Supporting Information

Synthesis of cyclometalated 1,3,5-triphenylpyrazole palladium dimer and its activity towards cross coupling reactions

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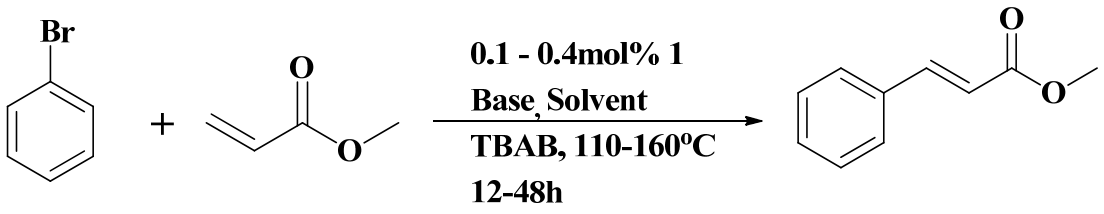
Reagents and solvents were purified according to standard procedures. Palladium acetate, 1,3-diphenyl-1,3-propanedione and phenylhydrazine were purchased from Sigma-Aldrich. Glacial acetic acid was obtained from Spectrochem. All glassware including Schlenk tubes were cleaned using base bath (potassium hydroxide in isopropanol solution), and acid bath (hydrochloric acid in distilled water). In some instance we used hydrofluoric acid to clean the Schlenk tubes. The stir-bars were cleaned using aqua regia solution. All 400 MHz ^{1}H, 100 MHz ^{13}C spectra were recorded on a Bruker ARX 400 spectrometer operating at 400 MHz. All ^{1}H and ^{13}C NMR spectra were referenced internally to solvent signals. ESI mass spectra were recorded on Bruker, microTOF-QII mass spectrometer. Elemental analyses were carried out by using a Thermo quest CE instrument model EA/110 CHNS-O elemental analyzer. Single-crystal X-ray diffraction data were collected on a Bruker APEX-II diffractometer equipped with an Oxford Instruments low-temperature attachment. The data were collected at 296 K using, Mo-Kα radiation (0.71073 Å). Crystallographic data for **1** and details of X-ray diffraction experiments and crystal structure refinements are given in Table 1. SADABS[1] absorption corrections were applied in both cases.[1] The structures were solved and refined with SHELX suite of programs.[2]All non-hydrogen atoms were refined with anisotropic displacement coefficients. The H atoms were placed at calculated positions and were refined as riding atoms. Crystallographic data for the structure of **1** have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-1040304. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; email: deposit@ccdc.cam.ac.uk).

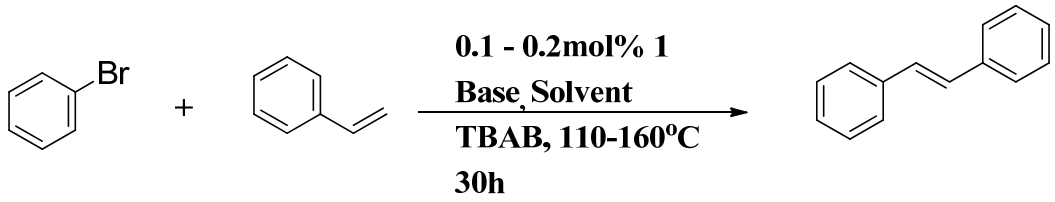
Table S1: Optimization of Heck cross coupling reaction of Bromobenzene and Methyl acrylate using palladacycle[a]



Entry	Cat. (mol%)	Base	Solvent	TBAB (mol%)	Temp. (^{0}C)	Time (h)	Yield[b] (%)	TON[d]
1	0.1	K_2CO_3	DMF	-	110	12	Trace	-
2	0.1	K_2CO_3	DMF	-	130	12	12	124
3	0.1	K_2CO_3	DMF	-	130	30	21	210
4	0.1	K_2CO_3	DMF	-	140	30	22	221
5	0.1	K_2CO_3	DMF	10	140	30	32	321
6	0.1	K_3PO_4	DMF	10	140	30	54	541
7	0.1	K_3PO_4	DMF	10	160	30	57	570
8	**0.2**	**K_3PO_4**	**DMF**	**10**	**160**	**30**	**62**	**310**
9	0.2	K_3PO_4	DMAc	10	160	30	45	226
10	0.2	$K_3PO_4.H_2O$	DMF	10	160	30	15	77
11	0.4	K_3PO_4	DMF	10	160	30	49[c]	123
12	0.4	K_3PO_4	DMAc	10	160	30	65	162
13	0.2	K_3PO_4	DMF	20	160	30	61	311
14	0.2	K_3PO_4	DMF	20	160	48	63	313
15	**0.2**	**K_3PO_4**	**NMP**	**10**	**160**	**30**	**81**	**404**

[a]Reaction conditions: 1 equiv of bromobenzene, 2 equiv of Methyl acrylate, 2 equiv of base. TBAB : Tetrabutylammoniumbromide, DMAc : Dimethylacetamide, NMP : N-methyl-2-pyrrolidone; [b]Isolated yield after chromatography; [c]Biphenyl product was also observed. [d]Turn over number, based on number of moles of the isolated product;.

Table S2 : Heck cross coupling reaction of Bromobenzene and Styrene using palladacycle[a]



Entry	Cat. (mol%)	Base	Solvent	TBAB (mol%)	Temp. (^{0}C)	Time (h)	Yield[b] (%)	TON[c]
1	0.1	K_2CO_3	DMF	10	110	30	51	511
2	0.2	K_3PO_4	DMF	10	160	30	96	475
3	0.2	K_3PO_4	NMP	10	160	30	99	498

[a]Reaction conditions: 1 equiv of Bromobenzene, 2 equiv of Styrene, 2 equiv of base; [b]Isolated yield after chromatography. [c]Turn over number, based on number of moles of the isolated product

Table S3 : Heck cross coupling reaction of iodobenzene and methyl acrylate using palladacycle **(1)**

Entry	Base	Solvent	Temp. (^{0}C)	Time (h)	Yield[c] (%)	TON[d]
1[a]	K_2CO_3	DMF	110	48	86	1.88 X 10^6
2[a]	K_3PO_4	NMP	160	30	96	1.92 X 10^6
3[b]	K_2CO_3	DMF	90	48	91	9 X 10^5
4[e]	K_2CO_3	NMP	140	10	-	-

[a]Reaction conditions: 2.45 mmol of iodobenzene, 4.90 mmol of methylacrylate, 4.90 mmol of base and 1.2 X 10^{-6} mmol of precatalyst 1 in 4 ml solvent

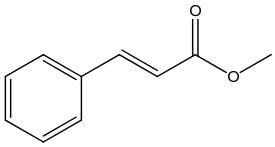
[b] Reaction conditions: 2.45 mmol of iodobenzene, 4.90 mmol of methylacrylate, 4.90 mmol of base 2.5×10^{-6} mmol of precatalyst in 4 ml solvent

[c]Isolated yield after chromatography

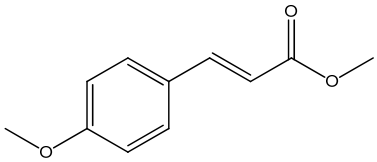
[d]Turn over number (TON), based on number of moles of the isolated product

[e]Reaction conditions: 2.45 mmol of iodobenzene, 4.90 mmol of methylacrylate, and 4.90 mmol of base

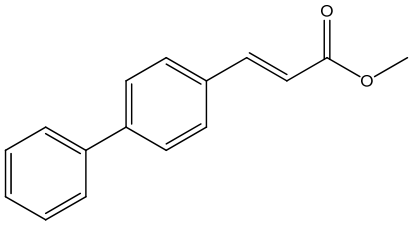
Characterization data of the products in Table 2 and Table 3:



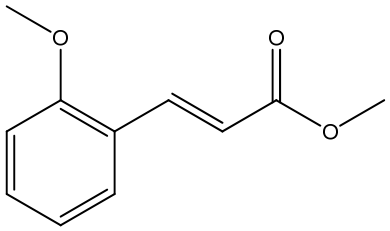
White solid (m.p.37 ^{0}C), HR-MS (ESI): calcd. for $C_{10}H_{10}O_2$ ($[M + H]^+$) : 163.0754 , found : 163.0762 ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.70 (d, J = 16 Hz, 1H, CH=CH), 7.54-7.51 (m, 2H, ArH), 7.39 (t, J = 4 Hz, 3H, ArH), 6.45 (d, J = 16 Hz, 1H, CH=CH), 3.81 (s, 3H, OMe). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 167.45, 144.89, 134.40, 130.30, 128.90, 128.08, 117.82, 51.71.



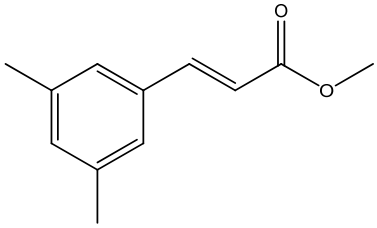
White solid (m.p. 92 ^{0}C), HR-MS (ESI): calcd. for $C_{11}H_{12}O_3$ ($[M + Na]^+$) : 215.0679 , found : 215.0689. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.66 (d, J = 16 Hz, 1H, CH=CH), 7.48 (d, J = 8 Hz, 2H, ArH), 6.91 (d, J = 8 Hz, 2H, ArH), 6.32 (d, J = 16 Hz, 1H, CH=CH), 3.83 (s, 3H, OMe), 3.77 (s, 3H, OMe). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 167.75, 161.40, 144.52, 129.72, 127.10, 115.25, 114.32, 55.34, 51.55.



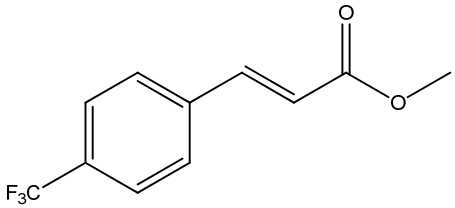
White solid (m.p.148 ^{0}C), HR-MS (ESI): calcd. for $C_{16}H_{14}O_2$ ($[M + H]^+$) : 239.1067 , found : 239.1064. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.75 (d, J = 16 Hz, 1H, CH=CH), 7.58-7.64 (m, 6H, ArH) , 7.48-7.44 (t, J = 8 Hz, 2H, ArH) , 7.36-7.40 (t, J = 8 Hz, 2H, ArH), 6.49 (d, J = 16 Hz, 1H, CH=CH), 3.83 (s, 3H, OMe). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 167.50, 144.43, 143.09, 140.15, 133.35, 128.93, 128.60, 127.88, 127.56, 127.06, 117.66, 51.75.



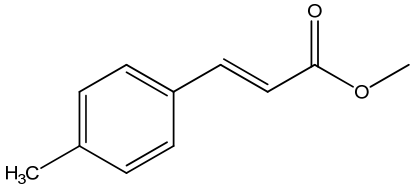
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.00 (d, J = 16 Hz, 1H, CH=CH), 7.50 (d, J = 8 Hz, 1H, ArH) , 7.35 (t, J = 8 Hz, 1H, ArH), 6.90-6.98 (m, 2H, ArH), 6.53 (d, J = 16 Hz, 1H, CH=CH), 3.88 (s, 3H, OMe), 3.80 (s, 3H, OMe). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 167.96, 158.36, 140.30, 131.50, 128.92, 123.37, 120.70, 118.32, 111.15, 55.47, 51.60.



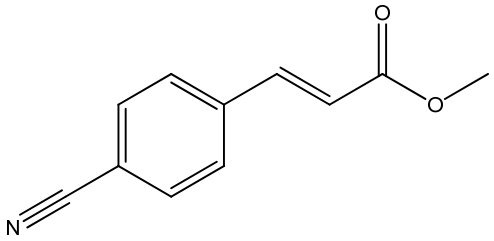
White solid (m.p.49 ^{0}C), HR-MS (ESI): calcd. for $C_{12}H_{14}O_2$ ($[M + H]^+$) : 191.1067 , found : 191.1067. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.64 (d, J = 16 Hz, 1H, CH=CH), 7.13 (s, 2H, ArH), 7.01 (s, 1H, ArH), 6.36 (d, J = 16 Hz, 1H, CH=CH), 3.80 (s, 3H, OMe), 2.32 (s, 6H, Me). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 167.54, 145.22, 138.38, 134.32, 132.10, 125.98, 117.32, 51.58, 21.16.



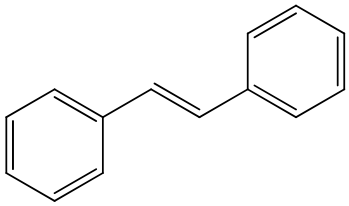
Light yellow solid (m.p.76 ^{0}C), HR-MS (ESI): calcd. for $C_{11}H_9O_2F_3$ ($[M + H]^+$) : 231.0627, found : 231.0649. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.69 (d, J = 16 Hz, 1H, CH=CH),7.64-7.61 (m, 4H, ArH), 6.50 (d, J = 16 Hz, 1H, CH=CH), 3.81 (s, 3H, OMe). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 166.83, 142.96, 137.75, 128.17, 125.86, 125.17, 122.46, 120.36, 51.88.



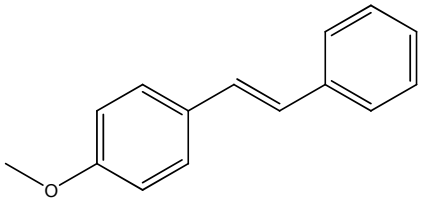
White solid (m.p.59 ^{0}C), HR-MS (ESI): calcd. for $C_{11}H_{12}O_2$ ($[M + H]^+$) : 177.0910 , found : 177.0924. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.70 (d, J = 16 Hz, 1H, CH=CH), 7.44 (d, J = 8 Hz, 2H, ArH), 7.21 (d, J = 8 Hz, 2H, ArH), 6.42 (d, J = 16 Hz, 1H, CH=CH), 3.82 (s, 3H, OMe), 2.39 (s, 3H, Me). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 167.62, 144.88, 140.72, 131.67, 129.63, 128.08, 116.70, 51.62, 21.46.



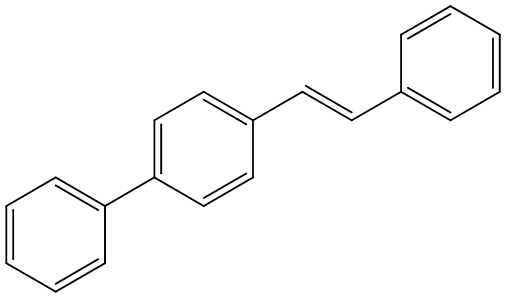
White solid (m.p.106 ^{0}C), HR-MS (ESI): calcd. for $C_{11}H_9O_2N$ ($[M + H]^+$) : 188.0706 , found : 188.0703. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.58-7.67 (m, 5H), 6.50 (d, J = 16 Hz), 3.81 (s, 3H, OMe). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 166.57, 142.41, 138.65, 132.66, 128.41, 121.38, 118.34, 113.42, 52.02.



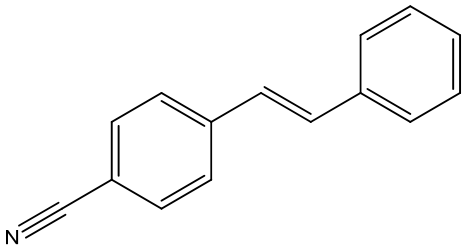
White solid (m.p.124 ^{0}C). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.66-7.64 (m, 4H, ArH), 7.51-7.35 (m, 6H, ArH), 7.26-7.18 (.m, 2H, CH=CH). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 137.47, 128.84, 127.76, 126.68.



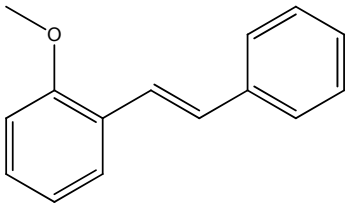
White solid (m.p.134 ^{0}C), HR-MS (ESI): calcd. for $C_{15}H_{14}O$ ($[M + H]^+$) : 212.1151 , found : 212.1127. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.53-7.47 (m, 4H, ArH), 7.37 (t, J = 8 Hz, 2H, ArH), 7.26 (t, J = 8 Hz, 1H, ArH), 7.12 (d, J = 16 Hz, 1H,CH=CH), 6.98 (d, J = 16 Hz, 1H,CH=CH), 6.93 (d, J = 8 Hz, 2H, ArH), 3.85 (s, 3H, OMe). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 159.34, 137.69, 130.18, 128.68, 128.25, 127.76, 127.25, 126.65, 126.30, 114.18, 55.35.



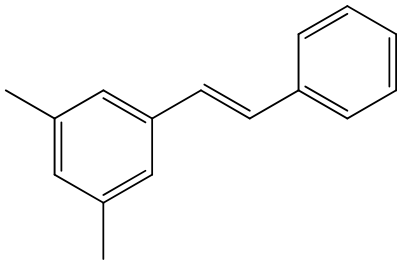
White solid (m.p.219 ^{0}C). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.65-7.59 (m, 6H, ArH), 7.55 (d, J = 8 Hz, 2H, ArH), 7.46 (t, J = 8 Hz, 2H, ArH), 7.41- 7.35 (m, 3H, ArH), 7.30-7.25 (m, 1H, ArH), 7.17 (s, 2H, CH=CH). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 139.99, 139.66, 136.65, 135.71, 128.13, 128.07, 128.03, 127.52, 126.98, 126.68, 126.66, 126.27, 126.25, 125.86.



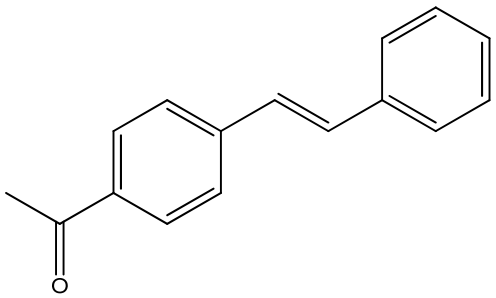
White solid (m.p.119 ^{0}C), HR-MS (ESI): calcd. for $C_{15}H_{11}N$ ([M + H]$^+$) : 206.0964 , found : 206.0963. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.65-7.53 (m, 6H, ArH), 7.40 (t, J = 8 Hz, 2H, ArH), 7.32 (t, J = 8 Hz, 1H, ArH), 7.20 (d, J = 16 Hz, 1H, CH=CH), 7.07 (d, J = 16 Hz, 1H, CH=CH). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 141.86, 136.30, 132.51, 132.43, 128.88, 128.67, 126.93, 126.88, 126.74, 119.05, 110.59.



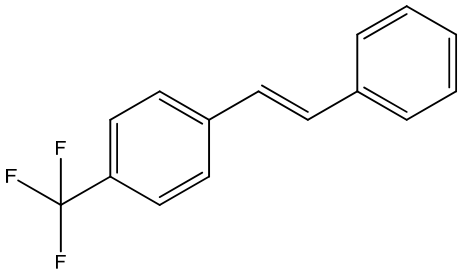
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.63-7.48 (m, 4H, ArH), 7.36 (t, J = 8 Hz, 2H, ArH), 7.28-7.24 (m, 2H, ArH), 7.13 (d, J = 16 Hz, 1H, CH=CH), 6.99 (t, J = 8 Hz, 1H, ArH), 6.92 (d, J = 16 Hz, 1H, CH=CH), 3.90 (s, 3H, OMe). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 156.94, 137.99, 129.13, 128.68, 128.60, 127.37, 126.58, 126.47, 126.43, 123.52, 120.77, 110.97, 55.55.



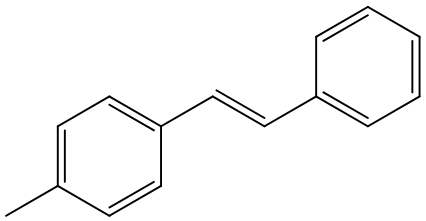
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.52 (d, J = 8 Hz, 2H, ArH), 7.37 (t, J = 8 Hz, 2H, ArH), 7.26 (t, J = 8 Hz, 1H, ArH), , 7.16 (s, 2H, ArH), 7.14-7.04 (m, 2H, CH=CH), 6.93 (s, 1H, ArH), 2.36 (s, 6H, Me). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 137.44, 136.84, 136.55, 128.75, 128.20, 127.98, 127.61, 126.78, 125.77, 123.75, 20.63.



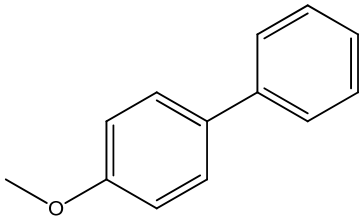
Light yellow solid (m.p.144 ^{0}C). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.96 (d, J = 8 Hz, 2H, ArH), 7.60-7.54 (m, 4H, ArH), 7.39 (t, J = 8 Hz, 2H, ArH), 7.31 (t, J = 8 Hz, 1H, ArH), 7.23 (d, J = 16 Hz, 1H, CH=CH), 7.13 (d, J = 16 Hz, 1H, CH=CH), 2.61 (s, 3H, Me). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 197.53, 142.03, 136.71, 135.96, 131.48, 128.90, 128.82, 128.34, 127.46, 126.84, 126.52, 26.61.



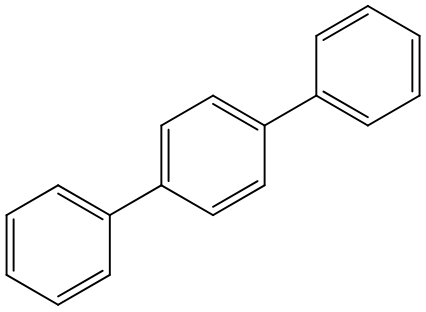
White solid (m.p.136 ^{0}C). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.59 (s, 4H, ArH), 7.52 (d, J = 8 Hz, 2H, ArH), 7.37 (t, J = 8 Hz, 2H, ArH), 7.29(t, J = 8 Hz, 1H, ArH), 7.18 (d, J = 16 Hz, 1H, CH=CH), 7.12(d, J = 16 Hz, 1H, CH=CH). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 140.82, 136.65, 131.22, 128.82, 128.31, 127.14, 126.80, 126.59, 125.70, 125.66, 125.63, 125.59.



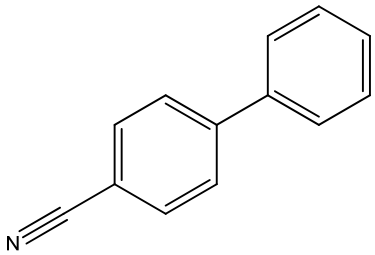
White solid (m.p.122 ^{0}C). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.55 (d, J = 8 Hz, 2H, ArH), 7.46 (d, J = 8 Hz, 2H, ArH), 7.40 (t, J = 8 Hz, 2H, ArH),, 7.31-7.18 (m, 4H, ArH), 7.17-7.08 (m, 2H, CH=CH), 2.41 (s, 3H, Me). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 137.55, 134.58, 129.43, 128.68, 128.65, 127.73, 127.43, 126.46, 126.43, 21.29.



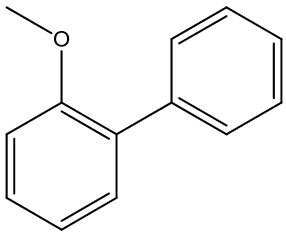
White solid (m.p.89 ^{0}C). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.65-7.55 (m, 4H, ArH), 7.51-7.43 (m, 2H, ArH), 7.40-7.34 (m, 1H, ArH), 7.07-7.00 (m, 2H, ArH), 3.90 (s, 3H, OMe). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 159.26, 140.91, 140.87, 133.84, 133.82, 128.84, 128.24, 126.83, 114.32, 55.39.



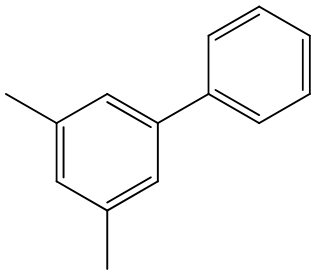
White solid (m.p.211 ^{0}C). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.71-7.67 (m, 8H, ArH), 7.49 (t, J = 8 Hz, 4H, ArH), 7.39 (t, J = 8 Hz, 3H, ArH). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 140.74, 140.15, 128.85, 127.54, 127.38, 127.09.



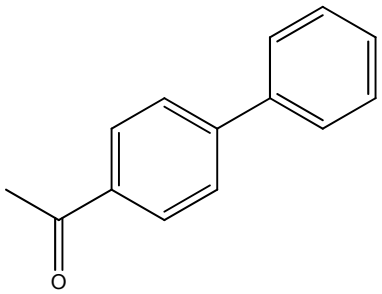
White solid (m.p.88 ^{0}C), HR-MS (ESI): calcd. for $C_{13}H_9N$ ([M + H]$^{+}$) : 180.0808 , found : 180.0807. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.74-7.67 (m, 4H, ArH), 7.60 (d, J = 8 Hz, 2H, ArH), 7.51-7.41 (m, 3H, ArH). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 145.67, 139.18, 139.02, 132.60, 129.13, 128.68, 127.74, 127.24, 118.96, 110.92.



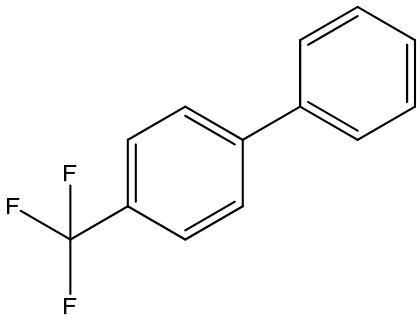
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.54 (d, J = 8 Hz, 2H, ArH), 7.42 (t, J = 8Hz, 2H, ArH), 7.35-7.31 (m, 3H, ArH), 7.06-6.99 (m, 2H, ArH), 3.82 (s, 3H, OMe). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 156.48, 155.06, 138.56, 130.91, 130.74, 129.56, 128.62, 127.99, 126.92, 120.84, 111.24, 55.57.



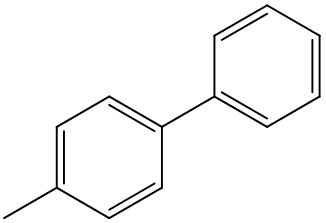
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.62 (d, J = 8 Hz, 2H, ArH), 7.46 (t, J = 8 Hz, 2H, ArH), 7.37 (m, 1H, ArH), 7.25 (s, 2H, ArH), 7.05 (s, 1H, ArH), 2.43 (s, 6H, Me). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 141.49, 141.29, 138.27, 128.91, 128.65, 127.21, 127.10, 125.14, 21.44.



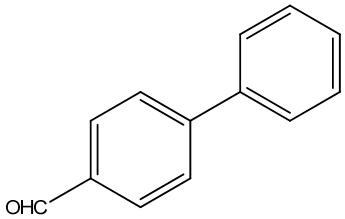
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.04 (d, J = 8 Hz, 2H, ArH), 7.73- 7.65 (m, 4H, ArH), 7.50 (t, J = 8 Hz, 2H, ArH), 7.45-7.41 (m, 1H, ArH), 2.67 (s, 3H, Me). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 197.80, 145.80, 139.89, 135.87, 128.98, 128.94, 128.26, 127.29, 127.24, 26.68.



White solid (m.p.69 ^{0}C). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.71 (s, 4H, ArH), 7.62 (d, J = 8 Hz, 2H, ArH), 7.51-7.40 (m, 3H, ArH). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 144.76, 139.79, 129.00, 128.20, 127.44, 127.30, 125.74, 125.71.



White solid (m.p.49 ^{0}C). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.65 (d, J = 8 Hz, 2H, ArH), 7.54 (d, J = 8 Hz, 2H, ArH), 7.49 (t, J = 8 Hz, 2H, ArH), 7.39 (t, J = 8 Hz, 1H, ArH),, 7.32 (d, J = 8 Hz, 2H, ArH),, 2.46 (s, 3H, Me). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 141.21, 138.41, 137.06, 129.53, 128.76, 127.04, 127.02, 21.15.



White solid (m.p.60 ^{0}C), HR-MS (ESI): calcd. for $C_{13}H_{10}O$ ($[M + H]^{+}$) : 183.0804 , found : 183.0808. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 10.07 (s, 1H, CHO), 7.94 (d, J = 8 Hz, 2H, ArH), 7.76 (d, J = 8 Hz, 2H, ArH) , 7.65 (d, J = 8 Hz, 2H, ArH), 7.51-7.41 (m, 3H, ArH). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 191.97, 147.23, 139.74, 135.21, 130.29, 129.03, 128.49, 127.71, 127.39.

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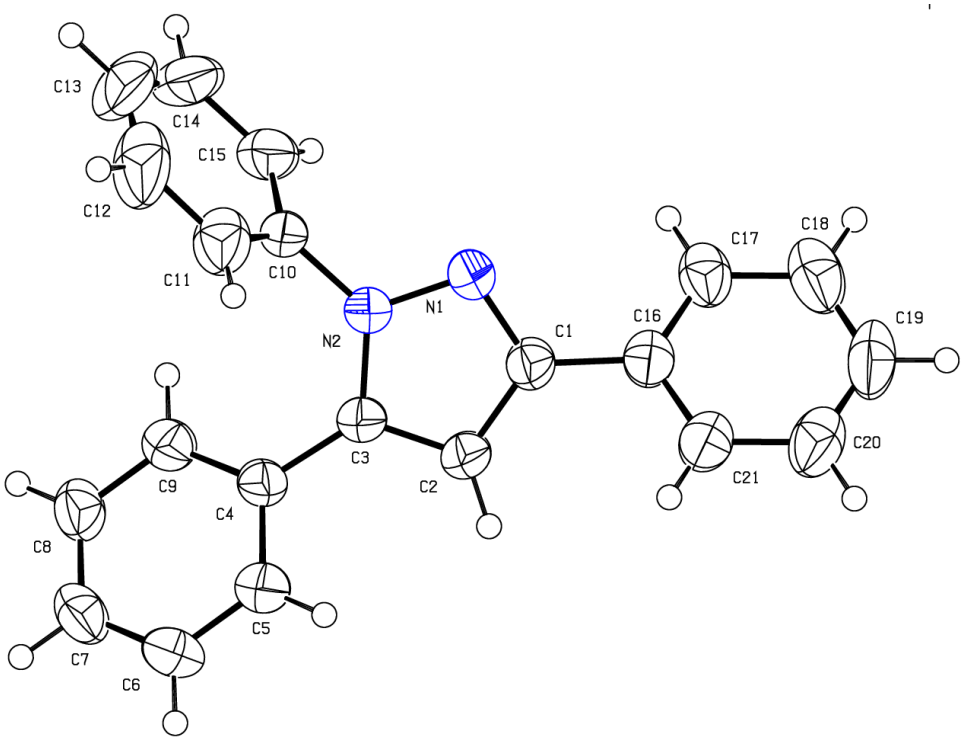
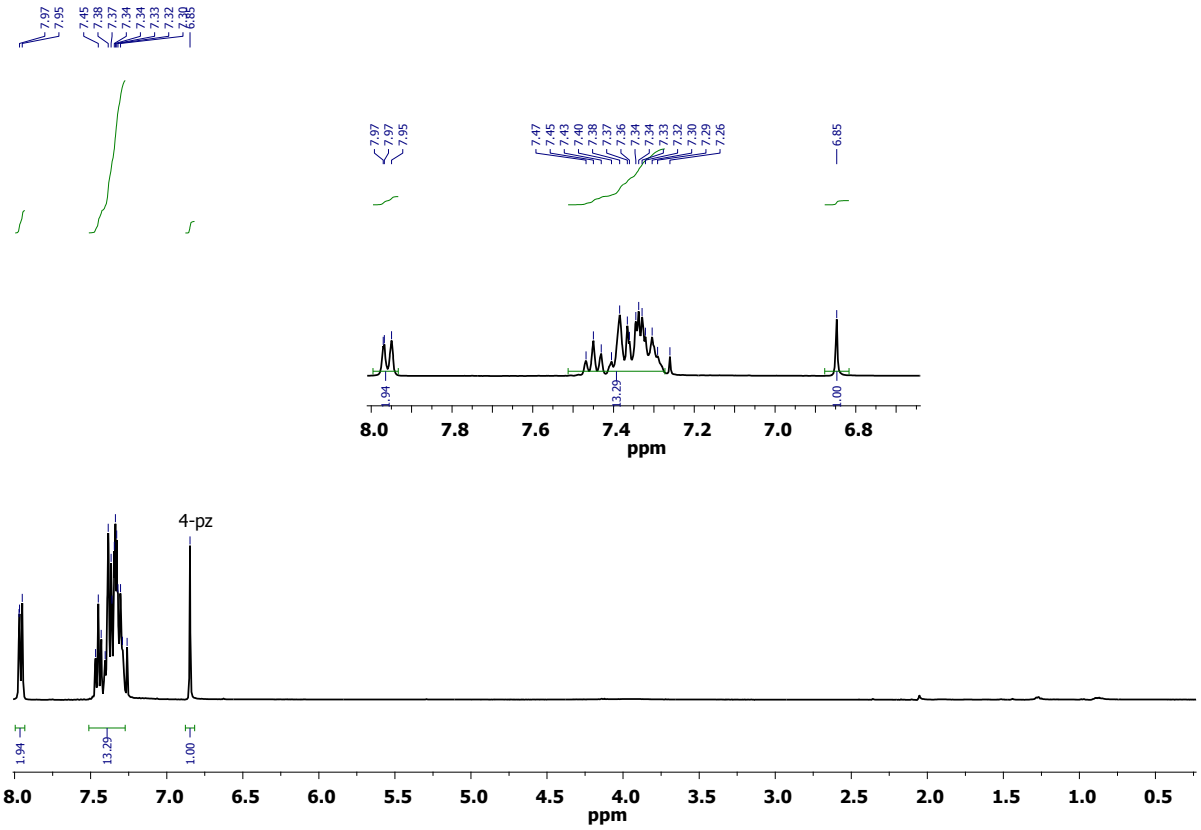
Reference:

1. G. M. Sheldrick, SADABS Program for Correction of Area Detector Data; University of Göttingen: Göttingen, Germany, 1999.
2. SHELXTL, Package v. 6.10, BrukerAXS, Madison and WI.

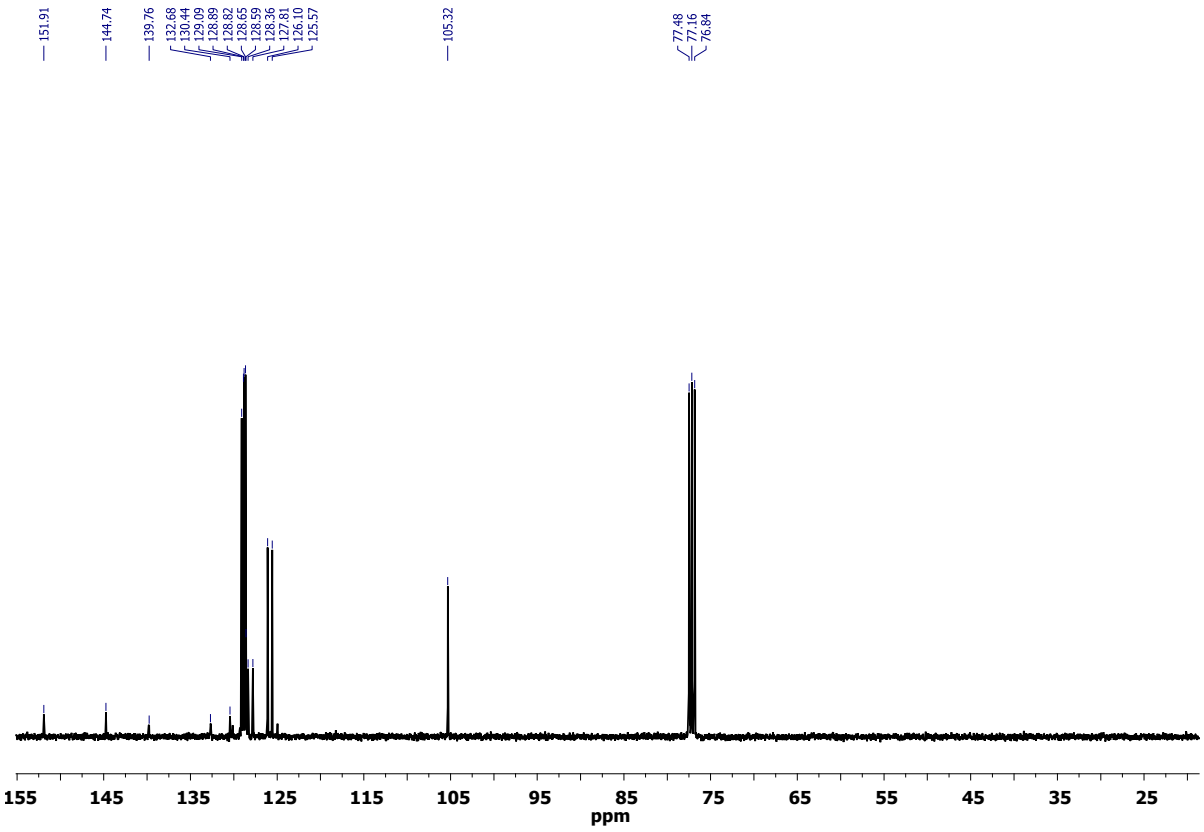
Molecular Structure of **1,3,5-triphenyl pyrazole**



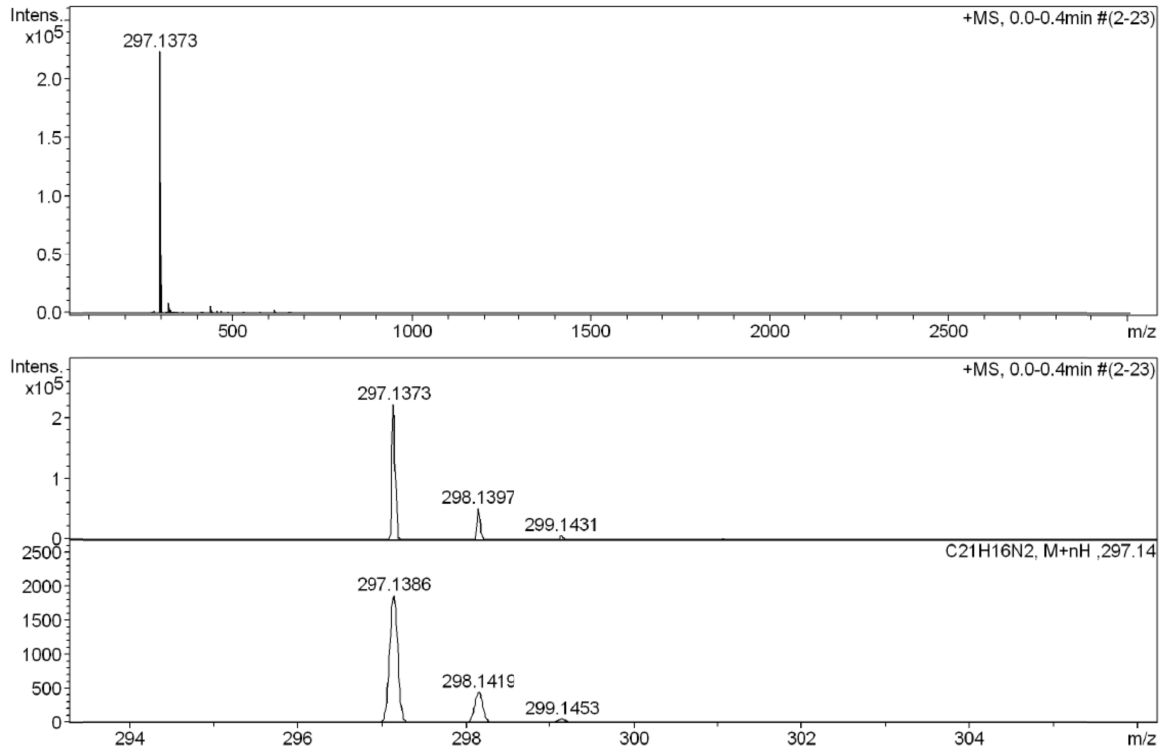
^{1}H NMR of **1,3,5-triphenyl pyrazole**



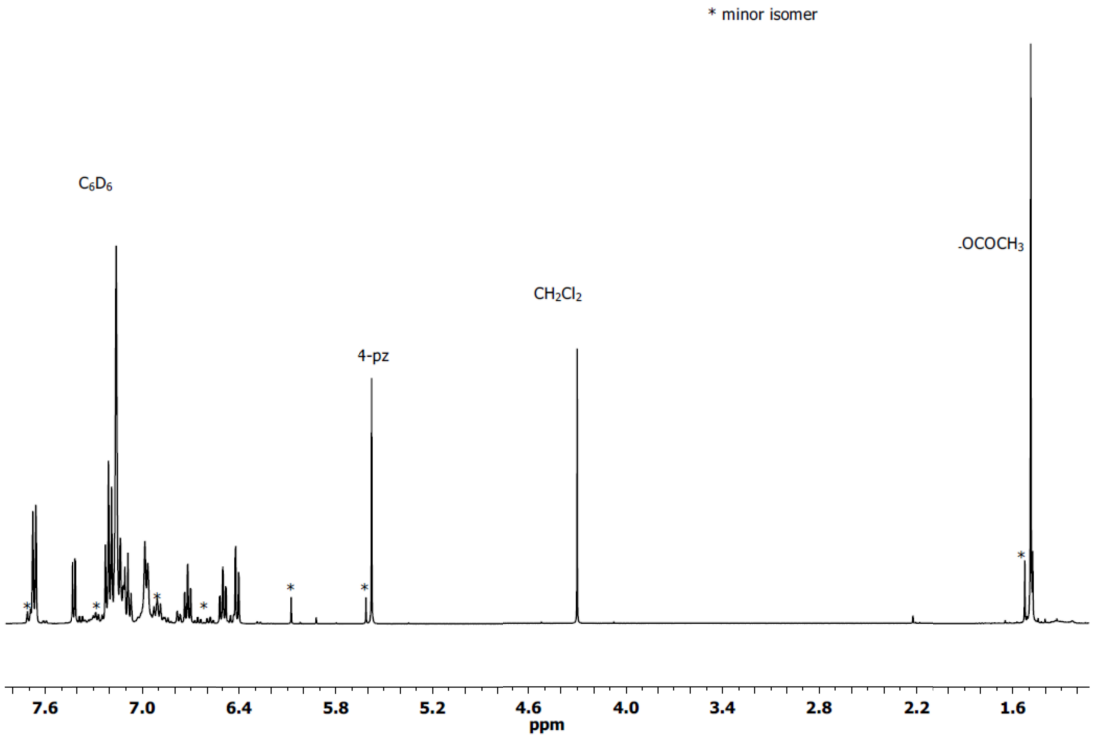
^{3}C NMR of **1,3,5-triphenyl pyrazole**



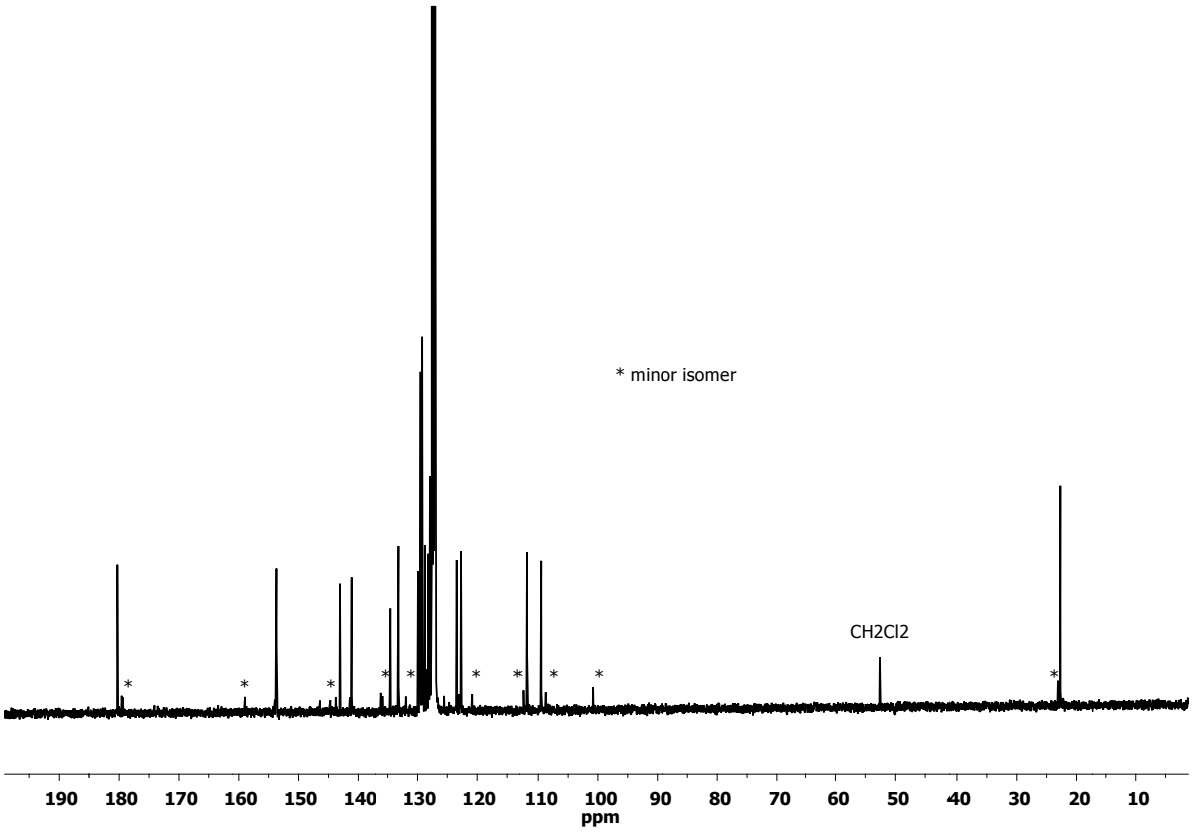
HRMS of **1,3,5-triphenyl pyrazole**



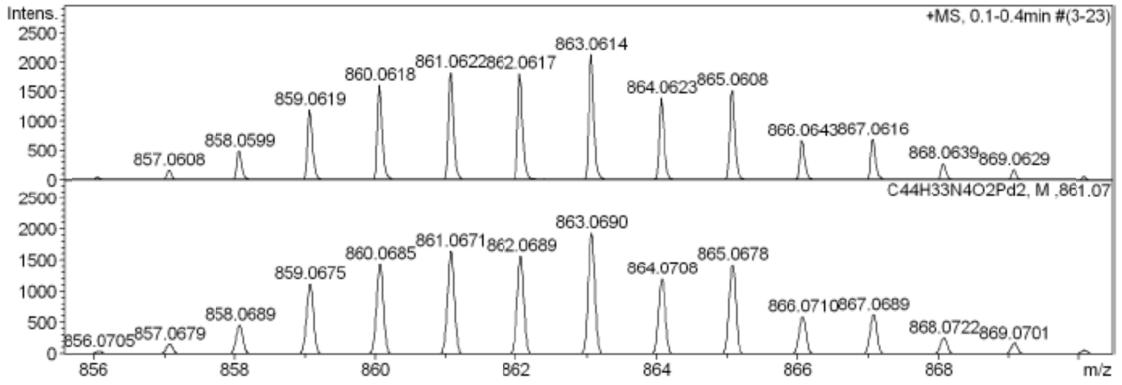
^{1}H NMR of Palladacycle (**1**)



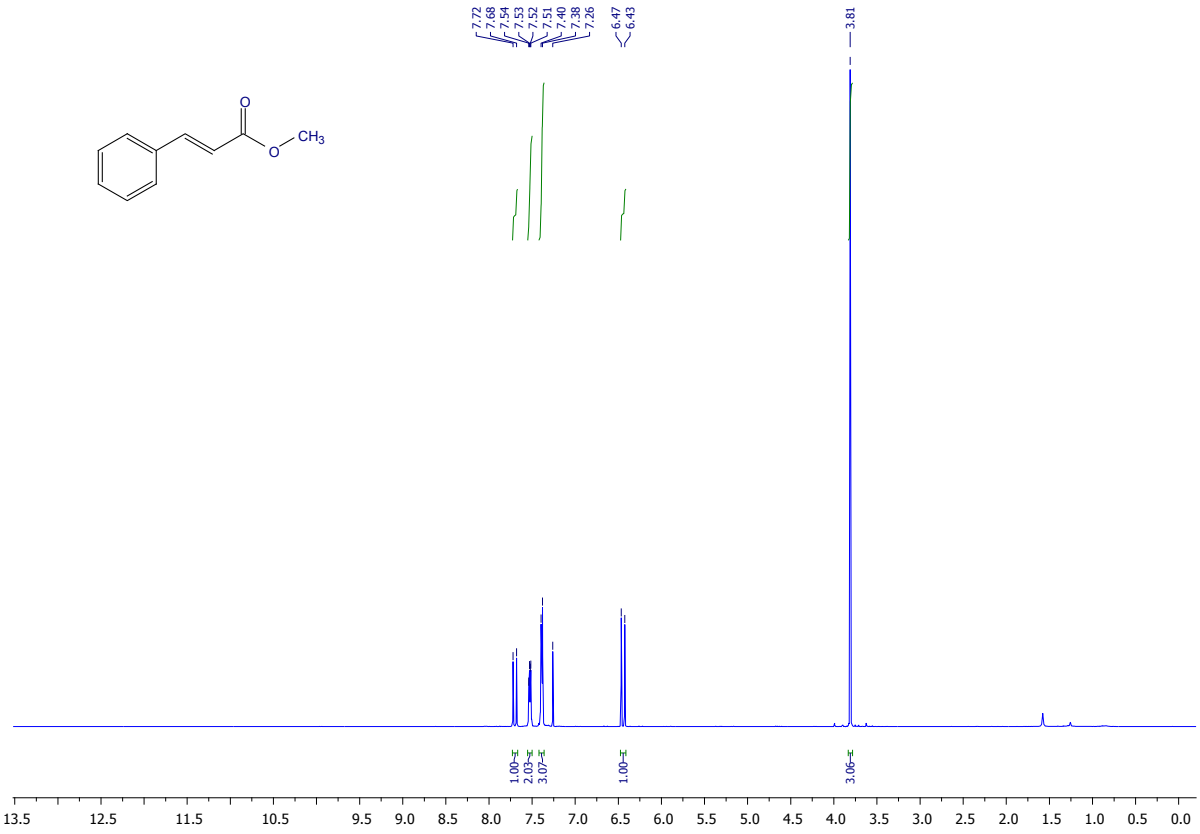
^{13}C NMR of Palladacycle (**1**)



HRMS of Palladacycle (**1)**



^{1}H & ^{13}C NMR of the isolated products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7.68
7.54
7.53
7.52
7.51
7.40
7.38
7.26
6.47
6.43
3.81
O
O
CH3
1.00
2.03
3.07
1.00
3.06
13.5
12.5
11.5
10.5
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
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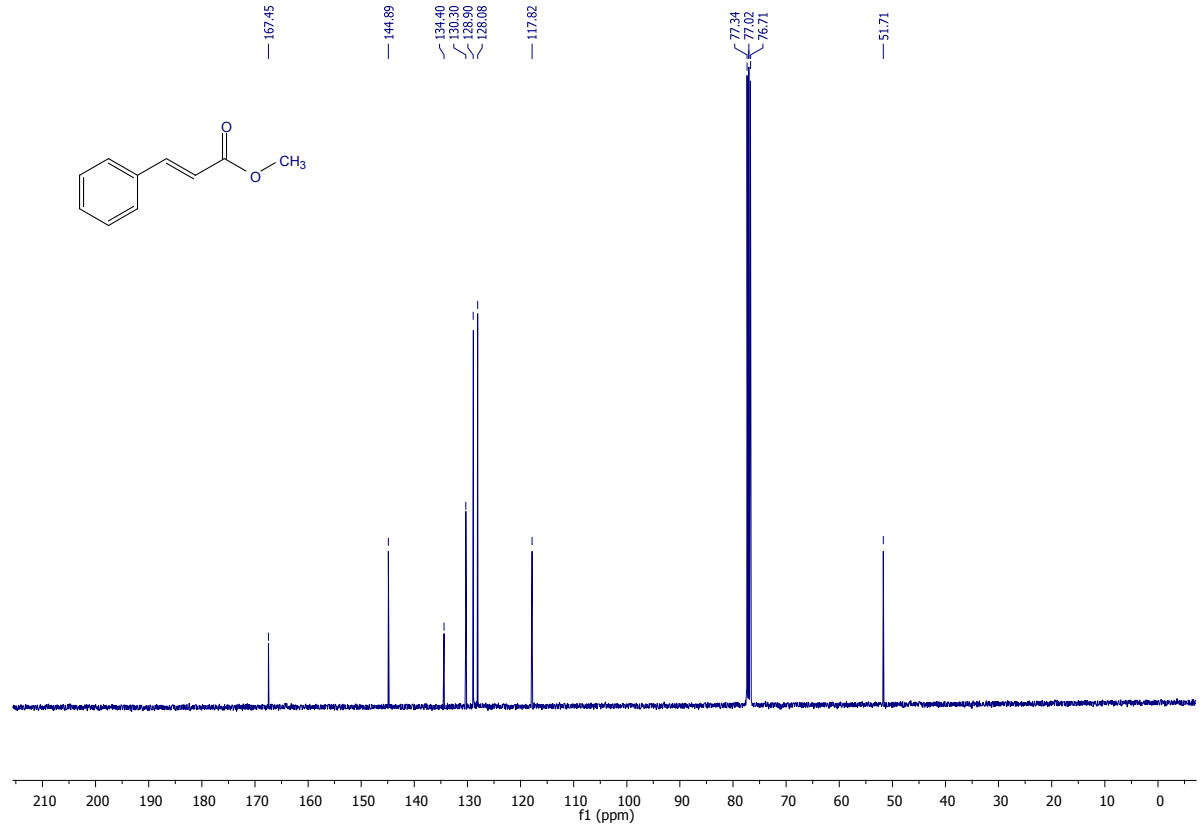
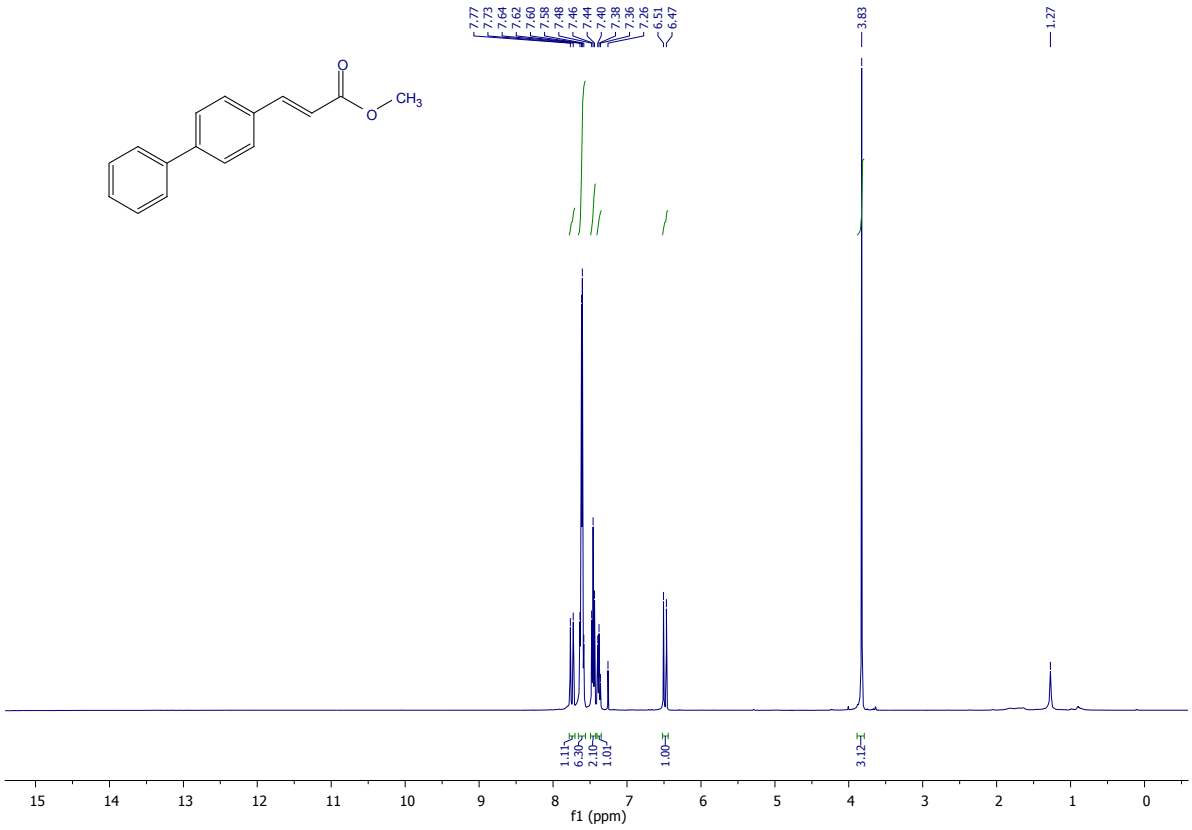
2.0
1.5
1.0
0.5
0.0


167.45
144.89
134.40
130.30
128.90
128.08
117.82
77.34
77.02
76.71
51.71
O
O
CH3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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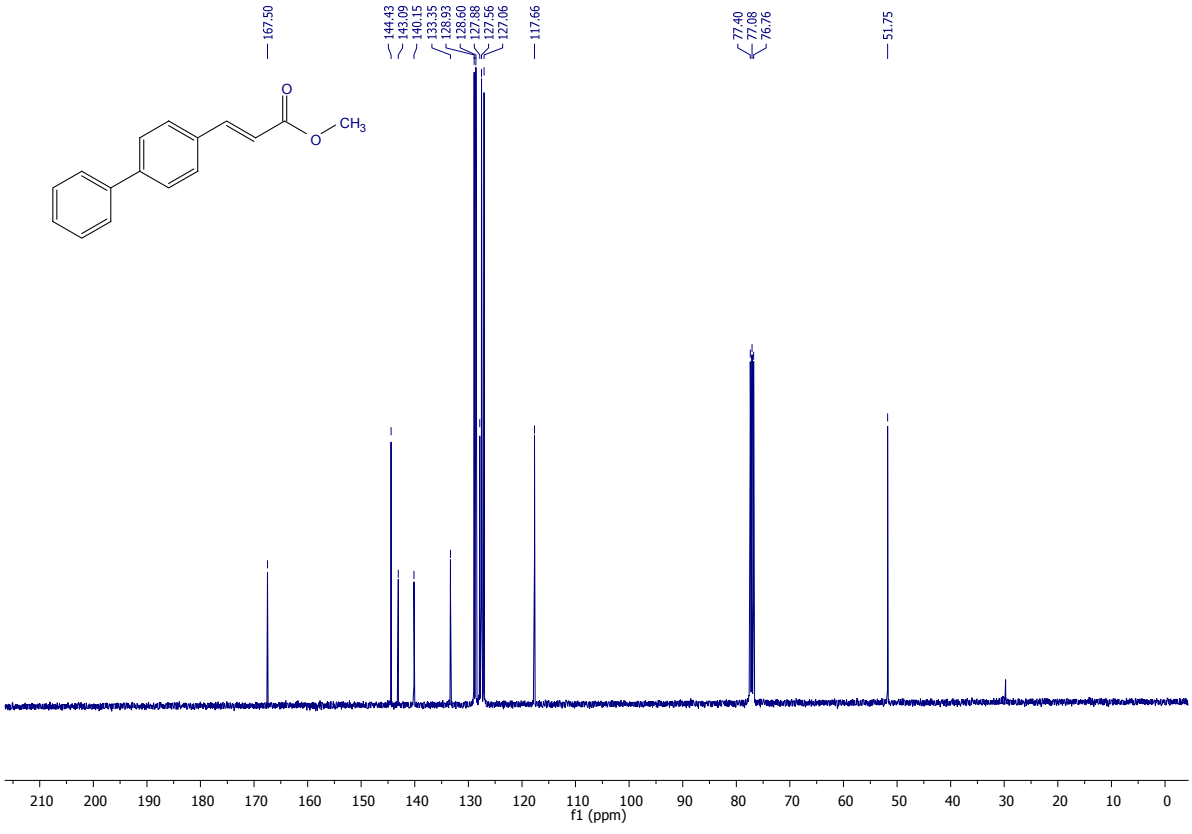
7.62
7.60
7.58
7.48
7.46
7.44
7.40
7.38
7.36
7.26
6.51
6.47
3.83
1.27
O
O
CH3
1.11
6.30
2.10
1.01
1.00
3.12
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)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140.15
133.35
128.93
128.60
127.88
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127.06
117.66
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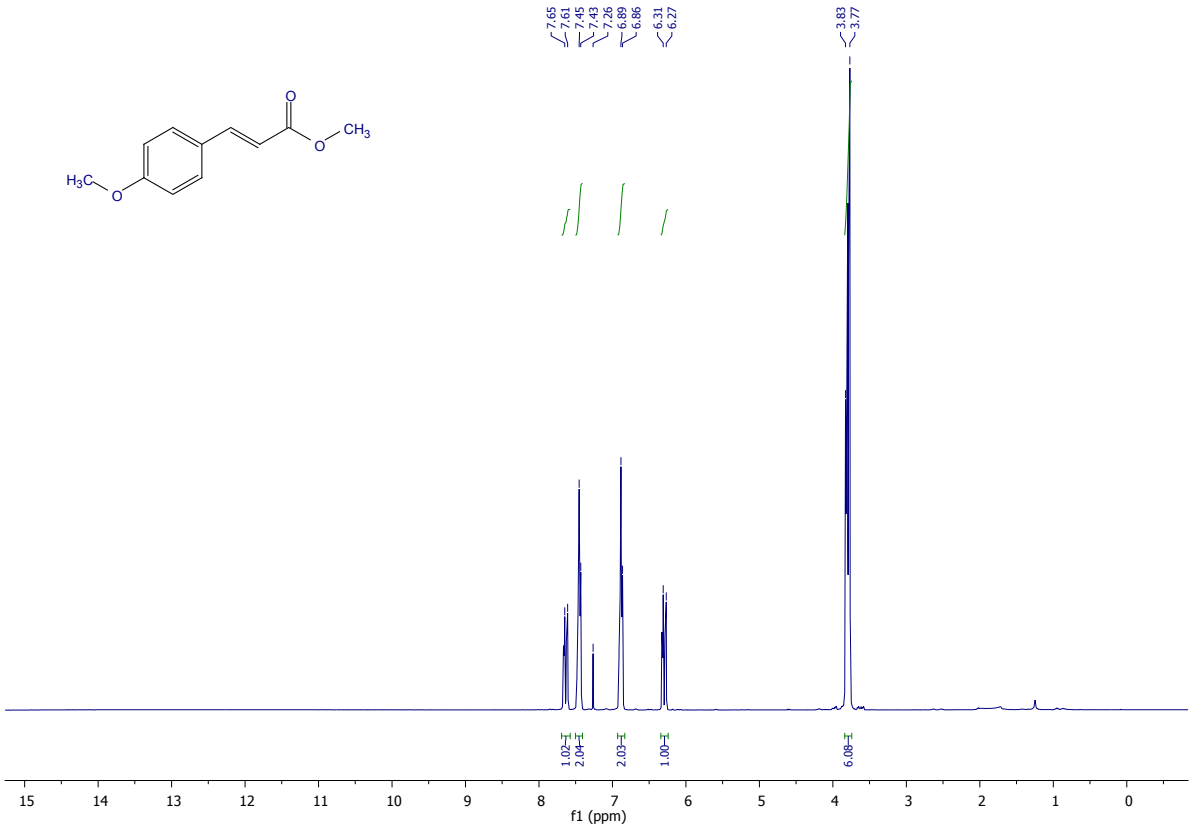
76.76
51.75
O
O
CH3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.61
7.45
7.43
7.26
6.89
6.86
6.31
6.27
3.83
3.77
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O
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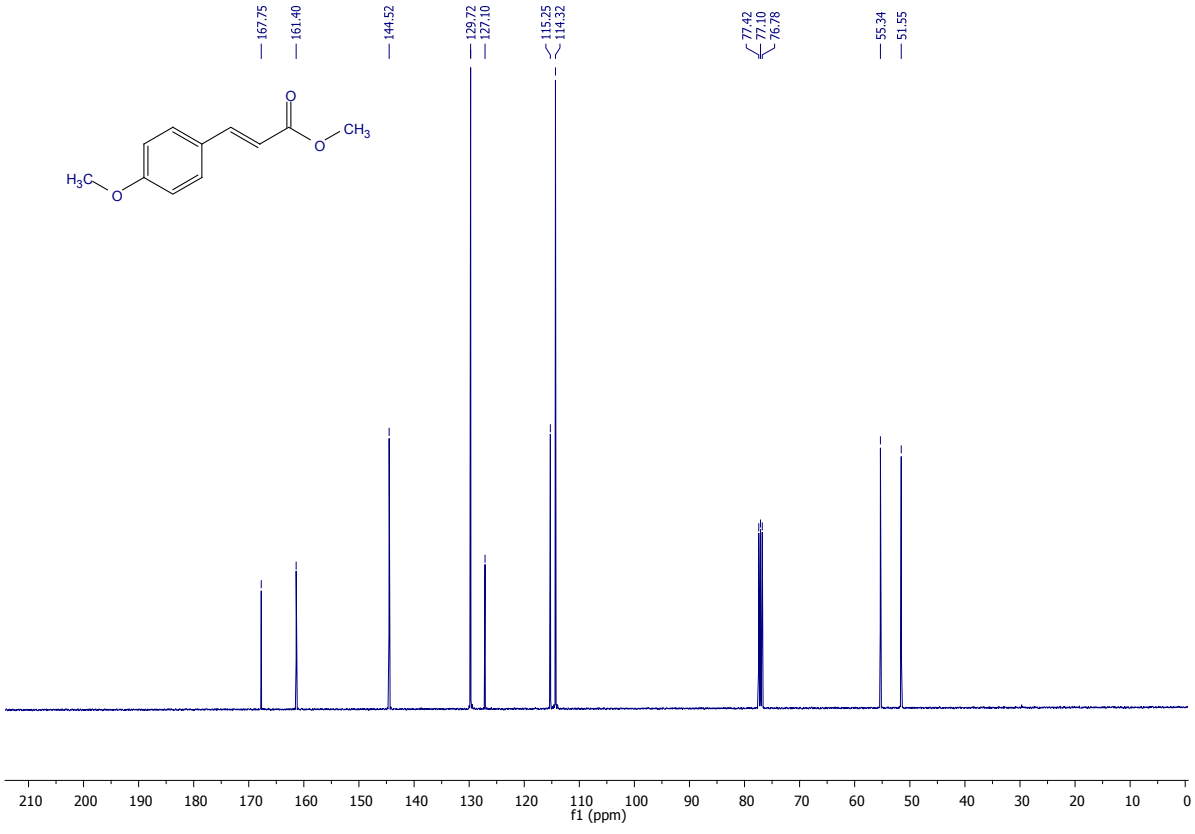
H3C
O
1.02
2.04
2.03
1.00
6.08
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)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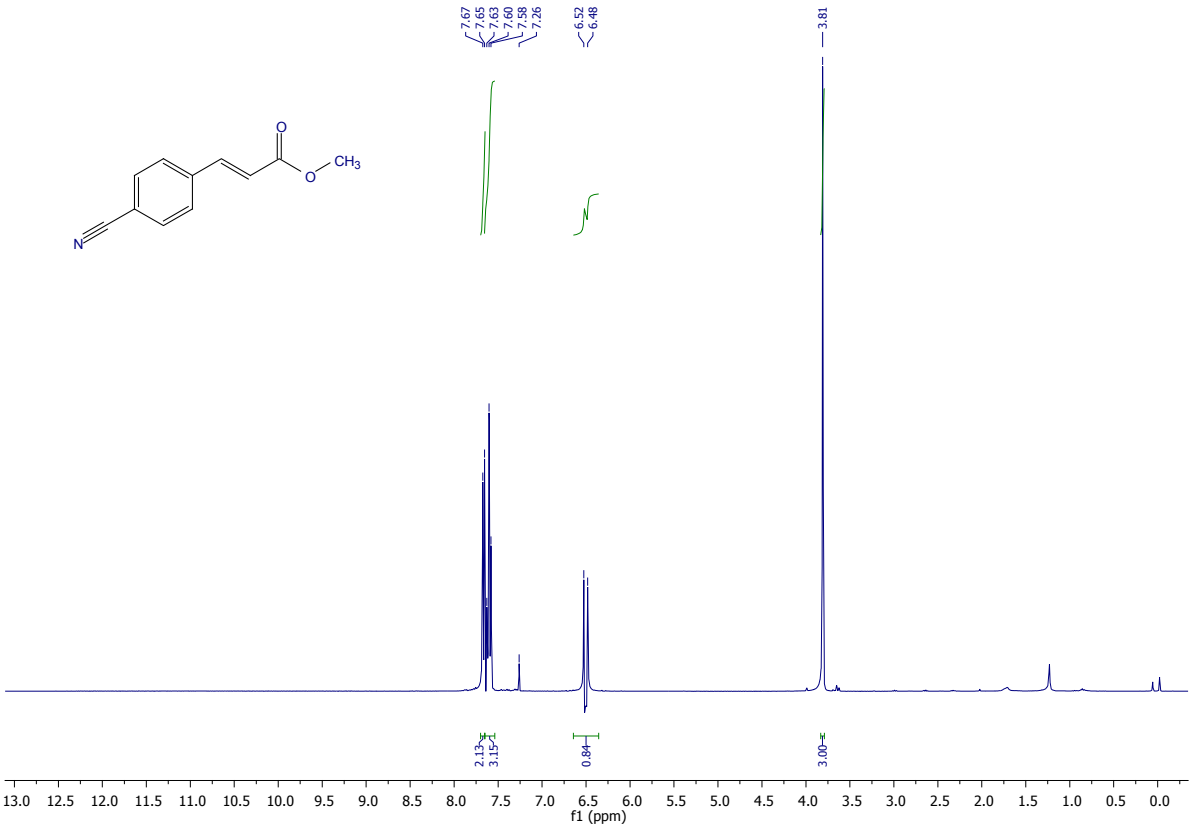
161.40
144.52
129.72
127.10
115.25
114.32
77.42
77.10
76.78
55.34
51.55
O
O
CH3
H3C
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.58
7.26
6.52
6.48
3.81
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O
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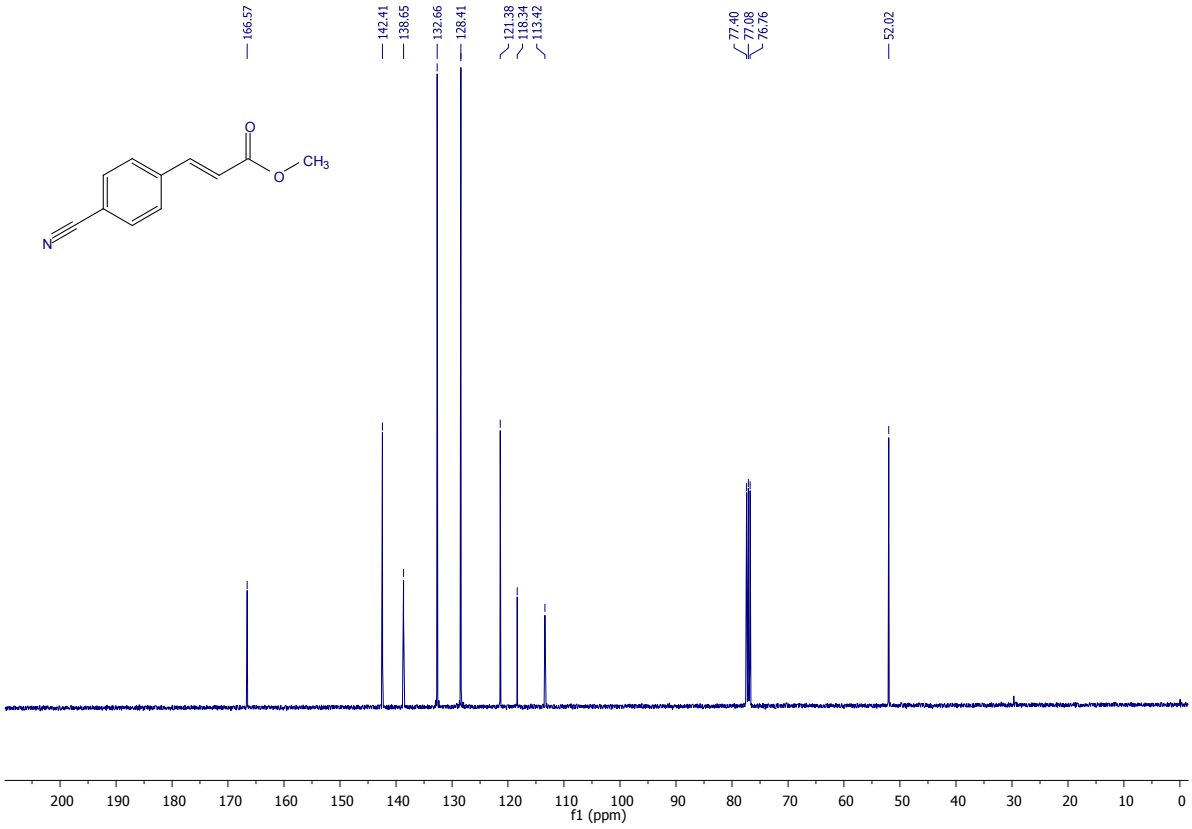
N
2.13
3.15
0.84
3.00
13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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132.66
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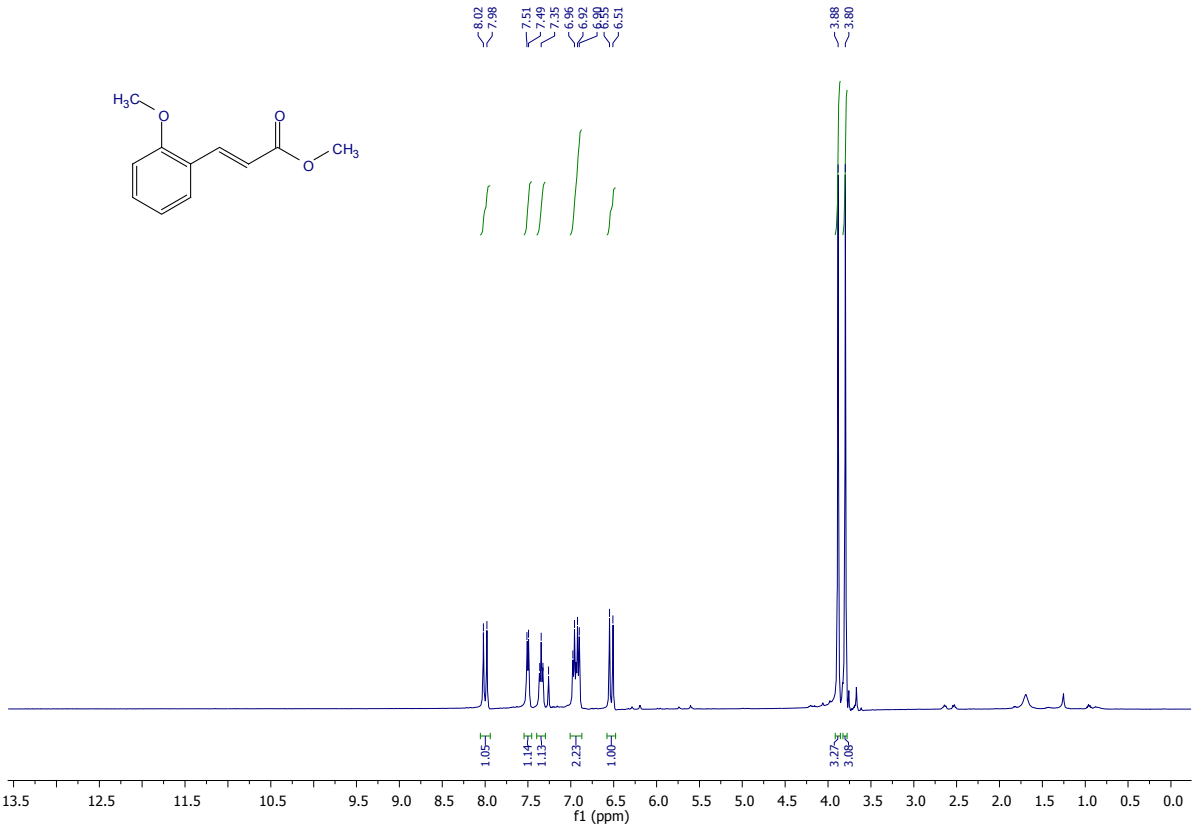
121.38
118.34
113.42
77.40
77.08
76.76
52.02
O
O
CH3
N
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.98
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7.49
7.35
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6.90
6.55
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3.80
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2.23
1.00
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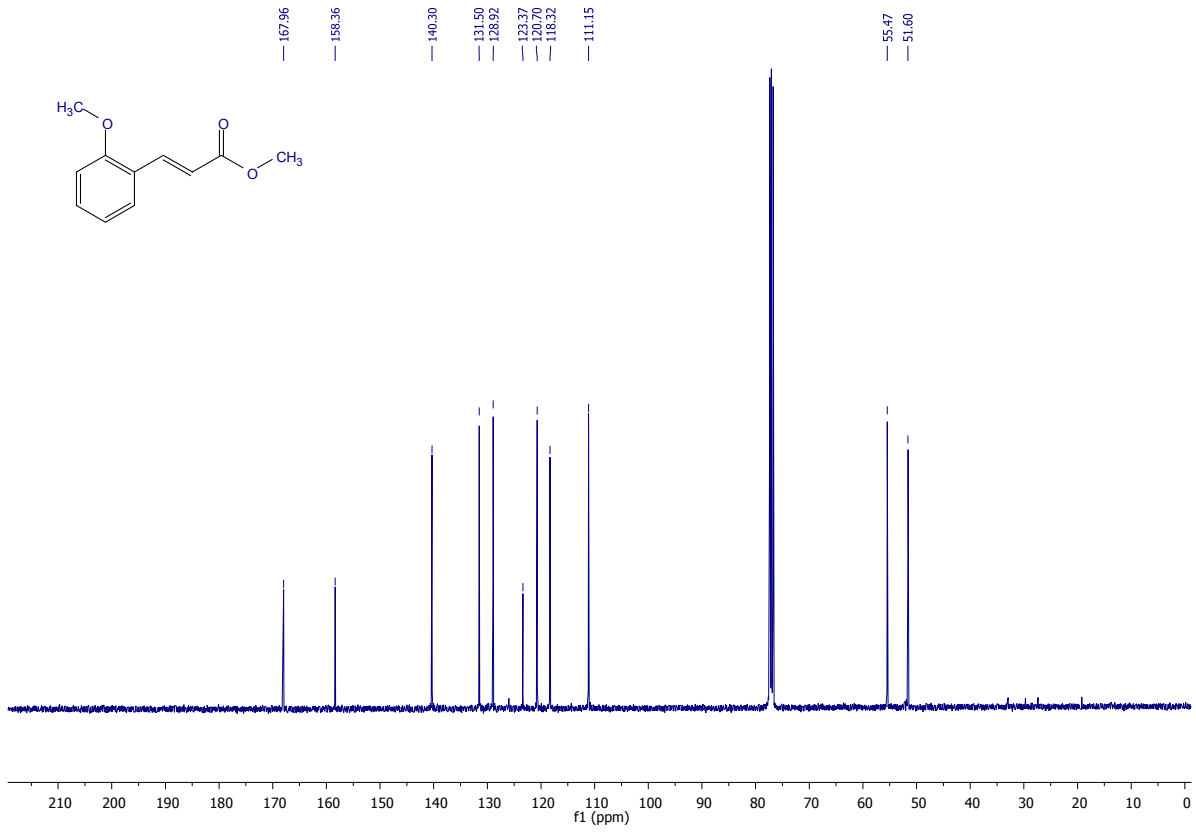
3.08
f1 (ppm)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128.92
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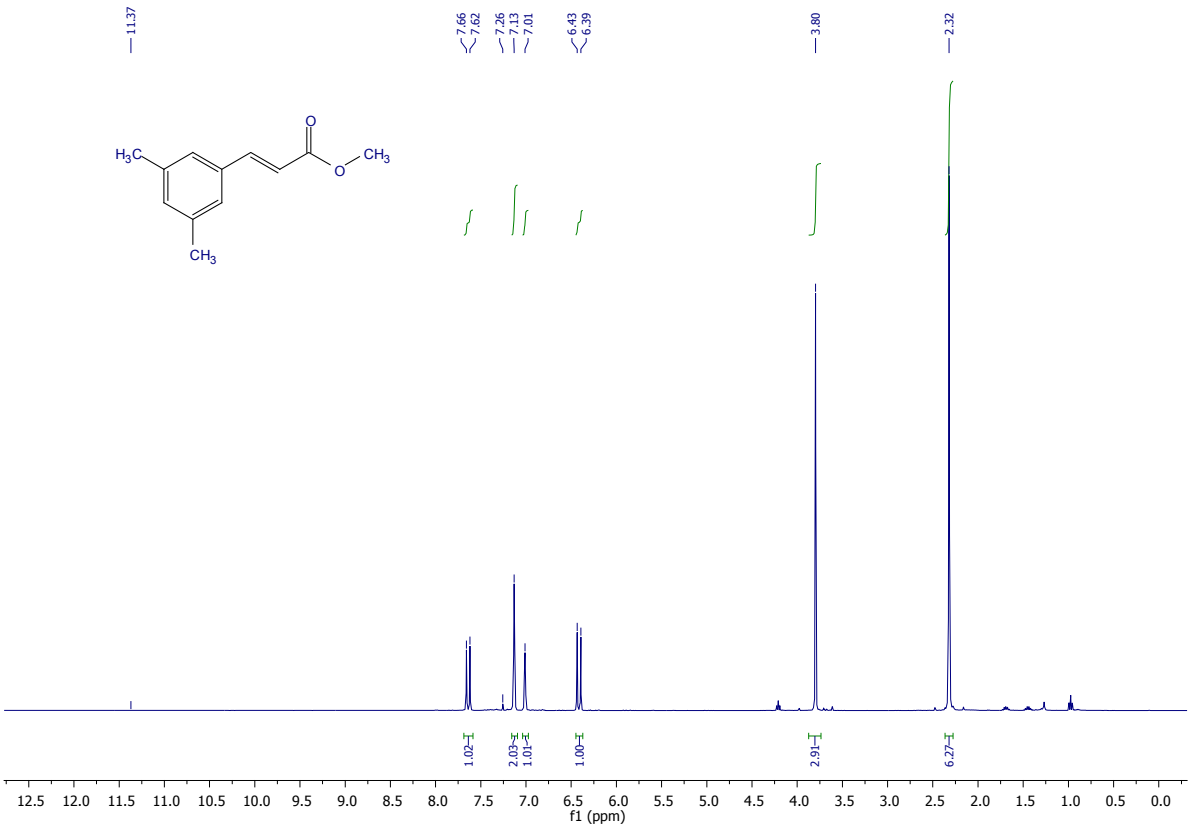
120.70
118.32
111.15
55.47
51.60
f1 (ppm)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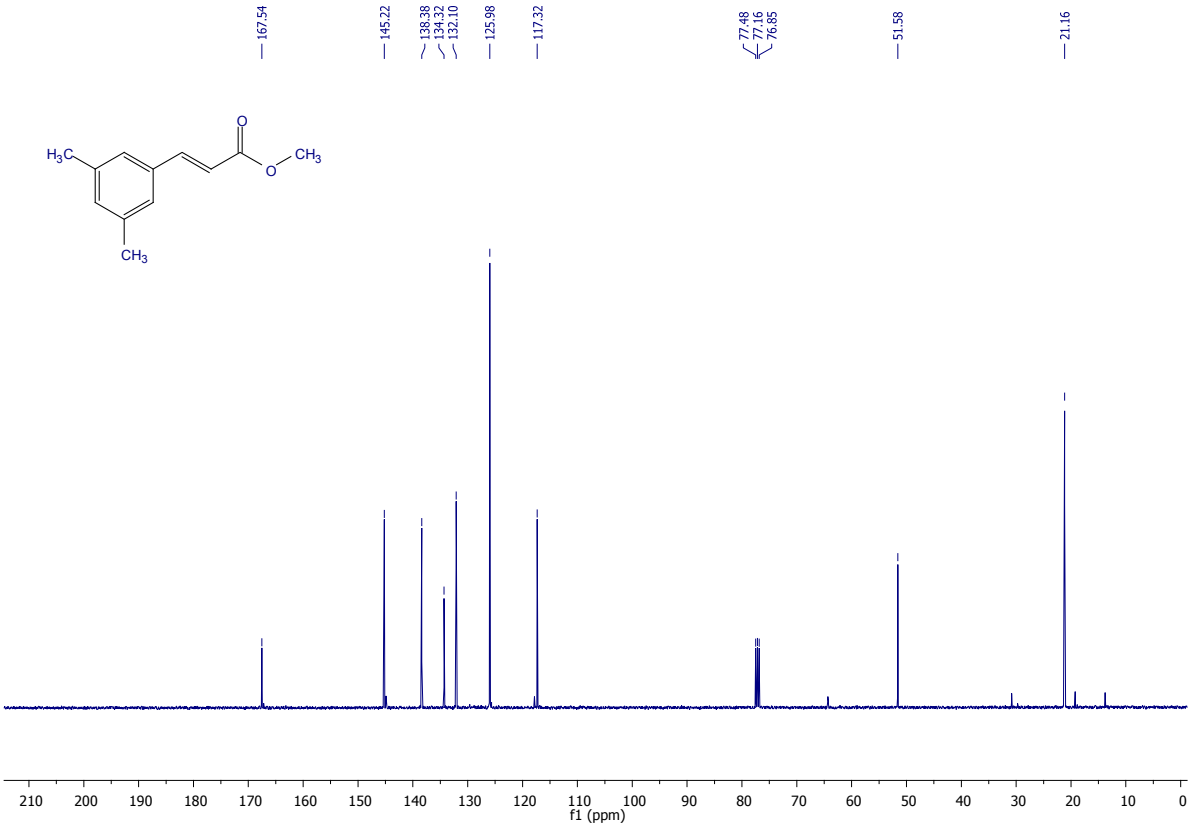
3.80
2.32
O
H3C
O
CH3
CH3
1.02
2.03
1.01
1.00
2.91
6.27
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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H3C
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CH3
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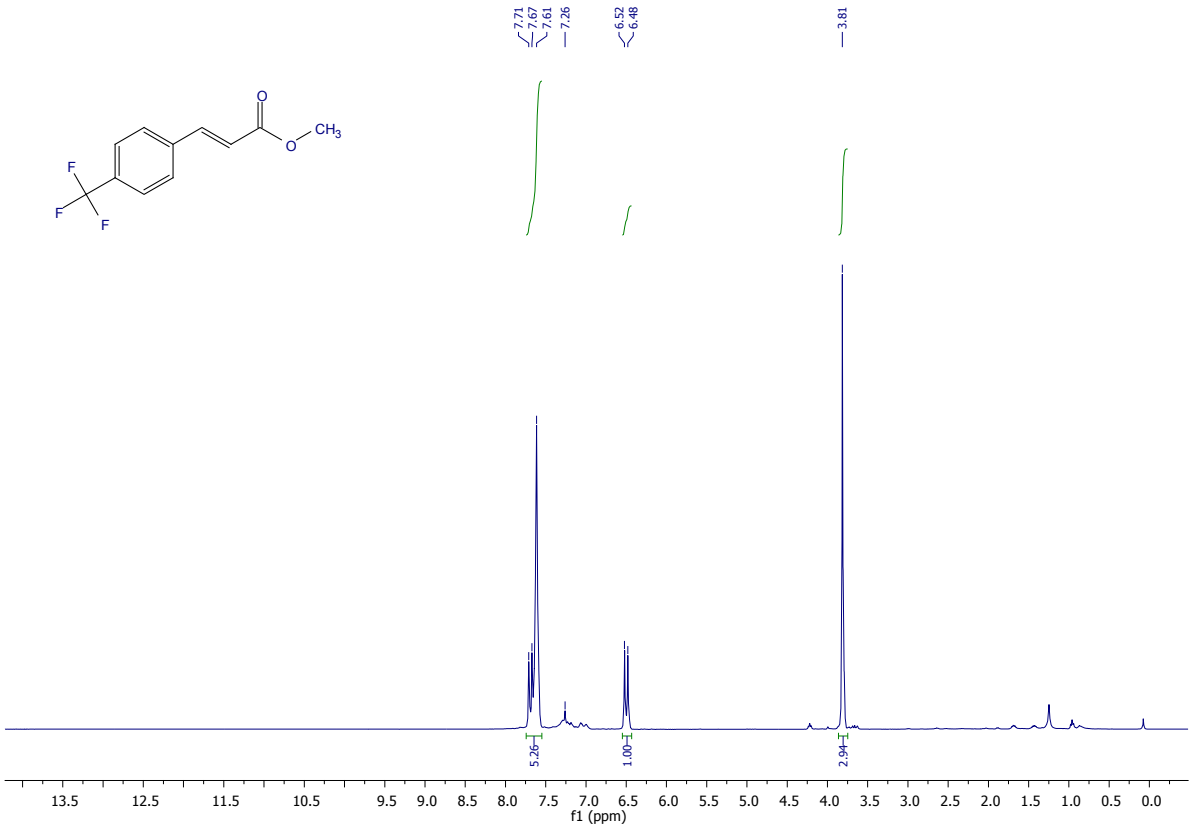
f1 (ppm)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F
F
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2.94
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12.5
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10.5
9.5
9.0
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8.0
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6.5
6.0
5.5
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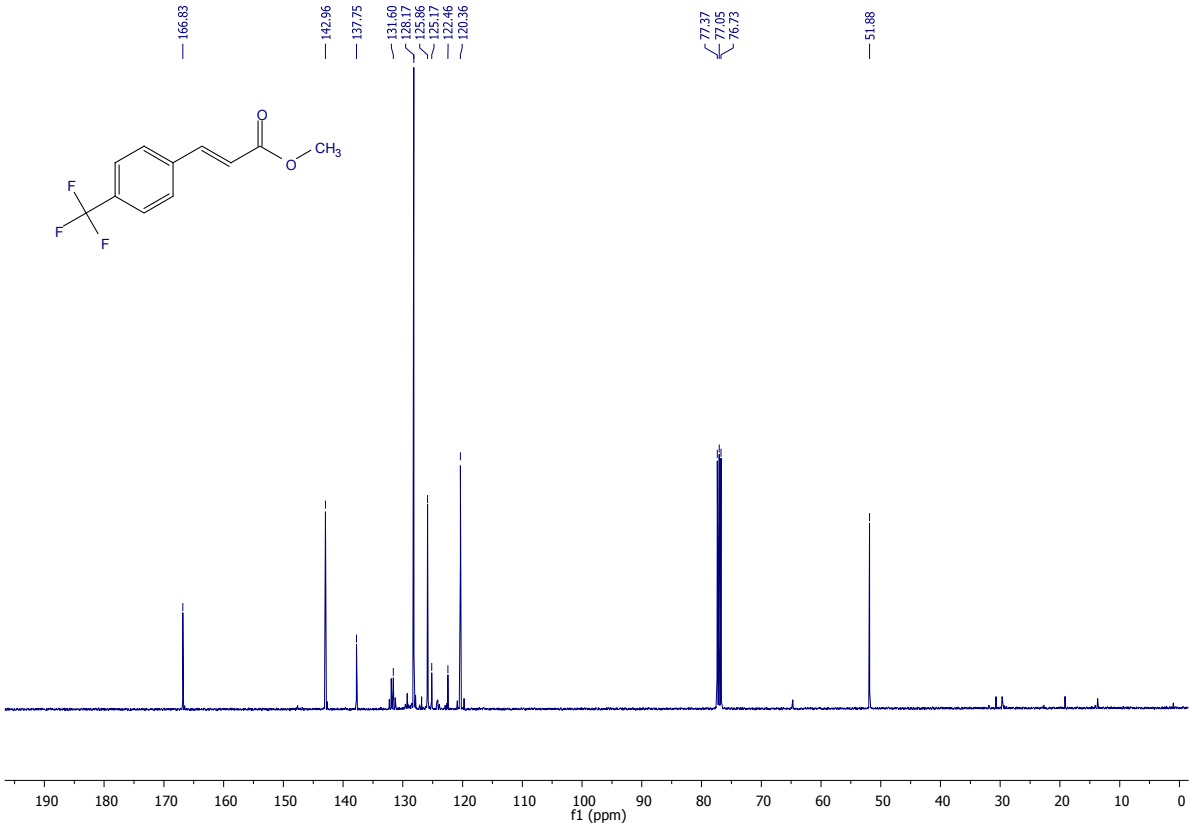
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77.05
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51.88
O
O
CH3
F
F
F
190
180
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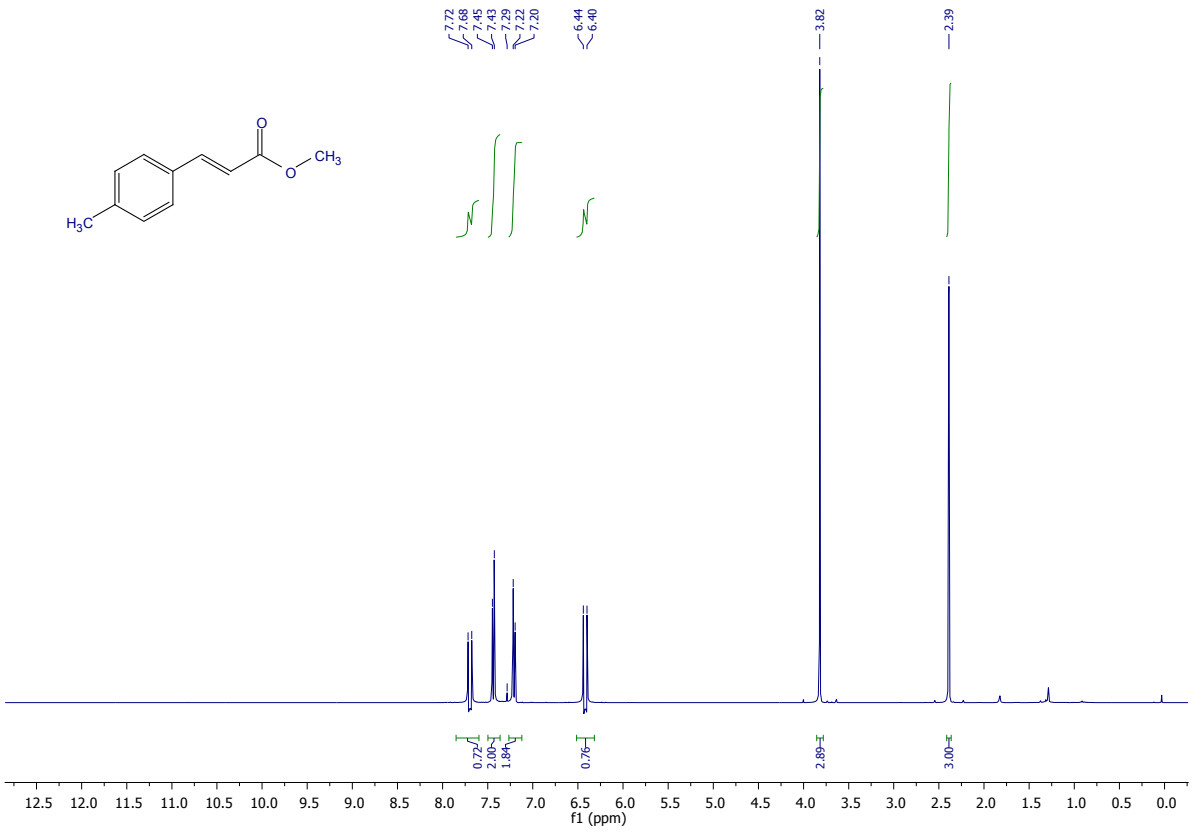
50
40
30
20
10
0
f1 (ppm)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7.68
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3.82
2.39
O
O
CH3
H3C
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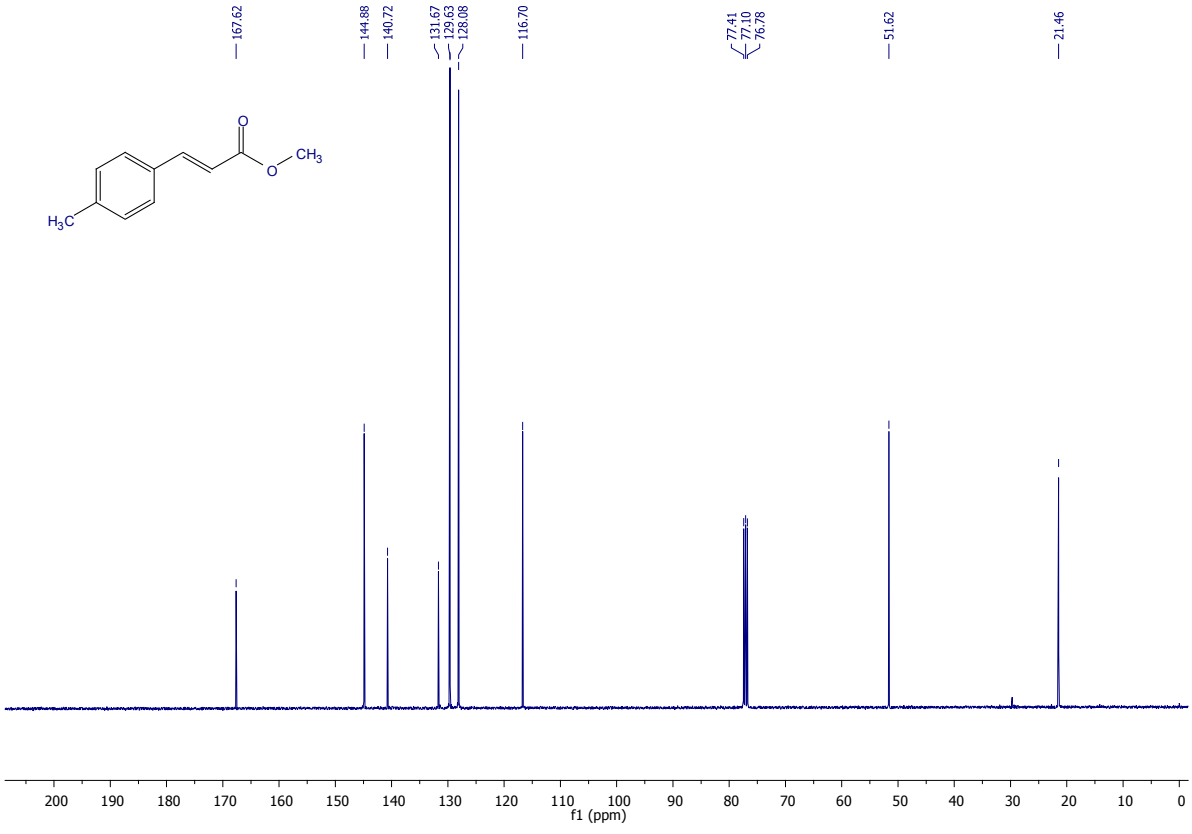
2.00
1.84
0.76
2.89
3.00
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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21.46
O
O
CH3
H3C
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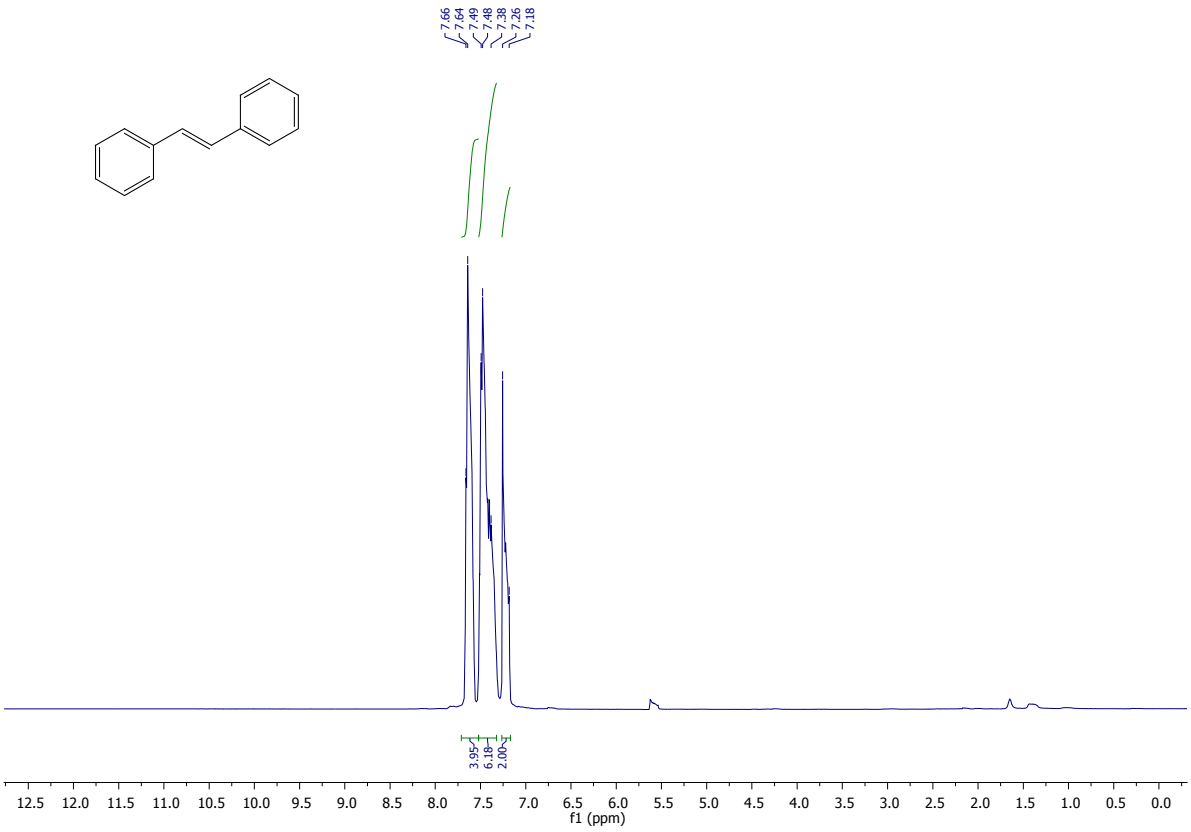
f1 (ppm)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7.64
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7.38
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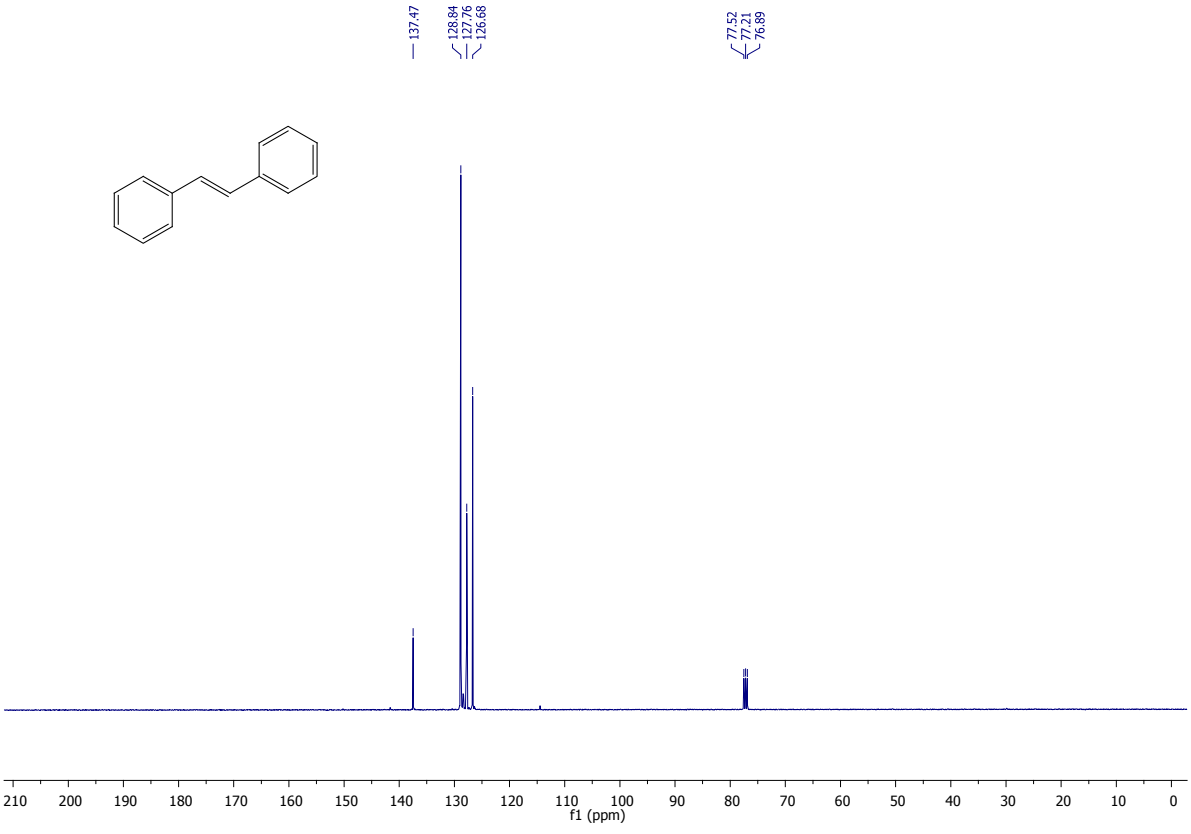
3.95
6.18
2.00
f1 (ppm)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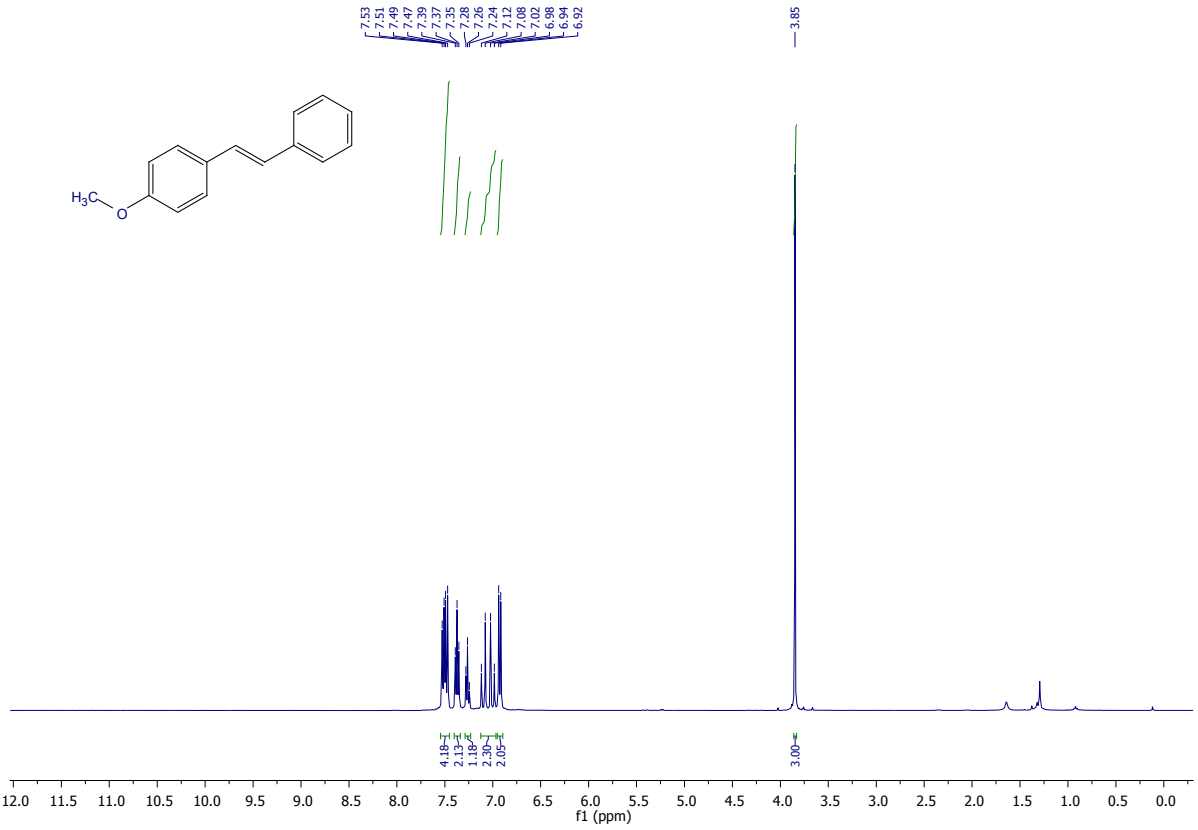
126.68
77.52
77.21
76.89
f1 (ppm)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7.49
7.47
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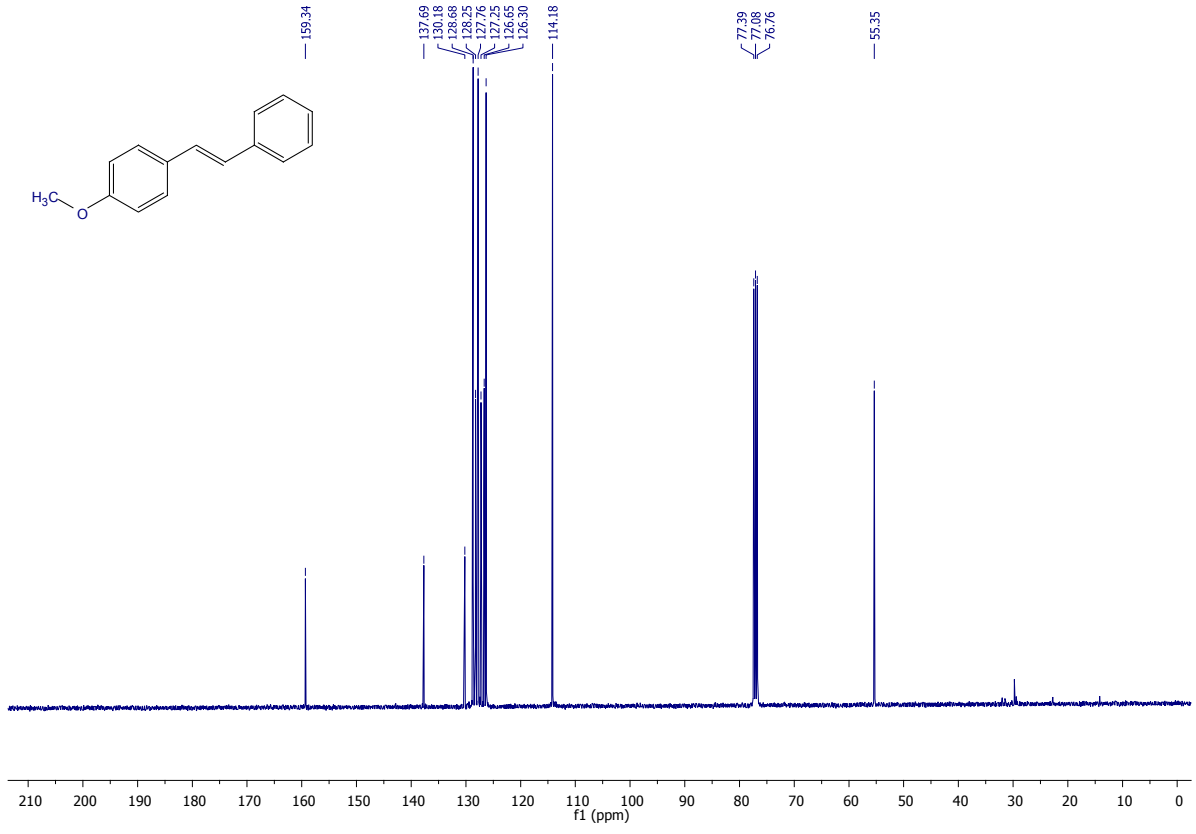
7.37
7.35
7.28
7.26
7.24
7.12
7.08
7.02
6.98
6.94
6.92
3.85
H3C
O
4.18
2.13
1.18
2.30
2.05
3.00
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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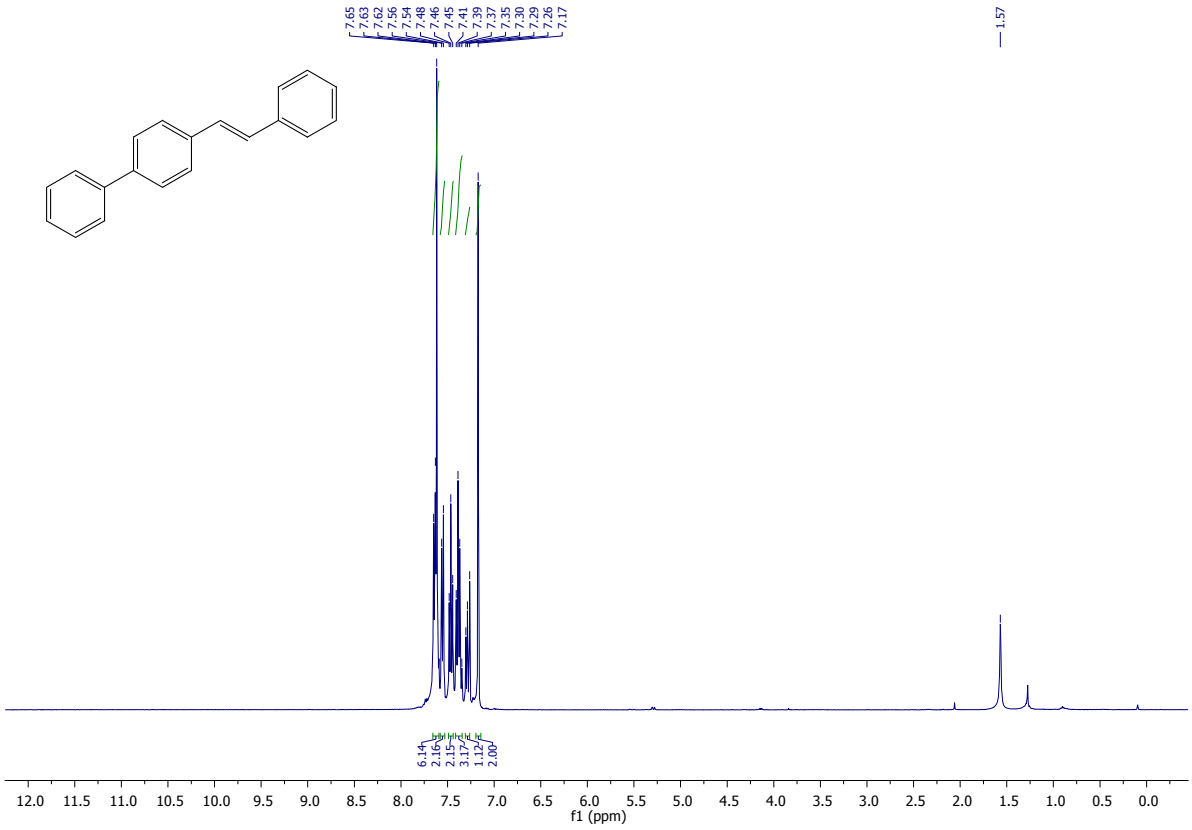
127.76
127.25
126.65
126.30
114.18
77.39
77.08
76.76
55.35
H3C
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.45
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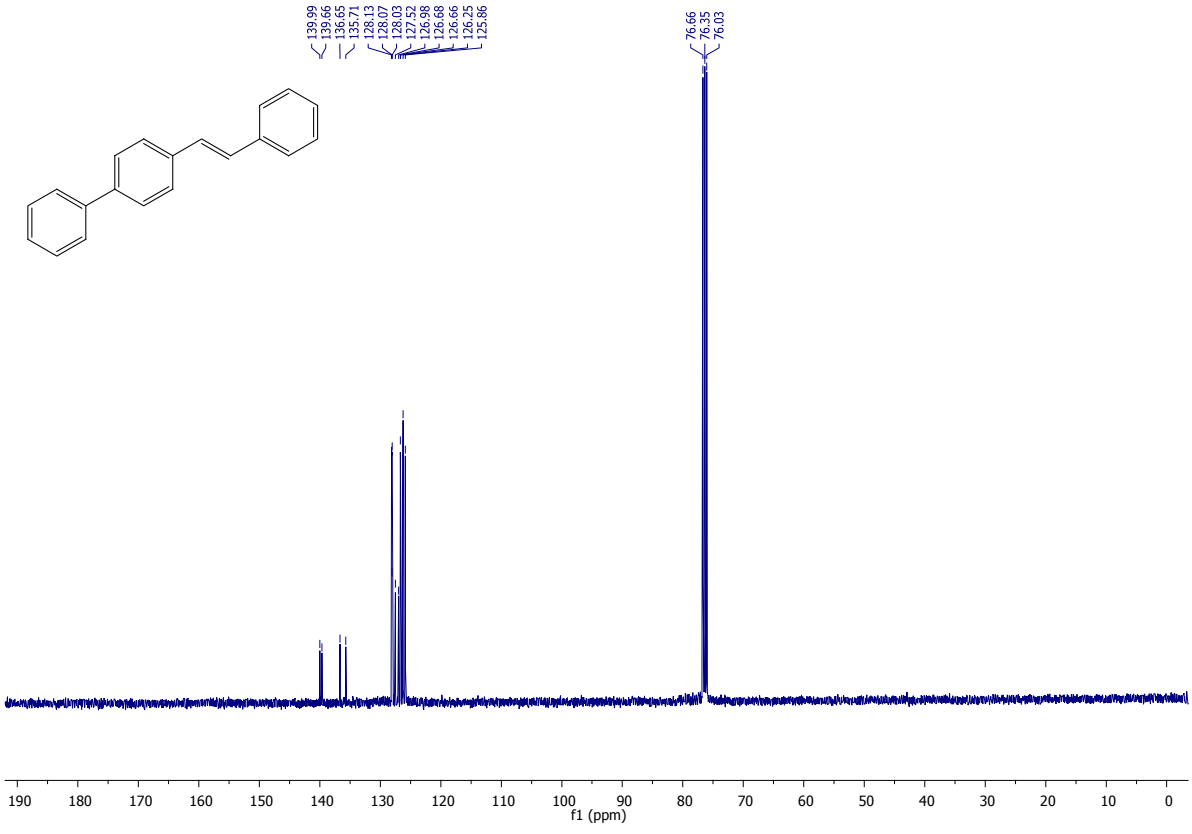
7.39
7.37
7.35
7.30
7.29
7.26
7.17
1.57
6.14
2.16
2.15
3.17
1.12
2.00
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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128.07
128.03
127.52
126.98
126.68
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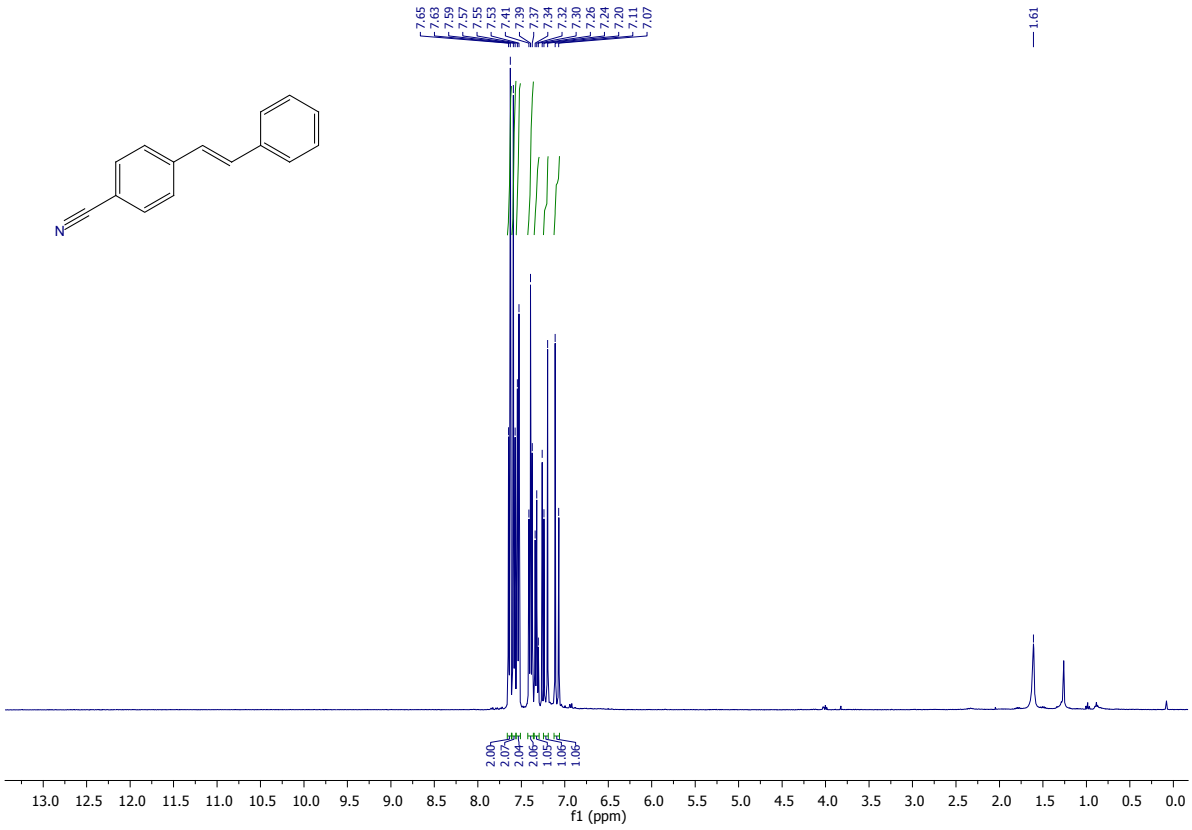
125.86
76.66
76.35
76.03
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.53
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7.39
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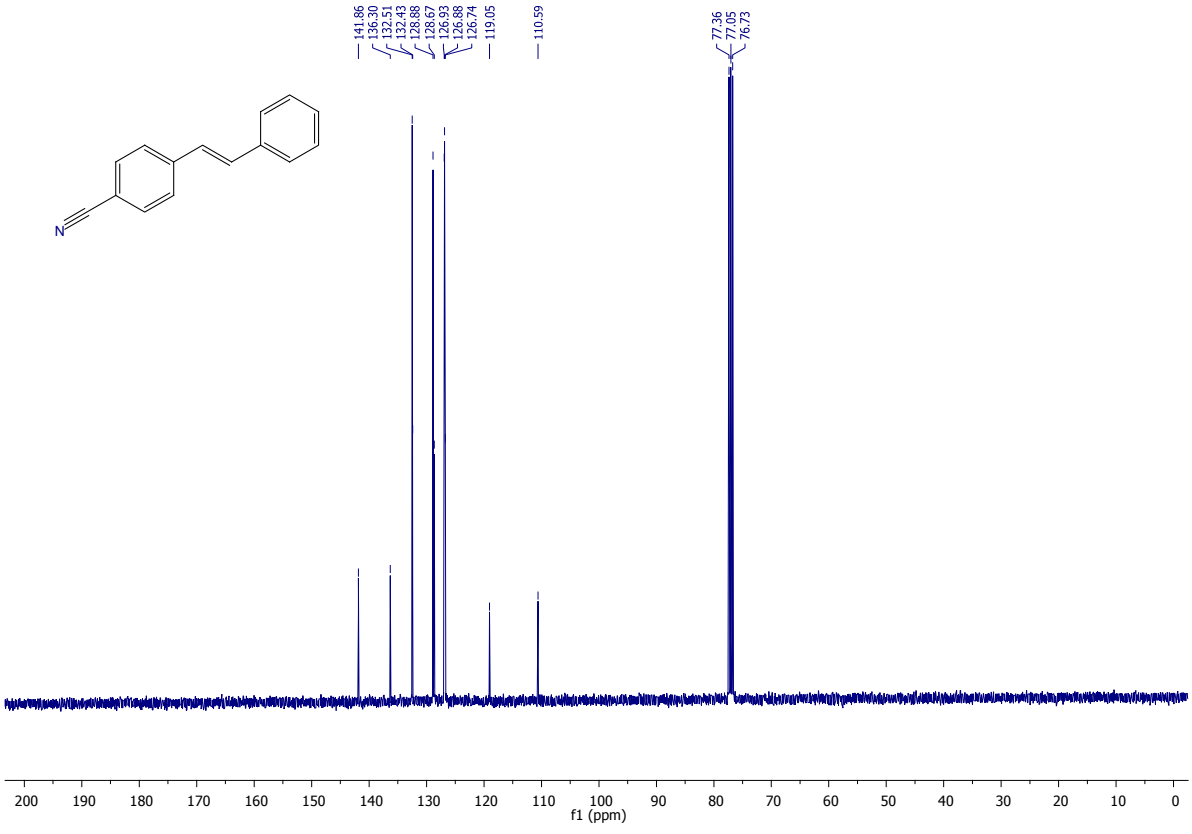
7.34
7.32
7.30
7.26
7.24
7.20
7.11
7.07
1.61
N
2.00
2.07
2.04
2.06
1.05
1.06
1.06
13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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132.43
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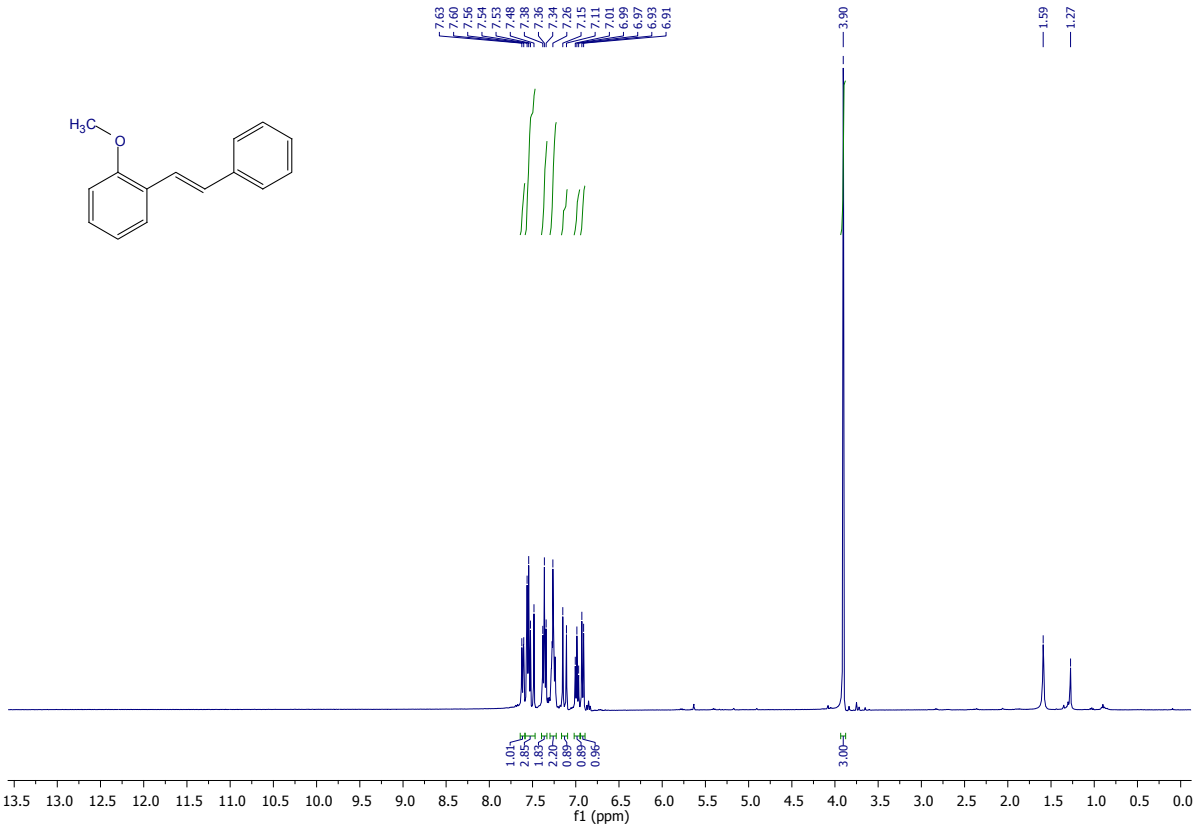
128.67
126.93
126.88
126.74
119.05
110.59
77.36
77.05
76.73
N
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.60
7.56
7.54
7.53
7.48
7.38
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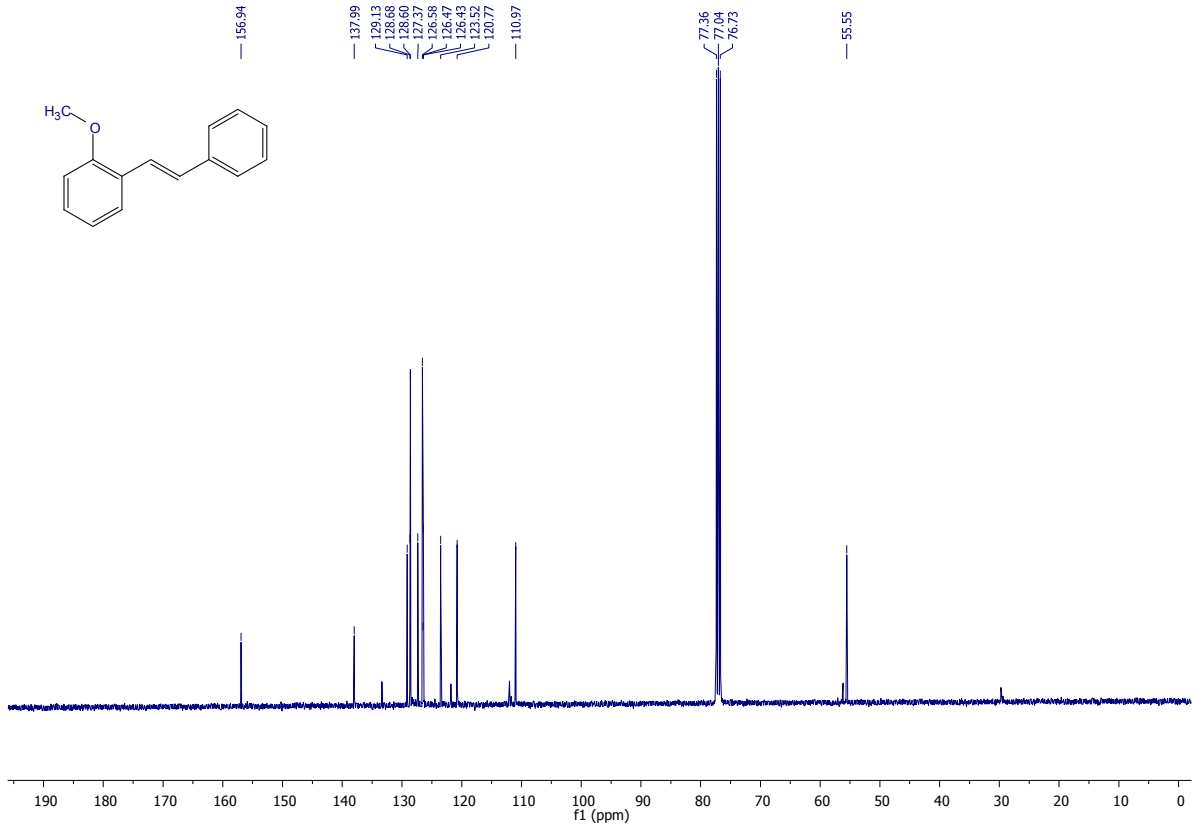
7.34
7.26
7.15
7.11
7.01
6.99
6.97
6.93
6.91
3.90
1.59
1.27
H3C
O
1.01
2.85
1.83
2.20
0.89
0.89
0.96
3.00
13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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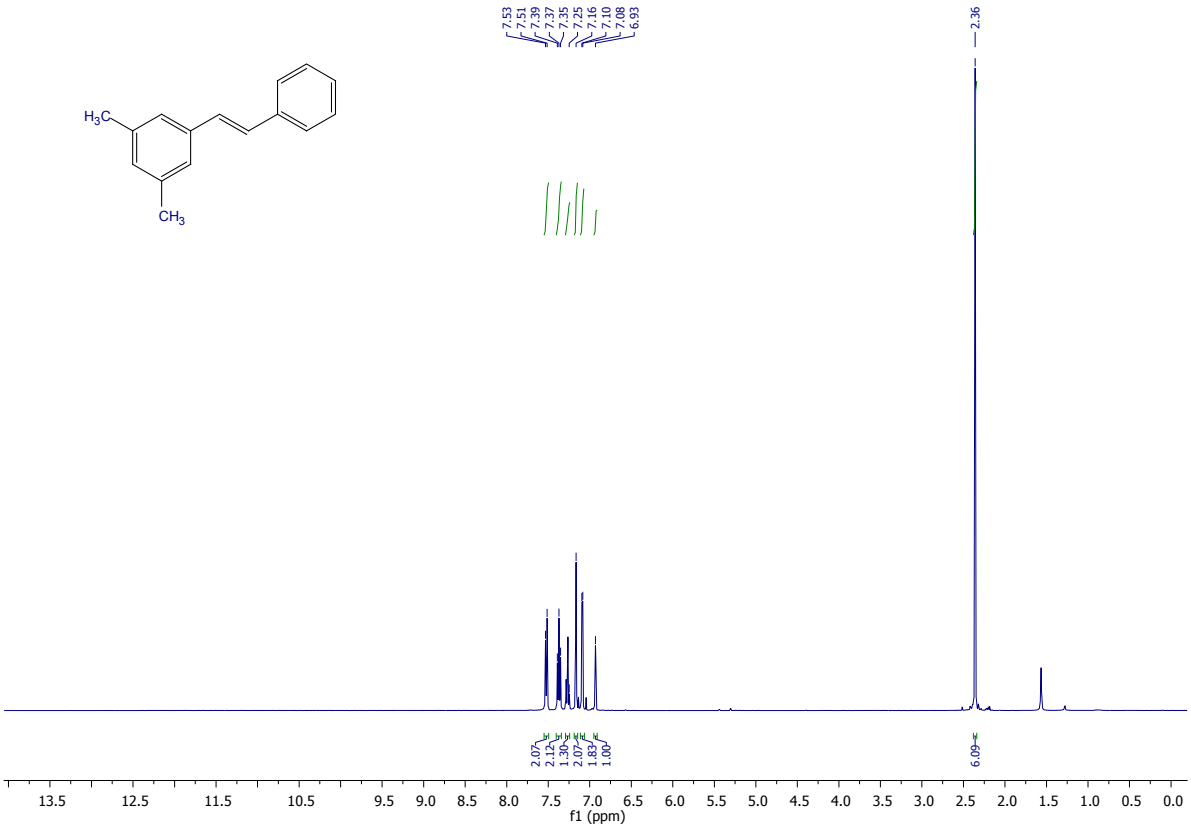
129.13
128.68
128.60
127.37
126.58
126.47
126.43
123.52
120.77
110.97
77.36
77.04
76.73
55.55
H3C
O
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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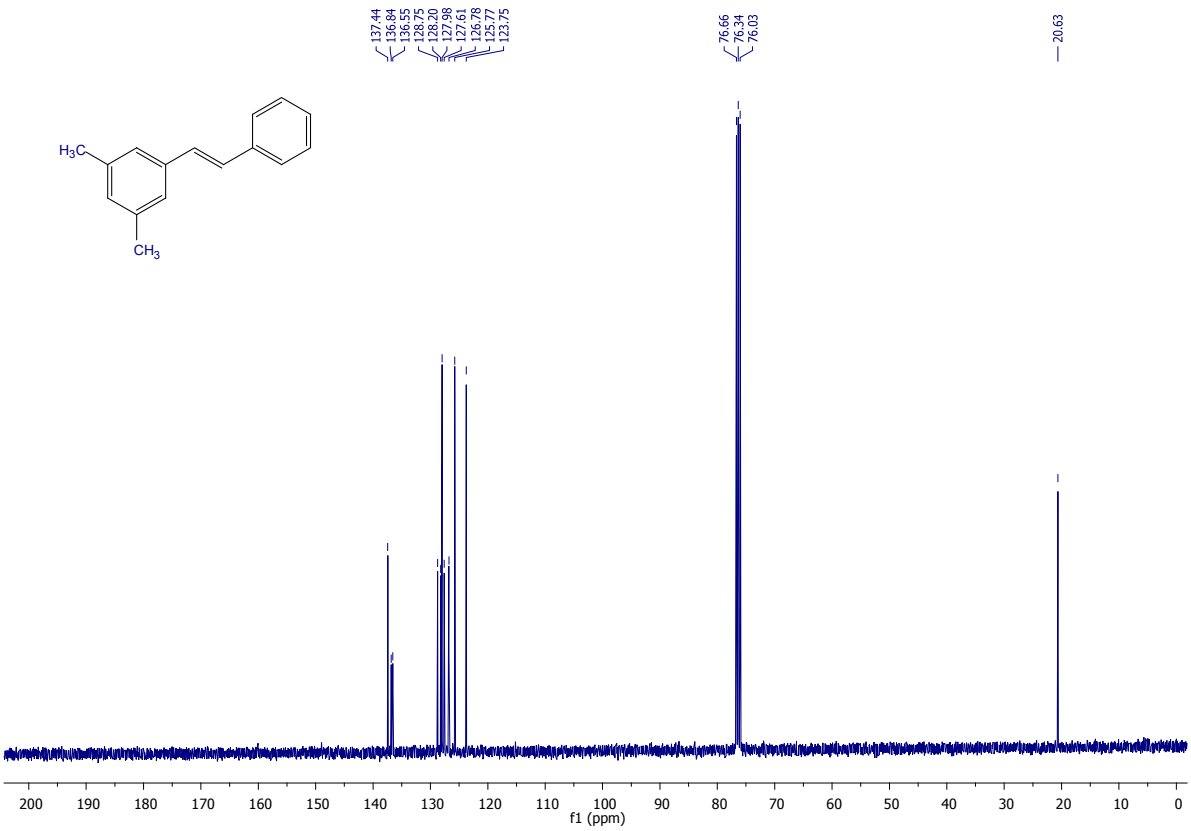
7.51
7.39
7.37
7.35
7.25
7.16
7.10
7.08
6.93
2.36
H3C
CH3
2.07
2.12
1.30
2.07
1.83
1.00
6.09
13.5 12.5 11.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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127.61
126.78
125.77
123.75
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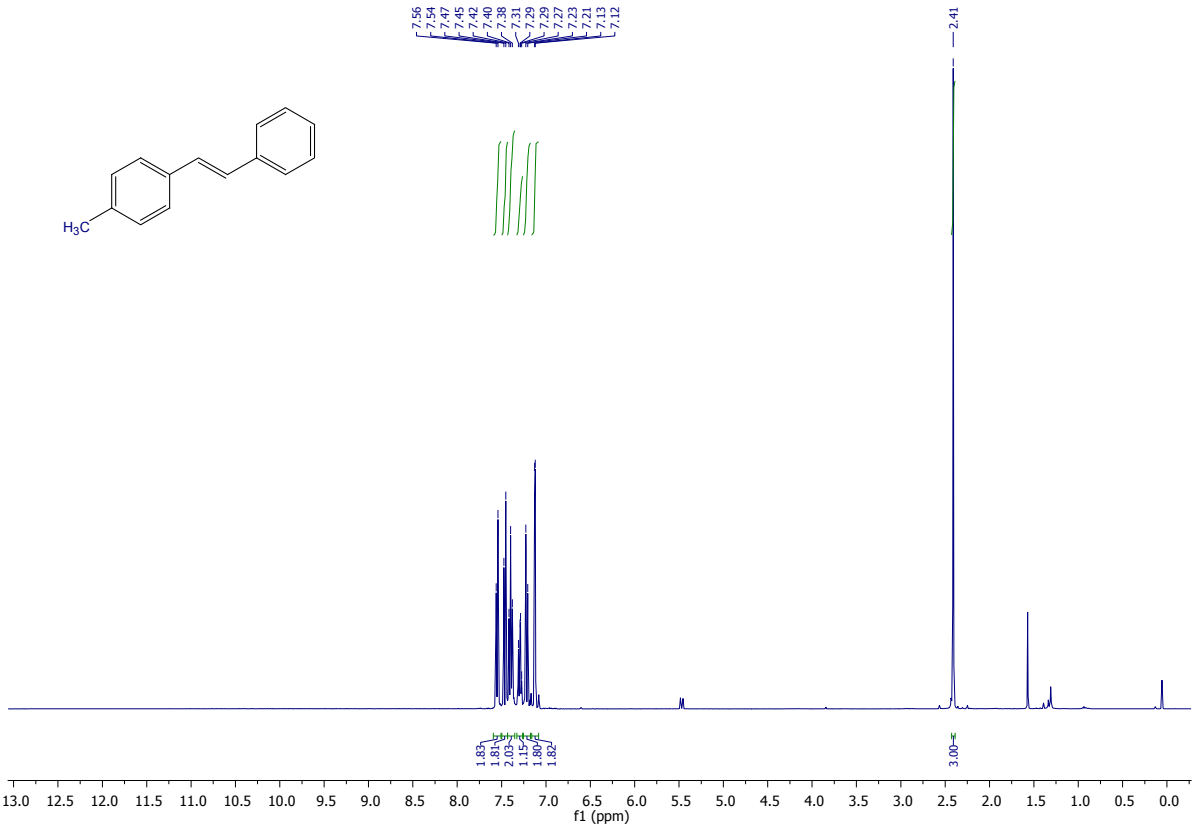
76.03
20.63
H3C
CH3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.54
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7.45
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7.40
7.38
7.31
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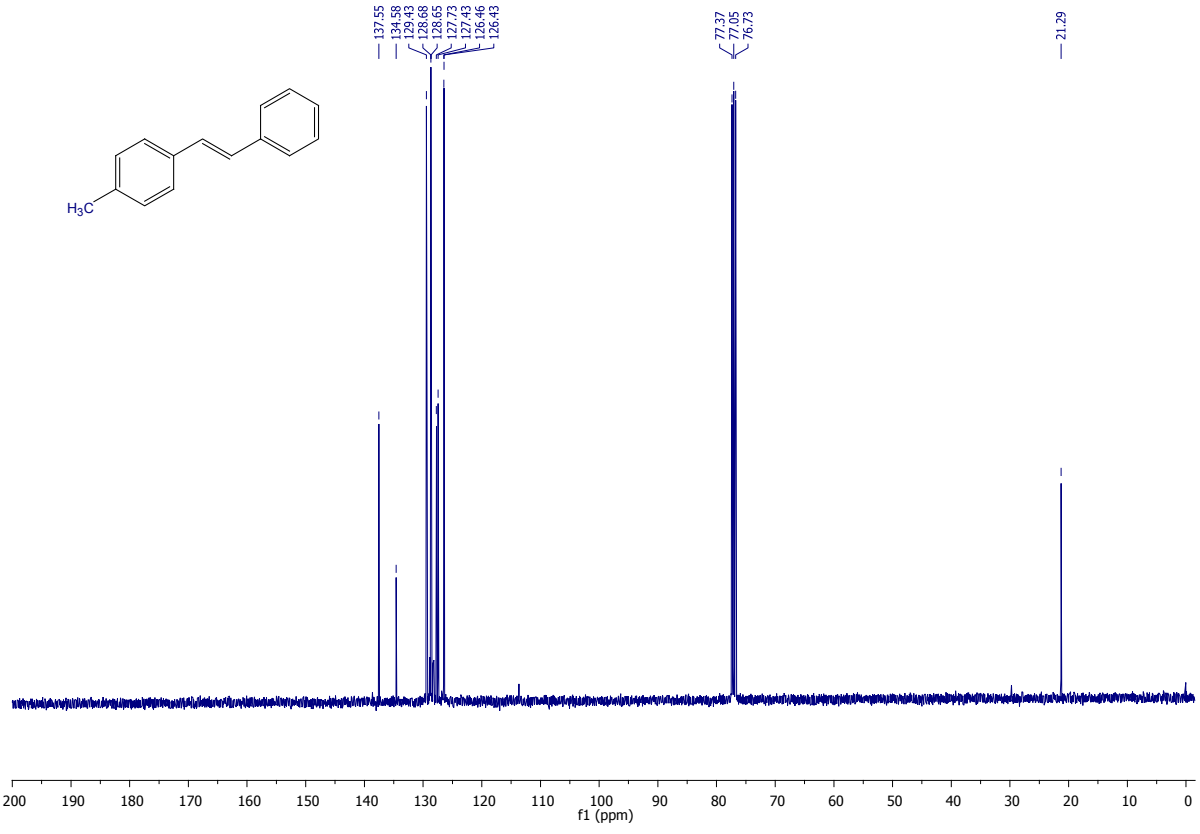
7.29
7.27
7.23
7.21
7.13
7.12
2.41
H3C
1.83
1.81
2.03
1.15
1.80
1.82
3.00
13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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134.58
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128.65
127.73
127.43
126.46
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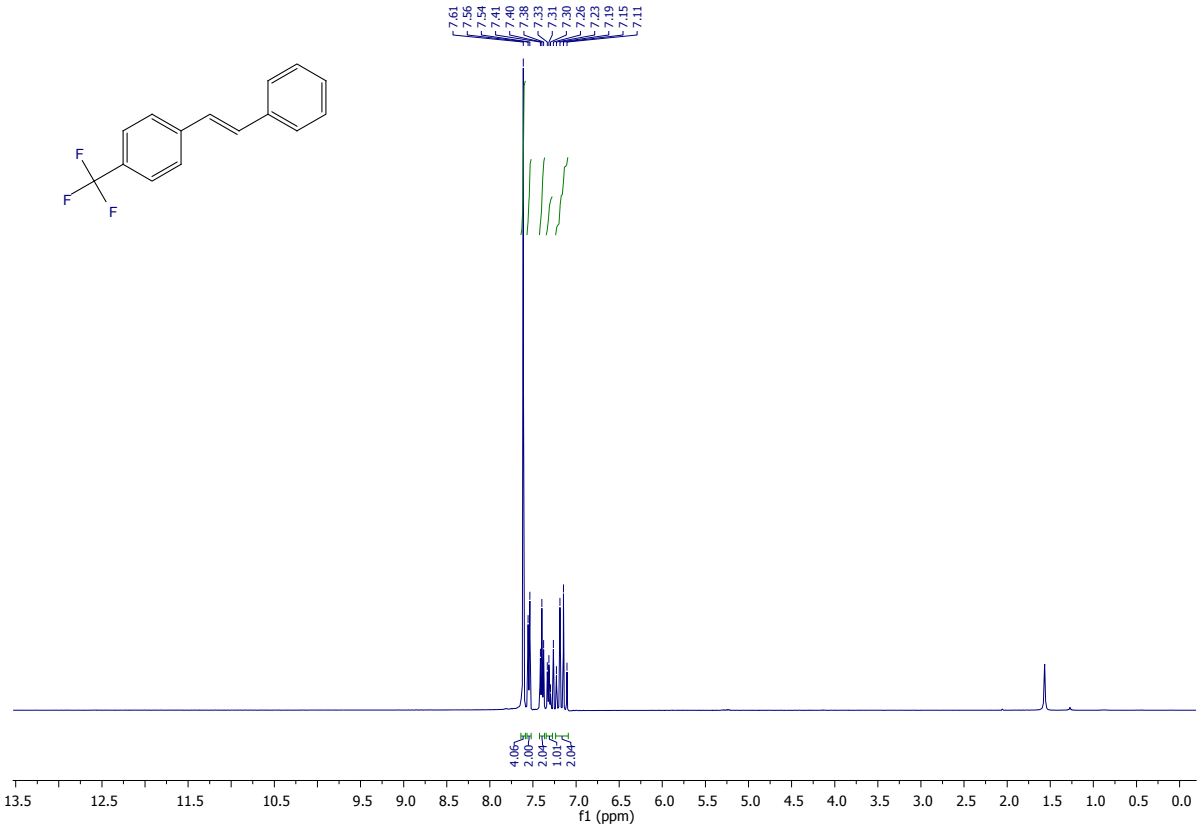
77.05
76.73
21.29
H3C
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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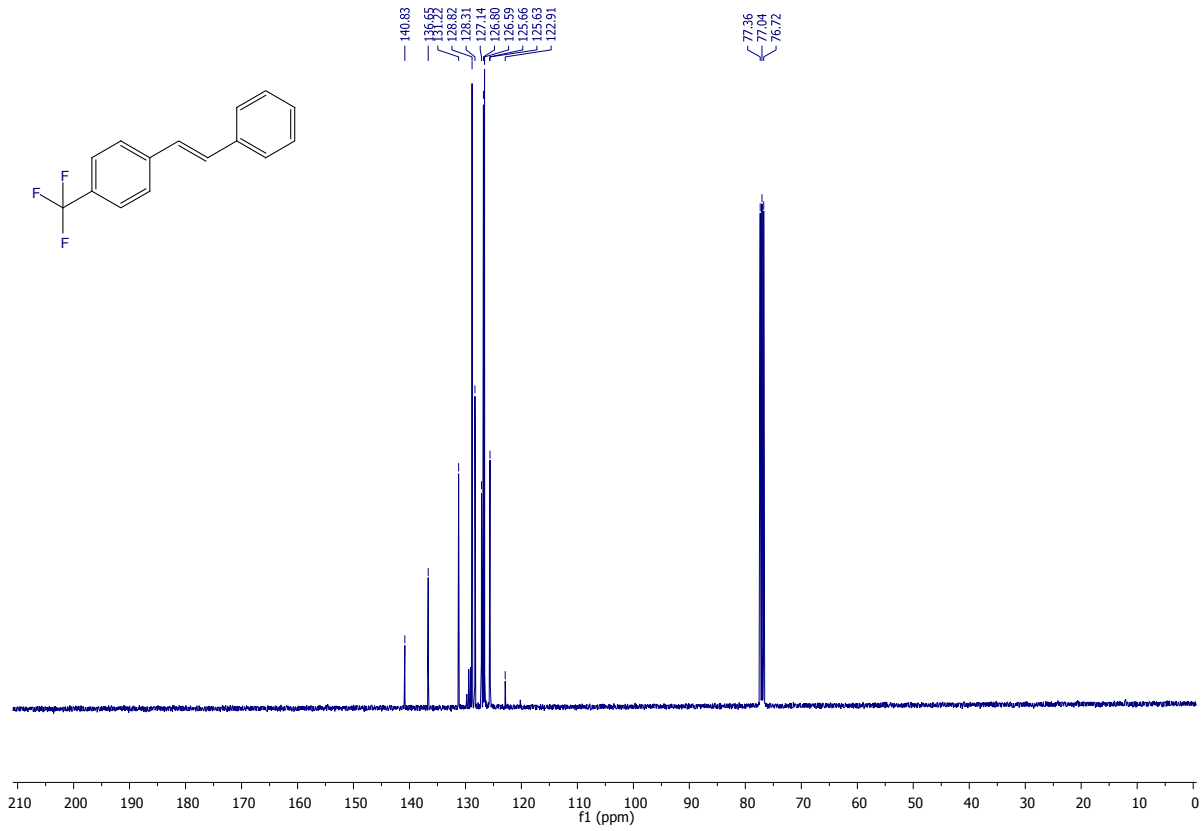
7.56
7.54
7.41
7.40
7.38
7.33
7.31
7.30
7.26
7.23
7.19
7.15
7.11
F
F
F
4.06
2.00
2.04
1.01
2.04
f1 (ppm)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136.65
133.27
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128.31
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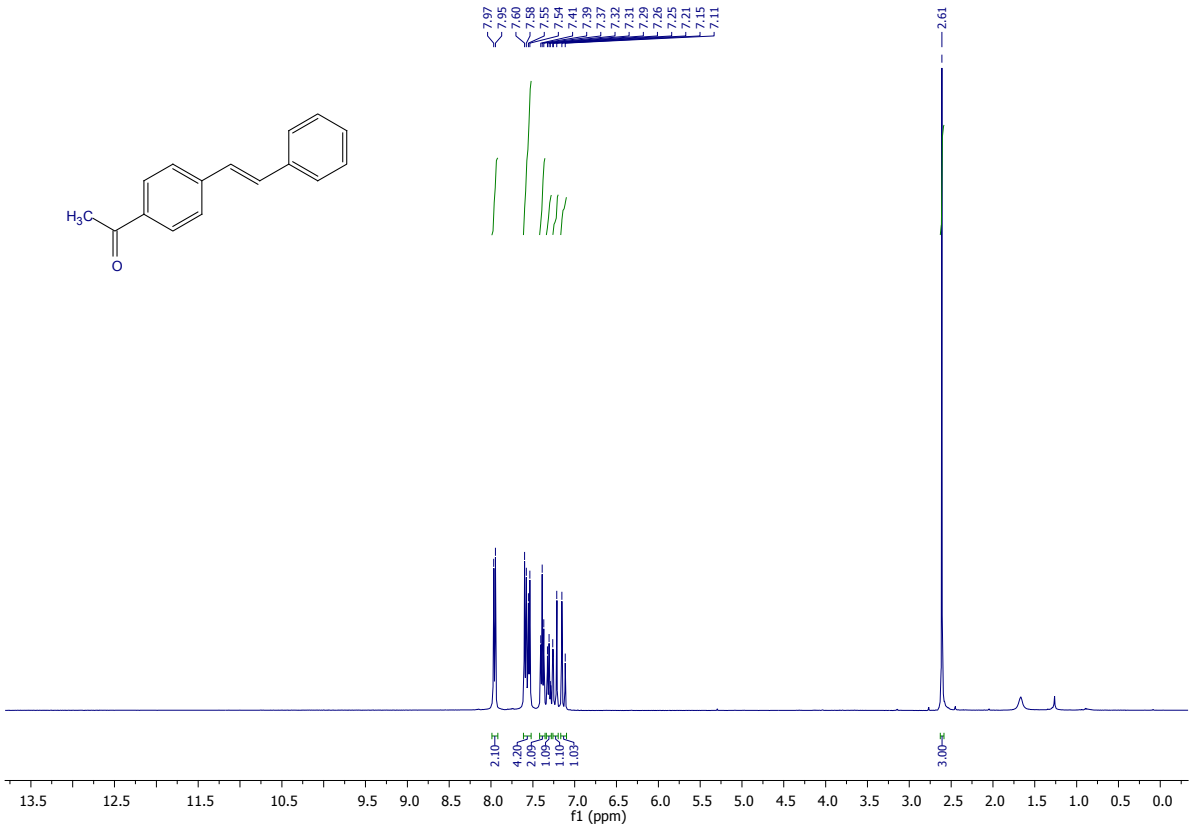
125.63
122.91
77.36
77.04
76.72
F
F
F
f1 (ppm)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7.54
7.41
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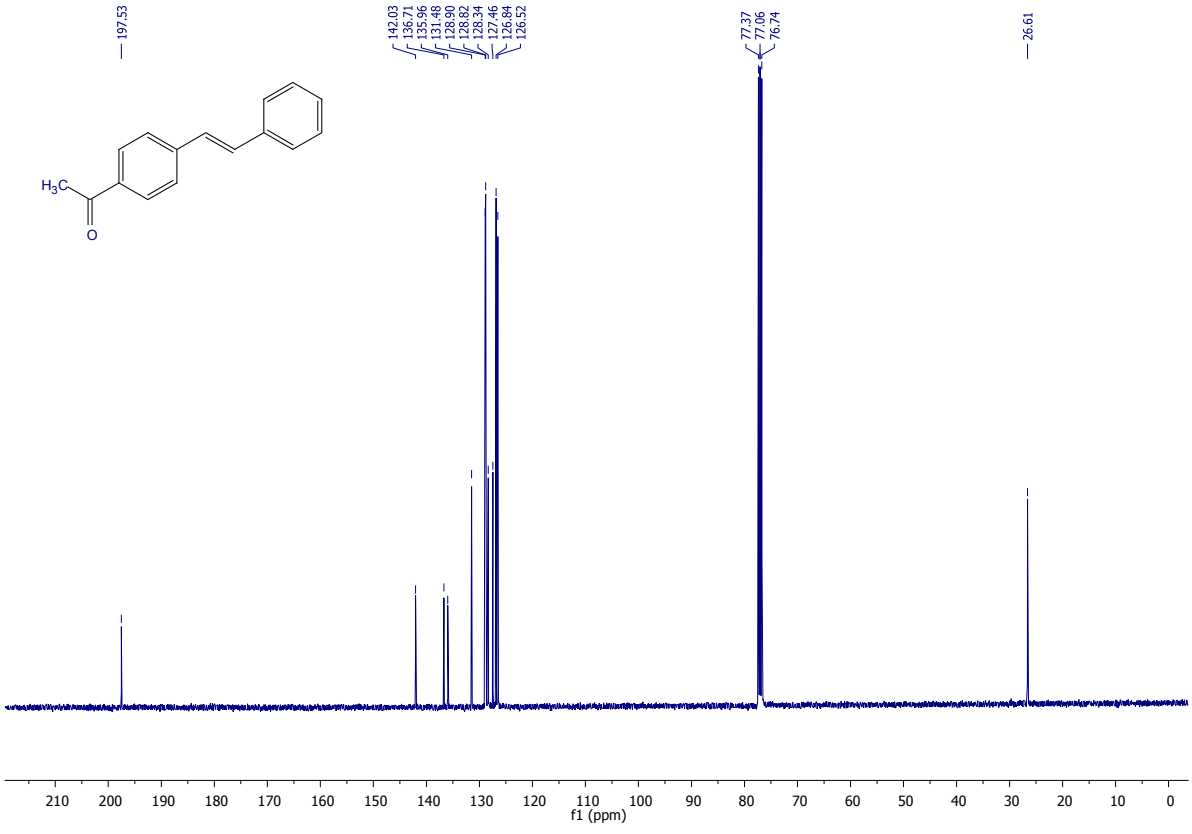
7.37
7.32
7.31
7.29
7.26
7.25
7.21
7.15
7.11
2.61
H3C
O
2.10
4.20
2.09
1.09
1.10
1.03
3.00
13.5
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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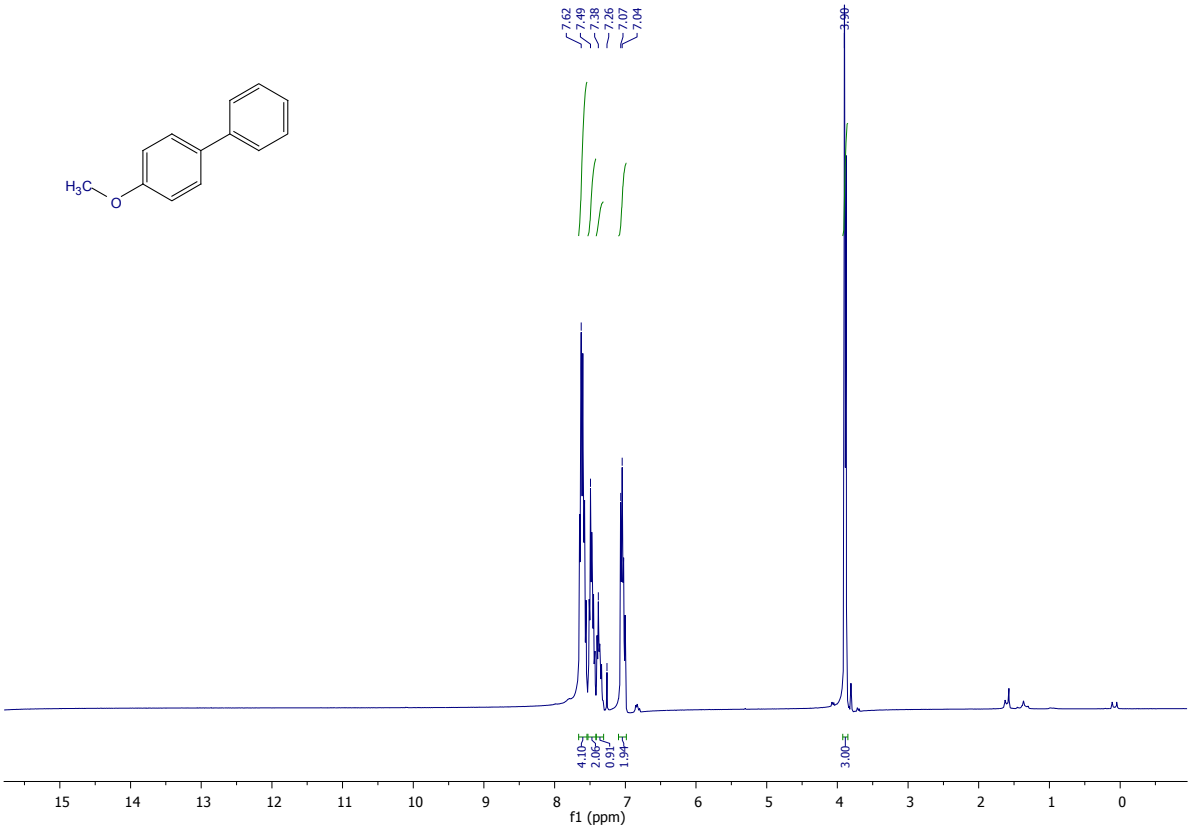
128.90
128.82
128.34
127.46
126.84
126.52
77.37
77.06
76.74
26.61
H3C
O
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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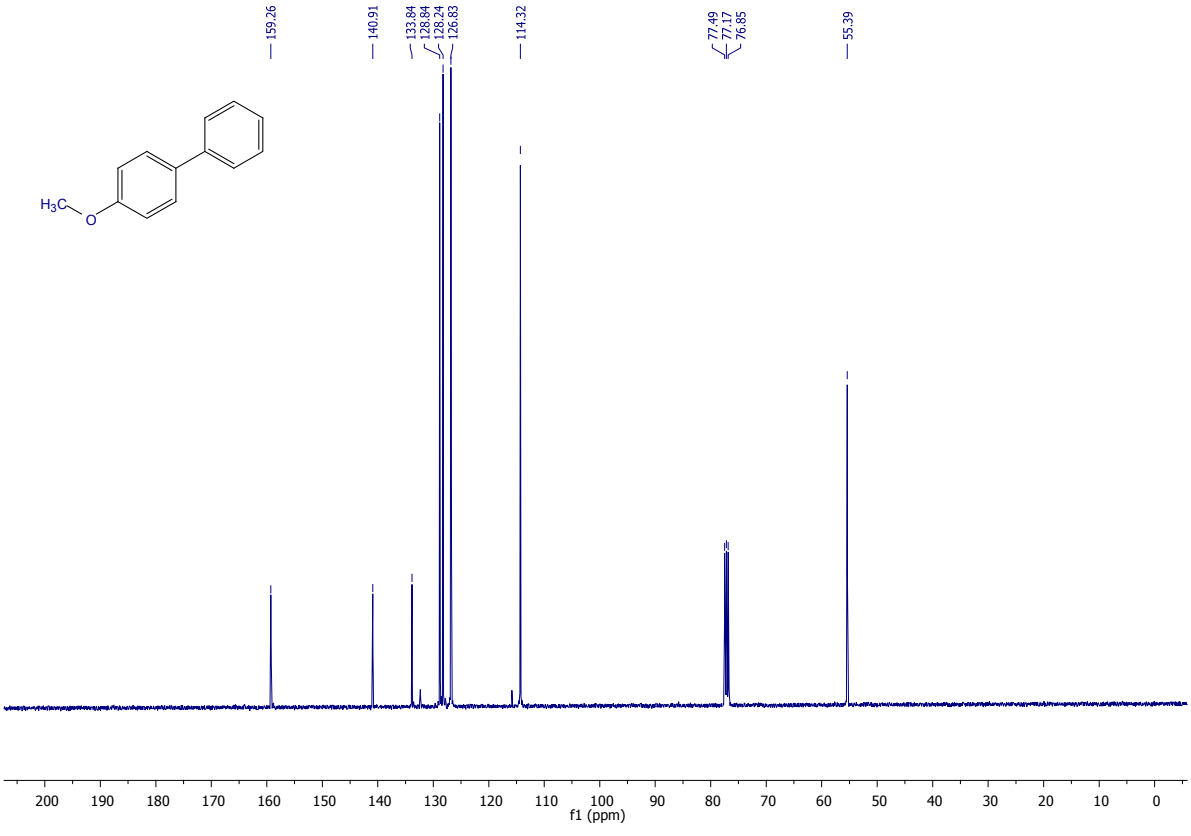
4.10
2.06
0.91
1.94
3.00
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)
H3C
O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114.32
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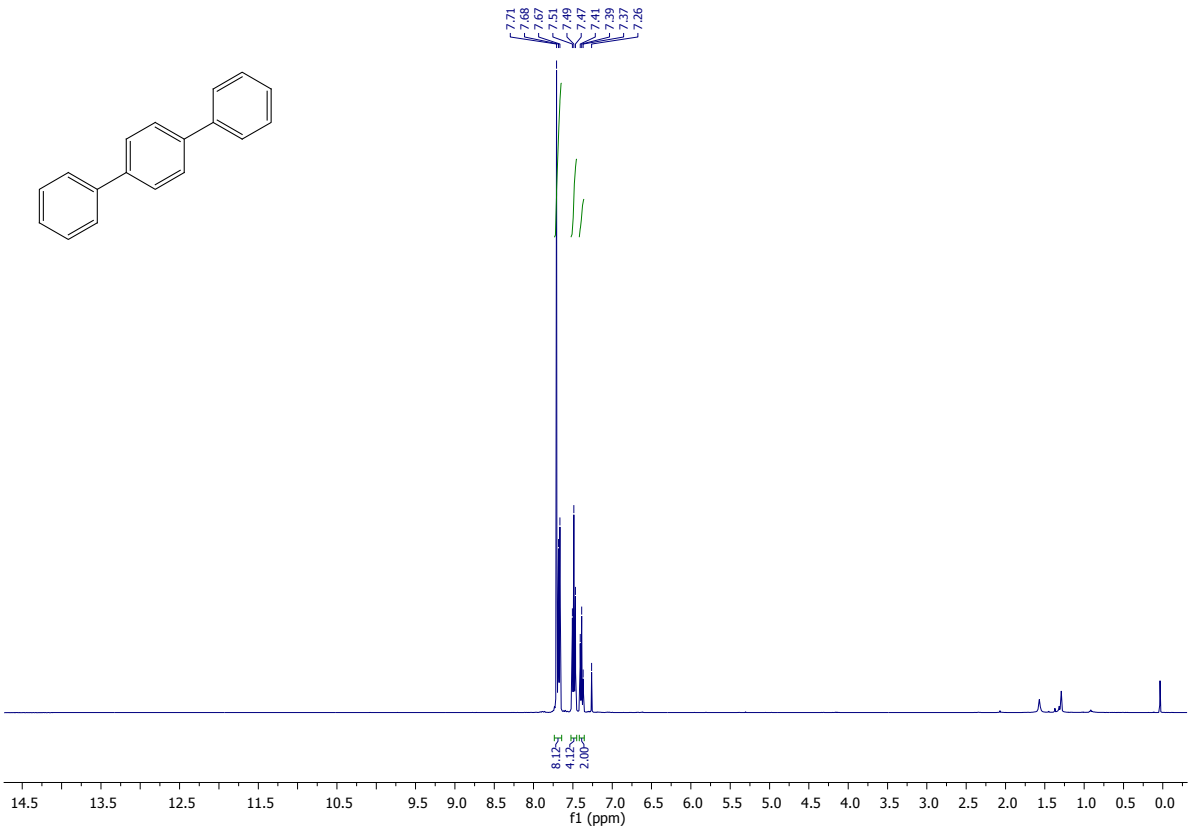
77.17
76.85
55.39
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
H3C
O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7.67
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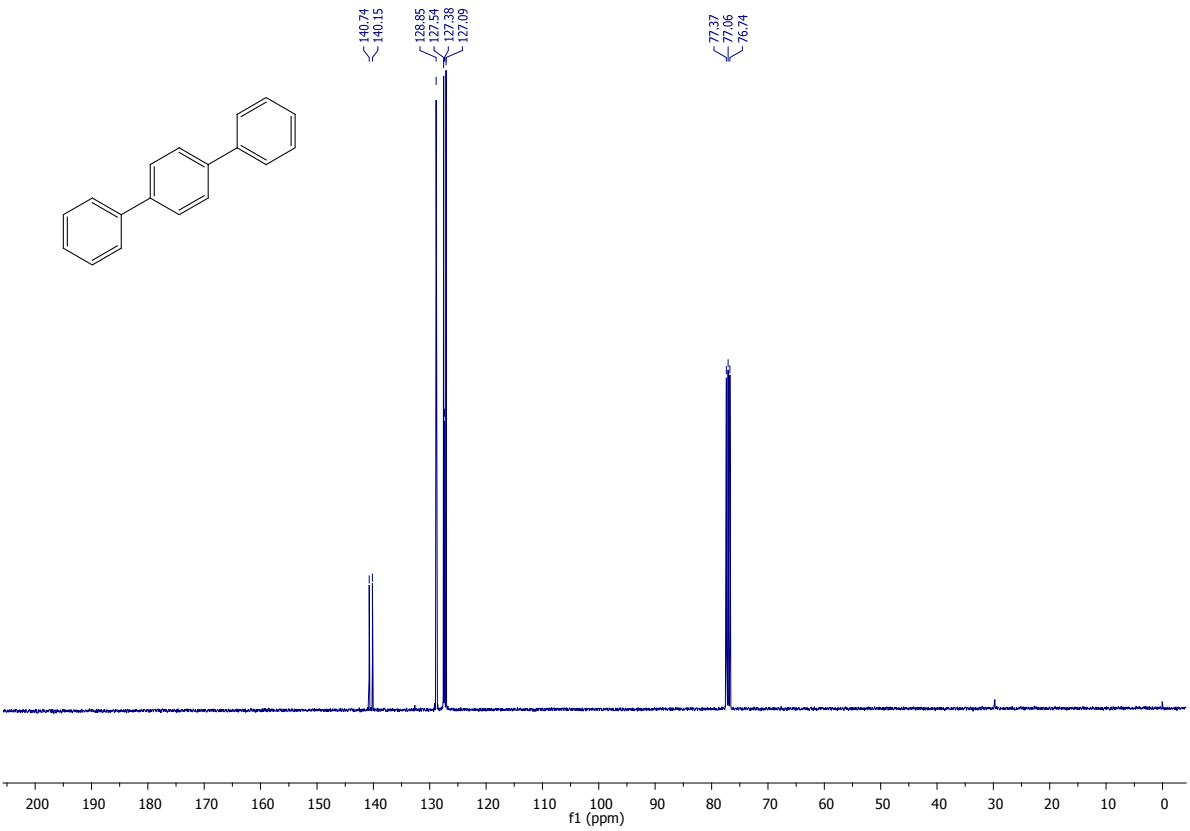
7.49
7.47
7.41
7.39
7.37
7.26
8.12
4.12
2.00
14.5 13.5 12.5 11.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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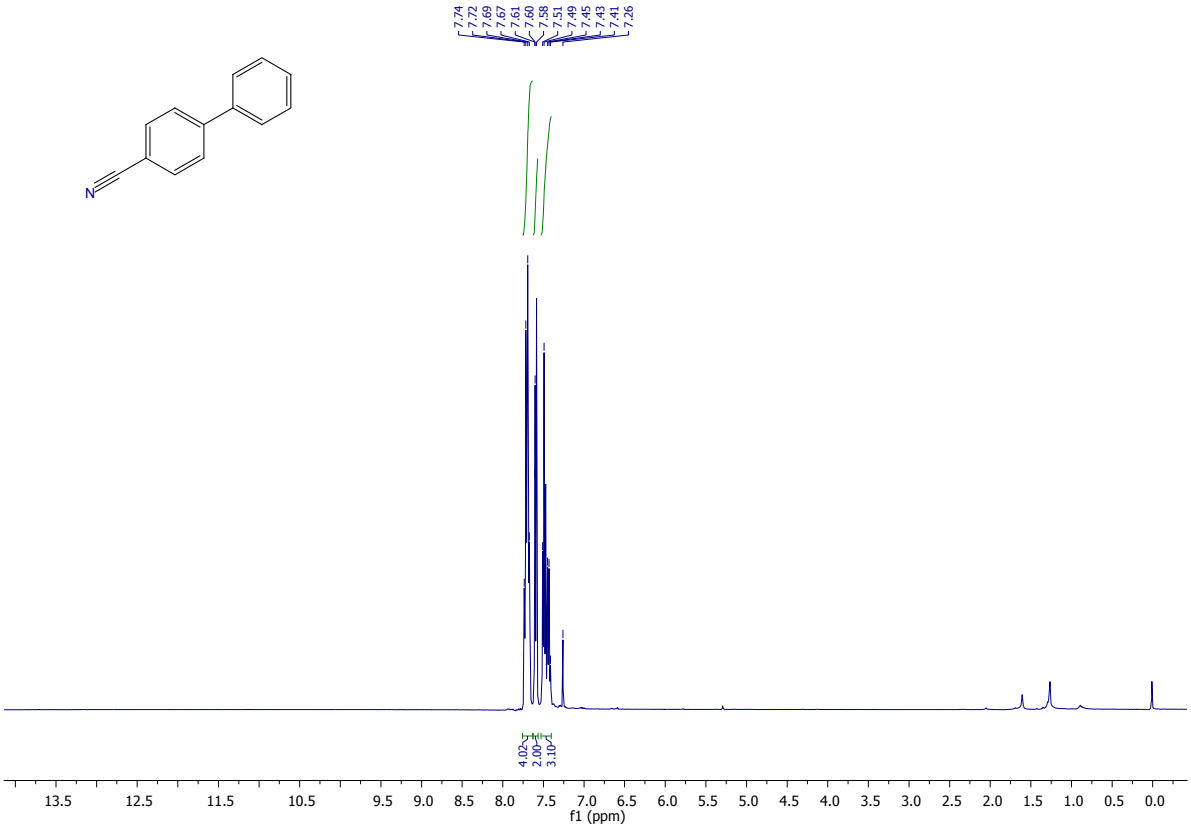
140.15
128.85
127.54
127.38
127.09
77.37
77.06
76.74
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.72
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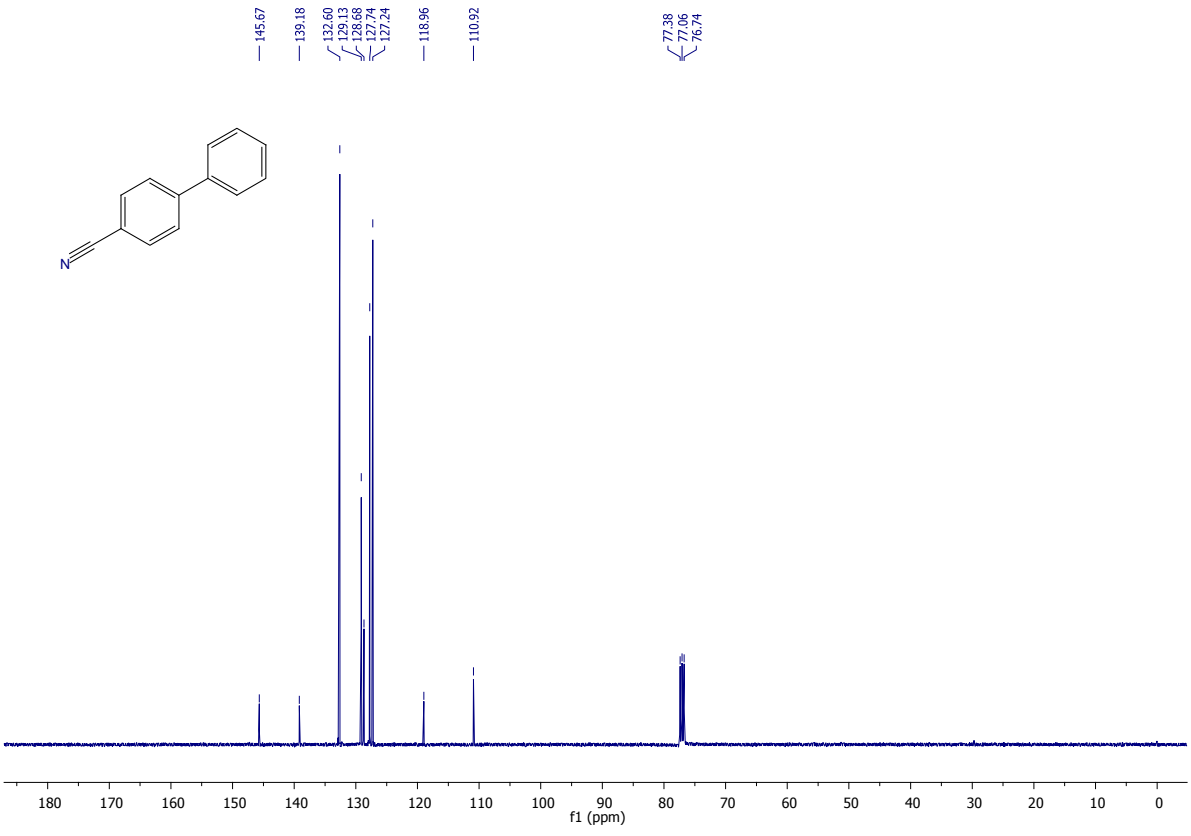
7.61
7.60
7.58
7.51
7.49
7.45
7.43
7.41
7.26
N
4.02
2.00
3.10
13.5 12.5 11.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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128.68
127.74
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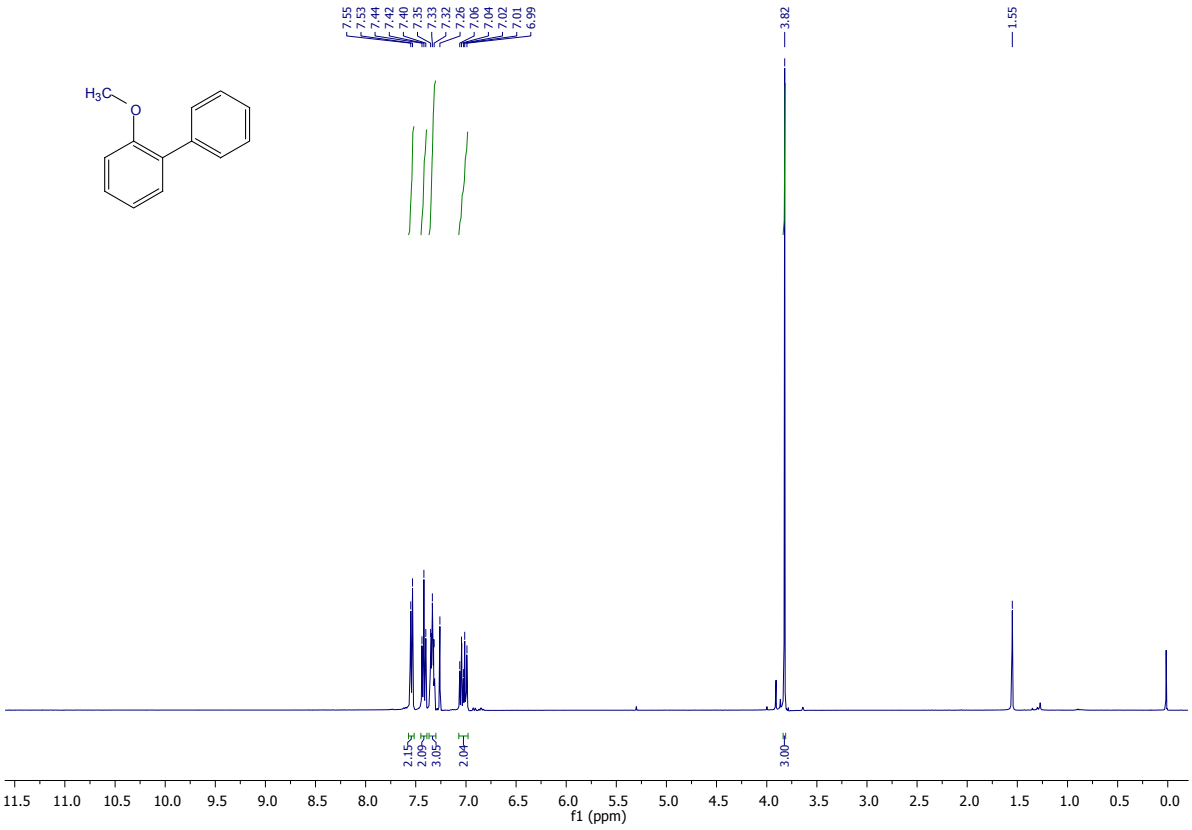
118.96
110.92
77.38
77.06
76.74
N
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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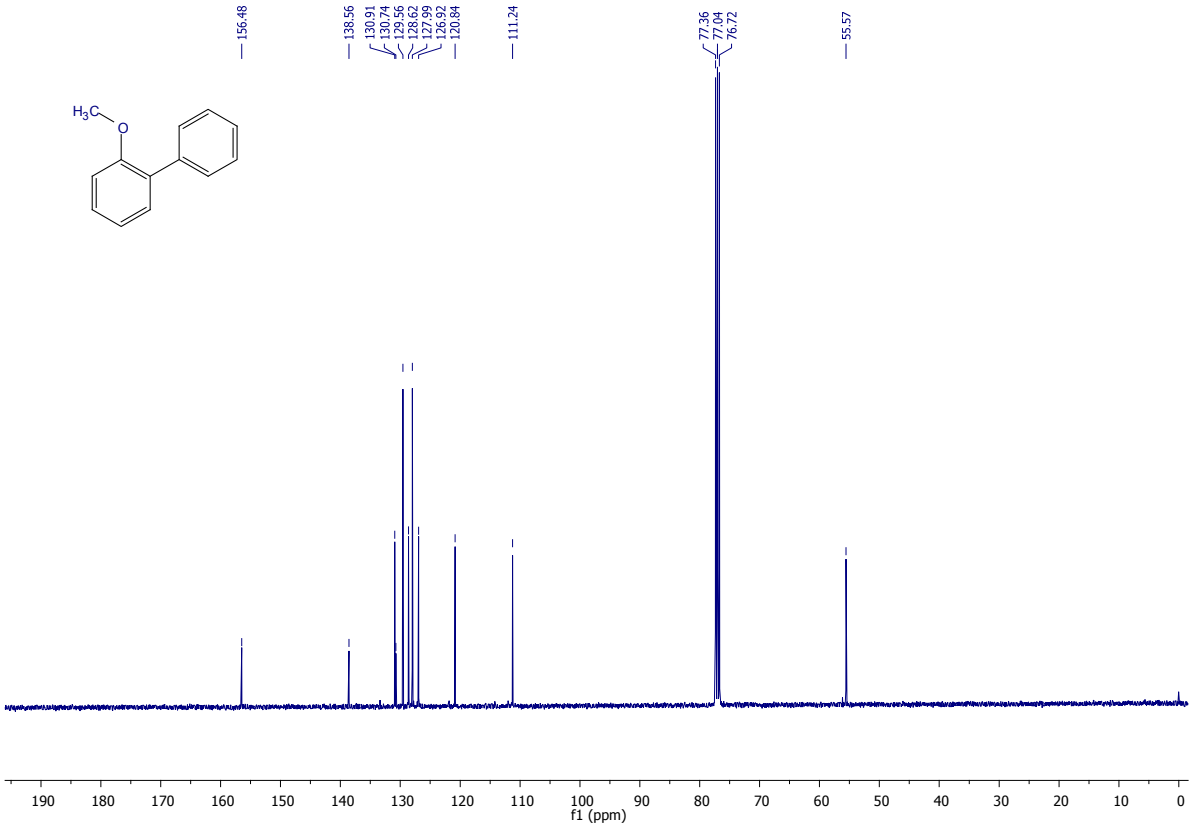
7.33
7.32
7.26
7.06
7.04
7.02
7.01
6.99
3.82
1.55
H3C
O
2.15
2.09
3.05
2.04
3.00
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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128.62
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126.92
120.84
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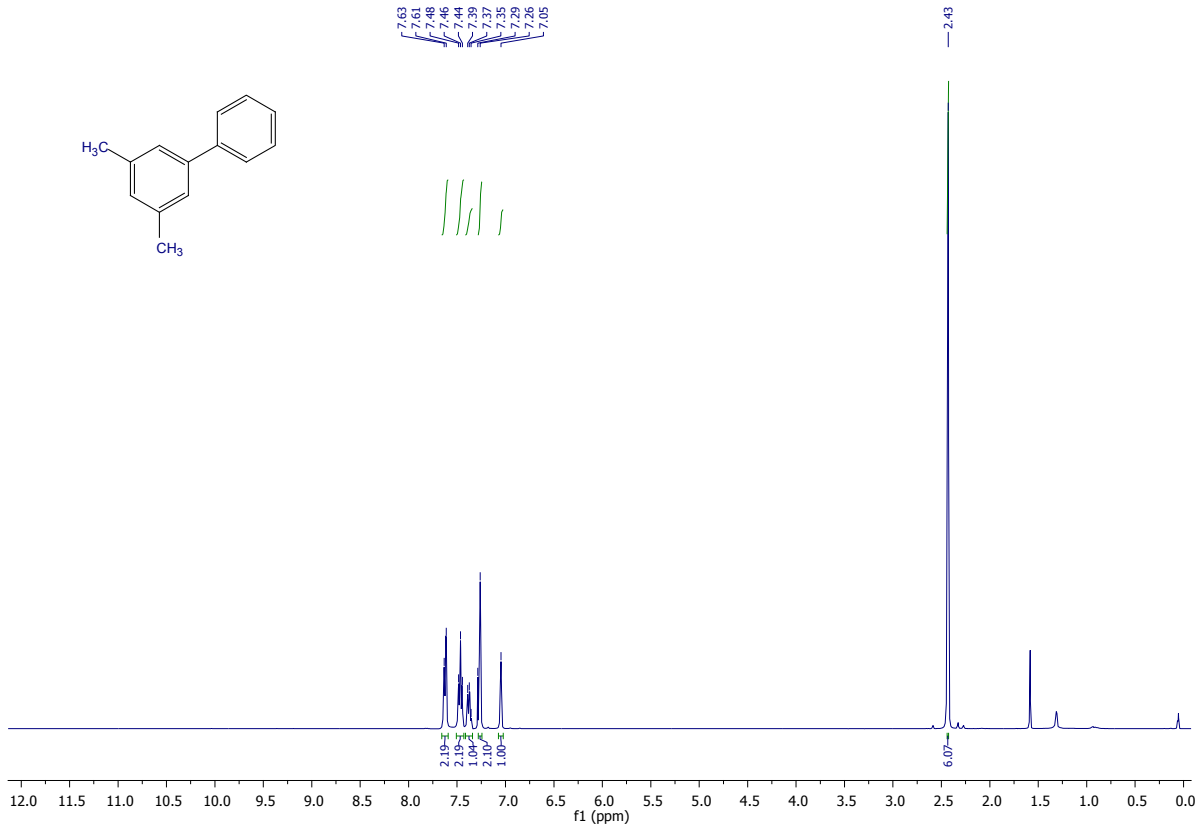
77.36
77.04
76.72
55.57
H3C
O
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.46
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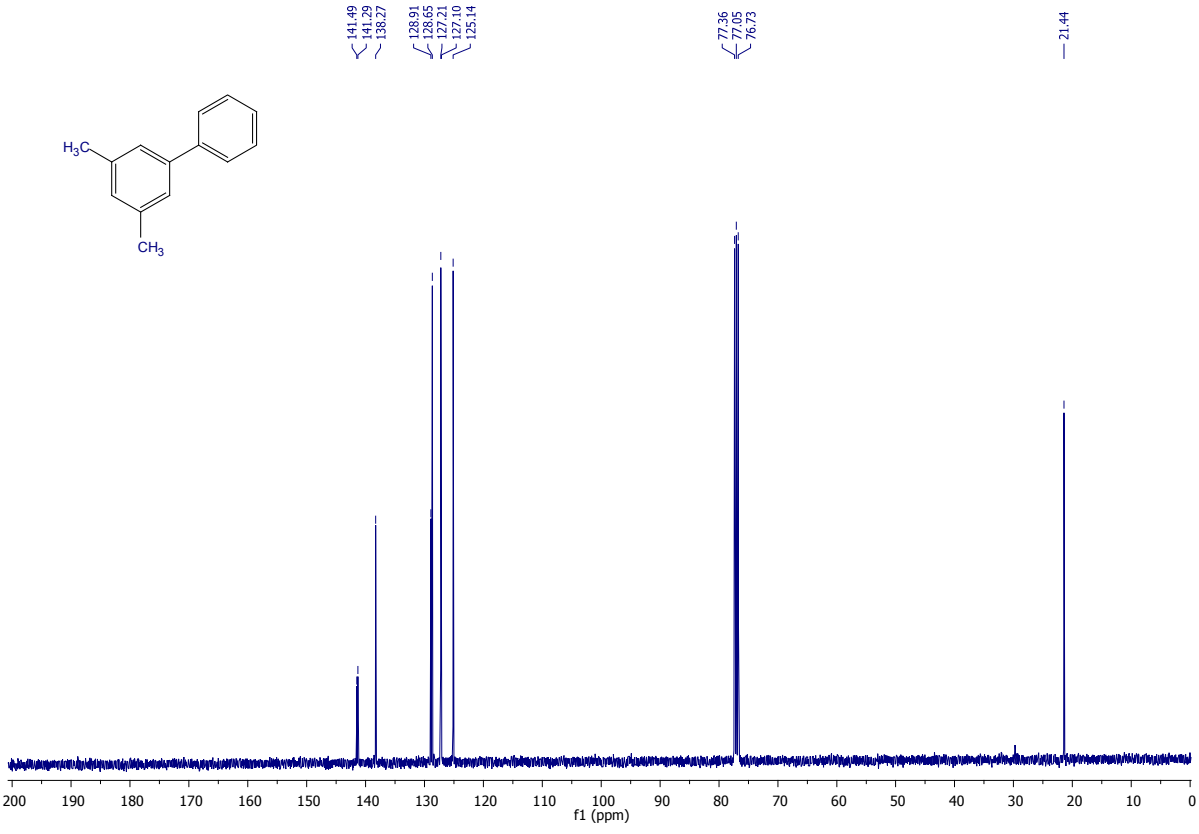
7.37
7.35
7.29
7.26
7.05
2.43
H3C
CH3
2.19
2.19
1.04
2.10
1.00
6.07
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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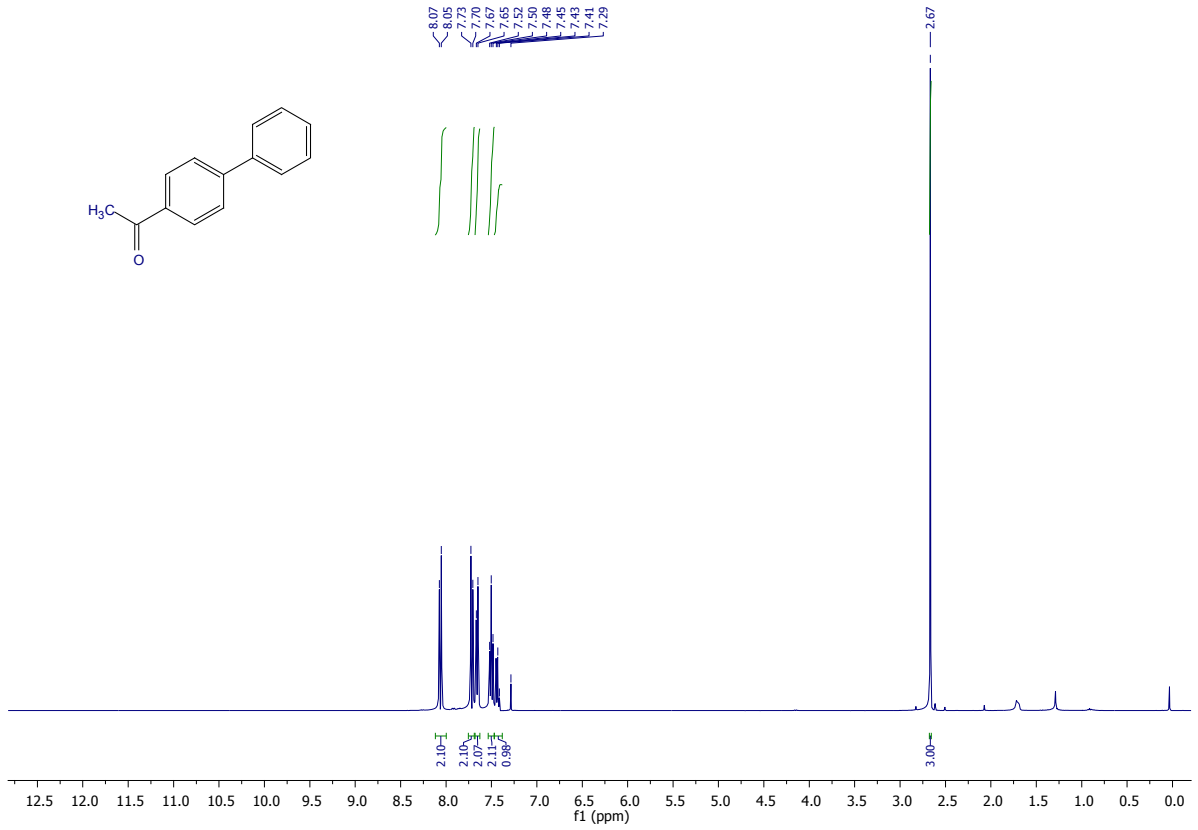
128.91
128.65
127.21
127.10
125.14
77.36
77.05
76.73
21.44
H3C
CH3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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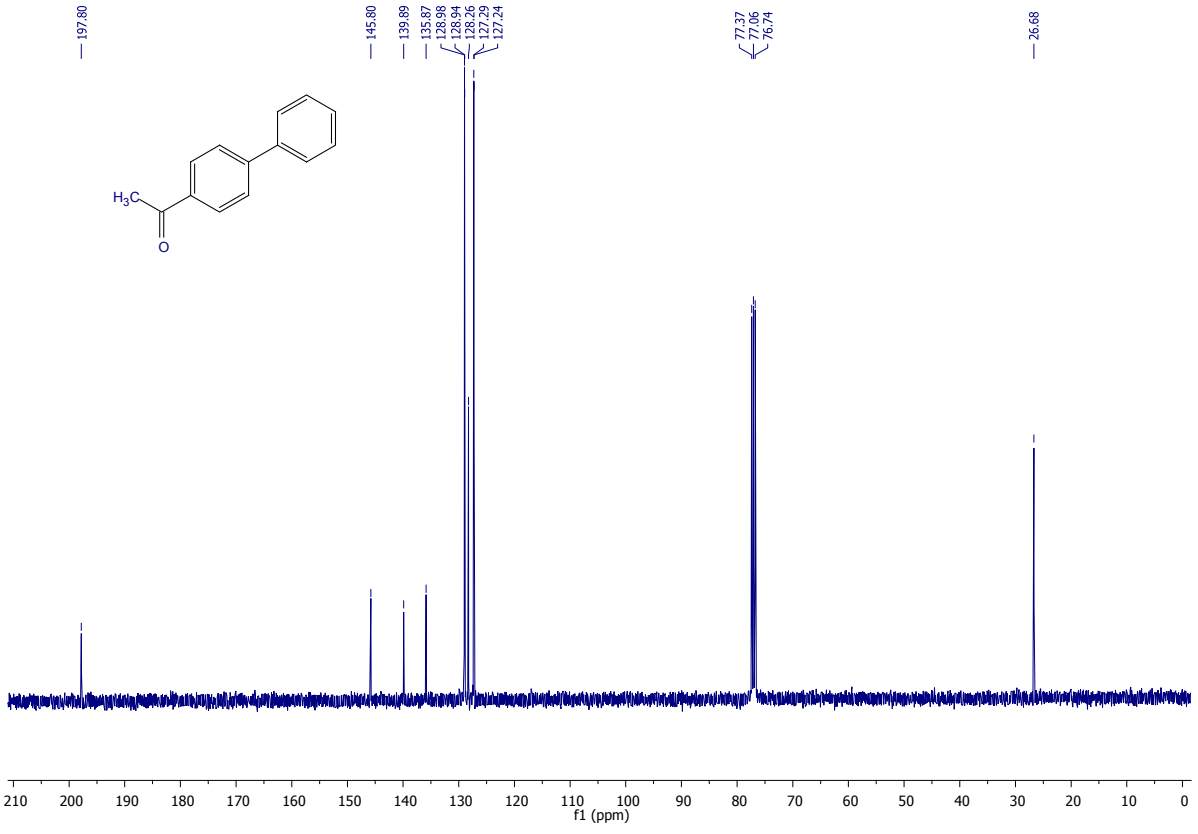
7.50
7.48
7.45
7.43
7.41
7.29
2.67
H3C
O
2.10
2.10
2.07
2.11
0.98
3.00
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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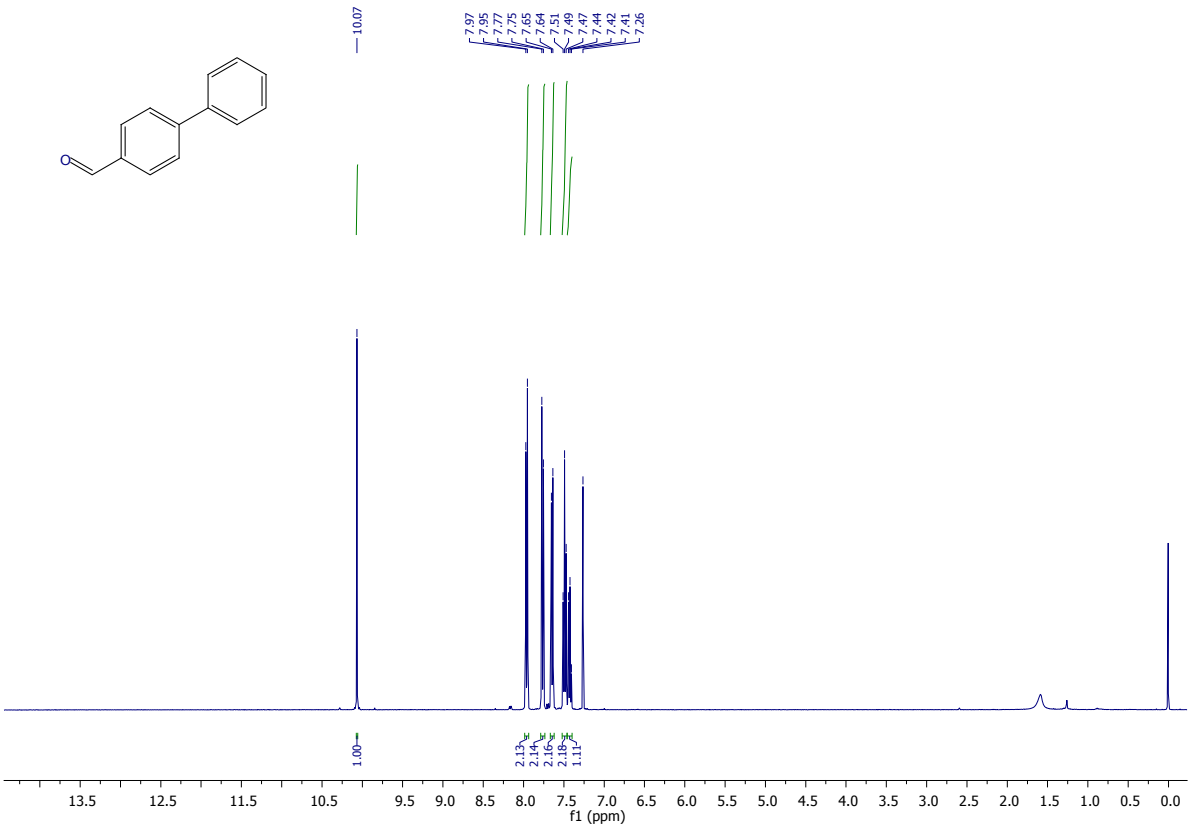
128.94
128.26
127.29
127.24
77.37
77.06
76.74
26.68
H3C
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.51
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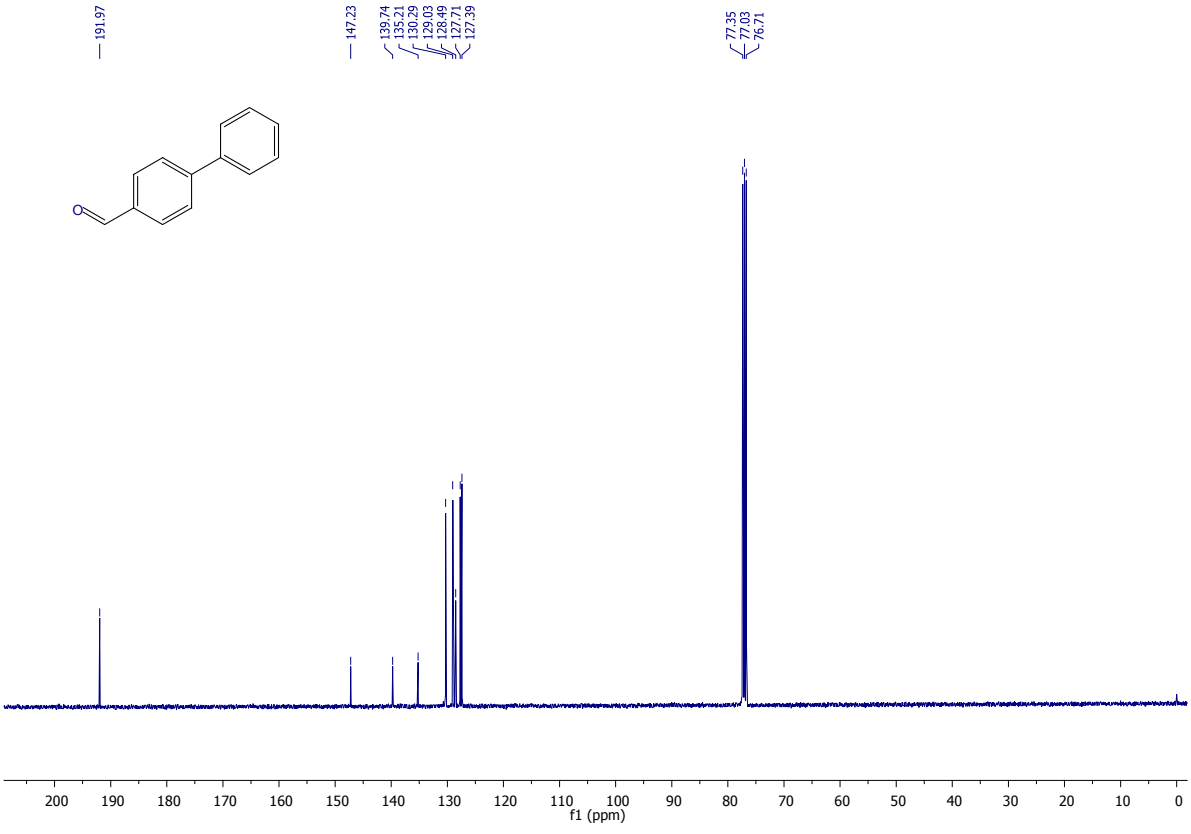
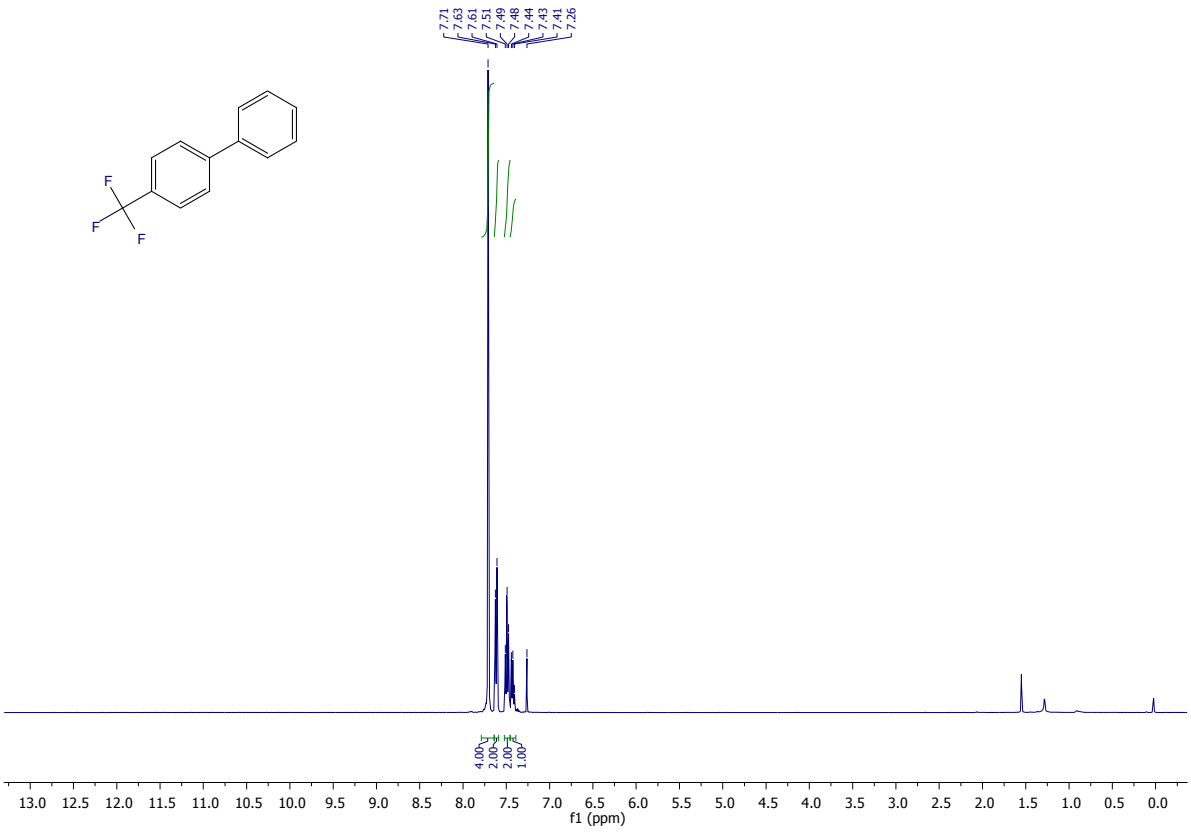
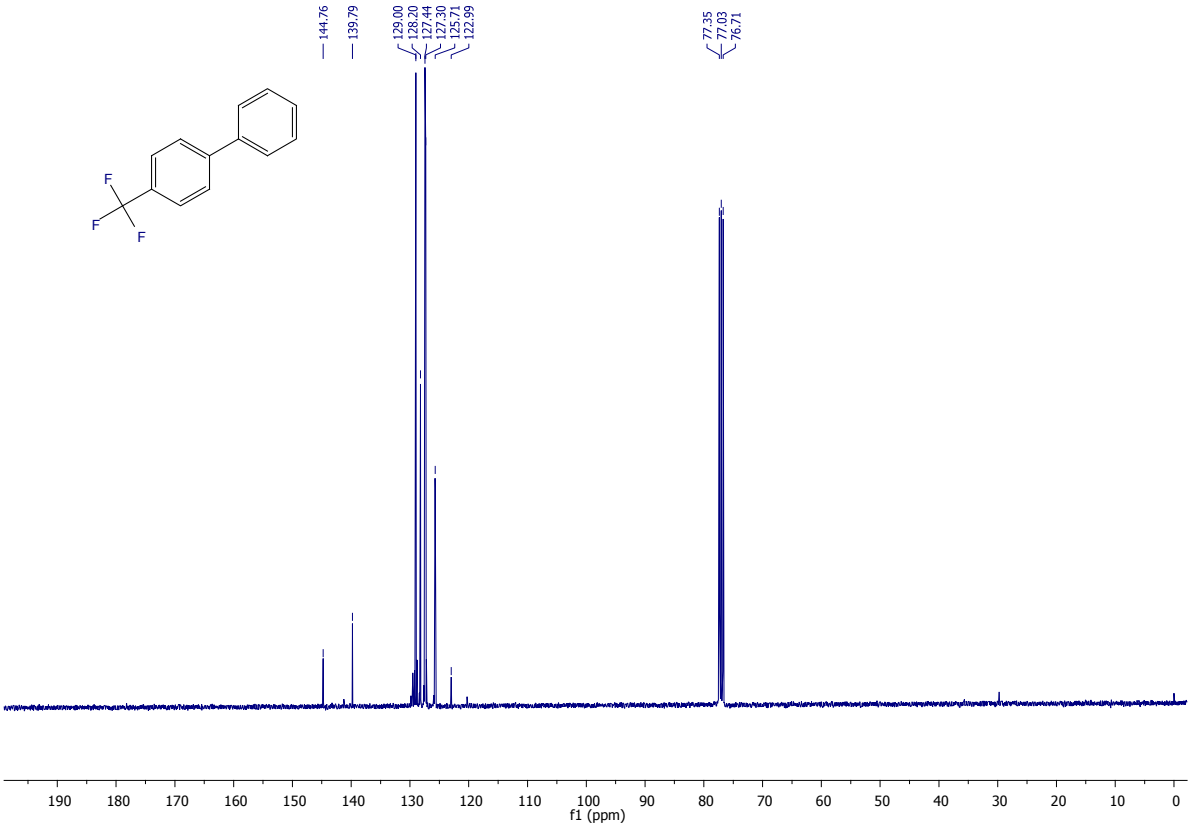
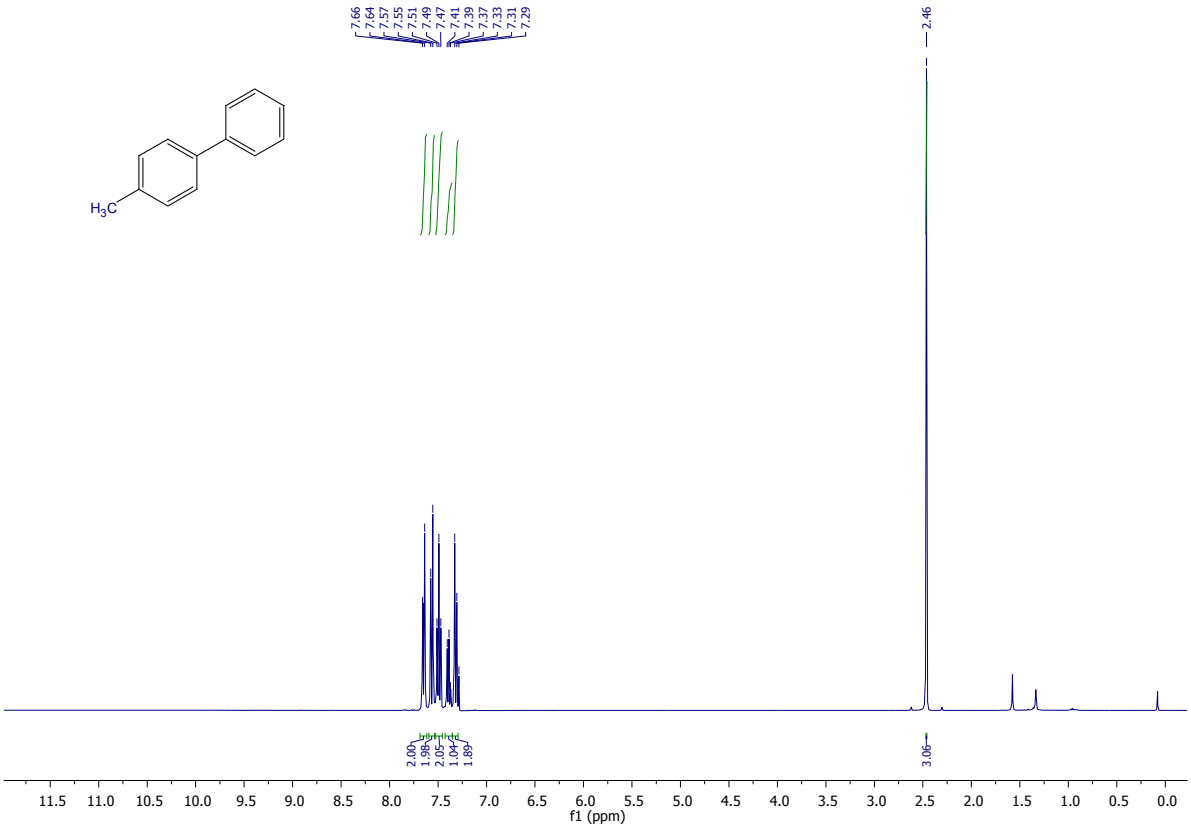
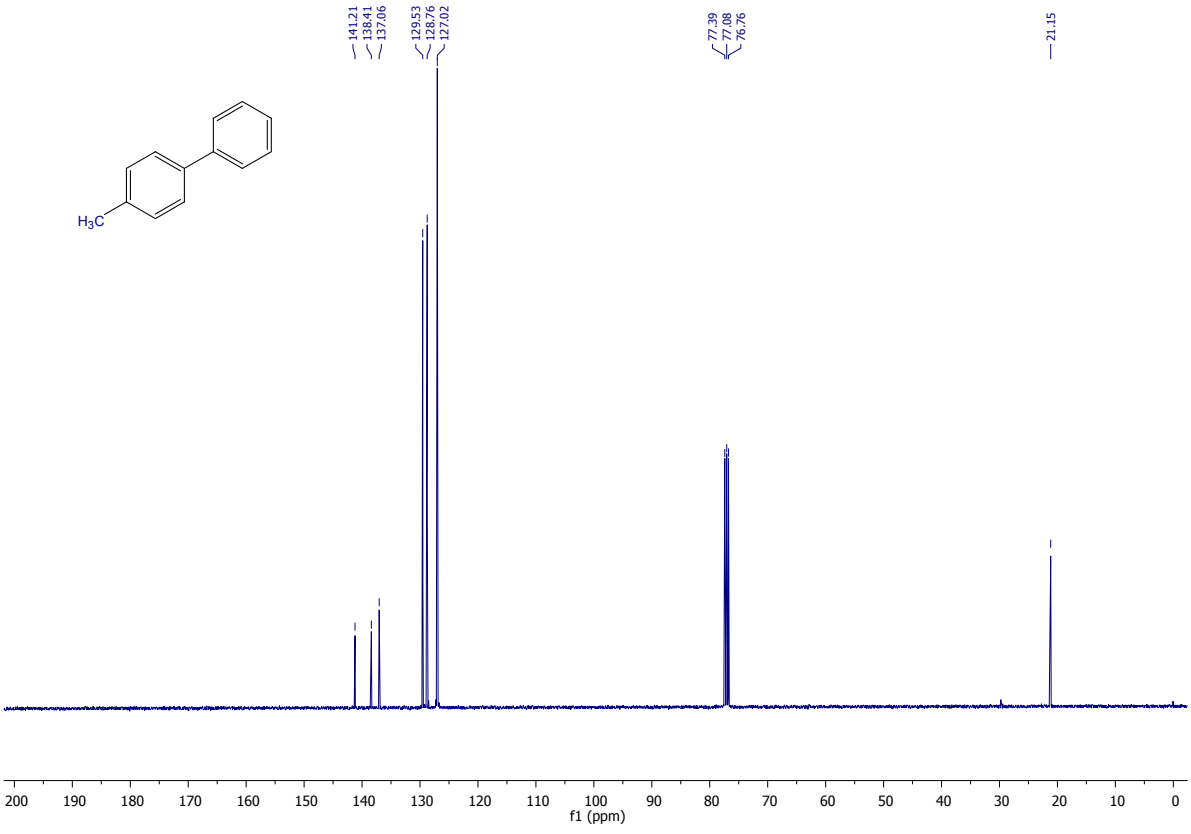
7.47
7.44
7.42
7.41
7.26
O
1.00
2.13
2.14
2.16
2.18
1.11
13.5
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


191.97
147.23
139.74
135.21
130.29
129.03
128.49
127.71
127.39
77.35
77.03
76.71
O
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.71
7.63
7.61
7.51
7.49
7.48
7.44
7.43
7.41
7.26
F
F
F
4.00
2.00
2.00
1.00
13.0 12.5 12.0 11.5 11.0 10.5 10.0 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 0.0
f1 (ppm)


144.76
139.79
129.00
128.20
127.44
127.30
125.71
122.99
77.35
77.03
76.71
F
F
F
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.66
7.64
7.57
7.55
7.51
7.49
7.47
7.41
7.39
7.37
7.33
7.31
7.29
2.46
H3C
2.00
1.98
2.05
1.04
1.89
3.06
11.5 11.0 10.5 10.0 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 0.0
f1 (ppm)


141.21
138.41
137.06
129.53
128.76
127.02
77.39
77.08
76.76
21.15
H3C
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)