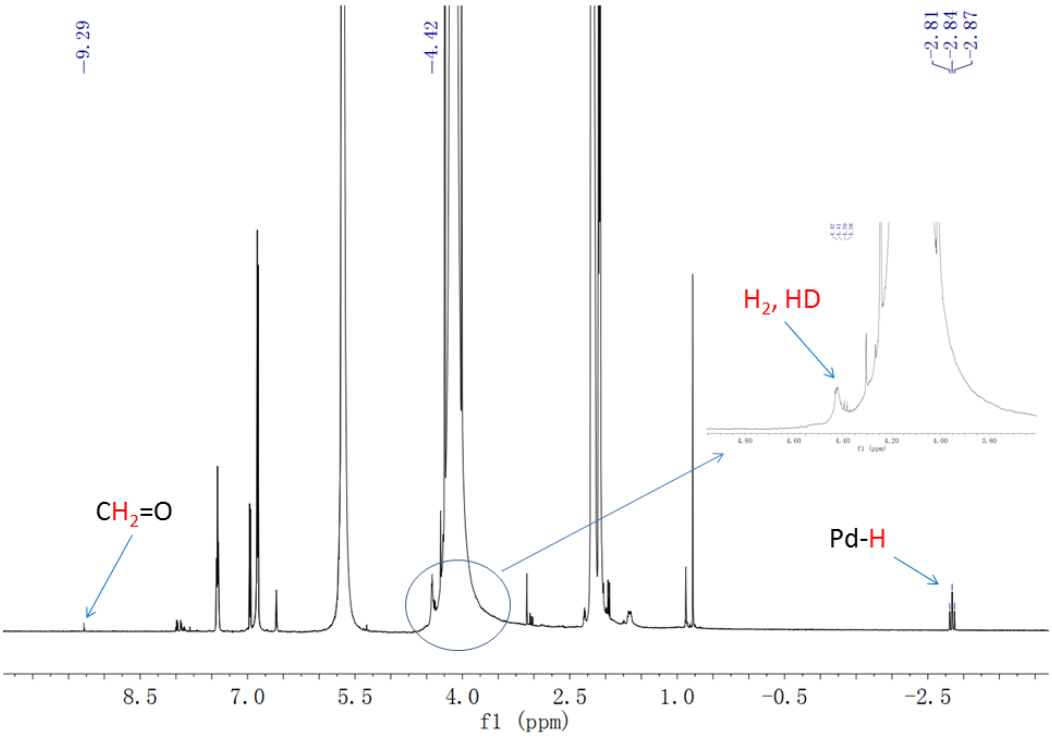



**Fig. S11** $^{1}$H NMR spectrum of the reaction of complex **1** with methanol (600 MHz, methanol-$d_4$). Spectrum recorded 5 h after adding complex **1** to methanol/methanol-$d_4$ (1:4) in a NMR tube (EXP II).

**Reaction of [2,6-($^{t}$Bu$_2$PNH)$_2$C$_6$H$_3$]PdH (1) with H$_2$O**

Complex **1** (0.01 mmol) was dissolved in 0.5 mL of benzene-$d_6$ in a NMR tube and $H_2O$ (0.50 mmol) was added. The NMR tube was sealed and kept at room temperature and the reaction was monitored by NMR spectra.

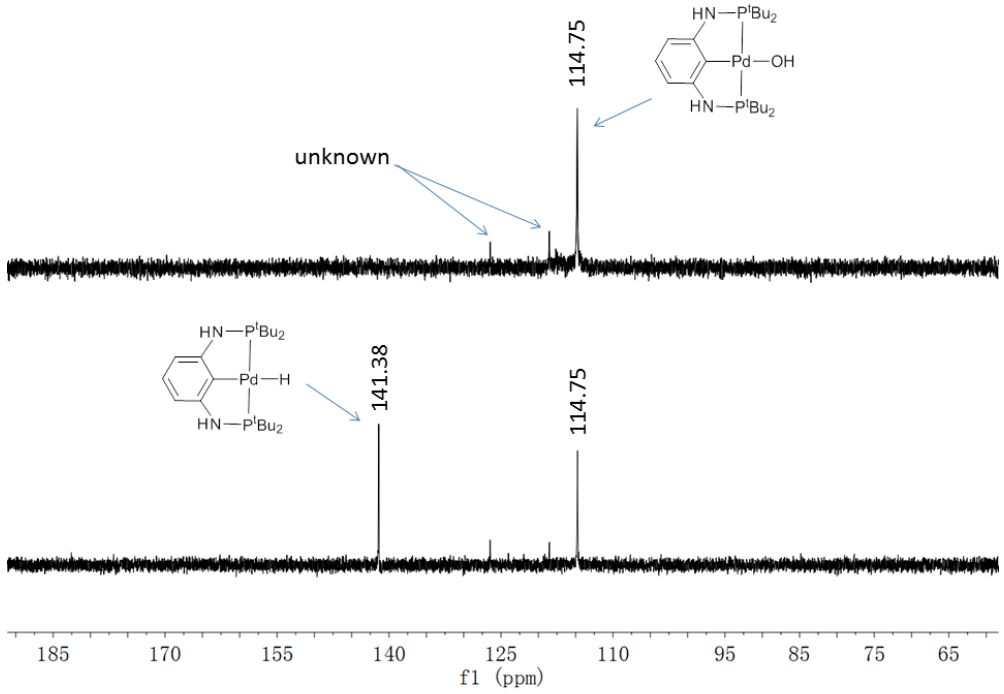



**Fig. S12** $^{31}$P{$^{1}$H} NMR spectrum of the reaction of complex **1** with water (243 MHz, $C_6D_6$). Bottom: spectrum recorded 24 h after mixing complex **1** with 50 equiv. of water; top: spectrum recorded 96 h after mixing complex **1** with 50 equiv. of water.

**Synthesis and characterization of [2,6-($^t$Bu$_2$PNH)$_2$C$_6$H$_3$]PdOH (2)**

A mixture of complex **Pd-NO$_3$** (282 mg, 0.5 mmol), NaOH (500 mg, 12.5 mmol) and THF (20 mL) was sonicated at room temperature for 5 h. The resulting suspension was centrifuged and the solvent was evaporated under reduced pressure. The solid residue was extracted with *n*-hexane (15 mL × 3). The combined extraction solution was concentrated and recrystallized. Complex [2,6-($^t$Bu$_2$PNH)$_2$C$_6$H$_3$]PdOH (**2**) was obtained as a white solid (190 mg, 73% yield). $^1$H NMR (600 MHz, benzene-$d_6$, $\delta$): 6.98 (t, 1H, $J_{H\text{-}H}$ = 7.7 Hz, Ar*H*), 6.20 (d, 2H, $J_{H\text{-}H}$ = 7.7 Hz, Ar*H*), 3.90 (s, 2H, N*H*), 1.28–1.30 (m, 36H, C(C*H*$_3$)$_3$), -1.35 (s, br., 1H, O*H*). $^{13}$C{$^1$H} NMR (151 MHz, benzene-$d_6$, $\delta$): 158.49 (t, $J_{C\text{-}P}$ = 12.2 Hz, Ar*C*), 126.24 (s, Ar*C*), 124.06 (s, Ar*C*), 102.13 (t, $J_{C\text{-}P}$ = 6.7 Hz, Ar*C*), 37.69 (t, $J_{C\text{-}P}$ = 8.4 Hz, *C*(CH$_3$)$_3$), 28.32 (t, $J_{C\text{-}P}$ = 3.6 Hz, C(*C*H$_3$)$_3$). $^{31}$P{$^1$H} NMR (243 MHz, benzene-$d_6$, $\delta$): 114.67 (s). HRMS (ESI): *m/z* calculated for $C_{22}H_{42}N_2OP_2Pd$ + $H^+$ [M + H]$^+$ 519.1880, found 519.1839; *m/z* calculated for [$C_{22}H_{42}N_2OP_2Pd$]$^+$ [M]$^+$ 518.1802, found 518.1807.

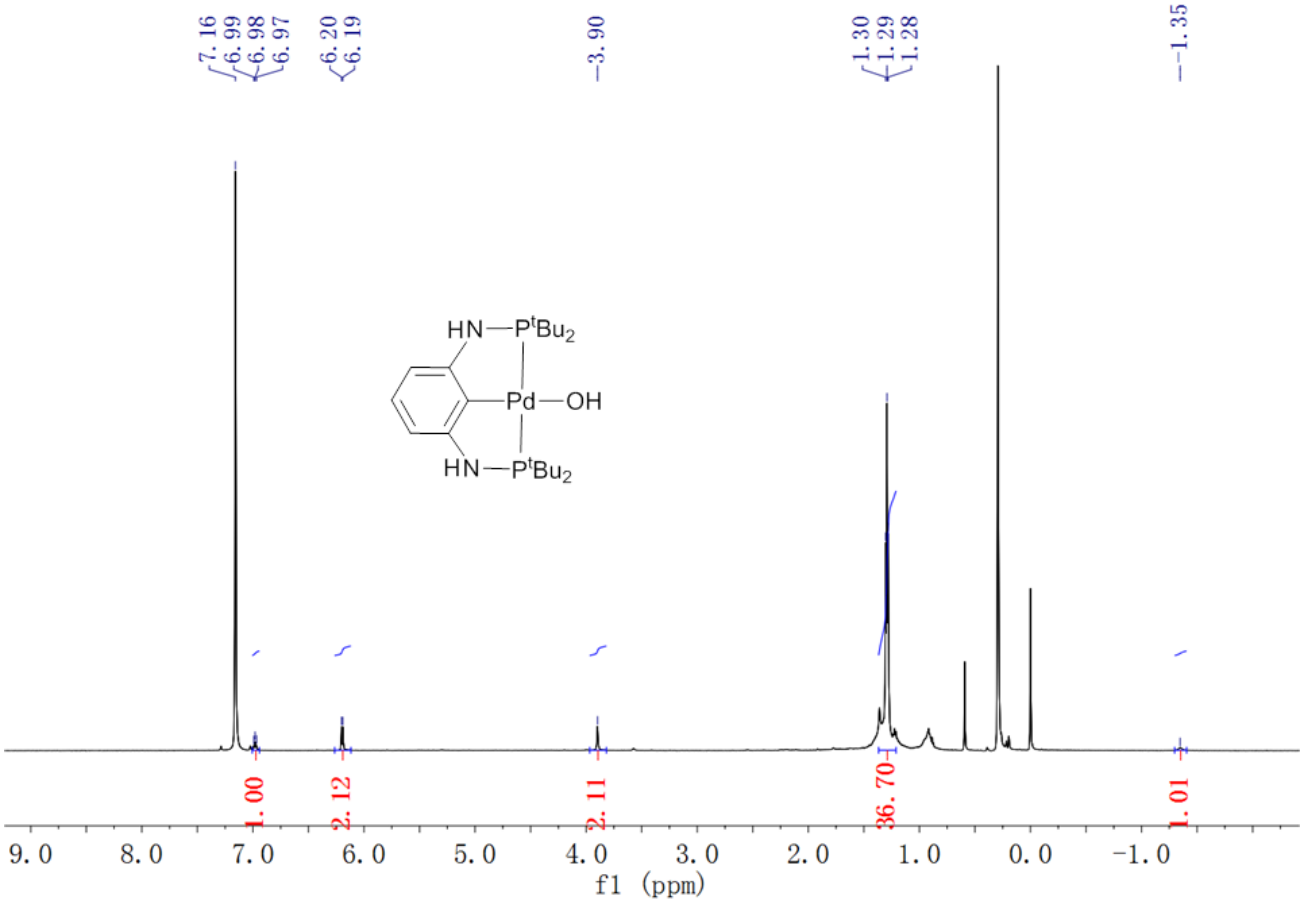



**Fig. S13** $^1$H NMR spectrum of complex **2** (600 MHz, $C_6D_6$)

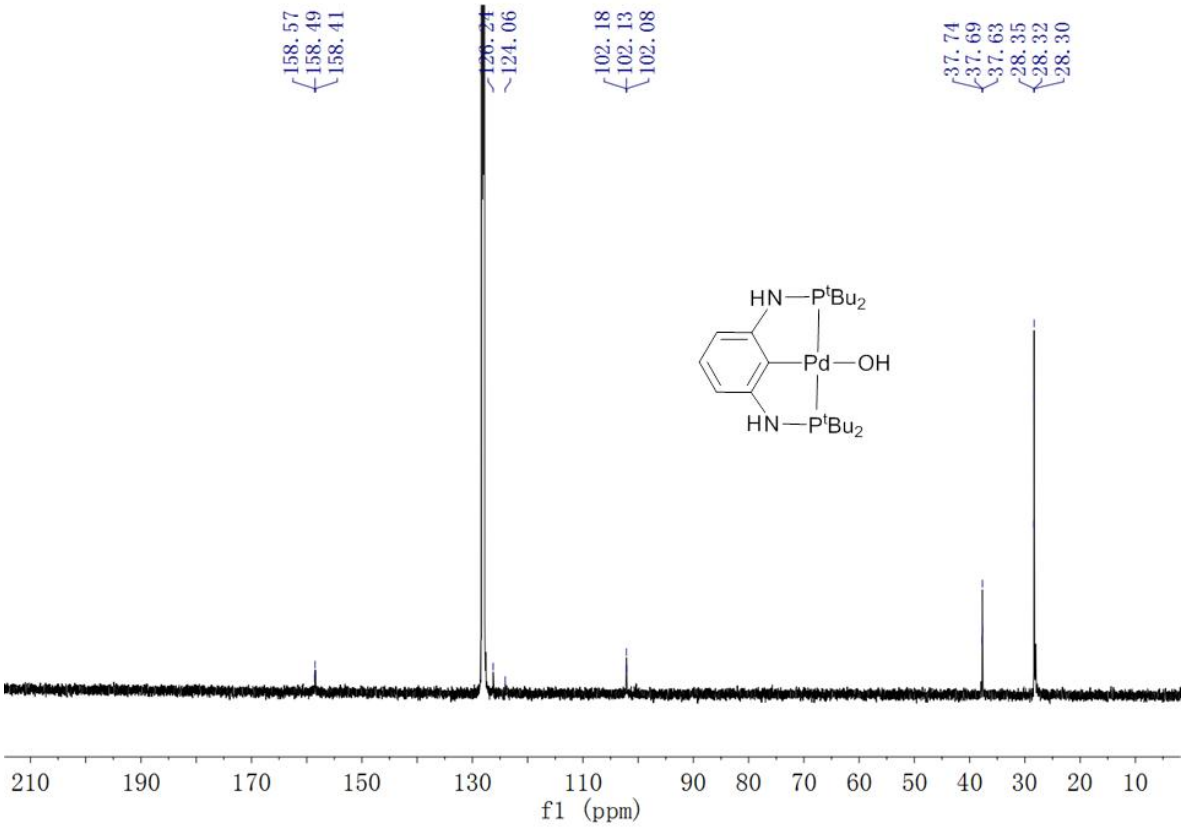



**Fig. S14** $^{13}C\{^{1}H\}$ NMR spectrum of complex **2** (151 MHz, $C_6D_6$)

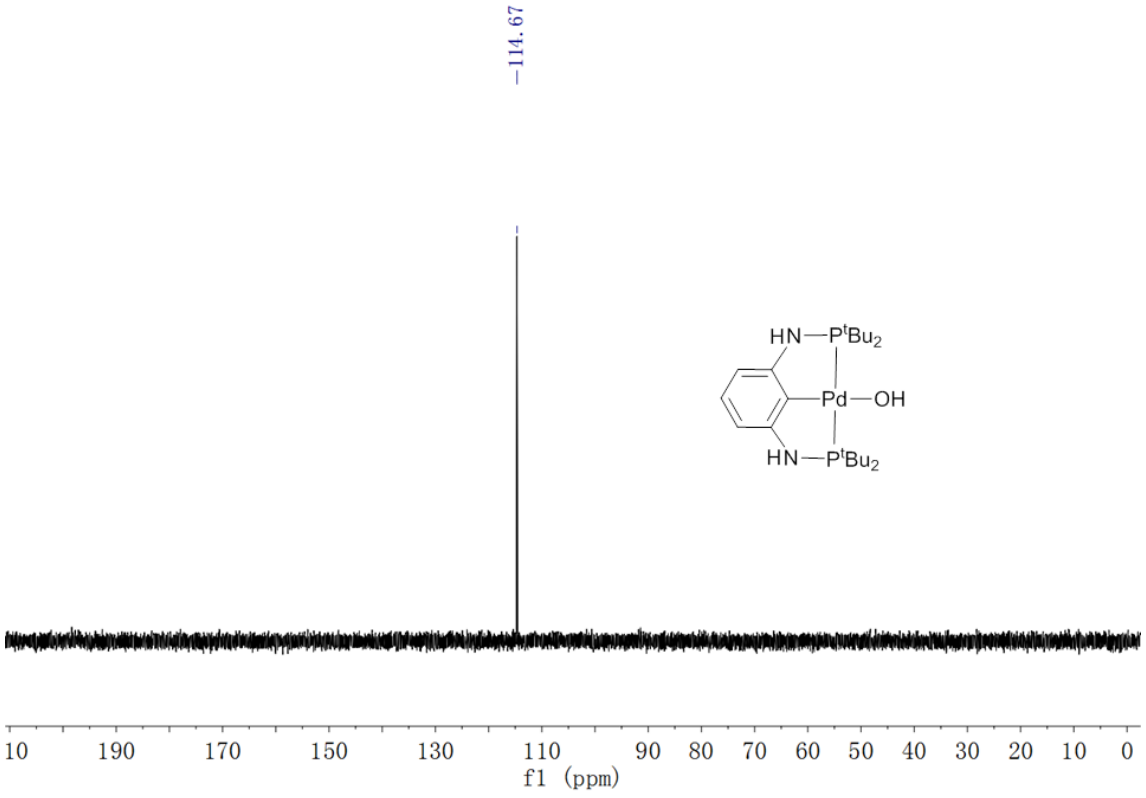



**Fig. S15** $^{31}P\{^{1}H\}$ NMR spectrum of complex **2** (243 MHz, $C_6D_6$)

**Synthesis and characterization of [2,6-($^t$Bu$_2$PNH)$_2$C$_6$H$_3$]PdNHC(O)CH$_3$ (3)**

*Route (I):* Complex **1** (100 mg, 0.20 mmol) and acetamide (21 μL, 0.40 mmol) were dissolved in 20 mL of THF. The solution was refluxed for 48 h. The reaction mixture was slowly cooled to room temperature and [2,6-($^t$Bu$_2$PNH)$_2$C$_6$H$_3$]PdNHC(O)CH$_3$ (**3**) precipitated from the solution as solid product (80 mg, 71% yield).

*Route (II):* Complex **1** (20 mg, 0.04 mmol) was dissolved in acetonitrile (2 mL), and then $H_2O$ (4 μL, 0.20 mmol) was added. The mixture was kept at room temperature without stirring overnight. Complex **3** precipitated as a dark yellow crystalline solid (9 mg, 40% yield).

*Route (III):* Complex **2** (0.02 mmol) was dissolved in 0.5 mL of benzene-$d_6$ in a NMR tube and acetonitrile (5 μL, 0.10 mmol) was added. The NMR tube was heated to 80 ℃ and the reaction was monitored by $^{31}$P{$^1$H} NMR spectrum. After 15 h, complex **2** was cleanly converted into complex **3**. The NMR tube was slowly cooled to room temperature in 24 h. Complex **3** precipitated from the solution as a crystalline solid (10 mg, 89% yield).

$^1$H NMR (600 MHz, DMSO-$d_6$, $\delta$): 6.50 (t, 1H, $J_{H\text{-}H}$ = 7.8 Hz, Ar*H*), 6.30 (s, 2H, PN*H*), 6.04 (d, 2H, $J_{H\text{-}H}$ = 7.8 Hz, Ar*H*), 1.72 (s, 3H, C$H_3$), 1.29–1.31 (m, 36H, C(C$H_3$)$_3$). $^{31}$P{$^1$H} NMR (243 MHz, DMSO-$d_6$, $\delta$): 117.20 (s). HRMS (ESI): *m/z* calculated for $C_{24}H_{43}N_3OP_2Pd$ + $H^+$ [M + H]$^+$ 560.2146, found 560.2102; *m/z* calculated for $C_{24}H_{43}N_3OP_2Pd^+$ [M]$^+$ 559.2067, found 559.2058.

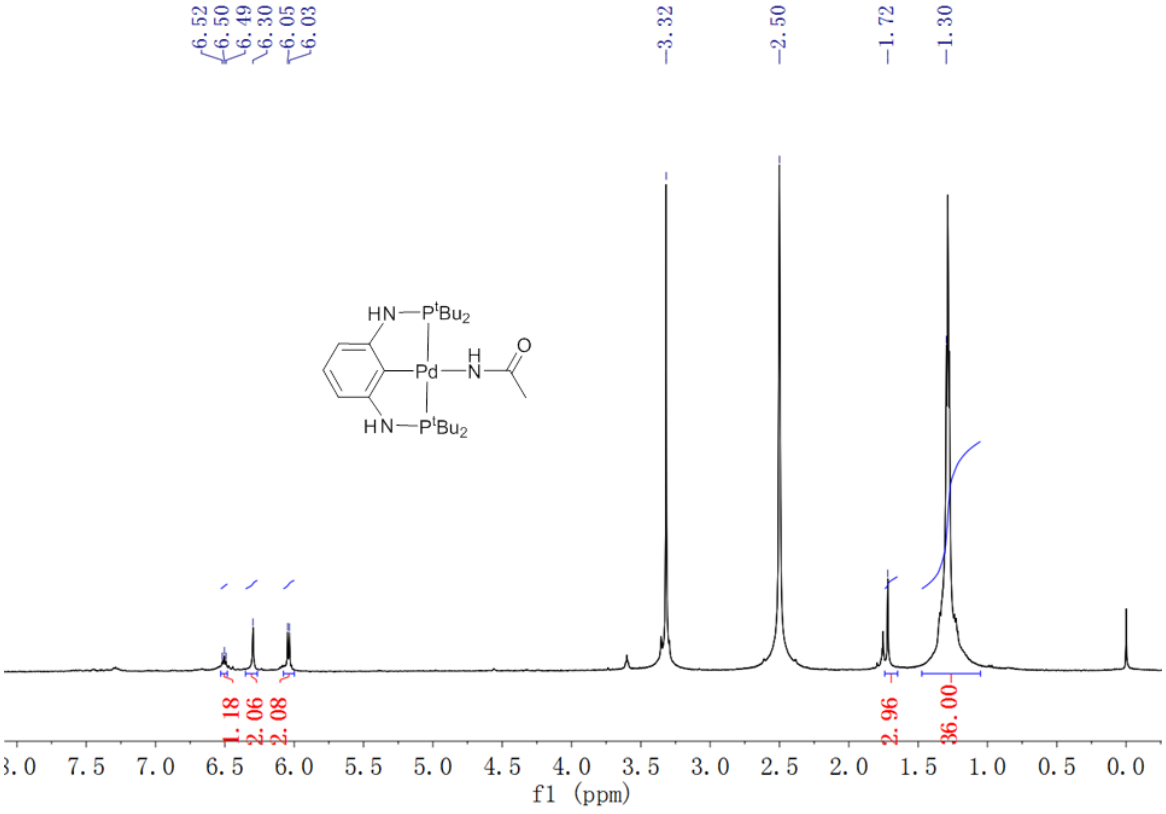



**Fig. S16** $^1$H NMR spectrum of complex **3** (600 MHz, DMSO-$d_6$).

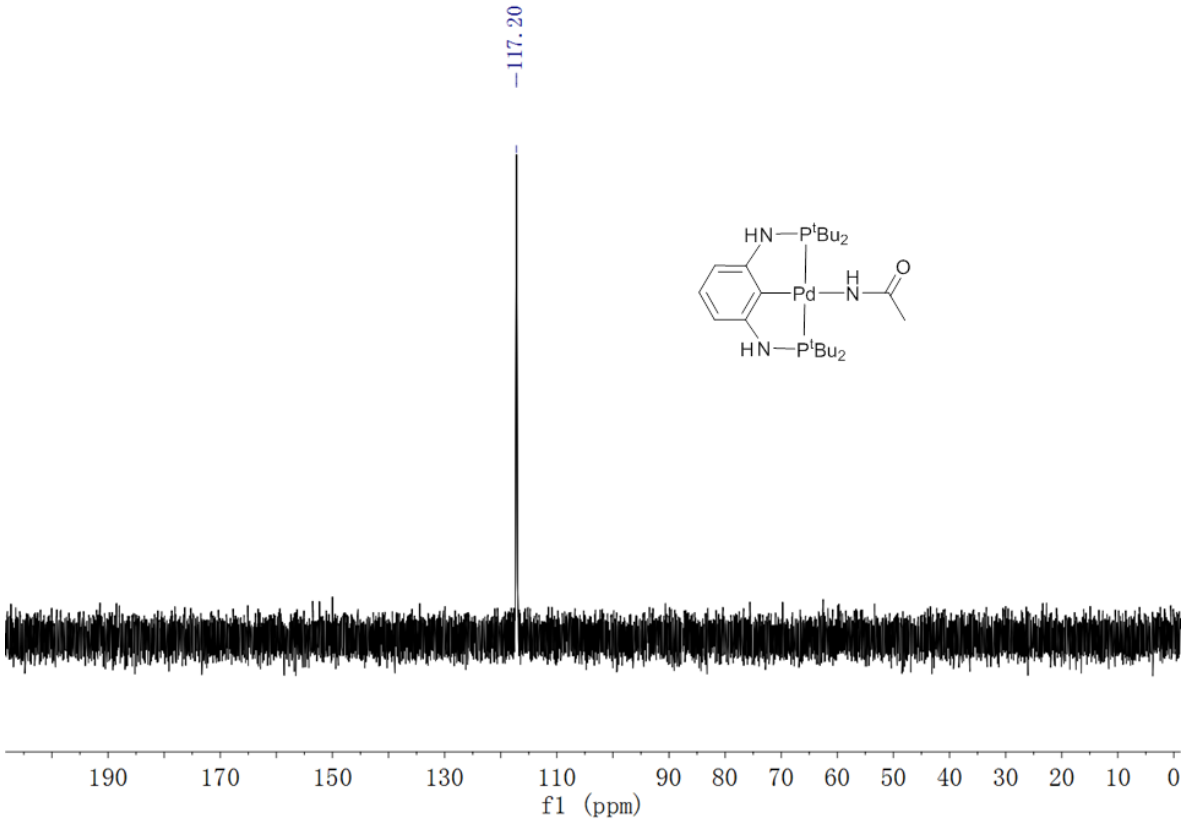



**Fig. S17** $^{31}P\{^{1}H\}$ NMR spectrum of complex **3** (243 MHz, DMSO-$d_6$).

**X-ray crystal structure determination**

The crystal structures of complexes **1**, **2**, **3**, and **Pd-NO$_3$** were determined on a SuperNova diffractometer (Oxford Diffraction). The intensity data were collected at 150 or 170 K using monochromated Cu-Kα radiation (λ = 1.54184 Å). The frames were integrated with the Bruker APEX2 software package using a narrow-frame algorithm. The data were corrected for decay, Lorentz, and polarization effects and absorption and beam corrections based on the multi-scan technique. The structures were solved by a combination of direct methods in SHELXTL and difference Fourier techniques and refined by full-matrix least-squares procedures interfaced with the program OLEX2.[S2,S3] Non-hydrogen atoms were refined with anisotropic displacement parameters. The H-atoms were either located or calculated and subsequently treated with a riding model. The crystals suitable for X-ray diffraction analysis were obtained in benzene solution for **1**, THF/*n*-hexane solution for **Pd-NO$_3$** and **2**, acetonitrile/$H_2O$ solution for **3**, respectively. Complex **Pd-NO$_3$** co-crystallized with a THF molecule, complex **2** co-crystallized with three molecules of $H_2O$, and complex **3** co-crystallized with two molecules of $CH_3CN$. Summaries of the crystallographic data and structure refinement for these complexes are provided in the Tables S1 and S2.

**Table S1. Summary of crystal data and structure refinement for complexes 1 and 2**

| Complex | **1** | **2** $3H_2O$ |
|---|---|---|
| CCDC number | 2191732 | 2191734 |
| Empirical formula | $C_{22}H_{42}N_2P_2Pd$ | $C_{22}H_{48}N_2O_4P_2Pd$ |
| Formula weight | 502.91 | 572.96 |
| Temp, K | 150.00(10) | 149.99(10) |
| Crystal system | orthorhombic | orthorhombic |
| Space group | Pbca | Pbca |
| *a*, Å | 11.4139(2) | 16.9062(2) |
| *b*, Å | 15.3554(3) | 14.9710(2) |
| *c*, Å | 28.0400(5) | 21.5306(3) |
| $\alpha$ (°) | 90 | 90 |
| $\beta$ (°) | 90 | 90 |
| $\gamma$ (°) | 90 | 90 |
| Volume, Å$^3$ | 4914.43(16) | 5449.45(12) |
| Z | 8 | 8 |
| $d_{calc}$, g cm$^{-3}$ | 1.359 | 1.397 |
| $\lambda$, Å | 1.54184 | 1.54184 |
| $\mu$, mm$^{-1}$ | 7.376 | 6.831 |
| No. of data collected | 12651 | 14725 |
| No. of unique data | 4655 | 5210 |
| $R_{int}$ | 0.0428 | 0.0282 |
| Goodness-of-fit on $F^2$ | 1.067 | 1.047 |
| $R_1$, w$R_2$ ($I > 2\sigma(I)$) | 0.0455, 0.1153 | 0.0312, 0.0778 |
| $R_1$, w$R_2$ (all data) | 0.0541, 0.1222 | 0.0366, 0.0809 |

**Table S2. Summary of crystal data and structure refinement for complexes 3 and Pd-$NO_3$**

| Complex | **3** ·2$CH_3CN$ | **Pd-$NO_3$** ·THF |
|---|---|---|
| CCDC number | 2191735 | 2191733 |
| Empirical formula | $C_{28}H_{51}N_5OP_2Pd$ | $C_{26}H_{49}N_3O_4P_2Pd$ |
| Formula weight | 642.07 | 636.02 |
| Temp, K | 170.00(10) | 149.99(10) |
| Crystal system | monoclinic | monoclinic |
| Space group | $P2_1/c$ | $P2_1/n$ |
| *a*, Å | 11.71590(10) | 11.34860(10) |
| *b*, Å | 14.45290(10) | 22.9353(2) |
| *c*, Å | 19.6929(2) | 11.59380(10) |
| $\alpha$ (°) | 90 | 90 |
| $\beta$ (°) | 95.1230(10) | 95.3590(10) |
| $\gamma$ (°) | 90 | 90 |
| Volume, $Å^3$ | 3321.25(5) | 3004.48(5) |
| Z | 4 | 4 |
| $d_{calc}$, g $cm^{-3}$ | 1.284 | 1.406 |
| $\lambda$, Å | 1.54184 | 1.54184 |
| $\mu$, $mm^{-1}$ | 5.622 | 6.266 |
| No. of data collected | 14789 | 13423 |
| No. of unique data | 6346 | 5747 |
| $R_{int}$ | 0.0265 | 0.0323 |
| Goodness-of-fit on $F^2$ | 1.081 | 1.035 |
| $R_1$, w$R_2$ ($I > 2\sigma(I)$) | 0.0335, 0.0865 | 0.0351, 0.0889 |
| $R_1$, w$R_2$ (all data) | 0.0371, 0.0885 | 0.0386, 0.0913 |

**General procedure for the catalytic reactions**

Nitrile (1.0 mmol), THF (1.0 mL), water (1.0 mL), and complex **1** (5.0 mg, 0.01 mmol) were mixed in a reaction tube. The tube was then sealed and the reaction mixture was stirred at 80 ℃. The reaction was monitored by GC-MS and stopped at the required time or until the nitrile substrate disappeared completely. THF and water were then removed under reduced pressure. The resulting residue was extracted with $CH_2Cl_2$ (3 × 5 mL) and filtered. Removal of $CH_2Cl_2$ from the combined extraction solutions produced the crude amide product which was washed with cold diethyl ether or *n*-hexane and dried in vacuo. The isolated amide products were characterized by $^1H$, $^{13}C\{^1H\}$ NMR spectra and high resolution mass spectrometry (HRMS). The NMR spectra are presented in Fig. S18–S67.

**Characterization of the isolated amide products**

(**4a**)

White solid (46 mg, 78% yield), M.P. 80–83 ℃. $^{1}$H NMR (600 MHz, $CD_3OD$, $\delta$): 1.96 (s, 3H, C$H_3$). $^{13}$C{$^{1}$H} NMR (151 MHz, $CD_3OD$, $\delta$): 176.39 (*C*O), 22.08 (*C*$H_3$). HRMS (ESI): *m/z* calculated for $C_2H_6NO$ $[M + H]^+$ 60.0444; Found 60.0445. These spectral data correspond to previously reported data.[S4]

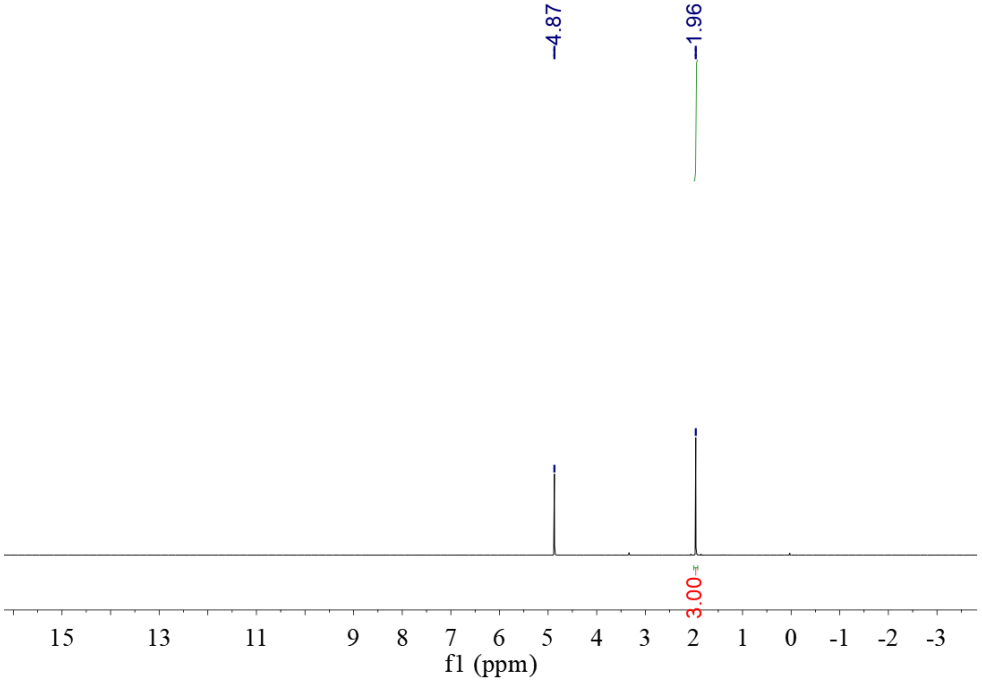



**Fig. S18** $^{1}$H NMR spectrum of the isolated **4a** (600 MHz, $CD_3OD$)

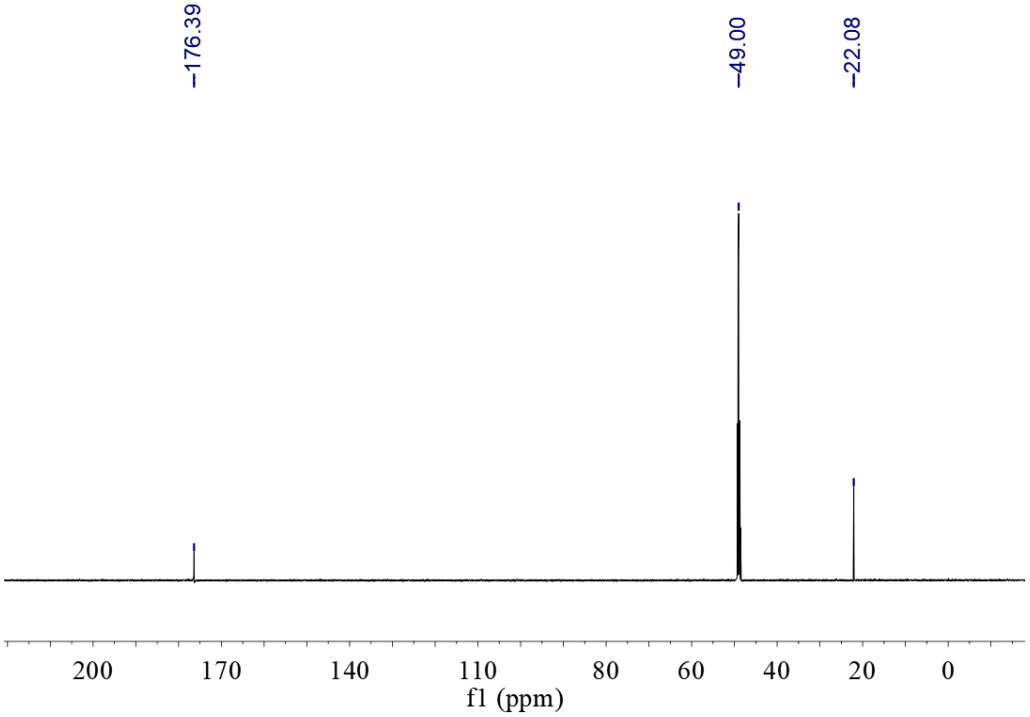
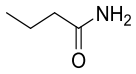



**Fig. S19** $^{13}$C{$^{1}$H} NMR spectrum of the isolated **4a** (151 MHz, $CD_3OD$)




(**4b**)

White solid (75 mg, 86% yield), M.P. 115–116 ℃. $^{1}$H NMR (600 MHz, $CD_3OD$, $\delta$): 2.20 (t, $J$ = 7.8 Hz, 2H, C$H_2$), 1.66 (m, 2H, C$H_2$), 0.98 (t, $J$ = 7.8 Hz, 3H, C$H_3$). $^{13}$C{$^{1}$H} NMR (151 MHz, $CD_3OD$, $\delta$): 179.12 (*C*O), 38.42 (*C*$H_2$), 20.22 (*C*$H_2$), 13.97 (*C*$H_3$). HRMS (ESI): *m/z* calculated for $C_4H_{10}NO$ $[M + H]^+$ 88.0757; Found 88.0764. These spectral data correspond to previously reported data.[S7]

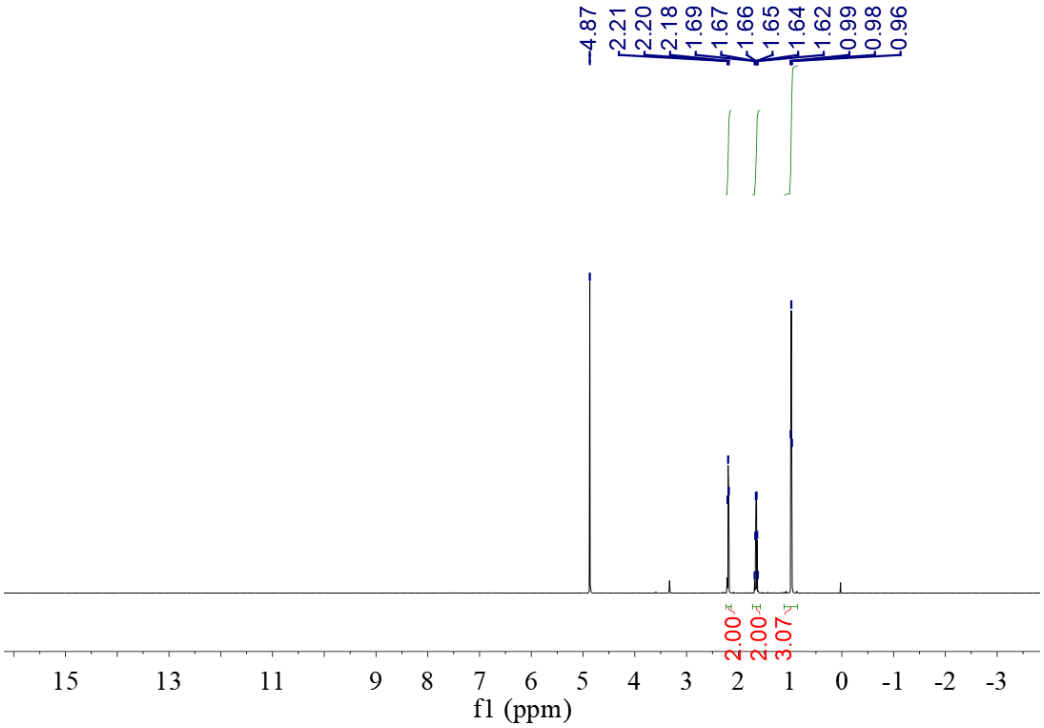



**Fig. S20** $^{1}$H NMR spectrum of the isolated **4b** (600 MHz, $CD_3OD$)

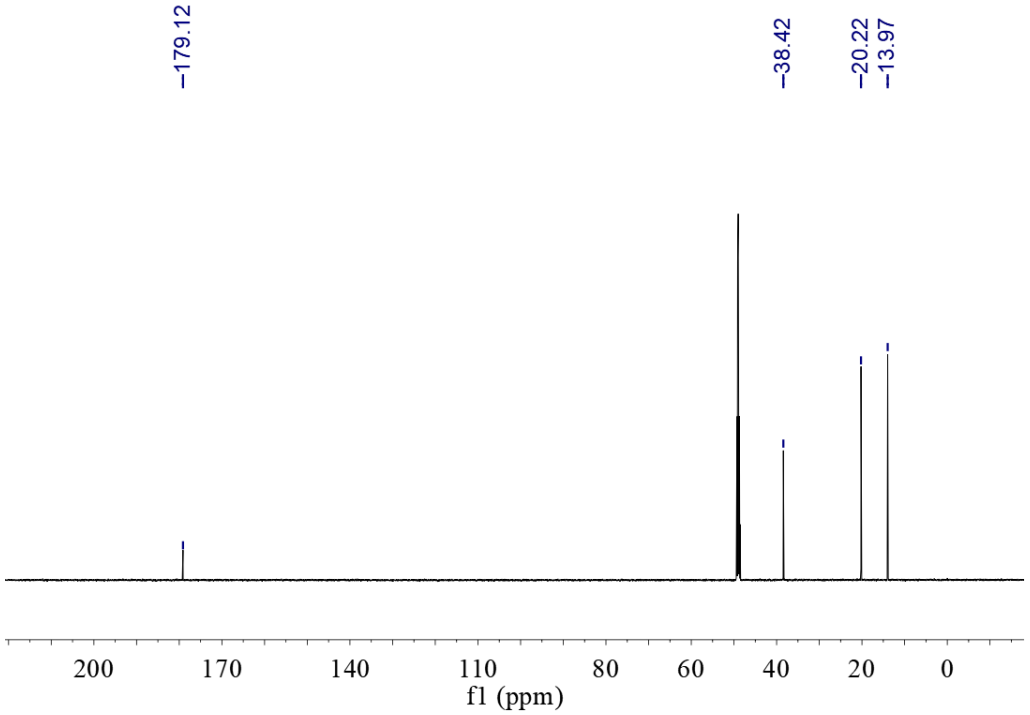
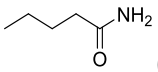



**Fig. S21** $^{13}$C{$^{1}$H} NMR spectrum of the isolated **4b** (151 MHz, $CD_3OD$)




(**4c**)

White solid (73 mg, 72% yield), M.P. 104–106 ℃. $^{1}$H NMR (600 MHz, $CD_3OD$, $\delta$): 2.22 (t, $J$ = 7.2 Hz, 2H, C$H_2$), 1.61 (m, 2H, C$H_2$), 1.39 (m, 2H, C$H_2$), 0.96 (t, $J$ = 7.2 Hz, 3H, C$H_3$). $^{13}$C{$^{1}$H} NMR (151 MHz, $CD_3OD$, $\delta$): 179.31 (*C*O), 36.26 (*C*$H_2$), 29.05 (*C*$H_2$), 23.37 (*C*$H_2$), 14.10 (*C*$H_3$). HRMS (ESI): *m/z* calculated for $C_5H_{12}NO$ $[M + H]^+$ 102.0913; Found 102.0915. These spectral data correspond to previously reported data.[S7]

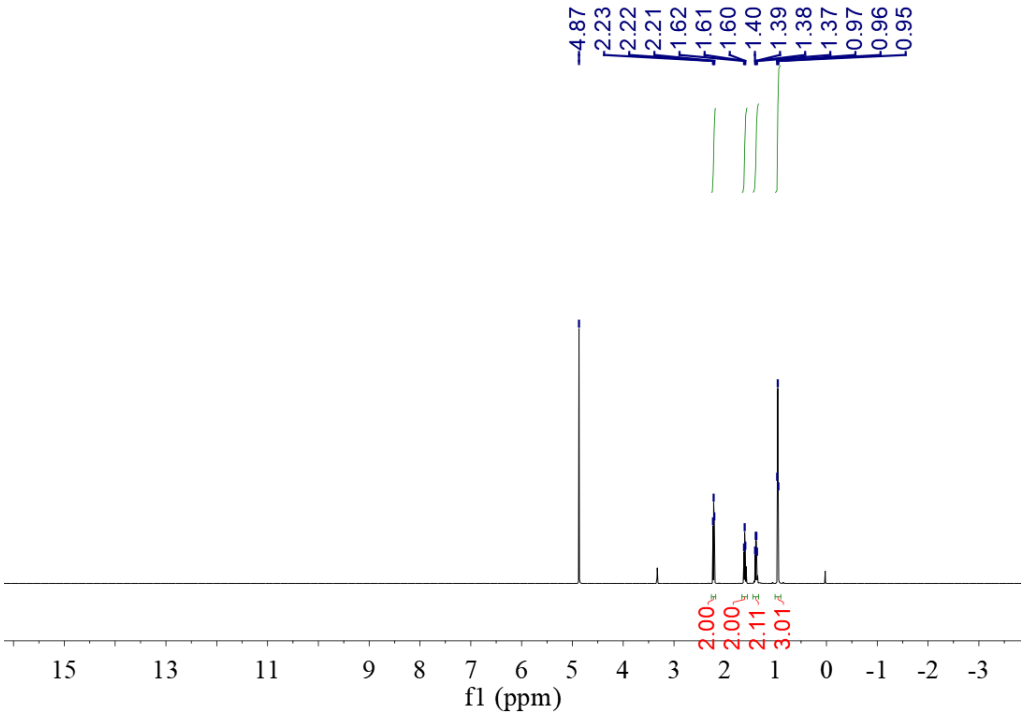



**Fig. S22** $^{1}$H NMR spectrum of the isolated **4c** (600 MHz, $CD_3OD$)

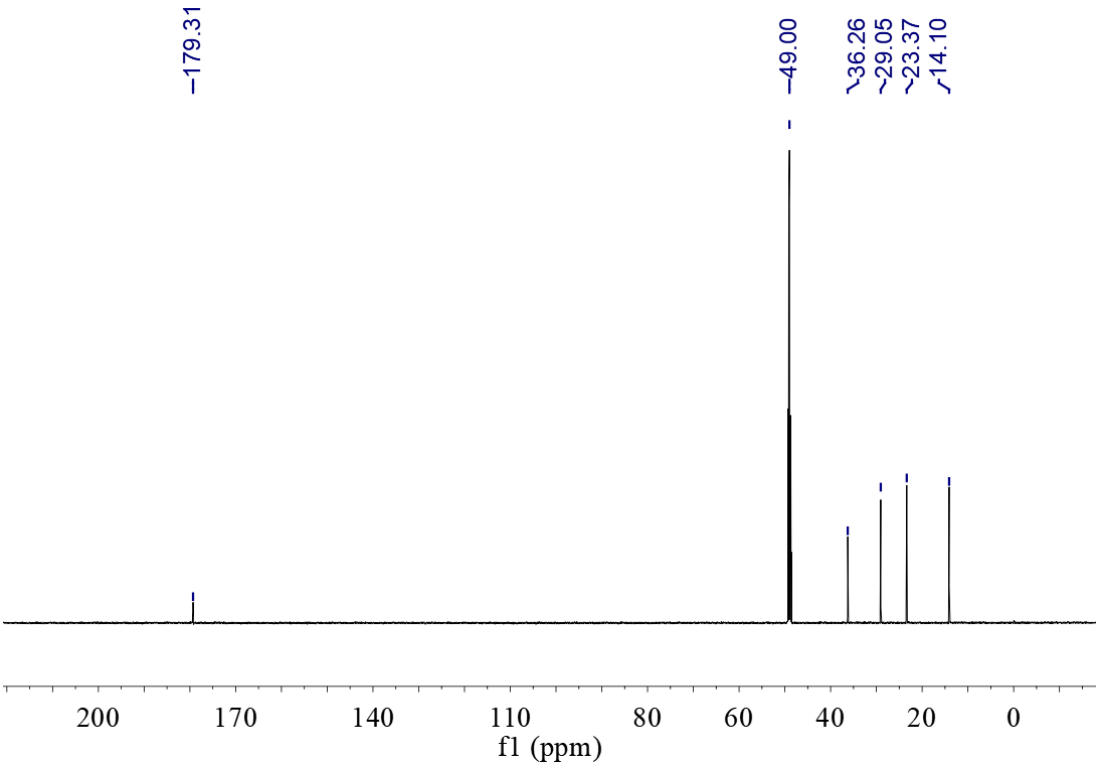
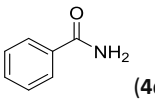



**Fig. S23** $^{13}$C{$^{1}$H} NMR spectrum of the isolated **4c** (151 MHz, $CD_3OD$)



(**4d**)

White solid (115 mg, 95% yield), M.P. 128–130 ℃. $^{1}$H NMR (600 MHz, $CD_3OD$, $\delta$): 7.88 (d, $J$ = 7.8 Hz, 2H, Ar*H*), 7.54 (t, $J$ = 7.8 Hz, 1H, Ar*H*), 7.46 (t, $J$ = 7.8 Hz, 2H, Ar*H*). $^{13}$C{$^{1}$H} NMR (151 MHz, $CD_3OD$, $\delta$): 172.41 (*C*O), 134.94 (Ar*C*), 132.90 (Ar*C*), 129.50 (Ar*C*), 128.62 (Ar*C*). HRMS (ESI): *m/z* calculated for $C_7H_8NO$ $[M + H]^+$ 122.0600; Found 122.0601. These spectral data correspond to previously reported data.[S4]

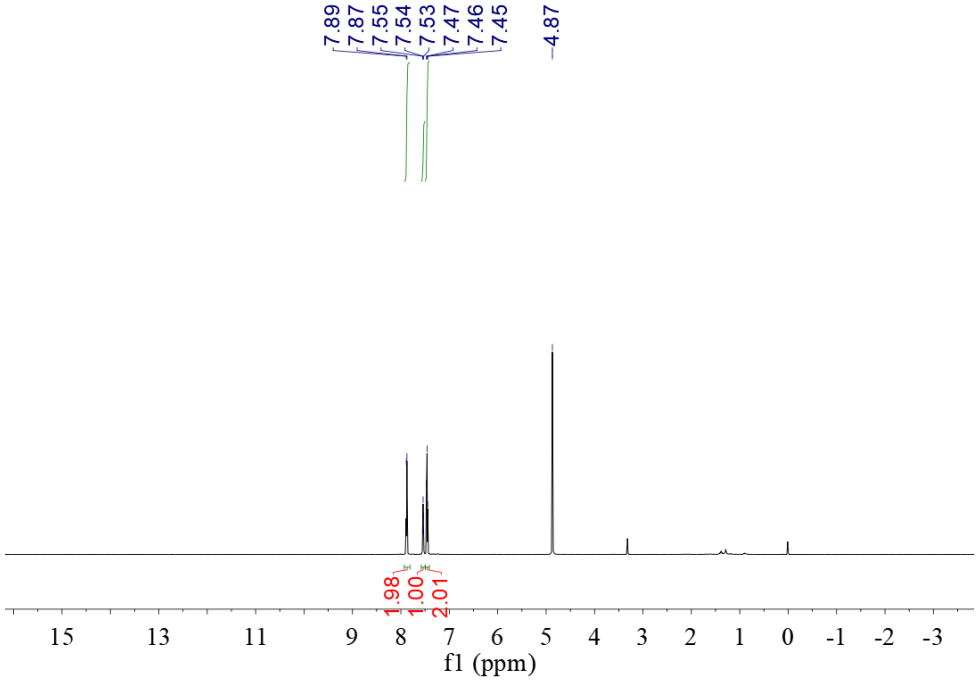



**Fig. S24** $^{1}$H NMR spectrum of the isolated **4d** (600 MHz, $CD_3OD$)

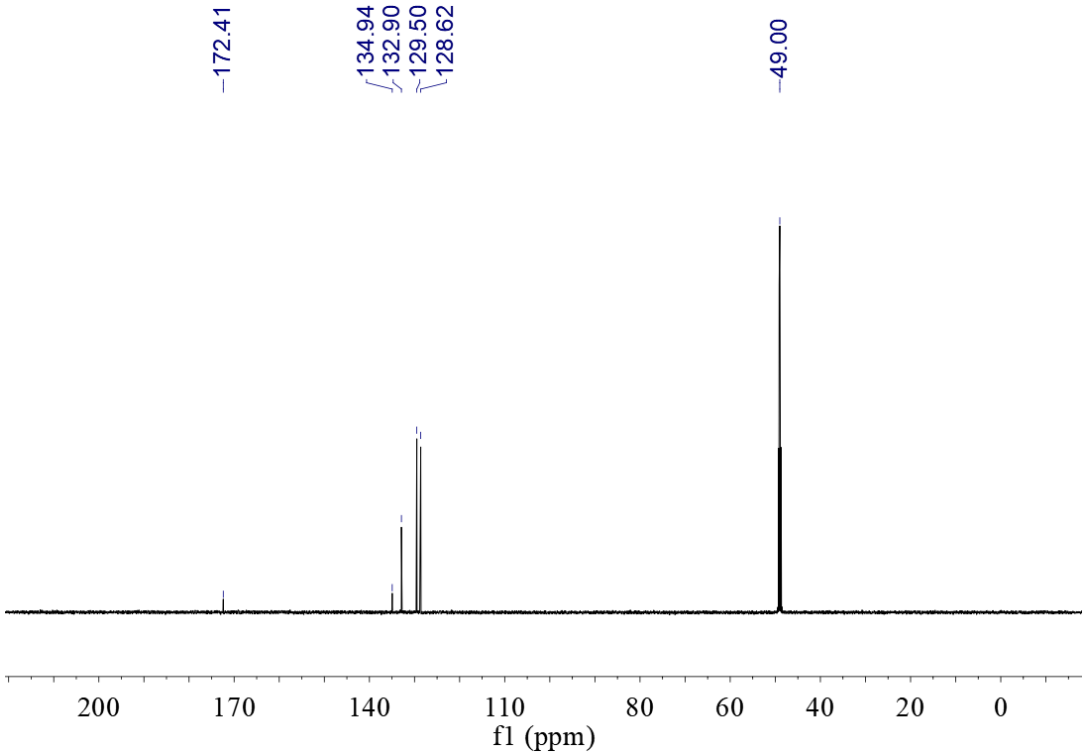
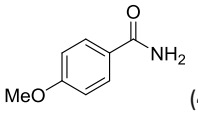



**Fig. S25** $^{13}$C{$^{1}$H} NMR spectrum of the isolated **4d** (151 MHz, $CD_3OD$)




(**4e**)

White solid (149 mg, 98% yield), M.P. 164–168 ℃. $^{1}$H NMR (600 MHz, $CD_3OD$, $\delta$): 7.86 (d, $J$ = 9 Hz, 2H, Ar*H*), 6.98 (d, $J$ = 7.8 Hz, 2H, Ar*H*), 3.85 (s, 3H, C$H_3$). $^{13}$C{$^{1}$H} NMR (151 MHz, $CD_3OD$, $\delta$): 172.02 (*C*O), 164.12 (Ar*C*), 130.60 (Ar*C*), 126.90 (Ar*C*), 114.66 (Ar*C*), 55.89 (*C*$H_3$). HRMS (ESI): *m/z* calculated for $C_8H_{10}NO_2$ $[M + H]^+$ 152.0706; Found 152.0705. These spectral data correspond to previously reported data.[S4]

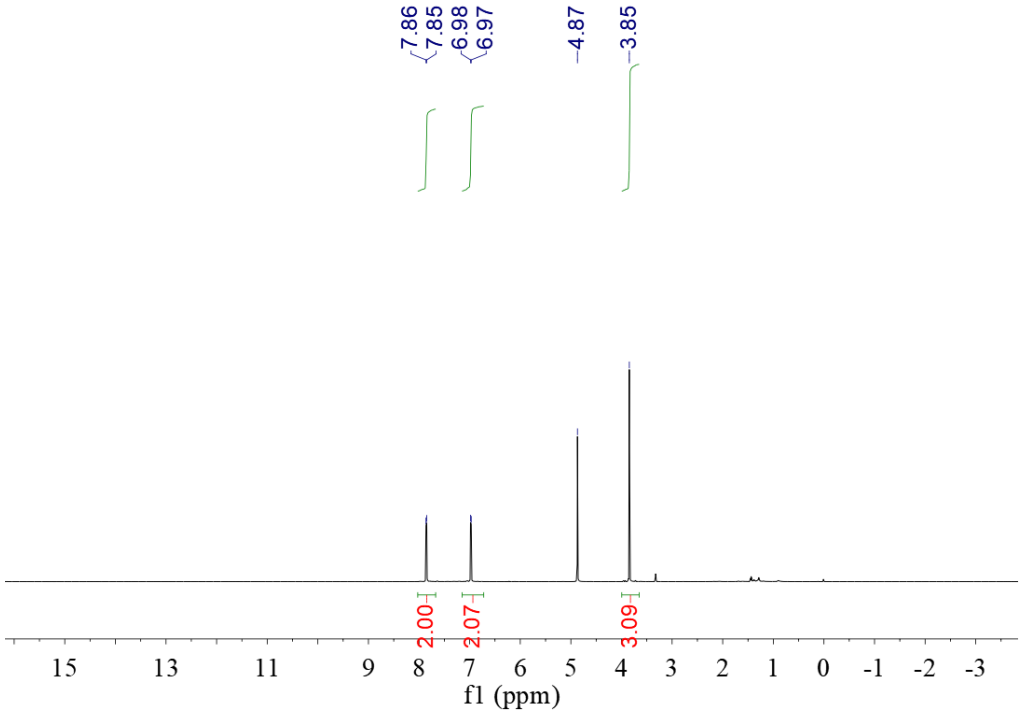



**Fig. S26** $^{1}$H NMR spectrum of the isolated **4e** (600 MHz, $CD_3OD$)

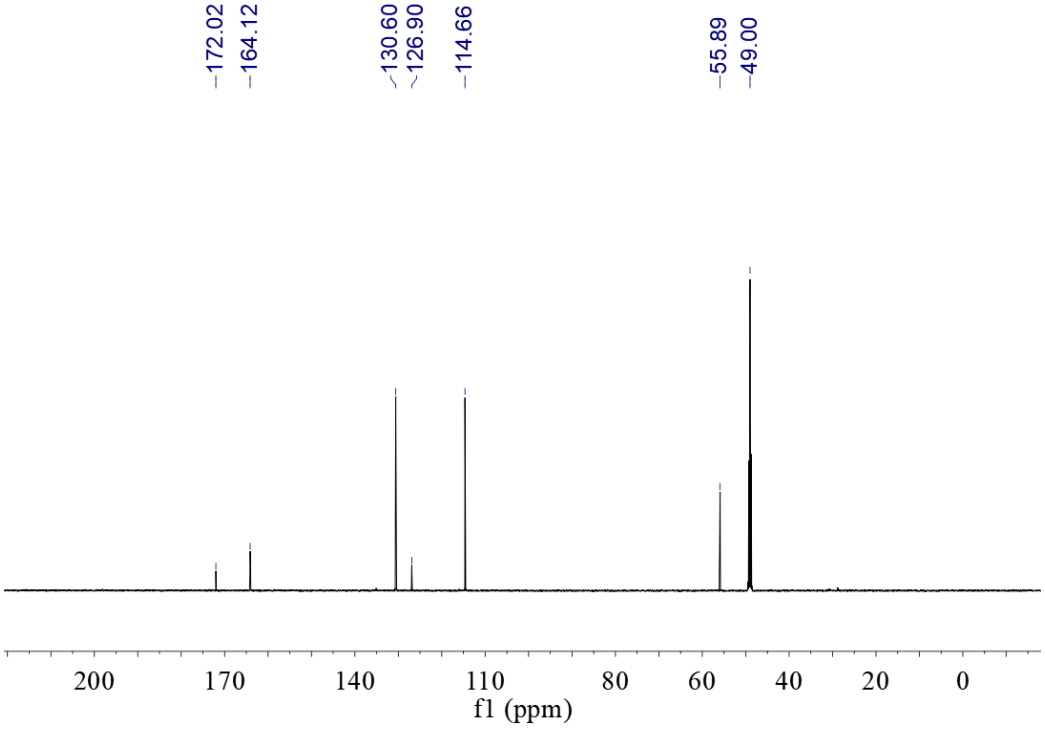
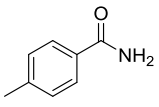



**Fig. S27** $^{13}$C{$^{1}$H} NMR spectrum of the isolated **4e** (151 MHz, $CD_3OD$)



(**4f**)

White solid (130 mg, 96% yield), M.P. 161–163 ℃. $^{1}$H NMR (600 MHz, $CD_3OD$, $\delta$): 7.78 (d, $J$ = 8.4 Hz, 2H, Ar*H*), 7.28 (d, $J$ = 8.4 Hz, 2H, Ar*H*), 2.39 (s, 3H, C$H_3$). $^{13}$C{$^{1}$H} NMR (151 MHz, $CD_3OD$, $\delta$): 172.40 (*C*O), 143.63 (Ar*C*), 132.04 (Ar*C*), 130.09 (Ar*C*), 128.70 (Ar*C*), 21.43 (*C*$H_3$). HRMS (ESI): *m/z* calculated for $C_8H_{10}NO$ $[M + H]^+$ 136.0758; Found 136.0754. These spectral data correspond to previously reported data.[S4]

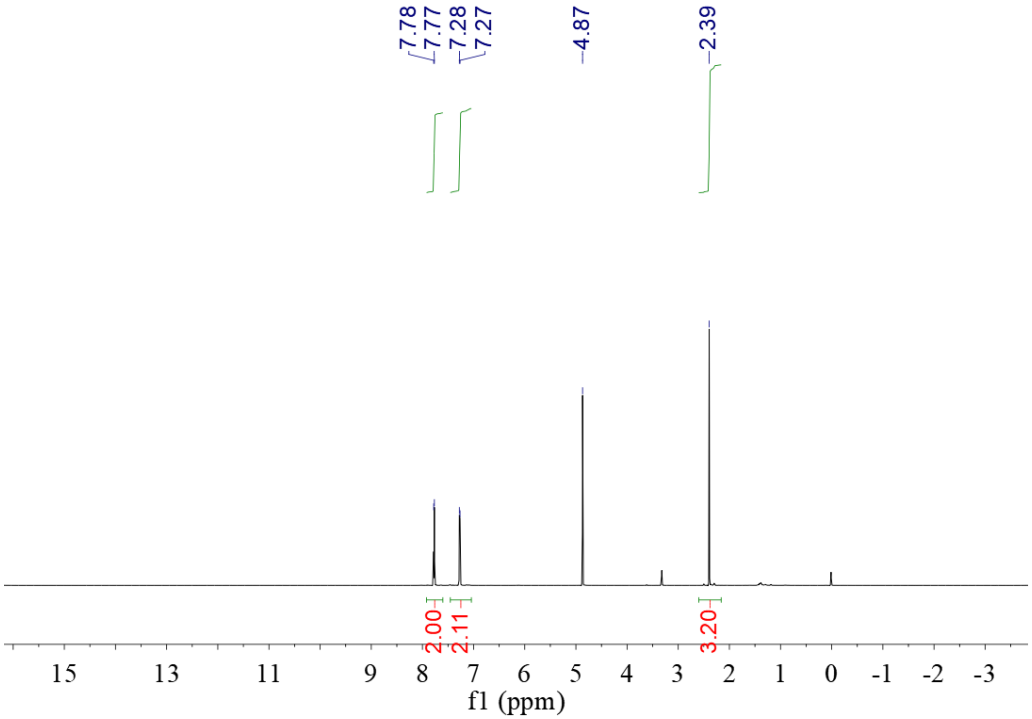



**Fig. S28** $^{1}$H NMR spectrum of the isolated **4f** (600 MHz, $CD_3OD$)

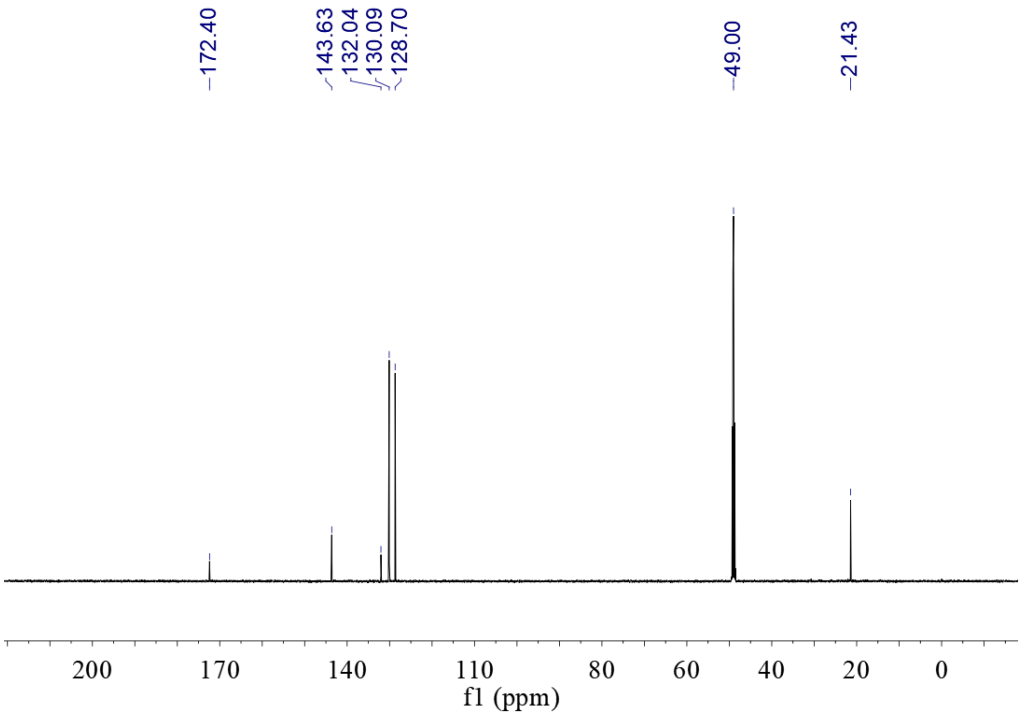
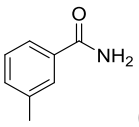



**Fig. S29** $^{13}$C{$^{1}$H} NMR spectrum of the isolated **4f** (151 MHz, $CD_3OD$)



(**4g**)

White solid (130 mg, 96% yield), M.P. 94–96 ℃. $^{1}$H NMR (600 MHz, $CD_3OD$, $\delta$): 7.69 (s, 1H, Ar*H*), 7.66 (d, $J$ = 6.6 Hz, 2H, Ar*H*), 7.31 (m, 2H, Ar*H*), 2.35 (s, 3H, C$H_3$). $^{13}$C{$^{1}$H} NMR (151 MHz, $CD_3OD$, $\delta$): 172.56 (*C*O), 139.39 (Ar*C*), 134.80 (Ar*C*), 133.52 (Ar*C*), 129.36 (Ar*C*), 129.14 (Ar*C*), 125.71 (Ar*C*), 21.34 (*C*$H_3$). HRMS (ESI): *m/z* calculated for $C_8H_{10}NO$ $[M + H]^+$ 136.0757; Found 136.0759. These spectral data correspond to previously reported data.[S7]

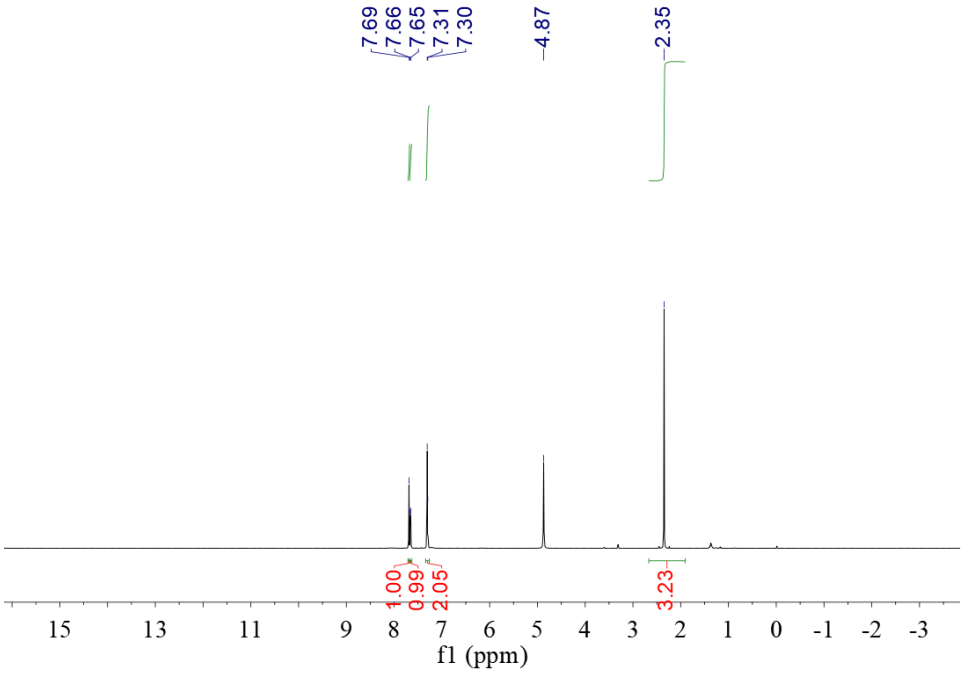



**Fig. S30** $^{1}$H NMR spectrum of the isolated **4g** (600 MHz, $CD_3OD$)

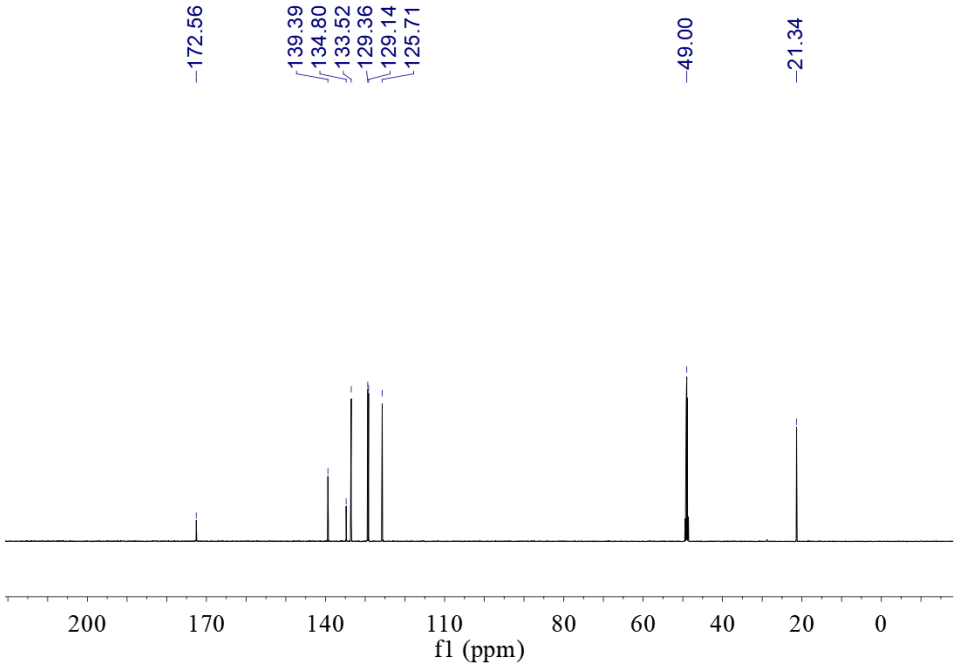
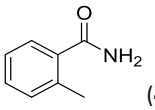



**Fig. S31** $^{13}$C{$^{1}$H} NMR spectrum of the isolated **4g** (151 MHz, $CD_3OD$)



(**4h**)

White solid (34 mg, 26% yield), M.P. 145–148 ℃. $^{1}$H NMR (600 MHz, $CD_3OD$, $\delta$): 7.42 (d, $J$ = 7.8 Hz, 1H, Ar*H*), 7.34 (t, $J$ = 7.8 Hz, 1H, Ar*H*), 7.26 (d, $J$ = 7.8 Hz, 1H, Ar*H*), 7.23 (t, $J$ = 7.8 Hz, 1H, Ar*H*), 2.45 (s, 3H, $CH_3$). $^{13}$C{$^{1}$H} NMR (151 MHz, $CD_3OD$, $\delta$): 175.69 (*C*O), 137.43 (Ar*C*), 136.76 (Ar*C*), 131.81 (Ar*C*), 130.97 (Ar*C*), 128.08 (Ar*C*), 126.69 (Ar*C*), 19.84 ($CH_3$). HRMS (ESI): *m/z* calculated for $C_8H_{10}NO$ $[M + H]^+$ 136.0757; Found 136.0754. These spectral data correspond to previously reported data.[S4]

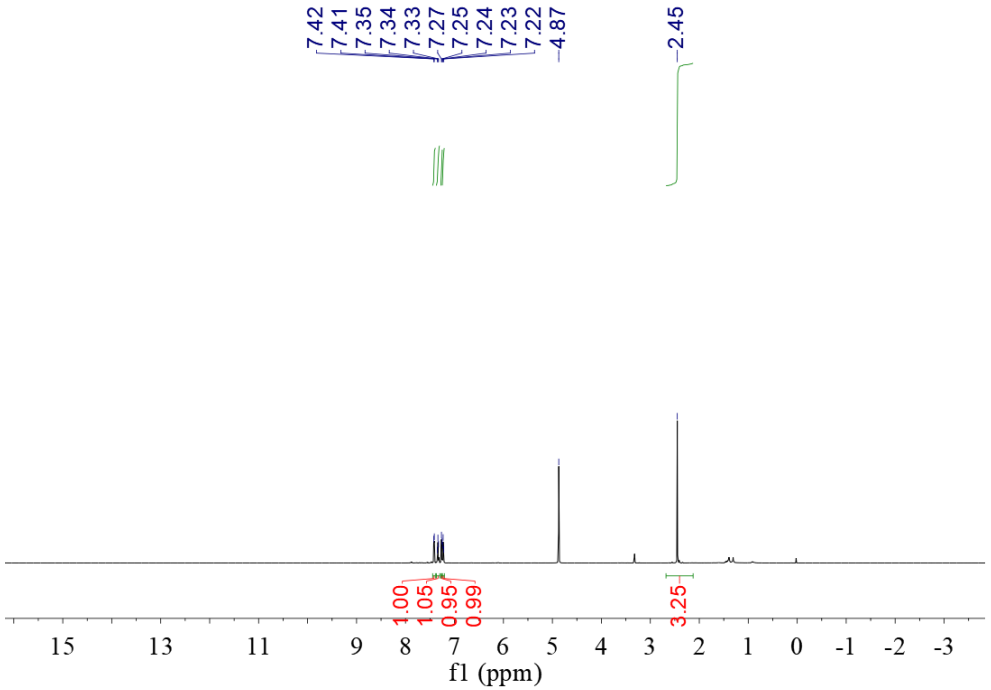



**Fig. S32** $^{1}$H NMR spectrum of the isolated **4h** (600 MHz, $CD_3OD$)

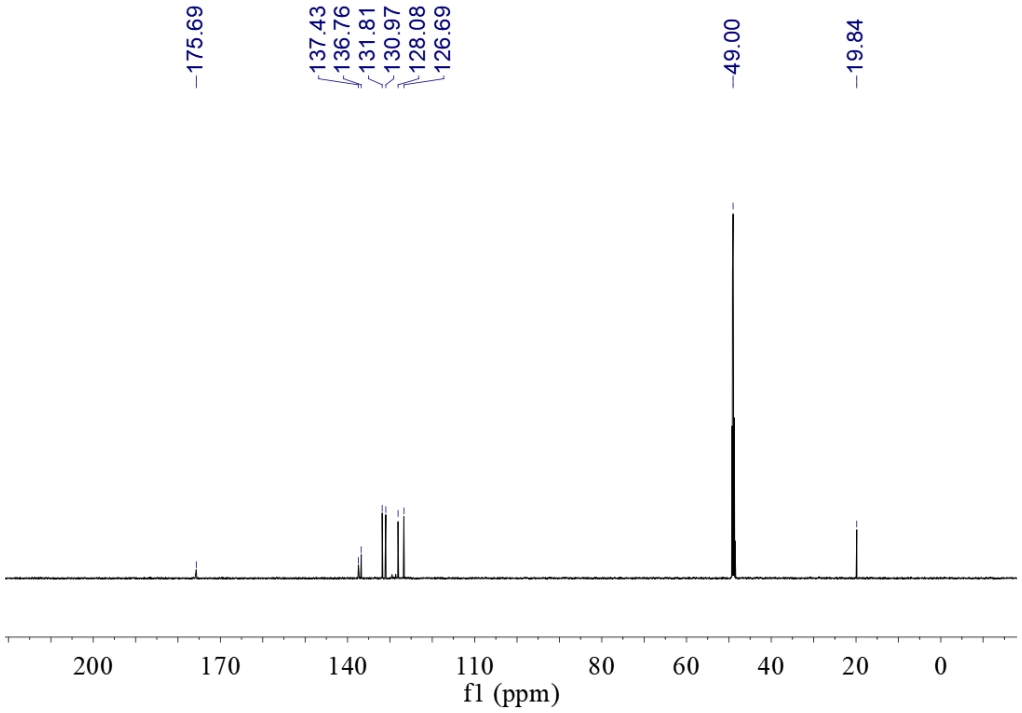
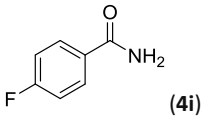



**Fig. S33** $^{13}$C{$^{1}$H} NMR spectrum of the isolated **4h** (151 MHz, $CD_3OD$)



(**4i**)

White solid (131 mg, 94% yield), M.P. 154–156 ℃. $^{1}$H NMR (600 MHz, $CD_3OD$, $\delta$): 7.92–7.94 (m, 2H, Ar*H*), 7.15–7.18 (m, 2H, Ar*H*). $^{13}C\{^{1}H\}$ NMR (151 MHz, $CD_3OD$, $\delta$): 171.14 (*C*O), 166.29 (d, $^{1}J_{C\text{-}F}$ = 251 Hz, Ar*C*), 131.20–131.34 (m, Ar*C*), 116.28 (d, $^{2}J_{C\text{-}F}$ = 22 Hz, Ar*C*). $^{19}F\{^{1}H\}$ NMR (565 MHz, $CD_3OD$, $\delta$): -106.21. HRMS (ESI): *m/z* calculated for $C_7H_7FNO$ $[M + H]^+$ 140.0506; Found 140.0509. These spectral data correspond to previously reported data.[S6]

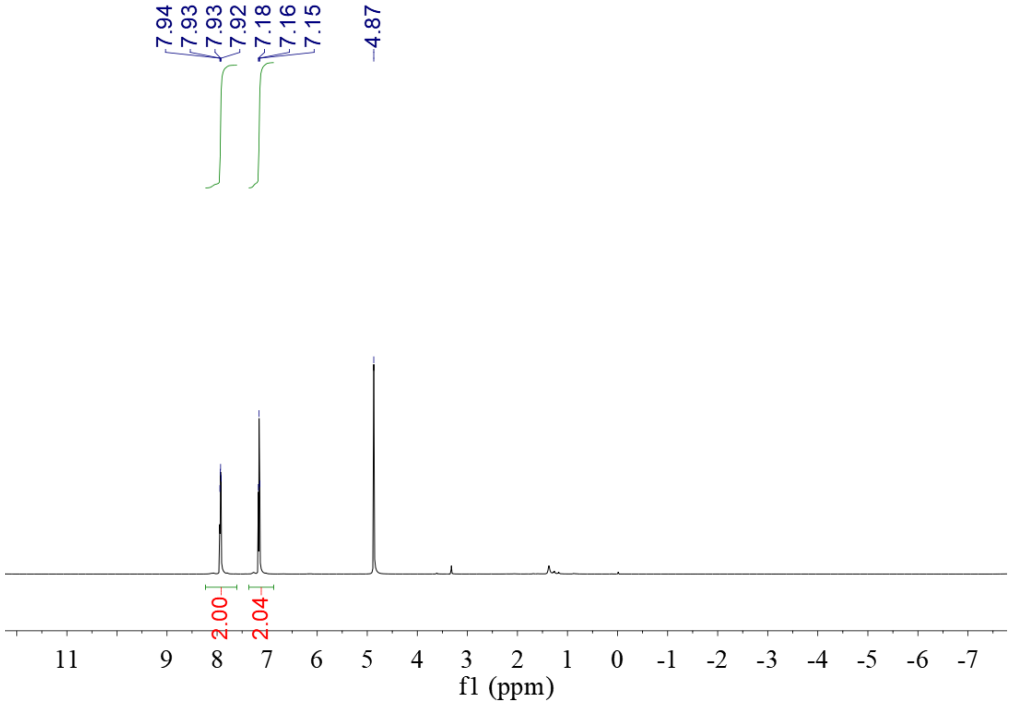



**Fig. S34** $^{1}$H NMR spectrum of the isolated **4i** (600 MHz, $CD_3OD$)

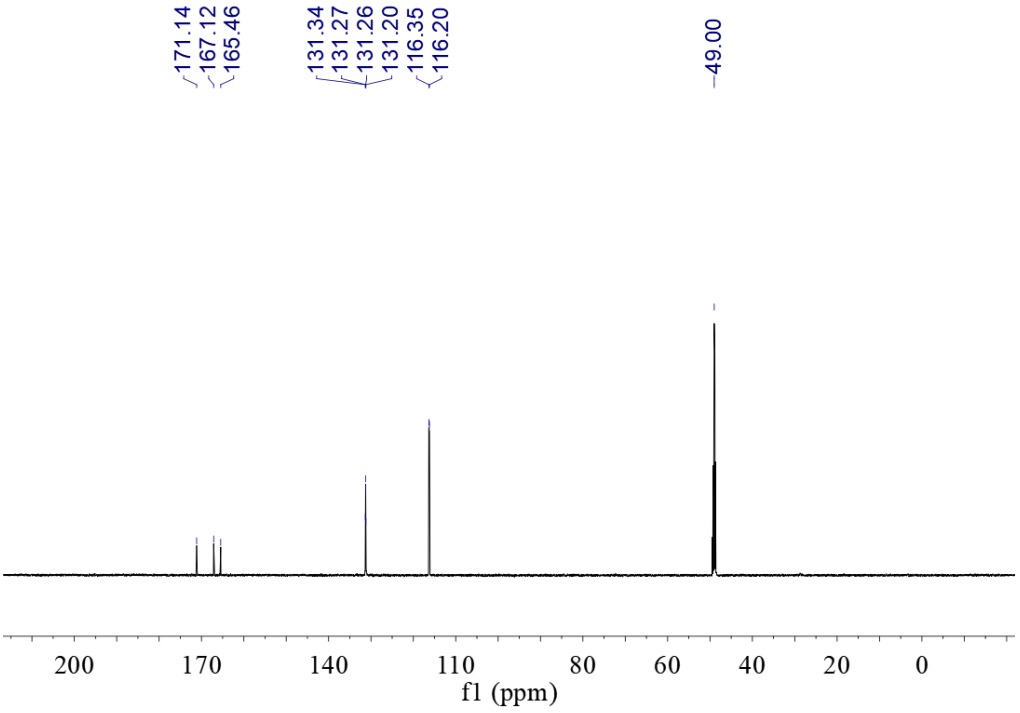
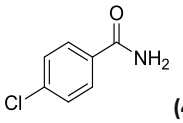



**Fig. S35** $^{13}C\{^{1}H\}$ NMR spectrum of the isolated **4i** (151 MHz, $CD_3OD$)



**(4j)**

White solid (127 mg, 82% yield), M.P. 173–175 ℃. $^{1}$H NMR (600 MHz, $CD_3OD$, $\delta$): 7.86 (d, $J$ = 8.4 Hz, 2H, Ar*H*), 7.46 (d, $J$ = 9 Hz, 2H, Ar*H*). $^{13}C\{^{1}H\}$ NMR (151 MHz, $CD_3OD$, $\delta$): 171.09 (*C*O), 138.96 (Ar*C*), 133.60 (Ar*C*), 130.33 (Ar*C*), 129.64 (Ar*C*). HRMS (ESI): *m/z* calculated for $C_7H_7ClNO$ $[M + H]^+$ 156.0211; Found 156.0210. These spectral data correspond to previously reported data.[S5]

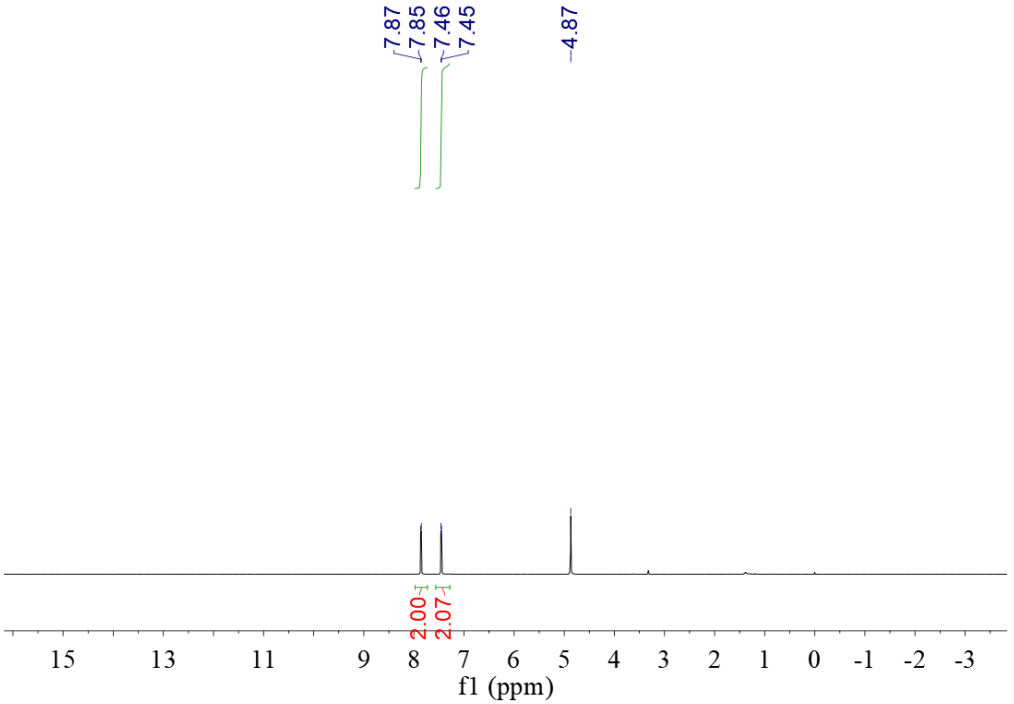



**Fig. S36** $^{1}$H NMR spectrum of the isolated **4j** (600 MHz, $CD_3OD$)

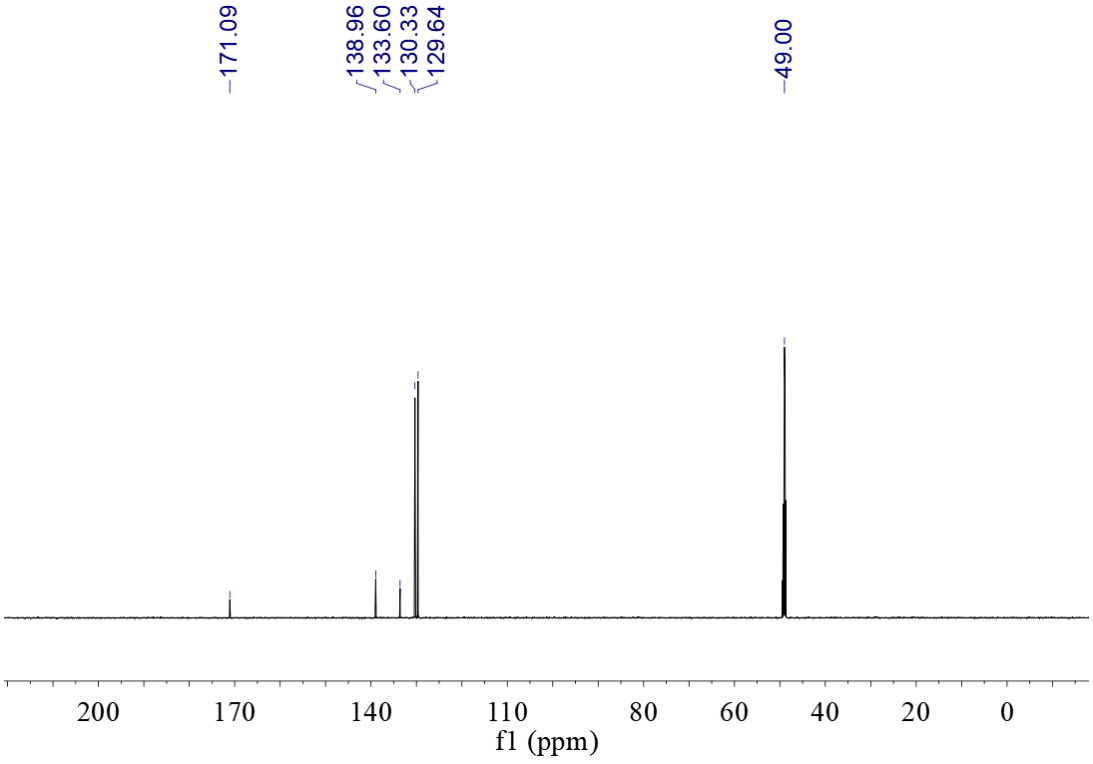
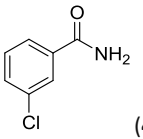



**Fig. S37** $^{13}C\{^{1}H\}$ NMR spectrum of the isolated **4j** (151 MHz, $CD_3OD$)



(**4k**)

White solid (101 mg, 65% yield), M.P. 132–134 ℃. $^{1}$H NMR (600 MHz, $CD_3OD$, $\delta$): 7.90 (s, 1H, Ar*H*), 7.81 (d, *J* = 7.8 Hz, 1H, Ar*H*), 7.55 (d, *J* = 7.8 Hz, 1H, Ar*H*), 7.45 (t, *J* = 7.8 Hz, 1H, Ar*H*). $^{13}$C{$^{1}$H} NMR (151 MHz, $CD_3OD$, $\delta$): 170.66 (*C*O), 136.97 (Ar*C*), 135.56 (Ar*C*), 132.74 (Ar*C*), 131.10 (Ar*C*), 128.78 (Ar*C*), 126.96 (Ar*C*). HRMS (ESI): *m/z* calculated for $C_7H_7ClNO$ $[M + H]^+$ 155.0211; Found 155.0212. These spectral data correspond to previously reported data.[S4]

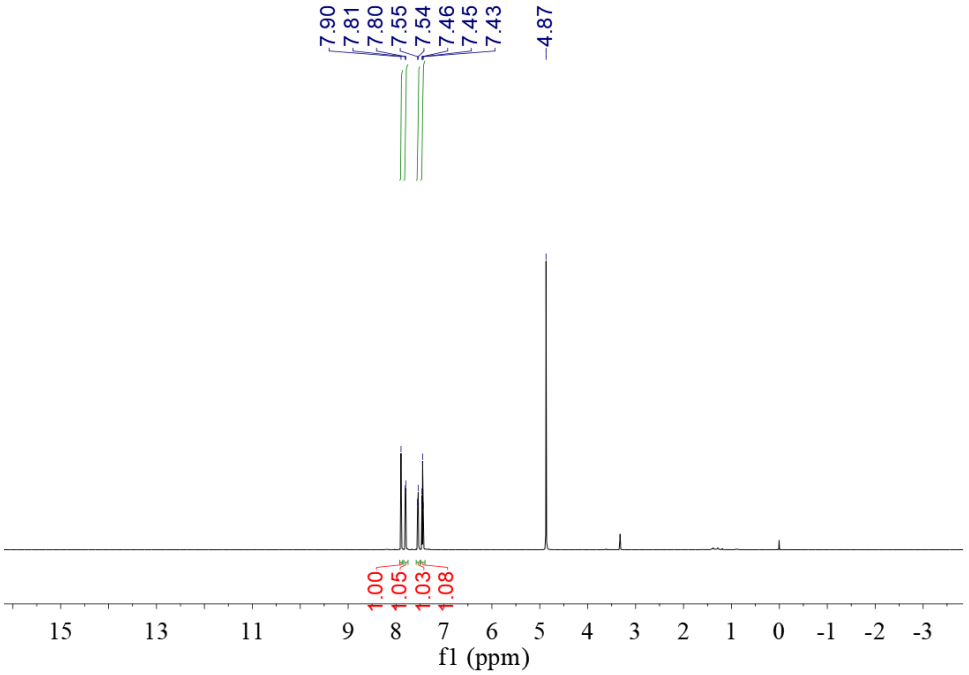



**Fig. S38** $^{1}$H NMR spectrum of the isolated **4k** (600 MHz, $CD_3OD$)

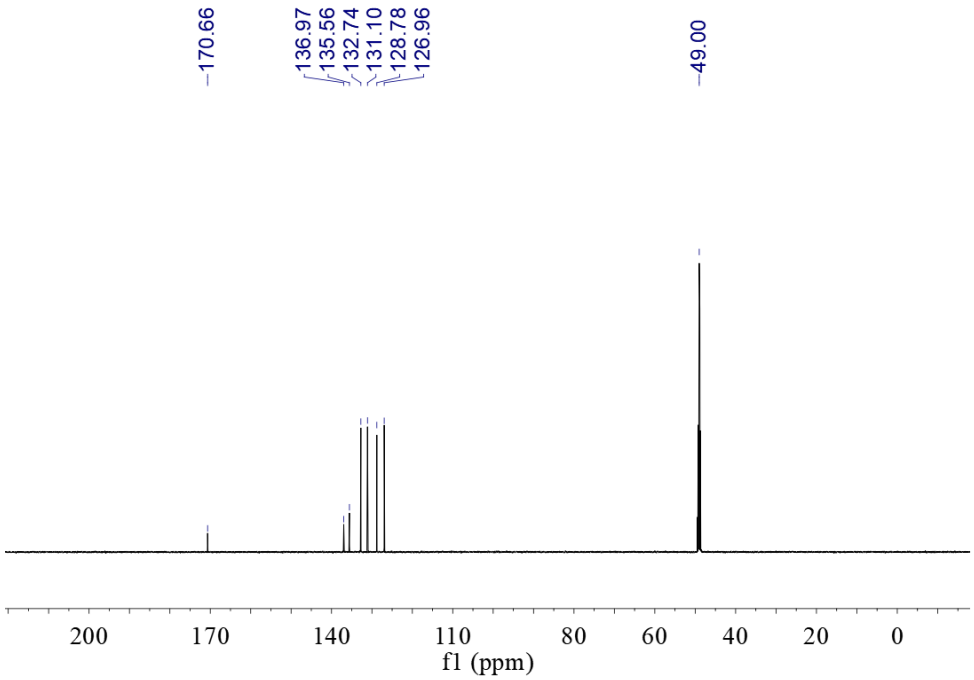
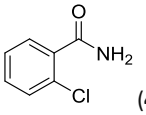



**Fig. S39** $^{13}$C{$^{1}$H} NMR spectrum of the isolated **4k** (151 MHz, $CD_3OD$)



(**4l**)

White solid (127 mg, 82% yield), M.P. 142–145 ℃. $^{1}$H NMR (600 MHz, $CD_3OD$, $\delta$): 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, $CD_3OD$, $\delta$): 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*). HRMS (ESI): *m/z* calculated for $C_7H_7ClNO$ $[M + H]^+$ 156.0211; Found 156.0211. These spectral data correspond to previously reported data.[S4]

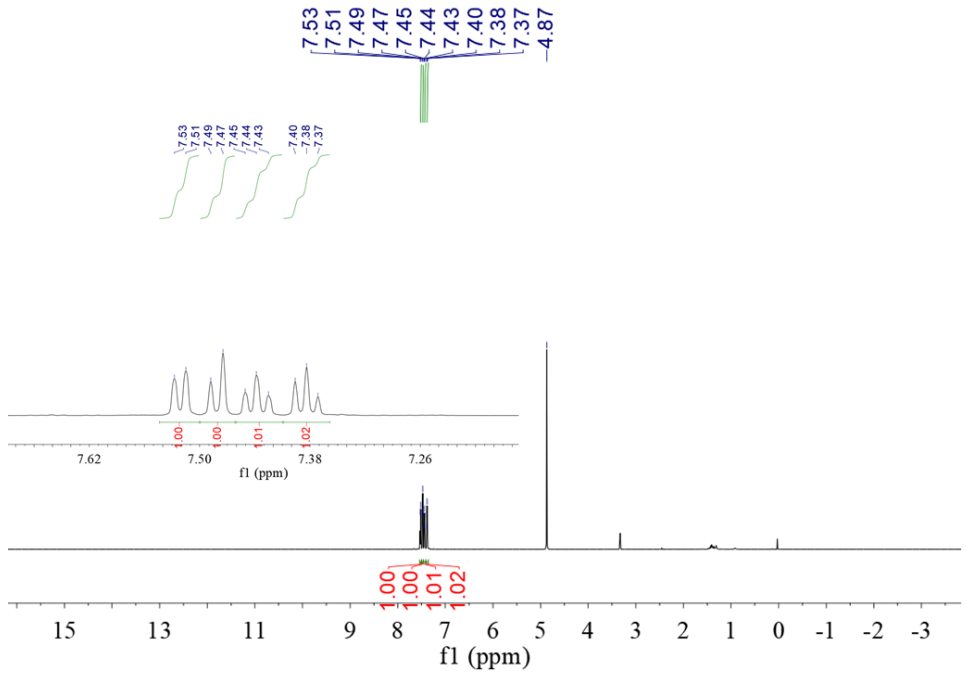



**Fig. S40** $^{1}$H NMR spectrum of the isolated **4l** (600 MHz, $CD_3OD$)

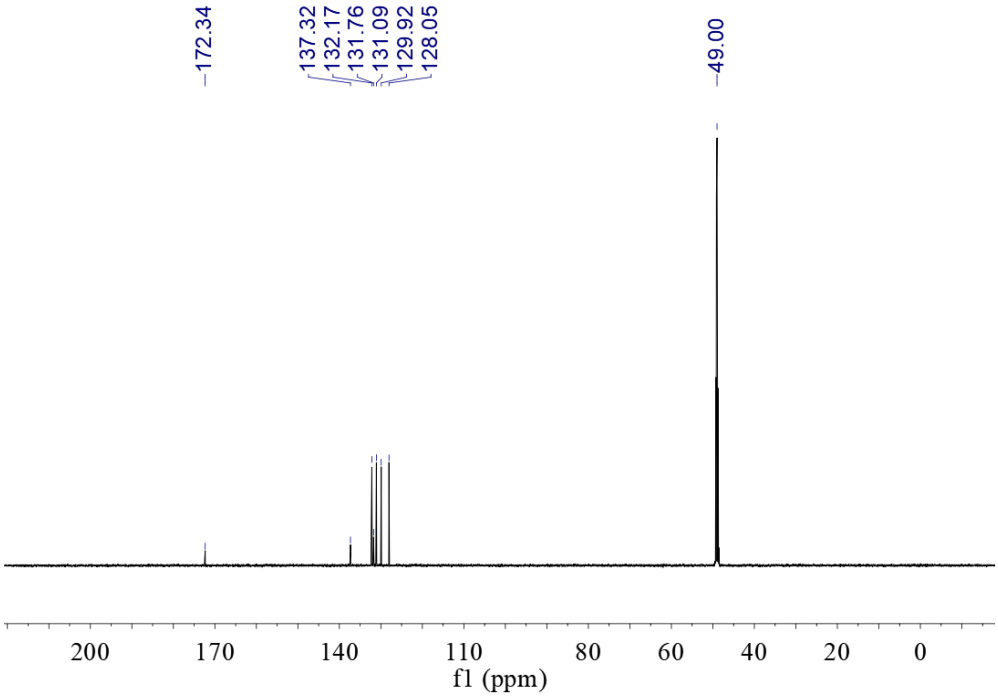
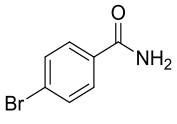



**Fig. S41** $^{13}$C{$^{1}$H} NMR spectrum of the isolated **4l** (151 MHz, $CD_3OD$)




(**4m**)

White solid (192 mg, 96% yield), M.P. 190–193 ℃. $^{1}$H NMR (600 MHz, $CD_3OD$, $\delta$): 7.79 (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, $CD_3OD$, $\delta$): 171.21 (*C*O), 134.11 (Ar*C*), 132.73 (Ar*C*), 130.51 (Ar*C*), 127.35 (Ar*C*). HRMS (ESI): *m/z* calculated for $C_7H_7BrNO$ $[M + H]^+$ 199.9706; Found 199.9701. These spectral data correspond to previously reported data.[S4]

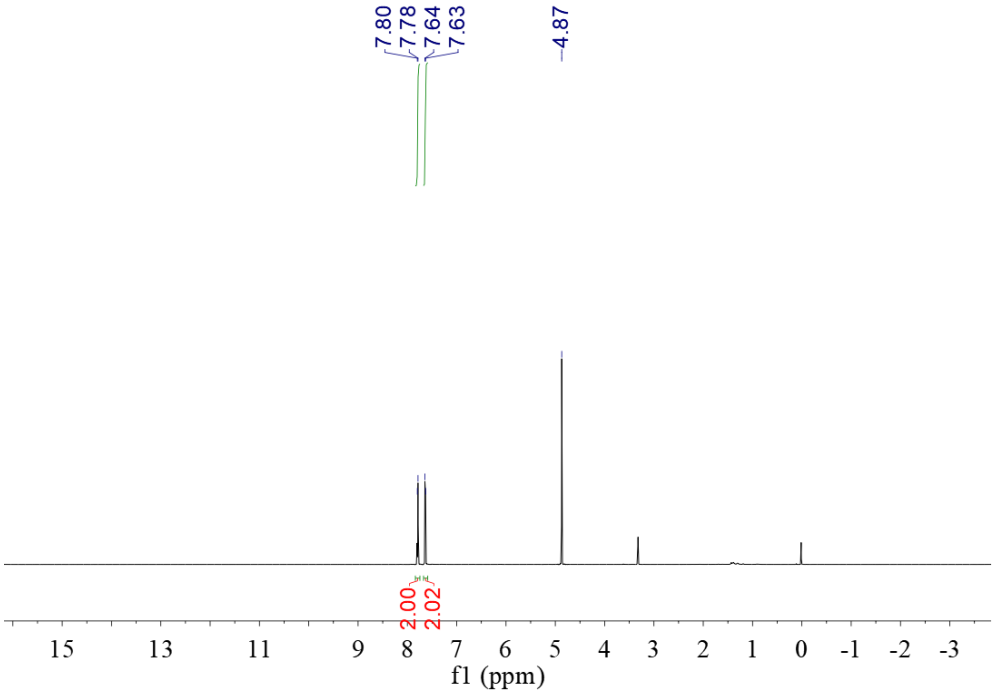



**Fig. S42** $^{1}$H NMR spectrum of the isolated **4m** (600 MHz, $CD_3OD$)

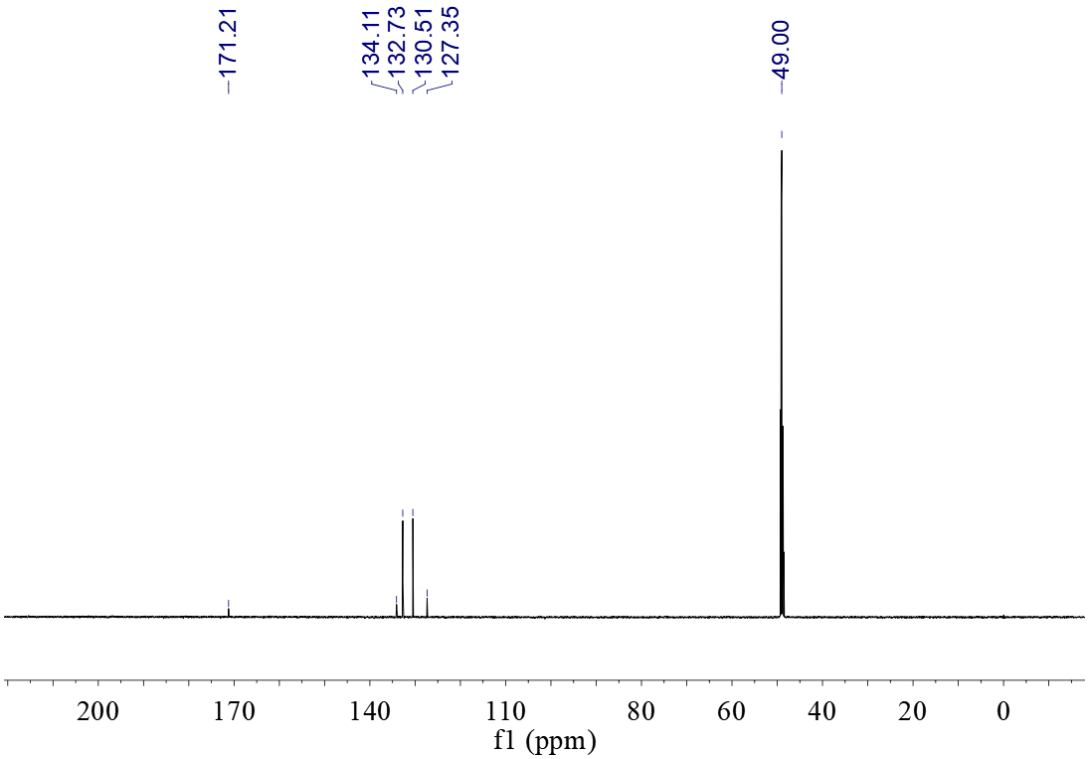
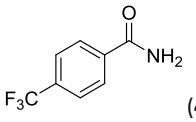



**Fig. S43** $^{13}C\{^{1}H\}$ NMR spectrum of the isolated **4m** (151 MHz, $CD_3OD$)



(**4n**)

White solid (166 mg, 88% yield), M.P. 183–186 ℃. $^{1}$H NMR (600 MHz, $CD_3OD$, $\delta$): 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, $CD_3OD$, $\delta$): 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, $CD_3OD$, $\delta$): -64.48. HRMS (ESI): *m/z* calculated for $C_8H_7F_3NO$ $[M + H]^+$ 190.0474; Found 190.0467. These spectral data correspond to previously reported data.[S5]

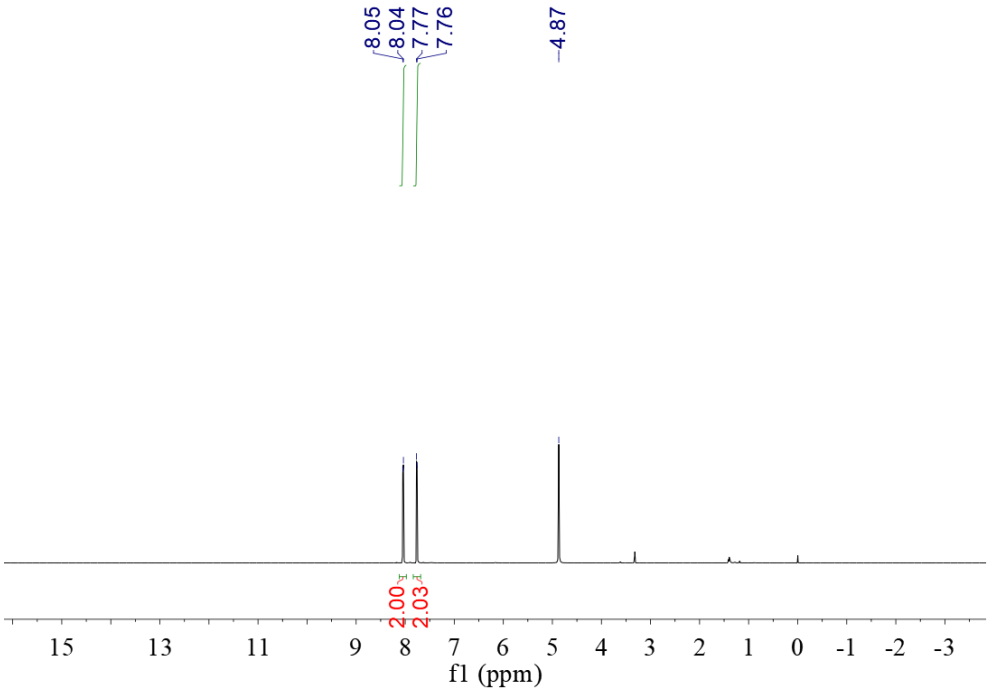



**Fig. S44** $^{1}$H NMR spectrum of the isolated **4n** (600 MHz, $CD_3OD$)

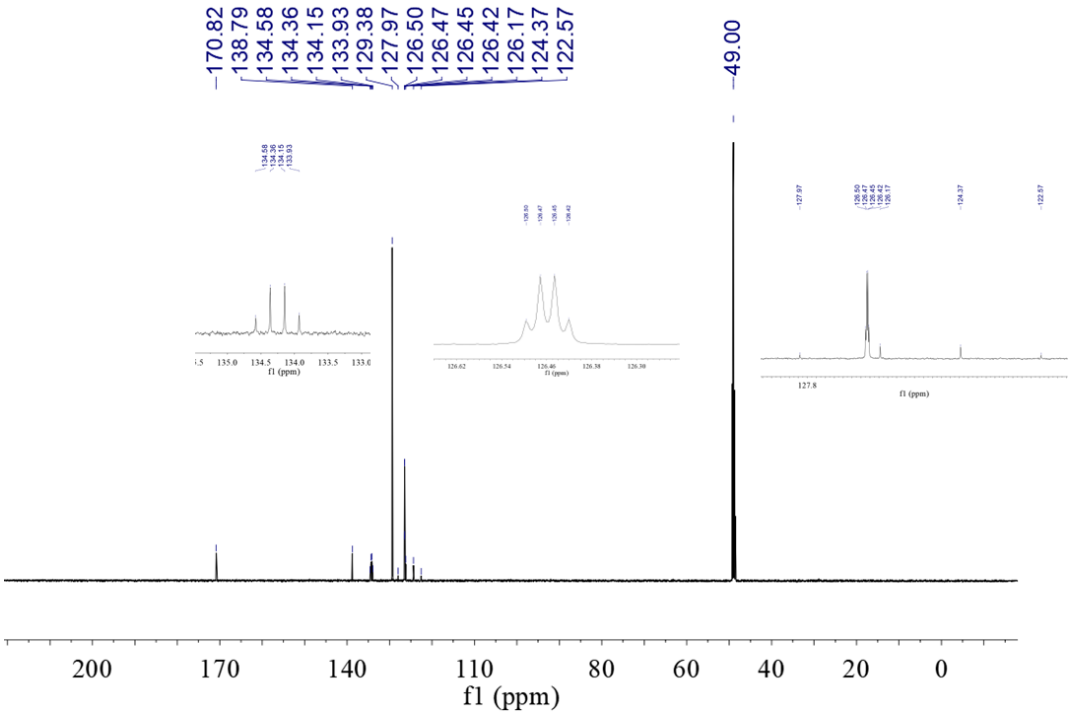
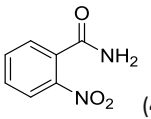



**Fig. S45** $^{13}C\{^{1}H\}$ NMR spectrum of the isolated **4n** (151 MHz, $CD_3OD$)



(**4o**)

White solid (121 mg, 73% yield), M.P. 175–178 ℃. $^{1}$H NMR (600 MHz, $CD_3OD$, $\delta$): 8.09 (dd, $J$ = 8.2, 1.0 Hz, 1H, Ar*H*), 7.78 (td, $J$ = 7.5, 1.2 Hz, 1H, Ar*H*), 7.70 (td, $J$ = 8.1, 1.4 Hz, 1H, Ar*H*), 7.65 (dd, $J$ = 7.5, 1.4 Hz, 1H, Ar*H*). $^{13}$C{$^{1}$H} NMR (151 MHz, $CD_3OD$, $\delta$): 171.78 (*C*O), 148.18 (Ar*C*), 134.72 (Ar*C*), 138.84 (Ar*C*), 131.81 (Ar*C*), 129.94 (Ar*C*), 125.40 (Ar*C*). HRMS (ESI): *m/z* calculated for $C_7H_7N_2O_3$ $[M + H]^+$ 168.0529; Found 168.0526. These spectral data correspond to previously reported data.[S6]

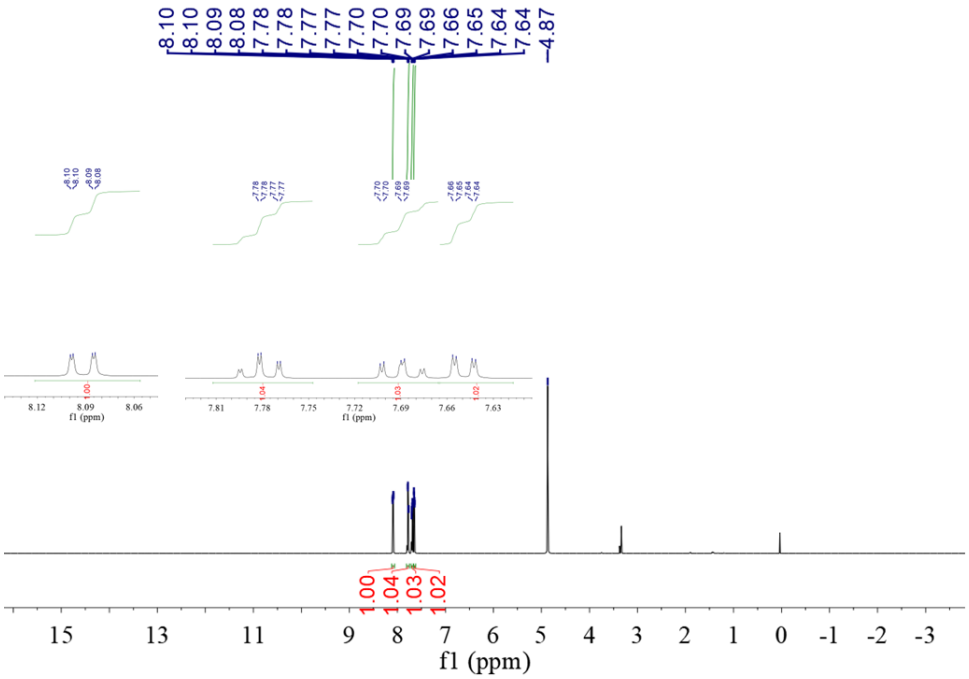



**Fig. S46** $^{1}$H NMR spectrum of the isolated **4o** (600 MHz, $CD_3OD$)

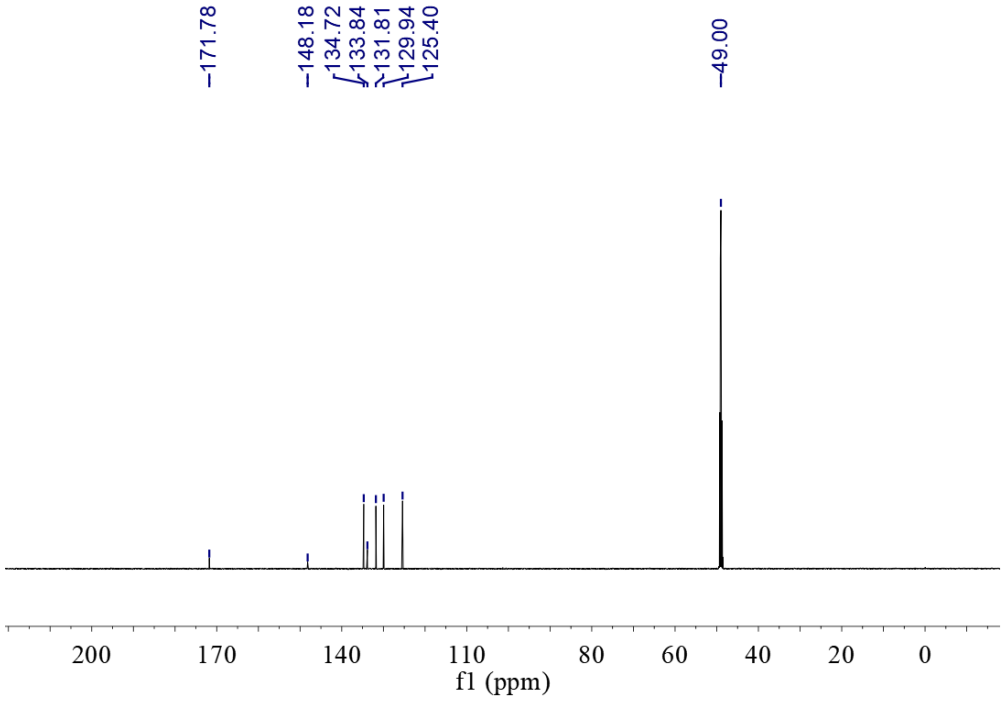
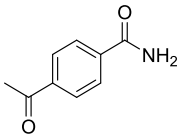



**Fig. S47** $^{13}$C{$^{1}$H} NMR spectrum of the isolated **4o** (151 MHz, $CD_3OD$)



(**4p**)

Yellow solid (155 mg, 95% yield), M.P. 188–192 ℃. $^{1}$H NMR (600 MHz, DMSO-$d_6$, $\delta$): 8.15 (s, br, 1H, N*H*), 7.98–8.02 (m, 4H, Ar*H*), 7.57 ppm (s, br, 1H, N*H*), 2.61 (s, 3H, C$H_3$). $^{13}$C{$^{1}$H} NMR (151 MHz, DMSO-$d_6$, $\delta$): 197.74 ($NH_2CO$), 167.17 ($CH_3CO$), 138.68 (Ar*C*), 138.12 (Ar*C*), 128.10 (Ar*C*), 127.79 (Ar*C*), 26.95 ($CH_3$). HRMS (ESI): *m/z* calculated for $C_9H_{10}NO_2$ [M + H]$^+$ 164.0706; Found 164.0707. These spectral data correspond to previously reported data.[S4]

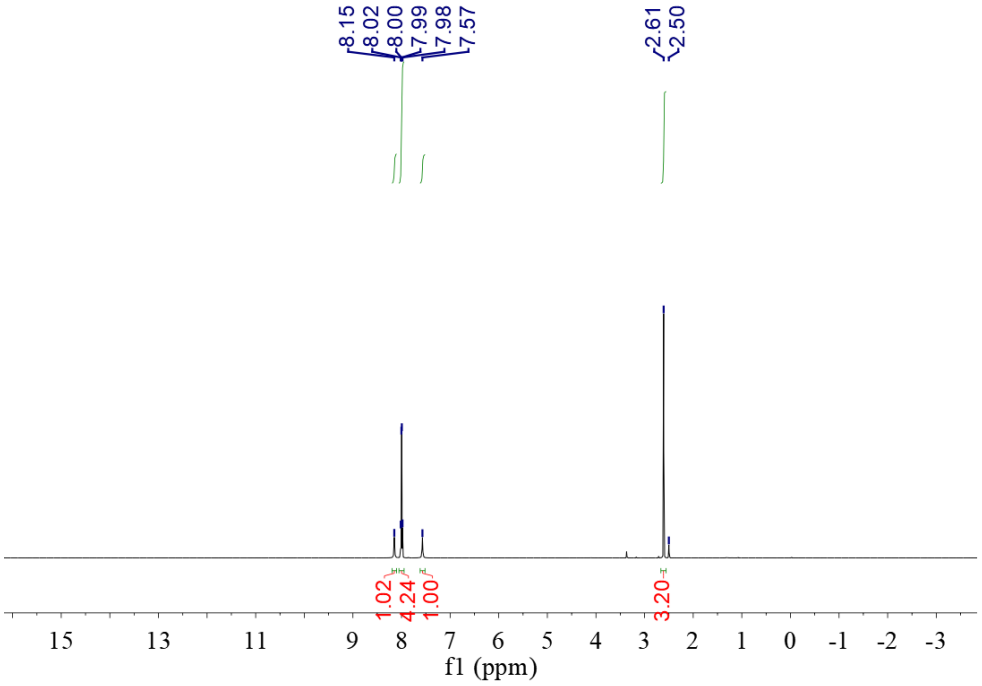



**Fig. S48** $^{1}$H NMR spectrum of the isolated **4p** (600 MHz, DMSO-$d_6$)

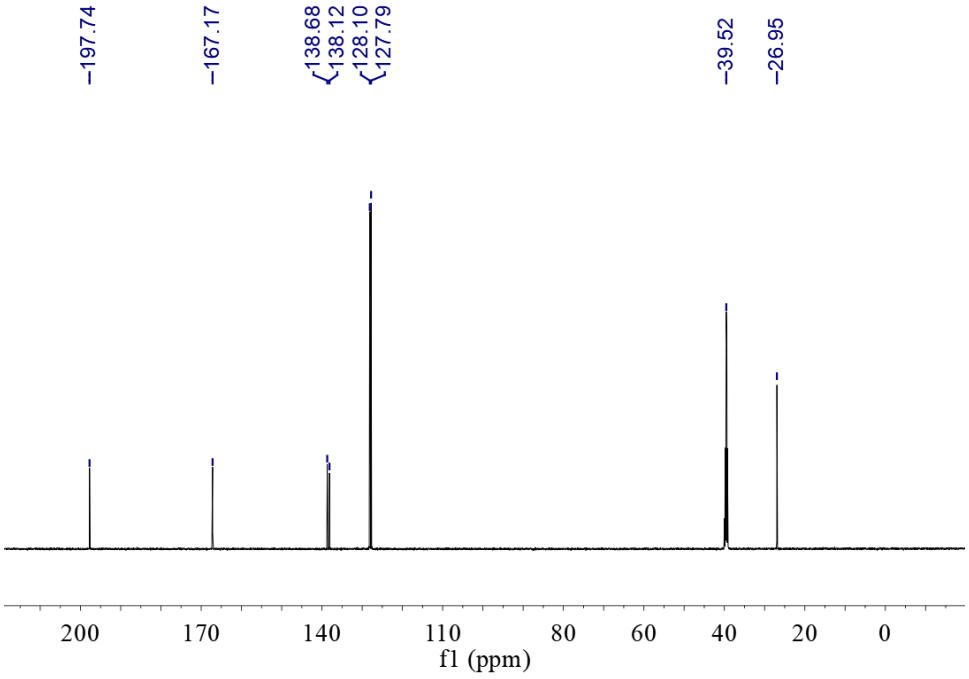
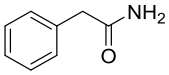



**Fig. S49** $^{13}$C{$^{1}$H} NMR spectrum of the isolated **4p** (151 MHz, DMSO-$d_6$)




(**4q**)

White solid (126 mg, 93% yield), M.P. 156–158 ℃. $^{1}$H NMR (600 MHz, $CD_3OD$, $\delta$): 7.31–7.32 (m, 4H, Ar*H*), 7.24–7.26 (m, 1H, Ar*H*), 3.52 (s, 2H, C$H_2$). $^{13}$C{$^{1}$H} NMR (151 MHz, $CD_3OD$, $\delta$): 176.96 (*C*O), 136.91 (Ar*C*), 130.14 (Ar*C*), 129.56 (Ar*C*), 127.89 (Ar*C*), 43.41 (*C*$H_2$). HRMS (ESI): *m/z* calculated for $C_8H_{10}NO$ $[M + H]^+$ 136.0757; Found 136.0756. These spectral data correspond to previously reported data.[S5]

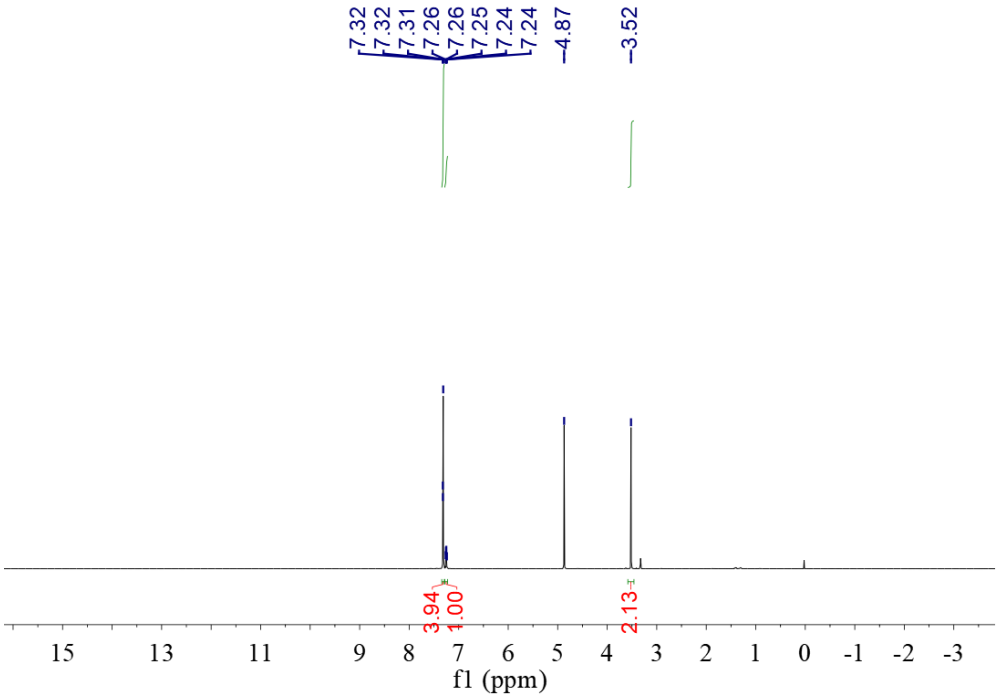



**Fig. S50** $^{1}$H NMR spectrum of the isolated **4q** (600 MHz, $CD_3OD$)

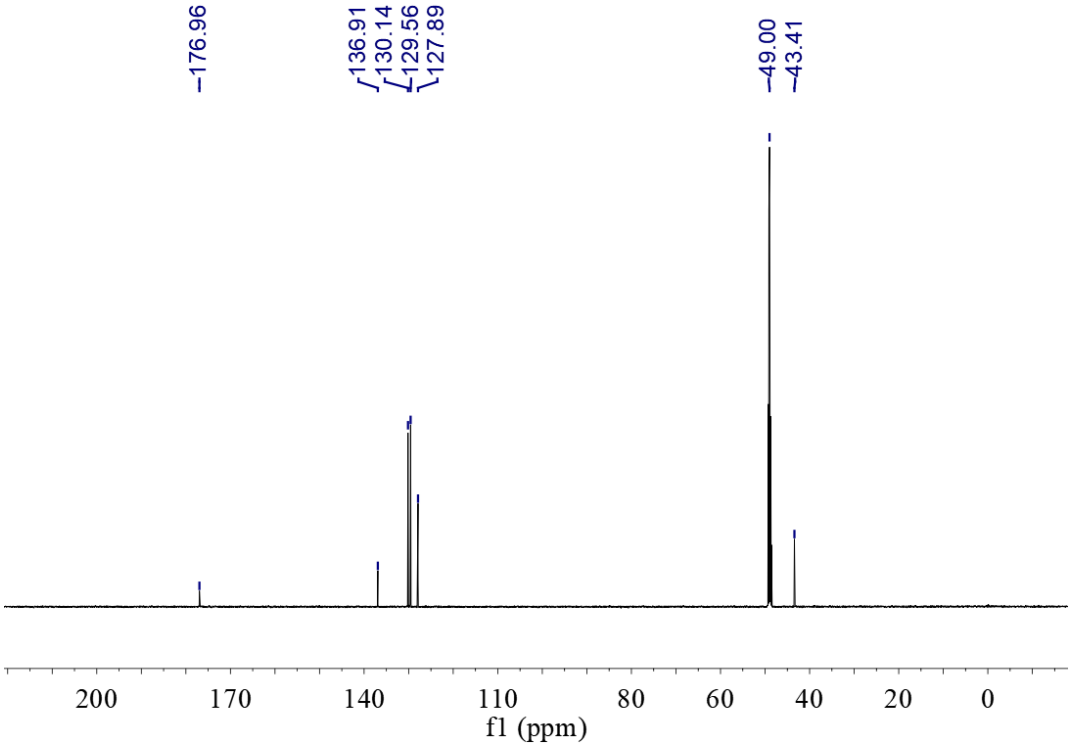
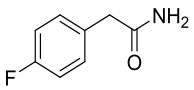



**Fig. S51** $^{13}$C{$^{1}$H} NMR spectrum of the isolated **4q** (151 MHz, $CD_3OD$)



(**4r**)

White solid (150 mg, 98% yield), M.P. 158–159 ℃. $^{1}$H NMR (600 MHz, $CD_3OD$, $\delta$): 7.30–7.33 (m, 2H, Ar*H*), 7.03–7.05 (m, 2H, Ar*H*), 3.50 (s, 2H, C$H_2$). $^{13}$C{$^{1}$H} NMR (151 MHz, $CD_3OD$, $\delta$): 176.69 (*C*O), 163.31 (d, $^{1}J_{C\text{-}F}$ = 243.7 Hz, Ar*C*), 132.89 (d, $^{3}J_{C\text{-}F}$ = 3.2 Hz, Ar*C*), 131.91 (d, $^{4}J_{C\text{-}F}$ = 3.2 Hz, Ar*C*), 116.12 (d, $^{2}J_{C\text{-}F}$ = 21.6 Hz, Ar*C*), 42.39 (*C*$H_2$). $^{19}$F{$^{1}$H} NMR (565 MHz, $CD_3OD$, $\delta$): -118.33. HRMS (ESI): *m/z* calculated for $C_8H_9NO$ $[M + H]^+$ 154.0603; Found 154.0605. These spectral data correspond to previously reported data.[S7]

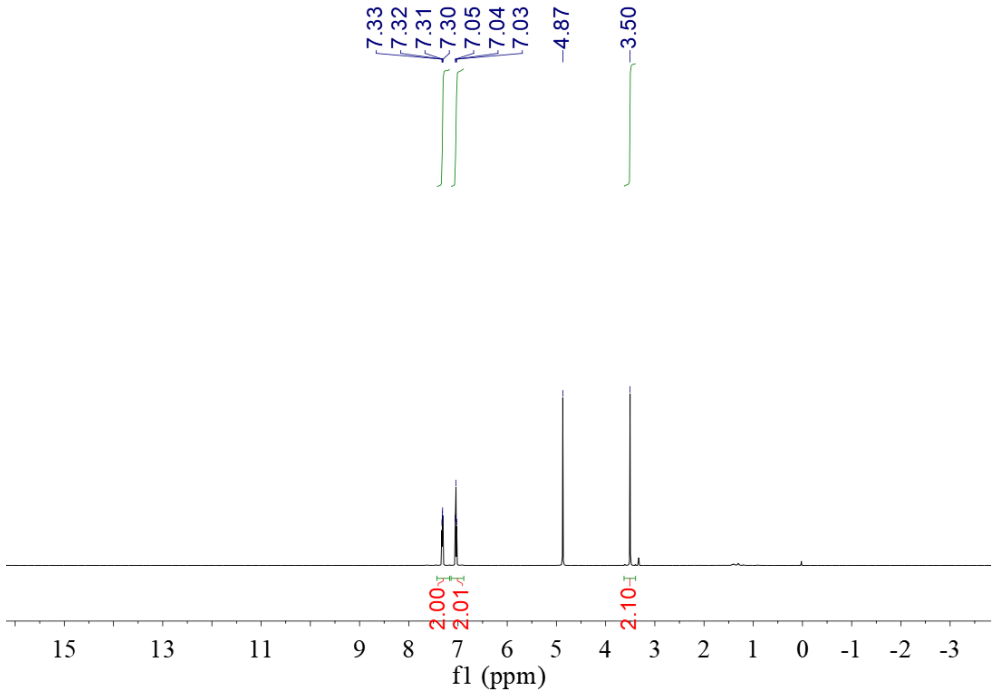



**Fig. S52** $^{1}$H NMR spectrum of the isolated **4r** (600 MHz, $CD_3OD$)

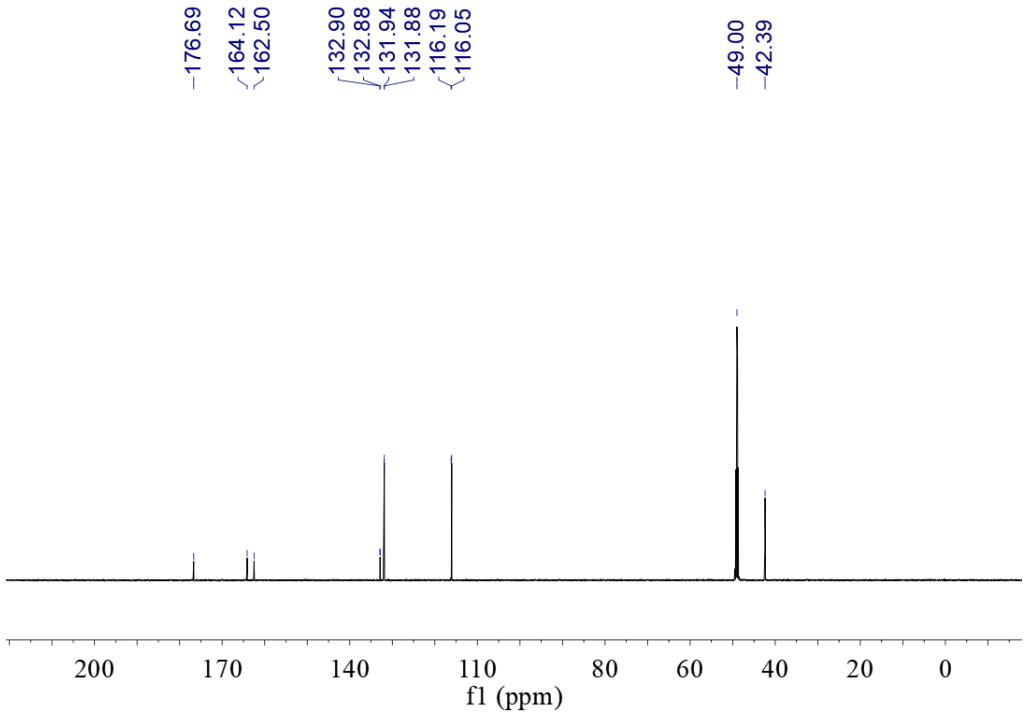
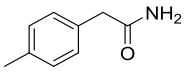



**Fig. S53** $^{13}$C{$^{1}$H} NMR spectrum of the isolated **4r** (151 MHz, $CD_3OD$)




(**4s**)

White solid (128 mg, 86% yield), M.P. 184–186 ℃. $^{1}$H NMR (600 MHz, $CD_3OD$, $\delta$): 7.19 (d, $J$ = 7.8 Hz, 2H, Ar*H*), 7.13 (d, $J$ = 7.8 Hz, 2H, Ar*H*), 3.47 (s, 2H, C$H_2$), 2.32 (s, 3H, C$H_3$). $^{13}$C{$^{1}$H} NMR (151 MHz, $CD_3OD$, $\delta$): 177.23 (*C*O), 137.58 (Ar*C*), 133.79 (Ar*C*), 130.18 (Ar*C*), 130.03 (Ar*C*), 43.02 (*C*$H_2$), 21.08 (*C*$H_3$). HRMS (ESI): *m/z* calculated for $C_9H_{12}NO$ $[M + H]^+$ 150.0913; Found 150.0910. These spectral data correspond to previously reported data.[S8]

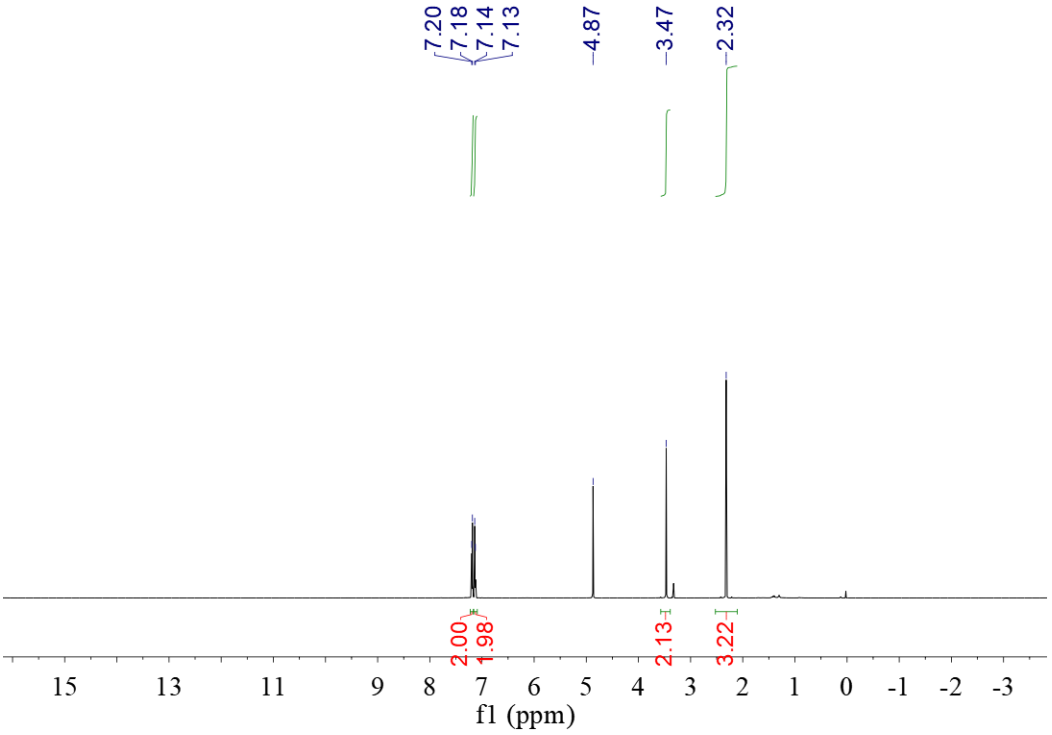



**Fig. S54** $^{1}$H NMR spectrum of the isolated **4s** (600 MHz, $CD_3OD$)

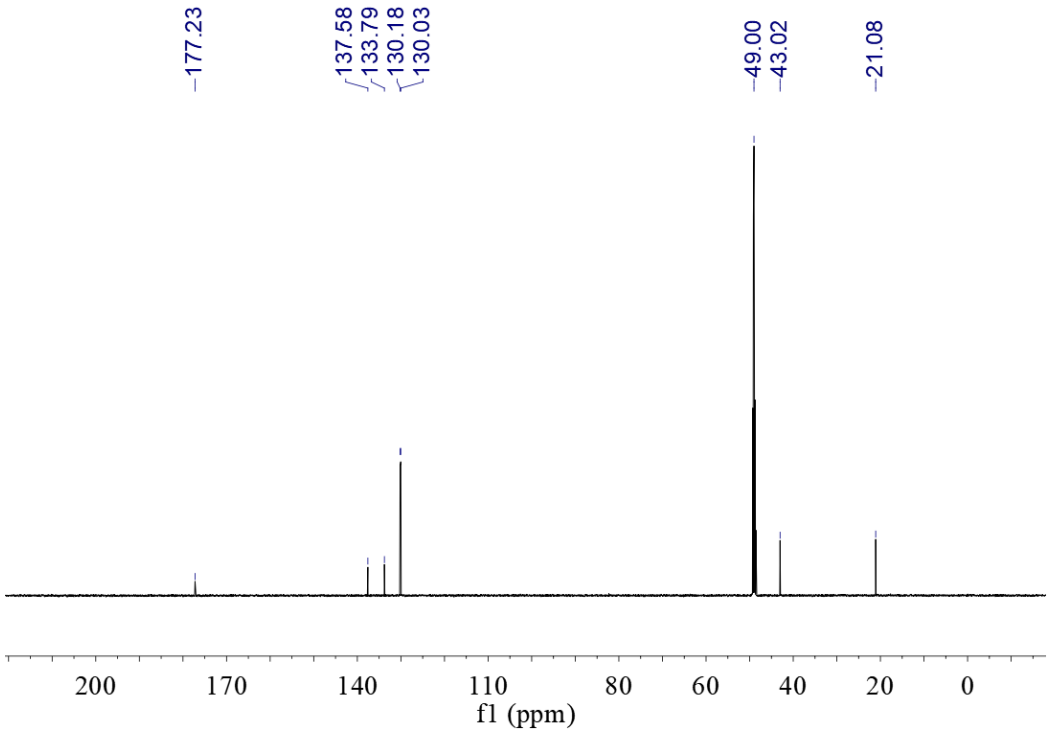
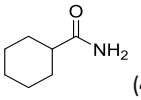



**Fig. S55** $^{13}$C{$^{1}$H} NMR spectrum of the isolated **4s** (151 MHz, $CD_3OD$)



(**4t**)

White solid (106 mg, 83% yield), M.P. 184–185 ℃. $^{1}$H NMR (600 MHz, $CD_3OD$, $\delta$): 2.22 (tt, $J$ = 12.0, 3.4 Hz, 1H, CH), 1.91–1.75 (m, 4H, C$H_2$), 1.71 (dd, $J$ = 7.6, 6.0 Hz, 1H, C$H_2$), 1.45 (dt, $J$ = 21.6, 6.3 Hz, 2H, C$H_2$), 1.38–1.29 (m, 2H, C$H_2$), 1.26 (ddt, $J$ = 12.6, 6.4, 2.9 Hz, 1H, C$H_2$). $^{13}$C{$^{1}$H} NMR (151 MHz, $CD_3OD$, $\delta$): 182.24 (*C*O), 45.92 (*C*H), 30.74 (*C*$H_2$), 26.91 (*C*$H_2$), 26.81 (*C*$H_2$). HRMS (ESI): *m/z* calculated for $C_7H_{14}NO$ $[M + H]^+$ 127.0992; Found 127.0993. These spectral data correspond to previously reported data.[S5]

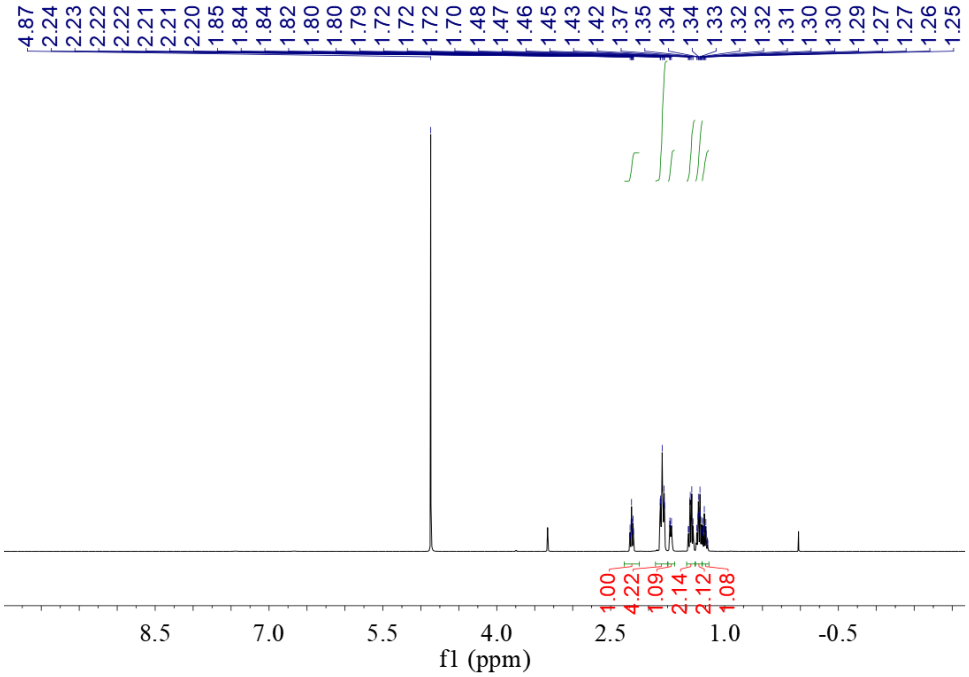



**Fig. S56** $^{1}$H NMR spectrum of the isolated **4t** (600 MHz, $CD_3OD$)

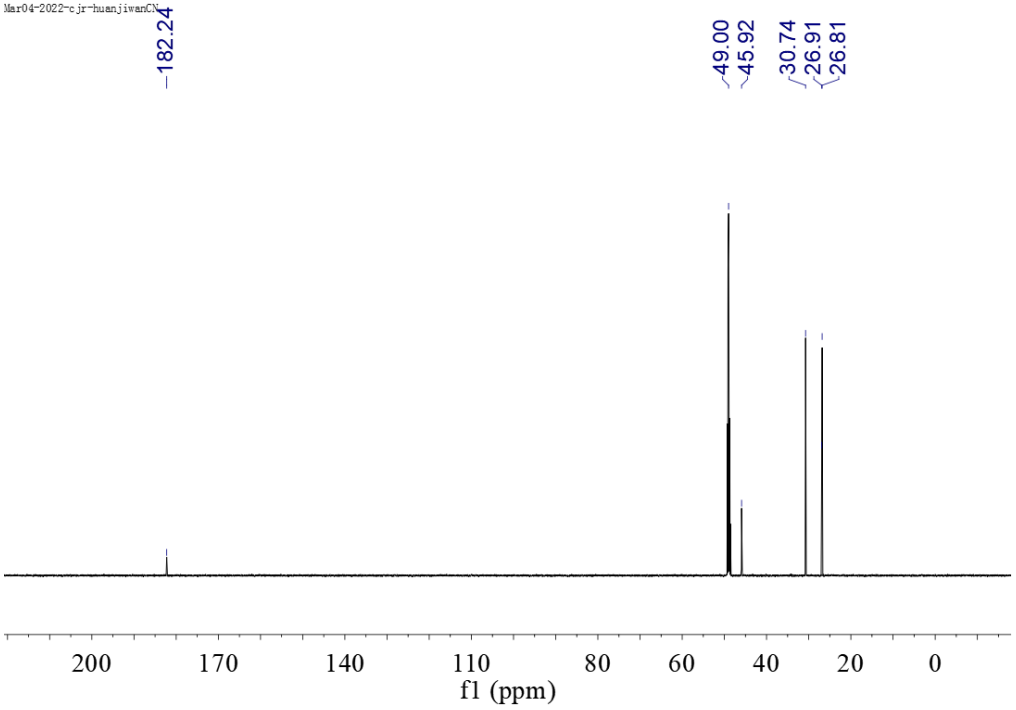
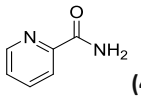



**Fig. S57** $^{13}$C{$^{1}$H} NMR spectrum of the isolated **4t** (151 MHz, $CD_3OD$)



**(4u)**

White solid (94 mg, 77% yield), M.P. 109–110 ℃. $^{1}$H NMR (600 MHz, $CD_3OD$, $\delta$): 8.64 (d, $J$ = 4.7 Hz, 1H), 8.12 (d, $J$ = 7.8 Hz, 1H), 7.96 (t, $J$ = 7.7 Hz, 1H), 7.61–7.49 (m, 1H). $^{13}$C{$^{1}$H} NMR (151 MHz, $CD_3OD$, $\delta$): 169.28 (*C*O), 151.03 (Ar*C*), 149.83 (Ar*C*), 138.66 (Ar*C*), 127.80 (Ar*C*), 123.24 (Ar*C*). HRMS (ESI): *m/z* calculated for $C_6H_7N_2O$ [M + H]$^{+}$ 123.0553; Found 123.0555. These spectral data correspond to previously reported data.[S4]

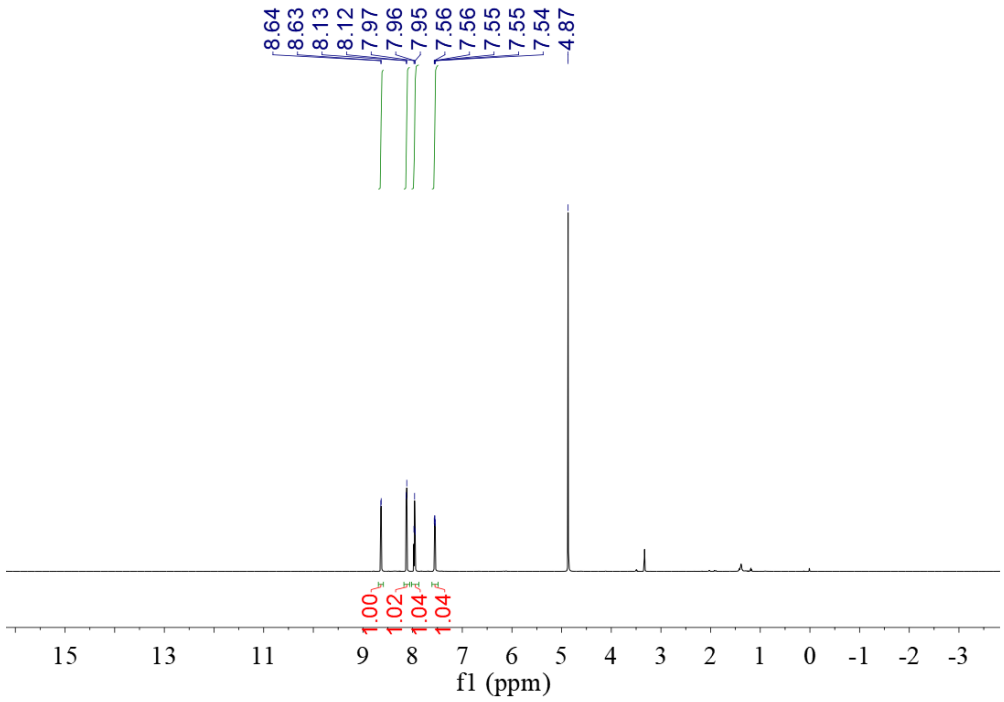



**Fig. S58** $^{1}$H NMR spectrum of the isolated **4u** (600 MHz, $CD_3OD$)

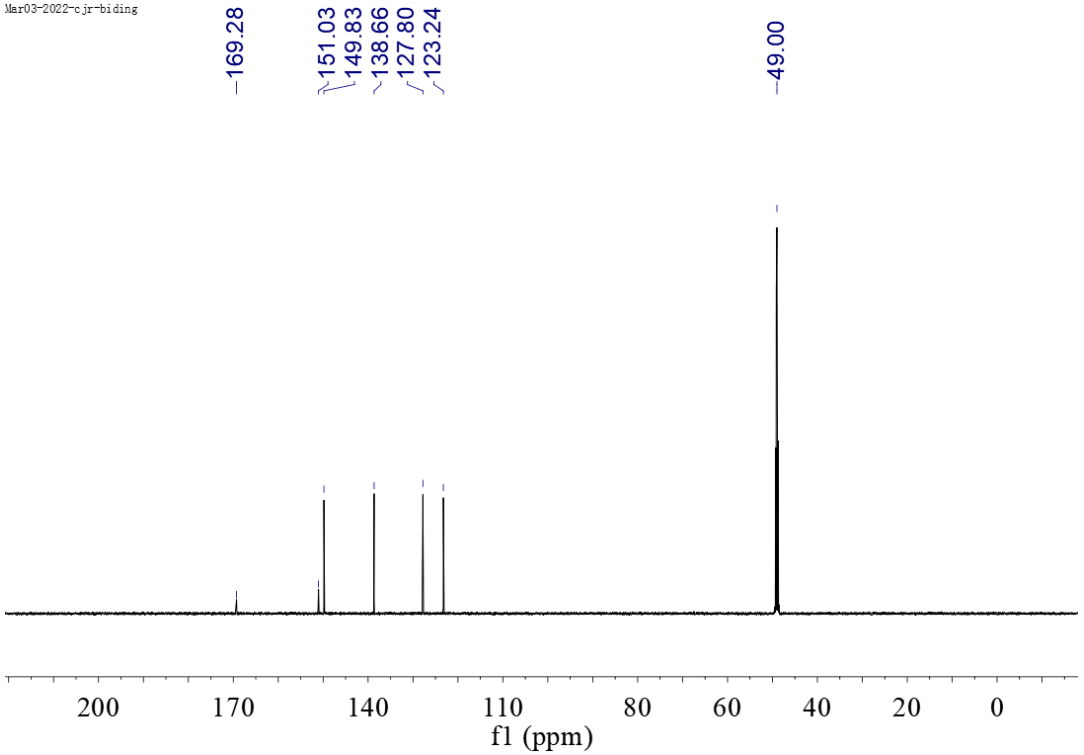
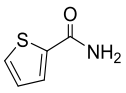



**Fig. S59** $^{13}$C{$^{1}$H} NMR spectrum of the isolated **4u** (151 MHz, $CD_3OD$)



(**4v**)

White solid (120 mg, 94% yield), M.P. 181–183 ℃. $^{1}$H NMR (600 MHz, $CD_3OD$, $\delta$): 7.72 (d, $J$ = 3.7 Hz, 1H), 7.66 (d, $J$ = 5.0 Hz, 1H), 7.13 (t, $J$ = 4.3 Hz, 1H). $^{13}C\{^{1}H\}$ NMR (151 MHz, $CD_3OD$, $\delta$): 166.63 (*C*O), 139.85 (Ar*C*), 132.15 (Ar*C*), 130.54 (Ar*C*), 128.82 (Ar*C*). HRMS (ESI): *m/z* calculated for $C_5H_6NOS$ $[M + H]^+$ 128.0165; Found 128.0160. These spectral data correspond to previously reported data.[S5]

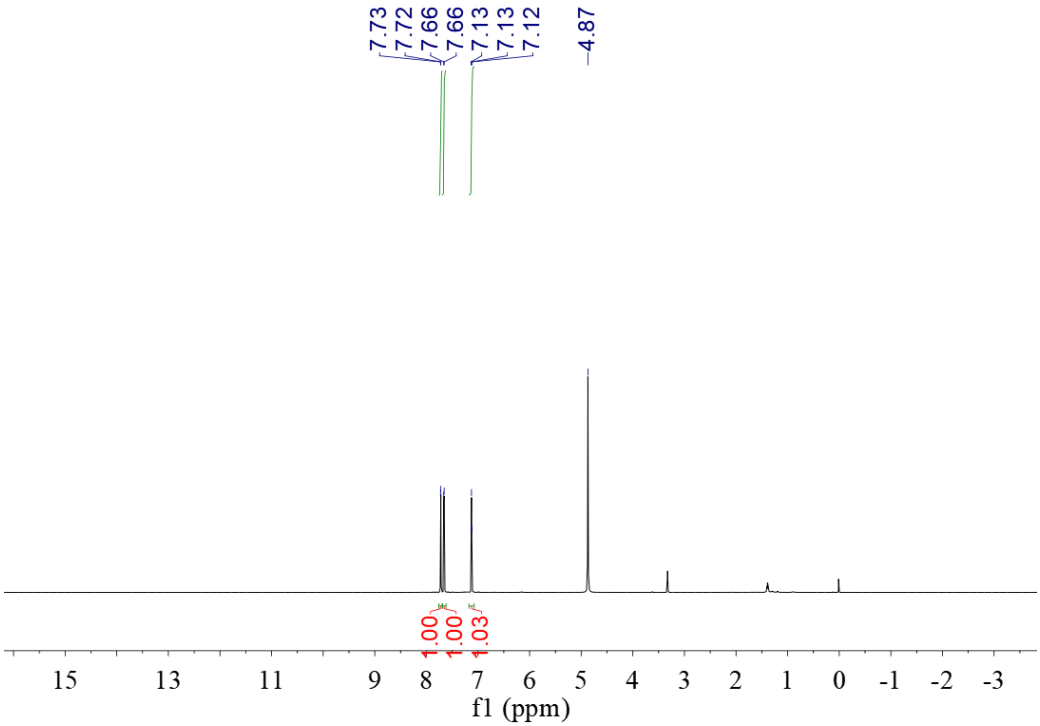



**Fig. S60** $^{1}$H NMR spectrum of the isolated **4v** (600 MHz, $CD_3OD$)

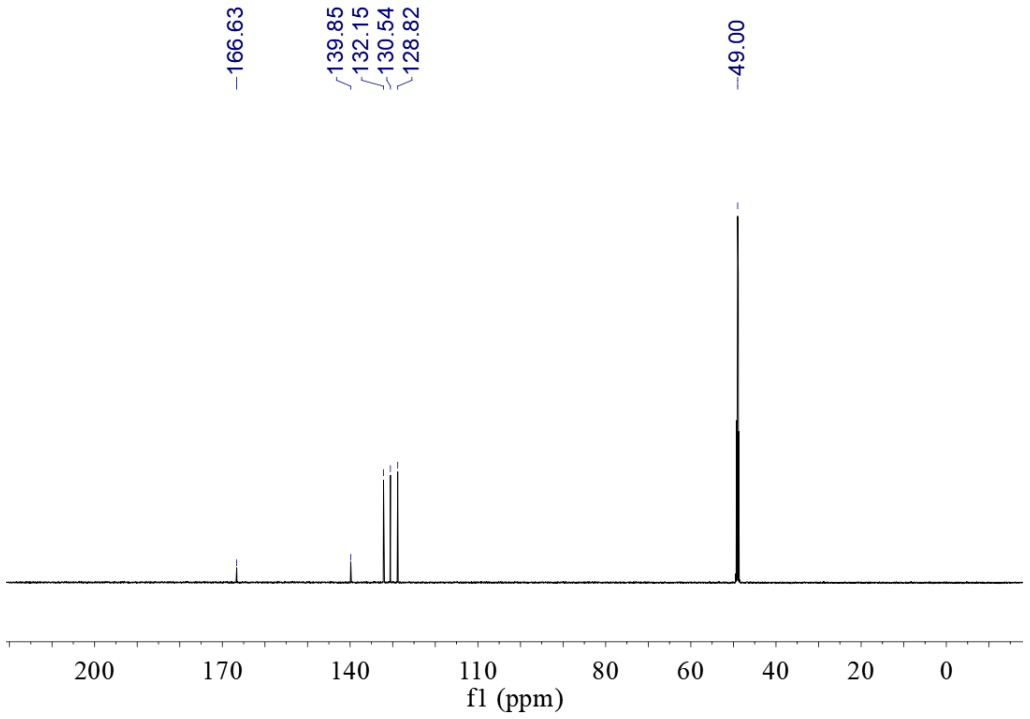
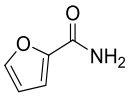



**Fig. S61** $^{13}C\{^{1}H\}$ NMR spectrum of the isolated **4v** (151 MHz, $CD_3OD$)



(**4w**)

White solid (96 mg, 86% yield), M.P. 140–142 ℃. $^{1}$H NMR (600 MHz, $CD_3OD$, $\delta$): 7.66 (d, $J$ = 1.6 Hz, 1H), 7.16 (d, $J$ = 3.5 Hz, 1H), 6.58 (dd, $J$ = 3.3, 1.6 Hz, 1H). $^{13}$C{$^{1}$H} NMR (151 MHz, $CD_3OD$, $\delta$): 162.89 (*C*O), 148.81 (Ar*C*), 146.46 (Ar*C*), 115.82 (Ar*C*), 112.97 (Ar*C*). HRMS (ESI): *m/z* calculated for $C_5H_6NO_2$ $[M + H]^+$ 112.0393; Found 112.0394. These spectral data correspond to previously reported data.[S5]

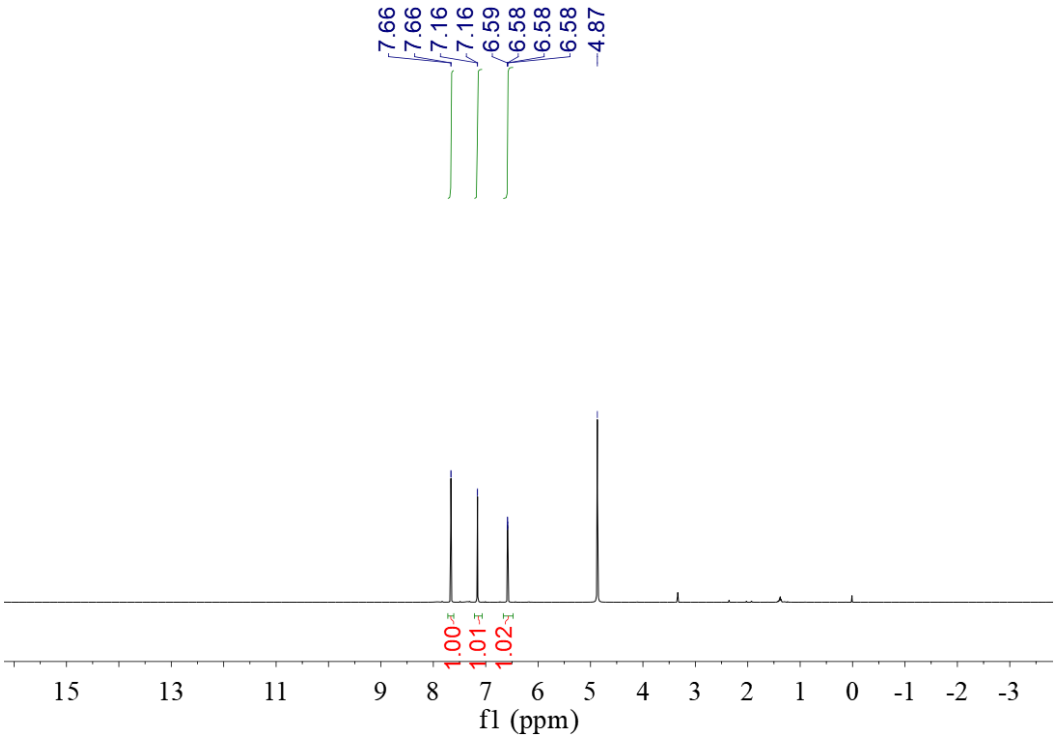



**Fig. S62** $^{1}$H NMR spectrum of the isolated **4w** (600 MHz, $CD_3OD$)

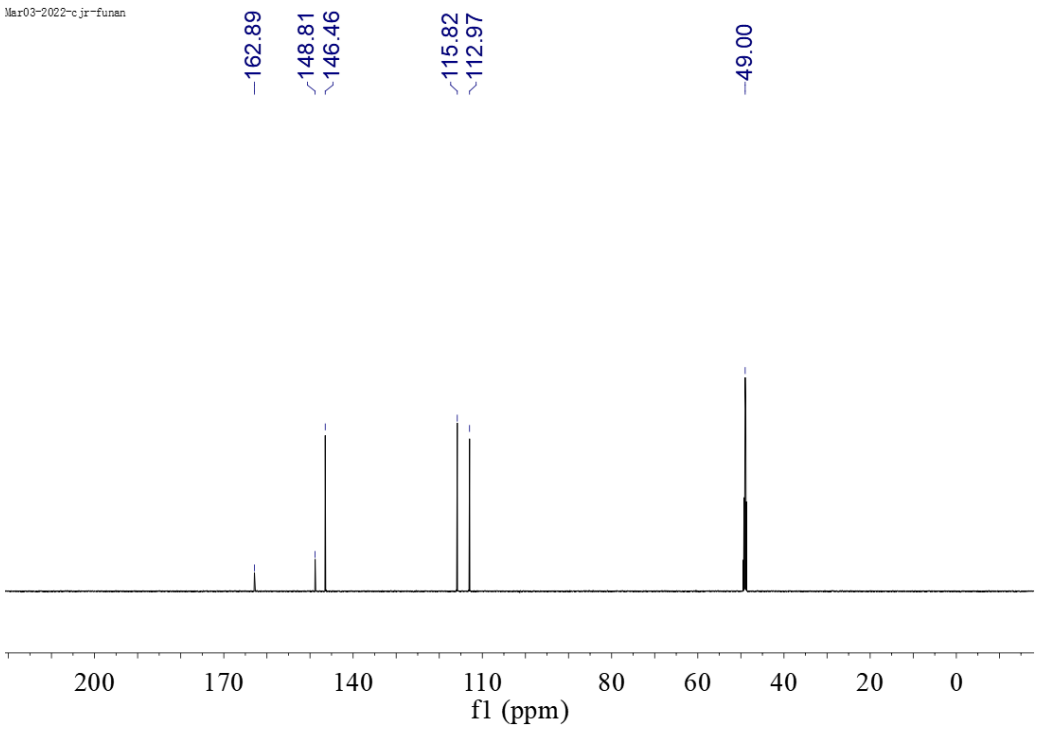
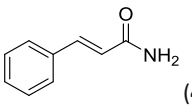



**Fig. S63** $^{13}$C{$^{1}$H} NMR spectrum of the isolated **4w** (151 MHz, $CD_3OD$)



(**4x**)

White solid (113 mg, 77% yield), M.P. 149–151 ℃. $^{1}$H NMR (600 MHz, $CD_3OD$, $\delta$): 7.65–7.48 (m, 3H), 7.46–7.29 (m, 3H), 6.66 (d, $J$ = 15.9 Hz, 1H). $^{13}C\{^{1}H\}$ NMR (151 MHz, $CD_3OD$, $\delta$): 170.92 (*C*O), 142.69, 136.14, 130.92, 129.93, 128.88, 121.40. HRMS (ESI): *m/z* calculated for $C_9H_{10}NO$ $[M + H]^+$ 148.0757; Found 148.0758. These spectral data correspond to previously reported data.[S5]

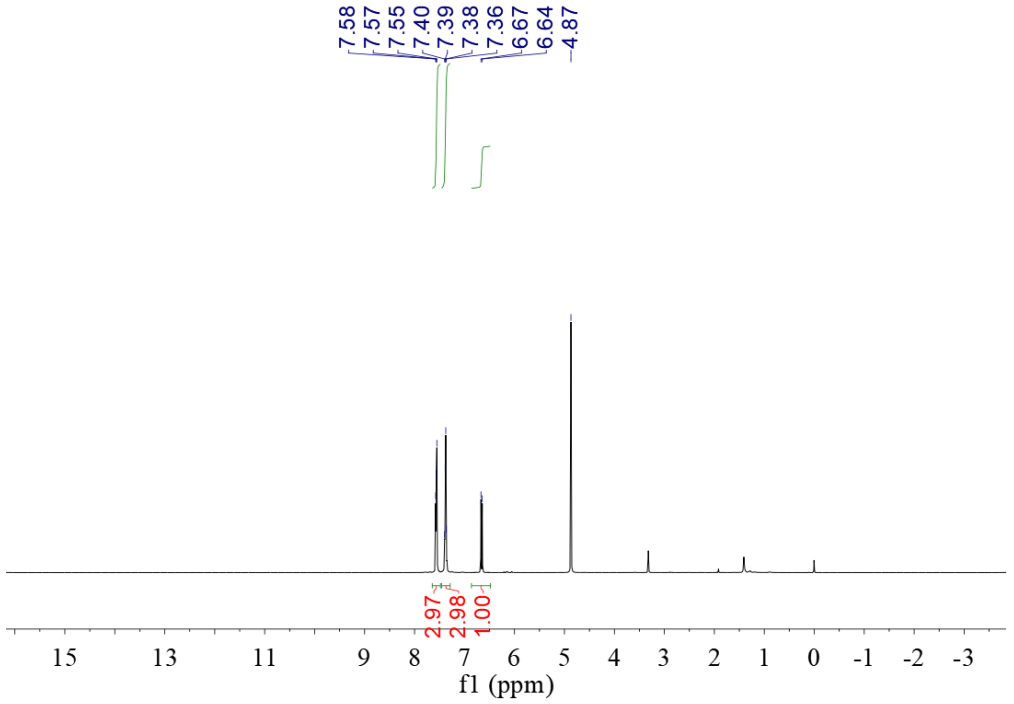



**Fig. S64** $^{1}$H NMR spectrum of the isolated **4x** (600 MHz, $CD_3OD$)

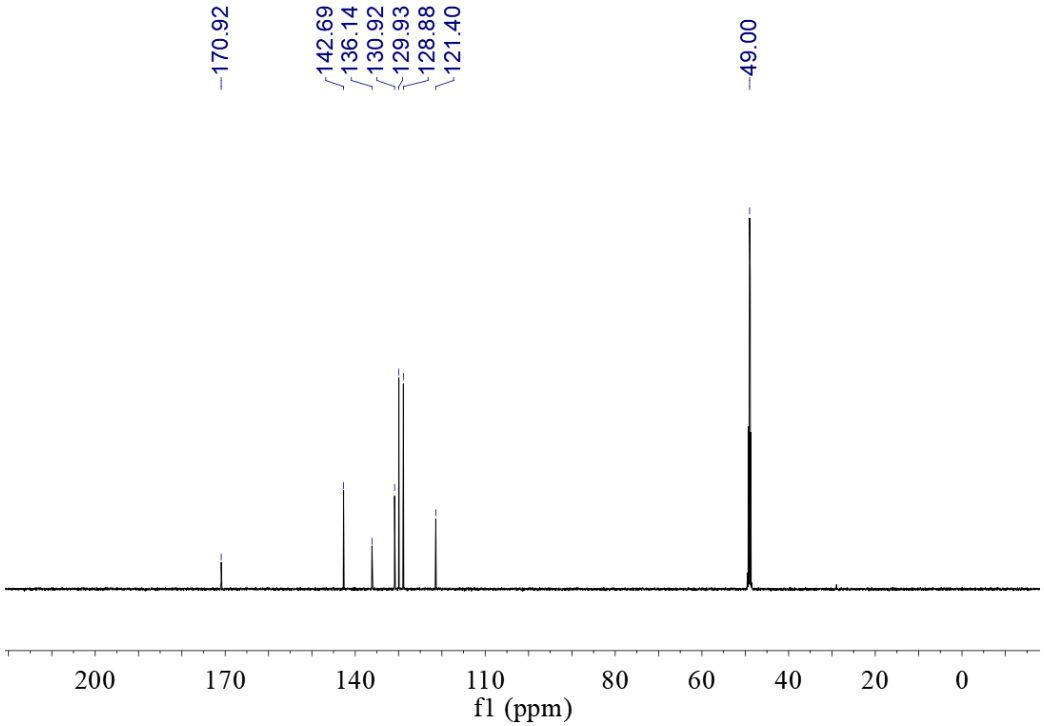
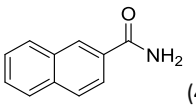



**Fig. S65** $^{13}C\{^{1}H\}$ NMR spectrum of the isolated **4x** (151 MHz, $CD_3OD$)



(**4y**)

White solid (156 mg, 91% yield), M.P. 191–192 ℃. $^{1}$H NMR (600 MHz, DMSO-$d_6$, $\delta$): 8.49 (s, 1H, Ar*H*), 8.14 (s, br, 1H, N*H*), 8.04–7.92 (m, 4H, Ar*H*), 7.66–7.54 (m, 2H, Ar*H*), 7.47 (s, br, 1H, N*H*). $^{13}$C{$^{1}$H} NMR (151 MHz, DMSO-$d_6$, $\delta$): 167.96 (*C*O), 134.16 (Ar*C*), 132.15 (Ar*C*), 131.65 (Ar*C*), 127.81 (Ar*C*), 127.76 (Ar*C*), 127.58 (Ar*C*), 127.56 (Ar*C*), 126.64 (Ar*C*), 124.39 (Ar*C*). HRMS (ESI): *m/z* calculated for $C_{11}H_{10}NO$ $[M + H]^+$ 173.0835; Found 173.0832. These spectral data correspond to previously reported data.[S5]

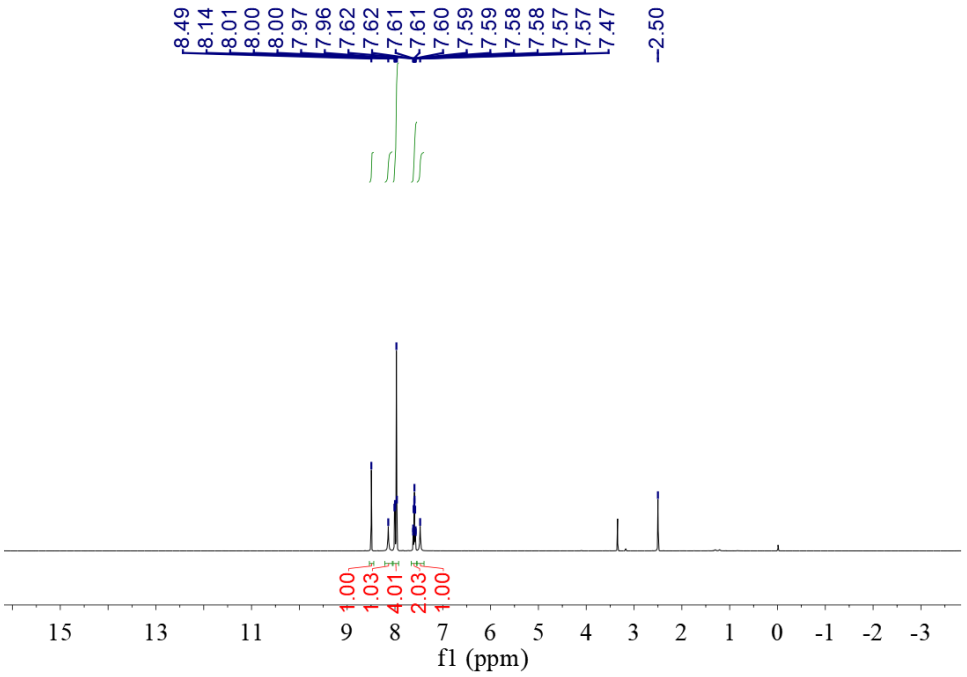



**Fig. S66** $^{1}$H NMR spectrum of the isolated **4y** (600 MHz, DMSO-$d_6$)

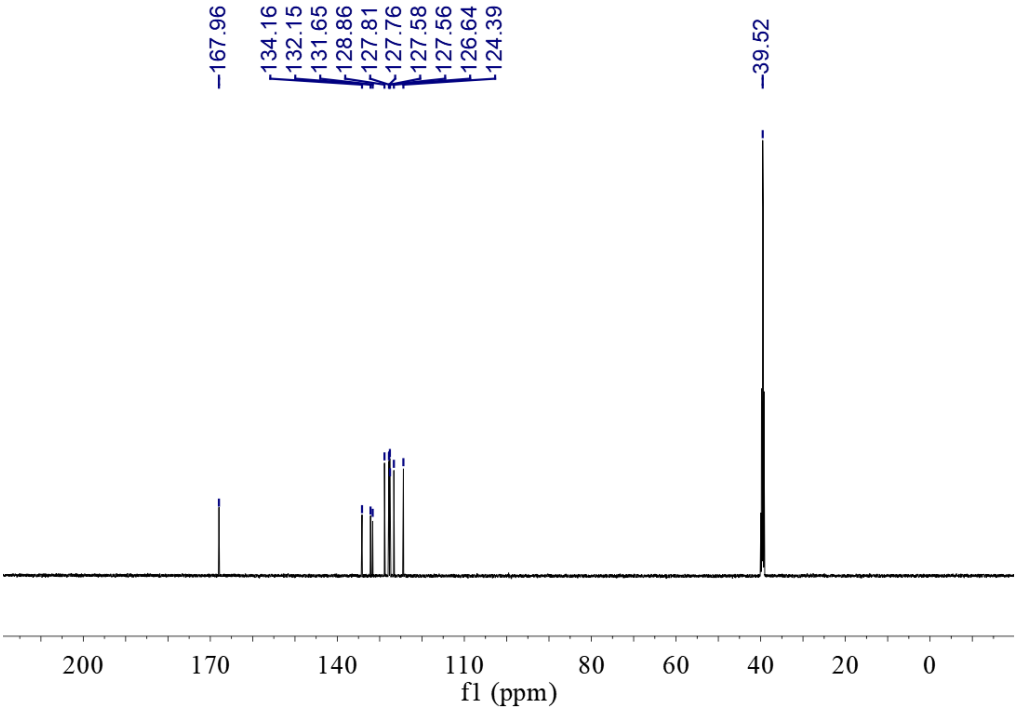



**Fig. S67** $^{13}$C{$^{1}$H} NMR spectrum of the isolated **4y** (151 MHz, DMSO-$d_6$)

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