Supporting Information for:

Nickel-Catalyzed Hydrocarboxylation of Alkynes with Formic Acid

Jing Hou[a], Ming-Lei Yuan[a], Jian-Hua Xie[a], Qi-Lin Zhou*[,a,b]

[a] *State Key Laboratory and Institute of Elemento-organic Chemistry, Nankai University, Tianjin 300071, China*

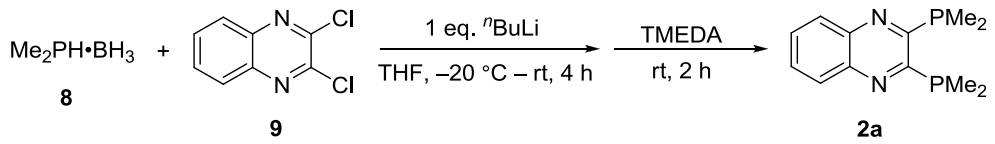
[b] *Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), Tianjin 300071, China*

CONTENTS:

General: Unless otherwise noted, the manipulations which are sensitive to moisture or air were performed in an argon-filled glove box MBRAUN labstar or using standard Schlenk techniques. NMR spectra were recorded on a Bruker AV 400 spectrometer at 400 MHz (^{1}H NMR), 100 MHz (^{13}C NMR) and 162 MHz (^{31}P NMR). Chemical shifts were reported in ppm down field from internal Me_4Si. Data are presented in the following space: chemical shift, multiplicity, coupling constant in hertz (Hz), and signal area integration in natural numbers. GC analyses were performed using a Hewlett Packard Model HP 7890 Series instruments. Acetylene gas (99.95%) was purchased from Boc Gas Inc., Tianjin. All the solvents used for reactions were distilled under argon after drying over an appropriate drying agent. All substrates containing stabilizing agents were distilled prior to use. All reagents were commercially supplied and used as received unless stated otherwise. **1d**[1], **3b – 3c**[2], **4**[3] **and 5c – 5d**[4] were synthesized according to the literatures.

(A) Preparation and Analysis of New Ligands

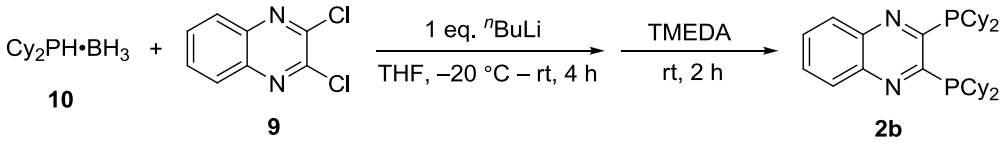
1. Preparation of 2,3-bis(dimethylphosphino)quinoxaline (2a)



A solution of ^{n}BuLi (4.2 mL of 2.4 M hexane solution, 10.0 mmol) was added dropwise to a stirred solution of dimethylphosphine–borane (**8**) (890 mg, 10 mmol) in THF (30 mL) at –20 ℃ under nitrogen. After 1 h, a solution of 2, 3-dichloroquinoxaline (**9**) (660 mg, 3.3 mmol) in THF (10 mL) was added in one portion with vigorous stirring and the mixture was warmed to room temperature. After stirring for an additional 3 h, tetramethylethylenediamine (5 mL) was added and the stirring was continued for 2 h. The reaction was quenched with 1 M HCl and the mixture was extracted with hexane. The combined extracts were washed with 1 M HCl and brine, and dried over Na_2SO_4. The solvent was removed in vacuum and the residue was purified by chromatography on silica gel (PE/EtOAc = 30/1) to give 2,3-bis(dimethylphosphino)quinoxaline (**2a**) (250 mg, 30 %) as a yellow solid.

Mp. 72 – 74 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (dd, *J* = 6.3, 3.5 Hz, 2H), 7.69 (dd, *J* = 6.4, 3.4 Hz, 2H), 1.48 (t, *J* = 1.8 Hz, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.20 – 166.35 (m), 142.19, 129.36, 129.20, 25.61. ^{31}P NMR (162 MHz, $CDCl_3$) δ –44.5 (s). HRMS (ESI) calcd for $C_{12}H_{17}N_2P_2^+$ ([M + H] $^+$): 251.0867; Found: 251.0865.

2. Preparation of 2,3-bis(dicyclohexylphosphino)quinoxaline (2b)



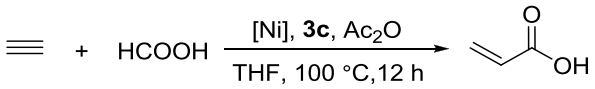
A solution of ^{n}BuLi (4.2 mL of 2.4 M hexane solution, 10.0 mmol) was added dropwise to a stirred solution of dicyclohexylphosphine–borane (**10**) (848 mg, 4 mmol) in THF (15 mL) at –20 ℃ under nitrogen. After 1 h, a solution of 2, 3-dichloroquinoxaline (**9**) (263 mg, 1.3 mmol)

in THF (5 mL) was added in one portion with vigorous stirring and the mixture was warmed to room temperature. After stirring for an additional 3 h, tetramethylethylenediamine (5 mL) was added and the stirring was continued for 2 h. The reaction was quenched with 1 M HCl and the mixture was extracted with hexane. The combined extracts were washed with 1 M HCl and brine, and dried over Na_2SO_4. The solvent was removed in vacuum and the residue was purified by chromatography on silica gel (PE/EtOAc = 30/1) to give 2,3-bis(dicyclohexylphosphino)-quinoxaline (**2b**) (120 mg, 17 %) as an orange solid.

Mp. 168 – 170 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ. 8.11 (dd, *J* = 6.3, 3.4 Hz, 2H), 7.74 (dd, *J* = 6.4, 3.4 Hz, 2H), 2.30 – 2.50 (m, 4H), 1.90 – 2.05 (m, 4H), 1.73 – 1.85 (m, 4H), 1.55 – 1.72 (m, 12H), 1.10 – 1.40 (m, 20H). ^{13}C NMR (101 MHz, $CDCl_3$) δ. 165.83 – 165.91 (m), 141.58, 129.55, 129.24, 34.52 (t, *J* = 4.6 Hz), 29.98 (t, *J* = 5.7 Hz), 29.76 (t, *J* = 7.1 Hz), 27.30 (dd, *J* = 10.5, 5.1 Hz), 25.61. ^{31}P NMR (162 MHz, $CDCl_3$) δ –5.6 (s). HRMS (ESI) calcd for $C_{12}H_{17}N_2P_2^+$ ($[M + H]^+$): 523.3371; Found:523.3368.

(B) Complementary Reaction Condition Optimizations

Table S1. Investigation on phosphine ligands for hydrocarboxylation of acetylene [a]



Entry	Ligand	L/Pd	TON[b]
1	-	-	NR
2	PPh_3	2	NR
3	PCy_3	2	NR
4	$P(OPh)_3$	2	NR
5	PBn_3	2	NR
6	dppe	1	NR
7	dppb	1	NR
8	dppf	1	NR
9	d^{t}bpf	1	NR

10	DPEphos	1	NR
11	Xantphos	1	NR
12	Triphos	1	NR

[a] Reaction conditions: $P(C_2H_2)$ = 10 atm, $Ni(acac)_2$ (5 μmol), Ligand (5 μmol), Ac_2O (0.75 mmol), HCOOH (1.5 mmol), in THF (3 mL) at 100 ℃ for 12 h. [b] Yield determined by GC analysis using *n*-hexadecane as internal standard; NR = no reaction. DPEphos = bis(diphenylphosphino-phenyl)ether; Xantphos = 4,5-bis(diphenyphosl-phino)-9,9-dimethyl-xanthene.

Table S2. Effect of solvents on the hydrocarboxylation of acetylene[a]

Entry	Solvent	TON[b]
1	THF	240
2	Et_2O	200
3	Dioxane	123
4	DME	95
5	DMF	25

[a] Reaction conditions: $P(C_2H_2)$ = 10 atm, $Ni(acac)_2$ (5 μmol), **3c** (10 μmol), HCOOH (1.5 mmol), in Solvent (3 mL) at 100 ^oC for 12 h. [b] Yield determined by GC analysis using *n*-Hexadecane as internal standard;

Table S3. Effect of the dosage of Ac_2O on the hydrocarboxylation of acetylene.[a]

Entry	[Ac_2O] (μmol)	TON[b]
1	750	170
2	375	245
3	180	240
4	90	238
5	45	240
6	22	80

[a] Reaction conditions: $P(C_2H_2)$ = 10 atm, $Ni(acac)_2$ (5 μmol), **3c** (10 μmol), HCOOH (1.5 mmol), in THF (3 mL) at 100 ^oC for 12 h. [b] Yield determined by GC analysis using *n*-Hexadecane as internal standard;

Table S4. Effect of initial pressure on the hydrocarboxylation of acetylene.[a]

Entry	P (atm)	TON[b]
1	1	300
2	3	300
3	5	290
4	7	277
5	10	240

[a] Reaction conditions: $Ni(acac)_2$ (5 μmol), **3c** (10 μmol), Ac_2O (45 μmol), HCOOH (1.5 mmol), in THF (3 mL) at 100 °C for 12 h. [b] Yield determined by GC analysis using *n*-Hexadecane as internal standard;

Table S5. Effect of reaction temperature on the hydrocarboxylation of acetylene[a]

Entry	T (°C)	TON[b]
1	25	30
2	40	140
3	60	300
4	80	300
5	100	300
6	120	280

[a] Reaction conditions: initial pressure $P(C_2H_2)$ = 1 atm, $Ni(acac)_2$ (5 μmol), **3c** (10 μmol), Ac_2O (45 μmol), HCOOH (1.5 mmol), in THF (3 mL) at 100 °C for 12 h. [b] Yield determined by GC analysis using *n*-Hexadecane as internal standard.

Table S6. Effect of the ratio of 3c/[Ni] on the hydrocarboxylation of acetylene under the condition of S/C = 10000[a]

Entry	**3c**/[Ni]	P (C_2H_2)	T (°C)	TON[b]
1	2	1	60	300
2	8	1	60	460
3	14	1	60	430
4	20	1	60	308

5	2	1	100	650
6	8	1	100	930
7	14	1	100	1400
8	20	1	100	2350
9	26	1	100	670
10	2	10	100	340
11	8	10	100	3500
12	14	10	100	4400
13	20	10	100	7700
14	26	10	100	2700

[a] Reaction conditions: initial pressure $Ni(acac)_2$ (0.15 μmol), Ac_2O (45 μmol), HCOOH (1.5 mmol), in THF (3 mL) at 100 ^oC for 12 h. [b] Yield determined by GC analysis using *n*-Hexadecane as internal standard

(C) General Procedure for Hydrocarboxylation of Acetylene

General procedure for the hydrocarboxylation of acetylene. In a glove box, a glass vessel was charged with $Ni(acac)_2$ (1.3 mg, 5 μmol), **3c** (2.8 mg, 10 μmol). The vessel was placed into the autoclave and the autoclave was purged three times with argon. A solution of HCOOH (69 mg, 1.5 mmol) and Ac_2O (4.6 mg, 45 μmol) in dry THF (3 mL) was added through the injection port. The autoclave was replaced with acetylene for three times before it was finally charged with 10 atm acetylene. The reaction mixture was stirred at 100 ℃. After 12 h the autoclave was cooled to the room temperature, and the pressure was released. After adding *n*-hexadecane as an internal standard, the mixture was filtered through a short silica column and submitted to analysis of yield of acrylic acid by GC (using column HP-INNOWAX, 30 m× 0.25 mm × 0.25 μm, flame ionization detector (FID) operating at 250 ℃. Injector temperature was set at 230 ℃. The carrier gas was nitrogen with a flow rate of 1.0 mL/min). The following temperature program was used in the analysis: 120 ℃ (4 min) – 10 ^oC/min – 250 ℃ (10 min). Using these conditions, the following retention times were observed: *n*-hexadecane (6.380 min), acrylic acid (6.997 min).

General procedure for the hydrocarboxylation of other alkynes. The general hydrocarboxylation procedure will be illustrated with a specific example. In a glove box, a glass vessel was charged with $Ni(acac)_2$ (2.6 mg, 10 μmol), **3c** (5.6 mg, 20 μmol). The vessel was placed into the autoclave and then the autoclave was purged three times with argon. A solution of phenylacetylene (51 mg, 0.5 mmol), HCOOH (69 mg, 1.5 mmol) and Ac_2O (15.3 mg, 0.15 mol) in dry THF (3 mL) was added through the injection port. The reaction mixture was stirred at 100 ℃. After 12 h the autoclave was cooled to the room temperature. The reaction mixture was transferred to a round bottom flask and the solvent was evaporated in vacuum. The residue was purified with silica gel chromatography using PE/EA (2/1, v/v) as an eluent.

(D) Gas Chromatogram of Hydrocarboxylation of Acetylene with FA

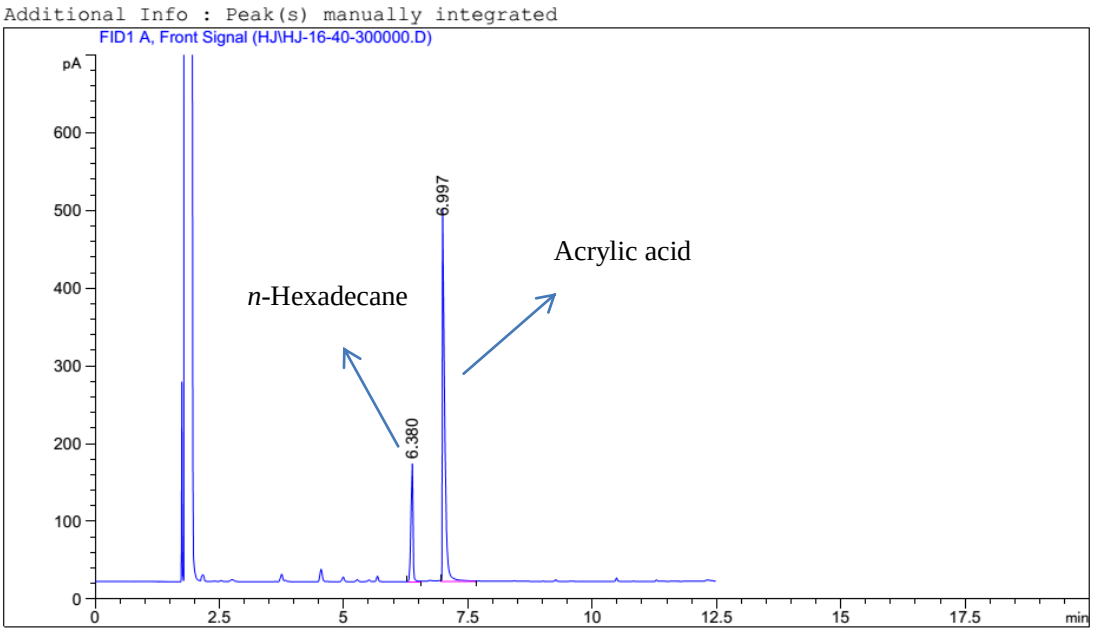
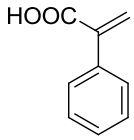


Figure S1. Representative chromatogram (Table S5, entry 3) (Temperature program was used in the analysis: 120 ℃ (4 min) – 10 ℃/min – 250 ℃ (10 min))

(E) Analytical Data of the Hydrocarboxylation Products

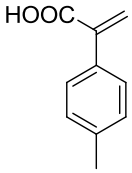
2-phenylacrylic acid (6a)



White solid, 88% yield (mixture of **6a** and **7a**, **6a** /**7a** = 97/3). NMR of **6a**: ^1H

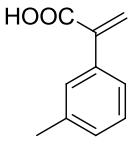
NMR (400 MHz, $CDCl_3$): δ 12.47 (brs, 1H), 7.42 – 7.50 (m, 2H), 7.32 – 7.42 (m, 3H), 6.57 (s, 1H), 6.05 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.51, 140.55, 136.00, 129.60, 128.43, 128.33, 128.10.

2-*p*-tolylacrylic acid (6b)



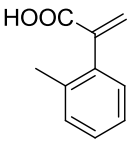
White solid, 89% yield (mixture of **6b** and **7b**, **6b** /**7b** = 97/3). NMR of **6b**: ^1H NMR (400 MHz, $CDCl_3$): δ 12.24 (brs, 1H), 7.35 (d, *J* = 7.1 Hz, 2H), 7.19 (d, *J* = 7.3 Hz, 2H), 6.51 (s, 1H), 6.01 (s, 1H), 2.38 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.60, 140.43, 138.25, 133.16, 128.82, 128.80, 128.30, 21.16.

2-*m*-tolylacrylic acid (6c)



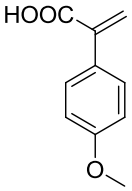
White solid, 85% yield (mixture of **6c** and **7c**, **6c**/**7c** = 96/4). NMR of **6c**: ^1H NMR (400 MHz, $CDCl_3$): δ 12.34 (brs, 1H), 7.25 – 7.35 (m, 3H), 7.20 – 7.25 (m, 1H), 6.57 (s, 1H), 6.05 (s, 1H), 2.42 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.39, 140.75, 137.74, 136.03, 129.22, 129.11, 128.03, 125.53, 21.39

2-*o*-tolylacrylic acid (6d)



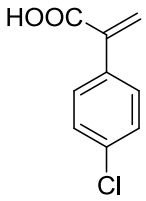
White solid, 28% yield (mixture of **6d** and **7d**, **6d**/**7d** = 98/2). NMR of **6d**: ^1H NMR (400 MHz, $CDCl_3$): δ 11.83 (brs, 1H), 7.10 – 7.30 (m, 4H), 6.64 (d, *J* = 1.5 Hz, 1H), 5.84 (d, *J* = 1.5 Hz, 1H), 2.24 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.98, 141.10, 136.42, 136.18, 130.90, 129.91, 129.52, 128.38, 125.67, 19.85.

2-(4-methoxyphenyl)acrylic acid (6e)



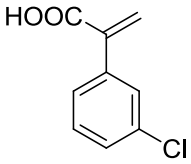
White solid, 84% yield (mixture of **6e** and **7e**, **6e** /**7e** = 93/7). NMR of **6e**: ^1H NMR (400 MHz, $CDCl_3$): δ 12.18 (brs, 1H), 7.40 (d, *J* = 7.5 Hz, 2H), 6.91 (d, *J* = 7.6 Hz, 2H), 6.48 (s, 1H), 3.83 (s, 3H), 5.98 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.63, 159.63, 139.89, 129.65, 128.46, 128.03, 113.50, 55.23

2-(4-chlorophenyl)acrylic acid (6f)



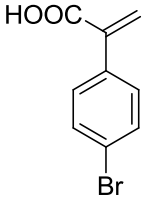
White solid, 83% yield (mixture of **6f** and **7f**, **6f** /**7f** = 97/3). NMR of **6f**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 12.48 (brs, 1H), 7.30 – 7.42 (m, 4H), 6.57 (s, 1H), 6.04 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.99, 139.54, 134.50, 134.47, 130.06, 129.86, 128.39.

2-(3-chlorophenyl)acrylic acid (6g)



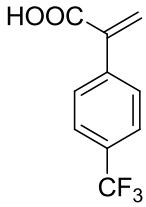
White solid, 80% yield (mixture of **6g** and **7g**, **6g**/**7g** = 95/5). NMR of **6g**: ^{1}H NMR (400 MHz, $CDCl_3$): 12.46 (brs, 1H), δ 6.46 (s, 1H), 6.62 (s, 1H), 7.28 – 7.38 (m, 3H), 7.26 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.90, 139.34, 137.64, 133.98, 130.68, 129.36, 128.58, 128.43, 126.67.

2-(4-bromophenyl)acrylic acid (6h)



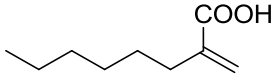
White solid, 80% yield (mixture of **6h** and **7h**, **6h**/**7h** = 95/5). NMR of **6h**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 12.16 (brs, 1H), 7.49 (s, 2H), 7.30 (s, 2H), 6.57 (s, 1H), 6.04 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.91, 139.48, 134.83, 131.30, 130.14, 130.10, 122.69.

2-(4-(trifluoromethyl)phenyl)acrylic acid (6i)



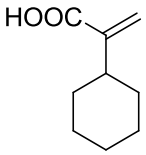
White solid, 80% yield (mixture of **6i** and **7i**, **6i**/**7i** = 95/5). NMR of **6i**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 12.38 (brs, 1H), 7.64 (d, *J* = 8.0 Hz, 2H), 7.57 (d, *J* = 8.1 Hz, 2H), 6.67 (s, 1H), 6.11 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.82, 139.49, 131.36, 128.90, 125.13, 125.10.

2-methyleneoctanoic acid (6j)



Colourless oil, 64% yield (mixture of **6j** and **7j**, **6j**/**7j** = 93/7). NMR of **6j**: ^{1}H NMR (400 MHz, $CDCl_3$): ^{1}H NMR (400 MHz, $CDCl_3$): δ 12.39 (brs, 1H), 6.29 (s, 1H), 5.64 (s, 1H), 2.29 – 2.31 (m, 2H), 1.42 – 1.53 (m, 2H), 1.22 – 1.38 (m, 6H), 0.85 – 0.92 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.3, 140.3, 126.9, 31.6, 31.4, 28.9, 28.3, 22.6, 14.1.

2-cyclohexylacrylic acid (6k)



White solid, 61% yield (mixture of **6k** and **7k**, **6k**/**7k** = 87/13). NMR of **6k**: ^{1}H NMR (400 MHz, $CDCl_3$): 12.14 (brs, 1H), δ 6.29 (s, 1H), 5.60 (s, 1H), 2.40 – 2.46 (m, 1H), 1.65 – 1.90 (m, 5H), 1.05 – 1.40 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.13, 145.59, 124.67, 38.69, 32.48, 26.55, 26.16.

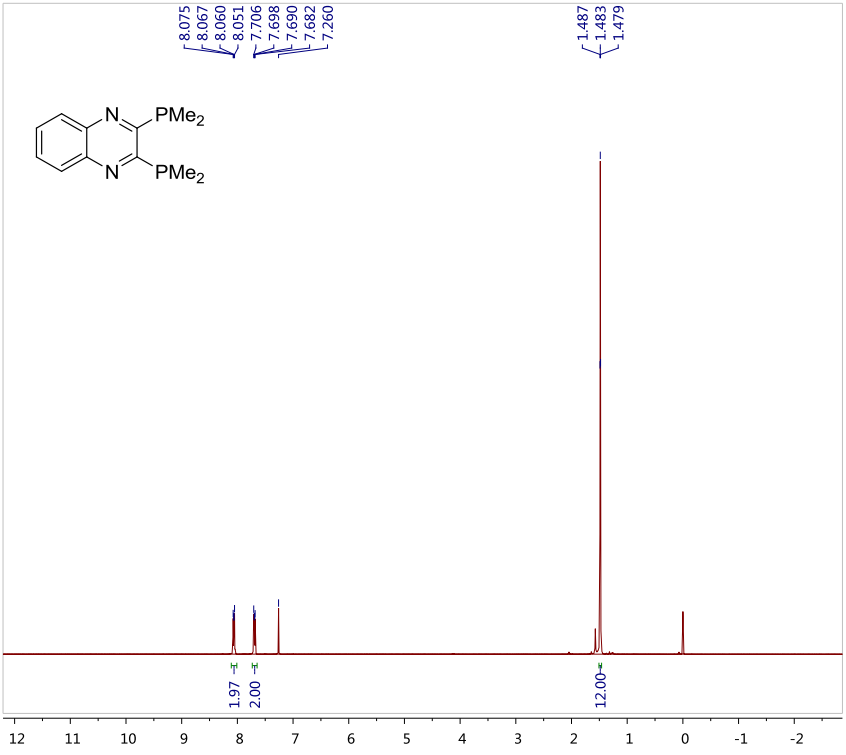
[1] W. Scherer, V. Herz, A. Bruck, C. Hauf, F.Reiner, S. Altmannshofer, D. Leusser, and D. Stalke, *Angew. Chem. Int. Ed.* 2011, **50**, 2845 –2849.

[2] E. P. Kyba, M. C. Kerby, and S. P. Rines, *Organometallics*, 1986, **5**, 1189–1194.

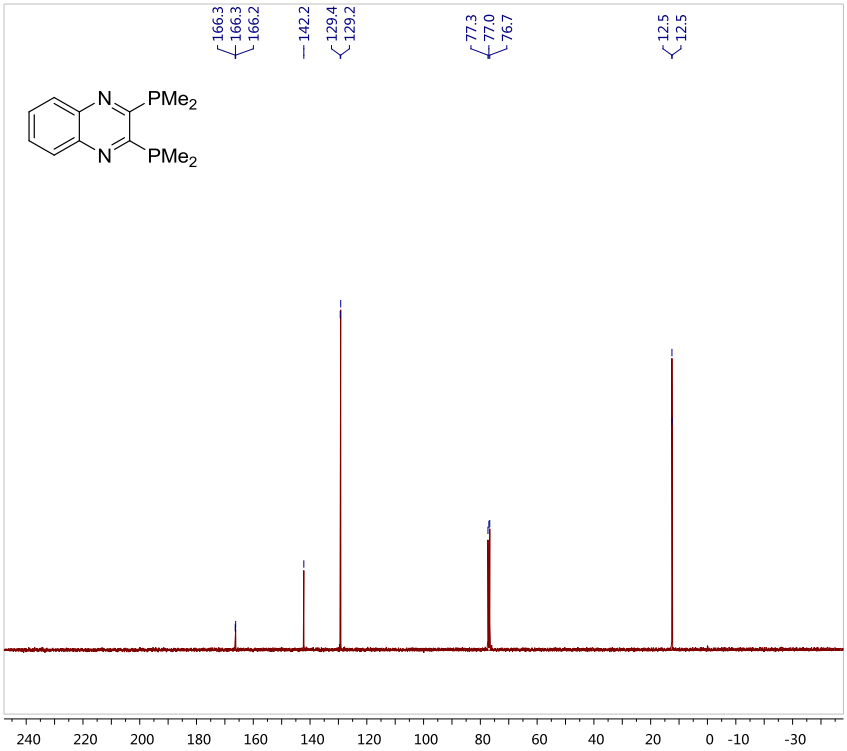
[3] R. Takise, K. Muto, J. Yamaguchi, and K. Itami, *Angew. Chem. Int. Ed.* 2014, **126**, 6909–6912.

[4] C. Xu, W. Du, Y. Zeng, B. Dai, and H. Guo, *Org. Lett.* 2014, **16**, 948–951.

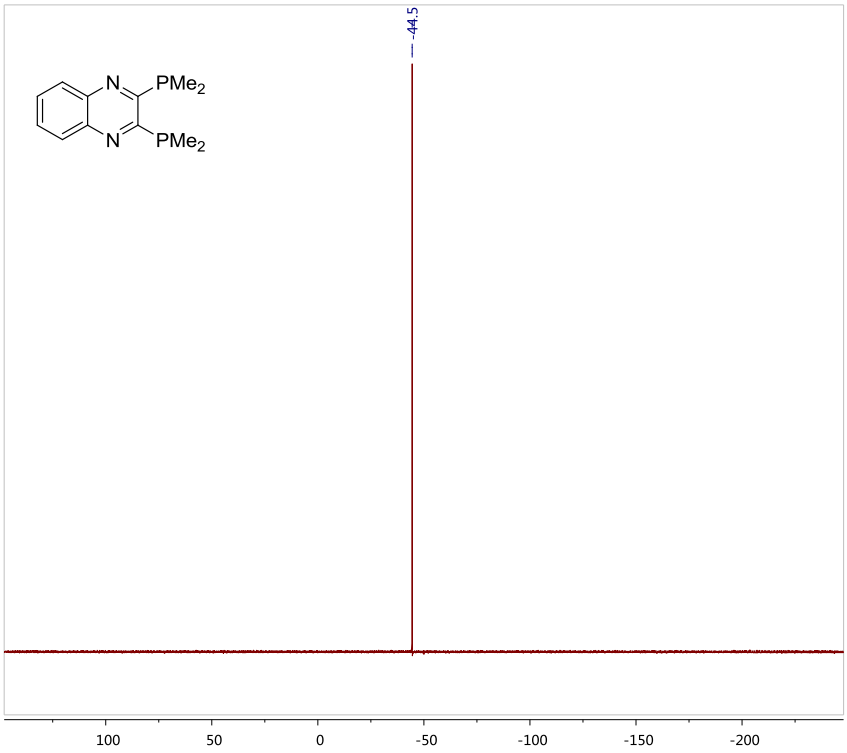
(F) NMR Spectra of New Compounds and Products



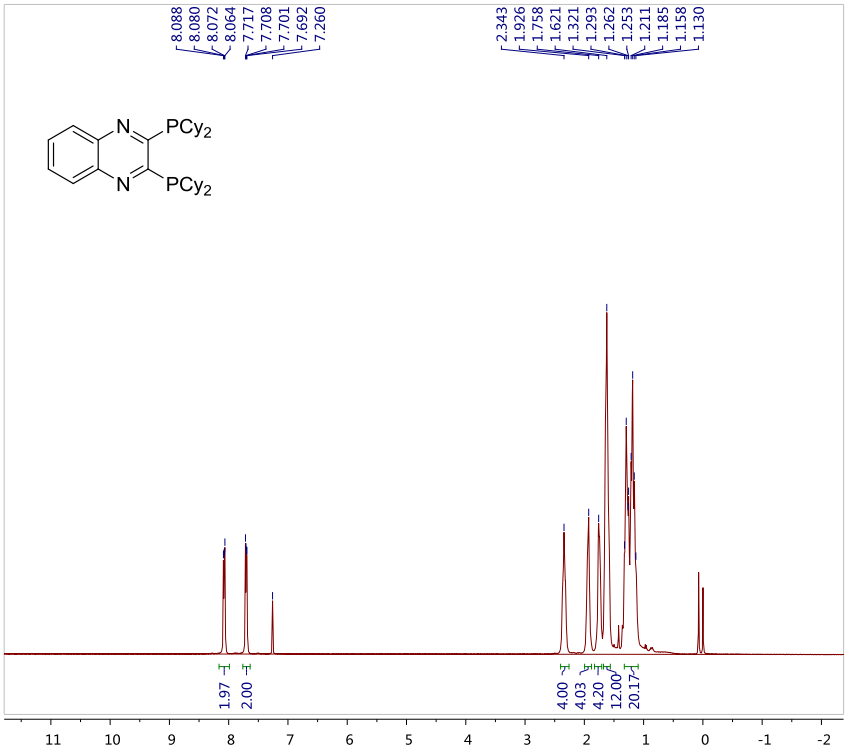
	Parameter	Value
1	Data File Name	Z:/ Data/ NMR/ 2015年/ 2015-07/ hj-15-92/ 1/ fid
2	Title	hj-15-92
3	Comment	PROTON
4	Origin	Bruker BioSpin GmbH
5	Owner	nmr
6	Site	
7	Spectrometer	spect
8	Author	
9	Solvent	CDCl3
10	Temperature	297.2
11	Pulse Sequence	zg30
12	Experiment	1D
13	Number of Scans	8
14	Receiver Gain	203
15	Relaxation Delay	1.0000
16	Pulse Width	13.7000
17	Acquisition Time	1.9999
18	Acquisition Date	2015-07-06T19:17:00
19	Modification Date	2015-07-06T19:17:00
20	Spectrometer Frequency	400.13
21	Spectral Width	8223.7
22	Lowest Frequency	-1640.9
23	Nucleus	1H
24	Acquired Size	16446
25	Spectral Size	65536



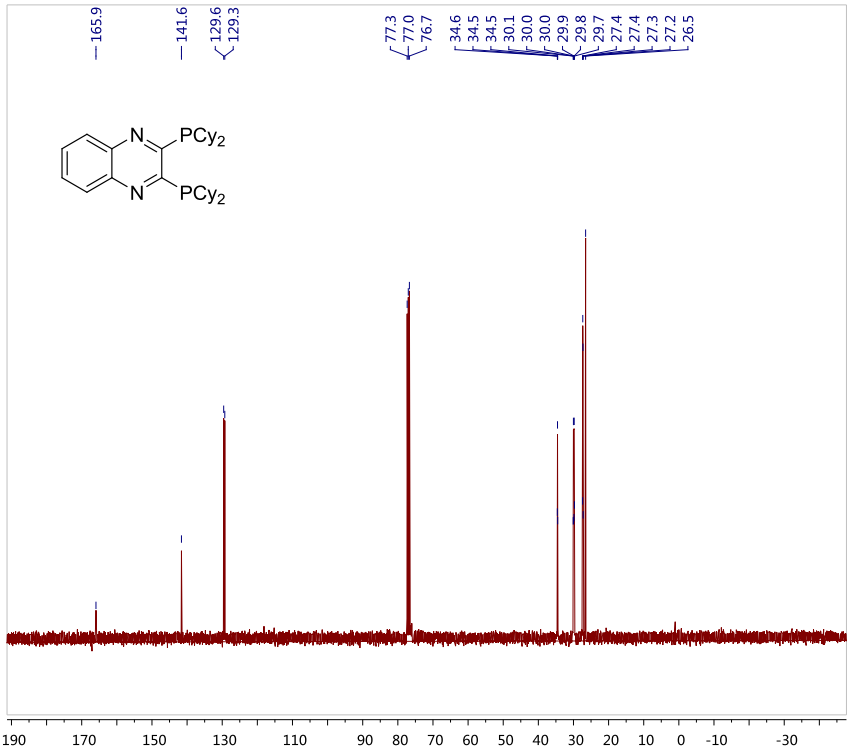
	Parameter	Value
1	Data File Name	Z:/ Data/ NMR/ 2016-01/ hj-2016-1-17-Me/ 1/ fid
2	Title	hj-2016-1-17-Me
3	Comment	C13CPD
4	Origin	Bruker BioSpin GmbH
5	Owner	common
6	Site	
7	Spectrometer	spect
8	Author	
9	Solvent	CDCl3
10	Temperature	2494.6
11	Pulse Sequence	zgpg30
12	Experiment	1D
13	Number of Scans	903
14	Receiver Gain	203
15	Relaxation Delay	1.0000
16	Pulse Width	12.0000
17	Acquisition Time	0.5506
18	Acquisition Date	2016-01-16T09:27:00
19	Modification Date	2016-01-16T09:51:00
20	Spectrometer Frequency	100.64
21	Spectral Width	29761.9
22	Lowest Frequency	-4817.6
23	Nucleus	13C
24	Acquired Size	16384
25	Spectral Size	32768



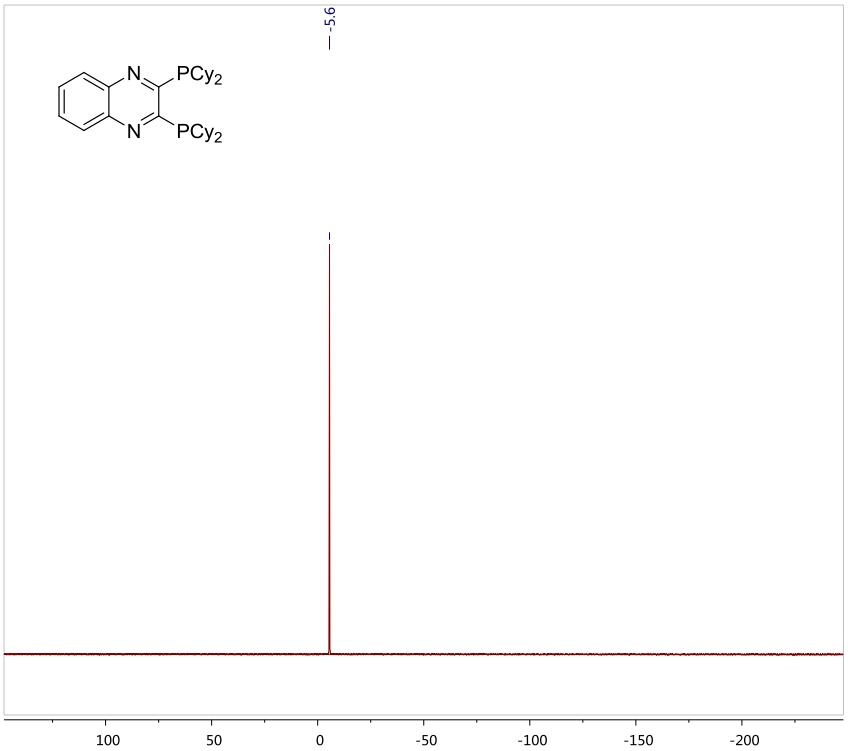
	Parameter	Value
1	Data File Name	Z:/ Data/ NMR/ 2015 4F/ 2015-07/ hj-15-92/ 2/ fid
2	Title	hj-15-92
3	Comment	P31CPD
4	Origin	Bruker BioSpin GmbH
5	Owner	nmr
6	Site	
7	Spectrometer	spect
8	Author	
9	Solvent	CDCl3
10	Temperature	297.6
11	Pulse Sequence	zgpg30
12	Experiment	1D
13	Number of Scans	16
14	Receiver Gain	203
15	Relaxation Delay	1.0000
16	Pulse Width	11.0000
17	Acquisition Time	0.5112
18	Acquisition Date	2015-07-06T19:19:00
19	Modification Date	2015-07-06T19:19:00
20	Spectrometer Frequency	161.98
21	Spectral Width	64102.6
22	Lowest Frequency	-40150.1
23	Nucleus	31P
24	Acquired Size	32768
25	Spectral Size	65536



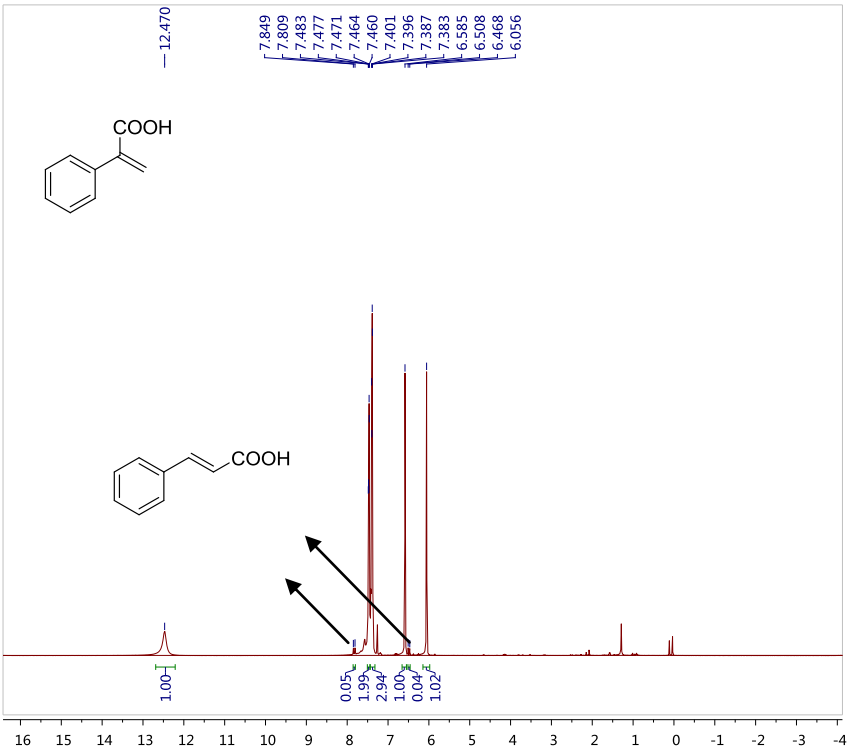
	Parameter	Value
1	Data File Name	Z:/ Data/ NMR/ 2016-01/ hj-2016-1-17-Cy/ 1/ pdata/ 1/ 1r
2	Title	hj-2016-1-17-Cy
3	Comment	PROTON
4	Origin	Bruker BioSpin GmbH
5	Owner	common
6	Site	
7	Spectrometer	spect
8	Author	
9	Solvent	CDCl3
10	Temperature	2501.0
11	Pulse Sequence	zg30
12	Experiment	1D
13	Number of Scans	8
14	Receiver Gain	101
15	Relaxation Delay	1.0000
16	Pulse Width	13.5000
17	Acquisition Time	1.9923
18	Acquisition Date	2016-01-16T09:08:00
19	Modification Date	2016-01-16T09:08:00
20	Spectrometer Frequency	400.23
21	Spectral Width	8223.7
22	Lowest Frequency	-1640.3
23	Nucleus	1H
24	Acquired Size	16384
25	Spectral Size	32768



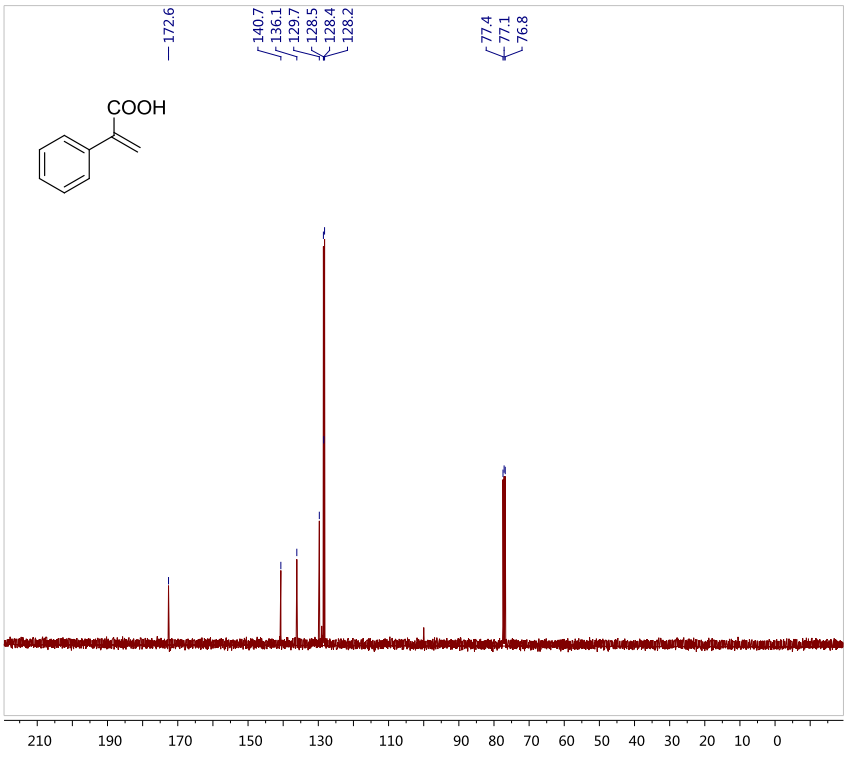
	Parameter	Value
1	Data File Name	Z:/ Data/ NMR/ 2016-01/ hj-2016-1-17-Cy/ 2/ fid
2	Title	hj-2016-1-17-Cy
3	Comment	C13CPD
4	Origin	Bruker BioSpin GmbH
5	Owner	common
6	Site	
7	Spectrometer	spect
8	Author	
9	Solvent	CDCl3
10	Temperature	2496.0
11	Pulse Sequence	zgpg30
12	Experiment	1D
13	Number of Scans	453
14	Receiver Gain	203
15	Relaxation Delay	1.0000
16	Pulse Width	12.0000
17	Acquisition Time	0.5506
18	Acquisition Date	2016-01-16T09:09:00
19	Modification Date	2016-01-16T09:21:00
20	Spectrometer Frequency	100.64
21	Spectral Width	29761.9
22	Lowest Frequency	-4817.6
23	Nucleus	13C
24	Acquired Size	16384
25	Spectral Size	32768



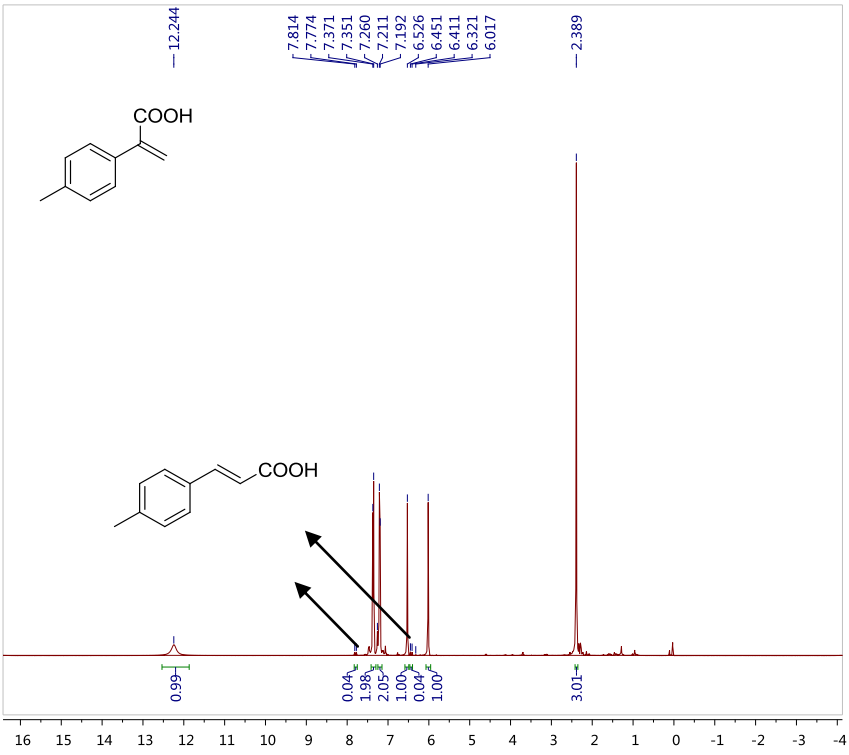
	Parameter	Value
1	Data File Name	Z:/ Data/ NMR/ 2015年/ 2015-06/ hj-15-88-5/ 2/ fid
2	Title	hj-15-88-5
3	Comment	
4	Origin	Bruker BioSpin GmbH
5	Owner	nmr
6	Site	
7	Spectrometer	spect
8	Author	
9	Solvent	CDCl3
10	Temperature	293.5
11	Pulse Sequence	zgpg30
12	Experiment	1D
13	Number of Scans	16
14	Receiver Gain	205
15	Relaxation Delay	2.0000
16	Pulse Width	7.8000
17	Acquisition Time	0.5112
18	Acquisition Date	2015-06-18T19:58:10
19	Modification Date	2015-06-18T19:58:00
20	Spectrometer Frequency	161.98
21	Spectral Width	64102.6
22	Lowest Frequency	-40150.1
23	Nucleus	31P
24	Acquired Size	32768
25	Spectral Size	65536



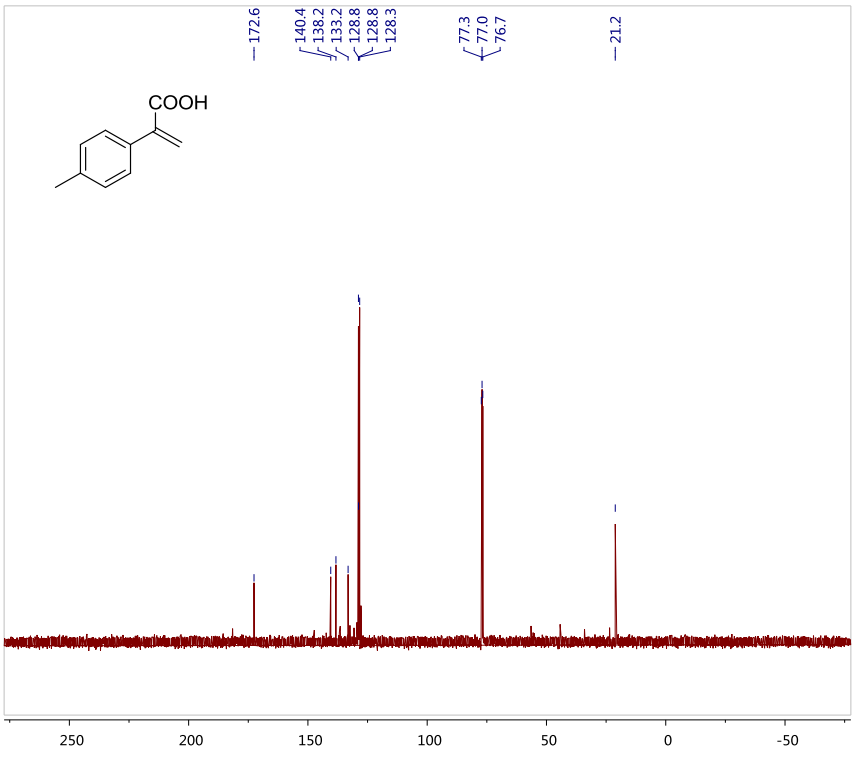
	Parameter	Value
1	Data File Name	Z:/ Data/ NMR/ 2016-01/ hj-2016-Ph/ 1/ fid
2	Title	hj-2016-Ph
3	Comment	PROTON
4	Origin	Bruker BioSpin GmbH
5	Owner	common
6	Site	
7	Spectrometer	spect
8	Author	
9	Solvent	CDCl3
10	Temperature	291.5
11	Pulse Sequence	zg30
12	Experiment	1D
13	Number of Scans	8
14	Receiver Gain	72
15	Relaxation Delay	1.0000
16	Pulse Width	13.5000
17	Acquisition Time	2.9999
18	Acquisition Date	2016-01-26T14:14:00
19	Modification Date	2016-01-26T14:14:00
20	Spectrometer Frequency	400.13
21	Spectral Width	8223.7
22	Lowest Frequency	-1664.5
23	Nucleus	1H
24	Acquired Size	24670
25	Spectral Size	65536



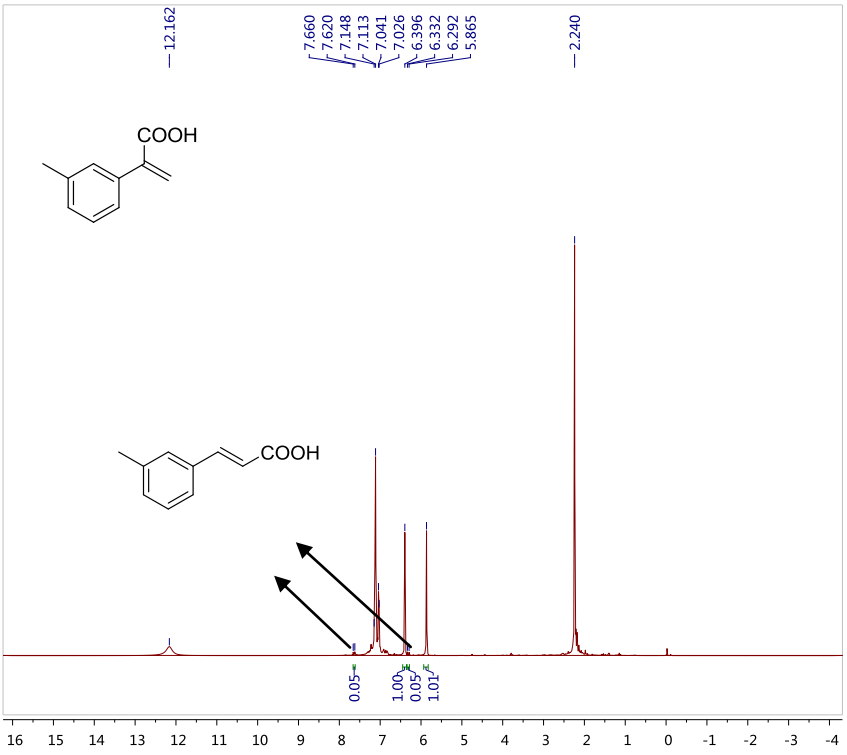
	Parameter	Value
1	Data File Name	Z:/ Data/ NMR/ 2016-03/ hj-2016-3-11-Ph/ 1/ fid
2	Title	hj-2016-3-11-Ph
3	Comment	C13CPD
4	Origin	Bruker BioSpin GmbH
5	Owner	nmr
6	Site	
7	Spectrometer	spect
8	Author	
9	Solvent	CDCl3
10	Temperature	292.0
11	Pulse Sequence	zgpg30
12	Experiment	1D
13	Number of Scans	18
14	Receiver Gain	29
15	Relaxation Delay	2.0000
16	Pulse Width	9.4000
17	Acquisition Time	1.3631
18	Acquisition Date	2016-03-12T09:27:48
19	Modification Date	2016-03-12T17:28:00
20	Spectrometer Frequency	100.61
21	Spectral Width	24038.5
22	Lowest Frequency	-1958.9
23	Nucleus	13C
24	Acquired Size	32768
25	Spectral Size	65536



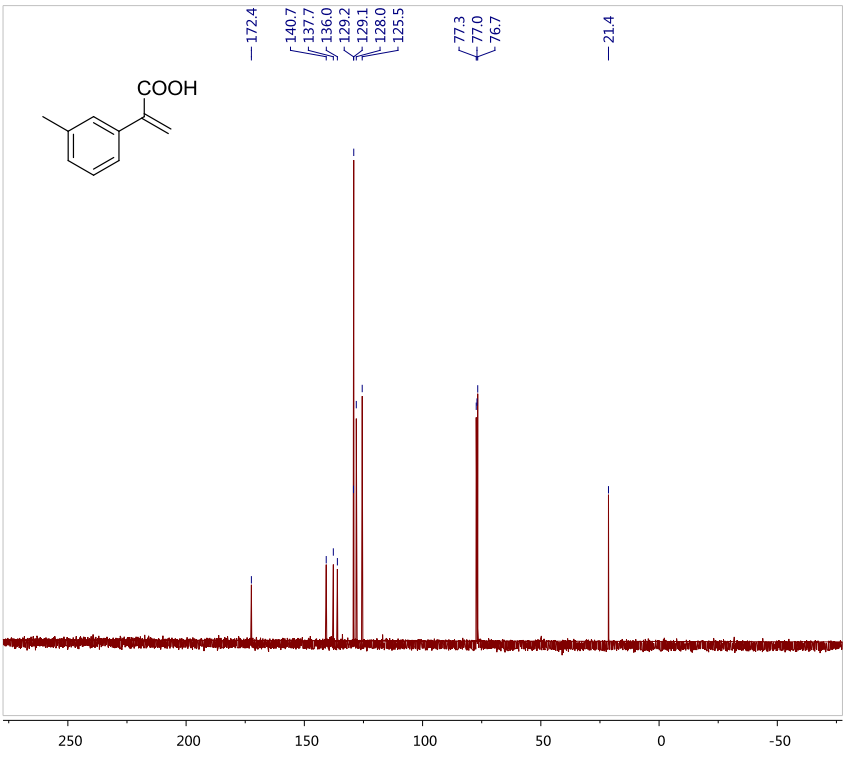
	Parameter	Value
1	Data File Name	Z:/ Data/ NMR/ 2016-01/ hj-2016-p-Me/ 1/ fid
2	Title	hj-2016-p-Me
3	Comment	PROTON
4	Origin	Bruker BioSpin GmbH
5	Owner	common
6	Site	
7	Spectrometer	spect
8	Author	
9	Solvent	CDCl3
10	Temperature	291.4
11	Pulse Sequence	zg30
12	Experiment	1D
13	Number of Scans	8
14	Receiver Gain	72
15	Relaxation Delay	1.0000
16	Pulse Width	13.5000
17	Acquisition Time	2.9999
18	Acquisition Date	2016-01-26T14:09:00
19	Modification Date	2016-01-26T14:09:00
20	Spectrometer Frequency	400.13
21	Spectral Width	8223.7
22	Lowest Frequency	-1663.2
23	Nucleus	1H
24	Acquired Size	24670
25	Spectral Size	65536



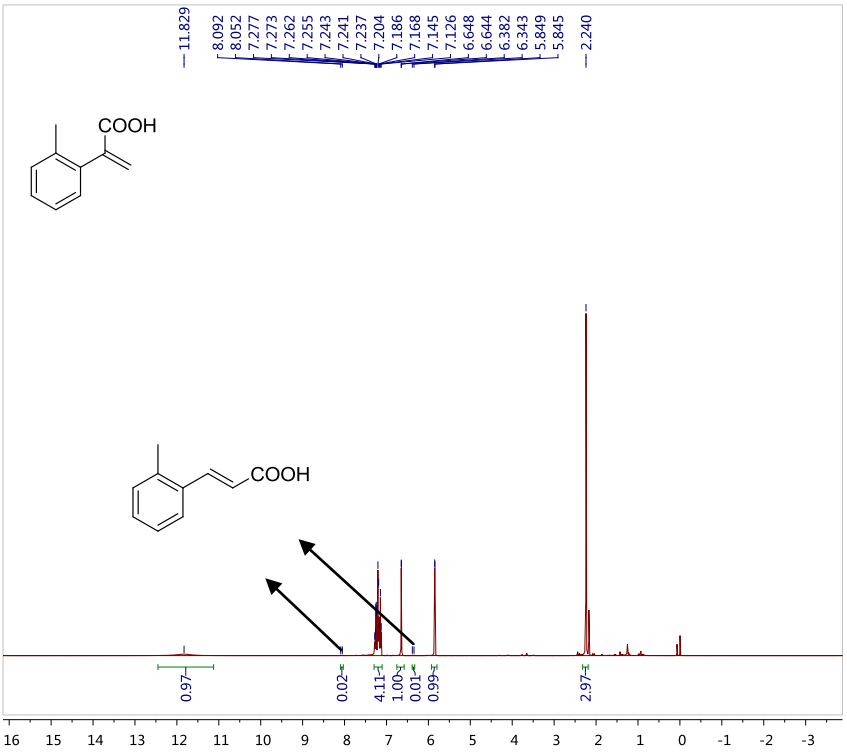
	Parameter	Value
1	Data File Name	Z:/ Data/ NMR/ 2016-03/ hj-2016-3-11-pMe/ 1/ fid
2	Title	hj-2016-3-11-pMe
3	Comment	C13CPD
4	Origin	Bruker BioSpin GmbH
5	Owner	common
6	Site	
7	Spectrometer	spect
8	Author	
9	Solvent	CDCl3
10	Temperature	295.0
11	Pulse Sequence	zgpg30
12	Experiment	1D
13	Number of Scans	48
14	Receiver Gain	203
15	Relaxation Delay	1.0000
16	Pulse Width	12.0000
17	Acquisition Time	0.4588
18	Acquisition Date	2016-03-12T09:32:00
19	Modification Date	2016-03-12T17:33:00
20	Spectrometer Frequency	100.61
21	Spectral Width	35714.3
22	Lowest Frequency	-7795.9
23	Nucleus	13C
24	Acquired Size	16384
25	Spectral Size	32768



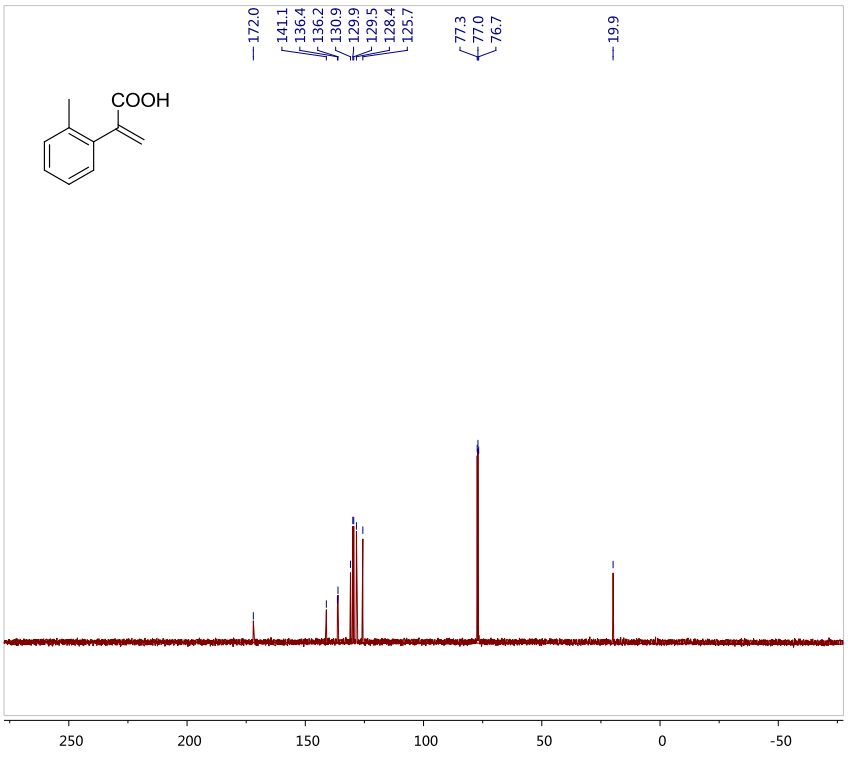
	Parameter	Value
1	Data File Name	Z:/ Data/ NMR/ 2016-01/ hj-16-50-2-m-Me/ 1/ fid
2	Title	hj-16-50-2-m-Me
3	Comment	PROTON
4	Origin	Bruker BioSpin GmbH
5	Owner	common
6	Site	
7	Spectrometer	spect
8	Author	
9	Solvent	CDCl3
10	Temperature	292.3
11	Pulse Sequence	zg30
12	Experiment	1D
13	Number of Scans	8
14	Receiver Gain	36
15	Relaxation Delay	1.0000
16	Pulse Width	13.5000
17	Acquisition Time	2.9999
18	Acquisition Date	2016-01-10T20:18:00
19	Modification Date	2016-01-10T20:18:00
20	Spectrometer Frequency	400.13
21	Spectral Width	8223.7
22	Lowest Frequency	-1718.8
23	Nucleus	1H
24	Acquired Size	24670
25	Spectral Size	65536



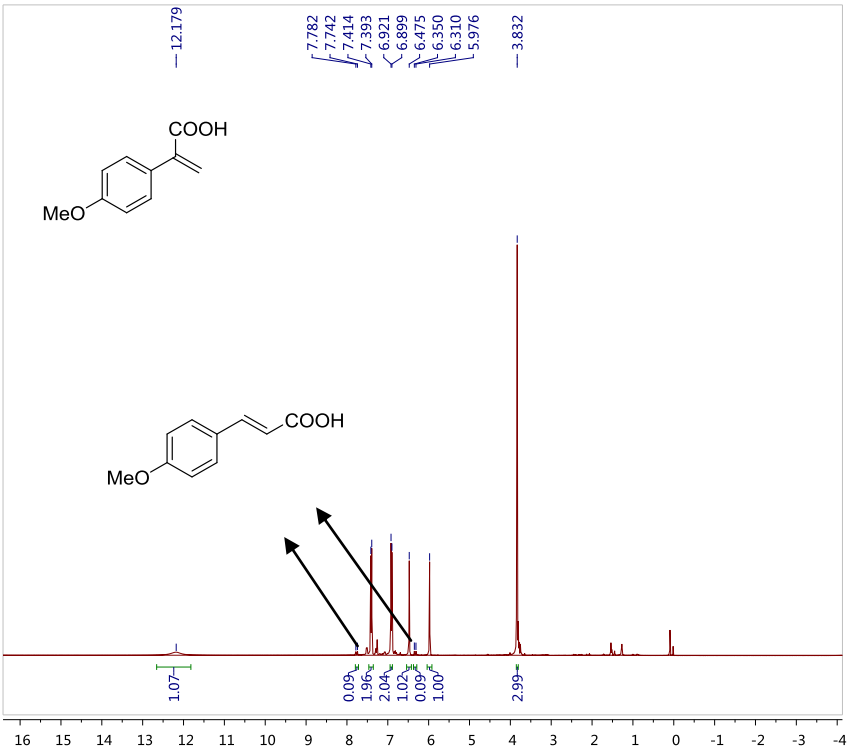
	Parameter	Value
1	Data File Name	Z:/ Data/ NMR/ 2014年/ 2014-06/ hj-14-6/ 2/ fid
2	Title	hj-14-6
3	Comment	C13CPD
4	Origin	Bruker BioSpin GmbH
5	Owner	nmr
6	Site	
7	Spectrometer	spect
8	Author	
9	Solvent	CDCl3
10	Temperature	296.3
11	Pulse Sequence	zgpg30
12	Experiment	1D
13	Number of Scans	107
14	Receiver Gain	133
15	Relaxation Delay	1.0000
16	Pulse Width	9.8000
17	Acquisition Time	0.4588
18	Acquisition Date	2014-06-26T16:49:20
19	Modification Date	2014-06-26T16:51:00
20	Spectrometer Frequency	100.61
21	Spectral Width	35714.3
22	Lowest Frequency	-7796.8
23	Nucleus	13C
24	Acquired Size	16384
25	Spectral Size	32768



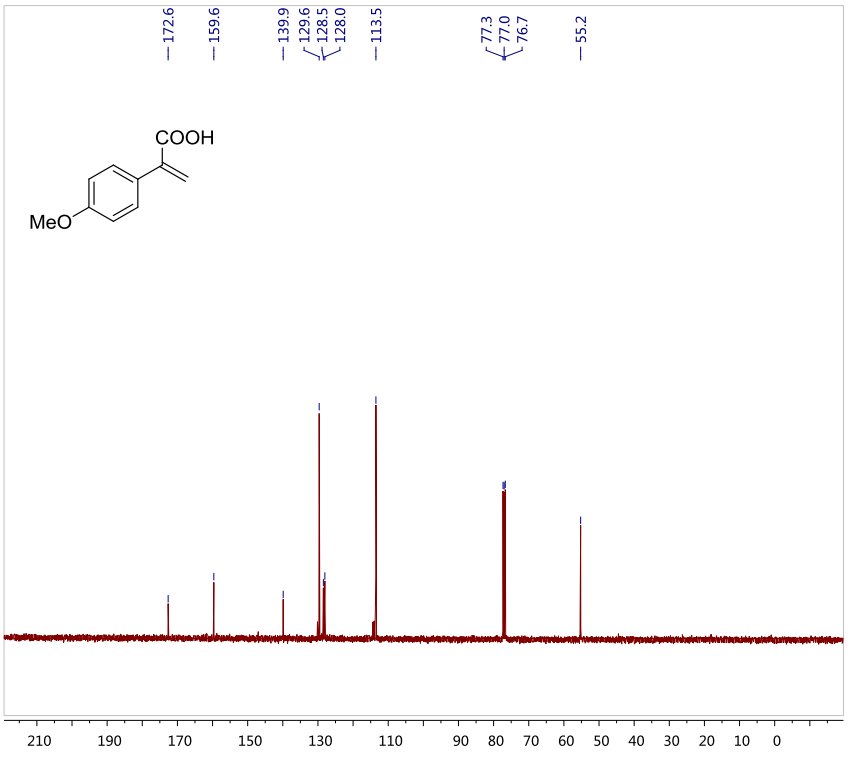
	Parameter	Value
1	Data File Name	Z:/ Data/ NMR/ 2016-01/ hj-2016-o-Me/ 1/ fid
2	Title	hj-2016-o-Me
3	Comment	PROTON
4	Origin	Bruker BioSpin GmbH
5	Owner	nmr
6	Site	
7	Spectrometer	spect
8	Author	
9	Solvent	CDCl3
10	Temperature	293.4
11	Pulse Sequence	zg30
12	Experiment	1D
13	Number of Scans	8
14	Receiver Gain	78
15	Relaxation Delay	1.0000
16	Pulse Width	9.1200
17	Acquisition Time	4.0894
18	Acquisition Date	2016-01-25T16:53:11
19	Modification Date	2016-01-25T16:53:00
20	Spectrometer Frequency	400.13
21	Spectral Width	8012.8
22	Lowest Frequency	-1535.4
23	Nucleus	1H
24	Acquired Size	32768
25	Spectral Size	65536



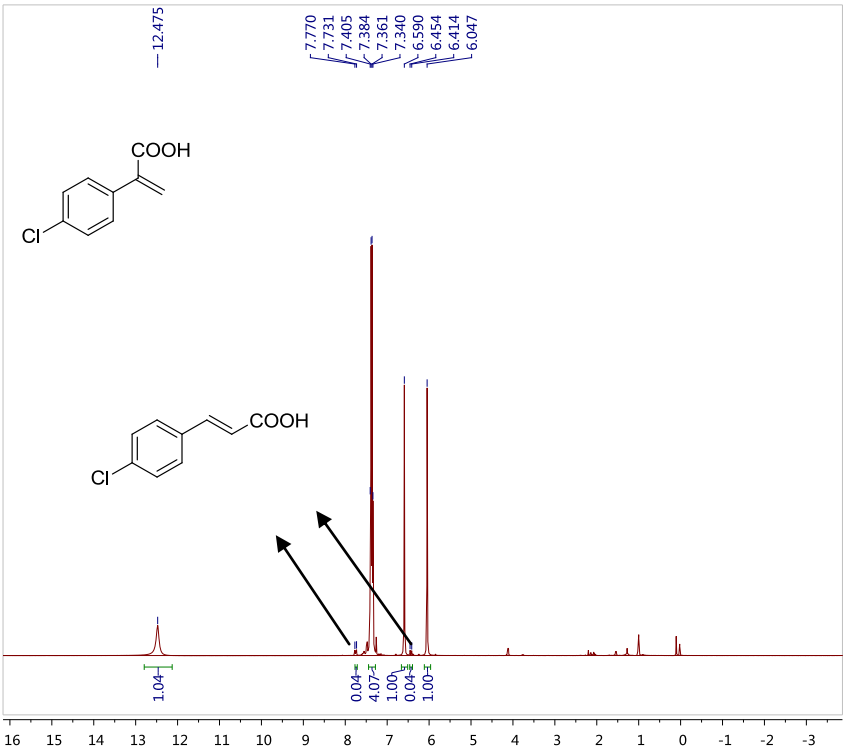
	Parameter	Value
1	Data File Name	Z:/ Data/ NMR/ 2016-03/ hj-2016-3-11-oMe/ 1/ fid
2	Title	hj-2016-3-11-oMe
3	Comment	C13CPD
4	Origin	Bruker BioSpin GmbH
5	Owner	common
6	Site	
7	Spectrometer	spect
8	Author	
9	Solvent	CDCl3
10	Temperature	294.9
11	Pulse Sequence	zgpg30
12	Experiment	1D
13	Number of Scans	196
14	Receiver Gain	203
15	Relaxation Delay	1.0000
16	Pulse Width	12.0000
17	Acquisition Time	0.4588
18	Acquisition Date	2016-03-12T09:18:00
19	Modification Date	2016-03-12T17:23:00
20	Spectrometer Frequency	100.61
21	Spectral Width	35714.3
22	Lowest Frequency	-7795.9
23	Nucleus	13C
24	Acquired Size	16384
25	Spectral Size	32768



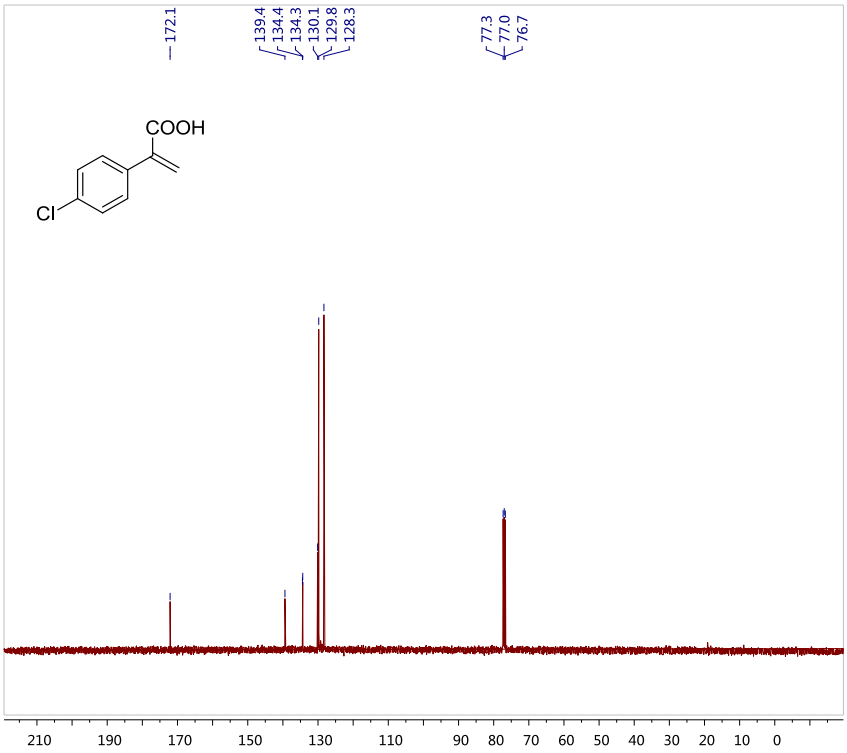
	Parameter	Value
1	Data File Name	Z:/ Data/ NMR/ 2016-01/ hj-201601017-OMe-P/ 1/ fid
2	Title	hj-201601017-OMe-P
3	Comment	PROTON
4	Origin	Bruker BioSpin GmbH
5	Owner	common
6	Site	
7	Spectrometer	spect
8	Author	
9	Solvent	CDCl3
10	Temperature	37.2
11	Pulse Sequence	zg30
12	Experiment	1D
13	Number of Scans	8
14	Receiver Gain	90
15	Relaxation Delay	1.0000
16	Pulse Width	13.5000
17	Acquisition Time	1.9923
18	Acquisition Date	2016-01-27T15:43:00
19	Modification Date	2016-01-27T15:43:00
20	Spectrometer Frequency	400.23
21	Spectral Width	8223.7
22	Lowest Frequency	-1690.0
23	Nucleus	1H
24	Acquired Size	16384
25	Spectral Size	32768



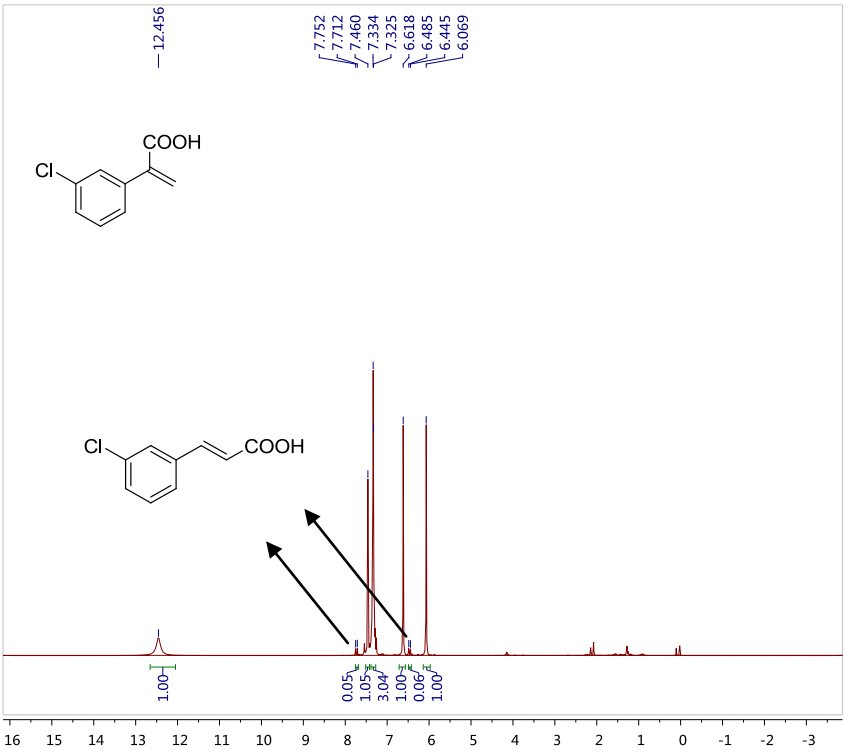
	Parameter	Value
1	Data File Name	Z:/ Data/ NMR/ 2016-03/ hj-2016-3-11-p-OMe/ 1/ fid
2	Title	hj-2016-3-11-p-OMe
3	Comment	C13CPD
4	Origin	Bruker BioSpin GmbH
5	Owner	nmr
6	Site	
7	Spectrometer	spect
8	Author	
9	Solvent	CDCl3
10	Temperature	292.3
11	Pulse Sequence	zgpg30
12	Experiment	1D
13	Number of Scans	39
14	Receiver Gain	29
15	Relaxation Delay	2.0000
16	Pulse Width	9.4000
17	Acquisition Time	1.3631
18	Acquisition Date	2016-03-12T09:23:07
19	Modification Date	2016-03-12T17:24:00
20	Spectrometer Frequency	100.61
21	Spectral Width	24038.5
22	Lowest Frequency	-1958.9
23	Nucleus	13C
24	Acquired Size	32768
25	Spectral Size	65536



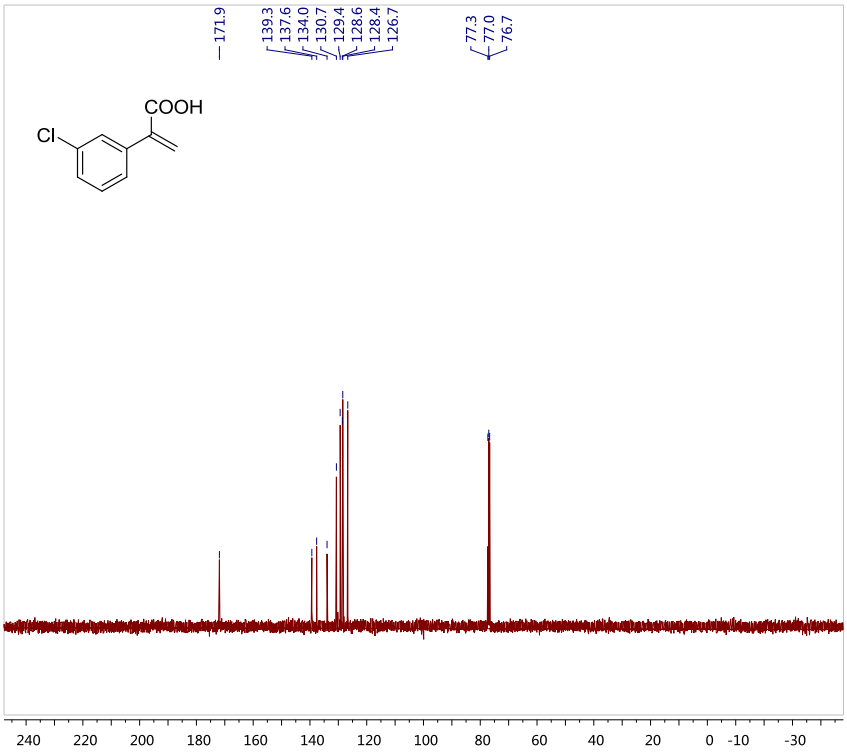
	Parameter	Value
1	Data File Name	Z:/ Data/ NMR/ 2016-01/ hj-16-53-p-Cl/ 1/ fid
2	Title	hj-16-53-p-Cl
3	Comment	PROTON
4	Origin	Bruker BioSpin GmbH
5	Owner	nmr
6	Site	
7	Spectrometer	spect
8	Author	
9	Solvent	CDCl3
10	Temperature	543.8
11	Pulse Sequence	zg30
12	Experiment	1D
13	Number of Scans	8
14	Receiver Gain	47
15	Relaxation Delay	1.0000
16	Pulse Width	9.1200
17	Acquisition Time	4.0894
18	Acquisition Date	2016-01-12T11:56:31
19	Modification Date	2016-01-12T11:56:00
20	Spectrometer Frequency	400.13
21	Spectral Width	8012.8
22	Lowest Frequency	-1535.4
23	Nucleus	1H
24	Acquired Size	32768
25	Spectral Size	65536



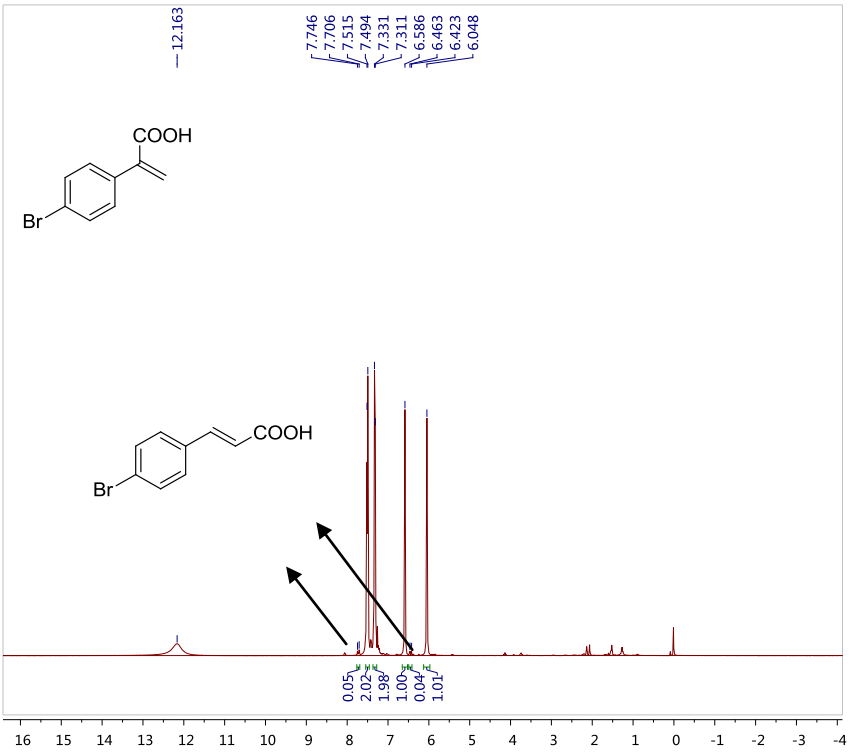
	Parameter	Value
1	Data File Name	Z:/ Data/ NMR/ 2016-01/ hj-16-53-p-Cl/ 2/ fid
2	Title	hj-16-53-p-Cl
3	Comment	C13CPD
4	Origin	Bruker BioSpin GmbH
5	Owner	nmr
6	Site	
7	Spectrometer	spect
8	Author	
9	Solvent	CDCl3
10	Temperature	544.3
11	Pulse Sequence	zgpg30
12	Experiment	1D
13	Number of Scans	19
14	Receiver Gain	29
15	Relaxation Delay	2.0000
16	Pulse Width	9.4000
17	Acquisition Time	1.3631
18	Acquisition Date	2016-01-12T11:57:32
19	Modification Date	2016-01-12T11:58:00
20	Spectrometer Frequency	100.61
21	Spectral Width	24038.5
22	Lowest Frequency	-1958.9
23	Nucleus	13C
24	Acquired Size	32768
25	Spectral Size	65536



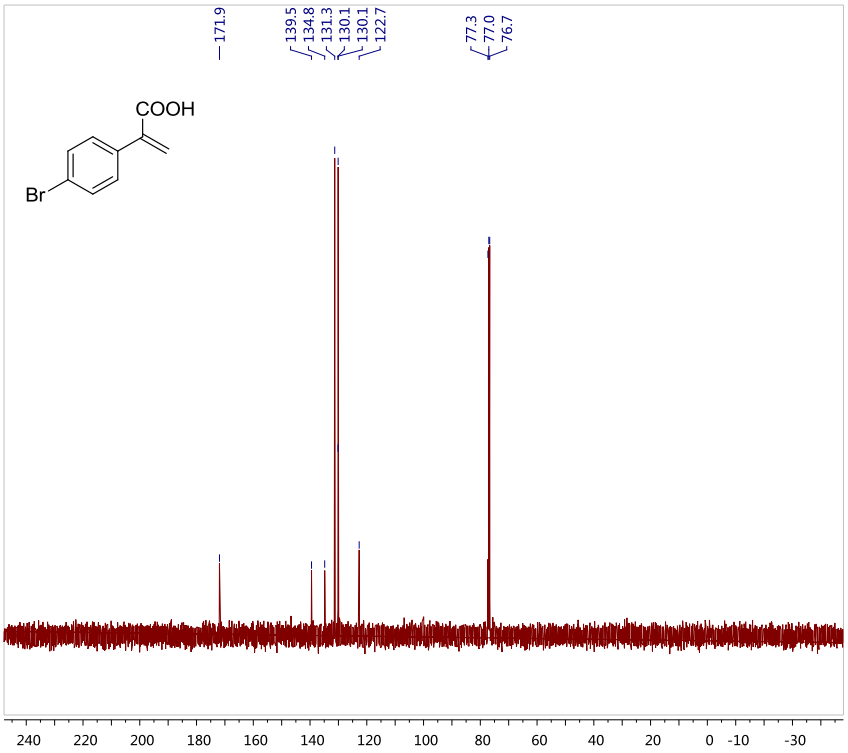
	Parameter	Value
1	Data File Name	Z:/ Data/ NMR/ 2016-01/ hj-16-53-m-Cl/ 1/ fid
2	Title	hj-16-53-m-Cl
3	Comment	PROTON
4	Origin	Bruker BioSpin GmbH
5	Owner	nmr
6	Site	
7	Spectrometer	spect
8	Author	
9	Solvent	CDCl3
10	Temperature	543.5
11	Pulse Sequence	zg30
12	Experiment	1D
13	Number of Scans	8
14	Receiver Gain	41
15	Relaxation Delay	1.0000
16	Pulse Width	9.1200
17	Acquisition Time	4.0894
18	Acquisition Date	2016-01-12T11:46:40
19	Modification Date	2016-01-12T11:46:00
20	Spectrometer Frequency	400.13
21	Spectral Width	8012.8
22	Lowest Frequency	-1535.4
23	Nucleus	1H
24	Acquired Size	32768
25	Spectral Size	65536



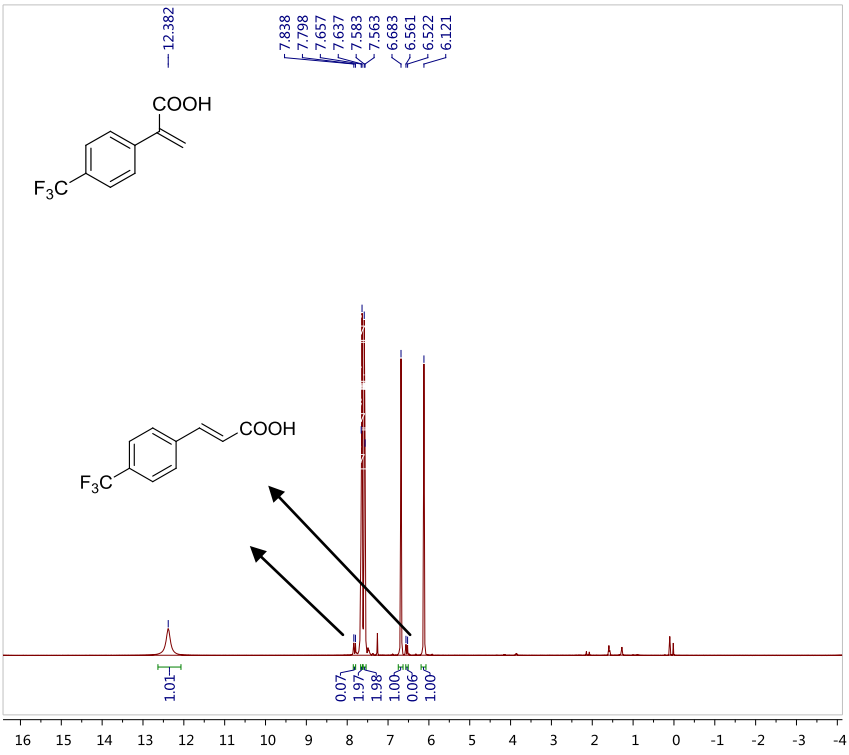
	Parameter	Value
1	Data File Name	Z:/ Data/ NMR/ 2016-01/ hj-16-53-m-Cl-2/ 1/ fid
2	Title	hj-16-53-m-Cl-2
3	Comment	C13CPD
4	Origin	Bruker BioSpin GmbH
5	Owner	common
6	Site	
7	Spectrometer	spect
8	Author	
9	Solvent	CDCl3
10	Temperature	2610.0
11	Pulse Sequence	zgpg30
12	Experiment	1D
13	Number of Scans	27
14	Receiver Gain	203
15	Relaxation Delay	1.0000
16	Pulse Width	12.0000
17	Acquisition Time	0.5506
18	Acquisition Date	2016-01-12T16:41:00
19	Modification Date	2016-01-12T16:42:00
20	Spectrometer Frequency	100.64
21	Spectral Width	29761.9
22	Lowest Frequency	-4817.6
23	Nucleus	13C
24	Acquired Size	16384
25	Spectral Size	32768



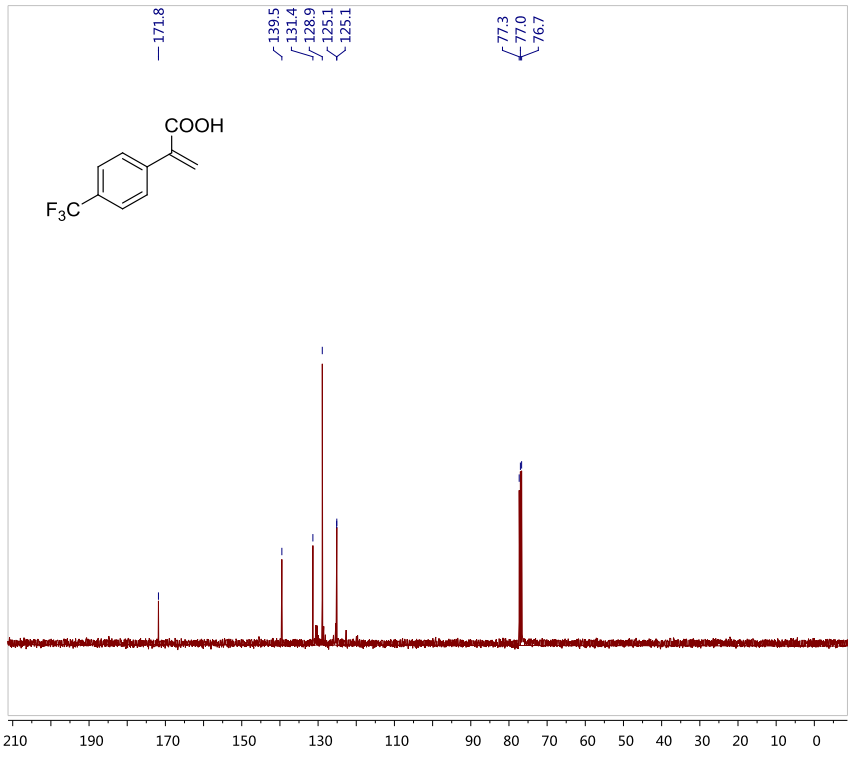
	Parameter	Value
1	Data File Name	Z:/ Data/ NMR/ 2016-01/ hj-16-53-3-p-Br/ 1/ fid
2	Title	hj-16-53-3-p-Br
3	Comment	PROTON
4	Origin	Bruker BioSpin GmbH
5	Owner	common
6	Site	
7	Spectrometer	spect
8	Author	
9	Solvent	CDCl3
10	Temperature	292.0
11	Pulse Sequence	zg30
12	Experiment	1D
13	Number of Scans	8
14	Receiver Gain	144
15	Relaxation Delay	1.0000
16	Pulse Width	13.5000
17	Acquisition Time	2.9999
18	Acquisition Date	2016-01-13T10:08:00
19	Modification Date	2016-01-13T10:08:00
20	Spectrometer Frequency	400.13
21	Spectral Width	8223.7
22	Lowest Frequency	-1655.6
23	Nucleus	1H
24	Acquired Size	24670
25	Spectral Size	65536



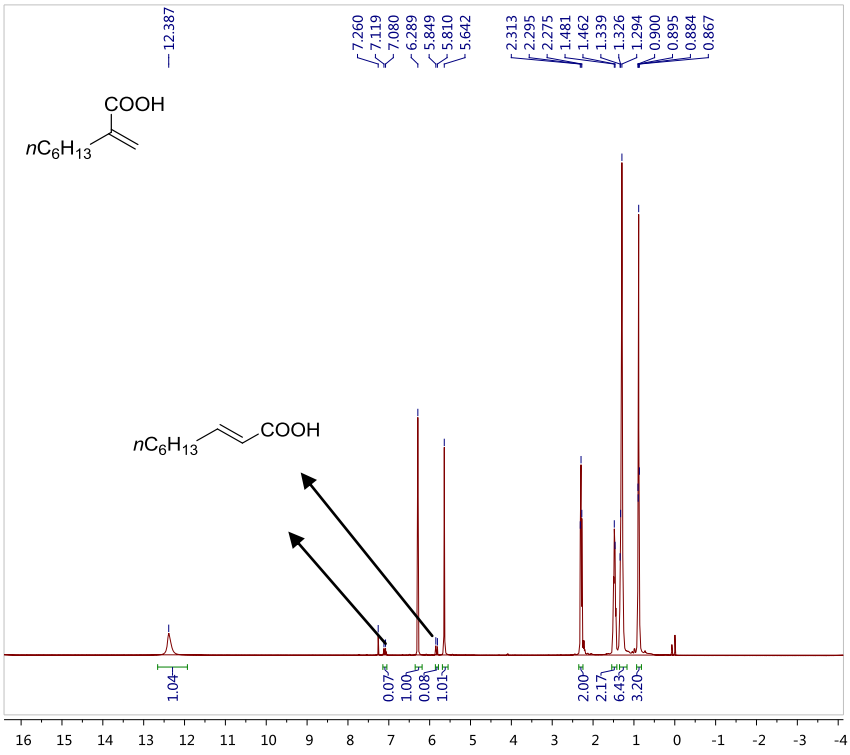
	Parameter	Value
1	Data File Name	Z:/ Data/ NMR/ 2016-01/ hj-16-53-3-p-Br/ 2/ fid
2	Title	hj-16-53-3-p-Br
3	Comment	C13CPD
4	Origin	Bruker BioSpin GmbH
5	Owner	common
6	Site	
7	Spectrometer	spect
8	Author	
9	Solvent	CDCl3
10	Temperature	292.1
11	Pulse Sequence	zgpg30
12	Experiment	1D
13	Number of Scans	31
14	Receiver Gain	203
15	Relaxation Delay	1.0000
16	Pulse Width	12.5000
17	Acquisition Time	0.5506
18	Acquisition Date	2016-01-13T10:09:00
19	Modification Date	2016-01-13T10:10:00
20	Spectrometer Frequency	100.61
21	Spectral Width	29761.9
22	Lowest Frequency	-4820.2
23	Nucleus	13C
24	Acquired Size	16384
25	Spectral Size	32768



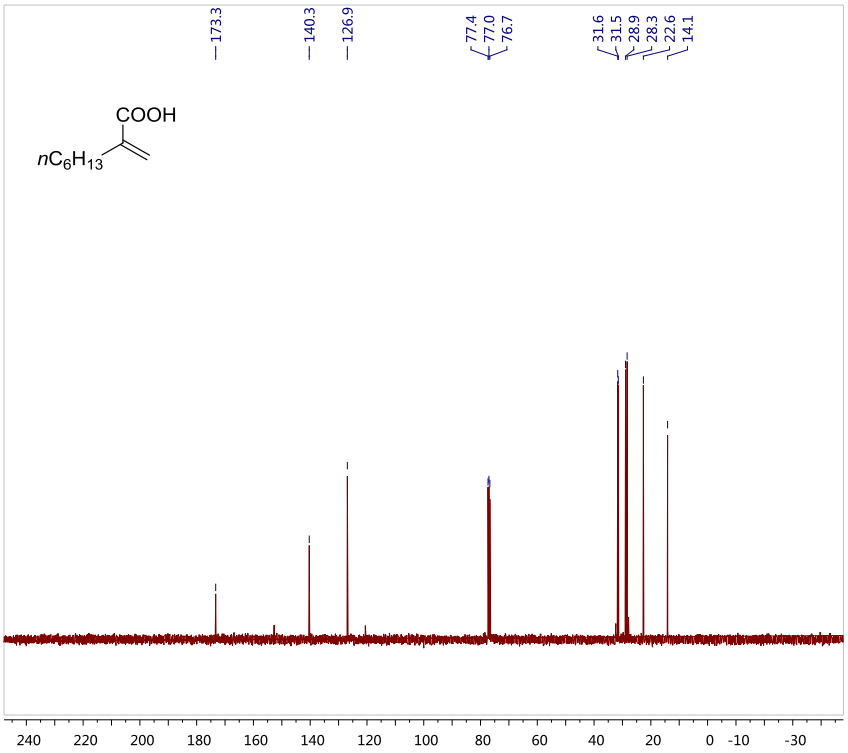
	Parameter	Value
1	Data File Name	Z:/ Data/ NMR/ 2016-01/ hj-2016-1-27-CF3/ 1/ fid
2	Title	hj-2016-1-27-CF3
3	Comment	PROTON
4	Origin	Bruker BioSpin GmbH
5	Owner	common
6	Site	
7	Spectrometer	spect
8	Author	
9	Solvent	CDCl3
10	Temperature	291.7
11	Pulse Sequence	zg30
12	Experiment	1D
13	Number of Scans	8
14	Receiver Gain	114
15	Relaxation Delay	1.0000
16	Pulse Width	13.5000
17	Acquisition Time	2.9999
18	Acquisition Date	2016-01-27T17:35:00
19	Modification Date	2016-01-27T17:35:00
20	Spectrometer Frequency	400.13
21	Spectral Width	8223.7
22	Lowest Frequency	-1691.7
23	Nucleus	1H
24	Acquired Size	24670
25	Spectral Size	65536



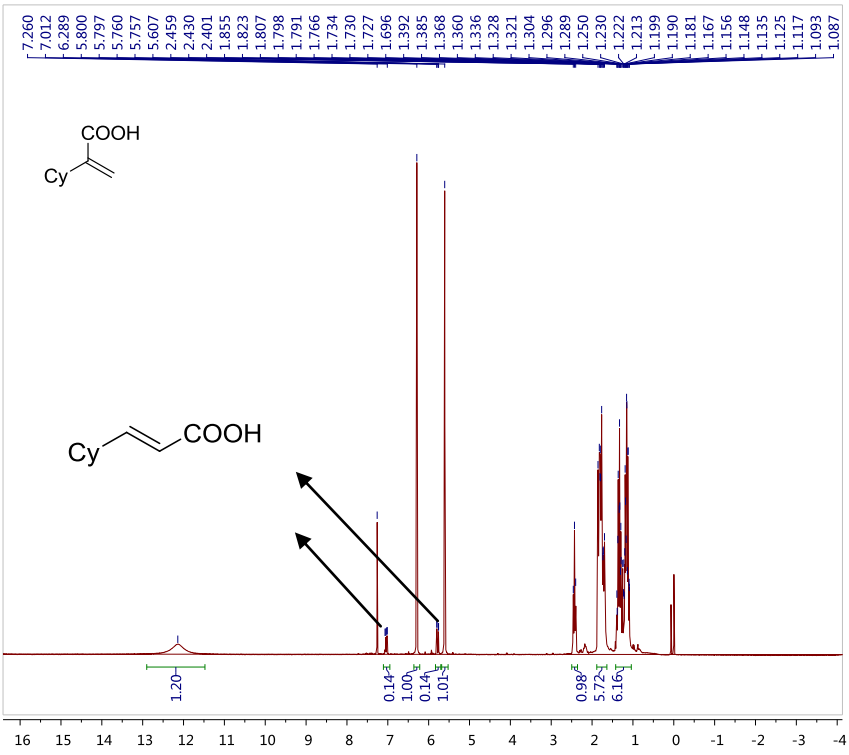
	Parameter	Value
1	Data File Name	Z:/ Data/ NMR/ 2016-03/ hj-2016-3-11-PCF3/ 1/ fid
2	Title	hj-2016-3-11-mMe
3	Comment	C13CPD
4	Origin	Bruker BioSpin GmbH
5	Owner	common
6	Site	
7	Spectrometer	spect
8	Author	
9	Solvent	CDCl3
10	Temperature	295.2
11	Pulse Sequence	zgpg30
12	Experiment	1D
13	Number of Scans	33
14	Receiver Gain	203
15	Relaxation Delay	1.0000
16	Pulse Width	12.0000
17	Acquisition Time	0.4588
18	Acquisition Date	2016-03-12T09:27:00
19	Modification Date	2016-03-12T17:27:00
20	Spectrometer Frequency	100.61
21	Spectral Width	35714.3
22	Lowest Frequency	-7795.9
23	Nucleus	13C
24	Acquired Size	16384
25	Spectral Size	32768



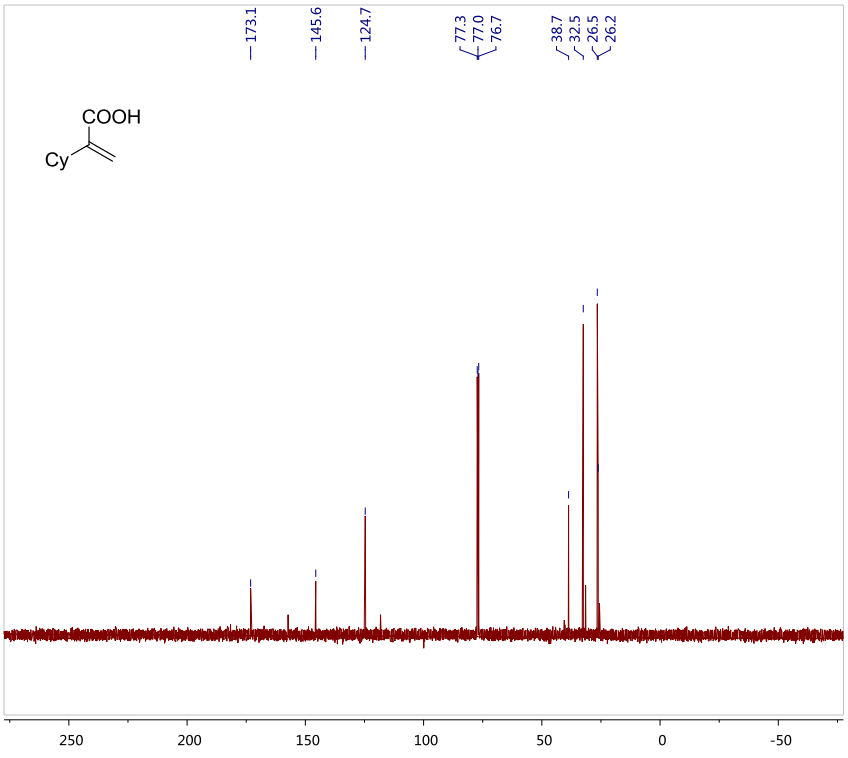
	Parameter	Value
1	Data File Name	Z:/ Data/ NMR/ 2016-01/ hj-2016-1-oct-C/ 2/ fid
2	Title	hj-2016-1-oct-C
3	Comment	PROTON
4	Origin	Bruker BioSpin GmbH
5	Owner	common
6	Site	
7	Spectrometer	spect
8	Author	
9	Solvent	CDCl3
10	Temperature	32.9
11	Pulse Sequence	zg30
12	Experiment	1D
13	Number of Scans	8
14	Receiver Gain	57
15	Relaxation Delay	1.0000
16	Pulse Width	13.5000
17	Acquisition Time	1.9923
18	Acquisition Date	2016-01-25T21:29:00
19	Modification Date	2016-01-25T21:29:00
20	Spectrometer Frequency	400.23
21	Spectral Width	8223.7
22	Lowest Frequency	-1640.3
23	Nucleus	1H
24	Acquired Size	16384
25	Spectral Size	32768



	Parameter	Value
1	Data File Name	Z:/ Data/ NMR/ 2016-01/ hj-2016-1-oct-C/ 1/ fid
2	Title	hj-2016-1-oct-C
3	Comment	C13CPD
4	Origin	Bruker BioSpin GmbH
5	Owner	common
6	Site	
7	Spectrometer	spect
8	Author	
9	Solvent	CDCl3
10	Temperature	33.0
11	Pulse Sequence	zgpg30
12	Experiment	1D
13	Number of Scans	52
14	Receiver Gain	203
15	Relaxation Delay	1.0000
16	Pulse Width	12.0000
17	Acquisition Time	0.5506
18	Acquisition Date	2016-01-25T21:27:00
19	Modification Date	2016-01-25T21:29:00
20	Spectrometer Frequency	100.64
21	Spectral Width	29761.9
22	Lowest Frequency	-4817.6
23	Nucleus	13C
24	Acquired Size	16384
25	Spectral Size	32768



	Parameter	Value
1	Data File Name	Z:/ Data/ NMR/ 2016-01/ hj-2016-cy/ 1/ fid
2	Title	hj-2016-cy
3	Comment	PROTON
4	Origin	Bruker BioSpin GmbH
5	Owner	common
6	Site	
7	Spectrometer	spect
8	Author	
9	Solvent	CDCl3
10	Temperature	33.1
11	Pulse Sequence	zg30
12	Experiment	1D
13	Number of Scans	8
14	Receiver Gain	101
15	Relaxation Delay	1.0000
16	Pulse Width	13.5000
17	Acquisition Time	1.9923
18	Acquisition Date	2016-01-25T21:23:00
19	Modification Date	2016-01-25T21:23:00
20	Spectrometer Frequency	400.23
21	Spectral Width	8223.7
22	Lowest Frequency	-1640.3
23	Nucleus	1H
24	Acquired Size	16384
25	Spectral Size	32768



	Parameter	Value
1	Data File Name	Z:/ Data/ NMR/ 2016-01/ lj-16-56-cy/ 2/ fid
2	Title	lj-16-56-cy
3	Comment	C13CPD
4	Origin	Bruker BioSpin GmbH
5	Owner	common
6	Site	
7	Spectrometer	spect
8	Author	
9	Solvent	CDCl3
10	Temperature	296.0
11	Pulse Sequence	zgpg30
12	Experiment	1D
13	Number of Scans	42
14	Receiver Gain	203
15	Relaxation Delay	1.0000
16	Pulse Width	12.0000
17	Acquisition Time	0.4588
18	Acquisition Date	2016-01-14T10:49:00
19	Modification Date	2016-01-14T10:50:00
20	Spectrometer Frequency	100.61
21	Spectral Width	35714.3
22	Lowest Frequency	-7795.9
23	Nucleus	13C
24	Acquired Size	16384
25	Spectral Size	32768