# Electronic Supplementary Information

# Cu-catalyzed carboxylation of organoboronic acid pinacol esters with $CO_2$

Chihiro Maeda,* Takumi Cho, Ren Kumemoto, and Tadashi Ema*

*Division of Applied Chemistry, Graduate School of Natural Science and Technology, Okayama University, Tsushima, Okayama 700-8530, Japan.*

*E-mail: cmaeda@okayama-u.ac.jp; ema@cc.okayama-u.ac.jp*

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## [A] Instrumentation and Materials

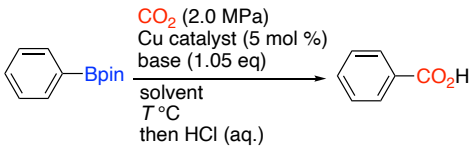
$^1$H and $^{13}$C NMR spectra were taken on a JEOL ECS400 or ECZ600 spectrometer, and chemical shifts are reported as the delta scale in ppm using an internal reference ($\delta$ = 7.26 for $^1$H NMR, 77.16 for $^{13}$C NMR, for $CDCl_3$, $\delta$ = 2.05 for $^1$H NMR, 29.84 for $^{13}$C NMR, for acetone-$d_6$, and $\delta$ = 2.50 for $^1$H NMR, 39.52 for $^{13}$C NMR, for DMSO-$d_6$). 1-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-9*H*-carbazole (**1j**),[1] 1,4-naphthalenediboronic acid bis(pinacol) ester (**1n**),[2] 2,7-pyrenediboronic acid bis(pinacol) ester (**1n**),[3] (*E*)-styrylboronic acid pinacol ester (**3a**),[4] (*E*)-(4-methoxystyryl)boronic acid pinacol ester (**3b**),[4] (phenylethynyl)boronic acid pinacol ester (**3g**),[5] 1,4-bis((*E*)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)benzene (**3h**),[4] 1,3-bis((*E*)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)benzene (**3i**),[4] 1,3,5-tris((*E*)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)benzene (**3j**),[4] 3,4-methylenedioxyphenylboronic acid pinacol ester,[6] and biphenyl-4-ylmethylboronic acid pinacol ester[7] were prepared according to literature procedures.

## [B] Experimental Procedures and Compound Data

**General procedure for the copper-catalyzed carboxylation of organoboronic acid pinacol esters with $CO_2$.** A 30 mL stainless autoclave containing organoboronic acid pinacol ester (0.5 mmol) and (IPr)CuCl (12.2 mg, 0.025 mmol, 5 mol%) was dried in vacuo and placed in a glove box (purge type) under $N_2$ atmosphere. $^t$BuOK (2.81 mg, 0.025 mmol, 5 mol%), CsF (152 mg, 1.00 mmol, dried at 80 °C for 12 h in vacuo and cooled to room temperature in advance) and dry 1,4-dioxane (1.0 mL) were added, and the autoclave was closed. The sealed autoclave was taken out from the glovebox and pressurized with 2.0 MPa of $CO_2$. The mixture was stirred at 150 °C for 24 h, and then the autoclave was cooled to room temperature, and the remaining $CO_2$ was vented slowly. The reaction mixture was acidified with 1 M HCl (aq), and the aqueous layer was extracted with EtOAc twice. The combined organic layer was washed with brine, dried over $Na_2SO_4$, and evaporated under reduced pressure. Purification by silica gel column chromatography gave the corresponding carboxylic acid.

**General procedure for the copper-catalyzed double carboxylation of organodiboronic acid bis(pinacol) esters with $CO_2$.** A 30 mL stainless autoclave containing organodiboronic acid bis(pinacol) ester (0.5 mmol) and (IPr)CuCl (24.4 mg, 0.050 mmol, 10 mol%) was dried in vacuo and placed in a glove box (purge type) under $N_2$ atmosphere. $^t$BuOK (5.61 mg, 0.050 mmol, 10 mol%), CsF (304 mg, 2.00 mmol, dried at 80 °C for 12 h in vacuo and cooled to room temperature in advance) and dry 1,4-dioxane (2.0 mL) were added, and the autoclave was closed. The sealed autoclave was taken out from the glovebox and pressurized with 2.0 MPa of $CO_2$. The mixture was stirred at 160 °C or 170 °C for 24 h, and then the autoclave was cooled to room temperature, and the remaining $CO_2$ was vented slowly. 10% NaOH (aq) was added to the reaction mixture, and the aqueous layer was washed with $Et_2O$ once. The aqueous layer was acidified with 5% $H_2SO_4$ (aq). For **2l**, **2o**, and **4h**−**j**, a powder precipitated was collected and washed with water and $CHCl_3$ to give the dicarboxylic acid. For **2o**, the crude product was dissolved in DMSO (10 mL), and MeI (1.2 mL, 2.0 mmol) and $K_2CO_3$ (276 mg, 2.00 mmol) were added. The mixture was stirred at 50 °C for 12 h. Water was added, and organic products were extracted with $CHCl_3$. Purification by silica gel column chromatography ($CHCl_3$) gave methyl ester **2o'**. For **2m**, **2n**, **2p**, and **2q**, the product was extracted with $Et_2O$ twice, and the combined organic layer was washed with brine, dried over $Na_2SO_4$, and evaporated under reduced pressure. Suction filtration of the precipitate gave the dicarboxylic acid.

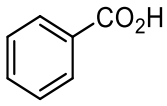
**Table S1** Initial screening of the reaction conditions of the Cu-catalyzed carboxylation of phenylboronic acid pinacol ester (**1a**) with $CO_2$.[a] A photograph of the 30 mL stainless autoclave is shown.




| Entry | Cu-catalyst | Solvent | Base | $T$ (°C) | Yield[b] (%) |
|---|---|---|---|---|---|
| 1[c] | IPrCuCl | toluene | KO$^t$Bu | 110 | 0 |
| 2 | IPrCuCl | toluene | KO$^t$Bu | 150 | 13 |
| 3 | IPrCuCl | THF | KO$^t$Bu | 150 | 26 |
| 4 | IPrCuCl | 1,4-dioxane | KO$^t$Bu | 150 | 48 |
| 5 | IPrCuCl | 1,4-dioxane | KO$^t$Bu | 130 | 21 |
| 6 | IPrCuCl | 1,4-dioxane | KO$^t$Bu | 170 | 53 |
| 7 | IMesCuCl | 1,4-dioxane | KO$^t$Bu | 150 | 5 |
| 8[d] | CuCl + Xantphos | 1,4-dioxane | KO$^t$Bu | 150 | 2 |
| 9[d] | CuCl + TMEDA | 1,4-dioxane | KO$^t$Bu | 150 | 0 |
| 10[d] | CuCl + 1,10-phen | 1,4-dioxane | KO$^t$Bu | 150 | 16 |
| 11 | IPrCuCl | 1,4-dioxane | NaO$^t$Bu | 150 | trace |
| 12 | IPrCuCl | 1,4-dioxane | $Cs_2CO_3$ | 150 | 28 |
| 13 | IPrCuCl | 1,4-dioxane | $^i$Pr$_2$NEt | 150 | 0 |
| 14 | IPrCuCl | 1,4-dioxane | KO$^t$Bu + CsF[e] | 150 | 36 |
| 15 | IPrCuCl | 1,4-dioxane | CsF[e] | 150 | 98 |

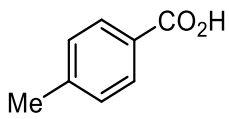
[a] Reaction conditions: **1a** (0.5 mmol), Cu-catalyst (5 mol%), base (1.05 equiv), solvent (1.0 mL), $CO_2$ (2.0 MPa), 110–170 °C, 24 h, in a 30 mL stainless autoclave. [b] Yields were determined by $^1$H NMR spectroscopy using 2-methoxynaphthalene as an internal standard. [c] 0.1 MPa $CO_2$ (balloon). [d] 5 mol% of ligand was used. [e] 2 equiv of CsF was used.

**benzoic acid (2a)**[8]



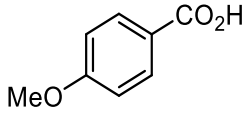

92% (56.1 mg, 459 μmol) white solid, $R_f$ = 0.15 ($CHCl_3$/MeOH = 20/1); $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 7.49 (t, $J$ = 7.6 Hz, 2H), 7.62 (tt, $J$ = 1.2, 7.6 Hz, 1H), 8.13 (dd, $J$ = 1.2, 8.4 Hz, 2H); $^{13}$C NMR ($CDCl_3$, 100 MHz) $\delta$ 128.6, 129.4, 130.4, 134.0, 172.1.

***p*-toluic acid (2b)**[9]



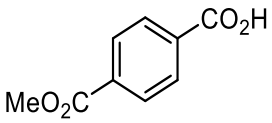

77% (52.2 mg, 383 μmol) white solid, $R_f$ = 0.13 ($CHCl_3$/MeOH = 20/1); $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 2.44 (s, 3H), 7.28 (d, $J$ = 7.6 Hz, 2H), 8.00 (d, $J$ = 8.0 Hz, 2H); $^{13}$C NMR ($CDCl_3$, 100 MHz) $\delta$ 21.9, 126.7, 129.4, 130.4, 144.8, 172.3.

***p*-anisic acid (2c)**[10]



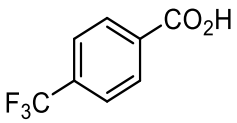

89% (67.6 mg, 444 μmol) white solid, $R_f$ = 0.18 ($CHCl_3$/MeOH = 20/1); $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 3.88 (s, 3H), 6.95 (d, $J$ = 9.2 Hz, 2H), 8.07 (d, $J$ = 9.2 Hz, 2H); $^{13}$C NMR ($CDCl_3$, 100 MHz) $\delta$ 55.6, 114.0, 122.0, 132.5, 164.3, 171.6.

**4-methoxycarbonylbenzoic acid (2d)**[11]



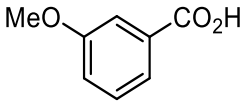
94% (84.3 mg, 468 μmol) white solid, $R_f$ = 0.10 ($CHCl_3$/MeOH = 20/1), and $R_f$ = 0.13 ($CHCl_3$/MeOH = 9/1); $^1$H NMR (DMSO-$d_6$, 400 MHz) $\delta$ 3.88 (s, 3H), 8.06 (s, 4H), 13.37 (s, 1H); $^{13}$C NMR (DMSO-$d_6$, 100 MHz) $\delta$ 52.5, 129.4, 129.7, 133.2, 135.0, 165.6, 166.7.

**4-trifluoromethylbenzoic acid (2e)**[10]



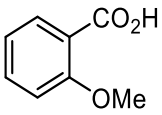
61% (58.3 mg, 307 μmol) white solid, $R_f$ = 0.07 ($CHCl_3$/MeOH = 20/1); $^1$H NMR (DMSO-$d_6$, 400 MHz) $\delta$ 7.88 (d, $J$ = 8.0 Hz, 2H), 8.13 (d, $J$ = 8.0 Hz, 2H), 13.49 (s, 1H); $^{13}$C NMR (DMSO-$d_6$, 100 MHz) $\delta$ 123.8 (q, $J$ = 271.5 Hz), 125.7 (q, $J$ = 2.9 Hz), 130.3, 132.5 (q, $J$ = 31.8 Hz), 135.1, 165.9.

***m*-anisic acid (2f)**[10]



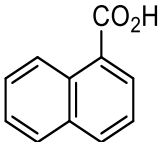
76% (58.1 mg, 382 μmol) white solid, $R_f$ = 0.13 ($CHCl_3$/MeOH = 20/1); $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 3.87 (s, 3H), 7.16 (ddd, $J$ = 1.2, 2.8, 8.4 Hz, 1H), 7.39 (t, $J$ = 8.4 Hz, 1H), 7.62−7.63 (m, 1H), 7.72 (d, $J$ = 7.6 Hz, 1H); $^{13}$C NMR ($CDCl_3$, 100 MHz) $\delta$ 55.6, 114.5, 120.6, 122.8, 129.7, 130.8, 159.7, 172.3.

***o*-anisic acid (2g)**[10]



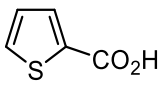
33% (25.0 mg, 164 μmol) white solid, $R_f$ = 0.13 ($CHCl_3$/MeOH = 20/1); $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 4.09 (s, 3H), 7.07 (d, $J$ = 8.0 Hz, 1H), 7.16 (t, $J$ = 7.2 Hz, 1H), 7.59 (dt, $J$ = 1.6, 7.2 Hz, 1H), 8.20 (dd, $J$ = 2.0, 8.0 Hz, 1H), 10.74 (s, 1H); $^{13}$C NMR ($CDCl_3$, 100 MHz) $\delta$ 56.8, 111.8, 117.7, 122.3, 133.9, 135.2, 158.2, 165.7.

**1-naphthoic acid (2h)**[10]



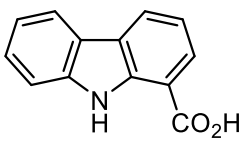
68% (58.4 mg, 339 μmol) white solid, $R_f$ = 0.13 ($CHCl_3$/MeOH = 20/1), and $R_f$ = 0.05 (hexane/EtOAc = 5/1); $^1$H NMR (DMSO-$d_6$, 400 MHz) $\delta$ 7.57−7.67 (m, 3H), 8.02 (d, $J$ = 7.2 Hz, 1H), 8.14−8.17 (m, 2H), 8.86 (d, $J$ = 8.8 Hz, 1H), 13.14 (s, 1H); $^{13}$C NMR (DMSO-$d_6$, 100 MHz) $\delta$ 124.9, 125.5, 126.2, 127.6, 127.7, 128.6, 129.9, 130.7, 133.0, 133.5, 168.7.

**thiophene-2-carboxylic acid (2i)**[10]



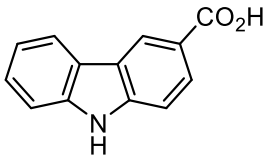
53% (34.1 mg, 266 μmol) white solid, $R_f$ = 0.05 ($CHCl_3$/MeOH = 20/1); $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 7.15 (dd, $J$ = 3.8, 4.4 Hz, 1H), 7.65 (dd, $J$ = 1.2, 5.2 Hz, 1H), 7.90 (dd, $J$ = 1.2, 3.6 Hz, 1H); $^{13}$C NMR ($CDCl_3$, 100 MHz) $\delta$ 128.3, 133.1, 134.2, 135.3, 168.0.

**carbazole-1-carboxylic acid (2j)**[12]



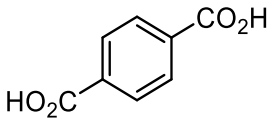
51% (53.8 mg, 255 μmol) white solid, $R_f$ = 0.30 ($CHCl_3$/MeOH = 9/1); $^1$H NMR (DMSO-$d_6$, 400 MHz) $\delta$ 7.18−7.27 (m, 2H), 7.42 (t, $J$ = 6.8 Hz, 1H), 7.74 (d, $J$ = 8.8 Hz, 1H), 8.00 (d, $J$ = 7.2 Hz, 1H), 8.16 (d, $J$ = 8.0 Hz, 1H), 8.39 (d, $J$ = 7.2 Hz, 1H), 11.32 (s, 1H), 13.17 (s, 1H); $^{13}$C NMR (DMSO-$d_6$, 100 MHz) $\delta$ 112.3, 112.8, 118.0, 119.3, 120.2, 121.7, 124.2, 125.2, 126.1, 127.5, 139.1, 140.3, 168.0.

**carbazole-3-carboxylic acid (2k)**[13]



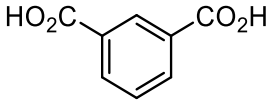
45%, (47.8 mg, 226 μmol) white solid, $R_f$ = 0.25 ($CHCl_3$/MeOH = 9/1); $^1$H NMR (DMSO-$d_6$, 400 MHz) $\delta$ 7.22 (t, $J$ = 7.6 Hz, 1H), 7.44 (t, $J$ = 7.2 Hz, 1H), 7.54 (d, $J$ = 9.2 Hz, 2H), 8.02 (dd, $J$ = 1.6, 8.4 Hz, 1H), 8.24 (d, $J$ = 8.0 Hz, 1H), 8.78 (s, 1H), 11.66 (s, 1H), 12.58 (s, 1H); $^{13}$C NMR (DMSO-$d_6$, 150 MHz) $\delta$ 110.6, 111.4, 119.5, 120.6, 121.0, 122.2, 122.49, 122.50, 126.3, 127.0, 140.3, 142.4, 168.1.

**terephthalic acid (2l)**[11]



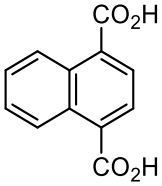
65% (54.1 mg, 326 μmol) white solid; $^1$H NMR (DMSO-$d_6$, 400 MHz) $\delta$ 8.04 (s, 4H), 13.29 (s, 2H); $^{13}$C NMR (DMSO-$d_6$, 100 MHz) $\delta$ 129.5, 134.5, 166.7.

**isophthalic acid (2m)**[14]



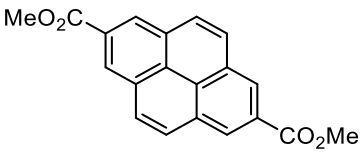
51% (42.7 mg, 257 μmol) white solid; $^1$H NMR (DMSO-$d_6$, 400 MHz) $\delta$ 7.64 (t, $J$ = 8.0 Hz, 1H), 8.16 (dd, $J$ = 2.0, 8.0 Hz, 2H), 8.48 (s, 1H), 13.25 (s, 2H); $^{13}$C NMR (DMSO-$d_6$, 100 MHz) $\delta$ 129.2, 130.1, 131.3, 133.5, 166.7.

**1,4-naphthalenedicarboxylic acid (2n)**[15]



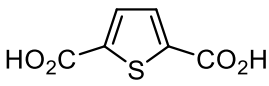
45% (48.7 mg, 225 μmol) white solid; $^1$H NMR (DMSO-$d_6$, 400 MHz) $\delta$ 7.70 (dd, $J$ = 3.6, 6.4 Hz, 2H), 8.10 (s, 2H), 8.78 (dd, $J$ = 3.6, 6.8 Hz, 2H), 13.51 (s, 2H); $^{13}$C NMR (DMSO-$d_6$, 100 MHz) $\delta$ 125.9, 127.6, 127.9, 130.8, 132.3, 168.5.

**dimethyl 2,7-pyrenedicarboxylate (2o')**[16]



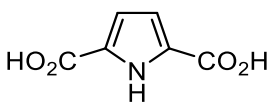
42% (66.6 mg, 209 μmol) light yellow solid; $^1$H NMR ($CDCl_3$, 600 MHz) $\delta$ 4.09 (s, 6H), 8.13 (s, 4H), 8.82 (s, 4H); $^{13}$C NMR ($CDCl_3$, 100 MHz) $\delta$ 52.6, 126.3, 128.6, 131.7, 167.5.

**2,5-thiophenedicarboxylic acid (2p)**[17]



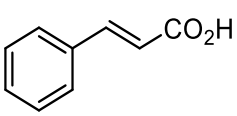
46% (40.0 mg, 232 μmol) white solid; $^1$H NMR (DMSO-$d_6$, 400 MHz) $\delta$ 7.71 (s, 2H), 13.59 (s, 2H); $^{13}$C NMR (DMSO-$d_6$, 100 MHz) $\delta$ 133.3, 139.8, 162.5.

**2,5-pyrroledicarboxylic acid (2q)**[18]



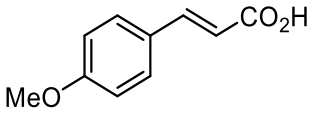
6% (5.0 mg, 32.2 μmol) gray solid; $^1$H NMR (DMSO-$d_6$, 400 MHz) $\delta$ 6.74 (d, $J$ = 1.2 Hz, 2H), 12.20 (s, 1H) 12.72 (s, 2H); $^{13}$C NMR (DMSO-$d_6$, 100 MHz) $\delta$ 115.1, 127.3, 161.3.

**(*E*)-cinnamic acid (4a)**[19]



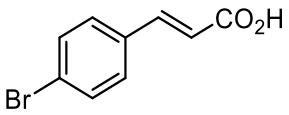
90% (69.5 mg, 469 μmol) white solid, $R_f$ = 0.15 ($CHCl_3$/MeOH = 20/1); $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 6.47 (d, $J$ = 15.6 Hz, 1H), 7.41−7.42 (m, 3H), 7.55−7.57 (m, 2H), 7.79 (d, $J$ = 16.0 Hz, 1H); $^{13}$C NMR ($CDCl_3$, 100 MHz) $\delta$ 117.4, 128.5, 129.1, 130.9, 134.2, 147.3, 172.6.

**(*E*)-4-methoxycinnamic acid (4b)**[20]



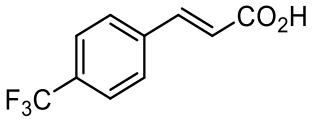
84% (75.9 mg, 426 μmol) white solid, $R_f$ = 0.07 ($CHCl_3$/MeOH = 30/1), and $R_f$ = 0.25 ($CHCl_3$/MeOH = 20/1); $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 3.85 (s, 3H), 6.32 (d, $J$ = 15.6 Hz, 1H), 6.92 (d, $J$ = 9.2 Hz, 2H), 7.51 (d, $J$ = 9.2 Hz, 2H), 7.74 (d, $J$ = 16.0 Hz, 1H); $^{13}$C NMR (DMSO-$d_6$, 100 MHz) $\delta$ 55.3, 114.6, 126.8, 130.0, 143.8, 161.0, 167.8.

**(*E*)-4-bromocinnamic acid (4c)**



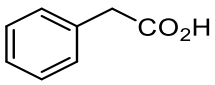
54% (61.7 mg, 272 μmol) white solid, $R_f$ = 0.05 ($CHCl_3$/MeOH = 20/1); $^1$H NMR (acetone-$d_6$, 400 MHz) $\delta$ 6.57 (d, $J$ = 16.0 Hz, 1H), 7.61−7.67 (m, 5H), 10.86 (s, 1H); $^{13}$C NMR (acetone-$d_6$, 100 MHz) $\delta$ 120.2, 124.7, 130.8, 132.9, 134.8, 144.0, 167.4; HRMS (ESI) $m/z$: [$M$–H]$^-$ Calcd for $C_9H_6O_2Br$ 224.9557; Found 224.9565.

**(*E*)-4-trifluoromethylcinnamic acid (4d)**[21]



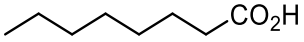
61% (36.1 mg, 167 μmol) from **3d** (250 μmol) white solid, $R_f$ = 0.07 ($CHCl_3$/MeOH = 20/1), and $R_f$ = 0.10 (EtOAc); $^1$H NMR (DMSO-$d_6$, 400 MHz) $\delta$ 6.68 (d, $J$ = 16.0 Hz, 1H), 7.66 (d, $J$ = 16.0 Hz, 1H), 7.76 (d, $J$ = 8.0 Hz, 2H), 7.92 (d, $J$ = 8.4 Hz, 2H), 12.62 (s, 1H); $^{13}$C NMR (DMSO-$d_6$, 100 MHz) $\delta$ 122.2, 124.1 (q, $J$ = 271.1 Hz), 125.7 (q, $J$ = 3.8 Hz), 128.9, 129.8 (q, $J$ = 31.8 Hz), 138.3, 142.1, 167.2.

**2-phenylacetic acid (4e)**[19]



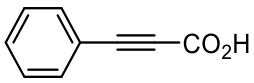
82% (55.8 mg, 410 μmol) white solid, $R_f$ = 0.20 ($CHCl_3$/MeOH = 9/1); $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 3.66 (s, 2H), 7.38−7.28 (m, 5H); $^{13}$C NMR ($CDCl_3$, 100 MHz) $\delta$ 127.5, 128.7, 129.5, 133.4, 178.1.

**octanoic acid (4f)**[22]



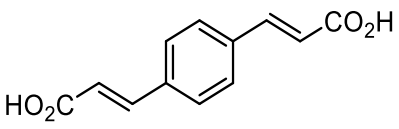
28% (18.5 mg, 128 μmol) colorless liquid; $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 0.88 (t, $J$ = 6.8 Hz, 3H), 1.16−1.38 (m, 8H), 1.56−1.70 (m, 2H), 2.35 (t, $J$ = 7.2 Hz, 2H); $^{13}$C NMR ($CDCl_3$, 100 MHz) $\delta$ 14.2, 22.7, 24.8, 29.1, 29.2, 31.8, 34.2, 180.3.

**3-phenylpropiolic acid (4g)**[19]



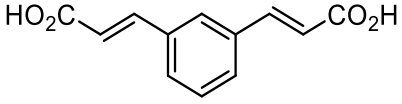
36% (26.7 mg, 183 μmol) white solid, $R_f$ = 0.05 ($CHCl_3$/MeOH = 20/1), and $R_f$ = 0.08 ($CHCl_3$/MeOH = 9/1); $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 7.40 (t, $J$ = 7.6 Hz, 2H), 7.49 (t, $J$ = 7.2 Hz, 1H), 7.62 (d, $J$ = 6.8 Hz, 2H); $^{13}$C NMR ($CDCl_3$, 100 MHz) $\delta$ 80.4, 89.5, 119.2, 128.8, 131.3, 133.5, 158.5.

**1,4-benzenediacrylic acid (4h)**[23]



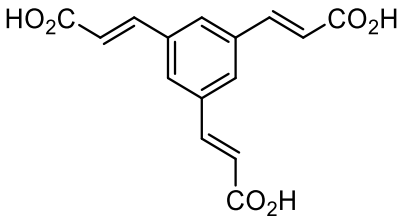
62% (64.1 mg, 294 μmol) light brown solid; $^1$H NMR (DMSO-$d_6$, 400 MHz) $\delta$6.60 (d, $J$ = 16.0 Hz, 2H), 7.60 (d, $J$ = 15.6 Hz, 2H), 7.73 (s, 4H) 12.46 (s, 2H); $^{13}$C NMR (DMSO-$d_6$, 150 MHz) $\delta$ 120.2, 128.7, 135.9, 143.1, 167.5.

**1,3-benzenediacrylic acid (4i)**



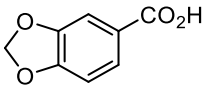
73% (79.7 mg, 365 μmol) light yellow solid; $^1$H NMR (DMSO-$d_6$, 400 MHz) $\delta$ 6.67 (d, $J$ = 16.0 Hz, 2H), 7.46 (t, $J$ = 8.0 Hz, 1H), 7.60 (d, $J$ = 16.0 Hz, 2H), 7.72 (dd, $J$ = 1.6, 8.0 Hz, 2H), 8.08 (s, 1H), 12.44 (s, 2H); $^{13}$C NMR (DMSO-$d_6$, 100 MHz) $\delta$ 120.2, 127.7, 129.5, 129.9, 135.0, 143.3, 167.6; HRMS (ESI) $m/z$: [$M$–H]$^-$ Calcd for $C_{12}H_{10}O_4$ 217.0506; Found 217.0515.

**1,3,5-benzenetriacrylic acid (4j)**



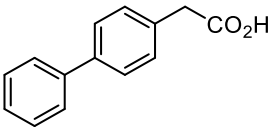
40% (19.3 mg, 67.0 μmol) from **3j** (167 μmol) brown solid; $^1$H NMR (DMSO-$d_6$, 400 MHz) $\delta$ 6.78 (d, $J$ = 16.0 Hz, 3H), 7.60 (d, $J$ = 16.4 Hz, 3H), 8.08 (s, 3H), 12.35 (s, 3H); $^{13}$C NMR could not detect peaks due to very low solubility; HRMS (ESI) $m/z$: $[M–2H]^{2–}$ Calcd for $C_{15}H_{10}O_6$ 143.0244; Found 143.0241.

**piperonylic acid**

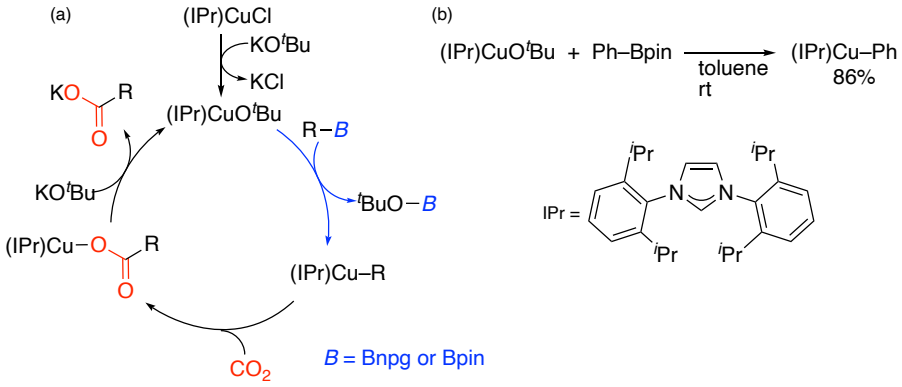


80% (66.2 mg, 398 μmol) white solid, $R_f$ = 0.11 ($CHCl_3$/MeOH = 20/1); $^1$H NMR (DMSO-$d_6$, 600 MHz) $\delta$ 6.12 (s, 2H), 7.00 (d, $J$ = 8.4 Hz, 1H), 7.36 (d, $J$ = 1.8 Hz, 1H), 7.54 (dd, $J$ = 1.8, 8.4 Hz, 1H), 12.77 (s, 1H); $^{13}$C NMR (DMSO-$d_6$, 150 MHz) $\delta$ 102.0, 108.1, 108.8, 124.6, 125.0, 147.5, 151.2, 166.6; HRMS (ESI) $m/z$: $[M–H]^–$ Calcd for $C_8H_5O_4$ 165.0193; Found 165.0187.

**felbinac**



45% (35.5 mg, 166 μmol) light yellow solid, $R_f$ = 0.11 ($CHCl_3$/MeOH = 20/1); $^1$H NMR ($CDCl_3$, 600 MHz) $\delta$ 3.71 (s, 2H), 7.35–7.38 (m, 3H), 7.42–7.45 (m, 2H), 7.56–7.59 (m, 4H); $^{13}$C NMR ($CDCl_3$, 150 MHz) $\delta$ 40.6, 127.2, 127.5, 127.6, 128.9, 129.9, 132.4, 140.5, 140.8, 176.5; HRMS (ESI) $m/z$: $[M–H]^–$ Calcd for $C_{14}H_{11}O_2$ 211.0765; Found 211.0760.




**Scheme S1** (a) A proposed reaction mechanism for the Cu-catalyzed carboxylation of boronic esters.[24] (b) Stoichiometric transmetalation of (IPr)CuO$^t$Bu with PhBpin.[25] IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene.

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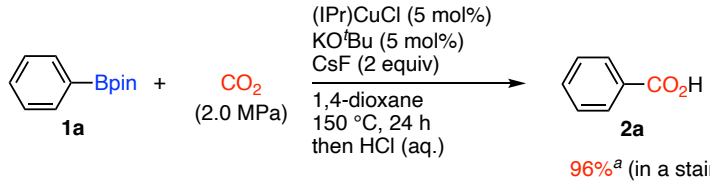
**[D] Comparison with the Reported Reaction Conditions**

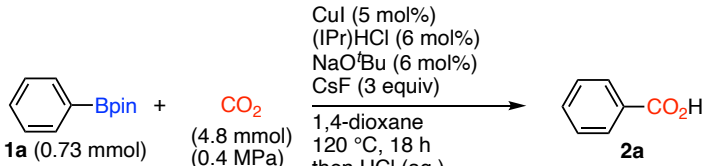
We conducted the Cu-catalyzed carboxylation under Bayer's reaction condition in a stainless autoclave. Unfortunately, we could not reproduce the high yields they achieved by using a specialized glassware (Scheme S2). In addition, double carboxylation did not take place at all under the reaction condition (Scheme S3).

**(a) Carboxylation under our optimized condition (this work)**



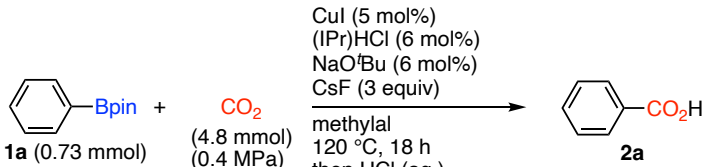

96%[a] (in a stainless autoclave)

**(b) Carboxylation under Bayer's condition in 1,4-dioxane**




54%[a] (in a stainless autoclave)
76%[b,c] (in a specialized glassware)

**(c) Carboxylation under Bayer's condition in methylal**

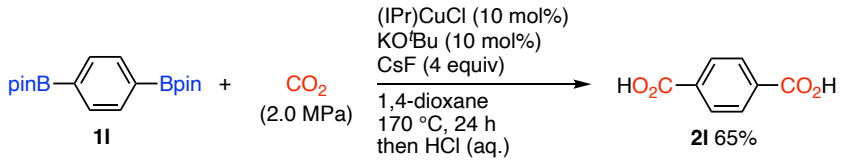



41%[a] (in a stainless autoclave)
81%[b,c] (in a specialized glassware)

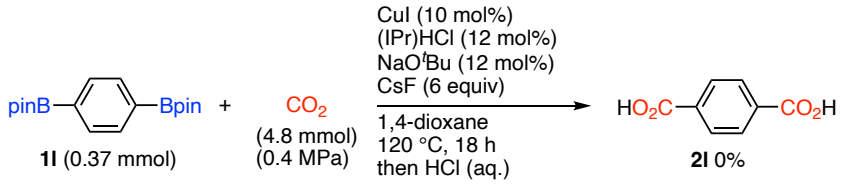
[a] NMR yield. [b] Isolated yield. [c] Reference data: *Chem. Eur. J.*, 2020, **26**, 6064.

**Scheme S2**

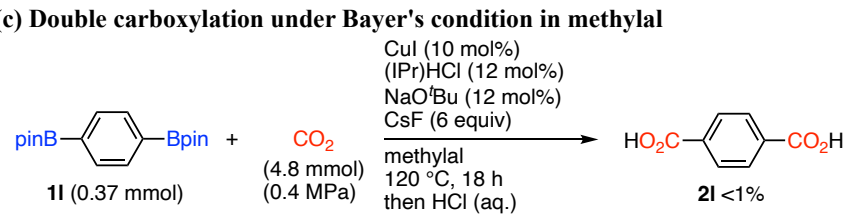
**(a) Double carboxylation under our optimized condition (this work)**




**(b) Double carboxylation under Bayer's condition in 1,4-dioxane**

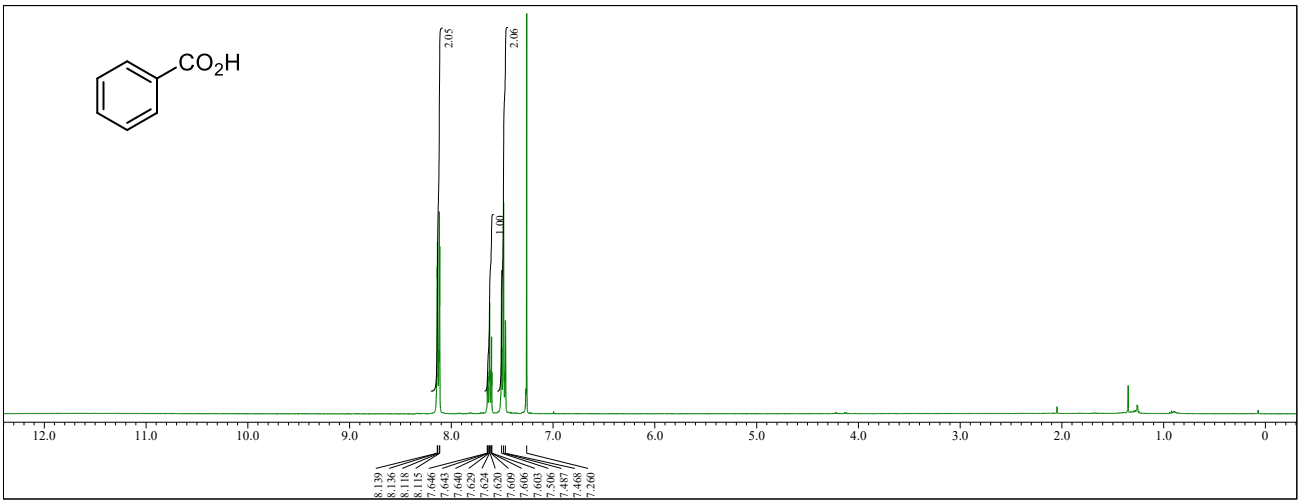



**(c) Double carboxylation under Bayer's condition in methylal**

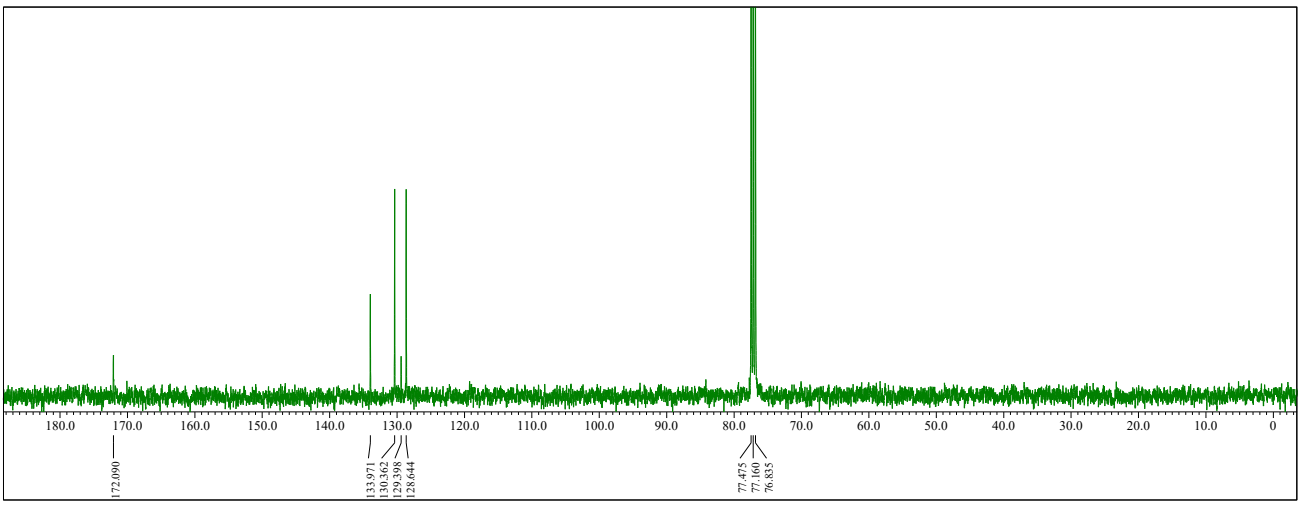



**Scheme S3**

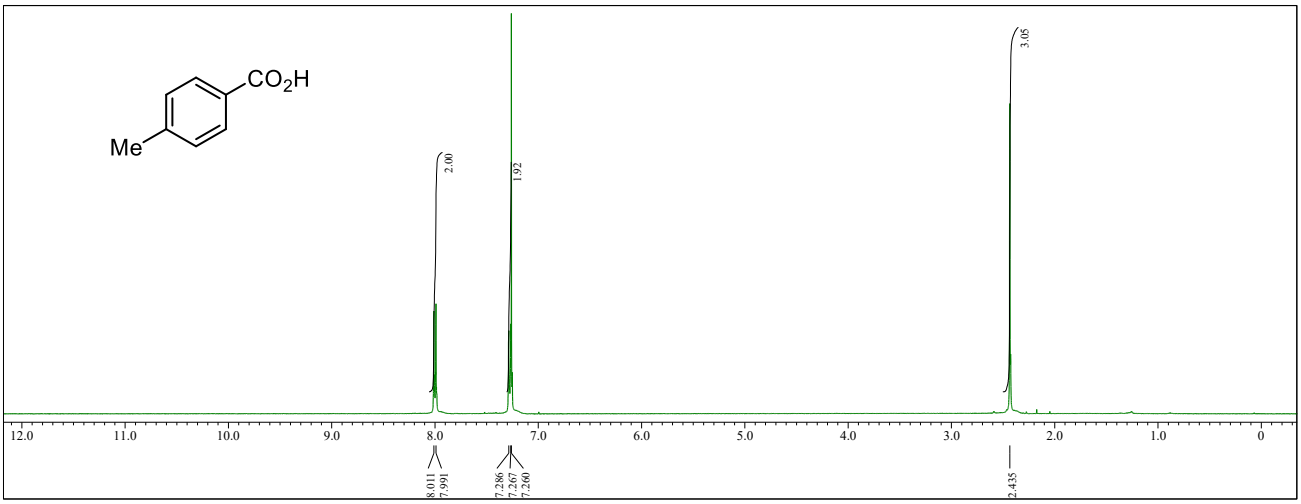
## [E] NMR Spectra



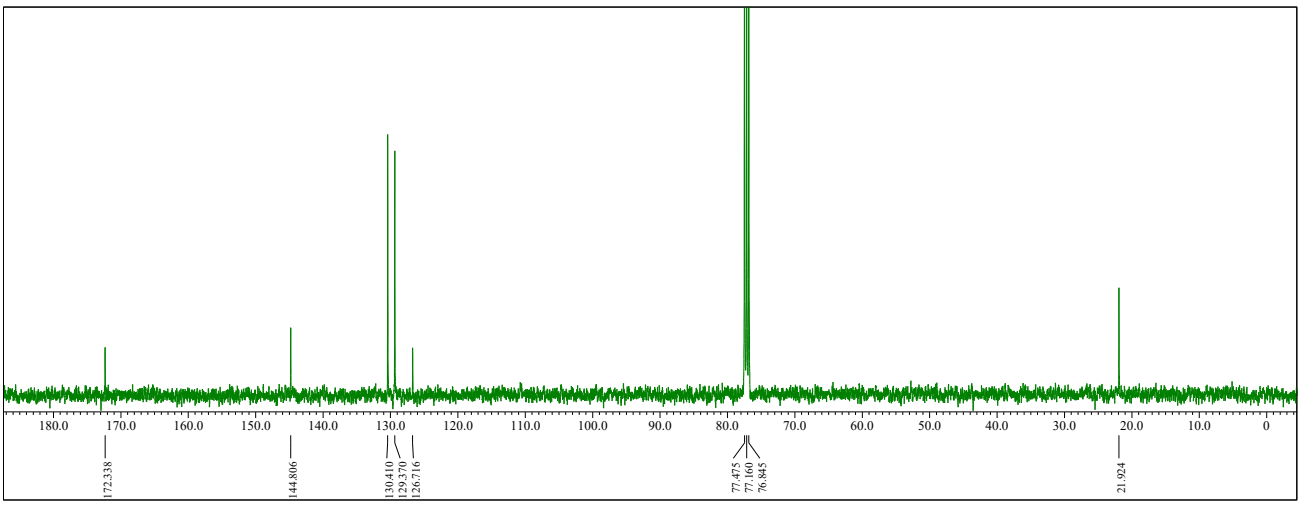

400 MHz $^{1}$H NMR spectrum of **2a** in $CDCl_3$.



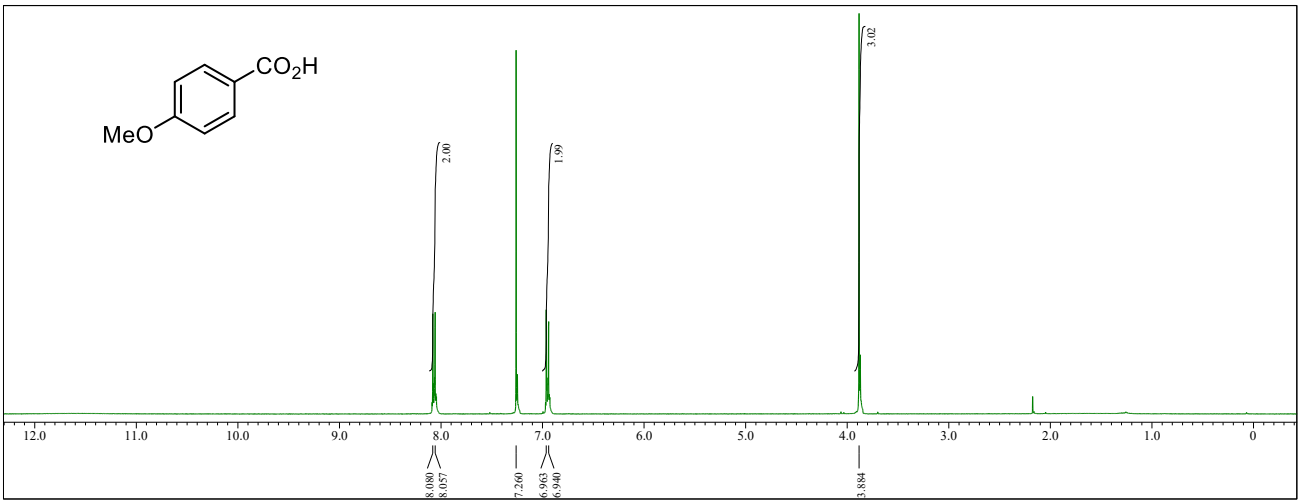

100 MHz $^{13}$C NMR spectrum of **2a** in $CDCl_3$.



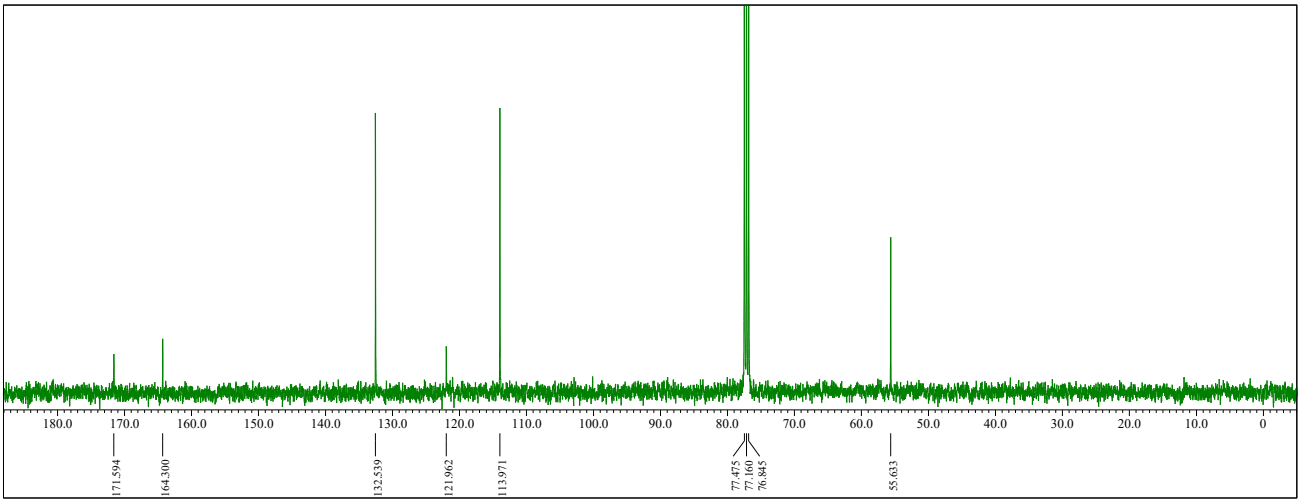

400 MHz $^{1}$H NMR spectrum of **2b** in $CDCl_3$.



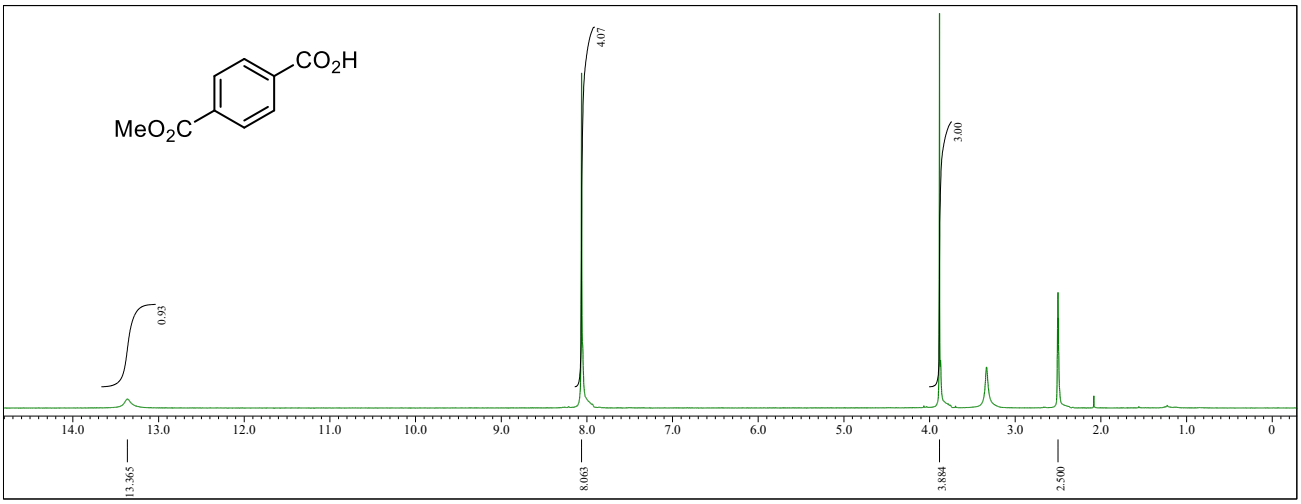

100 MHz $^{13}$C NMR spectrum of **2b** in $CDCl_3$.




400 MHz $^{1}$H NMR spectrum of **2c** in $CDCl_3$.

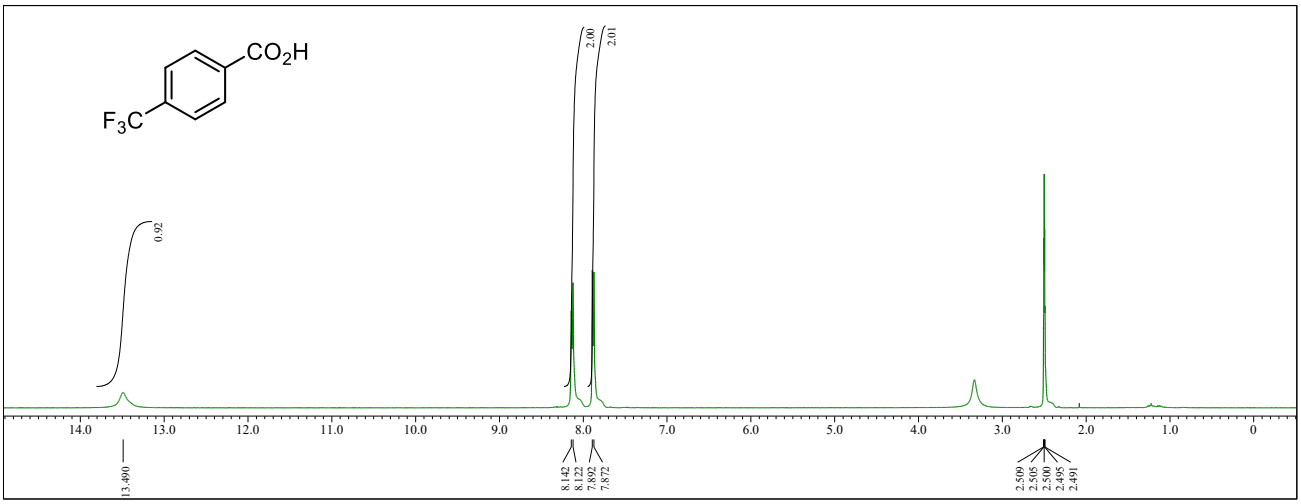



100 MHz $^{13}$C NMR spectrum of **2c** in $CDCl_3$.

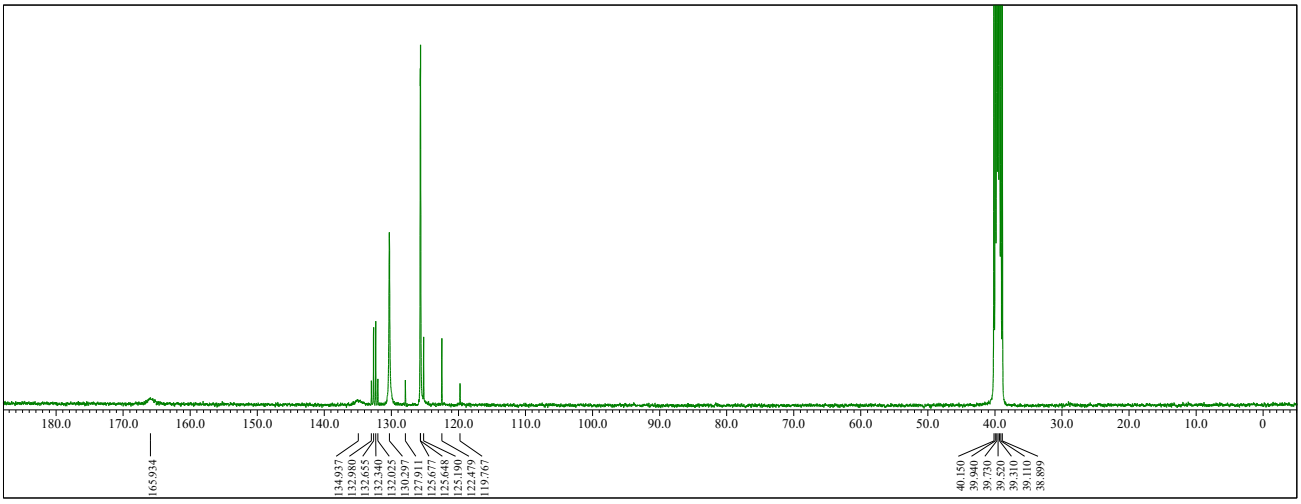



400 MHz $^{1}$H NMR spectrum of **2d** in DMSO-$d_6$.

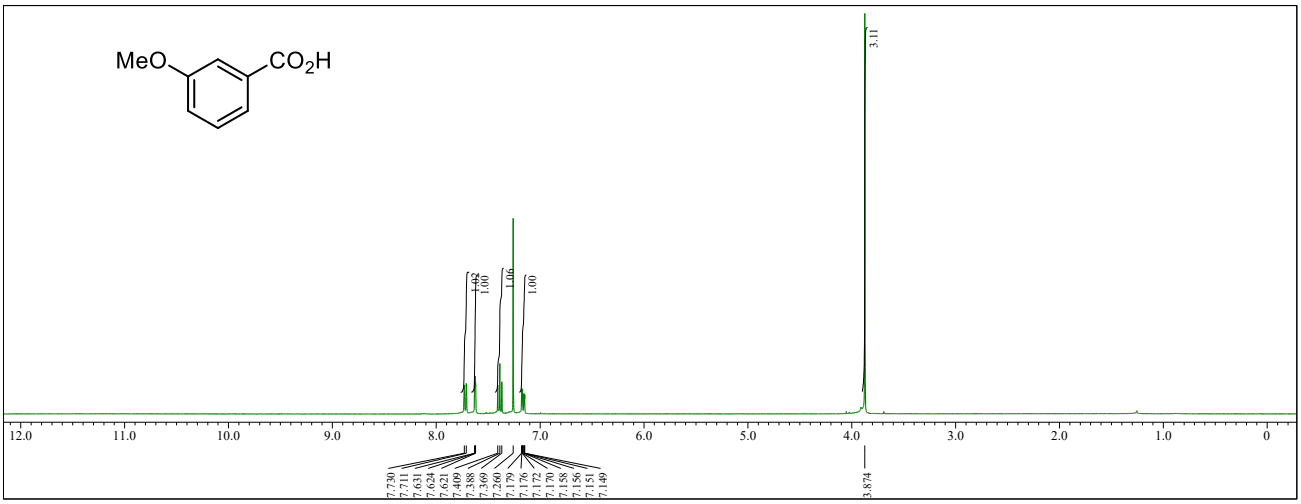

100 MHz $^{13}$C NMR spectrum of **2d** in DMSO-$d_6$.



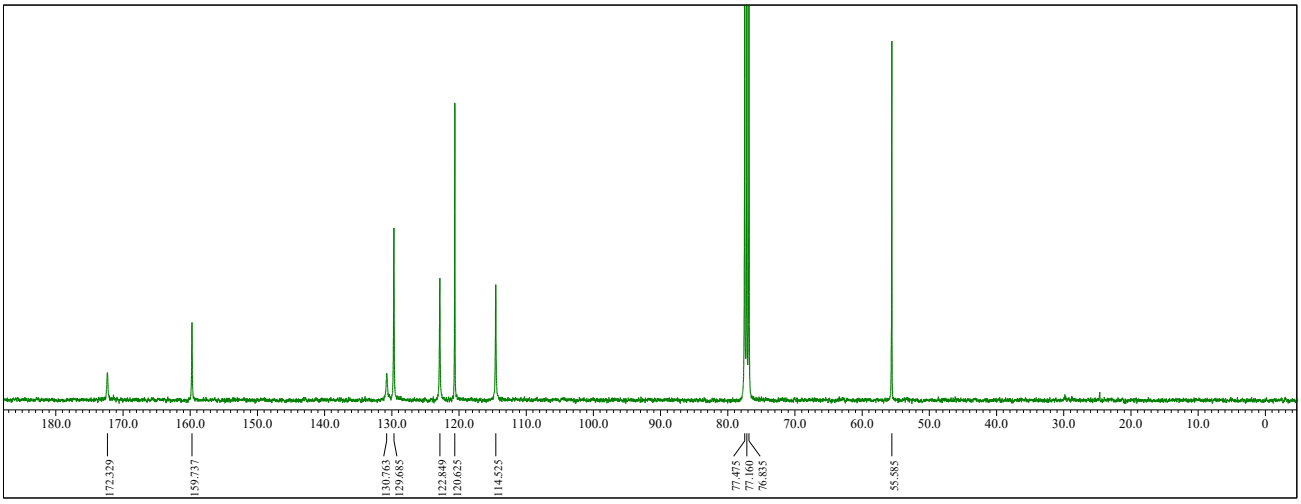

400 MHz $^{1}$H NMR spectrum of **2e** in DMSO-$d_6$.



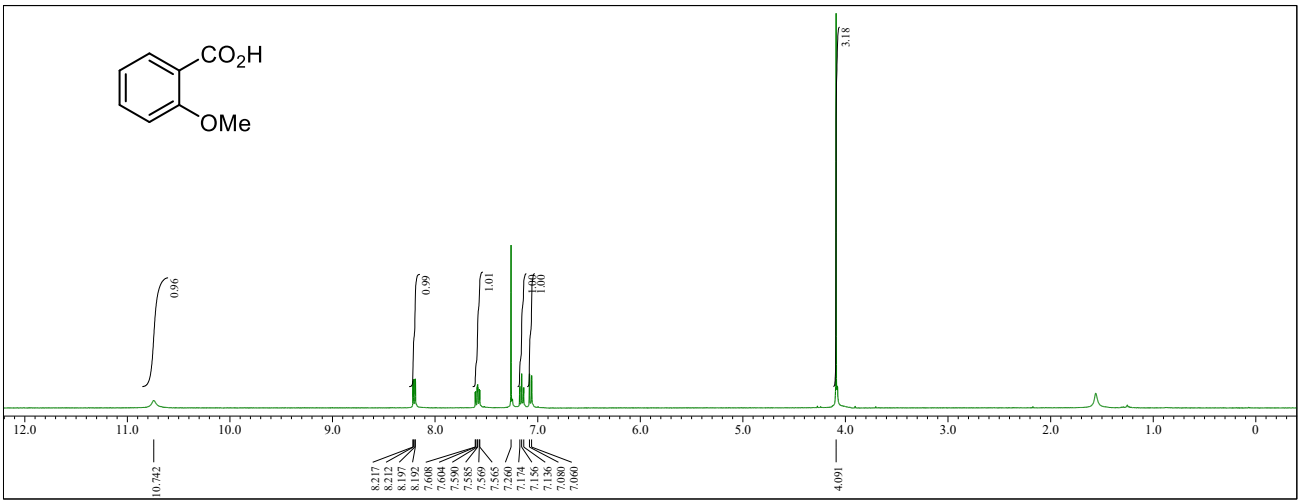

100 MHz $^{13}$C NMR spectrum of **2e** in DMSO-$d_6$.



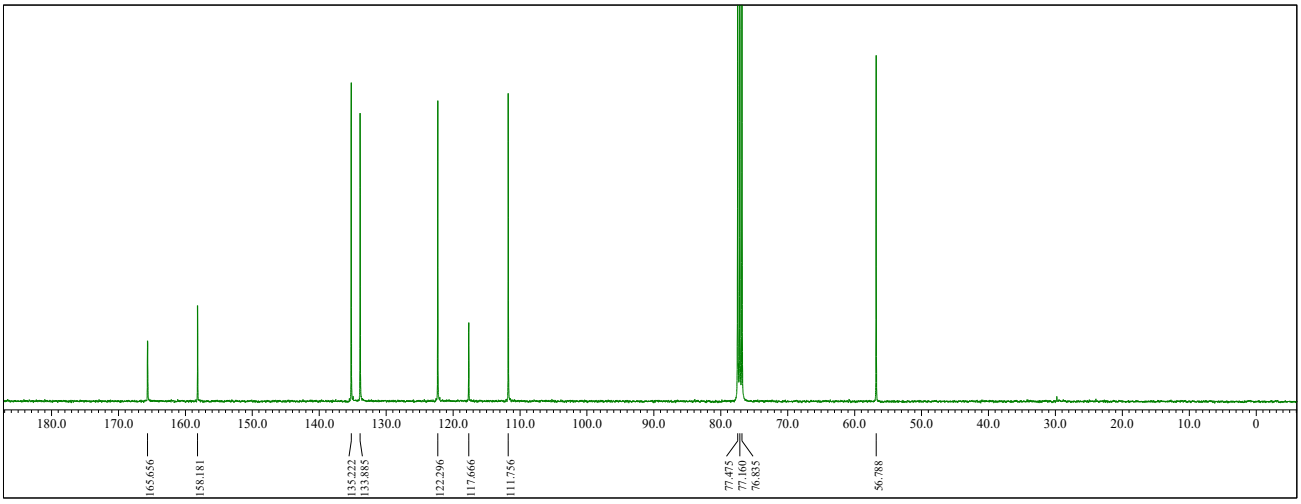

400 MHz $^{1}$H NMR spectrum of **2f** in $CDCl_3$.



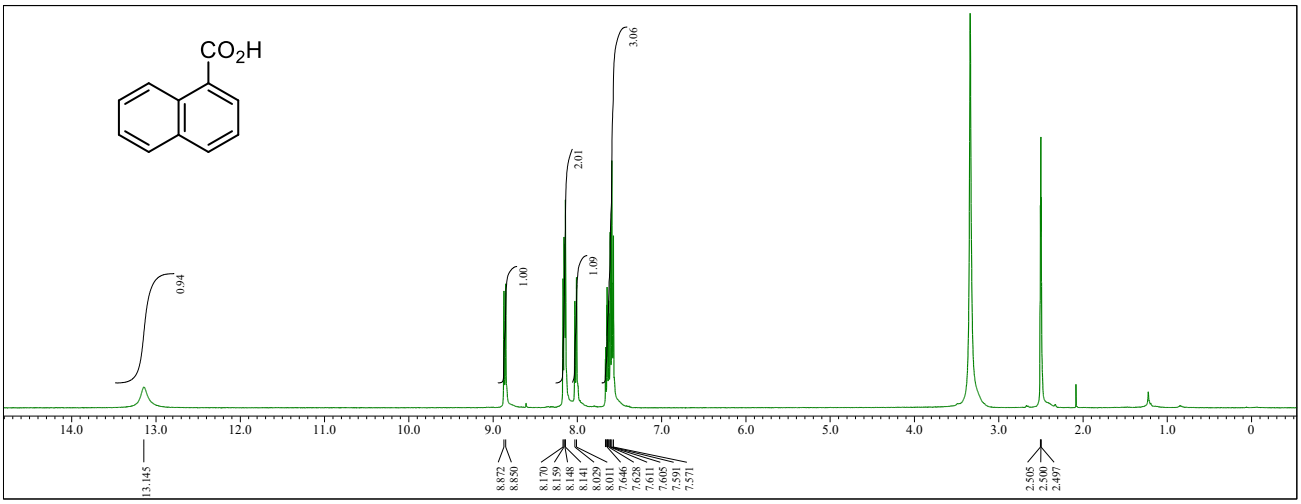

100 MHz $^{13}$C NMR spectrum of **2f** in $CDCl_3$.



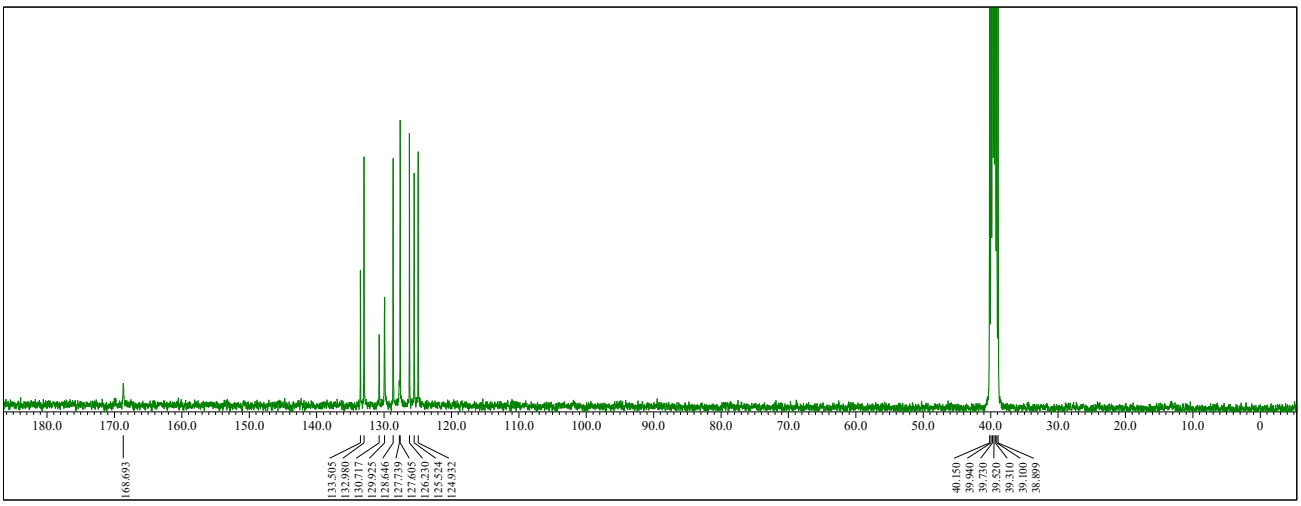

400 MHz $^{1}$H NMR spectrum of **2g** in $CDCl_3$.



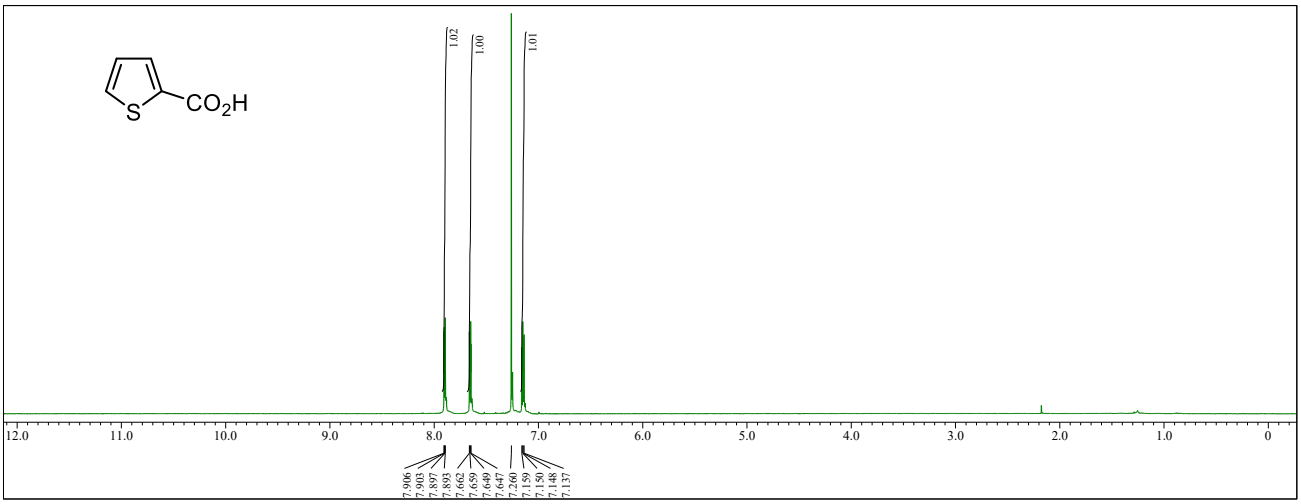

100 MHz $^{13}$C NMR spectrum of **2g** in $CDCl_3$.



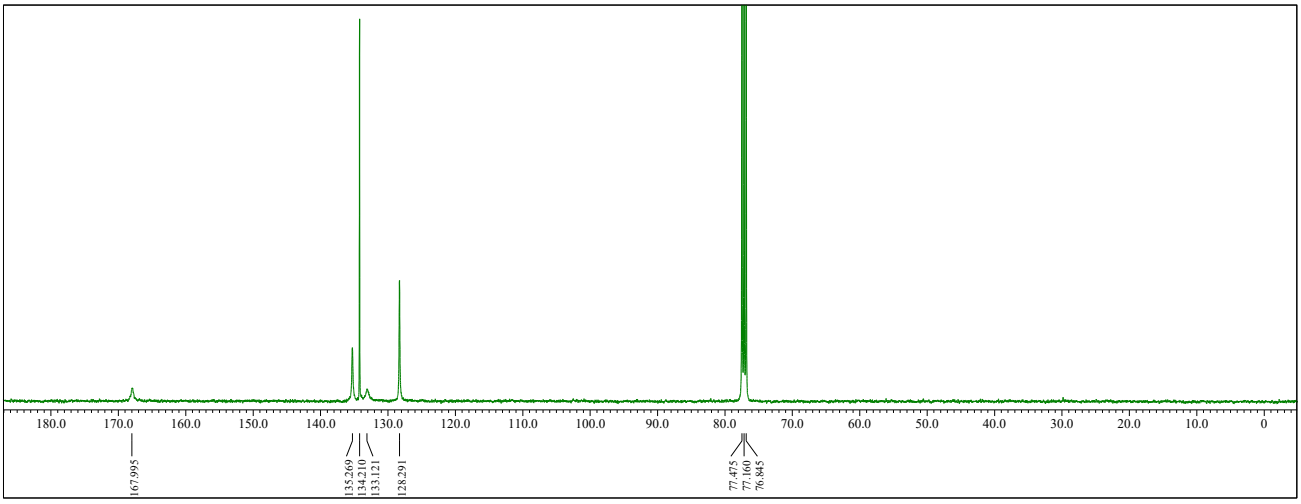

400 MHz $^{1}$H NMR spectrum of **2h** in DMSO-$d_6$.



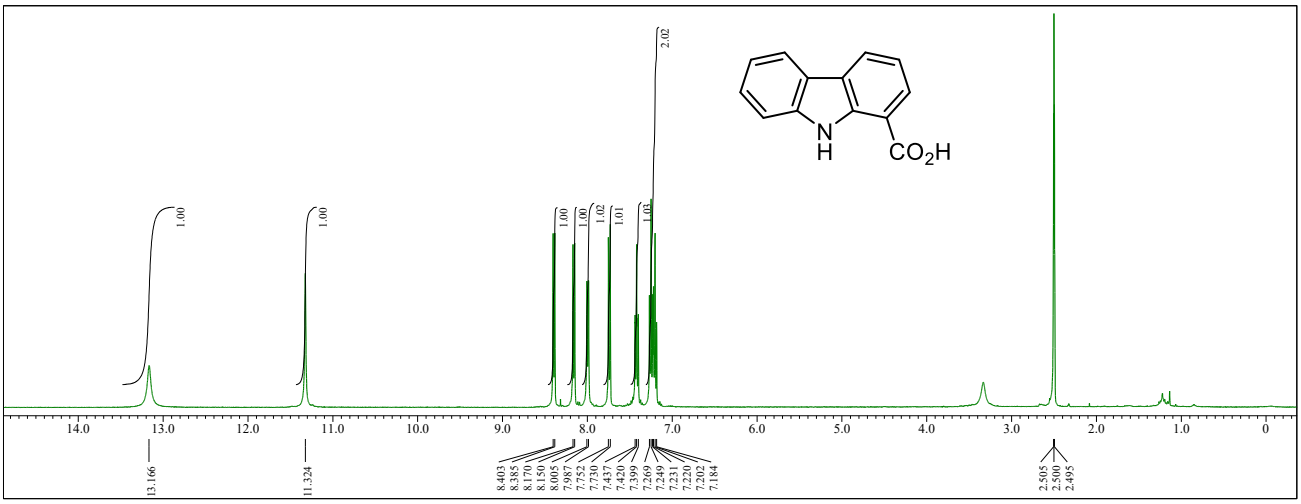

100 MHz $^{13}$C NMR spectrum of **2h** in DMSO-$d_6$.



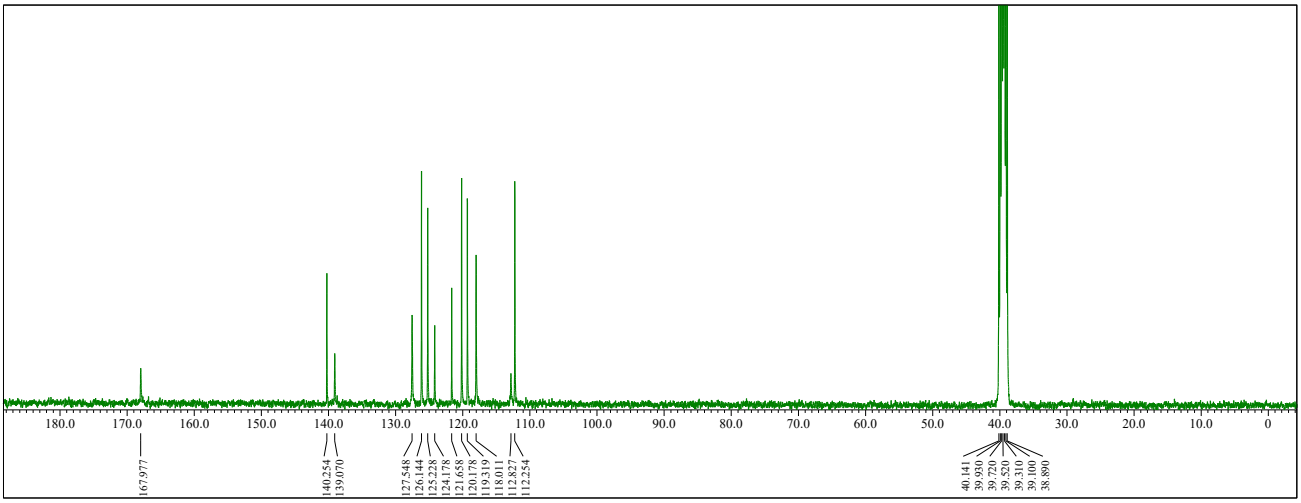

400 MHz $^{1}$H NMR spectrum of **2i** in $CDCl_3$.



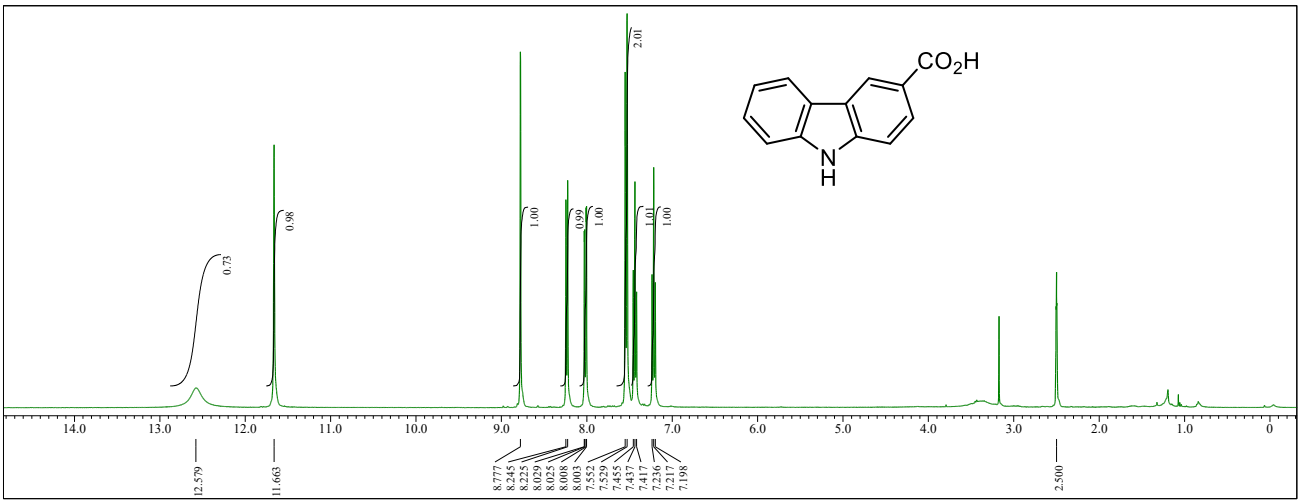

100 MHz $^{13}$C NMR spectrum of **2i** in $CDCl_3$.



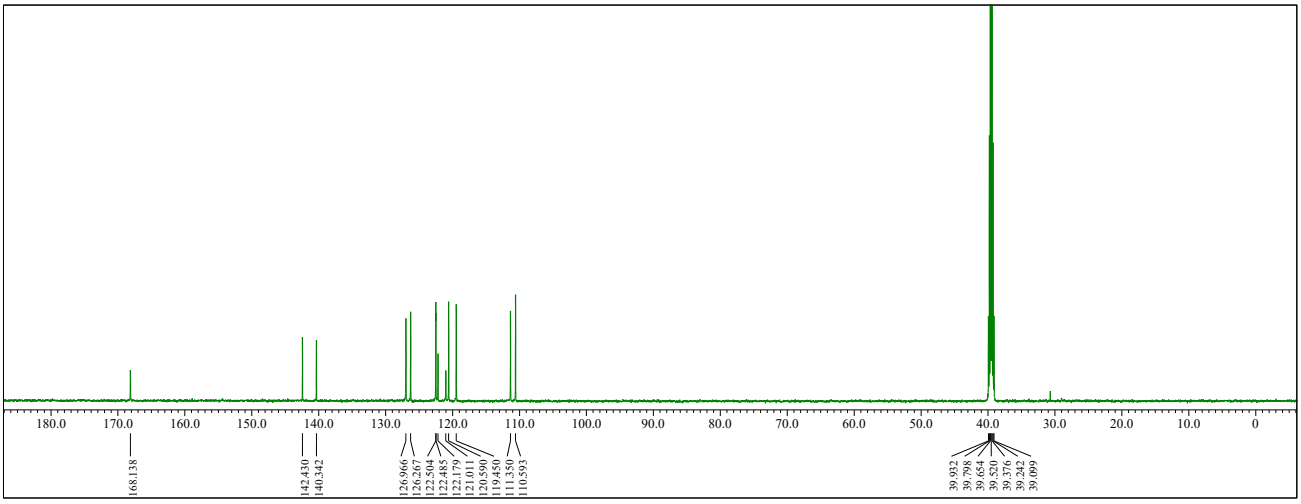

400 MHz $^{1}$H NMR spectrum of **2j** in DMSO-$d_6$.



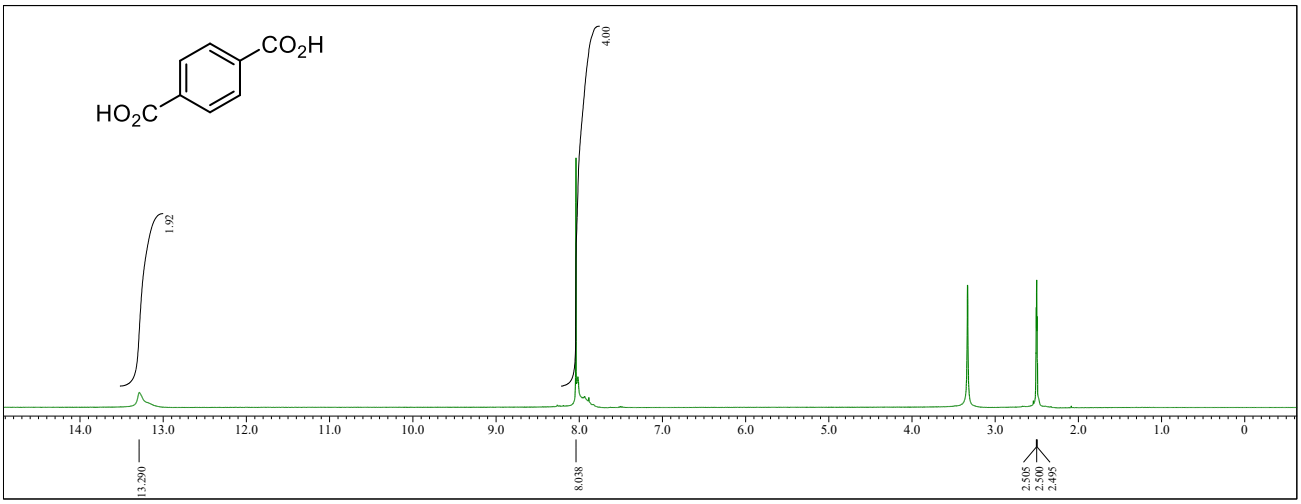
100 MHz $^{13}$C NMR spectrum of **2j** in DMSO-$d_6$.



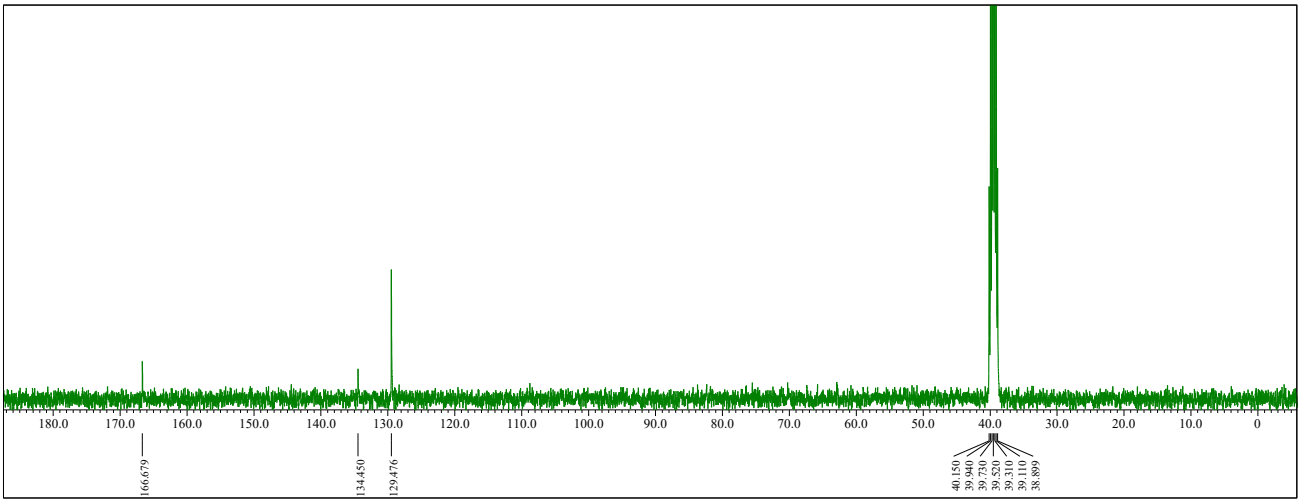

400 MHz $^{1}$H NMR spectrum of **2k** in DMSO-$d_6$.



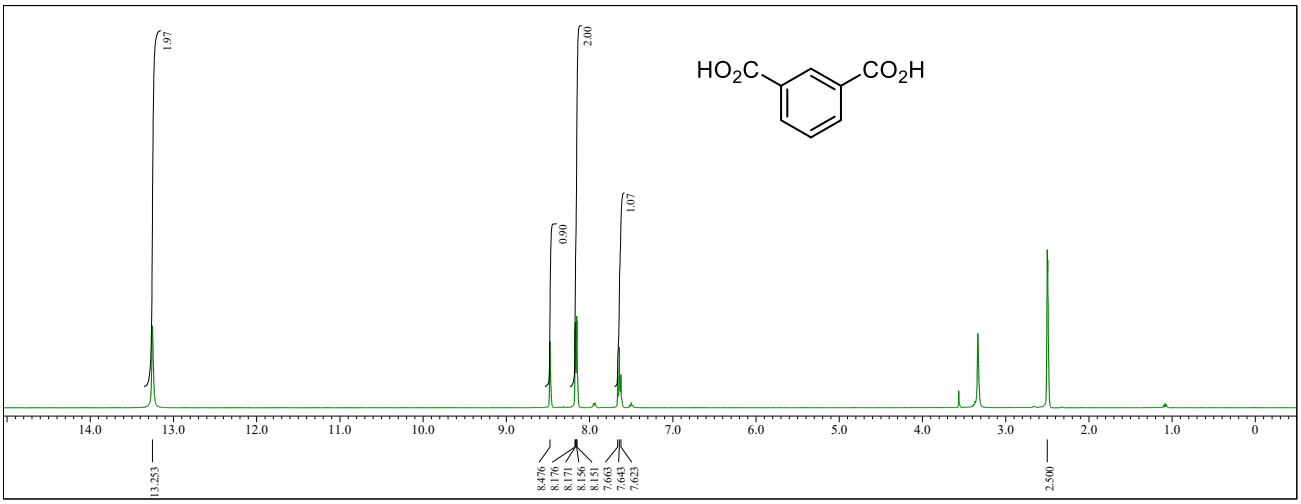

150 MHz $^{13}$C NMR spectrum of **2k** in DMSO-$d_6$.



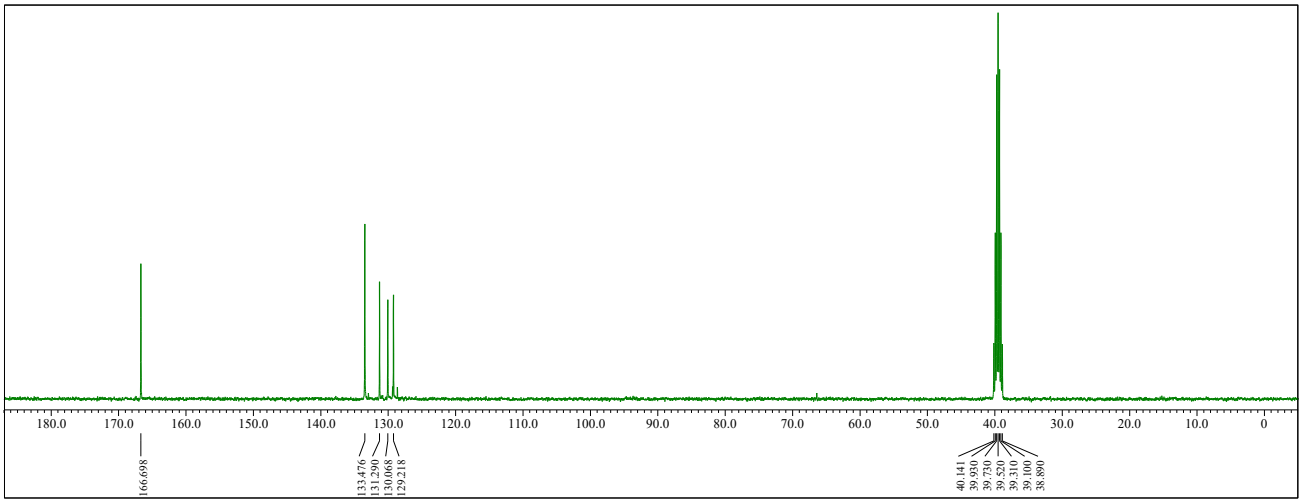

400 MHz $^{1}$H NMR spectrum of **2l** in DMSO-$d_6$.



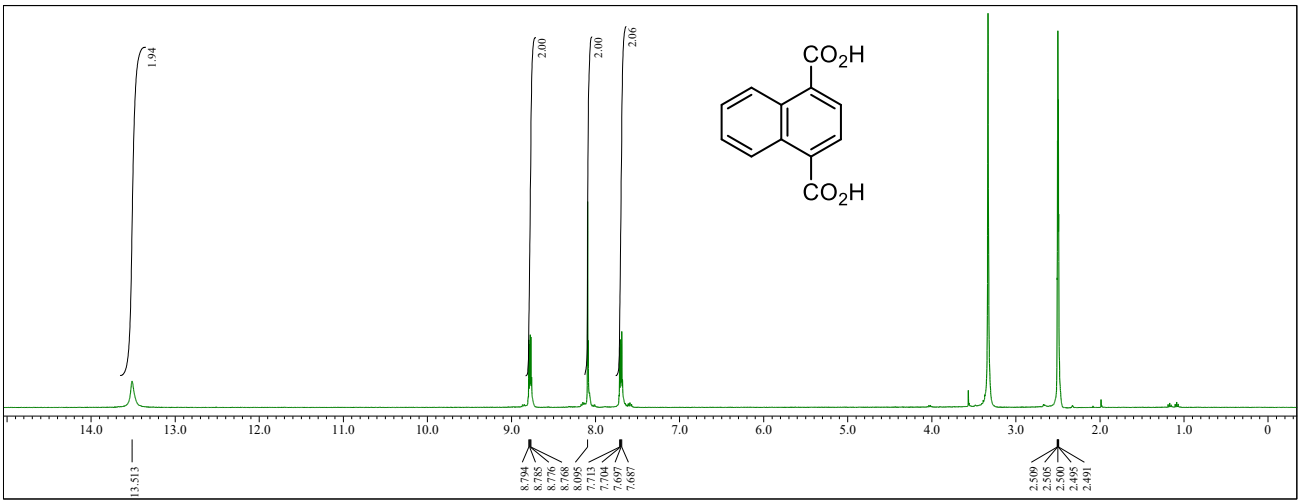

100 MHz $^{13}$C NMR spectrum of **2l** in DMSO-$d_6$.



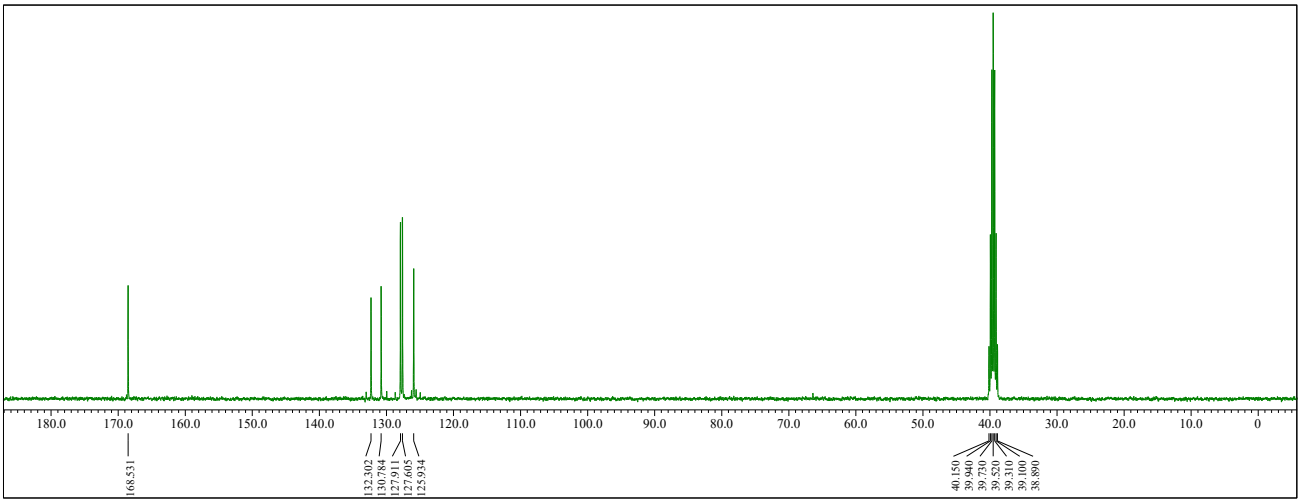

400 MHz $^{1}$H NMR spectrum of **2m** in DMSO-$d_6$.



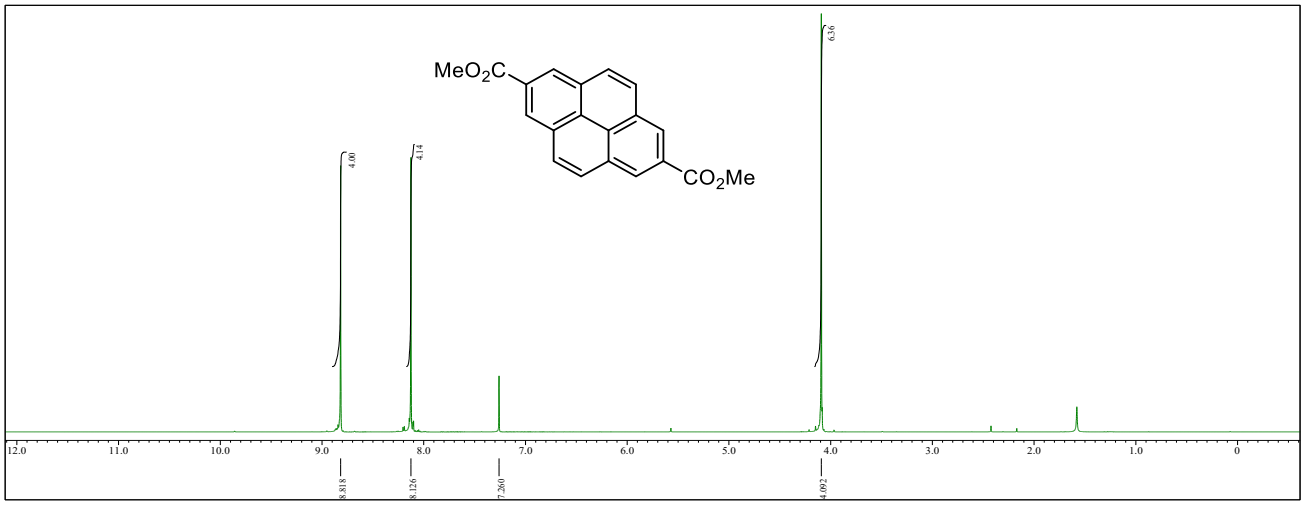

100 MHz $^{13}$C NMR spectrum of **2m** in DMSO-$d_6$.



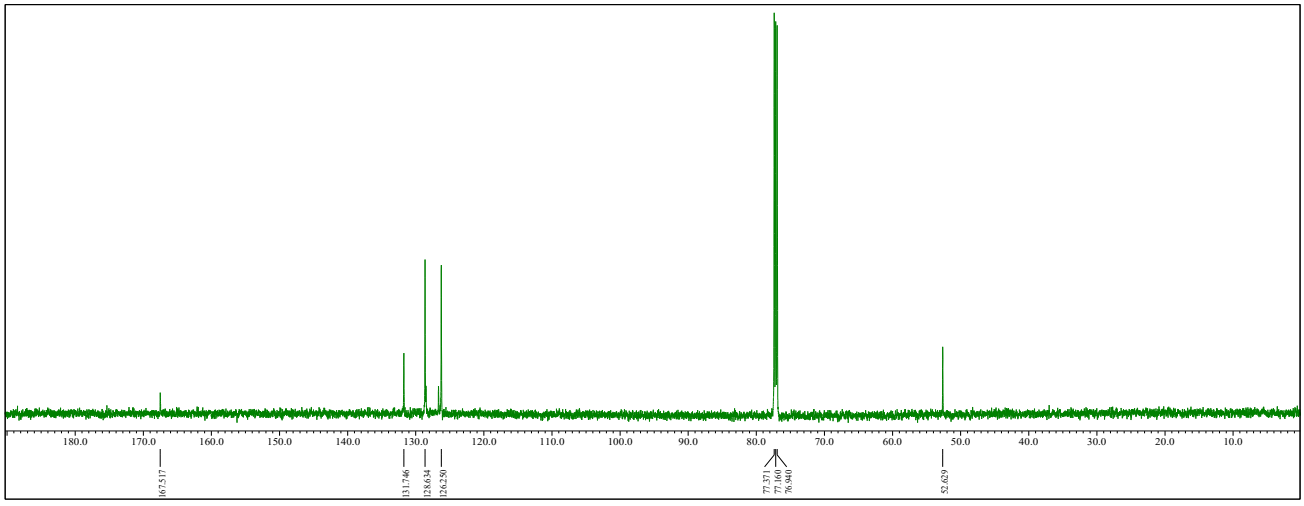

400 MHz $^{1}$H NMR spectrum of **2n** in DMSO-$d_6$.



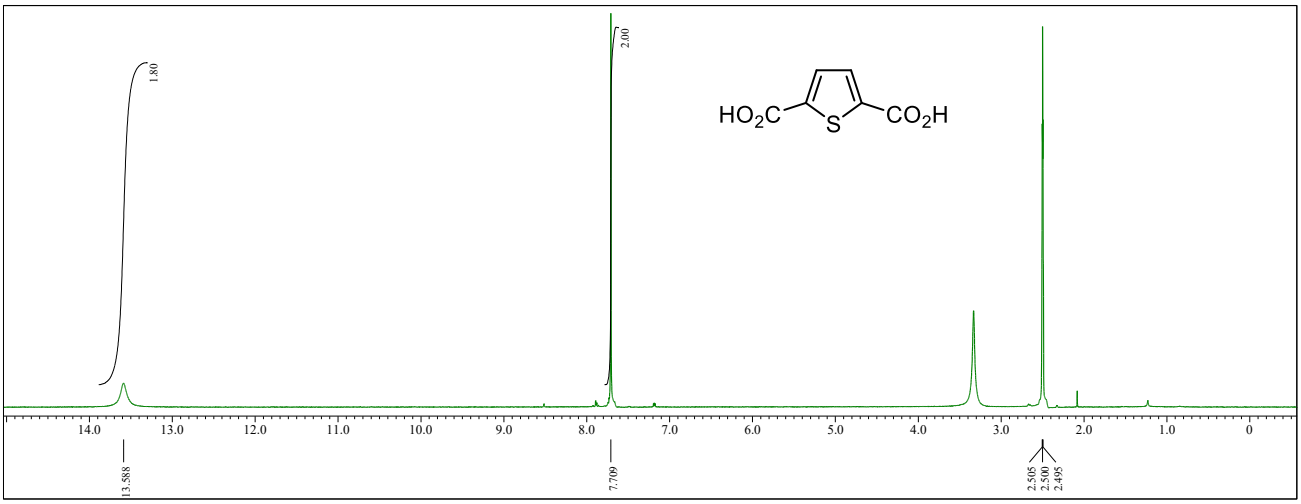

100 MHz $^{13}$C NMR spectrum of **2n** in DMSO-$d_6$.



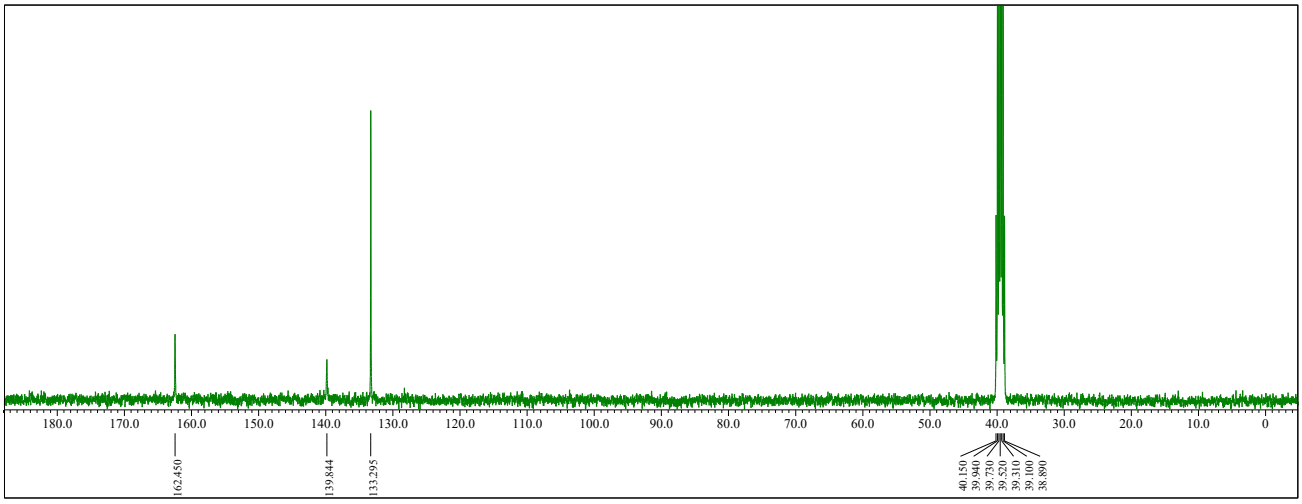

600 MHz $^{1}$H NMR spectrum of **2o'** in $CDCl_3$.



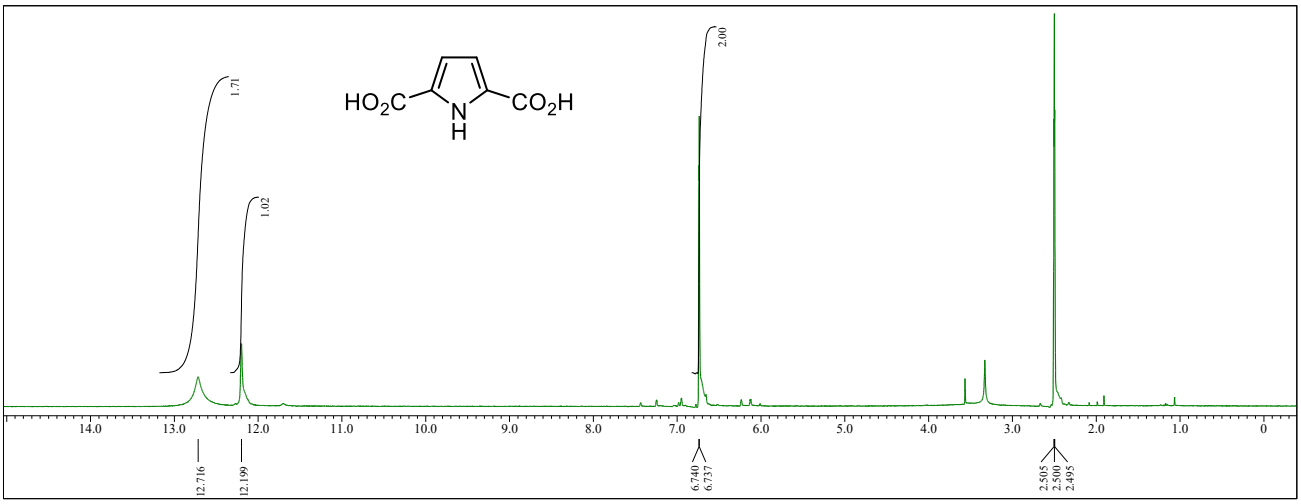

150 MHz $^{13}$C NMR spectrum of **2o'** in $CDCl_3$.



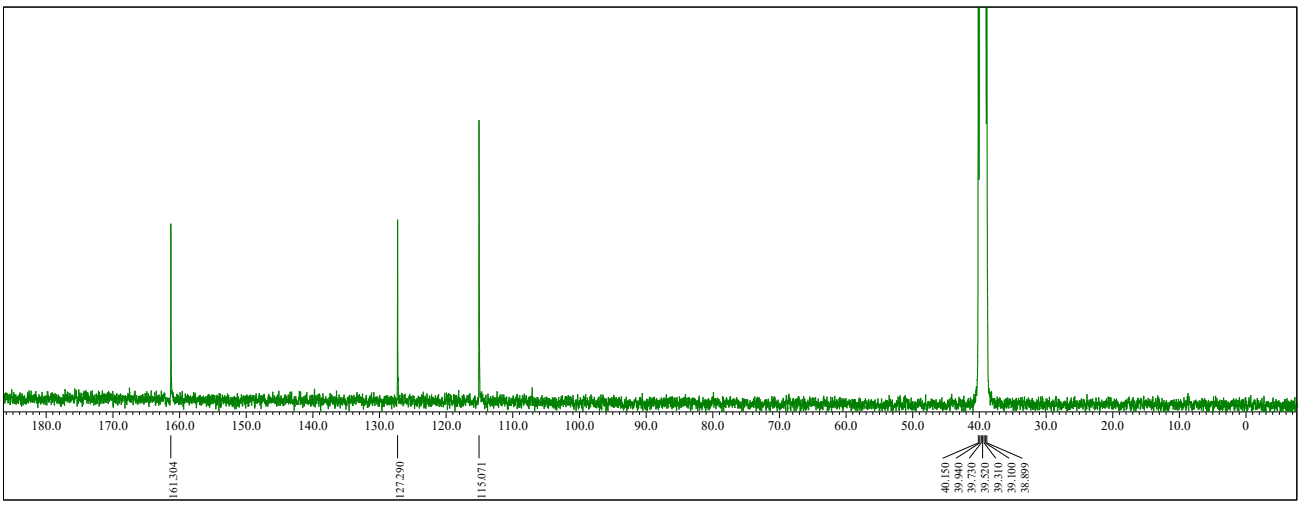

400 MHz $^{1}$H NMR spectrum of **2p** in DMSO-$d_6$.



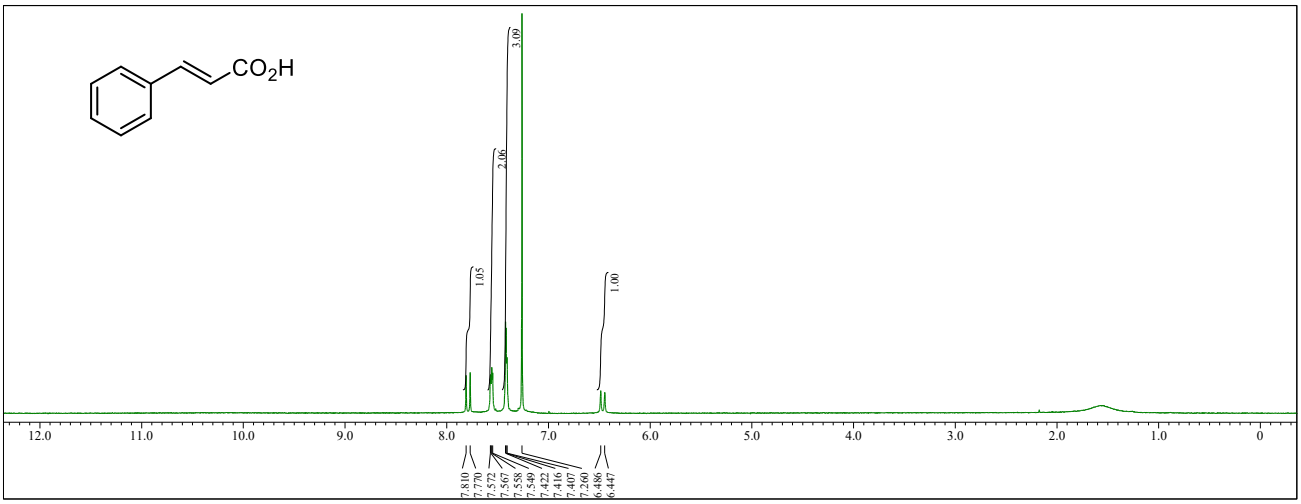

100 MHz $^{13}$C NMR spectrum of **2p** in DMSO-$d_6$.



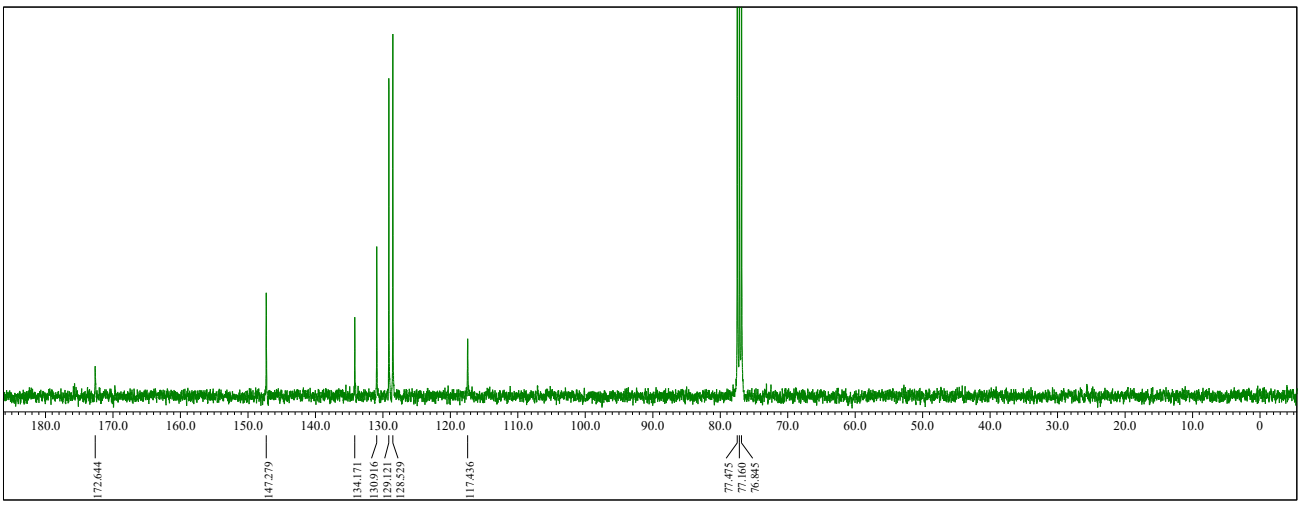

400 MHz $^{1}$H NMR spectrum of **2q** in DMSO-$d_6$.



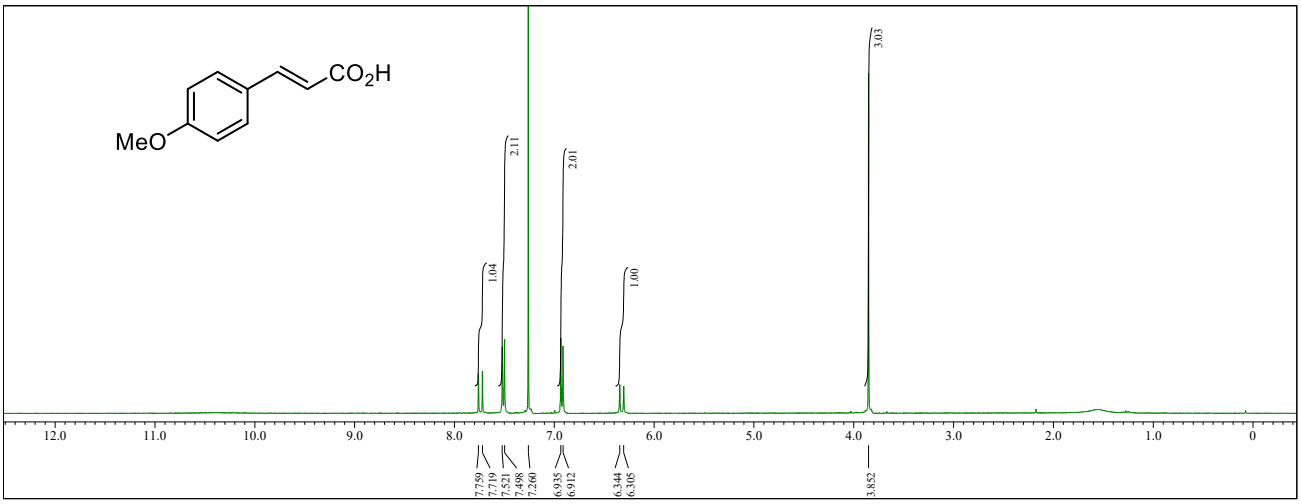

100 MHz $^{13}$C NMR spectrum of **2q** in DMSO-$d_6$.



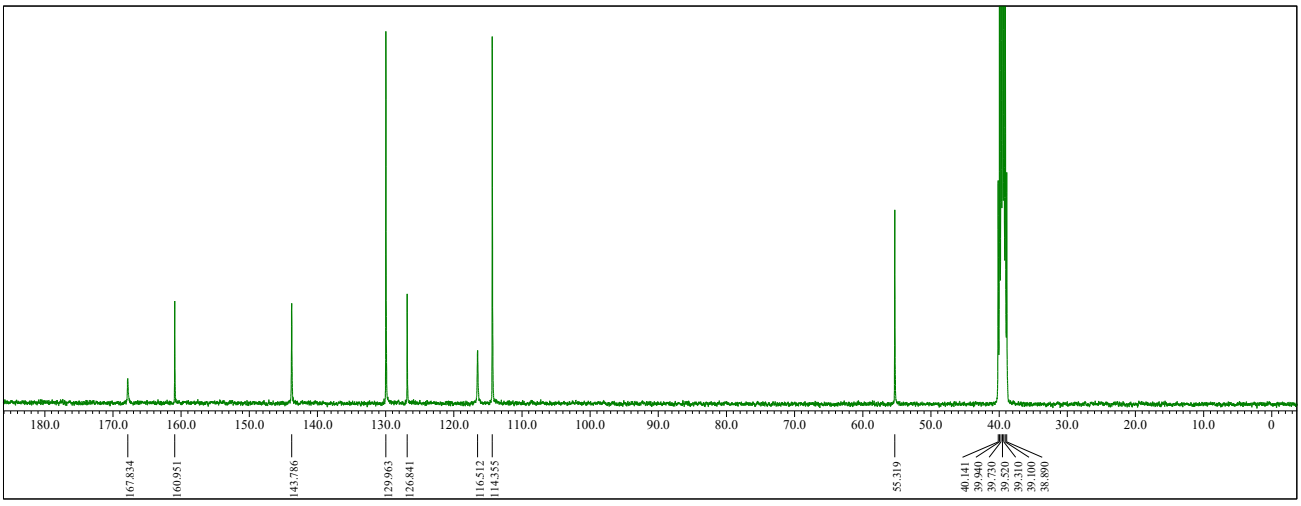

400 MHz $^{1}$H NMR spectrum of **4a** in $CDCl_3$.



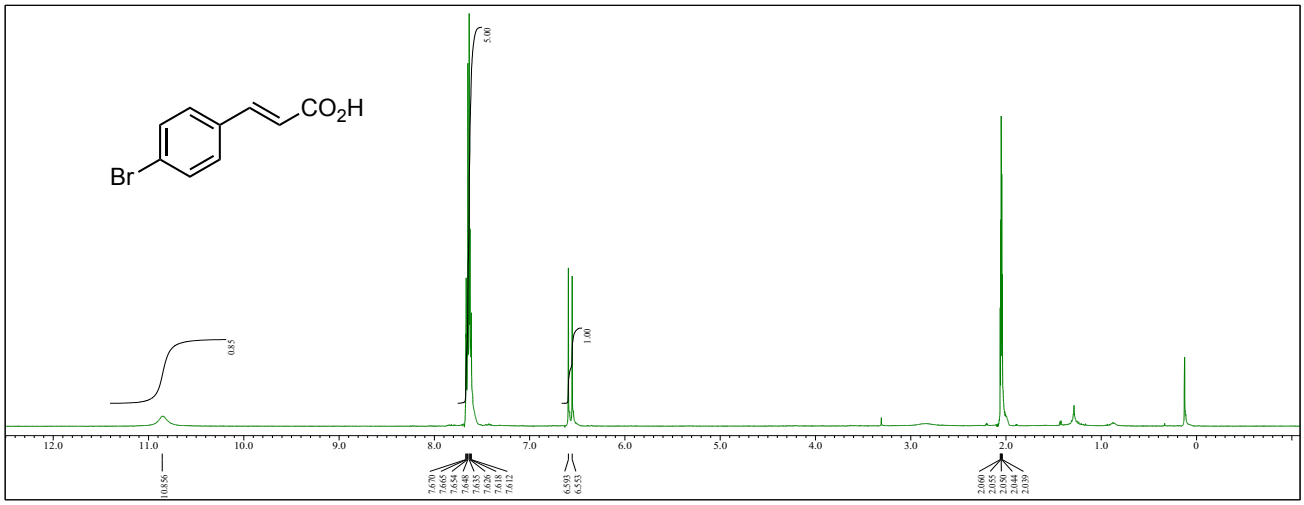

100 MHz $^{13}$C NMR spectrum of **4a** in $CDCl_3$.



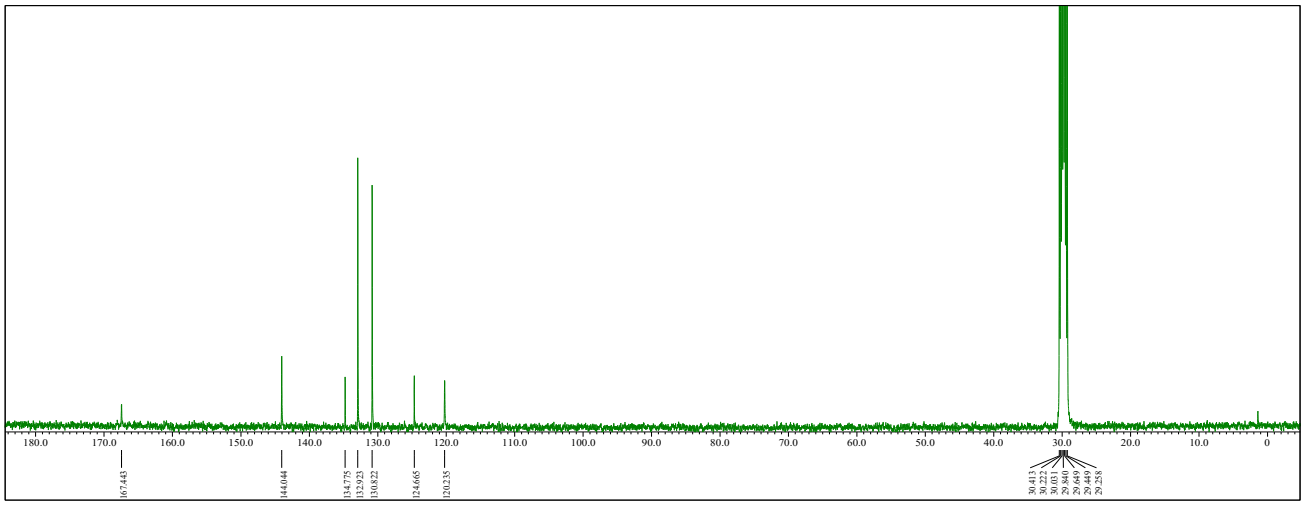

400 MHz $^{1}$H NMR spectrum of **4b** in $CDCl_3$.



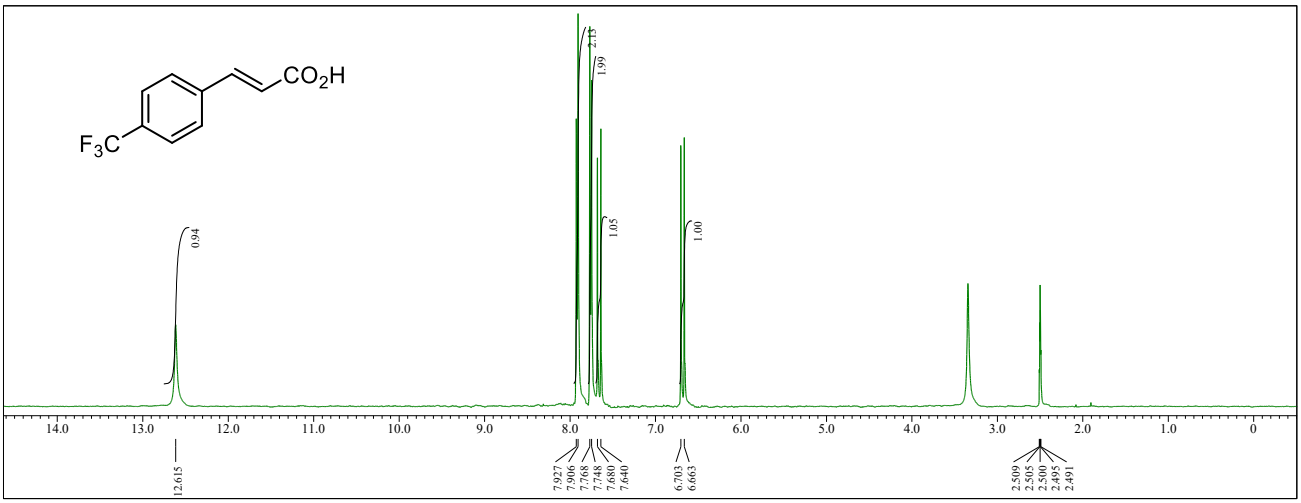

100 MHz $^{13}$C NMR spectrum of **4b** in DMSO-$d_6$.



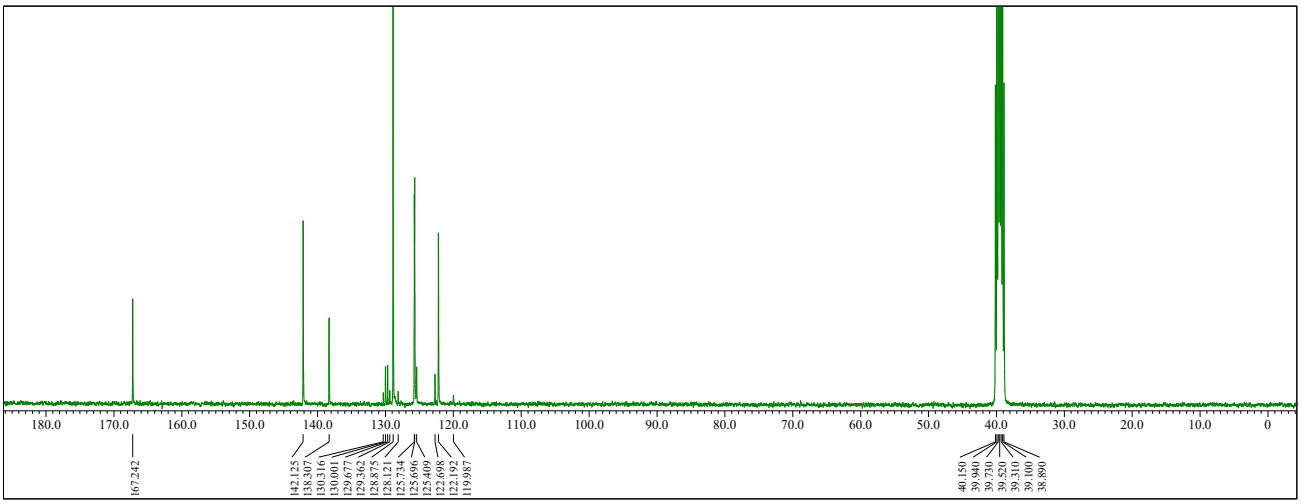

400 MHz $^{1}$H NMR spectrum of **4c** in acetone-$d_6$.



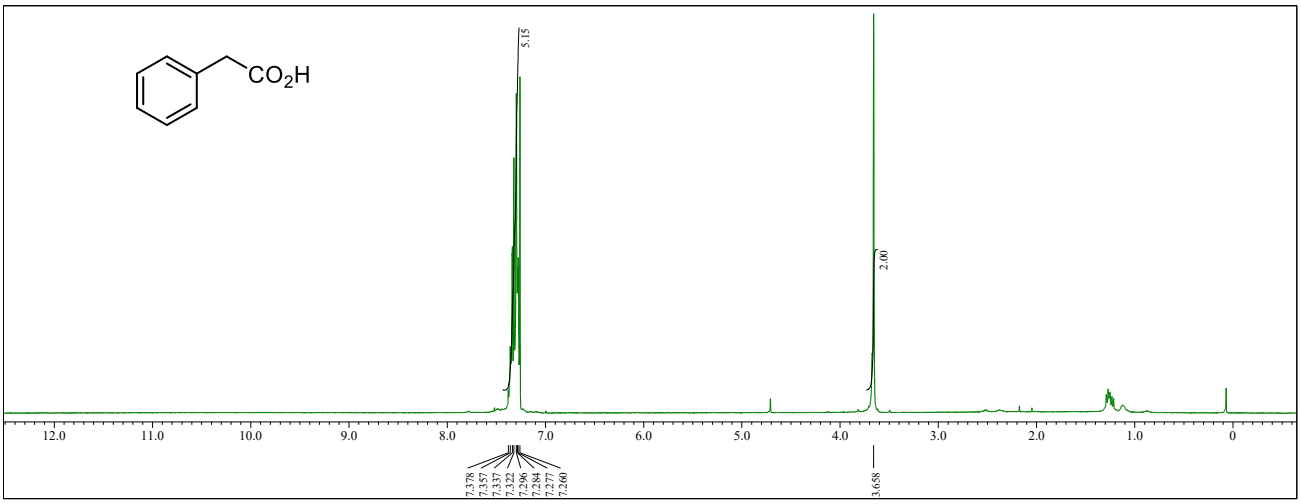
100 MHz $^{13}$C NMR spectrum of **4c** in acetone-$d_6$.



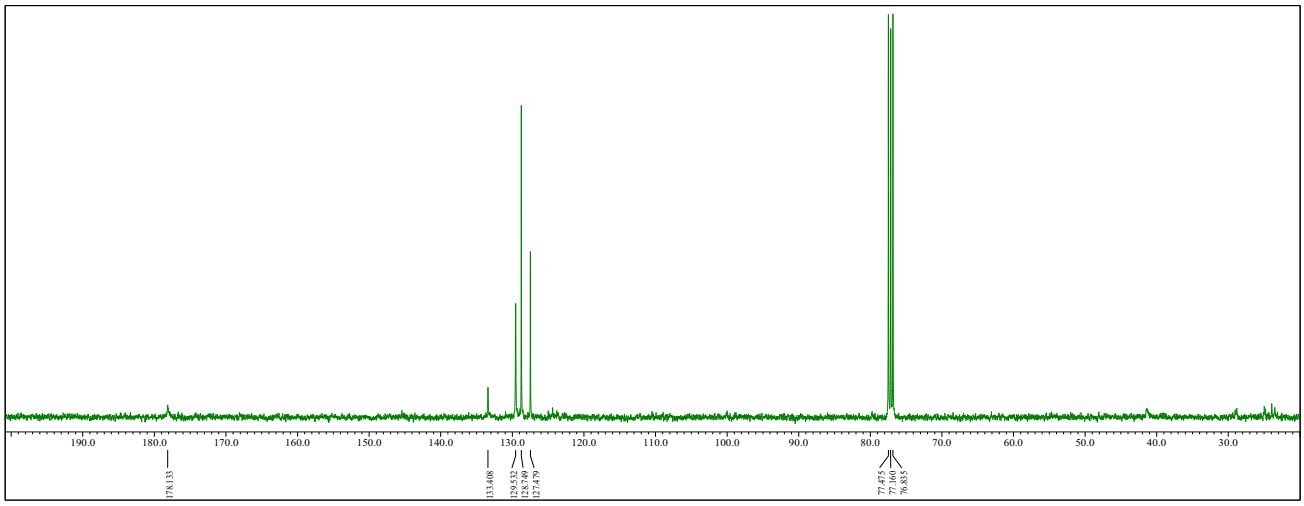

400 MHz $^{1}$H NMR spectrum of **4d** in DMSO-$d_6$.



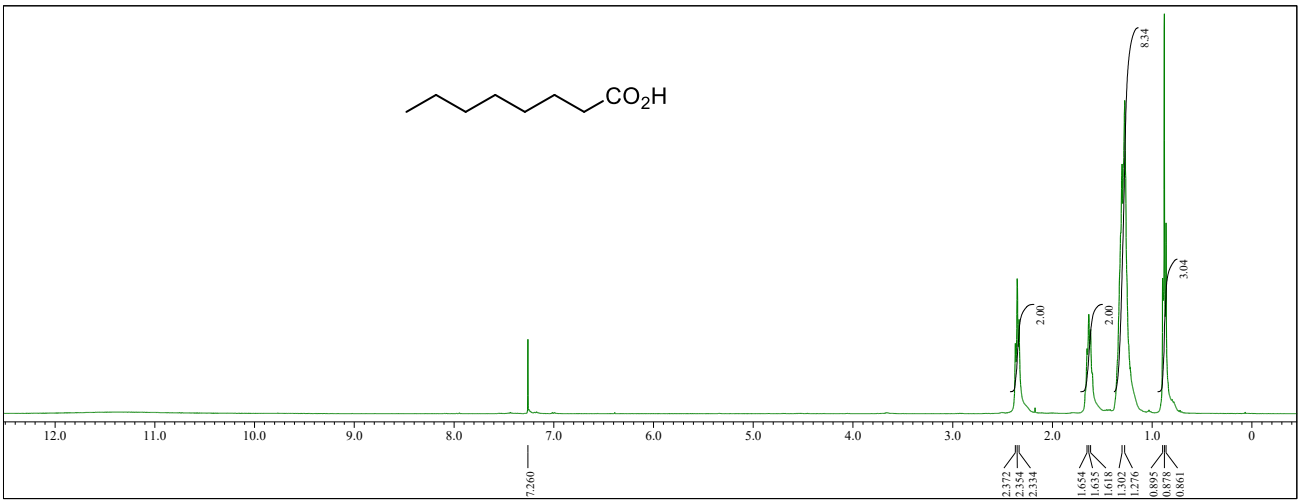

100 MHz $^{13}$C NMR spectrum of **4d** in DMSO-$d_6$.



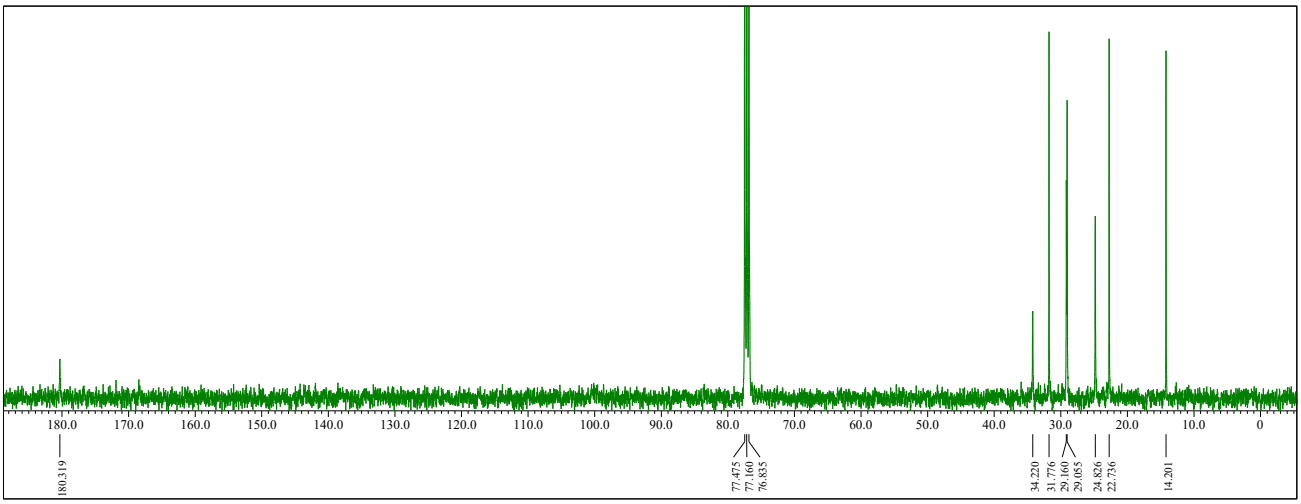

400 MHz $^{1}$H NMR spectrum of **4e** in $CDCl_3$.



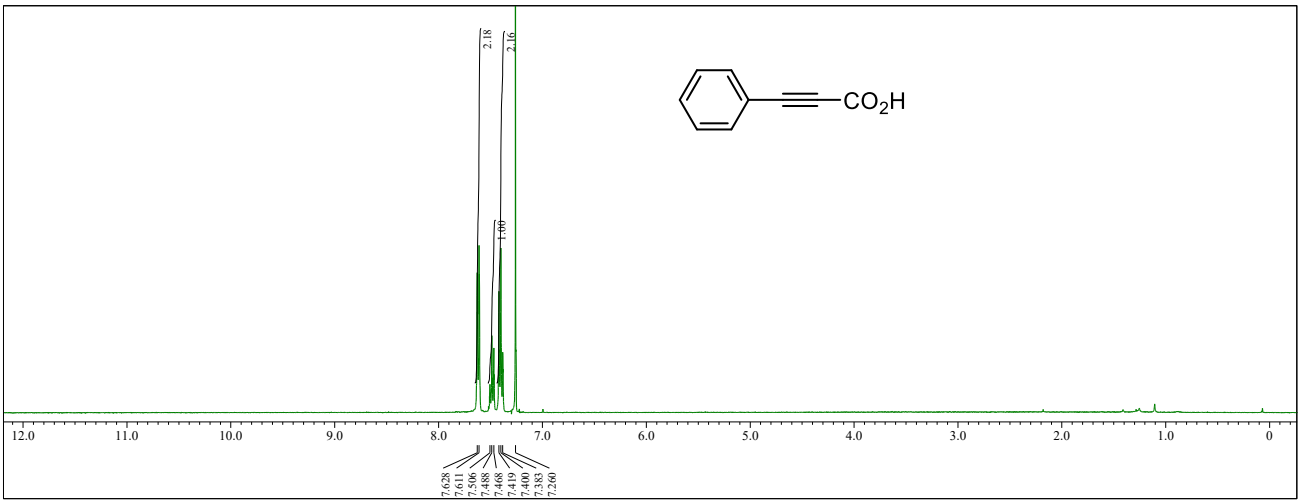

100 MHz $^{13}$C NMR spectrum of **4e** in $CDCl_3$.



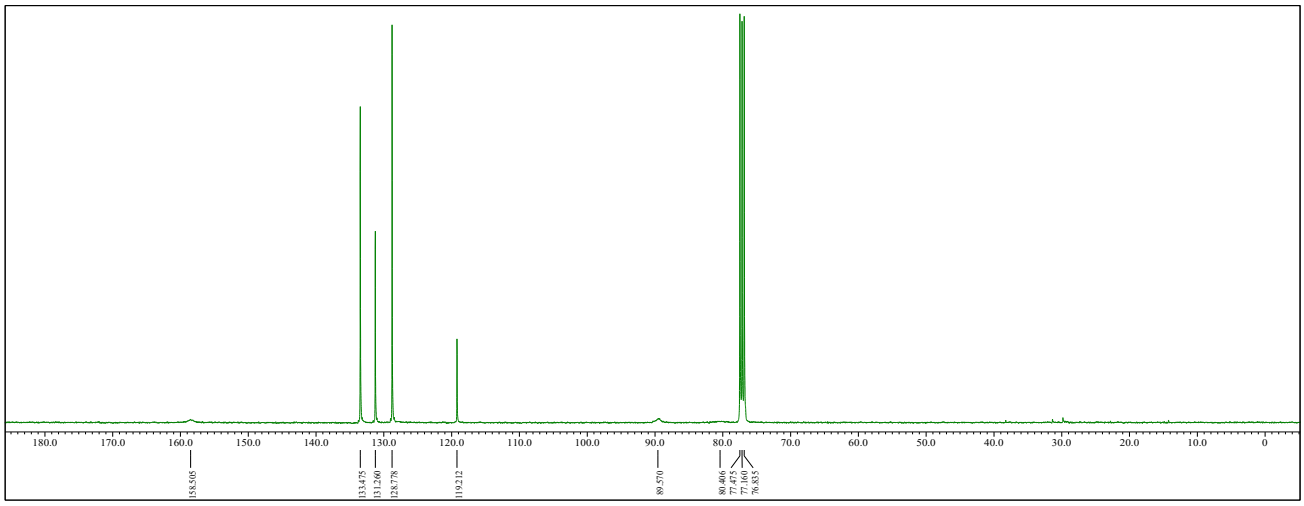

400 MHz $^{1}$H NMR spectrum of **4f** in $CDCl_3$.



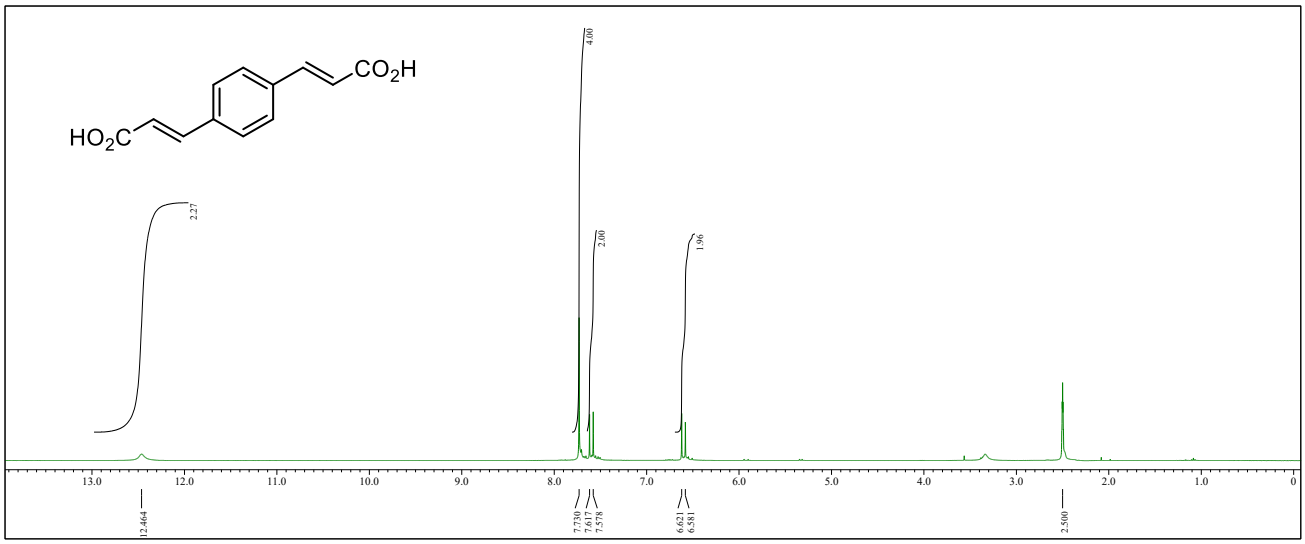

100 MHz $^{13}$C NMR spectrum of **4f** in $CDCl_3$.



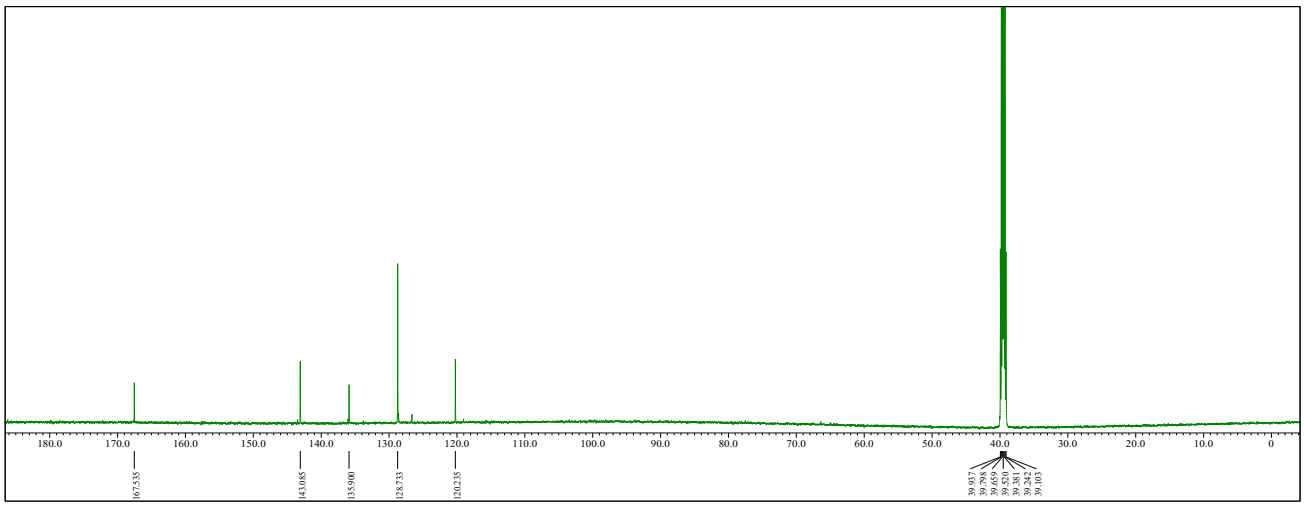

400 MHz $^{1}$H NMR spectrum of **4g** in $CDCl_3$.



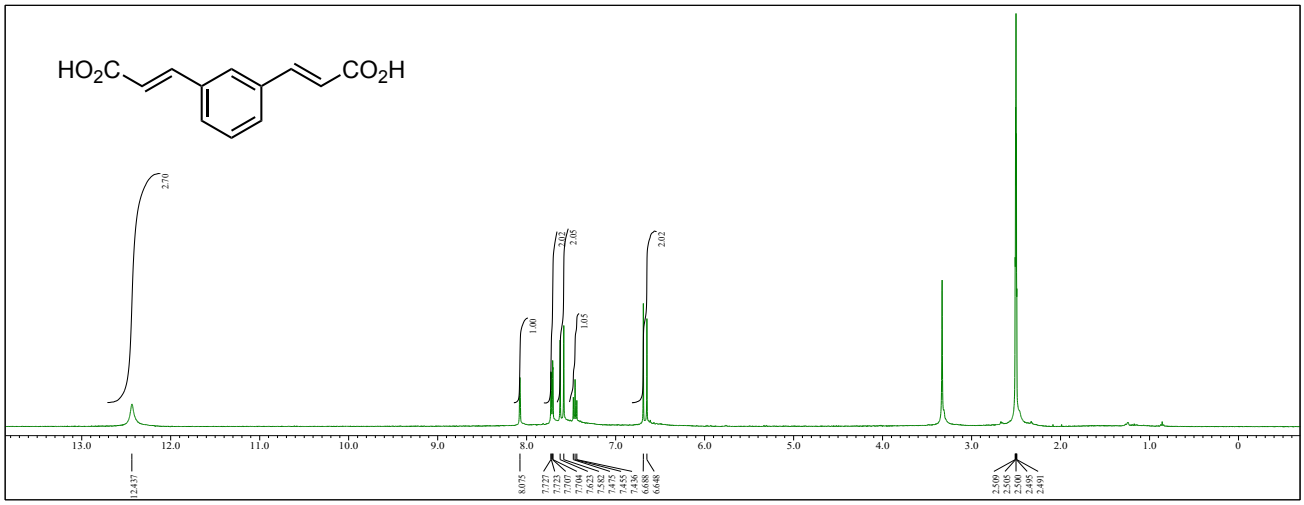

100 MHz $^{13}$C NMR spectrum of **4g** in $CDCl_3$.



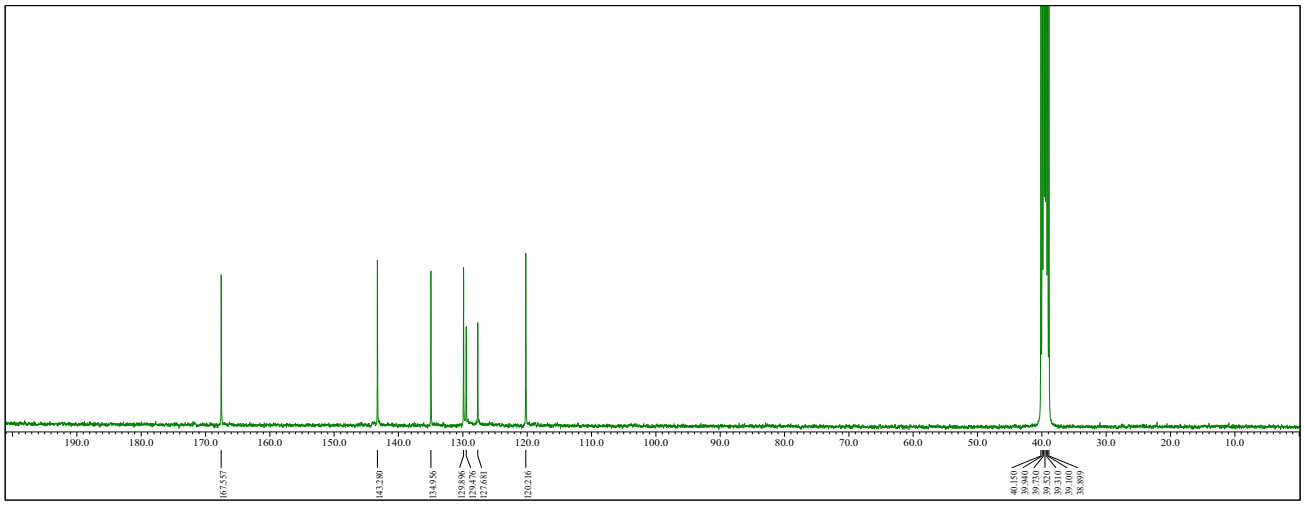

400 MHz $^{1}$H NMR spectrum of **4h** in DMSO-$d_6$.



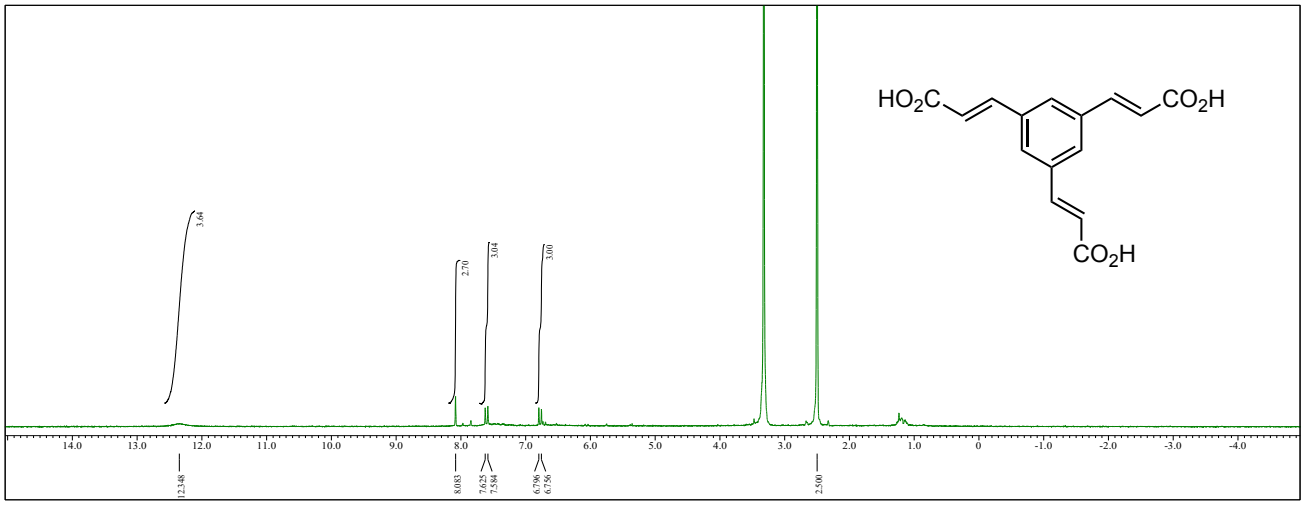

150 MHz $^{13}$C NMR spectrum of **4h** in DMSO-$d_6$.



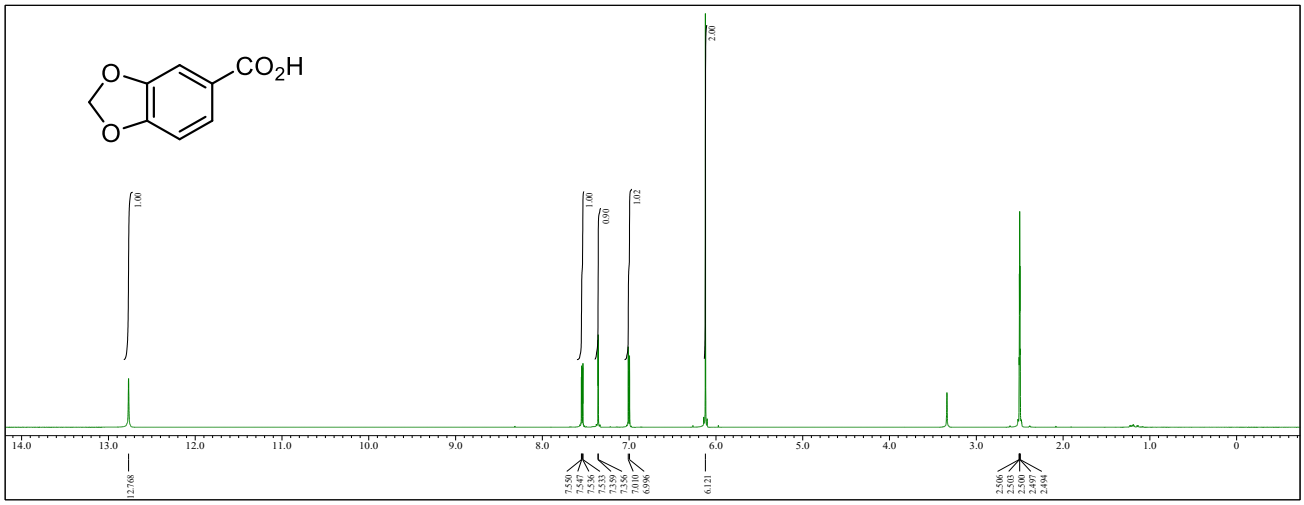

400 MHz $^{1}$H NMR spectrum of **4i** in DMSO-$d_6$.



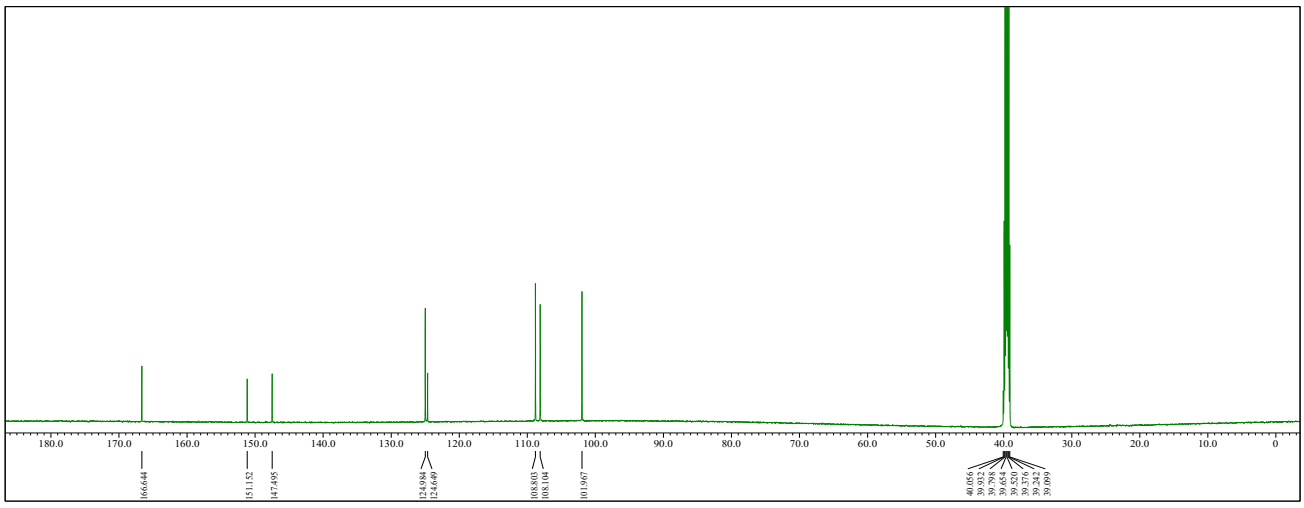
100 MHz $^{13}$C NMR spectrum of **4i** in DMSO-$d_6$.



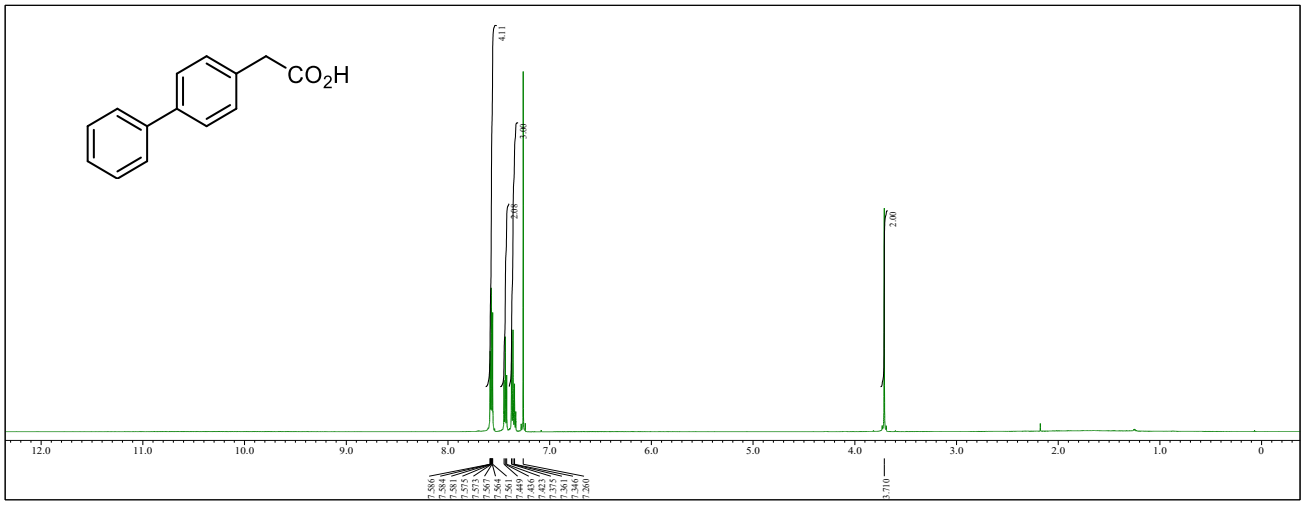

400 MHz $^{1}$H NMR spectrum of **4j** in DMSO-$d_6$.



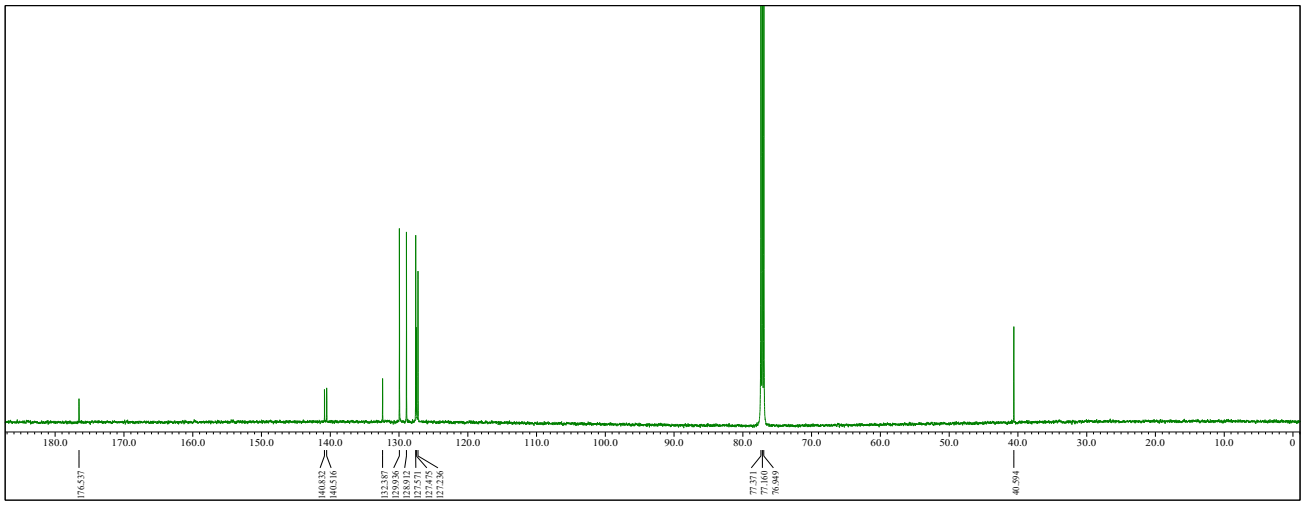

600 MHz $^{1}$H NMR spectrum of piperonylic acid in DMSO-$d_6$.




150 MHz $^{13}$C NMR spectrum of piperonylic acid in DMSO-$d_6$.




600 MHz $^{1}$H NMR spectrum of felbinac in $CDCl_3$.




150 MHz $^{13}$C NMR spectrum of felbinac in $CDCl_3$.