Electronic Supplementary Material (ESI) for ChemComm.

Palladium-catalyzed ring opening of norbornene: efficient synthesis of methylenecyclopentane derivatives

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Supporting Information

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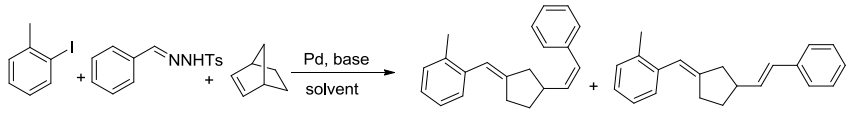
1. General remarks

For product purification by flash column chromatography, silica gel (200~300 mesh) and light petroleum ether (bp. 60~90) are used. ^{1}H NMR spectra were recorded on a Bruker advance Ⅲ 400 MHz in $CDCl_3$ and ^{13}C NMR spectra were recorded on 100 MHz in $CDCl_3$ using TMS as internal standard. Mass spectra were determined on a Hewlett Packard 5988A spectrometer by direct inlet at 70 eV. High-resolution mass spectral analysis (HRMS) data were measured on a Bruker Apex II. Element analysis (EA) data were measured on a Vario EL. Melting points were determined on a microscopic apparatus and were uncorrected. Copies of their ^{1}H NMR and ^{13}C NMR spectra were provided. Dioxane and THF were dried over Na. The starting materials were purchased from Aldrich, Acros, Alfa or TCI and used without further purification.

2. Optimization of the reaction conditions[a]



1a **2a** **3a** **3a'**

Entry	Pd	Base	Solvent	Yield (**3a** +**3a'**, %[b])
1[c]	$Pd(PPh_3)_4$	Cs_2CO_3	MeCN	trace
2[c]	$Pd(PPh_3)_4$	Cs_2CO_3	dioxane	18(1:1.5)
3[c]	$Pd(PPh_3)_4$	Cs_2CO_3	DMSO	0
4[c]	$Pd(PPh_3)_4$	Cs_2CO_3	toluene	60 (1:2.0)
5[c]	$Pd(PPh_3)_4$	Cs_2CO_3	DMF	trace
6[d]	**$Pd(PPh_3)_4$**	**Cs_2CO_3**	**THF**	**87 (1:1.8)**
7[d]	$Pd(PPh_3)_4$	K_2CO_3	THF	0
8[d]	$Pd(PPh_3)_4$	KO^tBu	THF	20(1:1.1)
9[d]	$Pd(PPh_3)_4$	LiO^tBu	THF	0
10[d]	$Pd(PPh_3)_4$	Na_2CO_3	THF	0
11[d]	$Pd(OAc)_2/PPh_3$	Cs_2CO_3	THF	68(1:1.7)
12[d]	$Pd_2(dba)_3$	Cs_2CO_3	THF	trace
13[d]	$Pd_2(dba)_3$ $CHCl_3$	Cs_2CO_3	THF	trace
14[d]	$Pd(TFA)_2/PPh_3$	Cs_2CO_3	THF	64(1:1.7)
15[d]	$PdCl_2(PPh_3)_2/PPh_3$	Cs_2CO_3	THF	65(1:1.8)
16[d]	$PdCl_2(MeCN)_2/PPh_3$	Cs_2CO_3	THF	68(1: 1.7)
17[d]	$Pd(OAc)_2$/xantphos	Cs_2CO_3	THF	17(1: 8.0)
18[d]	$Pd(OAc)_2$/xphos	Cs_2CO_3	THF	44(4.0: 1.0)
19[d]	$Pd(OAc)_2/PCy_3$	Cs_2CO_3	THF	<10
20[d]	$Pd(OAc)_2/[HPtBu_3]BF_4$	Cs_2CO_3	THF	trace
21[d,e]	$Pd(PPh_3)_4$	Cs_2CO_3	THF	69(1: 1.8)
22[d]	none	Cs_2CO_3	THF	0

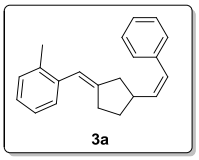
[a] Reaction conditions : **1a** (0.2 mmol), **2a** (0.3 mmol), norbornene (3.0 equiv.), Pd (5 mol%), ligand (10 mol%), base (2.5 equiv.), solvent (2 ml), 10 h. [b] Isolated yields. [c] The reaction was carried out at 90 ℃. [d] The reaction was carried out at 60 ℃. [e] The reaction was carried out with 2.5 mol% of $Pd(PPh_3)_4$.

3. Preparation of starting materials

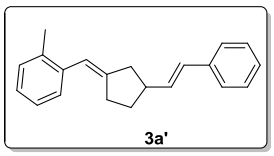
N-tosylhydrazones **2** and **4** were prepared according to a previously reported literature[1]. Aryl iodides **1** are commercially available.

4. General procedure for the preparation of the products 3 or 5

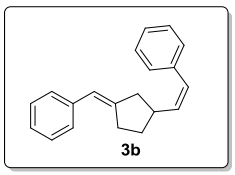
1 (0.2 mmol), **2** or **4** (0.3 mmol), $Pd(PPh_3)_4$ (5 mol%), Cs_2CO_3 (2.5 equiv.), norbornene (3.0 equiv.) were dissolved in 2 mL of degassed dry THF. The mixture was flushed with N_2 and heated at the indicated temperature for the indicated time. After cooling at room temperature, the mixture was diluted with diethyl ether, washed with water, dried over magnesium sulfate and purified by flash chromatography (silica, petroleum ether/AcOEt).



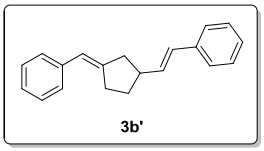
1-methyl-2-((E)-(3-((Z)-styryl)cyclopentylidene)methyl)benzene (3a): oil; ^{1}H NMR ($CDCl_3$, 400MHz) δ: 7.36-7.22 (m, 6H), 7.14-7.07 (m, 3H), 6.45-6.40 (m, 2H), 5.62 (dd, *J* = 10.0 Hz, *J* = 11.2 Hz, 1H), 3.15-3.11 (m, 1H), 2.77-2.71 (m, 1H), 2.61-2.57 (m, 1H) , 2.47-2.38 (m, 2H), 2.28 (s, 3H), 2.04-2.01 (m, 1H), 1.60-1.53 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 145.5, 137.7, 137.5, 136.7, 135.8, 129.8, 128.6, 128.4, 128.2, 127.9, 126.6, 126.1, 125.4, 119.3, 42.7, 38.0, 34.3, 30.3, 20.0. MS(EI): *m/z*(%): 274(100.0), 183(14.8), 170(68.1), 155(28.7), 129(68.8), 115 (25.4), 91(36.5).



1-methyl-2-((E)-(3-((E)-styryl)cyclopentylidene)methyl)benzene (3a'): oil; ^{1}H NMR ($CDCl_3$, 400MHz) δ: 7.36-7.27 (m, 5H), 7.20-7.14 (m, 3H), 7.11-7.07 (m, 1H), 6.45-6.41 (m, 2H), 6.23 (dd, *J* = 6.8 Hz, *J* = 16.0 Hz, 1H), 2.79-2.71 (m, 2H), 2.63-2.57 (m, 1H) , 2.49-2.40 (m, 2H), 2.29 (s, 3H), 2.01-1.99 (m, 1H), 1.64-1.54 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 145.4, 137.6, 137.5, 135.7, 134.0, 129.8, 128.7, 128.5, 127.9, 126.9, 126.1, 126.0, 125.4, 119.4, 42.7, 41.8, 33.5, 30.2, 20.0. Anal. Calcd. for $C_{21}H_{22}$: C, 91.92; H, 8.08. Found: C, 91.83; H, 8.28.

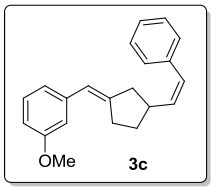


((Z)-2-((E)-3-benzylidenecyclopentyl)vinyl)benzene (3b) : oil; ^{1}H NMR ($CDCl_3$, 400MHz) δ: oil; ^{1}H NMR ($CDCl_3$, 400MHz) δ: 7.36-7.23 (m, 9H), 7.18-7.14 (m, 1H), 6.44 (d, *J* = 11.2 Hz, 1H), 6.36 (s, 1H), 5.61 (dd, *J* = 10.0 Hz, *J* = 11.2 Hz, 1H), 3.14-3.10 (m, 1H), 2.78-2.70 (m, 2H), 2.57-2.53 (m, 1H), 2.43-2.37 (m, 1H), 2.09-2.06 (m, 1H), 1.66-1.59 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 145.7, 138.5, 137.7, 136.5, 128.7, 128.7, 128.6, 128.5, 128.4, 128.2, 128.0, 126.6, 125.8, 121.4, 43.6, 38.0, 34.6, 30.8. MS(EI): *m/z*(%): 260(83.6), 169(40.1), 156(100.0), 141(38.6), 129(57.3), 115 (47.3), 91(61.4).



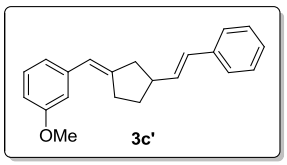
3b'

((E)-2-((E)-3-benzylidenecyclopentyl)vinyl)benzene (3b') : solid; m.p.90-92 ℃; ^{1}H NMR ($CDCl_3$, 400MHz) δ: oil; ^{1}H NMR ($CDCl_3$, 400MHz) δ: 7.37-7.29 (m, 6H), 7.24-7.15 (m, 4H), 6.44 (d, *J* = 15.6 Hz, 1H), 6.38 (s, 1H), 6.23 (dd, *J* = 7.2 Hz, *J* = 16.0 Hz, 1H), 2.79-2.70 (m, 3H), 2.60-2.57 (m, 1H), 2.49-2.43 (m, 1H), 2.10-2.07 (m, 1H), 1.70-1.65 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 145.7, 138.6, 137.6, 133.8, 128.9, 128.5, 128.2, 128.0, 127.0, 126.0, 125.8, 121.4, 42.8, 42.6, 33.8, 30.7. Anal. Calcd. for $C_{20}H_{20}$: C, 92.26; H, 7.74. Found: C, 92.05; H, 7.89.



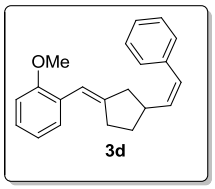
3c

1-methoxy-3-((E)-(3-((Z)-styryl)cyclopentylidene)methyl)benzene (3c): oil; ^{1}H NMR ($CDCl_3$, 400MHz) δ: 7.35-7.27 (m, 4H), 7.25-7.21 (m, 2H), 6.89 (d, *J* = 7.6 Hz, 1H), 6.85 (s, 1H), 6.73 (dd, *J* = 2.4 Hz, *J* = 8.0 Hz, 1H), 6.44 (d, *J* = 11.6 Hz, 1H), 6.33 (s, 1H), 5.60 (dd, *J* = 10.0 Hz, *J* = 11.2 Hz, 1H), 3.80 (s, 3H), 3.15-3.09 (m, 1H), 2.79-2.69 (m, 2H), 2.60-2.53 (m, 1H), 2.43-2.36 (m, 1H), 2.11-2.04 (m, 1H), 1.68-1.61 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 159.5, 146.1, 139.9, 137.7, 136.4, 129.1, 128.7, 128.6, 128.2, 126.6, 121.3, 120.7, 113.5, 111.3, 55.1, 43.6, 38.0, 34.6, 30.9. MS(EI): *m/z*(%): 290(100.0), 199(26.7), 186(71.8), 169(20.3), 159(39.7), 145 (22.7), 129(36.0), 91 (35.2). HRMS-ESI (m/z) $[M + H]^+$ calcd for $C_{21}H_{23}O_1$: 291.1743; Found, 291.1741.



3c'

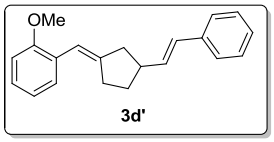
1-methoxy-3-((E)-(3-((E)-styryl)cyclopentylidene)methyl)benzene (3c'): solid; m.p. 62-64 ℃; ^{1}H NMR ($CDCl_3$, 400MHz) δ: oil; ^{1}H NMR ($CDCl_3$, 400MHz) δ: 7.36-7.18 (m, 6H), 6.91 (d, *J* = 7.6 Hz, 1H), 6.87 (s, 1H), 6.74 (dd, *J* = 2.0 Hz, *J* = 8.0 Hz, 1H), 6.46-6.42 (m, 1H), 6.35 (s, 1H), 6.23 (dd, *J* = 7.2 Hz, *J* = 16.0 Hz, 1H), 3.81 (s, 3H), 2.80-2.70 (m, 3H), 2.64-2.57 (m, 1H), 2.48-2.44 (m, 1H), 2.12-2.06 (m, 1H), 1.72-1.64 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 159.5, 146.1, 140.0, 137.6, 133.8, 129.1, 128.9, 128.5, 127.0, 126.0, 121.3, 120.7, 113.5, 111.3, 55.1, 42.8, 42.6, 33.8, 30.8. HRMS-ESI (m/z) $[M + H]^+$ calcd for $C_{21}H_{23}O_1$: 291.1743; Found, 291.1741.



3d

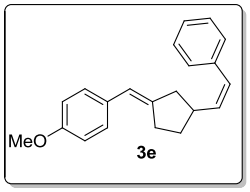
1-methoxy-2-((E)-(3-((Z)-styryl)cyclopentylidene)methyl)benzene (3d) : oil; ^{1}H NMR ($CDCl_3$, 400MHz) δ: oil; ^{1}H NMR ($CDCl_3$, 400MHz) δ: 7.35-7.15 (m, 7H), 6.94-6.90 (m, 1H), 6.85 (d, *J* = 8.4 Hz, 1H), 6.59 (s, 1H), 6.43 (d, *J* = 11.6 Hz, 1H), 5.61 (dd, *J* = 10.0 Hz, *J* = 11.2 Hz, 1H), 3.83 (s, 1H), 3.15-3.11 (m, 1H), 2.79-2.66 (m, 2H), 2.52-2.39 (m, 2H), 2.05-2.02 (m, 1H), 1.62-1.57 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 156.4, 145.6, 137.7,

136.8, 128.6, 128.6, 128.5, 128.2, 127.4, 127.2, 126.6, 120.1, 115.4, 110.3, 55.4, 43.1, 38.0, 34.5, 30.7. MS(EI): *m/z*(%): 290(100.0), 199(23.8), 186(71.8), 169(50.9), 159(39.7), 145 (22.7), 129(34.5), 91 (56.7), 44(42.8). HRMS-ESI (m/z) $[M + H]^+$ calcd for $C_{21}H_{23}O_1$: 291.1743; Found, 291.1741.



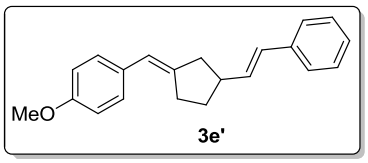
3d'

1-methoxy-2-((E)-(3-((E)-styryl)cyclopentylidene)methyl)benzene (3d') : solid; m.p. 90-92 ℃; ^{1}H NMR ($CDCl_3$, 400MHz) δ: oil; ^{1}H NMR ($CDCl_3$, 400MHz) δ: 7.36-7.27 (m, 5H), 7.21-7.15 (m, 2H), 6.93 (t, *J* = 7.2 Hz, 1H), 6.86 (d, *J* = 8.4 Hz, 1H), 6.61 (s, 1H), 6.44 (d, *J* = 16.0 Hz, 1H), 6.24 (dd, *J* = 6.8 Hz, *J* = 16.0 Hz, 1H), 3.83 (s, 3H), 2.80-2.66 (m, 3H), 2.57-2.43 (m, 2H), 2.06-2.01 (m, 1H), 1.68-1.60 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 156.4, 145.6, 137.7, 134.2, 128.7, 128.6, 128.5, 127.5, 127.1, 126.9, 126.0, 120.1, 115.5, 110.3, 55.4, 42.8, 42.2, 33.7, 30.6. HRMS-ESI (m/z) $[M + H]^+$ calcd for $C_{21}H_{23}O_1$: 291.1743; Found, 291.1741.



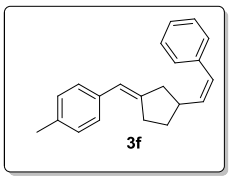
3e

1-methoxy-4-((E)-(3-((Z)-styryl)cyclopentylidene)methyl)benzene (3e) : oil; ^{1}H NMR ($CDCl_3$, 400MHz) δ: 7.35-7.27 (m, 4H), 7.24-7.21 (m, 3H), 6.86 (dd, *J* = 2.0 Hz, *J* = 6.8 Hz, 2H), 6.43 (d, *J* = 11.6 Hz, 1H), 6.30 (s, 1H), 5.60 (dd, *J* = 10.0 Hz, *J* = 11.6 Hz, 1H), 3.80 (s, 3H), 3.14-3.09 (m, 1H), 2.75-2.67(m, 2H), 2.54-2.49(m, 1H), 2.41-2.35(m, 1H), 2.08-2.04(m, 1H), 1.68-1.60(m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 157.6, 143.3, 137.7, 136.6, 131.4, 129.0, 128.6, 128.2, 126.6, 120.7, 113.6, 55.2, 43.5, 38.0, 34.6, 30.6. MS(EI): m/z(%): 290(100.0), 199(12.3), 186(38.0), 159(27.8), 129(24.4), 121 (42.0). HRMS-ESI (m/z) $[M + H]^+$ calcd for $C_{21}H_{23}O_1$: 291.1743; Found, 291.1741.



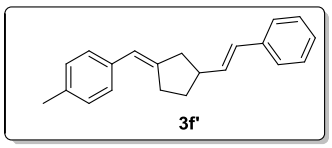
3e'

1-methoxy-4-((E)-(3-((E)-styryl)cyclopentylidene)methyl)benzene (3e') : solid; m.p.110-112 ℃; ^{1}H NMR ($CDCl_3$, 400MHz) δ: 7.35 (d, *J* = 7.2 Hz, 2H), 7.31-7.23 (m, 4H), 7.19 (t, *J* = 7.2 Hz, 1H), 6.87 (d, *J* = 8.4 Hz, 2H), 6.44 (d, *J* = 16.0 Hz, 1H), 6.32 (s, 1H), 6.23 (dd, *J* = 7.2 Hz, *J* = 16.0 Hz, 1H), 3.80 (s, 3H), 2.74-2.69(m, 3H), 2.59-2.51(m, 1H), 2.45-2.39(m, 1H), 2.08-2.04(m, 1H), 1.71-1.61(m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 157.6, 143.3, 137.6, 133.9, 131.4, 129.1, 128.8, 128.5, 126.9, 126.0, 120.7, 113.7, 55.2, 42.7, 42.7, 33.9, 30.6. HRMS-ESI (m/z) $[M + H]^+$ calcd for $C_{21}H_{23}O_1$: 291.1743; Found, 291.1741.

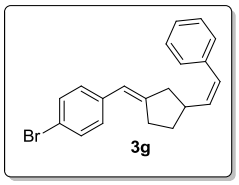


3f

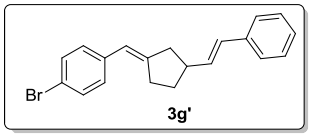
1-methyl-4-((E)-(3-((Z)-styryl)cyclopentylidene)methyl)benzene (3f) : solid; m.p.76-78 ℃; ^{1}H NMR ($CDCl_3$, 400MHz) δ: 7.35-7.27 (m, 4H), 7.24-7.18 (m, 3H), 7.12 (d, *J* = 8.0 Hz, 2H), 6.43 (d, *J* = 12.0 Hz, 1H), 6.32 (s, 1H), 5.60 (t, *J* = 10.4 Hz, 1H), 3.17-3.07(m, 1H), 2.76-2.68(m, 2H), 2.57-2.49(m, 1H), 2.41-2.35(m, 1H), 2.32(s, 3H), 2.10-2.04(m, 1H), 1.68-1.58(m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 144.6, 137.7, 136.6, 135.7, 135.4, 128.9, 128.6, 128.6, 128.2, 127.9, 126.6, 121.2, 43.5, 38.0, 34.6, 30.7, 21.1. MS(EI): *m/z*(%): 274(100.0), 170(70.8), 155(33.9), 144(16.0), 129(74.2), 105 (36.1), 91 (31.0).



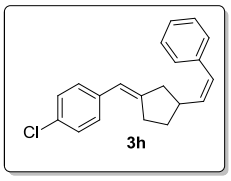
1-methyl-4-((E)-(3-((E)-styryl)cyclopentylidene)methyl)benzene (3f') : solid; m.p. 80-82 ℃; ^{1}H NMR ($CDCl_3$, 400MHz) δ: 7.35 (d, *J* = 7.6 Hz, 2H), 7.31-7.17 (m, 5H), 7.13 (d, *J* = 7.6 Hz, 2H), 6.44 (d, *J* = 16.0 Hz, 1H), 6.34 (s, 1H), 6.23 (dd, *J* = 7.2 Hz, *J* = 16.0 Hz, 1H), 2.77-2.69 (m, 3H), 2.61-2.53 (m, 1H), 2.47-2.40 (m, 1H), 2.33(s, 3H), 2.11-2.04 (m, 1H), 1.71-1.61 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 144.6, 137.6, 135.8, 135.4, 133.9, 128.9, 128.8, 128.6, 128.5, 128.2, 127.9, 126.9, 126.0, 121.2, 42.7, 42.6, 33.9, 30.7, 21.1. Anal. Calcd. for $C_{21}H_{22}$: C, 91.92; H, 8.08. Found: C, 91.80; H, 8.26.



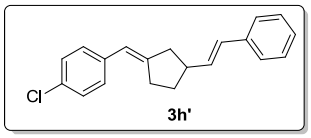
1-bromo-4-((E)-(3-((Z)-styryl)cyclopentylidene)methyl)benzene (3g) : solid; m.p. 85-87 ℃; ^{1}H NMR ($CDCl_3$, 400MHz) δ: 7.42 (d, *J* = 8.4 Hz, 2H), 7.35-7.21 (m, 5H), 7.14 (d, *J* = 8.4 Hz, 2H), 6.44 (d, *J* = 11.6 Hz, 1H), 6.28 (s, 1H), 5.59 (t, *J* = 10.8 Hz, 1H), 3.18-3.07 (m, 1H), 2.73-2.68 (m, 2H), 2.54-2.45 (m, 1H), 2.41-2.34 (m, 1H), 2.08-2.07 (m, 1H), 1.69-1.59 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 146.7, 137.6, 137.4, 136.2, 131.3, 129.5, 128.9, 128.6, 128.2, 126.7, 120.3, 119.4, 43.6, 38.0, 34.5, 30.8. MS(EI): *m/z*(%): 171(24.4), 169(66.7), 155(63.8), 141(32.6), 129(100.0), 115 (52.9), 91 (54.3).



1-bromo-4-((E)-(3-((E)-styryl)cyclopentylidene)methyl)benzene (3g') : solid; m.p. 128-130 ℃; ^{1}H NMR ($CDCl_3$, 400MHz) δ: 7.42 (d, *J* = 8.4 Hz, 2H), 7.36-7.15 (m, 7H), 6.44 (d, *J* = 16.0 Hz, 1H), 6.30 (s, 1H), 6.21 (dd, *J* = 7.2 Hz, *J* = 15.6 Hz, 1H), 2.78-2.67 (m, 3H), 2.57-2.39 (m, 2H), 2.11-2.07 (m, 1H), 1.72-1.62 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 146.7, 137.5, 137.4, 133.6, 131.3, 129.5, 129.0, 128.5, 127.0, 126.0, 120.4, 119.4, 42.8, 42.6, 33.8, 30.8. Anal. Calcd. for $C_{20}H_{19}Br$: C, 70.80; H, 5.64. Found: C, 71.01; H, 5.72.

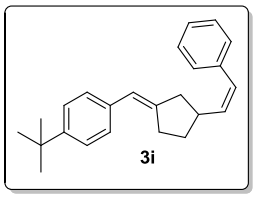


1-chloro-4-((E)-(3-((Z)-styryl)cyclopentylidene)methyl)benzene (3h) : solid; m.p.80-82 ℃; ^{1}H NMR ($CDCl_3$, 400MHz) δ: 7.35-7.19 (m, 9H), 6.44 (d, *J* = 11.6 Hz, 1H), 6.30 (s, 1H), 5.59 (dd, *J* = 10.0 Hz, *J* = 11.6 Hz, 1H), 3.15-3.09 (m, 1H), 2.74-2.67 (m, 2H), 2.55-2.35 (m, 2H), 2.09-2.04 (m, 1H), 1.69-1.61 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 146.5, 137.6, 137.0, 136.2, 131.3, 129.1, 128.9, 128.6, 128.3, 128.2, 126.7, 120.3, 43.6, 38.0, 34.5, 30.8. MS(EI): *m/z*(%): 294(87.2), 203(20.3), 190(100.0), 169(31.7), 159(39.7), 155 (54.8), 129(85.8), 91 (48.8).

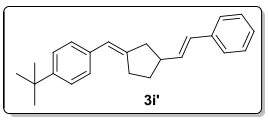


3h'

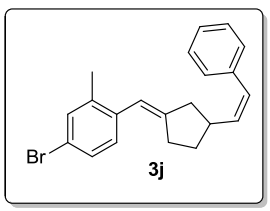
1-chloro-4-((E)-(3-((E)-styryl)cyclopentylidene)methyl)benzene (3h') : solid; m.p.132-134 ℃; ^{1}H NMR ($CDCl_3$, 400MHz) δ: 7.35 (d, *J* = 7.6 Hz, 2H), 7.31-7.18 (m, 7H), 6.44 (d, *J* = 15.6 Hz, 1H), 6.32 (s, 1H), 6.24 (dd, *J* = 7.2 Hz, *J* = 15.6 Hz, 1H), 2.79-2.68 (m, 3H), 2.59-2.40 (m, 2H), 2.12-2.07 (m, 1H), 1.73-1.63 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 146.5, 137.6, 137.0, 133.6, 131.3, 129.2, 129.0, 128.5, 128.3, 127.0, 126.0, 120.3, 42.8, 42.6, 33.8, 30.7. Anal. Calcd. for $C_{20}H_{19}Cl$: C, 81.48; H, 6.50. Found: C, 81.29; H, 6.63.


3i

1-(tert-butyl)-4-((E)-(3-((Z)-styryl)cyclopentylidene)methyl)benzene (3i) : oil; ^{1}H NMR ($CDCl_3$, 400MHz) δ: 7.35-7.27 (m, 6H), 7.25-7.22 (m, 3H), 6.43 (d, *J* = 11.6 Hz, 1H), 6.33 (s, 1H), 5.60 (dd, *J* = 10.0 Hz, *J* = 11.6 Hz, 1H), 3.17-3.06 (m, 1H), 2.78-2.68 (m, 2H), 2.59-2.50 (m, 1H), 2.42-2.35 (m, 1H), 2.10-2.04 (m, 1H), 1.68-1.56 (m, 1H), 1.31 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 148.7, 144.8, 137.7, 136.6, 135.7, 128.6, 128.2, 127.7, 126.6, 125.1, 121.1, 43.6, 38.0, 34.6, 34.4, 31.3, 30.7. MS(EI): *m/z*(%): 316(100.0), 301(28.9), 259(13.1), 212(35.3), 211(17.0), 197 (34.5), 169(30.4), 155 (34.5).

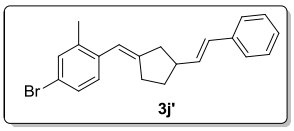

3i'

1-(tert-butyl)-4-((E)-(3-((E)-styryl)cyclopentylidene)methyl)benzene (3i') : solid; m.p. 88-90 ℃; ^{1}H NMR ($CDCl_3$, 400MHz) δ: 7.36-7.23 (m, 8H), 7.21-7.17 (m, 1H), 6.44 (d, *J* = 16.0 Hz, 1H), 6.35 (s, 1H), 6.23 (dd, *J* = 7.2 Hz, *J* = 16.0 Hz, 1H), 2.79-2.69 (m, 3H), 2.63-2.54 (m, 1H), 2.47-2.40 (m, 1H), 2.08-2.06 (m, 1H), 1.71-1.60 (m, 1H), 1.32 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 148.6, 144.8, 137.6, 135.8, 134.0, 128.8, 128.5, 127.7, 126.9, 126.0, 125.1, 121.1, 42.8, 42.7, 34.4, 33.9, 31.3, 30.7. Anal. Calcd. for $C_{24}H_{28}$: C, 91.08; H, 8.92. Found: C, 90.93; H, 8.84.

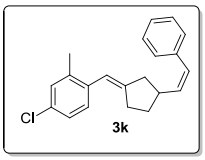


3j

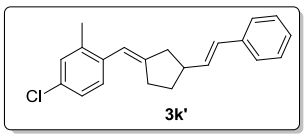
4-bromo-2-methyl-1-((E)-(3-((Z)-styryl)cyclopentylidene)methyl)benzene (3j) : oil; ^{1}H NMR ($CDCl_3$, 400MHz) δ: 7.36-7.22 (m, 7H), 7.13 (d, *J* = 8.4 Hz, 1H), 6.44 (d, *J* = 11.6 Hz, 1H), 6.30 (s, 1H), 5.61 (dd, *J* = 10.0Hz, *J* = 11.6 Hz, 1H), 3.16-3.11 (m, 1H), 2.75-2.69 (m, 1H), 2.54-2.51 (m, 1H), 2.42-2.33 (m, 2H), 2.24 (s, 3H), 2.04-2.01 (m, 1H), 1.60-1.53 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 146.5, 138.0, 137.7, 136.5, 136.4, 132.6, 129.5, 128.7, 128.6, 128.4, 128.2, 126.6, 119.5, 118.4, 42.8, 38.0, 34.2, 30.3, 19.8. MS(EI): *m/z*(%): 185(25.7), 183(28.6), 169(78.1), 154(24.4), 141 (56.5), 128(100.0), 115(47.8), 91 (58.8).



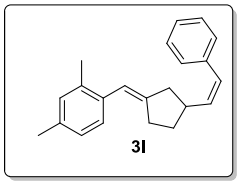
4-bromo-2-methyl-1-((E)-(3-((E)-styryl)cyclopentylidene)methyl)benzene (3j') : oil; ^{1}H NMR ($CDCl_3$, 400MHz) δ: 7.36-7.18 (m, 7H), 7.15 (d, *J* = 8.0 Hz, 1H), 6.44 (d, *J* = 15.6 Hz, 1H), 6.33 (s, 1H), 6.23 (dd, *J* = 7.2 Hz, *J* = 15.6 Hz, 1H), 2.80-2.70 (m, 2H), 2.58-2.52 (m, 1H), 2.45-2.36 (m, 2H), 2.25 (s, 3H), 2.06-2.00 (m, 1H), 1.66-1.56 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 146.4, 138.0, 137.6, 136.4, 133.8, 132.6, 129.5, 128.9, 128.5, 128.4, 127.0, 126.0, 119.5, 118.4, 42.7, 41.9, 33.4, 30.2, 19.8. Anal. Calcd. for $C_{21}H_{22}Br$: C, 71.39; H, 5.99. Found: C, 71.51; H, 6.18.



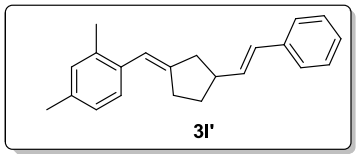
4-chloro-2-methyl-1-((E)-(3-((Z)-styryl)cyclopentylidene)methyl)benzene (3k) : oil; ^{1}H NMR ($CDCl_3$, 400MHz) δ: 7.36-7.17 (m, 6H), 7.2 (t, *J* = 4.0 Hz, 2H), 6.44 (d, *J* = 11.6 Hz, 1H), 6.32 (s, 1H), 5.60 (dd, *J* = 10.0 Hz, *J* = 11.6 Hz, 1H), 3.19-3.08 (m, 1H), 2.76-2.70 (m, 1H), 2.59-2.52 (m, 1H), 2.42-2.34 (m, 2H), 2.24 (s, 3H), 2.05-1.99 (m, 1H), 1.63-1.52 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 146.3, 137.7, 137.7, 136.5, 136.0, 131.3, 130.0, 129.1, 128.6, 128.6, 128.2, 126.6, 125.5, 118.3, 42.7, 38.0, 34.2, 30.3, 19.9. MS(EI): *m/z*(%): 310(33.8), 308(100.0), 217(15.9), 204(95.6), 169(63.2), 143 (60.3), 127(27.5), 91 (49.3).



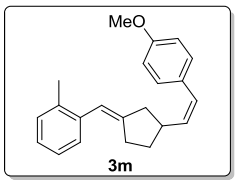
4-chloro-2-methyl-1-((E)-(3-((E)-styryl)cyclopentylidene)methyl)benzene (3k') : solid; m.p. 68-70 ℃; ^{1}H NMR ($CDCl_3$, 400MHz) δ: 7.37-7.35 (m, 2H), 7.31-7.28 (m, 2H), 7.24-7.18 (m, 2H), 7.14-7.10 (m, 2H), 6.44 (d, *J* = 16.0 Hz, 1H), 6.35 (s, 1H), 6.23 (dd, *J* = 7.2 Hz, *J* = 16.0 Hz, 1H), 2.80-2.71 (m, 2H), 2.59-2.52 (m, 1H), 2.45-2.37 (m, 2H), 2.25 (s, 3H), 2.05-2.00 (m, 1H), 1.66-1.58 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 146.3, 137.7, 137.6, 136.0, 133.9, 131.3, 129.7, 129.2, 128.9, 128.5, 127.0, 126.0, 125.5, 118.4, 42.7, 41.8, 33.5, 30.2, 19.9. Anal. Calcd. for $C_{21}H_{21}Cl$: C, 81.67; H, 6.85. Found: C, 81.70; H, 6.74.



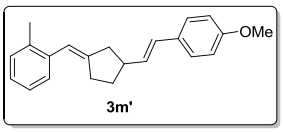
2,4-dimethyl-1-((E)-(3-((Z)-styryl)cyclopentylidene)methyl)benzene (3l) : oil; ^{1}H NMR ($CDCl_3$, 400MHz) δ: 7.36-7.17 (m, 6H), 6.96 (d, *J* = 8.0 Hz, 2H), 6.43 (d, *J* = 11.6 Hz, 1H), 6.37 (s, 1H), 5.61 (dd, *J* = 10.0 Hz, *J* = 11.6 Hz, 1H), 3.16-3.10 (m, 1H), 2.76-2.70 (m, 1H), 2.62-2.56 (m, 1H), 2.46-2.37 (m, 2H), 2.29 (s, 3H), 2.25 (s, 3H), 2.04-2.00 (m, 1H), 1.62-1.53 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 144.8, 137.7, 136.8, 135.6, 135.6, 134.6, 130.7, 128.6, 128.4, 128.2, 127.8, 126.7, 126.1, 119.1, 42.7, 38.0, 34.3, 30.3, 21.0, 20.0. MS(EI): *m/z*(%): 288(100.0), 184(51.0), 169(35.7), 158(24.4), 128(43.1), 91 (26.6), 44 (23.0).



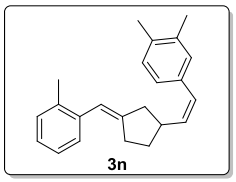
2,4-dimethyl-1-((E)-(3-((E)-styryl)cyclopentylidene)methyl)benzene (3l') : oil; ^{1}H NMR ($CDCl_3$, 400MHz) δ: 7.37-7.35 (m, 2H), 7.31-7.27 (m, 2H), 7.23-7.18 (m, 2H), 6.97 (d, *J* = 7.2 Hz, 2H), 6.46 (s, 1H), 6.41 (d, *J* = 8.8 Hz, 1H), 6.24 (dd, *J* = 8.4 Hz, *J* = 16.0 Hz, 1H), 2.77-2.71 (m, 2H), 2.64-2.57 (m, 1H), 2.49-2.40 (m, 2H), 2.30 (s, 3H), 2.26 (s, 3H), 2.03-2.00 (m, 1H), 1.63-1.57 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 144.7, 137.7, 135.6, 135.6, 134.6, 134.2, 130.7, 128.7, 128.5, 127.8, 126.9, 126.1, 126.0, 119.2, 42.7, 41.9, 33.5, 30.2, 21.0, 20.0. Anal. Calcd. for $C_{22}H_{24}$: C, 91.61; H, 8.39. Found: C, 91.76; H, 8.52.



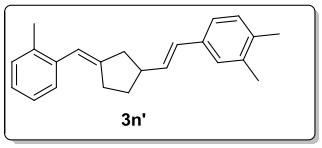
1-((E)-(3-((Z)-4-methoxystyryl)cyclopentylidene)methyl)-2-methylbenzene (3m) : oil; ^{1}H NMR ($CDCl_3$, 400MHz) δ: 7.29-7.22 (m, 3H), 7.15-7.09 (m, 3H), 6.89-6.87 (m, 2H), 6.39 (d, *J* = 8.8 Hz, 1H), 6.35 (s, 1H), 5.53 (dd, *J* = 8.8 Hz, *J* = 11.2 Hz, 1H), 3.81 (s, 3H), 3.16-3.11 (m, 1H), 2.77-2.72 (m, 1H), 2.63-2.57 (m, 1H), 2.45-2.34 (m, 2H), 2.28 (s, 3H), 2.04-2.01 (m, 1H), 1.61-1.51 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.3, 145.6, 137.5, 135.8, 135.3, 130.3, 129.8, 129.8, 128.0, 128.0, 126.1, 125.4, 119.3, 113.6, 55.3, 42.7, 38.0, 34.3, 30.3, 20.0. MS(EI): *m/z*(%): 304(100.0), 199(23.1), 170(48.5), 155(19.9), 134(35.2), 121 (50.8), 91(15.7), 44 (13.3). HRMS-ESI (m/z) $[M + H]^+$ calcd for $C_{22}H_{25}O_1$: 305.1900; Found, 305.1897.



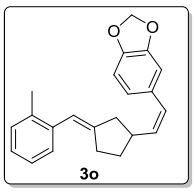
1-((E)-(3-((E)-4-methoxystyryl)cyclopentylidene)methyl)-2-methylbenzene (3m') : oil; ^{1}H NMR ($CDCl_3$, 400MHz) δ: 7.31-7.28 (m, 3H), 7.23-7.07 (m, 3H), 6.84 (d, *J* = 8.8 Hz, 2H), 6.41 (d, *J* = 5.6 Hz, 1H), 6.37 (s, 1H), 6.09 (dd, *J* = 6.8 Hz, *J* = 15.6 Hz, 1H), 3.79 (s, 3H), 2.77-2.71 (m, 2H), 2.63-2.56 (m, 1H), 2.49-2.38 (m, 2H), 2.29 (s, 3H), 2.04-1.99 (m, 1H), 1.64-1.54 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.7, 145.6, 137.6, 135.8, 132.0, 130.5, 129.8, 128.1, 128.0, 127.1, 126.1, 125.4, 119.3, 113.9, 55.3, 42.7, 42.0, 33.6, 30.2, 20.0. HRMS-ESI (m/z) $[M + H]^+$ calcd for $C_{22}H_{25}O_1$: 305.1900; Found, 305.1897.



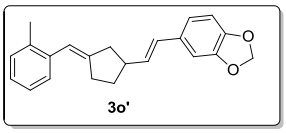
1,2-dimethyl-4-((Z)-2-((E)-3-(2-methylbenzylidene)cyclopentyl)vinyl)benzene (3n) : oil; ^{1}H NMR ($CDCl_3$, 400MHz) δ: 7.28 (d, *J* = 7.2 Hz, 1H), 7.14-7.04 (m, 6H), 6.39 (s, 1H), 6.36 (s, 1H), 5.56 (t, *J* = 11.2 Hz, 1H), 3.20-3.10 (m, 1H), 2.77-2.71 (m, 1H), 2.63-2.56 (m, 1H), 2.46-2.36 (m, 2H), 2.28 (s, 3H), 2.27 (s, 3H), 2.26 (s, 3H), 2.03-2.00 (m, 1H), 1.61-1.51 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 145.7, 137.5, 136.3, 136.0, 135.8, 135.3, 135.0, 130.0, 129.8, 129.5, 128.4, 128.0, 126.1, 126.0, 125.4, 119.3, 42.8, 38.1, 34.3, 30.3, 20.0, 19.9, 19.5. MS(EI): *m/z*(%): 302(100.0), 287(19.8), 236(25.1), 197(22.5), 183(19.9), 170 (72.0), 155(30.0), 143 (25.9).



1,2-dimethyl-4-((E)-2-((E)-3-(2-methylbenzylidene)cyclopentyl)vinyl)benzene (3n') : oil; ^{1}H NMR ($CDCl_3$, 400MHz) δ: 7.31-7.29(m, 1H), 7.17-7.04 (m, 6H), 6.41 (d, *J* = 5.6 Hz, 1H), 6.37 (s, 1H), 6.18 (dd, *J* = 7.2 Hz, *J* = 16.0 Hz, 1H), 2.78-2.73 (m, 2H), 2.63-2.57 (m, 1H), 2.49-2.39 (m, 2H), 2.29 (s, 3H), 2.25 (s, 3H), 2.24 (s, 3H), 2.04-2.00 (m, 1H), 1.64-1.54 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 145.6, 137.6, 136.5, 135.8, 135.3, 133.0, 129.8, 129.8, 128.6, 128.0, 127.2, 126.1, 125.4, 123.5, 119.3, 42.7, 41.9, 33.6, 30.2, 20.0, 19.8, 19.5. Anal. Calcd. for $C_{23}H_{26}$: C, 91.34; H, 8.66. Found: C, 91.30; H, 8.72.

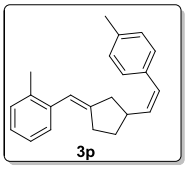


5-((Z)-2-((E)-3-(2-methylbenzylidene)cyclopentyl)vinyl)benzo[d][1,3]dioxole (3o) : oil; ^{1}H NMR ($CDCl_3$, 400MHz) δ: 7.29-7.25(m, 1H), 7.15-7.07(m, 3H), 6.81-6.74(m, 3H), 6.40 (s, 1H), 6.33 (d, *J* = 11.6 Hz, 1H), 5.95 (s, 2H), 5.53 (dd, *J* = 10.0 Hz, *J* = 11.2 Hz, 1H), 3.15-3.09 (m, 1H), 2.77-2.71 (m, 1H), 2.63-2.56 (m, 1H), 2.45-2.33 (m, 2H), 2.28 (s, 3H), 2.02-2.00 (m, 1H), 1.58-1.53 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 147.4, 146.2, 145.4, 137.5, 135.8, 131.8, 129.8, 128.1, 128.0, 126.1, 125.4, 122.2, 119.4, 108.9, 108.1, 100.9, 42.7, 38.0, 34.3, 30.3, 20.0. MS(EI): *m/z*(%): 318(100.0), 213(15.9), 182(20.9), 170(42.0), 148(44.5), 135 (24.3), 129(28.9), 115 (17.5). HRMS-ESI (m/z) $[M + H]^+$ calcd for $C_{22}H_{23}O_2$: 319.1693; Found, 319.1689.

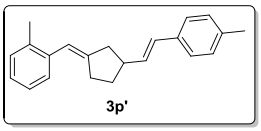


5-((E)-2-((E)-3-(2-methylbenzylidene)cyclopentyl)vinyl)benzo[d][1,3]dioxole (3o') : oil; ^{1}H NMR ($CDCl_3$, 400MHz) δ: 7.30-7.28(m, 1H), 7.17-7.08(m, 3H), 6.91 (d, *J* = 1.2 Hz, 1H), 6.78-6.72(m, 2H), 6.42 (s, 1H), 6.35 (d, *J* = 16.0 Hz, 1H), 6.06 (dd, *J* = 6.8 Hz, *J* = 15.6Hz, 1H), 5.92 (s, 2H), 2.77-2.70 (m, 2H), 2.60-2.56 (m, 1H), 2.48-2.40 (m, 2H), 2.29 (s, 3H), 2.02-1.98 (m, 1H), 1.60-1.55 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 148.0,

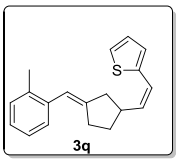
146.7, 145.5, 137.5, 135.8, 132.4, 132.2, 129.8, 128.3, 128.0, 126.1, 125.4, 120.3, 119.4, 108.2, 105.4, 100.9, 42.6, 42.0, 33.6, 30.2, 20.0. HRMS-ESI (m/z) $[M + H]^+$ calcd for $C_{22}H_{23}O_2$: 319.1693; Found, 319.1689.



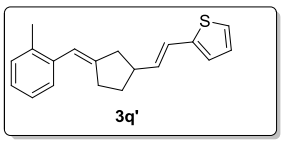
1-methyl-2-((E)-(3-((Z)-4-methylstyryl)cyclopentylidene)methyl)benzene (3p) : oil; ^{1}H NMR ($CDCl_3$, 400MHz) δ: 7.28 (d, *J* = 7.2 Hz, 1H), 7.20-7.07(m, 7H), 6.41-6.38(m, 2H), 5.70 (t, *J* = 10.4 Hz, 1H), 3.20-3.09 (m, 1H), 2.77-2.71 (m, 1H), 2.63-2.56 (m, 1H), 2.44-2.35 (m, 5H), 2.28 (s, 3H), 2.04-2.00 (m, 1H), 1.61-1.51 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 145.6, 137.5, 136.3, 136.1, 135.8, 134.8, 129.8, 128.9, 128.5, 128.3, 127.9, 126.1, 125.4, 119.3, 42.7, 38.1, 34.3, 30.3, 21.2, 20.0. MS(EI): *m/z*(%): 288(100.0), 183(42.5), 170(89.8), 155(41.3), 142(29.5), 129 (74.4), 105(60.1), 91(15.1).



1-methyl-2-((E)-(3-((E)-4-methylstyryl)cyclopentylidene)methyl)benzene (3p') : oil; ^{1}H NMR ($CDCl_3$, 400MHz) δ: 7.31-7.23(m, 3H), 7.17-7.08(m, 5H), 6.43 (s, 1H), 6.39 (s, 1H), 6.18 (dd, *J* = 7.2 Hz, *J* = 16.0Hz, 1H), 2.78-2.73(m, 2H), 2.63-2.57 (m, 1H), 2.49-2.39 (m, 2H), 2.32 (s, 3H), 2.29 (s, 3H), 2.03-2.00 (m, 1H), 1.64-1.54 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 145.6, 137.5, 136.6, 135.8, 134.8, 133.0, 129.8, 129.2, 128.5, 128.0, 126.1, 125.9, 125.4, 119.3, 42.7, 41.9, 33.6, 30.2, 21.1, 20.0. Anal. Calcd. for $C_{22}H_{24}$: C, 91.61; H, 8.39. Found: C, 91.72; H, 8.48.

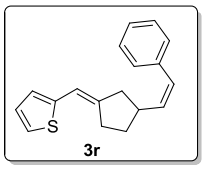


2-((Z)-2-((E)-3-(2-methylbenzylidene)cyclopentyl)vinyl)thiophene (3q) : oil; ^{1}H NMR ($CDCl_3$, 400MHz) δ: 7.31 (d, *J* = 7.2 Hz, 1H), 7.24 (s, 1H), 7.18-7.08 (m, 3H), 7.01-6.98 (m, 2H), 6.51 (d, *J* = 11.6 Hz, 1H), 6.43 (s, 1H), 5.55 (dd, *J* = 10.0 Hz, *J* = 11.2Hz, 1H), 3.39-3.33 (m, 1H), 2.87-2.81(m, 1H), 2.63-2.59 (m, 1H), 2.53-2.45 (m, 1H), 2.40-2.36 (m, 1H), 2.29 (s, 3H), 2.13-2.09 (m, 1H), 1.61-1.52 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 145.3, 140.3, 137.5, 135.8, 135.0, 129.9, 128.0, 127.3, 126.8, 126.1, 125.4, 124.9, 121.3, 119.5, 42.2, 38.8, 33.7, 30.3, 20.0. MS(EI): *m/z*(%): 270(73.4), 182(37.3), 170(100.0), 155(36.4), 135(18.5), 129 (65.4), 105(30.4), 97 (20.8).

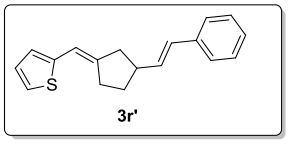


2-((E)-2-((E)-3-(2-methylbenzylidene)cyclopentyl)vinyl)thiophene (3q') : oil; ^{1}H NMR ($CDCl_3$, 400MHz) δ: 7.29 (d, *J* = 7.2 Hz, 1H), 7.15-7.08 (m, 4H), 6.94-6.88 (m, 2H), 6.56 (d, *J* = 15.6 Hz, 1H), 6.42 (s, 1H), 6.08 (dd, *J* = 7.2Hz, *J* = 15.6Hz, 1H), 2.76-2.73(m, 2H), 2.62-2.56 (m, 1H), 2.48-2.38 (m, 2H), 2.28 (s, 3H), 2.03-1.97 (m,

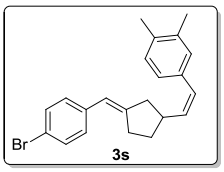
1H), 1.63-1.51 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 145.3, 142.9, 137.5, 135.8, 134.0, 129.8, 127.9, 127.2, 126.1, 125.4, 124.4, 123.2, 122.0, 119.5, 42.5, 41.7, 33.4, 30.1, 20.0. Anal. Calcd. for $C_{19}H_{20}S$: C, 81.38; H, 7.19. Found: C, 81.54; H, 7.31.



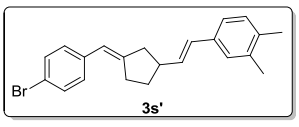
2-((E)-(3-((Z)-styryl)cyclopentylidene)methyl)thiophene (3r) : solid; m.p. 72-74 ℃; ^{1}H NMR ($CDCl_3$, 400MHz) δ: 7.35-7.19 (m, 6H), 6.99 (dd, *J* = 3.6Hz, *J* = 5.2Hz, 1H), 6.89 (d, *J* = 3.2 Hz, 1H), 6.44 (d, *J* = 11.6 Hz, 1H), 5.60 (dd, *J* = 10.0Hz, *J* = 12.0Hz, 1H), 3.18-3.12(m, 1H), 2.74-2.67(m, 2H), 2.51-2.47 (m, 1H), 2.42-2.36 (m, 1H), 2.13-2.11 (m, 1H), 1.72-1.67 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 144.1, 142.5, 137.6, 136.2, 128.8, 128.6, 128.2, 126.8, 126.6, 124.8, 123.9, 114.9, 43.1, 38.7, 34.4, 31.1. MS(EI): *m/z*(%): 266(100.0), 175(19.9), 162(43.8), 135(45.8), 129(31.0), 97 (28.0), 77 (10.2).



2-((E)-(3-((E)-styryl)cyclopentylidene)methyl)thiophene (3r') : oil; ^{1}H NMR ($CDCl_3$, 400MHz) δ: 7.36-7.20 (m, 6H), 7.02-7.00 (m, 1H), 6.91 (d, *J* = 3.2 Hz, 1H), 6.62 (s, 1H), 6.45 (d, *J* = 16.0 Hz, 1H), 6.23 (dd, *J* = 7.2Hz, *J* = 16.0Hz, 1H), 2.81-2.68 (m, 3H), 2.57-2.41 (m, 2H), 2.16-2.12 (m, 1H), 1.77-1.67 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 144.1, 142.6, 137.6, 133.6, 129.0, 128.5, 127.0, 126.9, 126.0, 124.8, 123.9, 114.9, 43.3, 42.3, 33.7, 31.1. Anal. Calcd. for $C_{18}H_{18}S$: C, 81.15; H, 6.81. Found: C, 81.04; H, 6.92.

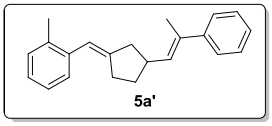


4-((Z)-2-((E)-3-(4-bromobenzylidene)cyclopentyl)vinyl)-1,2-dimethylbenzene (3s) : solid; m.p. 68-70 ℃; ^{1}H NMR ($CDCl_3$, 400MHz) δ: 7.42 (d, *J* = 8.4 Hz, 2H), 7.15 (d, *J* = 8.4 Hz, 2H), 7.10 (d, *J* = 8.0 Hz, 1H), 7.04 (d, *J* = 6.8 Hz, 2H), 6.39 (d, *J* = 11.2 Hz, 1H), 6.28 (s, 1H), 5.53 (dd, *J* = 10.0Hz, *J* = 11.6Hz, 1H), 3.16-3.10 (m, 1H), 2.73-2.66 (m, 2H), 2.54-2.45 (m, 1H), 2.40-2.31 (m, 1H), 2.26 (s, 3H), 2.25 (s, 3H), 2.11-2.05 (m, 1H), 1.68-1.57 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 146.9, 137.4, 136.3, 135.4, 135.2, 135.1, 131.3, 130.0, 129.5, 129.5, 128.8, 125.9, 120.2, 119.4, 43.7, 38.0, 34.5, 30.8, 19.9, 19.5. MS(EI): *m/z*(%): 368(99.2), 366(99.0), 234(86.1), 197(59.3), 169(43.0), 157 (47.5), 128(100.0), 119 (77.2).

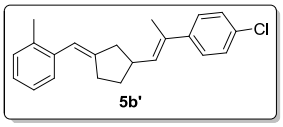


4-((E)-2-((E)-3-(4-bromobenzylidene)cyclopentyl)vinyl)-1,2-dimethylbenzene (3s') : solid; m.p. 110-112 ℃; ^{1}H NMR ($CDCl_3$, 400MHz) δ: 7.42 (d, *J* = 8.4 Hz, 2H), 7.17-7.14 (m, 3H), 7.10-7.04 (m, 2H), 6.38 (d, *J* = 16.0 Hz,

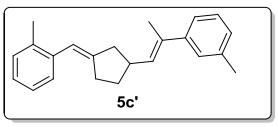
1H), 6.30 (s, 1H), 6.15 (dd, *J* = 7.2Hz, *J* = 15.6Hz, 1H), 2.76-2.67 (m, 3H), 2.57-2.48 (m, 1H), 2.45-2.38 (m, 1H), 2.24 (s, 3H), 2.23 (s, 3H), 2.12-2.04 (m, 1H), 1.71-1.61 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 146.9, 137.5, 136.6, 135.4, 135.2, 132.4, 131.3, 129.8, 129.5, 128.9, 127.2, 123.5, 120.3, 119.4, 42.9, 42.6, 33.8, 30.8, 19.8, 19.5. Anal. Calcd. for $C_{22}H_{23}Br$: C, 71.94; H, 6.31. Found: C, 72.19; H, 6.47.



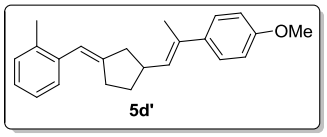
1-methyl-2-((E)-(3-((E)-2-phenylprop-1-en-1-yl)cyclopentylidene)methyl)benzene (5a') : oil; ^{1}H NMR ($CDCl_3$, 400MHz) δ: 7.41-7.39 (m, 2H), 7.33-7.30 (m, 3H), 7.25-7.21 (m, 1H), 7.18-7.10 (m, 3H), 6.42 (s, 1H), 5.75 (dd, *J* = 1.2Hz, *J* = 8.8Hz, 1H), 2.98-2.96 (m, 1H), 2.79-2.73 (m, 1H), 2.61-2.59 (m, 1H), 2.49-2.46 (m, 1H), 2.38-2.30 (m, 4H), 2.10 (s, 3H), 2.04-2.01 (m, 1H), 1.56-1.51 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 145.8, 143.7, 137.5, 135.8, 134.3, 132.5, 129.8, 128.2, 127.9, 126.6, 126.1, 125.6, 125.4, 119.2, 42.3, 38.9, 33.8, 30.3, 20.1, 16.1. Anal. Calcd. for $C_{22}H_{24}$: C, 91.61; H, 8.39. Found: C, 91.70; H, 8.52.



1-((E)-(3-((E)-2-(4-chlorophenyl)prop-1-en-1-yl)cyclopentylidene)methyl)-2-methylbenzene (5b') : oil; ^{1}H NMR ($CDCl_3$, 400MHz) δ: 7.33-7.25 (m, 5H), 7.16-7.10 (m, 3H), 6.42 (s, 1H), 5.73 (d, *J* = 8.8 Hz, 1H), 2.98-2.93 (m, 1H), 2.78-2.72 (m, 1H), 2.65-2.59 (m, 1H), 2.50-2.46 (m, 1H), 2.42-2.26 (m, 4H), 2.07-2.01 (m, 4H), 1.58-1.50 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 145.6, 142.1, 137.5, 135.8, 133.3, 133.0, 132.2, 129.9, 128.2, 127.9, 126.9, 126.1, 125.4, 119.3, 42.3, 38.9, 33.8, 30.3, 20.1, 16.0. Anal. Calcd. for $C_{22}H_{23}Cl$: C, 81.84; H, 7.18. Found: C, 81.67; H, 7.30.

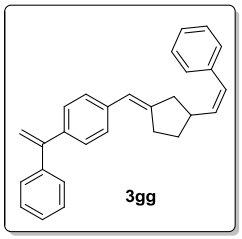


1-methyl-2-((E)-(3-((E)-2-(m-tolyl)prop-1-en-1-yl)cyclopentylidene)methyl)benzene (5c') : oil; ^{1}H NMR ($CDCl_3$, 400MHz) δ: 7.32-7.30 (m, 1H), 7.24-7.10 (m, 6H), 7.06-7.03 (m, 1H), 6.42 (s, 1H), 5.73 (dd, *J* = 1.2 Hz, *J* = 8.8 Hz, 1H), 2.97-2.93 (m, 1H), 2.78-2.72 (m, 1H), 2.60-2.58 (m, 1H), 2.48-2.46 (m, 1H), 2.38-2.34 (m, 4H), 2.29 (s, 3H), 2.09 (s, 3H), 2.03-2.00 (m, 1H), 1.56-1.51 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 145.8, 143.8, 137.6, 135.8, 134.4, 132.3, 129.8, 128.1, 128.0, 127.3, 126.4, 126.1, 125.4, 122.7, 119.2, 42.3, 38.8, 33.8, 30.3, 21.5, 20.1, 16.1. Anal. Calcd. for $C_{23}H_{26}$: C, 91.34; H, 8.66. Found: C, 91.28; H, 8.74.

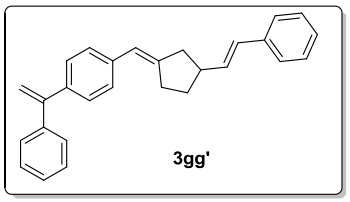


1-((E)-(3-((E)-2-(4-methoxyphenyl)prop-1-en-1-yl)cyclopentylidene)methyl)-2-methylbenzene (5d') : oil; ^{1}H NMR ($CDCl_3$, 400MHz) δ: 7.32-7.35 (m, 3H), 7.17-7.08 (m, 3H), 6.85 (d, *J* = 8.8 Hz, 2H), 6.42 (s, 1H), 5.67 (d, *J* = 8.8 Hz, 2H), 3.81 (s, 3H), 2.98-2.90 (m, 1H), 2.78-2.72 (m, 1H), 2.64-2.58 (m, 1H), 2.50-2.41 (m, 1H), 2.37-2.29

(m, 4H), 2.07-2.01 (m, 4H), 1.57-1.45 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.5, 145.9, 137.6, 136.3, 135.8, 133.7, 130.9, 129.8, 128.0, 126.6, 126.0, 125.4, 119.2, 113.5, 55.3, 42.4, 38.9, 33.9, 30.3, 20.1, 16.1. HRMS-ESI (m/z) $[M + H]^+$ calcd for $C_{23}H_{27}O_1$: 319.2056; Found, 319.2064.



1-(1-phenylvinyl)-4-((E)-(3-((Z)-styryl)cyclopentylidene)methyl)benzene (3gg) : oil; ^{1}H NMR ($CDCl_3$, 400MHz) δ: 7.35-7.24 (m, 13H), 7.22-7.21 (m, 1H), 6.44 (d, *J* = 11.6 Hz, 1H), 6.37 (s, 1H), 5.60 (dd, *J* = 10.0 Hz, *J* = 11.2 Hz, 1H), 5.47 (d, *J* = 1.2 Hz, 1H), 5.41 (d, *J* = 1.2 Hz, 1H), 3.14-3.10 (m, 1H), 2.76-2.70 (m, 2H), 2.58-2.53 (m, 1H), 2.44-2.37 (m, 1H), 2.10-2.07 (m, 1H), 1.67-1.61 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 149.7, 146.0, 141.5, 138.7, 138.0, 137.6, 136.4, 128.7, 128.6, 128.3, 128.2, 128.1, 128.1, 127.7, 127.6, 126.6, 121.0, 113.9, 43.7, 38.0, 34.6, 30.9. MS(EI): *m/z*(%): 362(100.0), 258(49.6), 193(25.5), 178(28.4), 129(50.7), 103 (44.3), 57(34.0), 44 (15.6).

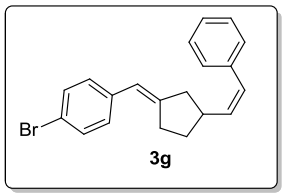


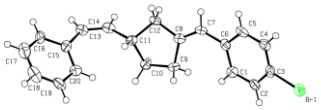
1-(1-phenylvinyl)-4-((E)-(3-((E)-styryl)cyclopentylidene)methyl)benzene (3gg') : oil; ^{1}H NMR ($CDCl_3$, 400MHz) δ: 7.37-7.27 (m, 13H), 7.23-7.18 (m, 1H), 6.45 (d, *J* = 15.6 Hz, 1H), 6.39 (s, 1H), 6.23 (dd, *J* = 7.2 Hz, *J* = 16.0 Hz, 1H), 5.48 (d, *J* = 1.2 Hz, 1H), 5.42 (d, *J* = 1.2 Hz, 1H), 2.80-2.73 (m, 3H), 2.64-2.57 (m, 1H), 2.49-2.42 (m, 1H), 2.13-2.06 (m, 1H), 1.73-1.65 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 149.7, 146.0, 141.5, 138.7, 137.5, 133.8, 128.9, 128.5, 128.3, 128.1, 128.1, 127.7, 127.7, 127.0, 126.0, 121.0, 113.9, 42.9, 42.7, 33.8, 30.9.

5. References:

(1) Fulton, J. R.; Aggarwal,V. K.; de Vicente, J. Eur. J. Org. Chem. 2005, 1479.

6. Crystallographic data of 3g and 3e'





Structure of 3g

Datablock:

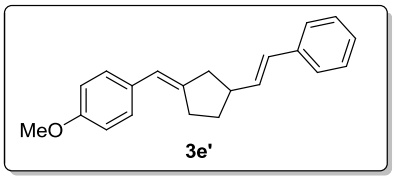
Bond precision:	C-C = 0.0111 A	Wavelength=0.71073	
Cell:	a=6.0119(6)	b=15.8060(14)	c=8.3765(8)
	alpha=90	beta=98.292(9)	gamma=90
Temperature:	291 K		
	Calculated	Reported	
Volume	787.65(13)	787.65(13)	
Space group	P n	P 1 n 1	
Hall group	-P 2yac	-P 2yac	
Moiety formula	C20 H19 Br	C20 H19 Br	
Sum formula	C20 H19 Br	C20 H19 Br	
Mr	339.25	339.26	
Dx,g cm-3	1.430	1.430	
Z	2	2	
Mu (mm-1)	2.601	2.601	
F000	348.0	348.0	
F000’	347.54		
h,k,lmax	7,19,10	7,19,10	
Nref	3107[1563]	2032	
Tmin,Tmax	0.395,0.695	0.021,1.000	
Tmin’	0.331		

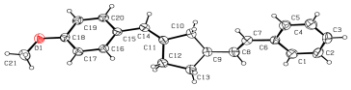
Correction method= MULTI-SCAN

Data completeness= 1.30/0.65 Theta(max)= 26.010

R(reflections)= 0.0508(1624) wR2(reflections)= 0.0999(2032)

S = 1.045 Npar= 190





Structure of 3e'

Datablock:

Bond precision:	C-C = 0.0042 A	Wavelength=0.71073	
Cell:	a=17.7810(8)	b=15.3478(9)	c=6.0728(2)
	alpha=90	beta=99.114(5)	gamma=90
Temperature:	295 K		
	Calculated	Reported	
Volume	1636.34(13)	1636.33(14)	
Space group	P 21/c	P 1 21/c 1	
Hall group	-P 2ybc	-P 2ybc	
Moiety formula	C21 H22 O	C21 H22 O	
Sum formula	C21 H22 O	C21 H22 O	
Mr	290.39	290.39	
Dx,g cm-3	1.179	1.179	
Z	4	4	
Mu (mm-1)	0.070	0.070	
F000	624.0	624.0	
F000’	624.25		
h,k,lmax	21,18,7	21,18,7	
Nref	3222	3215	
Tmin,Tmax	0.976,0.979	0.857,1.000	
Tmin’	0.976		

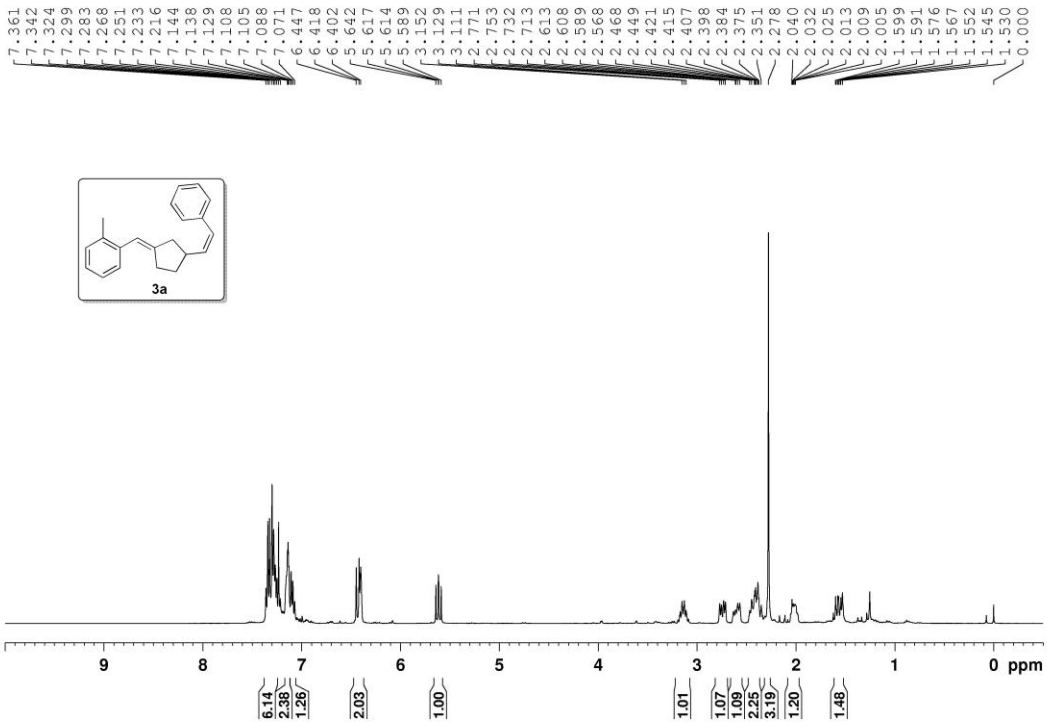
Correction method= MULTI-SCAN

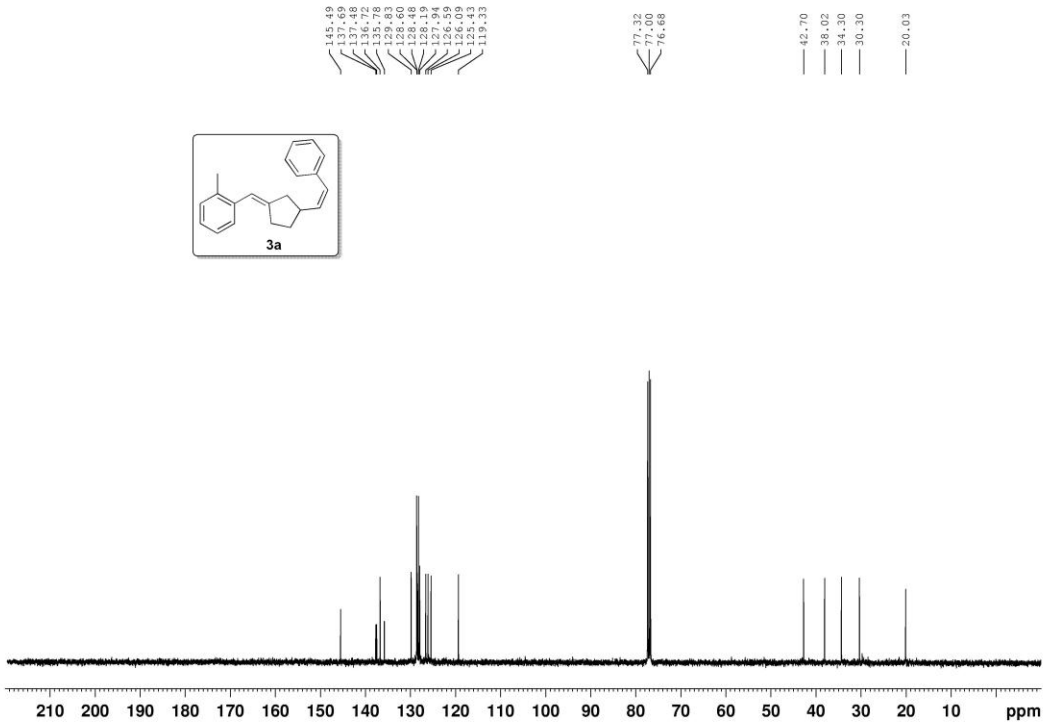
Data completeness= 0.998 Theta(max)= 26.020

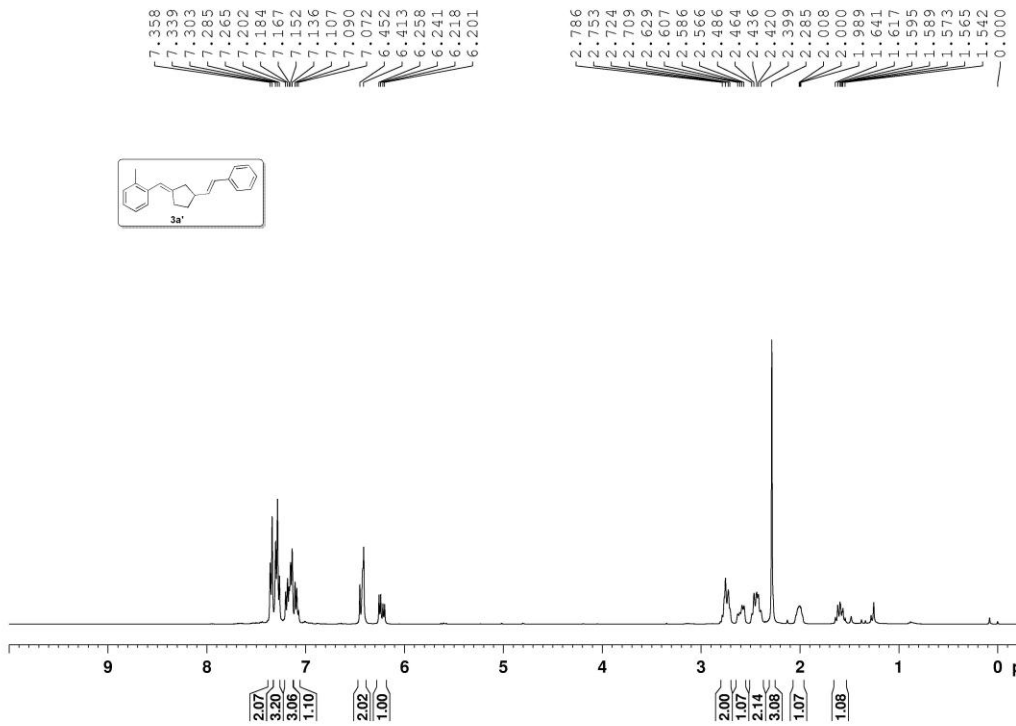
R(reflections)= 0.0705(1792) wR2(reflections)= 0.1875(3215)

S = 1.075 Npar= 209

7. ^{1}H NMR, ^{13}C NMR spectra for products 3a-3s, 3a'-3s', 5a'-5d', 3gg and 3gg'



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7.107
7.090
7.072
6.452
6.413
6.258
6.241
6.218
6.201
2.786
2.753
2.724
2.709
2.629
2.607
2.586
2.566
2.486
2.464
2.436
2.420
2.399
2.285
2.008
2.000
1.989
1.641
1.617
1.595
1.589
1.573
1.565
1.542
0.000
3a'
9
8
7
6
5
4
3
2
1
0 ppm
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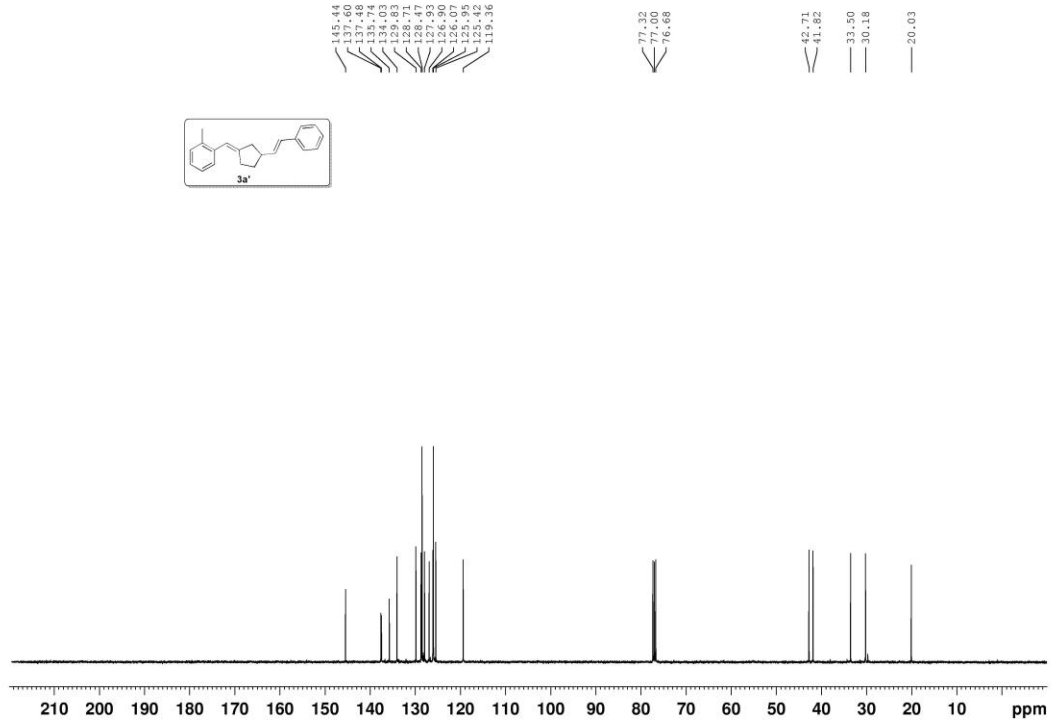
3.20
3.06
1.10
2.02
1.00
2.00
1.07
2.14
3.08
1.07
1.08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126.60
126.07
125.95
125.42
119.36
77.32
77.00
76.68
42.71
41.82
33.50
30.18
20.03
3a'
210
200
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150
140
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30
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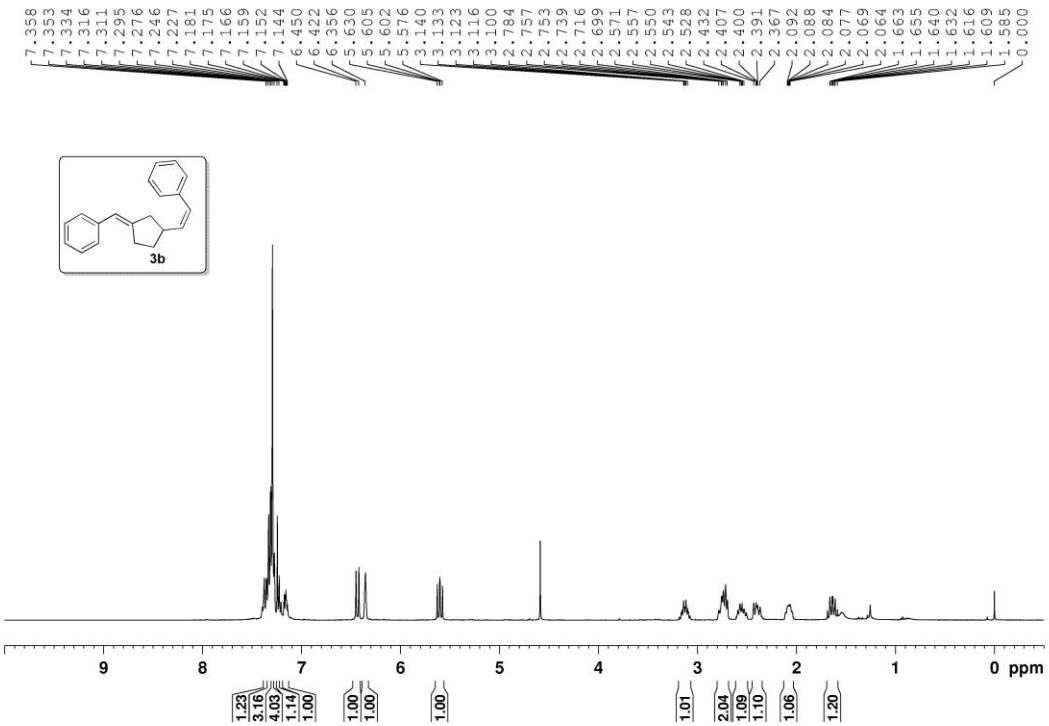
10
ppm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7.159
7.152
7.144
6.450
6.422
6.356
5.630
5.605
5.602
5.576
3.140
3.133
3.123
3.116
3.100
2.784
2.757
2.753
2.739
2.716
2.699
2.571
2.557
2.550
2.543
2.528
2.432
2.407
2.400
2.391
2.367
2.092
2.088
2.084
2.077
2.069
2.064
1.663
1.655
1.640
1.632
1.616
1.609
1.585
0.000
3b
9
8
7
6
5
4
3
2
1
0 ppm
1.23
3.16
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1.00
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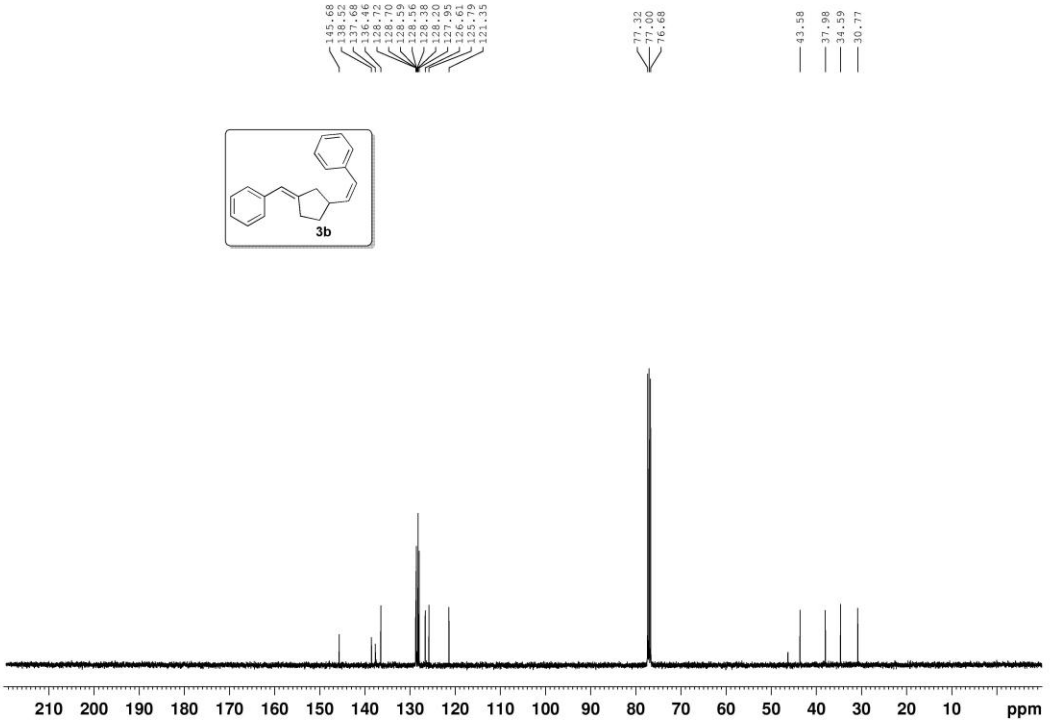
2.04
1.09
1.10
1.06
1.20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121.35
77.32
77.00
76.68
43.58
37.98
34.59
30.77
3b
210
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150
140
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90
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70
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50
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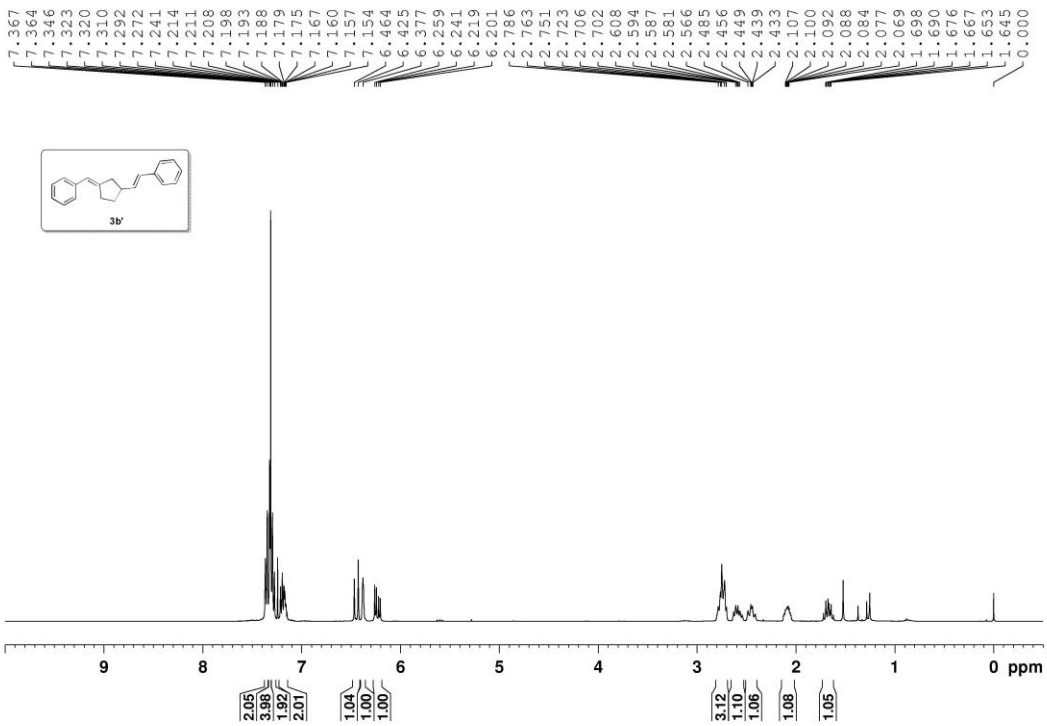
30
20
10
ppm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7.193
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7.179
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7.157
7.154
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6.377
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6.219
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2.723
2.706
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2.587
2.581
2.566
2.485
2.456
2.449
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2.433
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2.088
2.084
2.077
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8
7
6
5
4
3
2
1
0 ppm
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2.01
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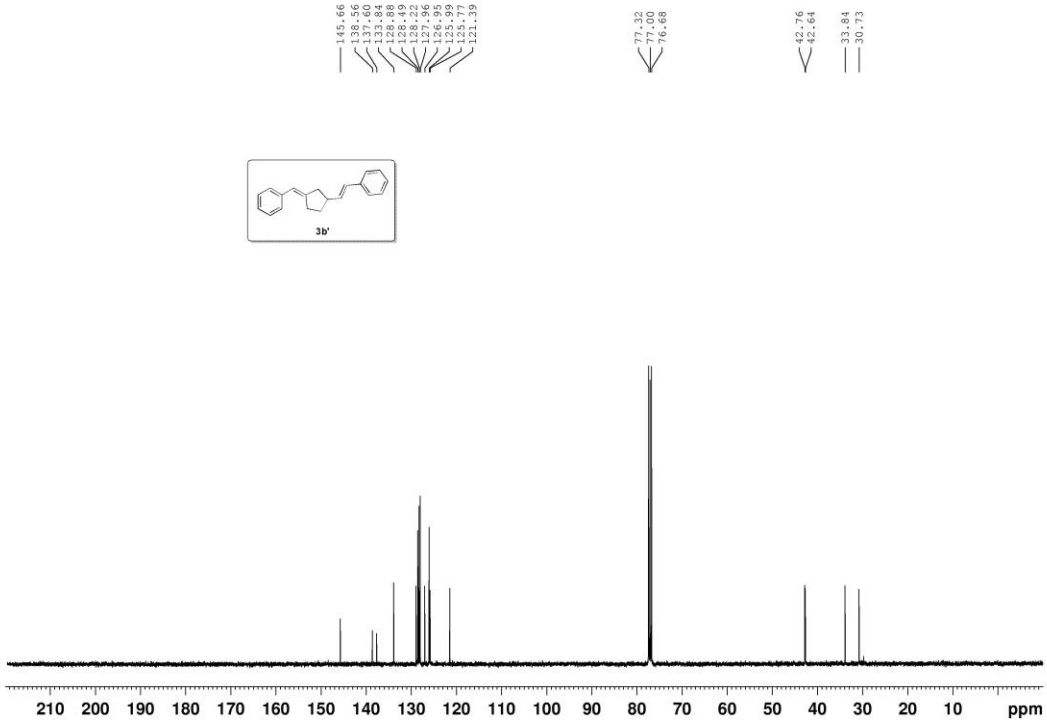
1.05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42.64
33.84
30.73
3b'
210
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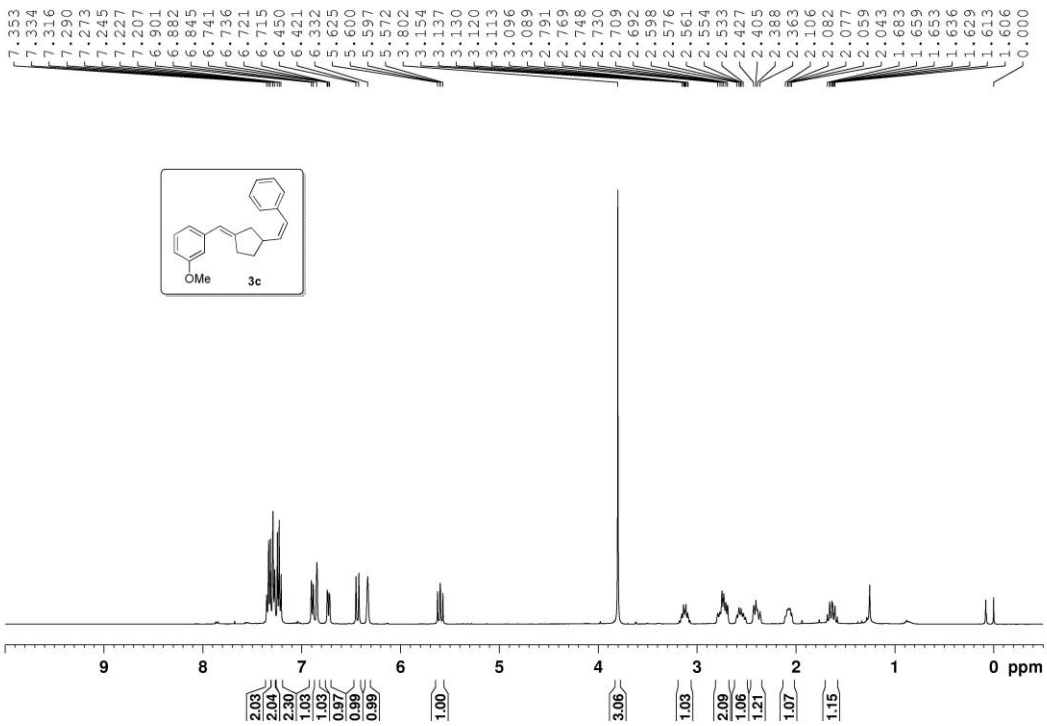
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6.721
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6.450
6.421
6.332
5.625
5.600
5.597
5.572
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3.154
3.137
3.130
3.120
3.113
3.096
3.089
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2.769
2.748
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2.106
2.082
2.077
2.059
2.043
1.683
1.659
1.653
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6
5
4
3
2
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0 ppm
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2.04
2.30
1.03
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1.21
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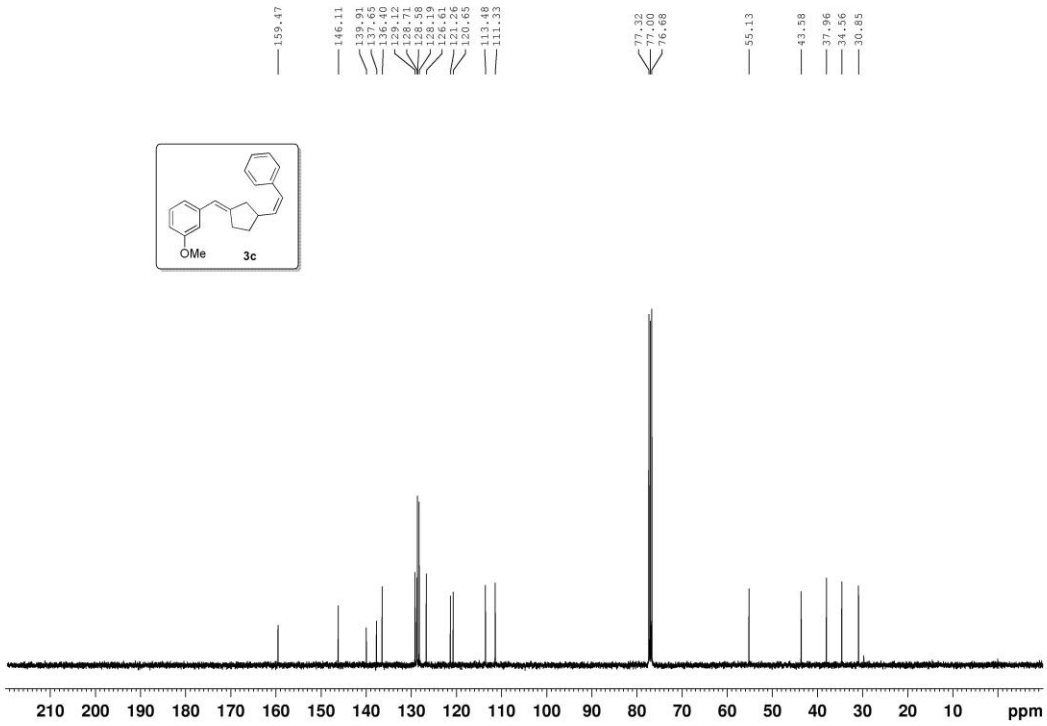
1.15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34.56
30.85
OMe
3c
210
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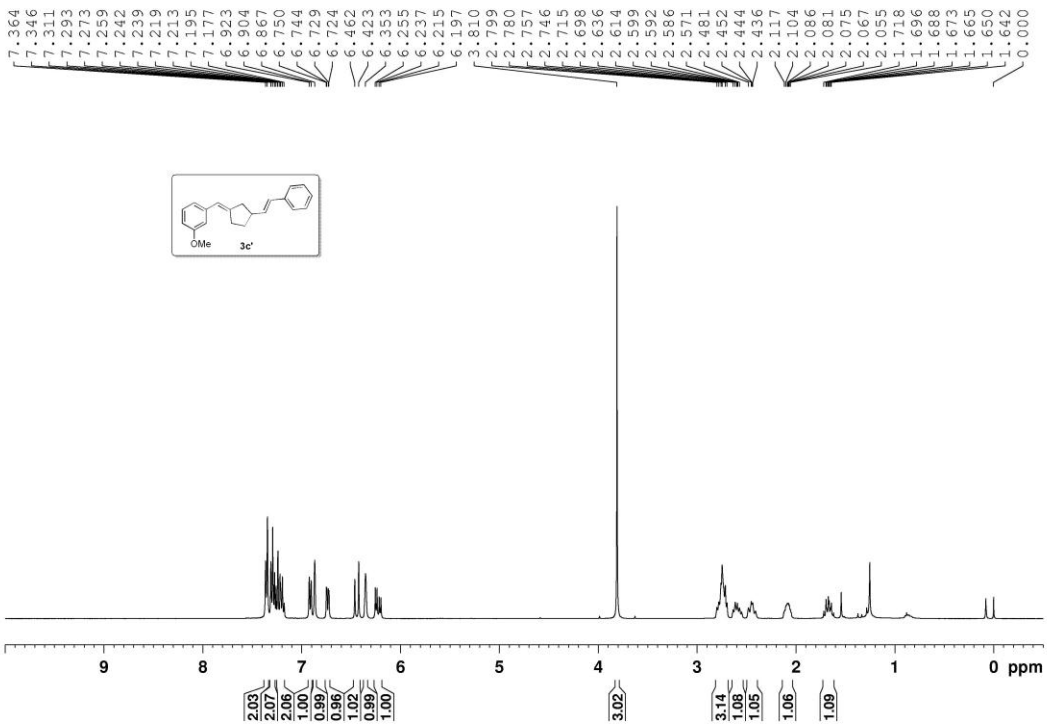
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6.867
6.750
6.744
6.729
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6.423
6.353
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6.215
6.197
3.810
2.799
2.780
2.757
2.746
2.715
2.698
2.636
2.614
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2.592
2.586
2.571
2.481
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2.444
2.436
2.117
2.104
2.086
2.081
2.075
2.067
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1.696
1.688
1.673
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3c'
9
8
7
6
5
4
3
2
1
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2.07
2.06
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3.02
3.14
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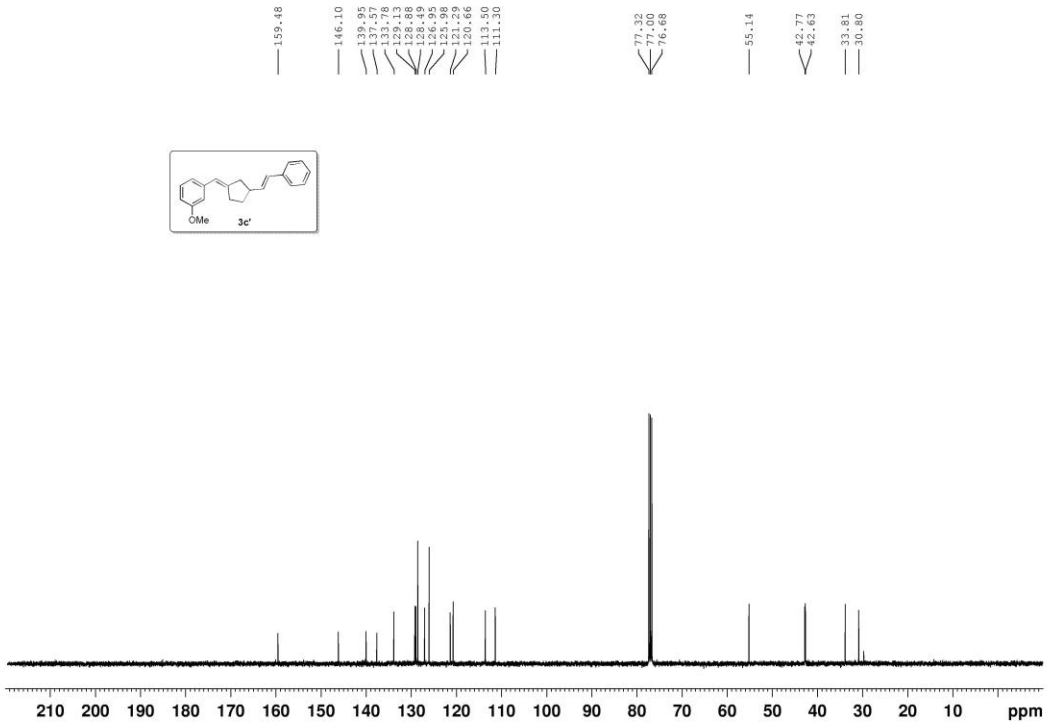
1.05
1.06
1.09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113.50
111.30
77.32
77.00
76.68
55.14
42.77
42.63
33.81
30.80
OMe
3c'
210
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140
130
120
110
100
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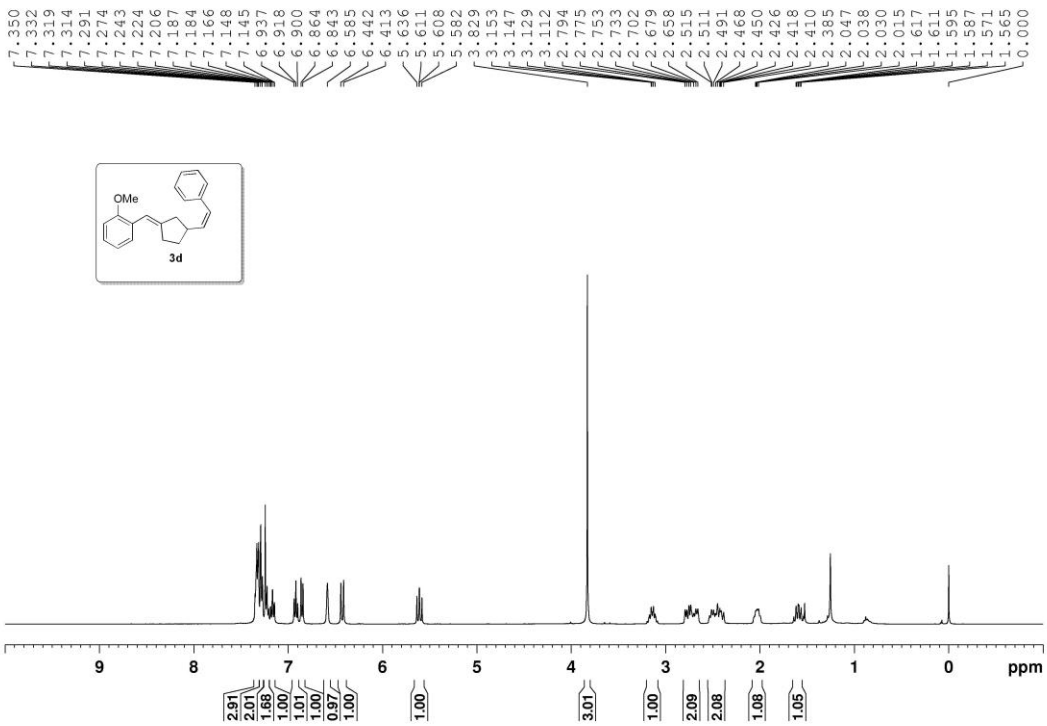
80
70
60
50
40
30
20
10
ppm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7.145
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6.918
6.900
6.864
6.843
6.585
6.442
6.413
5.636
5.611
5.608
5.582
3.829
3.153
3.147
3.129
3.112
2.794
2.775
2.753
2.733
2.702
2.679
2.658
2.515
2.511
2.491
2.468
2.450
2.426
2.418
2.410
2.385
2.047
2.038
2.030
2.015
1.617
1.611
1.595
1.587
1.571
1.565
0.000
OMe
3d
9
8
7
6
5
4
3
2
1
0
ppm
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1.68
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1.00
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1.00
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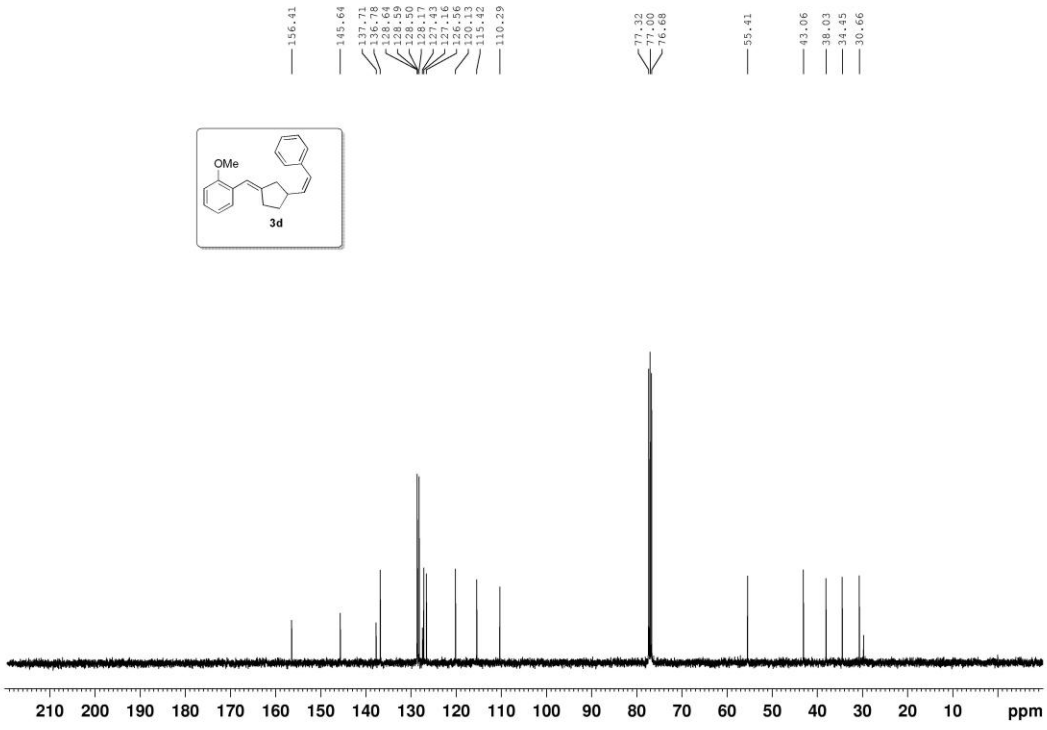
1.08
1.05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110.29
77.32
77.00
76.68
55.41
43.06
38.03
34.45
30.66
OMe
3d
210
200
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140
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120
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90
80
70
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50
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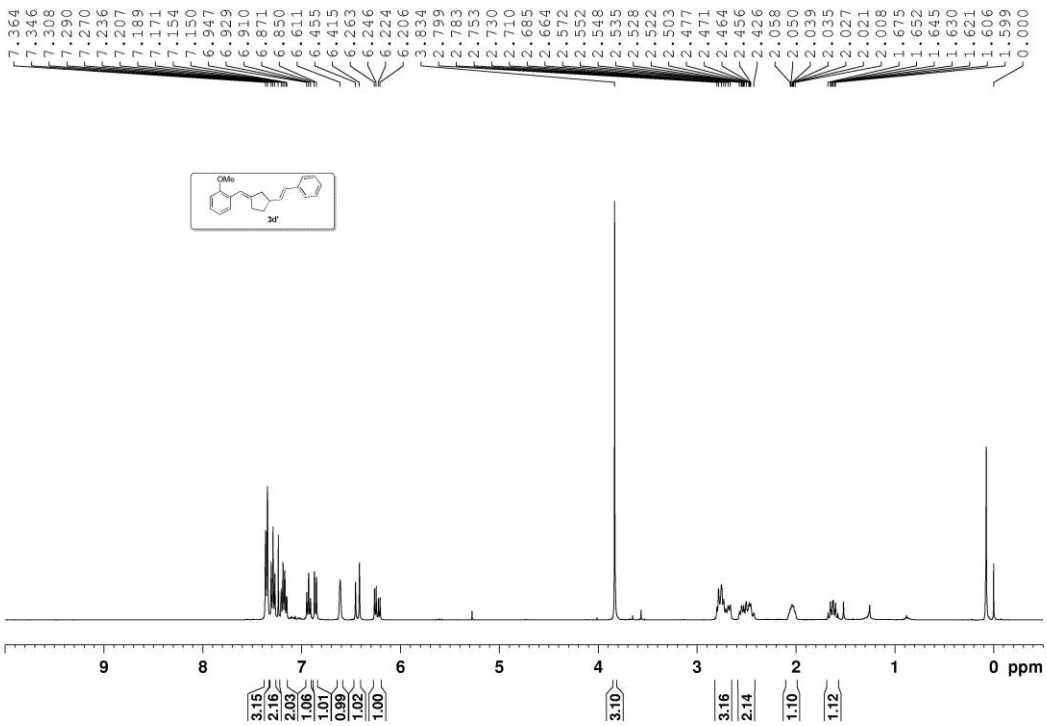
30
20
10
ppm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6.455
6.415
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2.522
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2.050
2.039
2.035
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2.021
2.008
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1.621
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1.599
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3d'
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6
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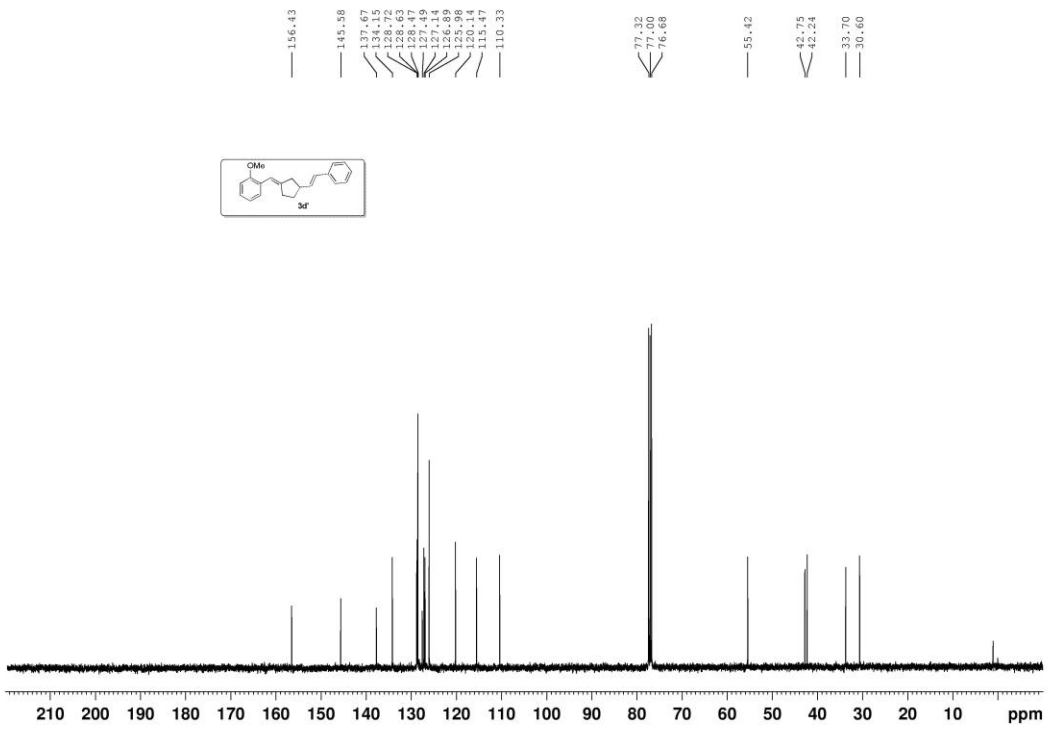
1.12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77.00
76.68
55.42
42.75
42.24
33.70
30.60
OMe
3d'
210
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10
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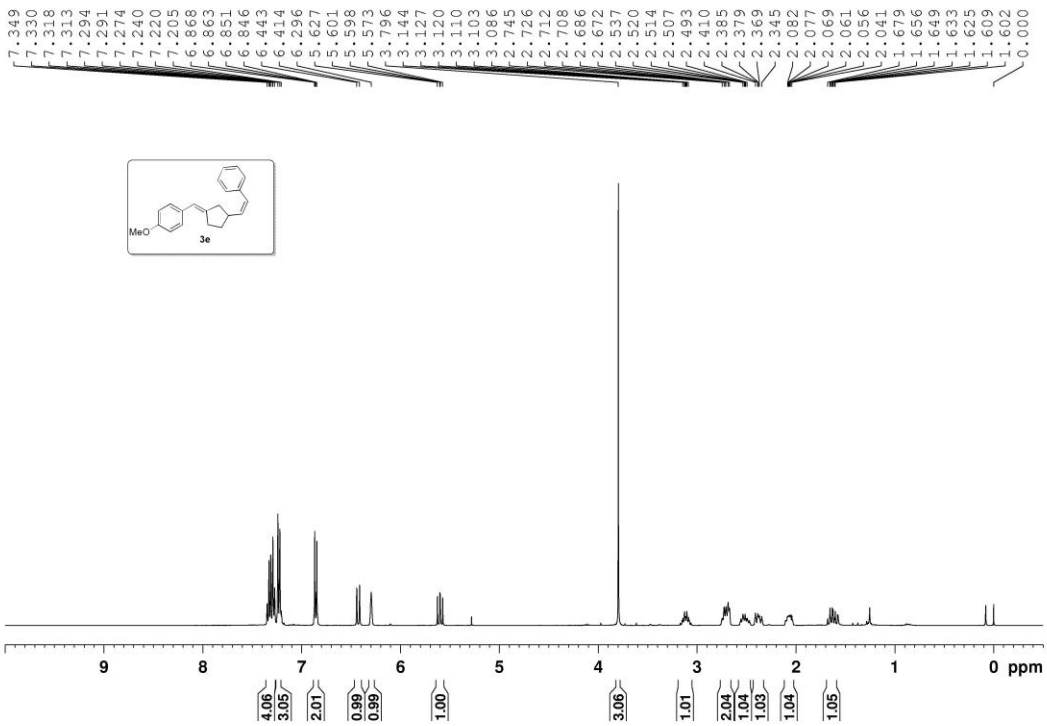
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2.726
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1.633
1.625
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0.000
MeO
3e
9
8
7
6
5
4
3
2
1
0 ppm
4.06
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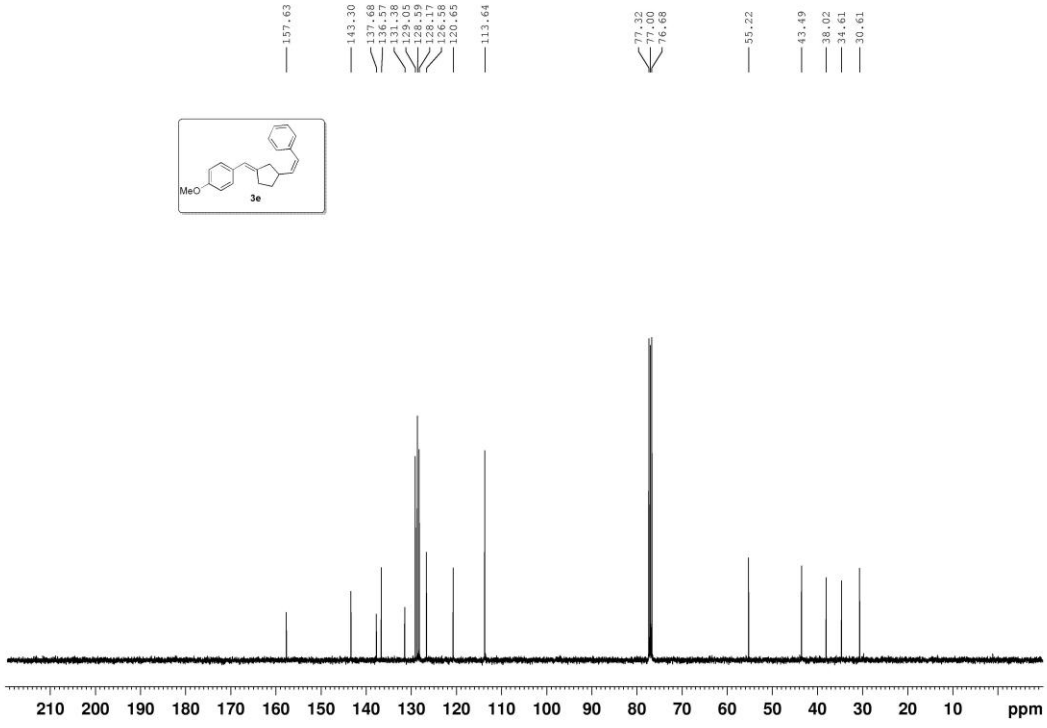
1.05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MeO
3e
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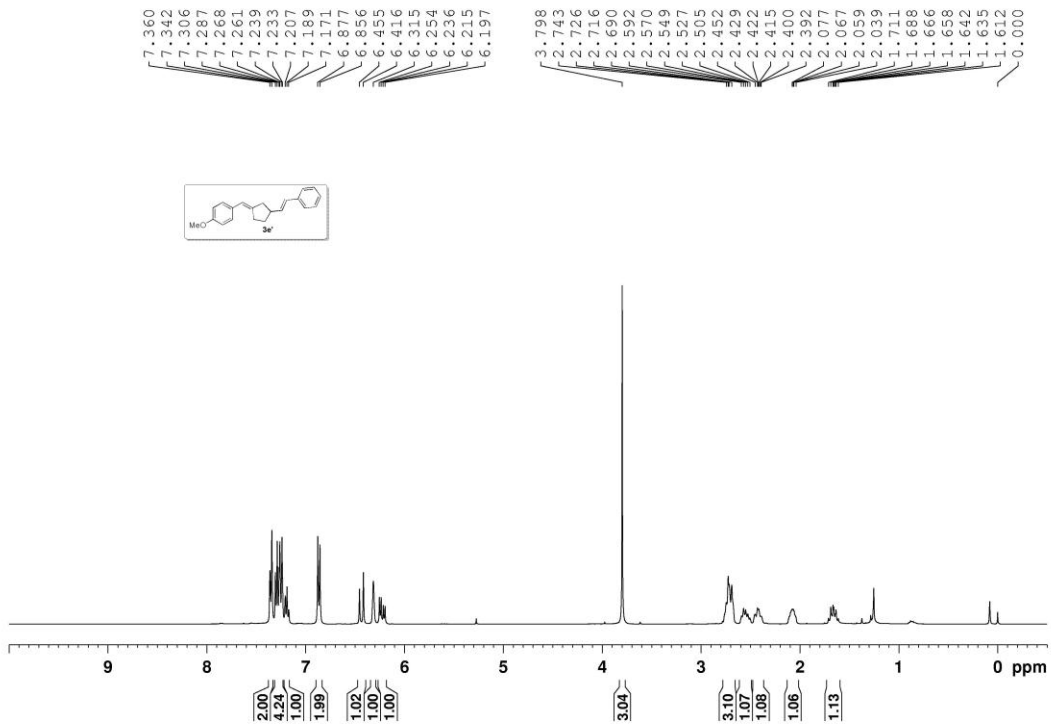
ppm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6.236
6.215
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MeO
3e'
9
8
7
6
5
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2
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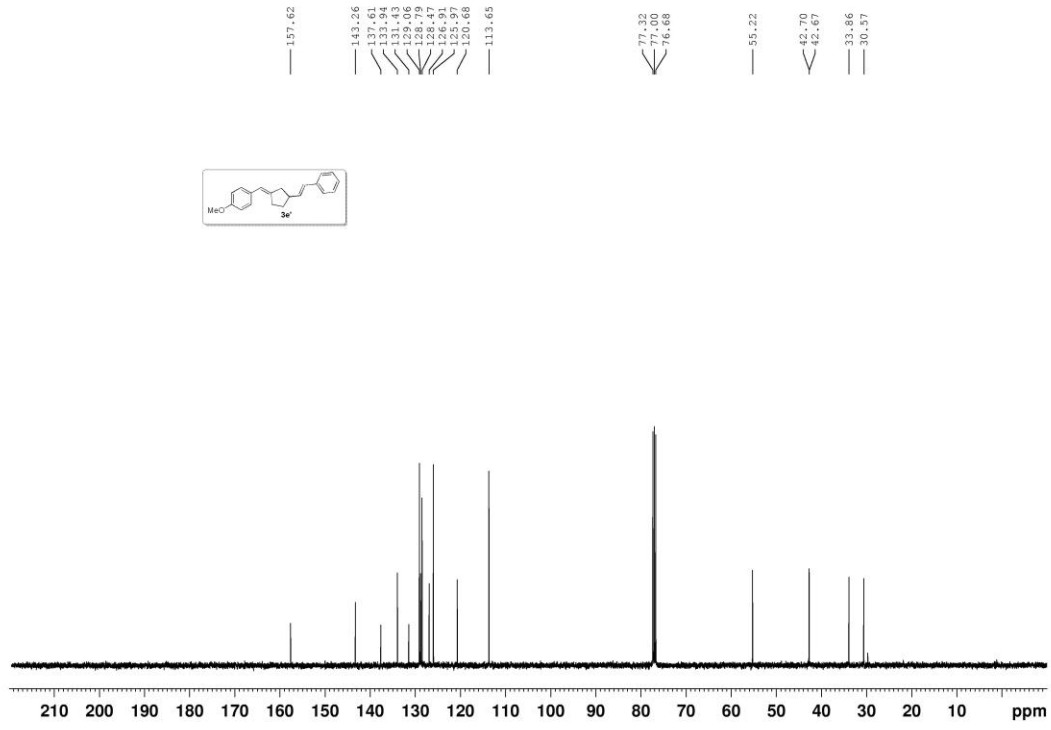
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120.68
113.65
77.32
77.00
76.68
55.22
42.70
42.67
33.86
30.57
MeO
3e'
210
200
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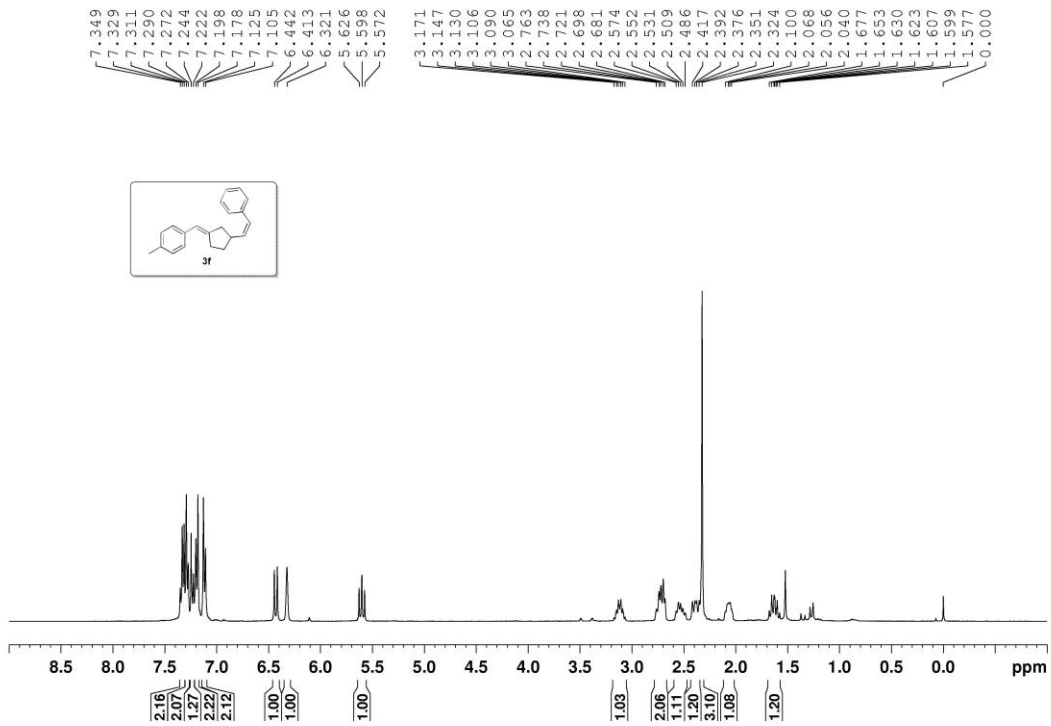
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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5.598
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3.147
3.130
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3.090
3.065
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2.738
2.721
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2.531
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2.056
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1.630
1.623
1.607
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1.577
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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
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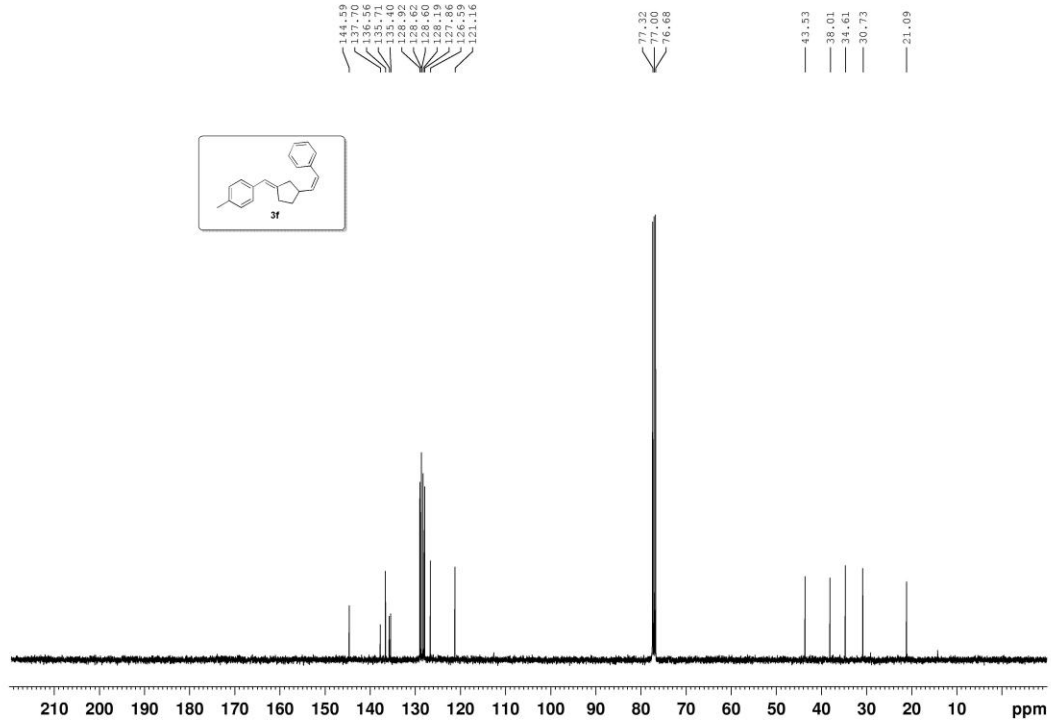
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128.60
128.19
127.86
126.59
121.16
77.32
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38.01
34.61
30.73
21.09
3f
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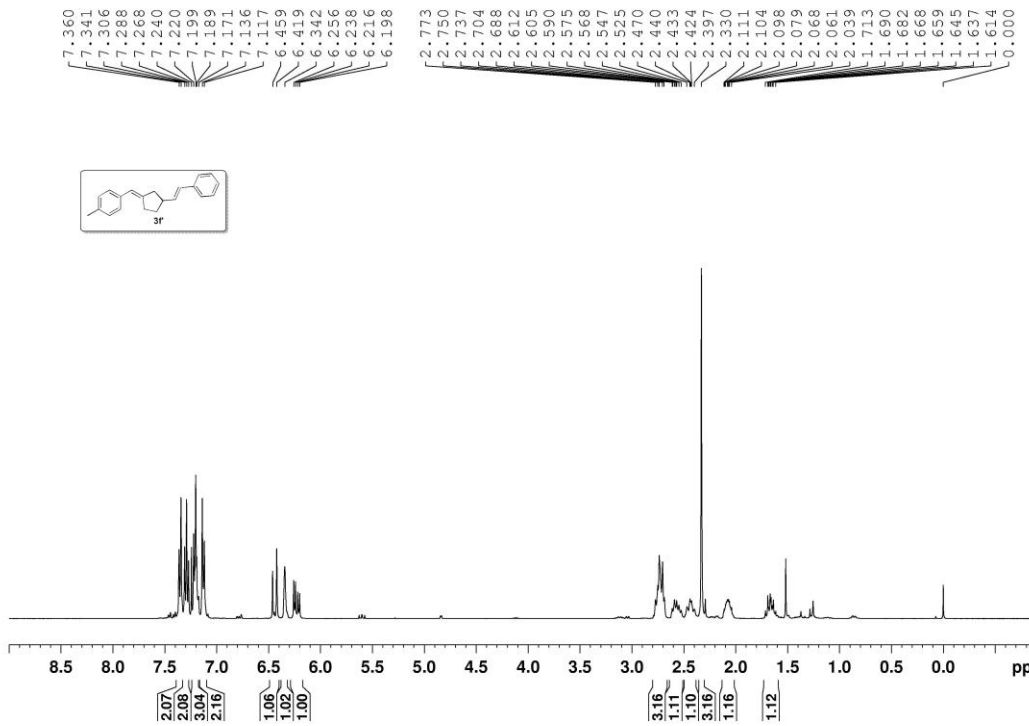
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7.171
7.136
7.117
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6.419
6.342
6.256
6.238
6.216
6.198
2.773
2.750
2.737
2.704
2.688
2.612
2.605
2.590
2.575
2.568
2.547
2.525
2.470
2.440
2.433
2.424
2.397
2.330
2.111
2.104
2.098
2.079
2.068
2.061
2.039
1.713
1.690
1.682
1.668
1.659
1.645
1.637
1.614
0.000
3r
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
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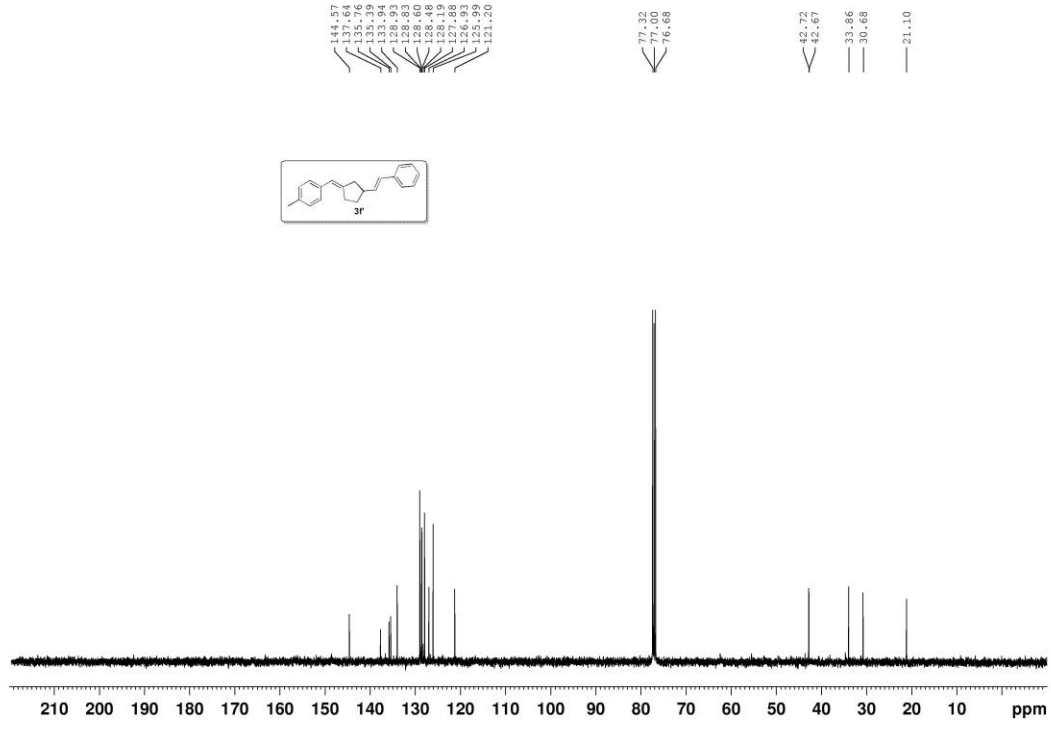
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126.93
125.99
121.20
77.32
77.00
76.68
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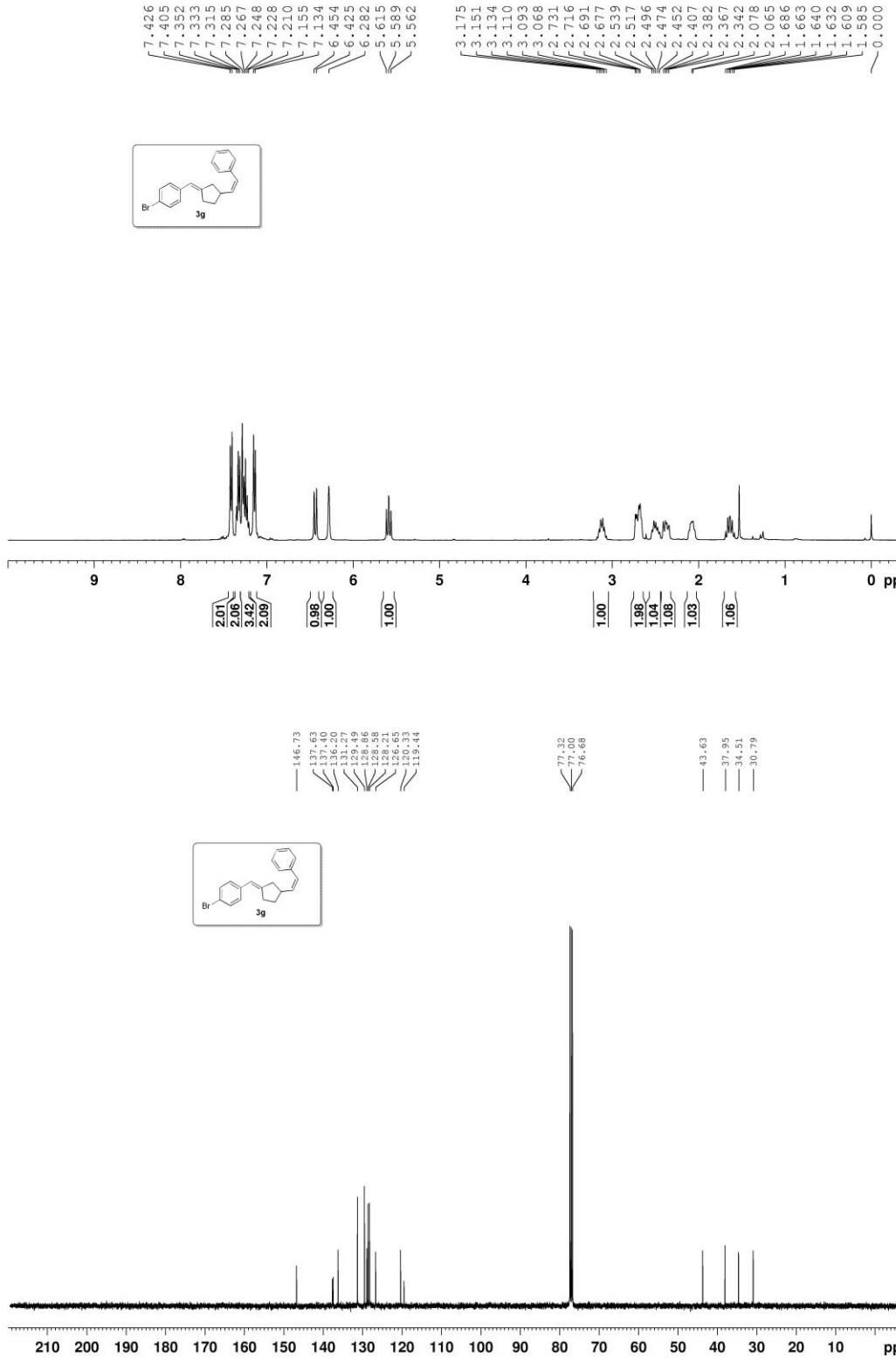
42.67
33.86
30.68
21.10
3r
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm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7.134
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6.425
6.282
5.615
5.589
5.562
3.175
3.151
3.134
3.110
3.093
3.068
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2.716
2.691
2.677
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2.496
2.474
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2.407
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2.065
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1.663
1.640
1.632
1.609
1.585
0.000
Br
3g
9
8
7
6
5
4
3
2
1
0 ppm
2.01
2.06
3.42
2.09
0.98
1.00
1.00
1.00
1.98
1.04
1.08
1.03
1.06
146.73
137.63
137.40
136.20
131.27
129.49
128.86
128.38
128.21
126.65
120.33
119.44
77.32
77.00
76.68
43.63
37.95
34.51
30.79
Br
3g
210
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150
140
130
120
110
100
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70
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50
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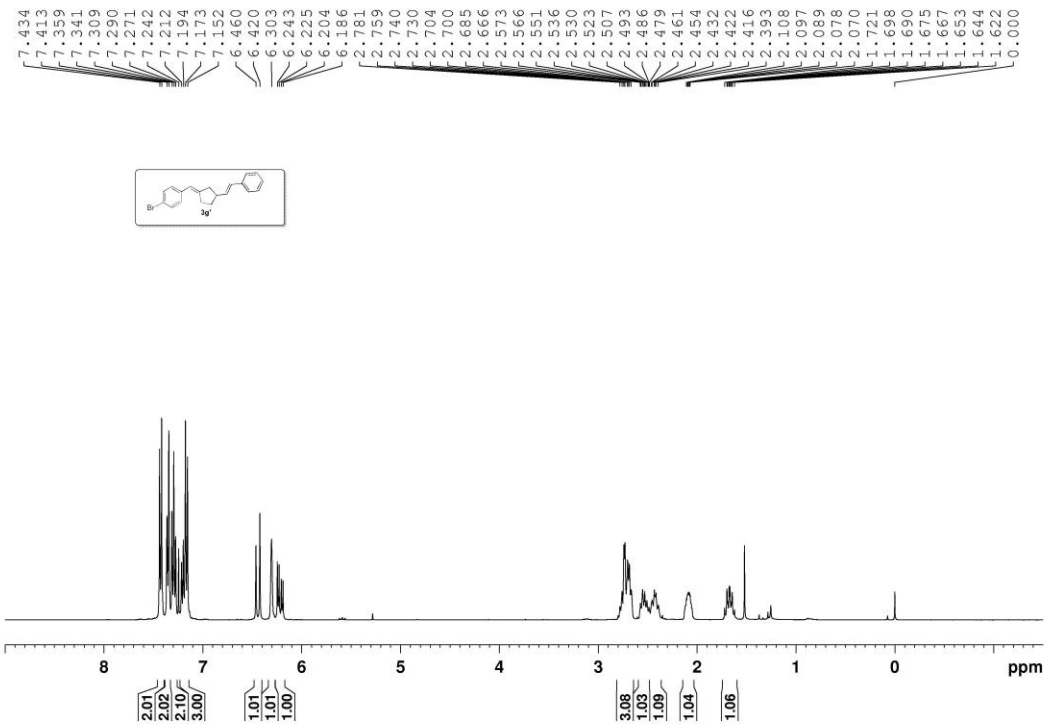
30
20
10
ppm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6.225
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2.486
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2.089
2.078
2.070
1.721
1.698
1.690
1.675
1.667
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1.644
1.622
0.000
Br
3g'
8
7
6
5
4
3
2
1
0
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1.01
1.00
3.08
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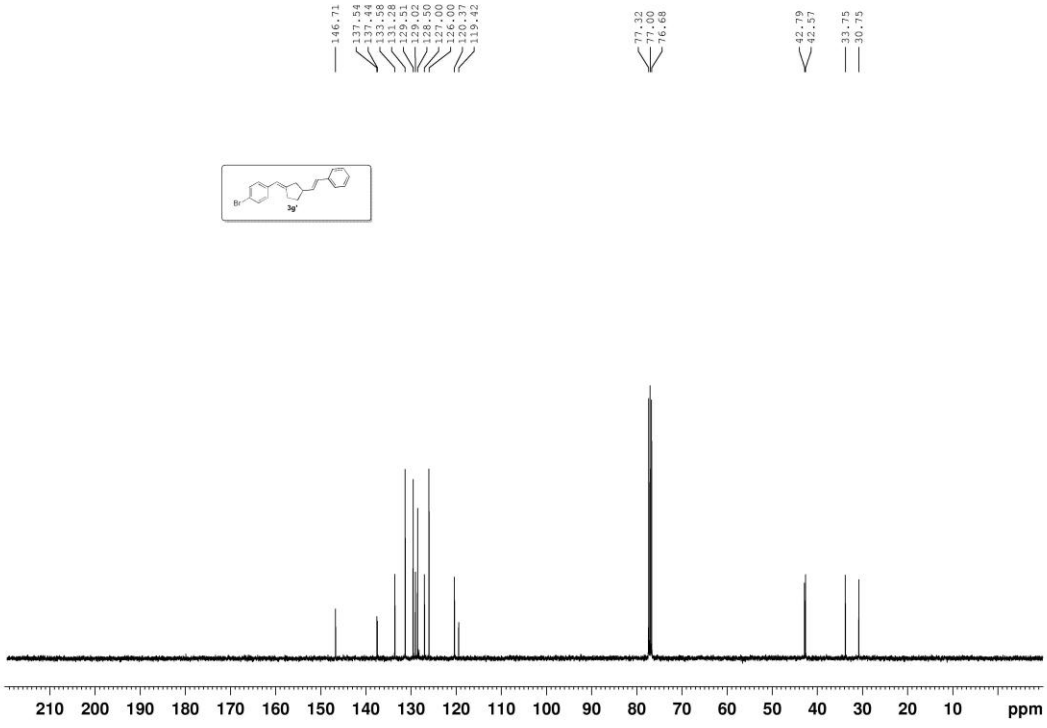
1.09
1.04
1.06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120.37
119.42
77.32
77.00
76.68
42.79
42.57
33.75
30.75
Br
3g'
210
200
190
180
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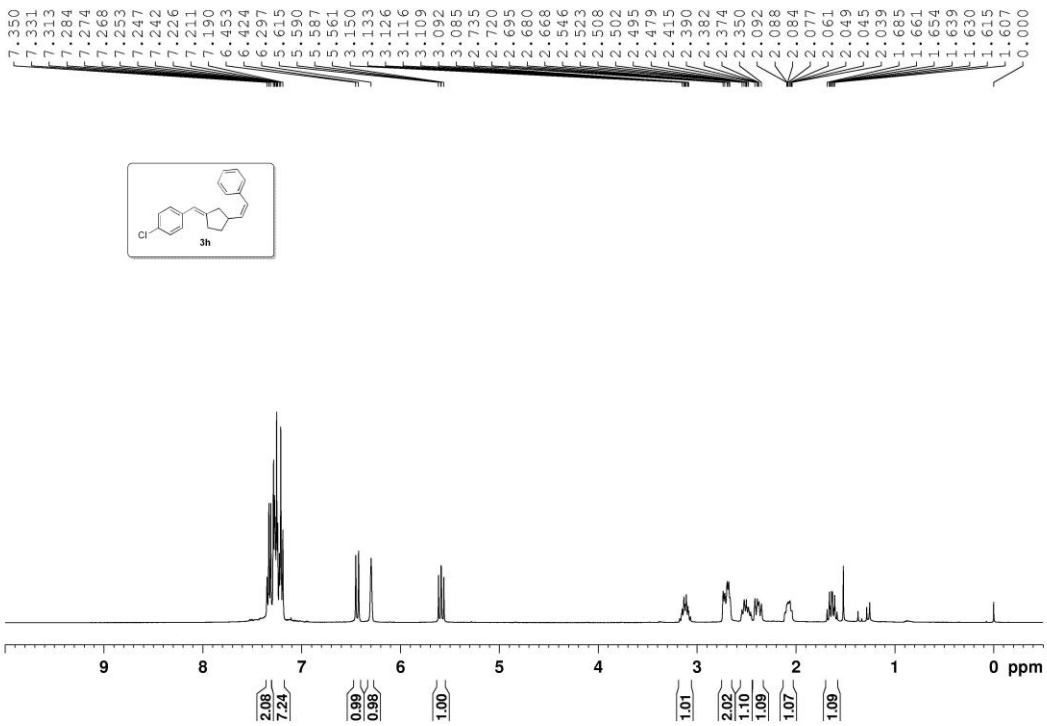
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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6.424
6.297
5.615
5.590
5.587
5.561
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3.126
3.116
3.109
3.092
3.085
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2.720
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2.680
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2.546
2.523
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2.502
2.495
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2.382
2.374
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2.092
2.088
2.084
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2.049
2.045
2.039
1.685
1.661
1.654
1.639
1.630
1.615
1.607
0.000
Cl
3h
9
8
7
6
5
4
3
2
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2.02
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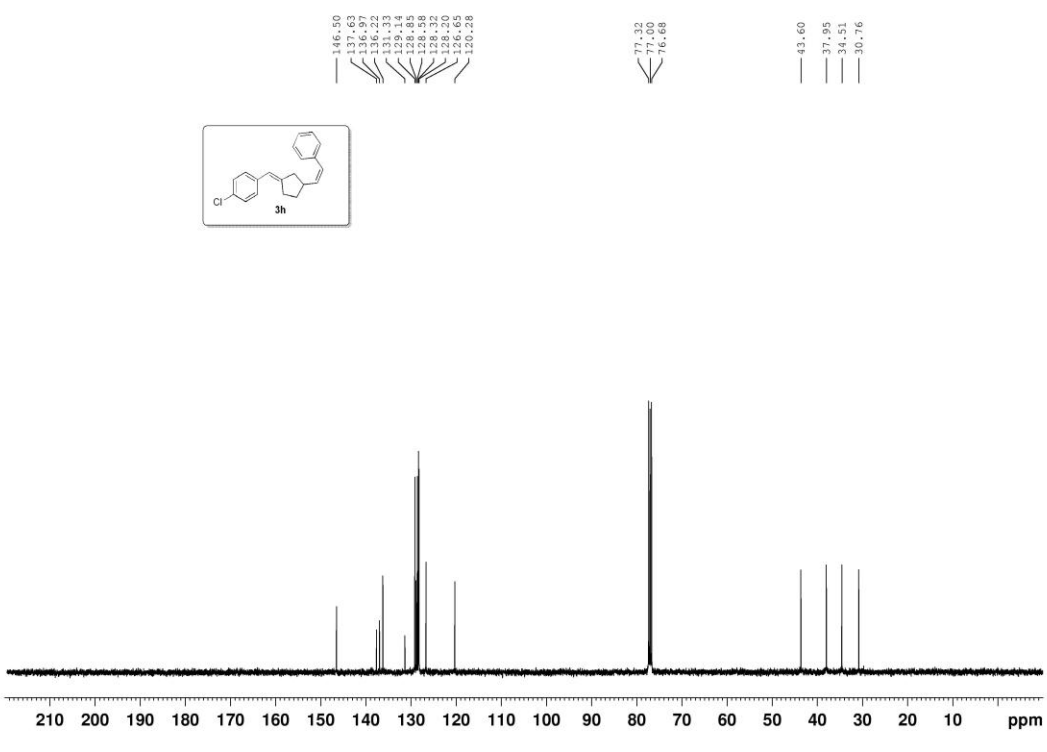
1.07
1.09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77.00
76.68
43.60
37.95
34.51
30.76
Cl
3h
210
200
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150
140
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120
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100
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70
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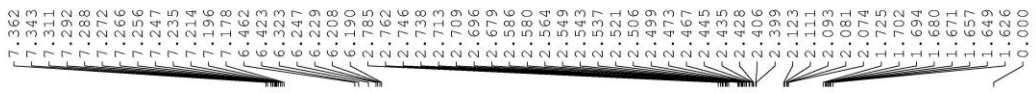
10
ppm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6.423
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6.247
6.229
6.208
6.190
2.785
2.762
2.746
2.738
2.713
2.709
2.696
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2.580
2.564
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2.543
2.537
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2.406
2.399
2.123
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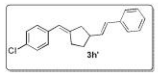
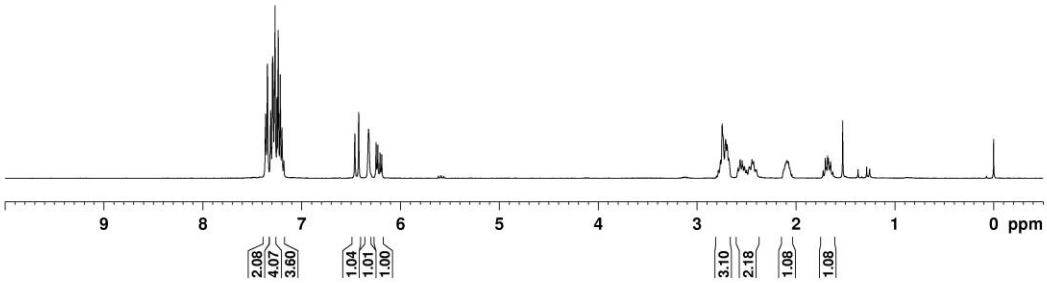

Cl
3h'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8
7
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5
4
3
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1.04
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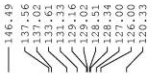
1.00
3.10
2.18
1.08
1.08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126.00
120.33


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77.00
76.69


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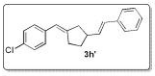
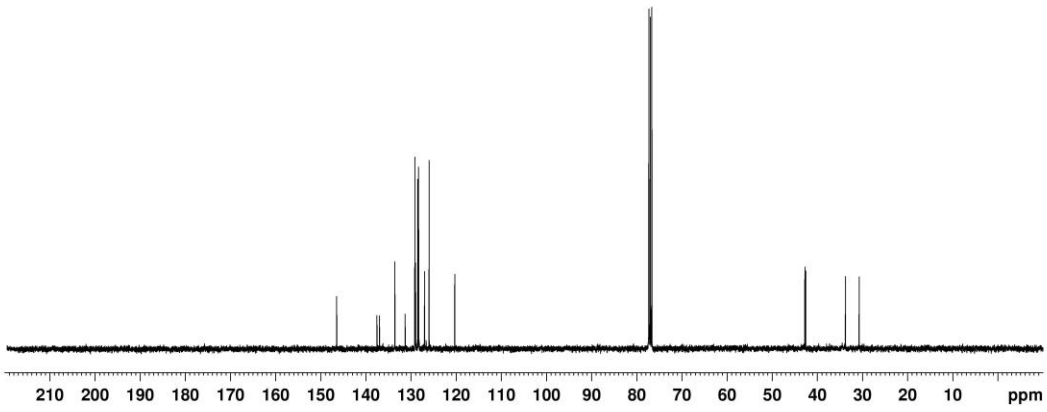
33.77
30.73


Cl
3h'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110
100
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60
50
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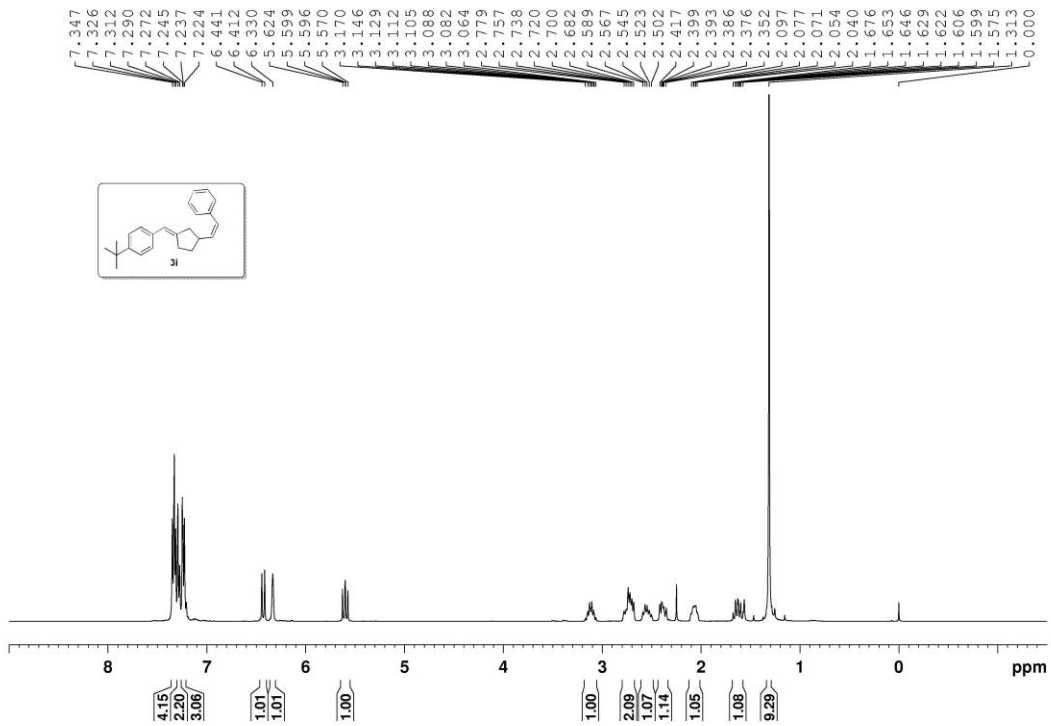
20
10
ppm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5.570
3.170
3.146
3.129
3.112
3.105
3.088
3.082
3.064
2.779
2.757
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2.720
2.700
2.682
2.589
2.567
2.545
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2.386
2.376
2.352
2.097
2.077
2.071
2.054
2.040
1.676
1.653
1.646
1.629
1.622
1.606
1.599
1.575
1.313
0.000
3l
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7
6
5
4
3
2
1
0
ppm
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1.01
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1.00
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1.07
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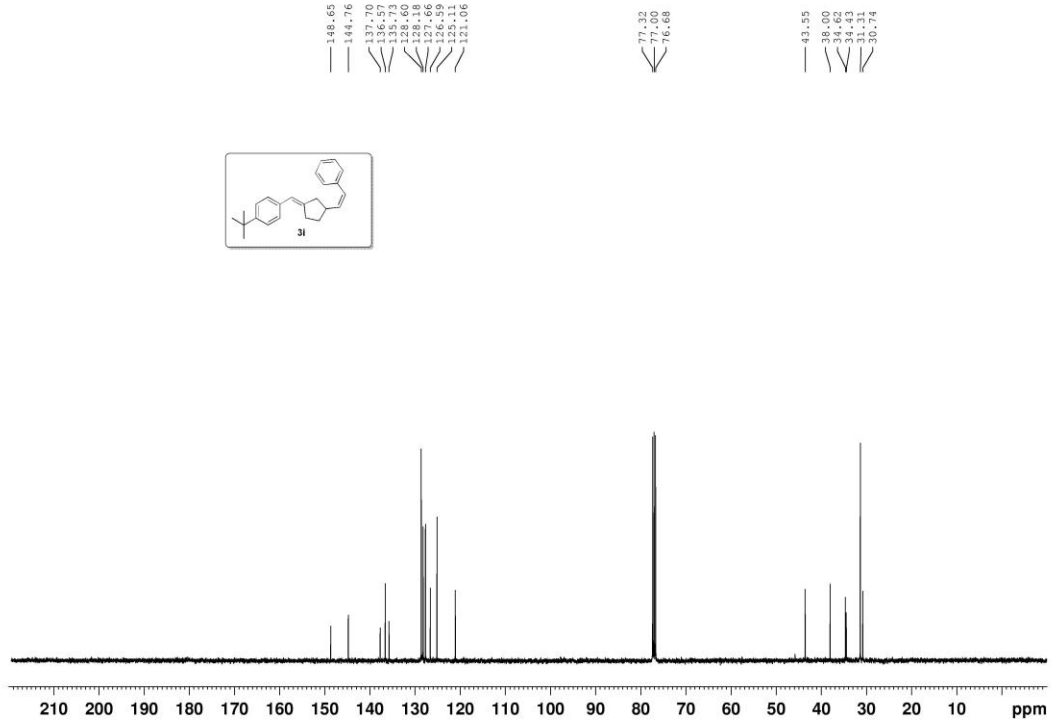
1.05
1.08
9.29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34.43
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3l
210
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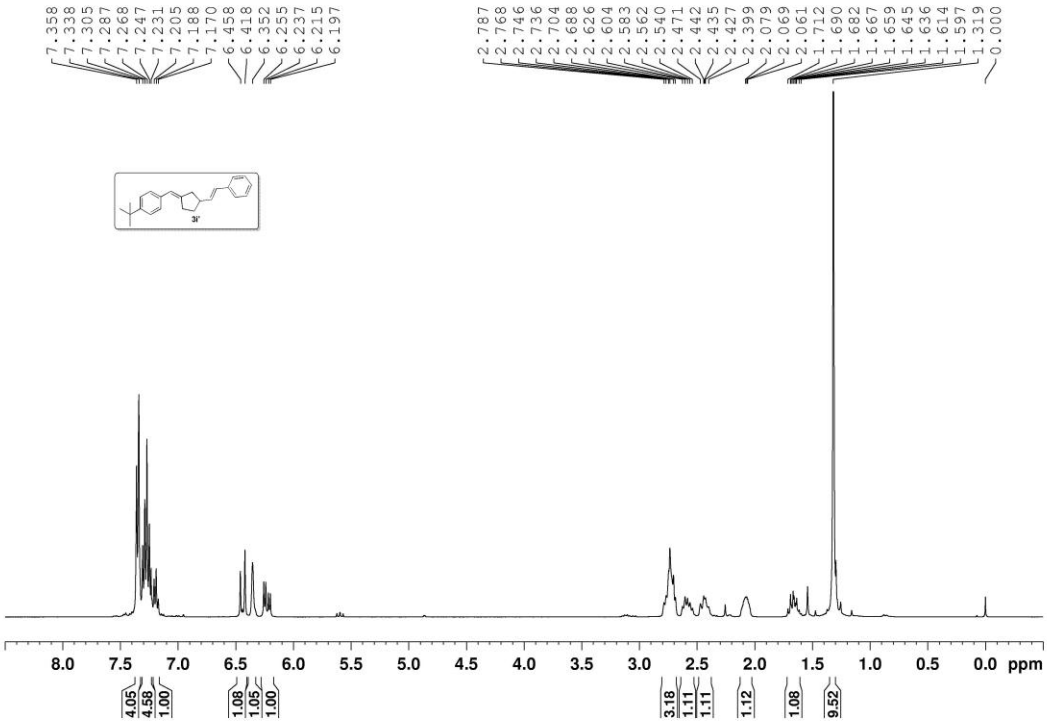
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6.237
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6.197
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2.768
2.746
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2.704
2.688
2.626
2.604
2.583
2.562
2.540
2.471
2.442
2.435
2.427
2.399
2.079
2.069
2.061
1.712
1.690
1.682
1.667
1.659
1.645
1.636
1.614
1.597
1.319
0.000
3r
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
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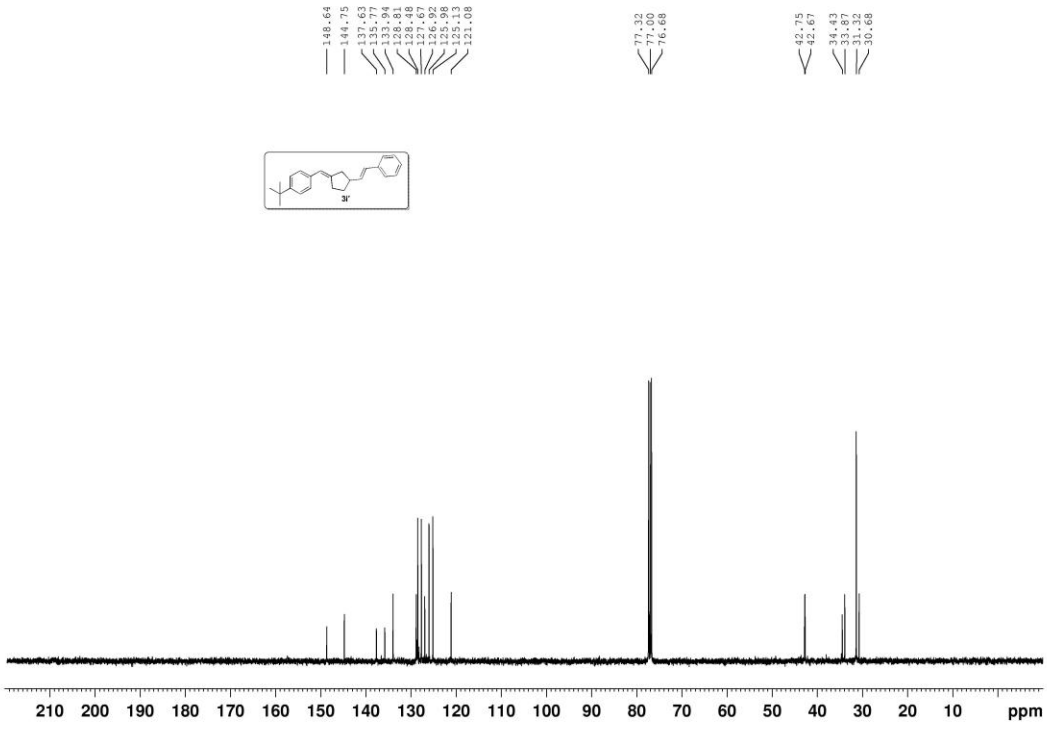
1.08
9.52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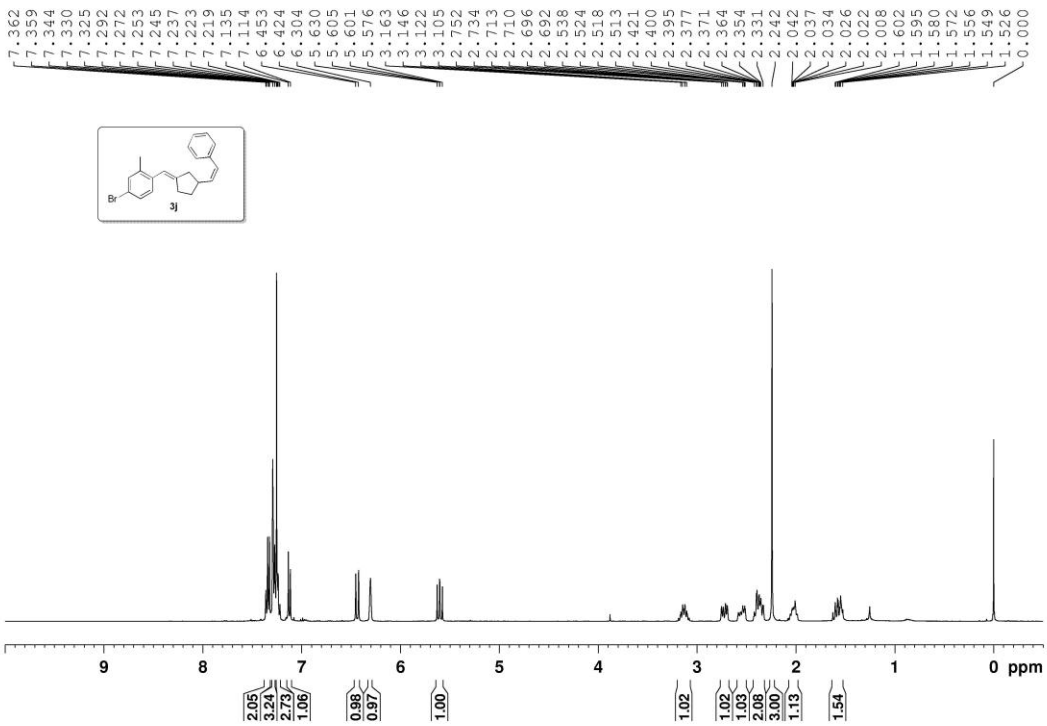
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2.692
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2.524
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2.513
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2.400
2.395
2.377
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2.354
2.331
2.242
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2.037
2.034
2.026
2.022
2.008
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1.595
1.580
1.572
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Br
3j
9
8
7
6
5
4
3
2
1
0 ppm
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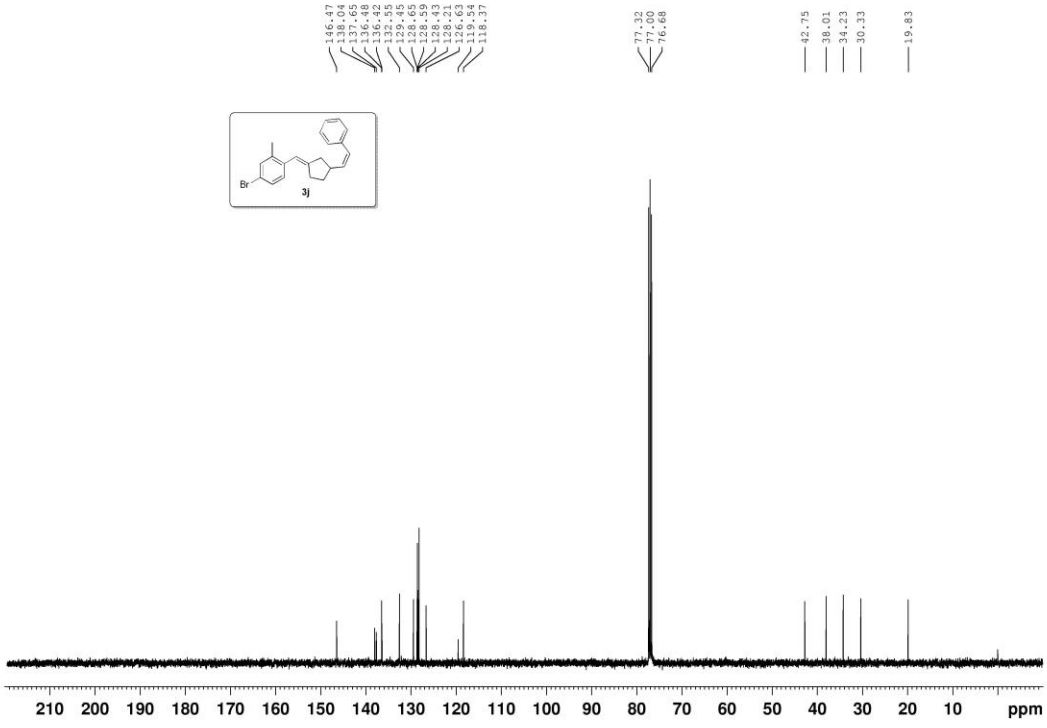
1.13
1.54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30.33
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Br
3j
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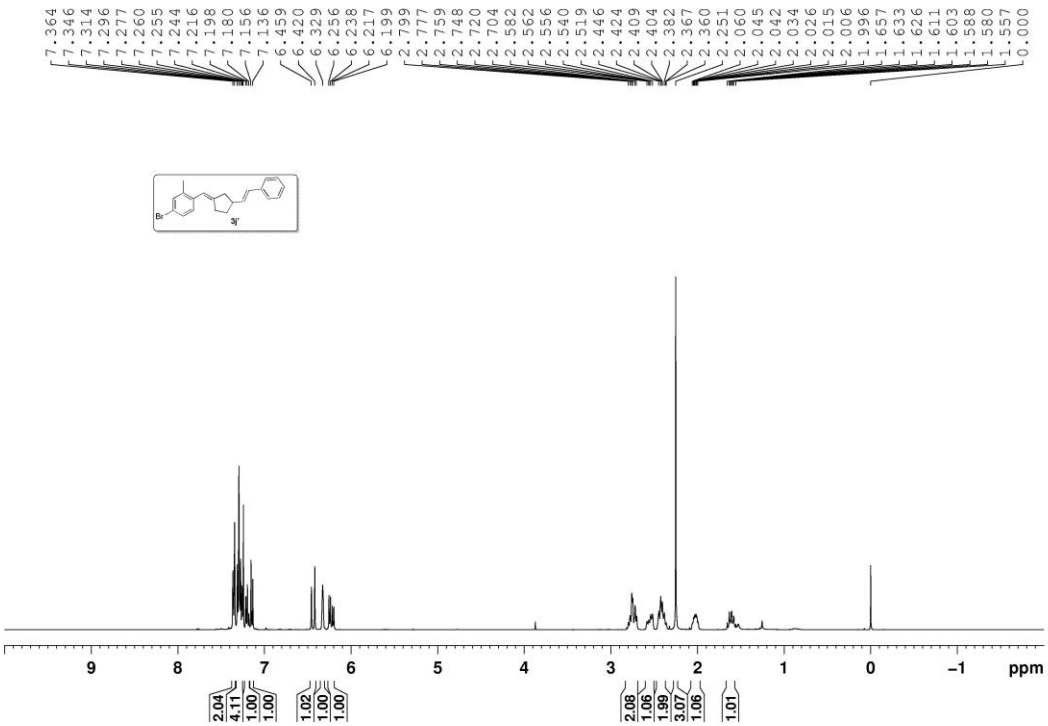
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1.626
1.611
1.603
1.588
1.580
1.557
0.000
Br
3j'
9
8
7
6
5
4
3
2
1
0
−1
ppm
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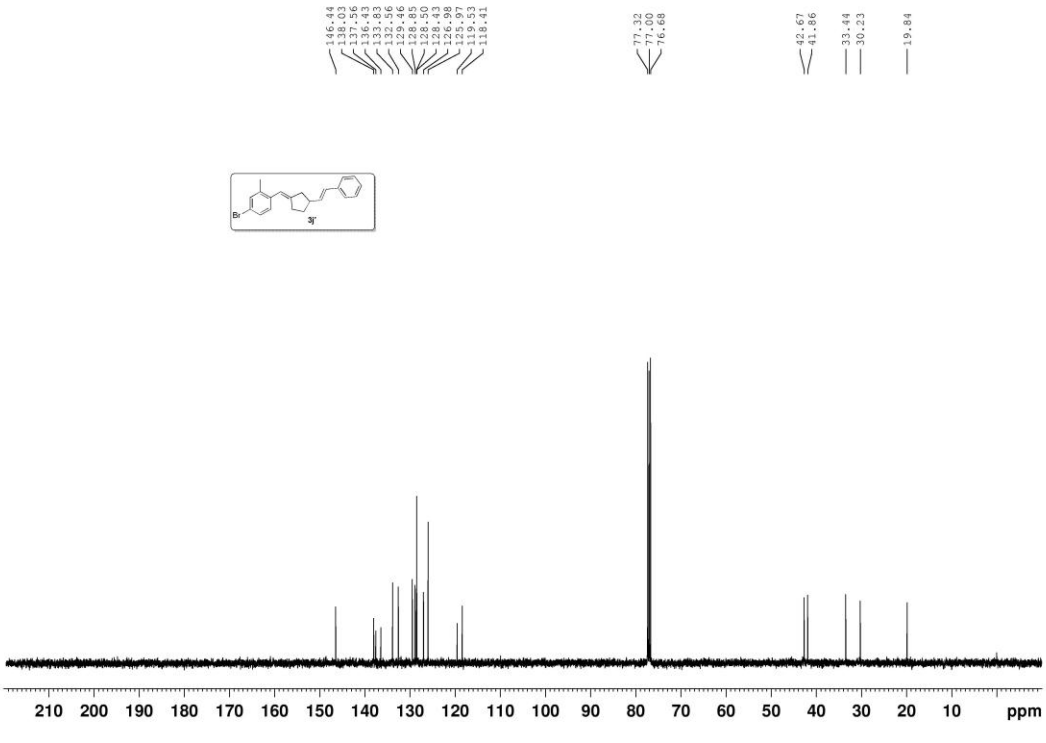
1.01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42.67
41.86
33.44
30.23
19.84
Br
3j'
210
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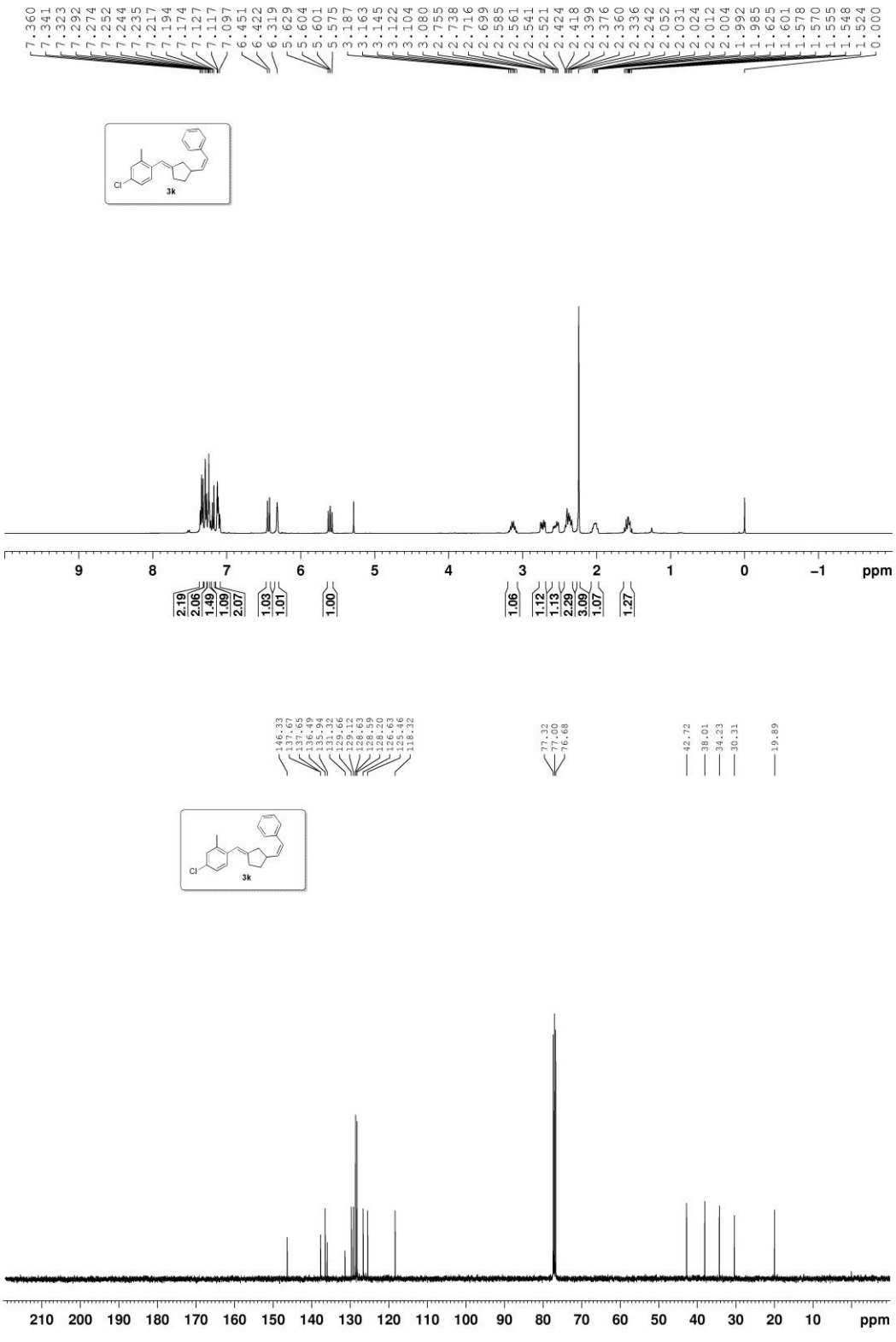
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3.122
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Cl
3k
9
8
7
6
5
4
3
2
1
0
−1
ppm
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1.03
1.01
1.00
1.06
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1.13
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77.32
77.00
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42.72
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19.89
Cl
3k
210
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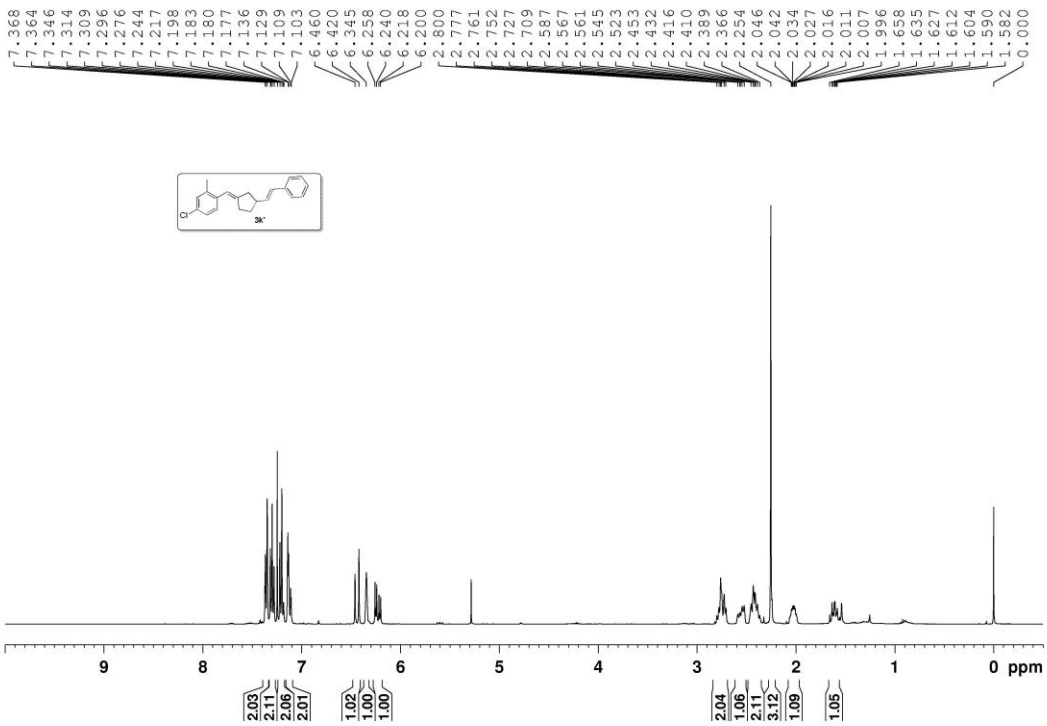
ppm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6.240
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2.042
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2.027
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1.590
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9
8
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6
5
4
3
2
1
0 ppm
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1.00
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1.06
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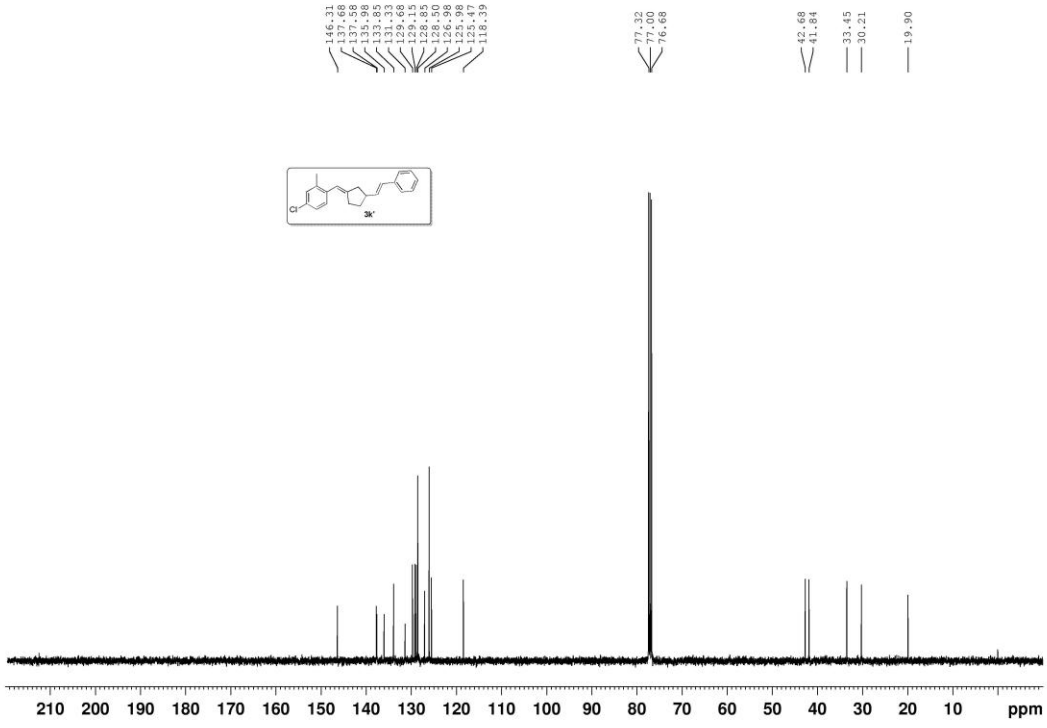
3.12
1.09
1.05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77.00
76.68
42.68
41.84
33.45
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19.90
3k'
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120
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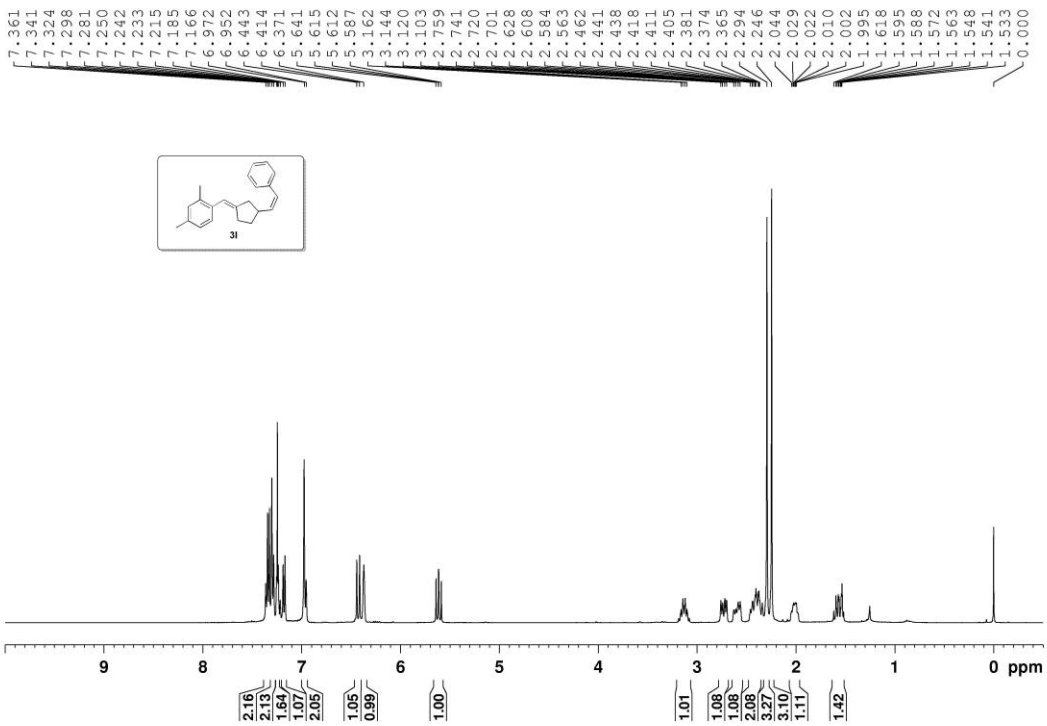
30
20
10
ppm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9
8
7
6
5
4
3
2
1
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2.13
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1.07
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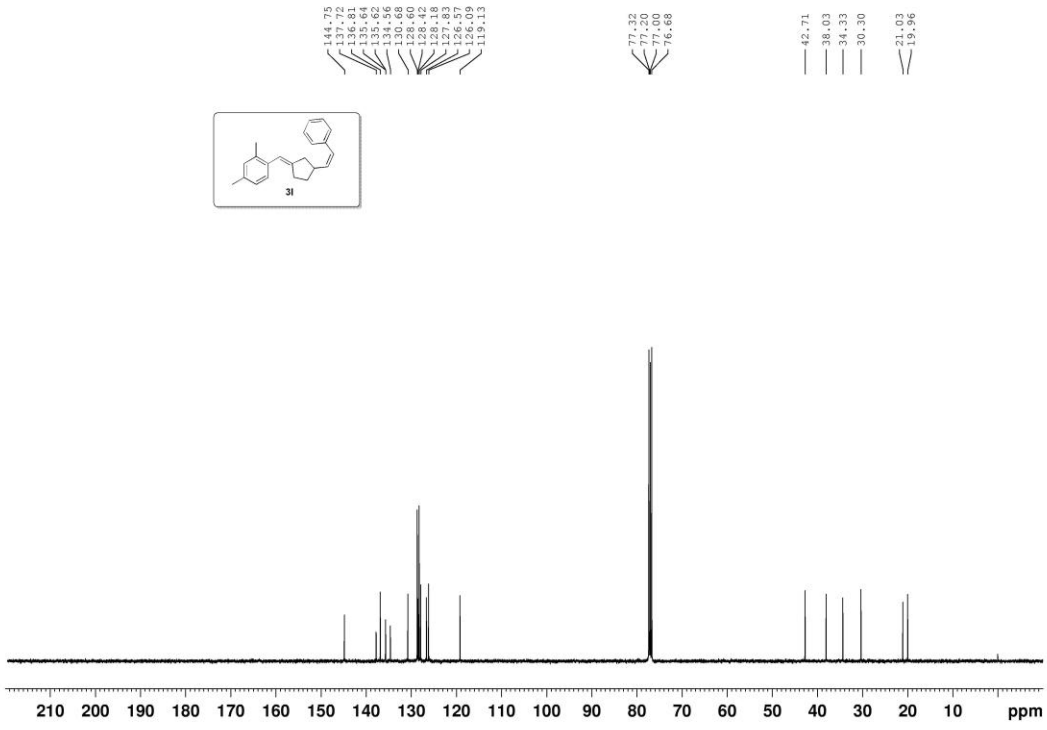
1.42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19.96
3l
210
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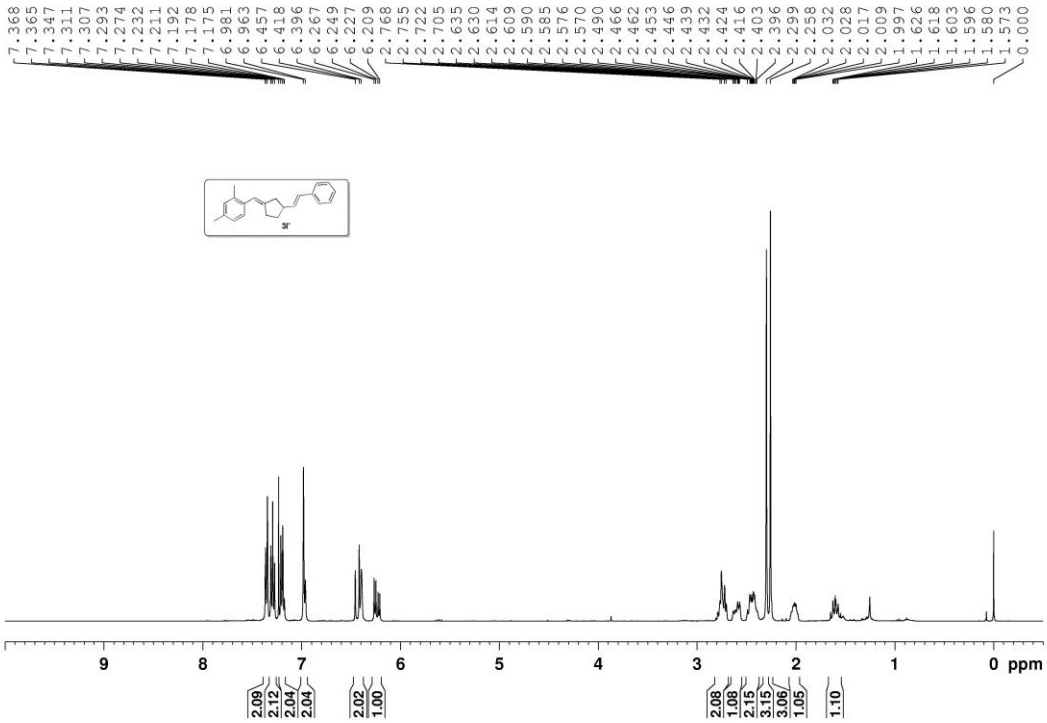
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3H'
9
8
7
6
5
4
3
2
1
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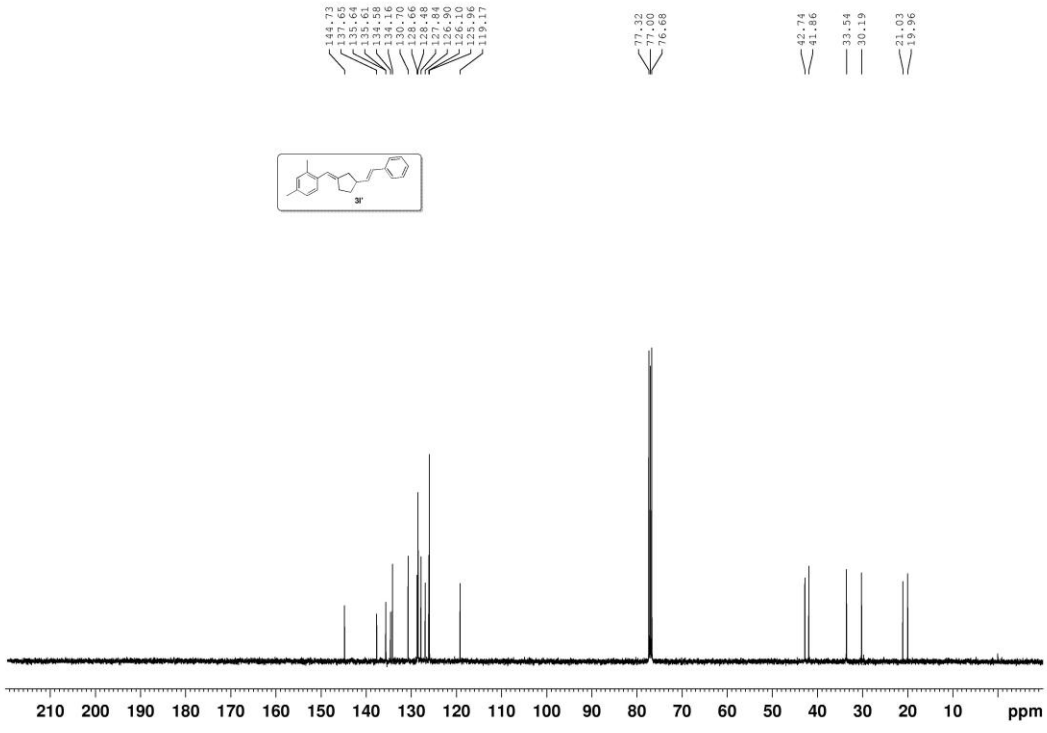
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21.03
19.96
3H'
210
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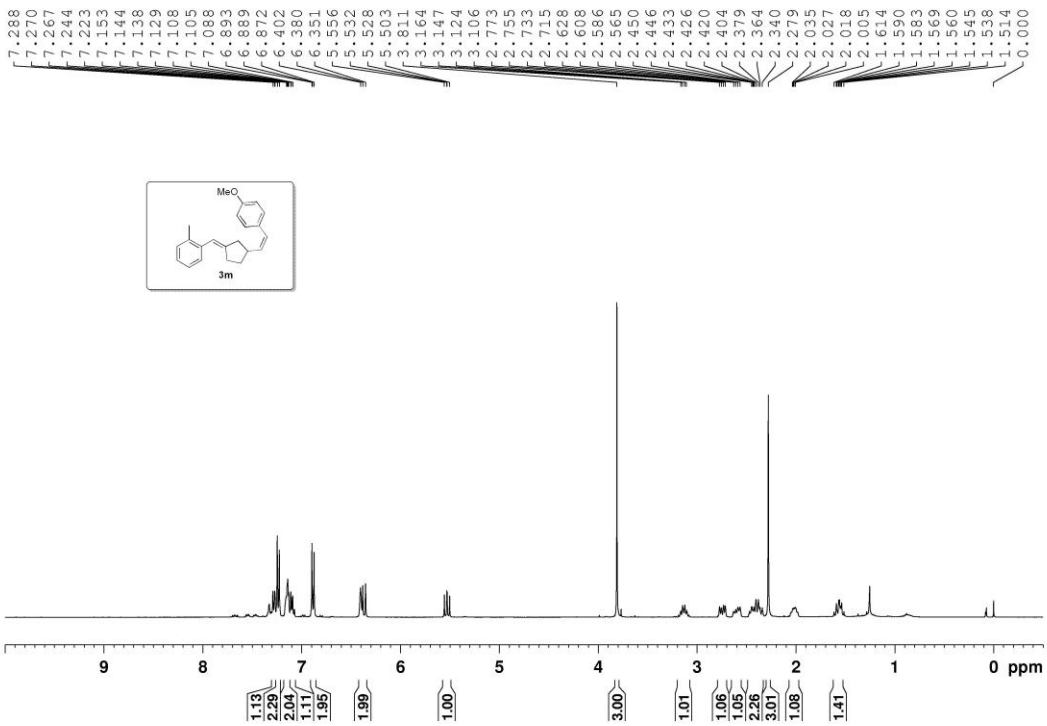
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MeO
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8
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6
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4
3
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1
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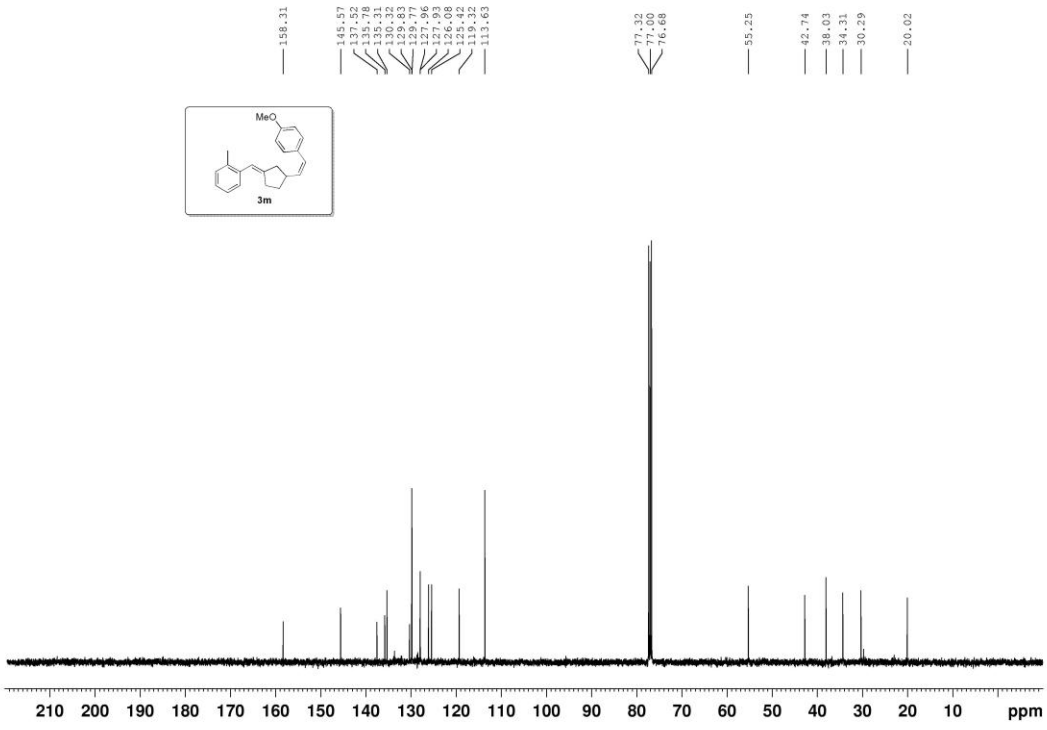
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30.29
20.02
MeO
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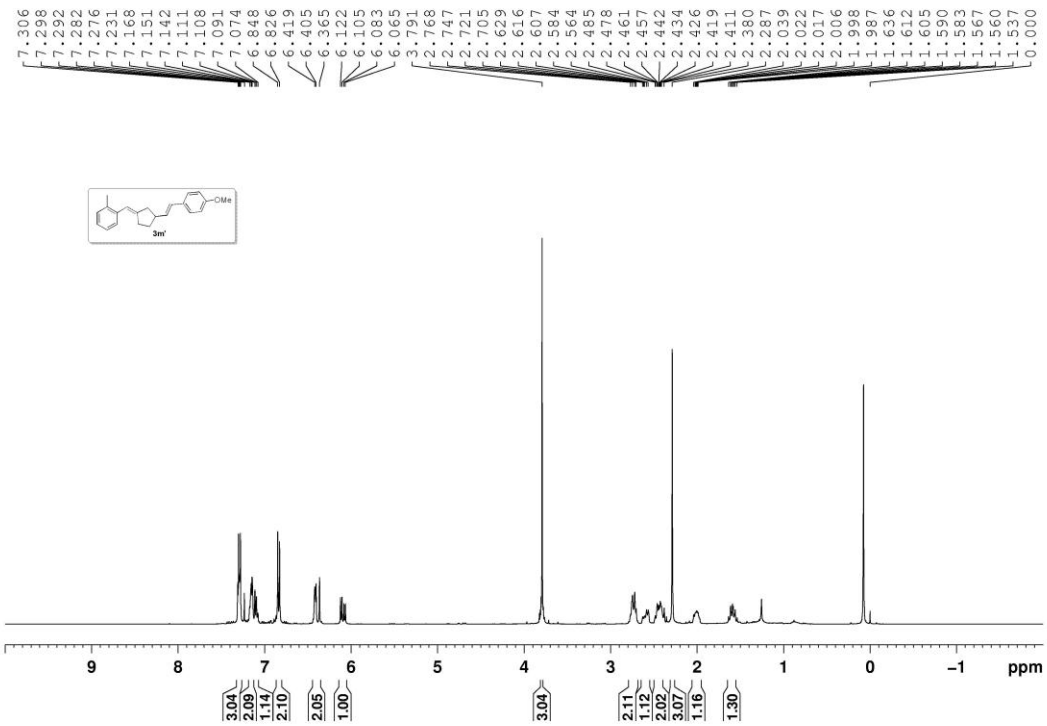
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1.590
1.583
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OMe
3m'
9
8
7
6
5
4
3
2
1
0
−1
ppm
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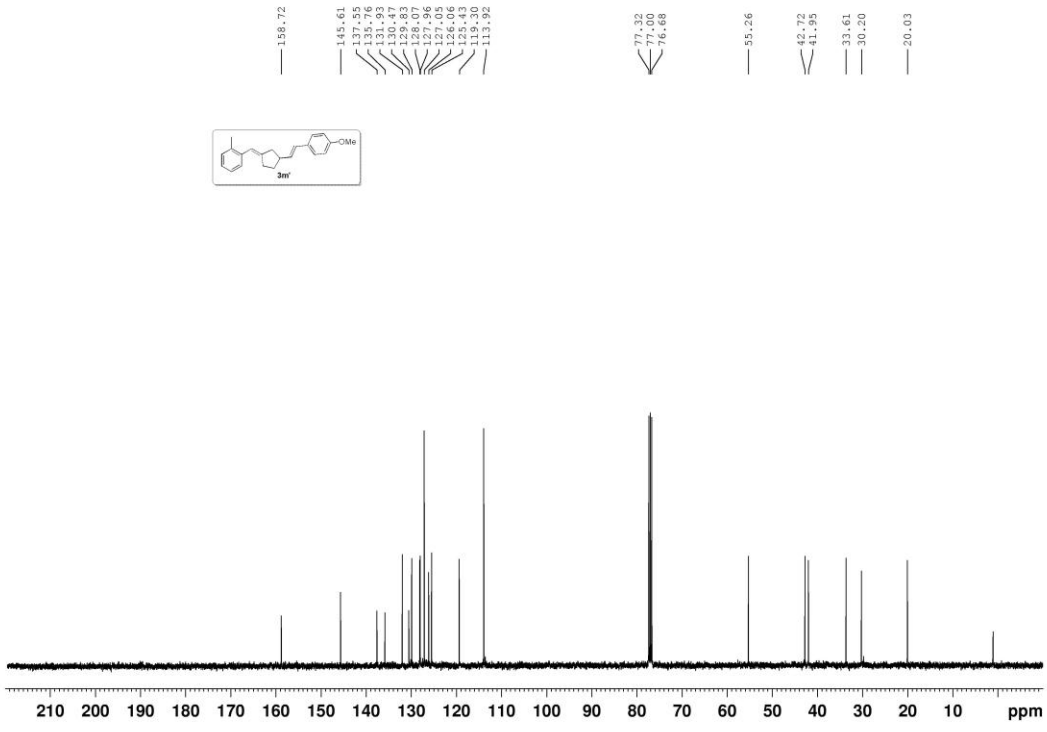
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77.00
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55.26
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41.95
33.61
30.20
20.03
OMe
3m'
210
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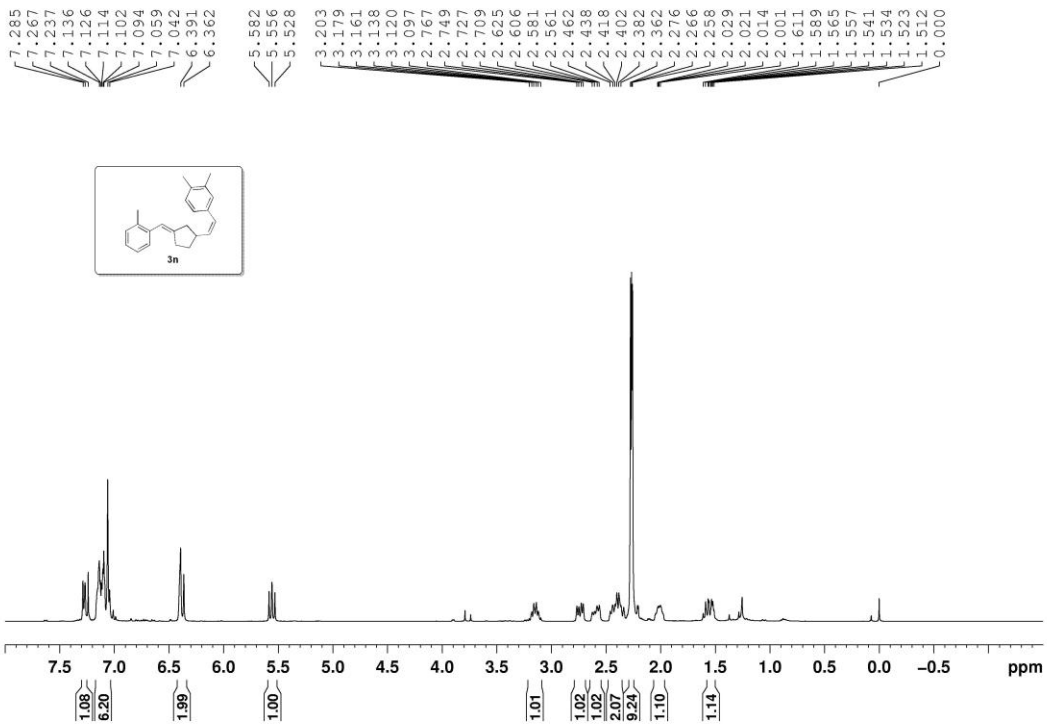
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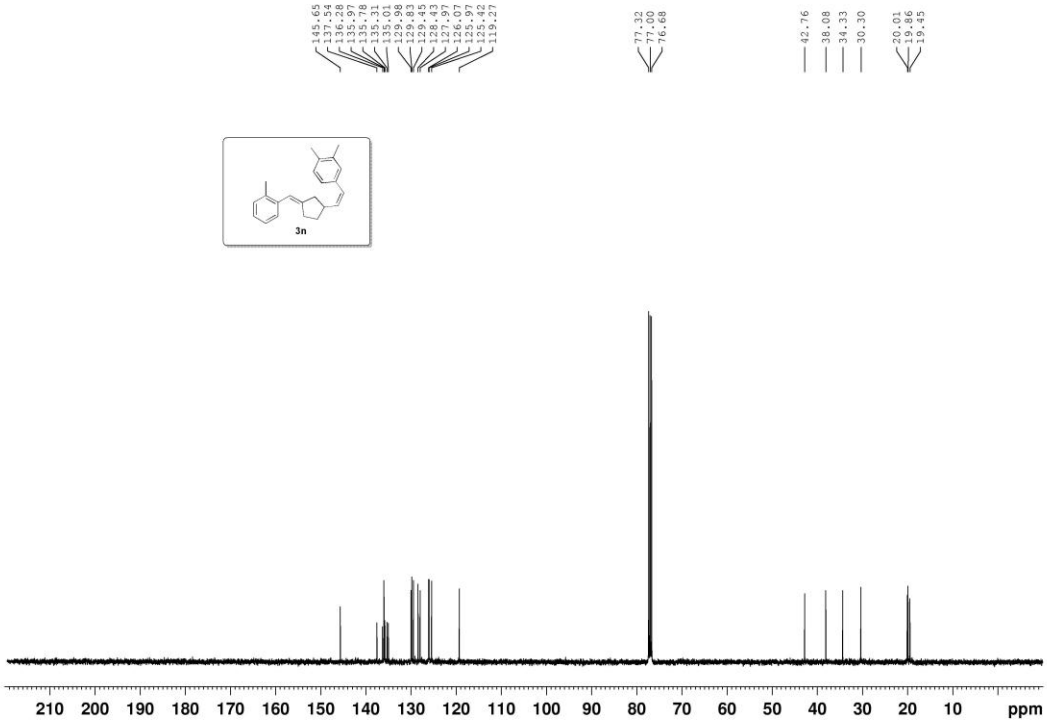
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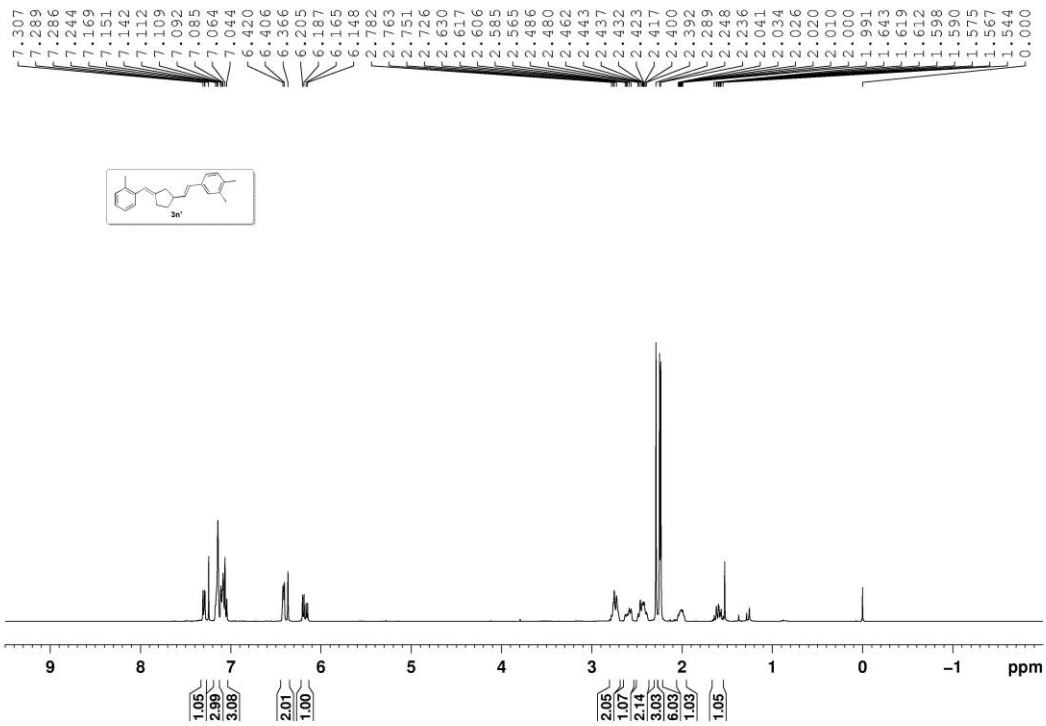
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2.010
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3n'
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5
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−1
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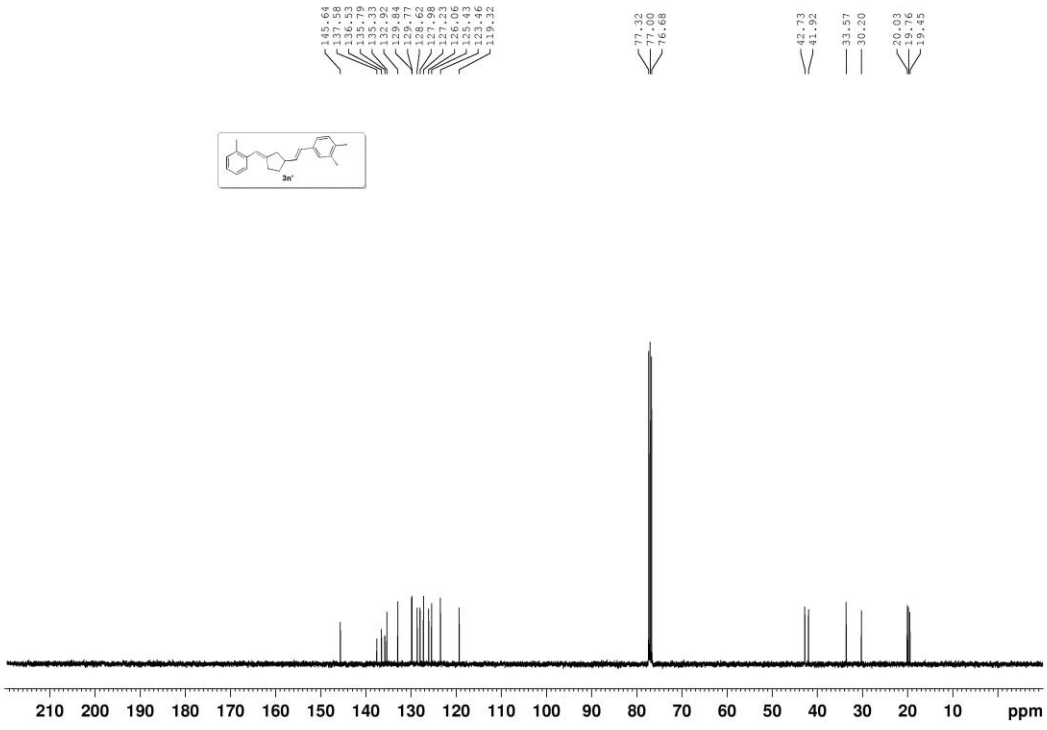
1.03
1.05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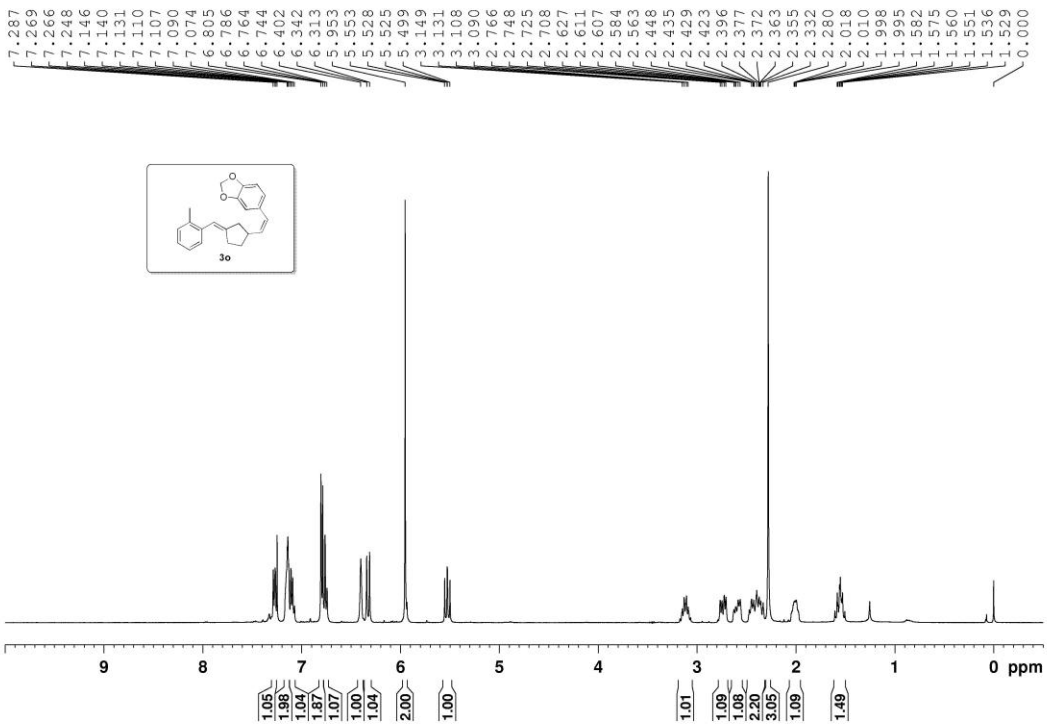
ppm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2.563
2.448
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2.423
2.396
2.377
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2.363
2.355
2.332
2.280
2.018
2.010
1.998
1.995
1.582
1.575
1.560
1.551
1.536
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3o
9
8
7
6
5
4
3
2
1
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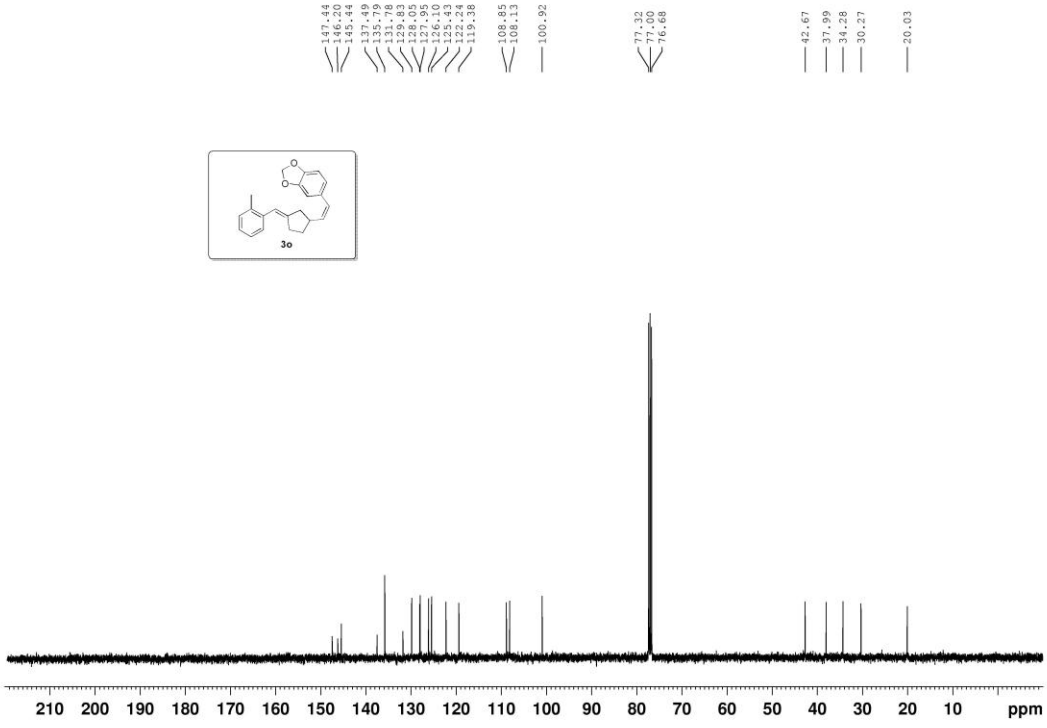
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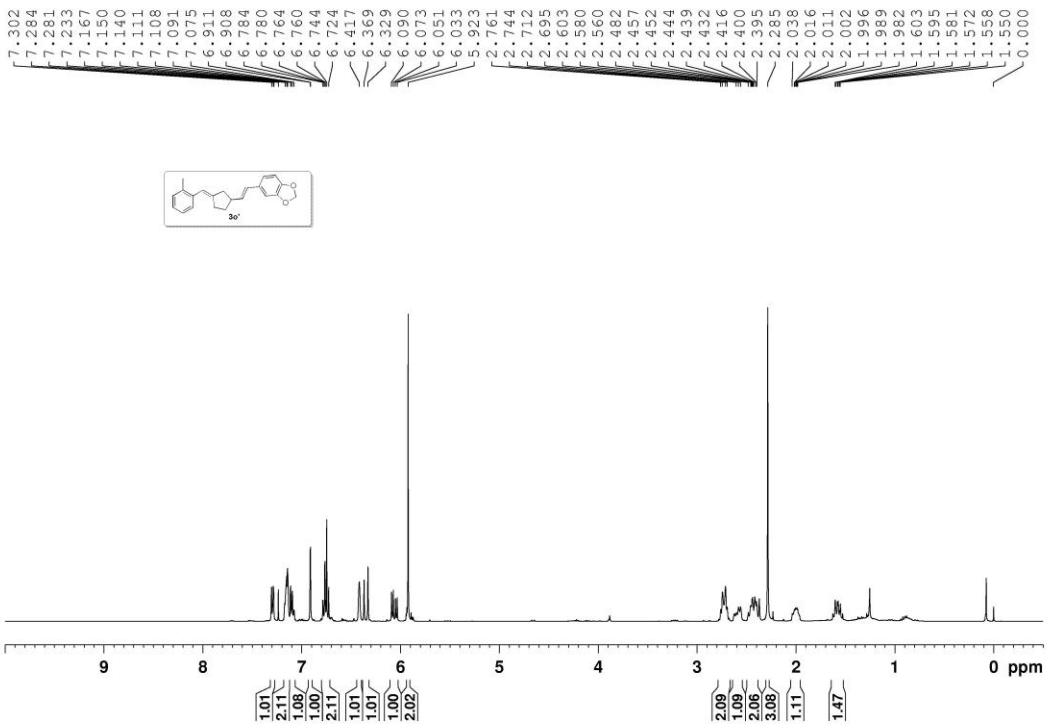
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9
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6
5
4
3
2
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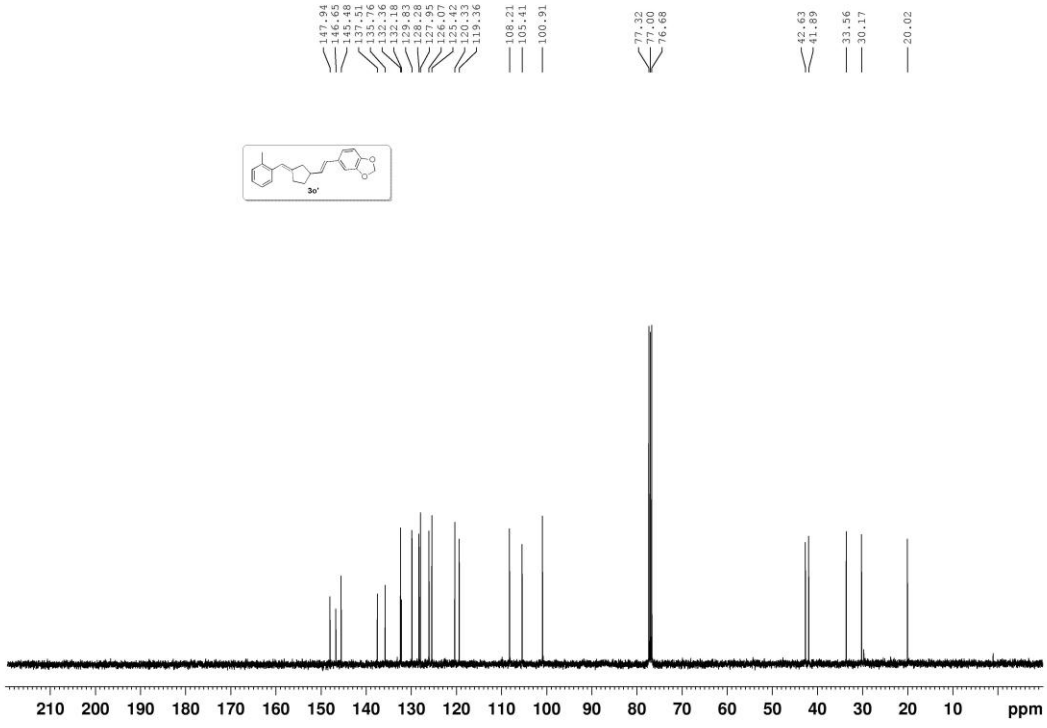
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20.02
3o'
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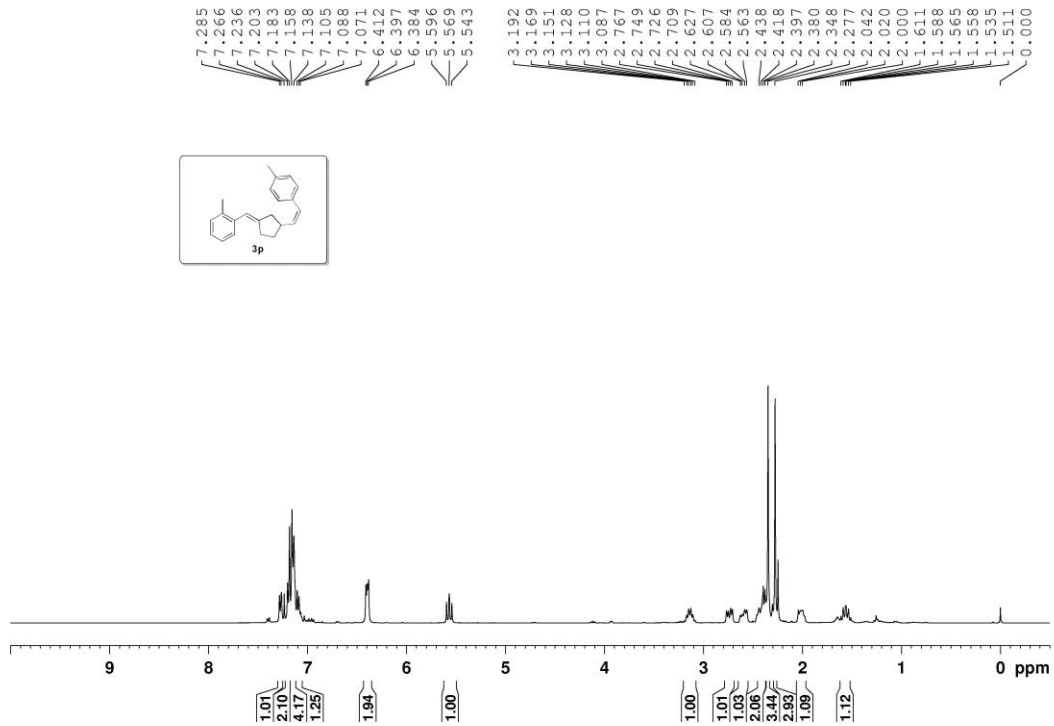
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3.169
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3.110
3.087
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2.726
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2.627
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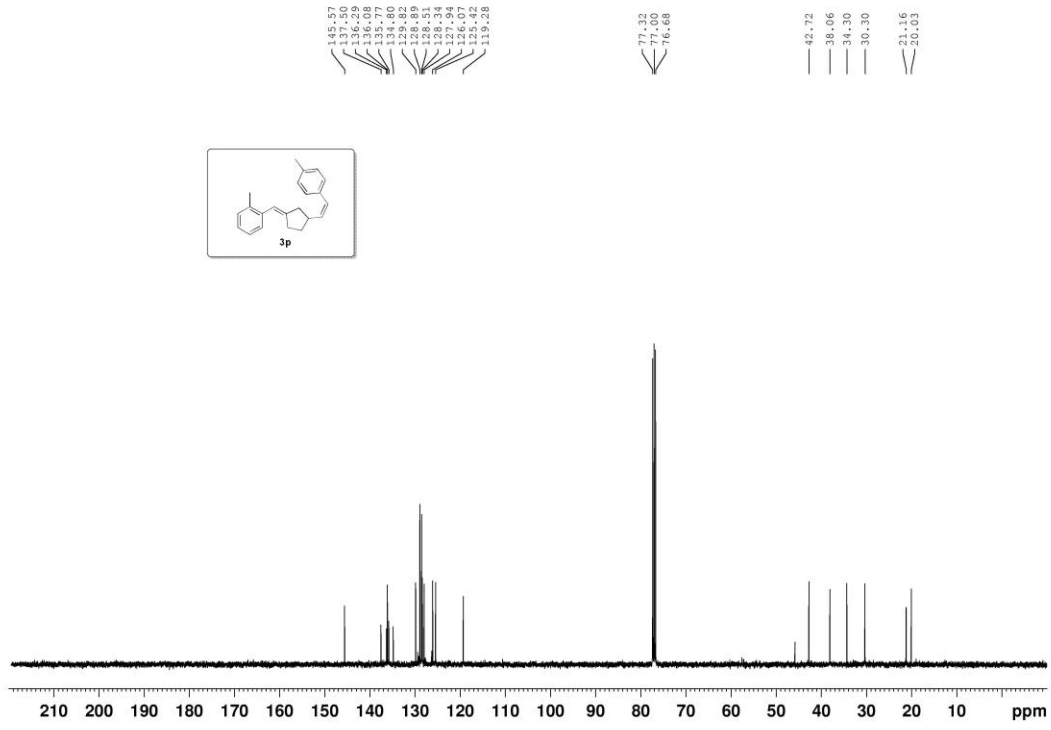
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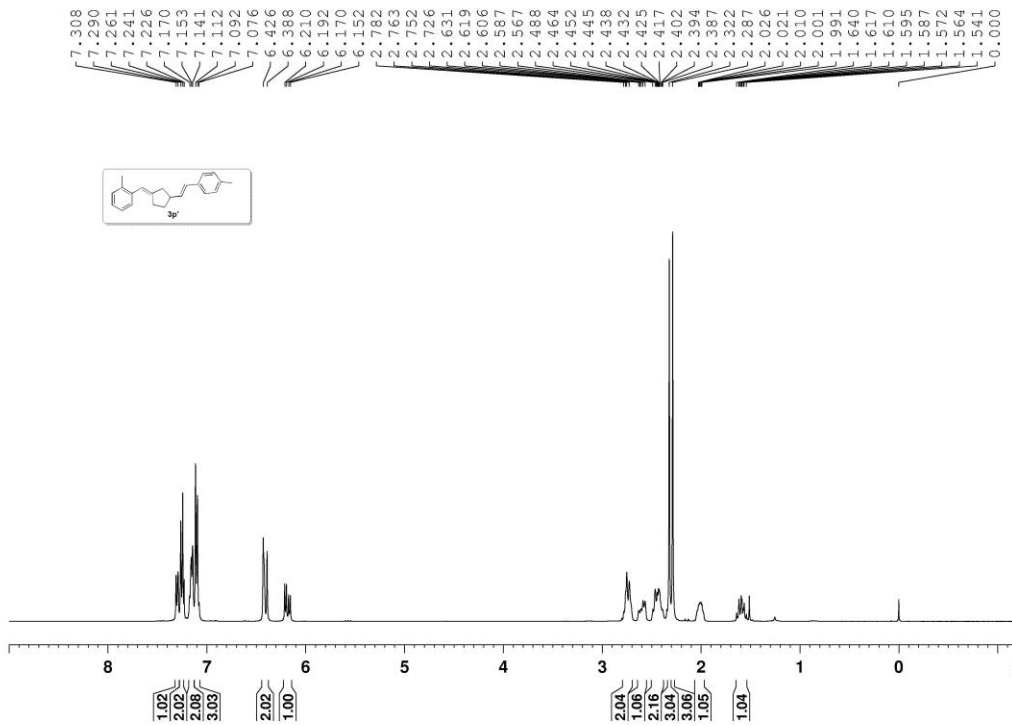
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6.192
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5
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1
0
ppm
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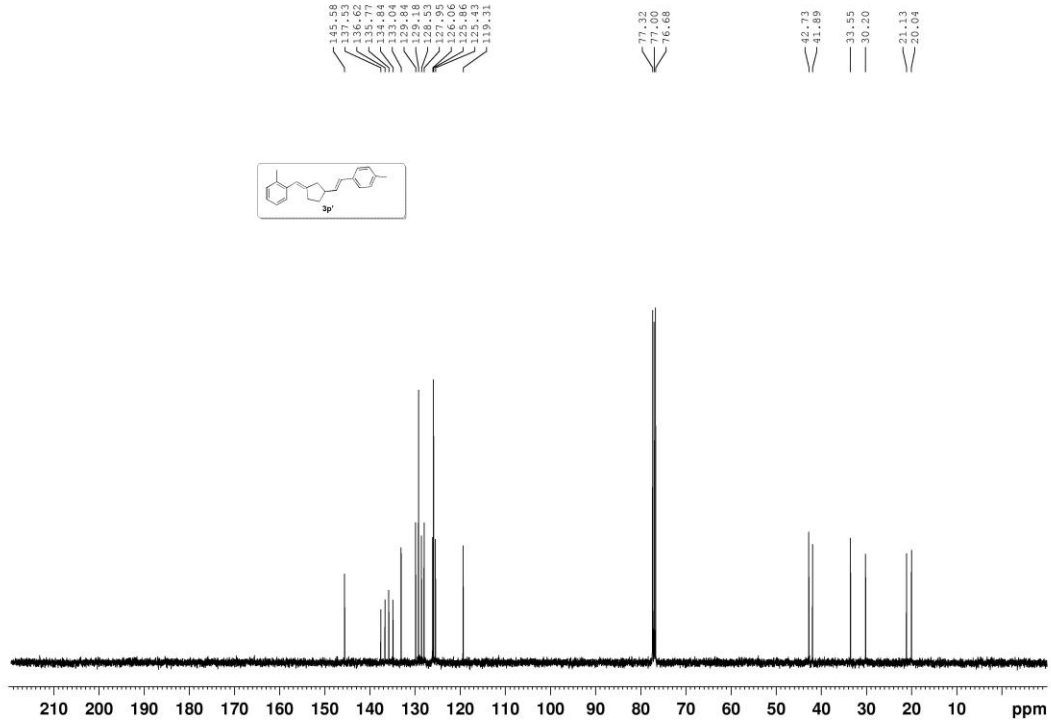
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42.73
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21.13
20.04
3p'
210
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150
140
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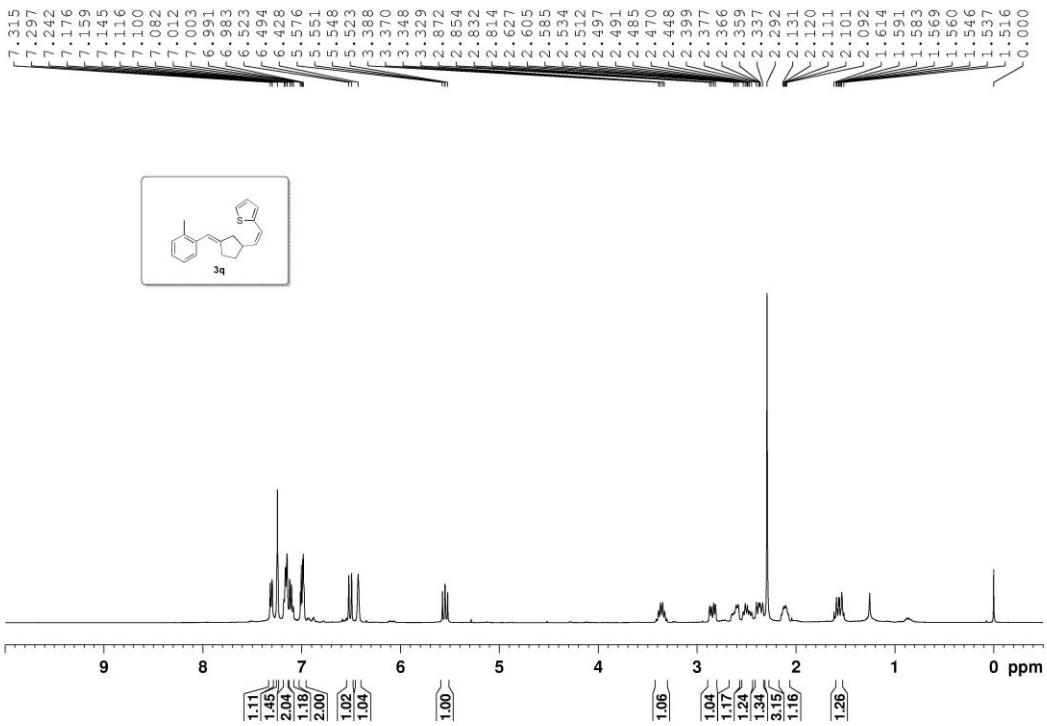
ppm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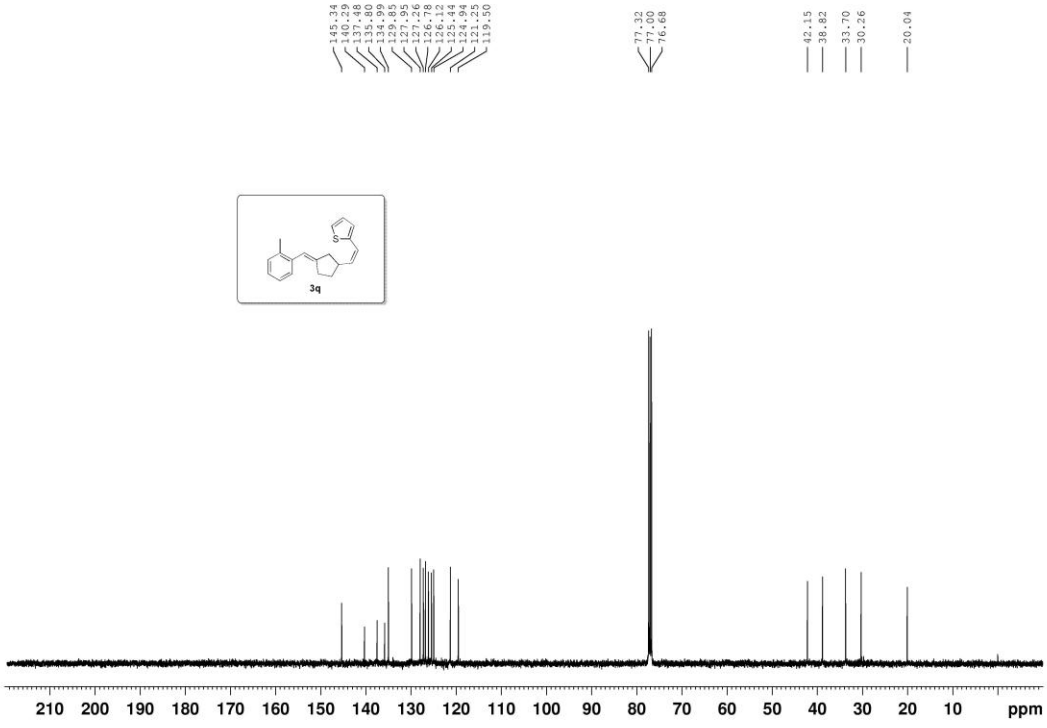
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77.00
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42.15
38.82
33.70
30.26
20.04
3q
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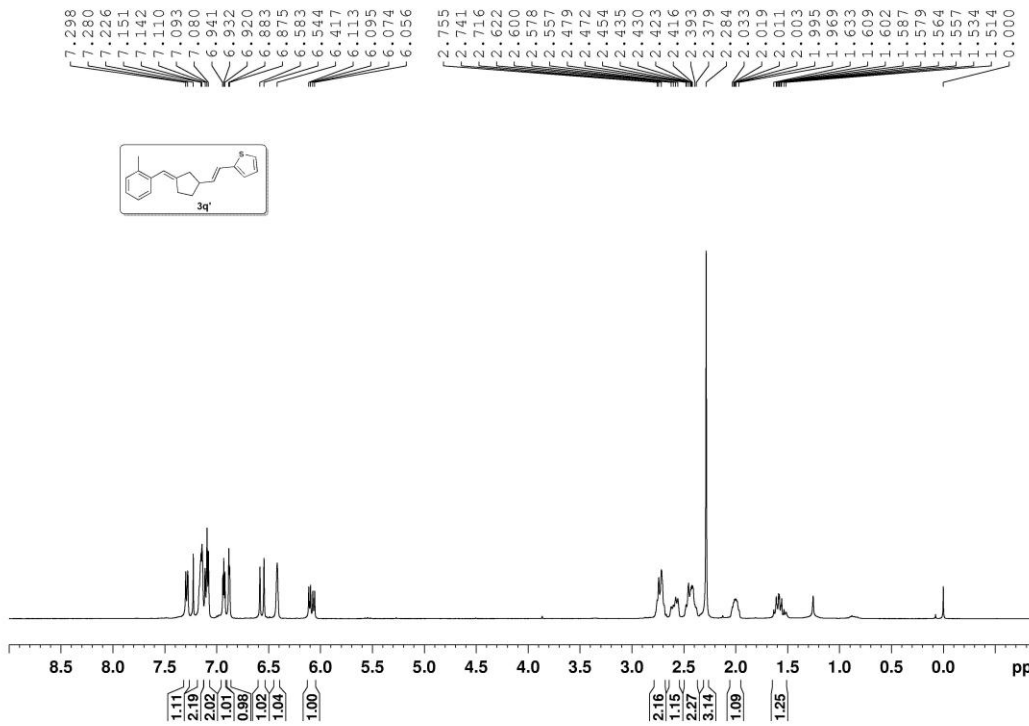
ppm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1.602
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3q'
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
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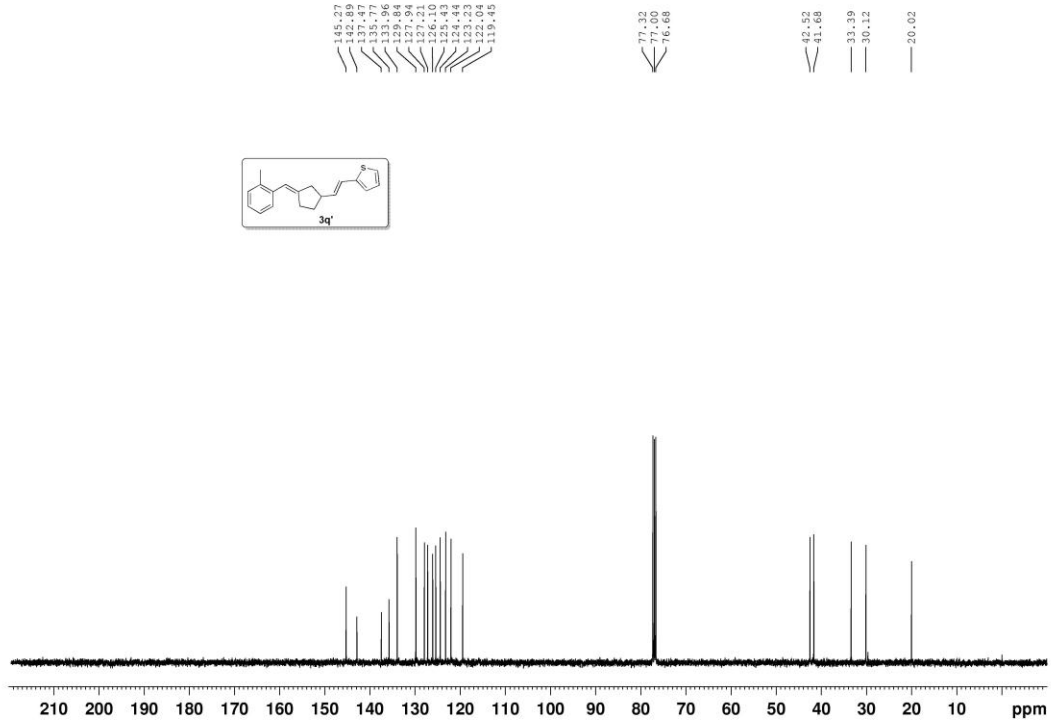
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77.00
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3q'
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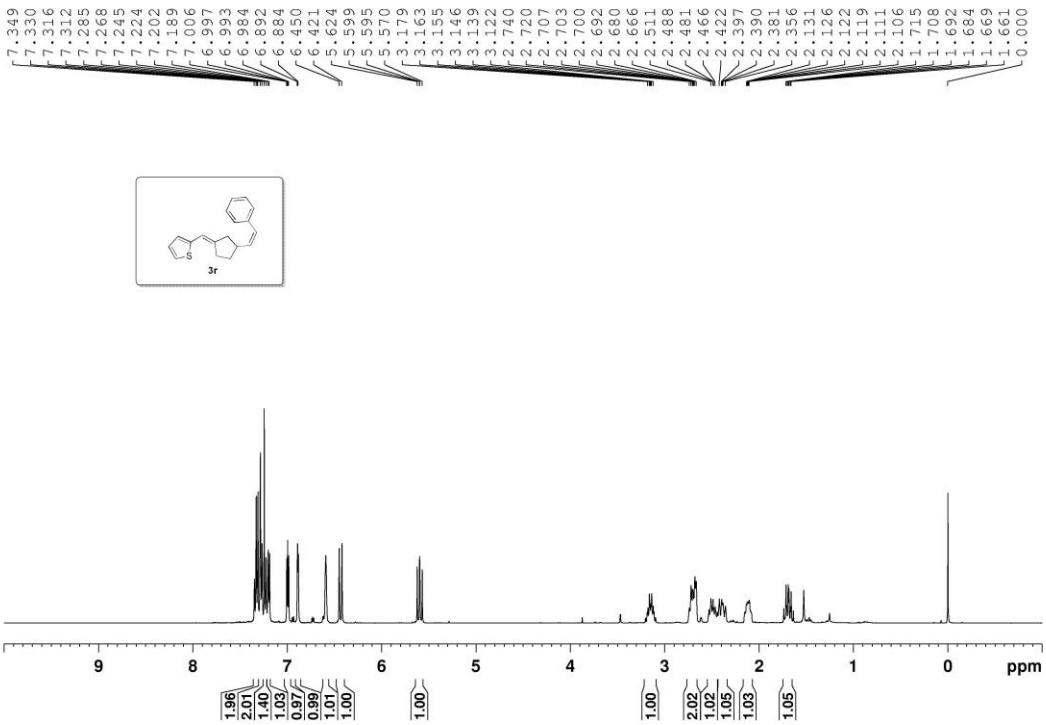
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5.570
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2.720
2.707
2.703
2.700
2.692
2.680
2.666
2.511
2.488
2.481
2.466
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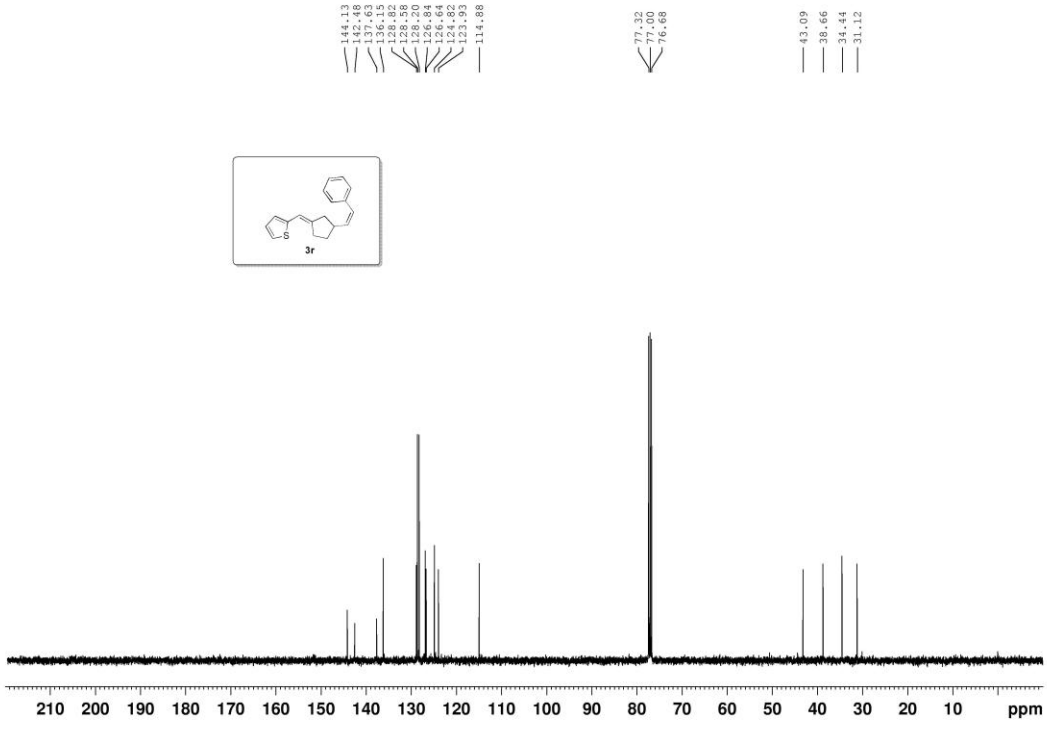
1.03
1.05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31.12
3r
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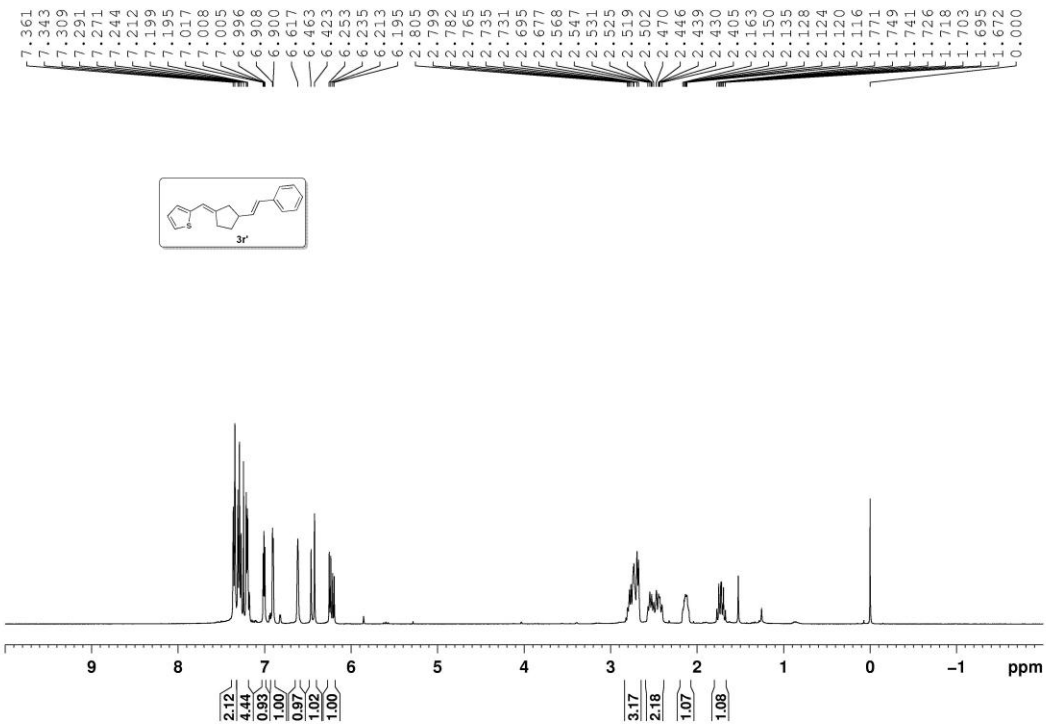
ppm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2.765
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2.731
2.695
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2.568
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2.531
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2.519
2.502
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3r'
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8
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6
5
4
3
2
1
0
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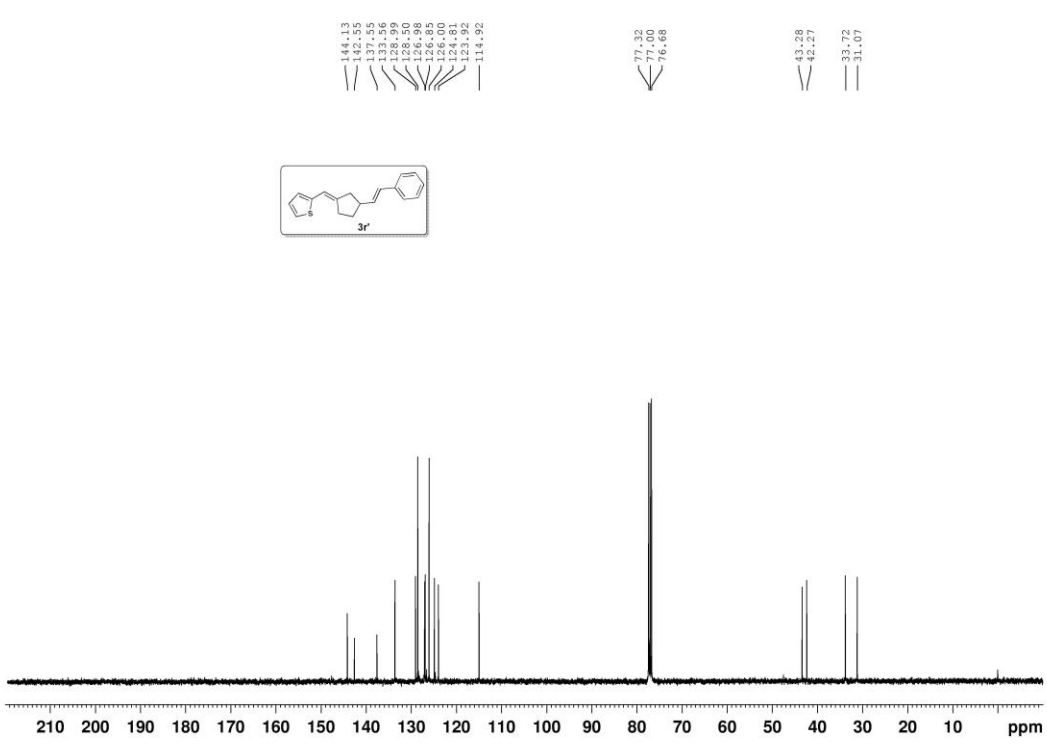
1.08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77.00
76.68
43.28
42.27
33.72
31.07
3r'
210
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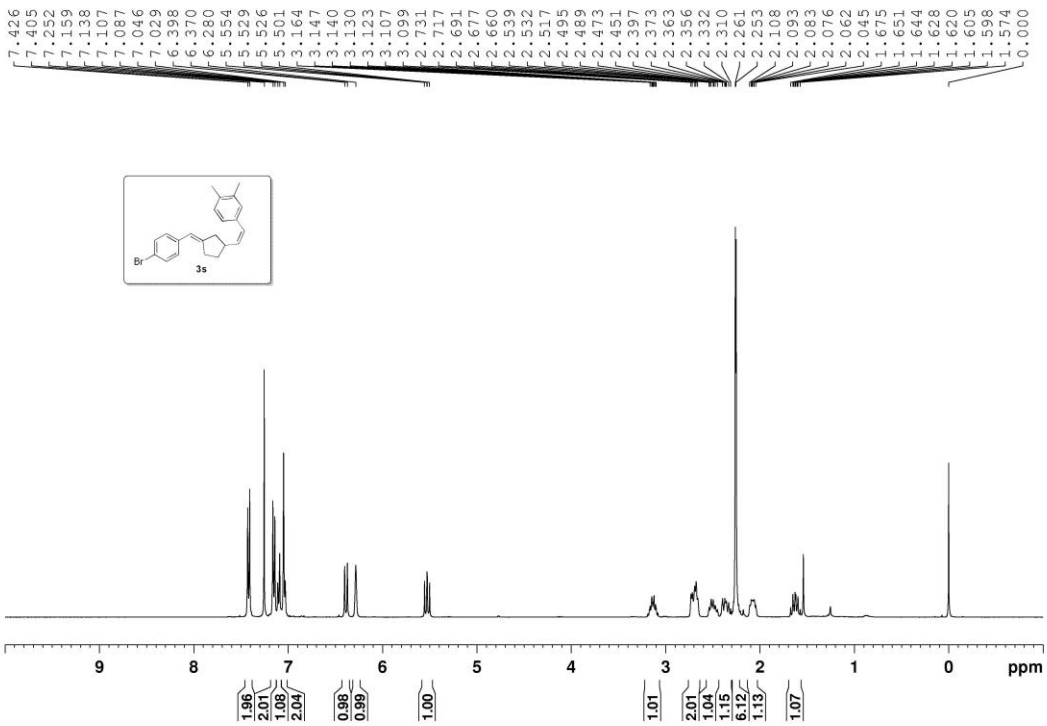
ppm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Br
3s
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ppm
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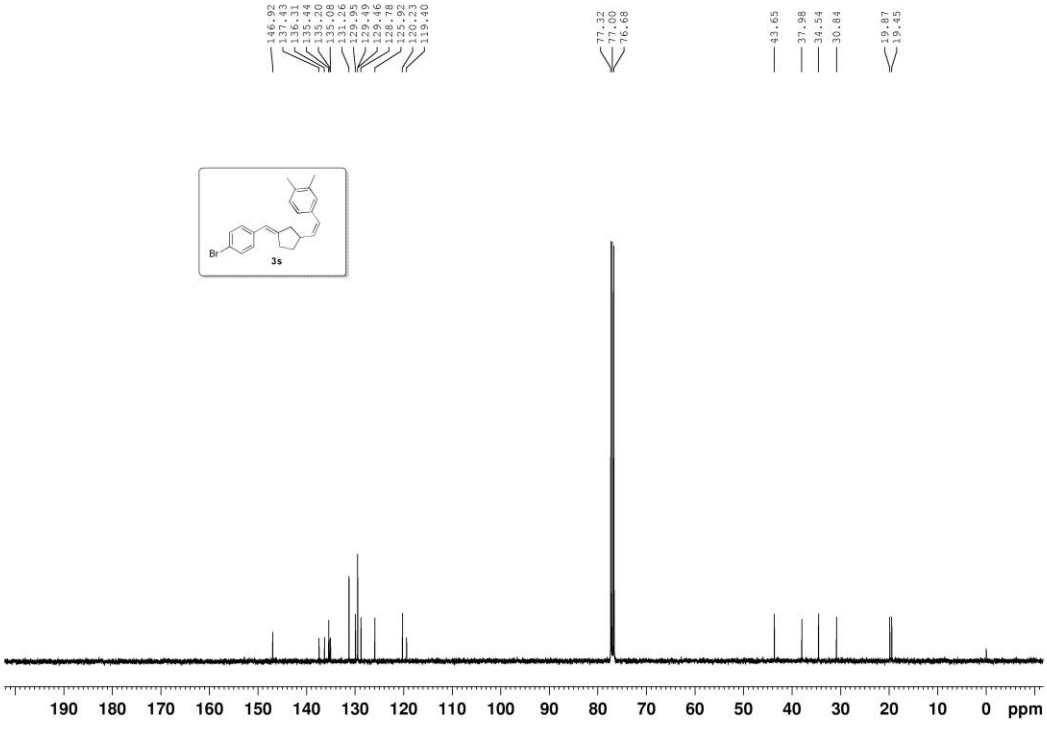
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77.32
77.00
76.68
43.65
37.98
34.54
30.84
19.87
19.45
Br
3s
190
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130
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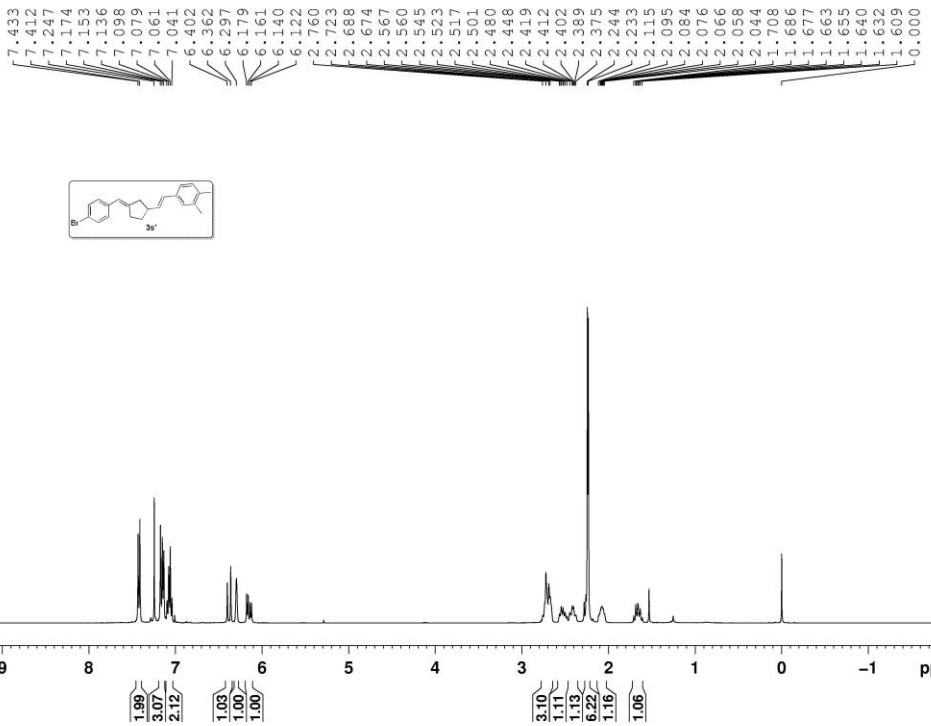
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6.362
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6.179
6.161
6.140
6.122
2.760
2.723
2.688
2.674
2.567
2.560
2.545
2.523
2.517
2.501
2.480
2.448
2.419
2.412
2.402
2.389
2.375
2.244
2.233
2.115
2.095
2.084
2.076
2.066
2.058
2.044
1.708
1.686
1.677
1.663
1.655
1.640
1.632
1.609
0.000
Br
3s'
9
8
7
6
5
4
3
2
1
0
−1
ppm
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2.12
1.03
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1.00
3.10
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1.13
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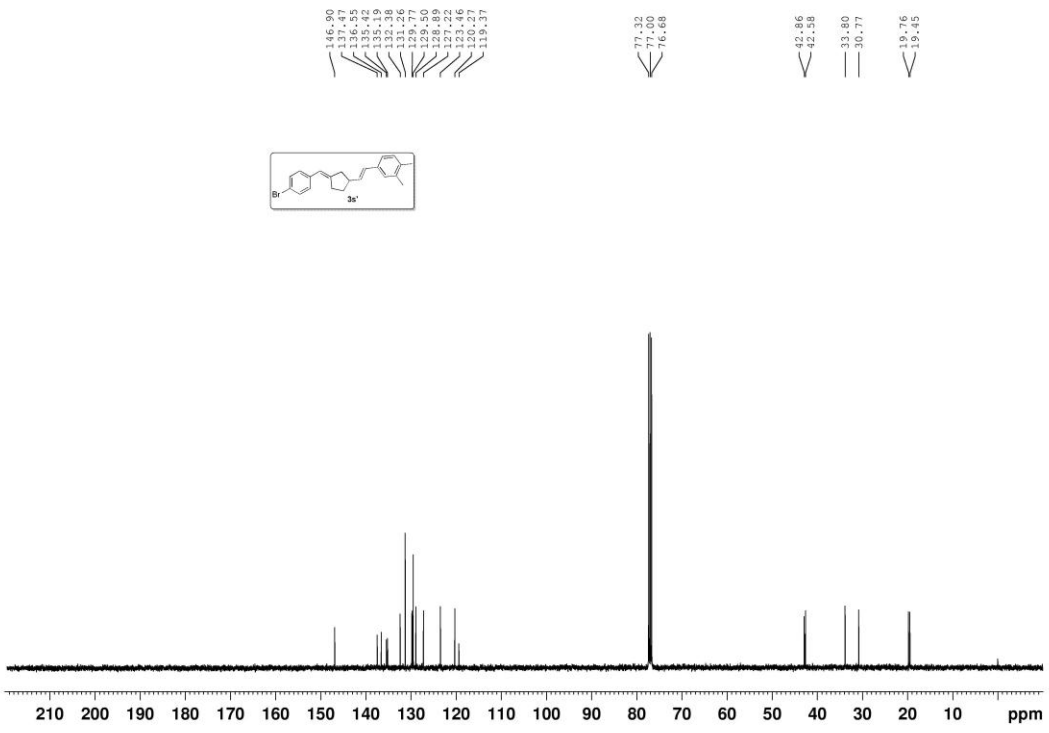
1.06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120.27
119.37
77.32
77.00
76.68
42.86
42.58
33.80
30.77
19.76
19.45
Br
3s'
210
200
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150
140
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120
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100
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80
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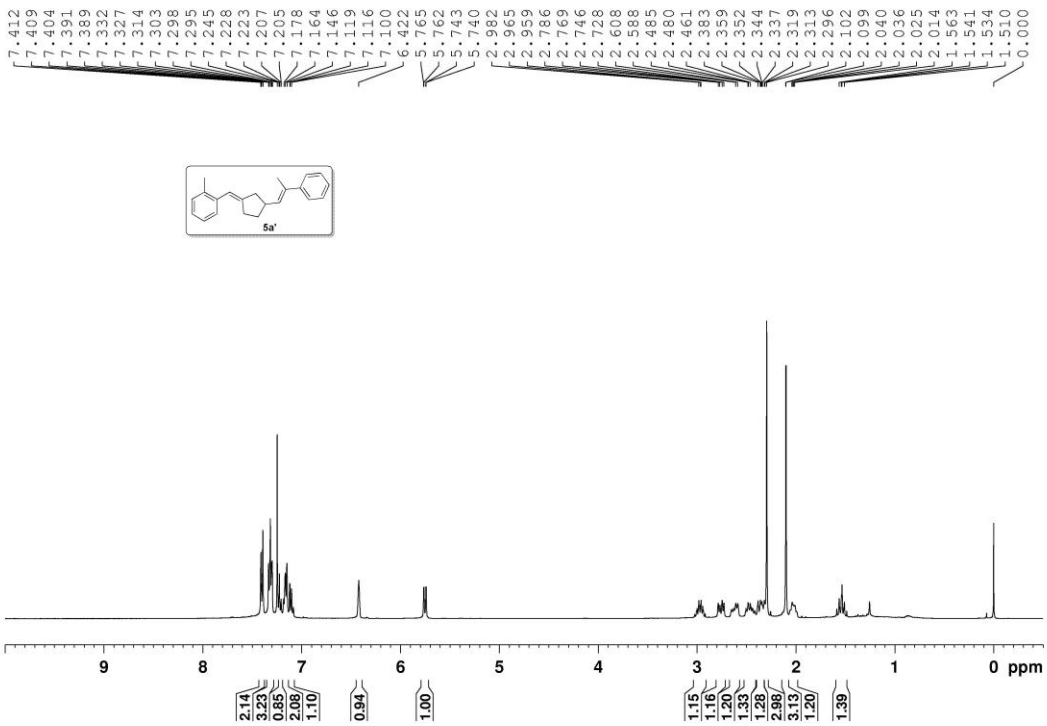
20
10
ppm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7.295
7.245
7.228
7.223
7.207
7.205
7.178
7.164
7.146
7.119
7.116
7.100
6.422
5.765
5.762
5.743
5.740
2.982
2.965
2.959
2.786
2.769
2.746
2.728
2.608
2.588
2.485
2.480
2.461
2.383
2.359
2.352
2.344
2.337
2.319
2.313
2.296
2.102
2.099
2.040
2.036
2.025
2.014
1.563
1.541
1.534
1.510
0.000
5a'
9
8
7
6
5
4
3
2
1
0 ppm
2.14
3.23
0.85
2.08
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1.28
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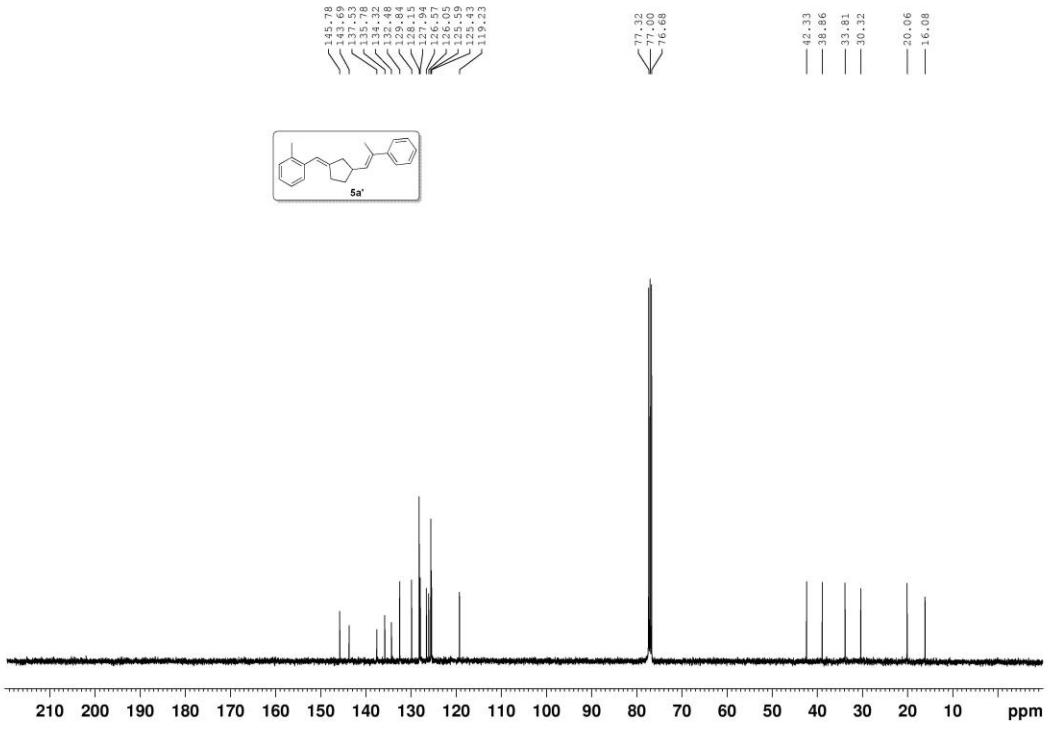
1.39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128.55
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126.57
126.05
125.59
125.43
119.23
77.32
77.00
76.68
42.33
38.86
33.81
30.32
20.06
16.08
5a'
210
200
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180
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150
140
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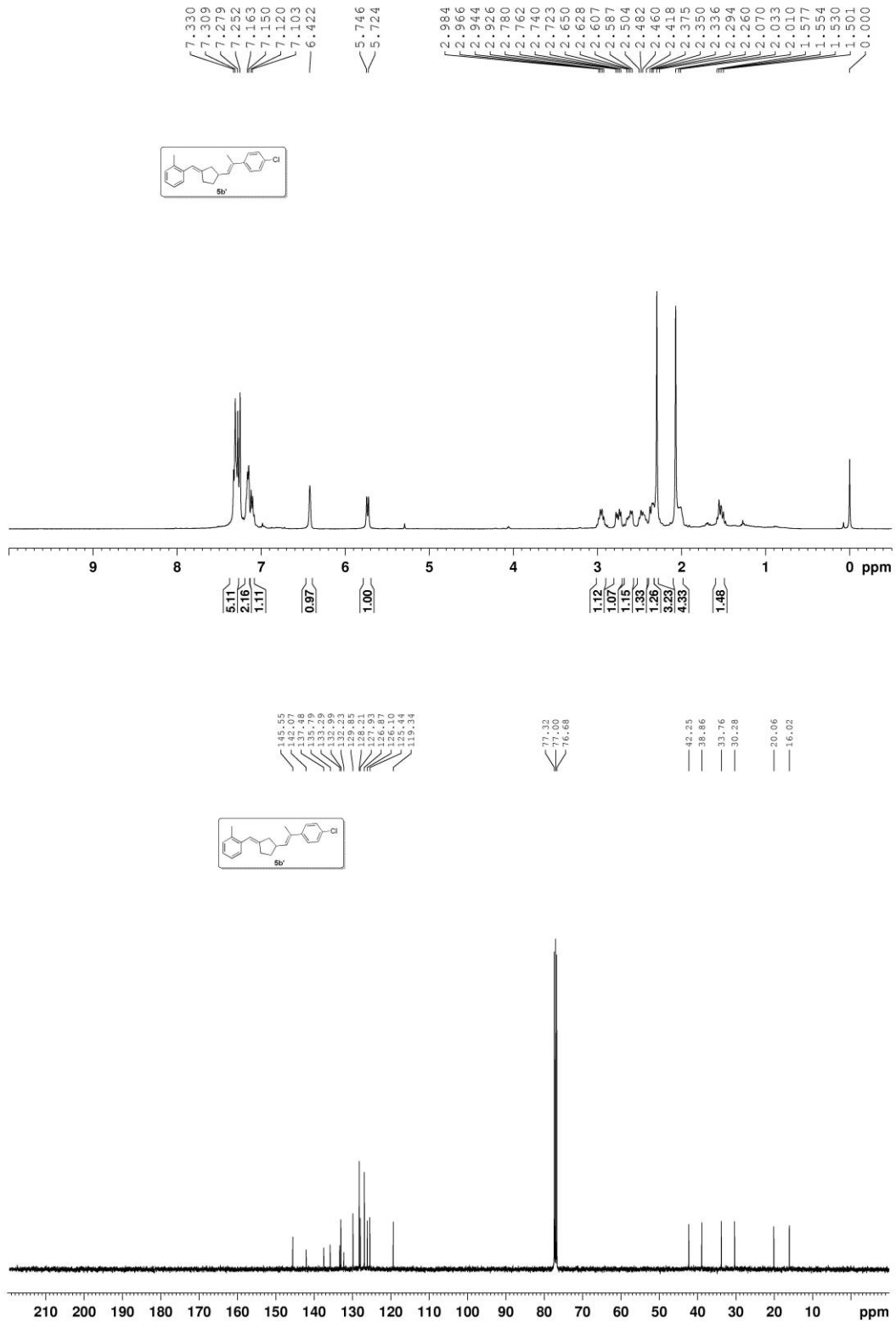
30
20
10
ppm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7.150
7.120
7.103
6.422
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5.724
2.984
2.966
2.944
2.926
2.780
2.762
2.740
2.723
2.650
2.628
2.607
2.587
2.504
2.482
2.460
2.418
2.375
2.350
2.336
2.294
2.260
2.070
2.033
2.010
1.577
1.554
1.530
1.501
0.000
Cl
5b'
9
8
7
6
5
4
3
2
1
0 ppm
5.11
2.16
1.11
0.97
1.00
1.12
1.07
1.15
1.33
1.26
3.23
4.33
1.48
145.55
140.20
137.48
135.79
133.29
132.99
132.23
129.55
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127.93
126.87
126.10
125.44
119.34
77.32
77.00
76.68
42.25
38.86
33.76
30.28
20.06
16.02
Cl
5b'
210
200
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150
140
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120
110
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30
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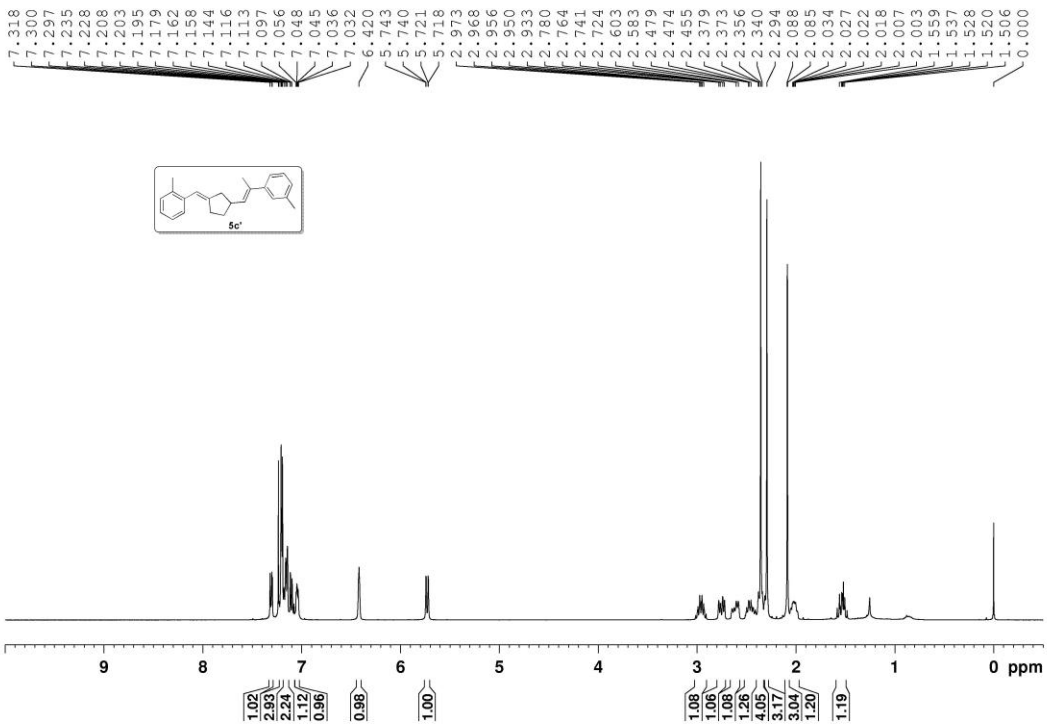
10
ppm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7.113
7.097
7.056
7.048
7.045
7.036
7.032
6.420
5.743
5.740
5.721
5.718
2.973
2.968
2.956
2.950
2.933
2.780
2.764
2.741
2.724
2.603
2.583
2.479
2.474
2.455
2.379
2.373
2.356
2.340
2.294
2.088
2.085
2.034
2.027
2.022
2.018
2.007
2.003
1.559
1.537
1.528
1.520
1.506
0.000
5c'
9
8
7
6
5
4
3
2
1
0 ppm
1.02
2.93
2.24
1.12
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1.08
1.26
4.05
3.17
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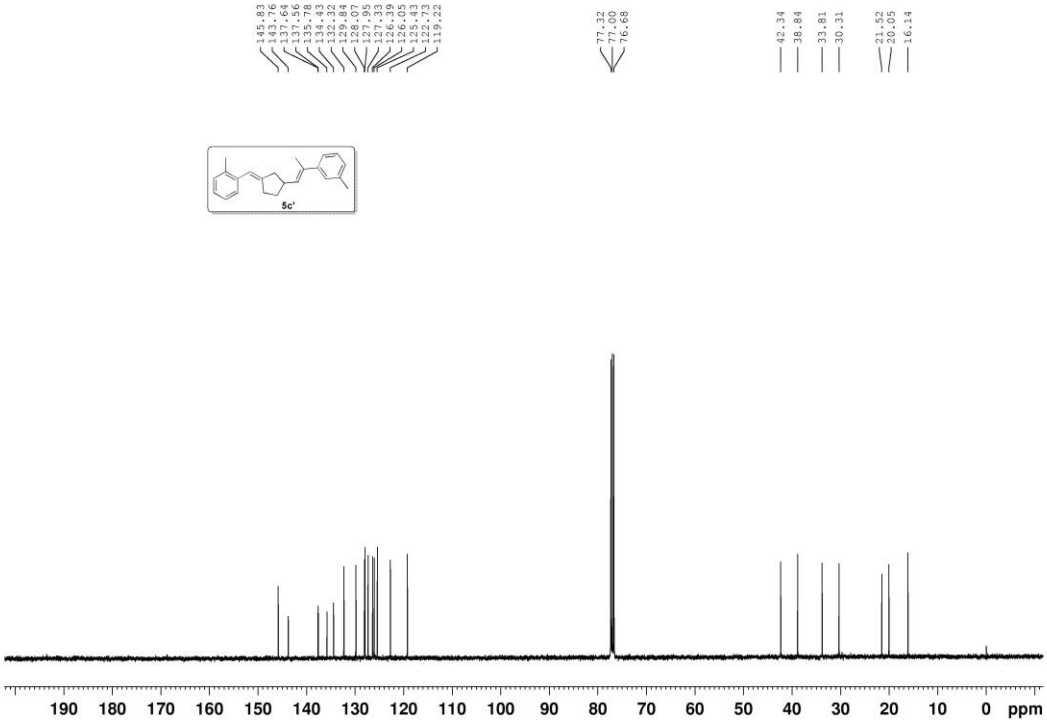
1.20
1.19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126.39
126.05
125.43
122.73
119.22
77.32
77.00
76.68
42.34
38.84
33.81
30.31
21.52
20.05
16.14
5c'
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150
140
130
120
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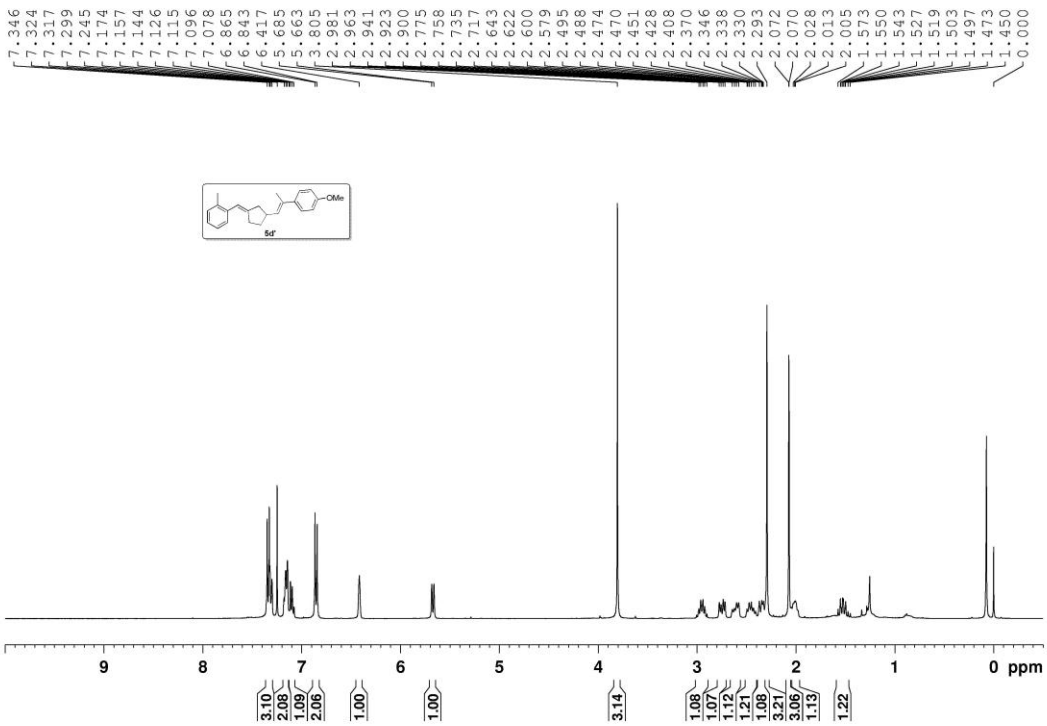
30
20
10
0 ppm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6.843
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5.685
5.663
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2.981
2.963
2.941
2.923
2.900
2.775
2.758
2.735
2.717
2.643
2.622
2.600
2.579
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2.488
2.474
2.470
2.451
2.428
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2.370
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2.070
2.028
2.013
2.005
1.573
1.550
1.543
1.527
1.519
1.503
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1.473
1.450
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OMe
5d'
9
8
7
6
5
4
3
2
1
0 ppm
3.10
2.08
1.09
2.06
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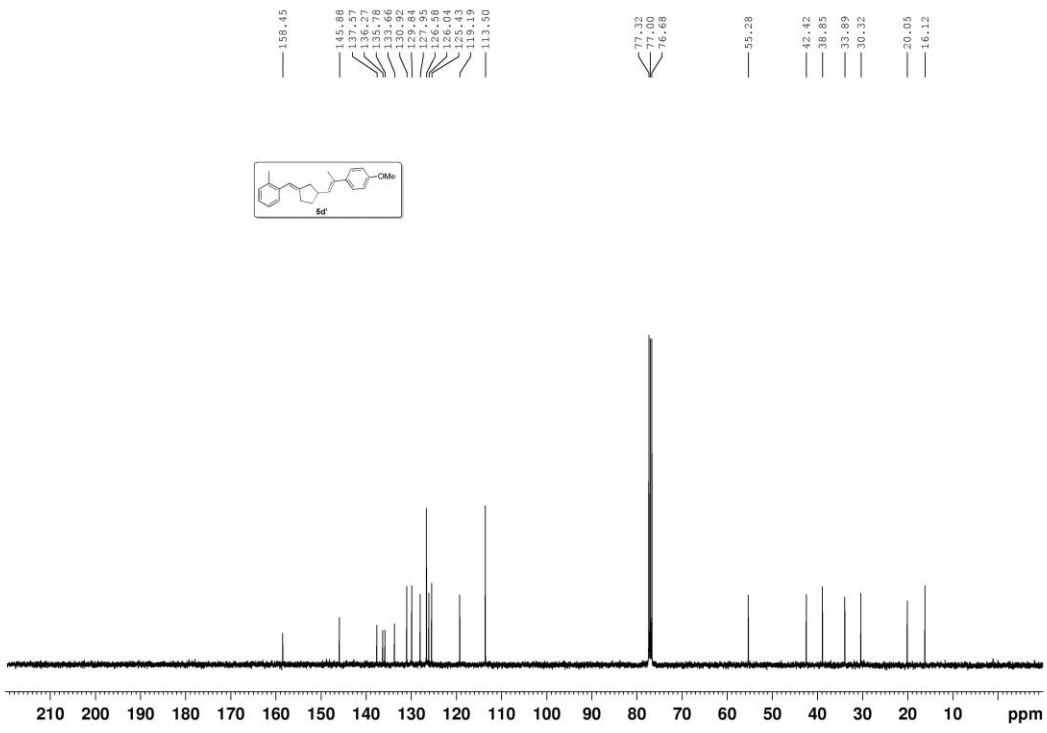
3.06
1.13
1.22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77.00
76.68
55.28
42.42
38.85
33.89
30.32
20.05
16.12
OMe
5d'
210
200
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180
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150
140
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120
110
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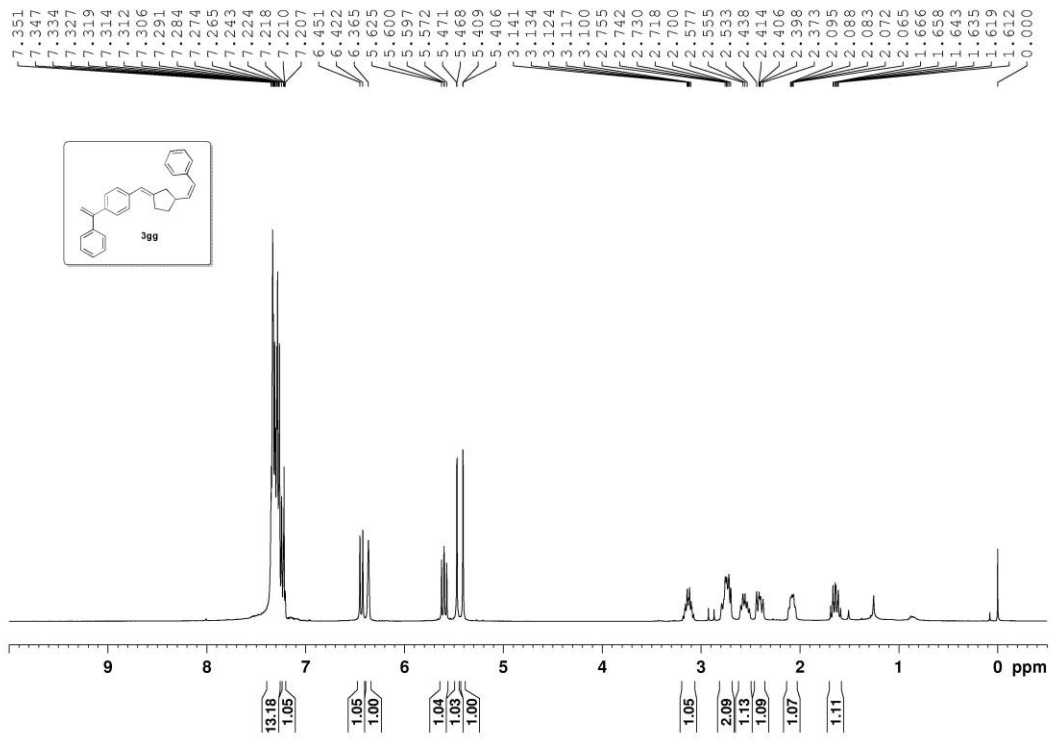
70
60
50
40
30
20
10
ppm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7.224
7.218
7.210
7.207
6.451
6.422
6.365
5.625
5.600
5.597
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5.471
5.468
5.409
5.406
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3.134
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3.117
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2.718
2.700
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2.088
2.083
2.072
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1.658
1.643
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1.619
1.612
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3gg
9
8
7
6
5
4
3
2
1
0 ppm
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1.03
1.00
1.05
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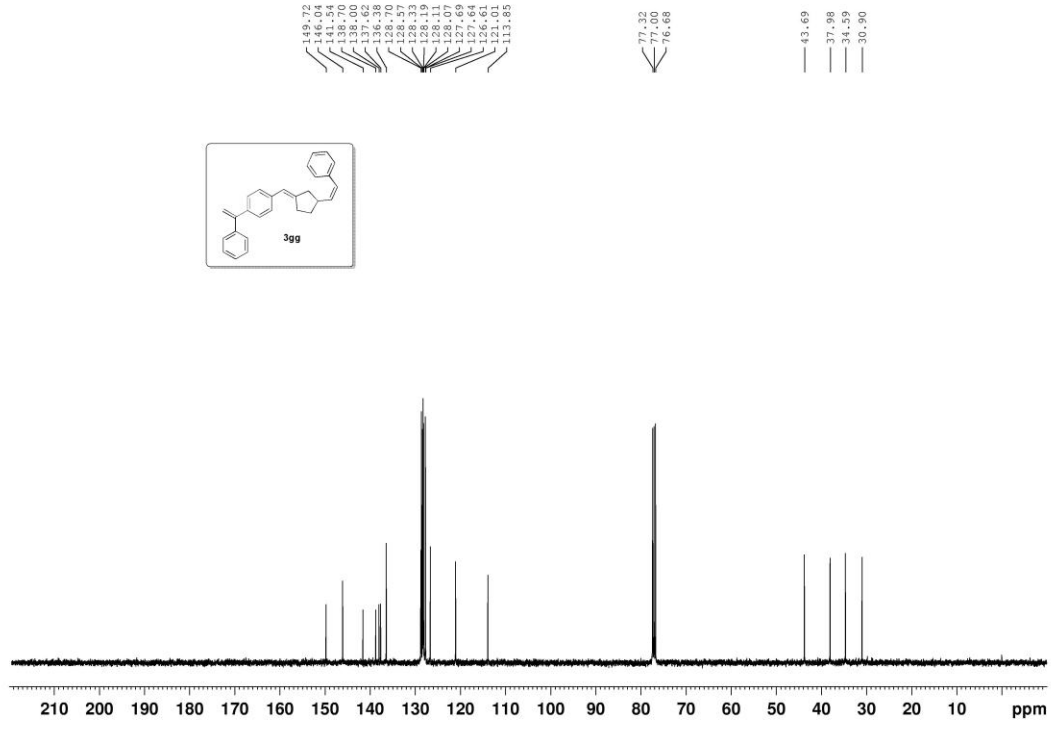
1.09
1.07
1.11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127.64
126.51
121.01
113.85
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77.00
76.68
43.69
37.98
34.59
30.90
3gg
210
200
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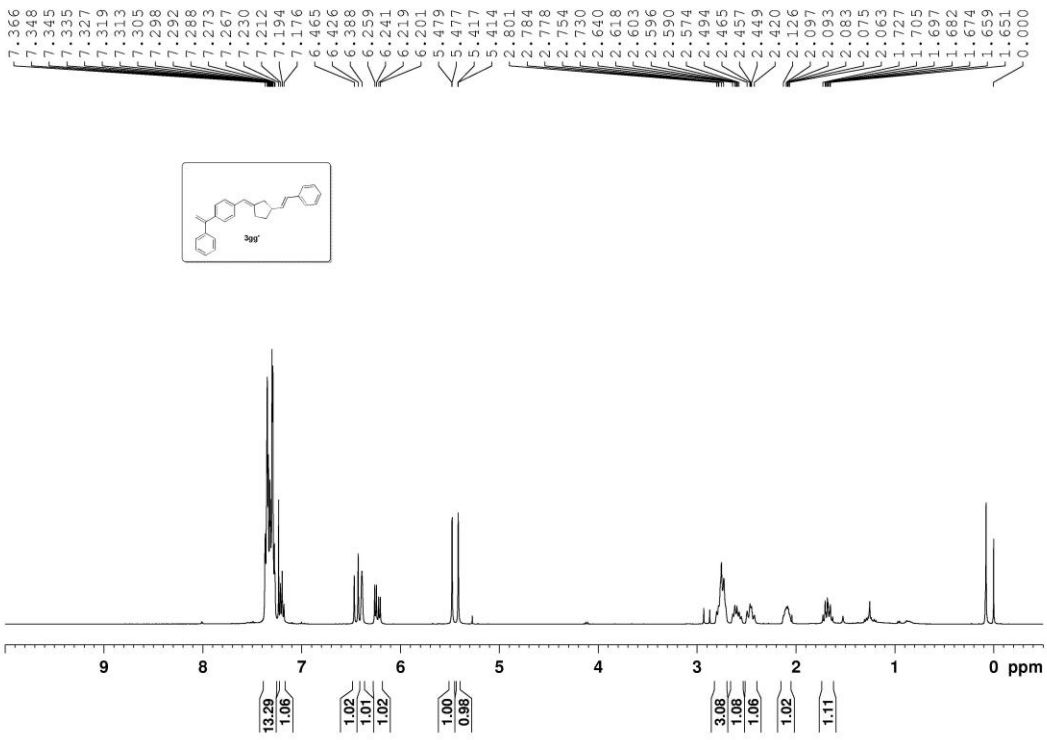
30
20
10
ppm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7.194
7.176
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6.426
6.388
6.259
6.241
6.219
6.201
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5.477
5.417
5.414
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2.754
2.730
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2.618
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2.596
2.590
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2.465
2.457
2.449
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2.097
2.093
2.083
2.075
2.063
1.727
1.705
1.697
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1.674
1.659
1.651
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3gg'
9
8
7
6
5
4
3
2
1
0 ppm
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1.02
1.00
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3.08
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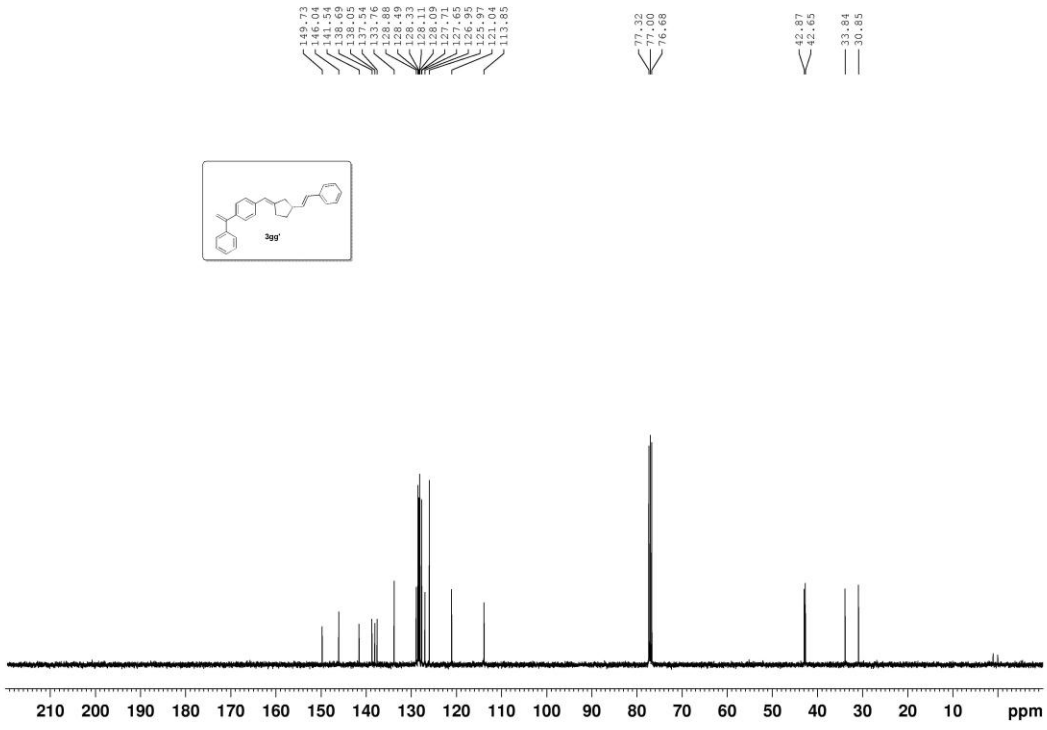
1.06
1.02
1.11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128.11
128.09
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127.65
126.95
125.97
123.04
113.85
77.32
77.00
76.68
42.87
42.65
33.84
30.85
3gg'
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

8. The NOE of 5d'