Supplementary Material

Photocatalyst-free Visible Light Promoted *E* → *Z* Isomerization of Alkenes

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Contents

1. General Information

All commercially available chemicals were used as received from Aldrich, TCI, Acros or Strem without further purification.^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Avance 400 Spectrometer (^{1}H 400 MHz and ^{13}C 100.6 MHz). The blue LED [30.0 W, λ= 455 nm] was used as a visible light source.

2. The general procedure

In an reaction tube containing a magnetic stirring bar was charged with a mixture solution of (*E*)-alkene (0.3 mmol) in MeCN (2 ml) and water (0.2 mL), followed by the addition of NaOH (12.0 mg, 0.3 mmol). The reaction mixture was open to air and stirred under the irradiation of 30 W blue LED at room temperature. After reaction 24 hours, the solution was concentrated in vacuum. The residue was purified by column chromatography using a mixture of petroleum ether and ethyl acetate as eluent to give the desired product.

3. screening of reaction conditions

Table 1. The screening of reaction conditions for the isomerization reaction[a]

Entry	Base	Solvent	Time	Yield(%)[b]	Z/E[c]
1	NaOH	MeCN/H_2O	24h	98	97:3
2	Na_2CO_3	MeCN/H_2O	24h	91	90:10
3	K_2CO_3	MeCN/H_2O	24h	93	62:38
4	$KHCO_3$	MeCN/H_2O	24h	91	66:34
5	Li_2CO_3	MeCN/H_2O	24h	86	41:59
6	Cs_2CO_3	MeCN/H_2O	24h	81	32:68
7	NH_2PF_6	MeCN/H_2O	24h	88	85:15
8	K_3PO_4	MeCN/H_2O	24h	94	42:58
9	Na_2PO_4	MeCN/H_2O	24h	84	28:72
10	NEt_3	MeCN/H_2O	24h	92	36:64

11	NaOH	THF/H_2O	24h	93	65:35
12	NaOH	DMF/H_2O	24h	86	53:47
13	NaOH	DMSO/H_2O	24h	78	44:56
14	NaOH	Dioxane/H_2O	24h	83	49:51
15	NaOH	Toluene /H_2O	24h	84	55:45
16	NaOH	*i*-PrOH /H_2O	24h	92	28:72
17[d]	NaOH	MeCN/H_2O	24h	96	/
18	/	MeCN/H_2O	24h	99	3:97
19[e]	NaOH	MeCN/H_2O	24h	91	36:64
20[f]	NaOH	MeCN/H_2O	24h	95	48:52
21[g]	NaOH	MeCN/H_2O	24h	93	26:74
22[h]	NaOH	MeCN/H_2O	24h	97	9:91

[a] Reaction conditions: ***E*-1a** (0.3 mmol), base (0.3 mmol), solvent (2mL), H_2O (0.2mL), 30W blue LED, air, rt.; [b] isolated yield; [c] determined by ^1H NMR of crude product; [d] No light. [e] MeCN/H_2O = 1:1; [f] MeCN/H_2O = 2:1; [g] MeCN/H_2O = 5:1; [h] MeCN/H_2O = 20:1;

3. Mechanistic Investigation

3.1 Deuteration experiment

In an reaction tube containing a magnetic stirring bar was charged with a mixture solution of (*E*)-stilbene (54.0 mg, 0.3 mmol) in MeCN (2 ml) and deuterium oxide (0.2 mL), followed by the addition of NaOH (12.0 mg, 0.3 mmol). After being degassed three times of nitrogen, the tube was heated and stirred under the irradiation of 30 W blue LED. After reaction 24 hours, the solution was concentrated in vacuum. The residue was purified by column chromatography using a mixture of petroleum ether and ethyl acetate as eluent to give the product.

3.2 The model reaction was carried under N_2

In an reaction tube containing a magnetic stirring bar was charged with a mixture solution of (*E*)-stilbene (54.0 mg, 0.3 mmol) in MeCN (2 ml) and water (0.2 mL), followed by the addition of NaOH (12.0 mg, 0.2 mmol). After being degassed three

times of nitrogen, the tube was heated and stirred under the irradiation of 30 W blue LED. After reaction 24 hours, the solution was concentrated in vacuum. The residue was purified by column chromatography using a mixture of petroleum ether and ethyl acetate as eluent to give the product.

3.3 Radical Control Experiment

In an oven-dried reaction tube with a magnetic stirring bar a solution of (*E*)-stilbene (54.0 mg, 0.3 mmol), MeCN (2 ml), water (0.2 mL), NaOH (12.0 mg, 0.3 mmol) and TEMPO (93.7 mg, 0.6 mmol). The reaction mixture was open to air and stirred under the irradiation of 30 W blue LED at room temperature for 24 h. After completion of the reaction, the solution was concentrated in vacuum. The residue was purified by column chromatography using a mixture of petroleum ether and ethyl acetate as eluent to give the product.

3.4 $O_2^{\cdot -}$ Radical Quenching Experiment

In an oven-dried reaction tube with a magnetic stirring bar a solution of (*E*)-stilbene (54.0 mg, 0.3 mmol), MeCN (2 ml), water (0.2 mL), NaOH (12.0 mg, 0.3 mmol) and DPPH (236.6 mg, 0.6 mmol). The reaction mixture was open to air and stirred under the irradiation of 30 W blue LED at room temperature for 24 h. After completion of the reaction, the solution was concentrated in vacuum. The residue was purified by column chromatography using a mixture of petroleum ether and ethyl acetate as eluent to give the product.

3.5 EPR experiments

a) standard conditions: A mixture of (*E*)-stilbene (54.0 mg, 0.3 mmol), MeCN (2 ml), water (0.2 mL), NaOH (12.0 mg, 0.3 mmol) and DMPO (10 uL) was open to air and stirred under the irradiation of 30 W blue LED at room temperature for 2 h. Afterwards, 20 uL of the mixture was quickly taken out into a small tube and analyzed by EPR.

b) without water under the standard conditions: A mixture of (*E*)-stilbene (54.0 mg, 0.3 mmol), MeCN (2 ml), NaOH (12.0 mg, 0.3 mmol) and DMPO (10 uL) was open to air and stirred under the irradiation of 30 W blue LED at room temperature

for 2 h. Afterwards, 20 uL of the mixture was quickly taken out into a small tube and analyzed by EPR.

c) without NaOH under the standard conditions: A mixture of (*E*)-stilbene (54.0 mg, 0.3 mmol), MeCN (2 ml), water (0.2 mL) and DMPO (10 uL) was open to air and stirred under the irradiation of 30 W blue LED at room temperature for 2 h. Afterwards, 20 uL of the mixture was quickly taken out into a small tube and analyzed by EPR.

d) without (*E*)-stilbene under the standard conditions: A mixture of NaOH (12.0 mg, 0.3 mmol), MeCN (2 ml), water (0.2 mL) and DMPO (10 uL) was open to air and stirred under the irradiation of 30 W blue LED at room temperature for 2 h. Afterwards, 20 uL of the mixture was quickly taken out into a small tube and analyzed by EPR.

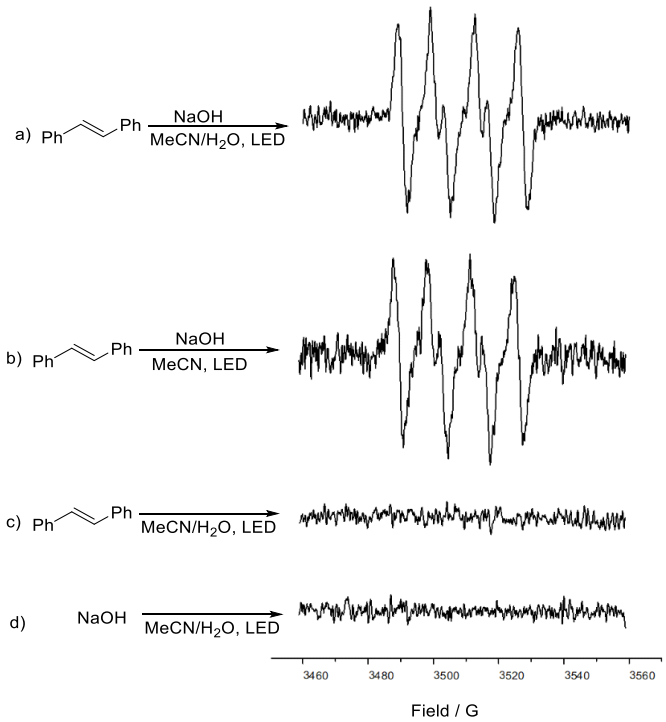
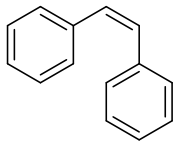


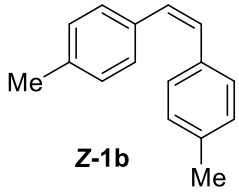
Figure 1. EPR spectra (X band, 9.4 GHz, rt) of (a) (*E*)-**1a** and NaOH in the mixture of CH_3CN and water, under blue LED irritation 2h; (b) (*E*)-**1a** and NaOH in CH_3CN, under blue LED irritation 2h; (c) (*E*)-**1a** in the mixture of CH_3CN and water, under blue LED irritation 2h; (d) NaOH in the mixture of CH_3CN and water, under blue LED irritation

4. Characterization Data of Products



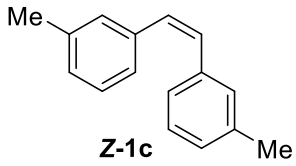
***Z*-1a**

(*Z*)-1,2-phenylethene (*Z*-1a)[1]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26-7.18 (m, 10H), 6.60 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 137.3, 130.3, 128.9, 128.2, 127.1.



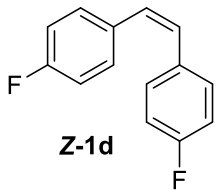
***Z*-1b**

(*Z*)-1,2-di-*p*-tolylethene.[1] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.15-7.13 (m, 2H), 7.09-7.05 (m, 2H), 6.94-6.89 (m, 4H), 6.71 (s, 2H), 2.28 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 136.5, 136.2, 130.0, 129.5, 129.1, 127.0, 125.4, 19.9.



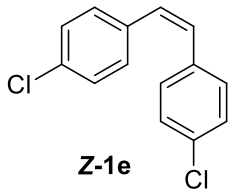
***Z*-1c**

(*Z*)-1,2-di-*m*-tolylethene.[2] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.16 (d, *J* = 8.1 Hz, 4H), 7.02 (d, *J* = 7.8 Hz, 4H), 6.51 (s, 2H), 2.31 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 136.8, 134.5, 129.5, 128.9, 128.8, 21.3.



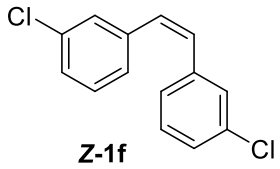
***Z*-1d**

(*Z*)-1,2-bis(4-fluorophenyl)ethene.[3] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.14-7.12 (m, 4H), 7.09-7.06 (m, 4H), 6.48 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 135.2, 133.0, 130.2, 129.6, 128.6.



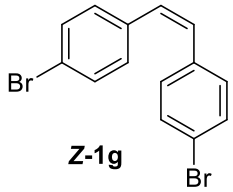
***Z*-1e**

(*Z*)-1,2-bis(4-chlorophenyl)ethane.[1] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.21-7.13 (m, 6H), 7.09-7.07 (m, 2H), 6.57 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 138.5, 134.2, 130.0, 129.6, 128.8, 127.5, 126.9.



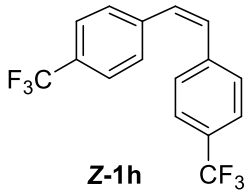
***Z*-1f**

(*Z*)-1,2-bis(3-chlorophenyl)ethene.[1] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26-7.15 (m, 6H), 7.13-7.03 (m, 3H), 6.56 (d, *J* = 1.04 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 138.5, 134.2, 130.0, 129.9, 129.6, 128.8, 128.6, 127.9, 127.5, 127.0, 126.4, 124.9.



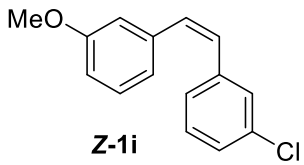
***Z*-1g**

(*Z*)-1,2-bis(4-bromophenyl)ethane.[4] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37-7.34 (m, 4H), 7.09-7.06 (m, 4H), 6.53 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 135.7, 131.5, 130.5, 129.7.



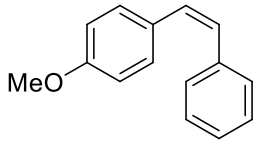
***Z*-1h**

(*Z*)-1,2-bis(4-(trifluoromethyl)phenyl)ethane.[5] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49 (d, *J* = 8.6 Hz, 4H), 7.30 (d, *J* = 8.0 Hz, 4H), 6.72 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 140.1, 130.7, 130.0, 129.6, 129.3, 129.1, 126.9, 125.5, 125.4, 125.37, 125.33, 122.7.



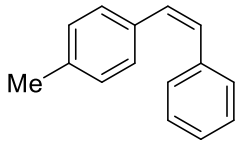
***Z*-1i**

(*Z*)-4-Chloro-4'-methoxystilbene.[6] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.22-7.11 (m, 4H), 6.81 (d, *J* = 7.62 Hz, 1H), 6.78-6.76 (m, 2H), 6.57 (dd, *J* = 37.46, 12.2 Hz, 2H), 3.67 (s, 3H) ; ^{13}C NMR ($CDCl_3$, 100 MHz): δ 159.4, 139.1, 137.9, 134.0, 131.4, 129.5, 129.4, 128.9, 128.8, 127.2, 127.1, 121.5, 113.7, 113.6, 55.1.



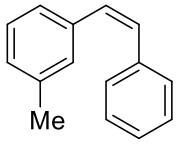
***Z*-2a**

(*Z*)-1-methoxy-4-styrylbenzene.[7] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.21-7.10 (m, 7H), 6.69-6.66 (m, 2H), 6.41 (s, 2H), 3.70 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 158.7, 137.6, 130.2, 129.8, 128.8, 128.7, 128.3, 126.9, 113.6, 55.2.



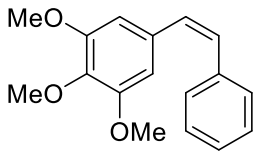
***Z*-2b**

(*Z*)-1-methyl-4-styrylbenzene.[8] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26-7.15 (m,5H), 7.10-7.03 (m,3H), 6.99-6.97 (m, 1H), 6.55 (s, 2H), 2.24 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 137.9, 137.4, 137.3, 130.5, 130.2, 129.7, 128.9, 128.3, 128.2, 127.9, 127.2, 125.9, 21.5.



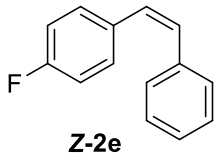
***Z*-2c**

(*Z*)-1-methyl-3-styrylbenzene.[9] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.18-7.10 (m, 8H), 7.03-7.01 (m, 1H), 6.64-6.56 (m, 2H), 2.25 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 137.3, 137.2, 136.2, 130.7, 130.2, 129.7, 129.1, 129.0, 128.3, 127.4, 127.2, 125.9, 20.1.



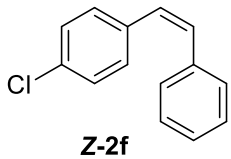
***Z*-2d**

(Z)-1,2,3-Trimethoxy-5-styrylbenzen.[10] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.17-7.10 (m, 4H), 7.06-7.03 (m, 1H), 6.46 (d, *J* = 12.16 Hz, 1H), 6.37-6.34 (m, 3H), 3.70 (s, 3H), 3.49 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 152.8, 137.5, 137.1, 132.5, 130.2, 130.0, 128.9, 128.3, 127.2, 106.1, 60.9, 55.8.



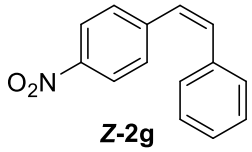
***Z*-2e**

(*Z*)-1-fluoro-4-styrylbenzene.[12] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25-7.18 (m, 7H), 6.93-6.87 (m, 2H), 6.56 (dd, *J* = 22.1, 12.2 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 163.0, 160.6, 137.0, 133.2, 133.1, 130.6, 130.5, 130.3, 129.1, 128.8, 128.3, 127.3, 115.3, 115.1.



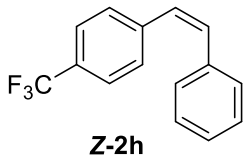
***Z*-2f**

(*Z*)-1-chloro-4-styrylbenzene.[1] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.22-7.15 (m 9H), 6.57 (dd, *J* = 40.4, 21.2 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 136.9, 135.7, 132.8, 131.0, 130.3, 129.0, 128.9, 128.5, 128.4, 127.4.



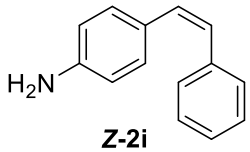
***Z*-2g**

(*Z*)-1-nitro-4-styrylbenzene.[13] ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.14 (dd, *J* = 6.96, 1.92 Hz, 2H), 7.55 (dd, *J* = 7.04, 1.72 Hz, 2H), 7.49-7.47 (m, 2H), 7.35-7.31 (m, 2H), 7.28-7.26 (m, 1H), 7.21-7.17 (m, 1H), 7.06 (d, *J* = 16.32 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 146.7, 143.9, 136.2, 133.3, 129.0, 127.1, 126.9, 126.3, 124.2.



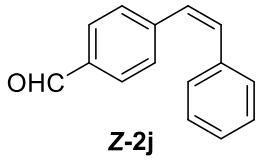
***Z*-2h**

(*Z*)-1-styryl-3-(trifluoromethyl)benzene.[15] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44 (d, *J* = 8.20 Hz, 2H), 7.31 (d, *J* = 8.56 Hz, 2H), 7.22-7.18 (m, 5H), 6.68 (d, *J* = 12.24 Hz, 1H), 6.56 (d, *J* = 12.24 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 141.0, 140.9, 136.6, 132.4, 129.2, 128.9, 128.8, 128.7, 128.5, 127.7, 126.3, 125.3, 125.2.



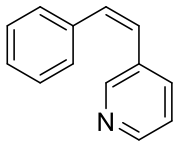
***Z*-2i**

(*Z*)-4-styrylaniline.[11] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31-7.28 (m, 2H), 7.25-7.17 (m, 3H), 7.08-7.05 (m, 2H), 6.54-6.51 (m, 2H), 6.45 (dd, *J* = 20.8, 12.24 Hz, 2H), 3.67 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 145.5, 138.0, 130.2, 130.1, 128.8, 128.2, 127.6, 127.5, 126.7, 114.7.



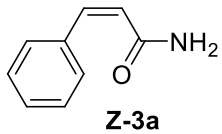
***Z*-2j**

(*Z*)-4-Styrylbenzaldehyde.[14] ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.95 (s, 1H), 7.73 (d, *J* = 7.48 Hz, 2H), 7.39 (d, *J* = 7.76 Hz, 2H), 7.26-7.24 (m, 7H), 6.76 (d, *J* = 12.28 Hz, 1H), 6.62 (d, *J* = 12.24 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 191.9, 143.8, 136.5, 134.9, 133.0, 129.7, 129.5, 129.0, 128.9, 128.4, 127.7.



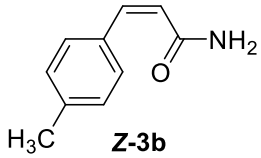
***Z*-2k**

(*Z*)-4-Styrylpyridine.[15] ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.44 (d, *J* = 5.96 Hz, 2H), 7.26-7.19 (m, 5H), 7.10 (d, *J* = 5.88 Hz, 2H), 6.79 (d, *J* = 12.28 Hz, 1H), 6.50 (d, *J* = 12.28 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 149.8, 145.0, 136.1, 134.1, 128.8, 128.5, 127.9, 127.6, 123.5.



Z-3a

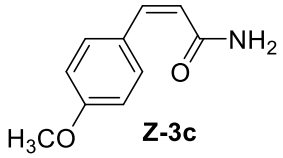
(*Z*)-3-phenylacrylamide.[16] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49-7.47 (m, 2H), 7.39-7.33 (m, 3H), 6.87 (d, *J* = 12.6Hz, 1H), 6.01 (d, *J* = 12.6 Hz, 1H), 5.43 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 168.8, 137.6, 134.8, 128.9, 128.8, 128.6, 123.8.



***Z*-3b**

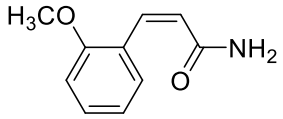
(Z)-3-(*p*-tolyl) acrylamide. Yellow Solid, mp. 119-121℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38 (d, *J* = 8.08 Hz, 2H), 7.17 (d, *J* = 8.0 Hz, 2H), 6.83 (d, *J* = 12.56 Hz, 1H), 5.94 (d, *J* = 12.52 Hz, 1H), 5.44 (d, *J* = 22.12 Hz, 2H). 2.36 (s, 3H); ^{13}C NMR

($CDCl_3$, 100 MHz): δ 169.0, 139.0, 137.7, 131.9, 129.3, 128.9, 123.0, 21.3. HRMS (ESI) calcd. for $C_{10}H_{12}NO$ $[M+H]^+$: 162.0913, found: 162.0915.



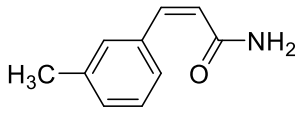
Z-3c

(*Z*)-3-(4-methoxyphenyl) acrylamide. White Solid, mp. 146-147 ℃. ^1H NMR (400 MHz, $CDCl_3$): δ 7.51-7.49 (m, 2H), 6.89-6.87 (m, 2H), 6.77 (d, *J* = 12.56 Hz, 1H), 5.87 (d, *J* = 12.56 Hz, 1H), 5.66 (d, *J* = 18.84 Hz, 2H), 3.82 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 169.3, 137.8, 130.9, 130.2, 127.2, 121.4, 113.8, 55.3. HRMS (ESI) calcd. for $C_{10}H_{12}NO_2$ $[M+H]^+$: 178.0863, found: 178.0864.



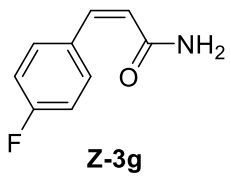
Z-3d

(*Z*)-3-(2-methoxyphenyl) acrylamide. Yellow oil, mp. 132-133 ℃. ^1H NMR (400 MHz, $CDCl_3$): δ 7.44 (d, *J* = 7.52 Hz, 1H), 7.32-7.28 (m, 1H), 7.00-6.97 (m, 1H), 6.94-6.88 (m, 2H), 6.20 (s, 1H), 5.97 (d, *J* = 12.56 Hz, 1H), 5.68 (s, 1H), 3.84 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 169.5, 157.0, 133.6, 130.4, 130.2, 124.1, 123.7, 120.5, 110.6, 55.4. HRMS (ESI) calcd. for $C_{10}H_{12}NO_2$$[M+H]^+$: 178.0863, found: 178.0862.



Z-3e

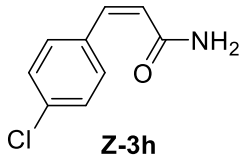
(*Z*)-3-(*m*-tolyl) acrylamide. White Solid, mp. 123-124 ℃. ^1H NMR (400 MHz, $CDCl_3$): δ 7.28-7.21 (m, 3H), 7.12 (d, *J* = 7.32 Hz, 1H), 6.78 (d, *J* = 12.6 Hz, 1H), 6.17 (s, 1H), 5.94 (d, *J* = 12.6 Hz, 1H), 5.74 (s, 1H), 2.34 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 169.5, 138.2, 137.7, 134.8, 129.5, 128.5, 125.9, 123.7, 21.4. HRMS (ESI) calcd. for $C_{10}H_{12}NO$ $[M+H]^+$: 162.0913, found:162.0914.



Z-3g

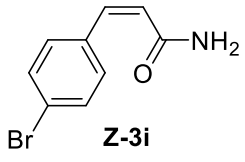
(*Z*)-3-(4-fluorophenyl) acrylamide. Colorless Oil. ^1H NMR (400 MHz, $CDCl_3$): δ 7.55-7.52 (m, 2H), 7.07-7.03 (m, 2H), 6.79 (d, *J* = 12.56 Hz, 1H), 5.97 (d, *J* = 12.6 Hz,

1H), 5.42 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 168.9, 136.9, 131.2, 131.1, 122.9, 115.6, 115.4. HRMS (ESI) calcd. for C_9H_9FNO $[M+H]^+$: 166.0663, found:166.0666.



Z-3h

(*Z*)-3-(4-chlorophenyl) acrylamide. Yellow Oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ7.48-7.46 (m, 2H), 7.34-7.32 (m, 2H), 6.77 (d, *J* = 12.6 Hz, 1H), 6.01 (d, *J* = 12.6 Hz, 1H), 5.45 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 168.4, 136.7, 133.1, 130.5, 128.7, 123.7. HRMS (ESI) calcd. for C_9H_9ClNO $[M+H]^+$: 182.0367, found:182.0368.



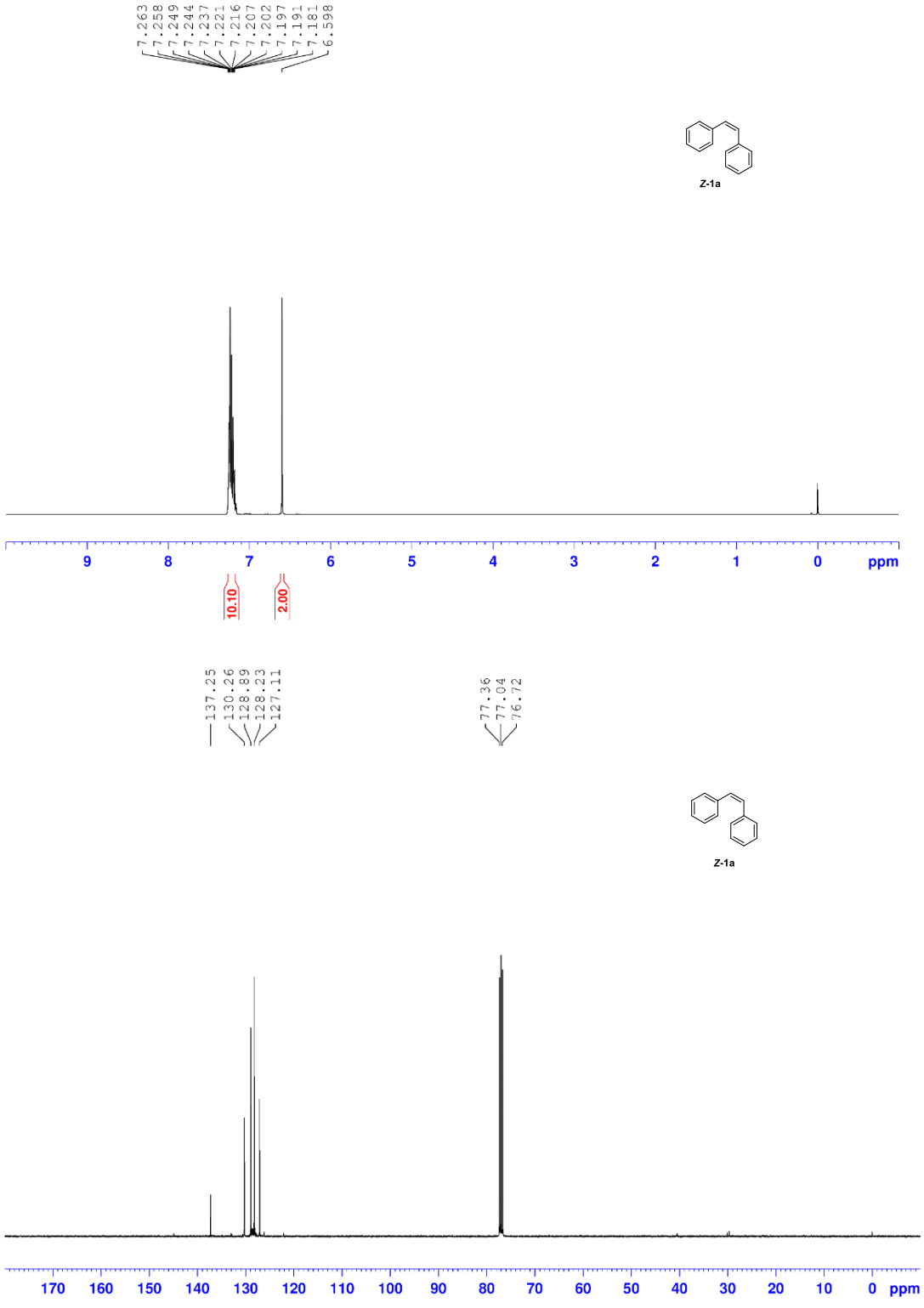
Z-3i

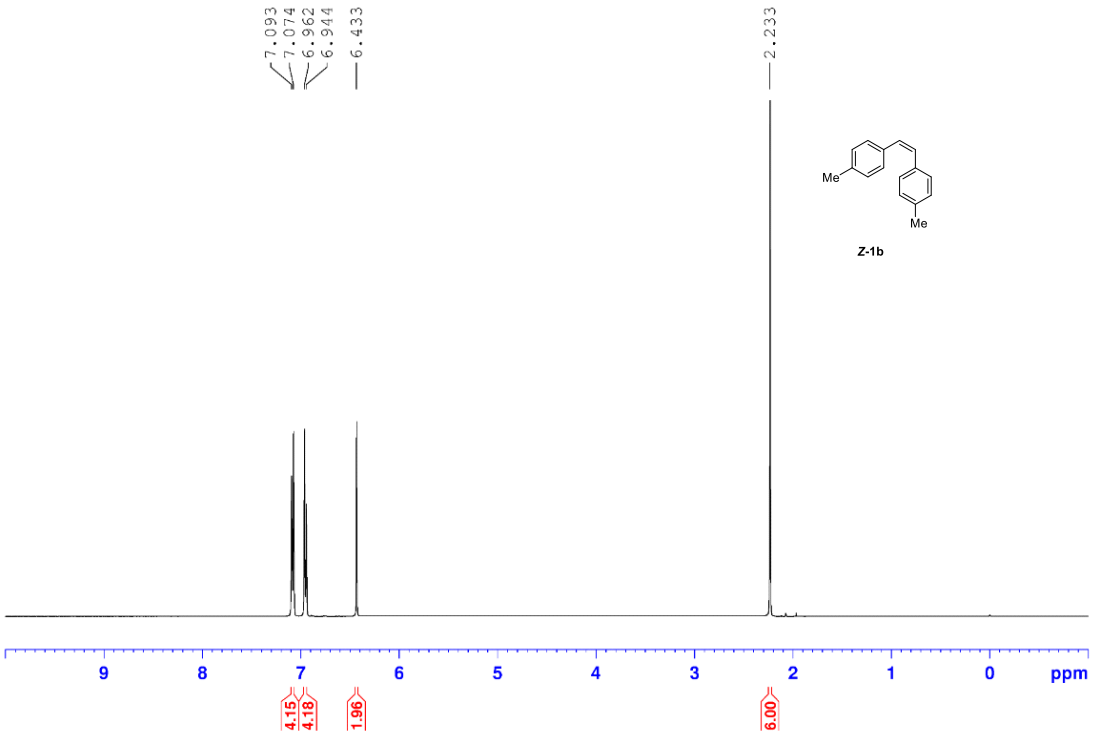
(*Z*)-3-(4-bromophenyl) acrylamide. Yellow Solid, mp. 156-158 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50-7.48 (m, 2H), 7.41-7.39 (m, 2H), 6.75 (d, *J* = 12.6 Hz, 1H), 6.02 (d, *J* = 12.56 Hz, 1H), 5.45 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 169.1, 136.7, 133.6, 131.6, 130.7, 123.9, 123.1. HRMS (ESI) calcd. for C_9H_9BrNO $[M+H]^+$: 225.9862, found:225.9866.

5. References

1. D. C. Fabry, M. A. Ronge, M. Rueping, *Chem. Eur. J.*, 2015, **21**, 5350-5354
2. C. C. Tai, M. S. Yu, Y. L. Chen, W. H. Chuang, T. H. Lin, G. P. A. Yap, T. G. Ong, *Chem. Commun.*, 2014, **50**, 4344–4346.
3. A. S. Saiyed, K. N. Patel, B .V. Kamath, A. V. Bedekar, *Tetrahedron Lett.*, 2012, **53**, 4692.
4. S. S. Li, L. Tao, F. Z. Wang, Y.-M. Liu, Y. Cao, *Adv. Synth. Catal.*, 2016, **358**, 1410.
5. G. Bellucci, R. Bianchini, C. Chiappe, R. S. Brown, S. Slebocka-Tilk, *J. Am. Chem. Soc.*, 1991, **113**, 8012.
6. J. Wu, D. Li, D. Zhang, *Synth. Commun.*, 2005, **35**, 2543-2551.
7. T. Schabel, C. Belger, B. Plietker, *Org. Lett.*, 2013, **15**, 2858−2861.
8. L. Ilies, T. Yoshida, E. Nakamura, *J. Am. Chem. Soc.*, 2012, **134**, 16951–16954.
9. S. Enthaler, M. Haberberger, E. Irran, *Chem. Asian J.*, 2011, **6**, 1613
10. F. Lara-Ochoa, G. Espinosa-Pérez, *Tetrahedron Lett.*, 2007, **48**, 7007.
11. S. Rao, K. R. Prabhu, *Chem. Eur. J.*, 2018, **24**, 13954.
12. T. N. Gieshoff, A. Welther, M. T. Kessler, M. H. G. Prechtl, A. J. von Wangelin, *Chem. Commun.*, 2014, **50**, 2261−2264.
13. C. Linde, N. Koliaï, P. O. Norrby,; B. Åkermark, *Chem. Eur. J.*, 2002, **8**, 2568-2573.
14. R. Nishibayashi,; T. Kurahashi, S. Matsubara, *Synlett*, 2014, **25**, 1287.
15. Z. Wang, S. F. Wnuk, *J. Org. Chem.*, 2005, **70**, 3281.
16. C. Q. Zhao, Y. G. Chen, H. Qiu, L. Wei, P. Fang, T. S. Mei, *Org. Lett.*, 2019, **21**, 5, 1412-1416

6. NMR spectra of products

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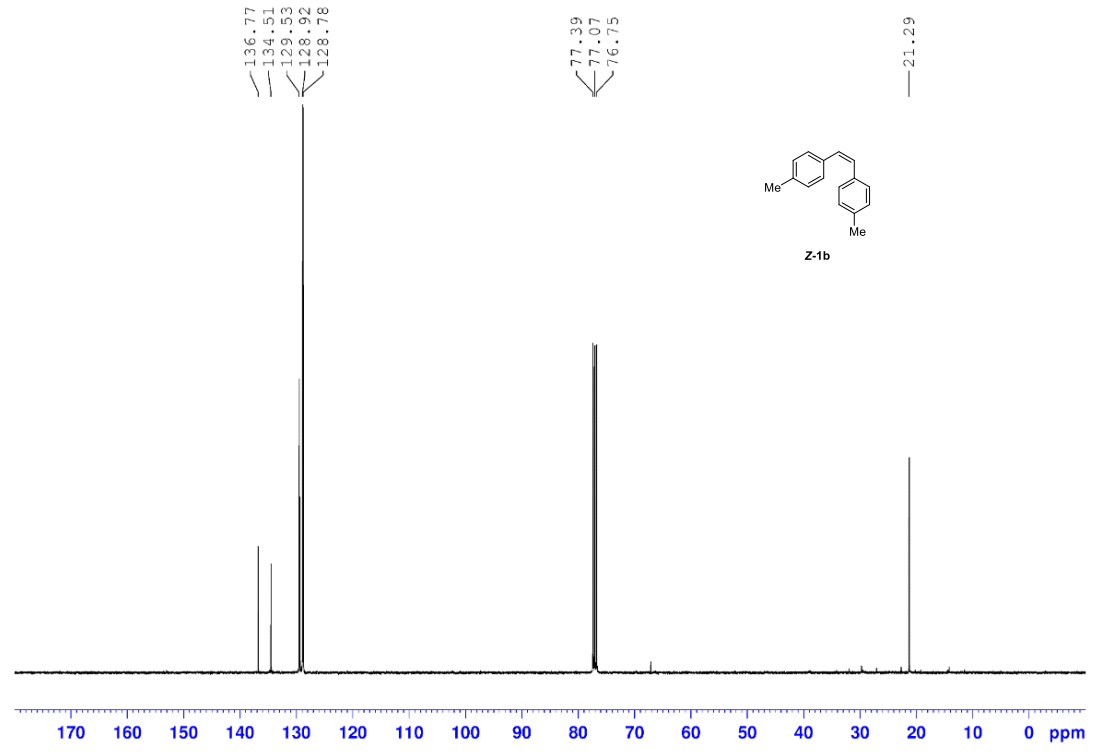
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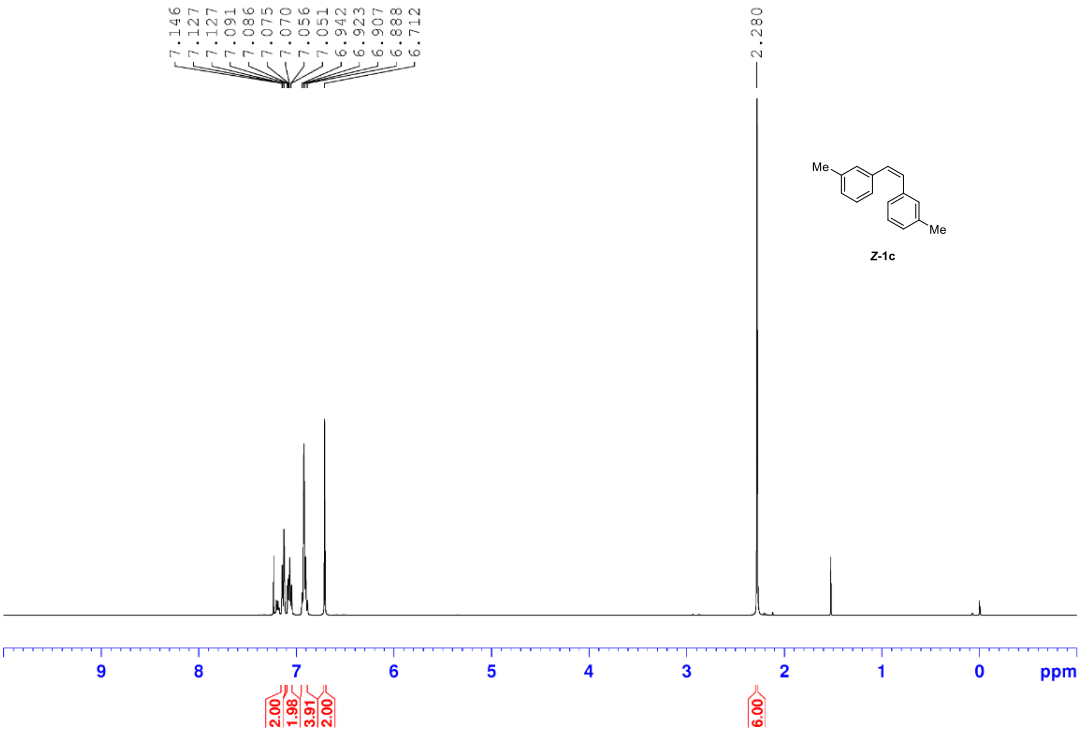
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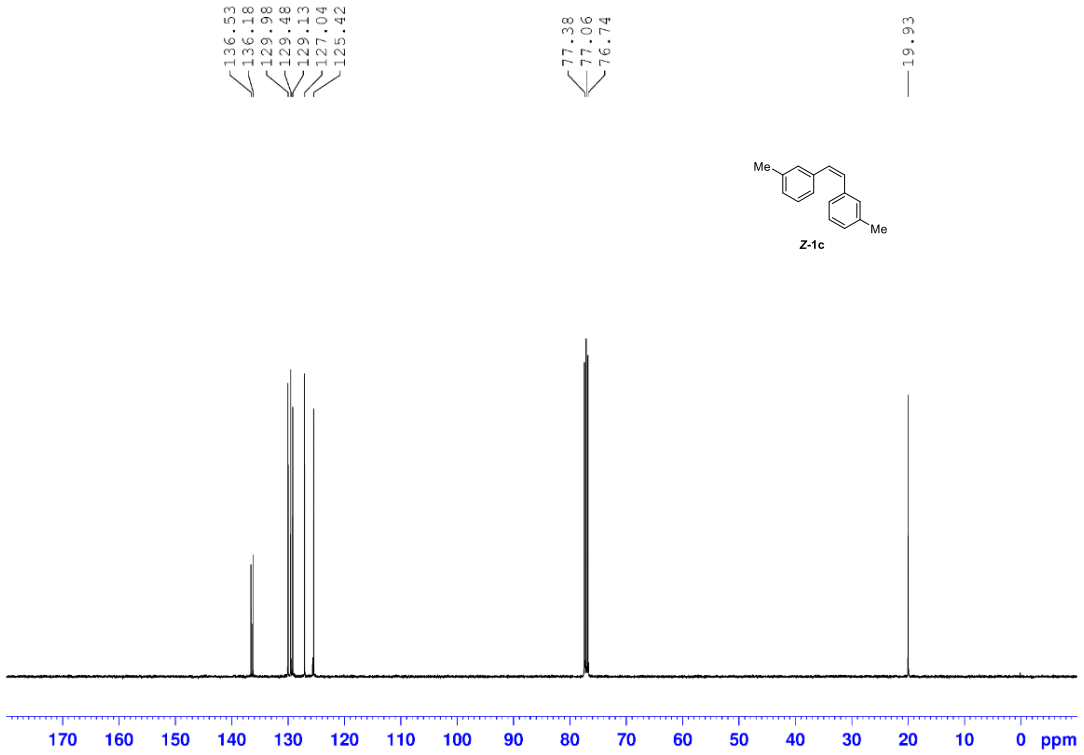
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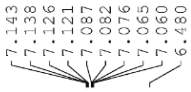
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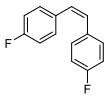
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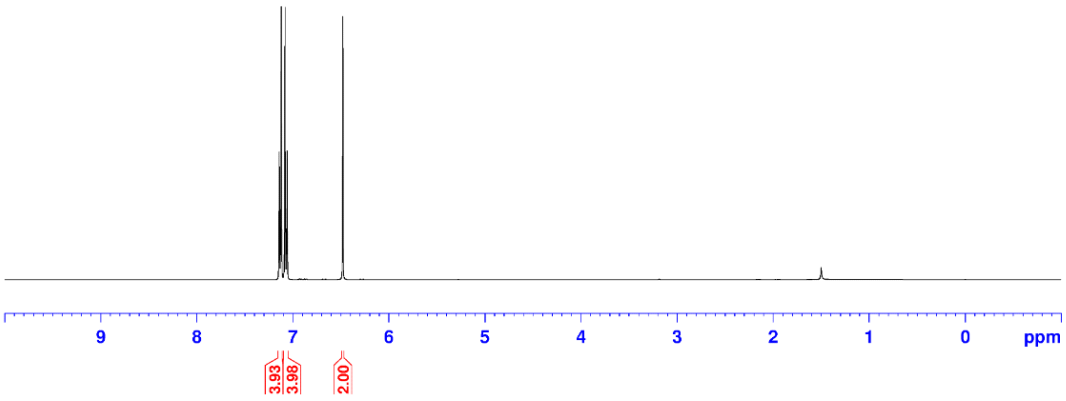
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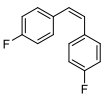
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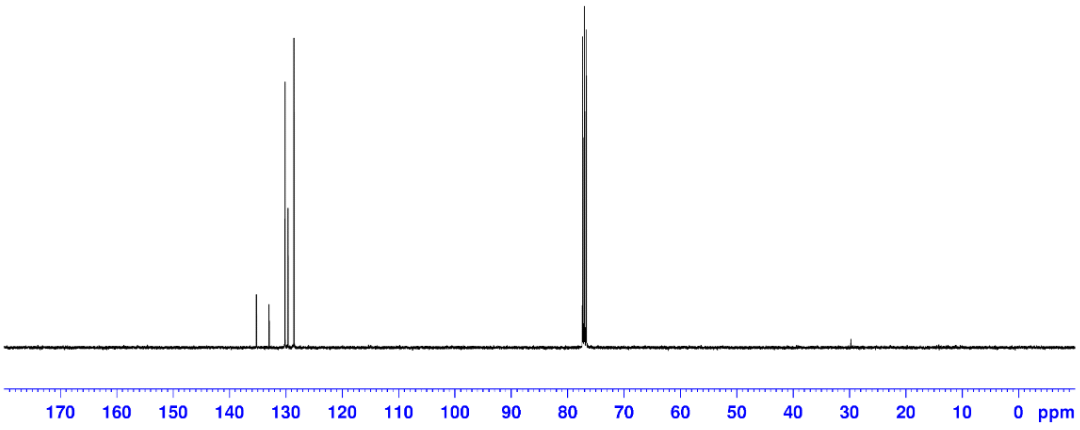
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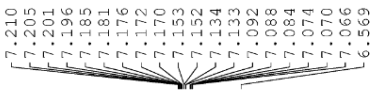
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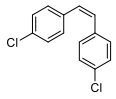
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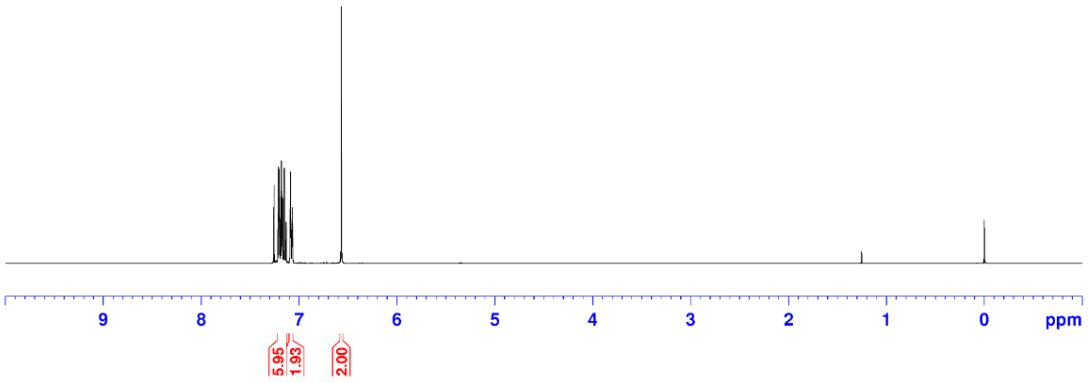
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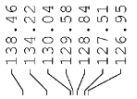
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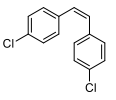
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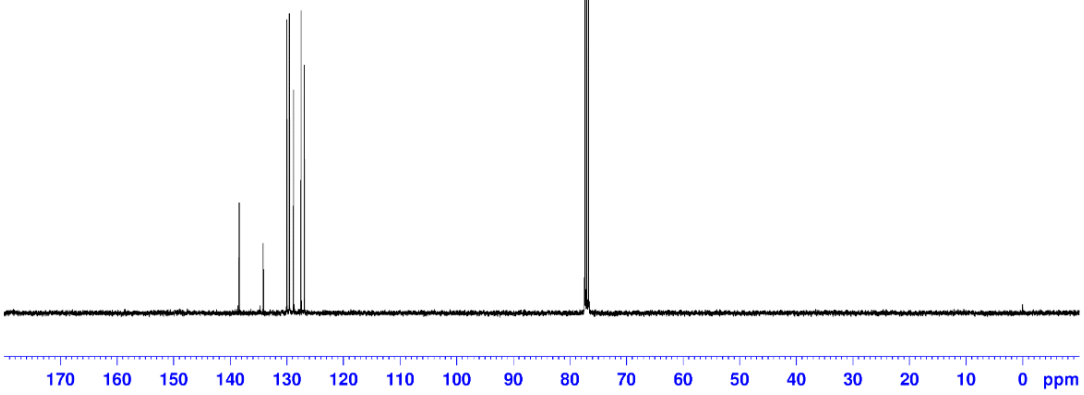
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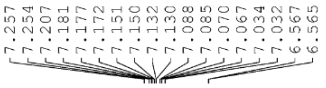
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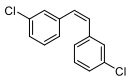
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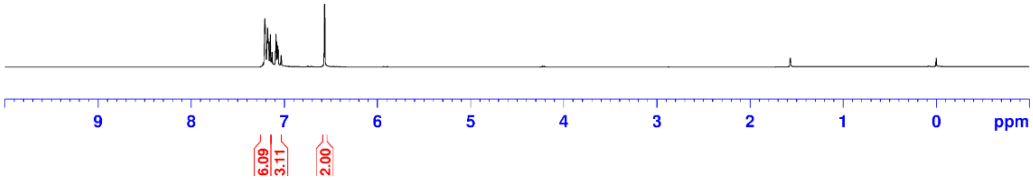
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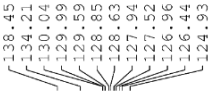
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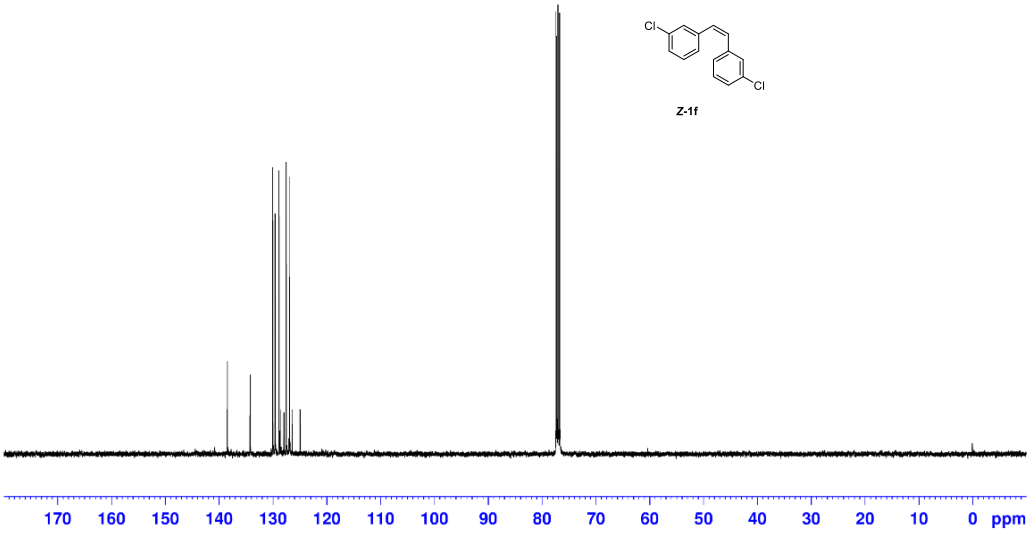
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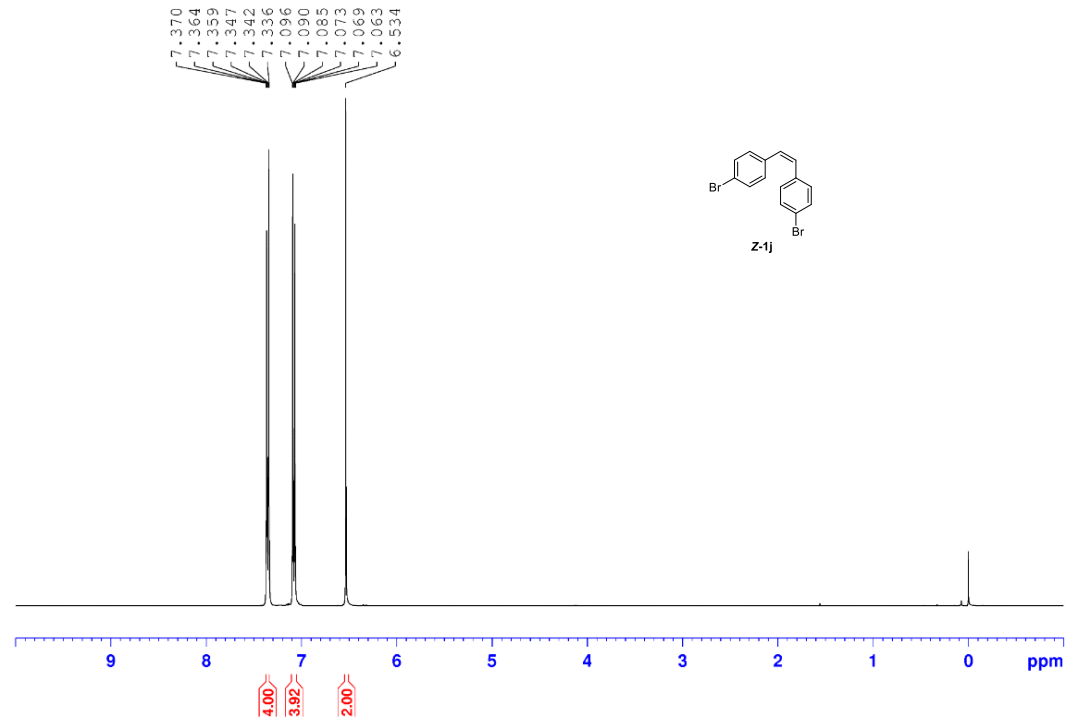
Cl
Cl

Z-1f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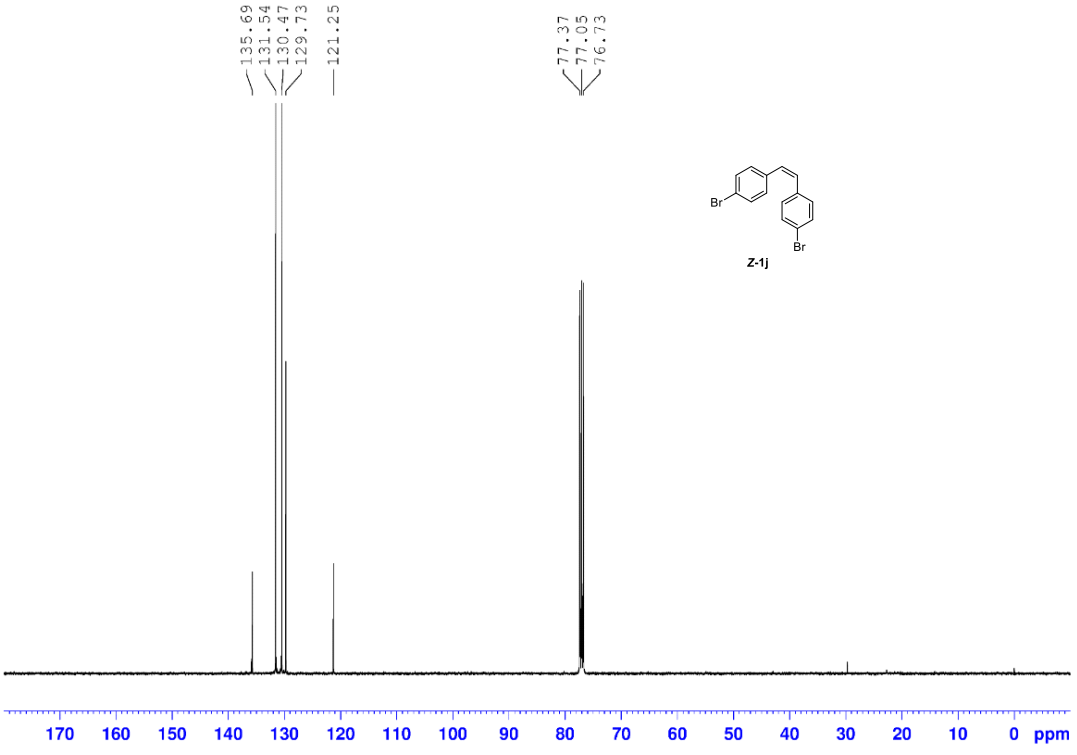
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130.47
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121.25
77.37
77.05
76.73
Br
Br
Z-1j
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140
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100
90
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60
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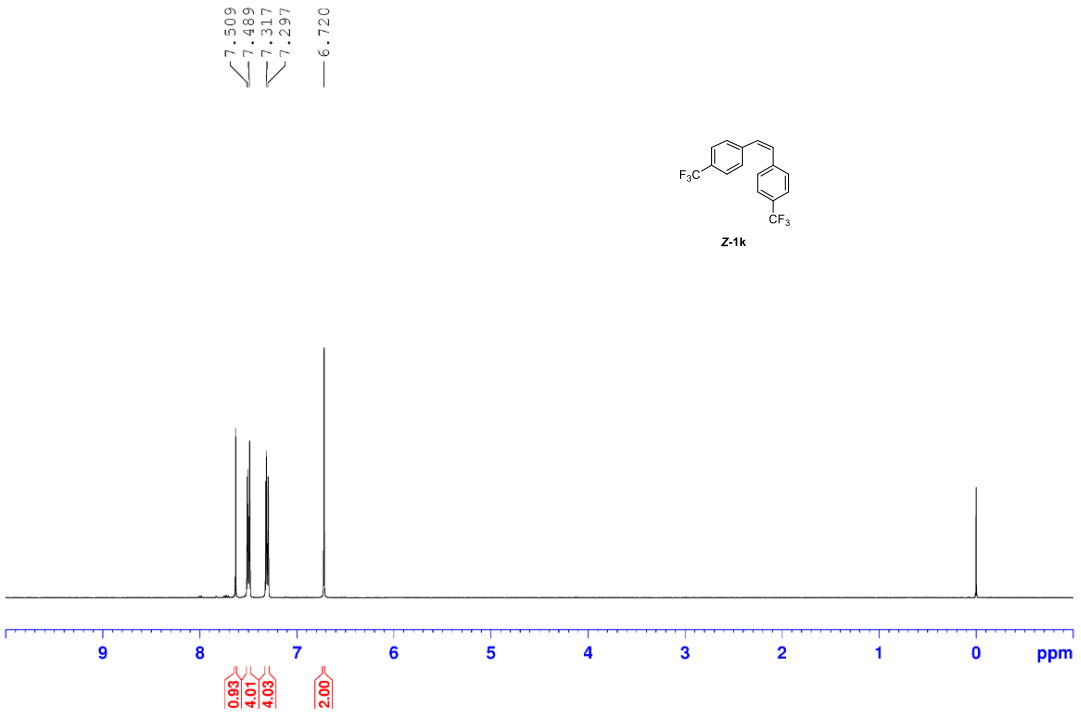
ppm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7.317
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F3C
CF3
Z-1k
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8
7
6
5
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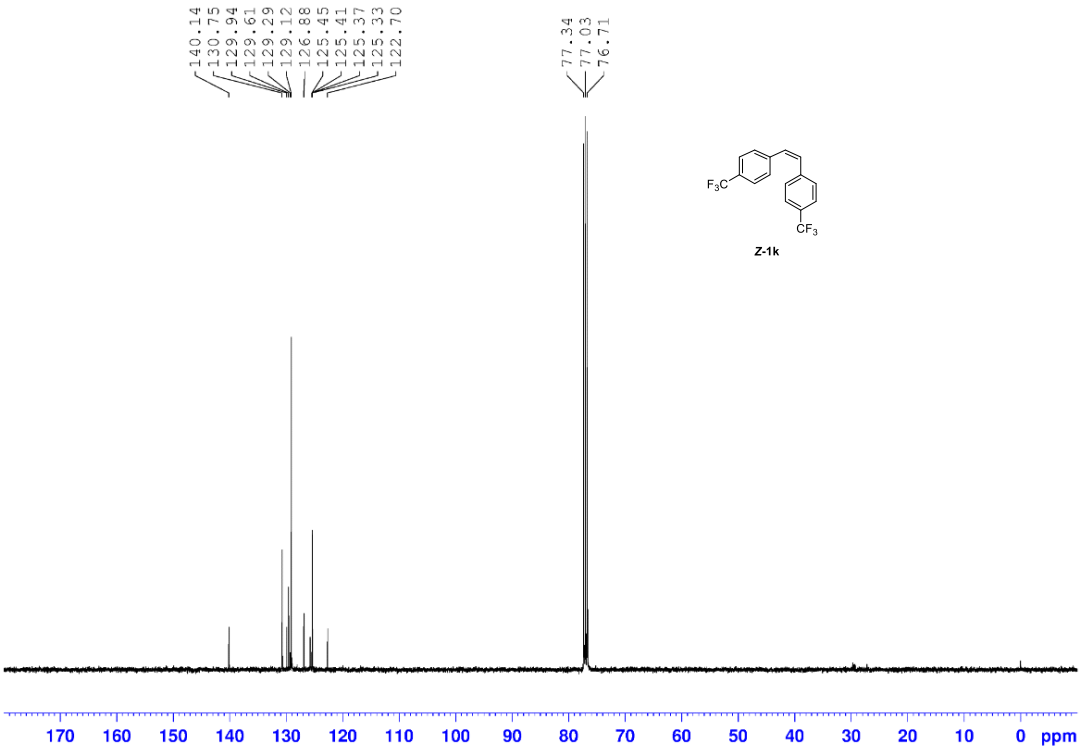
4.03
2.00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125.45
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125.37
125.33
122.70
77.34
77.03
76.71
F3C
CF3
Z-1k
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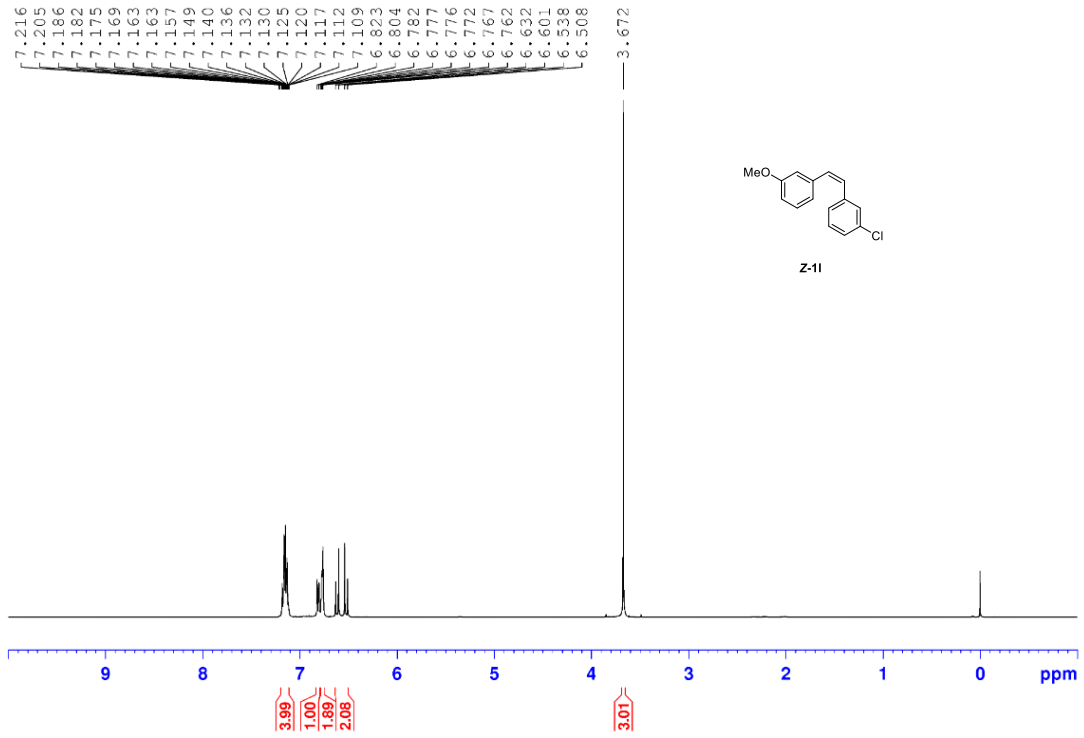
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7.163
7.163
7.157
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7.140
7.136
7.132
7.130
7.125
7.120
7.117
7.112
7.109
6.823
6.804
6.782
6.777
6.776
6.772
6.767
6.762
6.632
6.601
6.538
6.508
3.672
MeO
Cl
Z-1l
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4
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2
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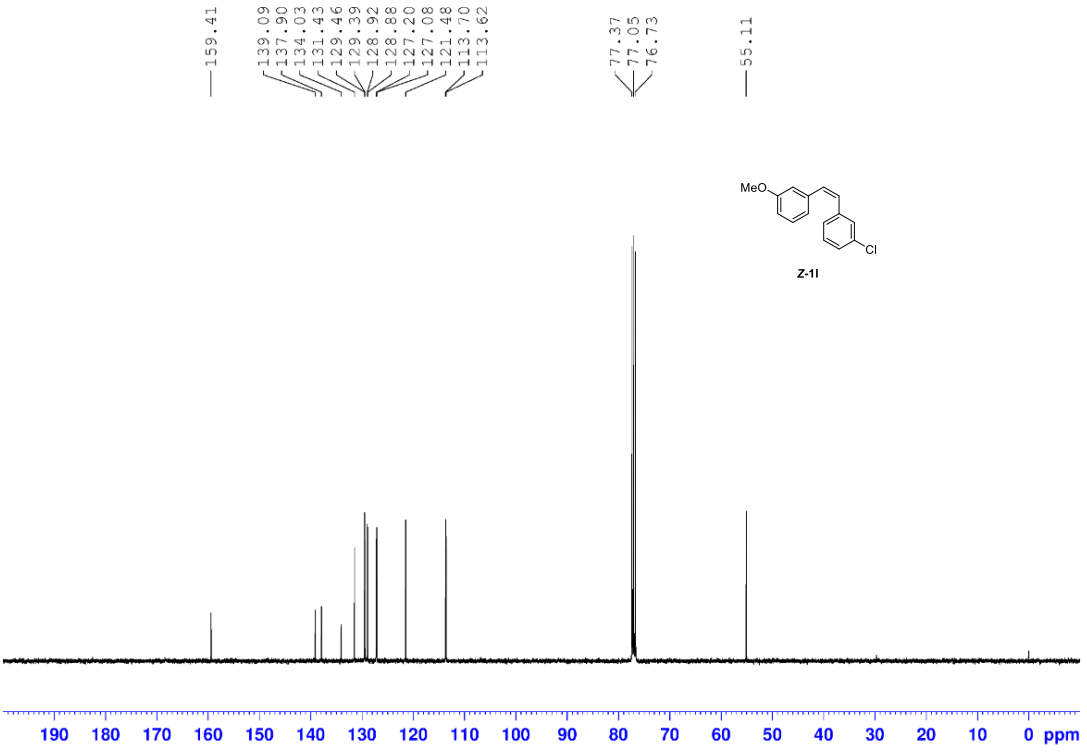
3.01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128.92
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127.20
127.08
121.48
113.70
113.62
77.37
77.05
76.73
55.11
MeO
Cl
Z-1l
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140
130
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110
100
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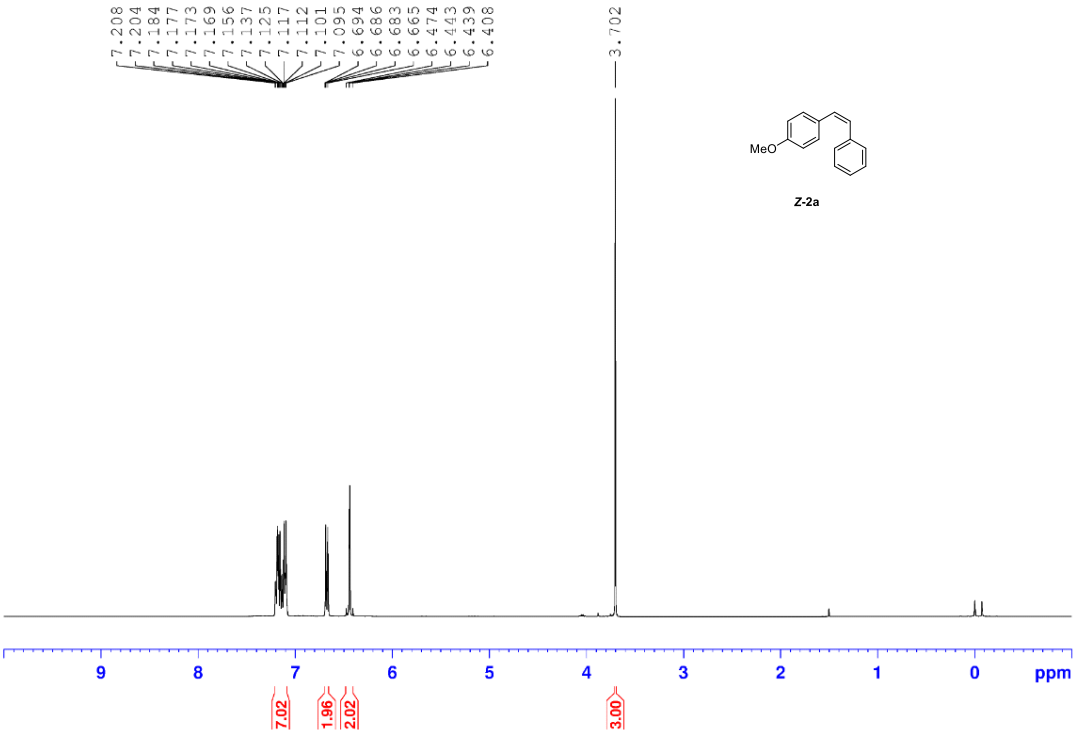
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7.156
7.137
7.125
7.117
7.112
7.101
7.095
6.694
6.686
6.683
6.665
6.474
6.443
6.439
6.408
3.702
MeO
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8
7
6
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4
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0
ppm
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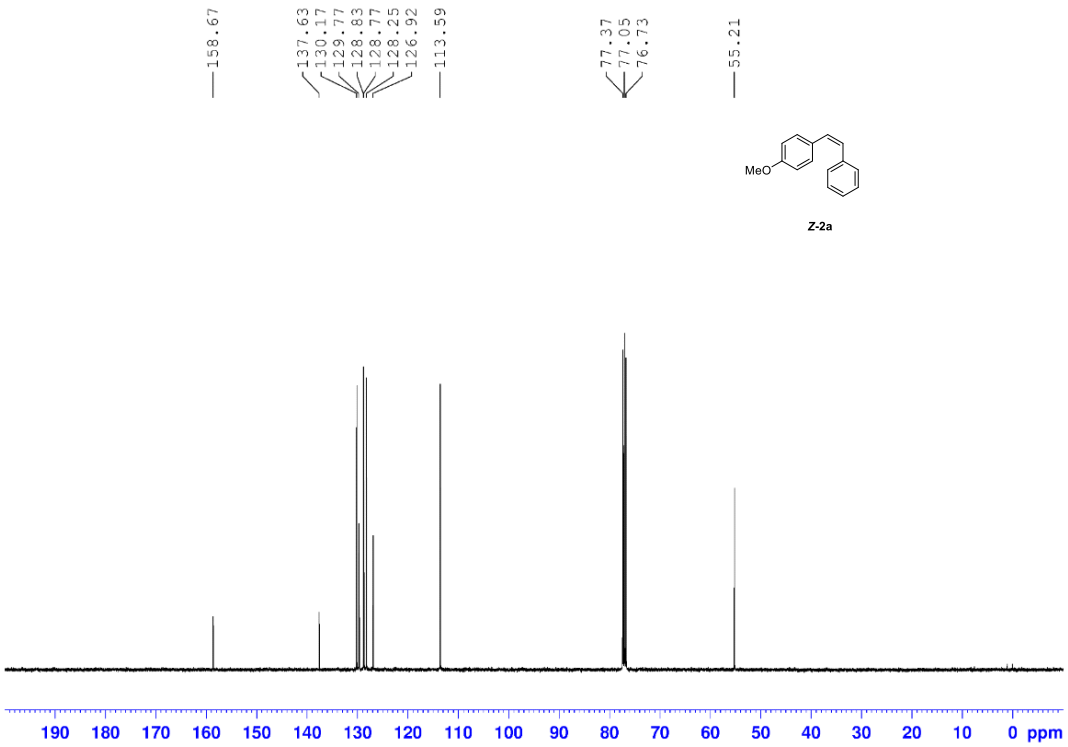
2.02
3.00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128.83
128.77
128.25
126.92
113.59
77.37
77.05
76.73
55.21
MeO
Z-2a
190
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150
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70
60
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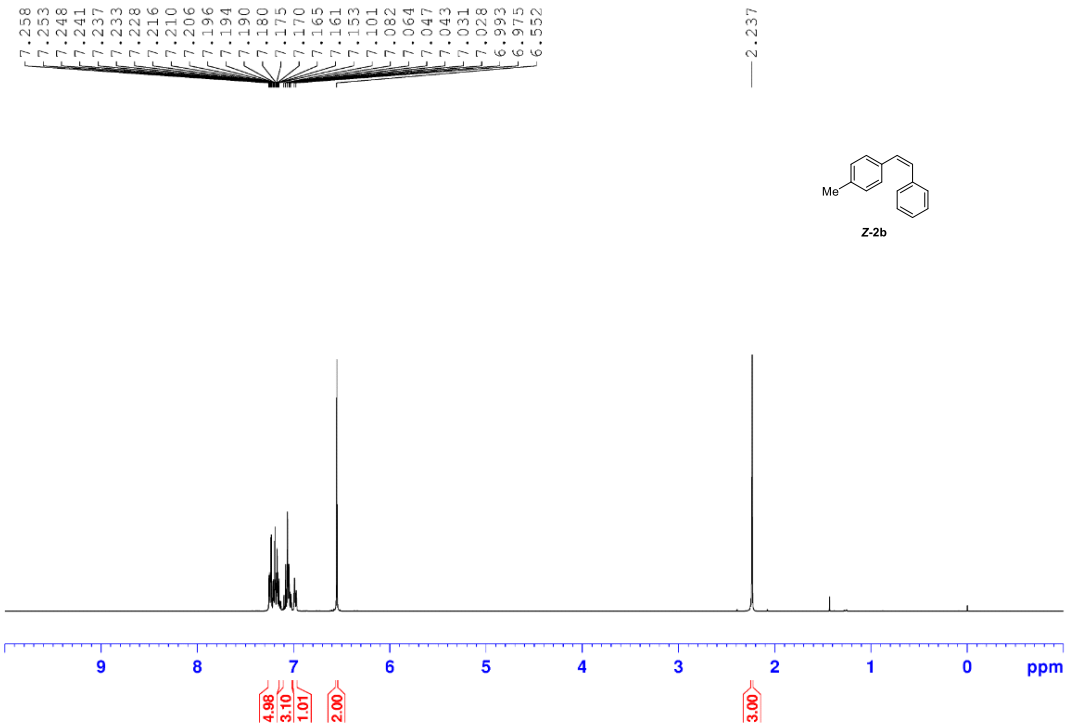
30
20
10
0 ppm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7.237
7.233
7.228
7.216
7.210
7.206
7.196
7.194
7.190
7.180
7.175
7.170
7.165
7.161
7.153
7.101
7.082
7.064
7.047
7.043
7.031
7.028
6.993
6.975
6.552
2.237
Me
Z-2b
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8
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6
5
4
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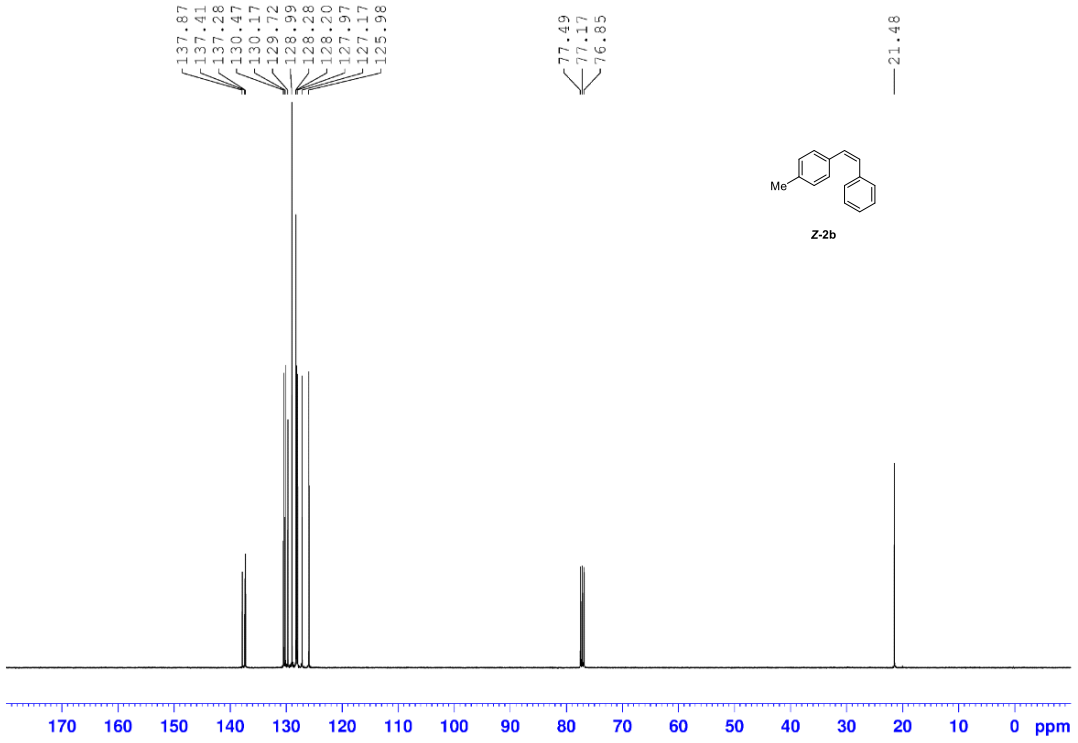
2
1
0
ppm
4.98
3.10
1.01
2.00
3.00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130.17
129.72
128.99
128.28
128.20
127.97
127.17
125.98
77.49
77.17
76.85
21.48
Me
Z-2b
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160
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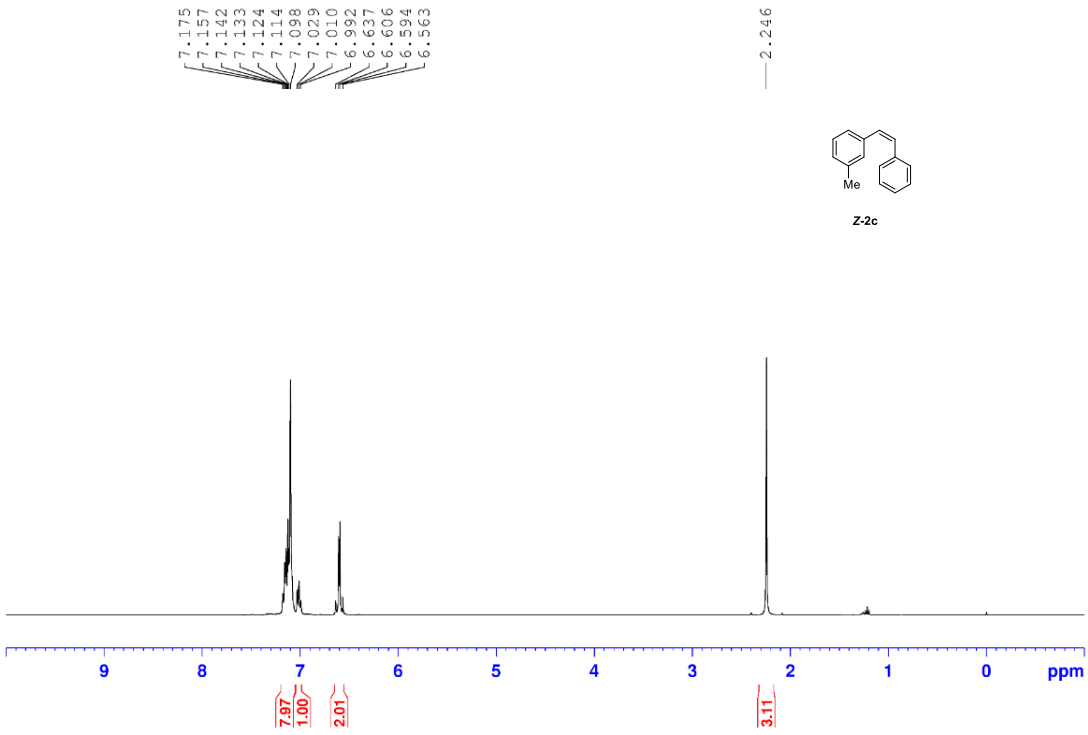
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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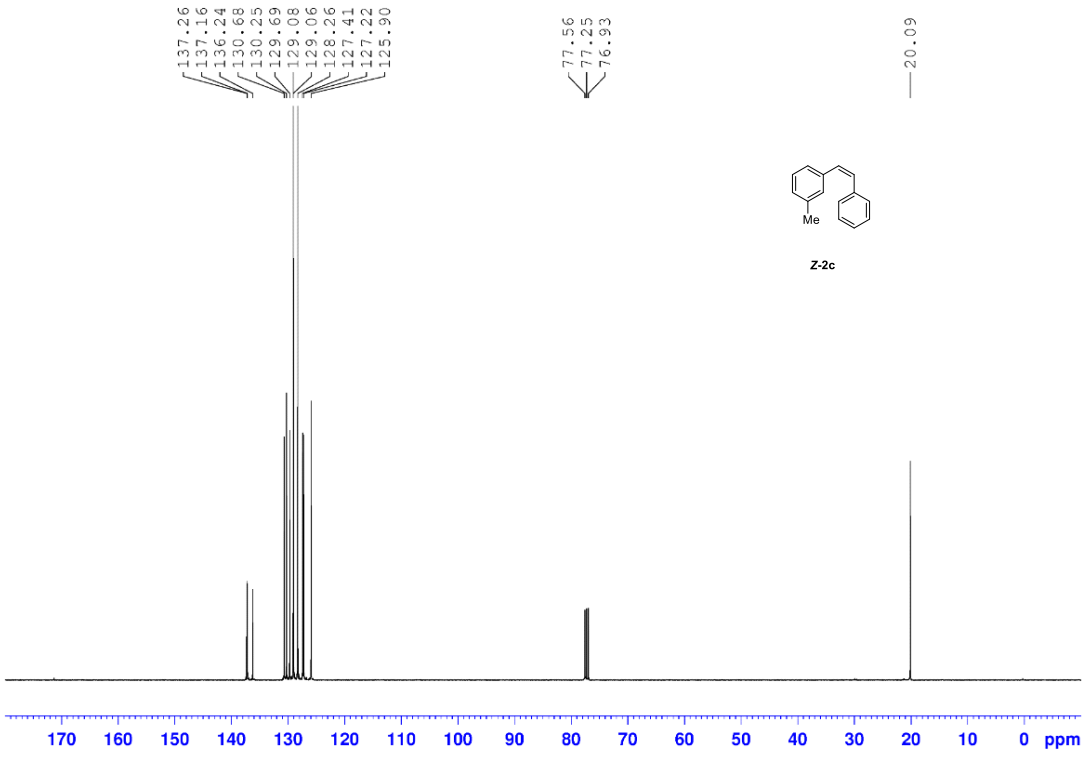
7.157
7.142
7.133
7.124
7.114
7.098
7.029
7.010
6.992
6.637
6.606
6.594
6.563
2.246
Me
Z-2c
9
8
7
6
5
4
3
2
1
0
ppm
7.97
1.00
2.01
3.11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137.16
136.24
130.68
130.25
129.69
129.08
129.06
128.26
127.41
127.22
125.90
77.56
77.25
76.93
20.09
Me
Z-2c
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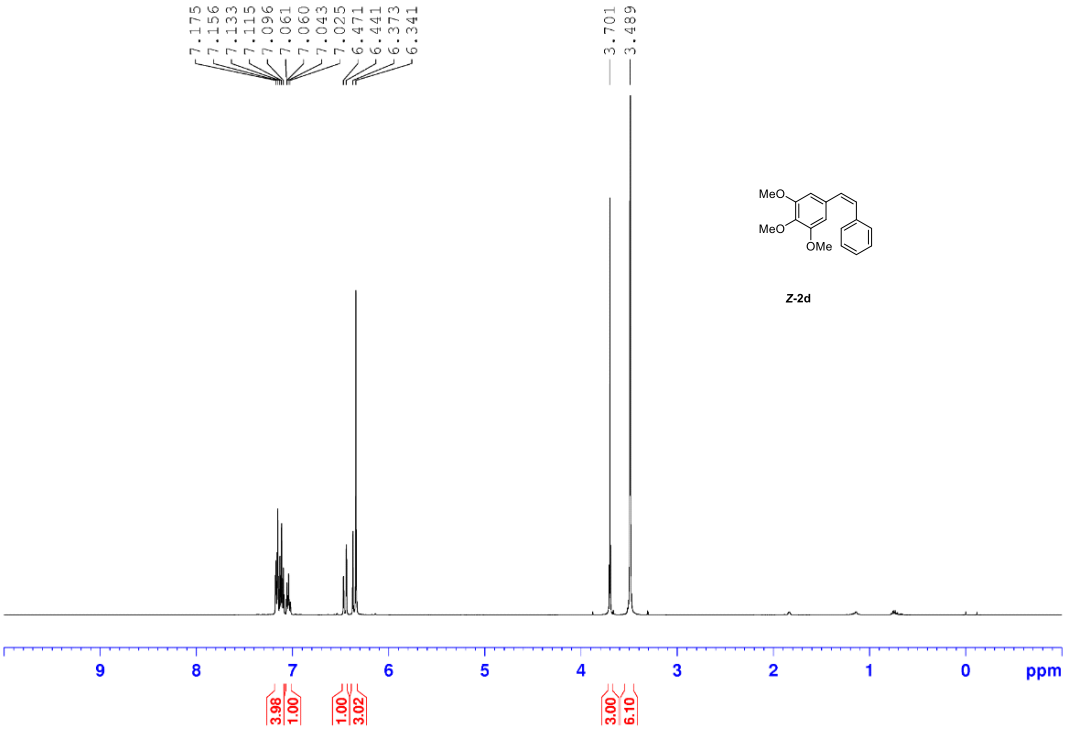
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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7.156
7.133
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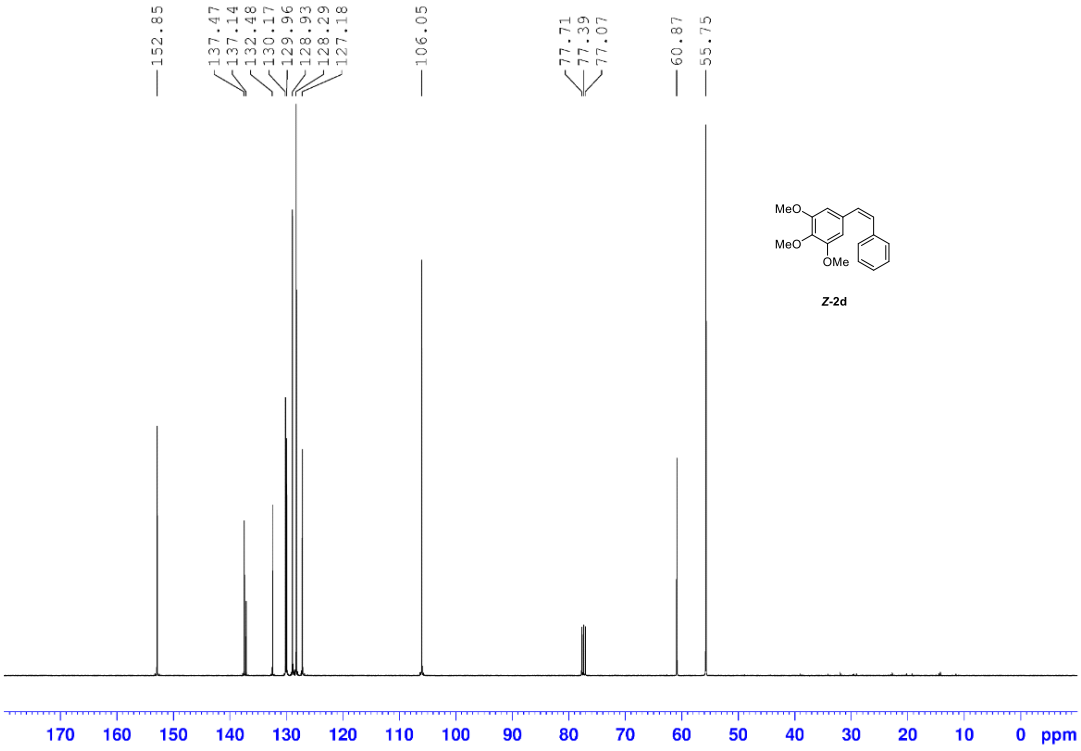
7.096
7.061
7.060
7.043
7.025
6.471
6.441
6.373
6.341
3.701
3.489
MeO
MeO
OMe
Z-2d
9
8
7
6
5
4
3
2
1
0
ppm
3.98
1.00
1.00
3.02
3.00
6.10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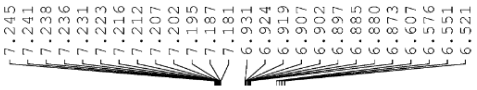
137.14
132.48
130.17
129.96
128.93
128.29
127.18
106.05
77.71
77.39
77.07
60.87
55.75
MeO
MeO
OMe
Z-2d
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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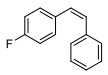
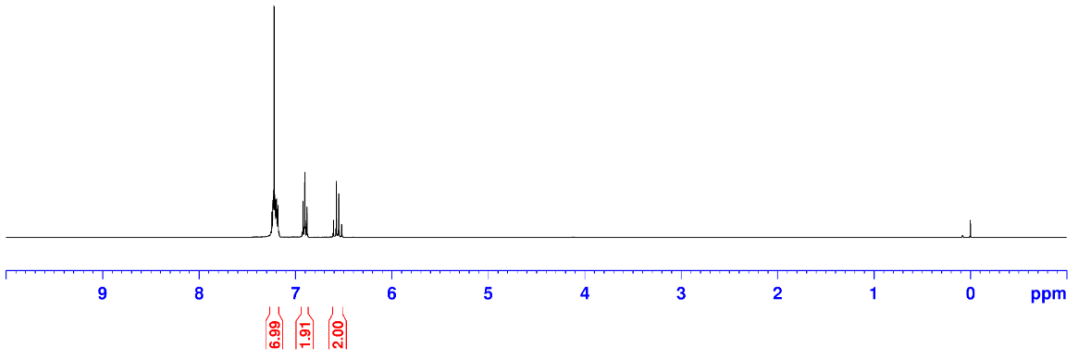
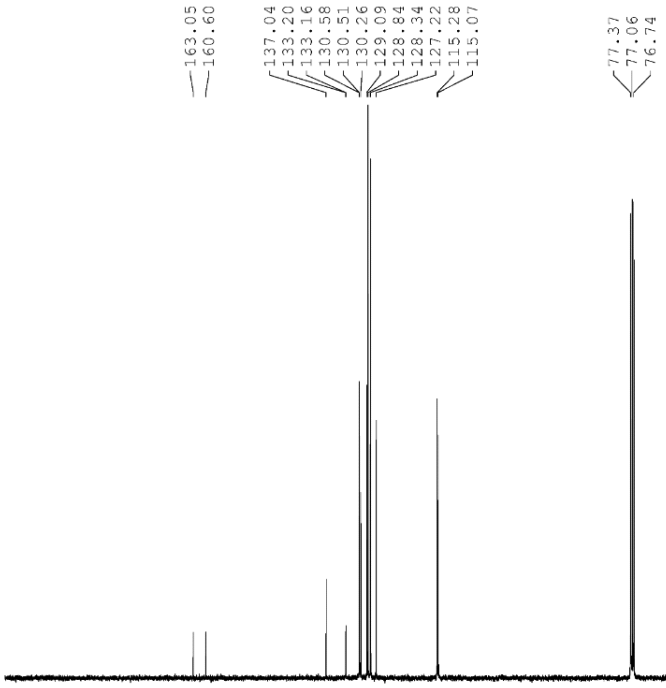
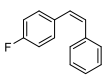
7.238
7.236
7.231
7.223
7.216
7.212
7.207
7.202
7.195
7.187
7.181
6.931
6.924
6.919
6.907
6.902
6.897
6.885
6.880
6.873
6.607
6.576
6.551
6.521


F

Z-2e

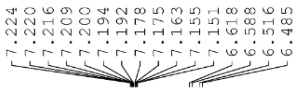

9
8
7
6
5
4
3
2
1
0
ppm
6.99
1.91
2.00


163.05
160.60
137.04
133.20
133.16
130.58
130.51
130.26
129.09
128.84
128.34
127.22
115.28
115.07
77.37
77.06
76.74


F

Z-2e


190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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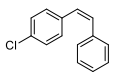
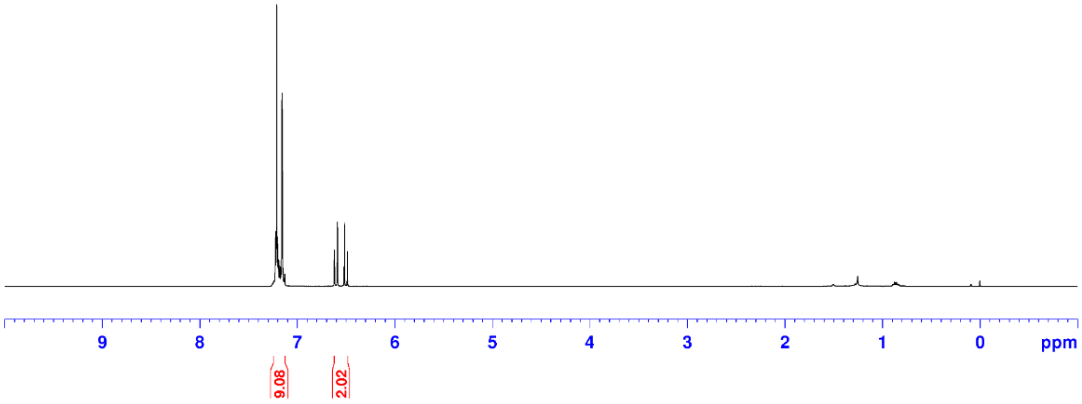
7.220
7.216
7.209
7.200
7.194
7.192
7.178
7.175
7.163
7.155
7.151
6.618
6.588
6.516
6.485


Cl

Z-2f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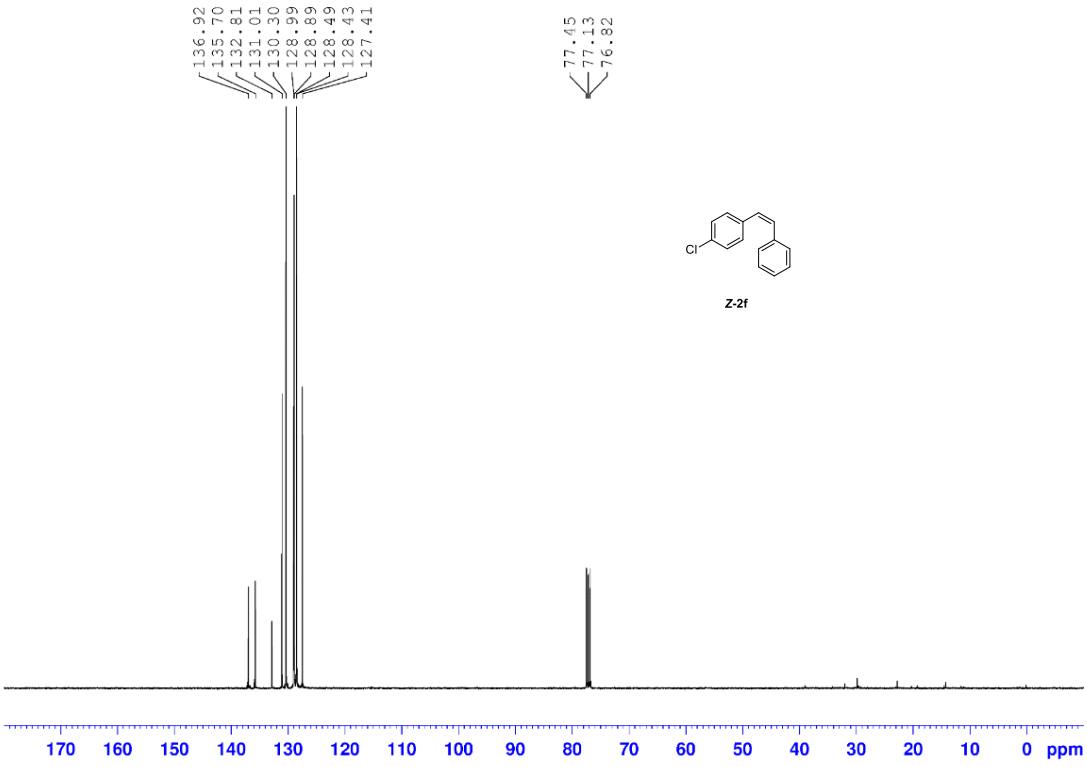
5
4
3
2
1
0
ppm
9.08
2.02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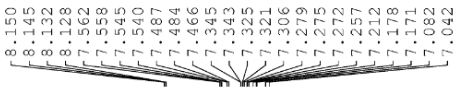
131.01
130.30
128.99
128.89
128.49
128.43
127.41
77.45
77.13
76.82
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

Cl

Z-2f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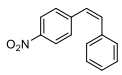
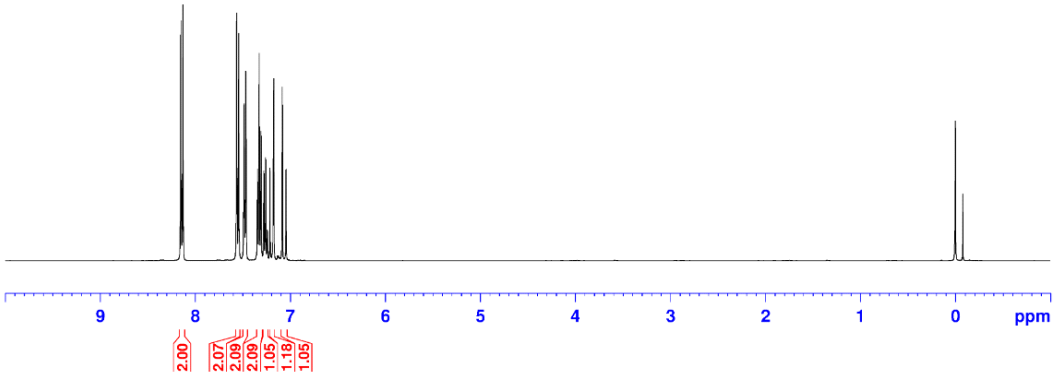
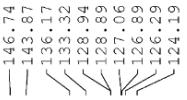
8.132
8.128
7.562
7.558
7.545
7.540
7.487
7.484
7.466
7.345
7.343
7.325
7.321
7.306
7.279
7.275
7.272
7.257
7.212
7.178
7.171
7.082
7.042


O2N

Z-2g


9
8
7
6
5
4
3
2
1
0
ppm
2.00
2.07
2.09
2.09
1.05
1.18
1.05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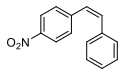
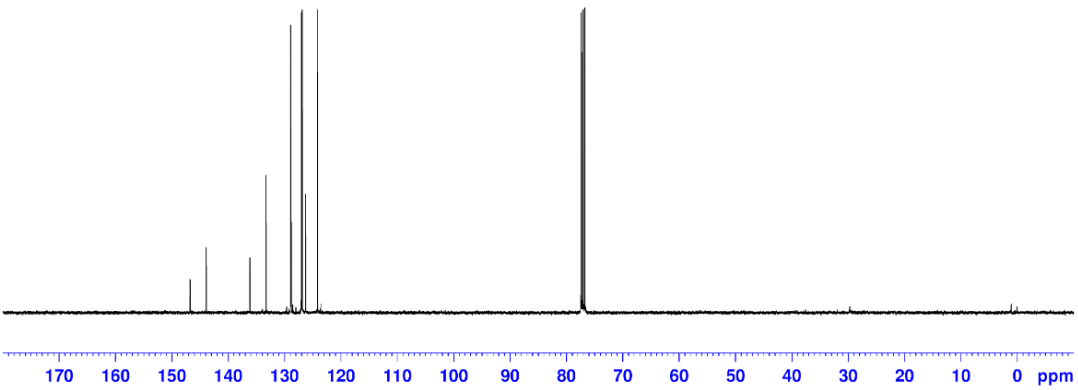
127.06
126.89
126.29
124.19


77.39
77.07
76.75


O2N

Z-2g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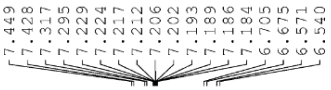
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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7.224
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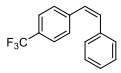
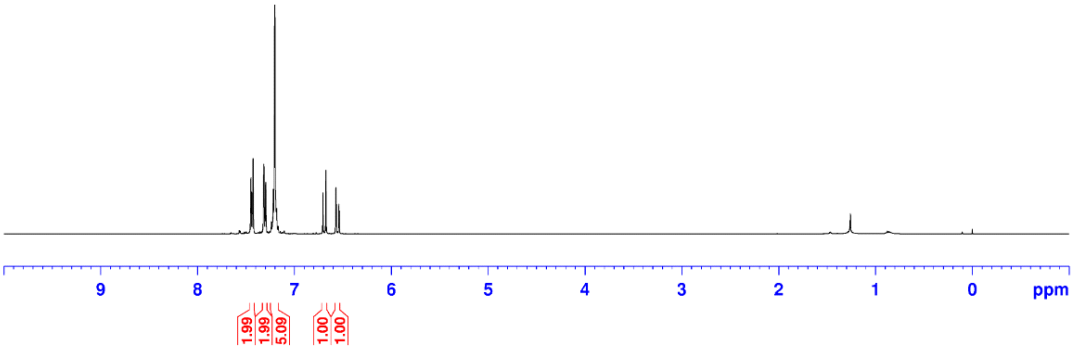
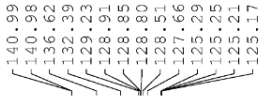
7.206
7.202
7.193
7.189
7.186
7.184
6.705
6.675
6.571
6.540


F3C

Z-2h


9
8
7
6
5
4
3
2
1
0
ppm

1.99
1.99
5.09
1.00
1.00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129.23
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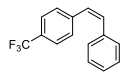
128.51
127.66
125.29
125.25
125.21
125.17


77.43
77.11
76.79


F3C

Z-2h

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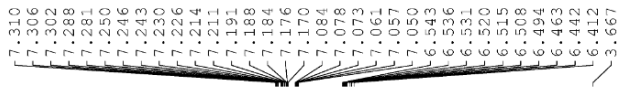
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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7.243
7.230
7.226
7.214
7.211
7.191
7.188
7.184
7.176
7.170
7.084
7.078
7.073
7.061
7.057
7.050
6.543
6.536
6.531
6.520
6.515
6.508
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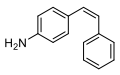
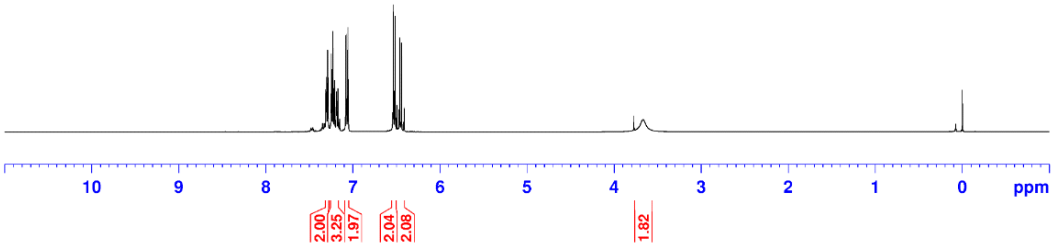
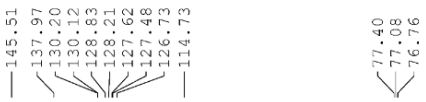
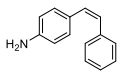
6.412
3.667


H2N

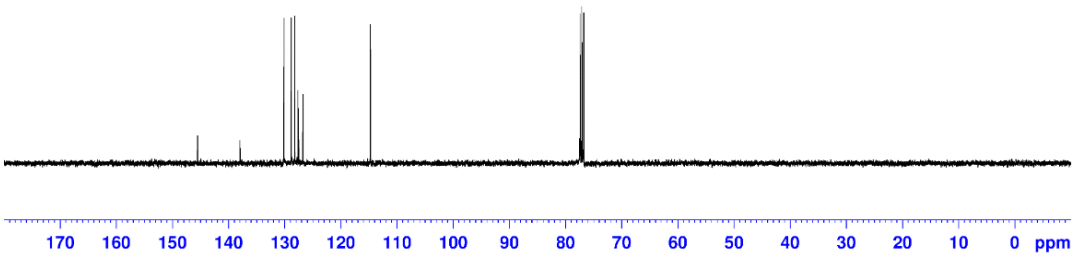
Z-2i

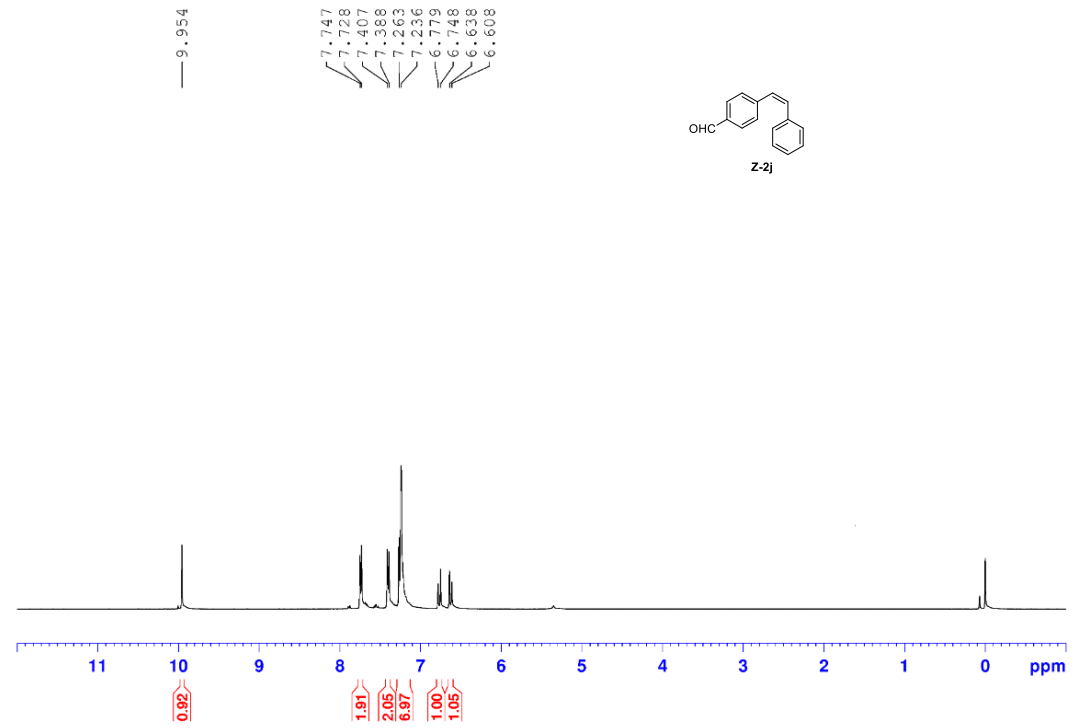

10
9
8
7
6
5
4
3
2
1
0
ppm
2.00
3.25
1.97
2.04
2.08
1.82

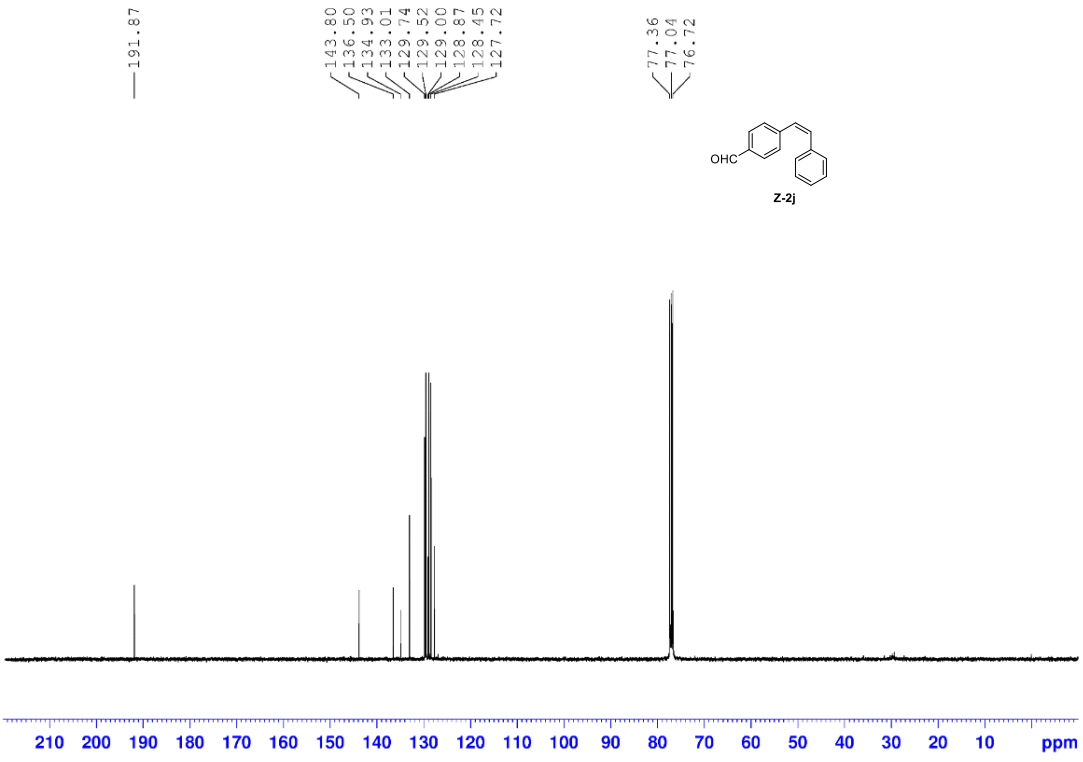

145.51
137.97
130.20
130.12
128.83
128.21
127.62
127.48
126.73
114.73
77.40
77.08
76.76

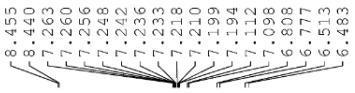

H2N

Z-2i


170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

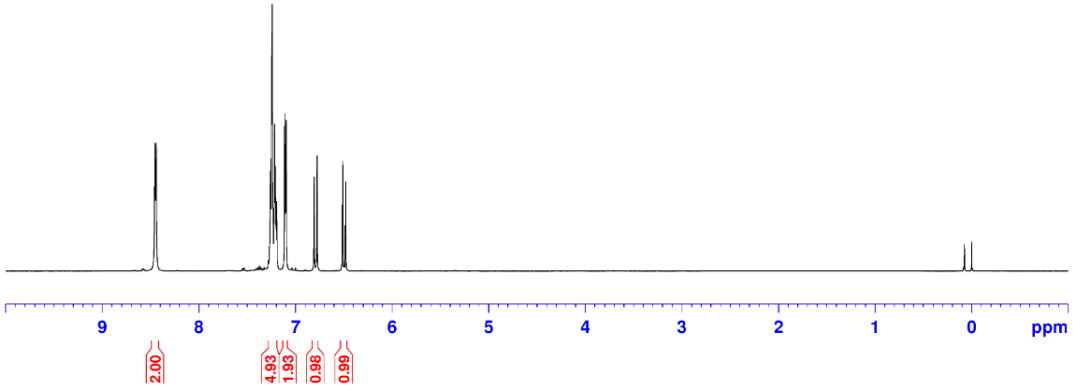

9.954
7.747
7.728
7.407
7.388
7.263
7.236
6.779
6.748
6.638
6.608
OHC
Z-2j
11
10
9
8
7
6
5
4
3
2
1
0
ppm
0.92
1.91
2.05
6.97
1.00
1.05

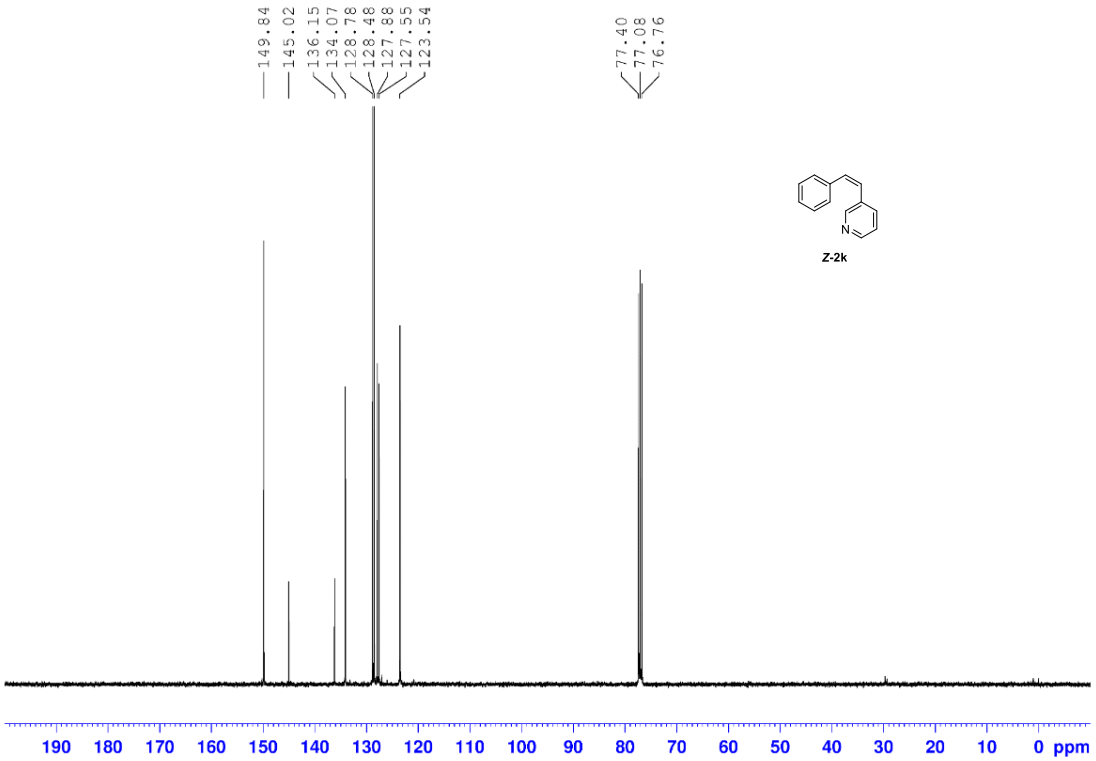

191.87
143.80
136.50
134.93
133.01
129.74
129.52
129.00
128.87
128.45
127.72
77.36
77.04
76.72
OHC
Z-2j
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


8.455
8.440
7.263
7.260
7.256
7.248
7.242
7.236
7.233
7.218
7.210
7.199
7.194
7.112
7.098
6.808
6.777
6.513
6.483


N

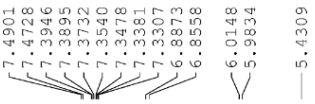
Z-2k

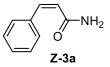

9
8
7
6
5
4
3
2
1
0
ppm
2.00
4.93
1.93
0.98
0.99


149.84
145.02
136.15
134.07
128.78
128.48
127.88
127.55
123.54
77.40
77.08
76.76
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm

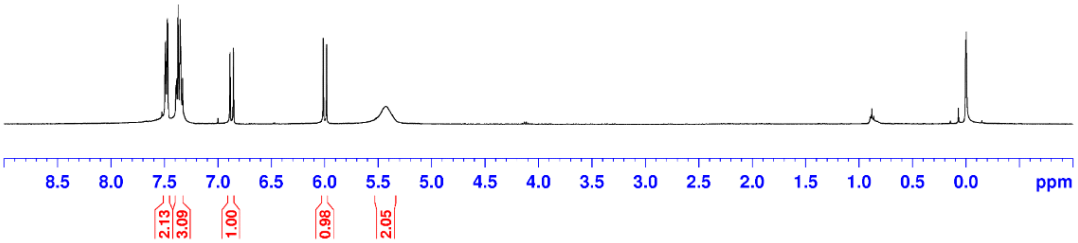
N

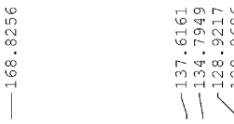
Z-2k

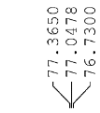

7.4901
7.4728
7.3946
7.3895
7.3732
7.3540
7.3478
7.3381
7.3307
6.8873
6.8558
6.0148
5.9834
5.4309

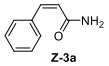

NH2
O

Z-3a

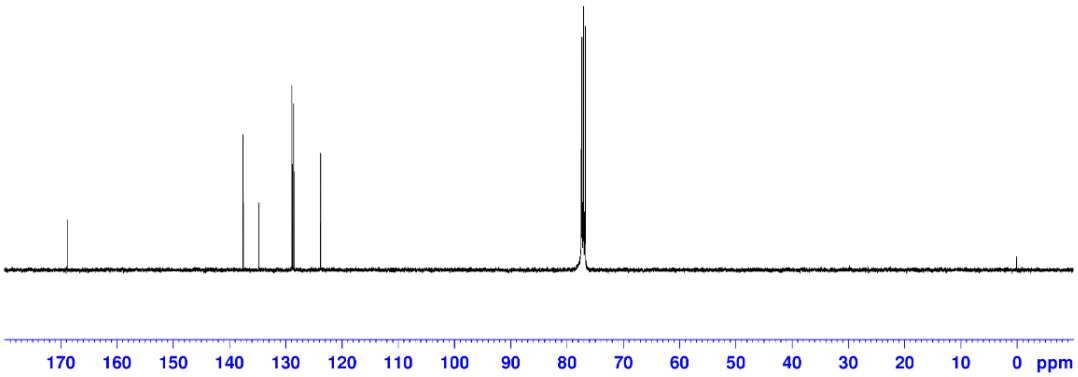

8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
2.13
3.09
1.00
0.98
2.05

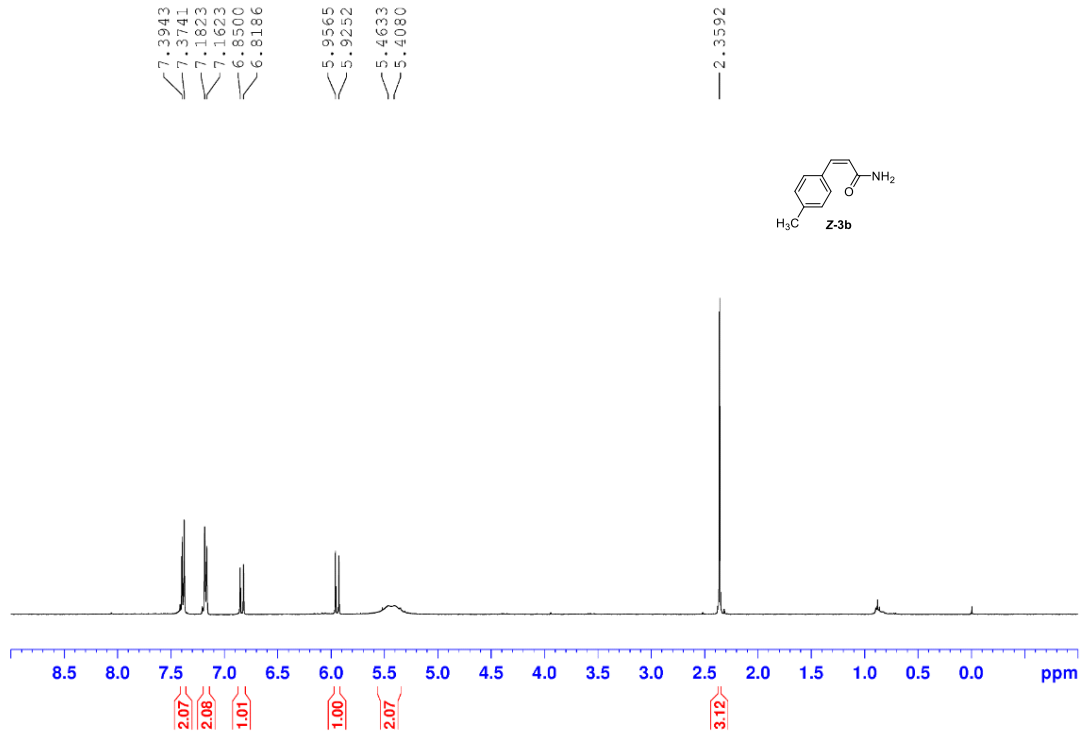

168.8256
137.6161
134.7949
128.9217
128.8686
128.6091
123.8349

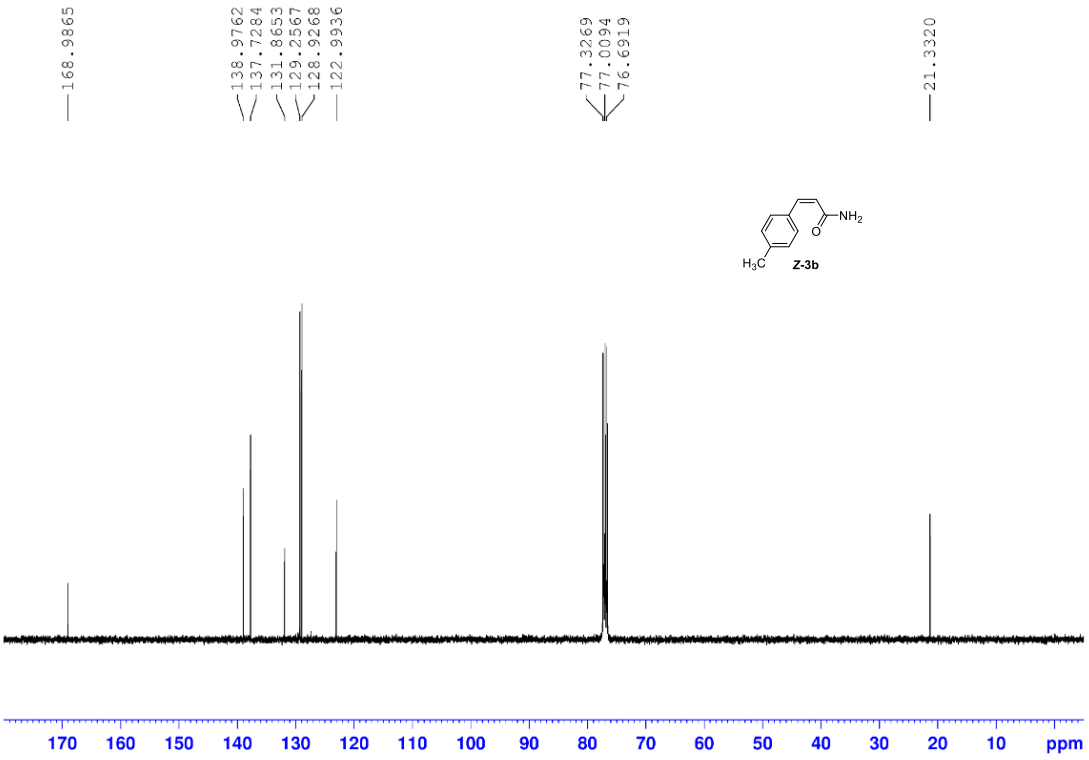

77.3650
77.0478
76.7300

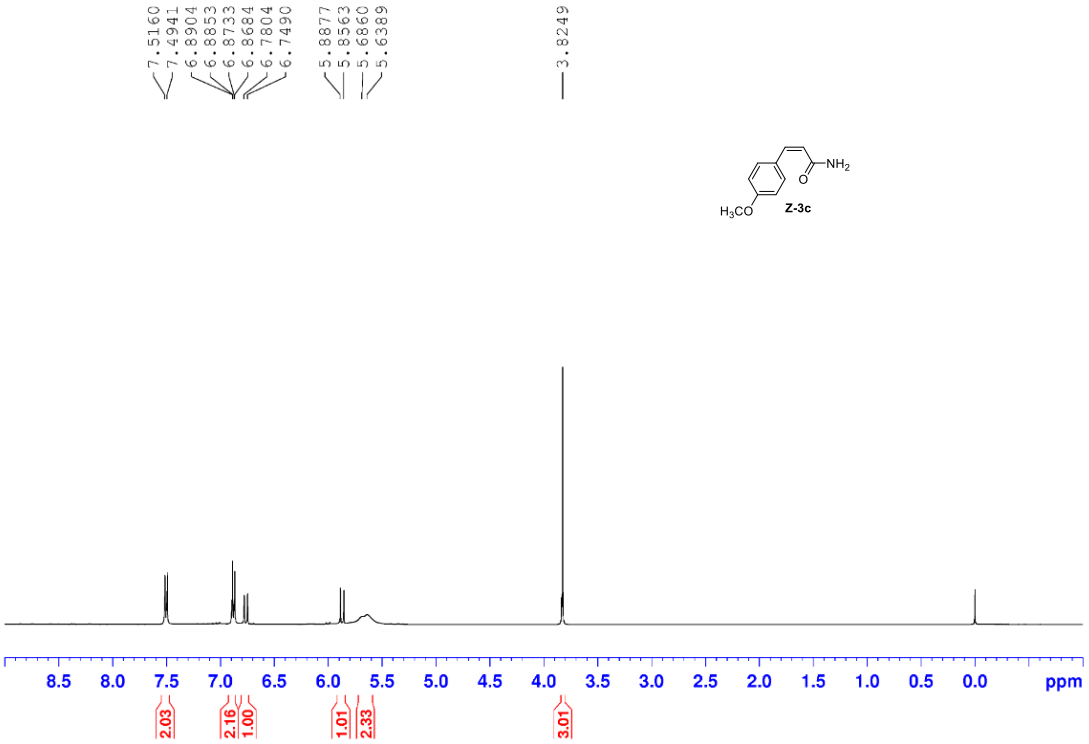

NH2
O

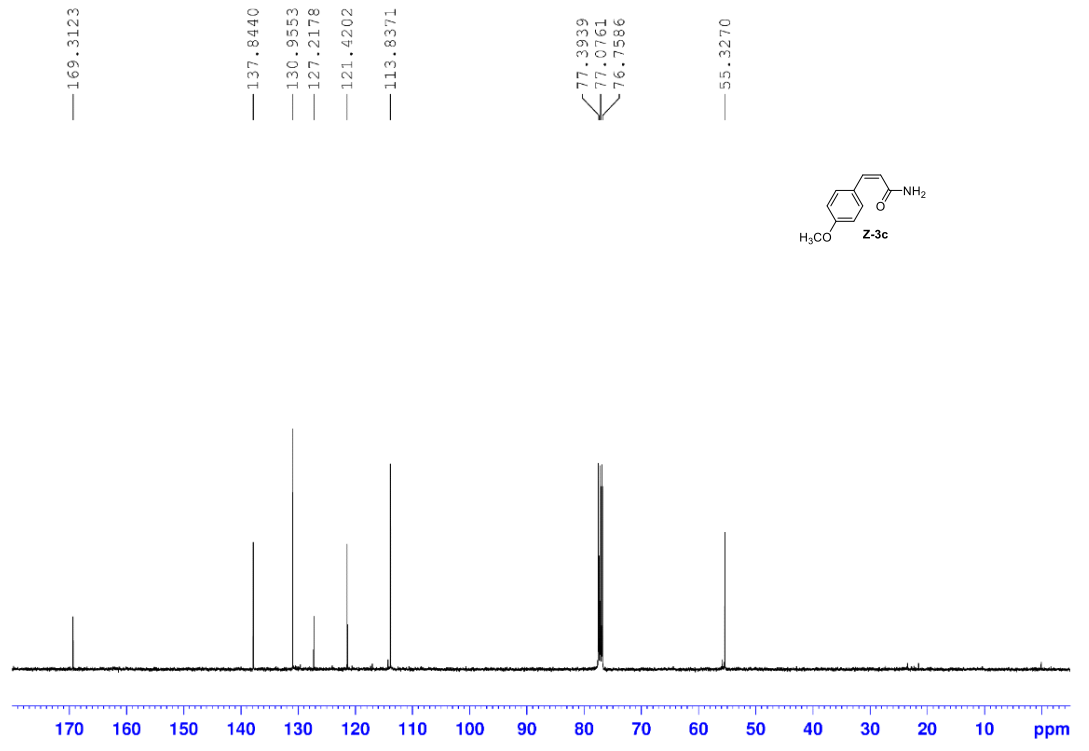
Z-3a

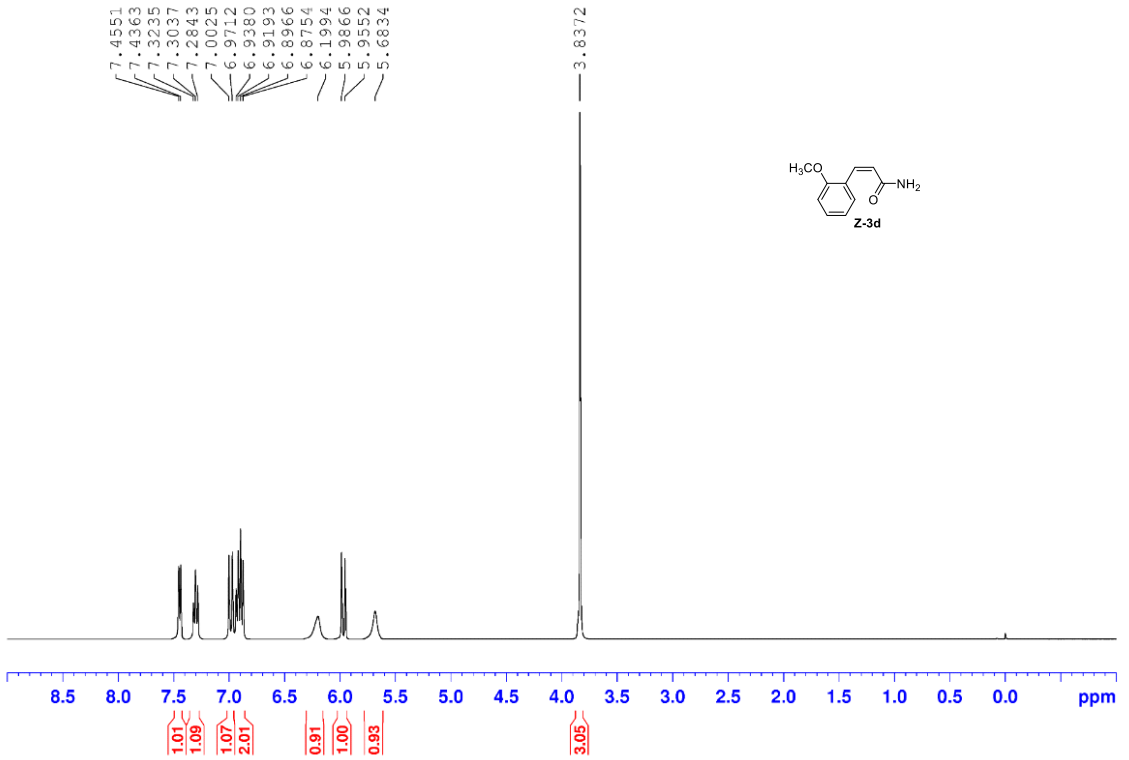

170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

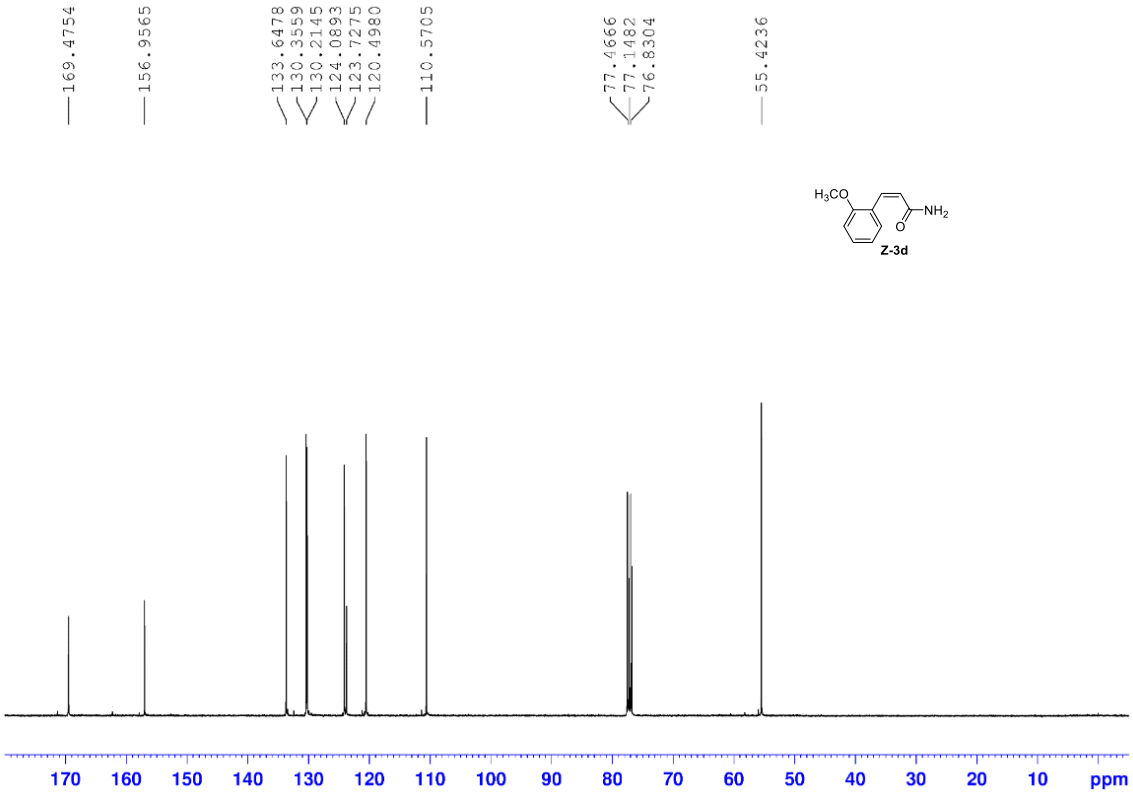

7.3943
7.3741
7.1823
7.1623
6.8500
6.8186
5.9565
5.9252
5.4633
5.4080
2.3592
NH2
O
H3C
Z-3b
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
2.07
2.08
1.01
1.00
2.07
3.12

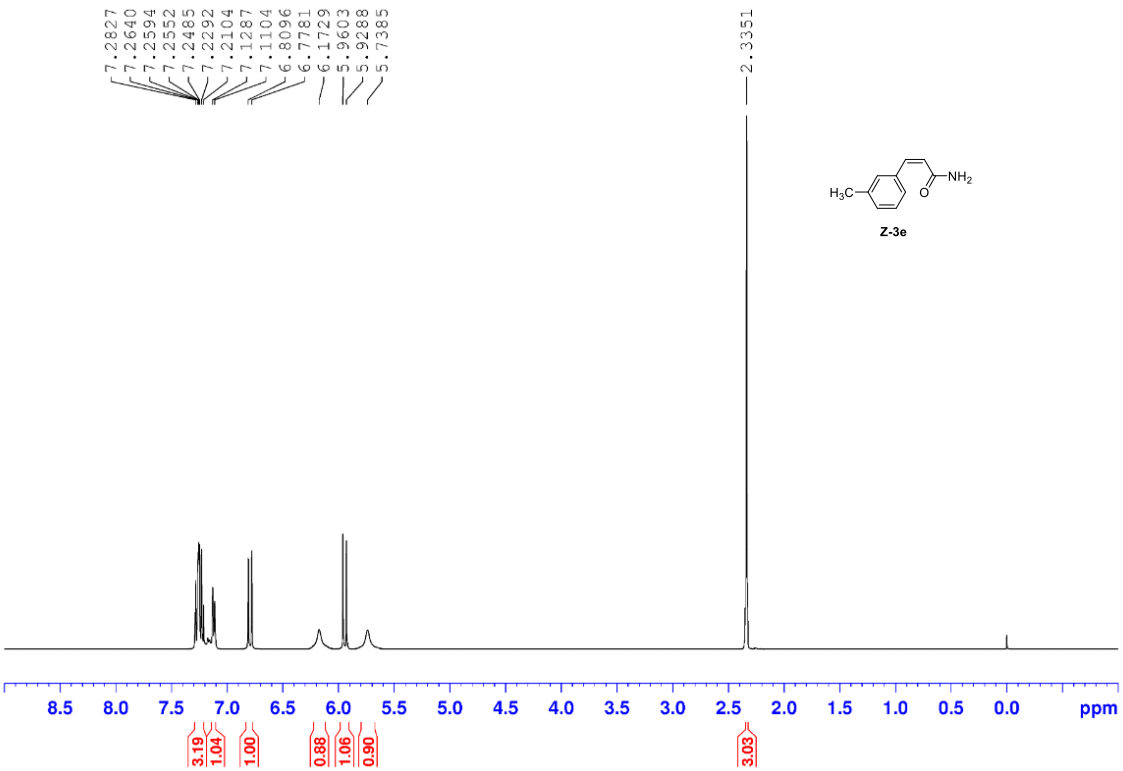

168.9865
138.9762
137.7284
131.8653
129.2567
128.9268
122.9936
77.3269
77.0094
76.6919
21.3320
NH2
O
H3C
Z-3b
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

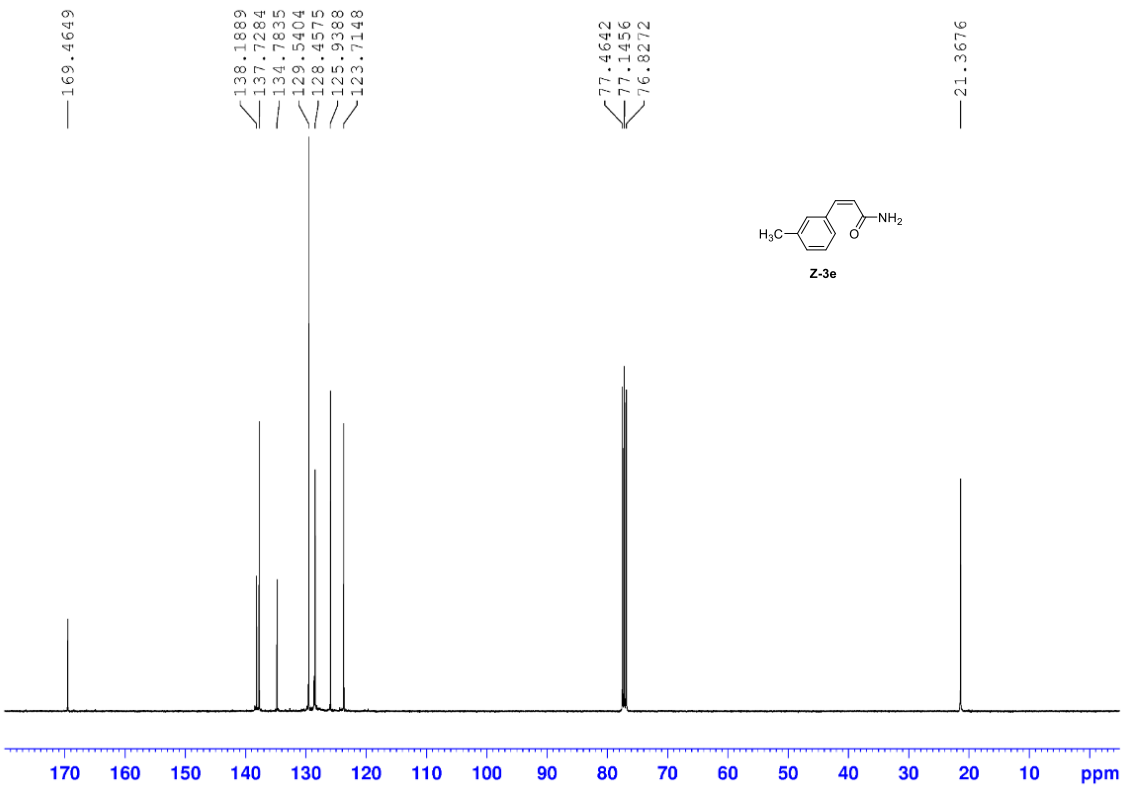

7.5160
7.4941
6.8904
6.8853
6.8733
6.8684
6.7804
6.7490
5.8877
5.8563
5.6860
5.6389
3.8249
NH2
O
H3CO
Z-3c
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
2.03
2.16
1.00
1.01
2.33
3.01

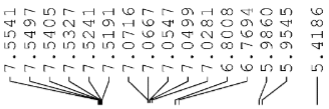

169.3123
137.8440
130.9553
127.2178
121.4202
113.8371
77.3939
77.0761
76.7586
55.3270
NH2
O
H3CO
Z-3c
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

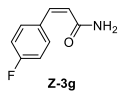

7.4551
7.4363
7.3235
7.3037
7.2843
7.0025
6.9712
6.9380
6.9193
6.8966
6.8754
6.1994
5.9866
5.9552
5.6834
3.8372
H3CO
NH2
O
Z-3d
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.01
1.09
1.07
2.01
0.91
1.00
0.93
3.05


169.4754
156.9565
133.6478
130.3559
130.2145
124.0893
123.7275
120.4980
110.5705
77.4666
77.1482
76.8304
55.4236
H3CO
NH2
O
Z-3d
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

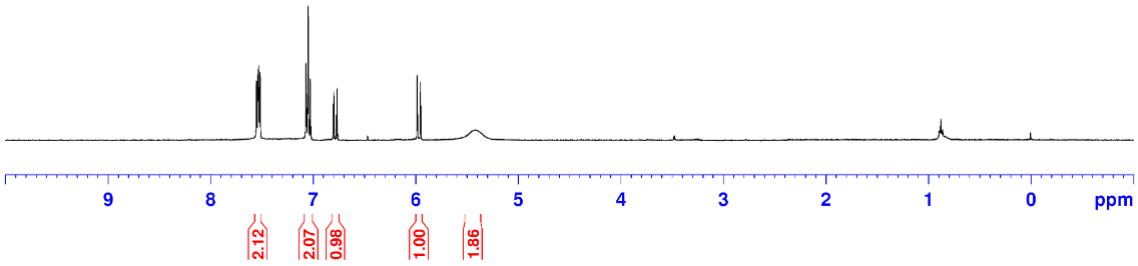

7.2827
7.2640
7.2594
7.2552
7.2485
7.2292
7.2104
7.1287
7.1104
6.8096
6.7781
6.1729
5.9603
5.9288
5.7385
2.3351
H3C
NH2
O
Z-3e
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
3.19
1.04
1.00
0.88
1.06
0.90
3.03


169.4649
138.1889
137.7284
134.7835
129.5404
128.4575
125.9388
123.7148
77.4642
77.1456
76.8272
21.3676
H3C
NH2
O
Z-3e
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

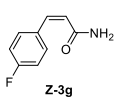

7.5541
7.5497
7.5405
7.5327
7.5241
7.5191
7.0716
7.0667
7.0547
7.0499
7.0281
6.8008
6.7694
5.9860
5.9545
5.4186


NH2
O
F

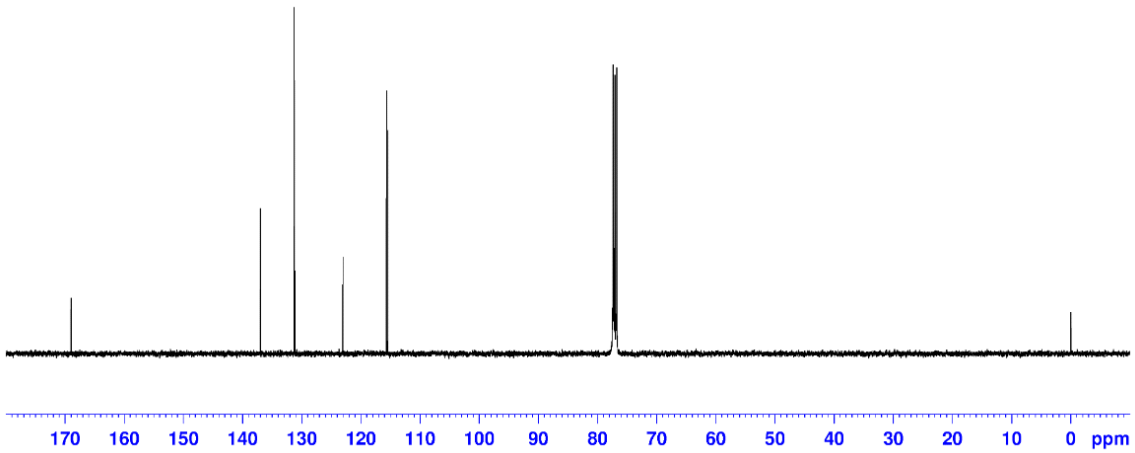
Z-3g

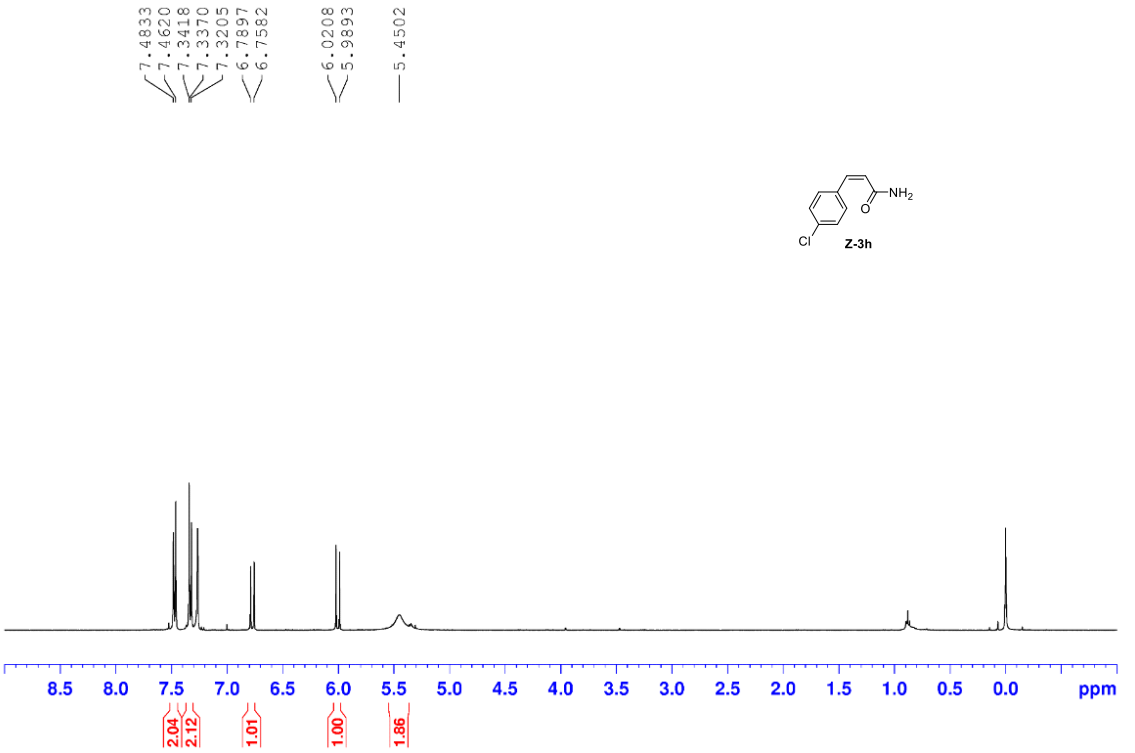

9
8
7
6
5
4
3
2
1
0
ppm
2.12
2.07
0.98
1.00
1.86

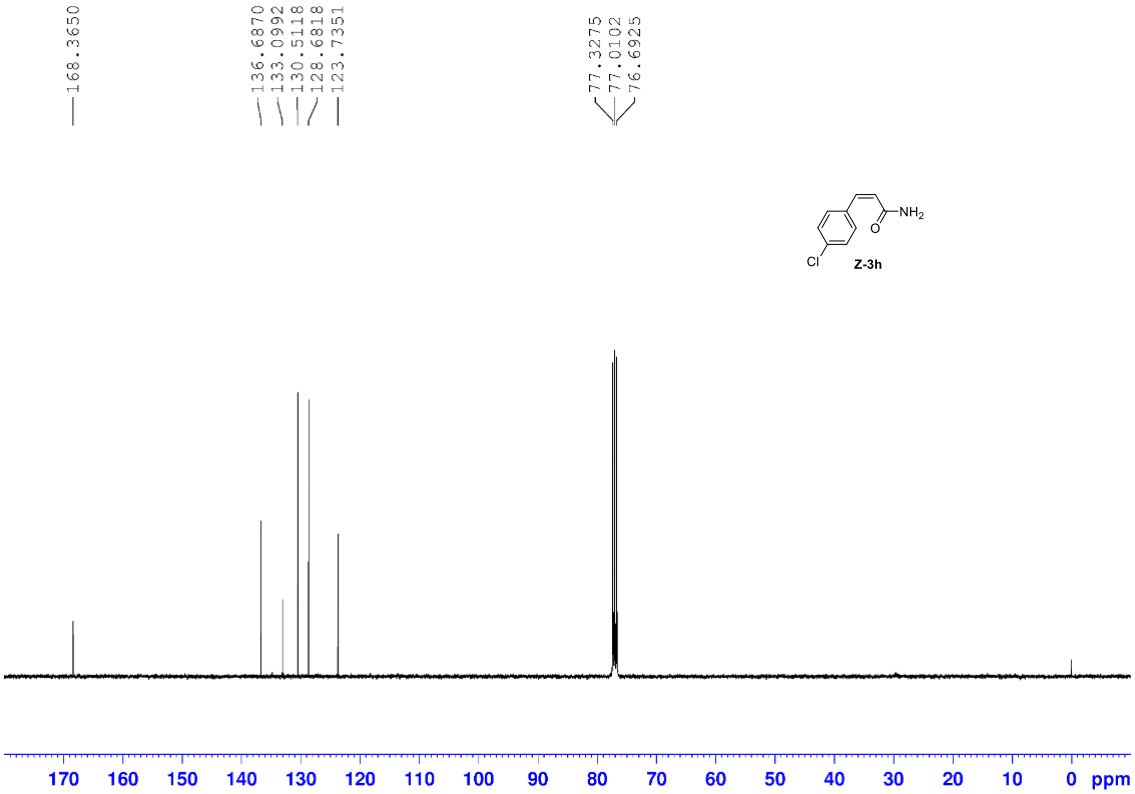

168.9768
136.9545
131.2387
131.1544
122.9887
115.6119
115.3963
77.3270
77.0092
76.6920

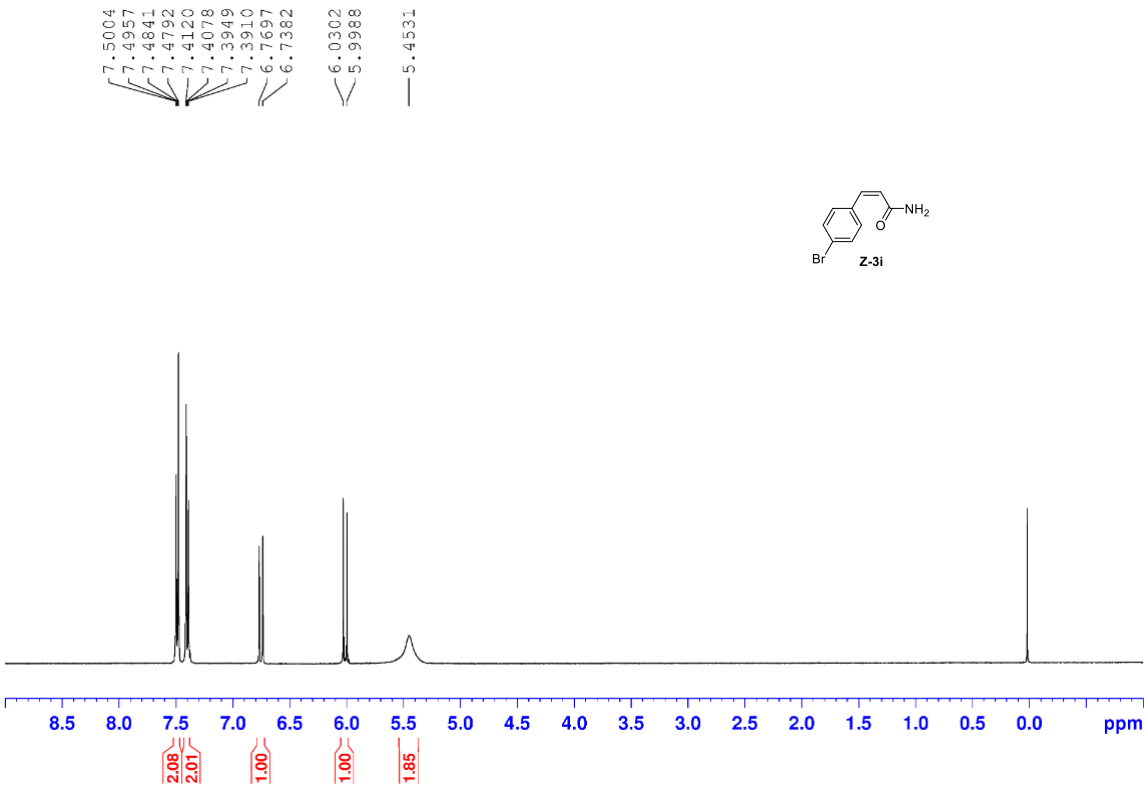

NH2
O
F

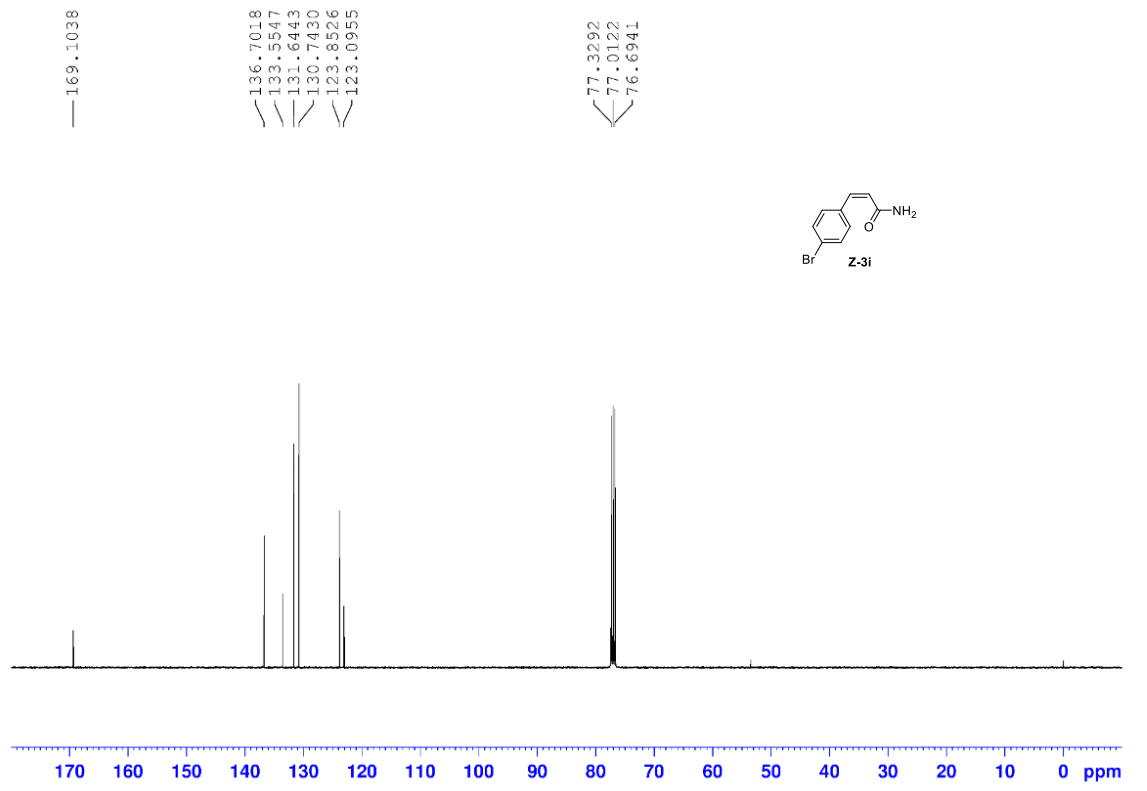
Z-3g


170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


7.4833
7.4620
7.3418
7.3370
7.3205
6.7897
6.7582
6.0208
5.9893
5.4502
NH2
O
Cl
Z-3h
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 ppm
2.04
2.12
1.01
1.00
1.86


168.3650
136.6870
133.0992
130.5118
128.6818
123.7351
77.3275
77.0102
76.6925
NH2
O
Cl
Z-3h
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


7.5004
7.4957
7.4841
7.4792
7.4120
7.4078
7.3949
7.3910
6.7697
6.7382
6.0302
5.9988
5.4531
NH2
O
Br
Z-3i
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 ppm
2.08
2.01
1.00
1.00
1.85


169.1038
136.7018
133.5547
131.6443
130.7430
123.8526
123.0955
77.3292
77.0122
76.6941
NH2
O
Br
Z-3i
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm