Cu(I)-Catalyzed Diamination of Conjugated Olefins with Tunable Anionic Counterions. A Possible Approach to Asymmetric Diamination

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Supporting Information

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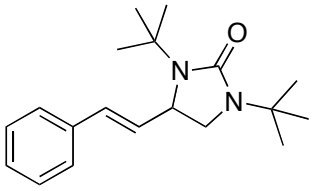
General Methods. All commercially available reagents and solvents were used without further purification. Chromatography was performed on silica gel (200-400 mesh) column. ^{1}H NMR spectra were recorded on 300 MHz NMR spectrometer and ^{13}C NMR spectra were recorded on 100 MHz NMR spectrometer. IR spectra were recorded on a FT-IR spectrometer. Melting points were uncorrected.

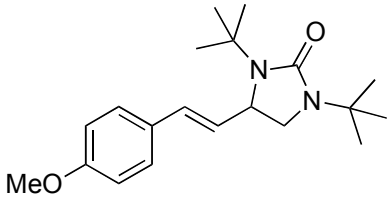
Table 2, entry 1



White solid; mp 157-158 ^{o}C; $[\alpha]_D^{25}$ = +13.9 (*c* 1.0, $CHCl_3$) (55% ee); IR (film) 1673 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41-7.23 (m, 5H), 6.50 (d, *J* = 16.2 Hz, 1H), 6.36 (dd, *J* = 16.2, 8.4 Hz, 1H), 4.17 (dt, *J* = 8.4, 2.1 Hz, 1H), 3.44 (t, *J* = 8.4 Hz, 1H), 3.01 (dd, *J* = 8.4, 2.1 Hz, 1H), 1.38 (s, 9H), 1.33 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.7, 136.6, 131.7, 130.8, 128.8, 128.0, 126.5, 55.4, 53.9, 53.1, 48.3, 29.0, 27.5.

Du, H.; Zhao, B.; Yuan, W.; Shi, Y. *Org. Lett.* **2008**, *10*, 4231.

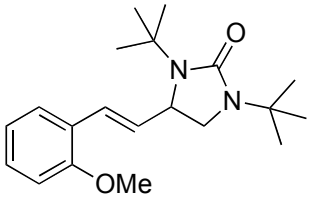
Table 2, entry 2



White solid; mp 111-112 ^{o}C; $[\alpha]_D^{25}$ = +17.0 (*c* 1.0, $CHCl_3$) (58% ee); IR (film) 1690 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.31 (ddd, *J* = 8.4, 3.0, 1.8 Hz, 2H), 6.87 (ddd, *J* = 8.4, 3.0, 1.8 Hz, 2H), 6.43 (d, *J* = 16.2 Hz, 1H), 6.22 (dd, *J* = 16.2, 8.7 Hz, 1H), 4.14 (ddd, *J* = 8.7, 8.1, 2.4, Hz, 1H), 3.81 (s, 3H), 3.42 (t, *J* = 8.1 Hz, 1H), 3.00 (dd, *J* = 8.1, 2.4 Hz, 1H), 1.37 (s, 9H), 1.33 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.7, 159.5, 130.2, 129.45, 129.39, 127.7, 114.2, 55.52, 55.46, 53.9, 53.1, 48.4, 29.0, 27.5.

Du, H.; Zhao, B.; Yuan, W.; Shi, Y. *Org. Lett.* **2008**, *10*, 4231.

Table 2, entry 3



White solid; mp 122-123 ^{o}C; $[\alpha]_D^{25}$ = +27.5 (*c* 1.0, $CHCl_3$) (61% ee); IR (film) 1691 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.44 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.24 (dt, *J* = 7.8, 1.5 Hz, 1H), 6.94 (t, *J* = 7.2 Hz, 1H), 6.88 (d, *J* = 8.4 Hz, 1H), 6.83 (d, *J* = 16.2 Hz, 1H), 6.36 (dd, *J* = 16.2, 9.0 Hz, 1H), 4.18 (ddd, *J* = 9.0, 7.8, 2.4 Hz, 1H), 3.85 (s, 3H), 3.43 (dd, *J* = 8.4, 7.8 Hz, 1H), 3.02 (dd, *J* = 8.4, 2.4 Hz, 1H), 1.39 (s, 9H), 1.32 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.7, 156.7, 132.2, 129.0, 126.7, 125.6, 125.4, 120.8, 111.0, 55.9, 55.6, 53.9, 53.0, 48.4, 29.0, 27.6.

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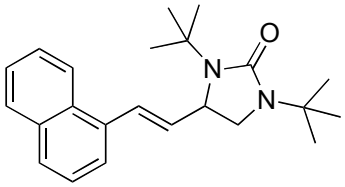
Table 2, entry 4



White solid; mp 129-130 ^{o}C; $[\alpha]_D^{25}$ = +17.4 (*c* 1.0, $CHCl_3$) (49% ee); IR (film) 1689 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.07 (dd, *J* = 7.2, 2.1 Hz, 1H), 7.86 (dd, *J* = 6.9, 2.1 Hz, 1H), 7.81 (d, *J* = 7.8 Hz, 1H), 7.60 (d, *J* = 7.2 Hz, 1H), 7.65-7.44 (m, 3H), 7.29 (d, *J* =15.6 Hz, 1H), 6.42 (dd, *J* =15.6, 8.7 Hz, 1H), 4.32 (ddd, *J* = 8.7, 8.1, 2.1 Hz, 1H), 3.51 (dd, *J* = 8.4, 8.1 Hz, 1H), 3.11 (dd, *J* = 8.4, 2.1 Hz, 1H), 1.45 (s, 9H), 1.35 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.6, 134.8, 134.3, 133.7, 131.2, 128.8, 128.3, 128.0, 126.3, 126.0, 125.8, 124.0, 123.6, 55.5, 54.0, 53.1, 48.3, 29.1, 27.6.

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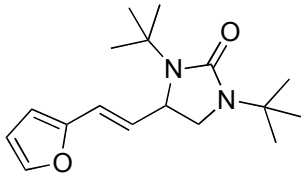
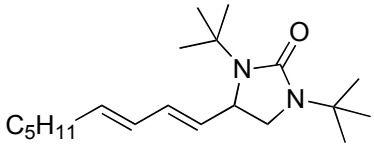
Table 2, entry 5



White solid; mp 143-144 °C; $[\alpha]_D^{25}$ = +8.4 (*c* 1.0, $CHCl_3$) (49% ee); IR (film) 1675 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) 7.35 (d, *J* = 1.8 Hz, 1H), 6.37 (dd, *J* = 3.3, 1.8 Hz, 1H), 6.31-6.29 (m, 2H), 6.24 (d, *J* = 3.3 Hz, 1H), 4.14-4.07 (m, 1H), 3.42 (t, *J* = 8.1 Hz, 1H), 2.96 (dd, *J* = 8.4, 2.4 Hz, 1H), 1.37 (s, 9H), 1.32 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) 160.6, 152.2, 142.3, 130.4, 119.2, 111.5, 108.2, 55.0, 53.9, 53.1, 48.3, 28.9, 27.5.

Du, H.; Zhao, B.; Yuan, W.; Shi, Y. *Org. Lett.* **2008**, *10*, 4231.

Table 2, entry 6



Colorless oil; $[\alpha]_D^{25}$ = +1.0 (*c* 1.0, $CHCl_3$) (55% ee); IR (film) 1694 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 6.13-5.96 (m, 2H), 5.75-5.63 (m, 2H), 3.98 (dt, *J* = 8.4, 2.4 Hz, 1H), 3.36 (t, *J* = 8.1 Hz, 1H), 2.92 (dd, *J* = 8.1, 2.4 Hz, 1H), 2.12-2.04 (m, 2H), 1.40-1.24 (m, 24H), 0.90 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.7, 135.8, 132.7, 131.3, 129.3, 55.1, 53.8, 53.0, 48.4, 32.8, 31.6, 29.0, 28.9, 27.6, 22.7, 14.2.

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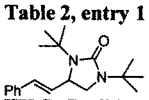
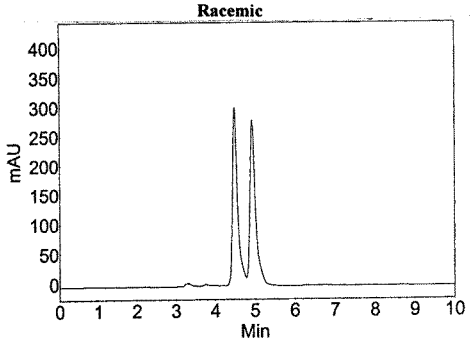
The chromatograms for the determination of enantioselectivity

Table 2, entry 1



HPLC Conditions: Column: Chiralpak AD-H (Column No. ADH0CE-FD069), Daicel Chemical Industries, Ltd.. **Eluent**: Hexanes/IPA (98/2); **Flow rate:** 1.0 mL/min; **Detection:** UV220 nm

Racemic



Index	Time [Min]	Area % [%]
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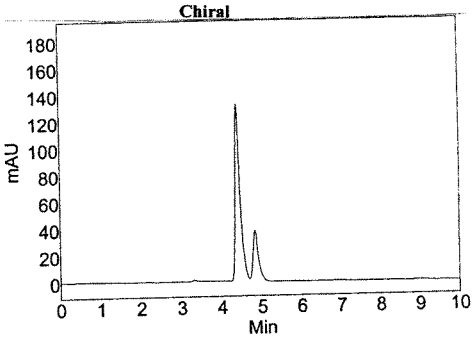
2	4.93	50.339
Total		100.000

Chiral



Index	Time [Min]	Area % [%]
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2	4.83	22.739
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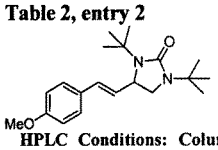
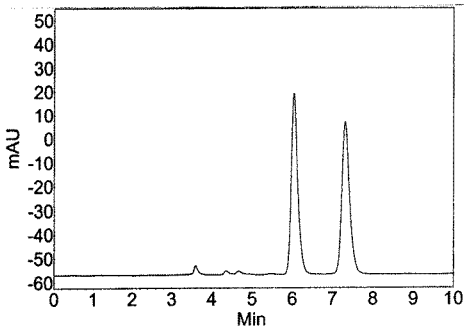
Table 2, entry 2



HPLC Conditions: Column: Chiralpak AD-H (Column No. ADH0CE-FD069), Daicel Chemical Industries, Ltd.. **Eluent**: Hexanes/IPA (98/2); **Flow rate:** 1.0 mL/min; **Detection:** UV220 nm

Racemic



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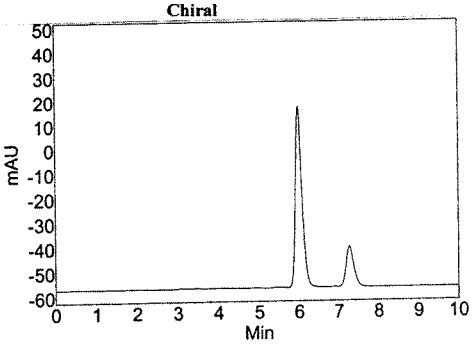
Chiral



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Total		100.000

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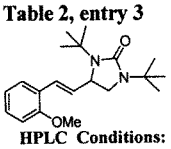
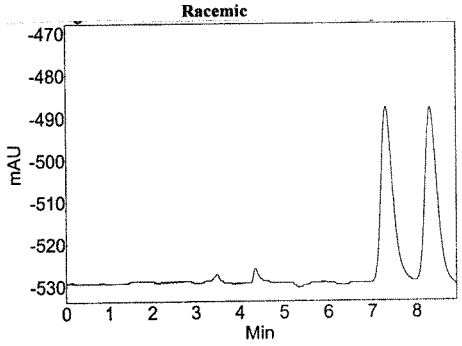


HPLC Conditions: Column: Chiralpak AD-H (Column No. ADH0CE-FD069), Daicel Chemical Industries, Ltd.. **Eluent**: Hexanes/IPA (200/1); **Flow rate:** 1.0 mL/min; **Detection:** UV220 nm

Racemic



Index	Time [Min]	Area % [%]
1	7.31	49.607
2	8.32	50.393
Total		100.000

Chiral

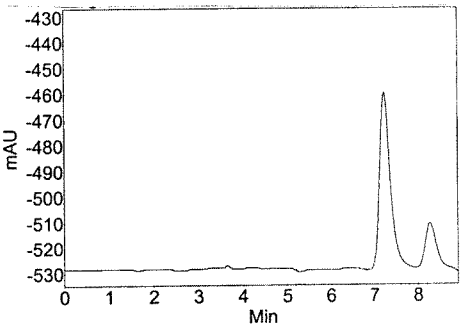


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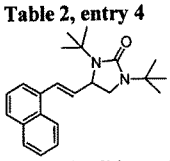
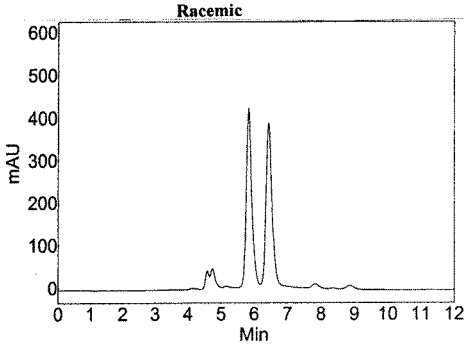
Table 2, entry 4



HPLC Conditions: Column: Chiralpak AD-H (Column No. ADH0CE-FD069), Daicel Chemical Industries, Ltd.. **Eluent**: Hexanes/IPA (98/2); **Flow rate:** 1.0 mL/min; **Detection:** UV220 nm

Racemic



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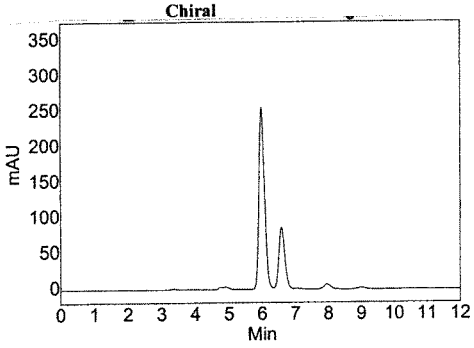
Chiral



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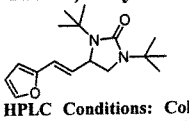
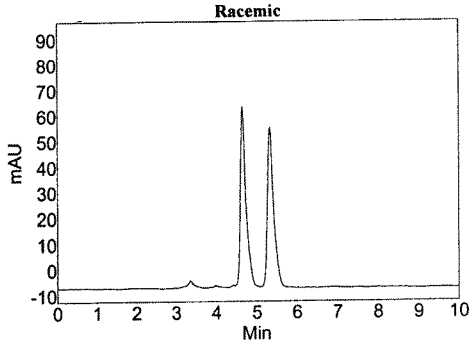


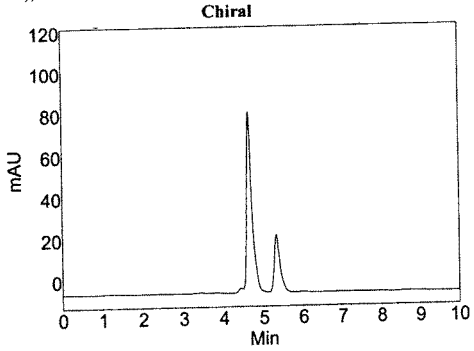
HPLC Conditions: Column: Chiralpak AD-H (Column No. ADH0CE-FD069), Daicel Chemical Industries, Ltd.. **Eluent**: Hexanes/IPA (98/2); **Flow rate:** 1.0 mL/min; **Detection:** UV220 nm

Racemic



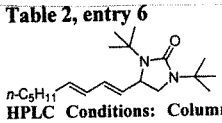
Index	Time [Min]	Area % [%]
1	4.65	50.261
2	5.33	49.739
Total		100.000

Chiral



Index	Time [Min]	Area % [%]
2	4.64	74.607
1	5.32	25.393
Total		100.000

Table 2, entry 6



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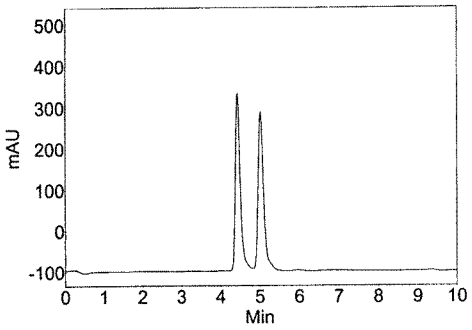

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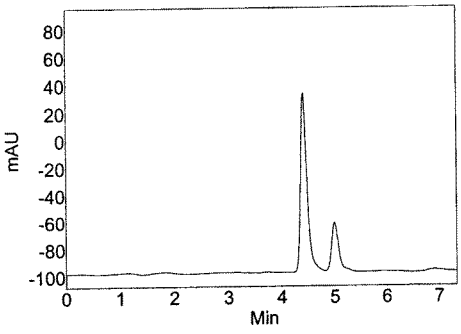

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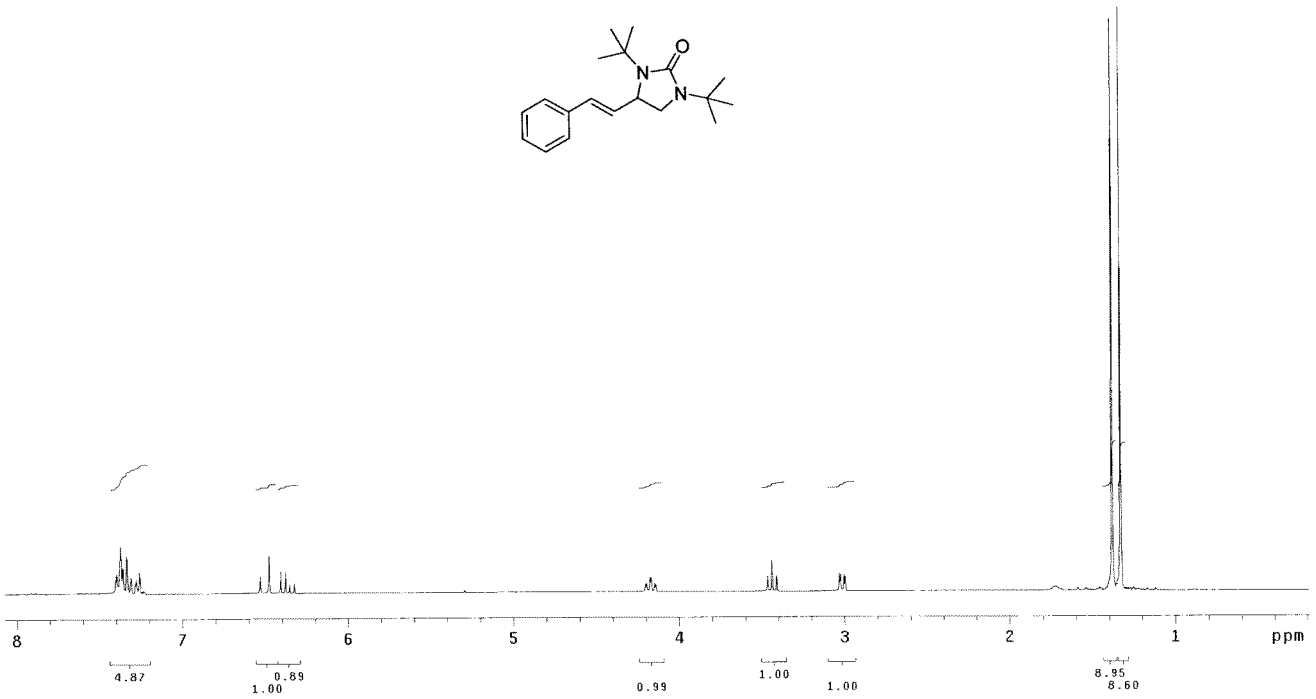


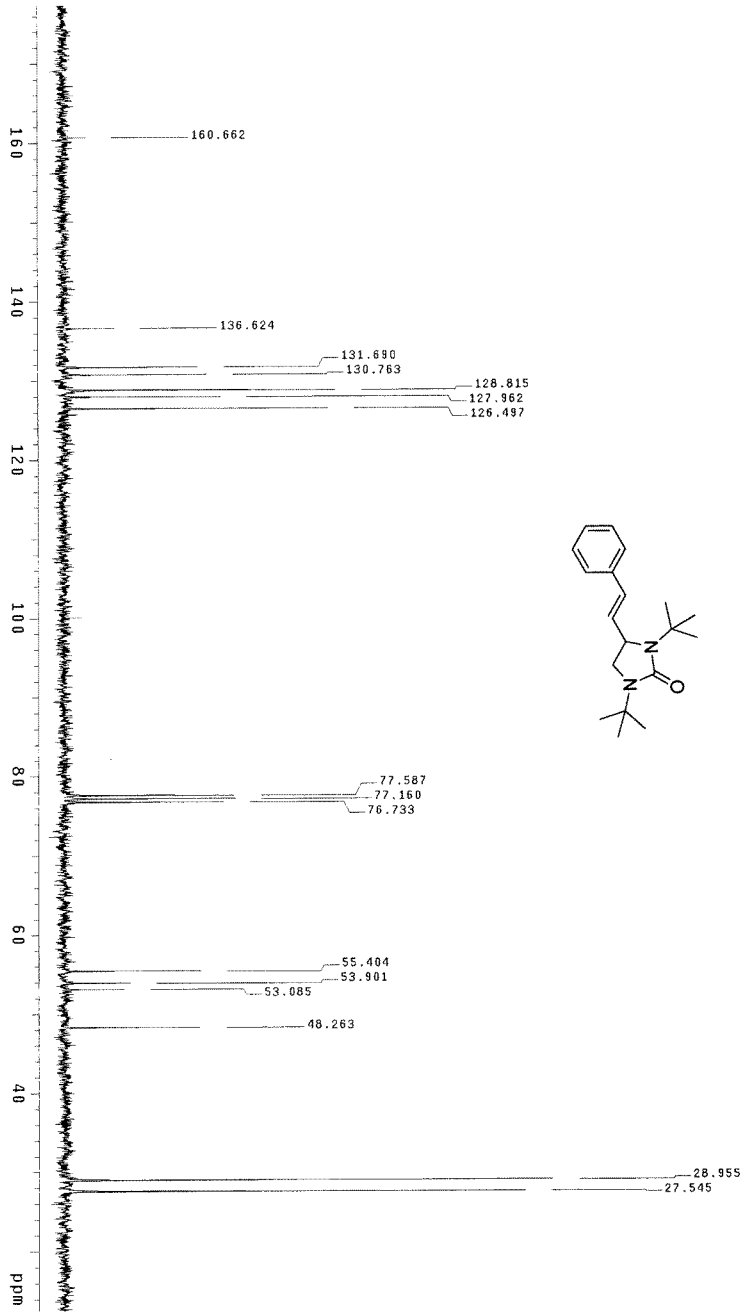
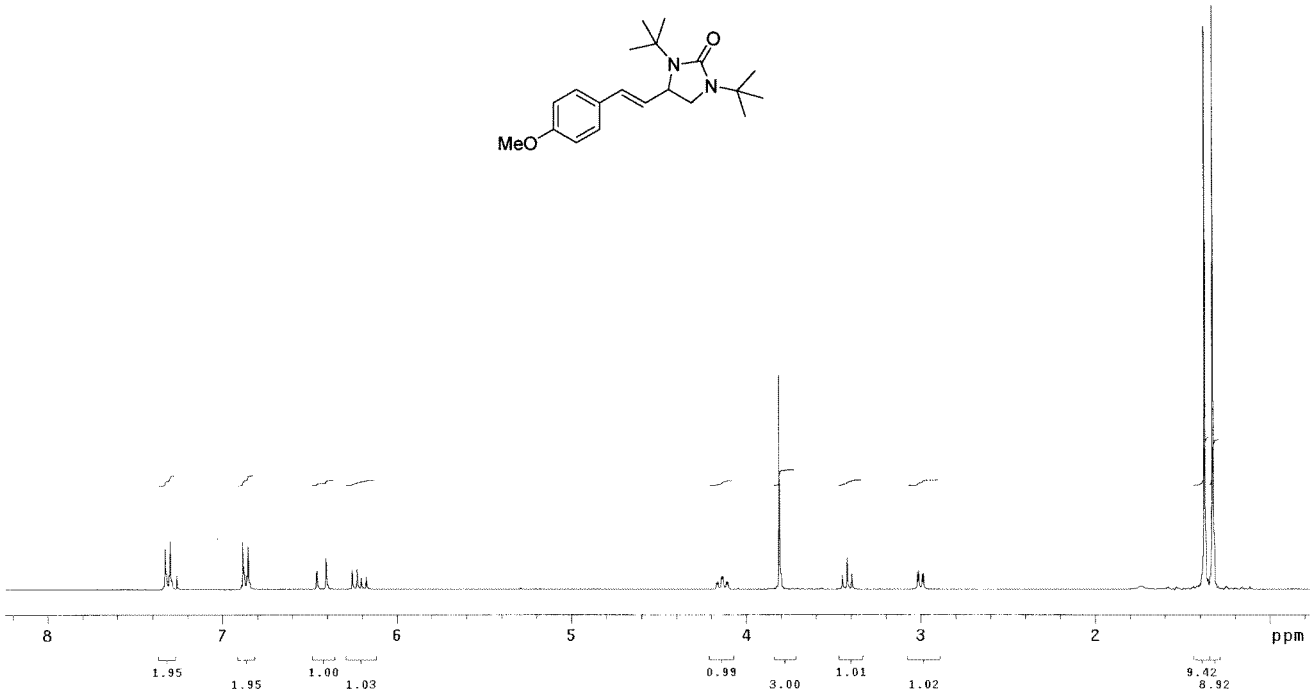
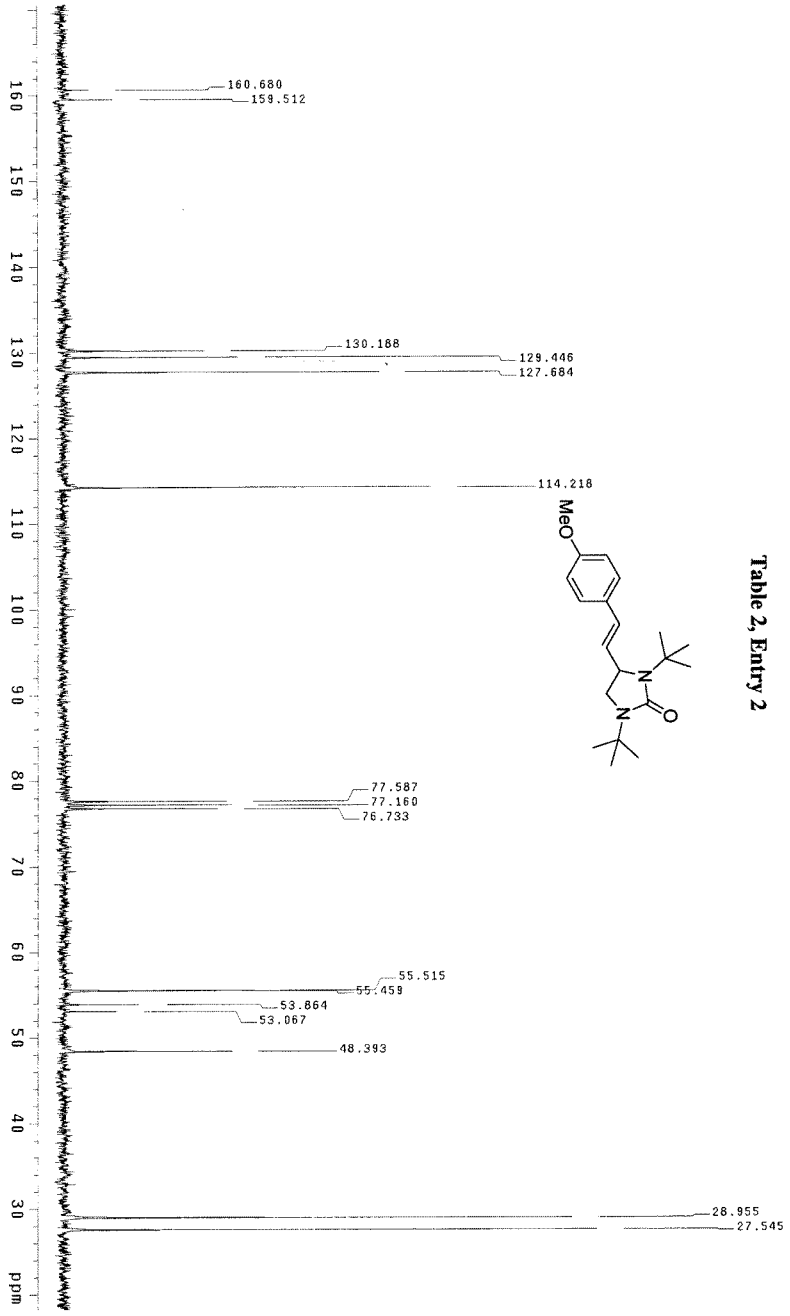


Table 2, Entry 1

Table 2, Entry 2





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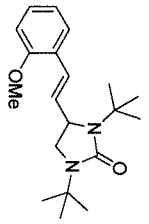

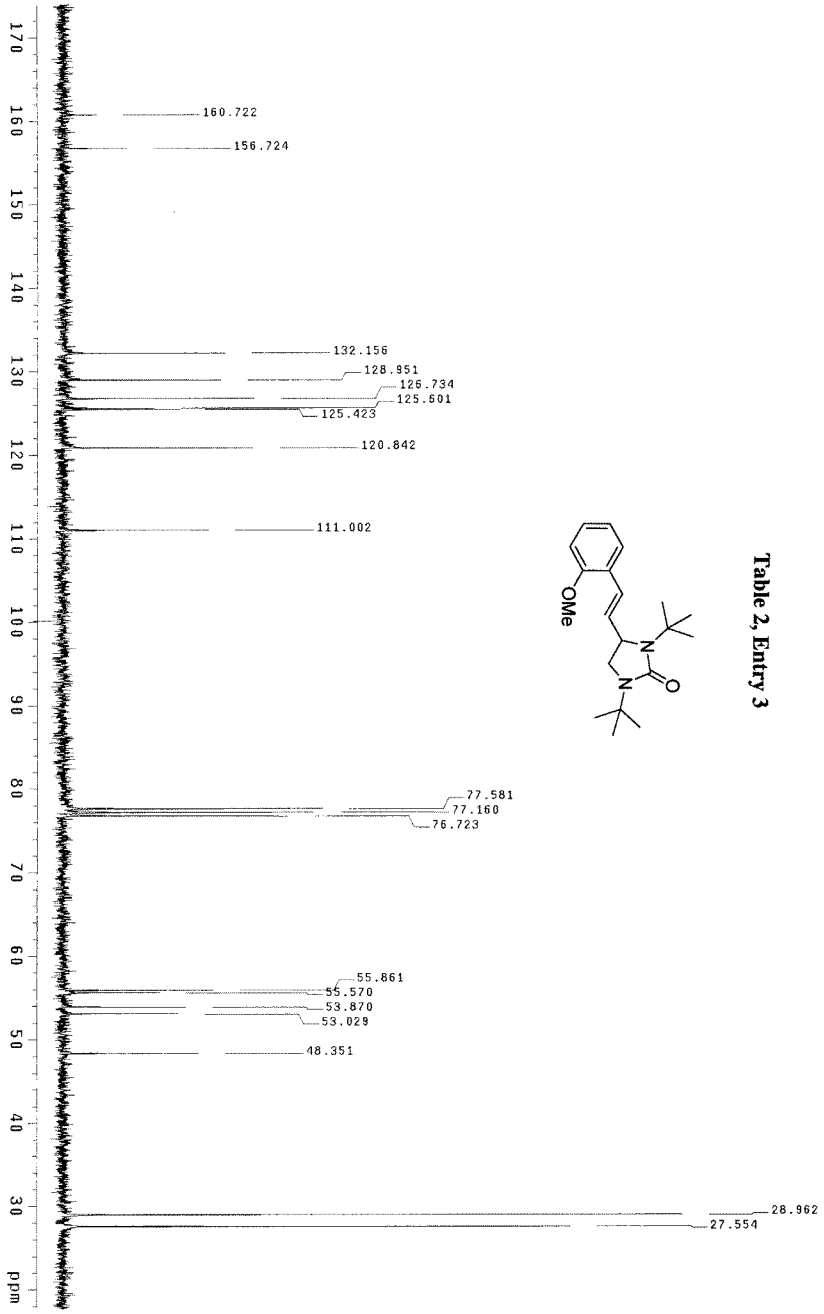

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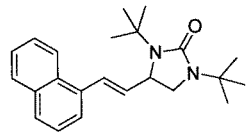
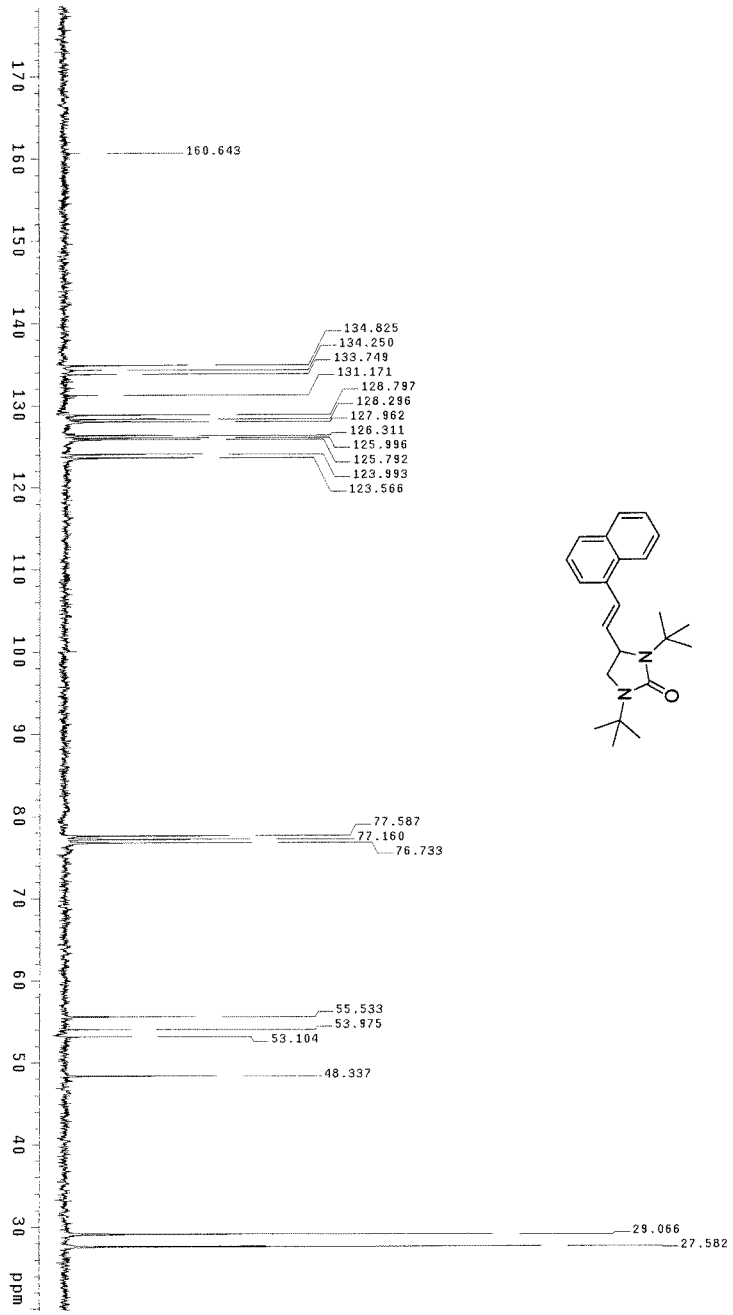
Table 2, Entry 4





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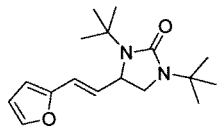

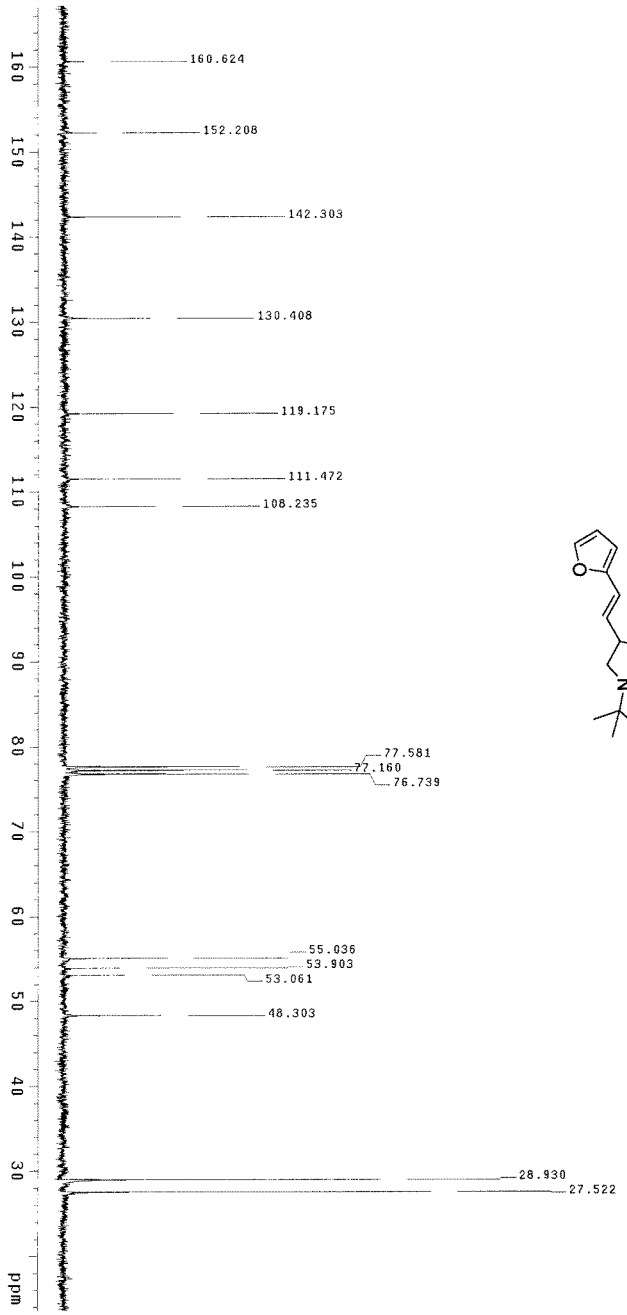

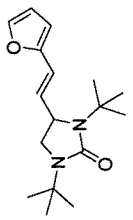

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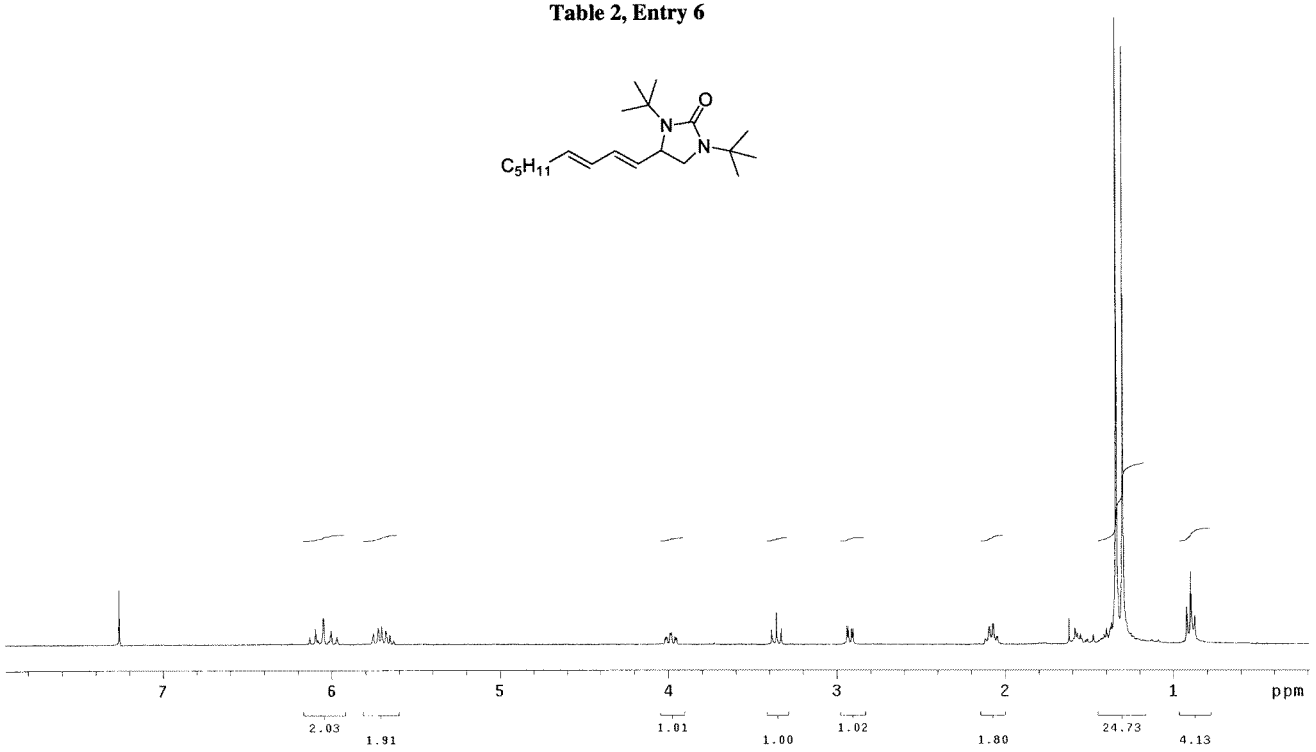
Table 2, Entry 6



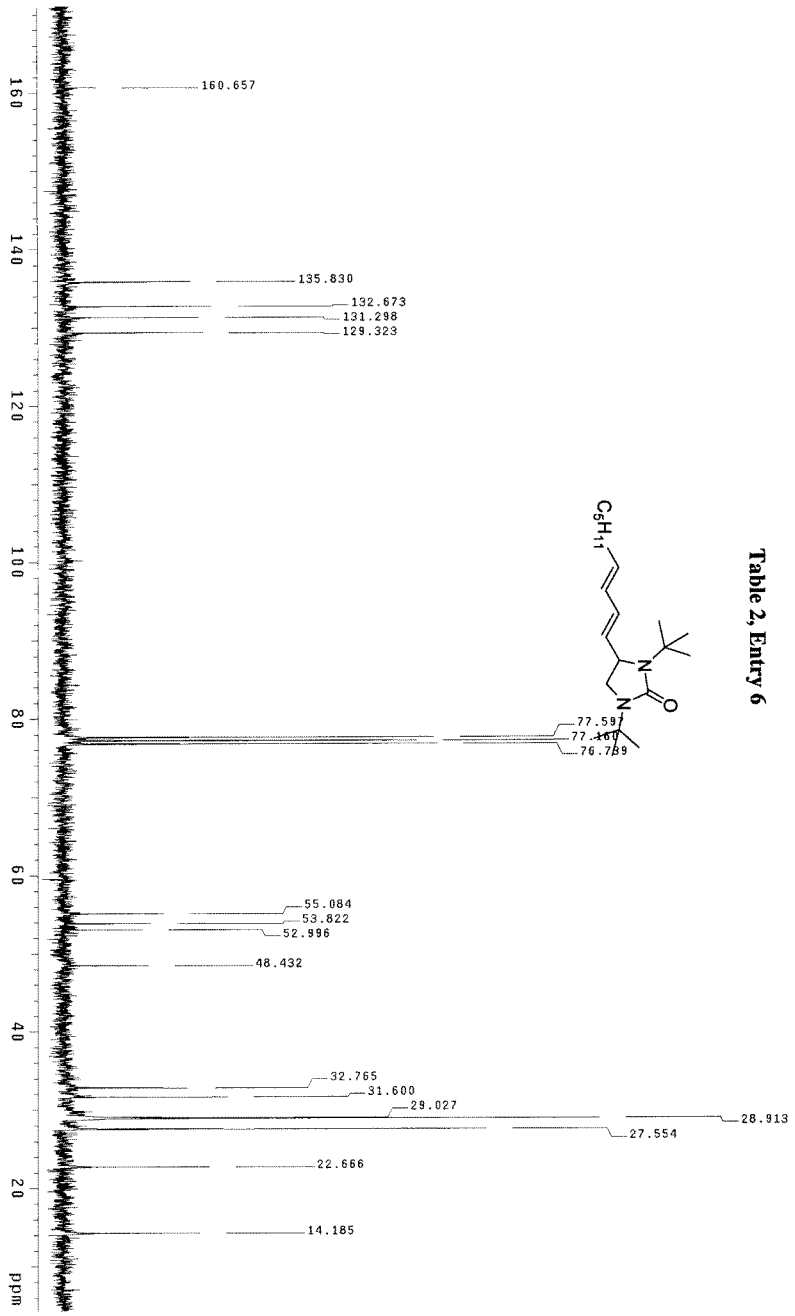


Table 2, Entry 6