Copper-Catalyzed Skeletal Rearrangement of *O*-propargilic Alkylaldoximes via N-O Bond Cleavage

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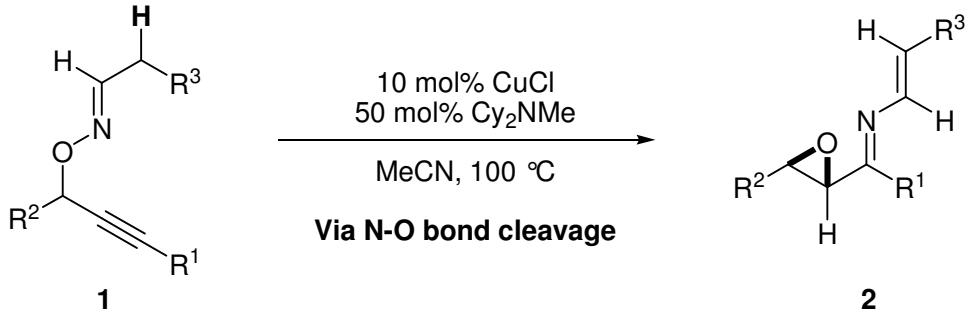
(Supporting Information)



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Contents

1. General information.

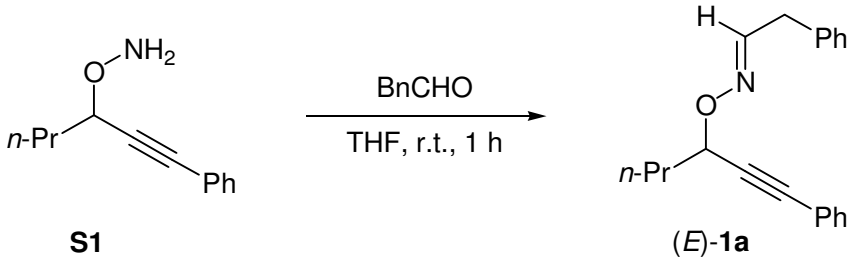
^{1}H NMR spectra were recorded on a JEOL JNM α-500 (500MHz) spectrometer. Chemical shifts are reported in ppm from the solvent resonance as the internal standard ($CDCl_3$: 7.26 ppm). Data are reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, qui =quintet, sext = sextet, sept = septet, br = broad, m = multiplet) and coupling constants (Hz). ^{13}C NMR spectra were recorded on a JEOL JNM α-500 (125.65 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm from the solvent resonance as the internal standard ($CDCl_3$: 77.00 ppm). Infrared (IR) spectra were recorded on a JASCO FT/IR-4100 spectrometer. High-resolution mass spectra were performed on a Bruker Daltonics APEX III FT-ICR-MS spectrometer at the Instrumental Analysis Center for Chemistry, Graduate School of Science, Tohoku University. Column chromatography was performed with Kanto Chemical silica gel 60 N (spherical, neutral, 40-50 μm) or FUJI SILYSIA CHEMICAL LTD. silica gel Chromatorex® NH DM2035. Analytical thin layer chromatography (TLC) was performed on Merck precoated TLC plates (silica gel 60 F_{254}). All manipulations were conducted under an argon atmosphere using standard Schlenk techniques.

Materials.

Anhydrous CH_2Cl_2, DMF, MeCN, EtOAc, 1,4-dioxane, THF, toluene, EtOH, hexane (WAKO) were purchased and used as received.

CuBr (WAKO, 99.9%) were purchased and used as received. CuCl (WAKO) was purified by recrystallization prior to use.

2. Representative procedure for the synthesis of (*E*)-1a.



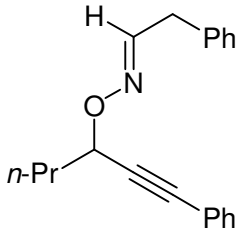
S1 (*E*)-**1a**

(*E*)-2-phenylacetaldehyde *O*-1-phenylhex-1-yn-3-yl oxime ((*E*)-**1a**). Alkoxylamine **S1** (946 mg, 5.0 mmol) was dissolved in THF (5.0 mL). 2-phenylacetaldehyde (5.1 mmol) was added at room temperature and the reaction mixture was stirred for 1h. The solvent was then removed under reduced pressure and the residue was purified by flash column chromatography (Hexane/EtOAc = 15/1 as eluent) to give **1a** (997 mg, *E*/*Z* = 72/28, 82% total yield).

Alkoxylamines were prepared following the reported procedure.[1]

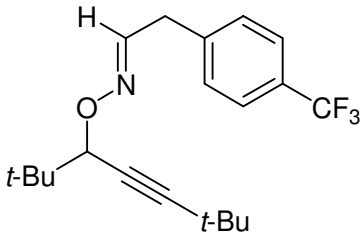
[1] Nakamura, I.; Araki, T.; Zhang, D.; Kudo, Y.; Kwon, E.; Terada, M. *Org. Lett.*, **2011**, *13*, 3616

3. Analytical data of 1.



(*E*)-**1a**

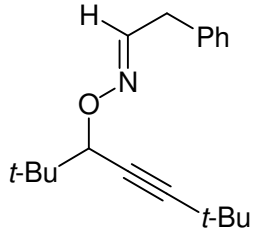
(*E*)-2-Phenylacetaldehyde *O*-1-phenylhex-1-yn-3-yl oxime ((*E*)-1a). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 (t, *J* = 6.5 Hz, 1H), 7.48-7.42 (m, 2H), 7.32-7.27 (m, 5H), 7.26-7.20 (m, 3H), 5.00 (t, *J* = 6.5 Hz, 1H), 3.57 (dd, *J* = 15.5 Hz, *J* = 6.5Hz, 1H), 3.54 (dd, *J* = 15.5 Hz, *J* = 6.5Hz, 1H), 1.95-1.81 (m, 2H), 1.58 (sext, *J* = 7.5 Hz, 2H), 0.99 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (125.65 MHz, $CDCl_3$) δ 150.03, 136.27, 131.84, 128.81, 128.68, 128.24, 128.15, 126.79, 122.86, 88.32, 85.60, 73.39, 36.58, 35.91, 18.52, 13.85. IR (ATR) 2959, 2932, 2872, 1598, 1489, 1598, 1489, 1455, 1340, 1109, 1067, 1002, 989, 961, 933 cm^{-1}. HRMS (ESI) calcd. for $C_{20}H_{21}NONa$ $[M + Na]^+$ 314.1515, found. 314.1515.



(*E*)-**1b**

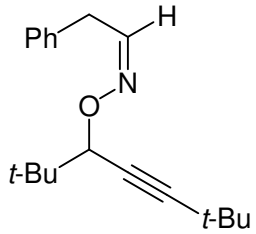
(*E*)-2-(4-(Trifluoromethyl)phenyl)acetaldehyde *O*-2,2,6,6-tetramethylhept-4-yn-3-yl oxime ((*E*)-1b). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.5 Hz, 2H), 7.50 (t, *J* = 6.5 Hz, 1H), 7.35 (d, *J* = 8.5 Hz, 2H), 4.44 (s, 1H), 3.62 (dd, *J* = 15.5 Hz, *J* = 6.5Hz, 1H), 3.57 (dd, *J* = 15.5 Hz, *J* = 6.5 Hz,

1H), 1.24 (s, 9H), 1.01 (s, 9H). ^{13}C NMR (125.65 MHz, $CDCl_3$) δ 147.89, 140.68, 129.20 (q, *J* = 32 Hz), 129.20, 125.54 (q, *J* = 3.8 Hz), 124.16 (q, *J* = 272 Hz), 95.12, 82.39, 76.37, 35.70, 35.40, 31.02, 27.47, 25.95. IR (ATR) 2968, 1618, 1322, 1164, 1126, 1066, 994 cm^{-1}. HRMS (ESI) calcd. for $C_{20}H_{26}F_3NONa$ $[C_{20}H_{26}F_3NO + Na]^+$ 376.1859, found. 376.1857.



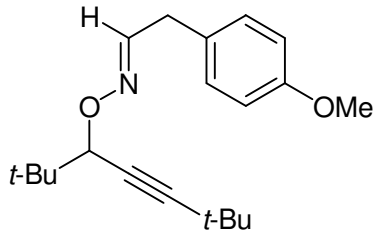
(*E*)-**1c**

(*E*)-2-Phenylacetaldehyde *O*-2,2,6,6-tetramethylhept-4-yn-3-yl oxime ((*E*)-1c). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 (t, *J* = 6.5 Hz, 1H), 7.32-7.29 (m, 2H), 7.25-7.22 (m, 3H), 4.44 (s, 1H), 3.56 (dd, *J* = 15.0 Hz, *J* = 6.5 Hz, 1H), 3.51 (dd, *J* = 15.0 Hz, *J* = 6.5 Hz, 1H), 1.24 (s, 9H), 1.01 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.06, 136.53, 128.85, 128.63, 126.73, 94.93, 82.18, 76.47, 35.89, 35.39, 31.04, 27.46, 25.97. IR (ATR) 2967, 1603, 1362, 995 cm^{-1}. HRMS (ESI) calcd. for $C_{19}H_{27}NONa$ $[C_{19}H_{27}NO + Na]^+$ 308.1985, found. 308.1985.



(*Z*)-**1c**

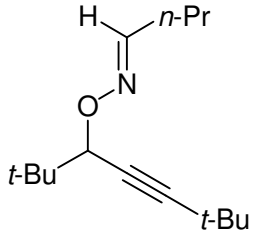
(*Z*)-2-Phenylacetaldehyde *O*-2,2,6,6-tetramethylhept-4-yn-3-yl oxime ((*Z*)-1c). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33-7.29 (m, 2H), 7.25-7.22 (m, 3H), 6.85 (t, *J* = 5.5 Hz, 1H), 4.47 (s, 1H), 3.76 (dd, *J* = 16.5 Hz, *J* = 5.5 Hz, 1H), 3.66 (dd, *J* = 16.5 Hz, *J* = 5.5 Hz, 1H), 1.24 (s, 9H), 1.04 (s, 9H). ^{13}C NMR (125.65 MHz, $CDCl_3$) δ 149.54, 136.97, 128.78, 128.64, 126.53, 94.81, 82.44, 76.52, 35.84, 32.47, 31.05, 27.46, 26.02. IR (ATR) 2967, 1362, 1362, 995, 894 cm^{-1}. HRMS (ESI) calcd. for $C_{19}H_{27}NONa$ $[C_{19}H_{27}NO + Na]^+$ 308.1985, found. 308.1984.



(*E*)-**1d**

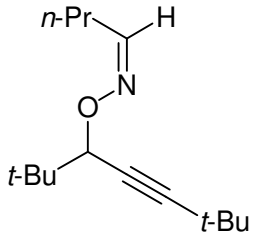
(*E*)-2-(4-Methoxyphenyl)acetaldehyde *O*-2,2,6,6-tetramethylhept-4-yn-3-yl oxime ((*E*)-1d). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 (t, *J* = 6.5 Hz, 1H), 7.16-7.13 (m, 2H), 6.86-6.83 (m, 2H), 4.43 (s, 1H), 3.79 (s, 3H), 3.50 (dd, *J* = 15.0 Hz, *J* = 6.5 Hz, 1H), 3.45 (dd, *J* = 15.0 Hz, *J* = 6.5 Hz, 1H), 1.24 (s, 9H), 1.00 (s, 9H). ^{13}C NMR (125.65 MHz, $CDCl_3$) δ 158.47, 149.35, 129.83, 128.46, 114.05, 94.90, 82.12, 76.48, 55.26, 35.40, 35.01, 31.04, 27.45, 25.95. IR (ATR) 2966, 1511, 1245, 995 cm^{-1}. HRMS

(ESI) calcd. for $C_{20}H_{29}NO_2Na$ $[C_{20}H_{29}NO_2 + Na]^+$ 338.2091, found. 338.2090.



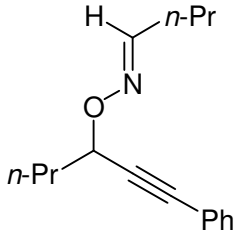
(*E*)-**1e**

(*E*)-Butyraldehyde *O*-2,2,6,6-tetramethylhept-4-yn-3-yl oxime ((*E*)-1e). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 (t, *J* = 6.5 Hz, 1H), 4.38 (s, 1H), 2.18 (qd, *J* = 7.5 Hz, *J* = 2.0 Hz, 2H), 1.52 (sext, *J* = 7.5 Hz, d, *J* = 2.0 Hz, 2H), 1.22 (s, 9H), 1.00 (s, 9H), 0.96 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (125.65 MHz, $CDCl_3$) δ 150.75, 94.81, 81.92, 76.53, 35.41, 31.35, 31.04, 27.43, 25.97, 20.10, 13.56. IR (ATR) 2966, 1478, 1458, 1363, 1265, 1024, 1011, 994, 929 cm^{-1}. HRMS (ESI) calcd. for $C_{15}H_{27}NONa$ $[C_{15}H_{27}NO + Na]^+$ 260.1985, found. 260.1984.



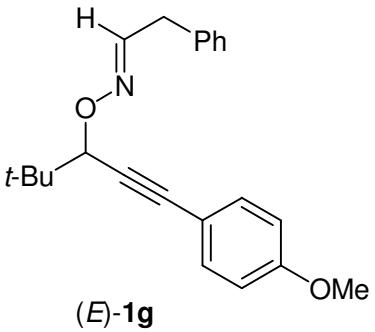
(*Z*)-**1e**

(*Z*)-Butyraldehyde *O*-2,2,6,6-tetramethylhept-4-yn-3-yl oxime ((*Z*)-1e). ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.67 (t, *J* = 6.5 Hz, 1H), 4.38 (s, 1H), 2.39-2.27 (m, 2H), 1.51 (sext, *J* = 7.5 Hz, 2H), 1.22 (s, 9H), 1.01 (s, 9H), 0.96 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (125.65 MHz, $CDCl_3$) δ 151.79, 94.501, 82.06, 76.65, 35.51, 31.04, 27.73, 27.43, 25.98, 19.60, 13.88.



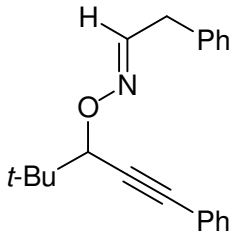
(*E*)-**1f**

(*E*)-Butyraldehyde *O*-1-phenylhex-1-yn-3-yl oxime ((*E*)-1f). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46-7.43 (m, 3H), 7.29-7.27 (m, 3H), 4.95 (t, *J* = 7.0 Hz, 1H), 2.21 (q, *J* = 6.5 Hz, 2H), 1.93-1.79 (m, 2H), 1.61-1.50 (m, 4H), 0.99 (t, *J* = 7.0 Hz, 3H), 0.96 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (125.65 MHz, $CDCl_3$) δ 151.69, 131.83, 128.18, 128.12, 122.92, 88.37, 85.53, 73.13, 36.64, 31.43, 20.08, 18.51, 13.85, 13.56.



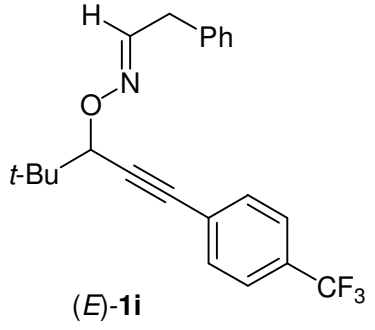
(*E*)-**1g**

(*E*)-2-Phenylacetaldehyde *O*-1-(4-methoxyphenyl)-4,4-dimethylpent-1-yn-3-yl oxime ((*E*)-1g). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 (t, 0.99 (t, *J* = 7.0 Hz, 1H), 7.39 (m, 2H), 7.30-7.27 (m, 2H), 7.25-7.21 (m, 3H), 6.84-6.81 (m, 2H), 4.68 (s, 1H), 3.80 (s, 3H) 3.58 (dd, *J* = 15.0 Hz, *J* = 7.0 Hz, 1H) 3.55 (dd, *J* = 15.0 Hz, *J* = 7.0 Hz, 1H), 1.09 (s, 9H). ^{13}C NMR (125.65 MHz, $CDCl_3$) δ 159.47, 149.60, 136.39, 133.26, 128.85, 128.66, 126.76, 115.24, 113.74, 86.09, 86.05, 82.52, 55.25, 35.89, 35.63, 26.05. IR (ATR) 2957, 1605, 1569, 1508, 1290, 1245, 1171, 1031, 992 cm^{-1}. HRMS (ESI) calcd. for $C_{22}H_{25}NO_2Na$ $[C_{22}H_{25}NO_2 + Na]^+$ 358.1778, found. 358.1776.



(*E*)-**1h**

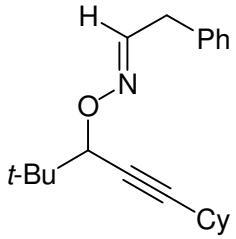
(*E*)-2-Phenylacetaldehyde *O*-4,4-dimethyl-1-phenylpent-1-yn-3-yl oxime ((*E*)-1h). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 (t, *J* = 6.5 Hz,1H), 7.48-7.42 (m, 2H), 7.31-7.27 (m, 5H), 7.24-7.21 (m, 3H), 4.69 (s, 1H), 3.58 (dd, *J* = 15.0 Hz, *J* = 6.5 Hz, 1H), 3.54 (dd, *J* = 15.0 Hz, *J* = 6.5 Hz, 1H), 1.10 (s, 9H). ^{13}C NMR (125.65 MHz, $CDCl_3$) δ 149.72, 136.35, 131.83, 128.85, 128.67, 128.13, 128.12, 126.77, 123.10, 87.59, 86.21, 82.42, 35.89, 35.61, 26.04. IR (ATR) 2957, 1598, 1489, 1326, 1068, 995, 931 cm^{-1}. HRMS (ESI) calcd. for $C_{21}H_{23}NONa$ $[C_{21}H_{23}NO + Na]^+$ 328.1672, found. 328.1672.



(*E*)-**1i**

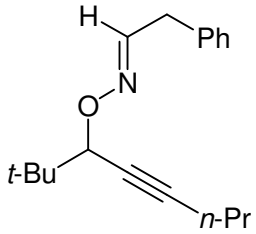
(*E*)-2-Phenylacetaldehyde *O*-4,4-dimethyl-1-(4-(trifluoromethyl)phenyl)pent-1-yn-3-yl oxime ((*E*)-1i). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58-7.45 (m, 5H), 7.32-7.27 (m, 2H), 7.26-7.21 (m, 3H), 4.70 (s, 1H), 3.58 (dd, *J* = 15.0 Hz, *J* = 6.5 Hz, 1H), 3.55 (dd, *J* = 15.0 Hz, *J* = 6.5 Hz, 1H), 1.10 (s, 9H). ^{13}C NMR (125.65 MHz, $CDCl_3$) δ 149.99, 136.25, 132.03, 129.91 (q, *J* = 32 Hz), 128.83, 128.71, 126.88, 126.85, 125.10 (q, *J* = 3.8 Hz), 123.92 (q, *J* = 272 Hz), 90.31, 84.90, 82.27, 35.88, 35.61, 26.01. IR (ATR) 2966, 1615, 1489, 1320, 1165, 1125, 1105, 1067, 997 cm^{-1}. HRMS (ESI) calcd. for

$C_{22}H_{22}F_3NONa$ $[C_{22}H_{22}F_3NO + Na]^+$ 396.1546, found. 396.1544.



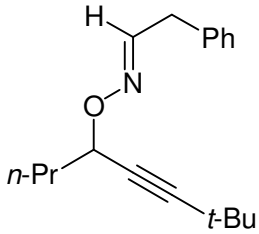
(*E*)-**1j**

(*E*)-2-Phenylacetaldehyde *O*-1-cyclohexyl-4,4-dimethylpent-1-yn-3-yl oxime ((*E*)-1j). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 (t, *J* = 6.5 Hz, 1H), 7.31-7.29 (m, 2H), 7.26-7.22 (m, 3H), 4.46 (d, *J* = 2.0 Hz, 1H), 3.55 (dd, *J* = 15.0 Hz, *J* = 6.5 Hz, 1H), 3.53 (dd, *J* = 15.0 Hz, *J* = 6.5 Hz, 1H), 2.5-2.4 (m, 1H), 1.82-1.75 (m, 2H), 1.74-1.66 (m, 2H), 1.53-1.43 (m, 3H), 1.38-1.25 (m, 3H), 1.02 (s, 9H). ^{13}C NMR (125.65 MHz, $CDCl_3$) δ 149.20, 136.51, 128.85, 128.63, 126.73, 90.86, 82.27, 78.04, 35.90, 35.39, 32.65, 32.60, 29.03, 25.98, 25.96, 24.71. IR (ATR) 2952, 2929, 2854, 1449, 1363, 1326, 993 cm^{-1}. HRMS (ESI) calcd. for $C_{21}H_{29}NONa$ $[C_{21}H_{29}NO + Na]^+$ 334.2141, found. 334.2141.



(*E*)-**1k**

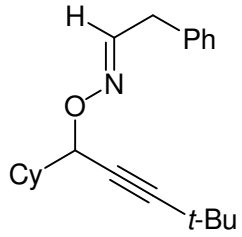
(*E*)-2-Phenylacetaldehyde *O*-2,2-dimethyloct-4-yn-3-yl oxime ((*E*)-1k). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 (t, *J* = 6.5 Hz, 1H), 7.32-7.29 (m, 2H), 7.25-7.21 (m, 3H), 4.46 (t, *J* = 2.0 Hz, 1H), 3.55 (d, *J* = 6.5 Hz, 2H), 2.24 (dt, *J* = 2.0 Hz, *J* = 6.5 Hz, 2H), 1.55 (sext, *J* = 7.5 Hz, 2H), 1.02 (s, 9H), 0.99(t, *J* = 7.5 Hz, 3H). ^{13}C NMR (125.65 MHz, $CDCl_3$) δ 149.30, 136.47, 128.84, 128.64, 126.74, 86.74, 82.29, 78.21, 35.91, 35.34, 25.95, 22.16, 20.87, 13.50. IR (ATR) 3726, 3706, 3624, 3599, 2960, 2933, 2905, 2870, 1455, 1326, 994 cm^{-1}. HRMS (ESI) calcd. for $C_{18}H_{25}NONa$ $[C_{18}H_{25}NO + Na]^+$ 294.1828, found. 294.1827.



(*E*)-**1l**

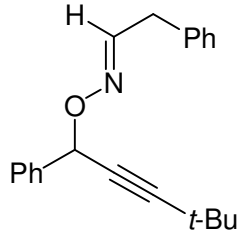
(*E*)-2-Phenylacetaldehyde *O*-7,7-dimethyloct-5-yn-4-yl oxime ((*E*)-1l). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 (t, *J* = 6.5 Hz, 1H), 7.32-7.29 (m, 2H), 7.25-7.21 (m, 3H), 4.77 (dd, *J* = 7.5 Hz, *J* = 7.0 Hz, 1H), 3.56 (dd, *J* = 15.0 Hz, *J* = 6.5 Hz, 1H), 3.51 (dd, *J* = 15.0 Hz, *J* = 6.5 Hz, 1H), 1.82-1.75 (m, 1H), 1.73-1.66 (m, 1H), 1.48 (sext, *J* = 7.5 Hz, 1H), 1.23 (s, 9H), 0.95 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (125.65 MHz, $CDCl_3$) δ 149.47, 136.40, 128.81, 128.64, 126.75, 94.64, 77.32, 73.24, 36.91, 35.91, 31.00, 27.39, 18.43, 13.87. IR (ATR) 2965, 2931, 2871, 1495, 1455, 1263, 1005, 962, 935 cm^{-1}.

HRMS (ESI) calcd. for $C_{18}H_{25}NONa$ $[C_{18}H_{25}NO + Na]^+$ 294.1828, found. 294.1826.



(*E*)-**1m**

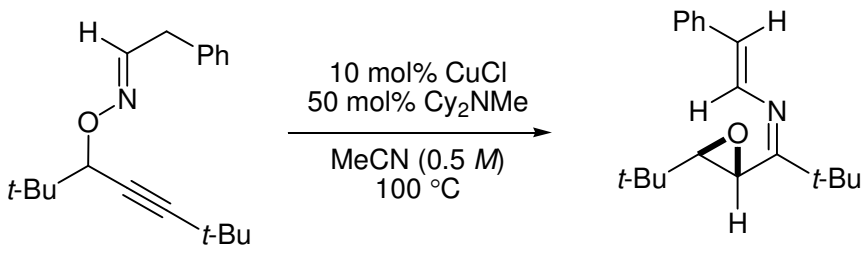
(*E*)-2-Phenylacetaldehyde O-1-cyclohexyl-4,4-dimethylpent-2-ynyl oxime ((*E*)-1m). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 (t, *J* = 6.5 Hz, 1H), 7.32-7.30 (m, 2H), 7.25-7.21 (m, 3H), 4.59 (d, *J* = 6.0 Hz, 2H), 3.56 (dd, *J* = 15.0 Hz, *J* = 6.5 Hz, 1H), 3.51 (dd, *J* = 15.0 Hz, *J* = 6.5 Hz, 1H), 1.85-1.64 (m, 6H), 1.31-1.06 (m, 5H), 1.24 (s, 9H). ^{13}C NMR (125.65 MHz, $CDCl_3$) δ 149.37, 136.45, 128.81, 128.63, 126.73, 95.39, 78.04, 76.05, 41.64, 35.92, 31.05, 29.06, 27.73, 27.46, 26.52, 26.01, 25.89. IR (ATR) 2967, 2925, 2853, 1495, 1453, 1335, 1263, 997, 978, 961 cm^{-1}. HRMS (ESI) calcd. for $C_{21}H_{29}NONa$ $[C_{21}H_{29}NO + Na]^+$ 334.2141, found. 334.2140.



(*E*)-**1n**

(*E*)-2-Phenylacetaldehyde *O*-4,4-dimethyl-1-phenylpent-2-ynyl oxime ((*E*)-1n). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57-7.53 (m, 2H), 7.52 (t, *J* = 6.5 Hz, 1H), 7.39-7.32 (m, 3H), 7.31-7.26 (m, 2H), 7.24-7.17 (m, 3H), 5.84 (s, 1H), 3.55 (dd, *J* = 15.0 Hz, *J* = 6.5 Hz, 1H), 3.50 (dd, *J* = 15.0 Hz, *J* = 6.5 Hz, 1H), 1.31 (s, 9H). ^{13}C NMR (125.65 MHz, $CDCl_3$) δ 150.29, 138.39, 136.22, 128.82, 128.62, 128.37, 128.31, 128.00, 126.76, 96.78, 76.20, 75.23, 35.86, 30.90, 27.58. IR (ATR) 3063, 3030, 2967, 2928, 2900, 2866, 1603, 1494, 1454, 1295, 1273, 1259, 976, 961, 933 cm^{-1}. HRMS (ESI) calcd. for $C_{21}H_{23}NONa$ $[C_{21}H_{23}NO + Na]^+$ 328.1672, found. 328.1671.

4. Representative procedure for the CuCl-catalyzed synthesis of 2c.

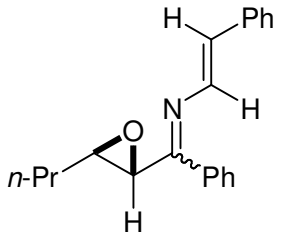


(*E*)-**1c** **2c**

To a solution of CuCl (3.0 mg, 0.03 mmol) and Cy_2NMe (29.3 mg, 0.15mmol) in MeCN (0.6 mL) in a pressure vial was added the the oxime (*E*)-**1c** (85.6 mg, 0.30 mmol) under argon atmosphere and the mixture was stirred at 100 °C for 3h. The reaction mixture was washed NH_4Cl aq. After removing

solvents in vacuo, the residue was purified by FUJI SILYSIA CHEMICAL LTD. silica gel Chromatorex® NH DM2035 (Hexane/Et_2O = 500/1 as eluent) to give **2c** (74.5 mg, 87%).

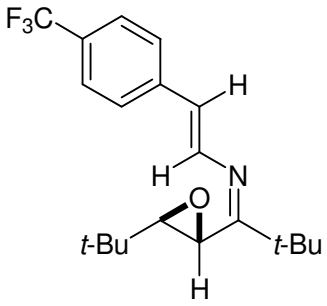
5. Analytical data of 2.



2a

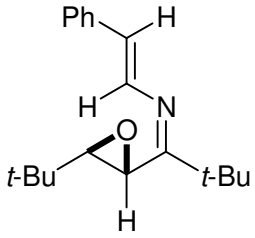
(1*E*,*NZ*)-2-phenyl-*N*-(phenyl(3-propyloxiran-2-yl)methylene)ethenamine (2a). (*E*/*Z* = 69/31, mixture); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.19 (d, *J* = 13.4 Hz, 1H, *Z*), 7.94-7.92 (m, 2.07H, *Z*), 7.51-7.49 (m, 2H, *E*), 7.44-7.41 (m, 6H, *E*), 7.44-7.41 (m, 3H, *E*), 7.41-7.34 (m, 3H, *E*), 7.41-7.34 (m, 1.17H, *Z*), 7.28-7.19 (m, 12H, *E*), 7.28-7.19 (m, 5.60H, *Z*), 6.98-6.96 (m, 2H, *E*), 6.98-6.96 (m, 1.16H, *Z*), 3.77 (d, *J* = 2.4 Hz, 0.99H, *Z*), 3.60 (d, *J* = 2.1 Hz, 1H, *E*), 3.04-3.00 (m, 1.02H, *Z*), 2.86-2.84 (m, 1H, *E*), 2.98-2.90 (m, 1.03H, *Z*), 1.67-1.46 (m, 11H, *E*), 1.67-1.46 (m, 4.83H, *Z*), 1.04 (t, *J* = 7.4 Hz, 3.14H, *Z*), 0.95 (t, *J* = 7.4 Hz, 9H, *E*). ^{13}C NMR (149.40 MHz, $CDCl_3$) δ 167.42, 161.37, 137.20, 136.42, 136.13, 135.77, 134.83, 133.27, 132.76, 132.09, 130.36, 129.32, 128.74, 128.60, 128.40, 128.33, 128.27, 128,00, 127.91, 127.66, 126.96, 126.89, 60.65, 58.85, 58.34, 55.52, 34.13, 33.76, 19.33, 19.25, 14.02, 13.95. Acidic hydrolysis of **2a** with 1N HCl afforded the corresponding oxiranylketone, phenyl(3-propyloxiran-2-yl)methanone, of which ^{1}H and ^{13}C NMR spectra were identified to those in a literature.[1]

[1] Mukaiyama, T.; Pudhom, K.; Yamane, K.; Arai, H. *Bull. Chem. Soc. Jpn.* **2003**, *76*, 413.



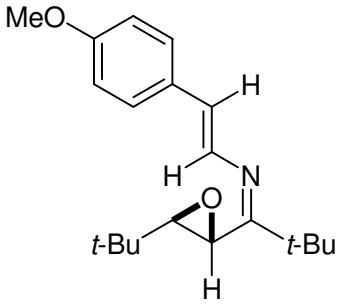
2b

(1*E*,*NZ*)-*N*-(1-(3-*tert*-butyloxiran-2-yl)-2,2-dimethylpropylidene)-2-(4-(trifluoromethyl)phenyl)ethenamine (2b). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (d, *J* = 14.0 Hz, 1H), 7.55 (d, *J* = 8.5 Hz, 2H), 7.46 (d, *J* = 8.5 Hz, 2H), 6.53 (d, *J* = 14.0 Hz, 1H), 3.56 (d, *J* = 2.5 Hz, 1H), 2.73 (d, *J* = 2.5 Hz, 1H), 1.25 (s, 9H), 0.99 (s, 9H). ^{13}C NMR (125.65 MHz, $CDCl_3$) δ 174.94, 140.40, 136.71, 128.72 (q, *J* = 32 Hz), 126.37, 125.55 (q, *J* = 3.8 Hz), 125.22, 124.25, 124.27 (q, *J* = 32 Hz), 66.08, 54.55, 40.38, 31.21, 28.17, 25.80. IR (ATR) 2963, 2905, 2869, 1593, 1365, 1171, 1117, 1109, 1067, 946, 831 cm^{-1}. HRMS (ESI) calcd. for $C_{20}H_{26}F_3NONa$ $[C_{20}H_{26}F_3NO + Na]^+$ 376.1859, found. 376.1858.



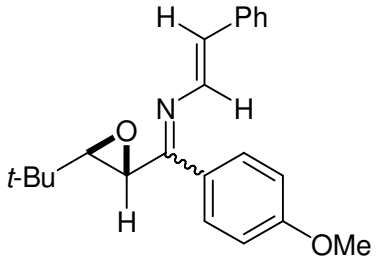
2c

(1*E*,*NZ*)-*N*-(1-(3-*tert*-butyloxiran-2-yl)-2,2-dimethylpropylidene)-2-phenylethenamine (2c). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (d, *J* = 13.5 Hz, 1H), 7.40-7.38 (m, 2H), 7.32-7.29 (m, 2H), 7.23-7.19 (m, 1H), 6.63 (d, *J* = 13.5 Hz, 1H), 3.55 (d, *J* = 2.5 Hz, 1H), 2.23 (d, *J* = 2.5 Hz, 1H), 1.25 (s, 9H), 1.01 (s, 9H). ^{13}C NMR (125.65 MHz, $CDCl_3$) δ 173.53, 136.66, 134.26, 128.60, 128.51, 127.26, 126.49, 66.11, 54.53, 40.32, 31.20, 28.14, 25.84. IR (ATR) 3726, 3705, 3623, 3599, 2958, 2905, 2868, 1590, 1479, 1363, 941 cm^{-1}. HRMS (ESI) calcd. for $C_{19}H_{27}NONa$ $[C_{19}H_{27}NO + Na]^+$ 308.1985, found. 308.1985.



2d

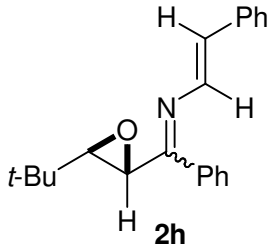
(1*E*,*NZ*)-*N*-(1-(3-*tert*-butyloxiran-2-yl)-2,2-dimethylpropylidene)-2-(4-methoxyphenyl)ethenamin e (2d). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83 (d, *J* = 13.5 Hz, 1H), 7.35-7.32 (m, 2H), 6.87-6.84 (m, 2H), 6.63 (d, *J* = 13.5 Hz, 1H), 3.80 (s, 3H), 3.54 (d, *J* = 2.5 Hz, 1H), 2.72 (d, *J* = 2.5 Hz, 1H), 1.24 (s, 9H), 1.02 (s, 9H). ^{13}C NMR (125.65 MHz, $CDCl_3$) δ 172.33, 159.09, 132.42, 129.31, 129.05, 127.75, 114.10, 66.08, 55.24, 54.50, 40.26, 31.21, 28.15, 25.86. IR (ATR) 2956, 2905, 2868, 2835, 1607, 1509, 1245, 1173, 1033 cm^{-1}. HRMS (ESI) calcd. for $C_{20}H_{29}NO_2Na$ $[C_{20}H_{29}NO_2 + Na]^+$ 338.2091, found. 338.2090.



2g

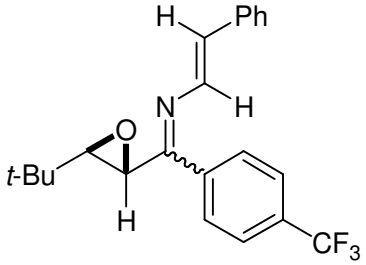
(1*E*)-*N*-((3-*tert*-butyloxiran-2-yl)(4-methoxyphenyl)methylene)-2-phenylethenamine (2g). (*E*/*Z* = 59/41, mixture); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.15 (d, *J* = 13.5 Hz, 0.68H, *Z*), 7.94-7.92 (m, 1.36H, *Z*), 7.47 (d, *J* = 7.5 Hz, 1.36H, *Z*), 7.36-7.32 (m, 1.38H, *Z*), 7.30-7.18 (m, 3H, *Z*), 7.30-7.18 (m, 5H, *E*), 6.98-6.90 (m, 2H, *Z*), 6.98-6.90 (m, 3H, *E*), 3.86 (s, 3H, *E*), 3.84 (s, 2.14H, *Z*), 2.82 (d, *J* = 2.5 Hz,

0.67H, *Z*), 2.67 (d, *J* = 2.5 Hz, 1H, *E*), 1.09 (s, 6.14H, *Z*), 0.96 (s, 9H, *E*). ^{13}C NMR (125.65 MHz, $CDCl_3$) δ 167.25, 161.51, 161.44, 160.25, 136.56, 136.31, 136.06, 134.68, 131.67, 131.22, 129.96, 129.90, 129.57, 128.68, 128.56, 127.70, 126.77, 126.76, 125.54, 113.77, 113.59, 66.30, 66.27, 57.72, 55.33, 55.27, 53.03, 31.32, 31.07, 25.91, 25.83. IR (ATR) 2957, 1604, 1509, 1249, 1173, 1029, 942 cm^{-1}. HRMS (ESI) calcd. for $C_{22}H_{25}NO_2Na$ $[C_{22}H_{25}NO_2 + Na]^+$ 358.1778, found. 358.1777.



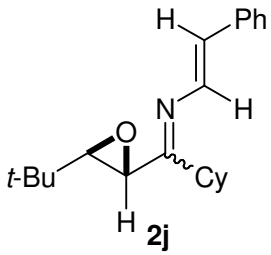
2h

(1*E*)-*N*-((3-*tert*-butyloxiran-2-yl)(phenyl)methylene)-2-phenylethenamine (2h). (*E*/*Z* = 69/31, mixture); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.19 (d, *J* = 13.5 Hz, 0.44H, *Z*), 7.95-7.92 (m, 0.89H, *Z*), 7.49-7.40 (m, 3H, *Z*), 7.49-7.40 (m, 3H, *E*), 7.37-7.33 (m, 2H, *E*) 7.28-7.18(m, 6H, *E*), 7.28-7.18(m, 2H, *Z*), 6.97 (d,), 6.97 (d, *J* = 13.5 Hz, 1H, *E*), 6.97 (d, *J* = 13.5 Hz, 0.45H, *Z*), 3.90 (d, *J* = 2.5 Hz, 0.43H, *Z*), 3.70 (d, *J* = 2.5 Hz, 1H, *E*), 2.83 (d, *J* = 2.5 Hz, 0.46H, *Z*), 2.67 (d, *J* = 2.5 Hz, 1H, *E*), 1.09 (s, 4.02H, *Z*), 0.96(s, 9H, *E*). ^{13}C NMR (125.65 MHz, $CDCl_3$) δ 167.68, 162.13, 137.30, 136.36, 136.12, 135.75, 134.52, 133.43, 132.78, 132.01, 130.24, 129.27, 128.72, 128.57, 128.42, 128.20, 128.18, 127.96, 127.88, 128.82, 126.92, 126.85, 66.34, 66.17, 57.68, 53.04, 31.34, 31.08, 25.91, 25.81. IR (ATR) 3057, 3025, 2957, 2867, 1479, 1445, 1364 cm^{-1}. HRMS (ESI) calcd. for $C_{21}H_{23}NONa$ $[C_{21}H_{23}NO + Na]^+$ 328.1672, found. 328.1671.



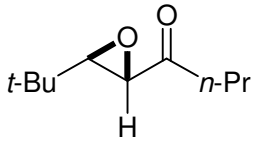
2i

(1*E*)-*N*-((3-*tert*-butyloxiran-2-yl)(4-(trifluoromethyl)phenyl)methylene)-2-phenylethenamine (2i). (*E*/*Z* = 57/43, mixture); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.16 (d, *J* = 13.5 Hz, 0.76H, *Z*), 8.05(d, *J* = 8.0 Hz, 1.54H, *Z*), 7.72 (d, *J* = 8.0 Hz, 2H, *E*), 7.65 (d, *J* = 8.0 Hz, 1.66H, *Z*), 7.49 (d, *J* = 8.0 Hz, 1.60H, *Z*), 7.40-7.34 (m, 1.62H, *Z*), 7.40-7.34 (m, 2H, *E*), 7.31-7.20 (m, 3.26H, *Z*), 7.31-7.20 (m, 4H, *E*), 7.03 (d, *J* = 13.5 Hz, 0.79H, *Z*), 7.02 (d, *J* = 13.5 Hz, 1H, *E*), 3.89 (d, *J* = 2.5 Hz, 0.78H, *Z*), 3.72 (d, *J* = 2.5 Hz, 1H, *E*), 2.82 (d, *J* = 2.5 Hz, 0.77H, *Z*), 2.56 (d, *J* = 2.5 Hz, 1H, *E*), 1.09 (s, 7.09H, *Z*), 0.96 (s, 9H, *E*). ^{13}C NMR (125.65 MHz, $CDCl_3$) δ 165.81, 160.66, 140.47, 136.67, 135.98, 135.68, 134.93, 134.35, 134.07, 133.38, 131.41, 131.15, 128.81, 128.72, 128.66, 128.36, 128.26, 128.19, 127.07, 126.97, 125.44 (q, *J* = 3.8 Hz), 125.07 (q, *J* = 3.8 Hz), 124.88, 122.92, 122.71, 66.45, 65.77, 57.67, 52.63, 31.34, 31.05, 25.86, 25.75. IR (ATR) 2959, 1617, 1481, 1321, 1165, 1123, 1109, 1067, 1016, 942 cm^{-1}. HRMS (ESI) calcd. for $C_{22}H_{22}F_3NONa$ $[C_{22}H_{22}F_3NO + Na]^+$ 396.1546, found. 396.1544.



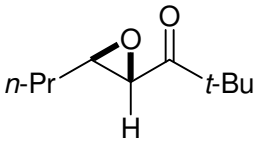
2j

(1*E*)-*N*-((3-*tert*-butyloxiran-2-yl)(cyclohexyl)methylene)-2-phenylethenamine (2j). (2j/3j = 93/7; (*E*)-2j/*Z*-(2j) = 26/74, mixture) ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 (d, *J* = 13.5 Hz, 1H, *Z*), 7.68 (d, *J* = 13.5 Hz, 0.34H, *E*), 7.42-7.30 (m, 4H, *Z*), 7.42-7.30 (m, 2.62H, *E*), 7.25-7.20 (m, 1H, *Z*), 7.25-7.20 (m, 0.44H, *E*), 6.79 (d, *J* = 13.5 Hz, 0.34H, *E*), 6.65 (d, *J* = 13.5 Hz, 1H, *Z*), 3.58 (d, *J* = 2.5 Hz, 1H, *Z*), 3.52 (d, *J* = 2.5 Hz, 0.32H, *E*), 2.79 (m, 0.46H, ((*E*)-2J+3J)), 2.71 (d, *J* = 2.5 Hz, 1H, *Z*), 2.32 (m, 1H, *Z*), 1.97-1.65 (m, 6H, *Z*), 1.97-1.65 (m, 2.12H, *E*), 1.58-1.50 (m, 1H, *Z*), 1.58-1.50 (m, 0.49H, *E*), 1.40-1.18 (m, 5H, *Z*), 1.40-1.18 (m, 5H, *Z*), 1.40-1.18 (m, 1.72H, *E*), 1.01 (s, 9H, *Z*), 0.99 (s, 3.56H, *E*). ^{13}C NMR (125.65 MHz, $CDCl_3$) δ 173.74, 136.48, 134.03, 133.10, 129.72, 128.66, 128.60, 128.28, 127.46, 127.39, 126.58, 126.38, 67.81, 65.91, 53.85, 53.11, 42.10, 40.86, 31.20, 29.68, 29.54, 26.43, 26.04, 26.03, 25.86, 25.72, 25.65. IR (ATR) 2953, 2928, 2852, 1591, 1447, 1364, 939, 897 cm^{-1}. HRMS (ESI) calcd. for $C_{21}H_{29}NONa$ $[C_{21}H_{29}NO + Na]^+$ 334.2141, found. 334.2140.



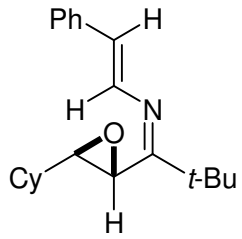
3k

1-(3-*tert*-butyloxiran-2-yl)butan-1-one (3k). ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.31 (d, *J* = 2.5 Hz, 1H), 2.84 (d, *J* = 2.5 Hz, 1H), 2.47-2.40 (m, 1H), 2.32-2.25 (m, 1H), 1.67-1.55 (m, 2H), 0.96 (s, 9H), 0.92 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (125.65 MHz, $CDCl_3$) δ 208.23, 65.92, 56.90, 39.08, 31.17, 25.61, 16.70, 13.66. IR (ATR) 2960, 2934, 2869, 1708, 1365 cm^{-1}. HRMS (ESI) calcd. for $C_{10}H_{18}O_2Na$ $[C_{10}H_{18}O_2 + Na]^+$ 193.1199, found. 193.1199.



3l

2,2-dimethyl-1-(3-propyloxiran-2-yl)propan-1-one (3l). ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.61 (d, *J* = 2.5 Hz, 1H), 2.94 (td, *J* = 5.5 Hz, *J* = 2.5 Hz, 1H), 1.66-1.59 (m, 2H), 1.58-1.45 (m, 2H), 1.23 (s, 9H), 0.98 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (125.65 MHz, $CDCl_3$) δ 209.52, 59.90, 55.27, 43.55, 33.93, 25.80, 19.16, 13.84. IR (ATR) 2961, 2935, 2874, 1618, 1489, 1322, 1163, 1122, 1110, 1065 cm^{-1}. HRMS (ESI) calcd. for $C_{10}H_{18}O_2Na$ $[C_{10}H_{18}O_2 + Na]^+$ 193.1199, found. 193.1198.



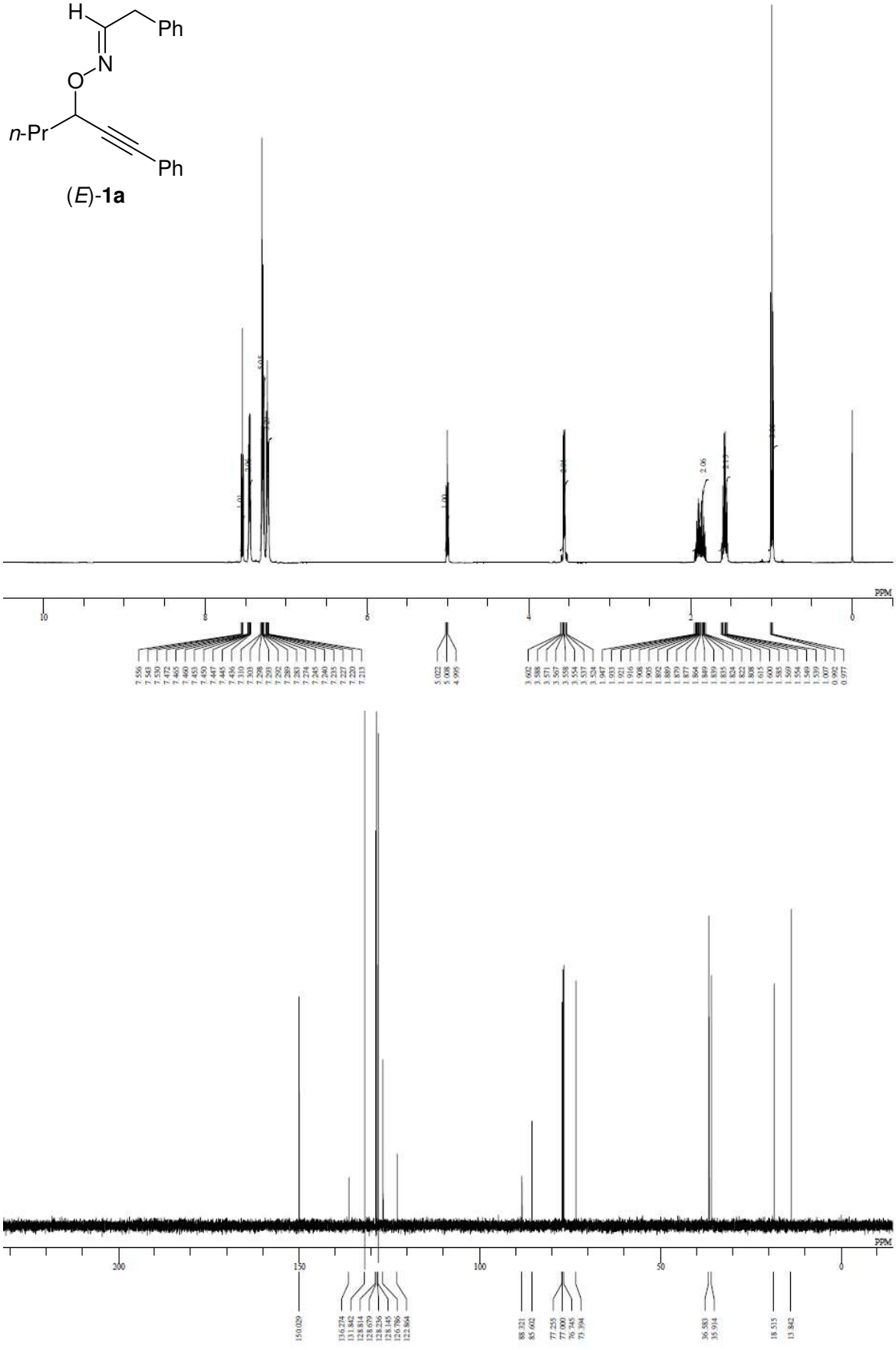
2m

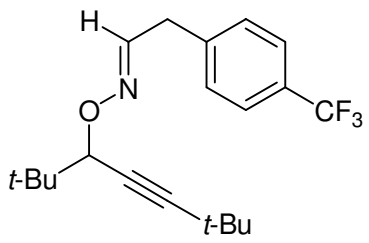
(1*E*,*NZ*)-*N*-(1-(3-cyclohexyloxiran-2-yl)-2,2-dimethylpropylidene)-2-phenylethenamine1 (2m). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (d, *J* = 13.5 Hz, 1H), 7.40 (m, 2H), 7.38 (m, 2H), 7.20 (m, 1H), 6.62 (d, *J* = 13.5 Hz, 1H), 3.49 (d, *J* = 2.5 Hz, 1H), 2.75 (dd, *J* = 2.5 Hz, *J* = 2.5 Hz,1H), 1.88-1.85 (m, 2H), 1.80-1.76 (m, 2H), 1.71-1.67 (m, 1H), 1.44-1.42 (m, 1H), 1.41-1.08 (m, 6H), 1.21 (s, 9H). ^{13}C NMR (125.65 MHz, $CDCl_3$) δ 173.30, 136.68, 134.49, 128.57, 128.45, 127.26, 126.52, 62.67, 55.82, 40.31, 40.06, 29.39, 29.09, 28.18, 26.14, 25.61, 25.52. IR (ATR) 2925, 2852, 1588, 1447, 941 cm^{-1}. HRMS (ESI) calcd. for $C_{21}H_{29}NONa$ $[C_{21}H_{29}NO + Na]^+$ 334.2141, found. 334.2140.

3n: ^{1}H and ^{13}C NMR spectra were identified to those in a literature.[2]

[2] Nemoto, T.; Ohshima, T.; Yamaguchi, K.; Shibasaki, M. *J. Am. Chem. Soc.* **2001**, *123*, 2725.

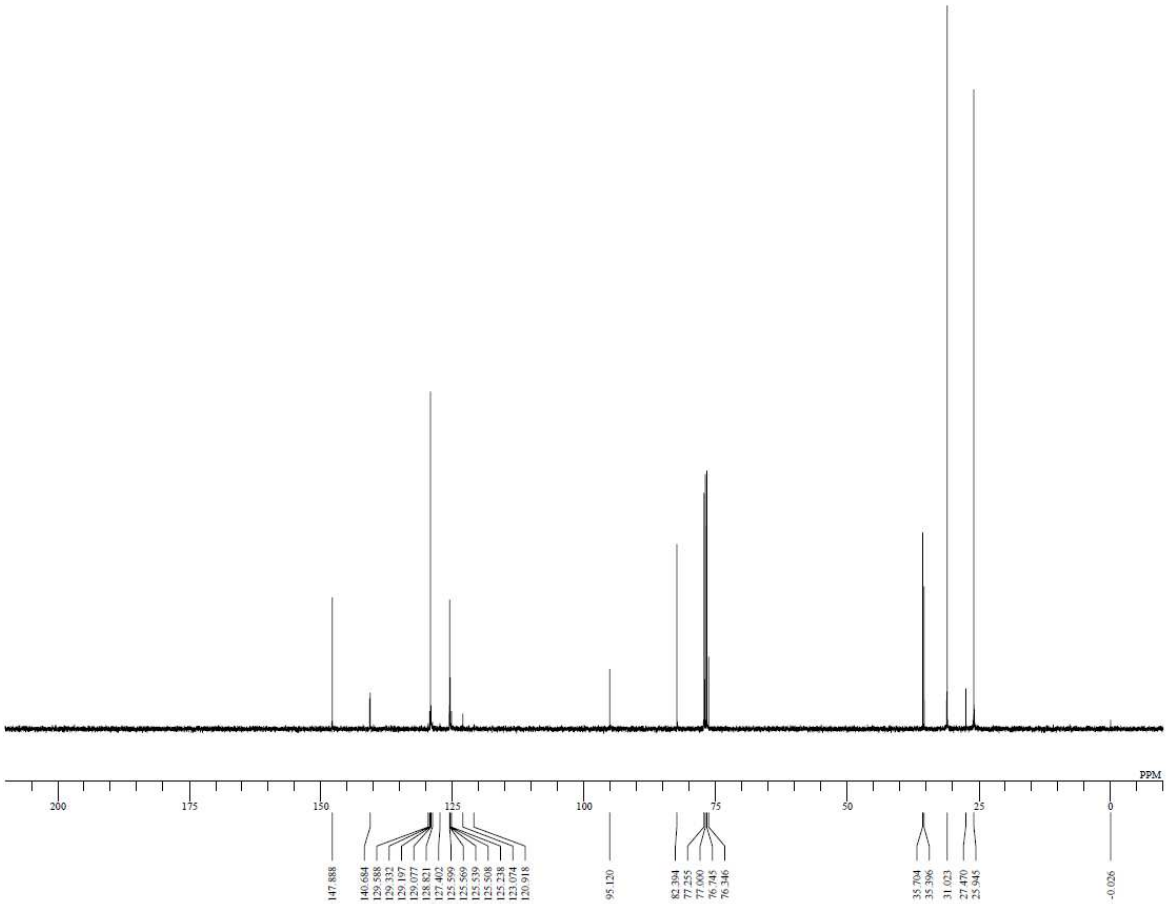
6. ^{1}H and ^{13}C NMR charts of 1 and 2.




H
N
O
CF3
t-Bu
t-Bu

(*E*)-**1b**

9.170
9.033
2.003
1.979
2.022
1.000
2.046
PPM
10
8
6
4
2
0
7.573
7.556
7.509
7.497
7.484
7.362
7.345
7.259
4.444
3.645
3.631
3.614
3.601
3.595
3.583
3.564
3.552
1.362
1.237
1.129
1.107
1.005
0.877
0.000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175
150
125
100
75
50
25
0
147.888
140.684
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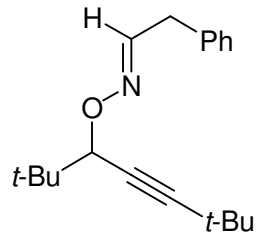
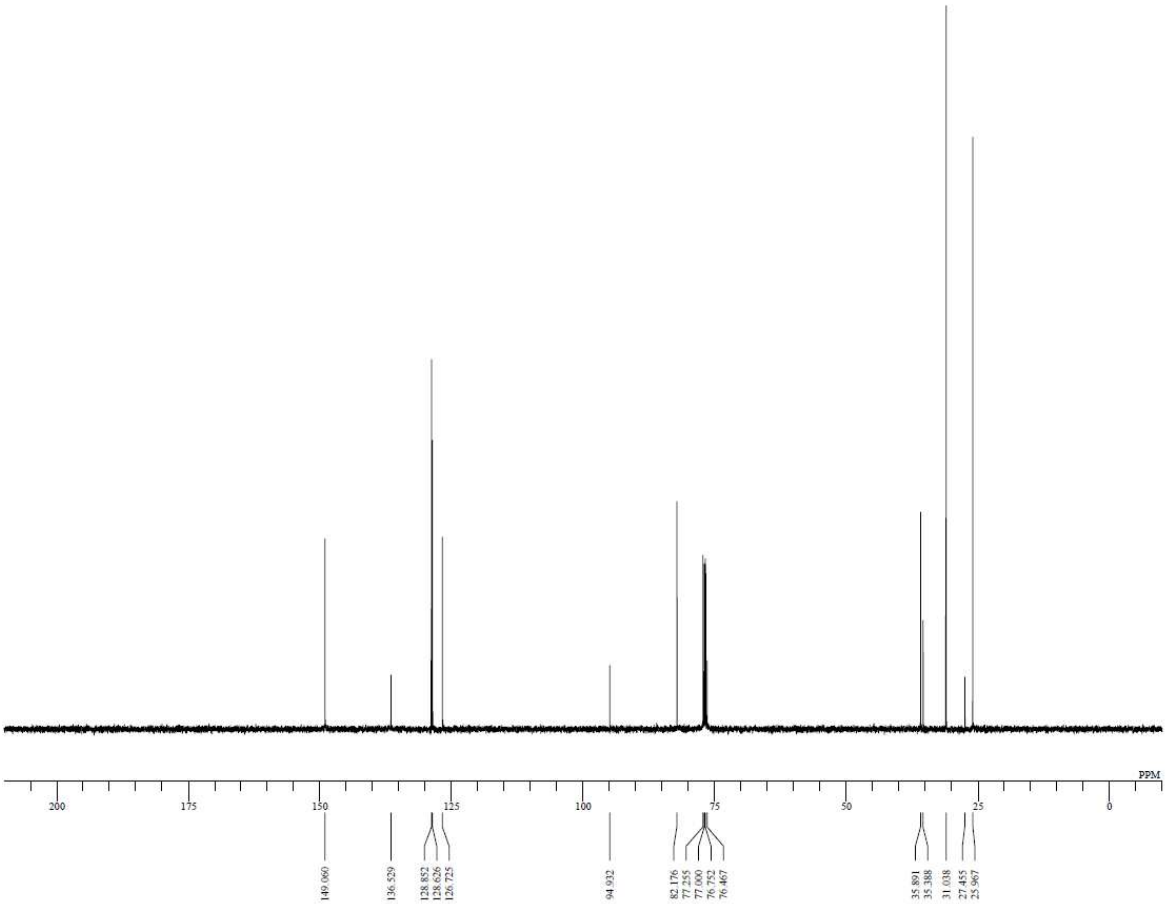
129.332
129.197
129.077
128.821
127.402
125.599
125.569
125.539
125.508
125.238
123.074
120.918
95.120
82.394
77.255
77.000
76.745
76.346
35.704
35.396
31.023
27.470
25.945
-0.026


H
Ph
N
O
t-Bu
t-Bu

(*E*)-**1c**

1.015
2.077
3.007
1.000
2.105
9.041
9.004
PPM
10
8
6
4
2
0
7.510
7.497
7.484
7.311
7.318
7.310
7.306
7.304
7.298
7.291
7.249
7.246
7.237
7.233
7.222
4.442
3.584
3.571
3.554
3.541
3.532
3.520
3.502
3.489
1.238
1.005
0.000


PPM
200
175
150
125
100
75
50
25
0
149.060
126.529
128.852
128.626
126.725
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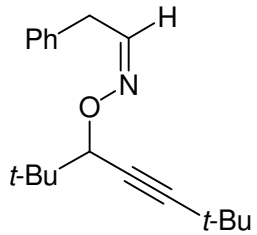
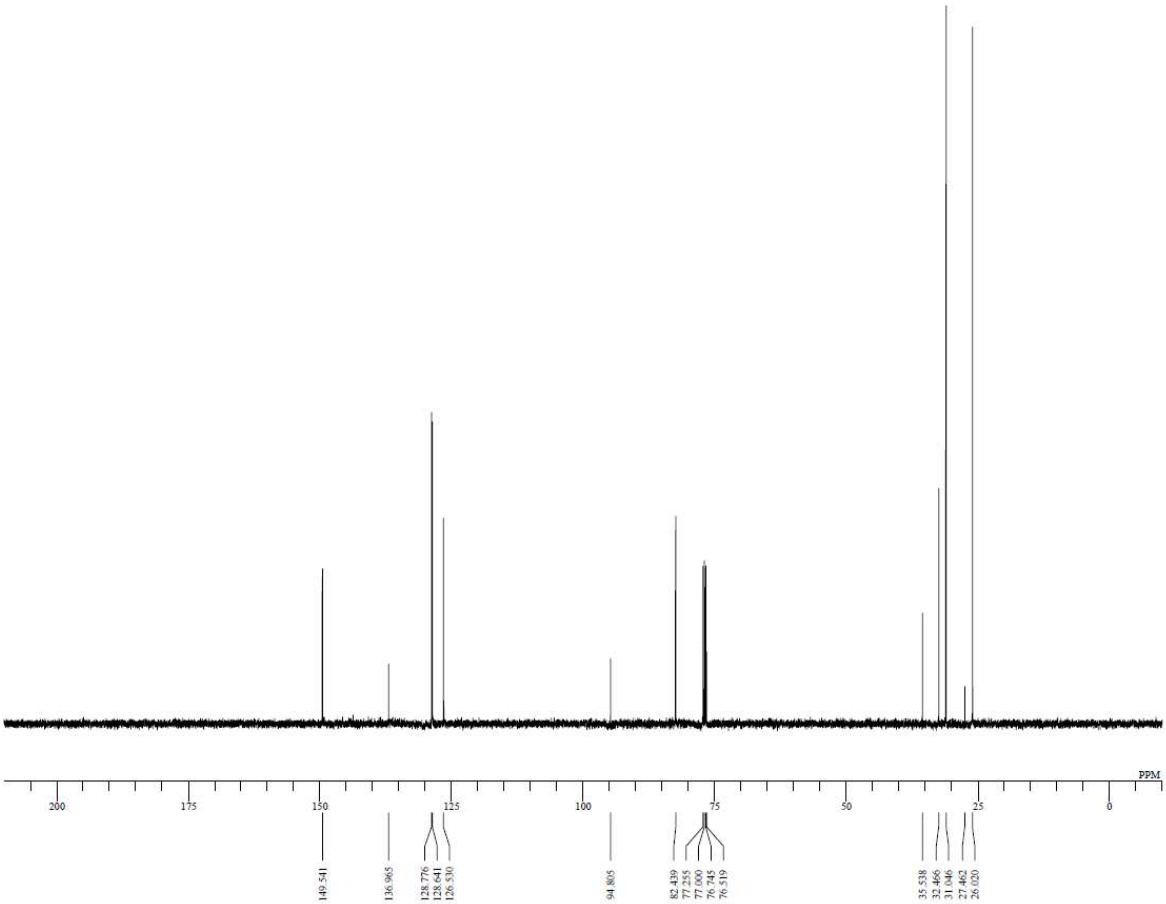
76.467
35.891
35.388
31.038
27.455
25.967


Ph
H
N
O
t-Bu
t-Bu

(*Z*)-**1c**

9.087
8.923
2.964
2.970
0.994
1.000
2.103
PPM
10
8
6
4
2
0
7.324
7.321
7.309
7.303
7.293
7.248
7.247
7.239
7.238
7.233
7.224
7.223
7.222
6.857
6.846
6.836
4.473
3.785
3.774
3.752
3.741
3.679
3.669
3.646
3.635
1.244
1.040
0.000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200
175
150
125
100
75
50
25
0
149.541
136.965
128.776
128.641
126.530
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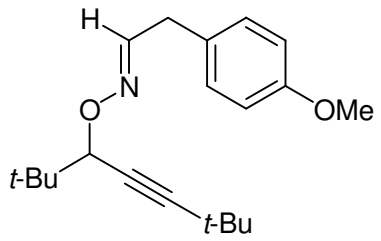
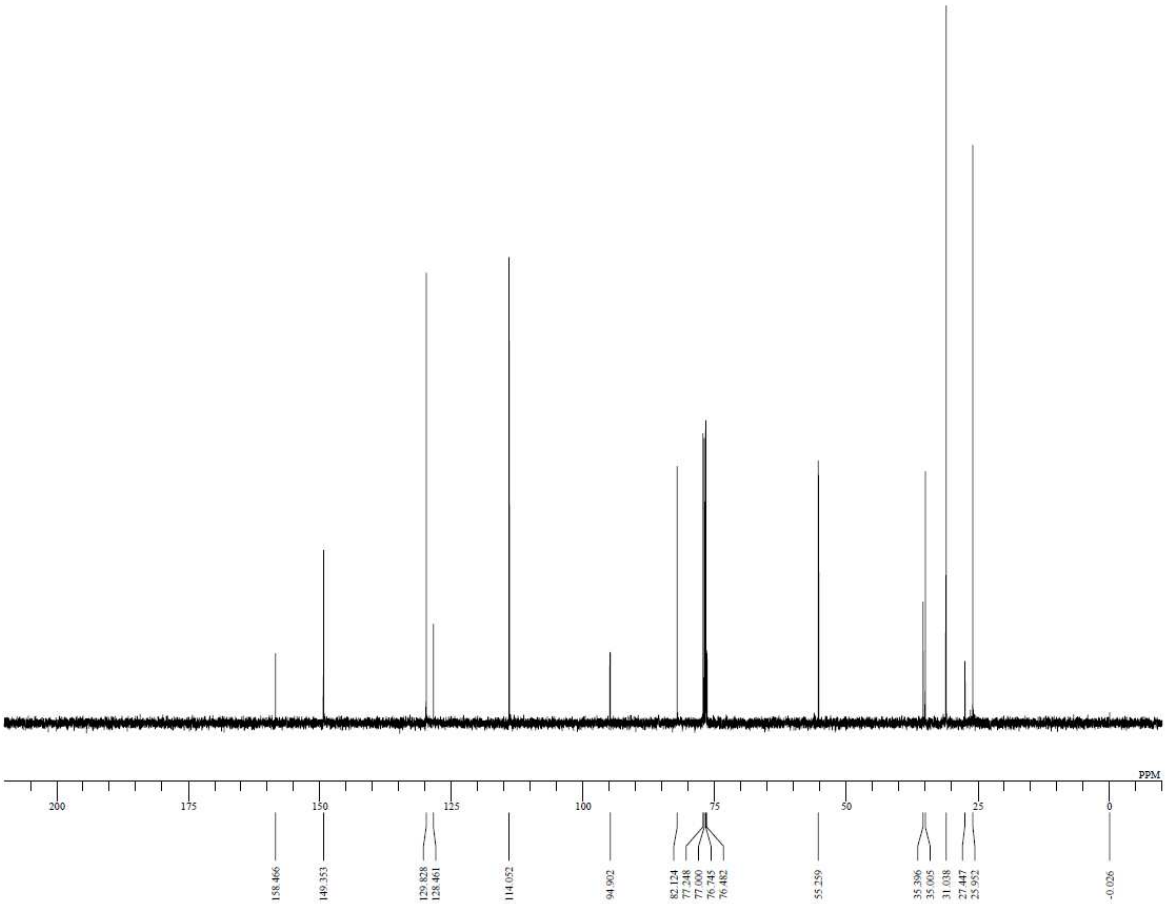
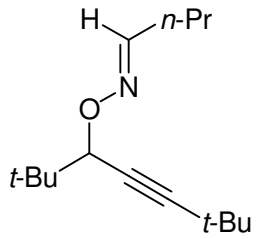
76.519
35.538
32.466
31.046
27.462
26.020


H
N
O
OMe
t-Bu
t-Bu

(*E*)-**1d**

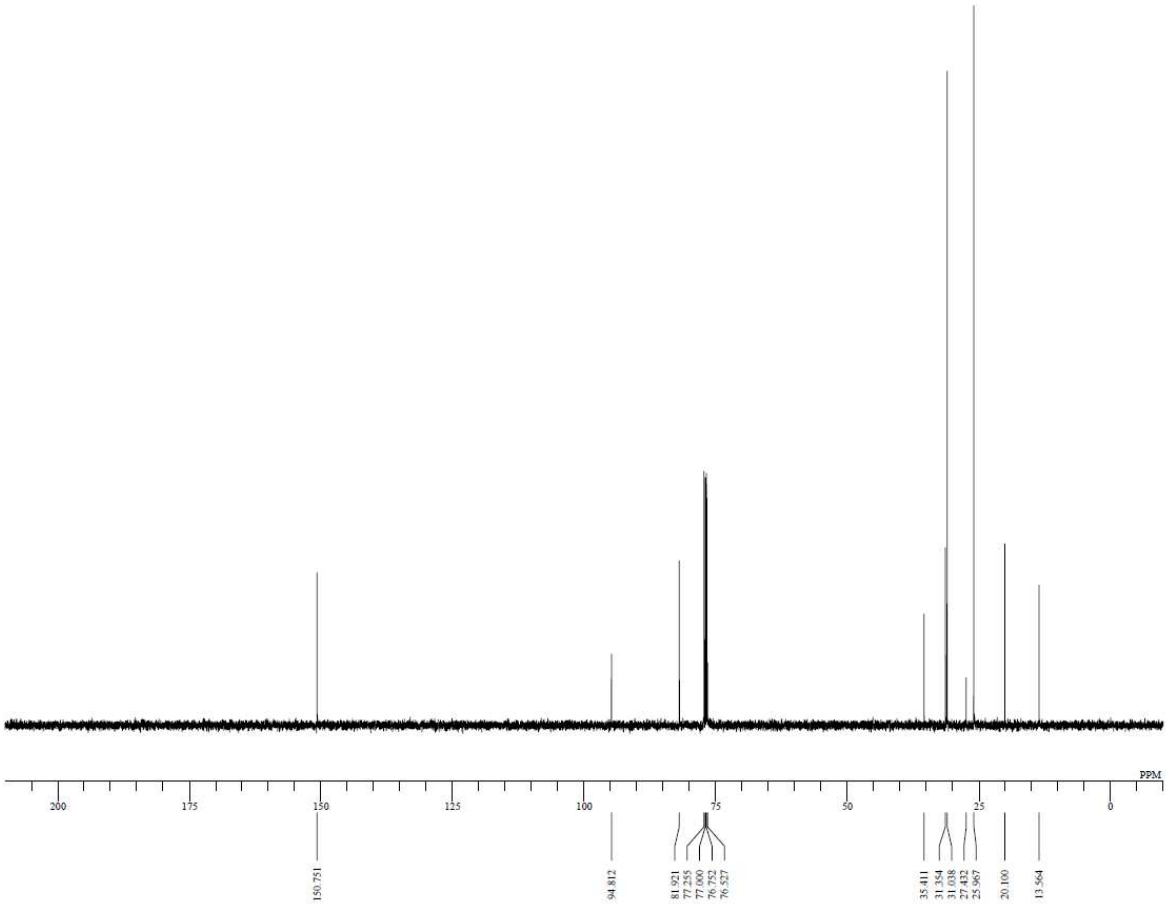
1.000
2.051
2.068
1.000
3.093
2.065
9.055
9.103
PPM
10
8
6
4
2
0
7.478
7.465
7.452
7.257
7.157
7.152
7.147
7.138
7.134
7.128
6.859
6.853
6.849
6.840
6.836
6.830
4.432
3.928
3.787
3.641
3.517
3.514
3.488
3.474
3.470
3.457
3.440
3.427
1.364
1.239
1.125
1.109
1.001
0.874
0.000

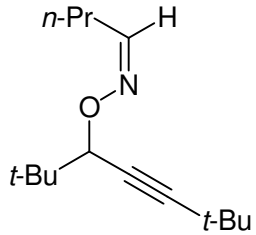

PPM
200
175
150
125
100
75
50
25
0
158.466
149.353
129.828
128.461
114.052
94.902
82.124
77.248
77.000
76.745
76.482
55.259
35.396
35.005
31.038
27.447
25.952
-0.026


H
n-Pr
N
O
t-Bu
t-Bu

(*E*)-**1e**

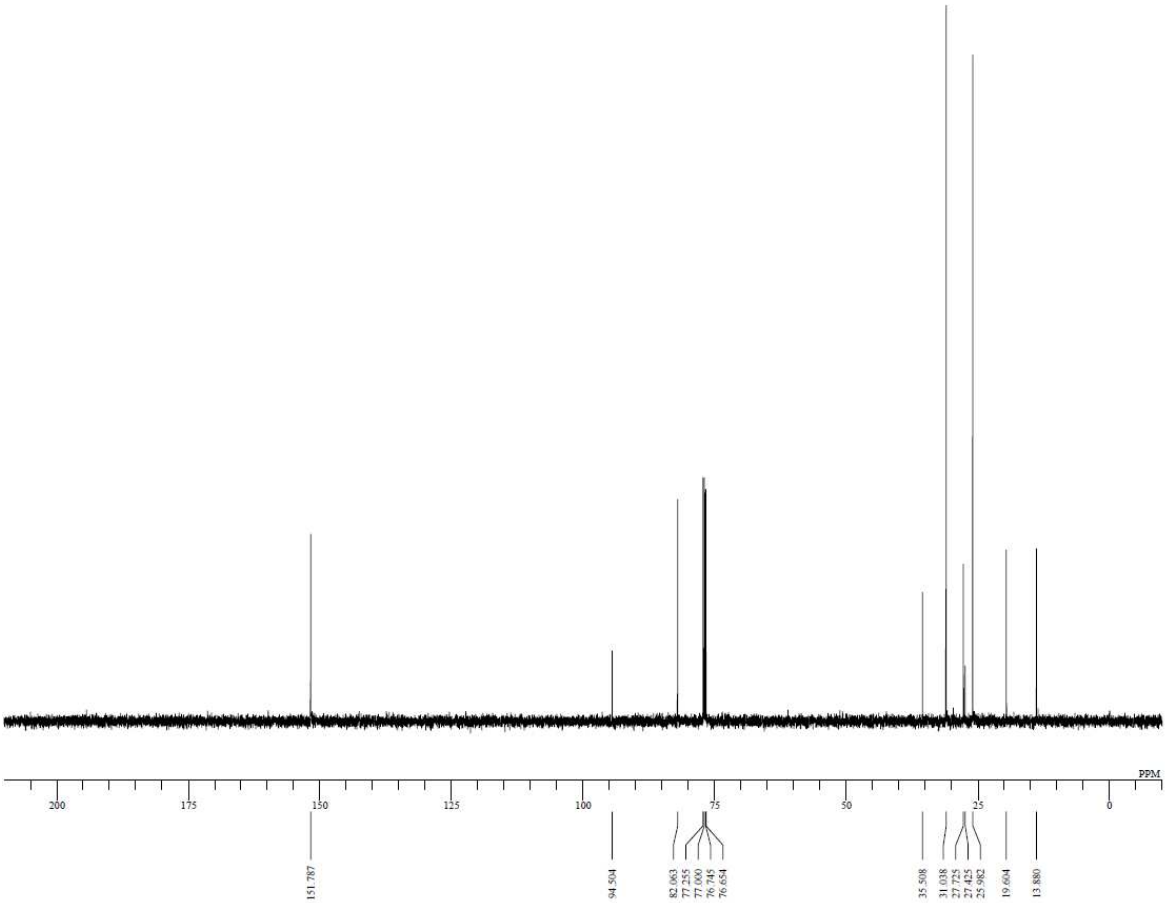
9.104
9.121
3.320
2.038
2.052
1.015
1.000
PPM
10
8
6
4
2
0
7.415
7.403
7.390
7.265
4.381
2.202
2.200
2.186
2.173
2.172
2.158
1.605
1.560
1.556
1.545
1.541
1.530
1.526
1.515
1.511
1.501
1.497
1.486
1.483
1.346
1.221
1.121
1.092
0.997
0.971
0.956
0.941
0.869
0.000


PPM
200
175
150
125
100
75
50
25
0
150.751
94.812
81.921
77.355
77.000
76.752
76.527
35.411
31.354
31.038
27.432
25.967
20.100
13.564


n-Pr
H
N
O
t-Bu
t-Bu

(*Z*)-**1e**

0.968
1.000
2.019
2.007
9.273
9.042
3.201
PPM
10
8
6
4
2
0
7.266
6.683
6.672
6.661
4.380
2.385
2.374
2.370
2.359
2.354
2.343
2.339
2.333
2.329
2.324
2.318
2.314
2.313
2.303
2.298
2.286
2.282
2.272
1.634
1.550
1.535
1.520
1.506
1.491
1.476
1.347
1.222
1.132
1.093
1.009
0.973
0.958
0.943
0.881
0.000


PPM
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175
150
125
100
75
50
25
0
151.787
94.504
82.063
77.255
77.000
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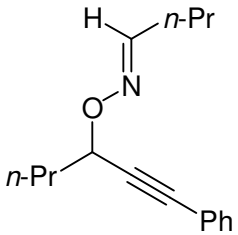
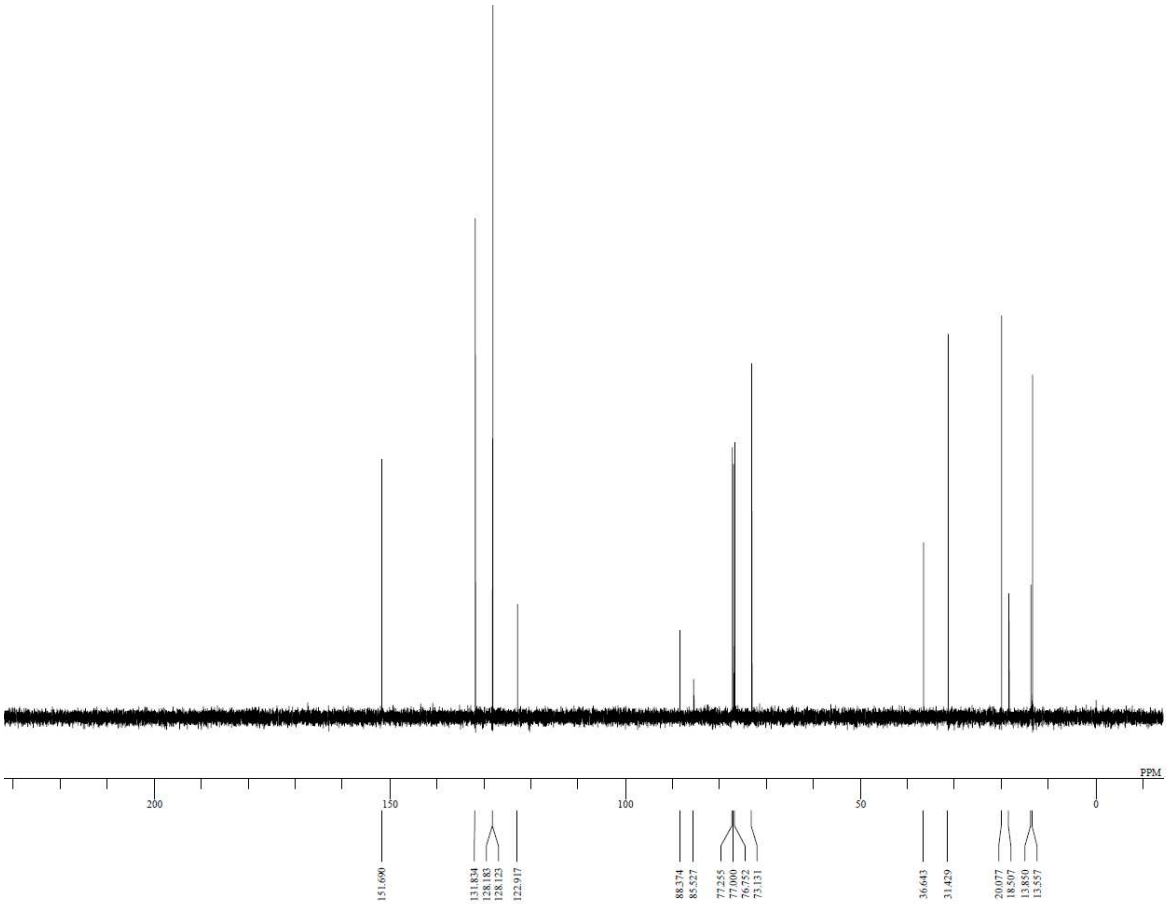
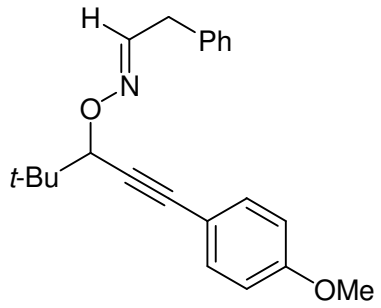
27.725
27.425
25.982
19.604
13.880


H
n-Pr
N
O
n-Pr
Ph

(*E*)-**1f**

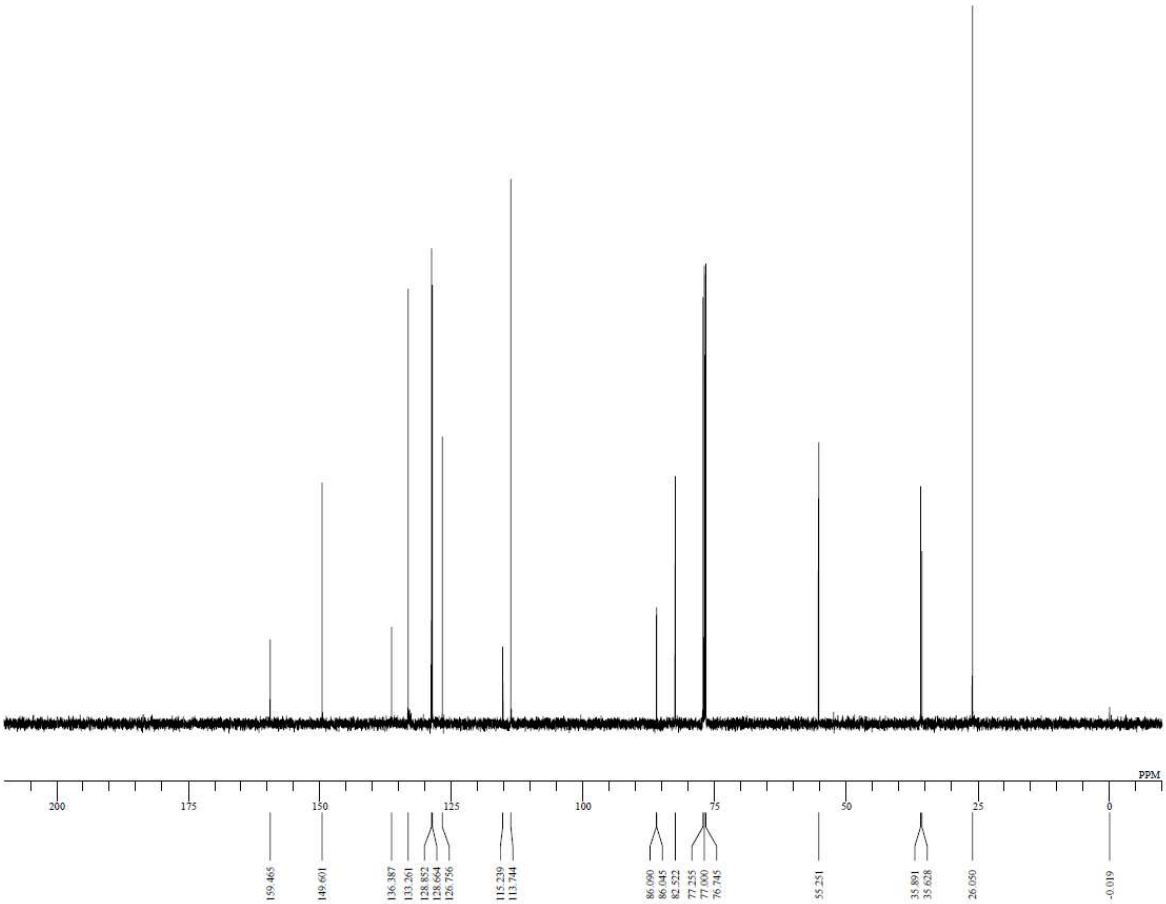
3.04
2.90
1.00
2.74
2.58
5.55
PPM
10
8
6
4
2
0
7.458
7.455
7.449
7.445
7.441
7.439
7.434
7.432
7.300
7.292
7.287
7.283
7.281
7.278
7.274
7.271
4.967
4.951
4.939
2.226
2.213
2.200
2.197
2.184
1.927
1.912
1.900
1.887
1.868
1.872
1.868
1.858
1.856
1.844
1.827
1.818
1.814
1.804
1.800
1.786
1.605
1.591
1.582
1.576
1.560
1.557
1.541
1.527
1.512
1.498
1.490
1.041
0.985
0.975
0.971
0.960
0.945


PPM
200
150
100
50
0
151.690
131.834
128.183
128.123
122.917
88.374
85.527
77.255
77.000
76.752
73.131
36.643
31.429
20.077
18.507
13.850
13.557


H
Ph
N
O
t-Bu
OMe

(*E*)-**1g**

9.142
3.109
3.037
2.086
2.069
2.057
2.074
1.028
1.000
PPM
10
8
6
4
2
0
7.563
7.549
7.537
7.411
7.409
7.405
7.404
7.388
7.382
7.304
7.294
7.287
7.280
7.274
7.251
7.241
7.228
7.214
6.839
6.838
6.833
6.816
6.810
4.676
3.804
3.600
3.587
3.570
3.566
3.556
3.552
3.535
3.521
1.567
1.212
1.088
0.960
0.000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200
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150
125
100
75
50
25
0
159.465
149.601
136.387
133.261
128.852
128.664
126.756
115.239
113.744
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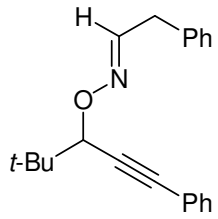
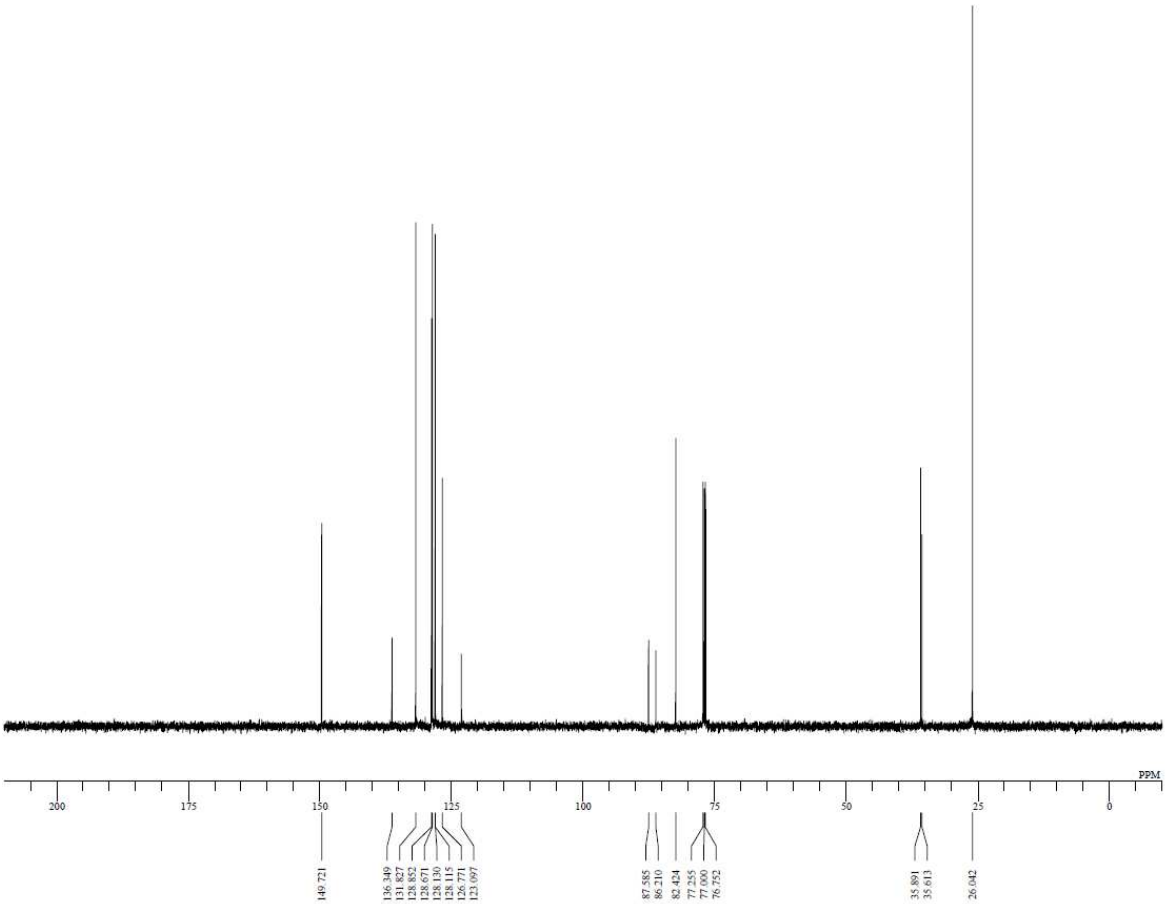
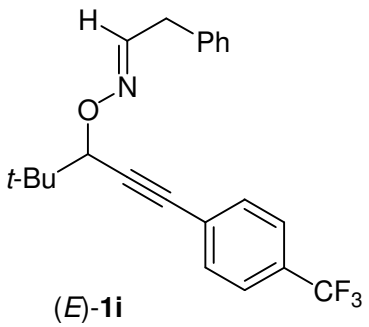
86.045
82.522
77.255
77.000
76.745
55.251
35.891
35.628
26.050
-0.019


H
Ph
N
O
t-Bu
Ph

(*E*)-**1h**

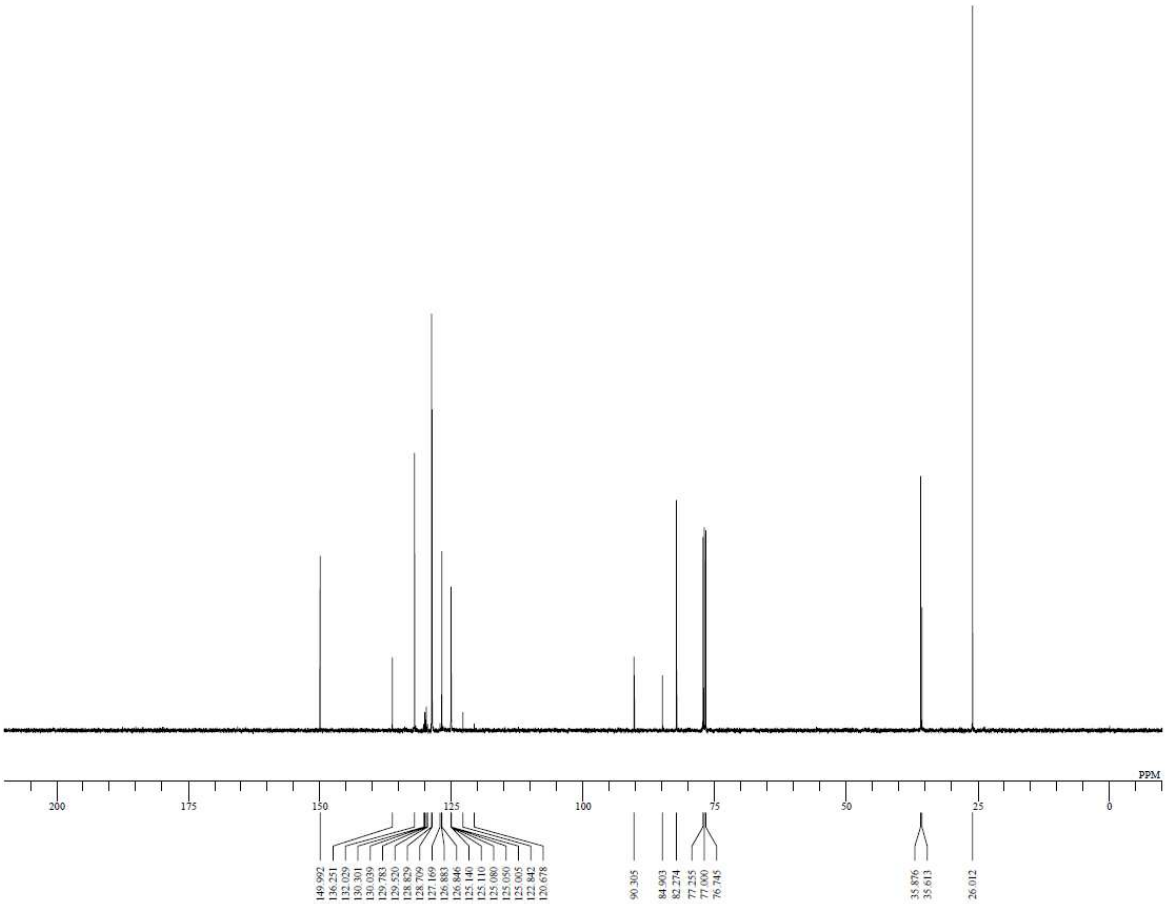
9.003
5.121
3.387
2.650
0.993
1.000
2.110
PPM
10
8
6
4
2
0
7.568
7.555
7.542
7.469
7.464
7.459
7.457
7.454
7.452
7.450
7.447
7.441
7.308
7.301
7.295
7.292
7.288
7.284
7.283
7.275
7.270
7.219
7.235
7.226
7.219
7.214
7.210
7.208
4.693
3.601
3.588
3.571
3.563
3.558
3.550
3.533
3.520
1.572
1.098
0.000

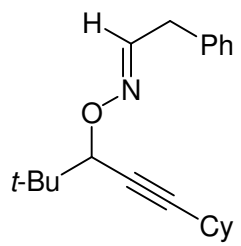

PPM
200
175
150
125
100
75
50
25
0
149.721
136.349
131.827
128.852
128.671
128.130
128.115
126.771
123.697
87.585
86.210
82.424
77.255
77.000
76.752
35.891
35.613
26.042


H
Ph
N
O
t-Bu
CF3

(*E*)-**1i**

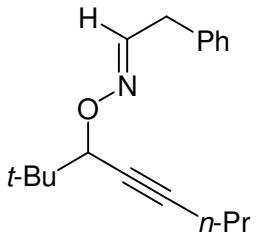
5.006
3.243
1.987
1.000
2.057
8.928
PPM
10
8
6
4
2
0
7.580
7.570
7.567
7.552
7.539
7.535
7.533
7.312
7.309
7.306
7.299
7.297
7.294
7.285
7.280
7.279
7.253
7.251
7.246
7.240
7.236
7.224
4.843
4.696
4.543
3.701
3.696
3.688
3.684
3.605
3.591
3.574
3.569
3.561
3.556
3.539
3.526
3.443
3.438
3.430
3.425
1.576
1.223
1.069
0.971
0.000


PPM
200
175
150
125
100
75
50
25
0
149.992
136.251
132.029
130.301
130.039
129.783
129.520
128.829
128.709
127.169
126.883
126.846
125.140
125.110
125.080
125.050
123.605
122.943
120.678
90.305
84.903
82.274
77.255
77.000
76.745
35.876
35.613
26.012


H
Ph
N
O
t-Bu
Cy

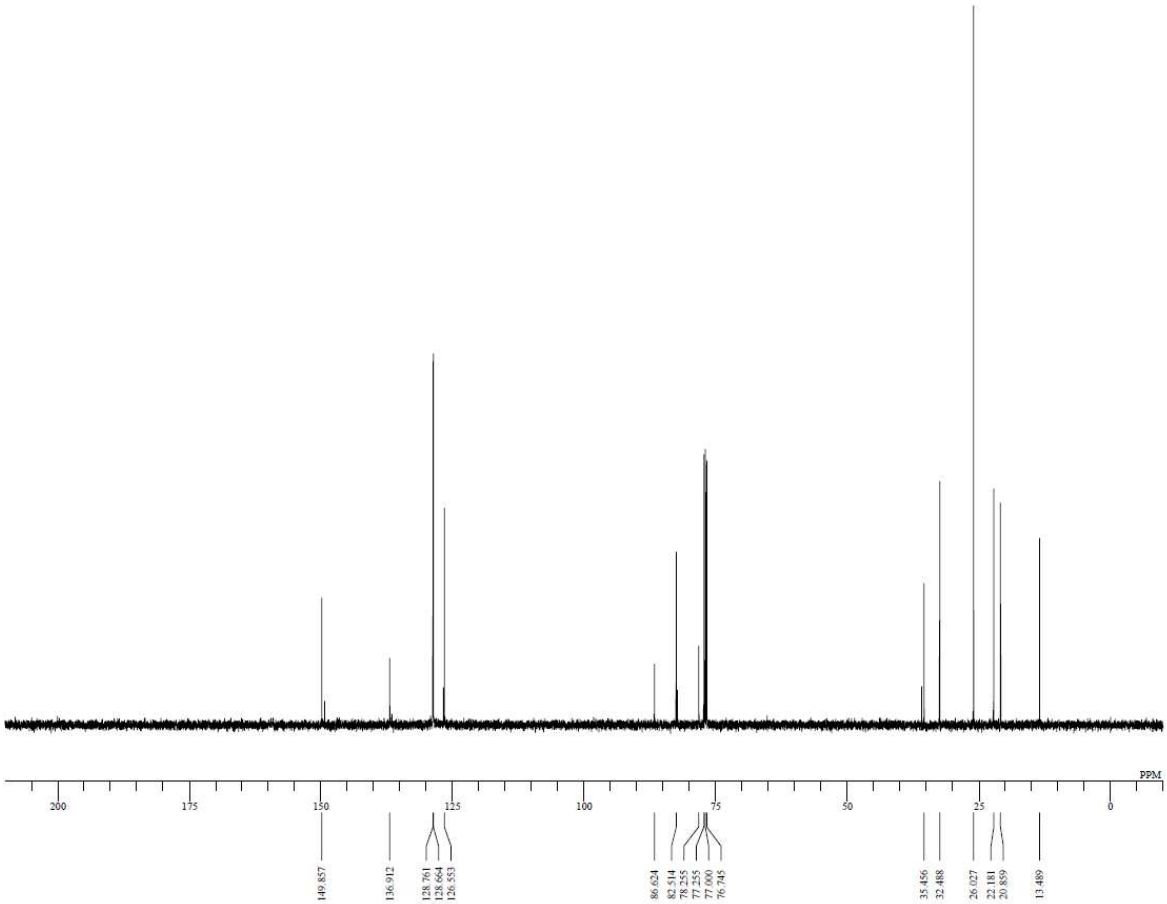
(*E*)-**1j**

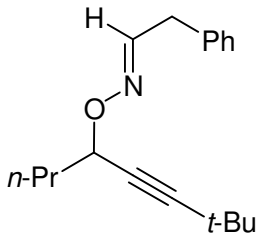
0.980
1.986
3.020
1.000
2.021
0.983
2.016
2.068
3.050
3.089
8.986
PPM
10
8
6
4
2
0
7.516
7.503
7.490
7.332
7.319
7.309
7.307
7.296
7.292
7.255
7.250
7.248
7.234
7.233
7.220
4.464
4.460
3.582
3.568
3.551
3.545
3.538
3.512
3.503
2.463
1.804
1.798
1.787
1.772
1.767
1.758
1.728
1.715
1.708
1.702
1.696
1.690
1.684
1.676
1.670
1.581
1.513
1.508
1.495
1.489
1.478
1.471
1.465
1.353
1.333
1.317
1.313
1.301
1.294
1.287
1.275
1.140
1.016
0.889
0.000
PPM
200
175
150
125
100
75
50
25
0
149.195
136.507
128.852
128.626
126.725
90.861
82.266
78.044
77.255
77.000
76.745
35.899
35.388
32.646
32.601
29.025
25.982
25.960
24.705
-0.019


H
Ph
N
O
t-Bu
n-Pr

(*E*)-**1k**

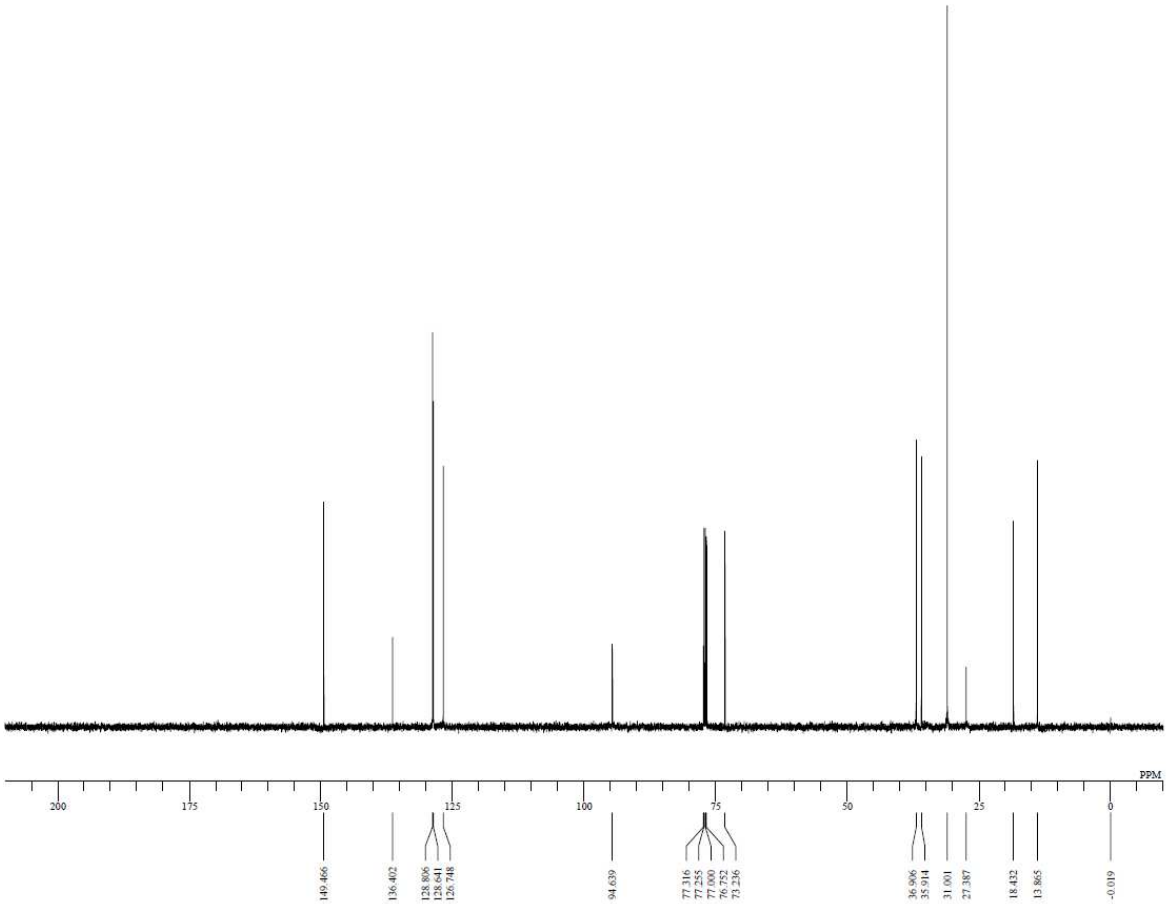
0.985
2.000
3.019
1.000
2.021
2.035
2.223
12.000
PPM
10
8
6
4
2
0
7.521
7.518
7.495
7.323
7.312
7.308
7.297
7.294
7.254
7.250
7.235
7.231
7.218
4.460
4.456
4.452
3.553
3.540
2.252
2.248
2.238
2.234
2.224
2.220
1.588
1.574
1.560
1.545
1.531
1.516
1.142
1.018
1.009
0.994
0.979
0.890
0.000

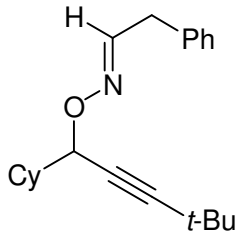

PPM
200
175
150
125
100
75
50
25
0
149.857
136.912
128.761
128.664
126.553
86.624
82.514
78.255
77.255
77.000
76.745
35.456
32.488
26.027
22.181
20.859
13.489


H
Ph
N
O
n-Pr
t-Bu

(*E*)-**1l**

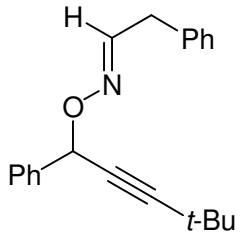
0.985
2.011
3.020
1.000
2.042
1.022
0.996
2.013
9.051
3.009
PPM
10
8
6
4
2
0


PPM
200
175
150
125
100
75
50
25
0


H
Ph
N
O
Cy
t-Bu

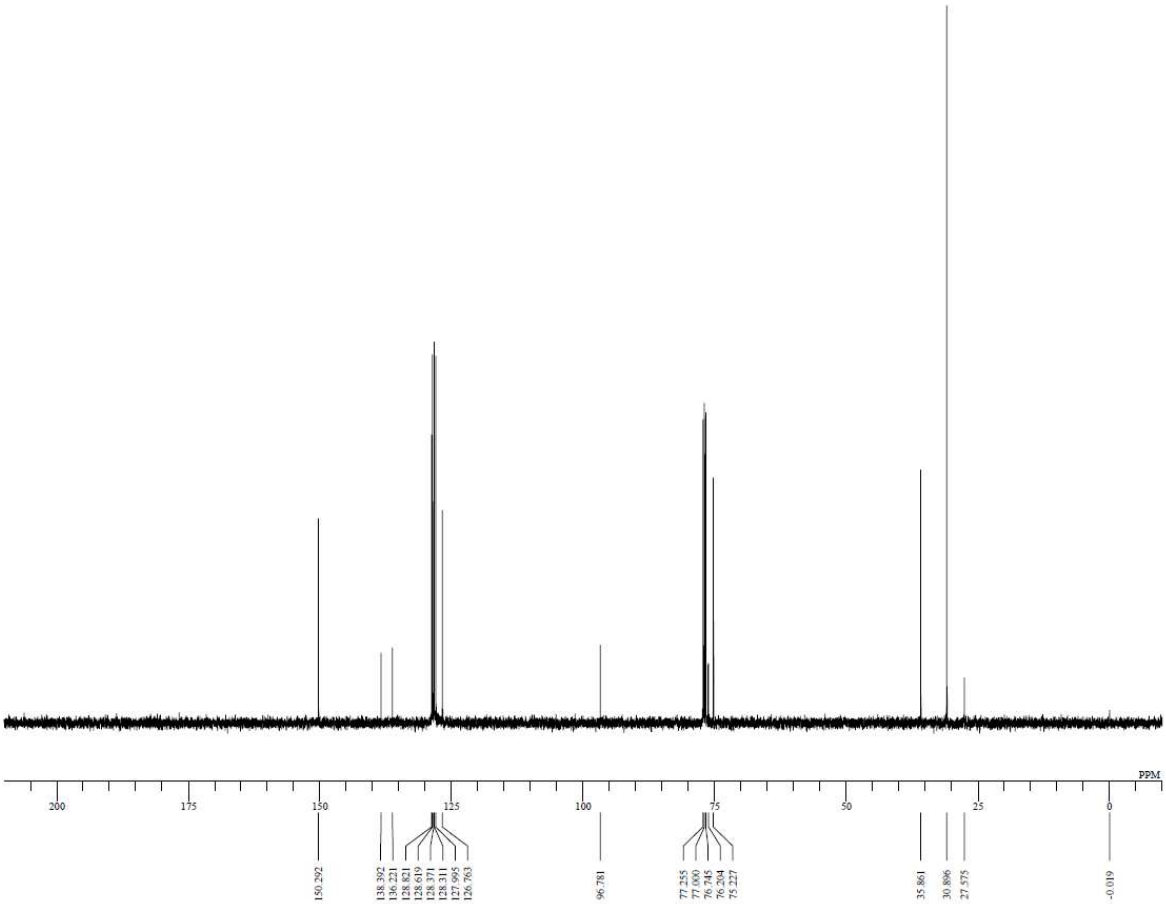
(*E*)-**1m**

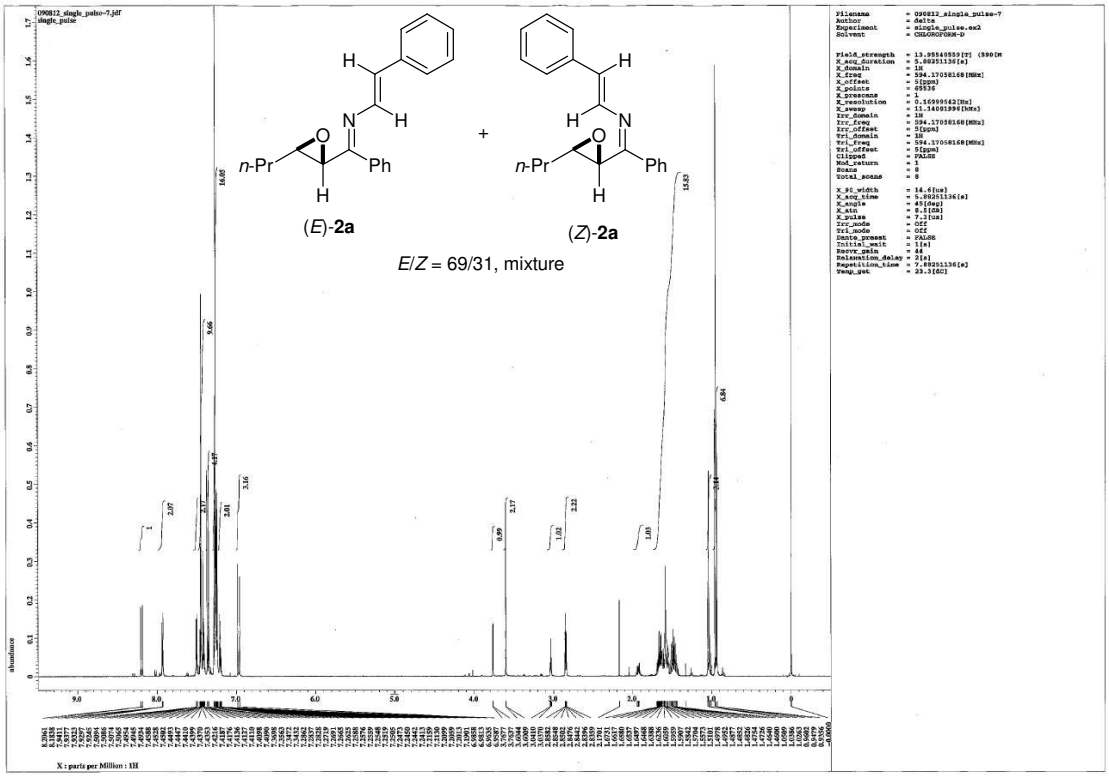
14.517
6.211
3.042
2.010
0.990
1.000
2.039
PPM
10
8
6
4
2
0
PPM
200
175
150
125
100
75
50
25
0

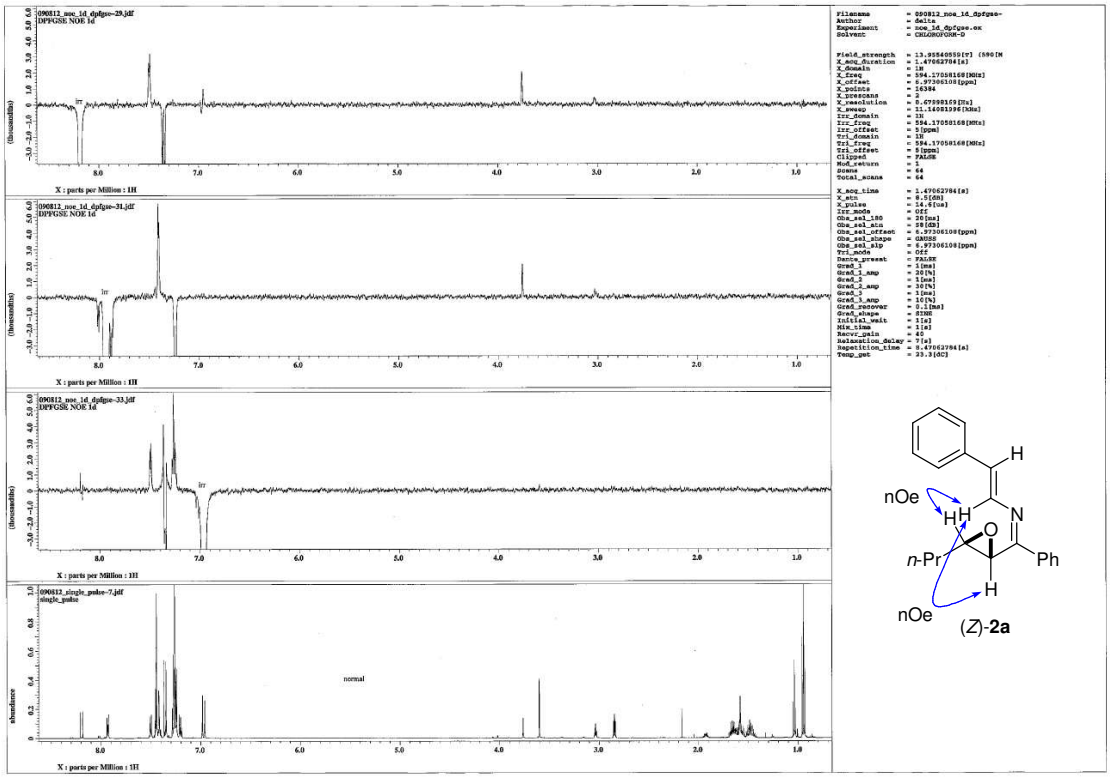

H
Ph
N
O
Ph
t-Bu

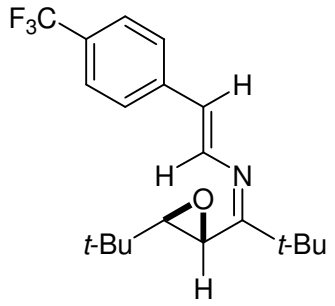
(*E*)-**1n**

9.007
3.106
2.298
2.089
1.990
1.136
1.094
0.384
1.000
2.102
PPM
10
8
6
4
2
0
7.561
7.558
7.554
7.544
7.543
7.538
7.534
7.521
7.518
7.386
7.383
7.380
7.369
7.366
7.357
7.355
7.350
7.343
7.340
7.337
7.331
7.326
7.319
7.314
7.311
7.308
7.304
7.302
7.299
7.292
7.289
7.286
7.276
7.273
7.269
7.244
7.242
7.239
7.236
7.229
7.225
7.220
7.213
7.210
7.207
7.190
7.187
7.173
7.172
5.835
3.573
3.559
3.542
3.529
3.522
3.509
3.492
3.479
1.549
1.402
1.386
1.311
1.277
1.202
1.148
0.000


PPM
200
175
150
125
100
75
50
25
0
150.292
138.392
136.221
128.571
128.610
128.371
128.311
127.995
126.763
96.781
77.255
77.000
76.745
76.204
75.227
35.861
30.896
27.575
-0.019

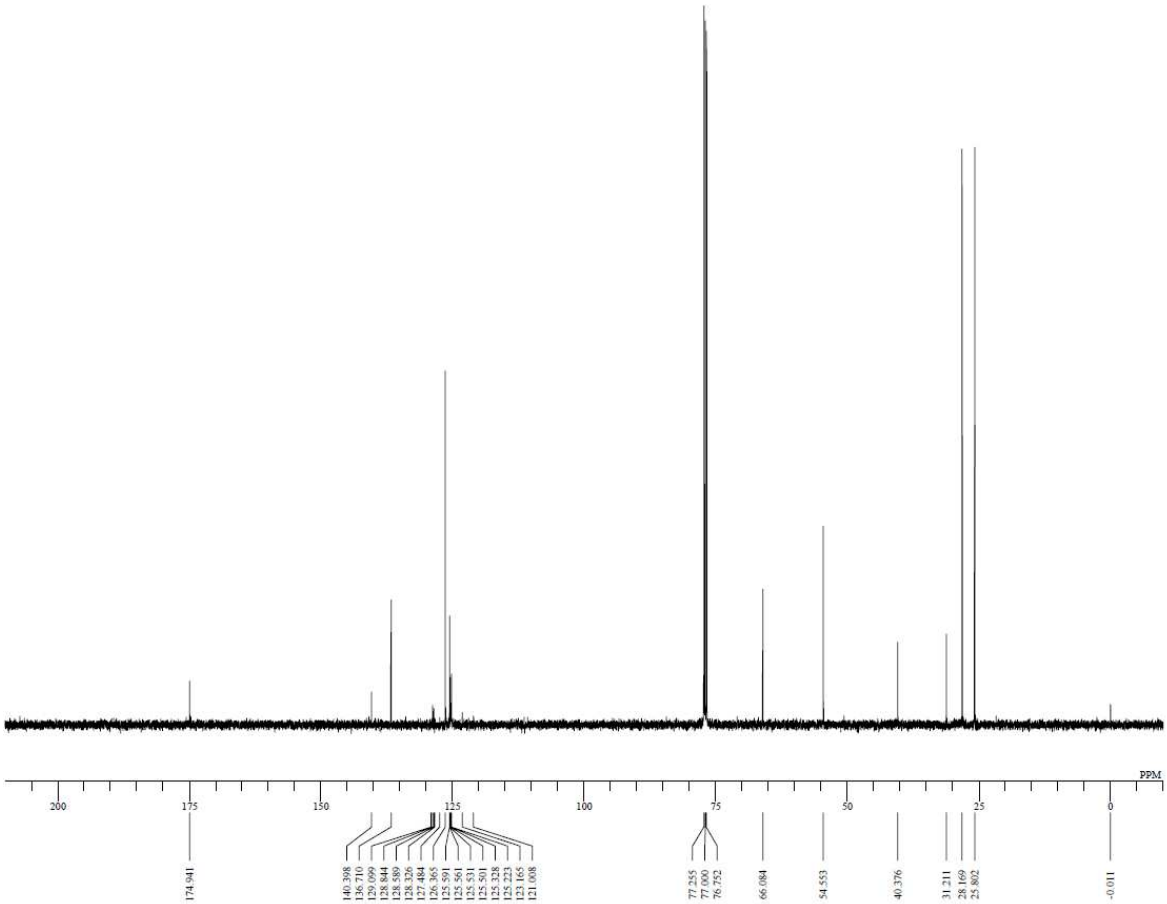

(E)-2a
(Z)-2a
E/Z = 69/31, mixture

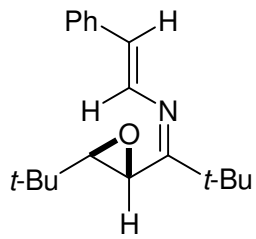

nOe
nOe
(Z)-2a


F3C
H
H
N
O
t-Bu
t-Bu
H

2b

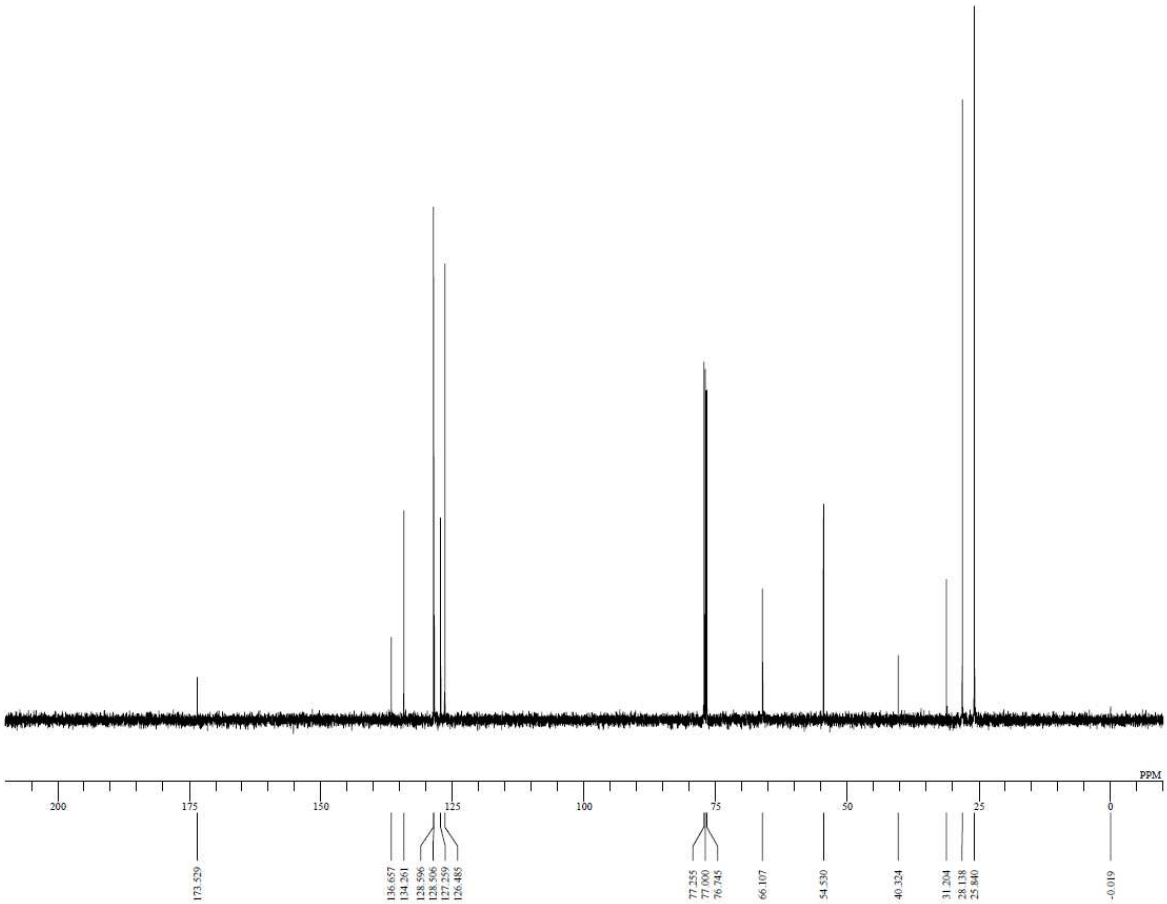
1.008
2.111
2.062
0.993
1.017
1.000
9.134
9.020
PPM
10
8
6
4
2
0
8.018
7.991
7.555
7.538
7.468
7.451
7.260
6.545
6.517
3.560
3.555
2.728
2.723
1.557
1.252
0.994
0.000

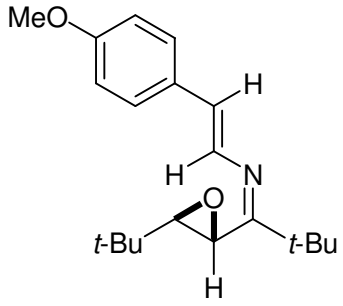

PPM
200
175
150
125
100
75
50
25
0
174.941
140.398
136.710
129.099
128.844
128.589
128.326
127.484
126.365
125.591
125.561
125.531
125.501
125.328
125.223
123.165
121.008
77.255
77.000
76.752
66.084
54.553
40.376
31.211
28.169
25.802
-0.011


Ph
H
H
N
O
t-Bu
t-Bu
H

2c

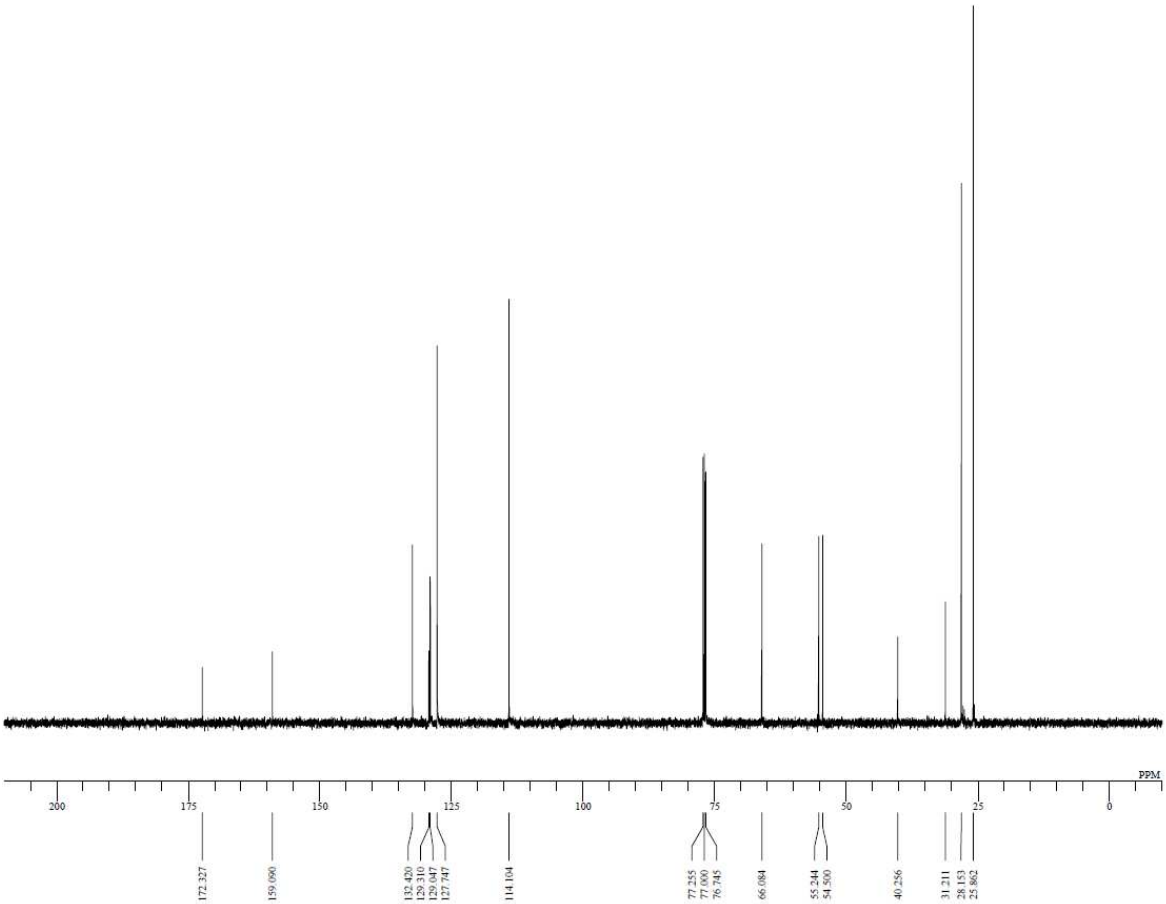
9.076
8.997
2.034
2.169
1.088
0.999
0.989
1.012
1.000
PPM
10
8
6
4
2
0
7.935
7.908
7.398
7.395
7.381
7.319
7.315
7.304
7.292
7.289
7.254
7.227
7.224
7.222
7.213
7.210
7.206
7.197
7.195
7.193
6.640
6.613
3.548
3.543
2.729
2.724
1.581
1.249
1.009
0.000

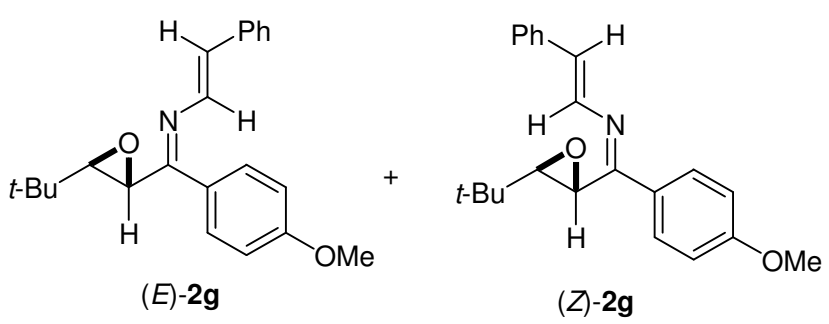

PPM
200
175
150
125
100
75
50
25
0
173.529
136.657
134.261
128.596
128.506
127.259
126.485
77.255
77.000
76.745
66.107
54.530
40.324
31.204
28.138
25.840
-0.019


MeO
H
H
N
O
t-Bu
t-Bu
H

2d

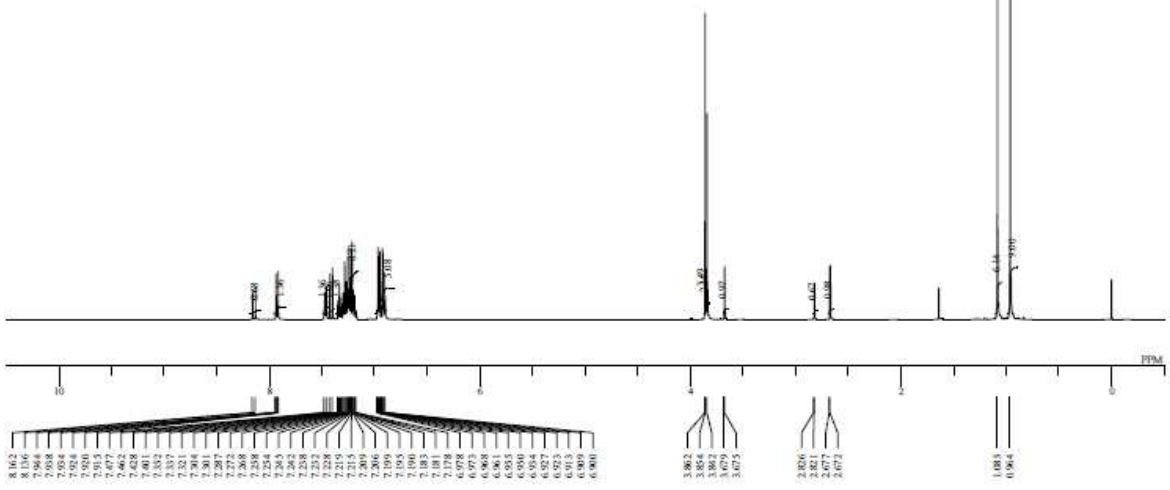
1.010
2.032
2.068
0.996
3.083
1.000
1.015
9.171
8.889
PPM
10
8
6
4
2
0
7.846
7.820
7.346
7.340
7.336
7.326
7.322
7.317
7.256
6.867
6.861
6.855
6.844
6.838
6.648
6.621
3.804
3.541
3.536
2.725
2.720
1.606
1.242
1.017
0.000

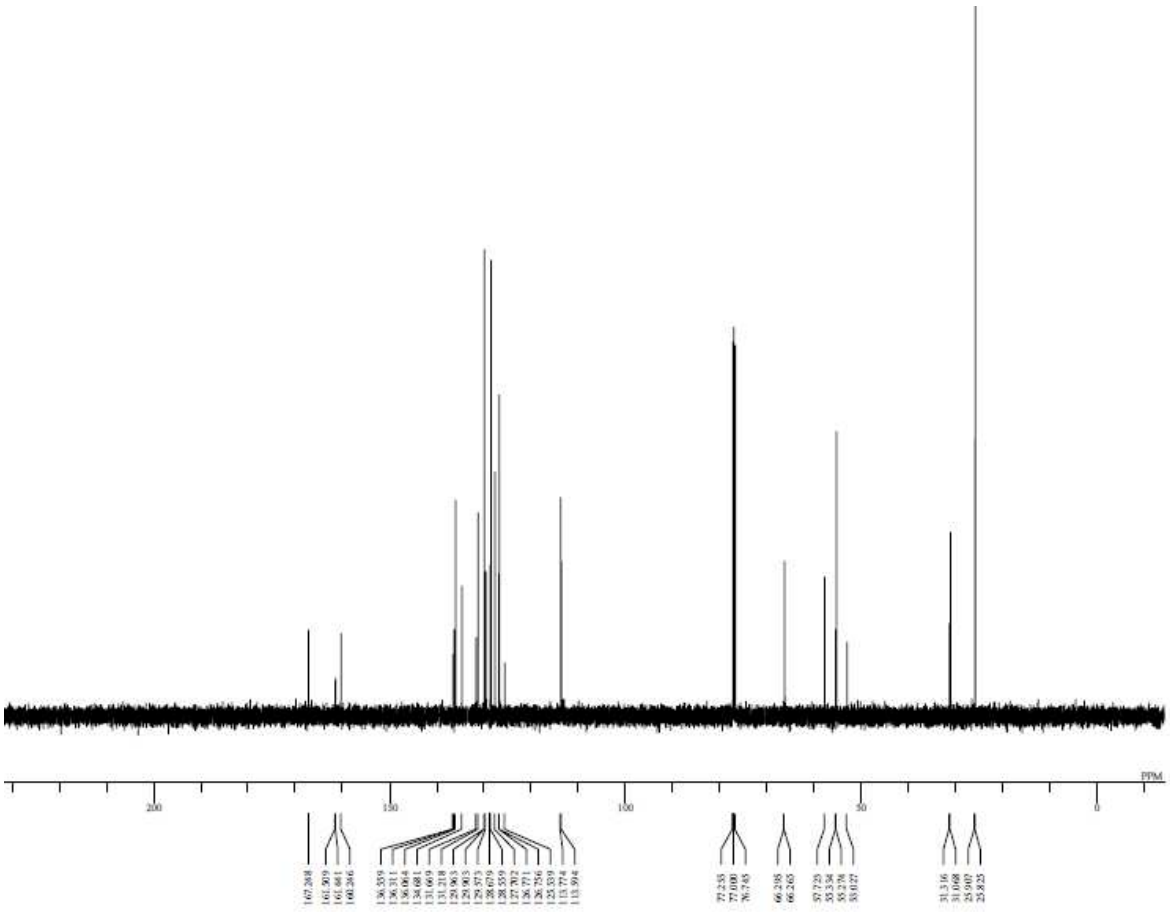

PPM
200
175
150
125
100
75
50
25
0
172.327
159.090
132.420
129.310
129.047
127.747
114.104
77.255
77.000
76.745
66.084
55.244
54.500
40.256
31.211
28.153
25.862

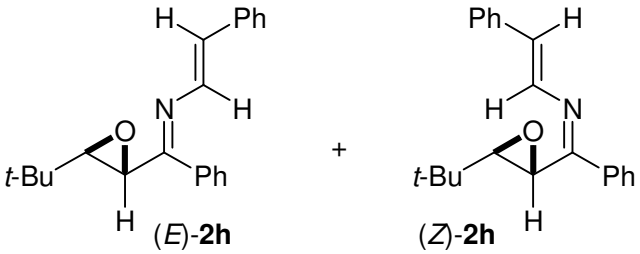


(*E*)-**2g** (*Z*)-**2g**

E/*Z* = 59/41, mixture

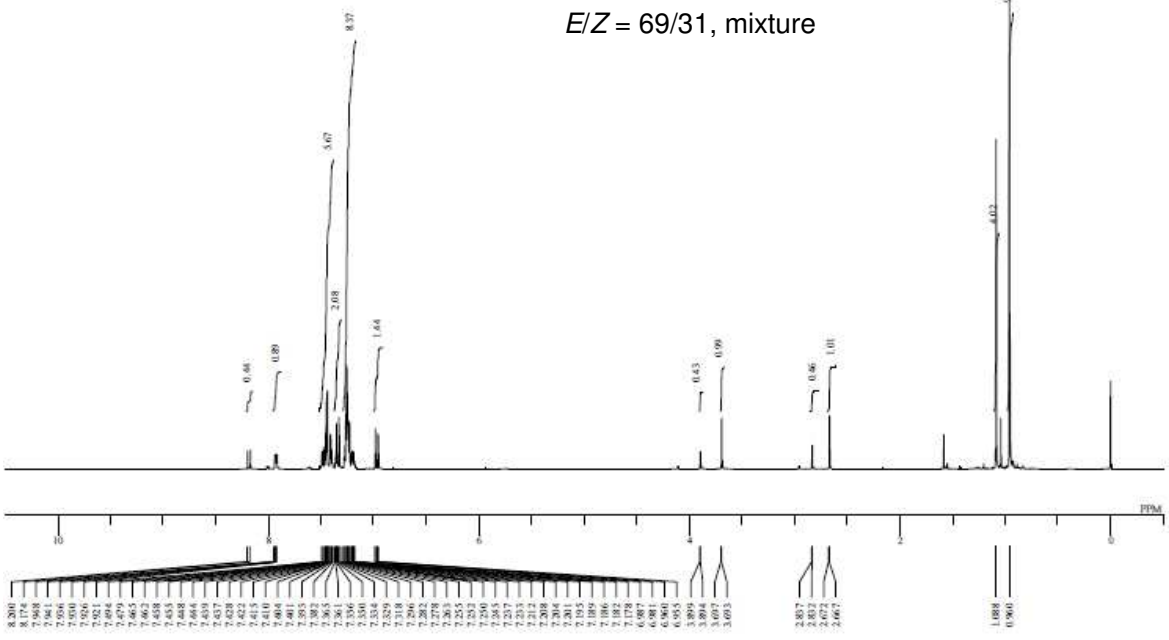


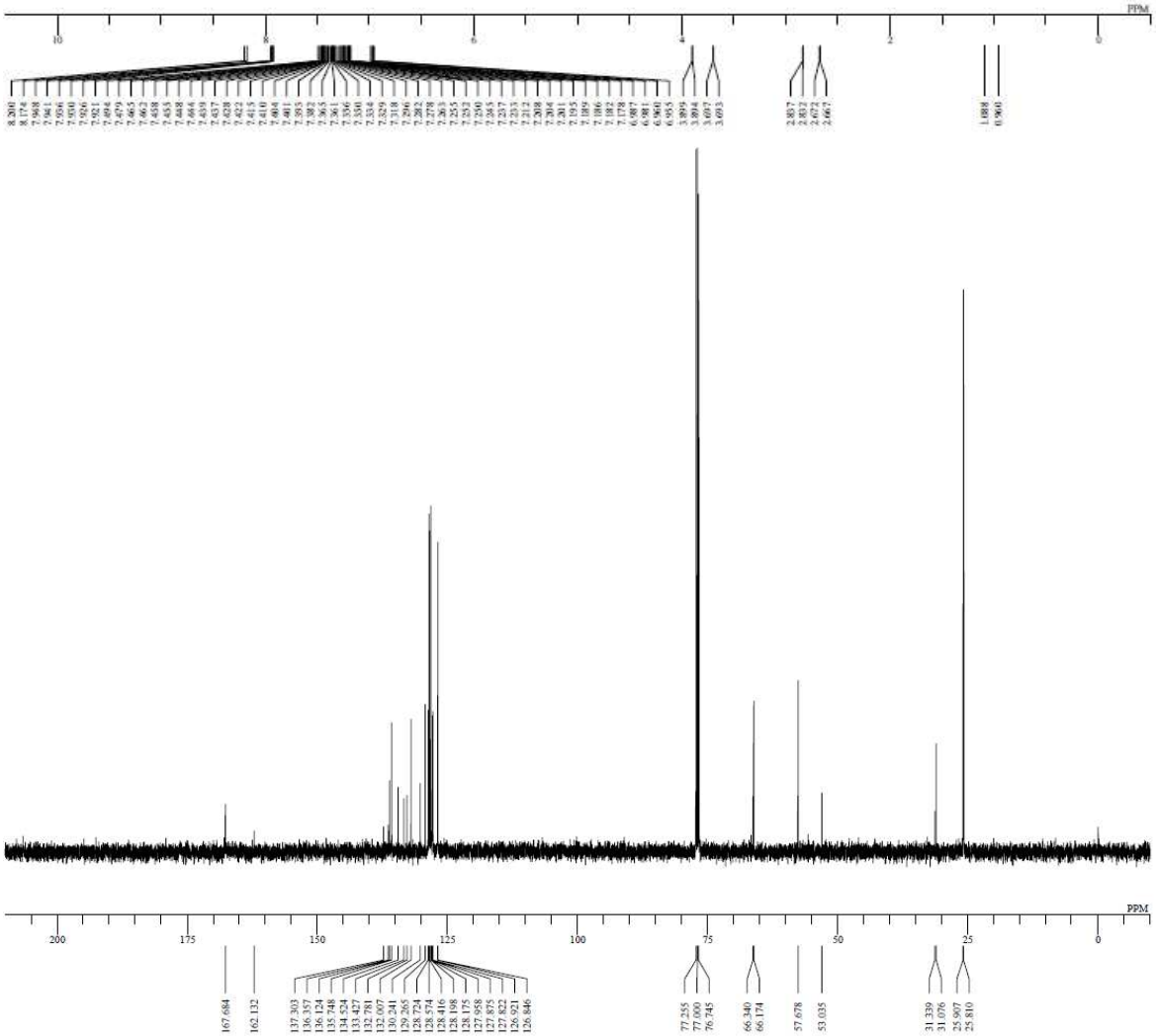


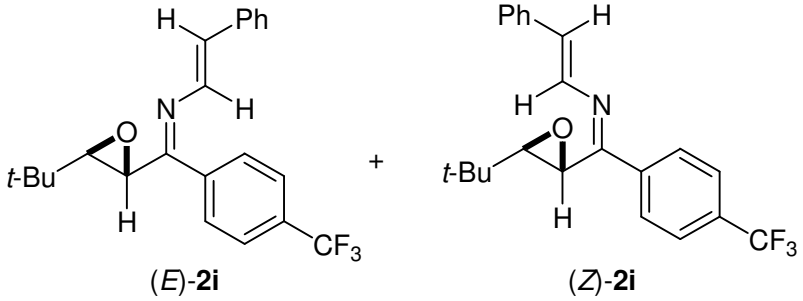


(*E*)-**2h** (*Z*)-**2h**

E/*Z* = 69/31, mixture

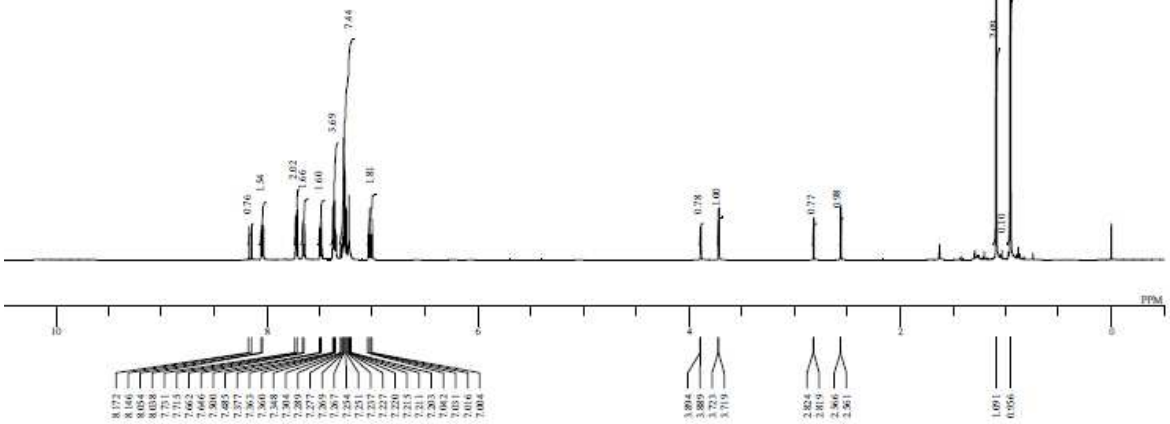


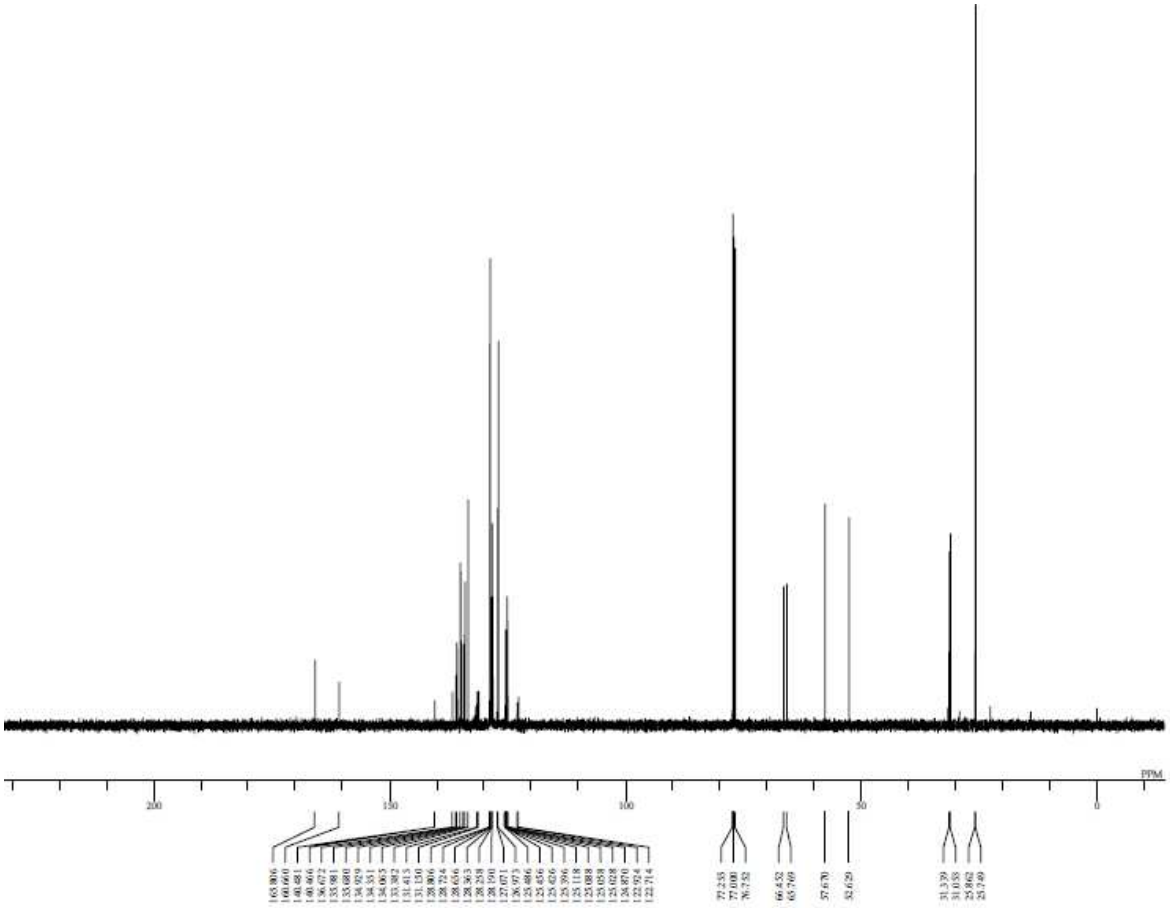


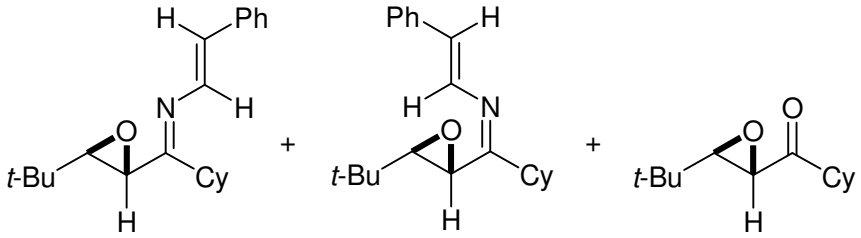


(*E*)-**2i** (*Z*)-**2i**

E/*Z* = 57/43, mixture

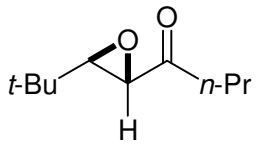






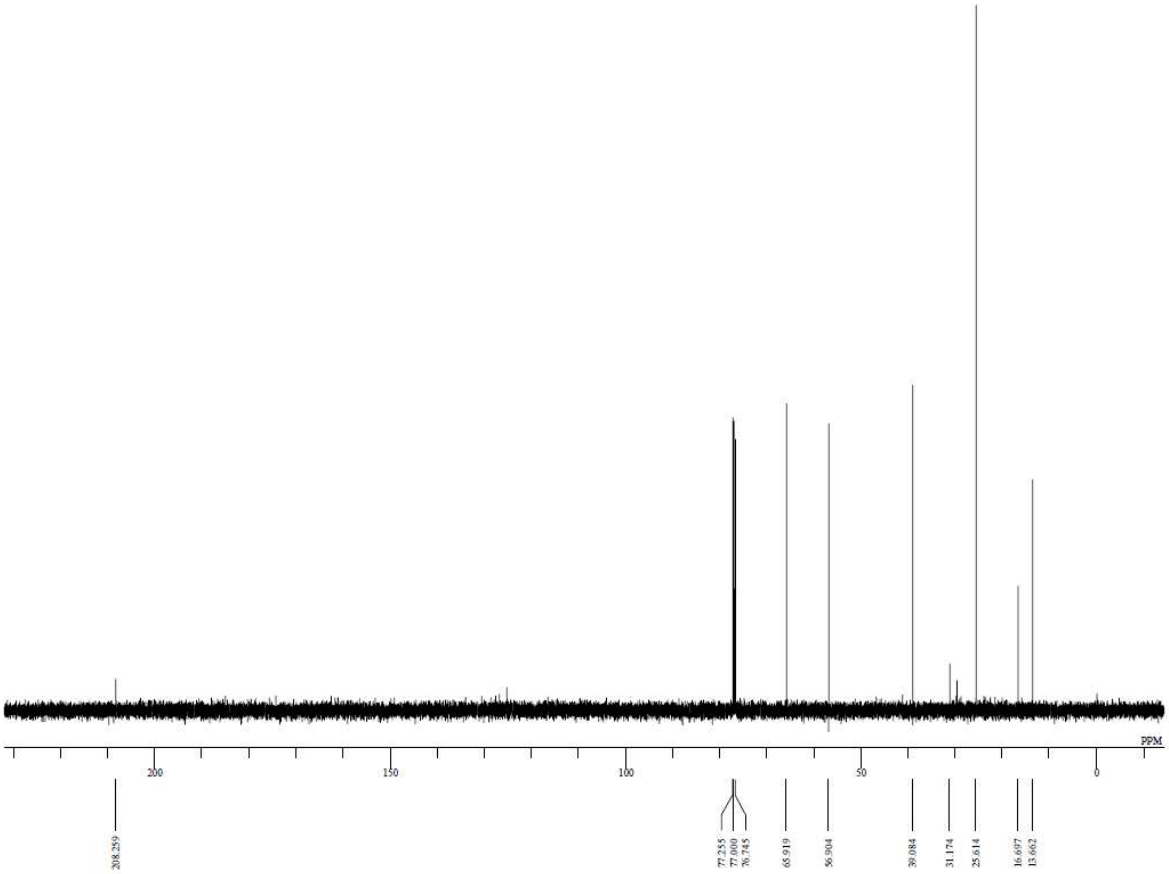
(*E*)-**2j** (*Z*)-**2j** **3j**

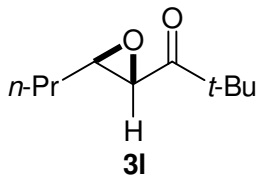
2j/**3j = 93**/**7;** (*E*)-**2j**/(*Z*)-**3j = 26**/**74;** mixture


O
O
t-Bu
n-Pr
H

3k

1.00
1.01
0.99
1.10
2.42
8.91
3.66
PPM
10
8
6
4
2
0
3.312
3.308
2.841
2.836
2.466
2.455
2.450
2.437
2.432
2.419
2.416
2.405
2.316
2.301
2.287
2.282
2.269
2.266
2.255
1.667
1.655
1.640
1.625
1.611
1.596
1.580
1.582
1.567
1.554
0.959
0.957
0.922
0.908
0.000


PPM
200
150
100
50
0
208.259
77.255
77.000
76.745
65.919
56.904
39.084
31.174
25.614
16.697
13.662


O
O
n-Pr
t-Bu
H

3l

1.00
0.99
2.18
2.17
9.42
3.16
PPM
10
8
6
4
2
0
3.616
3.612
2.950
2.946
2.939
2.935
2.928
2.924
1.649
1.645
1.638
1.633
1.627
1.617
1.605
1.561
1.550
1.547
1.538
1.535
1.523
1.520
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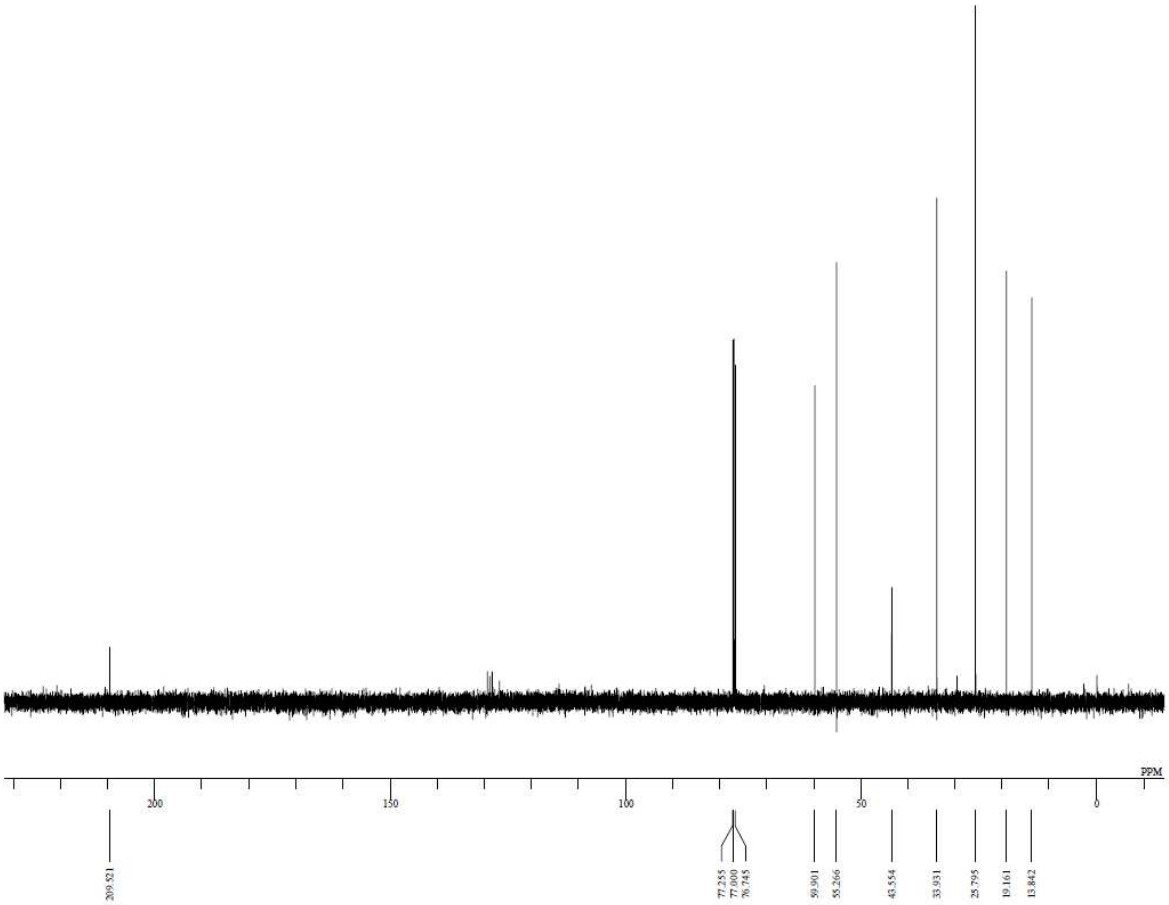
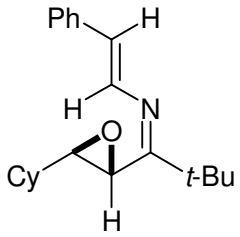
1.495
1.479
1.467
1.464
1.457
1.231
0.997
0.982
0.968


PPM
200
150
100
50
0
209.521
77.255
77.000
76.745
59.901
55.266
43.554
33.931
25.795
19.161
13.842


Ph
H
H
N
O
Cy
t-Bu
H

2m

15.820
1.013
2.093
2.172
1.086
0.993
1.000
1.011
2.101
2.226
1.791
1.127
PPM
10
8
6
4
2
0
PPM
200
175
150
125
100
75
50
25
0
173.303
136.680
134.486
128.566
128.446
127.259
126.515
77.255
77.000
76.745
62.674
55.822
40.309
40.061
29.386
29.093
28.184
26.140
25.607
25.517