Polystyrene Supported Palladium Nanoparticles Catalyzed Cinnamic Acid Synthesis using Maleic Anhydride as Substitute of Acrylic Acid

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1. General Information

High quality reagents and analytical grade solvents were purchased from Sigma Aldrich, TCI Chemicals, Merck and Sd Fine Chem. Ltd. Amberlite® IRA 900 Cl^- resin (PS) was procured from Acros Organics. Reactions were monitored using TLC which was performed on pre coated silica gel plates 60 F_{254} (purchased from Merck) in UV light detector. Silica gel (60-120 mesh size) for column chromatography purchased from Merck was used for the purification of compounds. ^1H and ^{13}C NMR spectra were recorded using a Bruker Avance 600 spectrometer operating at 300/600 MHz (^1H) and 75/150 MHz (^{13}C) NMR spectra were recorded at 25 °C in CD_3OD [residual CH_3OH (δ_H 3.33 and 4.86 ppm) and CH_3OH (δc 49.00 ppm)], DMSO-d_6 [residual DMSO (δ_H 2.50 and 3.42 ppm) and DMSO (δ_C 39.54 ppm)] with TMS as internal standard. Chemical shifts were recorded in δ (ppm) relative to the TMS and NMR solvent signal, coupling constants (*J*) are given in Hz and multiplicities of signals are reported as follows: s, singlet; d, doublet; t, triplet; m, multiplet; br, broad singlet. Melting points were determined by using MR-VIS$^+$ melting point apparatus and are uncorrected.

2. Preparation of polystyrene supported Palladium (0) (Pd@PS) nanoparticles as catalyst

The solution of 30 mg $NaBH_4$ in 10 mL distilled water was added to 1g of Amberlite® IRA 900 Cl^- resin (PS) in 50 mL round bottom flask. The resulting mixture was stirred for 4 h at room temperature. Then the partially borohydride exchanged resin was washed with water till the pH became neutral and later with acetone to remove excess of water from polymer surface. This exchanged polystyrene resin (PS-$BH4^-$) was dried under reduced pressure.

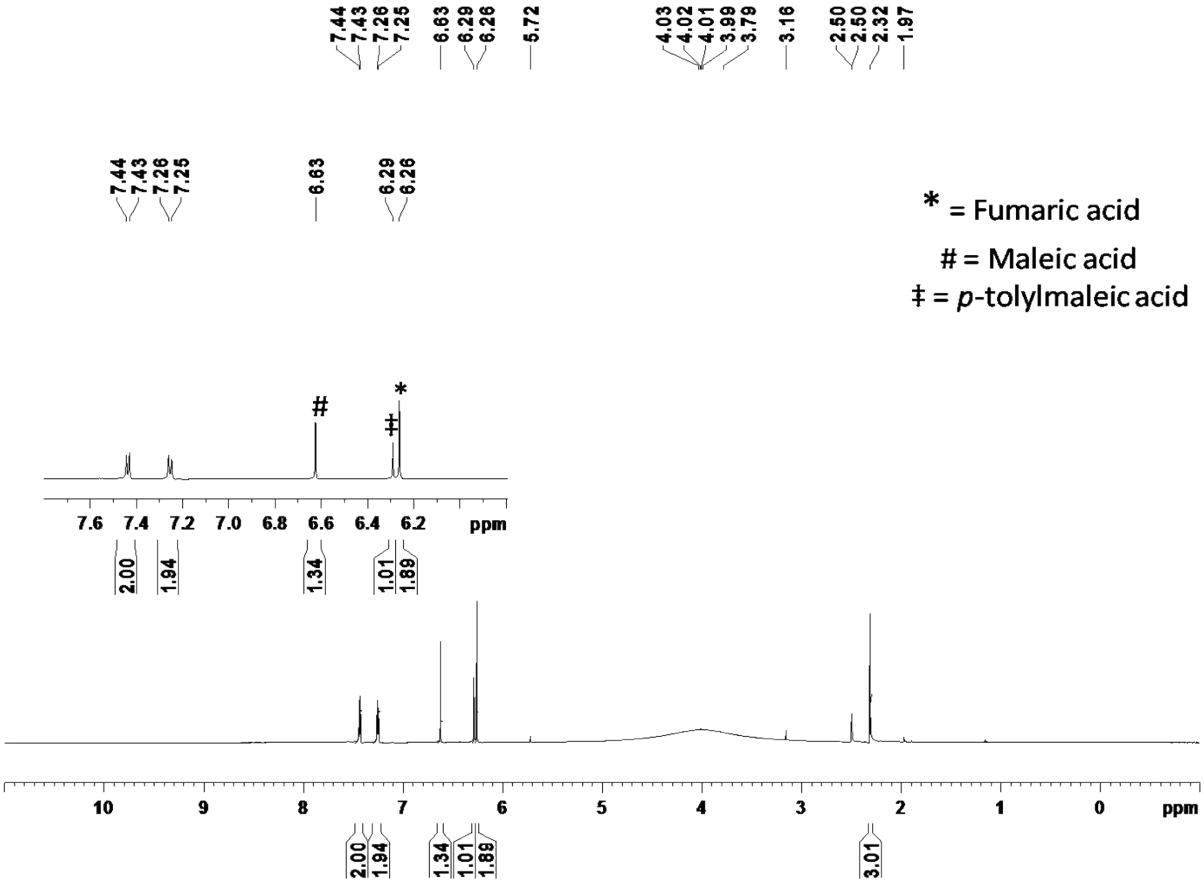
The PS-BH_4^- (1g) was added to the hot suspension of palladium acetate (10 mg) in DMF (10 mL) and the mixture was stirred for 1 h or till the brown colour solution changed to colourless and PS-BH_4^- simultaneously turned black giving Pd@PS catalyst. After cooling, the Pd@PS catalyst was filtered through cotton bed, washed with water and acetone and dried under reduced pressure.

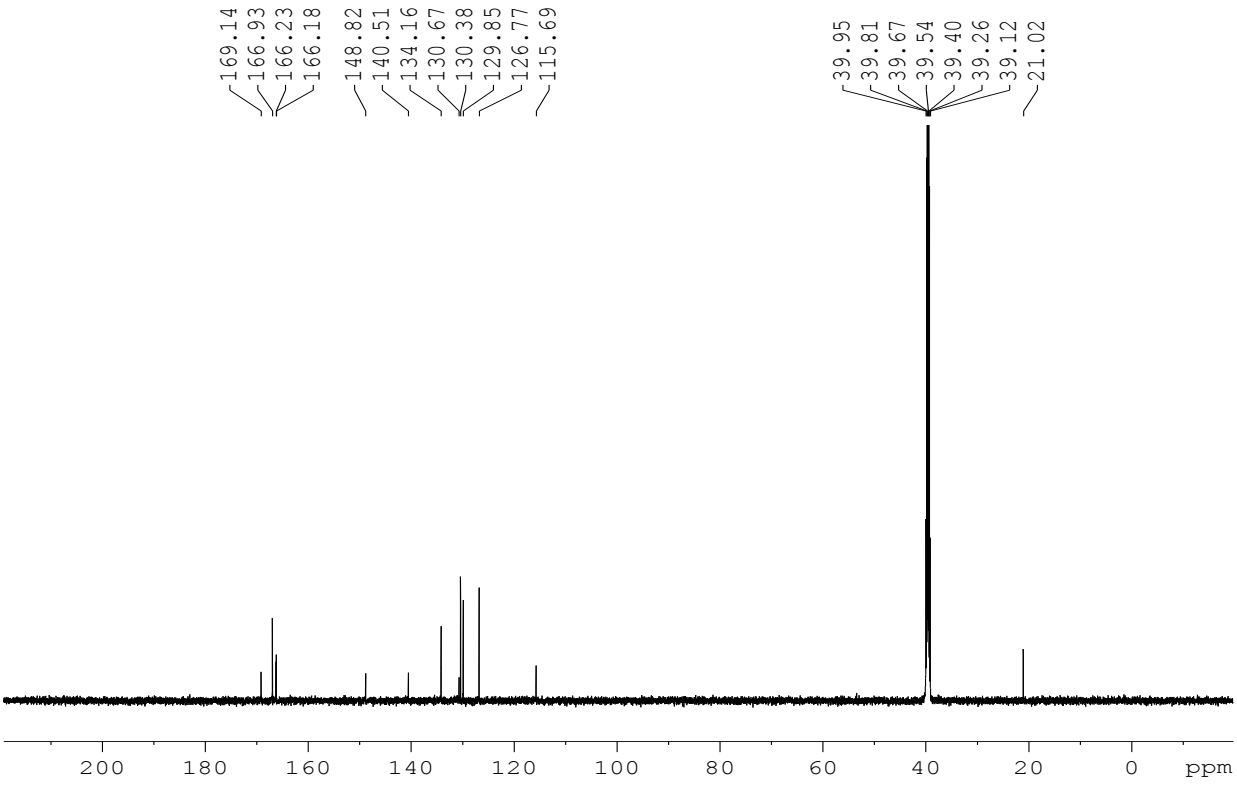
3. Mechanistic investigation

NMR investigation for intermediate and byproduct analysis

The reaction was performed under standard conditions using 1a (500 mg, 2.29 mmol), maleic anhydride (673 mg, 6.87 mmol), K_2CO_3 (316 mg, 2.29 mmol) and Pd@PS (1028 mg, 2 mol% of Pd) for 6h. The reaction residue after isolation of desired product was analysed by NMR studies that clearly indicated the presence of maleic acid, fumaric acid and *p*-tolylmaleic acid.

^{1}H and ^{13}C NMR spectra:





Mechanistic investigation through FT-IR analysis:

We conducted the set of control experiments to establish the role of polymer support in the reaction. We treated the polymer support (PS) with maleic anhydride and K_2CO_3 (same equivalents as of standard reaction) under the optimized reaction conditions for 1 h. The PS was filtered, washed with distilled water and acetone respectively and then dried under vacuum. Further, PS was grinded into the fine powder and analyzed using FT-IR (Figure S1, '**b**'). Similar experiment was performed using Pd@PS catalyst (Figure S1, 'd'). All the recorded FT-IR spectras including maleic acid (hydrolysed product of maleic anhydride) are summarized in Figure S1 and S2.

The initial FT-IR spectra of PS and Pd@PS were found to be similar (Figure S1, '**b**' and '**d**'). The IR spectrum of PS after treatment with maleic anhydride under reaction conditions showed the presence of new intense peaks in 1600-1200 cm^{-1} region (Figure S1, '**c**'). While, the spectrum of Pd@PS (e) after treatment with maleic anhydride was also found similar to '**c**' (Figure S1, '**c**' and '**e**').

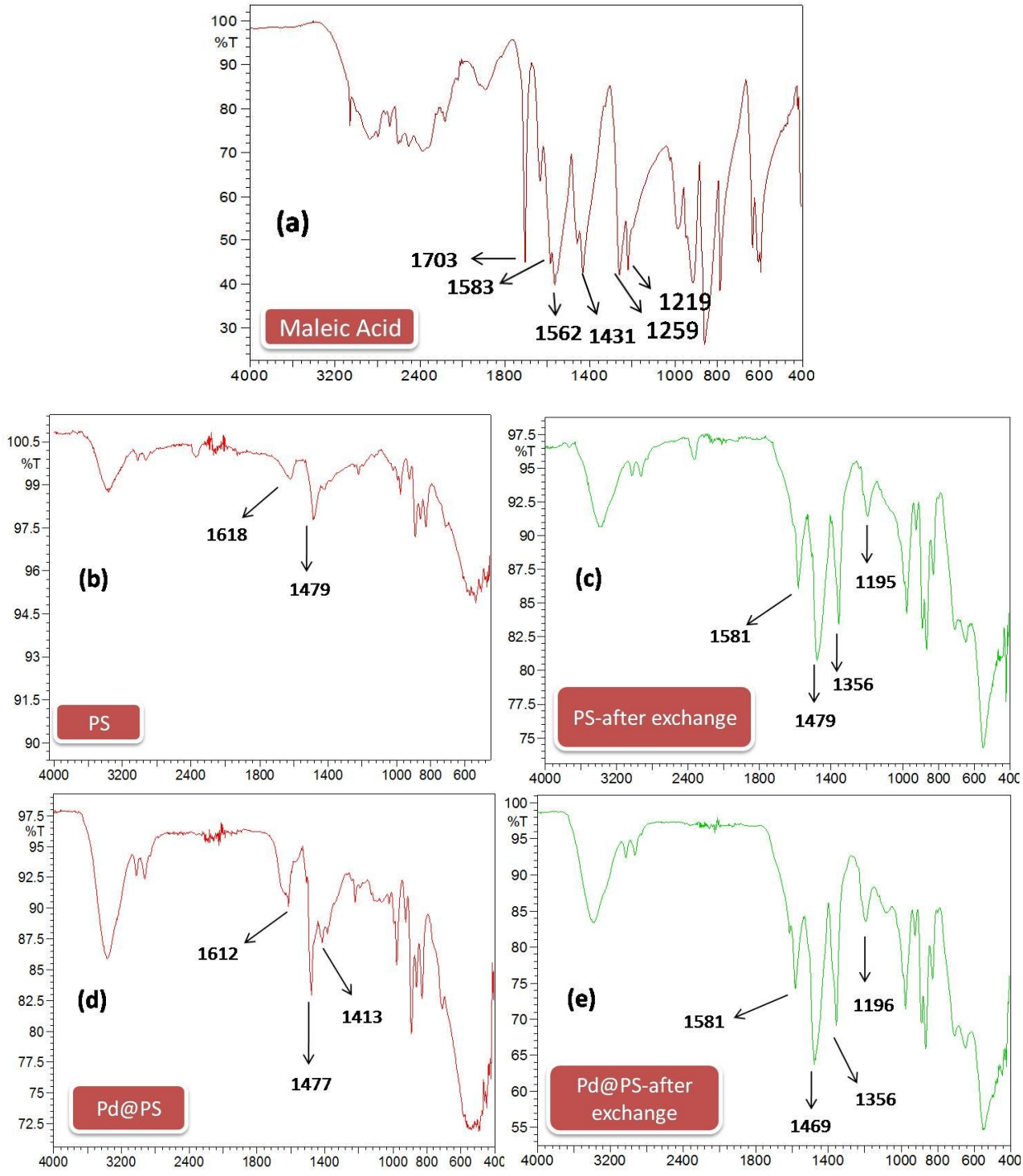
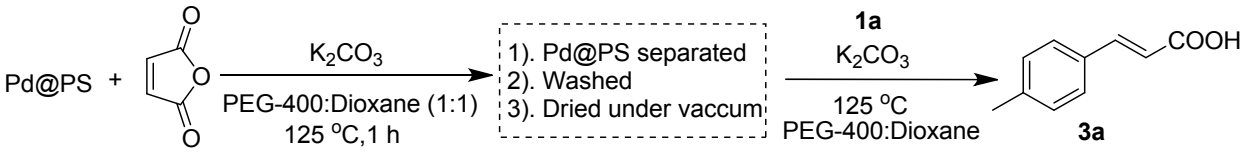


Figure S1. (a) FTIR spectra of Maleic acid; (b) FTIR spectra of polymer support (PS); (c) FTIR spectra of PS after exchange with maleic anhydride for 1 h; (d) FTIR spectra of Pd@PS (e) FTIR spectra of Pd@PS after exchange with maleic anhydride for 1 h.

In another experiment, the Pd@PS-exchanged with maleic anhydride (as described above), was subjected to the reaction with 4-iodotoluene under optimized conditions. The formation of desired product **3a** was observed. The Pd@PS recovered after the reaction was also subjected to FT-IR analysis and the recorded IR spectra did not show the presence of intense peaks at 1581, 1356 and 1192 (Figure S2). This observation further proved the partial exchange of maleic acid with polymer support hence facilitating the reaction at the polymer surface.



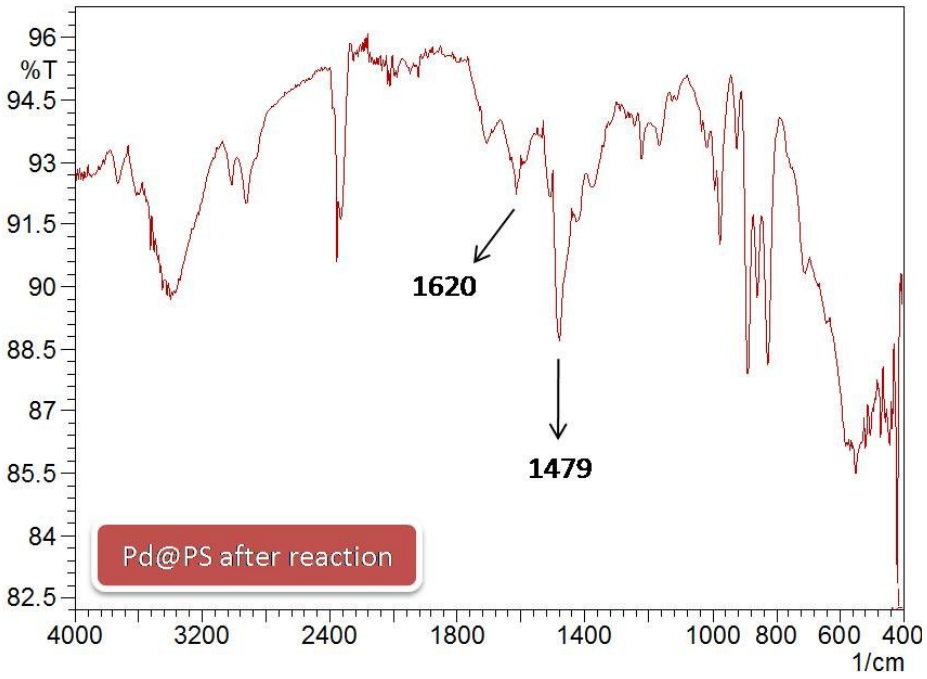
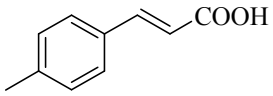


Figure S2. The FT-IR spectrum of Pd@PS after the reaction with **1a**.

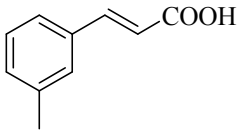
4. Typical experimental procedures for synthesis of cinnamic acid derivatives from aryl halides and characterization data:

(*E*)-3-*p*-tolylacrylic acid (3a)



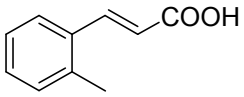
4-iodotoluene **1a** (100 mg, 0.459 mmol), maleic anhydride **2** (135 mg, 1.376 mmol), K_2CO_3 (63 mg, 0.459 mmol), and Pd@PS (309 mg, 3 mol % of Pd) were taken in an oven dried screw capped reaction tube in 2 mL solvent mixture of PEG-400:Dioxane (1:1). The resultant reaction mixture was stirred at 125 ^oC for 12 h. The progress of reaction was monitored using TLC. The reaction mixture was cooled to ambient temperature and quenched with water and then extracted using ethyl acetate (4 X 5 mL). The resulting organic layer was treated with anhy. Na_2SO_4 and dried under reduced pressure. The corresponding (*E*)-3-*p*-tolylacrylic acid **3a** was obtained in 60 mg, 80% yield as white solid after purification by column chromatography on silica gel (60-120 mesh) using Hexane:EtOAc (70:30) as elute; on the other hand, 4-bromotoluene (100 mg, 0.585 mmol), maleic anhydride **2** (172 mg, 1.76 mmol), K_2CO_3 (161 mg, 1.169 mmol), and Pd@PS (394 mg, 3 mol% of Pd) under same reaction conditions at 130 ^oC, after column chromatography with Hexane:EtOAc (70:30), gave **3a** as white solid (61 mg, 64%); mp 198-199 ^oC (lit.[1] mp 199-200 ^oC); ^1H NMR (300 MHz, DMSO-d_6) δ 2.31 (s, 3H), 6.45 (d, J = 15.99 Hz, 1H), 7.21 (d, J = 7.92 Hz, 2H), 7.51-7.57 (m, 3H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 21.1, 118.1, 128.3, 129.6, 131.5, 140.3, 144.1, 167.8; IR (KBr) 2924, 2853, 1682, 1624, 1513, 1424 cm^{-1}.

(*E*)-3-*m*-tolylacrylic acid (3b)



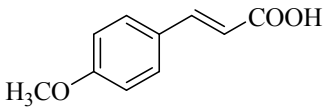
Prepared as described for **3a**; 3-iodotoluene **1b** (100 mg, 0.459 mmol) gave **3b,** after purification with silica gel column chromatography (Hexane:EtOAc = 75:25) as white solid (58 mg, 78%); mp 117-118 ^oC (lit.[2] mp 116-118 ^oC); ^1H NMR (300 MHz, DMSO-d_6) δ 2.31 (s, 3H), 6.50 (d, J = 15.9 Hz, 1H), 7.20-7.32 (m, 2H), 7.45- 7.57 (m, 3H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 20.8, 119.0, 125.4, 128.6, 128.8, 130.9, 134.2, 138.2, 144.1, 167.6; IR (KBr) 2922, 2853, 1686, 1630, 1430 cm^{-1}.

(*E*)-3-*o*-tolylacrylic acid (3c)



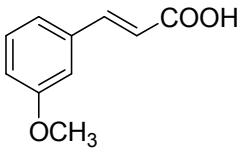
Prepared as described for **3a**; 2-iodotoluene **1c** (100 mg, 0.459 mmol) gave **3c,** after purification with silica gel column chromatography (Hexane:EtOAc = 70:30) as white solid (53 mg, 71%); mp 174-176 ^{o}C (lit.[1] mp 175-176 ^{o}C); ^{1}H NMR (300 MHz, DMSO-d_6) δ 2.37 (s, 3H), 6.41 (d, J = 15.9 Hz, 1H), 7.20-7.32 (m, 3H), 7.69 (d, J = 7.2 Hz, 1H), 7.81 (d, J = 15.9 Hz, 1H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 19.2, 128.2, 126.4, 126.5, 129.9, 130.7, 132.9, 137.1, 141.2, 167.5. IR (KBr) 2947, 2847, 1686, 1622, 1488, 1424 cm^{-1}.

(*E*)-3-(4-methoxyphenyl)acrylic acid (3d)



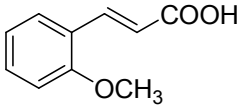
Prepared as described for **3a**; 4-iodoanisole **1d** (100 mg, 0.427 mmol) gave **3d,** after purification with silica gel column chromatography (Hexane:EtOAc = 70:30) as white solid (58 mg, 77%); mp 174-176 ^{o}C (lit.[1] mp 175-176 ^{o}C); ^{1}H NMR (600 MHz, DMSO-d_6) δ 3.78 (s, 3H), 6.37 (d, J = 15.96 Hz, 1H), 6.96 (d, J = 8.28 Hz, 2H), 7.54 (d, J = 15.96 Hz, 1H), 7.62 (d, J = 8.28 Hz, 2H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 55.3, 114.4, 116.5, 126.9, 129.9, 143.8, 161.0, 167.9; IR (KBr) 2972, 2938, 2843, 1684, 1623, 1513, 1432 cm^{-1}.

(*E*)-3-(3-methoxyphenyl)acrylic acid (3e)



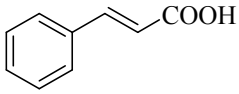
Prepared as described for **3a**; 3-iodoanisole **1e** (100 mg, 0.427 mmol) gave **3e,** after purification with silica gel column chromatography (Hexane:EtOAc = 70:30) as white solid (56 mg, 74%); mp 116-117 ^{o}C (lit.[2] mp 117-119 ^{o}C); ^{1}H NMR (600 MHz, DMSO-d_6) δ 3.78 (s, 3H), 6.54 (d, J = 15.96 Hz, 1H), 6.97-6.98 (dd, J_1 = 8.15, J_2 = 2.2 Hz, 1H), 7.23-7.25 (m, 2H), 7.32 (t, J = 7.8 Hz, 1H), 7.55 (d, J = 16.02 Hz, 1H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 55.3, 112.9, 116.3, 119.6, 120.8, 129.9, 135.7, 143.9, 159.6, 167.6; IR (KBr) 2923, 2854, 1694, 1631, 1582, 1491, 1454, 1434 cm^{-1}.

(*E*)-3-(2-methoxyphenyl)acrylic acid (3f)



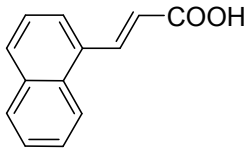
Prepared as described for **3a**; 2-iodoanisole **1f** (100 mg, 0.427 mmol) gave **3f,** after purification with silica gel column chromatography (Hexane:EtOAc = 70:30) as white solid (53 mg, 70%); mp 182-183 ^{o}C (lit.[2] mp 182-184 ^{o}C); ^{1}H NMR (600 MHz, DMSO-d_6) δ 3.86 (s, 3H), 6.51 (d, J = 16.14 Hz, 1H), 6.98 (t, J = 7.5 Hz, 1H), 7.08 (d, J = 8.3 Hz, 1H), 7.39-7.42 (m, 1H), 7.66-7.67 (dd, J_1 = 7.68, J_2 = 1.44 Hz, 1H), 7.84 (d, J = 16.2 Hz, 1H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 55.6, 111.7, 119.3, 120.8, 122.5, 128.4, 131.8, 138.8, 157.8, 167.9; IR (KBr) 2974, 2946, 2842, 1683, 1620, 1490, 1463, 1427 cm^{-1}.

Cinnamic acid (3g)



Prepared as described for **3a**; iodobenzene **1g** (100 mg, 0.49 mmol) gave **3g,** after purification with silica gel column chromatography (Hexane:EtOAc = 70:30) as white solid (60 mg, 82%); also bromobenzene (100 mg, 0.637 mmol), maleic anhydride **2** (187 mg, 1.91 mmol), K_2CO_3 (176 mg, 1.27 mmol), and Pd@PS (429 mg, 3 mol% of Pd) under same reaction conditions gave **3g,** after purification with silica gel column chromatography (Hexane:EtOAc = 70:30) as white solid (58 mg, 61%); mp 132-134 ^{o}C (lit.[1] mp 133-134 ^{o}C); ^{1}H NMR (600 MHz, DMSO-d_6) δ 6.531 (d, J = 15.6 Hz, 1H), 7.404-7.41 (m, 3H), 7.59 (d, J = 16.02 Hz, 1H), 7.67-7.68 (m, 2H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 119.2, 128.2, 128.9, 130.3, 134.3, 144.0, 167.6; IR (KBr) 3024, 2924, 2854, 1691, 1631, 1453 cm^{-1}.

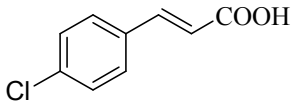
(*E*)-3-(naphthalen-3-yl)acrylic acid (3h)



Prepared as described for **3a**; 1-iodonaphthalene **1h** (100 mg, 0.395 mmol) gave **3h**, after purification with silica gel column chromatography (Hexane:EtOAc = 75:25) as white solid (62 mg, 79%); mp 212-213 ^{o}C (lit.[1] mp 213-214 ^{o}C); ^{1}H NMR (600 MHz, DMSO-d_6) δ 6.60 (d, J = 15.72 Hz, 1H), 7.54-7.63 (m, 3H), 7.94 (d, J = 7.2 Hz, 1H), 7.97-8.01 (m, 2H), 8.19 (d, J = 8.4 Hz, 1H), 8.40 (d, J = 15.72 Hz, 1H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 121.9,

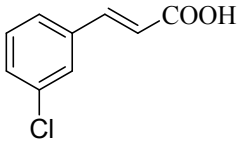
122.1, 125.2, 126.3, 127.2, 128.7, 130.4, 130.8, 131.0, 133.3, 140.2, 167.5; IR (KBr) 3048, 2971, 2836, 1682, 1619, 1511, 1424 cm^{-1}.

(*E*)-3-(4-chlorophenyl)acrylic acid (3i)



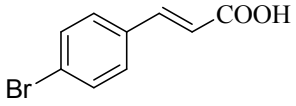
Prepared as described for **3a**; 1-chloro-4-iodobenzene **1i** (100 mg, 0.419 mmol) gave **3i,** after purification with silica gel column chromatography (Hexane:EtOAc = 65:35) as white solid (65 mg, 85%); also 1-bromo-4-chlorobenzene (100 mg, 0.523 mmol), maleic anhydride **2** (154 mg, 1.57 mmol), K_2CO_3 (176 mg, 1.27 mmol), and Pd@PS (352 mg, 3 mol% of Pd) under same reaction conditions at 130 ^oC gave **3i,** after purification with silica gel column chromatography (Hexane:EtOAc = 65:35) as white solid (70 mg, 74%); mp 247-248 ^oC (lit.[2] mp 247-249 ^oC); ^1H NMR (300 MHz, DMSO-d_6) δ 6.54 (d, J = 16.05 Hz, 1H), 7.45 (d, J = 8.4 Hz, 2H), 7.57 (d, J = 16.02 Hz, 1H), 7.70 (d, J = 8.4 Hz, 2H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 120.1, 128.9, 129.9, 133.2, 134.7, 142.5, 167.4; IR (KBr) 2977, 2830, 1691, 1628, 1490, 1426 cm^{-1}.

(*E*)-3-(3-chlorophenyl)acrylic acid (3j)



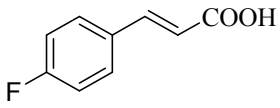
1-bromo-3-chlorobenzene **1j** (100 mg, 0.523 mmol), maleic anhydride **2** (154 mg, 1.57 mmol), K_2CO_3 (176 mg, 1.27 mmol), and Pd@PS (352 mg, 3 mol% of Pd) under aforementioned reaction conditions at 130 ^oC gave **3j,** after purification with silica gel column chromatography (Hexane:EtOAc = 75:25) as white solid (68 mg, 72%); mp 173-175 ^oC (lit.[3] mp 175-176 ^oC); ^1H NMR (600 MHz, DMSO-d_6) δ 6.60 (d, J = 16.02 Hz, 1H), 7.41-7.46 (m, 2H), 7.56 (d, J = 16.02 Hz, 1H), 7.65 (d, J = 7.32 Hz, 1H), 7.79 (s, 1H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 120.9, 126.7, 127.7, 129.7, 130.6, 133.7, 136.5, 142.2, 167.2; IR (KBr) 2992, 1696, 1630, 1570, 1480, 1430 cm^{-1}.

(*E*)-3-(4-bromophenyl)acrylic acid (3k)



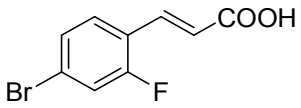
Prepared as described for **3a**; 1-bromo-4-iodobenzene **1k** (100 mg, 0.35 mmol) gave **3k,** after purification with silica gel column chromatography (Hexane:EtOAc = 65:35) as white solid (65 mg, 82%); mp 251-253 ^{o}C (lit.[4] mp 253 ^{o}C); ^{1}H NMR (600 MHz, DMSO-d_6) δ 6.56 (d, J = 16.02 Hz, 1H), 7.56 (d, J = 16.02 Hz, 1H), 7.60 (d, J = 8.52 Hz, 2H), 7.64 (d, J = 8.52 Hz, 2H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 120.2, 123.6, 130.2, 131.9, 133.6, 142.7, 167.5; IR (KBr) 2978, 2835, 1689, 1626, 1485, 1425 cm^{-1}.

(*E*)-3-(4-fluorophenyl)acrylic acid (3l)



Prepared as described for **3a**; 1-fluoro-4-iodobenzene **1l** (100 mg, 0.45 mmol) gave **3l,** after purification with silica gel column chromatography (Hexane:EtOAc = 65:35) as white solid (64 mg, 86%); also 1-fluoro-4-bromobenzene (100 mg, 0.571 mmol), maleic anhydride **2** (168 mg, 1.71 mmol), K_2CO_3 (158 mg, 1.14 mmol), and Pd@PS (385 mg, 3 mol% of Pd) under same reaction conditions gave **3l,** after purification with silica gel column chromatography (Hexane:EtOAc = 65:35) as white solid (67 mg, 71%); mp 209-210 ^{o}C (lit.[5] mp 209-211 ^{o}C); ^{1}H NMR (600 MHz, DMSO-d_6) δ 6.49 (d, J = 16.02 Hz, 1H), 7.23 (t, J = 8.7 Hz, 2H), 7.59 (d, J = 16.02 Hz, 1H), 7.74-7.76 (m, 2H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 115.9 (d, J = 21.69 Hz), 119.2, 130.5 (d, J = 8.60 Hz), 130.9 (d, J = 3.03 Hz), 142.7, 163.2 (d, J = 246.62 Hz), 167.6; IR (KBr) 2929, 2847, 1686, 1628, 1599, 1508, 1427 cm^{-1}.

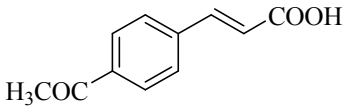
(*E*)-3-(4-bromo-2-fluorophenyl)acrylic acid (3m)



Prepared as described for **3a**; 4-bromo-2-fluoro-1-iodobenzene **1m** (100 mg, 0.332 mmol) gave **3m,** after purification with silica gel column chromatography (Hexane:EtOAc = 60:40) as white solid (63 mg, 78%); mp 218-219 ^{o}C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 6.60 (d, J = 16.14 Hz, 1H), 7.44-7.45 (dd, J_1 = 8.4, J_2 = 1.8 Hz, 1H), 7.57 (d, J = 16.2 Hz, 1H), 7.60 -7.62 (dd, J_1 = 10.32 , J_2 = 1.86 Hz, 1H), 7.77 (t, J = 8.28 Hz, 1H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 119.5 (d, J = 25.15 Hz), 121.4 (d, J = 11.31 Hz), 122.6 (d, J = 5.38Hz), 123.8 (d, J = 9.95Hz), 128.3 (d, J = 3.21 Hz), 130.6 (d, J = 2.94 Hz), 134.7 (d, J = 2.83 Hz),

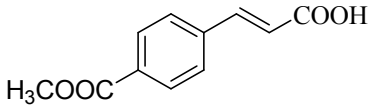
160.2 (d, 254.38 Hz), 167.2; IR (KBr) 3069, 2926, 2852, 1692, 1625, 1599, 1565, 1482, 1415 cm^{-1}.

(*E*)-3-(4-acetylphenyl)acrylic acid (3n)



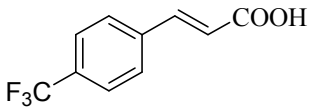
Prepared as described for **3a**; 4-iodoacetophenone **1n** (100 mg, 0.40 mmol) gave **3n**, after purification with silica gel column chromatography (Hexane:EtOAc = 60:40) as white solid (48 mg, 63%); mp 223-225 ^{o}C (lit.[1] mp 224-226 ^{o}C); ^{1}H NMR (600 MHz, DMSO-d_6) δ 2.59 (s, 3H), 6.67 (d, J = 16.2 Hz, 1H), 7.64 (d, J = 16.20 Hz, 1H), 7.83 (d, J = 8.4 Hz, 2H), 7.97 (d, J = 8.4 Hz, 2H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 26.9, 121.8, 128.4, 128.7, 137.6, 138.6, 142.6, 167.3, 197.5; IR (KBr) 3343, 2960, 2922, 2852, 1682, 1630, 1603, 1563, 1424 cm^{-1}.

(*E*)-3-(4-(methoxycarbonyl)phenyl)acrylic acid (3o)



Prepared as described for **3a**; methyl 4-iodobenzoate **1o** (100 mg, 0.382 mmol) gave **3o**, after purification with silica gel column chromatography (Hexane:EtOAc = 60:40) as white solid (57 mg, 73%); mp 245-246 ^{o}C (lit.[2] mp 245-247 ^{o}C); ^{1}H NMR (600 MHz, DMSO-d_6) δ 3.86 (s, 3H), 6.65 (d, J = 16.02 Hz, 1H), 7.63 (d, J = 16.02 Hz, 1H), 7.82 (d, J = 8.4 Hz, 2H), 7.96 (d, J = 8.4 Hz, 1H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 52.2, 121.9, 128.4, 129.6, 130.6, 138.8, 142.4, 165.7, 167.2; IR(KBr) 3414, 2955, 2846, 1712, 1686, 1631, 1567, 1429 cm^{-1}.

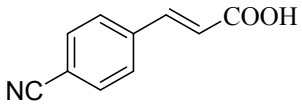
(*E*)-3-(4-(trifluoromethyl)phenyl)acrylic acid (3p)



Prepared as described for **3a**; methyl 1-(trifluoromethyl)-4-iodobenzene **1p** (100 mg, 0.368 mmol) gave **3p**, after purification with silica gel column chromatography (Hexane:EtOAc = 60:40) as white solid (59 mg, 74%); mp 231-232 ^{o}C (lit.[5] mp 231-233 ^{o}C); ^{1}H NMR (600 MHz, DMSO-d_6) δ 6.67 (d, J = 16.02 Hz, 1H), 7.65 (d, J = 16.02 Hz, 1H), 7.75 (d, J = 8.29 Hz, 2H), 7.91 (d, J = 8.16 Hz, 2H), ^{13}C NMR (150/75 MHz, DMSO-d_6) δ 122.2, 125.6 (q,

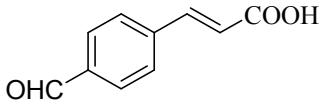
J = 3.77 Hz), 128.7, 129.4, 129.8 (q, J = 31.70 Hz), 138.2, 141.9, 167.1; IR (KBr) 2990, 2841, 1696, 1632, 1581, 1427 cm^{-1}.

(*E*)-3-(4-cyanophenyl)acrylic acid (3q)



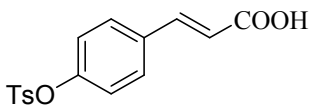
Prepared as described for **3a**; 4-iodobenzonitrile **1q** (100 mg, 0.437 mmol) gave **3q**, after purification with silica gel column chromatography (Hexane:EtOAc = 60:40) as white solid (54 mg, 71%); also 4-bromobenzonitrile (100 mg, 0.549 mmol),), maleic anhydride **2** (161 mg, 1.65 mmol), K_2CO_3 (152 mg, 1.1 mmol), and Pd@PS (370 mg, 3 mol% of Pd) under same reaction conditions at 130 ^oC gave **3q,** after purification with silica gel column chromatography (Hexane:EtOAc = 60:40) as white solid (65 mg, 68%) mp 253-255 ^oC (lit.[3] mp 254-255 ^oC); ^1H NMR (300 MHz, DMSO-d_6) δ 6.71 (d, J = 16.05Hz, 1H), 7.63 (d, J = 16.05 Hz, 1H), 7.85-7.91 (m, 4H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 112.1, 118.5, 122.8, 128.8, 132.7, 138.8, 141.8, 167.1; IR (KBr) 2967, 2837, 2226, 1691, 1626, 1562, 1509, 1424 cm^{-1}.

(*E*)-3-(4-formylphenyl)acrylic acid (3r)



Prepared as described for **3a**; 4-iodobenzaldehyde (100 mg, 0.43 mmol) gave **3r**, after purification with silica gel column chromatography (Hexane:EtOAc = 55:45) as white solid (54 mg, 72%); also 4-bromobenzaldehyde (100 mg, 0.540 mmol),), maleic anhydride **2** (159 mg, 1.62 mmol), K_2CO_3 (149 mg, 1.08 mmol), and Pd@PS (370 mg, 3 mol% of Pd) under same reaction conditions at 130 ^oC gave **3r,** after purification with silica gel column chromatography (Hexane:EtOAc = 55:45) as white solid (60 mg, 63%); mp 250-252 ^oC; ^1H NMR (600 MHz, DMSO-d_6) δ 6.70 (d, J = 16.08 Hz, 1H), 7.65 (d, J = 16.02 Hz, 1H), 7.90-7.94 (m, 4H), 10.02 (s, 1H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 122.4, 128.8, 129.9, 136.8, 139.9, 142.4, 167.2, 192.7; IR (KBr) 2983, 2842, 1692, 1630, 1605, 1569, 1419 cm^{-1}.

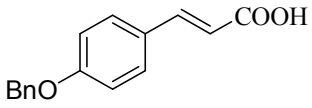
(*E*)-3-(4-(4-methylbenzenesulfonoyl)phenyl)acrylic acid (3s)



Prepared as described for **3a**; 4-iodophenyl 4-methylbenzenesulfonate **1s** (100 mg, 0.267 mmol) gave **3s**, after purification with silica gel column chromatography

(Hexane:EtOAc = 65:35) as white solid (65 mg, 76%); mp 202-203 ^{o}C (lit.[6] mp 201-202 ^{o}C); ^{1}H NMR (600 MHz, CD_3OD) δ 2.44 (s, 3H), 6.43 (d, J = 15.96 Hz, 1H), 7.01 (d, J = 8.58 Hz, 2H), 7.41 (d, J = 8.1 Hz, 2H), 7.55 (d, J = 8.58 Hz, 2H), 7.60 (d, J = 16.02 Hz, 1H), 7.69 (d, J = 8.16 Hz, 2H); ^{13}C NMR (150 MHz, CD_3OD) δ 20.6, 119.7, 122.9, 128.6, 129.5, 130.1, 132.5, 134.0, 143.4, 146.4, 151.2, 168.9; IR (KBr) 2978, 1688, 1631, 1596, 1504, 1428 cm^{-1}.

(*E*)-3-(4-(benzyloxy)phenyl)acrylic acid (3t)



Prepared as described for **3a**; 1-((4-iodophenoxy)methyl)benzene **1t** (100 mg, 0.32 mmol) gave **3t**, after purification with silica gel column chromatography (Hexane:EtOAc = 65:35) as white solid (61 mg, 75%); mp 208-210 ^{o}C (lit.[7] mp 209-211 ^{o}C); ^{1}H NMR (600 MHz, DMSO-d_6) δ 5.15 (s, 2H), 6.38 (d, J = 15.96 Hz, 1H), 7.04 (d, J = 8.76 Hz, 2H), 7.33 (t, J = 7.26 Hz, 1H), 7.39 (t, J =7.5 Hz, 2H), 7.45 (d, J = 7.26 Hz, 2H), 7.54 (d, J = 15.96 Hz, 1H), 7.63 (d, J = 8.76 Hz, 2H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 69.3, 115.2, 116.6, 127.0, 127.7, 127.9, 128.5, 129.9, 136.7, 143.7, 160.0, 167.8; IR (KBr) 3031, 2930, 2836, 1668, 1601, 1512, 1430 cm^{-1}.

5. Typical experimental procedure for reaction of 4-iodotoluene in gram scale:

For gram scale reaction, 4-iodotoluene **1a** (1 g, 4.58 mmol), maleic anhydride (1.35 g, 13.76 mmol), K_2CO_3 (633 mg, 4.48 mmol) and Pd@PS (2059 g, 2 mol% of Pd) were treated under the aforementioned conditions to give **3a** after purification with silica gel column chromatography (Hexane:EtOAc = 70:30) as final product (520 mg, 70%).

6. Recyclability Experiments

The recyclability experiment of Pd@PS was carried out using 4-iodotoluene as model substrate under the optimum reaction conditions. The catalyst was recovered, washed with water and then with acetone, dried under reduced pressure after each cycle before applying it in the next reaction. The catalyst was successfully applied upto 5th cycle as the isolated yield of product **3a** showed less decrease upto 5th cycle.

Cycles	Yield 3a (%)
1	80
2	80
3	77
4	75
5	69

7. TEM analysis of Pd@PS after 5th cycle:

TEM analysis of Pd@PS after recyclability experiments was performed to find outs the size and dispersion of Pd NPs. The TEM image at 50 nm showed the presence of Pd NPs and the corresponding particle size distribution histogram confirmed the average number of NPs having size in range of 1-3 nm. The study reveals that the size of nanoparticles of Pd@PS remains unaffected after 5th cycle of reaction. But, NPs were not well dispersed as of fresh Pd@PS catalyst. The nanoparticles clustering might be the reason for loss of catalytic activity.

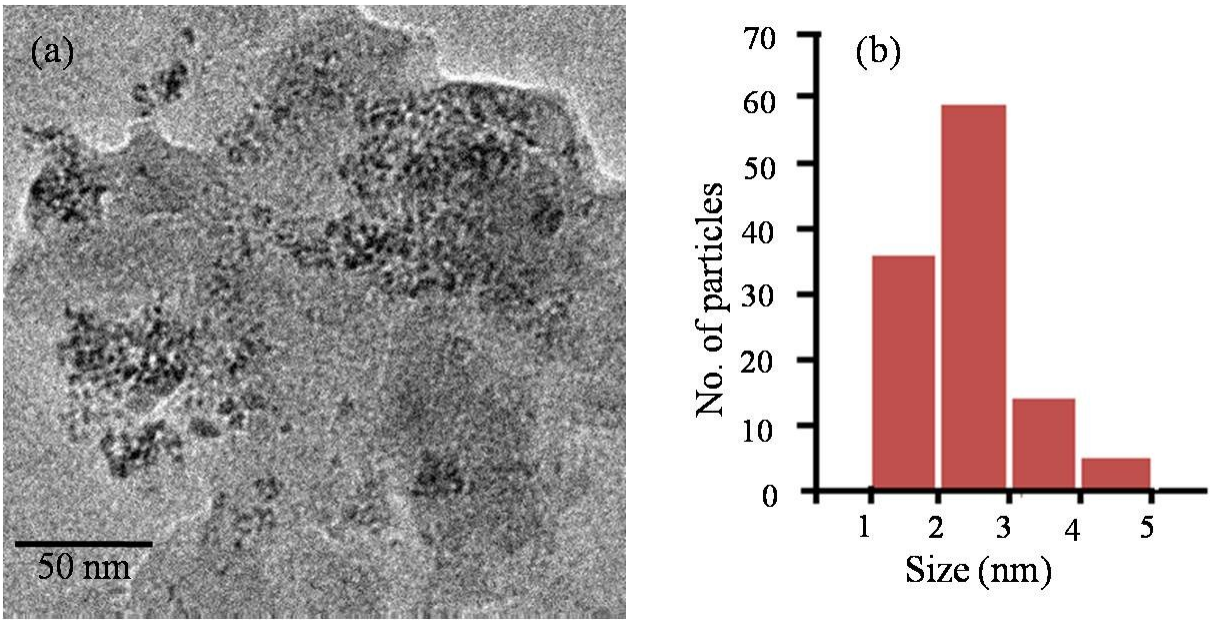


Figure S3. (a) TEM at 50 nm (b) Particle size distribution histogram from (a)

8. ICP-AES studies

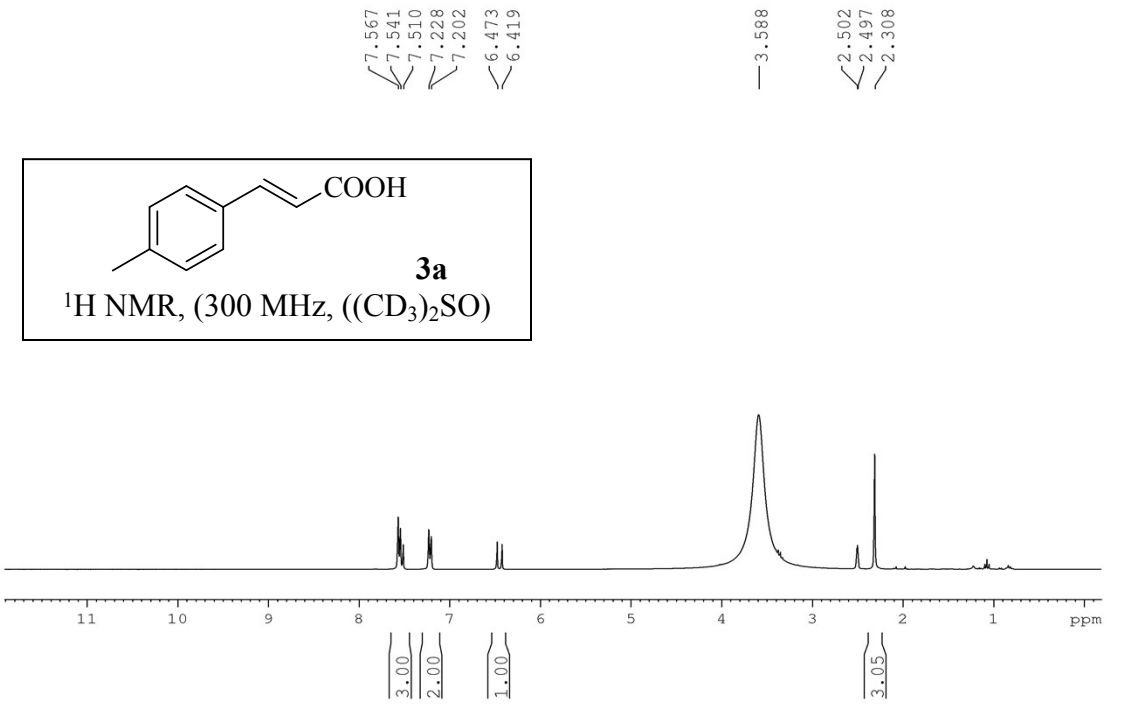
ICP-AES analysis was performed for the reaction mixture using 4-iodotoluene as model substrate under standard reaction conditions. The reaction mixture after complete digestion under acidic conditions was subjected for ICP-AES analysis which showed leaching less than 1 ppm.

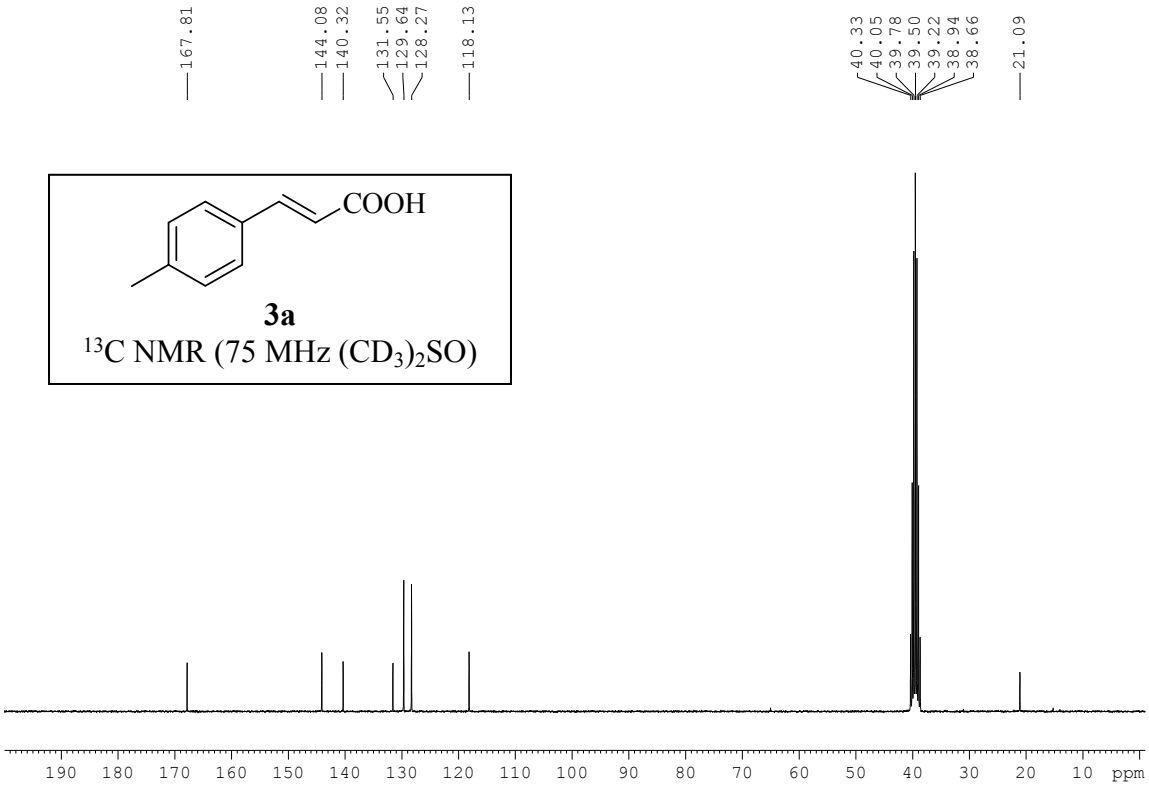
9. Mercury Test

The reaction of 4-iodotoluene under standard reaction conditions was screened for mercury test. We conducted the test using 500 equiv. of Hg(0) with respect to Pd@PS (3 mol% of Pd). Initially we stirred the Hg(0) and Pd@PS catalyst for half an hour followed by the addition of 4-iodotoluene (1 equiv.), maleic anhydride (3 equiv.) and K_2CO_3 (1 equiv.) in PEG-400:Dioxane (1:1) and reaction was performed under optimized reaction conditions. The product **3a** was isolated in 18% yield indicating the poisoning of catalyst.

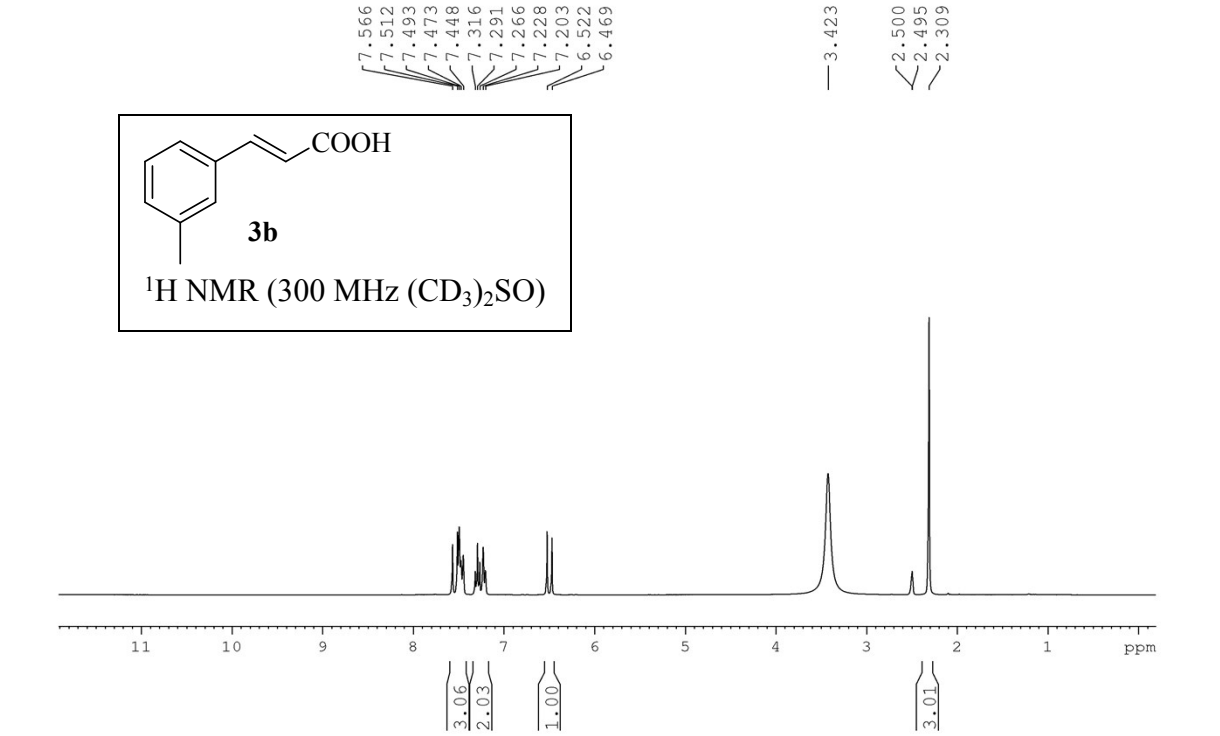
10. NMR (^{1}H and ^{13}C) Spectra

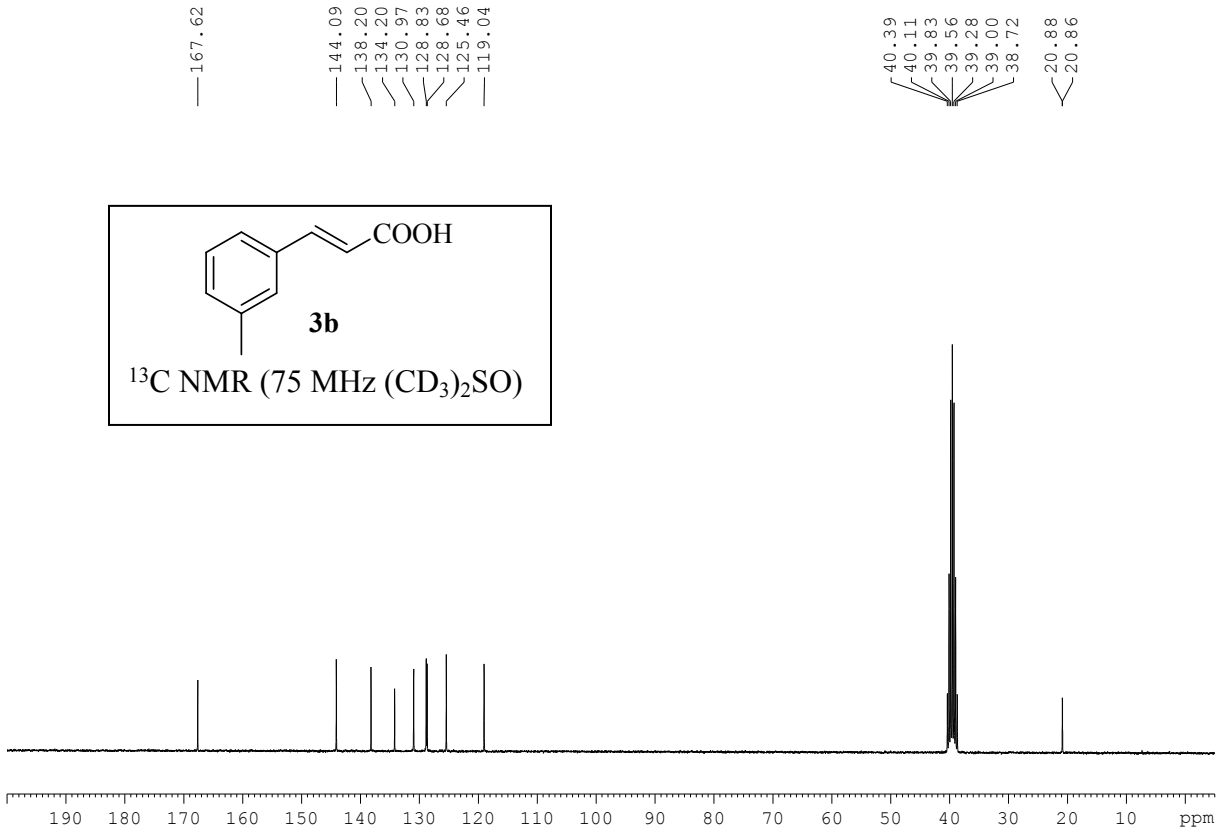
(*E*)-3-*p*-tolylacrylic acid (3a)



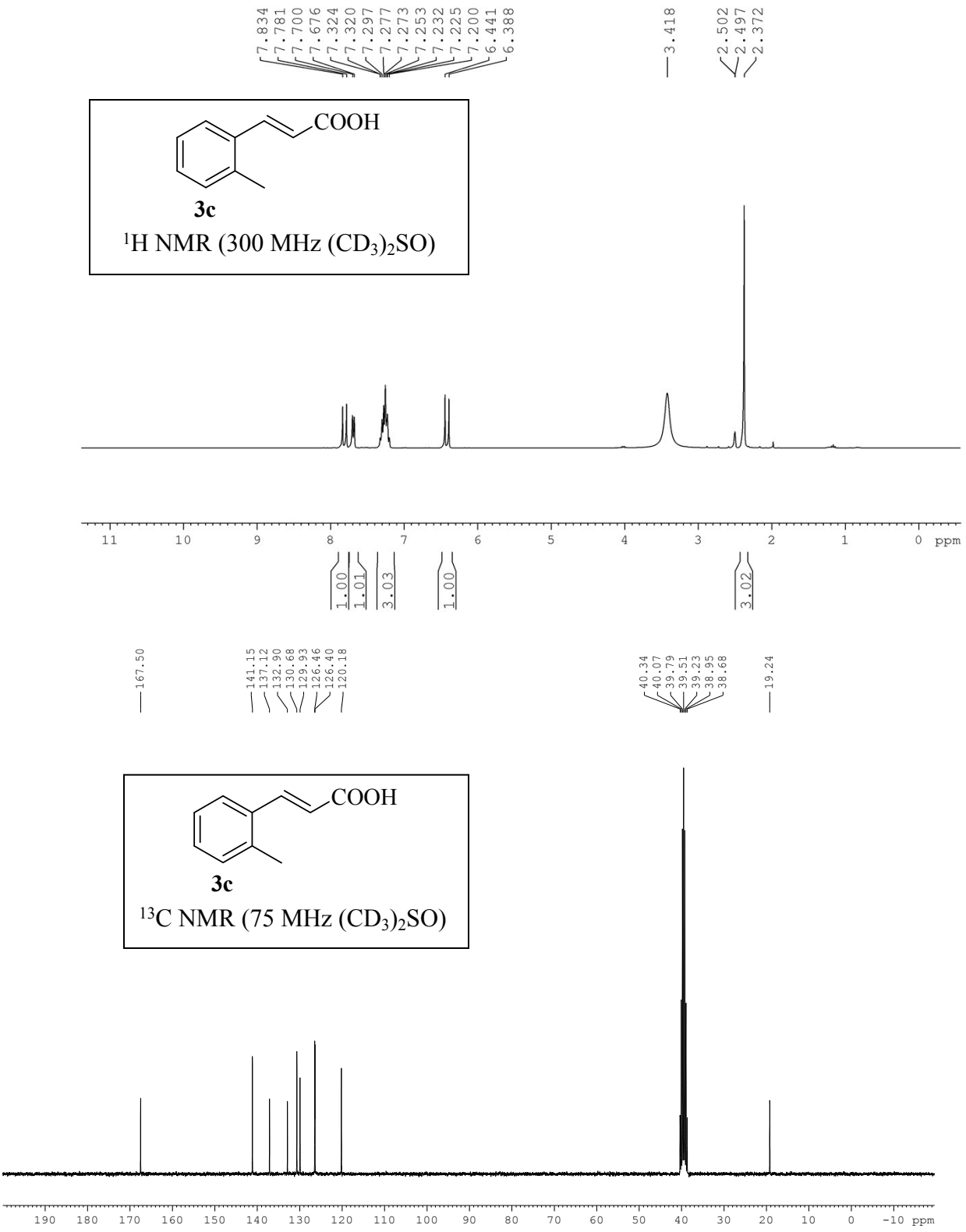


(*E*)-3-*m*-tolylacrylic acid (3b)

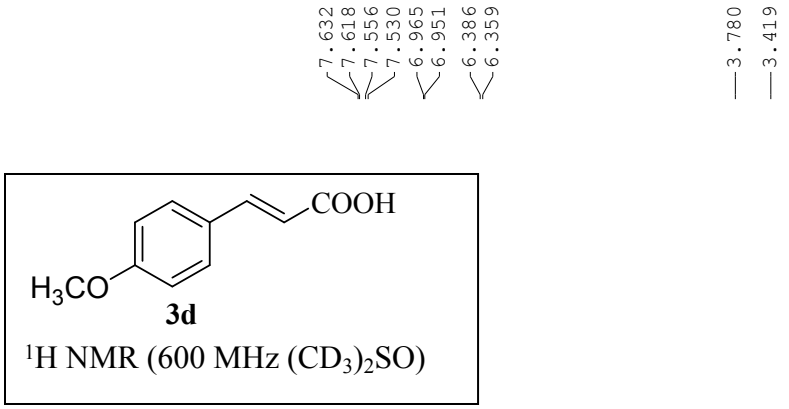


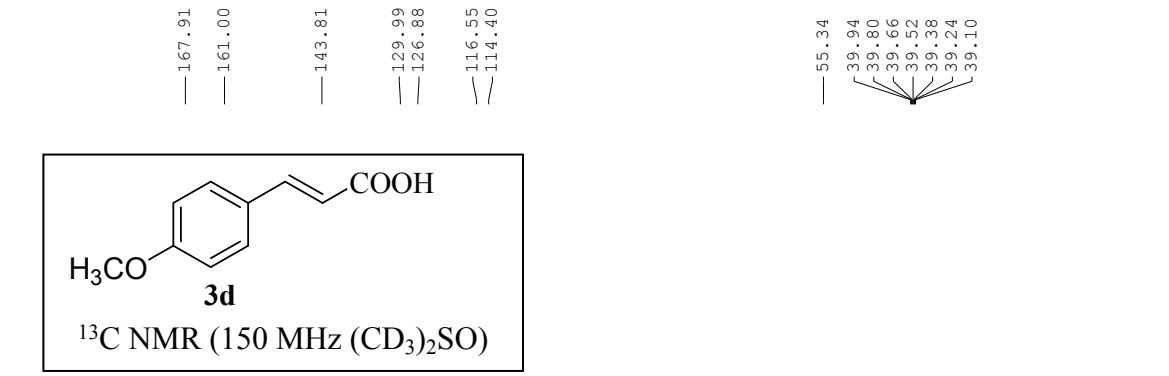


(E)-3-o-tolylacrylic acid (3c)

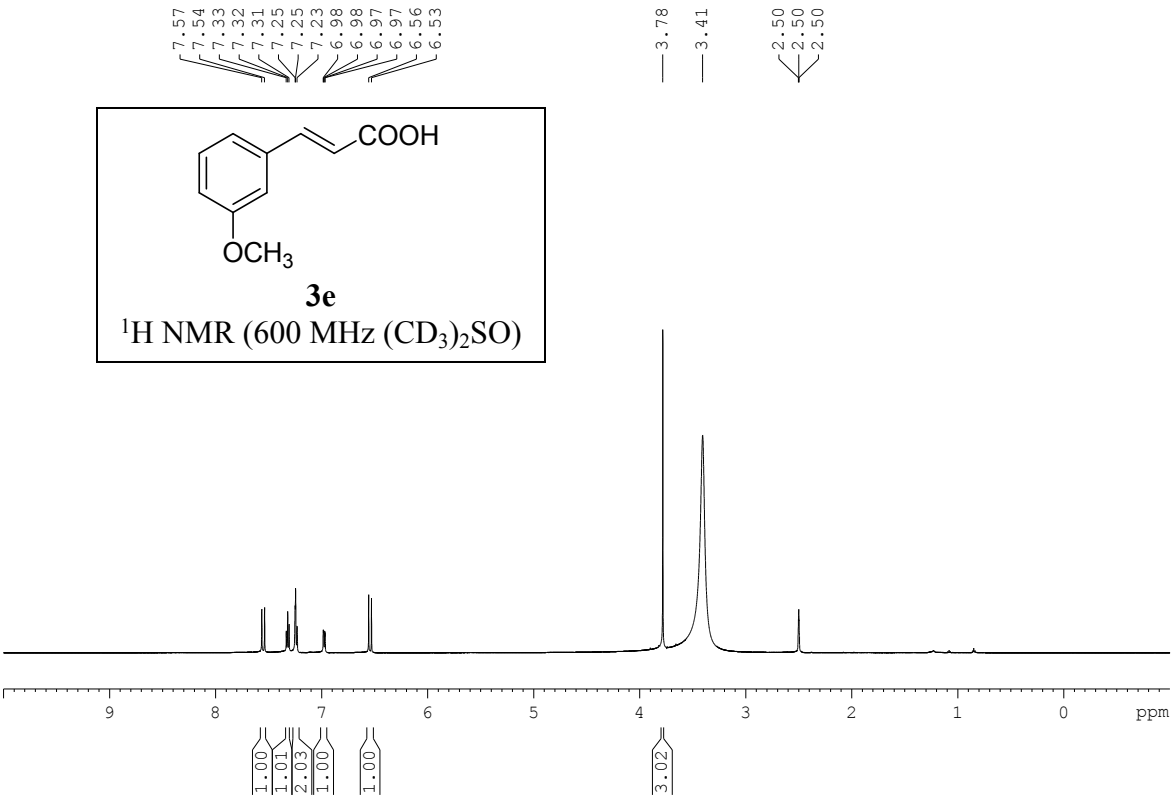


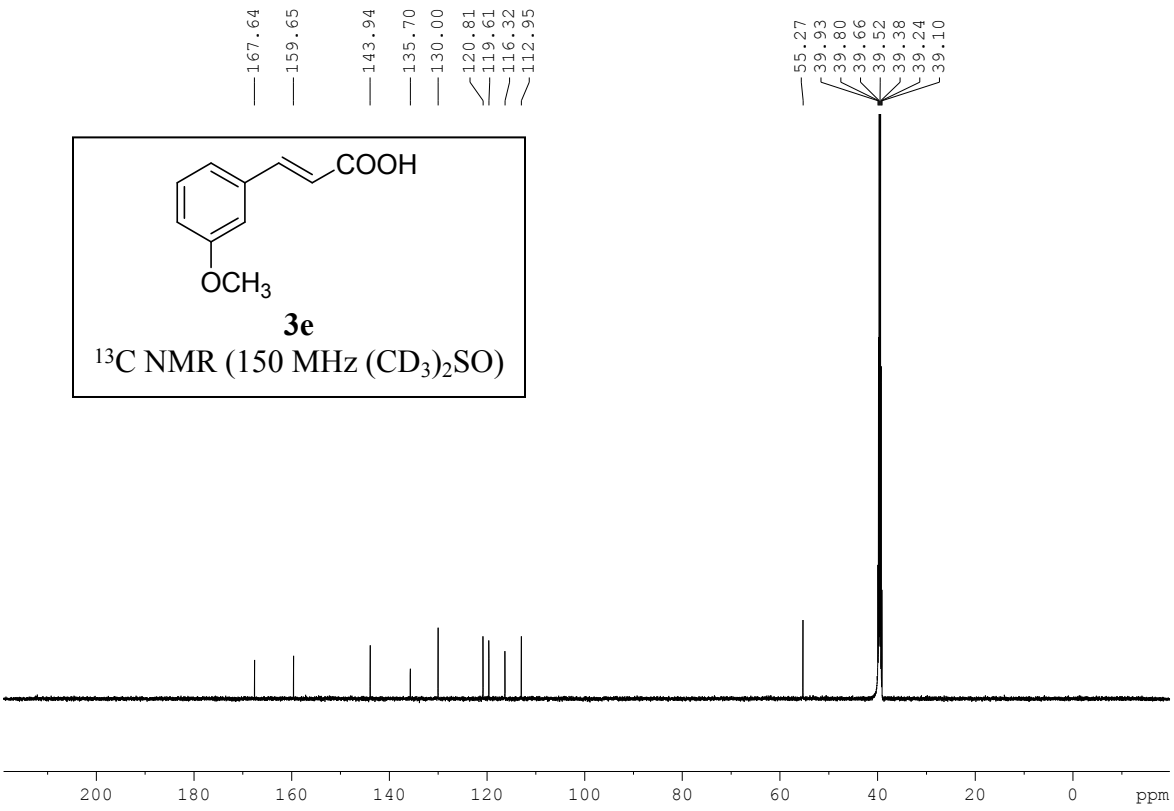
(*E*)-3-(4-methoxyphenyl)acrylic acid (3d)



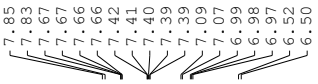


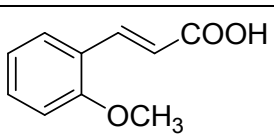
(*E*)-3-(3-methoxyphenyl)acrylic acid (3e)





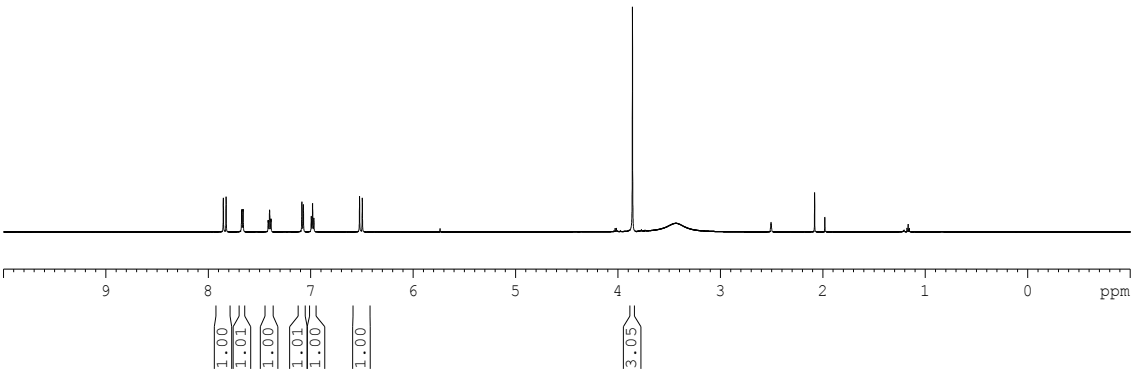
(*E*)-3-(2-methoxyphenyl)acrylic acid (3f)

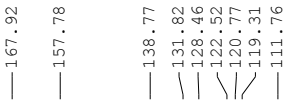


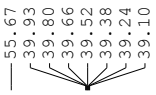


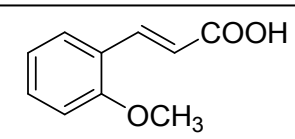
3f

^{1}H NMR (600 MHz $(CD_3)_2SO$)



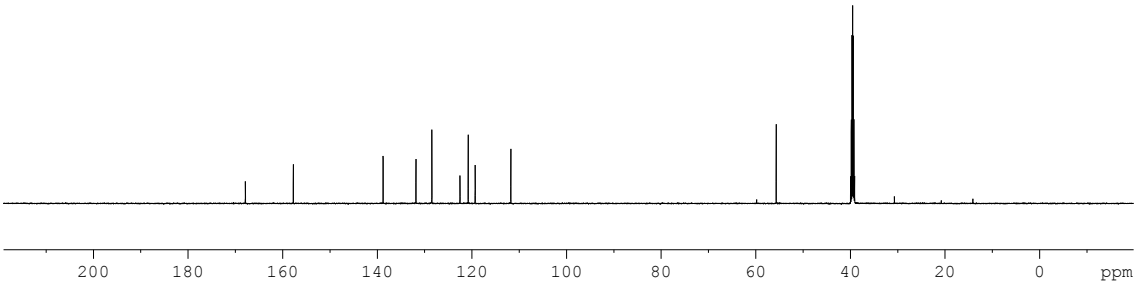




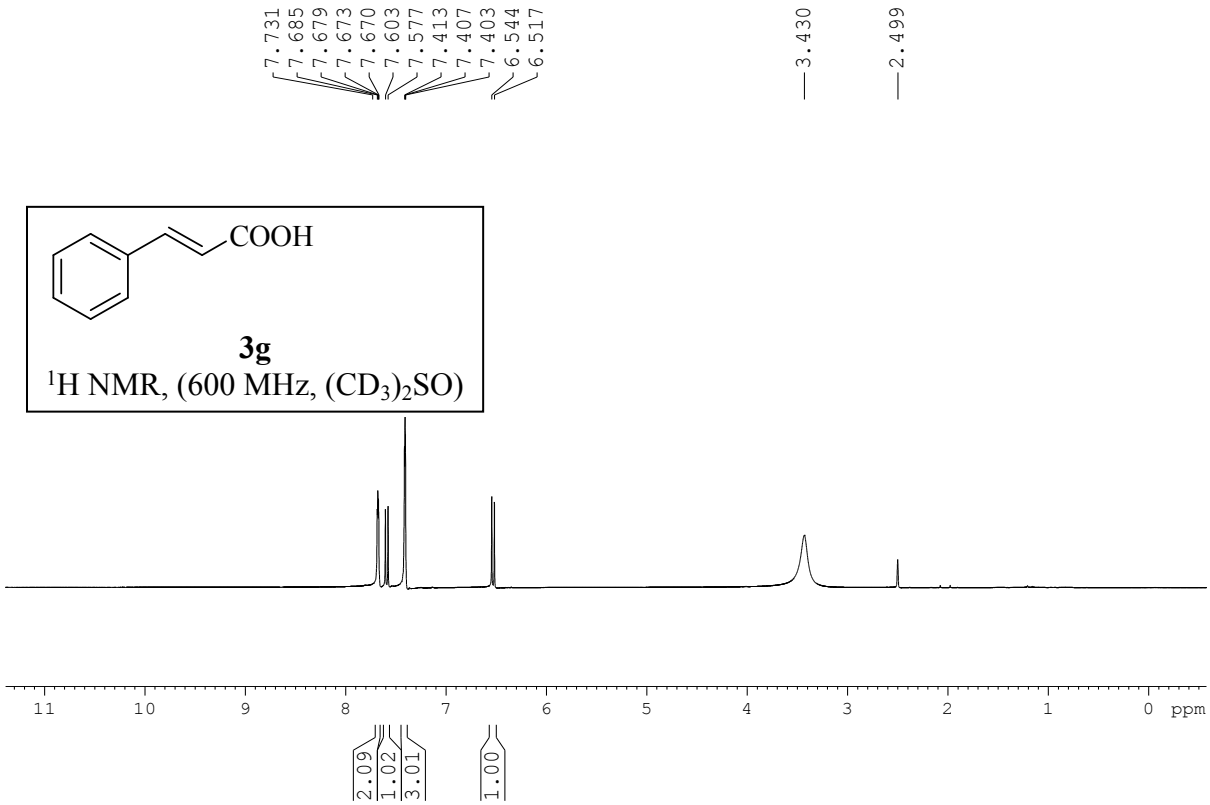


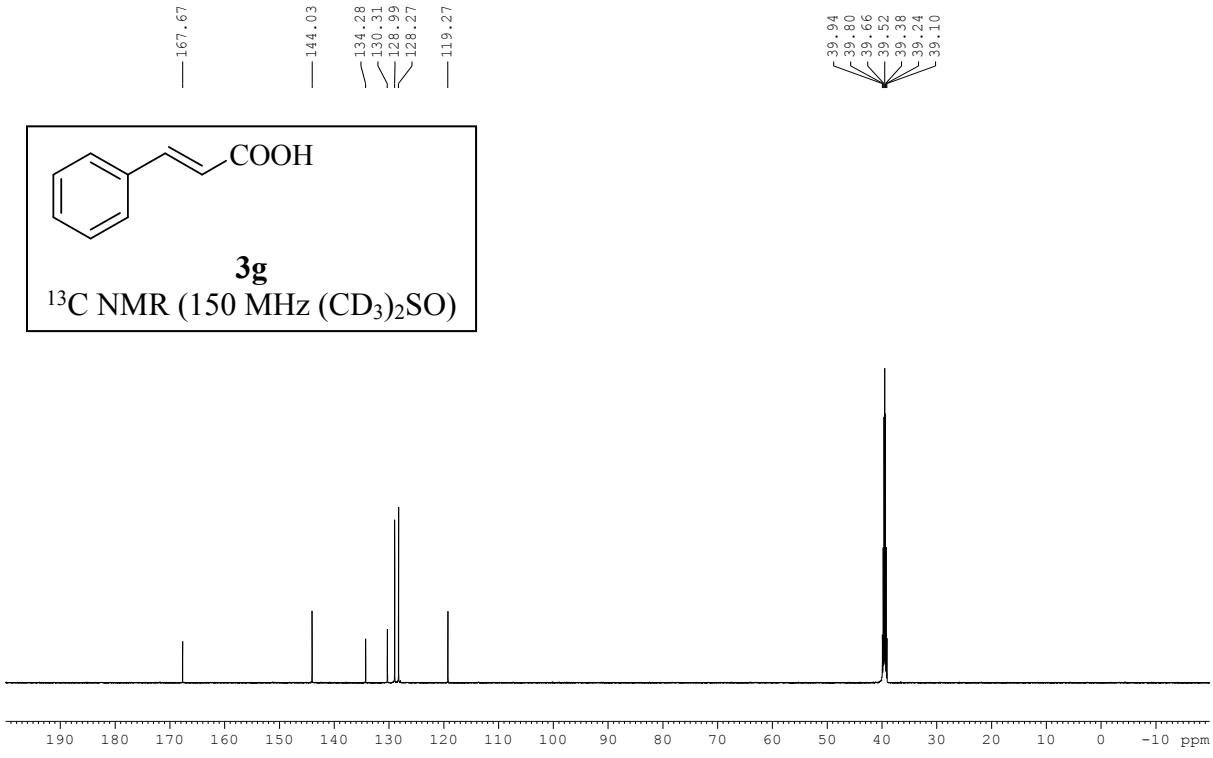
3f

^{13}C NMR (150 MHz $(CD_3)_2SO$)

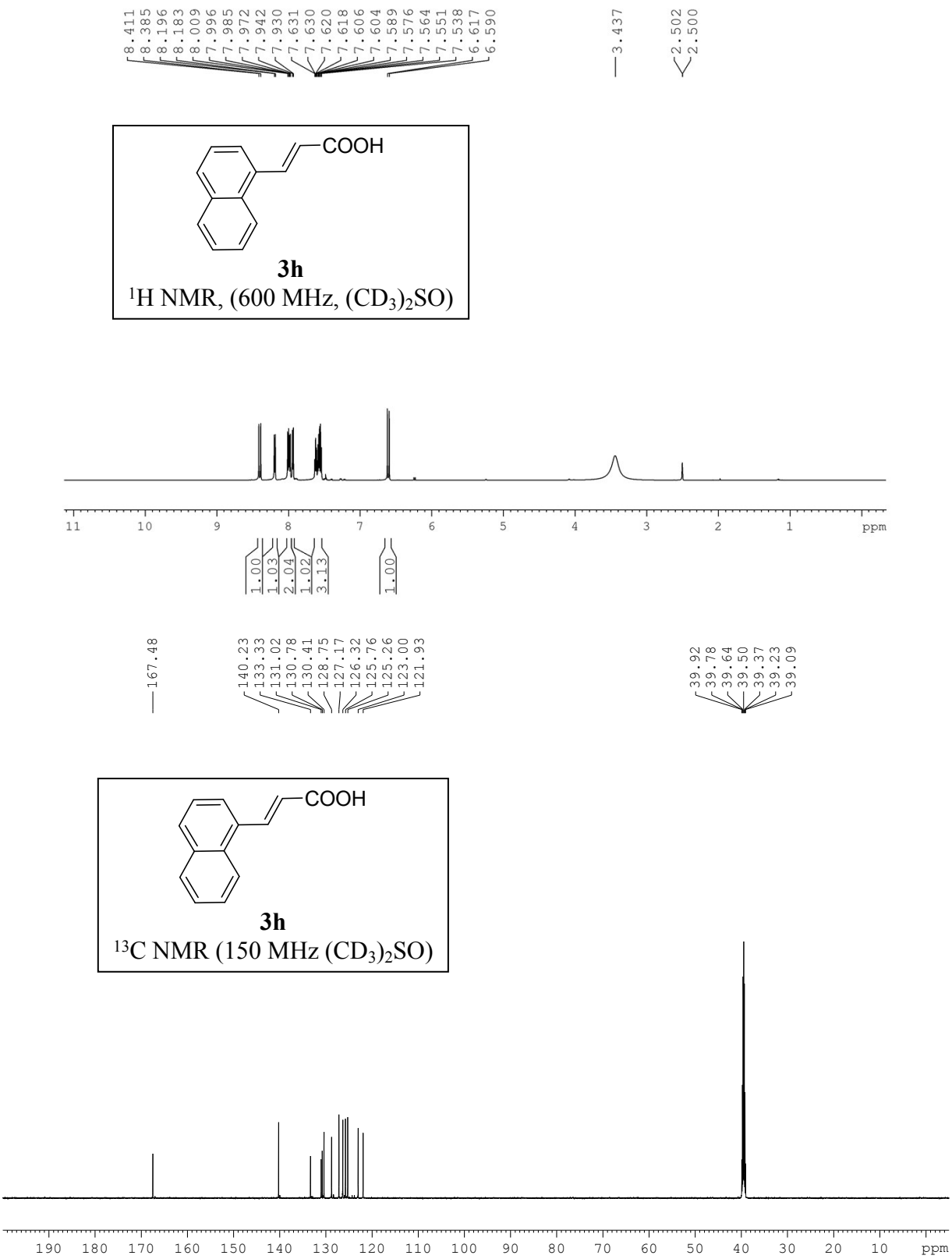


Cinnamic acid (3g)

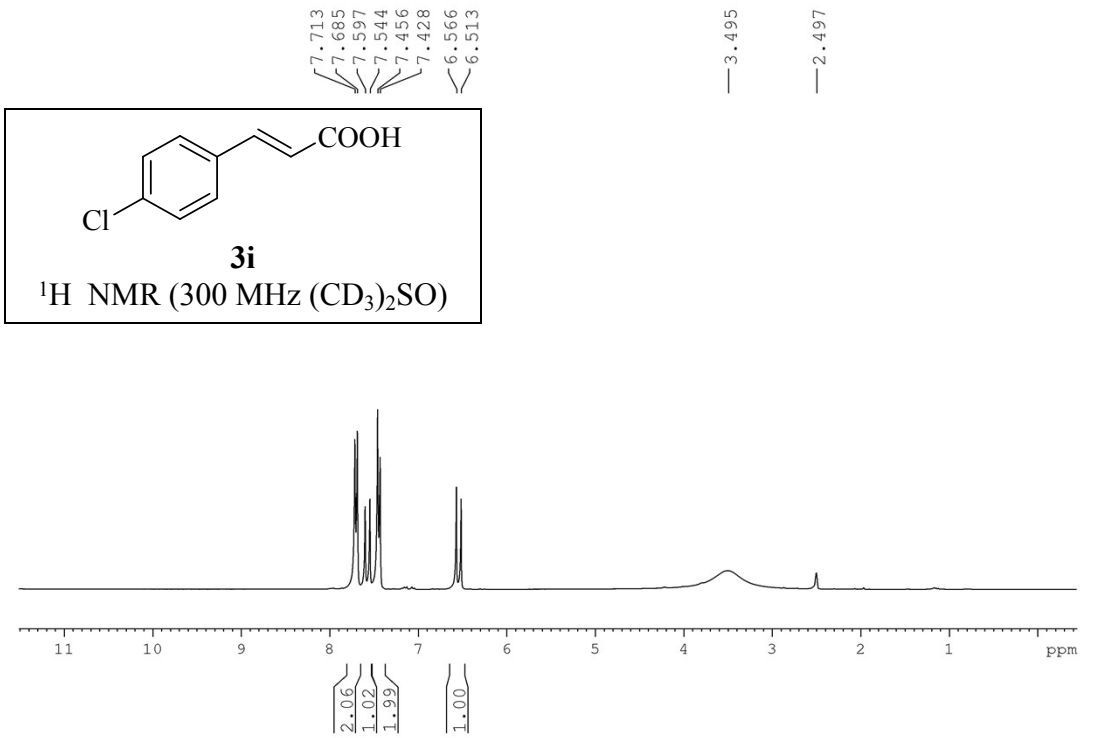


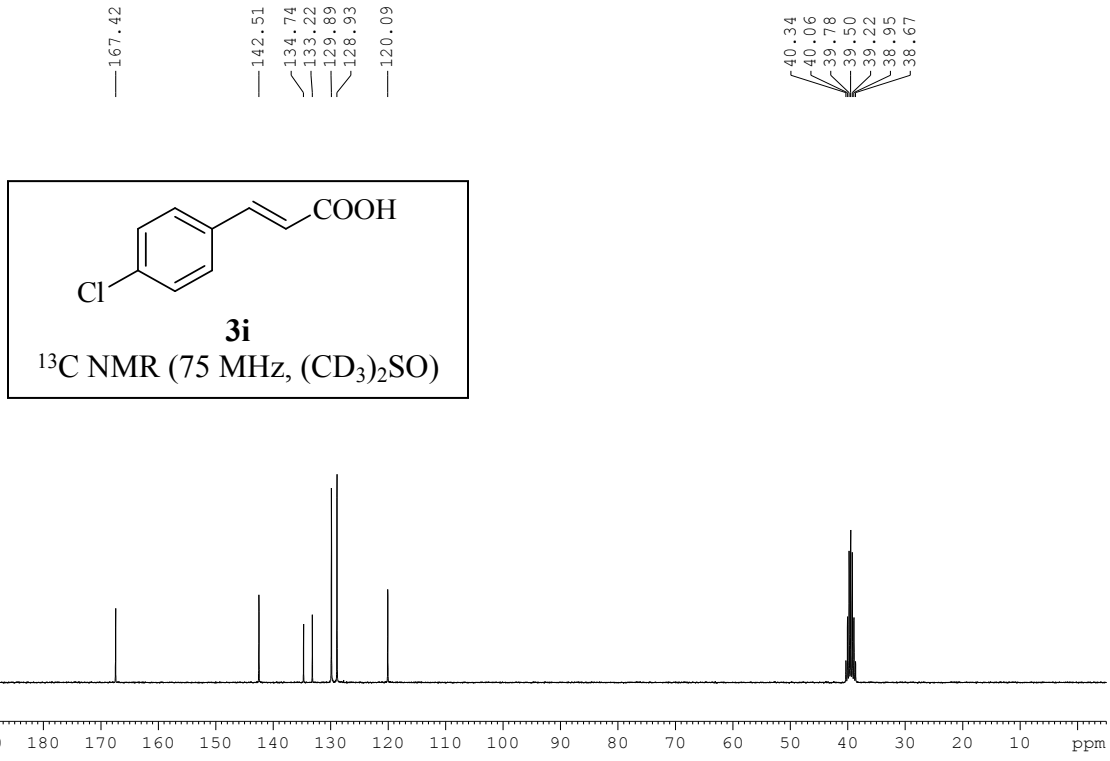


(*E*)-3-(naphthalen-3-yl)acrylic acid (3h)

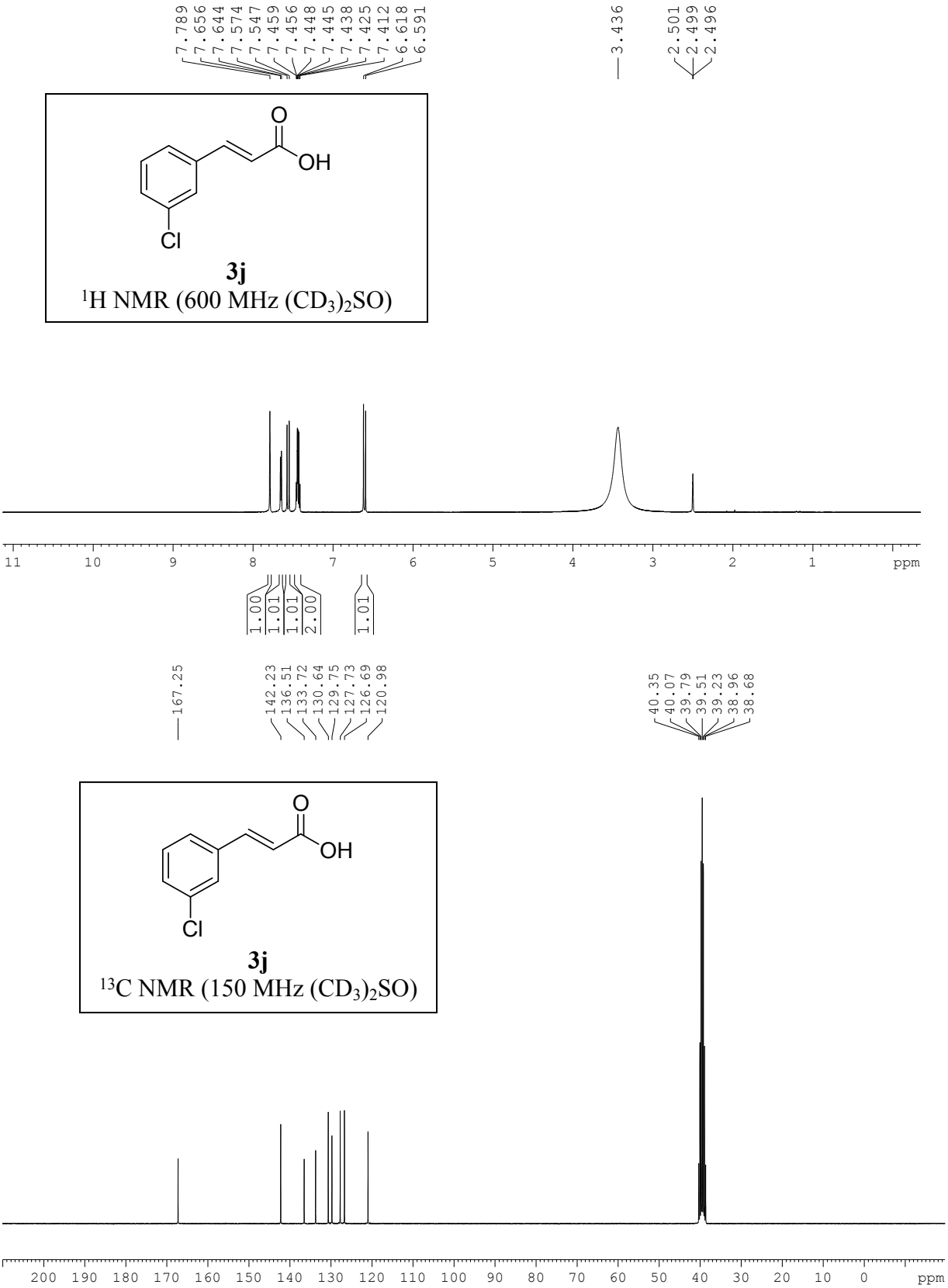


(*E*)-3-(4-chlorophenyl)acrylic acid (3i)

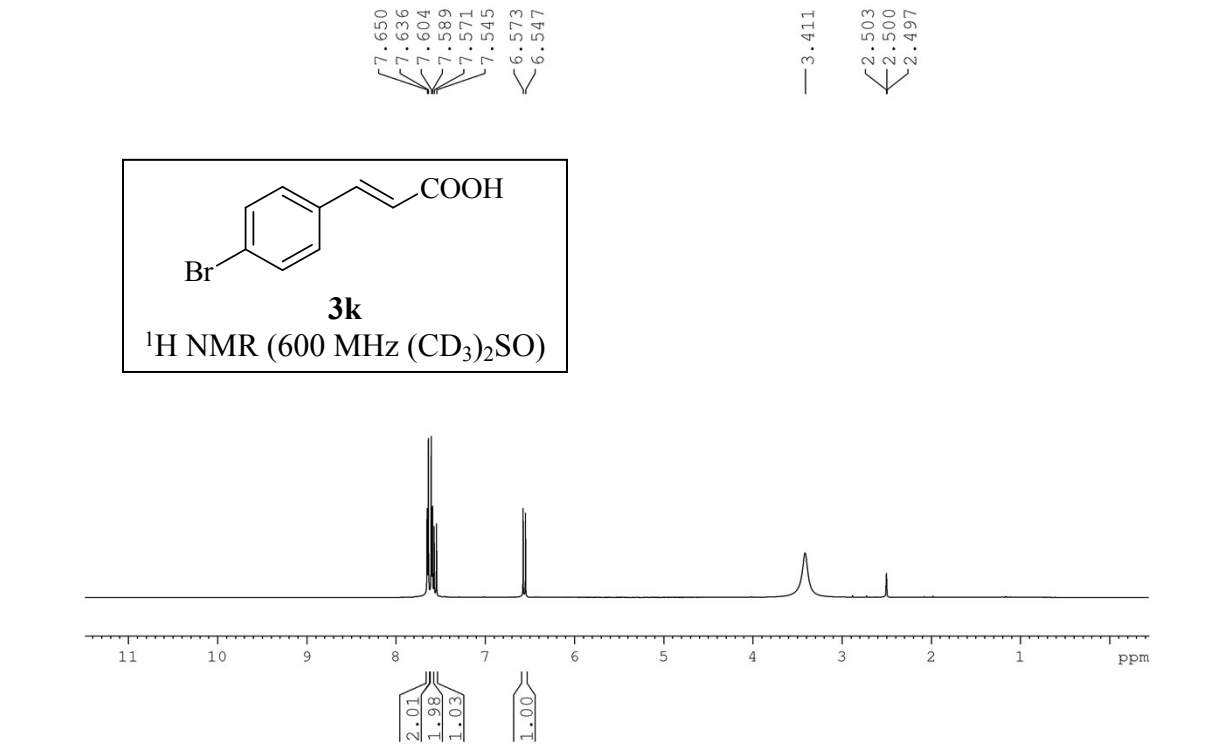


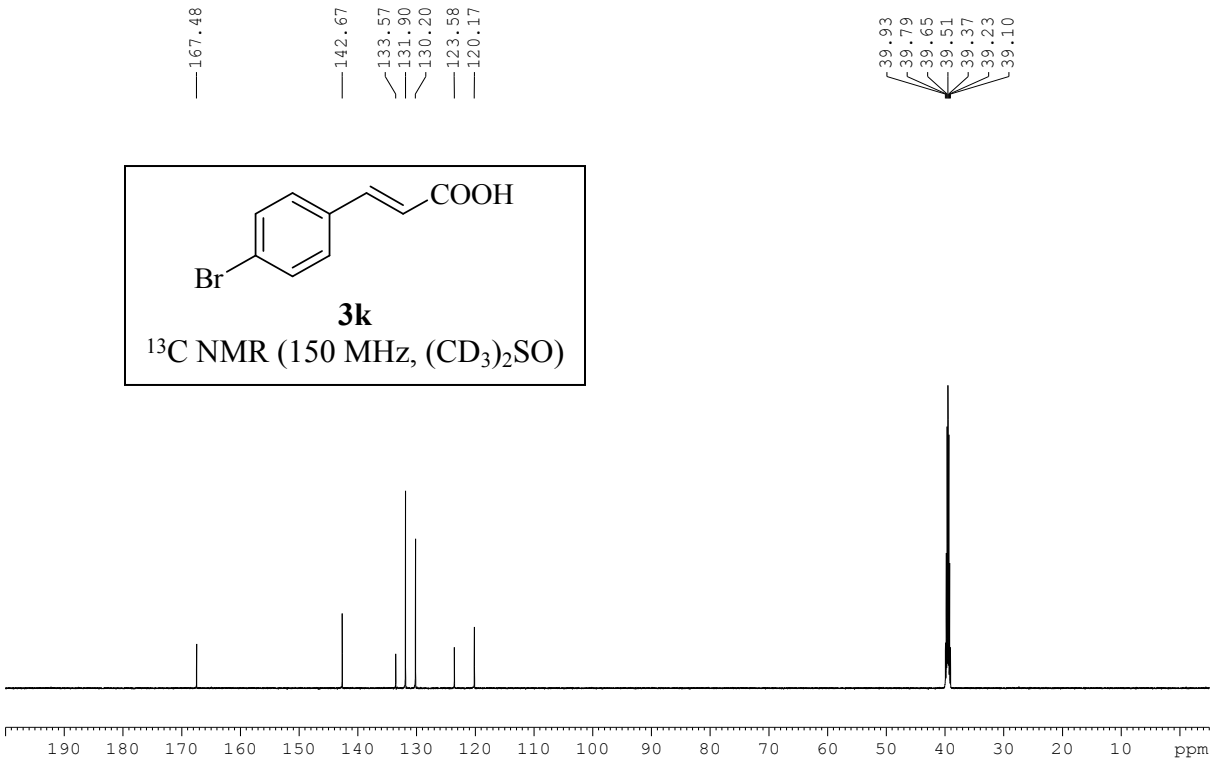


(*E*)-3-(3-chlorophenyl)acrylic acid (3j)

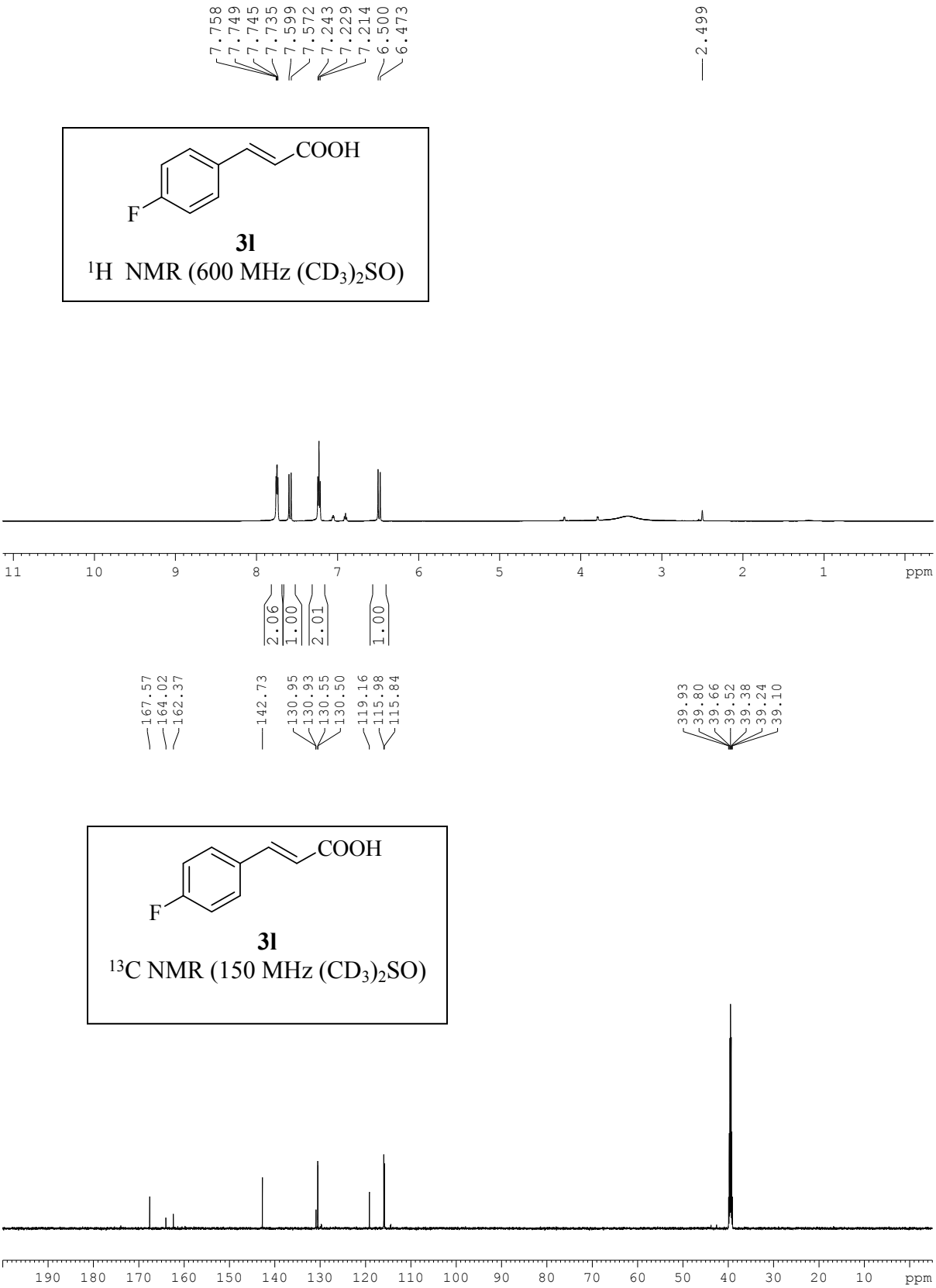


(*E*)-3-(4-bromophenyl)acrylic acid (3k)

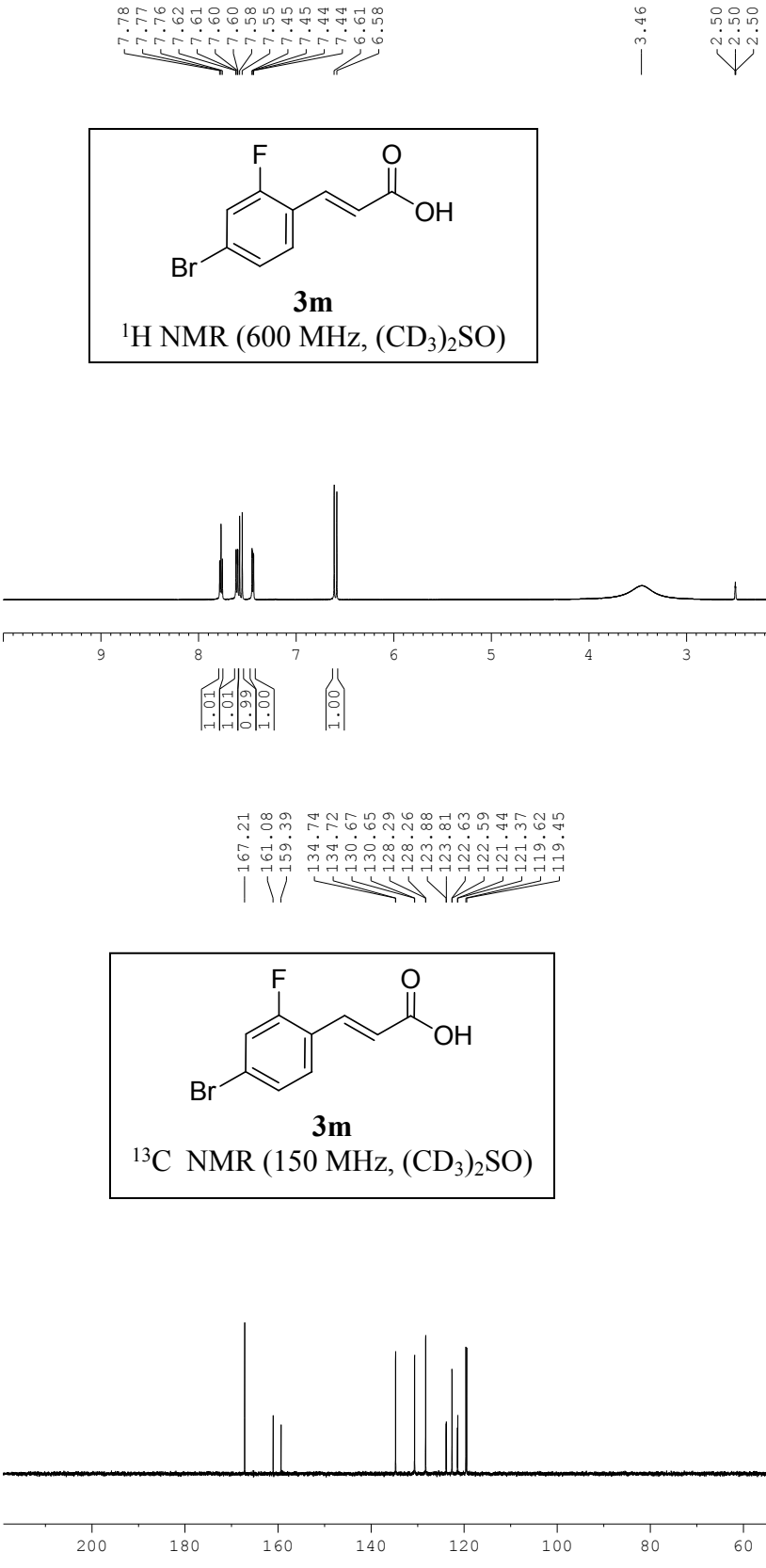




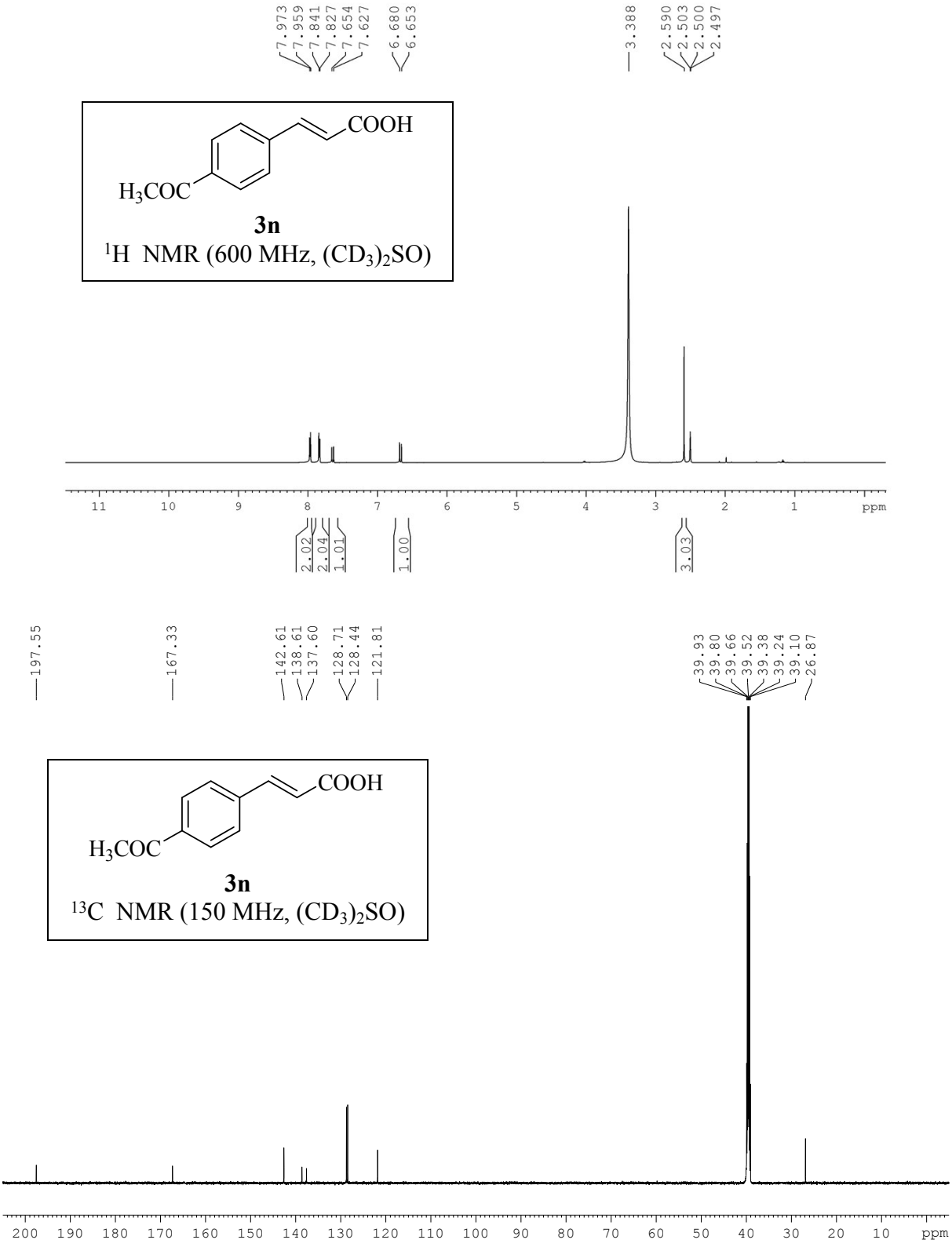
(*E*)-3-(4-fluorophenyl)acrylic acid (3l)



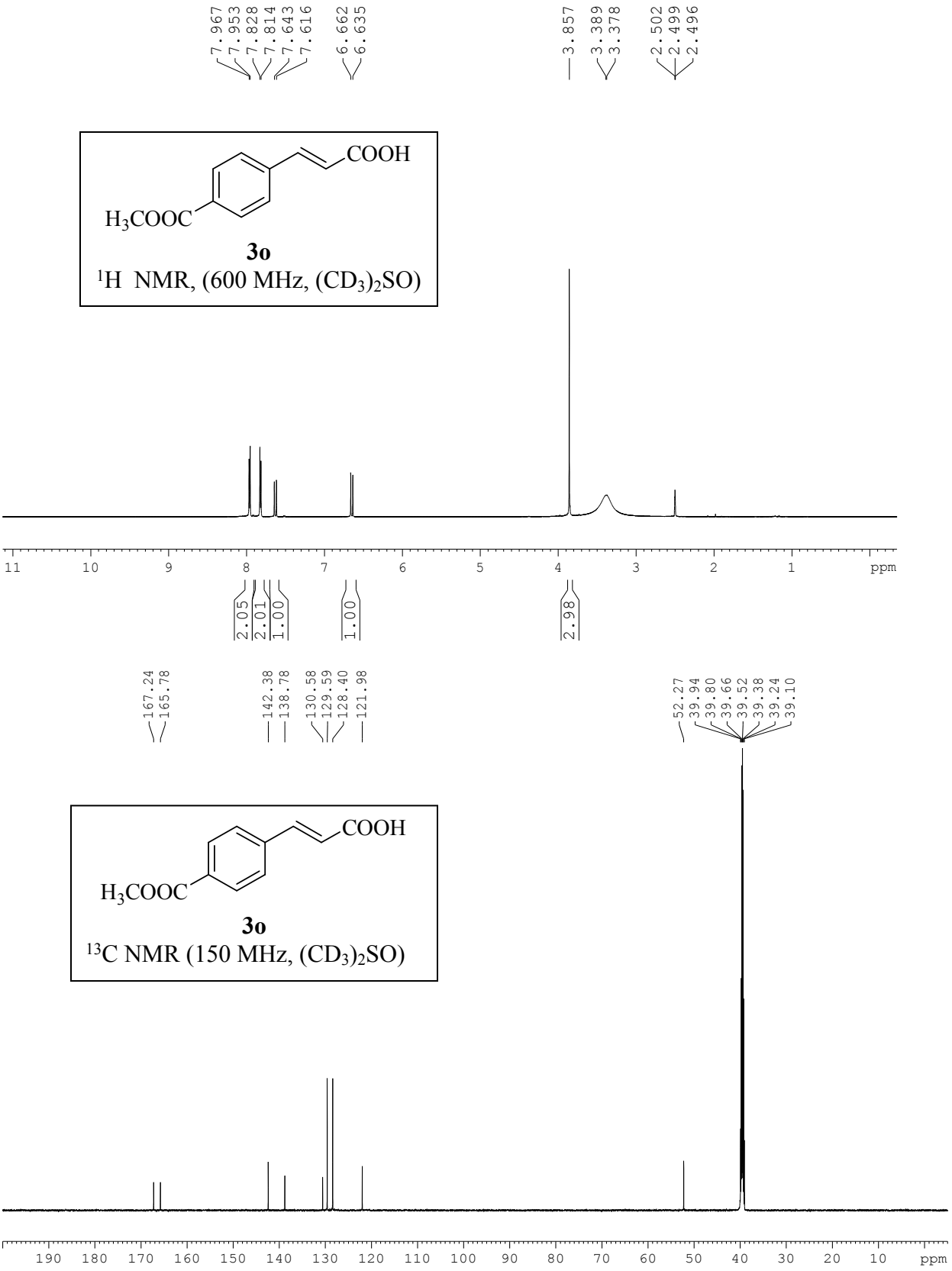
(*E*)-3-(4-bromo-2-fluorophenyl)acrylic acid (3m)



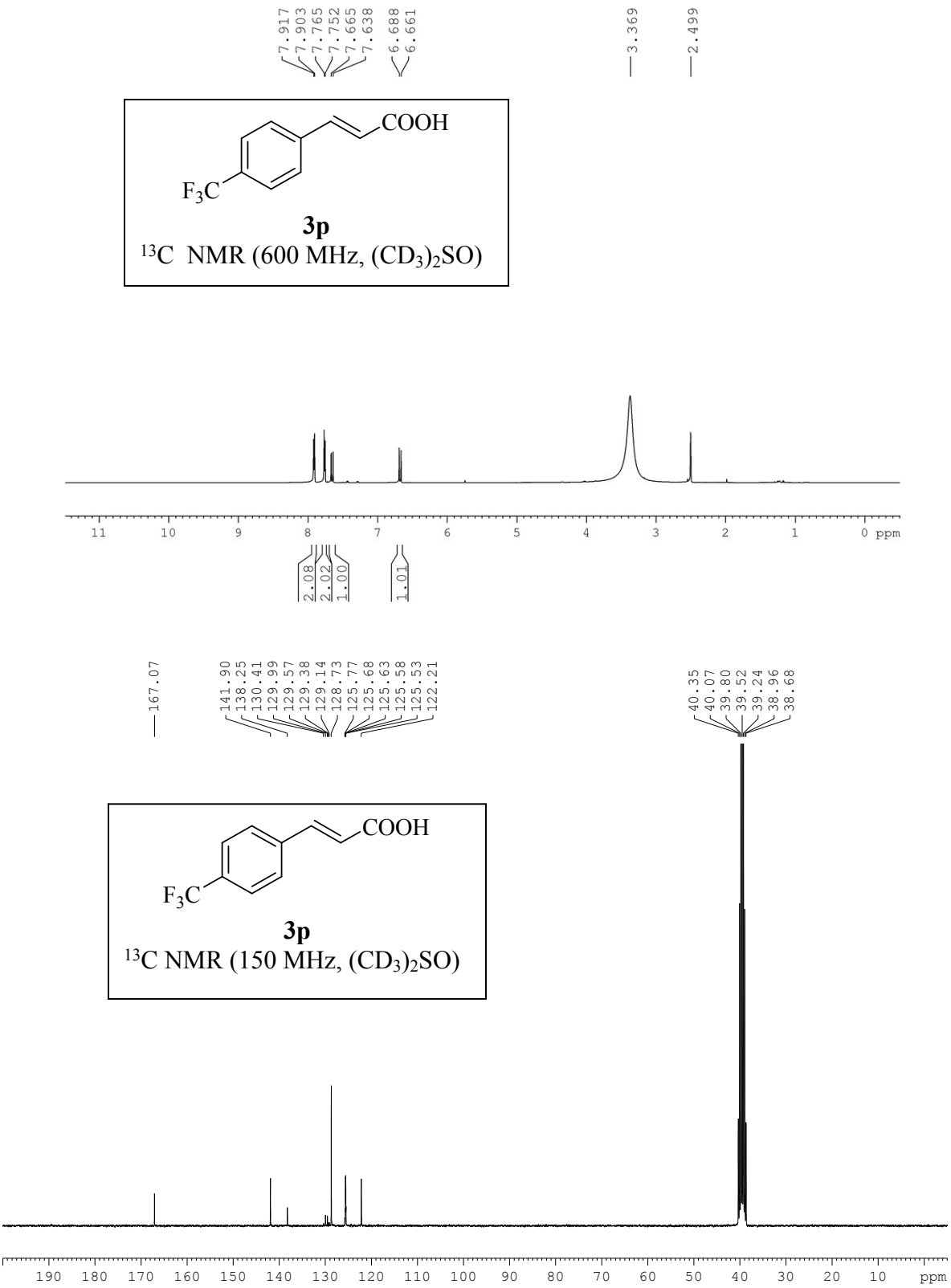
(*E*)-3-(4-acetylphenyl)acrylic acid (3n)



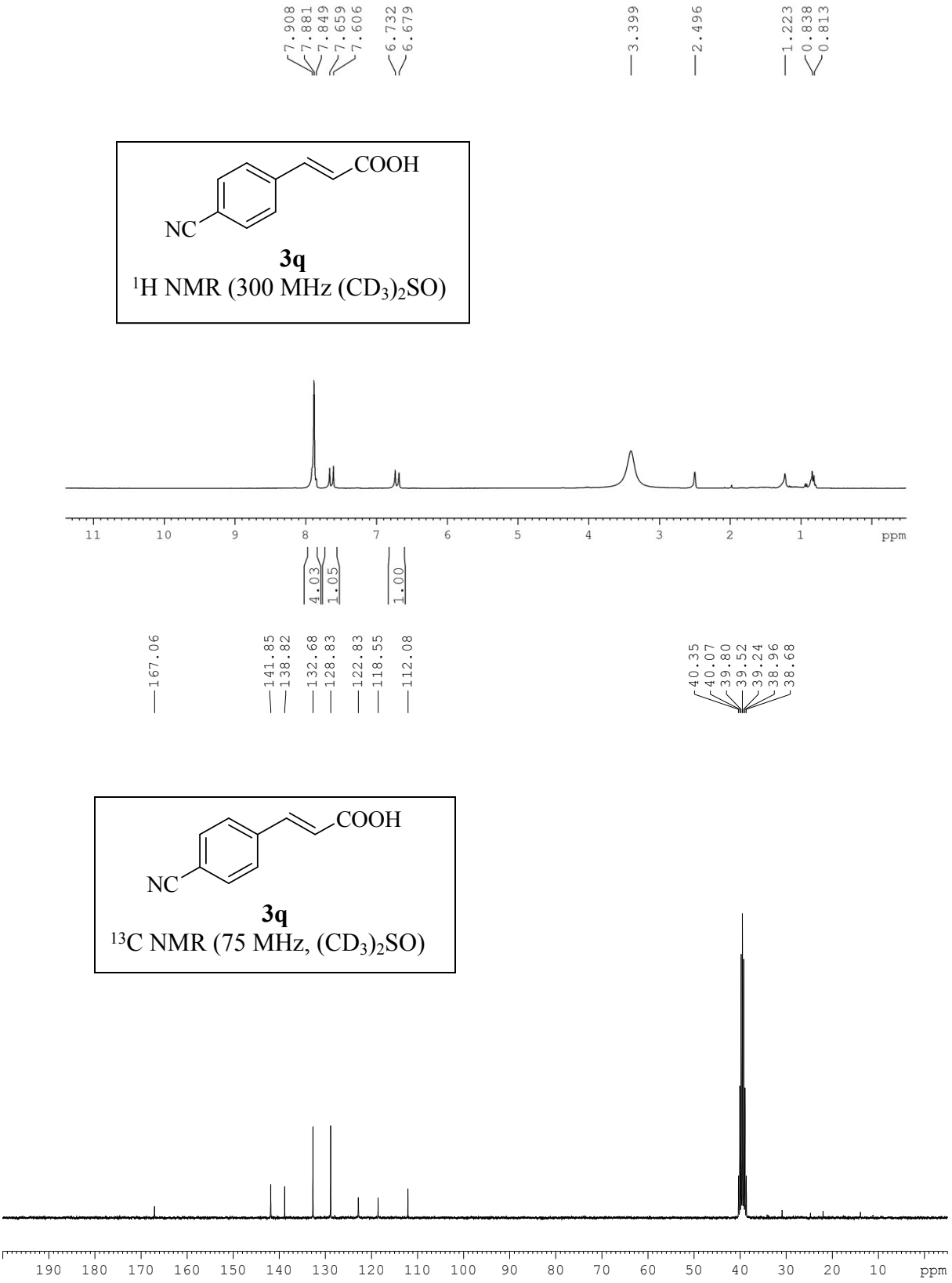
(*E*)-3-(4-(methoxycarbonyl)phenyl)acrylic acid (3o)



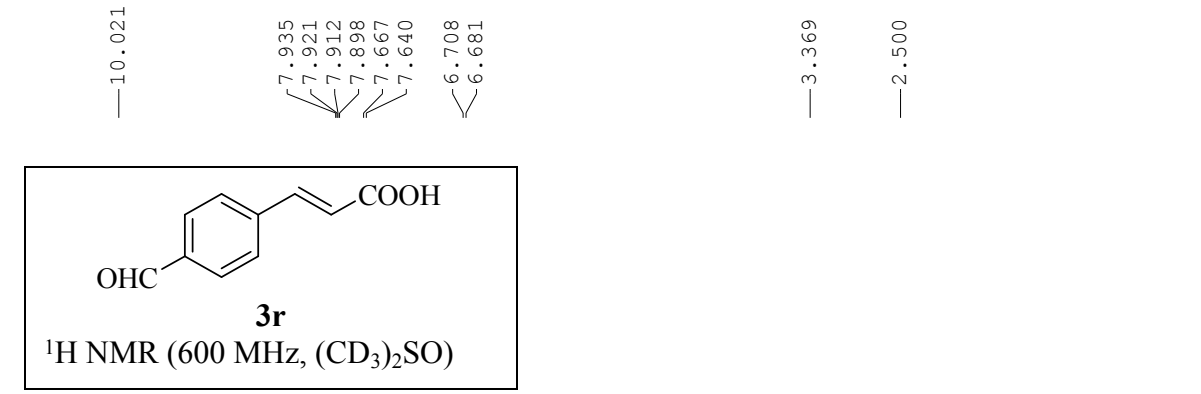
(*E*)-3-(4-(trifluoromethyl)phenyl)acrylic acid (3p)

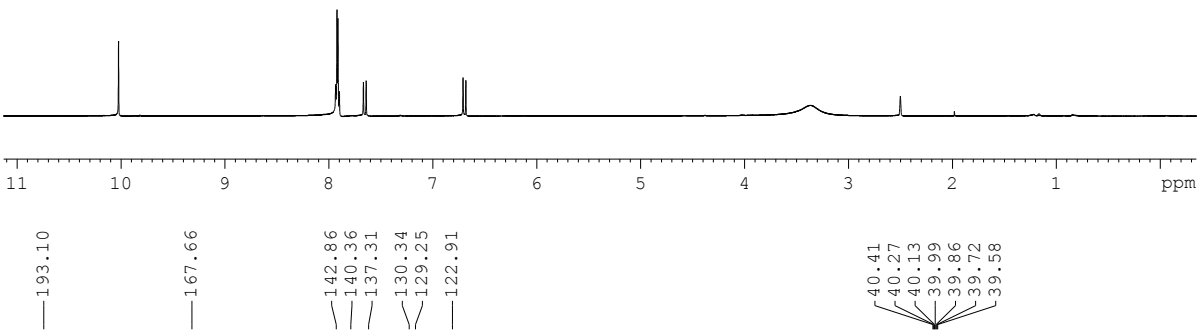


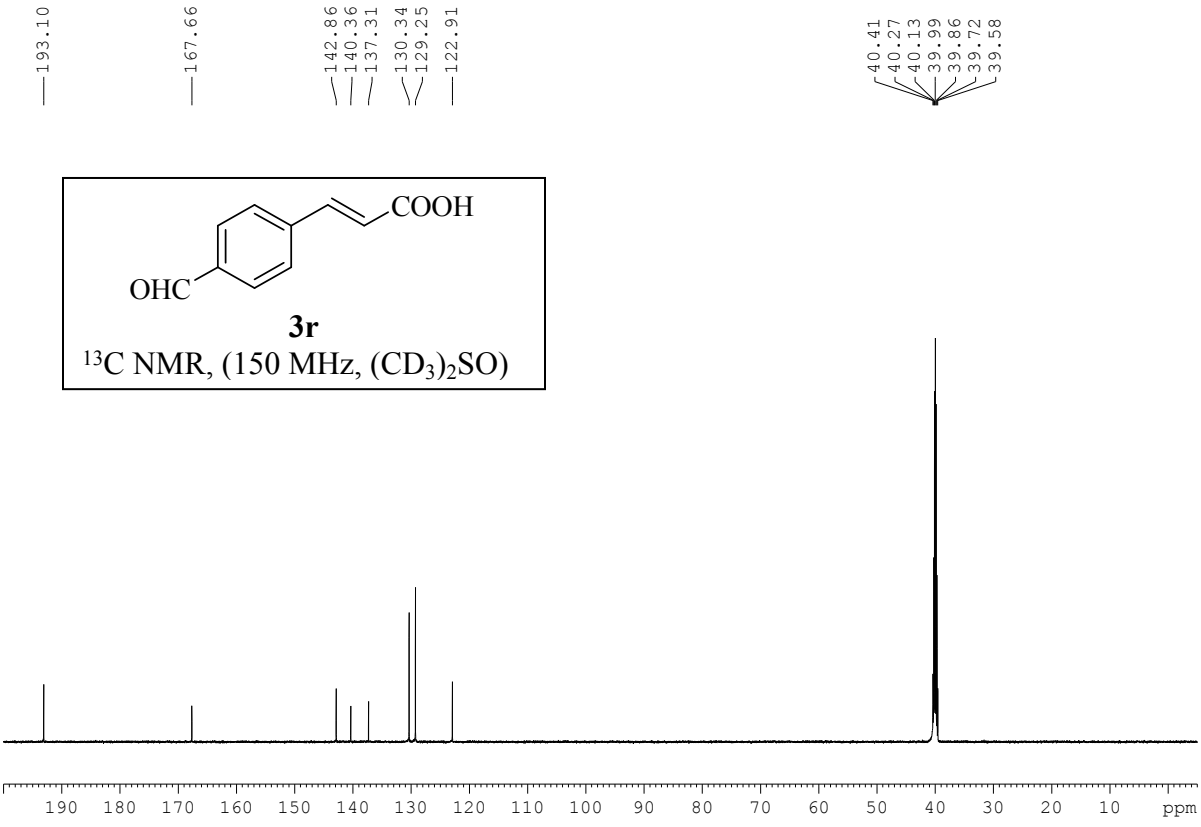
(*E*)-3-(4-cyanophenyl)acrylic acid (3q)



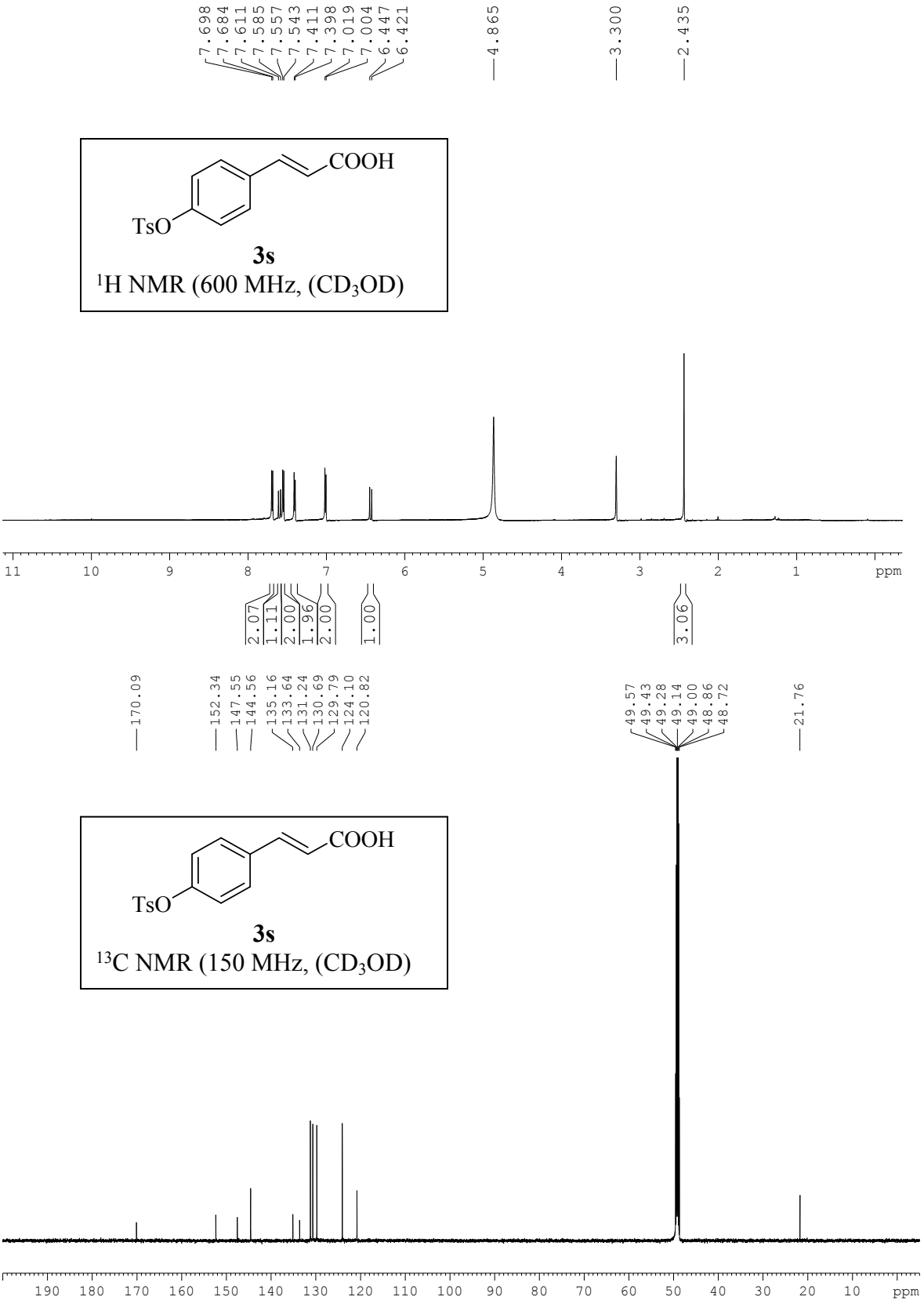
(*E*)-3-(4-formylphenyl)acrylic acid (3r)



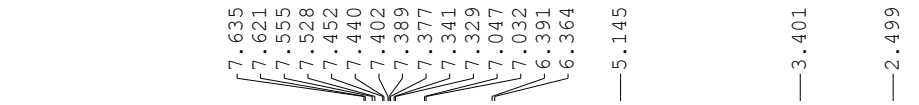


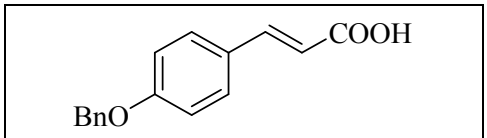


(*E*)-3-(4-(4-methylbenzenesulfonoyl)phenyl)acrylic acid (3s)



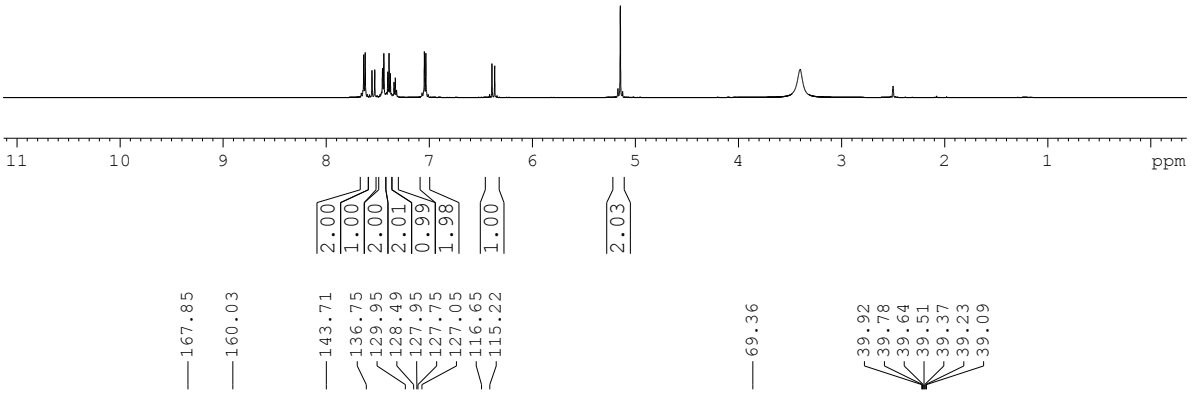
(*E*)-3-(4-(benzyloxy)phenyl)acrylic acid (3t)

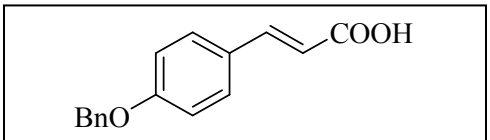




3t

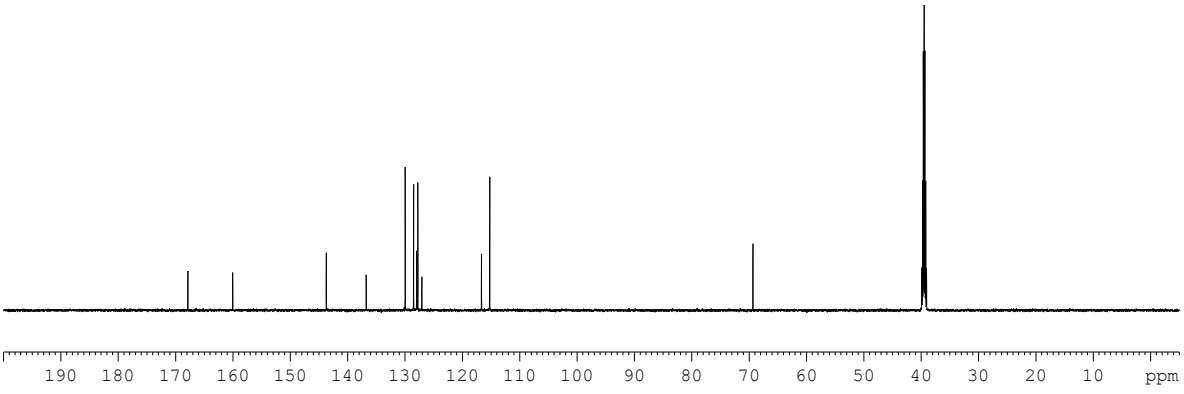
^{1}H NMR (600 MHz, $(CD_3)_2SO$)





3t

^{13}C NMR, (150 MHz, $(CD_3)_2SO$)



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