Supporting Information for

Ni-catalyzed Regioselective Hydrocarboxylation of Alkynes with CO_2 by Using Simple Alcohols as Proton Sources

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Table of contents

General considerations S2

Optimizations details S3

Ni-catalyzed hydrocarboxylation of alkynes (Table 2) S9

Mechanistic experiments (Schemes 2-3) S20

X-Ray crystallographic data for 3a, 3c and 3u S24

^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra S61

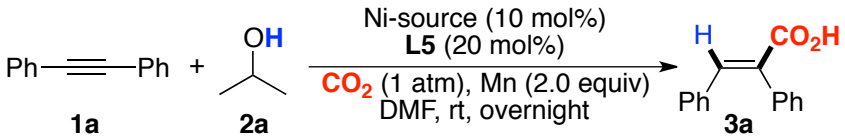
General considerations

Reagents: All reactions were conducted in Schlenk tubes. $NiCl_2 \cdot$glyme was purchased from Strem. All other Nickel catalysts, Mn were purchased from Aldrich or Strem. Bathocuproine was purchased from TCI. Anhydrous DMF was purchased from Acros and directly used as received (Note: it is worth noting that old batches of DMF resulted in significant lower yields of products).

Analytical methods: ^{1}H NMR and ^{13}C NMR spectra and melting points (where applicable) are included for all compounds. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker 400 MHz and a Bruker 500 MHz at 20 ^{o}C. All ^{1}H NMR spectra are reported in parts per million (ppm) downfield of TMS and were measured relative to the signals for $CHCl_3$ (7.26 ppm), DMSO (2.50 ppm). All ^{13}C NMR spectra were reported in ppm relative to residual $CHCl_3$ (77.2 ppm), DMSO (39,5 ppm) and were obtained with ^{1}H decoupling. Coupling constants, ***J***, are reported in hertz. Melting points were measured using open glass capillaries in a Büchi B540 apparatus. Infrared spectra were recorded on a Bruker Tensor 27. Mass spectra were recorded on a Waters LCT Premier spectrometer. Gas chromatographic analyses were performed on Hewlett-Packard 6890 gas chromatography instrument with a FID detector using 25m x 0.20 mm capillary column with cross-linked methyl siloxane as the stationary phase. High Pressure Liquid Chromatographic (HPLC) analyses were performed on Agilent Technologies Model 1260 Infinity HPLC chromatography instrument equipped with Agilent Eclipse Plus C18 (3.5 um, 4.6 x 100 mm) column and UV/V is detector. Flash chromatography was performed with EM Science silica gel 60 (230-400 mesh) and using bromocresol as TLC stain. The yields reported in table 2 refer to isolated yields and represent an average of at least two independent runs. The procedures described in this section are representative. Thus, the yields may differ slightly from those given in the manuscript

Optimization details

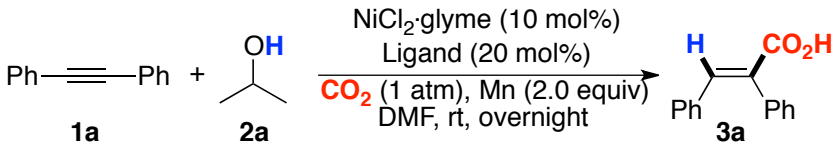
Table S1: Screening of nickel catalysts.[a]



Entry	Ni-source	Conversion (%)[b]	Yield (%)[b]
1	$NiCl_2$·glyme	100	85
2	$NiBr_2$·diglyme	100	72
3	$Ni(ClO_4)_2·6H_2O$	0	0
4	$Ni(OTf)_2$	0	0
5	$Ni(acac)_2$	0	0
6	NiI_2	78	35
7	$NiBr_2$	92	66
8	NiF_2	0	0
9	$NiCl_2$	100	74
10	$NiCO_3$	0	0

[a] Reaction conditions: **1a** (0.25 mmol), **2a** (0.5 mmol), Ni-cat. (10 mol%), ligand (20 mol%), Mn (2.0 equiv), DMF (1 mL), rt, overnight. [b] Determined by HPLC using naphthalene as internal standard.

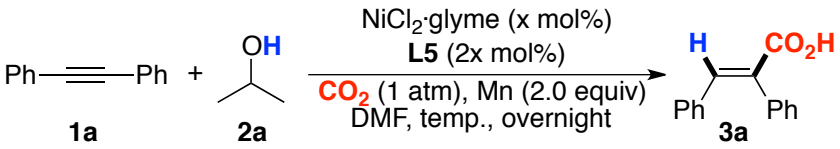
Table S2: Screening of ligands.[a]



Entry	Ligand	Conversion (%)[b]	Yield (%)[b]
1	2,2'-bipyridine	0	0
2	2,4-Lutidine	0	0
3	6,6'-dimethyl-2,2'-bipridine	98	75
4	1,10-phenanthroline	0	0
5	1,7-phenanthroline	0	0
6	Bathophenanthroline	0	0
7	Neocuproine	88	66
8	i-Pr-Box	0	0

[a] Reaction conditions: **1a** (0.25 mmol), **2a** (0.5 mmol), $NiCl_2$·glyme. (10 mol%), Ligand (20 mol%), Mn (2.0 equiv), DMF (1 mL), rt, overnight. [b] Determined by HPLC using naphthalene as internal standard.

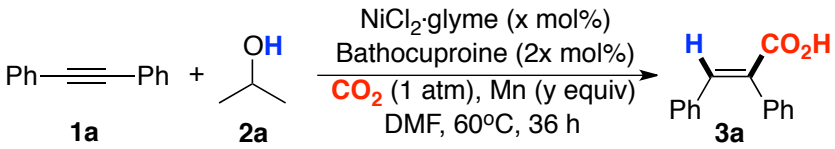
Table S3: Screening of catalyst loadings and temperature.[a]



Entry	x (mol%)	Temp. (°C)	Conversion (%)[b]	Yield (%)[b]
1	5	rt	73	72
2	2.5	rt	42	42
3	1	rt	5	3
4	5	50	98	88
5	5	60	99	90

[a] Reaction conditions: **1a** (0.25 mmol), **2a** (0.5 mmol), $NiCl_2$·glyme. (x mol%), ligand (2x mol%), Mn (2.0 equiv), DMF (1 mL), overnight. [b] Determined by HPLC using naphthalene as internal standard.

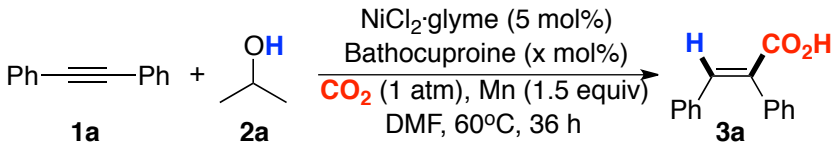
Table S4: Catalyst loadings and amount of Mn.[a]



Entry	x (mol%)	Mn (equiv)	Conv. (%)[b]	Yield (%)[b]
1	5	2.0	100	99 (94[c])
2	2.5	2.0	100	85
3	5	1.5	100	99 (94[c])
4	5	1.2	100	88
5	5	1.0	100	83

[a] Reaction conditions: **1a** (0.25 mmol), **2a** (0.5 mmol), $NiCl_2$·glyme. (x mol%), ligand (2x mol%), Mn (y equiv), DMF (1 mL), 60 °C, 36 h. [b] Determined by HPLC using naphthalene as internal standard. [c] Isolated yield.

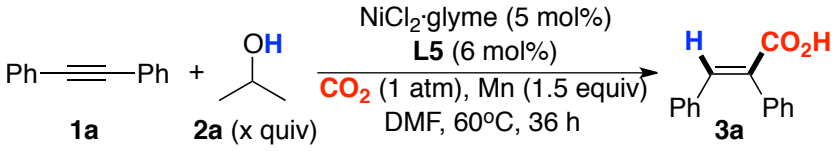
Table S5: Metal to ligand ratio.[a]



Entry	Ligand (mol%)	Conversion. (%)[b]	Yield (%)[b]
1	9	100	99 (94[c])
2	6	100	99 (94[c])
3	5.5	100	96 (92[c])
4	5	100	84

[a] Reaction conditions: **1a** (0.25 mmol), **2a** (0.5 mmol), $NiCl_2$·glyme. (5 mol%), ligand (x mol%), Mn (1.5 equiv), DMF (1 mL), 60°C, 36 h. [b] Determined by HPLC using naphthalene as internal standard. [c] Isolated yield.

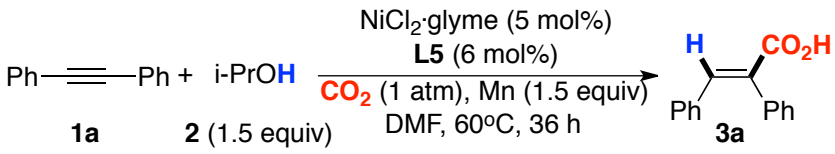
Table S6: Amount of *i*-PrOH (2a).[a]



Entry	**2a** (equiv)	Conversion (%)[b]	Yield (%)[b]
1	1.5	100	99 (94[c])
2	1.2	100	88
3	1.0	100	83

[a] Reaction conditions: **1a** (0.25 mmol), **2a** (x mmol), $NiCl_2$·glyme. (5 mol%), ligand (6 mol%), Mn (1.5 equiv), DMF (1 mL), 60°C, 36 h. [b]H Determined by HPLC using naphthalene as internal standard. [c] Isolated yield.

Table S7: Deviation from the standard conditions.[a]

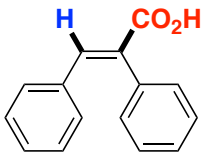


Entry	Deviation	Conversion. (%)[b]	Yield (%)[b]
1	MeOH instead of *i*-PrOH	100	47
2	EtOH instead of *i*-PrOH	100	52
3	*t*-BuOH instead of *i*-PrOH	38	37
4	BnOH instead of *i*-PrOH	100	37
5	Phenol instead of *i*-PrOH	100	45
6	1,1,1,3,3,3-hexafluoroisopropanol (HFIP) instead of *i*-PrOH	100	50
7	$Ni(COD)_2$ as catalyst	88	78
8	DMA (DMSO) as the solvent	41 (75)	36 (66)
9	Zn as reducing agent	32	20
10	BHT (1 equiv) as additive	100	74

[a] Reaction conditions: **1a** (0.25 mmol), **2a** (0.375 mmol), $NiCl_2$·glyme. (5 mol%), ligand (6 mol%), Mn (1.5 equiv), DMF (1 mL), 60°C, 36 h. [b] Determined by HPLC using naphthalene as internal standard.

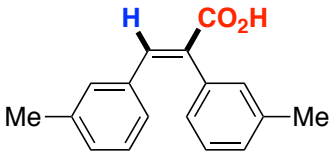
Ni-catalyzed hydrocarboxylation of alkynes (Table 2)

General procedure: A Schlenk tube containing a stirring bar was charged with diphenylacetylene (89.2 mg, 0.50 mmol), **L5** (10.8 mg, 0.03 mmol), Mn powder (41.2 mg, 0.75 mmol) and $NiCl_2 \cdot$glyme (5.5 mg, 0.025 mmol). The tube was then evacuated and back-filled with CO_2 three times. *i*-PrOH (57.4 μL, 0.75 mmol) and DMF (2 mL) were then added by syringe under a CO_2 flow. Once added, the Schlenk tube was closed at atmospheric pressure of CO_2 (1atm) and stirred for 36 h at 60°C. The mixture was quenched with HCl (2M) and extracted with DCM. The combined organic layers were washed with brine and dried over anhydrous $MgSO_4$ and evaporated. The residue was purified by flash chromatography (hexanes/ethyl acetate = 10/1 to 1/1).



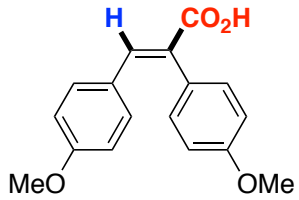
3a

(*E*)-2,3-diphenylacrylic acid (3a): Following the general procedure using **1a** to afford **3a** (105.4 mg, 95% yield) as a white solid. The spectroscopic data correspond to those previously reported in the literature.[1] M.P. = 170 – 171°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (s, 1H), 7.43 – 7.34 (m, 3H), 7.29 – 7.20 (m, 3H), 7.20 – 7.12 (m, 2H), 7.10 – 7.05 (m, 2H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.2, 142.6, 135.5, 134.5, 131.8, 131.0, 130.0, 129.7, 128.9, 128.4, 128.2 ppm.



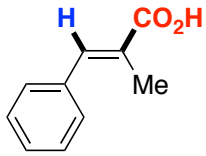
3b

(*E*)-2,3-di-*m*-tolylacrylic acid (3b): Following the general procedure using **1b** to afford **3b** (103.4 mg, 84% yield) as a white solid. The spectroscopic data correspond to those previously reported in the literature.[1] M.P. = 151 – 153°C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 (s, 1H), 7.28 (t, J = 7.6 Hz, 1H), 7.19 (d, J = 7.6 Hz, 1H), 7.10 – 6.99 (m, 4H), 6.94 (s, 1H), 6.90 – 6.83 (m, 1H), 2.36 (s, 3H), 2.21 (s, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.6, 142.6, 138.5, 138.0, 135.5, 134.4, 132.1, 131.7, 130.5, 130.4, 128.9, 128.7, 128.3, 128.0, 126.9, 21.6, 21.4 ppm.



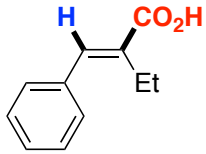
3c

(*E*)-2,3-bis(4-methoxyphenyl)acrylic acid (3c): Following the general procedure using **1c** to afford **3c** (98.1 mg, 70% yield) as a white solid. The spectroscopic data correspond to those previously reported in the literature.[1] M.P. = 208 – 211°C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.88 (s, 1H), 7.18 (d, *J* = 8.8 Hz, 2H), 7.06 (d, *J* = 8.8 Hz, 2H), 6.93 (d, *J* = 8.8 Hz, 2H), 6.71 (d, *J* = 8.8 Hz, 2H), 3.85 (s, 3H), 3.77 (s, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.5, 160.7, 159.4, 142.2, 132.8, 131.2, 128.8, 128.0, 127.3, 114.5, 113.9, 55.4 (2C) ppm.



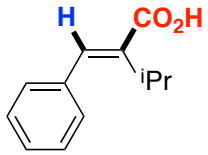
3d

(*E*)-2-methyl-3-phenylacrylic acid (3d): Following the general procedure using **1d** and *t*-BuOH (**2c**) to afford **3d** (68.9 mg, 85% yield) as a white solid. The spectroscopic data correspond to those previously reported in the literature.[1] M.P. = 78 – 80°C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 (s, 1H), 7.54 – 7.40 (m, 4H), 7.40 – 7.33 (m, 1H), 2.19 (d, *J* = 1.5 Hz, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.8, 141.3, 135.7, 130.0, 128.9, 128.6, 127.7, 13.9 ppm.



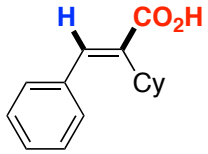
3e

(*E*)-2-benzylidenebutanoic acid (3e): Following the general procedure using **1e** and *t*-BuOH (**2c**) to afford **3e** (71.4 mg, 84% yield) as a white solid. The spectroscopic data correspond to those previously reported in the literature.[2] M.P. = 98 – 100°C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83 (s, 1H), 7.50 – 7.40 (m, 4H), 7.40 – 7.30 (m, 1H), 2.60 (q, *J* = 7.4 Hz, 2H), 1.25 (t, *J* = 7.4 Hz, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.4, 141.0, 135.6, 134.1, 129.6, 128.9, 128.7, 20.7, 13.9 ppm.



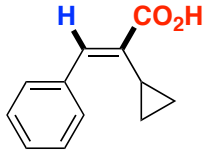
3f

(*E*)-2-benzylidene-3-methylbutanoic acid (3f): Following the general procedure using **1f** and *t*-BuOH (**2c**) to afford **3f** (78.0 mg, 83% yield) as a white solid. M.P. = 111 – 113°C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 (s, 1H), 7.44 – 7.39 (m, 2H), 7.37 – 7.32 (m, 3H), 3.21 (m, 1H), 1.30 (d, J = 7.0 Hz, 6H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.8, 140.6, 138.4, 135.9, 129.1, 128.6, 128.4, 27.6, 21.3 ppm. IR (neat, cm^{-1}): 2956, 1671, 1418, 1258, 692. HRMS *calcd.* for ($C_{12}H_{14}O_2$-H): 189.0921, *found*: 189.0927.



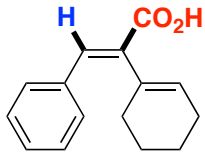
3g

(*E*)-2-cyclohexyl-3-phenylacrylic acid (3g): Following the general procedure using **1g** and *t*-BuOH (**2c**) to afford **3g** (100.2 mg, 89% yield) as a white solid. The spectroscopic data correspond to those previously reported in the literature.[3] M.P. = 184 – 186°C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 (s, 1H), 7.41 (dd, J = 8.1, 6.7 Hz, 2H), 7.37 – 7.30 (m, 3H), 2.81 (tt, J = 12.0, 3.3 Hz, 1H), 2.18 – 1.90 (m, 2H), 1.77 (m, 2H), 1.70 – 1.55 (m, 3H), 1.39 – 1.12 (m, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.6, 140.7, 137.7, 136.0, 129.2, 128.6, 128.5, 38.6, 30.8, 26.8, 26.0 ppm.



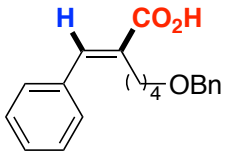
3h

(*E*)-2-cyclopropyl-3-phenylacrylic acid (3h): Following the general procedure using **1h** and *t*-BuOH (**2c**) to afford **3h** (68.7 mg, **3h:3h´** = 13:1, 75% yield) as a white solid. M.P. = 54-55°C. Spectroscopic data for the major isomer (**3h**): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 (d, J = 2.0 Hz, 1H), 7.63 (d, J = 6.9 Hz, 2H), 7.47 – 7.40 (m, 2H), 7.41 – 7.33 (m, 1H), 1.80-1.74 (m, 1H), 1.00 – 0.86 (m, 2H), 0.52-0.49 (dt, J = 6.1, 4.5 Hz, 2H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.4, 142.6, 135.0, 132.5, 130.7, 129.0, 128.2, 10.0, 9.3 ppm. IR (neat, cm^{-1}): 3005, 1669, 609, 273, 774, 690. HRMS *calcd.* for ($C_{12}H_{12}O_2$-H): 187.0765, *found*: 187.0763.



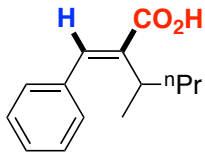
3i

(*E*)-2-(cyclohex-1-en-1-yl)-3-phenylacrylic acid (3i): Following the general procedure using **1i** to afford **3i** (84.4 mg, **3i**:**3i´** = 5:1, 76% yield) as a white solid. M.P. = 81 – 82°C. Spectroscopic data for the major isomer (**3i**): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67 (s, 1H), 7.64 – 7.58 (m, 2H), 7.40 – 7.30 (m, 3H), 5.67 (dt, *J* = 3.8, 2.0 Hz, 1H), 2.25 – 2.16 (m, 2H), 2.12 (d, *J* = 3.7 Hz, 2H), 1.84 – 1.73 (m, 2H), 1.70 (dt, *J* = 8.4, 2.5 Hz, 2H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.8, 140.6, 135.1, 134.4, 133.2, 130.6, 129.5, 128.7, 128.5, 28.1, 25.6, 22.9, 21.9 ppm. IR (neat, cm^{-1}): 2931, 1670, 1414, 1258, 918, 688. HRMS *calcd*. for ($C_{15}H_{16}O_2$-H): 227.1078, *found*: 227.1075.



3j

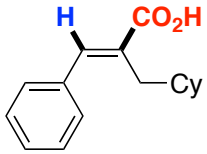
(*E*)-2-benzylidene-6-(benzyloxy)hexanoic acid (3j): Following the general procedure using **1j** and *t*-BuOH (**2c**) to afford **3j** (150.5 mg, 99% yield) as a white solid. M.P. = 65 – 67°C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 (s, 1H), 7.64 – 7.31 (m, 10H), 4.58 (s, 2H), 3.66 – 3.44 (m, 2H), 2.66 (t, *J* = 7.3 Hz, 2H), 1.79 (m, 4H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.2, 141.3, 138.6, 135.5, 132.7, 129.5, 128.8, 128.7, 128.4, 127.7, 127.6, 73.0, 70.0, 29.8, 27.1, 25.8 ppm. IR (neat, cm^{-1}): 2938, 2851, 1673, 1615, 1262, 728, 694. HRMS *calcd*. for ($C_{20}H_{22}O_3$-H): 309.1496, *found*: 309.1502.



3k

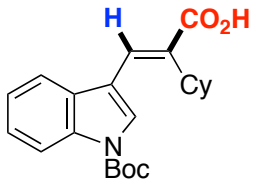
(*E*)-2-benzylidene-3-methylhexanoic acid (3k): Following the general procedure using **1k** and *t*-BuOH (**2c**) to afford **3k** (80.7 mg, 77% yield) as a white solid. The spectroscopic data correspond to those previously reported in the literature.[1] M.P. = 72 – 54°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (s, 1H), 7.48 – 7.37 (m, 2H), 7.37 – 7.29 (m, 3H), 3.03 (m, 1H), 1.87 – 1.67 (m, 1H), 1.59 – 1.45 (m, 1H), 1.31 (d, *J* = 7.0

Hz, 3H), 1.28 – 1.11 (m, 2H), 0.81 (t, J = 7.3 Hz, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.7, 141.3, 137.3, 135.9, 128.9, 128.4, 128.2, 37.0, 32.5, 21.2, 19.4, 14.1 ppm.



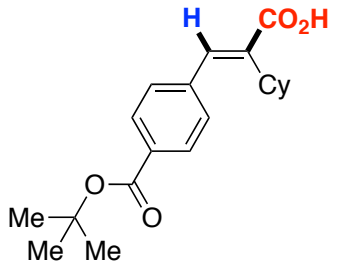
3l

(*E*)-2-(cyclohexylmethyl)-3-phenylacrylic acid (3l): Following the general procedure using **1l** and *t*-BuOH (**2c**) to afford **3l** (114.9 mg, 95% yield) as a white solid. M.P. = 105 – 107°C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (s, 1H), 7.50 – 7.38 (m, 4H), 7.38 – 7.32 (m, 1H), 2.54 (d, J = 7.1 Hz, 2H), 1.85 – 1.55 (m, 6H), 1.30 – 1.05 (m, 3H), 1.07 – 0.78 (m, 2H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.1, 141.9, 135.9, 132.0, 129.7, 128.7, 128.6, 37.9, 34.3, 33.4, 26.6, 26.5 ppm. IR (neat, cm^{-1}): 2921, 2848, 1663, 1446, 1262, 1217, 686. HRMS *calcd*. for ($C_{16}H_{20}O_2$-H): 243.1391, *found*: 243.1385.



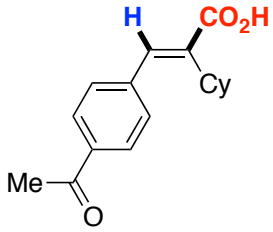
3m

(*E*)-3-(1-(*tert*-butoxycarbonyl)-1*H*-indol-3-yl)-2-cyclohexylacrylic acid (3m): Following the general procedure using **1m** and *t*-BuOH (**2c**) to afford **3m** (131.2 mg, 73% yield) as a white solid. M.P. = 188 – 191°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, J = 8.4 Hz, 1H), 7.84 (s, 1H), 7.78 (d, J = 1.1 Hz, 1H), 7.70 (d, J = 7.8 Hz, 1H), 7.39 (dd, J = 8.4, 1.3 Hz, 1H), 7.35 – 7.29 (m, 1H), 2.94 (tt, J = 12.1, 3.2 Hz, 1H), 2.19 – 2.02 (m, 2H), 1.95 – 1.79 (m, 2H), 1.75-1.68 (m, 12H), 1.38-1.32 (m, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.5, 149.6, 137.1, 135.1, 130.5, 130.1, 125.6, 125.3, 123.4, 119.2, 115.7, 115.4, 84.6, 40.1, 30.5, 28.4, 27.0, 26.2 ppm. IR (neat, cm^{-1}): 2927, 1729, 1669, 1451, 1372, 1144, 743. HRMS *calcd*. for ($C_{22}H_{27}NO_4$-H): 368.1867, *found*: 368.1865.



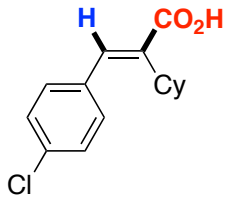
3n

(*E*)-3-(4-(*tert*-butoxycarbonyl)phenyl)-2-cyclohexylacrylic acid (3n): Following the general procedure using **1n** and *t*-BuOH (**2c**) to afford **3n** (102.4 mg, 66% yield) as a white solid. M.P. = 149 – 151°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.3 Hz, 2H), 7.72 (s, 1H), 7.34 (d, *J* = 8.3 Hz, 2H), 2.72 (tt, *J* = 12.0, 3.3 Hz, 1H), 2.07 – 1.91 (m, 2H), 1.82 – 1.69 (m, 2H), 1.61 (m, 12H), 1.30 – 1.12 (m, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.4, 165.5, 140.1, 139.6, 139.2, 131.8, 129.7, 128.9, 81.5, 38.9, 30.8, 28.4, 26.7, 25.9 ppm. IR (neat, cm^{-1}): 2927, 1713, 1678, 1292, 1161, 1115. HRMS *calcd*. for ($C_{20}H_{26}O_4$-H): 329.1758, *found*: 329.1760.



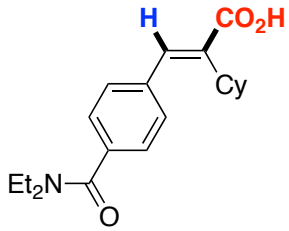
3o

(*E*)-3-(4-acetylphenyl)-2-cyclohexylacrylic acid (3o): Following the general procedure using **1o** and *t*-BuOH (**2c**) to afford **3o** (102.1 mg, 75% yield; **3o:3o'**=6:1) as a white solid. **3o** could be isolated in pure form by column chromatography: M.P. = 156 – 158°C. Spectroscopic data for the major isomer (**3o**): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.3 Hz, 2H), 7.71 (s, 1H), 7.39 (d, *J* = 8.3 Hz, 2H), 2.79 – 2.66 (m, 1H), 2.63 (s, 3H), 2.08 – 1.91 (m, 2H), 1.87 – 1.69 (m, 2H), 1.69 – 1.55 (m, 3H), 1.32 – 1.10 (m, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.8, 173.4, 140.7, 139.6, 139.2, 136.6, 129.2, 128.6, 38.9, 30.8, 26.8, 26.7, 25.9 ppm. IR (neat, cm^{-1}): 2924, 2850, 1668, 1602, 1258, 821. HRMS *calcd*. for ($C_{17}H_{20}O_3$-H): 271.1340, *found*: 271.1340.



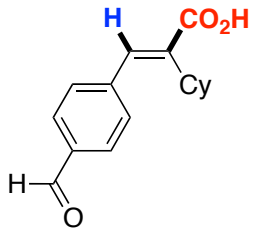
3p

(*E*)-3-(4-chlorophenyl)-2-cyclohexylacrylic acid (3p): Following the general procedure using **1p** and *t*-BuOH (**2c**) to afford **3p** (68.7 mg, 76% yield; **3p:3p'**=18:1) as a white solid. Spectroscopic data for the major isomer (**3p**): M.P. = 122 – 123°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (s, 1H), 7.40 (d, *J* = 8.2 Hz, 2H), 7.27 (d, *J* = 8.2 Hz, 2H), 2.75 (t, *J* = 12.0 Hz, 1H), 2.08 – 1.98 (m, 2H), 1.79 (d, *J* = 11.2 Hz, 2H), 1.65 (m, 3H), 1.35 – 1.18 (m, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.7, 139.3, 138.4, 134.4, 134.3, 130.5, 128.9, 38.7, 30.8, 26.8, 26.0 ppm. IR (neat, cm-1): 2925, 2852, 1673, 1238, 816. HRMS *calcd*. for ($C_{15}H_{16}ClO_2$-H): 263.0844, *found*: 263.0838.



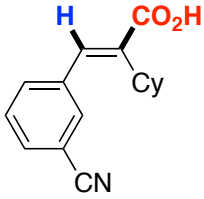
3q

(*E*)-2-cyclohexyl-3-(4-(diethylcarbamoyl)phenyl)acrylic acid (3q): Following the general procedure using **1q** to afford **3q** (126.8 mg, 78% yield) as a white solid. M.P. = 149 – 151°C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 (s, 1H), 7.41 (d, *J* = 8.1 Hz, 2H), 7.32 (d, *J* = 8.1 Hz, 2H), 3.57 (brs, 2H), 3.30 (brs, 2H), 2.74 (tt, *J* = 12.0, 3.3 Hz, 1H), 2.08 – 1.92 (m, 2H), 1.83 – 1.68 (m, 2H), 1.69 – 1.51 (m, 3H), 1.39 – 0.97 (m, 9H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.0, 171.1, 139.2, 138.9, 136.9, 136.9, 129.2, 126.6, 43.6, 39.6, 38.7, 30.8, 26.7, 25.9, 14.4, 13.0 ppm. IR (neat, cm^{-1}): 2925, 1697, 1589, 1209, 839, 765. HRMS *calcd*. for ($C_{20}H_{27}NO_3$-H): 328.1918, *found*: 328.1915.



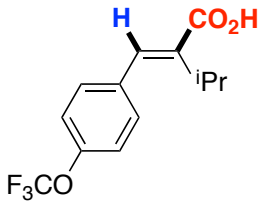
3r

(*E*)-2-cyclohexyl-3-(4-formylphenyl)acrylic acid (3r): Following the general procedure using 2-(4-(cyclohexylethynyl)phenyl)-1,3-dioxolane and *t*-BuOH (**2c**) to afford **3r** (107.2 mg, 85% yield over two steps; **3r:3r′**=15:1) as a white solid. Spectroscopic data for the major isomer (**3r**): M.P. = 177 – 178°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.04 (s, 1H), 7.92 (d, *J* = 8.2 Hz, 2H), 7.72 (s, 1H), 7.46 (d, *J* = 8.1 Hz, 2H), 2.84 – 2.57 (m, 1H), 2.16 – 1.90 (m, 2H), 1.82 – 1.69 (m, 2H), 1.69 – 1.39 (m, 3H), 1.37 – 0.90 (m, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.9, 173.4, 142.1, 140.0, 139.0, 135.9, 130.0, 129.6, 39.0, 30.8, 26.7, 25.9 ppm. IR (neat, cm^{-1}): 2930, 2848, 1698, 1667, 1598, 1199, 835, 666. HRMS *calcd*. for ($C_{16}H_{18}O_3$-H): 257.1183, *found*: 257.1181.



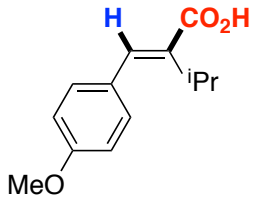
3s

(*E*)-3-(3-cyanophenyl)-2-cyclohexylacrylic acid (3s): Following the general procedure using **1s** to afford **3s** (93.2 mg, 73% yield) as a white solid. M.P. = 159 – 161°C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 – 7.61 (m, 2H), 7.56 (s, 1H), 7.54 – 7.49 (m, 2H), 2.62 (tt, *J* = 12.0, 3.3 Hz, 1H), 2.03 – 1.92 (m, 2H), 1.82 – 1.73 (m, 2H), 1.66 (dt, *J* = 10.3, 3.0 Hz, 1H), 1.64 – 1.54 (m, 2H), 1.35 – 1.07 (m, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.2, 140.1, 137.7, 137.2, 133.2, 132.4, 131.8, 129.5, 118.6, 113.0, 38.9, 30.8, 26.6, 25.8 ppm. IR (neat, cm^{-1}): 2926, 2856, 2233, 1677, 1265, 919, 797. HRMS *calcd*. for ($C_{16}H_{17}NO_2$-H): 254.1187, *found*: 254.1190.



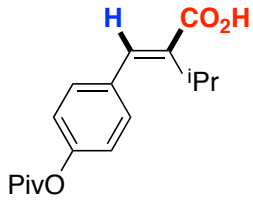
3t

(*E*)-3-methyl-2-(4-(trifluoromethoxy)benzylidene)butanoic acid (3t): Following the general procedure using **1t** and *t*-BuOH (**2c**) to afford **3t** (107 mg, 80% yield) as a white solid. M.P. = 82 – 84°C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73 (s, 1H), 7.38 (d, *J* = 8.3 Hz, 2H), 7.28 (d, *J* = 8.3 Hz, 2H), 3.17 (m, 1H), 1.33 (d, *J* = 7.0 Hz, 6H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.8, 149.1, 139.2, 139.0, 134.4, 130.6, 120.63 (q, *J* = 257.6 Hz). 121.0 27.7, 23.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ -57.90 ppm. IR (neat, cm^{-1}): 2963, 1676, 1247, 1203, 1159. HRMS *calcd*. for ($C_{13}H_{13}F_3O_3$-H): 273.0744, *found*: 273.0747.



3u

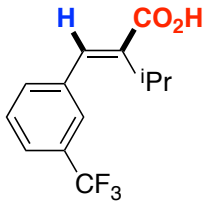
(*E*)-2-(4-methoxybenzylidene)-3-methylbutanoic acid (3u): Following the general procedure using **1u** and *t*-BuOH (**2c**) to afford **3u** (66.3 mg, 63% yield) as a white solid. M.P. = 125 – 127°C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 (s, 1H), 7.32 (d, *J* = 8.7 Hz, 2H), 6.94 (d, *J* = 8.7 Hz, 2H), 3.84 (s, 3H), 3.25 (m, 1H), 1.30 (d, *J* = 6.9 Hz, 6H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.9, 159.9, 140.2, 136.6, 131.0, 128.3, 114.1, 55.5, 27.5, 21.2 ppm. IR (neat, cm^{-1}): 2957, 1665, 1602, 1509, 1247, 1169, 829. HRMS *calcd*. for ($C_{13}H_{16}O_3$-H): 219.1027, *found*: 219.1023.



3v

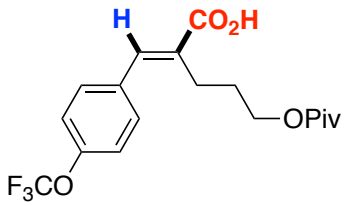
(*E*)-3-methyl-2-(4-(pivaloyloxy)benzylidene)butanoic acid (3v): Following the general procedure using **1v** and *t*-BuOH (**2c**) to afford **3v** (123.4 mg, 79% yield) as a white solid. M.P. = 165 – 167°C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 (s, 1H), 7.33 (d, *J* = 8.5 Hz, 2H), 7.10 (d, *J* = 8.5 Hz, 2H), 3.17 (m, 1H), 1.37 (s, 9H), 1.28 (d, *J* = 7.0

Hz, 6H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 177.2, 173.2, 151.1, 139.6, 138.5, 133.3, 130.3, 121.8, 39.3, 27.6, 27.3, 21.2 ppm. IR (neat, cm^{-1}): 2963, 1752, 1683, 1262, 1166, 1109. HRMS *calcd*. for ($C_{17}H_{22}O_4$-H): 289.1445, *found*: 289.1446.



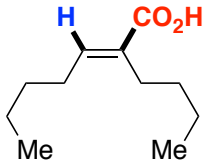
3w

(*E*)-3-methyl-2-(3-(trifluoromethyl)benzylidene)butanoic acid (3w): Following the general procedure using **1w** and *t*-BuOH (**2c**) to afford **3w** (96.8 mg, 75% yield) as a white solid. M.P. = 107-109°C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 (s, 1H), 7.61 (d, *J* = 7.6 Hz, 1H), 7.58 (s, 1H), 7.56-7.52 (m, 1H), 7.51 (d, *J* = 7.7 Hz, 1H), 3.10 (m, 1H), 1.31 (d, *J* = 7.0 Hz, 6H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.6, 140.1, 138.7, 136.7, 132.2, 131.2 (q, *J* = 32.4 Hz), 129.2, 131.2 (q, *J* = 272.3 Hz), 125.8 (q, *J* = 3.8 Hz), 125.1 (q, *J* = 3.8 Hz), 27.8 , 21.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.94 ppm. IR (neat, cm^{-1}): 2968, 1680, 1329, 1286, 1120, 805, 700. HRMS *calcd*. for ($C_{13}H_{13}F_3O_2$-H): 257.0795, *found*: 257.0801.



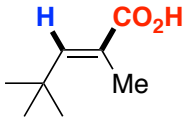
3x

(*E*)-5-(pivaloyloxy)-2-(4-(trifluoromethoxy)benzylidene)pentanoic acid (3x): Following the general procedure using **1x** and *t*-BuOH (**2c**) to afford **3x** (162.9 mg, 87% yield) as a white solid. M.P. = 78-79°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (s, 1H), 7.45 (d, *J* = 8.3 Hz, 2H), 7.27 (d, *J* = 8.3 Hz, 2H), 4.15 (t, *J* = 6.1 Hz, 2H), 2.73 – 2.53 (m, 2H), 2.03 – 1.87 (m, 2H), 1.20 (s, 9H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.8, 173.6, 149.5 (q, *J* = 1.8 Hz), 140.4, 134.0, 132.5, 131.0, 121.1, 120.6 (q, *J* = 257.8 Hz), 64.2, 38.9, 28.3, 27.3, 24.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ -57.91 ppm. IR (neat, cm^{-1}): 2974, 1726, 1686, 1246, 1150, 849. HRMS *calcd*. for ($C_{18}H_{21}F_3O_5$-H): 373.1268, *found*: 373.1265.



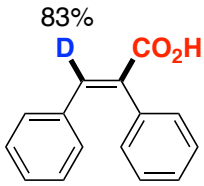
3y

(*E*)-2-butylhept-2-enoic acid (3y): Following the general procedure using **1y** and *t*-BuOH (**2c**) to afford **3y** (55.3 mg, 60% yield) as a white solid. The spectroscopic data correspond to those previously reported in the literature.[4] ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.90 (t, *J* = 7.5 Hz, 1H), 2.32 – 2.26 (m, 2H), 2.19 – 2.23 (m, 2H), 1.70 – 1.25 (m, 8H), 0.86 – 0.94 (m, 6H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.1, 145.7, 132.0, 31.7, 31.1, 28.6, 26.4, 22.9, 22.7, 14.1 (2C) ppm.



3z

(*E*)-2,4,4-trimethylpent-2-enoic acid (3z): Following the general procedure using **1z** and *t*-BuOH (**2c**) to afford **3z** (15.2 mg, 21% yield) as a yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.97 (m, 1H), 1.97 (d, *J* = 1.3 Hz, 3H), 1.20 (d, *J* = 0.7 Hz, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.9, 153.9, 125.8, 33.2, 29.9, 12.9. IR (neat, cm^{-1}): 2959, 1682, 1636, 1277, 1251. HRMS *calcd*. for ($C_8H_{14}O_2$): 142.0994, *found*: 142.0954



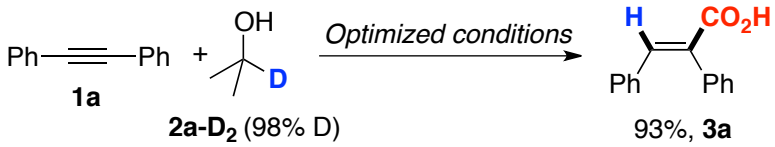
3a-D1

(*E*)-3-D-2,3-diphenylacrylic acid (3ab): Following the general procedure using **1a** to afford **3a-D1** (52.9 mg, 47% yield) as a white solid. M.P. = 166 – 168°C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (s, 0.17H), 7.46 – 7.34 (m, 3H), 7.26 (s, 3H), 7.17 (dd, *J* = 8.3, 1.4 Hz, 2H), 7.12 – 7.01 (m, 2H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.0, 142.6, 135.5, 134.4, 131.7, 131.0, 130.0, 129.7, 128.9, 128.5, 128.2 ppm. IR (neat, cm^{-1}): 1671, 1424, 1330, 1259, 695. HRMS *calcd*. for ($C_{15}H_{11}DO_2$-H): 224.0827, *found*: 224.0827.

Mechanistic experiments (Scheme 2)

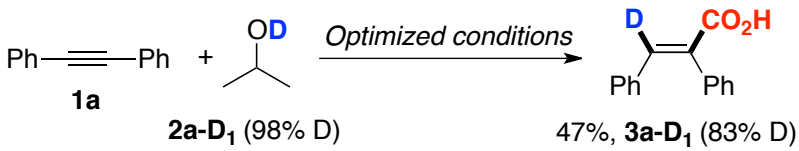
(1) Reaction of 1a with different secondary alcohols

→ **Reaction with 2a-D[2]**



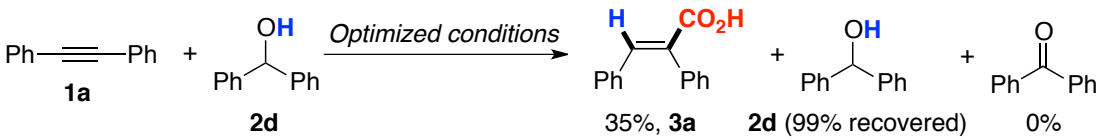
Following the general procedure using **1a** and **2a-D$_2$** to afford **3a** (104.3 mg, 93% yield) as a white solid.

→ **Reaction with 2a-D[1]**



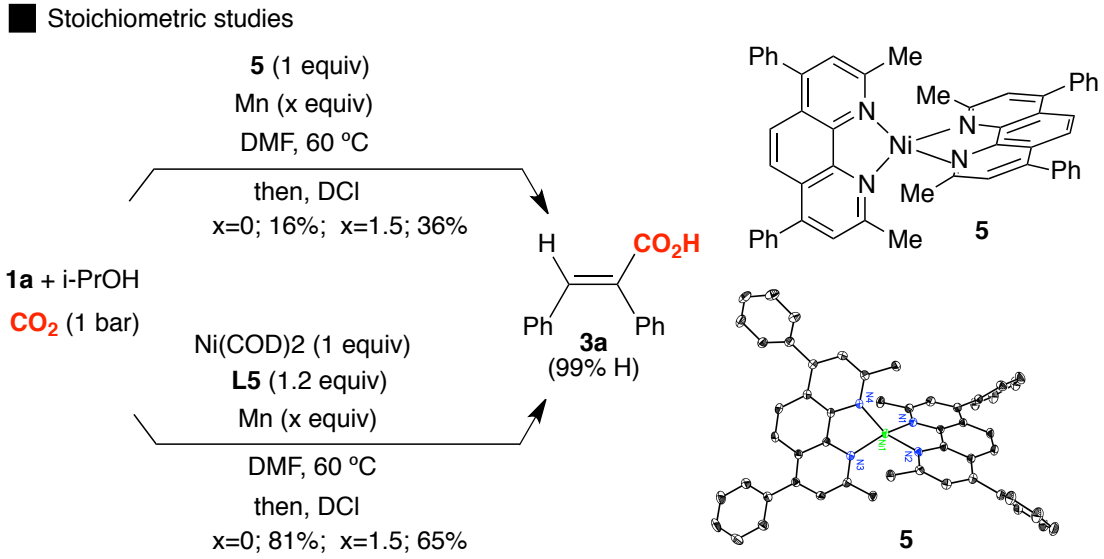
Following the general procedure using **1a** and **2a-D$_1$** to afford **3a-D$_1$** (52.7 mg, 47% yield) as a white solid.

→ **Reaction with 2d**



Following the general procedure using **1a** and **2d** to afford **3a** (39.3 mg, 35% yield) as a white solid.

(2) Stoichiometric experiments



→ Reaction with complex-5

A Schlenk tube containing a stirring bar was charged with diphenylacetylene (44.6 mg, 0.25 mmol), complex-**5** (194.9 mg, 0.25 mmol) inside of glovebox. The tube was then evacuated and back-filled with CO_2 three times. *i*-PrOH (28.7 μL, 0.375 mmol) and DMF (2 mL) were then added by syringe under a CO_2 flow. Once added, the Schlenk tube was closed at atmospheric pressure of CO_2 (1atm) and stirred for 36 h at 60°C. The mixture was quenched with DCl (2M) and extracted with DCM. The combined organic layers were washed with brine and dried over anhydrous $MgSO_4$ and evaporated. The residue was purified by flash chromatography (hexanes/ethyl acetate = 10/1 to 1/1).

a) Following the above procedure, Mn (20.6 mg, 0.375 mmol) was used, 3a was obtained in 36% isolated yield as a white solid.
b) Following the above procedure, no Mn (20.6 mg, 0.375 mmol) was used, 3a was obtained in 16% isolated yield as a white solid.

→ Reaction with $Ni(COD)_2$

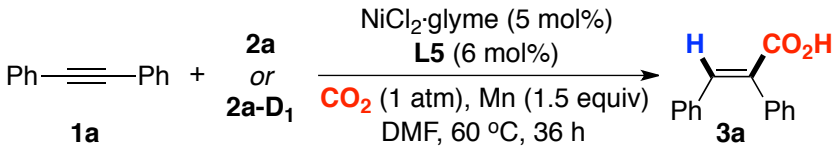
A Schlenk tube containing a stirring bar was charged with diphenylacetylene (44.6 mg, 0.25 mmol), Bathocuproine (108 mg, 0.30 mmol) and $Ni(COD)_2$ (69 mg, 0.25 mmol) inside of glovebox. The tube was then evacuated and back-filled with CO_2 three times. *i*-PrOH (28.7 μL, 0.375 mmol) and DMF (2 mL) were then added by syringe under a CO_2 flow. Once added, the Schlenk tube was closed at atmospheric

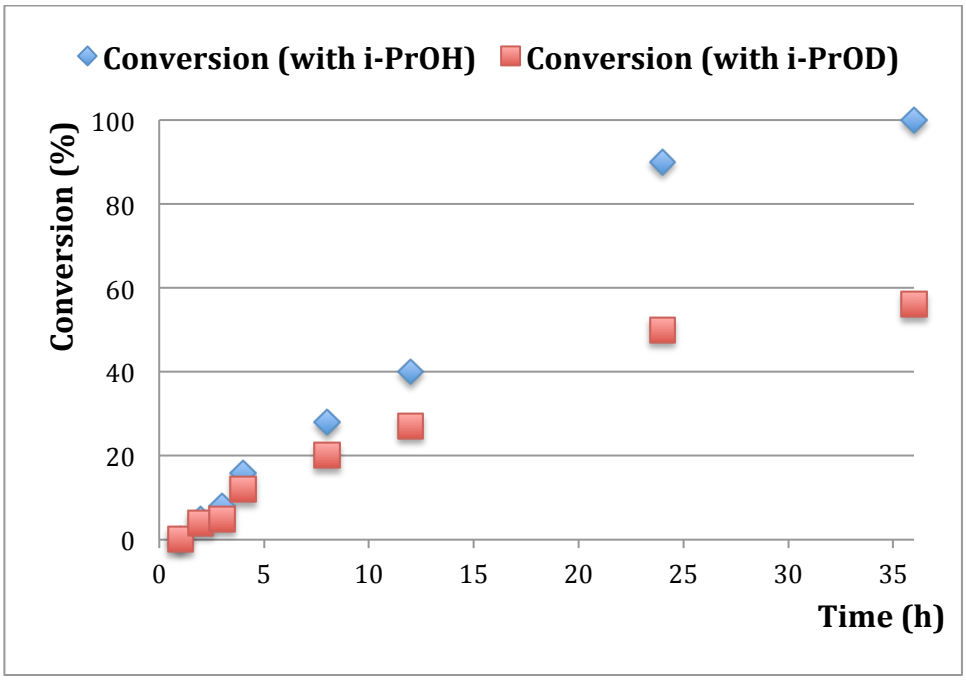
pressure of CO_2 (1atm) and stirred for 36 h at 60°C. The mixture was quenched with DCl (2M) and extracted with DCM. The combined organic layers were washed with brine and dried over anhydrous $MgSO_4$ and evaporated. The residue was purified by flash chromatography (hexanes/ethyl acetate = 10/1 to 1/1).

a) Following the above procedure, Mn (20.6 mg, 0.375 mmol) was used, 3a was obtained in 65% isolated yield as a white solid.

b) Following the above procedure, no Mn (20.6 mg, 0.375 mmol) was used, 3a was obtained in 81% isolated yield as a white solid.

3) Reaction rate of 2a *vs* 2a-D_1





Following the general procedure, the yields were measured by HPLC using naphthalene as internal standard. The results clearly indicate that **2a** reacts at a significant higher rate than **2a-D_1**. Taking into consideration initial rates (<30% conversion), the k_H/k_D was found to be 1.1.

References:

1) Fujihara, T.; Xu, T. H.; Semba, K.; Terao, J.; Tsuji, T. *Angew. Chem. Int. Ed.* **2011**, *50*, 523.
2) Zargarian, D.; Alper, H. *Organometallics* **1993**, *12*, 712.
3) Kowalski, C. J.; Sakdarat, S. *J. Org. Chem.* **1990**, *55*, 1977.
4) Back, T. G.; Minksztym, K. *Chem. Commun.* **1997**, 1759.

X-Ray crystallographic data

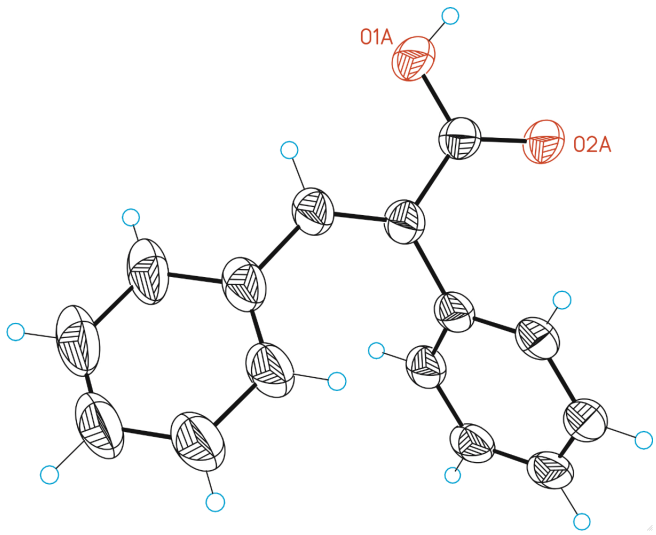


Table 1. Crystal data and structure refinement for **3a**.

Identification code	**3a**	
Empirical formula	C15.50 H13 O2.17	
Formula weight	233.92	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 5.8667(11)Å	á= 119.655(10)°.
	b = 38.923(6)Å	â = 92.878(9)°.
	c = 38.924(6)Å	ã = 92.933(9)°.
Volume	7685(2) $Å^3$	
Z	24	
Density (calculated)	1.213 Mg/m^3	
Absorption coefficient	0.080 mm^{-1}	
F(000)	2960	
Crystal size	0.20 x 0.20 x 0.20 mm^3	
Theta range for data collection	2.418 to 25.373°.	
Index ranges	-5<=h<=7,-46<=k<=33,-40<=l<=46	
Reflections collected	37942	
Independent reflections	24861[R(int) = 0.0455]	
Completeness to theta =25.373°	98.4%	
Absorption correction	Multi-scan	
Max. and min. transmission	0.998 and 0.768	

Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	24861/ 1889/ 2528
Goodness-of-fit on F^2	1.024
Final R indices [I>2sigma(I)]	R1 = 0.0797, wR2 = 0.1670
R indices (all data)	R1 = 0.1739, wR2 = 0.2075
Largest diff. peak and hole	0.383 and -0.396 e.Å^{-3}

Table 2. Bond lengths [Å] and angles [°] for **3a**.

Bond lengths----	
O1A-C1A	1.326(6)
O2A-C1A	1.228(6)
C1A-C2A	1.469(7)
C2A-C9A	1.339(6)
C2A-C3A	1.482(6)
C3A-C4A	1.390(6)
C3A-C8A	1.401(7)
C4A-C5A	1.380(6)
C5A-C6A	1.372(7)
C6A-C7A	1.375(6)
C7A-C8A	1.381(6)
C9A-C10A	1.455(8)
C10A-C15A	1.390(7)
C10A-C11A	1.400(9)
C11A-C12A	1.389(7)
C12A-C13A	1.396(9)
C13A-C14A	1.362(11)
C14A-C15A	1.384(9)
O1X-C1X	1.326(6)
O2X-C1X	1.231(7)
C1X-C2X	1.468(8)
C2X-C9X	1.339(7)
C2X-C3X	1.484(7)
C3X-C4X	1.390(7)
C3X-C8X	1.400(7)
C4X-C5X	1.380(7)
C5X-C6X	1.372(8)

C6X-C7X	1.375(7)
C7X-C8X	1.381(7)
C9X-C10X	1.457(8)
C10X-C15X	1.391(8)
C10X-C11X	1.401(9)
C11X-C12X	1.388(8)
C12X-C13X	1.396(10)
C13X-C14X	1.361(12)
C14X-C15X	1.384(10)
O1B-C1B	1.236(5)
O2B-C1B	1.315(4)
C1B-C2B	1.466(6)
C2B-C9B	1.337(6)
C2B-C3B	1.501(5)
C3B-C8B	1.372(6)
C3B-C4B	1.395(5)
C4B-C5B	1.381(6)
C5B-C6B	1.371(6)
C6B-C7B	1.382(6)
C7B-C8B	1.380(5)
C9B-C10B	1.446(6)
C10B-C15B	1.397(6)
C10B-C11B	1.406(6)
C11B-C12B	1.375(6)
C12B-C13B	1.402(6)
C13B-C14B	1.370(6)
C14B-C15B	1.366(7)
O1C-C1C	1.304(5)
O2C-C1C	1.224(5)
C1C-C2C	1.494(5)
C2C-C9C	1.332(5)
C2C-C3C	1.481(5)
C3C-C4C	1.378(5)
C3C-C8C	1.397(6)
C4C-C5C	1.380(6)
C5C-C6C	1.372(6)
C6C-C7C	1.382(6)
C7C-C8C	1.369(6)

C9C-C10C	1.481(5)
C10C-C11C	1.387(6)
C10C-C15C	1.398(6)
C11C-C12C	1.389(6)
C12C-C13C	1.377(7)
C13C-C14C	1.355(7)
C14C-C15C	1.410(6)
O1D-C1D	1.216(5)
O2D-C1D	1.320(4)
C1D-C2D	1.481(6)
C2D-C9D	1.335(5)
C2D-C3D	1.490(5)
C3D-C4D	1.384(5)
C3D-C8D	1.391(5)
C4D-C5D	1.381(5)
C5D-C6D	1.375(6)
C6D-C7D	1.379(6)
C7D-C8D	1.380(5)
C9D-C10D	1.466(6)
C10D-C11D	1.391(6)
C10D-C15D	1.398(6)
C11D-C12D	1.414(7)
C12D-C13D	1.371(7)
C13D-C14D	1.365(6)
C14D-C15D	1.387(6)
O1E-C1E	1.308(5)
O2E-C1E	1.236(5)
C1E-C2E	1.480(6)
C2E-C9E	1.338(6)
C2E-C3E	1.496(5)
C3E-C8E	1.385(5)
C3E-C4E	1.394(6)
C4E-C5E	1.375(6)
C5E-C6E	1.382(6)
C6E-C7E	1.385(6)
C7E-C8E	1.384(5)
C9E-C10E	1.462(6)
C10E-C11E	1.392(6)

C10E-C15E	1.393(6)
C11E-C12E	1.372(7)
C12E-C13E	1.374(7)
C13E-C14E	1.387(6)
C14E-C15E	1.383(6)
O1F-C1F	1.229(6)
O2F-C1F	1.329(5)
C1F-C2F	1.456(7)
C2F-C9F	1.330(7)
C2F-C3F	1.499(6)
C3F-C4F	1.385(6)
C3F-C8F	1.388(6)
C4F-C5F	1.388(6)
C5F-C6F	1.378(7)
C6F-C7F	1.367(7)
C7F-C8F	1.379(6)
C9F-C10F	1.451(8)
C10F-C11F	1.398(7)
C10F-C15F	1.402(8)
C11F-C12F	1.394(9)
C12F-C13F	1.392(10)
C13F-C14F	1.378(9)
C14F-C15F	1.391(8)
O1Y-C1Y	1.231(7)
O2Y-C1Y	1.327(6)
C1Y-C2Y	1.456(8)
C2Y-C9Y	1.328(8)
C2Y-C3Y	1.499(6)
C3Y-C4Y	1.385(7)
C3Y-C8Y	1.388(7)
C4Y-C5Y	1.386(7)
C5Y-C6Y	1.378(8)
C6Y-C7Y	1.368(7)
C7Y-C8Y	1.383(7)
C9Y-C10Y	1.453(9)
C10Y-C11Y	1.398(8)
C10Y-C15Y	1.404(9)
C11Y-C12Y	1.396(10)

C12Y-C13Y	1.394(11)
C13Y-C14Y	1.378(9)
C14Y-C15Y	1.392(9)
O1G-C1G	1.222(5)
O2G-C1G	1.320(5)
C1G-C2G	1.479(5)
C2G-C9G	1.339(5)
C2G-C3G	1.483(5)
C3G-C4G	1.383(6)
C3G-C8G	1.400(5)
C4G-C5G	1.378(6)
C5G-C6G	1.389(6)
C6G-C7G	1.364(6)
C7G-C8G	1.375(6)
C9G-C10G	1.468(6)
C10G-C11G	1.396(6)
C10G-C15G	1.407(6)
C11G-C12G	1.391(6)
C12G-C13G	1.368(7)
C13G-C14G	1.366(7)
C14G-C15G	1.400(6)
O1H-C1H	1.322(4)
C1H-O2H	1.233(4)
C1H-C2H	1.469(5)
C2H-C9H	1.346(5)
C2H-C3H	1.486(5)
C3H-C8H	1.386(5)
C3H-C4H	1.392(5)
C4H-C5H	1.393(6)
C5H-C6H	1.362(6)
C6H-C7H	1.376(6)
C7H-C8H	1.388(5)
C9H-C10H	1.465(5)
C10H-C11H	1.389(5)
C10H-C15H	1.404(5)
C11H-C12H	1.369(6)
C12H-C13H	1.383(6)
C13H-C14H	1.390(6)

C14H-C15H	1.372(6)
O1I-C1I	1.229(4)
O2I-C1I	1.323(4)
C1I-C2I	1.468(6)
C2I-C9I	1.339(5)
C2I-C3I	1.495(5)
C3I-C8I	1.385(5)
C3I-C4I	1.387(5)
C4I-C5I	1.378(5)
C5I-C6I	1.377(6)
C6I-C7I	1.379(6)
C7I-C8I	1.385(5)
C9I-C10I	1.466(6)
C10I-C11I	1.390(6)
C10I-C15I	1.395(5)
C11I-C12I	1.372(6)
C12I-C13I	1.380(6)
C13I-C14I	1.374(6)
C14I-C15I	1.389(6)
O1J-C1J	1.230(5)
O2J-C1J	1.313(4)
C1J-C2J	1.474(5)
C2J-C9J	1.352(5)
C2J-C3J	1.483(5)
C3J-C8J	1.391(6)
C3J-C4J	1.391(5)
C4J-C5J	1.394(5)
C5J-C6J	1.371(6)
C6J-C7J	1.371(6)
C7J-C8J	1.382(6)
C9J-C10J	1.465(5)
C10J-C11J	1.392(6)
C10J-C15J	1.392(5)
C11J-C12J	1.382(6)
C12J-C13J	1.377(6)
C13J-C14J	1.375(6)
C14J-C15J	1.385(6)
O1K-C1K	1.327(5)

O2K-C1K	1.228(6)
C1K-C2K	1.459(7)
C2K-C9K	1.348(7)
C2K-C3K	1.494(6)
C3K-C4K	1.381(6)
C3K-C8K	1.394(6)
C4K-C5K	1.377(6)
C5K-C6K	1.372(7)
C6K-C7K	1.366(7)
C7K-C8K	1.391(6)
C9K-C10K	1.444(8)
C10K-C15K	1.402(8)
C10K-C11K	1.410(7)
C11K-C12K	1.378(9)
C12K-C13K	1.380(10)
C13K-C14K	1.401(9)
C14K-C15K	1.378(8)
O1K'-C1K'	1.326(6)
O2K'-C1K'	1.231(7)
C1K'-C2K'	1.460(8)
C2K'-C9K'	1.346(7)
C2K'-C3K'	1.495(7)
C3K'-C4K'	1.380(7)
C3K'-C8K'	1.393(7)
C4K'-C5K'	1.380(7)
C5K'-C6K'	1.372(7)
C6K'-C7K'	1.365(8)
C7K'-C8K'	1.388(7)
C9K'-C10'	1.444(8)
C10'-C15'	1.402(9)
C10'-C11'	1.410(8)
C11'-C12'	1.379(10)
C12'-C13'	1.382(10)
C13'-C14'	1.399(9)
C14'-C15'	1.378(8)
O1L-C1L	1.233(5)
O2L-C1L	1.315(5)
C1L-C2L	1.479(6)

C2L-C9L	1.340(6)
C2L-C3L	1.499(5)
C3L-C8L	1.381(5)
C3L-C4L	1.392(5)
C4L-C5L	1.395(5)
C5L-C6L	1.375(6)
C6L-C7L	1.378(6)
C7L-C8L	1.379(5)
C9L-C10L	1.453(6)
C10L-C11L	1.393(6)
C10L-C15L	1.397(6)
C11L-C12L	1.385(6)
C12L-C13L	1.392(6)
C13L-C14L	1.370(7)
C14L-C15L	1.381(7)
O1S-C1S	1.226(6)
C1S-C3S	1.469(5)
C1S-C2S	1.502(5)
O1S'-C1S'	1.184(8)
C1S'-C2S'	1.513(5)
C1S'-C3S'	1.513(5)
O1T-C1T	1.239(7)
C1T-C3T	1.442(6)
C1T-C2T	1.498(7)
O1U-C1U	1.238(7)
C1U-C3U	1.444(6)
C1U-C2U	1.498(7)
O1V-C1V	1.234(8)
C1V-C3V	1.450(7)
C1V-C2V	1.498(7)
O1V'-C1V'	1.236(8)
C1V'-C3V'	1.452(7)
C1V'-C2V'	1.499(7)

Angles----------

O2A-C1A-O1A	121.1(6)
O2A-C1A-C2A	122.5(5)
O1A-C1A-C2A	116.3(5)

C9A-C2A-C1A	118.8(5)
C9A-C2A-C3A	126.2(5)
C1A-C2A-C3A	114.9(4)
C4A-C3A-C8A	118.5(5)
C4A-C3A-C2A	119.4(5)
C8A-C3A-C2A	122.0(5)
C5A-C4A-C3A	121.2(5)
C6A-C5A-C4A	119.4(5)
C5A-C6A-C7A	120.7(5)
C6A-C7A-C8A	120.4(5)
C7A-C8A-C3A	119.9(5)
C2A-C9A-C10A	128.6(5)
C15A-C10A-C11A	118.0(6)
C15A-C10A-C9A	119.9(7)
C11A-C10A-C9A	122.1(5)
C12A-C11A-C10A	121.0(6)
C11A-C12A-C13A	119.3(8)
C14A-C13A-C12A	120.1(7)
C13A-C14A-C15A	120.7(7)
C14A-C15A-C10A	120.9(8)
O2X-C1X-O1X	120.5(8)
O2X-C1X-C2X	122.4(7)
O1X-C1X-C2X	117.1(7)
C9X-C2X-C1X	119.6(6)
C9X-C2X-C3X	125.7(7)
C1X-C2X-C3X	114.6(7)
C4X-C3X-C8X	118.8(6)
C4X-C3X-C2X	119.4(7)
C8X-C3X-C2X	121.8(7)
C5X-C4X-C3X	121.3(7)
C6X-C5X-C4X	119.0(7)
C5X-C6X-C7X	121.0(7)
C6X-C7X-C8X	120.4(7)
C7X-C8X-C3X	119.5(7)
C2X-C9X-C10X	128.1(8)
C15X-C10X-C11X	117.9(7)
C15X-C10X-C9X	120.0(8)
C11X-C10X-C9X	122.1(7)

C12X-C11X-C10X	121.2(8)
C11X-C12X-C13X	119.2(9)
C14X-C13X-C12X	120.0(8)
C13X-C14X-C15X	120.8(8)
C14X-C15X-C10X	120.8(9)
O1B-C1B-O2B	121.5(4)
O1B-C1B-C2B	122.8(4)
O2B-C1B-C2B	115.7(4)
C9B-C2B-C1B	119.9(4)
C9B-C2B-C3B	125.1(4)
C1B-C2B-C3B	114.9(4)
C8B-C3B-C4B	119.0(4)
C8B-C3B-C2B	119.6(3)
C4B-C3B-C2B	121.2(4)
C5B-C4B-C3B	120.0(4)
C6B-C5B-C4B	120.6(4)
C5B-C6B-C7B	119.6(4)
C8B-C7B-C6B	120.0(4)
C3B-C8B-C7B	120.9(4)
C2B-C9B-C10B	129.7(4)
C15B-C10B-C11B	116.9(5)
C15B-C10B-C9B	120.1(4)
C11B-C10B-C9B	122.8(4)
C12B-C11B-C10B	121.4(4)
C11B-C12B-C13B	119.8(5)
C14B-C13B-C12B	119.2(5)
C15B-C14B-C13B	120.9(5)
C14B-C15B-C10B	121.7(5)
O2C-C1C-O1C	123.4(4)
O2C-C1C-C2C	120.5(4)
O1C-C1C-C2C	116.0(4)
C9C-C2C-C3C	126.0(4)
C9C-C2C-C1C	119.3(4)
C3C-C2C-C1C	114.7(3)
C4C-C3C-C8C	118.6(4)
C4C-C3C-C2C	119.0(4)
C8C-C3C-C2C	122.2(4)
C3C-C4C-C5C	120.7(4)

C6C-C5C-C4C	120.5(5)
C5C-C6C-C7C	119.2(5)
C8C-C7C-C6C	120.8(4)
C7C-C8C-C3C	120.3(4)
C2C-C9C-C10C	127.9(4)
C11C-C10C-C15C	119.0(4)
C11C-C10C-C9C	122.0(4)
C15C-C10C-C9C	118.8(4)
C10C-C11C-C12C	120.8(5)
C13C-C12C-C11C	119.9(5)
C14C-C13C-C12C	120.4(5)
C13C-C14C-C15C	120.9(5)
C10C-C15C-C14C	118.9(5)
O1D-C1D-O2D	122.7(4)
O1D-C1D-C2D	121.9(4)
O2D-C1D-C2D	115.3(4)
C9D-C2D-C1D	120.3(4)
C9D-C2D-C3D	125.7(4)
C1D-C2D-C3D	113.9(4)
C4D-C3D-C8D	118.6(4)
C4D-C3D-C2D	122.4(4)
C8D-C3D-C2D	118.9(4)
C5D-C4D-C3D	120.6(4)
C6D-C5D-C4D	120.5(4)
C5D-C6D-C7D	119.4(4)
C6D-C7D-C8D	120.4(4)
C7D-C8D-C3D	120.5(4)
C2D-C9D-C10D	128.4(4)
C11D-C10D-C15D	118.2(4)
C11D-C10D-C9D	119.7(4)
C15D-C10D-C9D	122.1(4)
C10D-C11D-C12D	119.5(5)
C13D-C12D-C11D	120.5(5)
C14D-C13D-C12D	120.5(5)
C13D-C14D-C15D	119.7(5)
C14D-C15D-C10D	121.6(5)
O2E-C1E-O1E	123.1(4)
O2E-C1E-C2E	121.4(4)

O1E-C1E-C2E	115.5(4)
C9E-C2E-C1E	118.9(4)
C9E-C2E-C3E	126.2(4)
C1E-C2E-C3E	114.9(4)
C8E-C3E-C4E	119.3(4)
C8E-C3E-C2E	118.9(4)
C4E-C3E-C2E	121.7(4)
C5E-C4E-C3E	120.0(4)
C4E-C5E-C6E	121.4(4)
C5E-C6E-C7E	118.3(4)
C8E-C7E-C6E	121.2(4)
C7E-C8E-C3E	119.8(4)
C2E-C9E-C10E	128.8(4)
C11E-C10E-C15E	118.9(4)
C11E-C10E-C9E	118.6(4)
C15E-C10E-C9E	122.4(4)
C12E-C11E-C10E	120.3(5)
C11E-C12E-C13E	121.1(5)
C12E-C13E-C14E	119.1(5)
C15E-C14E-C13E	120.4(5)
C14E-C15E-C10E	120.1(4)
O1F-C1F-O2F	120.7(6)
O1F-C1F-C2F	123.1(5)
O2F-C1F-C2F	116.3(5)
C9F-C2F-C1F	119.3(5)
C9F-C2F-C3F	125.7(5)
C1F-C2F-C3F	114.8(5)
C4F-C3F-C8F	119.1(4)
C4F-C3F-C2F	122.5(4)
C8F-C3F-C2F	118.4(4)
C3F-C4F-C5F	119.9(5)
C6F-C5F-C4F	120.4(5)
C7F-C6F-C5F	119.7(5)
C6F-C7F-C8F	120.7(5)
C7F-C8F-C3F	120.2(5)
C2F-C9F-C10F	129.0(5)
C11F-C10F-C15F	118.5(6)
C11F-C10F-C9F	119.2(6)

C15F-C10F-C9F	122.2(5)
C12F-C11F-C10F	119.4(7)
C13F-C12F-C11F	121.2(7)
C14F-C13F-C12F	119.9(7)
C13F-C14F-C15F	119.2(8)
C14F-C15F-C10F	121.7(6)
O1Y-C1Y-O2Y	120.6(8)
O1Y-C1Y-C2Y	122.9(7)
O2Y-C1Y-C2Y	116.4(7)
C9Y-C2Y-C1Y	120.2(6)
C9Y-C2Y-C3Y	125.9(7)
C1Y-C2Y-C3Y	113.8(6)
C4Y-C3Y-C8Y	120.0(6)
C4Y-C3Y-C2Y	121.1(6)
C8Y-C3Y-C2Y	118.8(6)
C3Y-C4Y-C5Y	119.7(7)
C6Y-C5Y-C4Y	119.7(7)
C7Y-C6Y-C5Y	120.1(7)
C6Y-C7Y-C8Y	120.6(7)
C7Y-C8Y-C3Y	119.1(7)
C2Y-C9Y-C10Y	128.5(7)
C11Y-C10Y-C15Y	118.7(8)
C11Y-C10Y-C9Y	119.6(8)
C15Y-C10Y-C9Y	121.5(7)
C12Y-C11Y-C10Y	119.0(8)
C13Y-C12Y-C11Y	120.8(8)
C14Y-C13Y-C12Y	120.4(9)
C13Y-C14Y-C15Y	118.6(9)
C14Y-C15Y-C10Y	121.9(7)
O1G-C1G-O2G	121.8(4)
O1G-C1G-C2G	122.3(4)
O2G-C1G-C2G	115.9(4)
C9G-C2G-C1G	120.4(4)
C9G-C2G-C3G	125.6(4)
C1G-C2G-C3G	114.1(3)
C4G-C3G-C8G	118.3(4)
C4G-C3G-C2G	119.2(4)
C8G-C3G-C2G	122.2(4)

C5G-C4G-C3G	121.4(4)
C4G-C5G-C6G	119.5(5)
C7G-C6G-C5G	119.5(4)
C6G-C7G-C8G	121.4(4)
C7G-C8G-C3G	119.9(4)
C2G-C9G-C10G	128.2(4)
C11G-C10G-C15G	118.2(4)
C11G-C10G-C9G	122.2(4)
C15G-C10G-C9G	119.5(4)
C12G-C11G-C10G	120.7(4)
C13G-C12G-C11G	120.5(5)
C14G-C13G-C12G	120.0(5)
C13G-C14G-C15G	121.1(5)
C14G-C15G-C10G	119.5(5)
O2H-C1H-O1H	121.8(4)
O2H-C1H-C2H	122.7(4)
O1H-C1H-C2H	115.5(3)
C9H-C2H-C1H	119.3(4)
C9H-C2H-C3H	124.8(4)
C1H-C2H-C3H	115.8(3)
C8H-C3H-C4H	119.3(4)
C8H-C3H-C2H	119.2(3)
C4H-C3H-C2H	121.5(4)
C3H-C4H-C5H	119.2(4)
C6H-C5H-C4H	121.0(4)
C5H-C6H-C7H	120.2(4)
C6H-C7H-C8H	119.8(4)
C3H-C8H-C7H	120.5(4)
C2H-C9H-C10H	128.4(4)
C11H-C10H-C15H	117.7(4)
C11H-C10H-C9H	118.6(4)
C15H-C10H-C9H	123.6(4)
C12H-C11H-C10H	121.6(4)
C11H-C12H-C13H	120.5(4)
C12H-C13H-C14H	118.7(4)
C15H-C14H-C13H	121.0(4)
C14H-C15H-C10H	120.4(4)
O1I-C1I-O2I	121.6(4)

O1I-C1I-C2I	122.9(4)
O2I-C1I-C2I	115.5(4)
C9I-C2I-C1I	119.2(4)
C9I-C2I-C3I	125.5(4)
C1I-C2I-C3I	115.3(3)
C8I-C3I-C4I	119.1(4)
C8I-C3I-C2I	122.1(4)
C4I-C3I-C2I	118.8(4)
C5I-C4I-C3I	119.8(4)
C6I-C5I-C4I	120.9(4)
C5I-C6I-C7I	119.8(4)
C6I-C7I-C8I	119.7(4)
C7I-C8I-C3I	120.7(4)
C2I-C9I-C10I	128.3(4)
C11I-C10I-C15I	118.5(4)
C11I-C10I-C9I	118.1(4)
C15I-C10I-C9I	123.3(4)
C12I-C11I-C10I	121.3(4)
C11I-C12I-C13I	120.0(5)
C14I-C13I-C12I	119.7(5)
C13I-C14I-C15I	120.8(5)
C14I-C15I-C10I	119.7(4)
O1J-C1J-O2J	122.4(4)
O1J-C1J-C2J	122.1(4)
O2J-C1J-C2J	115.5(4)
C9J-C2J-C1J	118.8(4)
C9J-C2J-C3J	125.2(4)
C1J-C2J-C3J	116.0(3)
C8J-C3J-C4J	119.2(4)
C8J-C3J-C2J	122.2(4)
C4J-C3J-C2J	118.6(4)
C3J-C4J-C5J	119.8(4)
C6J-C5J-C4J	120.2(4)
C5J-C6J-C7J	120.4(4)
C6J-C7J-C8J	120.3(4)
C7J-C8J-C3J	120.2(4)
C2J-C9J-C10J	128.1(4)
C11J-C10J-C15J	118.7(4)

C11J-C10J-C9J	117.9(4)
C15J-C10J-C9J	123.3(4)
C12J-C11J-C10J	121.1(4)
C13J-C12J-C11J	119.1(5)
C14J-C13J-C12J	120.7(4)
C13J-C14J-C15J	120.3(5)
C14J-C15J-C10J	119.9(4)
O2K-C1K-O1K	121.6(5)
O2K-C1K-C2K	122.4(5)
O1K-C1K-C2K	116.0(5)
C9K-C2K-C1K	119.3(5)
C9K-C2K-C3K	125.1(5)
C1K-C2K-C3K	115.4(4)
C4K-C3K-C8K	118.9(5)
C4K-C3K-C2K	119.0(4)
C8K-C3K-C2K	122.0(5)
C5K-C4K-C3K	121.6(5)
C6K-C5K-C4K	119.4(5)
C7K-C6K-C5K	119.9(5)
C6K-C7K-C8K	121.5(5)
C7K-C8K-C3K	118.7(5)
C2K-C9K-C10K	128.5(5)
C15K-C10K-C11K	117.8(6)
C15K-C10K-C9K	123.2(5)
C11K-C10K-C9K	118.8(6)
C12K-C11K-C10K	120.0(7)
C11K-C12K-C13K	121.8(6)
C12K-C13K-C14K	118.8(7)
C15K-C14K-C13K	120.0(7)
C14K-C15K-C10K	121.6(6)
O2K'-C1K'-O1K'	120.9(8)
O2K'-C1K'-C2K'	122.6(7)
O1K'-C1K'-C2K'	116.3(7)
C9K'-C2K'-C1K'	120.8(6)
C9K'-C2K'-C3K'	125.2(7)
C1K'-C2K'-C3K'	114.0(6)
C4K'-C3K'-C8K'	119.6(6)
C4K'-C3K'-C2K'	119.9(6)

C8K'-C3K'-C2K'	120.4(6)
C3K'-C4K'-C5K'	120.9(6)
C6K'-C5K'-C4K'	119.3(7)
C7K'-C6K'-C5K'	120.5(7)
C6K'-C7K'-C8K'	121.0(7)
C7K'-C8K'-C3K'	118.7(7)
C2K'-C9K'-C10'	127.9(7)
C15'-C10'-C11'	117.9(7)
C15'-C10'-C9K'	123.0(7)
C11'-C10'-C9K'	118.9(8)
C12'-C11'-C10'	119.9(8)
C11'-C12'-C13'	121.5(8)
C12'-C13'-C14'	119.1(8)
C15'-C14'-C13'	119.8(8)
C14'-C15'-C10'	121.6(7)
O1L-C1L-O2L	122.5(4)
O1L-C1L-C2L	122.1(4)
O2L-C1L-C2L	115.3(4)
C9L-C2L-C1L	119.3(4)
C9L-C2L-C3L	126.2(4)
C1L-C2L-C3L	114.5(4)
C8L-C3L-C4L	119.4(4)
C8L-C3L-C2L	122.4(4)
C4L-C3L-C2L	118.0(4)
C3L-C4L-C5L	119.5(4)
C6L-C5L-C4L	120.4(4)
C5L-C6L-C7L	120.0(4)
C6L-C7L-C8L	120.2(4)
C7L-C8L-C3L	120.6(4)
C2L-C9L-C10L	128.9(4)
C11L-C10L-C15L	118.1(5)
C11L-C10L-C9L	122.6(4)
C15L-C10L-C9L	119.1(4)
C12L-C11L-C10L	121.0(5)
C11L-C12L-C13L	119.9(5)
C14L-C13L-C12L	119.4(5)
C13L-C14L-C15L	121.0(5)
C14L-C15L-C10L	120.5(5)

O1S-C1S-C3S	121.4(6)
O1S-C1S-C2S	124.9(7)
C3S-C1S-C2S	113.6(6)
O1S'-C1S'-C2S'	123.2(8)
O1S'-C1S'-C3S'	122.6(8)
C2S'-C1S'-C3S'	114.2(7)
O1T-C1T-C3T	119.5(8)
O1T-C1T-C2T	128.5(9)
C3T-C1T-C2T	111.6(8)
O1U-C1U-C3U	119.8(8)
O1U-C1U-C2U	128.4(9)
C3U-C1U-C2U	111.6(8)
O1V-C1V-C3V	120.3(9)
O1V-C1V-C2V	127.9(10)
C3V-C1V-C2V	111.8(8)
O1V'-C1V'-C3V'	119.6(10)
O1V'-C1V'-C2V'	127.0(11)
C3V'-C1V'-C2V'	111.2(9)

Table 3. Torsion angles [°] for **3a**.

O2A_a-C1A_a-C2A_a-C9A_a	172.3(9)
O1A-C1A-C2A-C9A	-7.8(11)
O2A-C1A-C2A-C3A	-10.2(11)
O1A-C1A-C2A-C3A	169.6(7)
C9A-C2A-C3A-C4A	64.8(9)
C1A-C2A-C3A-C4A	-112.4(7)
C9A-C2A-C3A-C8A	-120.1(8)
C1A-C2A-C3A-C8A	62.7(8)
C8A-C3A-C4A-C5A	0.1(9)
C2A-C3A-C4A-C5A	175.4(6)
C3A-C4A-C5A-C6A	-0.5(9)
C4A-C5A-C6A-C7A	0.5(10)
C5A-C6A-C7A-C8A	-0.2(10)
C6A-C7A-C8A-C3A	-0.2(9)
C4A-C3A-C8A-C7A	0.2(9)
C2A-C3A-C8A-C7A	-174.9(6)

C1A-C2A-C9A-C10A	-174.1(7)
C3A-C2A-C9A-C10A	8.8(12)
C2A-C9A-C10A-C15A	-152.6(7)
C2A-C9A-C10A-C11A	31.1(11)
C15A-C10A-C11A-C12A	0.1(11)
C9A-C10A-C11A-C12A	176.5(7)
C10A-C11A-C12A-C13A	2.5(12)
C11A-C12A-C13A-C14A	-2.4(12)
C12A-C13A-C14A-C15A	-0.2(12)
C13A-C14A-C15A-C10A	2.9(11)
C11A-C10A-C15A-C14A	-2.8(10)
C9A-C10A-C15A-C14A	-179.3(6)
O2X-C1X-C2X-C9X	170(2)
O1X-C1X-C2X-C9X	-8(3)
O2X-C1X-C2X-C3X	-13(3)
O1X-C1X-C2X-C3X	168.8(17)
C9X-C2X-C3X-C4X	66(2)
C1X-C2X-C3X-C4X	-111.0(17)
C9X-C2X-C3X-C8X	-115.5(18)
C1X-C2X-C3X-C8X	68(2)
C8X-C3X-C4X-C5X	-2(2)
C2X-C3X-C4X-C5X	176.9(13)
C3X-C4X-C5X-C6X	1(2)
C4X-C5X-C6X-C7X	0(2)
C5X-C6X-C7X-C8X	1(2)
C6X-C7X-C8X-C3X	-2(2)
C4X-C3X-C8X-C7X	2(2)
C2X-C3X-C8X-C7X	-176.5(13)
C1X-C2X-C9X-C10X	-170.2(17)
C3X-C2X-C9X-C10X	13(3)
C2X-C9X-C10X-C15X	-149.7(17)
C2X-C9X-C10X-C11X	32(3)
C15X-C10X-C11X-C12X	-1(2)
C9X-C10X-C11X-C12X	178.1(14)
C10X-C11X-C12X-C13X	0(2)
C11X-C12X-C13X-C14X	2(2)
C12X-C13X-C14X-C15X	-4(3)
C13X-C14X-C15X-C10X	3(3)

C11X-C10X-C15X-C14X	-1(2)
C9X-C10X-C15X-C14X	180.0(15)
O1B-C1B-C2B-C9B	171.3(4)
O2B-C1B-C2B-C9B	-7.1(6)
O1B-C1B-C2B-C3B	-11.5(6)
O2B-C1B-C2B-C3B	170.0(4)
C9B-C2B-C3B-C8B	65.0(6)
C1B-C2B-C3B-C8B	-112.0(5)
C9B-C2B-C3B-C4B	-120.8(5)
C1B-C2B-C3B-C4B	62.2(5)
C8B-C3B-C4B-C5B	-0.3(6)
C2B-C3B-C4B-C5B	-174.5(4)
C3B-C4B-C5B-C6B	0.6(7)
C4B-C5B-C6B-C7B	-0.9(7)
C5B-C6B-C7B-C8B	0.9(7)
C4B-C3B-C8B-C7B	0.3(7)
C2B-C3B-C8B-C7B	174.6(4)
C6B-C7B-C8B-C3B	-0.6(7)
C1B-C2B-C9B-C10B	-172.9(4)
C3B-C2B-C9B-C10B	10.2(8)
C2B-C9B-C10B-C15B	-152.0(5)
C2B-C9B-C10B-C11B	32.0(7)
C15B-C10B-C11B-C12B	0.5(7)
C9B-C10B-C11B-C12B	176.6(4)
C10B-C11B-C12B-C13B	0.5(7)
C11B-C12B-C13B-C14B	0.1(7)
C12B-C13B-C14B-C15B	-1.6(8)
C13B-C14B-C15B-C10B	2.6(8)
C11B-C10B-C15B-C14B	-2.0(7)
C9B-C10B-C15B-C14B	-178.3(5)
O2C-C1C-C2C-C9C	-171.0(4)
O1C-C1C-C2C-C9C	8.3(6)
O2C-C1C-C2C-C3C	10.3(6)
O1C-C1C-C2C-C3C	-170.4(4)
C9C-C2C-C3C-C4C	-67.3(6)
C1C-C2C-C3C-C4C	111.3(4)
C9C-C2C-C3C-C8C	117.6(5)
C1C-C2C-C3C-C8C	-63.8(5)

C8C-C3C-C4C-C5C	0.8(6)
C2C-C3C-C4C-C5C	-174.5(3)
C3C-C4C-C5C-C6C	0.0(6)
C4C-C5C-C6C-C7C	-1.1(6)
C5C-C6C-C7C-C8C	1.4(6)
C6C-C7C-C8C-C3C	-0.6(6)
C4C-C3C-C8C-C7C	-0.5(5)
C2C-C3C-C8C-C7C	174.6(3)
C3C-C2C-C9C-C10C	-8.6(7)
C1C-C2C-C9C-C10C	172.8(4)
C2C-C9C-C10C-C11C	-34.2(7)
C2C-C9C-C10C-C15C	150.2(5)
C15C-C10C-C11C-C12C	-1.7(7)
C9C-C10C-C11C-C12C	-177.3(4)
C10C-C11C-C12C-C13C	-0.2(7)
C11C-C12C-C13C-C14C	0.6(8)
C12C-C13C-C14C-C15C	0.9(8)
C11C-C10C-C15C-C14C	3.2(7)
C9C-C10C-C15C-C14C	178.9(4)
C13C-C14C-C15C-C10C	-2.8(7)
O1D-C1D-C2D-C9D	171.4(4)
O2D-C1D-C2D-C9D	-8.3(6)
O1D-C1D-C2D-C3D	-10.2(6)
O2D-C1D-C2D-C3D	170.1(4)
C9D-C2D-C3D-C4D	-117.9(5)
C1D-C2D-C3D-C4D	63.8(5)
C9D-C2D-C3D-C8D	66.9(6)
C1D-C2D-C3D-C8D	-111.4(4)
C8D-C3D-C4D-C5D	1.0(6)
C2D-C3D-C4D-C5D	-174.2(4)
C3D-C4D-C5D-C6D	-0.4(7)
C4D-C5D-C6D-C7D	-0.4(7)
C5D-C6D-C7D-C8D	0.5(7)
C6D-C7D-C8D-C3D	0.2(7)
C4D-C3D-C8D-C7D	-0.9(6)
C2D-C3D-C8D-C7D	174.5(4)
C1D-C2D-C9D-C10D	-173.0(4)
C3D-C2D-C9D-C10D	8.9(8)

C2D-C9D-C10D-C11D	-150.4(5)
C2D-C9D-C10D-C15D	33.4(7)
C15D-C10D-C11D-C12D	-2.5(7)
C9D-C10D-C11D-C12D	-178.9(4)
C10D-C11D-C12D-C13D	2.7(7)
C11D-C12D-C13D-C14D	-1.2(8)
C12D-C13D-C14D-C15D	-0.4(8)
C13D-C14D-C15D-C10D	0.5(7)
C11D-C10D-C15D-C14D	1.0(7)
C9D-C10D-C15D-C14D	177.3(4)
O2E-C1E-C2E-C9E	-171.6(4)
O1E-C1E-C2E-C9E	8.7(6)
O2E-C1E-C2E-C3E	10.2(6)
O1E-C1E-C2E-C3E	-169.6(4)
C9E-C2E-C3E-C8E	-65.3(6)
C1E-C2E-C3E-C8E	112.8(4)
C9E-C2E-C3E-C4E	119.8(5)
C1E-C2E-C3E-C4E	-62.1(5)
C8E-C3E-C4E-C5E	0.0(6)
C2E-C3E-C4E-C5E	174.8(4)
C3E-C4E-C5E-C6E	-0.8(6)
C4E-C5E-C6E-C7E	1.3(6)
C5E-C6E-C7E-C8E	-1.1(6)
C6E-C7E-C8E-C3E	0.3(6)
C4E-C3E-C8E-C7E	0.3(6)
C2E-C3E-C8E-C7E	-174.7(4)
C1E-C2E-C9E-C10E	172.9(4)
C3E-C2E-C9E-C10E	-9.1(8)
C2E-C9E-C10E-C11E	151.4(5)
C2E-C9E-C10E-C15E	-32.7(7)
C15E-C10E-C11E-C12E	2.1(7)
C9E-C10E-C11E-C12E	178.1(4)
C10E-C11E-C12E-C13E	-3.0(7)
C11E-C12E-C13E-C14E	1.7(8)
C12E-C13E-C14E-C15E	0.3(7)
C13E-C14E-C15E-C10E	-1.1(7)
C11E-C10E-C15E-C14E	-0.1(6)
C9E-C10E-C15E-C14E	-175.9(4)

O1F-C1F-C2F-C9F	-172.8(8)
O2F-C1F-C2F-C9F	6.0(10)
O1F-C1F-C2F-C3F	12.3(11)
O2F-C1F-C2F-C3F	-169.0(6)
C9F-C2F-C3F-C4F	120.7(8)
C1F-C2F-C3F-C4F	-64.7(8)
C9F-C2F-C3F-C8F	-62.4(9)
C1F-C2F-C3F-C8F	112.2(7)
C8F-C3F-C4F-C5F	0.3(10)
C2F-C3F-C4F-C5F	177.2(7)
C3F-C4F-C5F-C6F	-1.7(12)
C4F-C5F-C6F-C7F	2.4(13)
C5F-C6F-C7F-C8F	-1.8(12)
C6F-C7F-C8F-C3F	0.5(11)
C4F-C3F-C8F-C7F	0.3(10)
C2F-C3F-C8F-C7F	-176.8(6)
C1F-C2F-C9F-C10F	174.5(7)
C3F-C2F-C9F-C10F	-11.2(11)
C2F-C9F-C10F-C11F	153.3(7)
C2F-C9F-C10F-C15F	-29.8(11)
C15F-C10F-C11F-C12F	1.3(10)
C9F-C10F-C11F-C12F	178.3(6)
C10F-C11F-C12F-C13F	-0.7(11)
C11F-C12F-C13F-C14F	-1.8(12)
C12F-C13F-C14F-C15F	3.8(13)
C13F-C14F-C15F-C10F	-3.2(12)
C11F-C10F-C15F-C14F	0.7(11)
C9F-C10F-C15F-C14F	-176.2(7)
O1Y-C1Y-C2Y-C9Y	-168.2(19)
O2Y-C1Y-C2Y-C9Y	10(2)
O1Y-C1Y-C2Y-C3Y	9(2)
O2Y-C1Y-C2Y-C3Y	-172.1(15)
C9Y-C2Y-C3Y-C4Y	113.0(17)
C1Y-C2Y-C3Y-C4Y	-64.5(18)
C9Y-C2Y-C3Y-C8Y	-69(2)
C1Y-C2Y-C3Y-C8Y	113.4(16)
C8Y-C3Y-C4Y-C5Y	-6(2)
C2Y-C3Y-C4Y-C5Y	171.7(15)

C3Y-C4Y-C5Y-C6Y	8(3)
C4Y-C5Y-C6Y-C7Y	-9(3)
C5Y-C6Y-C7Y-C8Y	8(3)
C6Y-C7Y-C8Y-C3Y	-6(3)
C4Y-C3Y-C8Y-C7Y	5(2)
C2Y-C3Y-C8Y-C7Y	-172.4(14)
C1Y-C2Y-C9Y-C10Y	172.3(14)
C3Y-C2Y-C9Y-C10Y	-5(2)
C2Y-C9Y-C10Y-C11Y	146.5(16)
C2Y-C9Y-C10Y-C15Y	-38(2)
C15Y-C10Y-C11Y-C12Y	5(2)
C9Y-C10Y-C11Y-C12Y	-178.9(14)
C10Y-C11Y-C12Y-C13Y	-9(2)
C11Y-C12Y-C13Y-C14Y	9(2)
C12Y-C13Y-C14Y-C15Y	-4(2)
C13Y-C14Y-C15Y-C10Y	0(2)
C11Y-C10Y-C15Y-C14Y	-1(2)
C9Y-C10Y-C15Y-C14Y	-176.4(13)
O1G-C1G-C2G-C9G	-171.3(4)
O2G-C1G-C2G-C9G	7.8(6)
O1G-C1G-C2G-C3G	10.5(6)
O2G-C1G-C2G-C3G	-170.5(4)
C9G-C2G-C3G-C4G	-67.2(6)
C1G-C2G-C3G-C4G	110.9(4)
C9G-C2G-C3G-C8G	118.4(5)
C1G-C2G-C3G-C8G	-63.5(5)
C8G-C3G-C4G-C5G	0.7(6)
C2G-C3G-C4G-C5G	-173.9(4)
C3G-C4G-C5G-C6G	-0.9(6)
C4G-C5G-C6G-C7G	-0.2(7)
C5G-C6G-C7G-C8G	1.4(7)
C6G-C7G-C8G-C3G	-1.6(6)
C4G-C3G-C8G-C7G	0.5(6)
C2G-C3G-C8G-C7G	175.0(4)
C1G-C2G-C9G-C10G	172.8(4)
C3G-C2G-C9G-C10G	-9.2(8)
C2G-C9G-C10G-C11G	-33.4(7)
C2G-C9G-C10G-C15G	150.6(5)

C15G-C10G-C11G-C12G	-1.2(7)
C9G-C10G-C11G-C12G	-177.2(4)
C10G-C11G-C12G-C13G	-0.6(8)
C11G-C12G-C13G-C14G	0.5(9)
C12G-C13G-C14G-C15G	1.4(9)
C13G-C14G-C15G-C10G	-3.2(8)
C11G-C10G-C15G-C14G	3.0(7)
C9G-C10G-C15G-C14G	179.2(4)
O2H-C1H-C2H-C9H	170.8(4)
O1H-C1H-C2H-C9H	-8.2(6)
O2H-C1H-C2H-C3H	-10.8(6)
O1H-C1H-C2H-C3H	170.2(3)
C9H-C2H-C3H-C8H	65.0(6)
C1H-C2H-C3H-C8H	-113.3(4)
C9H-C2H-C3H-C4H	-117.4(5)
C1H-C2H-C3H-C4H	64.3(5)
C8H-C3H-C4H-C5H	-1.5(6)
C2H-C3H-C4H-C5H	-179.0(4)
C3H-C4H-C5H-C6H	1.4(6)
C4H-C5H-C6H-C7H	-0.4(7)
C5H-C6H-C7H-C8H	-0.5(7)
C4H-C3H-C8H-C7H	0.7(6)
C2H-C3H-C8H-C7H	178.2(4)
C6H-C7H-C8H-C3H	0.3(6)
C1H-C2H-C9H-C10H	-174.9(4)
C3H-C2H-C9H-C10H	6.9(7)
C2H-C9H-C10H-C11H	-154.5(4)
C2H-C9H-C10H-C15H	29.3(7)
C15H-C10H-C11H-C12H	-2.6(6)
C9H-C10H-C11H-C12H	-179.0(4)
C10H-C11H-C12H-C13H	1.8(7)
C11H-C12H-C13H-C14H	0.3(8)
C12H-C13H-C14H-C15H	-1.5(8)
C13H-C14H-C15H-C10H	0.7(7)
C11H-C10H-C15H-C14H	1.3(6)
C9H-C10H-C15H-C14H	177.6(4)
O1I-C1I-C2I-C9I	170.8(4)
O2I-C1I-C2I-C9I	-8.5(6)

O1I-C1I-C2I-C3I	-10.8(6)
O2I-C1I-C2I-C3I	169.9(3)
C9I-C2I-C3I-C8I	-116.8(5)
C1I-C2I-C3I-C8I	64.9(5)
C9I-C2I-C3I-C4I	64.0(5)
C1I-C2I-C3I-C4I	-114.3(4)
C8I-C3I-C4I-C5I	-0.9(6)
C2I-C3I-C4I-C5I	178.3(4)
C3I-C4I-C5I-C6I	1.5(6)
C4I-C5I-C6I-C7I	-0.7(7)
C5I-C6I-C7I-C8I	-0.5(7)
C6I-C7I-C8I-C3I	1.0(7)
C4I-C3I-C8I-C7I	-0.3(6)
C2I-C3I-C8I-C7I	-179.5(4)
C1I-C2I-C9I-C10I	-174.4(4)
C3I-C2I-C9I-C10I	7.4(7)
C2I-C9I-C10I-C11I	-154.9(4)
C2I-C9I-C10I-C15I	28.5(7)
C15I-C10I-C11I-C12I	-2.8(6)
C9I-C10I-C11I-C12I	-179.6(4)
C10I-C11I-C12I-C13I	2.4(7)
C11I-C12I-C13I-C14I	-0.2(7)
C12I-C13I-C14I-C15I	-1.4(7)
C13I-C14I-C15I-C10I	0.8(7)
C11I-C10I-C15I-C14I	1.2(6)
C9I-C10I-C15I-C14I	177.8(4)
O1J-C1J-C2J-C9J	170.7(4)
O2J-C1J-C2J-C9J	-8.2(6)
O1J-C1J-C2J-C3J	-10.6(6)
O2J-C1J-C2J-C3J	170.4(3)
C9J-C2J-C3J-C8J	-117.0(5)
C1J-C2J-C3J-C8J	64.4(5)
C9J-C2J-C3J-C4J	64.9(5)
C1J-C2J-C3J-C4J	-113.7(4)
C8J-C3J-C4J-C5J	-0.1(5)
C2J-C3J-C4J-C5J	178.1(3)
C3J-C4J-C5J-C6J	0.7(6)
C4J-C5J-C6J-C7J	-0.5(6)

C5J-C6J-C7J-C8J	-0.4(6)
C6J-C7J-C8J-C3J	1.1(6)
C4J-C3J-C8J-C7J	-0.8(5)
C2J-C3J-C8J-C7J	-178.9(4)
C1J-C2J-C9J-C10J	-174.7(4)
C3J-C2J-C9J-C10J	6.8(7)
C2J-C9J-C10J-C11J	-154.6(4)
C2J-C9J-C10J-C15J	29.3(6)
C15J-C10J-C11J-C12J	-3.3(6)
C9J-C10J-C11J-C12J	-179.6(4)
C10J-C11J-C12J-C13J	2.9(7)
C11J-C12J-C13J-C14J	-1.3(7)
C12J-C13J-C14J-C15J	0.0(7)
C13J-C14J-C15J-C10J	-0.4(7)
C11J-C10J-C15J-C14J	2.0(6)
C9J-C10J-C15J-C14J	178.1(4)
O2K-C1K-C2K-C9K	-172.7(7)
O1K-C1K-C2K-C9K	6.8(9)
O2K-C1K-C2K-C3K	11.8(10)
O1K-C1K-C2K-C3K	-168.7(6)
C9K-C2K-C3K-C4K	-63.6(9)
C1K-C2K-C3K-C4K	111.6(7)
C9K-C2K-C3K-C8K	120.6(7)
C1K-C2K-C3K-C8K	-64.1(8)
C8K-C3K-C4K-C5K	0.0(9)
C2K-C3K-C4K-C5K	-175.9(6)
C3K-C4K-C5K-C6K	1.0(10)
C4K-C5K-C6K-C7K	-2.1(10)
C5K-C6K-C7K-C8K	2.3(11)
C6K-C7K-C8K-C3K	-1.3(10)
C4K-C3K-C8K-C7K	0.1(9)
C2K-C3K-C8K-C7K	175.9(6)
C1K-C2K-C9K-C10K	174.0(6)
C3K-C2K-C9K-C10K	-10.9(11)
C2K-C9K-C10K-C15K	-30.7(11)
C2K-C9K-C10K-C11K	153.2(7)
C15K-C10K-C11K-C12K	2.7(10)
C9K-C10K-C11K-C12K	179.0(7)

C10K-C11K-C12K-C13K	-1.9(12)
C11K-C12K-C13K-C14K	-0.7(13)
C12K-C13K-C14K-C15K	2.6(12)
C13K-C14K-C15K-C10K	-1.8(12)
C11K-C10K-C15K-C14K	-0.9(11)
C9K-C10K-C15K-C14K	-177.0(7)
O2K'-C1K'-C2K'-C9K'	-166.7(17)
O1K'-C1K'-C2K'-C9K'	8(2)
O2K'-C1K'-C2K'-C3K'	11(2)
O1K'-C1K'-C2K'-C3K'	-174.2(13)
C9K'-C2K'-C3K'-C4K'	-70.3(19)
C1K'-C2K'-C3K'-C4K'	111.9(15)
C9K'-C2K'-C3K'-C8K'	113.3(16)
C1K'-C2K'-C3K'-C8K'	-64.6(17)
C8K'-C3K'-C4K'-C5K'	2(2)
C2K'-C3K'-C4K'-C5K'	-174.0(12)
C3K'-C4K'-C5K'-C6K'	-3(2)
C4K'-C5K'-C6K'-C7K'	3(2)
C5K'-C6K'-C7K'-C8K'	-2(3)
C6K'-C7K'-C8K'-C3K'	2(2)
C4K'-C3K'-C8K'-C7K'	-2(2)
C2K'-C3K'-C8K'-C7K'	174.5(12)
C1K'-C2K'-C9K'-C10'	172.3(14)
C3K'-C2K'-C9K'-C10'	-5(2)
C2K'-C9K'-C10'-C15'	-38(2)
C2K'-C9K'-C10'-C11'	147.1(15)
C15'-C10'-C11'-C12'	4(2)
C9K'-C10'-C11'-C12'	178.9(14)
C10'-C11'-C12'-C13'	-6(2)
C11'-C12'-C13'-C14'	4(2)
C12'-C13'-C14'-C15'	0(2)
C13'-C14'-C15'-C10'	-2(2)
C11'-C10'-C15'-C14'	0(2)
C9K'-C10'-C15'-C14'	-175.1(14)
O1L-C1L-C2L-C9L	-172.0(4)
O2L-C1L-C2L-C9L	7.2(6)
O1L-C1L-C2L-C3L	10.4(6)
O2L-C1L-C2L-C3L	-170.3(4)

C9L-C2L-C3L-C8L	120.3(5)
C1L-C2L-C3L-C8L	-62.3(6)
C9L-C2L-C3L-C4L	-64.6(6)
C1L-C2L-C3L-C4L	112.8(5)
C8L-C3L-C4L-C5L	0.7(7)
C2L-C3L-C4L-C5L	-174.6(4)
C3L-C4L-C5L-C6L	-0.2(7)
C4L-C5L-C6L-C7L	-1.1(7)
C5L-C6L-C7L-C8L	1.8(7)
C6L-C7L-C8L-C3L	-1.2(7)
C4L-C3L-C8L-C7L	0.0(7)
C2L-C3L-C8L-C7L	175.0(4)
C1L-C2L-C9L-C10L	173.1(4)
C3L-C2L-C9L-C10L	-9.6(8)
C2L-C9L-C10L-C11L	-31.9(7)
C2L-C9L-C10L-C15L	152.3(5)
C15L-C10L-C11L-C12L	0.2(6)
C9L-C10L-C11L-C12L	-175.7(4)
C10L-C11L-C12L-C13L	-1.7(6)
C11L-C12L-C13L-C14L	1.1(7)
C12L-C13L-C14L-C15L	1.1(7)
C13L-C14L-C15L-C10L	-2.7(7)
C11L-C10L-C15L-C14L	2.0(6)
C9L-C10L-C15L-C14L	178.0(4)

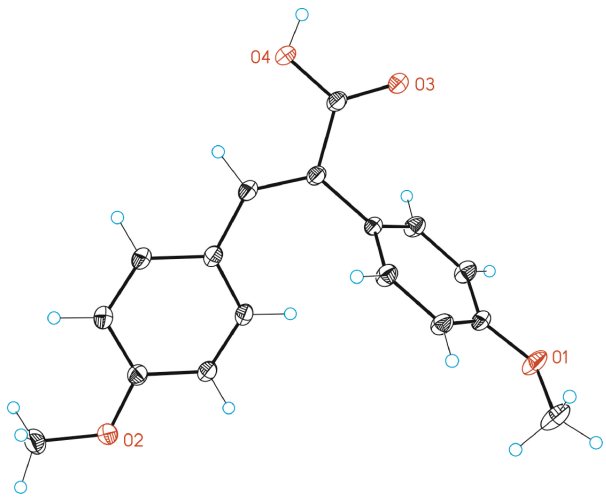


Table 1. Crystal data and structure refinement for **3c**.

Identification code	**3c**	
Empirical formula	C17 H16 O4	
Formula weight	284.30	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 5.8239(4)Å	a=
84.6047(18)°.		
	b = 9.0597(6)Å	b =
84.7115(18)°.		
	c = 13.9214(8)Å	g =
79.8913(19)°.		
Volume	717.78(8) $Å^3$	
Z	2	
Density (calculated)	1.315 Mg/m^3	
Absorption coefficient	0.093 mm^{-1}	
F(000)	300	
Crystal size	0.40 x 0.005 x 0.005 mm^3	
Theta range for data collection	2.291 to 32.609°.	
Index ranges	-7<=h<=8,-12<=k<=13,-14<=l<=21	
Reflections collected	11300	
Independent reflections	4668[R(int) = 0.0210]	
Completeness to theta =32.609°	89.1%	
Absorption correction	Empirical	
Max. and min. transmission	1.000 and 0.921	

Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4668/ 0/ 192
Goodness-of-fit on F^2	1.036
Final R indices [I>2sigma(I)]	R1 = 0.0449, wR2 = 0.1207
R indices (all data)	R1 = 0.0550, wR2 = 0.1285
Largest diff. peak and hole	0.587 and -0.235 e.Å^{-3}

Table 2. Bond lengths [Å] and angles [°] for **3c**.

Bond lengths----	
O1-C4	1.3673(12)
O1-C15	1.4253(15)
O2-C12	1.3574(13)
O2-C17	1.4337(14)
O3-C16	1.2308(13)
O4-C16	1.3225(12)
C1-C2	1.3904(14)
C1-C6	1.3985(14)
C1-C7	1.4890(13)
C2-C3	1.3943(14)
C3-C4	1.3923(15)
C4-C5	1.3954(15)
C5-C6	1.3864(14)
C7-C8	1.3570(14)
C7-C16	1.4812(14)
C8-C9	1.4608(15)
C9-C14	1.4005(14)
C9-C10	1.4090(14)
C10-C11	1.3808(15)
C11-C12	1.4041(15)
C12-C13	1.3943(15)
C13-C14	1.3912(15)
Angles----------	
C4-O1-C15	117.05(9)
C12-O2-C17	117.51(9)
C2-C1-C6	118.13(9)
C2-C1-C7	120.17(9)

C6-C1-C7	121.70(9)
C1-C2-C3	121.67(9)
C4-C3-C2	119.40(9)
O1-C4-C3	124.49(9)
O1-C4-C5	115.86(9)
C3-C4-C5	119.64(9)
C6-C5-C4	120.23(9)
C5-C6-C1	120.93(9)
C8-C7-C16	117.85(9)
C8-C7-C1	126.23(9)
C16-C7-C1	115.88(9)
C7-C8-C9	130.56(9)
C14-C9-C10	117.32(10)
C14-C9-C8	117.61(9)
C10-C9-C8	124.96(9)
C11-C10-C9	120.71(10)
C10-C11-C12	120.99(10)
O2-C12-C13	125.17(10)
O2-C12-C11	115.62(9)
C13-C12-C11	119.21(10)
C14-C13-C12	119.16(10)
C13-C14-C9	122.51(10)
O3-C16-O4	122.19(9)
O3-C16-C7	121.77(9)
O4-C16-C7	116.04(9)

Table 3. Torsion angles [°] for **3c**.

C6-C1-C2-C3	-0.34(16)
C7-C1-C2-C3	-179.28(10)
C1-C2-C3-C4	0.02(17)
C15-O1-C4-C3	0.11(17)
C15-O1-C4-C5	178.94(11)
C2-C3-C4-O1	178.58(10)
C2-C3-C4-C5	-0.22(17)
O1-C4-C5-C6	-178.15(10)
C3-C4-C5-C6	0.74(17)

C4-C5-C6-C1	-1.08(17)
C2-C1-C6-C5	0.86(16)
C7-C1-C6-C5	179.79(10)
C2-C1-C7-C8	-64.04(15)
C6-C1-C7-C8	117.05(12)
C2-C1-C7-C16	113.71(11)
C6-C1-C7-C16	-65.20(13)
C16-C7-C8-C9	176.34(10)
C1-C7-C8-C9	-5.95(18)
C7-C8-C9-C14	169.24(11)
C7-C8-C9-C10	-14.61(18)
C14-C9-C10-C11	-2.32(16)
C8-C9-C10-C11	-178.48(10)
C9-C10-C11-C12	-0.23(17)
C17-O2-C12-C13	-2.55(16)
C17-O2-C12-C11	177.86(10)
C10-C11-C12-O2	-177.68(10)
C10-C11-C12-C13	2.70(16)
O2-C12-C13-C14	177.90(10)
C11-C12-C13-C14	-2.52(16)
C12-C13-C14-C9	-0.09(17)
C10-C9-C14-C13	2.50(16)
C8-C9-C14-C13	178.95(10)
C8-C7-C16-O3	177.50(10)
C1-C7-C16-O3	-0.44(15)
C8-C7-C16-O4	-2.29(14)
C1-C7-C16-O4	179.76(9)

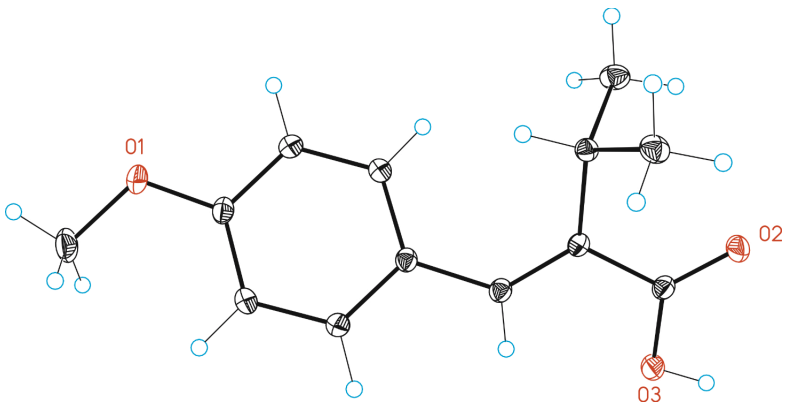


Table 1. Crystal data and structure refinement for **3u**.

Identification code	**3u**	
Empirical formula	C13 H16 O3	
Formula weight	220.26	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 5.2457(13)Å	a= 90°.
	b = 20.488(5)Å	b = 93.965(5)°.
	c = 10.644(3)Å	g = 90°.
Volume	1141.3(5) $Å^3$	
Z	4	
Density (calculated)	1.282 Mg/m^3	
Absorption coefficient	0.090 mm^{-1}	
F(000)	472	
Crystal size	0.40 x 0.30 x 0.30 mm^3	
Theta range for data collection	2.763 to 29.662°.	
Index ranges	-7<=h<=7,-28<=k<=28,-14<=l<=11	
Reflections collected	11376	
Independent reflections	3193[R(int) = 0.0279]	
Completeness to theta =29.662°	98.799995%	
Absorption correction	Empirical	
Max. and min. transmission	0.973 and 0.748	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3193/ 0/ 209	
Goodness-of-fit on F^2	1.058	
Final R indices [I>2sigma(I)]	R1 = 0.0363, wR2 = 0.0983	

R indices (all data)	R1 = 0.0412, wR2 = 0.1000
Largest diff. peak and hole	0.381 and -0.247 e.Å^{-3}

Table 2. Bond lengths [Å] and angles [°] for **3u**.

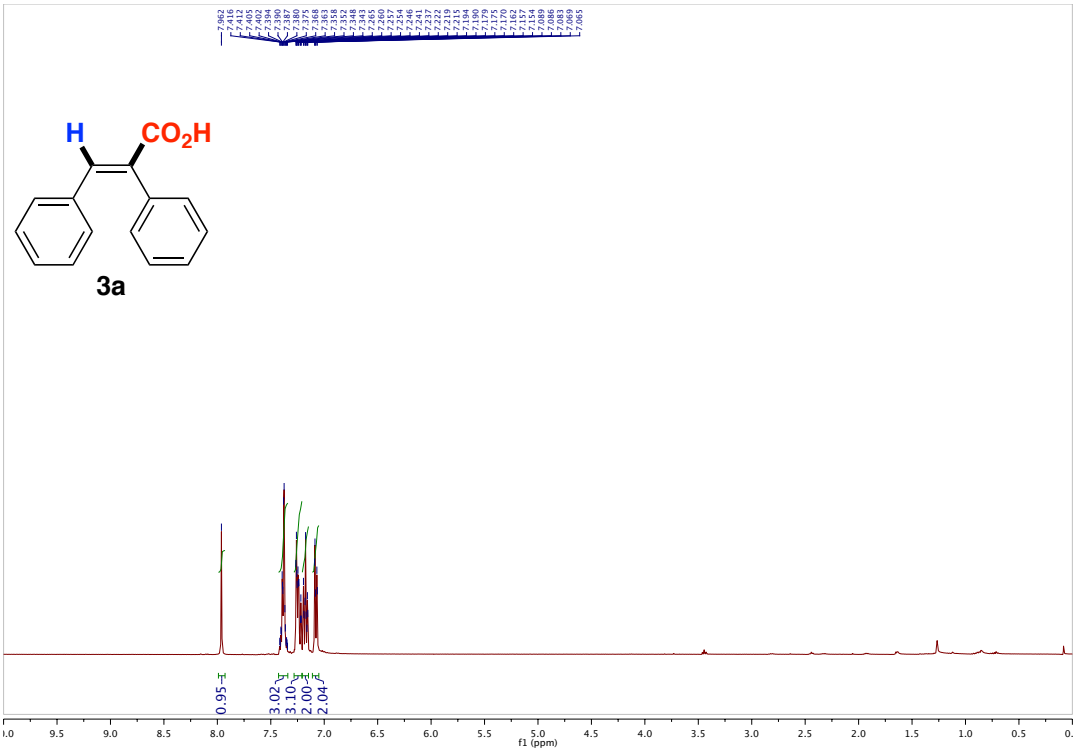
Bond lengths----	
C1-C6	1.3987(12)
C1-C2	1.4046(12)
C1-C8	1.4665(12)
C2-C3	1.3818(12)
C3-C4	1.3974(13)
C4-O1	1.3620(11)
C4-C5	1.3908(13)
C5-C6	1.3941(12)
C7-O1	1.4305(12)
C8-C9	1.3494(12)
C9-C13	1.4864(12)
C9-C10	1.5144(13)
C10-C12	1.5327(13)
C10-C11	1.5340(12)
C13-O2	1.2279(11)
C13-O3	1.3239(11)
Angles----------	
C6-C1-C2	117.62(8)
C6-C1-C8	118.82(8)
C2-C1-C8	123.38(8)
C3-C2-C1	121.03(8)
C2-C3-C4	120.40(8)
O1-C4-C5	124.65(8)
O1-C4-C3	115.57(8)
C5-C4-C3	119.77(8)
C4-C5-C6	119.27(8)
C5-C6-C1	121.87(8)
C9-C8-C1	129.15(8)
C8-C9-C13	117.28(8)
C8-C9-C10	125.18(8)
C13-C9-C10	117.55(7)

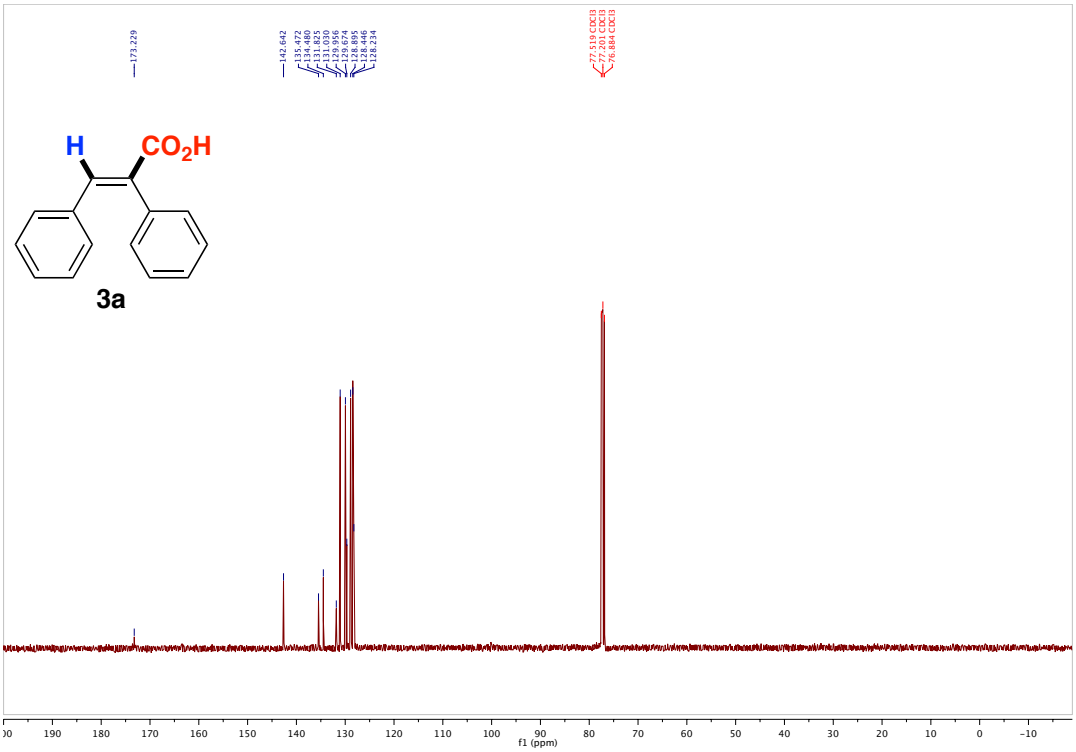
C9-C10-C12	113.33(7)
C9-C10-C11	111.62(7)
C12-C10-C11	111.64(7)
O2-C13-O3	122.14(8)
O2-C13-C9	122.45(8)
O3-C13-C9	115.37(8)
C4-O1-C7	117.22(8)

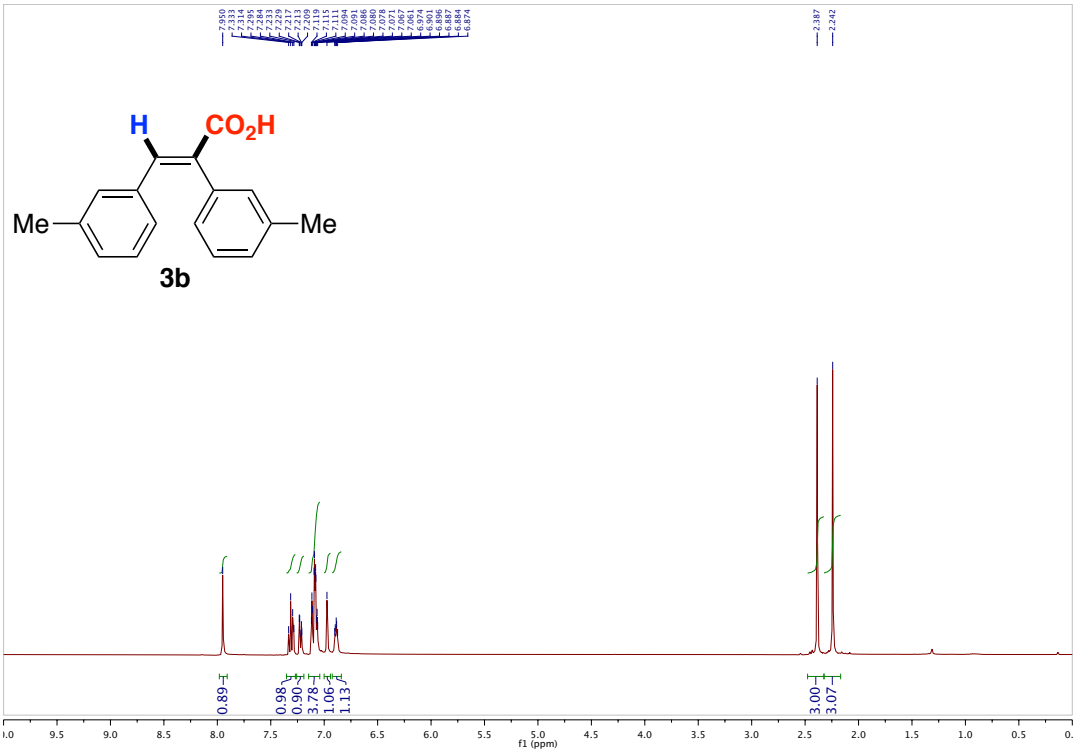
Table 3. Torsion angles [°] for **3u**.

C6-C1-C2-C3	2.23(13)
C8-C1-C2-C3	177.19(8)
C1-C2-C3-C4	-0.62(14)
C2-C3-C4-O1	-179.62(8)
C2-C3-C4-C5	-0.78(14)
O1-C4-C5-C6	179.22(8)
C3-C4-C5-C6	0.49(14)
C4-C5-C6-C1	1.22(14)
C2-C1-C6-C5	-2.54(13)
C8-C1-C6-C5	-177.74(8)
C6-C1-C8-C9	-152.83(9)
C2-C1-C8-C9	32.27(14)
C1-C8-C9-C13	-170.30(8)
C1-C8-C9-C10	9.16(15)
C8-C9-C10-C12	-111.97(10)
C13-C9-C10-C12	67.49(10)
C8-C9-C10-C11	120.95(9)
C13-C9-C10-C11	-59.60(10)
C8-C9-C13-O2	173.66(9)
C10-C9-C13-O2	-5.84(13)
C8-C9-C13-O3	-4.01(12)
C10-C9-C13-O3	176.49(7)
C5-C4-O1-C7	-9.90(13)
C3-C4-O1-C7	168.88(8)

^{1}H NMR , ^{13}C NMR and ^{19}F NMRspectra.



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Me
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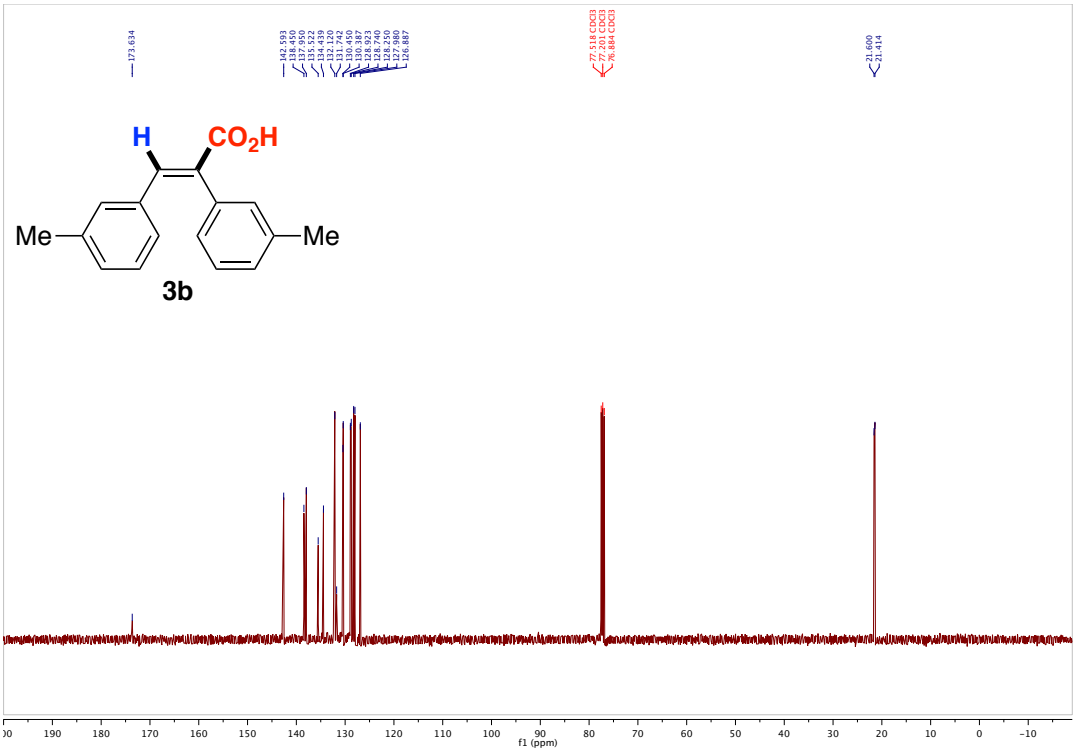
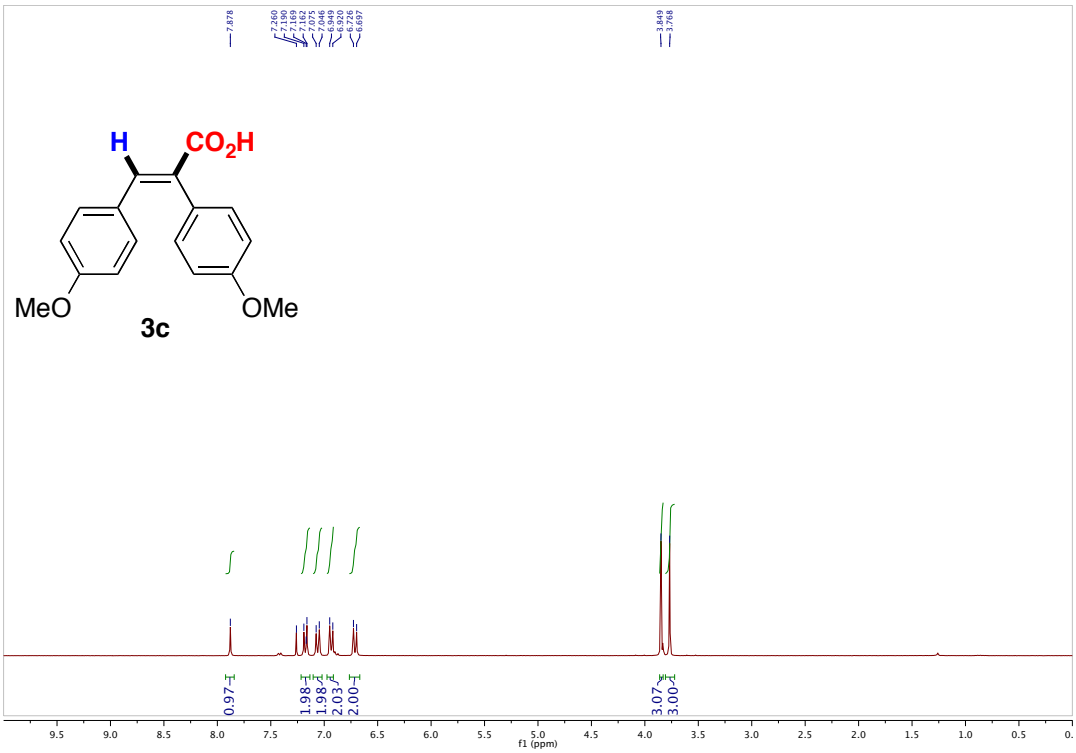
0.90
3.78
1.06
1.13
3.00
3.07
f1 (ppm)


H
CO2H
Me
Me
3b
f1 (ppm)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CO2H
MeO
OMe
3c
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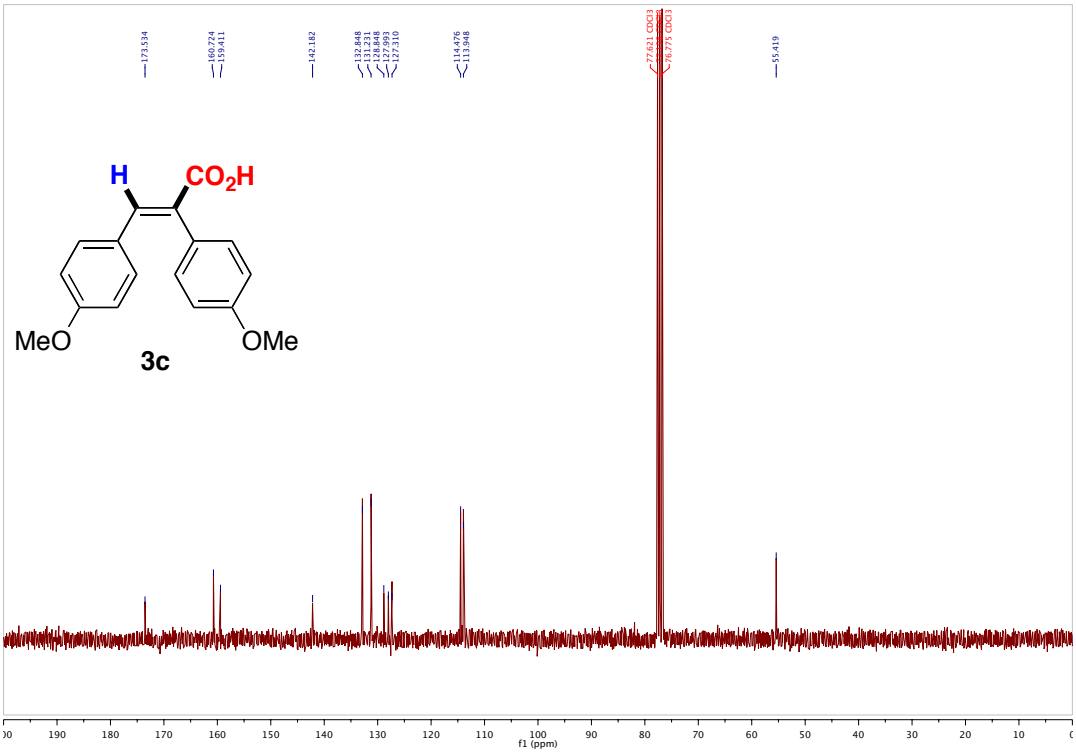
7.190
7.169
7.162
7.075
7.046
6.949
6.920
6.726
6.697
3.849
3.768
0.97
1.98
1.98
2.03
2.00
3.07
3.00
f1 (ppm)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CO2H
MeO
OMe
3c
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114.476
113.948
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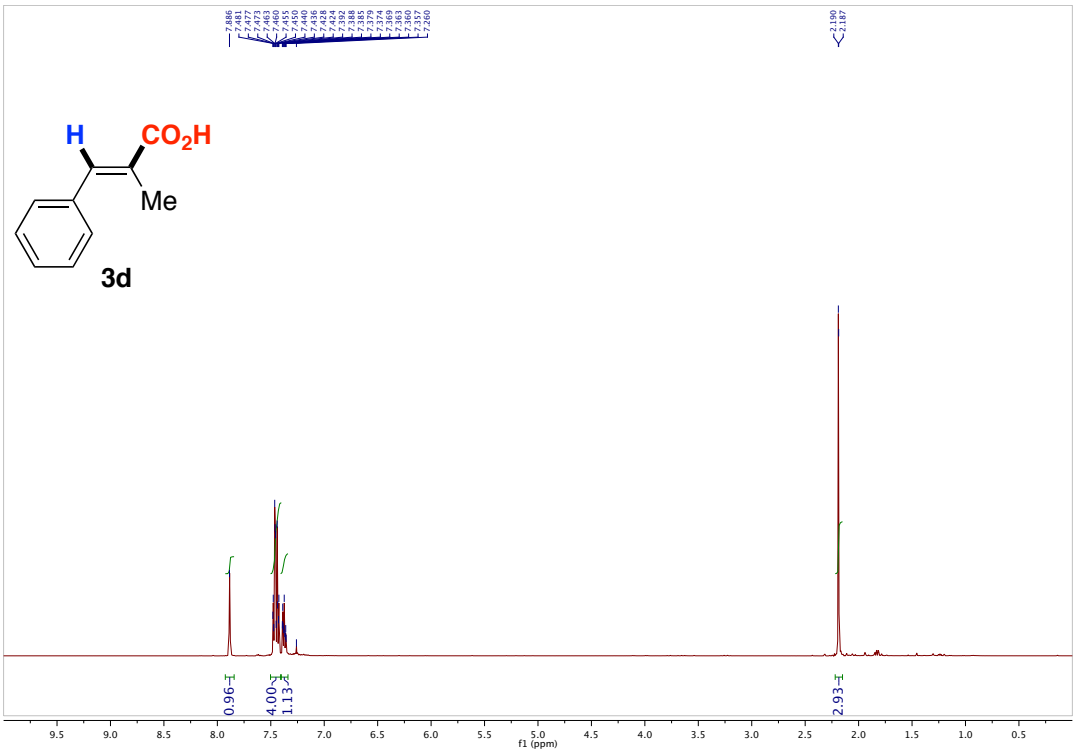
77.204 CDCl3
76.775 CDCl3
55.419
f1 (ppm)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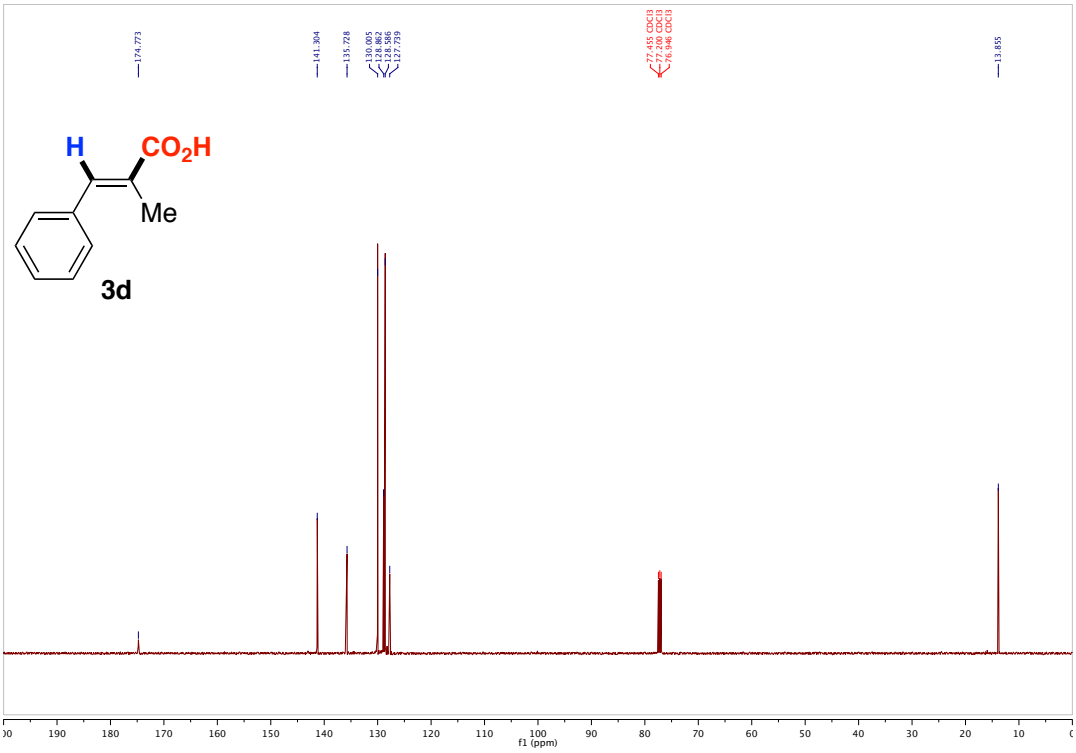
7.477
7.473
7.463
7.460
7.455
7.450
7.446
7.436
7.428
7.424
7.392
7.388
7.385
7.379
7.374
7.369
7.363
7.360
7.357
7.260
2.190
2.187
0.96
4.00
1.13
2.93
f1 (ppm)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Me
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128.862
128.556
127.739
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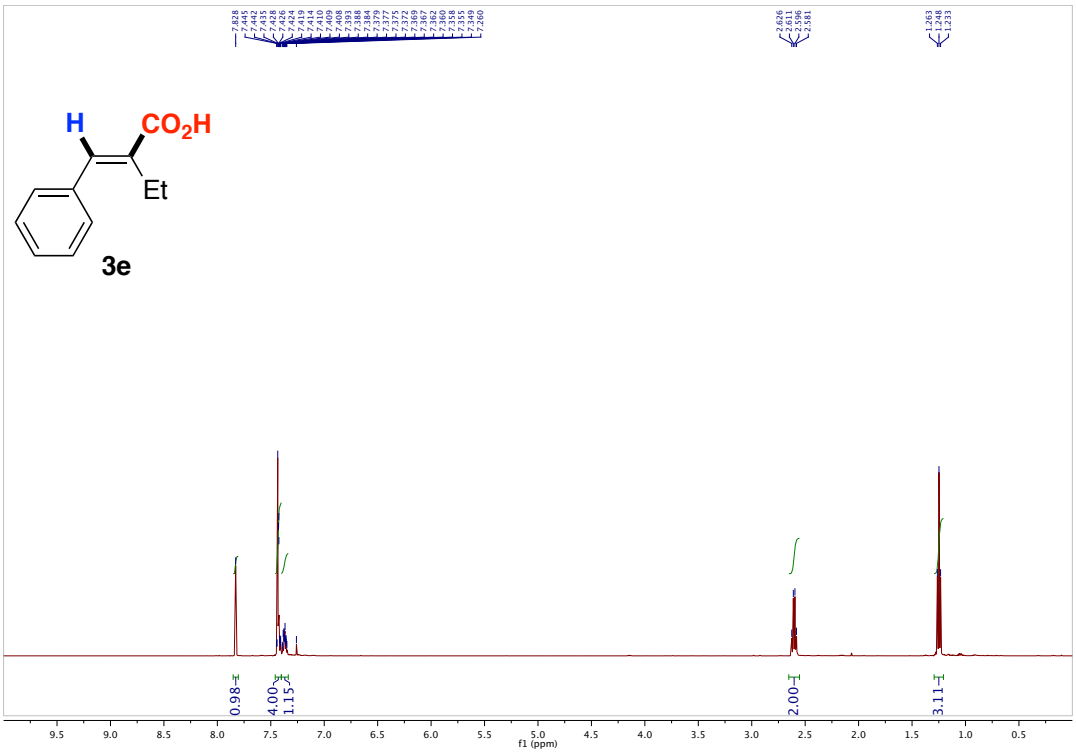
77.200 CDCl3
76.946 CDCl3
13.855
f1 (ppm)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Et
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1.15
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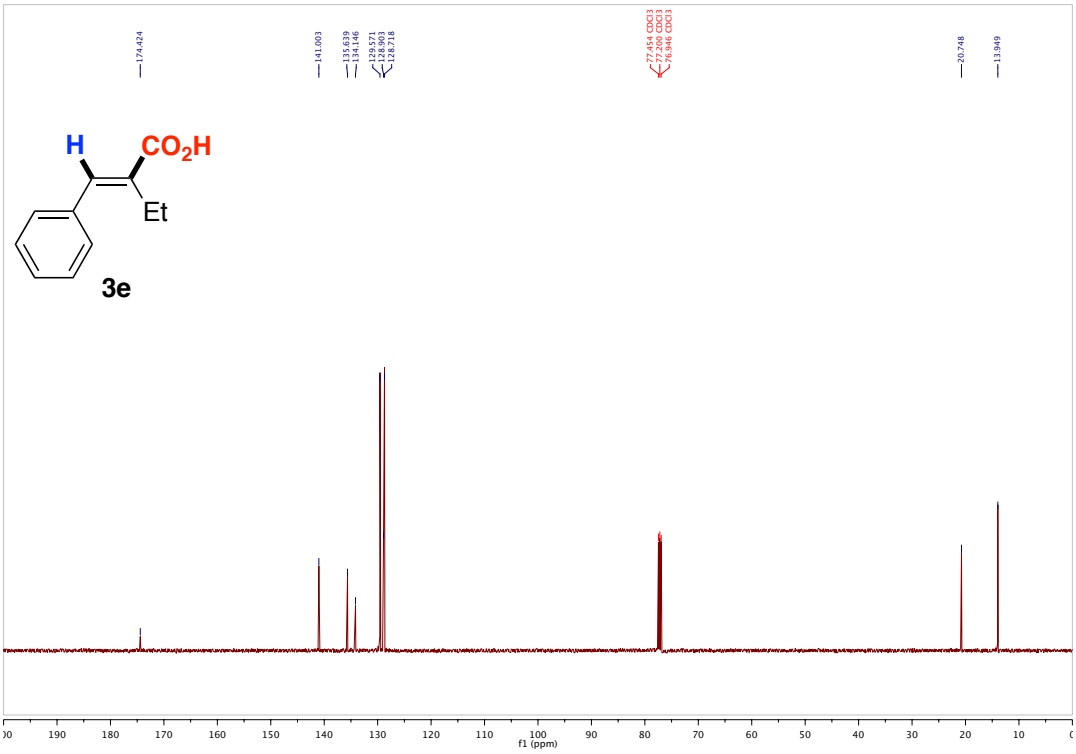
3.11
f1 (ppm)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3e
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141.003
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134.146
129.571
128.903
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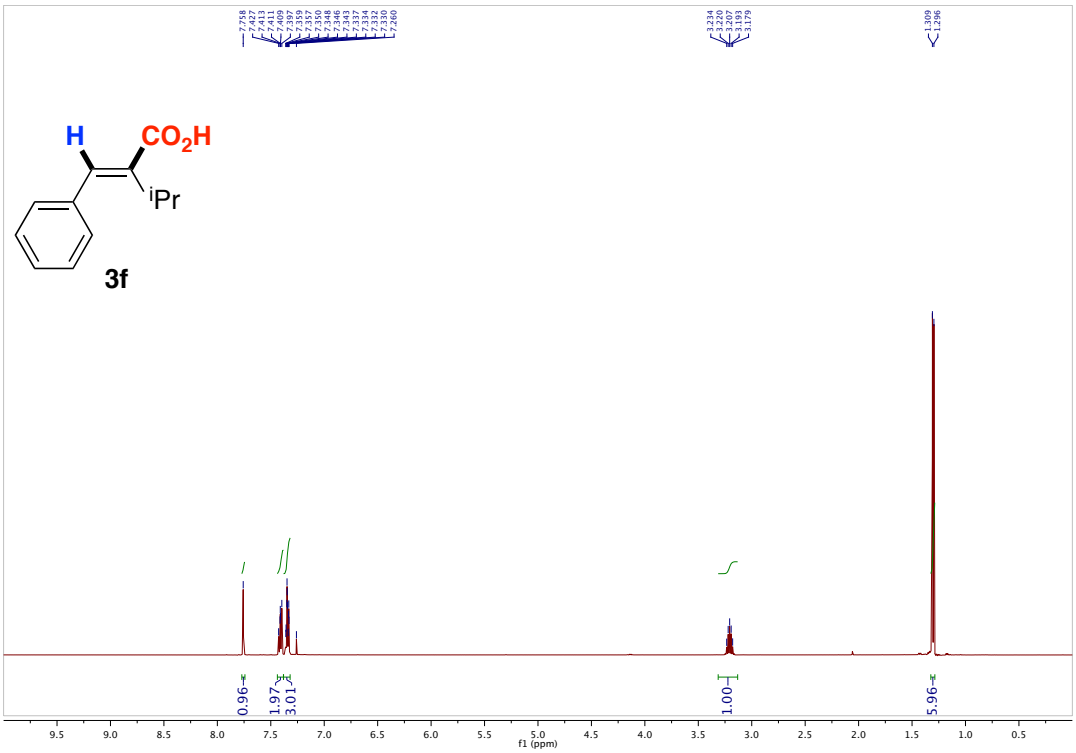
77.200 CDCl3
76.946 CDCl3
20.748
13.949
f1 (ppm)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7.411
7.409
7.357
7.359
7.357
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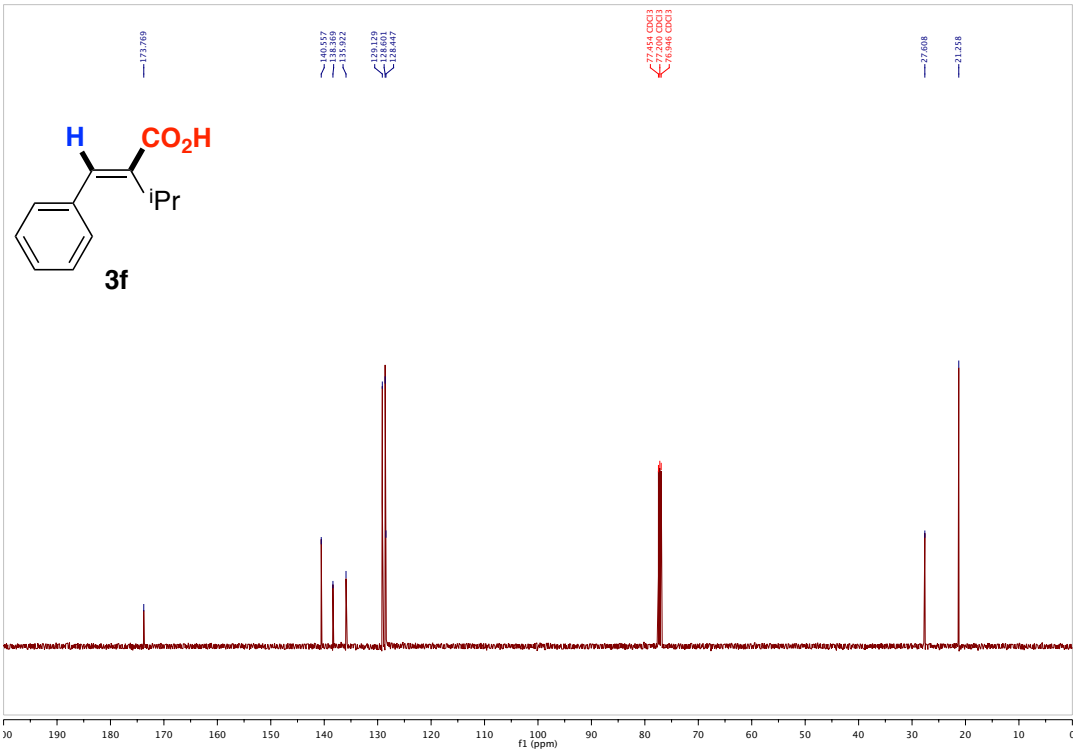
7.346
7.343
7.337
7.334
7.332
7.330
7.260
3.234
3.220
3.207
3.193
3.179
1.309
1.296
0.96
1.97
3.01
1.00
5.96
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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CO2H
iPr
3f
173.769
140.557
138.969
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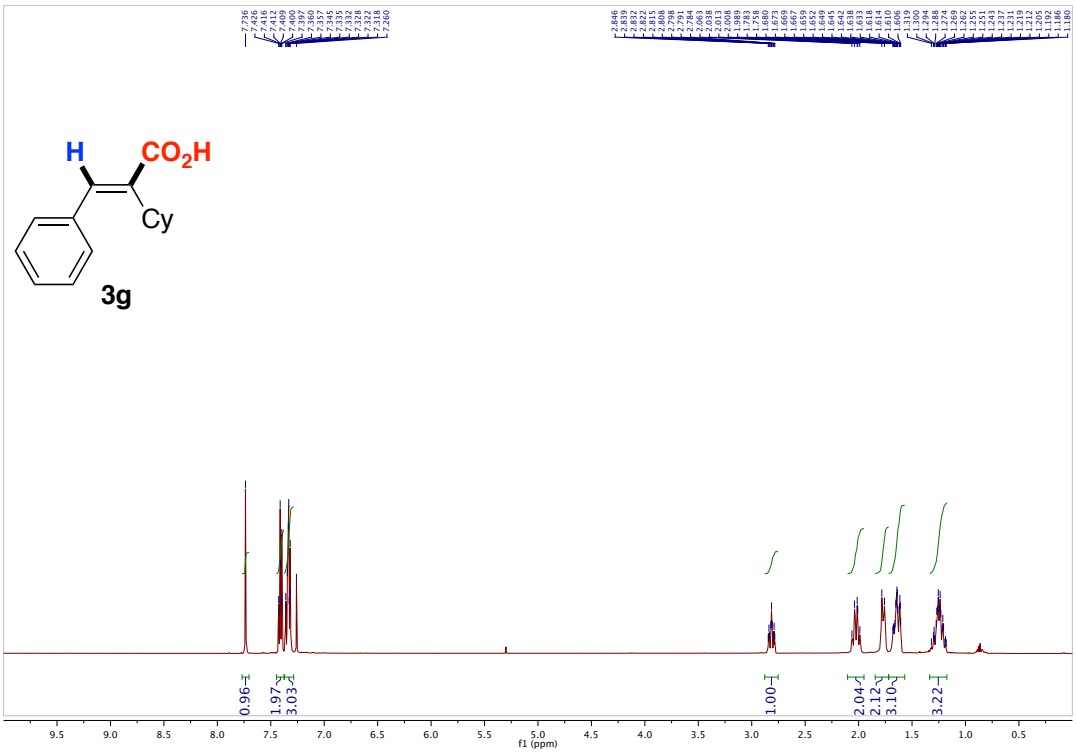
129.129
128.601
128.447
77.454 CDCl3
77.200 CDCl3
76.946 CDCl3
27.608
21.258
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)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CO2H
Cy
3g
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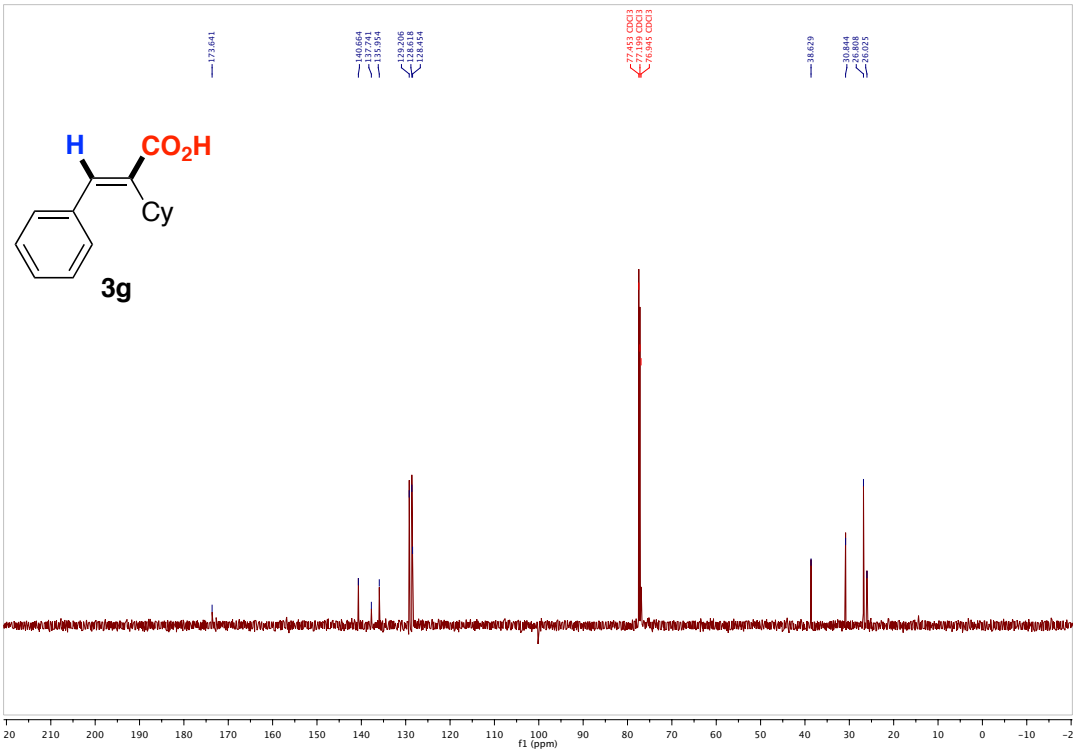
1.00
2.04
2.12
3.10
3.22
f1 (ppm)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Cy
3g
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129.206
128.618
128.454
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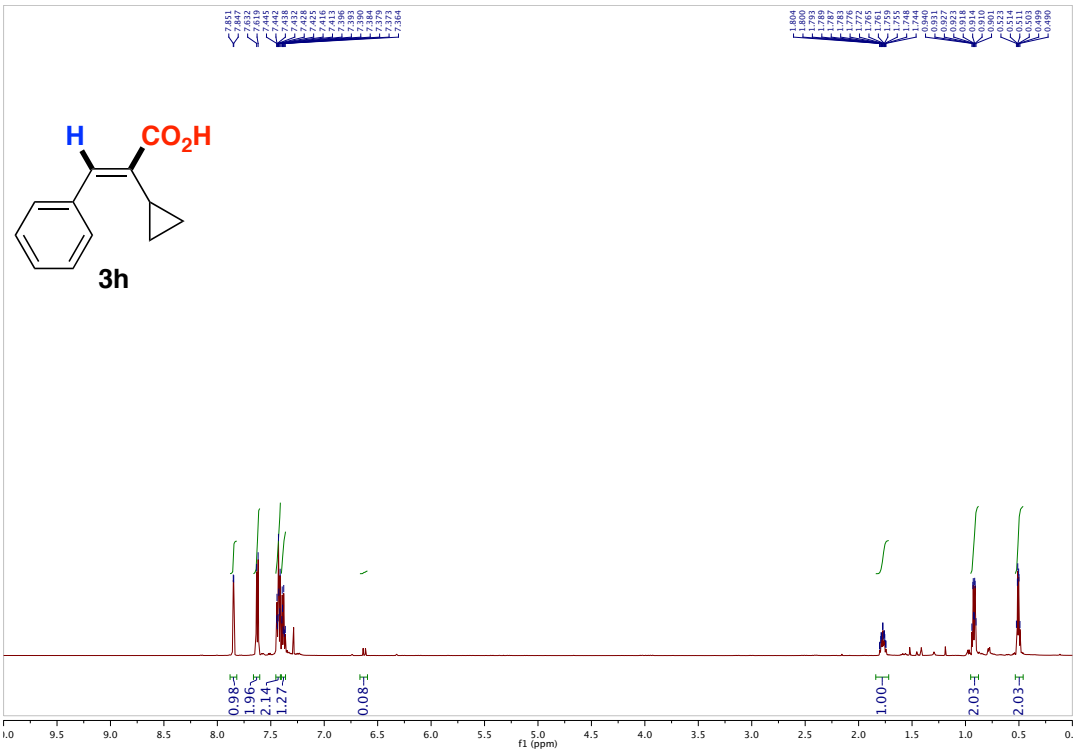
77.199 CDCl3
76.945 CDCl3
38.629
30.844
26.808
26.025
f1 (ppm)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CO2H
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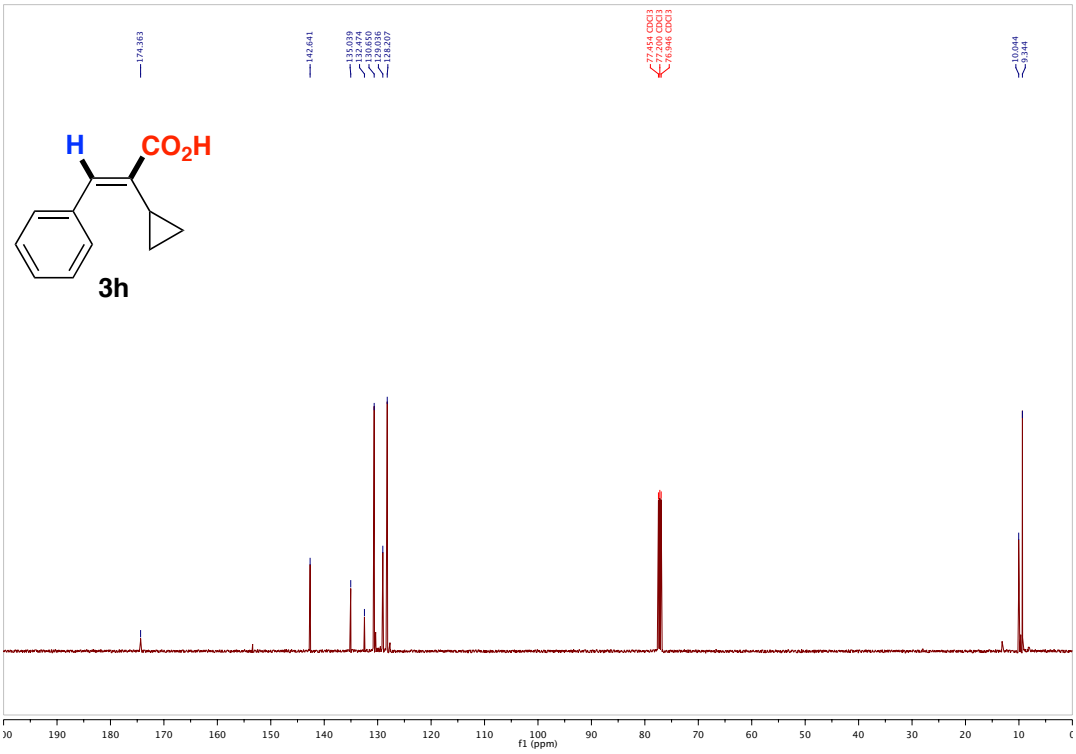
1.27
0.08
1.00
2.03
2.03
f1 (ppm)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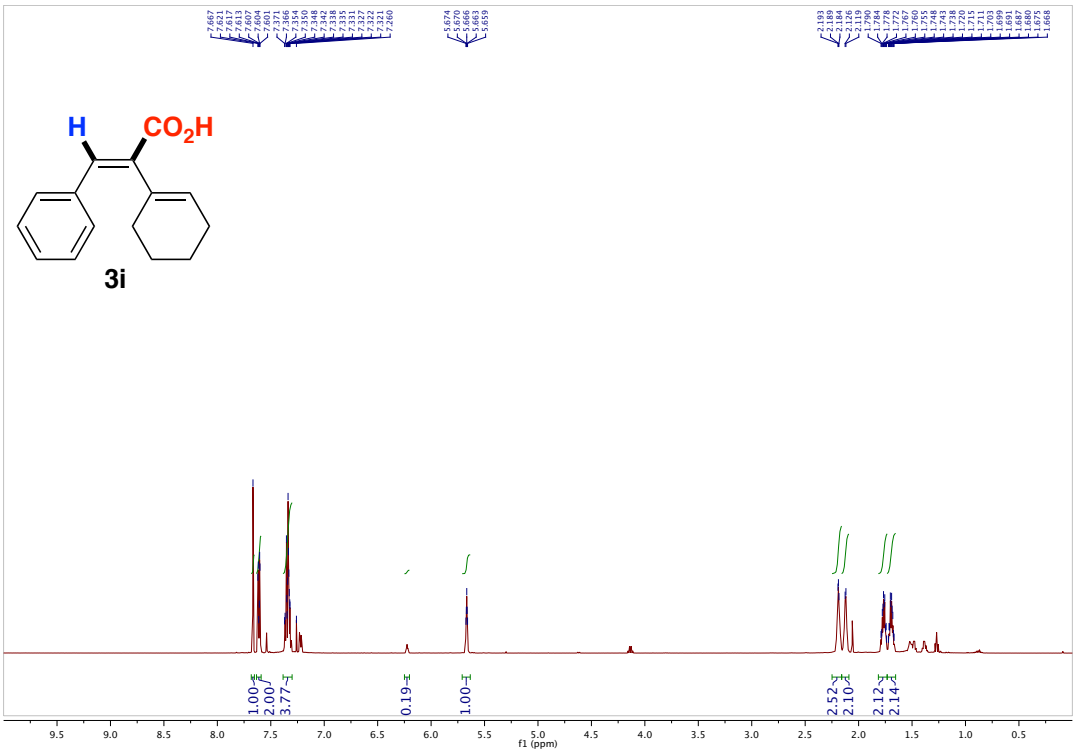
76.946 CDCl3
10.044
9.344
f1 (ppm)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CO2H
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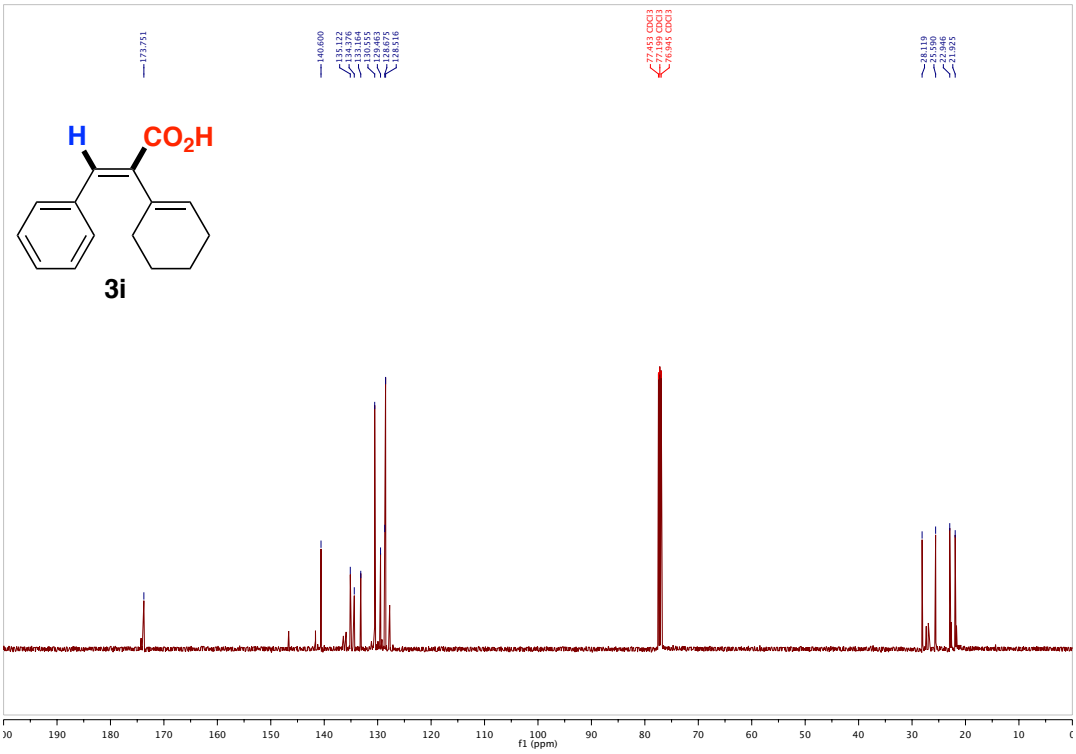
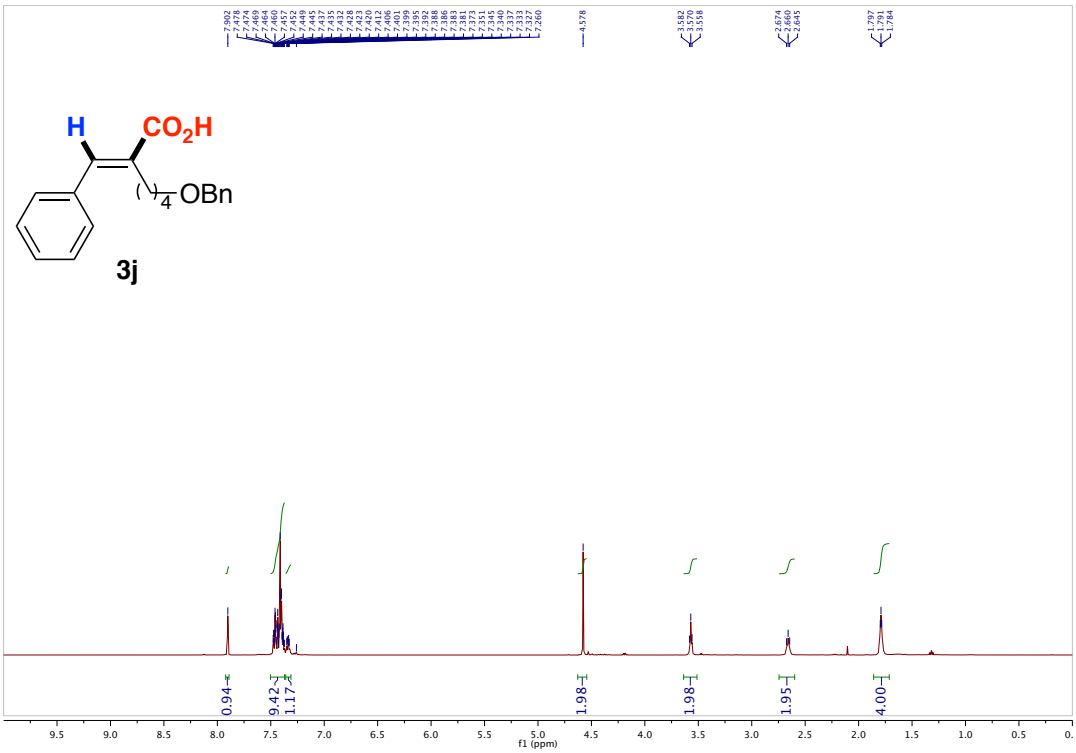
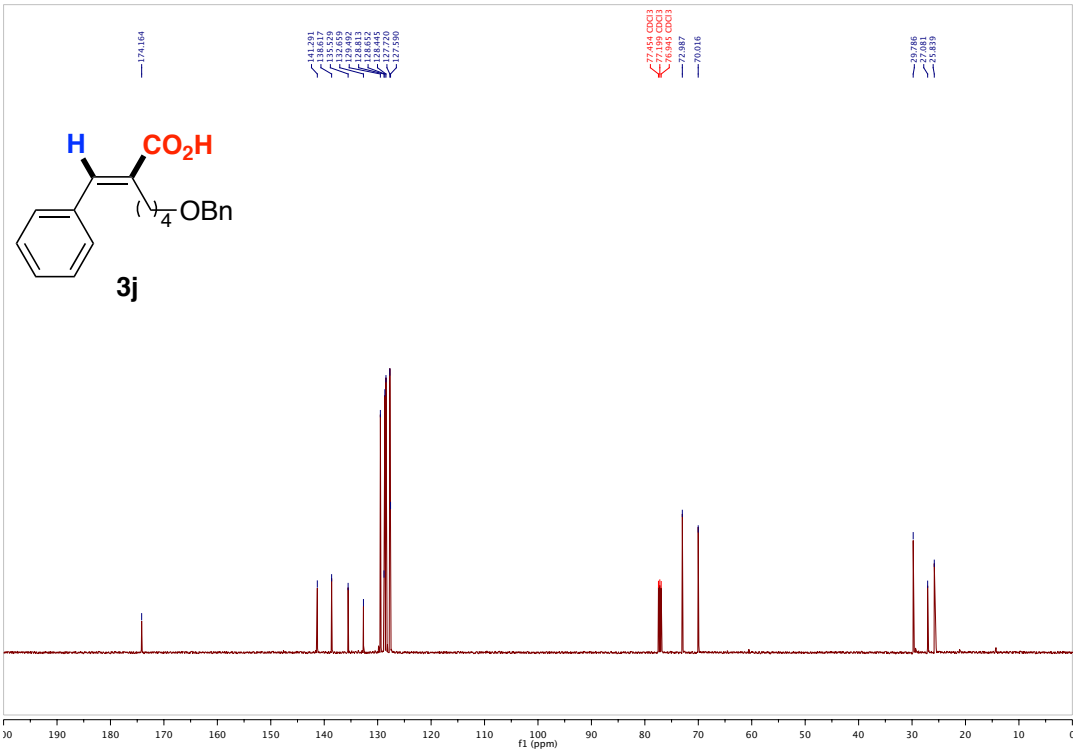
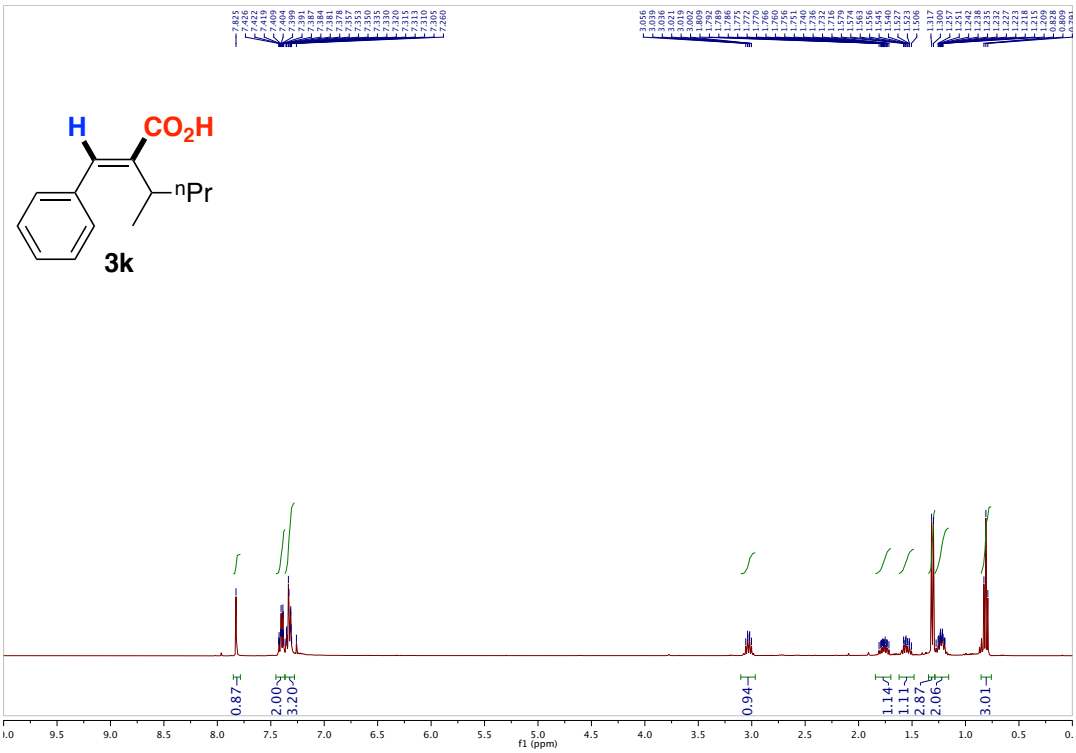
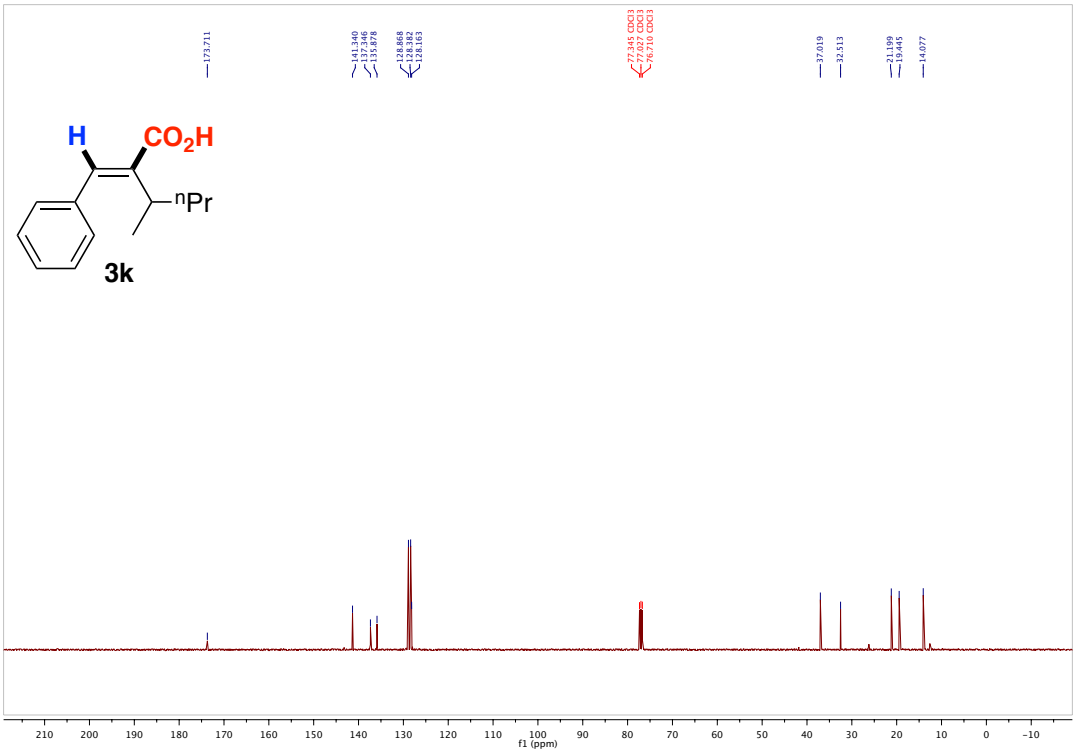
2.10
2.12
2.14
f1 (ppm)

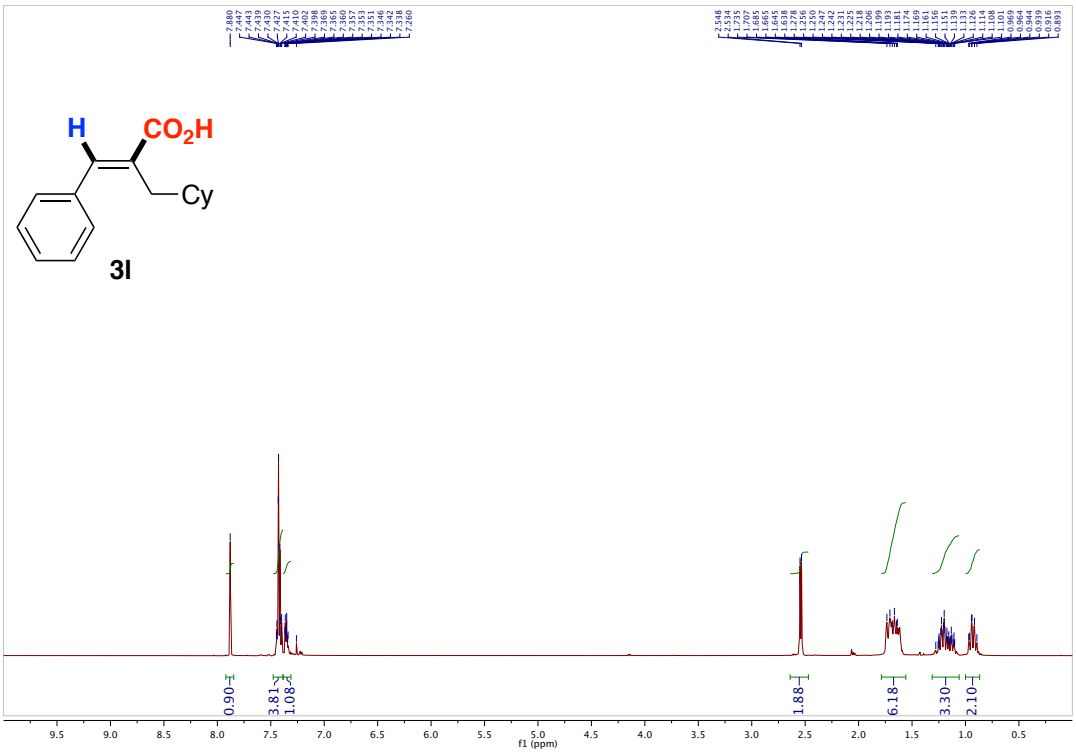

H
CO2H
3i
173.751
140.600
135.122
134.326
133.184
130.555
129.493
128.852
128.516
77.453 CDCl3
77.199 CDCl3
76.945 CDCl3
28.119
25.589
22.946
21.925
f1 (ppm)

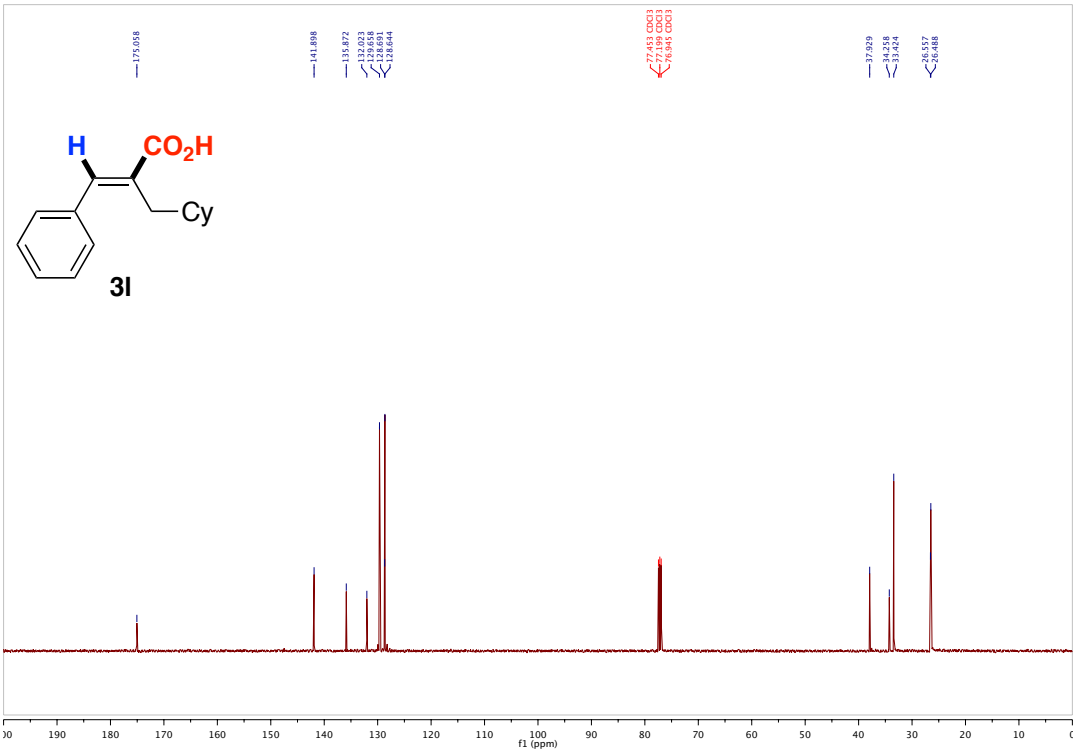

H
CO2H
4
OBn
3j
f1 (ppm)

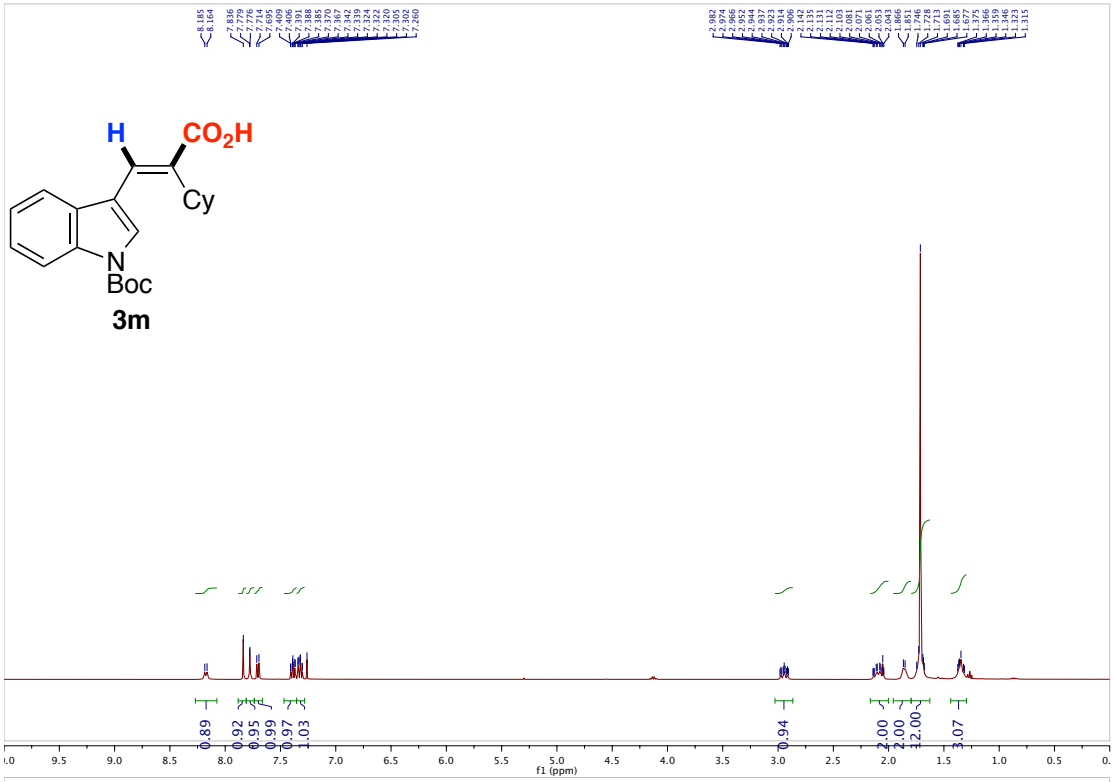

H
CO2H
4
OBn
3j
f1 (ppm)

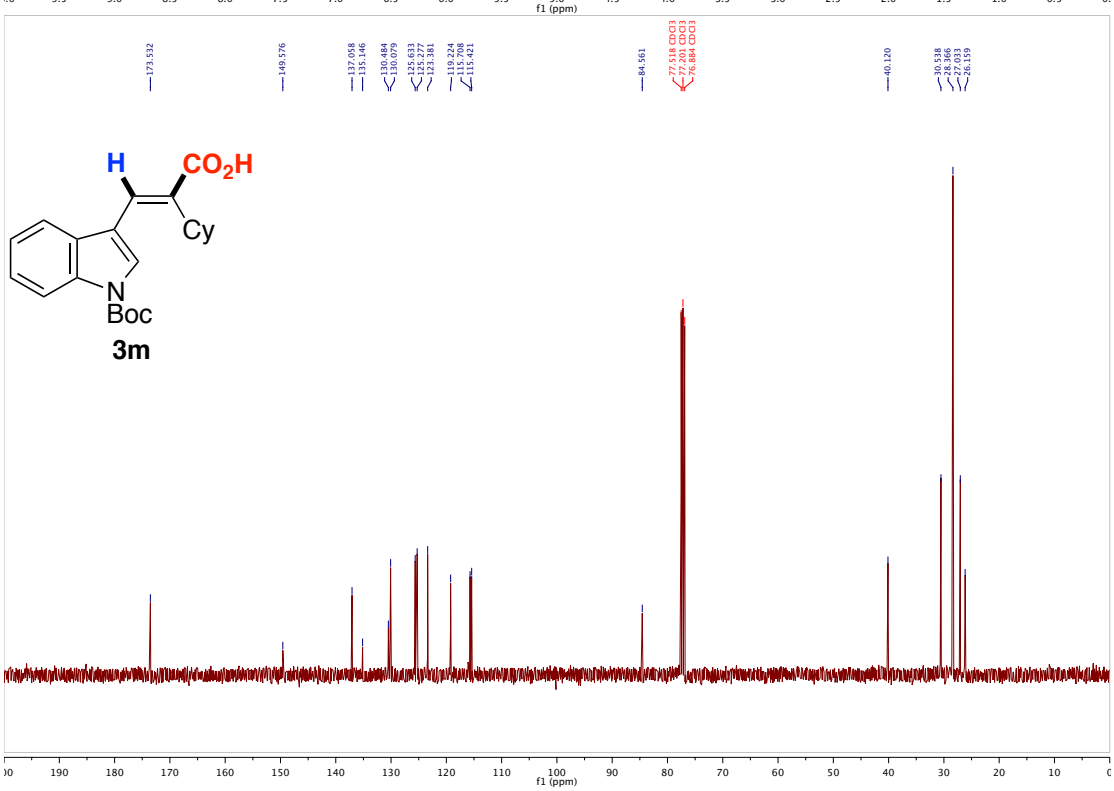

H
CO2H
nPr
3k
0.87
2.00
3.20
0.94
1.14
1.11
2.87
2.06
3.01
f1 (ppm)

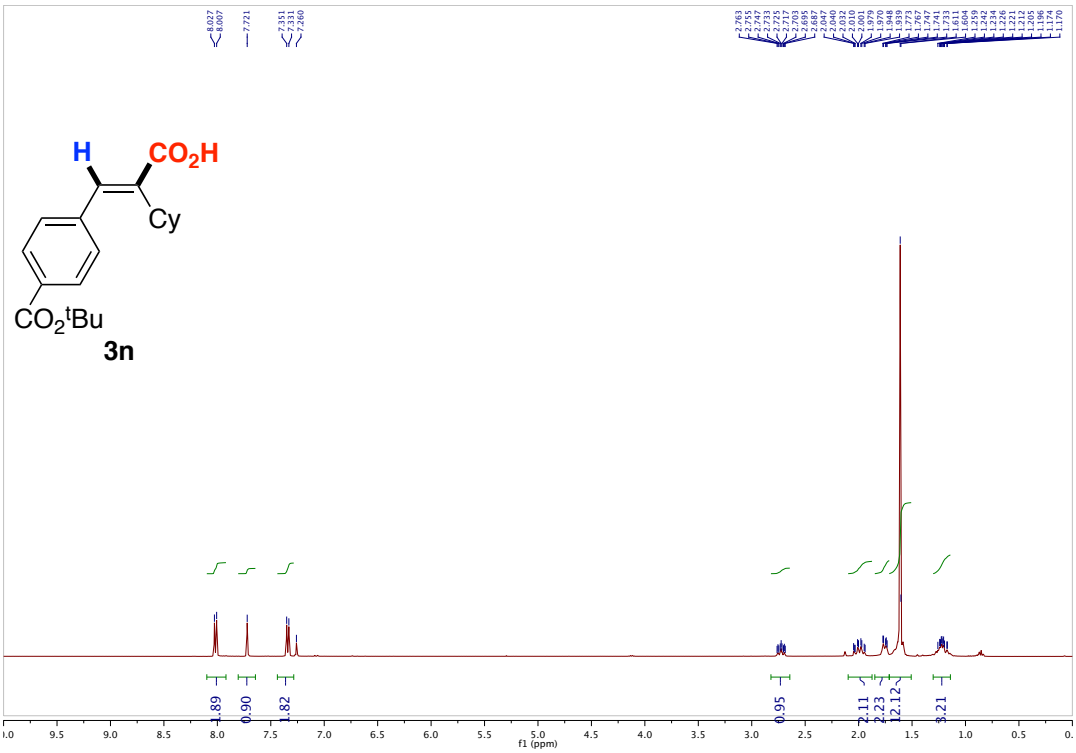

H
CO2H
nPr
3k
173.711
141.340
137.346
135.878
128.866
128.382
126.163
77.345 CDCl3
77.027 CDCl3
76.710 CDCl3
37.019
32.513
21.199
19.445
14.077
f1 (ppm)

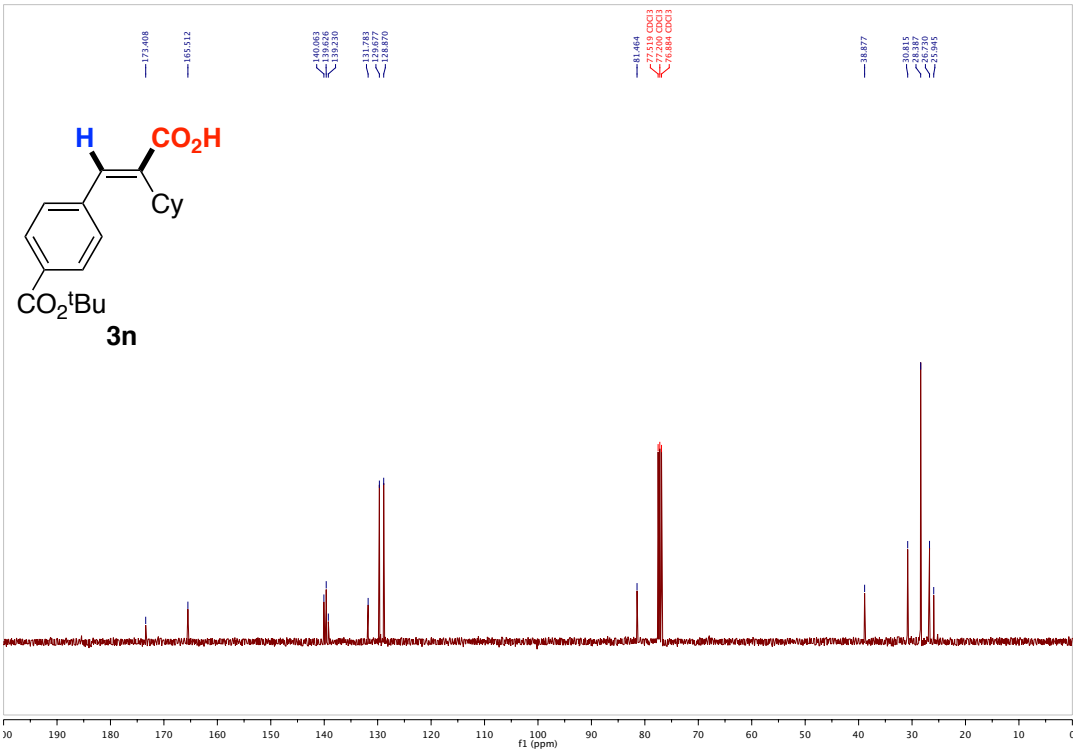

H
CO2H
Cy
3l
0.90
3.81
1.08
1.88
6.18
3.30
2.10
f1 (ppm)

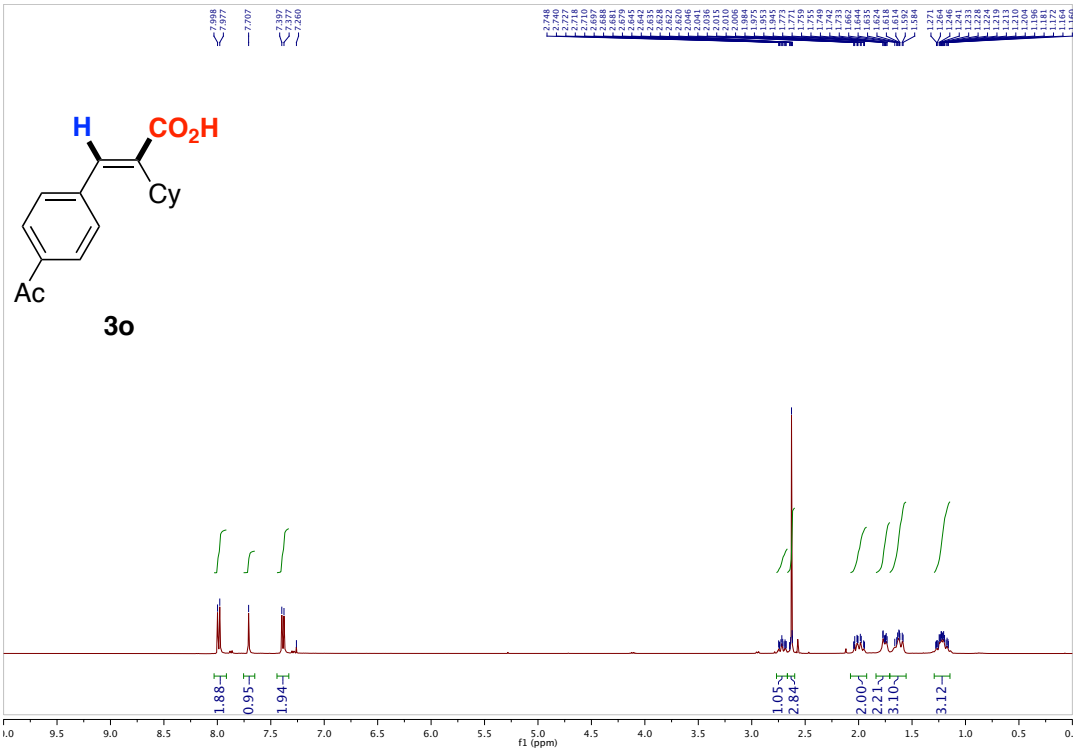

H
CO2H
Cy
3l
175.058
141.898
135.872
132.022
129.658
128.691
128.644
77.453 CDCl3
77.199 CDCl3
76.945 CDCl3
37.929
34.258
33.424
26.557
26.488
f1 (ppm)

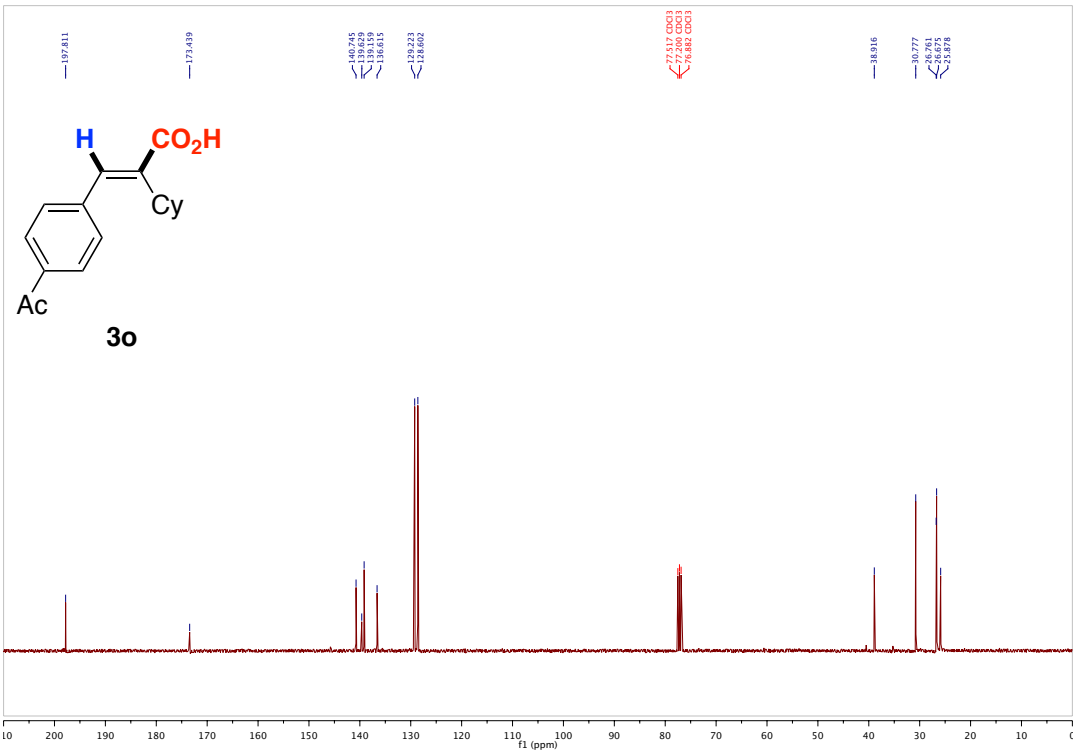

H
CO2H
Cy
N
Boc
3m
f1 (ppm)

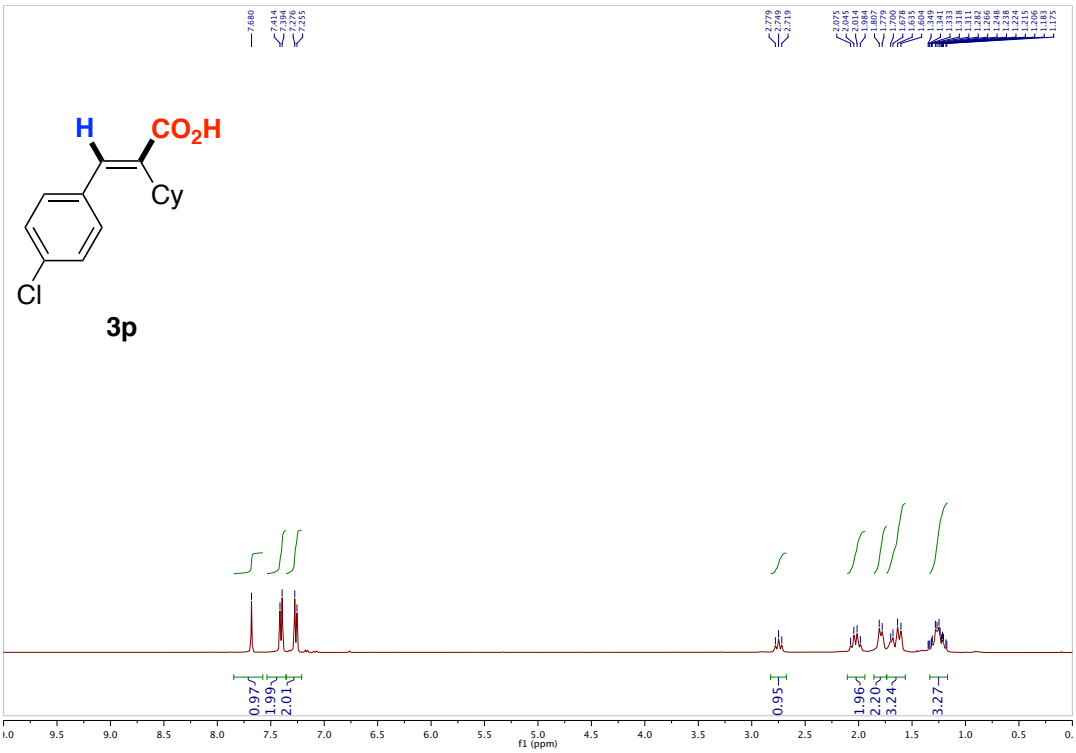

H
CO2H
Cy
N
Boc
3m
f1 (ppm)

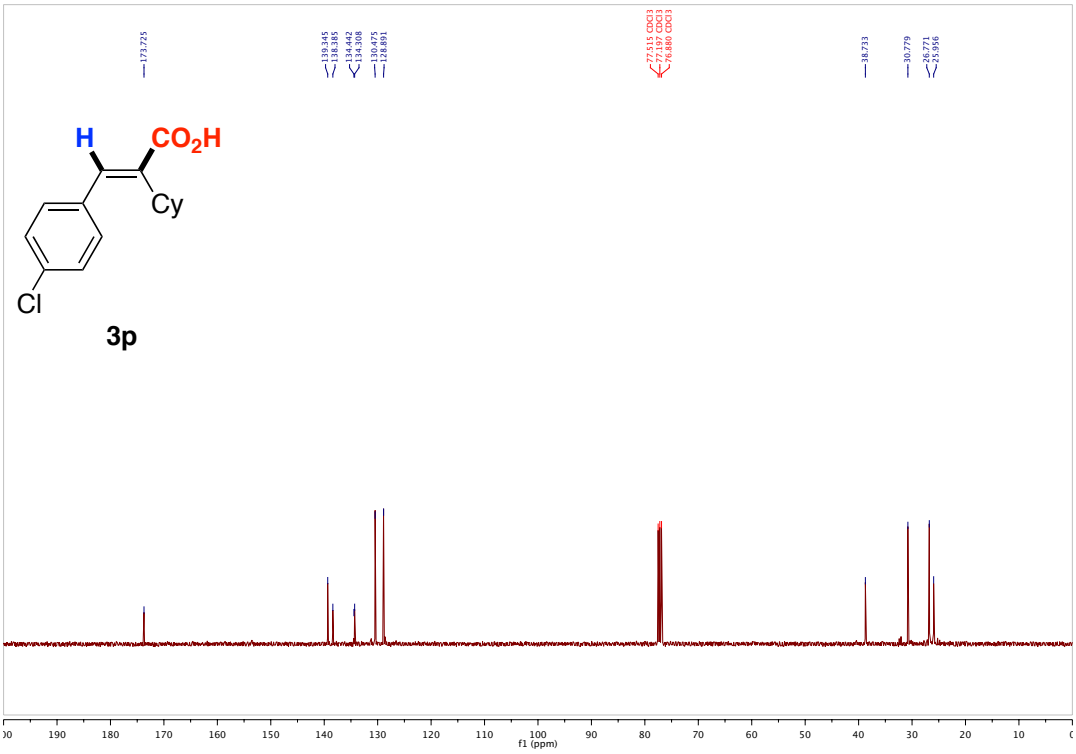

H
CO2H
Cy
CO2tBu
3n
f1 (ppm)

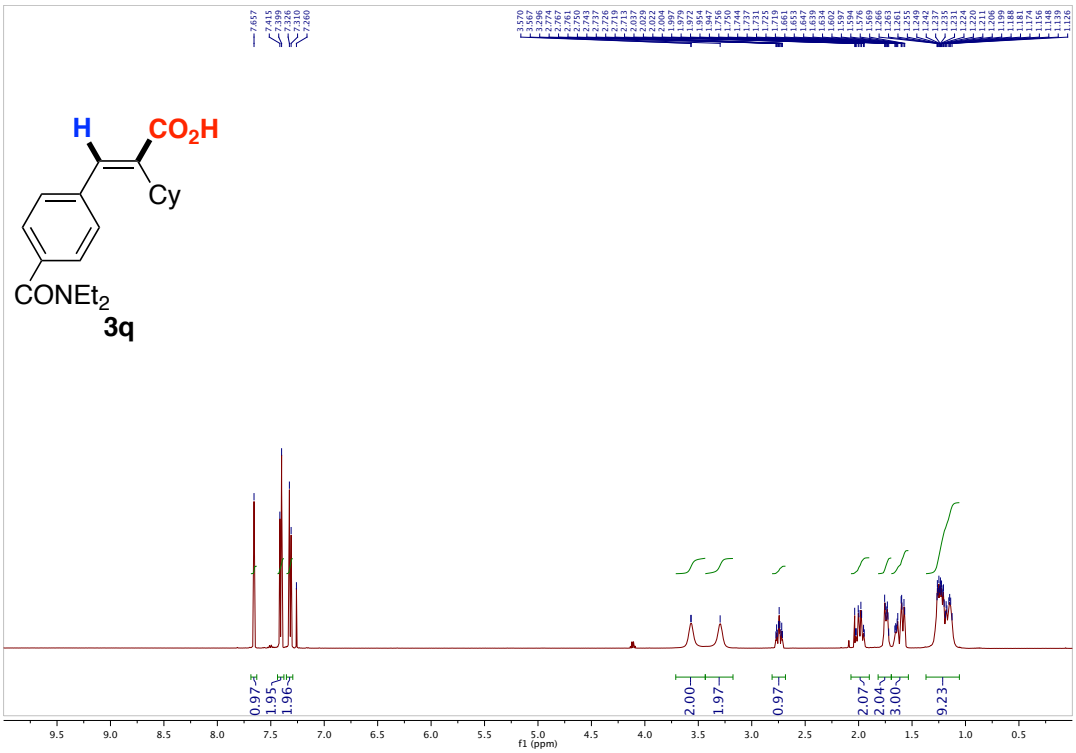

H
CO2H
Cy
CO2tBu
3n
f1 (ppm)

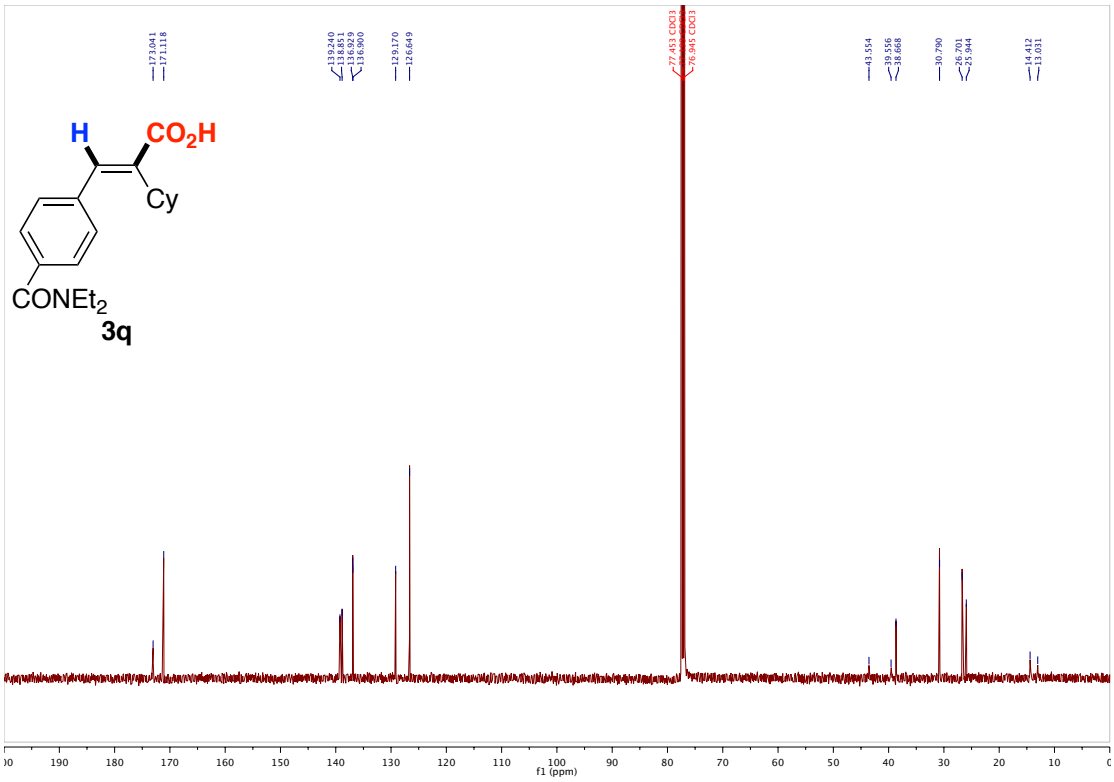

H
CO2H
Cy
Ac
3o
1.88
0.95
1.94
1.05
2.84
2.00
2.21
3.10
3.12
f1 (ppm)

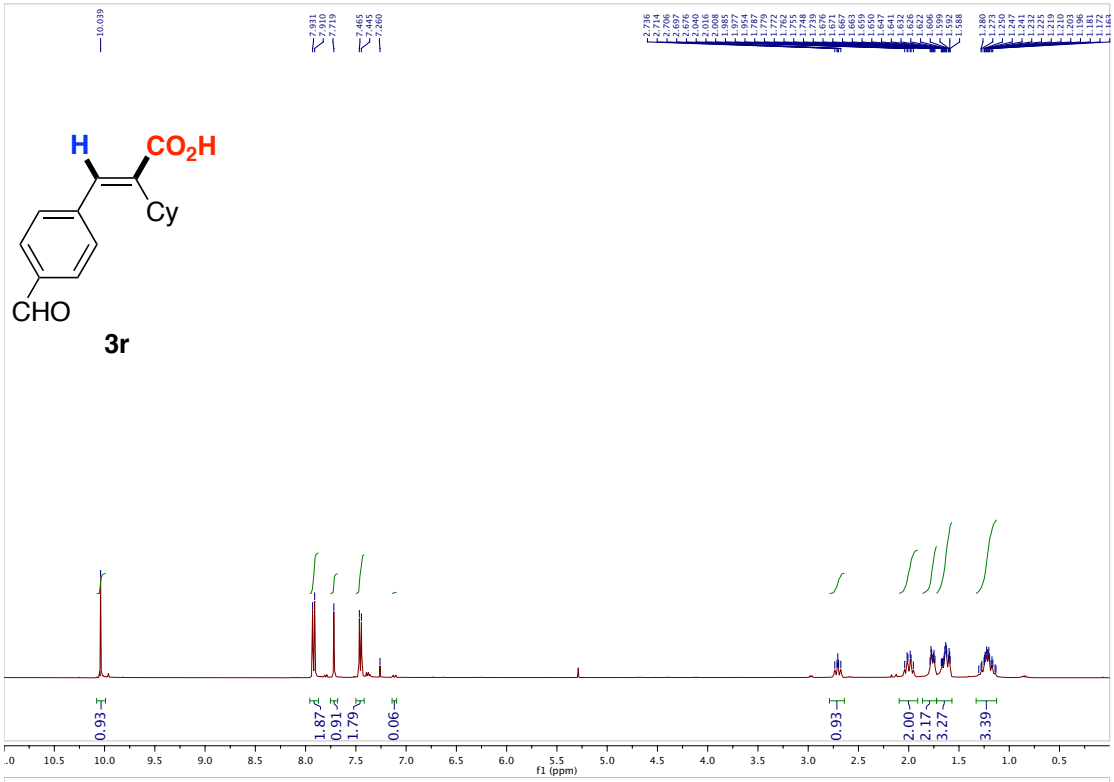

H
CO2H
Cy
Ac
3o
197.811
173.439
140.745
139.620
139.159
136.615
129.223
128.602
77.517 CDCl3
77.200 CDCl3
76.882 CDCl3
38.916
30.777
26.761
26.675
21.978
f1 (ppm)

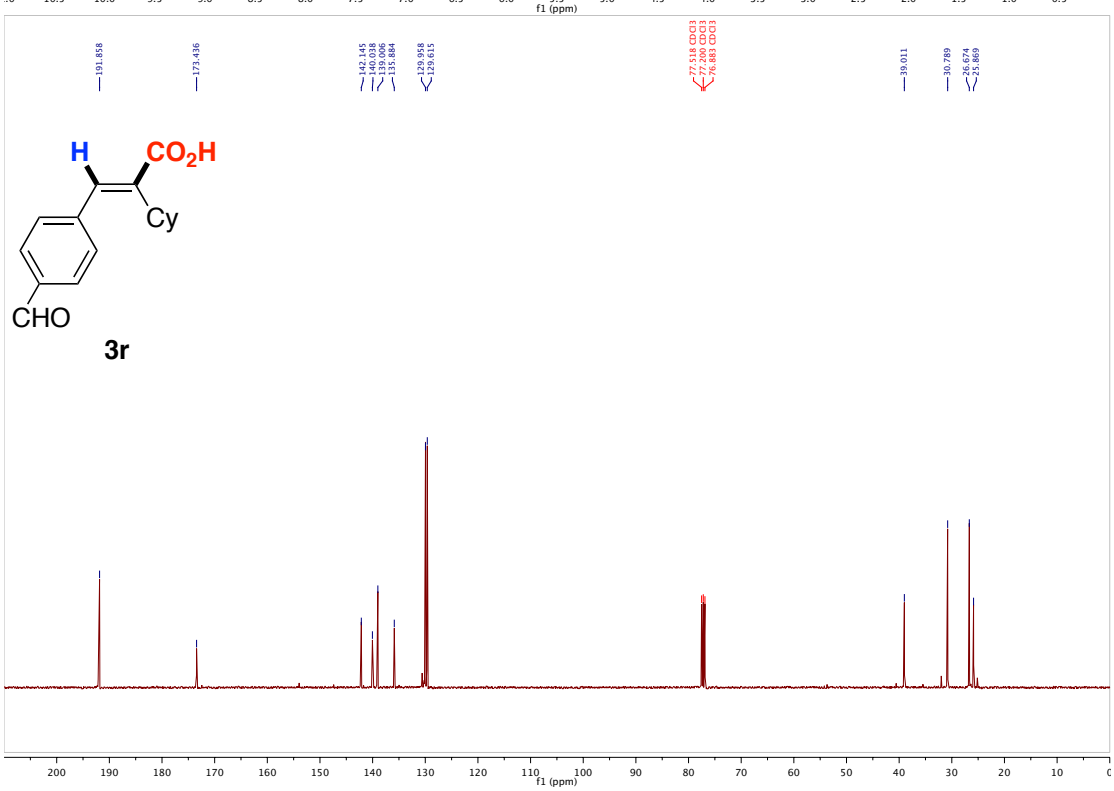

H
CO2H
Cy
Cl
3p
7.680
7.414
7.394
7.226
7.225
2.779
2.749
2.719
2.075
2.045
2.014
1.984
1.807
1.779
1.750
1.678
1.635
1.604
1.349
1.341
1.333
1.318
1.311
1.290
1.266
1.248
1.238
1.224
1.215
1.206
1.195
1.175
0.97
1.99
2.01
0.95
1.96
2.20
3.24
3.27
f1 (ppm)

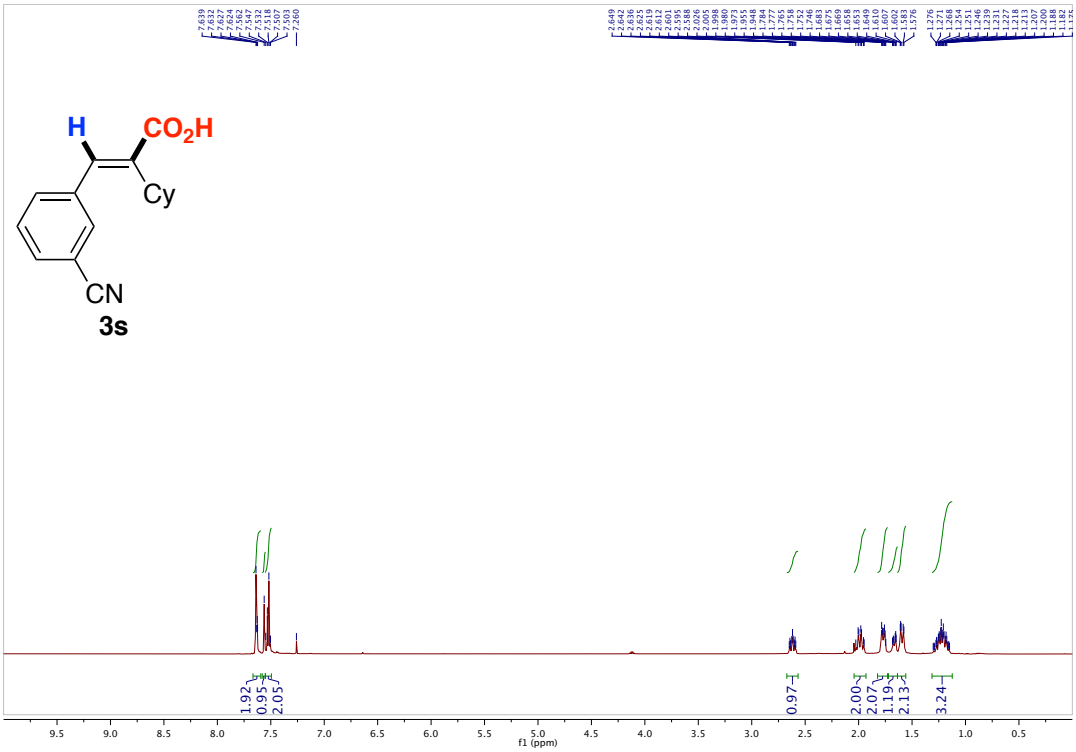

H
CO2H
Cy
Cl
3p
173.725
139.345
138.385
134.442
134.008
130.475
128.891
77.515 CDCl3
77.197 CDCl3
76.880 CDCl3
38.733
30.779
26.771
25.956
f1 (ppm)

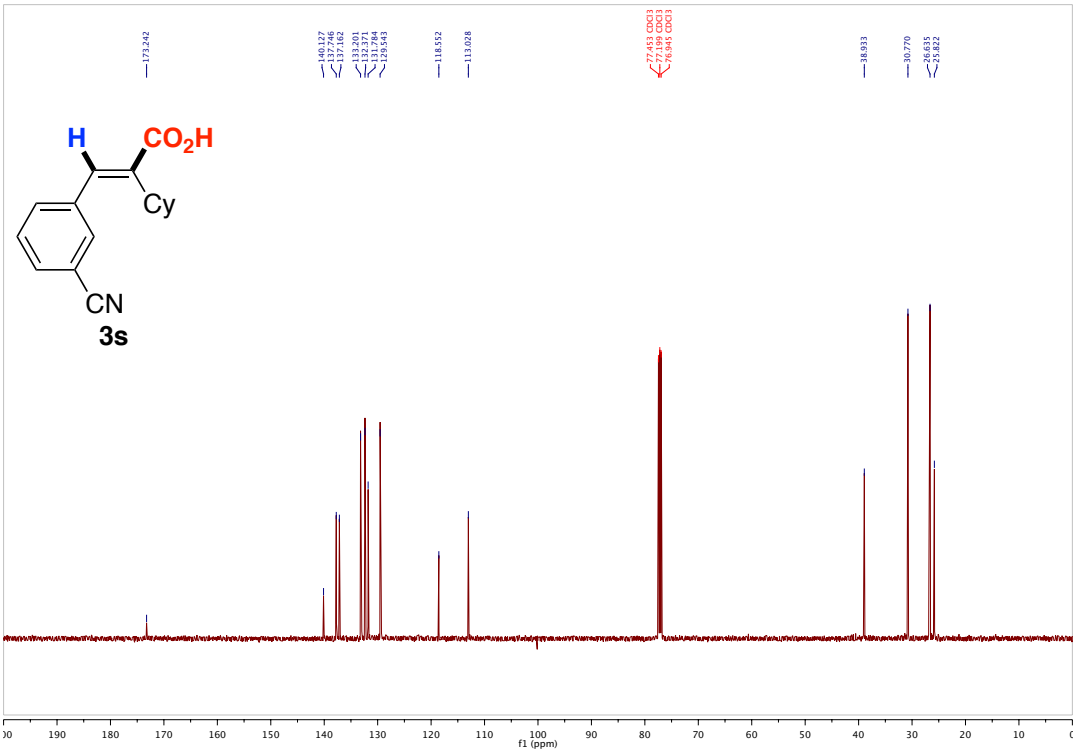

H
CO2H
Cy
CONEt2
3q
f1 (ppm)

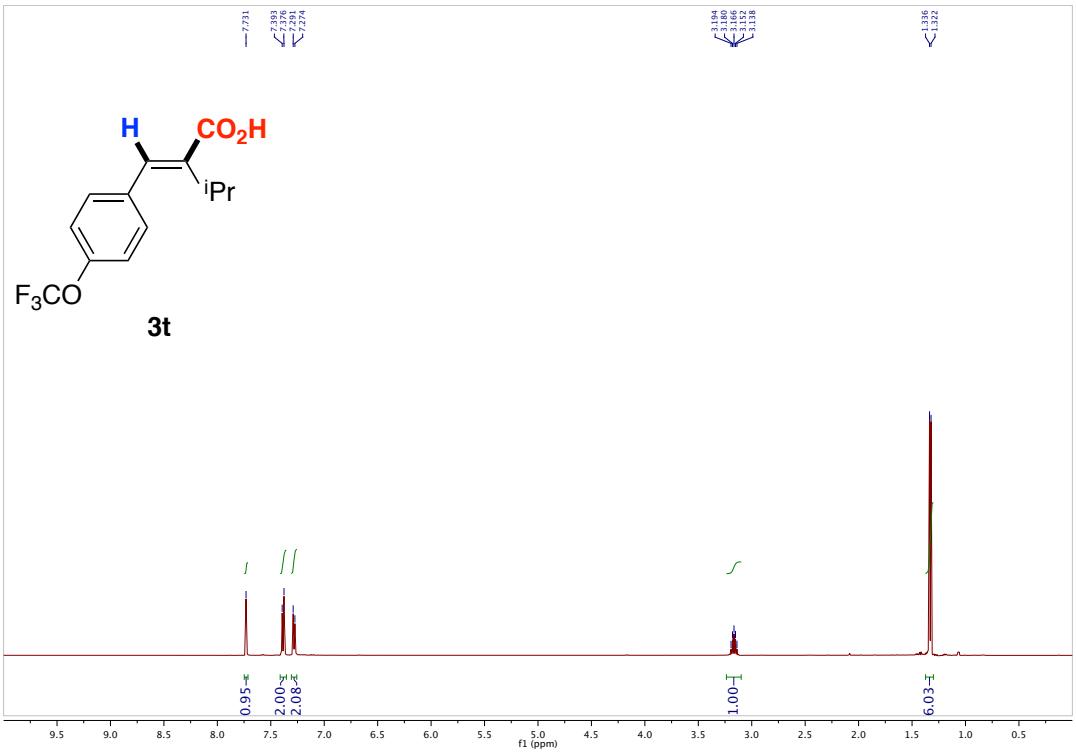

H
CO2H
Cy
CONEt2
3q
f1 (ppm)

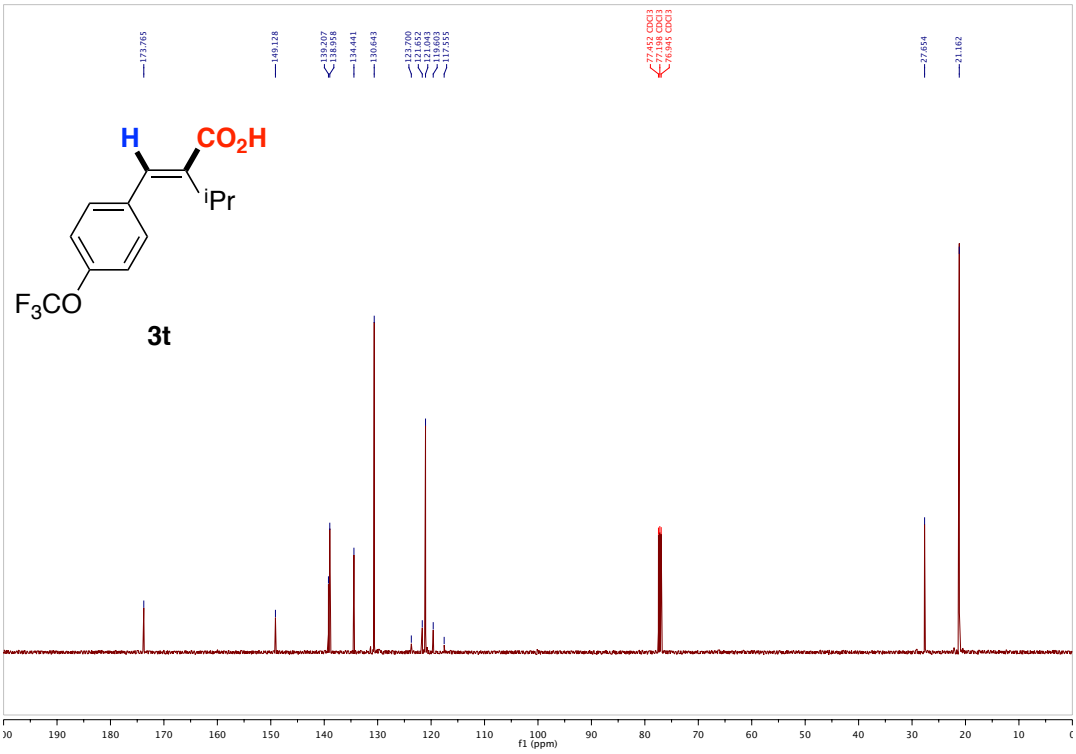

H
CO2H
Cy
CHO
3r
10.039
7.931
7.910
7.719
7.465
7.445
7.260
0.93
1.87
0.91
1.79
0.06
0.93
2.00
2.17
3.27
3.39
f1 (ppm)

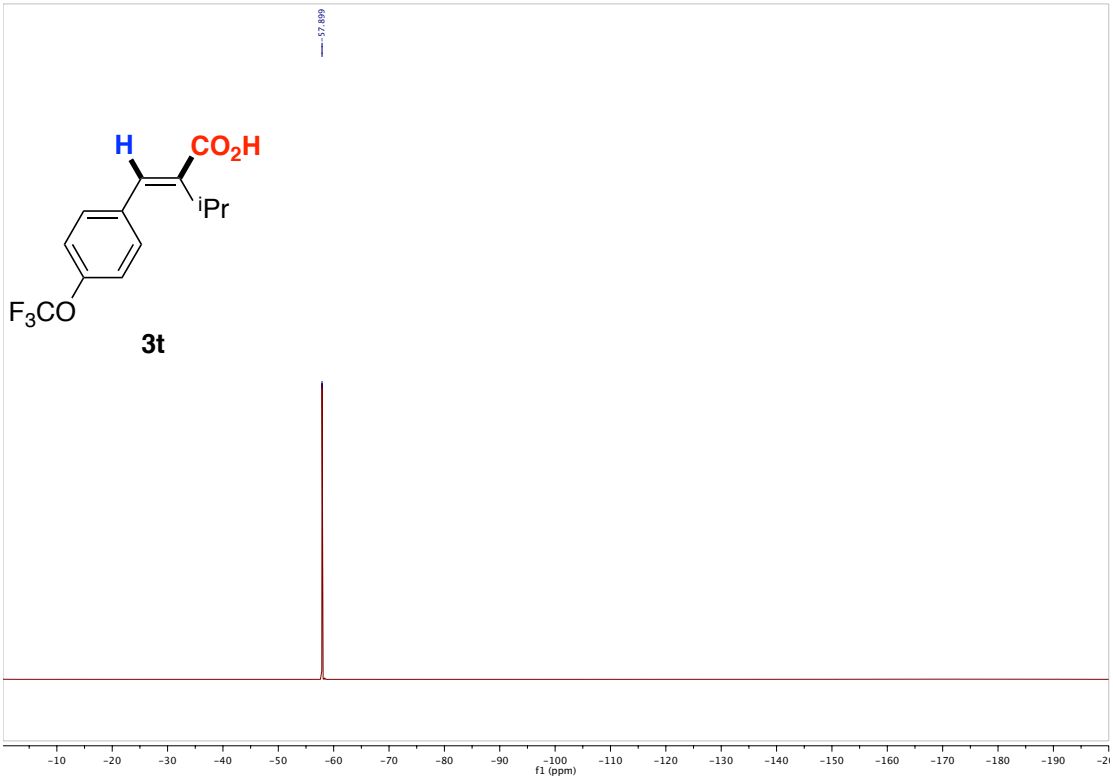

H
CO2H
Cy
CHO
3r
191.858
173.436
142.145
140.038
139.066
135.984
129.958
129.615
77.518 CDCl3
77.200 CDCl3
76.883 CDCl3
39.011
30.789
26.674
25.869
f1 (ppm)

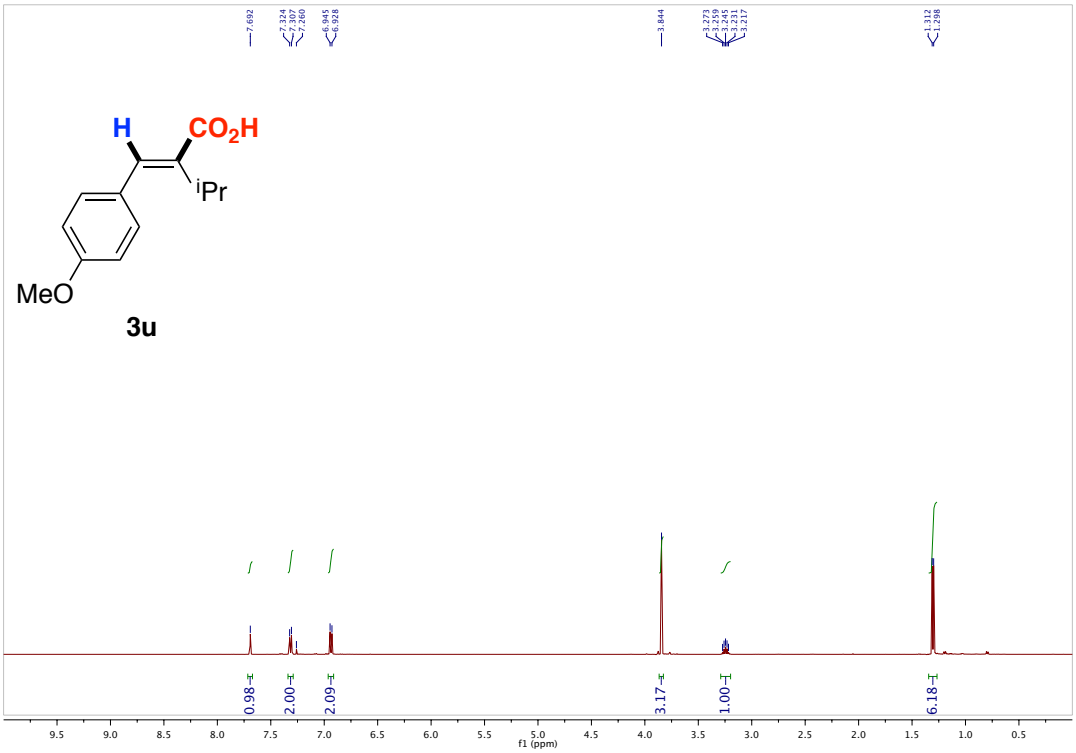

H
CO2H
Cy
CN
3s
1.92
0.95
2.05
0.97
2.00
2.07
1.19
2.13
3.24
f1 (ppm)

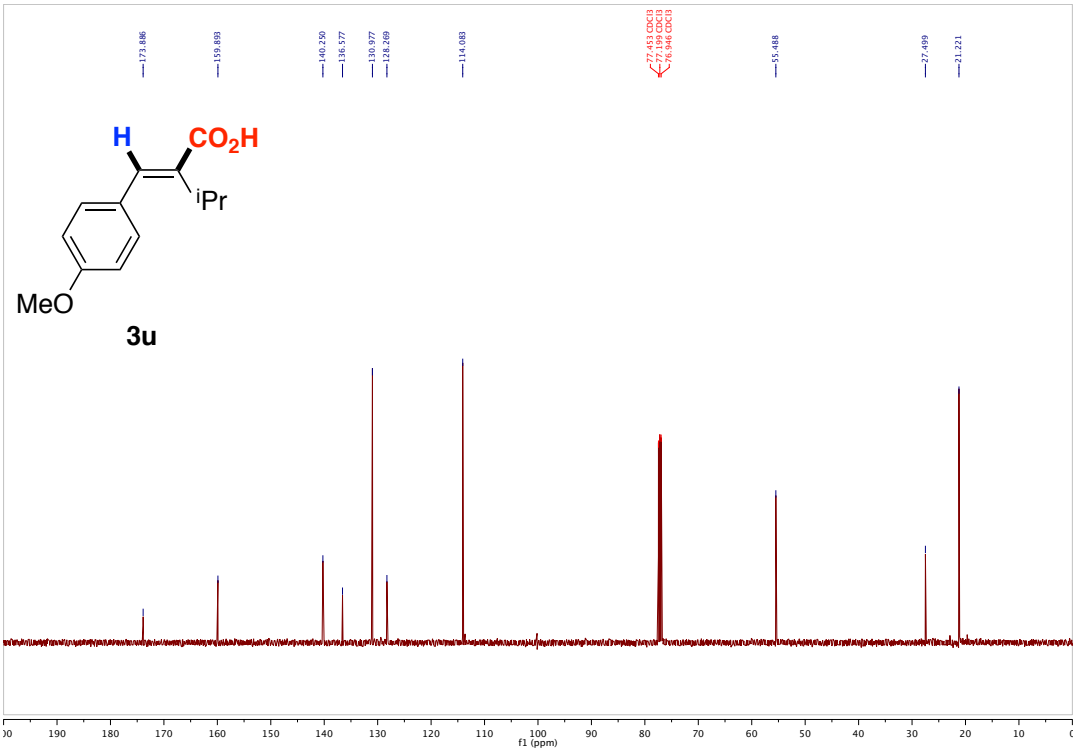

H
CO2H
Cy
CN
3s
173.242
140.127
137.946
137.162
133.201
132.371
131.784
129.543
118.552
113.028
77.453 CDCl3
77.199 CDCl3
76.945 CDCl3
38.933
30.770
26.635
25.822
f1 (ppm)

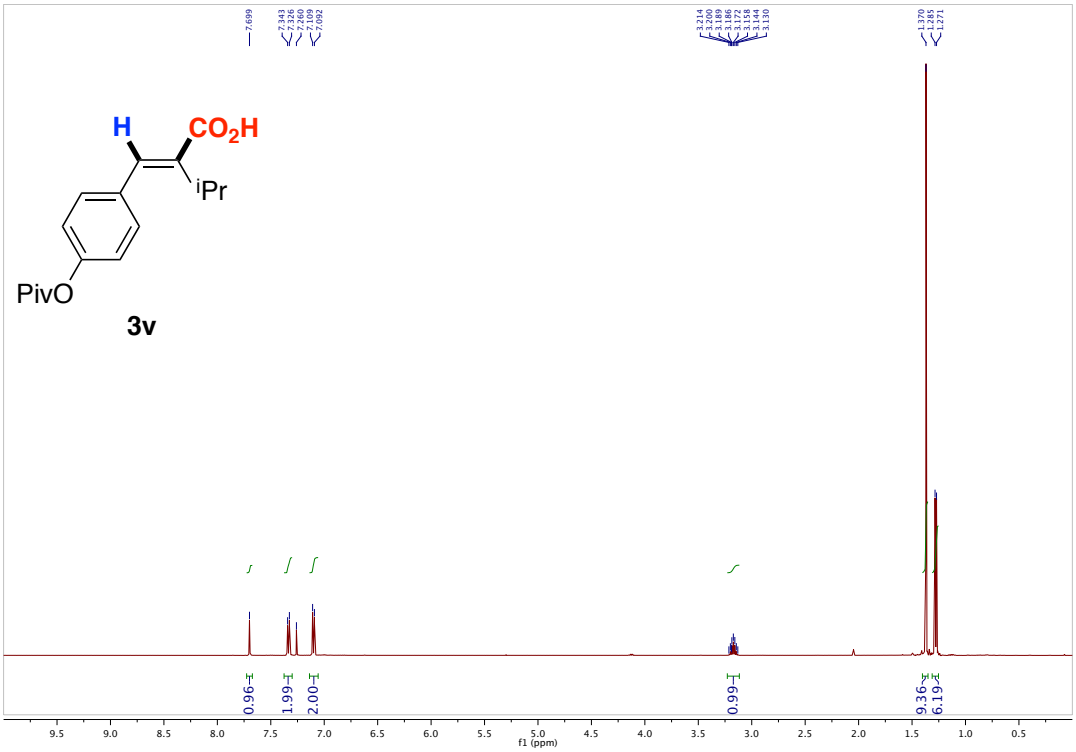

H
CO2H
iPr
F3CO
3t
7.731
7.393
7.376
7.291
7.224
3.194
3.180
3.166
3.152
3.138
1.336
1.322
0.95
2.00
2.08
1.00
6.03
f1 (ppm)

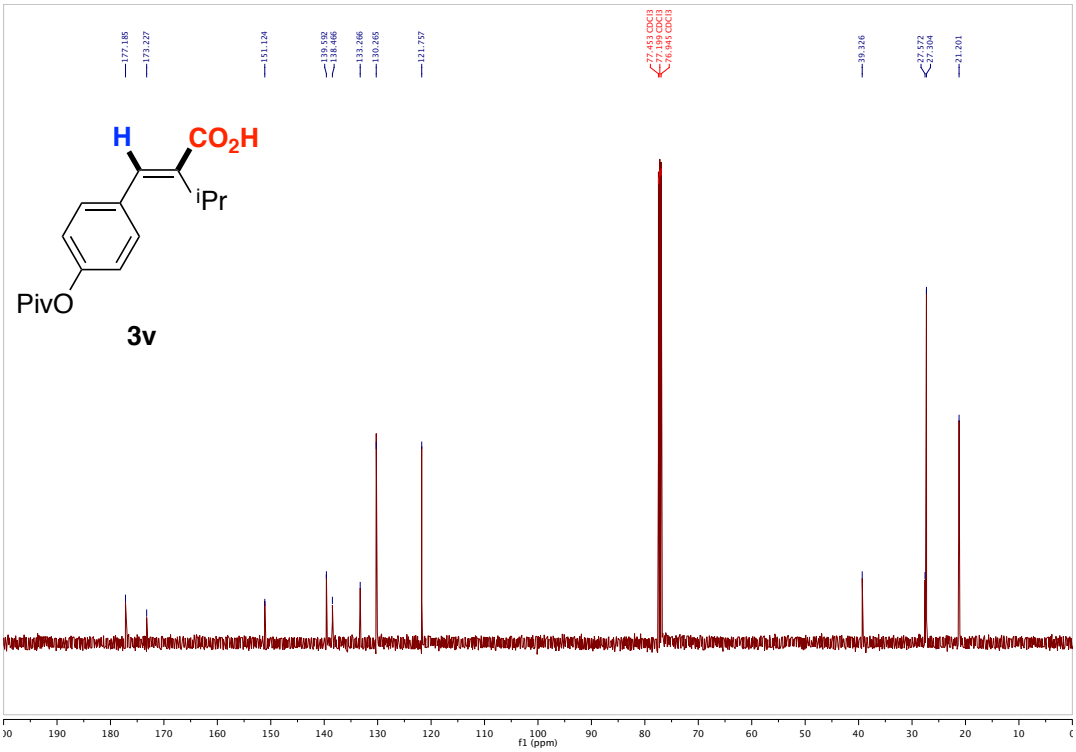

H
CO2H
iPr
F3CO
3t
173.765
149.128
139.207
138.958
134.441
130.643
123.700
121.652
121.043
119.603
117.355
77.452 CDCl3
77.198 CDCl3
76.945 CDCl3
27.654
21.162
f1 (ppm)

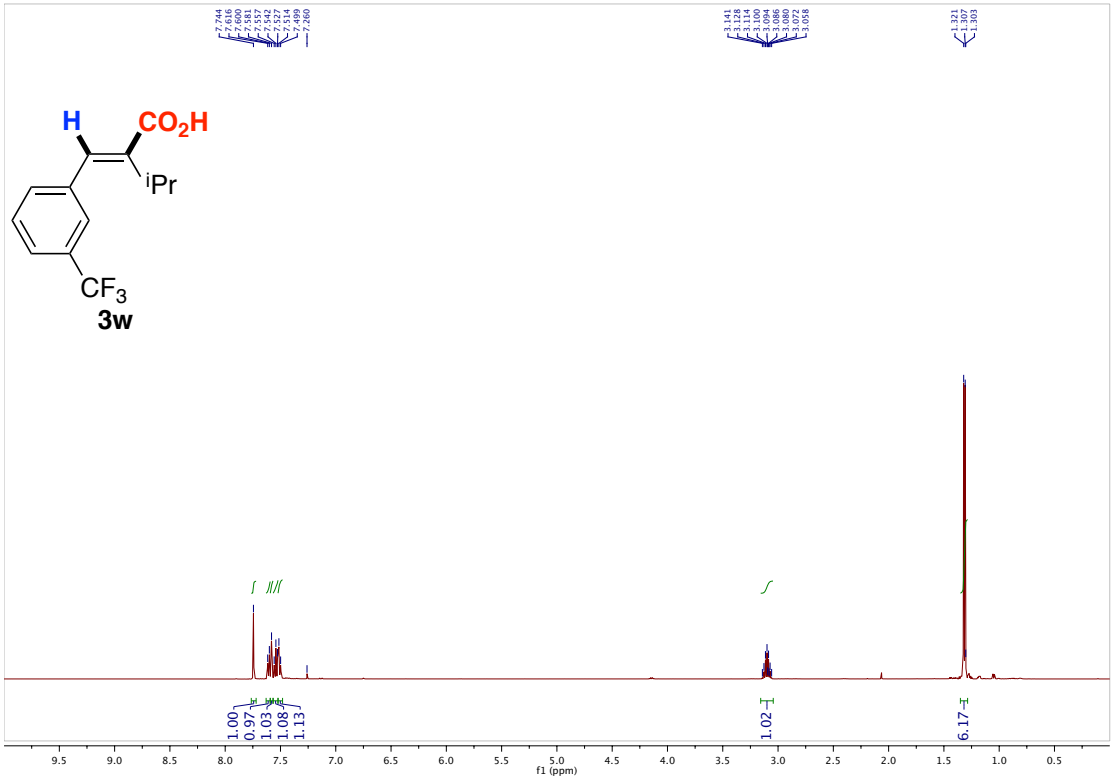

57.899
H
CO2H
iPr
F3CO
3t
f1 (ppm)

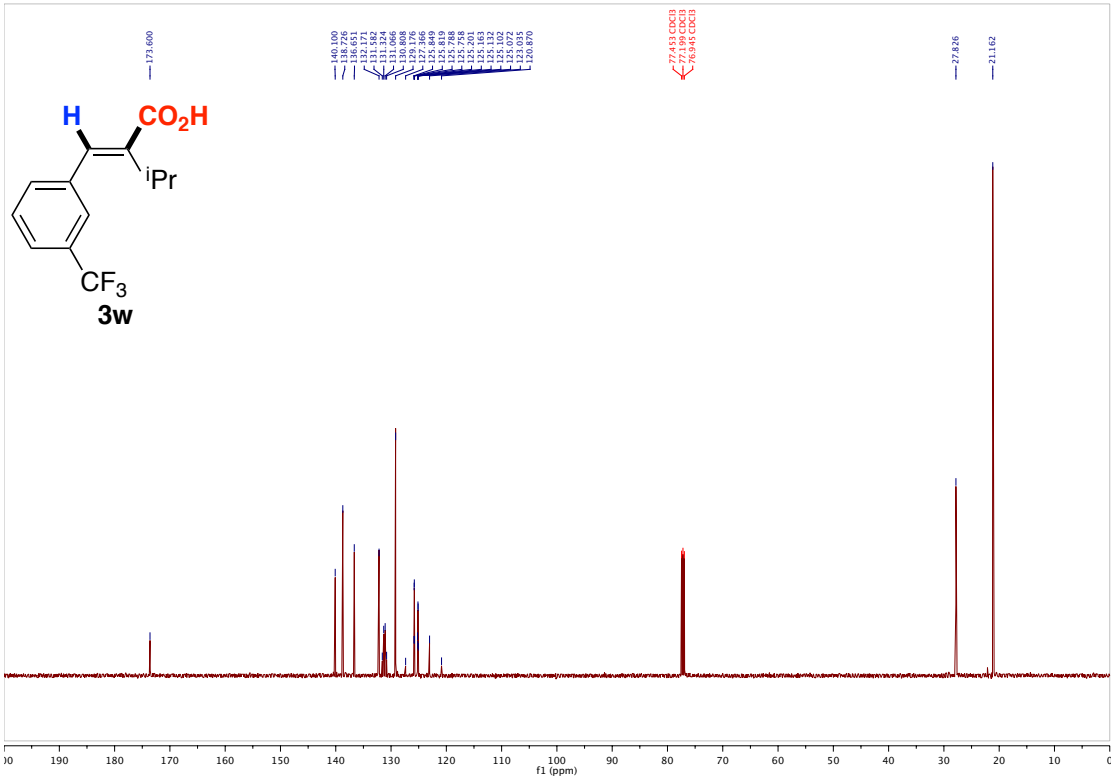

7.692
7.324
7.307
7.290
6.945
6.928
3.844
3.273
3.259
3.245
3.231
3.217
1.312
1.298
H
CO2H
iPr
MeO
3u
0.98
2.00
2.09
3.17
1.00
6.18
f1 (ppm)

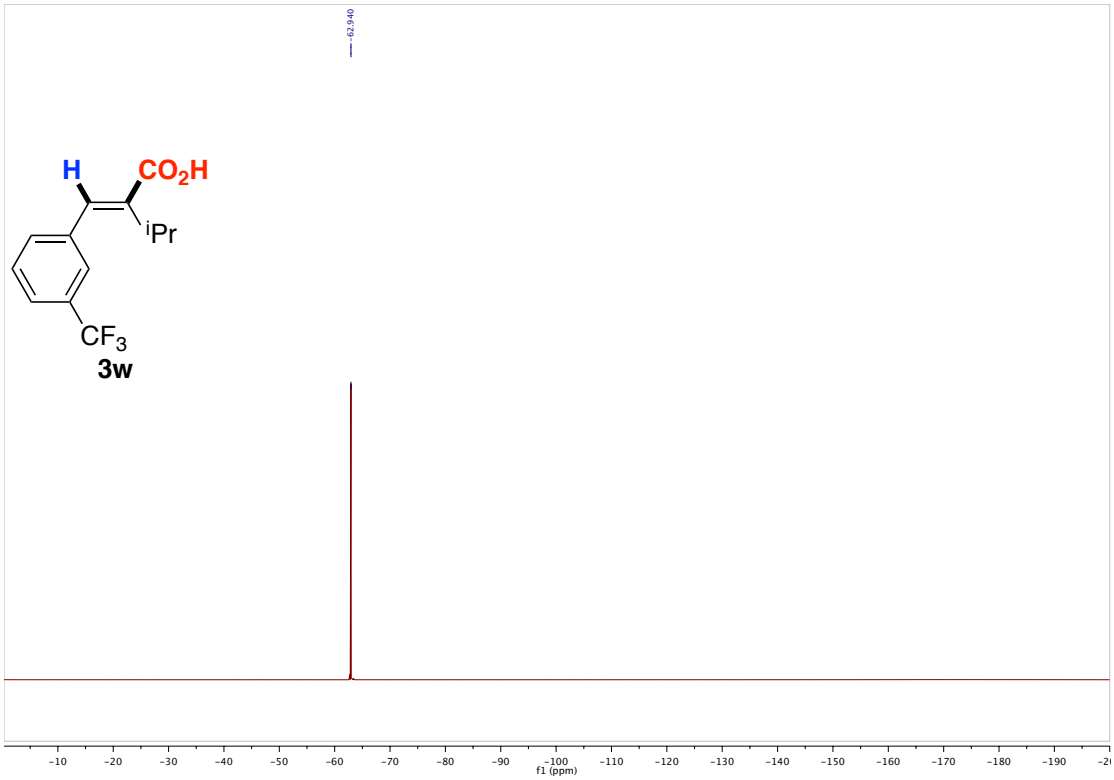

173.886
159.893
140.290
136.577
130.977
128.269
114.083
77.453 CDCl3
77.199 CDCl3
76.946 CDCl3
55.488
27.499
21.221
H
CO2H
iPr
MeO
3u
f1 (ppm)

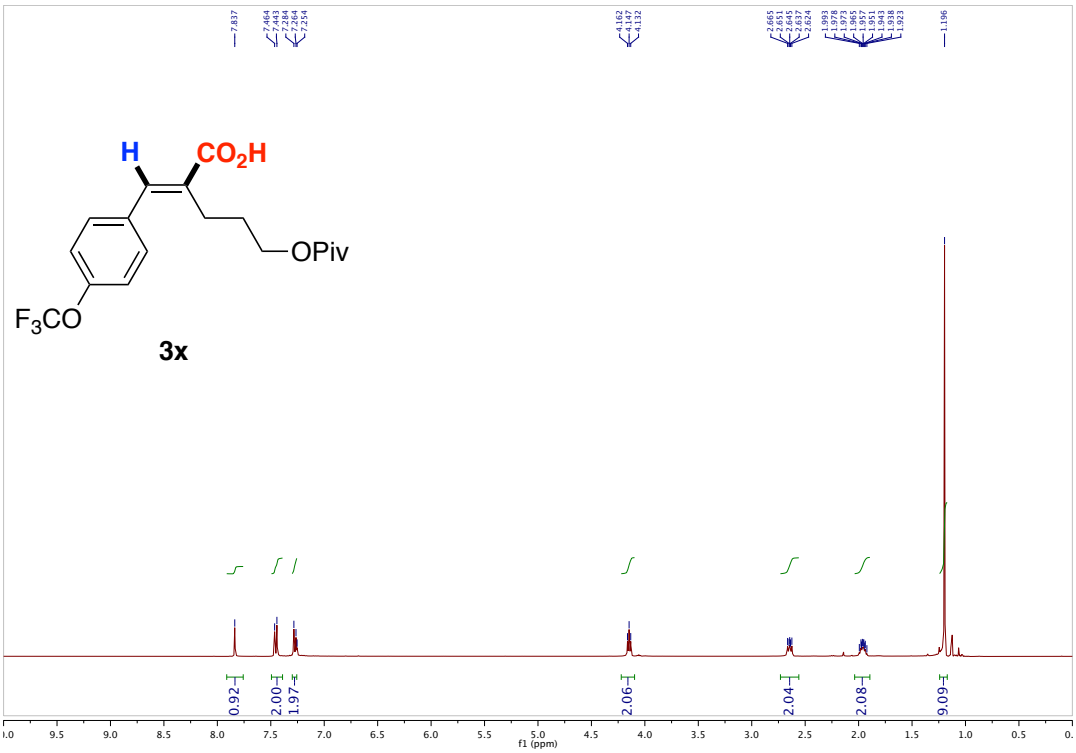

7.699
7.343
7.326
7.260
7.109
7.092
3.214
3.200
3.189
3.186
3.172
3.158
3.144
3.130
1.370
1.285
1.271
H
CO2H
iPr
PivO
3v
0.96
1.99
2.00
0.99
9.36
6.19
f1 (ppm)

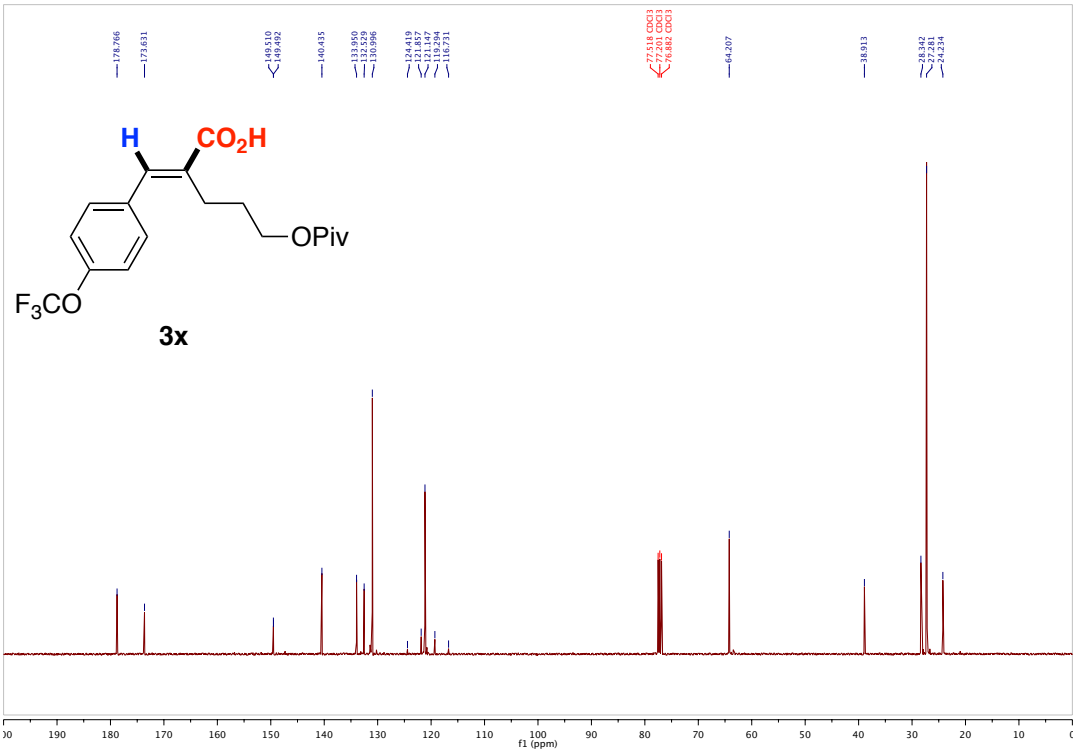

177.185
173.227
151.124
139.592
138.466
133.266
130.265
121.757
77.453 CDCl3
77.199 CDCl3
76.945 CDCl3
39.326
27.572
27.304
21.201
H
CO2H
iPr
PivO
3v
f1 (ppm)

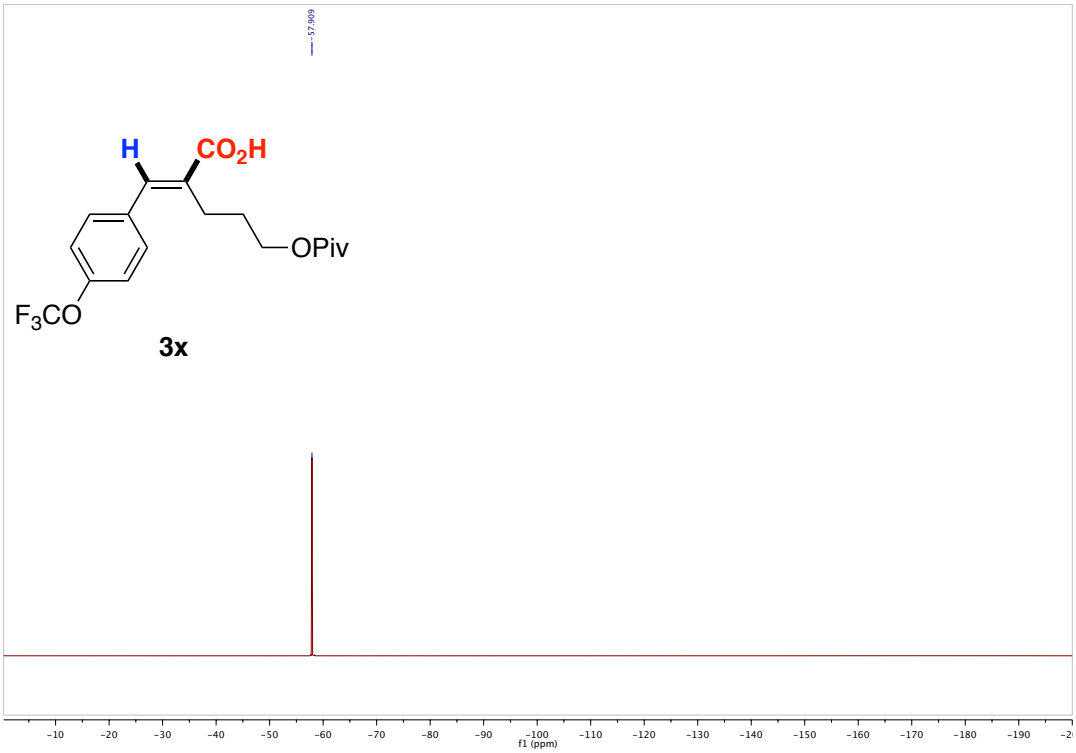

7.744
7.616
7.600
7.581
7.557
7.542
7.527
7.514
7.499
7.260
3.141
3.128
3.114
3.100
3.094
3.086
3.080
3.072
3.058
1.321
1.307
1.303
H
CO2H
iPr
CF3
3w
1.00
0.97
1.03
1.08
1.13
1.02
6.17
f1 (ppm)

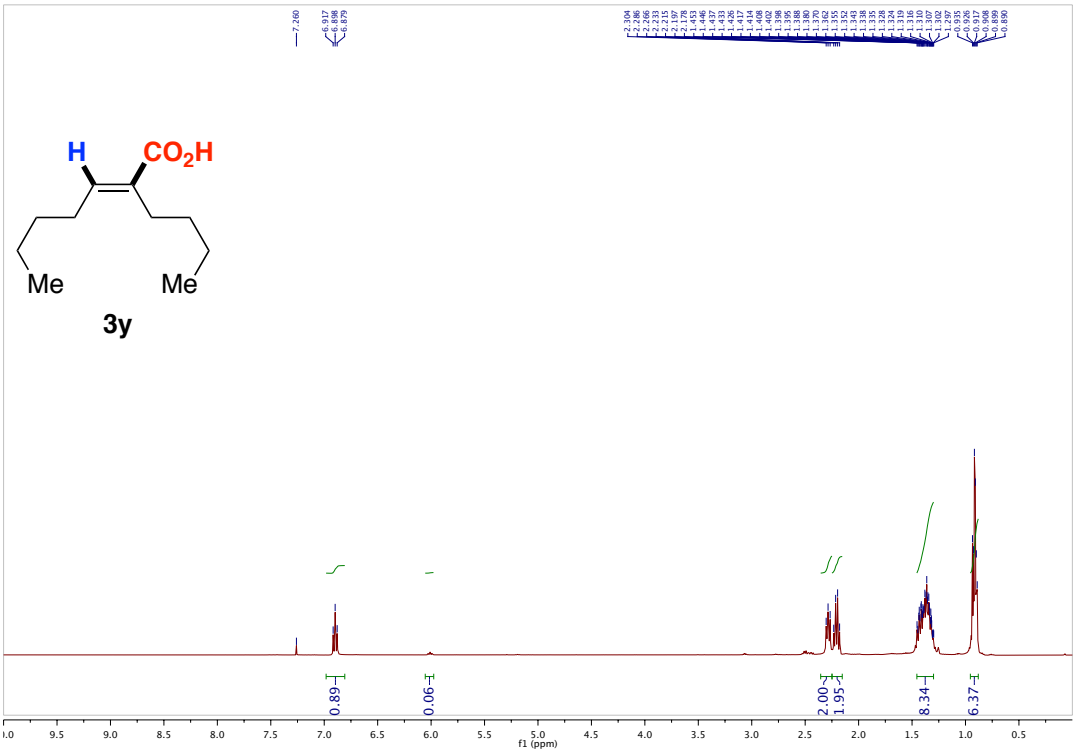

173.600
140.100
138.726
136.651
132.171
131.582
131.324
131.066
130.808
129.176
127.866
125.849
125.819
125.788
125.758
125.201
125.163
125.132
125.102
125.072
125.015
120.870
77.453 CDCl3
77.199 CDCl3
76.945 CDCl3
27.826
21.162
H
CO2H
iPr
CF3
3w
f1 (ppm)

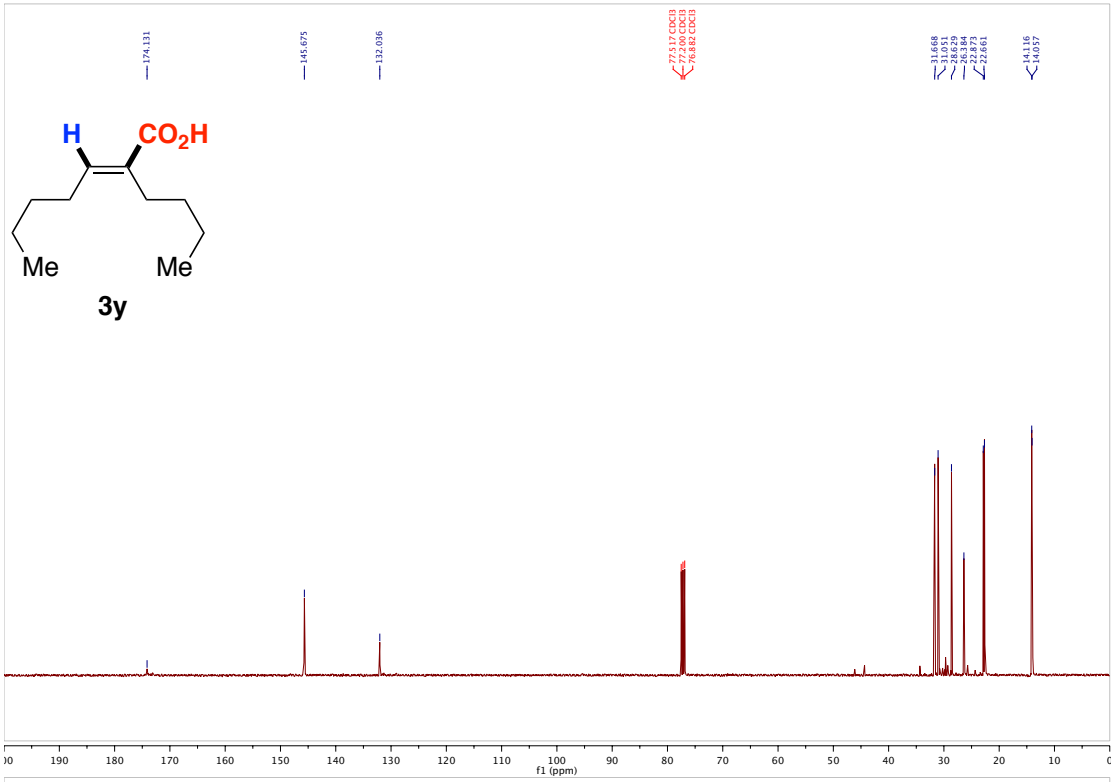

-62.940
H
CO2H
iPr
CF3
3w
f1 (ppm)

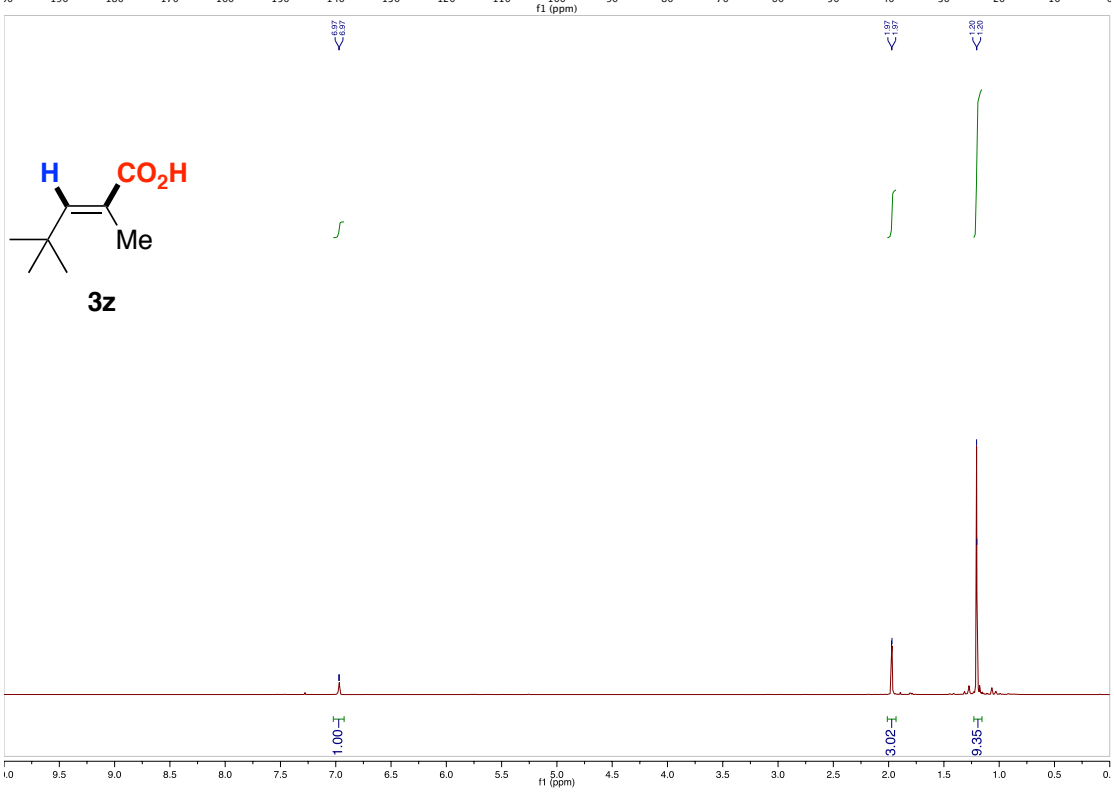

H
CO2H
OPiv
F3CO
3x
7.837
7.464
7.443
7.284
7.264
7.234
4.162
4.137
4.112
2.665
2.651
2.645
2.637
2.624
1.993
1.978
1.973
1.965
1.957
1.951
1.943
1.938
1.923
1.196
0.92
2.00
1.97
2.06
2.04
2.08
9.09
f1 (ppm)

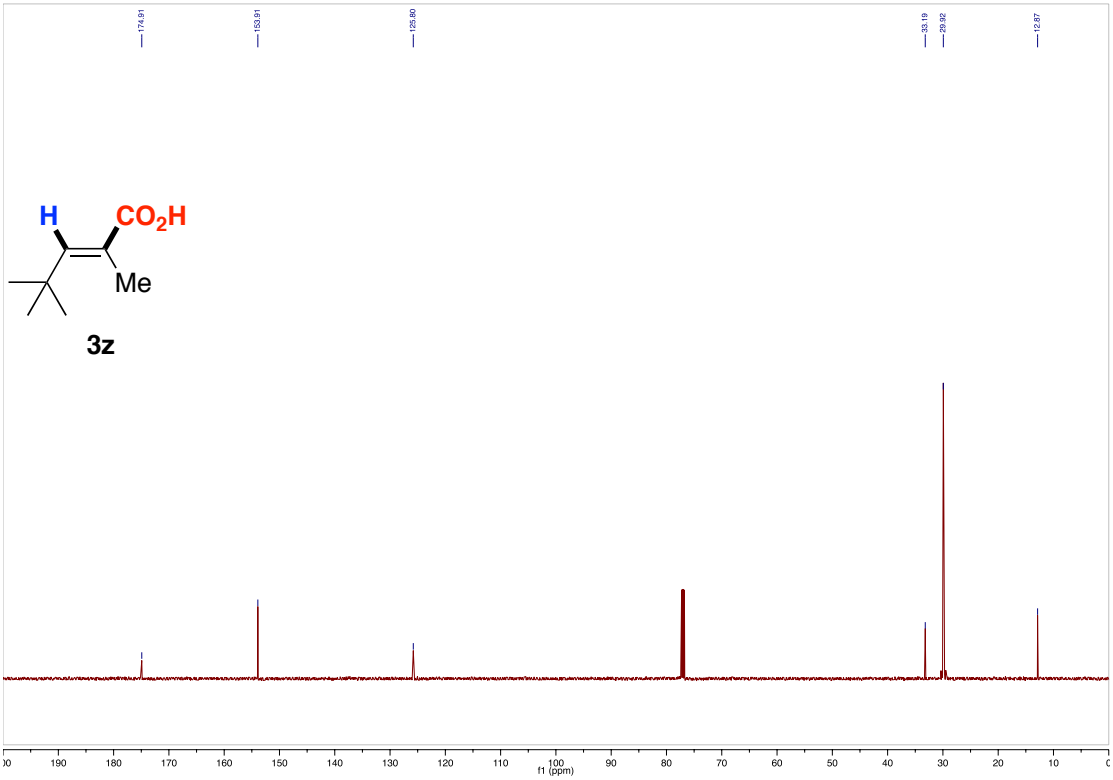

H
CO2H
OPiv
F3CO
3x
178.766
173.631
149.510
149.492
140.435
133.950
132.529
130.986
124.419
121.457
121.437
119.294
116.731
77.518 CDCl3
77.201 CDCl3
76.882 CDCl3
64.207
38.913
38.842
27.281
24.234
f1 (ppm)

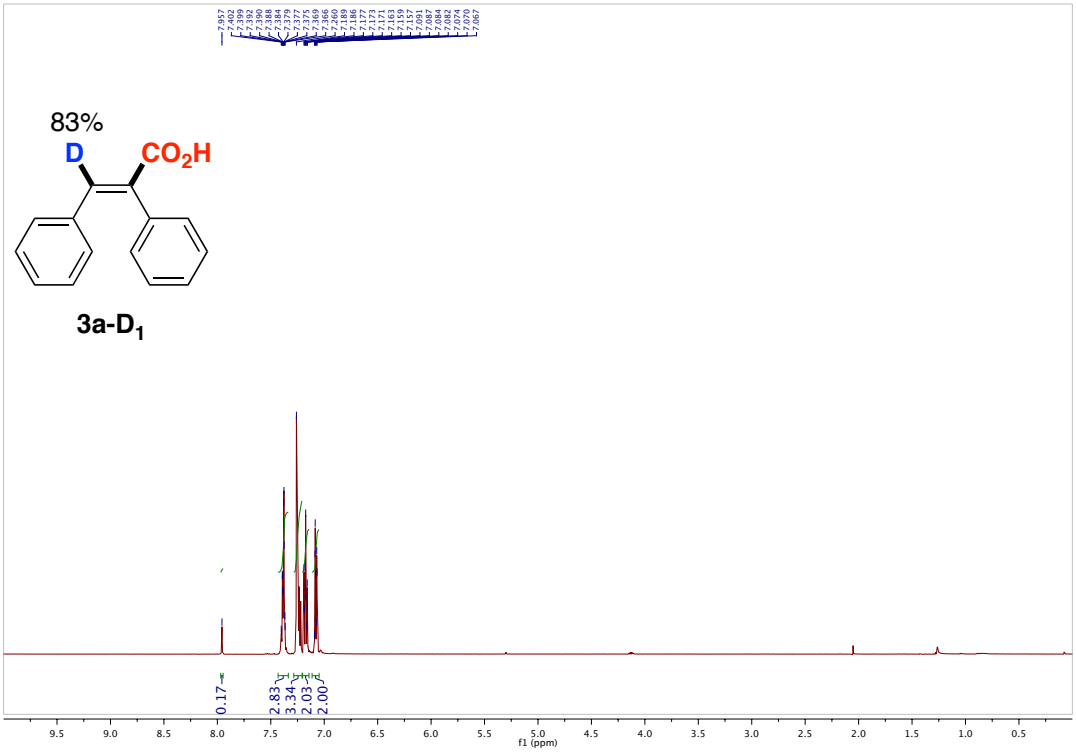

H
CO2H
OPiv
F3CO
3x
-57.909
f1 (ppm)

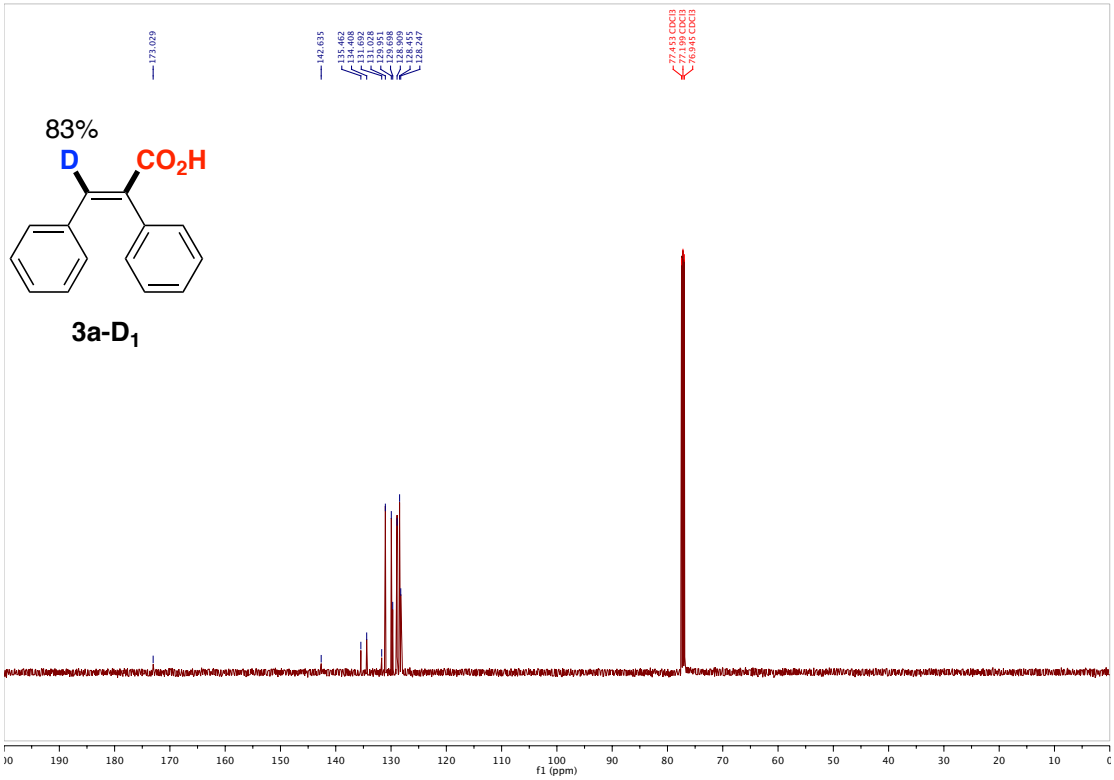

H
CO2H
Me
Me
3y
7.260
6.917
6.898
6.879
0.89
0.06
2.00
1.95
8.34
6.37
f1 (ppm)


174.131
145.675
132.036
77.517 CDCl3
77.200 CDCl3
76.882 CDCl3
31.668
31.051
28.629
28.384
22.873
22.661
14.116
14.057
H
CO2H
Me
Me
3y
f1 (ppm)


6.97
6.97
1.97
1.97
1.20
1.20
H
CO2H
Me
3z
1.00
3.02
9.35
f1 (ppm)


174.91
153.91
125.80
33.19
29.92
12.87
H
CO2H
Me
3z
f1 (ppm)


83%
D
CO2H
3a-D1
0.17
2.83
3.34
2.03
2.00
f1 (ppm)


173.029
142.635
135.462
134.698
131.692
131.028
130.351
129.698
128.909
128.455
128.247
77.453 CDCl3
77.199 CDCl3
76.945 CDCl3
83%
D
CO2H
3a-D1
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)