

# Supporting Information

## Stereodivergent Synthesis of $\beta$ -Iodoenol Carbamates with CO<sub>2</sub> via Photocatalysis

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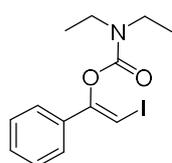
## A. General methods

$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded using a Bruker DRX-400 or Bruker DRX-500 spectrometer using  $\text{CDCl}_3$  as solvent and TMS as an internal standard. The chemical shifts are referenced to signals at 7.26 and 77.0 ppm, respectively. The data of HRMS was carried out on a high-resolution mass spectrometer (LCMS-IT-TOF). IR spectra were obtained either as potassium bromide plates or as liquid films between two potassium bromide plates with a Bruker TENSOR 27 spectrometer. Melting points were determined with a Büchi Melting Point B-545 instrument and are uncorrected. X-ray structural analyses were conducted on an x-ray analysis instrument. UV-vis absorption spectra were measured on a Shimadzu UV-2600 spectrophotometer. Photoluminescence spectra were recorded on a Horiba Fluoromax-4 spectrofluorometer. Blue LEDs (30W,  $\lambda_{\text{max}} = 450$  nm) and green LEDs (30W,  $\lambda_{\text{max}} = 530$  nm) powered by Constant Current Modules were used for the light irradiation. The light source was placed  $\sim 7$  mm from the reaction tube. The photoreactor was placed in an incubator, which was used to maintain the temperature at room temperature (25 °C). Substrates **1a-1s** were prepared according to the literature procedure,<sup>1-3</sup> and other reagents were commercially purchased and used without further purification.

## B. General procedure for the preparation of (*Z*)- $\beta$ -iodoenol carbamates

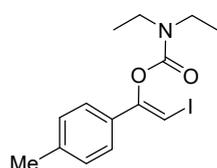
A 25 mL oven-dried Schlenk tube equipped with a magnetic stirring bar was charged with alkynylbenziodoxole **1** (0.1 mmol) and eosin Y (0.001 mmol). The tube was then evacuated, refilled with  $\text{CO}_2$  (1 atm) three times, and charged further with amine **2** (0.3 mmol), 1,8-diazabicyclo[5.4.0]undec-7-ene (0.1 mmol) and dimethyl sulfoxide (1 mL) successively via a syringe. The reaction mixture was stirred at room temperature for 0.5 h under 30 W green LEDs irradiation. After the reaction was completed, the reaction mixture was diluted with  $\text{H}_2\text{O}$  (20 mL) and extracted with ethyl acetate (15 mL $\times$ 3). The combined organic layers were dried over anhydrous  $\text{Na}_2\text{SO}_4$  and then filtered. The volatile compounds were removed under vacuum and the crude residue was separated by column chromatography on a silica gel column using petroleum ether/ethyl acetate (20:1-0:100) as eluent to give the desired product (*Z*)-**3**.

**(Z)-2-Iodo-1-phenylvinyl diethylcarbamate ((Z)-3aa)**



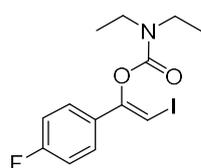
Pale yellow oil (24.5 mg, 71%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.46 – 7.40 (m, 2 H), 7.38 – 7.30 (m, 3 H), 6.55 (s, 1 H), 3.53 (q, *J* = 7.2 Hz, 2 H), 3.37 (q, *J* = 7.3 Hz, 2 H), 1.36 (t, *J* = 7.4 Hz, 3 H), 1.19 (t, *J* = 7.2 Hz, 3 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 155.2, 151.9, 134.6, 129.0, 128.6, 125.1, 68.0, 42.3, 42.1, 14.5, 13.3. IR (KBr): 3083, 2977, 2934, 2878, 1724, 1610, 1572, 1465, 1421, 1378, 1314, 1253, 1150, 1064, 1013, 954, 783, 747, 695, 646 cm<sup>-1</sup>. HRMS-ESI (*m/z*): calcd for C<sub>13</sub>H<sub>16</sub>INNaO<sub>2</sub> [M + Na]<sup>+</sup>: 368.0118; found: 368.0117.

**(Z)-2-Iodo-1-(*p*-tolyl)vinyl diethylcarbamate ((Z)-3ba)**



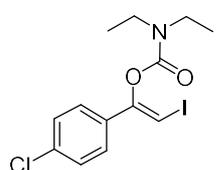
Pale yellow oil (26.6 mg, 74%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.32 (d, *J* = 7.2 Hz, 2 H), 7.14 (d, *J* = 7.6 Hz, 2 H), 6.46 (s, 1 H), 3.52 (q, *J* = 7.2 Hz, 2 H), 3.37 (q, *J* = 7.3 Hz, 2 H), 2.32 (s, 3 H), 1.35 (t, *J* = 6.8 Hz, 3 H), 1.19 (t, *J* = 6.8 Hz, 3 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 155.3, 151.9, 139.1, 131.9, 129.3, 125.1, 66.7, 42.2, 42.0, 21.3, 14.5, 13.3. IR (KBr): 3084, 2988, 2916, 2837, 1771, 1715, 1520, 1465, 1382, 1245, 1149, 1055, 1004, 917, 744, 656 cm<sup>-1</sup>. HRMS-ESI (*m/z*): calcd for C<sub>14</sub>H<sub>19</sub>INO<sub>2</sub> [M + H]<sup>+</sup>: 360.0455; found: 360.0449.

**(Z)-1-(4-Fluorophenyl)-2-iodovinyl diethylcarbamate ((Z)-3ca)**



White solid (24.0 mg, 66%). mp: 103 – 105 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.49 – 7.36 (m, 2 H), 7.08 – 6.97 (m, 2 H), 6.47 (s, 1 H), 3.52 (q, *J* = 7.2 Hz, 2 H), 3.36 (q, *J* = 7.1 Hz, 2 H), 1.35 (t, *J* = 7.2 Hz, 3 H), 1.19 (t, *J* = 7.2 Hz, 3 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 163.1 (d, *J* = 247.8 Hz), 154.4, 151.8, 131.0 (d, *J* = 3.3 Hz), 127.1 (d, *J* = 8.4 Hz), 115.7 (d, *J* = 21.8 Hz), 67.5, 42.3, 42.1, 14.5, 13.3. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>): δ = -111.8 – -111.9 (m). IR (KBr): 3082, 2977, 1718, 1611, 1509, 1375, 1311, 1243, 1149, 1055, 1002, 916, 838, 745, 653 cm<sup>-1</sup>. HRMS-ESI (*m/z*): calcd for C<sub>13</sub>H<sub>16</sub>FINO<sub>2</sub> [M + H]<sup>+</sup>: 364.0204; found: 364.0200.

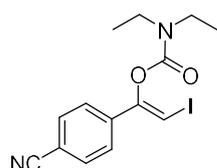
**(Z)-1-(4-Chlorophenyl)-2-iodovinyl diethylcarbamate ((Z)-3da)**



White solid (23.4 mg, 62%). mp: 115 – 116 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.38 – 7.33 (m, 2 H), 7.33 – 7.27 (m, 2 H), 6.55 (s, 1 H), 3.51 (q, *J* = 7.1 Hz, 2 H), 3.36 (q, *J* = 7.1 Hz, 2 H), 1.35 (t, *J* = 7.0 Hz, 3 H), 1.19 (t, *J* = 7.2

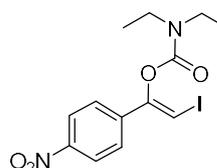
Hz, 3 H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 154.3, 151.7, 134.9, 133.1, 128.8, 126.4, 68.5, 42.3, 42.1, 14.5, 13.3$ . IR (KBr): 3080, 2981, 2930, 1780, 1712, 1614, 1550, 1471, 1425, 1375, 1251, 1151, 1066, 1006, 933, 833, 773, 648  $\text{cm}^{-1}$ . HRMS-ESI ( $m/z$ ): calcd for  $\text{C}_{13}\text{H}_{16}\text{ClINO}_2$  [ $\text{M} + \text{H}$ ] $^+$ : 379.9909; found: 379.9905.

**(Z)-1-(4-Cyanophenyl)-2-iodovinyl diethylcarbamate ((Z)-3ea)**



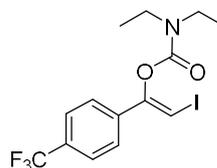
White solid (18.5 mg, 50%). mp: 119 – 120 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.67 - 7.59$  (m, 2 H), 7.56 – 7.48 (m, 2 H), 6.78 (s, 1 H), 3.53 (q,  $J = 7.1$  Hz, 2 H), 3.36 (q,  $J = 7.1$  Hz, 2 H), 1.36 (t,  $J = 7.0$  Hz, 3 H), 1.19 (t,  $J = 7.0$  Hz, 3 H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 153.7, 151.5, 138.7, 132.5, 125.6, 118.4, 112.4, 72.1, 42.4, 42.2, 14.5, 13.2$ . IR (KBr): 2994, 2894, 2829, 1767, 1700, 1549, 1383, 1307, 1244, 1149, 1054, 915, 849, 744, 660  $\text{cm}^{-1}$ . HRMS-ESI ( $m/z$ ): calcd for  $\text{C}_{14}\text{H}_{16}\text{IN}_2\text{O}_2$  [ $\text{M} + \text{H}$ ] $^+$ : 371.0251; found: 371.0246.

**(Z)-2-Iodo-1-(4-nitrophenyl)vinyl diethylcarbamate ((Z)-3fa)**



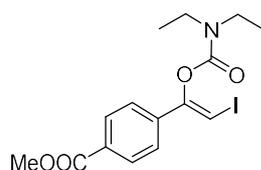
Pale yellow solid (26.5 mg, 68%). mp: 126 – 127 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 8.20$  (d,  $J = 8.0$  Hz, 2 H), 7.57 (d,  $J = 8.4$  Hz, 2 H), 6.85 (s, 1 H), 3.54 (q,  $J = 7.2$  Hz, 2 H), 3.36 (q,  $J = 7.2$  Hz, 2 H), 1.37 (t,  $J = 7.0$  Hz, 3 H), 1.19 (t,  $J = 6.8$  Hz, 3 H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 153.6, 151.5, 147.8, 140.5, 125.9, 124.0, 72.7, 42.5, 42.2, 14.5, 13.2$ . IR (KBr): 3091, 2986, 2923, 2845, 1771, 1707, 1582, 1511, 1334, 1245, 1149, 1057, 922, 855, 789, 738, 650  $\text{cm}^{-1}$ . HRMS-ESI ( $m/z$ ): calcd for  $\text{C}_{13}\text{H}_{16}\text{IN}_2\text{O}_4$  [ $\text{M} + \text{H}$ ] $^+$ : 391.0149; found: 391.0142.

**(Z)-2-Iodo-1-(4-(trifluoromethyl)phenyl)vinyl diethylcarbamate ((Z)-3ga)**



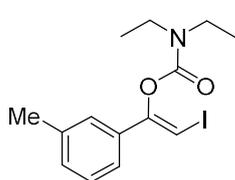
White solid (26.4 mg, 64%). mp: 98 – 100 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.60$  (d,  $J = 8.4$  Hz, 2 H), 7.53 (d,  $J = 8.4$  Hz, 2 H), 6.71 (s, 1 H), 3.54 (q,  $J = 7.2$  Hz, 2 H), 3.37 (q,  $J = 7.2$  Hz, 2 H), 1.36 (t,  $J = 7.2$  Hz, 3 H), 1.20 (t,  $J = 7.0$  Hz, 3 H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 154.1, 151.7, 137.9, 130.8$  (q,  $J = 32.4$  Hz), 125.7 (q,  $J = 3.8$  Hz), 125.40, 123.9 (q,  $J = 270.5$  Hz), 70.6, 42.4, 42.1, 14.5, 13.2.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ):  $\delta = -62.8$  (s). IR (KBr): 3100, 2993, 2892, 2823, 1770, 1703, 1538, 1393, 1320, 1244, 1151, 1056, 999, 916, 847, 747, 656  $\text{cm}^{-1}$ . HRMS-ESI ( $m/z$ ): calcd for  $\text{C}_{14}\text{H}_{16}\text{F}_3\text{INO}_2$  [ $\text{M} + \text{H}$ ] $^+$ : 414.0172; found: 414.0168.

**Methyl (Z)-4-(1-((diethylcarbamoyl)oxy)-2-iodovinyl)benzoate ((Z)-3ha)**



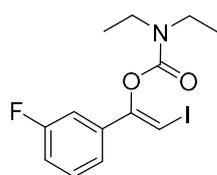
Pale yellow oil (30.6 mg, 76%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 8.00 (d,  $J$  = 8.4 Hz, 2 H), 7.48 (d,  $J$  = 8.4 Hz, 2 H), 6.73 (s, 1 H), 3.90 (s, 3 H), 3.53 (q,  $J$  = 6.9 Hz, 2 H), 3.36 (q,  $J$  = 6.9 Hz, 2 H), 1.36 (t,  $J$  = 7.0 Hz, 3 H), 1.19 (t,  $J$  = 7.0 Hz, 3 H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 166.4, 154.4, 151.7, 138.6, 130.3, 129.9, 125.0, 70.7, 52.2, 42.3, 42.1, 14.5, 13.2. IR (KBr): 3082, 2973, 1717, 1608, 1420, 1258, 1149, 1059, 1007, 933, 859, 753, 645  $\text{cm}^{-1}$ . HRMS-ESI ( $m/z$ ): calcd for  $\text{C}_{15}\text{H}_{19}\text{INO}_4$  [ $\text{M} + \text{H}$ ] $^+$ : 404.0353; found: 404.0349.

**(Z)-2-Iodo-1-(*m*-tolyl)vinyl diethylcarbamate ((Z)-3ia)**



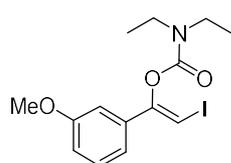
Pale yellow oil (21.9 mg, 61%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.24 (s, 1 H), 7.22 (d,  $J$  = 4.5 Hz, 2 H), 7.16 – 7.12 (m, 1 H), 6.51 (s, 1 H), 3.53 (q,  $J$  = 7.2 Hz, 2 H), 3.37 (q,  $J$  = 7.2 Hz, 2 H), 2.35 (s, 3 H), 1.36 (t,  $J$  = 7.0 Hz, 3 H), 1.19 (t,  $J$  = 7.0 Hz, 3 H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 155.4, 151.9, 138.3, 134.6, 129.9, 128.5, 125.9, 122.3, 67.6, 42.3, 42.1, 21.5, 14.5, 13.3. IR (KBr): 3117, 2996, 2900, 2823, 1922, 1843, 1771, 1687, 1538, 1390, 1248, 1155, 1053, 980, 920, 788, 657  $\text{cm}^{-1}$ . HRMS-ESI ( $m/z$ ): calcd for  $\text{C}_{14}\text{H}_{19}\text{INO}_2$  [ $\text{M} + \text{H}$ ] $^+$ : 360.0455; found: 360.0446.

**(Z)-1-(3-Fluorophenyl)-2-iodovinyl diethylcarbamate ((Z)-3ja)**



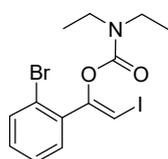
Pale yellow oil (22.9 mg, 63%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.31 (q,  $J$  = 7.3 Hz, 1 H), 7.22 (d,  $J$  = 8.0 Hz, 1 H), 7.11 (d,  $J$  = 10.0 Hz, 1 H), 7.02 (t,  $J$  = 8.4 Hz, 1 H), 6.61 (s, 1 H), 3.52 (q,  $J$  = 7.2 Hz, 2 H), 3.37 (q,  $J$  = 7.2 Hz, 2 H), 1.36 (t,  $J$  = 7.2 Hz, 3 H), 1.20 (t,  $J$  = 7.2 Hz, 3 H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 162.8 (d,  $J$  = 244.8 Hz), 154.1, 151.7, 136.7 (d,  $J$  = 7.4 Hz), 130.2 (d,  $J$  = 8.4 Hz), 120.9 (d,  $J$  = 3.0 Hz), 115.9 (d,  $J$  = 21.3 Hz), 112.2 (d,  $J$  = 23.3 Hz), 69.4, 42.3, 42.1, 14.5, 13.3.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  = -112.43 – -112.53 (m). IR (KBr): 3086, 2991, 2919, 2838, 1777, 1717, 1566, 1471, 1415, 1254, 1151, 1056, 956, 870, 777, 662  $\text{cm}^{-1}$ . HRMS-ESI ( $m/z$ ): calcd for  $\text{C}_{13}\text{H}_{16}\text{FINO}_2$  [ $\text{M} + \text{H}$ ] $^+$ : 364.0204; found: 364.0199.

**(Z)-2-Iodo-1-(3-methoxyphenyl)vinyl diethylcarbamate ((Z)-3ka)**



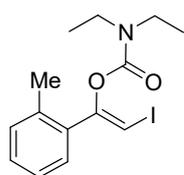
Pale yellow oil (27.0 mg, 72%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.27 – 7.22 (m, 1 H), 7.05 – 7.00 (m, 1 H), 6.97 – 6.93 (m, 1 H), 6.90 – 6.84 (m, 1 H), 6.54 (s, 1 H), 3.80 (s, 3 H), 3.52 (q, *J* = 7.2 Hz, 2 H), 3.36 (q, *J* = 7.2 Hz, 2 H), 1.36 (t, *J* = 7.0 Hz, 3 H), 1.19 (t, *J* = 7.2 Hz, 3 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 159.7, 155.1, 151.8, 135.9, 129.7, 117.7, 114.7, 110.9, 68.2, 55.2, 42.3, 42.1, 14.5, 13.3. IR (KBr): 3085, 2922, 2842, 1778, 1714, 1572, 1467, 1412, 1252, 1151, 1050, 945, 866, 757, 664 cm<sup>-1</sup>. HRMS-ESI (*m/z*): calcd for C<sub>14</sub>H<sub>19</sub>INO<sub>3</sub> [M + H]<sup>+</sup>: 376.0404; found: 376.0400.

**(Z)-1-(2-Bromophenyl)-2-iodovinyl diethylcarbamate ((Z)-3la)**



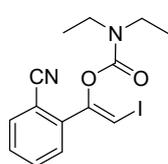
Pale yellow oil (28.3 mg, 67%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.55 (d, *J* = 8.0 Hz, 1 H), 7.46 (d, *J* = 7.6 Hz, 1 H), 7.30 (t, *J* = 7.6 Hz, 1 H), 7.19 (t, *J* = 7.8 Hz, 1 H), 6.25 (s, 1 H), 3.48 (q, *J* = 7.2 Hz, 2 H), 3.28 (q, *J* = 7.2 Hz, 2 H), 1.31 (t, *J* = 7.2 Hz, 3 H), 1.13 (t, *J* = 7.2 Hz, 3 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 154.3, 151.8, 136.4, 133.1, 131.4, 130.3, 127.2, 121.1, 70.9, 42.1, 14.4, 13.2. IR (KBr): 2982, 2922, 2839, 1778, 1719, 1550, 1467, 1418, 1253, 1150, 1064, 1012, 955, 752, 658 cm<sup>-1</sup>. HRMS-ESI (*m/z*): calcd for C<sub>13</sub>H<sub>16</sub>BrINO<sub>2</sub> [M + H]<sup>+</sup>: 423.9404; found: 423.9398.

**(Z)-2-Iodo-1-(*o*-tolyl)vinyl diethylcarbamate ((Z)-3ma)**



Pale yellow oil (26.9 mg, 75%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.38 – 7.34 (m, 1 H), 7.26 – 7.21 (m, 1 H), 7.19 – 7.14 (m, 2 H), 6.05 (s, 1 H), 3.45 (q, *J* = 7.2 Hz, 2 H), 3.29 (q, *J* = 7.2 Hz, 2 H), 2.40 (s, 3 H), 1.30 (t, *J* = 7.2 Hz, 3 H), 1.13 (t, *J* = 7.2 Hz, 3 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 155.7, 151.9, 135.8, 135.1, 130.5, 129.0, 128.9, 125.7, 69.1, 42.0, 41.9, 20.2, 14.4, 13.2. IR (KBr): 3081, 2983, 2924, 1782, 1715, 1621, 1551, 1467, 1411, 1243, 1147, 1052, 1006, 939, 746, 671, 614 cm<sup>-1</sup>. HRMS-ESI (*m/z*): calcd for C<sub>14</sub>H<sub>19</sub>INO<sub>2</sub> [M + H]<sup>+</sup>: 360.0455; found: 360.0449.

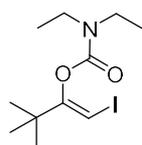
**(Z)-1-(2-Cyanophenyl)-2-iodovinyl diethylcarbamate ((Z)-3na)**



Pale yellow oil (18.1 mg, 49%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.69 – 7.64 (m, 1 H), 7.60 – 7.53 (m, 2 H), 7.47 – 7.40 (m, 1 H), 6.63 (s, 1 H), 3.55 (q, *J* = 7.1 Hz, 2 H), 3.31 (q, *J* = 7.1 Hz, 2 H), 1.35 (t, *J* = 7.2 Hz, 3 H), 1.15 (t, *J* = 7.2 Hz, 3 H).

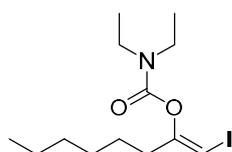
$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 152.5, 151.6, 138.7, 133.9, 132.8, 129.1, 128.5, 117.7, 109.5, 72.6, 42.2, 42.1, 14.3, 13.1$ . IR (KBr): 3084, 2994, 2915, 2838, 1780, 1702, 1543, 1396, 1246, 1146, 1047, 926, 753, 657  $\text{cm}^{-1}$ . HRMS-ESI ( $m/z$ ): calcd for  $\text{C}_{14}\text{H}_{16}\text{IN}_2\text{O}_2$  [ $\text{M} + \text{H}$ ] $^+$ : 371.0251; found: 371.0248.

**(Z)-1-Iodo-3,3-dimethylbut-1-en-2-yl diethylcarbamate ((Z)-3oa)**



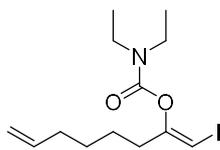
Pale yellow oil (13.7 mg, 42%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 5.96$  (s, 1 H), 3.45 – 3.29 (m, 4 H), 1.25 (t,  $J = 7.2$  Hz, 3 H), 1.19 (t,  $J = 7.0$  Hz, 3 H), 1.14 (s, 9 H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 164.2, 151.4, 65.1, 42.2, 42.0, 39.0, 28.0, 14.3, 13.3$ . IR (KBr): 3114, 2993, 2898, 2823, 1775, 1683, 1539, 1394, 1255, 1154, 1079, 975, 871, 781, 659  $\text{cm}^{-1}$ . HRMS-ESI ( $m/z$ ): calcd for  $\text{C}_{11}\text{H}_{21}\text{INO}_2$  [ $\text{M} + \text{H}$ ] $^+$ : 326.0611; found: 326.0609.

**(Z)-1-Iodo-oct-1-en-2-yl diethylcarbamate ((Z)-3pa)**



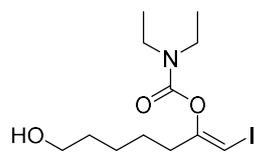
Pale yellow oil (10.9 mg, 31%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 5.71$  (s, 1 H), 3.35 (dt,  $J = 14.0, 7.2$  Hz, 4 H), 2.42 (t,  $J = 7.6$  Hz, 2 H), 1.52 – 1.43 (m, 2 H), 1.32 – 1.23 (m, 9 H), 1.18 (t,  $J = 7.0$  Hz, 3 H), 0.88 (t,  $J = 6.8$  Hz, 3 H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 158.3, 152.0, 64.3, 41.9, 34.6, 31.5, 28.6, 26.4, 22.3, 14.3, 14.0, 13.3$ . IR (KBr): 3084, 2932, 2864, 1718, 1640, 1428, 1264, 1243, 1154, 1099, 971, 911, 739, 649  $\text{cm}^{-1}$ . HRMS-ESI ( $m/z$ ): calcd for  $\text{C}_{13}\text{H}_{25}\text{INO}_2$  [ $\text{M} + \text{H}$ ] $^+$ : 354.0924; found: 354.0920.

**(Z)-1-Iodo-octa-1,7-dien-2-yl diethylcarbamate ((Z)-3qa)**



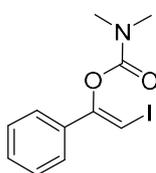
Pale yellow oil (21.8 mg, 62%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 5.77$  (ddt,  $J = 16.9, 10.1, 6.6$  Hz, 1 H), 5.71 (s, 1 H), 5.06 – 4.86 (m, 2 H), 3.35 (dq,  $J = 10.6, 7.1$  Hz, 4 H), 2.43 (t,  $J = 7.2$  Hz, 2 H), 2.10 – 1.99 (m, 2 H), 1.54 – 1.45 (m, 2 H), 1.45 – 1.36 (m, 2 H), 1.24 (t,  $J = 7.2$  Hz, 3 H), 1.18 (t,  $J = 7.0$  Hz, 3 H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 158.0, 151.9, 138.4, 114.6, 64.5, 42.1, 41.9, 34.4, 33.3, 28.1, 25.9, 14.3, 13.3$ . IR (KBr): 2981, 1754, 1373, 1243, 1151, 1057, 916, 826, 642  $\text{cm}^{-1}$ . HRMS-ESI ( $m/z$ ): calcd for  $\text{C}_{13}\text{H}_{23}\text{INO}_2$  [ $\text{M} + \text{H}$ ] $^+$ : 352.0768 ; found: 352.0764.

**(Z)-1-Iodo-octa-1,7-dien-2-yl diethylcarbamate ((Z)-3ra)**



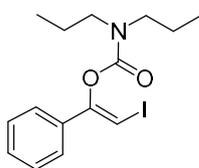
Pale yellow oil (26.6 mg, 75%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 5.72 (s, 1H), 3.60 (t,  $J$  = 6.5 Hz, 2 H), 3.34 (dq,  $J$  = 14.0, 7.1 Hz, 4 H), 2.41 (td,  $J$  = 7.4, 1.1 Hz, 2 H), 1.84 (s, 1 H), 1.59 – 1.45 (m, 4 H), 1.42 – 1.33 (m, 2 H), 1.23 (t,  $J$  = 7.0 Hz, 3 H), 1.16 (t,  $J$  = 7.0 Hz, 3 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 157.8, 151.9, 64.6, 62.4, 42.1, 41.9, 34.6, 32.2, 26.1, 24.9, 14.2, 13.3. IR (KBr): 3079, 2934, 2870, 1710, 1643, 1427, 1239, 1156, 1060, 970, 744, 625 cm<sup>-1</sup>. HRMS-ESI ( $m/z$ ): calcd for C<sub>12</sub>H<sub>23</sub>INO<sub>3</sub> [M + H]<sup>+</sup>: 356.0717; found: 356.0715.

**(Z)-2-Iodo-1-phenylvinyl dimethylcarbamate ((Z)-3ab)**



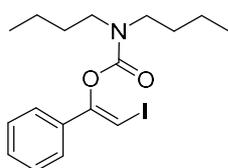
Yellow oil (22.4 mg, 71%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.47 – 7.42 (m, 2 H), 7.37 – 7.31 (m, 3 H), 6.54 (s, 1 H), 3.19 (s, 3 H), 3.01 (s, 3 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 155.2, 152.6, 134.4, 129.1, 128.6, 125.2, 68.0, 36.8, 36.6. IR (KBr): 3124, 2998, 2894, 2822, 1771, 1715, 1687, 1556, 1442, 1384, 1245, 1150, 1049, 979, 915, 745, 661 cm<sup>-1</sup>. HRMS-ESI ( $m/z$ ): calcd for C<sub>11</sub>H<sub>13</sub>INO<sub>2</sub> [M + H]<sup>+</sup>: 317.9985; found: 317.9981.

**(Z)-2-Iodo-1-phenylvinyl dipropylcarbamate ((Z)-3ac)**



Pale yellow oil (29.5 mg, 79%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.45 – 7.40 (m, 2 H), 7.37 – 7.31 (m, 3 H), 6.54 (s, 1 H), 3.42 (t,  $J$  = 7.5 Hz, 2 H), 3.27 (t,  $J$  = 7.5 Hz, 2 H), 1.80 (q,  $J$  = 7.4 Hz, 2 H), 1.63 (q,  $J$  = 7.4 Hz, 2 H), 1.00 (t,  $J$  = 7.5 Hz, 3 H), 0.91 (t,  $J$  = 7.5 Hz, 3 H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  = 155.3, 152.4, 134.6, 129.0, 128.6, 125.2, 67.9, 49.5, 49.4, 22.2, 21.1, 11.4, 11.2. IR (KBr): 3088, 2971, 2926, 1766, 1721, 1559, 1464, 1414, 1379, 1241, 1150, 1057, 914, 857, 745, 655 cm<sup>-1</sup>. HRMS-ESI ( $m/z$ ): calcd for C<sub>15</sub>H<sub>21</sub>INO<sub>2</sub> [M + H]<sup>+</sup>: 374.0612; found: 374.0604.

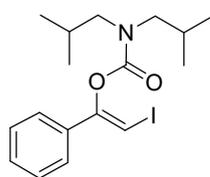
**(Z)-2-Iodo-1-phenylvinyl dibutylcarbamate ((Z)-3ad)**



Pale yellow oil (28.5 mg, 71%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.45 – 7.39 (m, 2 H), 7.37 – 7.30 (m, 3 H), 6.54 (s, 1 H), 3.44 (t,  $J$  = 7.8 Hz, 2 H), 3.30 (t,  $J$  = 7.6 Hz, 2 H), 1.80 – 1.72 (m, 2 H), 1.62 – 1.54 (m, 2 H), 1.47 – 1.39 (m, 2 H), 1.37 – 1.31 (m, 2 H), 0.99 (t,  $J$  = 7.2 Hz, 3 H), 0.92 (t,  $J$  = 7.4 Hz, 3 H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  = 155.3, 152.3, 134.6, 129.0, 128.6, 125.2, 67.9,

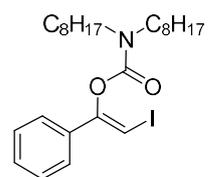
47.6, 47.5, 31.1, 29.9, 20.2, 20.0, 13.9, 13.8. IR (KBr): 3093, 2930, 2855, 1724, 1556, 1465, 1383, 1244, 1151, 1057, 915, 796, 746, 663  $\text{cm}^{-1}$ . HRMS-ESI ( $m/z$ ): calcd for  $\text{C}_{17}\text{H}_{25}\text{INO}_2$  [ $\text{M} + \text{H}$ ] $^+$ : 402.0924; found: 402.0920.

**(Z)-2-Iodo-1-phenylvinyl diisobutylcarbamate ((Z)-3ae)**



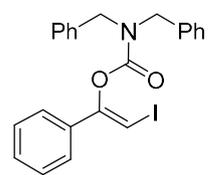
Pale yellow oil (29.7 mg, 74%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.45 – 7.39 (m, 2 H), 7.36 – 7.29 (m, 3 H), 6.54 (s, 1 H), 3.31 (d,  $J$  = 7.6 Hz, 2 H), 3.15 (d,  $J$  = 7.6 Hz, 2 H), 2.27 – 2.16 (m, 1 H), 2.12 – 2.00 (m, 1 H), 1.02 (d,  $J$  = 6.4 Hz, 6 H), 0.92 (d,  $J$  = 6.8 Hz, 6 H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 155.4, 152.9, 134.6, 129.0, 128.6, 125.2, 67.9, 55.4, 55.3, 27.5, 26.6, 20.3, 20.1. IR (KBr): 3084, 2956, 1724, 1613, 1462, 1419, 1237, 1152, 1067, 1002, 920, 857, 750, 693  $\text{cm}^{-1}$ . HRMS-ESI ( $m/z$ ): calcd for  $\text{C}_{17}\text{H}_{25}\text{INO}_2$  [ $\text{M} + \text{H}$ ] $^+$ : 402.0924; found: 402.0918.

**(Z)-2-Iodo-1-phenylvinyl dioctylcarbamate ((Z)-3af)**



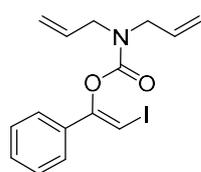
Pale yellow oil (38.5 mg, 75%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.44 – 7.40 (m, 2 H), 7.35 – 7.31 (m, 3 H), 6.54 (s, 1 H), 3.43 (t,  $J$  = 7.5 Hz, 2 H), 3.29 (t,  $J$  = 7.5 Hz, 2 H), 1.79 – 1.73 (m, 2 H), 1.62 – 1.56 (m, 2 H), 1.40 – 1.35 (m, 4 H), 1.31 – 1.25 (m, 16 H), 0.90 – 0.86 (m, 6 H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 155.3, 152.3, 134.6, 129.0, 128.6, 125.2, 67.9, 47.8, 47.7, 31.8, 31.8, 31.8, 29.4, 29.4, 29.3, 29.3, 29.3, 28.9, 27.9, 27.8, 27.1, 27.0, 26.7, 22.6, 22.6, 14.1. IR (KBr): 2937, 2861, 1738, 1634, 1552, 1451, 1387, 1243, 1152, 1058, 909, 836, 741, 687  $\text{cm}^{-1}$ . HRMS-ESI ( $m/z$ ): calcd for  $\text{C}_{25}\text{H}_{41}\text{INO}_2$  [ $\text{M} + \text{H}$ ] $^+$ : 514.2176; found: 514.2166.

**(Z)-2-Iodo-1-phenylvinyl dibenzylcarbamate ((Z)-3ag)**



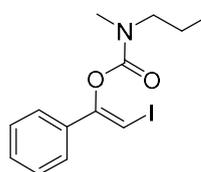
White solid (31.9 mg, 68%). mp: 103 – 104  $^{\circ}\text{C}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.46 – 7.32 (m, 15 H), 6.63 (s, 1 H), 4.68 (s, 2 H), 4.57 (s, 2 H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 155.3, 153.0, 136.7, 134.2, 129.2, 128.7, 128.6, 128.3, 127.7, 127.6, 125.2, 68.3, 50.0, 49.6. IR (KBr): 3087, 3002, 2920, 2845, 1767, 1714, 1555, 1450, 1392, 1311, 1247, 1111, 1050, 990, 914, 858, 743, 682, 603  $\text{cm}^{-1}$ . HRMS-ESI ( $m/z$ ): calcd for  $\text{C}_{23}\text{H}_{21}\text{INO}_2$  [ $\text{M} + \text{H}$ ] $^+$ : 470.0611; found: 470.0606.

**(Z)-2-Iodo-1-phenylvinyl diallylcarbamate ((Z)-3ah)**



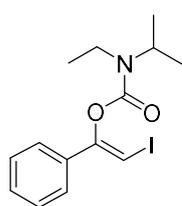
Pale yellow oil (25.5 mg, 69%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.46 – 7.40 (m, 2 H), 7.38 – 7.29 (m, 3 H), 6.56 (s, 1 H), 6.05 – 5.94 (m, 1 H), 5.88 – 5.75 (m, 1 H), 5.32 – 5.18 (m, 4 H), 4.11 (d,  $J$  = 5.5 Hz, 2 H), 3.95 (d,  $J$  = 6.0 Hz, 2 H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 155.1, 152.1, 134.3, 133.2, 132.8, 129.1, 128.6, 125.2, 117.6, 117.3, 68.1, 49.3, 49.1. IR (KBr): 3083, 2992, 2927, 2847, 1762, 1725, 1555, 1453, 1401, 1237, 1149, 1058, 993, 855, 747, 661  $\text{cm}^{-1}$ . HRMS-ESI ( $m/z$ ): calcd for  $\text{C}_{15}\text{H}_{17}\text{INO}_2$  [ $\text{M} + \text{H}$ ] $^+$ : 370.0298; found: 370.0292.

**(Z)-2-Iodo-1-phenylvinyl methyl(propyl)carbamate ((Z)-3ai)**



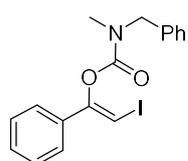
Pale yellow oil (23.1 mg, 67%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.43 (s, 2 H), 7.36 – 7.30 (m, 3 H), 6.54 (s, 1 H), 3.46 (t,  $J$  = 6.3 Hz, 1 H), 3.31 (t,  $J$  = 6.0 Hz, 1 H), 3.16 (s, 1.5 H), 2.98 (s, 1.5 H), 1.84 – 1.76 (m, 1 H), 1.68 – 1.58 (m, 1 H), 1.03 (t,  $J$  = 6.3 Hz, 1.5 H), 0.93 (t,  $J$  = 6.5 Hz, 1.5 H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 155.2, 152.4, 134.5, 134.4, 129.1, 128.6, 125.2, 67.8, 51.2, 51.1, 34.9, 34.5, 21.4, 20.5, 11.1, 11.3, 11.0. IR (KBr): 3109, 3000, 2899, 2819, 1772, 1717, 1548, 1390, 1243, 1150, 1054, 979, 914, 855, 746, 662  $\text{cm}^{-1}$ . HRMS-ESI ( $m/z$ ): calcd for  $\text{C}_{13}\text{H}_{17}\text{INO}_2$  [ $\text{M} + \text{H}$ ] $^+$ : 346.0298; found: 346.0295.

**(Z)-2-Iodo-1-phenylvinyl ethyl(isopropyl)carbamate ((Z)-3aj)**



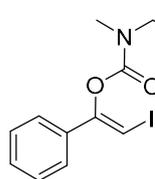
White solid (23.3 mg, 65%). mp: 115 – 117  $^{\circ}\text{C}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.48 – 7.40 (m, 2 H), 7.38 – 7.28 (m, 3 H), 6.56 (s, 0.6 H), 6.55 (s, 0.4 H), 4.59 – 4.41 (m, 0.4 H), 4.37 – 4.26 (m, 0.6 H), 3.43 (q,  $J$  = 7.1 Hz, 1.2 H), 3.28 (q,  $J$  = 7.1 Hz, 0.8 H), 1.40 – 1.34 (m, 3 H), 1.27 – 1.16 (m, 6 H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 155.3, 152.0, 134.6, 129.0, 128.6, 125.1, 67.9, 48.5, 48.3, 37.9, 37.7, 21.4, 20.5, 16.3, 14.8. IR (KBr): 3086, 2927, 2854, 1771, 1716, 1560, 1442, 1361, 1235, 1150, 1078, 1022, 905, 747, 696  $\text{cm}^{-1}$ . HRMS-ESI ( $m/z$ ): calcd for  $\text{C}_{14}\text{H}_{19}\text{INO}_2$  [ $\text{M} + \text{H}$ ] $^+$ : 360.0455; found: 360.0446.

**(Z)-2-Iodo-1-phenylvinyl benzyl(methyl)carbamate ((Z)-3ak)**



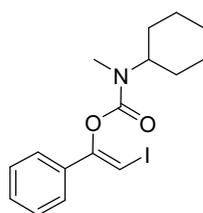
Pale yellow oil (24.8 mg, 63%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.52 – 7.28 (m, 10 H), 6.61 (s, 0.55 H), 6.57 (s, 0.45 H), 4.76 (s, 0.90 H), 4.56 (s, 1.10 H), 3.11 (s, 1.55 H), 3.00 (s, 1.45 H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 155.2, 155.2, 153.0, 152.4, 136.8, 134.3, 134.2, 129.1, 128.7, 128.6, 128.6, 127.9, 127.6, 127.5, 125.2, 125.2, 68.2, 68.1, 53.0, 52.8, 34.8, 34.1. IR (KBr): 3087, 3002, 2920, 2845, 1767, 1714, 1555, 1450, 1392, 1311, 1247, 1111, 1050, 990, 914, 858, 803, 743, 682  $\text{cm}^{-1}$ . HRMS-ESI ( $m/z$ ): calcd for  $\text{C}_{17}\text{H}_{17}\text{INO}_2$  [ $\text{M} + \text{H}$ ] $^+$ : 394.0298; found: 394.0294.

**(Z)-2-Iodo-1-phenylvinyl methyl(phenethyl)carbamate ((Z)-3al)**



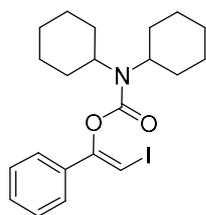
Pale yellow oil (21.2 mg, 52%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.44 – 7.41 (m, 1 H), 7.39 – 7.32 (m, 7 H), 7.31 – 7.24 (m, 2 H), 6.59 (s, 1 H), 3.79 (t,  $J$  = 7.4 Hz, 1 H), 3.63 (t,  $J$  = 7.4 Hz, 1 H), 3.16 – 3.10 (m, 3 H), 2.99 – 2.94 (m, 3 H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 155.1, 152.3, 138.6, 134.3, 134.2, 129.1, 128.9, 128.6, 128.6, 128.5, 126.5, 126.4, 125.1, 125.1, 68.1, 68.0, 51.3, 51.2, 35.3, 35.3, 34.9, 33.7. IR (KBr): 3083, 3012, 2928, 2835, 1778, 1719, 1557, 1490, 1394, 1250, 1176, 1114, 1052, 979, 917, 795, 744, 692  $\text{cm}^{-1}$ . HRMS-ESI ( $m/z$ ): calcd for  $\text{C}_{18}\text{H}_{19}\text{INO}_2$  [ $\text{M} + \text{H}$ ] $^+$ : 408.0455; found: 408.0443.

**(Z)-2-Iodo-1-phenylvinyl cyclohexyl(methyl)carbamate ((Z)-3am)**



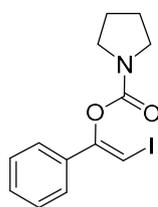
Pale yellow oil (25.0 mg, 65%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.47 – 7.40 (m, 2 H), 7.37 – 7.31 (m, 3 H), 6.54 (s, 1 H), 4.19 – 4.10 (m, 0.4 H), 4.06 – 3.88 (m, 0.6 H), 3.04 (s, 1.7 H), 2.88 (s, 1.3 H), 1.97 – 1.72 (m, 4 H), 1.68 – 1.31 (m, 5 H), 1.19 – 1.03 (m, 1 H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 155.4, 155.2, 152.3, 152.2, 134.5, 129.0, 128.6, 125.2, 125.1, 68.0, 67.9, 56.0, 55.4, 30.7, 30.0, 29.0, 28.8, 25.7, 25.6, 25.4. IR (KBr): 3122, 2998, 2923, 2839, 1770, 1711, 1548, 1447, 1393, 1318, 1244, 1154, 1101, 1052, 999, 914, 794, 747, 664  $\text{cm}^{-1}$ . HRMS-ESI ( $m/z$ ): calcd for  $\text{C}_{16}\text{H}_{21}\text{INO}_2$  [ $\text{M} + \text{H}$ ] $^+$ : 386.0611; found: 386.0602.

**(Z)-2-Iodo-1-phenylvinyl dicyclohexylcarbamate ((Z)-3an)**



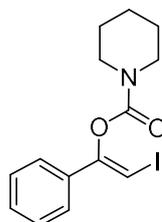
Yellow oil (25.8 mg, 57%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.45 – 7.39 (m, 2 H), 7.37 – 7.30 (m, 3 H), 6.55 (s, 1 H), 3.69 (s, 1 H), 3.52 (s, 1 H), 1.95 – 1.83 (m, 8 H), 1.81 – 1.75 (m, 2 H), 1.70 – 1.58 (m, 4 H), 1.42 – 1.34 (m, 2 H), 1.31 – 1.24 (m, 2 H), 1.21 – 1.05 (m, 2 H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 155.3, 151.3, 134.8, 128.9, 128.6, 125.1, 67.8, 56.3, 56.0, 32.0, 30.4, 26.3, 26.1, 25.4, 25.3. IR (KBr): 3118, 2999, 2925, 2847, 1767, 1697, 1541, 1449, 1382, 1241, 1158, 1095, 1047, 912, 792, 746, 656  $\text{cm}^{-1}$ . HRMS-ESI ( $m/z$ ): calcd for  $\text{C}_{21}\text{H}_{29}\text{INO}_2$  [ $\text{M} + \text{H}$ ] $^+$ : 454.1237; found: 454.1228.

**(Z)-2-Iodo-1-phenylvinyl pyrrolidine-1-carboxylate ((Z)-3ao)**



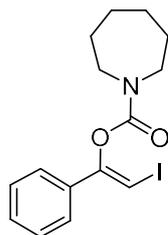
Pale yellow oil (23.3 mg, 68%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.49 – 7.42 (m, 2 H), 7.37 – 7.30 (m, 3 H), 6.54 (s, 1 H), 3.68 (t,  $J$  = 6.6 Hz, 2 H), 3.47 (t,  $J$  = 6.6 Hz, 2 H), 2.05 – 1.89 (m, 4 H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 155.2, 150.9, 134.5, 129.1, 128.6, 125.3, 68.0, 46.5, 25.8, 25.0. IR (KBr): 3120, 3000, 2919, 2835, 1774, 1715, 1546, 1393, 1247, 1155, 1060, 917, 860, 799, 745, 664  $\text{cm}^{-1}$ . HRMS-ESI ( $m/z$ ): calcd for  $\text{C}_{13}\text{H}_{13}\text{INO}_2$  [ $\text{M} - \text{H}$ ] $^-$ : 341.9996; found: 342.0001.

**(Z)-2-Iodo-1-phenylvinyl piperidine-1-carboxylate ((Z)-3ap)**



Pale yellow oil (23.2 mg, 65%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.46 – 7.41 (m, 2 H), 7.36 – 7.31 (m, 3 H), 6.54 (s, 1 H), 3.69 (s, 2 H), 3.49 (s, 2 H), 1.74 – 1.62 (m, 6 H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 155.2, 151.3, 134.5, 129.1, 128.6, 125.2, 67.9, 45.9, 45.3, 26.1, 25.6, 24.3. IR (KBr): 3092, 3001, 2925, 2843, 1775, 1713, 1554, 1419, 1224, 1139, 1060, 1018, 913, 848, 793, 744, 662  $\text{cm}^{-1}$ . HRMS-ESI ( $m/z$ ): calcd for  $\text{C}_{14}\text{H}_{17}\text{INO}_2$  [ $\text{M} + \text{H}$ ] $^+$ : 358.0298; found: 358.0291.

**(Z)-2-Iodo-1-phenylvinyl azepane-1-carboxylate ((Z)-3aq)**

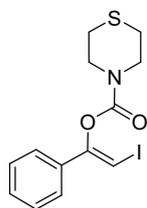


Pale yellow oil (28.6 mg, 77%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.46 – 7.42 (m, 2 H), 7.36 – 7.32 (m, 3 H), 6.54 (s, 1 H), 3.67 (t,  $J$  = 6.0 Hz, 2 H), 3.50 (t,  $J$  = 6.0 Hz, 2 H), 1.94 – 1.88 (m, 2 H), 1.78 – 1.73 (m, 2 H), 1.72 – 1.67 (m, 2 H), 1.66 – 1.61 (m, 2 H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 155.2, 152.2, 134.6, 129.0, 128.6, 125.2, 68.0, 47.5, 47.5, 28.6, 28.1, 27.4, 26.8. IR (KBr): 3083, 3002, 2923,

2851, 1774, 1715, 1559, 1645, 1410, 1248, 1165, 1106, 1062, 1001, 914, 845, 797, 679  $\text{cm}^{-1}$ .

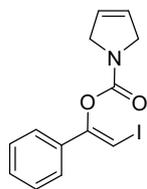
HRMS-ESI ( $m/z$ ): calcd for  $\text{C}_{15}\text{H}_{19}\text{INO}_2$  [ $\text{M} + \text{H}$ ] $^+$ : 372.0455; found: 372.0447.

**(Z)-2-Iodo-1-phenylvinyl thiomorpholine-4-carboxylate ((Z)-3ar)**



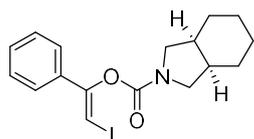
Yellow oil (22.8 mg, 61%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.45 – 7.39 (m, 2 H), 7.39 – 7.29 (m, 3 H), 6.58 (s, 1 H), 4.01 (s, 2 H), 3.81 (s, 2 H), 2.81 (s, 2 H), 2.70 (s, 2 H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 155.0, 151.1, 134.1, 129.3, 128.7, 125.1, 68.3, 47.5, 46.8, 27.6, 27.2. IR (KBr): 3124, 2999, 2915, 2839, 1767, 1699, 1549, 1382, 1243, 1161, 1058, 963, 915, 794, 745, 660  $\text{cm}^{-1}$ . HRMS-ESI ( $m/z$ ): calcd for  $\text{C}_{13}\text{H}_{15}\text{INO}_2\text{S}$  [ $\text{M} + \text{H}$ ] $^+$ : 375.9863; found: 375.9853.

**(Z)-2-Iodo-1-phenylvinyl 2,5-dihydro-1H-pyrrole-1-carboxylate ((Z)-3as)**



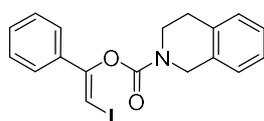
Yellow oil (24.5 mg, 72%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.50 – 7.43 (m, 2 H), 7.38 – 7.31 (m, 3 H), 6.57 (s, 1 H), 5.87 (s, 2 H), 4.52 – 4.47 (m, 2 H), 4.31 – 4.24 (m, 2 H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 155.1, 150.6, 134.3, 129.2, 128.6, 125.8, 125.5, 125.3, 68.2, 53.6. IR (KBr): 3122, 3002, 2908, 2839, 1775, 1692, 1547, 1472, 1392, 1250, 1162, 1069, 990, 851, 791, 736, 667  $\text{cm}^{-1}$ . HRMS-ESI ( $m/z$ ): calcd for  $\text{C}_{13}\text{H}_{13}\text{INO}_2$  [ $\text{M} + \text{H}$ ] $^+$ : 341.9985; found: 341.9979.

**(Z)-2-Iodo-1-phenylvinyl (3aR,7aS)-octahydro-2H-isoindole-2-carboxylate ((Z)-3at)**



Yellow oil (25.4 mg, 64%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.49 – 7.43 (m, 2 H), 7.37 – 7.31 (m, 3 H), 6.55 (s, 1 H), 3.69 – 3.54 (m, 2 H), 3.49 – 3.35 (m, 2 H), 2.36 – 2.21 (m, 2 H), 1.72 – 1.61 (m, 2 H), 1.60 – 1.48 (m, 4 H), 1.46 – 1.33 (m, 2 H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 155.1, 151.4, 134.4, 129.1, 128.6, 125.2, 68.1, 50.6, 50.3, 37.4, 36.6, 25.8, 25.7, 22.7, 22.7. IR (KBr): 3080, 2926, 2866, 1728, 1605, 1485, 1400, 1262, 1179, 1076, 916, 854, 742, 696, 605  $\text{cm}^{-1}$ . HRMS-ESI ( $m/z$ ): calcd for  $\text{C}_{17}\text{H}_{21}\text{INO}_2$  [ $\text{M} + \text{H}$ ] $^+$ : 398.0611; found: 398.0603.

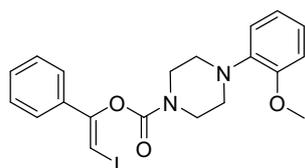
**(Z)-2-Iodo-1-phenylvinyl 3,4-dihydroisoquinoline-2(1H)-carboxylate ((Z)-3au)**



Pale yellow oil (29.2 mg, 72%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.53 – 7.45 (m, 2 H), 7.42 – 7.33 (m, 3 H), 7.30 – 7.16 (m, 4 H), 6.63 (s, 1 H), 4.98 (s, 1 H), 4.74 (s, 1 H), 4.02 (t,  $J$  = 5.8 Hz, 1 H), 3.82 (t,  $J$  = 5.8 Hz,

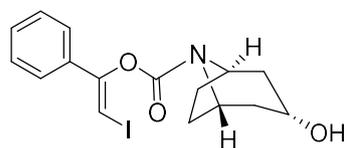
1 H), 3.08 (t,  $J = 6.0$  Hz, 1 H), 2.98 (t,  $J = 6.0$  Hz, 1 H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 155.1$ , 155.0, 151.7, 151.5, 134.4, 134.2, 134.2, 133.0, 132.5, 129.2, 128.8, 128.6, 128.6, 126.7, 126.6, 126.4, 126.4, 126.2, 125.2, 68.3, 46.4, 46.0, 42.5, 41.7, 29.2, 28.7. IR (KBr): 3075, 2999, 2918, 2853, 1773, 1713, 1609, 1493, 1408, 1221, 1069, 922, 838, 741, 609  $\text{cm}^{-1}$ . HRMS-ESI ( $m/z$ ): calcd for  $\text{C}_{18}\text{H}_{17}\text{INO}_2$   $[\text{M} + \text{H}]^+$ : 406.0298; found: 406.0292.

**(Z)-2-Iodo-1-phenylvinyl 4-(2-methoxyphenyl)piperazine-1-carboxylate ((Z)-3av)**



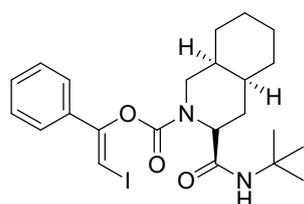
Pale yellow oil (28.3 mg, 61%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.50 - 7.44$  (m, 2 H), 7.40 - 7.32 (m, 3 H), 7.10 - 6.89 (m, 4 H), 6.59 (s, 1 H), 3.97 (s, 2 H), 3.90 (s, 3 H), 3.76 (s, 2 H), 3.17 (d,  $J = 28.4$  Hz, 4 H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 155.1$ , 152.3, 151.4, 134.2, 129.2, 128.7, 128.0, 125.2, 123.6, 121.1, 118.5, 111.4, 68.2, 55.5, 50.9, 50.6, 45.1, 44.4. IR (KBr): 3083, 2996, 2919, 2821, 1765, 1726, 1552, 1503, 1437, 1383, 1239, 1159, 1058, 914, 745  $\text{cm}^{-1}$ . HRMS-ESI ( $m/z$ ): calcd for  $\text{C}_{20}\text{H}_{22}\text{IN}_2\text{O}_3$   $[\text{M} + \text{H}]^+$ : 465.0670; found: 465.0667.

**(Z)-2-Iodo-1-phenylvinyl (1R,3r,5S)-3-hydroxy-8-azabicyclo[3.2.1]octane-8-carboxylate ((Z)-3aw)**



White solid (25.9 mg, 65%). mp: 150 - 151  $^{\circ}\text{C}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.47 - 7.40$  (m, 2 H), 7.38 - 7.31 (m, 3 H), 6.54 (s, 1 H), 4.59 - 4.46 (m, 1 H), 4.38 - 4.27 (m, 1 H), 4.26 - 4.17 (m, 1 H), 2.52 - 2.41 (m, 1 H), 2.35 - 2.18 (m, 3 H), 2.17 - 2.07 (m, 1 H), 2.06 - 1.94 (m, 1 H), 1.90 - 1.74 (m, 2 H), 1.68 (s, 1 H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 154.8$ , 149.1, 134.4, 129.1, 128.6, 125.1, 68.2, 65.0, 53.8, 53.2, 39.4, 38.6, 28.8, 27.7. IR (KBr): 3483, 3082, 2989, 2926, 1765, 1710, 1558, 1505, 1414, 1325, 1244, 1164, 1076, 1043, 913, 796, 746, 692  $\text{cm}^{-1}$ . HRMS-ESI ( $m/z$ ): calcd for  $\text{C}_{16}\text{H}_{19}\text{INO}_3$   $[\text{M} + \text{H}]^+$ : 400.0404; found: 400.0396.

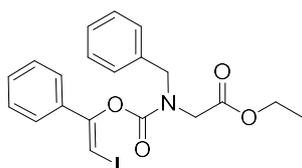
**(Z)-2-Iodo-1-phenylvinyl (3R,4aS,8aS)-3-(tert-butylcarbamoyl)octahydroisoquinoline-2(1H)-carboxylate ((Z)-3ax)**



Pale yellow oil (34.2 mg, 67%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.48 - 7.32$  (m, 5 H), 6.61 (s, 1 H), 6.00 (s, 1 H), 5.00 - 4.51 (m, 1 H), 4.22 - 3.78 (m, 1 H), 3.48 - 3.16 (m, 1 H), 2.51 - 2.27 (m, 1 H),

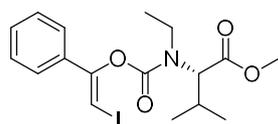
2.07 – 1.79 (m, 3 H), 1.72 – 1.26 (m, 18 H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ = 169.9, 155.1, 154.8, 152.5, 152.0, 134.0, 129.4, 128.8, 125.1, 68.6, 54.8, 54.3, 51.3, 42.8, 41.7, 34.7, 34.1, 33.5, 33.3, 31.5, 30.0, 29.2, 28.8, 27.0, 26.6, 26.2, 26.0, 21.6, 21.4. IR (KBr): 3357, 3082, 2925, 2859, 1719, 1676, 1530, 1451, 1407, 1360, 1231, 1179, 1128, 1066, 1017, 914, 859, 798, 748 cm<sup>-1</sup>. HRMS-ESI (*m/z*): calcd for C<sub>23</sub>H<sub>32</sub>IN<sub>2</sub>O<sub>3</sub> [M + H]<sup>+</sup>: 511.1452; found: 511.1450.

**Ethyl (Z)-N-benzyl-N-(((2-iodo-1-phenylvinyl)oxy)carbonyl)glycinate ((Z)-3ay)**



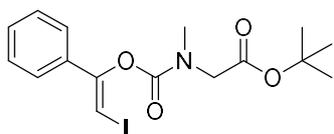
Pale yellow oil (31.2 mg, 67%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.52 – 7.48 (m, 1 H), 7.45 – 7.38 (m, 3 H), 7.38 – 7.30 (m, 6 H), 6.63 (d, *J* = 4.8 Hz, 1 H), 4.86 (s, 1 H), 4.66 (s, 1 H), 4.27 – 4.15 (m, 2 H), 4.13 (s, 1 H), 4.02 (s, 1 H), 1.30 – 1.23 (m, 3 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 169.2, 168.9, 155.0, 155.0, 152.8, 152.6, 136.2, 133.9, 133.9, 129.2, 129.2, 128.8, 128.7, 128.7, 128.3, 128.0, 127.9, 127.9, 125.2, 125.2, 68.3, 61.5, 61.3, 51.9, 51.8, 48.1, 47.9, 14.2, 14.1. IR (KBr): 3122, 2998, 2896, 2823, 1920, 1839, 1753, 1689, 1546, 1392, 1239, 1167, 1097, 1057, 1017, 972, 918, 866, 796, 746, 667, 605 cm<sup>-1</sup>. HRMS-ESI (*m/z*): calcd for C<sub>20</sub>H<sub>21</sub>INO<sub>4</sub> [M + H]<sup>+</sup>: 466.0510; found: 466.0503.

**Methyl (Z)-N-ethyl-N-(((2-iodo-1-phenylvinyl)oxy)carbonyl)-L-valinate ((Z)-3az)**



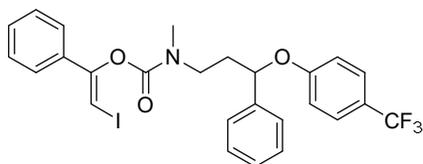
Pale yellow solid (17.2 mg, 40%). mp: 86 – 87 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.48 – 7.39 (m, 2 H), 7.37 – 7.30 (m, 3 H), 6.59 (s, 0.4 H), 6.58 (s, 0.6 H), 4.49 (d, *J* = 10.8 Hz, 0.4 H), 4.27 (d, *J* = 10.4 Hz, 0.6 H), 3.79 (s, 1.2 H), 3.72 (s, 1.8 H), 3.67 – 3.60 (m, 0.6 H), 3.57 – 3.49 (m, 0.6 H), 3.47 – 3.40 (m, 0.4 H), 3.37 – 3.27 (m, 0.4 H), 2.42 – 2.27 (m, 1 H), 1.40 – 1.33 (m, 2 H), 1.30 – 1.22 (m, 1 H), 1.17 – 1.12 (m, 2 H), 1.05 (d, *J* = 6.4 Hz, 1 H), 1.00 (dd, *J* = 6.8, 2.0 Hz, 3 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 171.4, 171.1, 155.1, 153.1, 151.7, 134.3, 129.1, 128.6, 128.6, 125.1, 68.2, 68.1, 65.0, 64.7, 52.0, 51.9, 40.6, 39.8, 28.0, 27.6, 20.0, 19.9, 19.7, 19.1, 14.8, 13.2. IR (KBr): 2961, 2848, 1717, 1587, 1411, 1243, 1117, 1060, 1005, 745, 694, 605 cm<sup>-1</sup>. HRMS-ESI (*m/z*): calcd for C<sub>17</sub>H<sub>23</sub>INO<sub>4</sub> [M + H]<sup>+</sup>: 432.0666; found: 432.0662.

**tert-Butyl (Z)-N-(((2-iodo-1-phenylvinyl)oxy)carbonyl)-N-methylglycinate ((Z)-3aaa)**



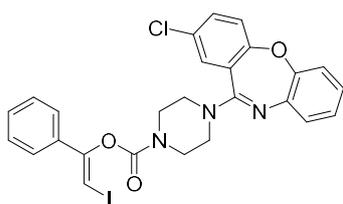
Pale yellow oil (27.9 mg, 67%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.48 – 7.43 (m, 2 H), 7.37 – 7.29 (m, 3 H), 6.63 – 6.55 (m, 1 H), 4.13 (s, 1 H), 3.98 (s, 1 H), 3.24 (s, 1.5 H), 3.06 (s, 1.5 H), 1.52 (s, 4.5 H), 1.47 (s, 4.5 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 168.2, 168.0, 155.0, 154.9, 152.9, 152.1, 134.0, 133.9, 129.1, 128.6, 128.6, 125.1, 82.1, 82.0, 68.1, 68.1, 51.6, 51.6, 36.2, 35.9, 28.1, 28.1. IR (KBr): 2977, 2837, 1717, 1602, 1511, 1462, 1423, 1374, 1303, 1251, 1152, 1055, 954, 866, 824, 753, 692 cm<sup>-1</sup>. HRMS-ESI (*m/z*): calcd for C<sub>16</sub>H<sub>21</sub>INO<sub>4</sub> [M + H]<sup>+</sup>: 418.0510; found: 418.0504.

**(Z)-2-Iodo-1-phenylvinyl methyl(3-phenyl-3-(4-(trifluoromethyl)phenoxy)propyl)carbamate ((Z)-3aba)**



Yellow oil (30.2 mg, 52%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.48 – 7.32 (m, 1 H), 6.93 (dd, *J* = 18.5, 8.4 Hz, 2 H), 6.80 (d, *J* = 8.4 Hz, 1 H), 6.59 (d, *J* = 11.6 Hz, 1H), 5.42 – 5.21 (m, 1 H), 3.88 – 3.68 (m, 1 H), 3.60 (t, *J* = 7.0 Hz, 1 H), 3.23 (s, 1.6 H), 3.03 (s, 1.4 H), 2.46 (q, *J* = 7.0 Hz, 1 H), 2.38 – 2.18 (m, 1 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 160.2, 159.1, 155.2, 155.1, 152.3, 152.6, 140.5, 140.4, 134.2, 129.2, 129.0, 128.8, 128.6, 128.1, 128.0, 126.9 – 126.7 (m), 125.7, 125.6, 125.2, 123.3 – 122.0 (m), 115.8, 115.4, 77.8, 68.3, 68.2, 46.7, 46.6, 37.6, 36.5, 35.6, 35.4. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>): δ = -61.32 (s), -61.55 (d, *J* = 9.4 Hz). IR (KBr): 3083, 2930, 1724, 1612, 1512, 1452, 1402, 1324, 1250, 1167, 1117, 1059, 837, 750, 698, 641 cm<sup>-1</sup>. HRMS-ESI (*m/z*): calcd for C<sub>26</sub>H<sub>23</sub>F<sub>3</sub>INO<sub>3</sub> [M - e]<sup>+</sup>: 581.0675; found: 581.0681.

**(Z)-2-Iodo-1-phenylvinyl 4-(2-chlorodibenzo[*b,f*][1,4]oxazepin-11-yl)piperazine-1-carboxylate ((Z)-3aca)**

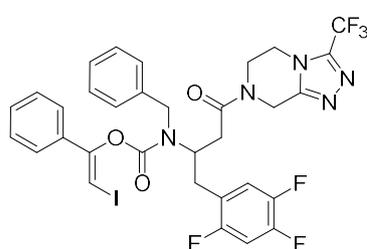


Pale yellow solid (24.0 mg, 41%). mp: 204 – 205 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.48 – 7.40 (m, 3 H), 7.39 – 7.33 (m, 4 H), 7.24 – 7.17 (m, 2 H), 7.16 – 7.09 (m, 2 H), 7.07 – 7.01 (m, 1 H), 6.60 (s, 1 H), 4.02 – 3.50 (m, 8 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 159.3, 158.8, 155.0, 151.8, 151.3, 134.0, 132.9, 130.5, 129.3, 128.8, 128.7, 127.1, 125.9, 125.1, 124.7, 122.9, 120.1, 68.4, 47.5, 44.6, 43.8. IR (KBr): 3122, 2997, 2923, 2838, 1920,

1838, 1766, 1725, 1560, 1471, 1392, 1234, 1154, 1105, 1059, 1012, 915, 841, 791, 747, 662  $\text{cm}^{-1}$ .

HRMS-ESI ( $m/z$ ): calcd for  $\text{C}_{26}\text{H}_{22}\text{ClIN}_3\text{O}_3$  [ $\text{M} + \text{H}$ ] $^+$ : 586.0389; found: 586.0385.

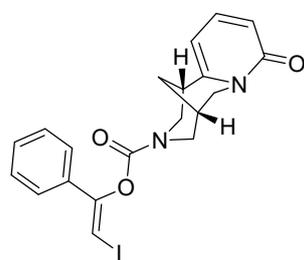
**(Z)-2-Iodo-1-phenylvinyl benzyl(4-oxo-4-(3-(trifluoromethyl)-5,6-dihydro-[1,2,4]triazolo [4,3-*a*]pyrazin-7(8*H*)-yl)-1-(2,4,5-trifluorophenyl)butan-2-yl)carbamate ((Z)-3ada)**



Pale yellow oil (36.9 mg, 48%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.53 – 7.17 (m, 10 H), 6.90 – 6.61 (m, 2 H), 6.58 (s, 1 H), 5.17 – 4.94 (m, 1 H), 4.91 – 4.54 (m, 2 H), 4.50 – 4.35 (m, 1 H), 4.28 – 3.91 (m, 3 H), 3.88 – 3.64 (m, 2 H), 3.61 – 3.40 (m, 1 H), 3.22 – 2.99 (m, 1 H), 2.97 – 2.84 (m, 1 H), 2.74 – 2.44 (m, 1 H).

$^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 169.5, 169.4, 156.9 – 156.7 (m), 155.1, 154.9, 153.0, 151.7, 150.2 – 150.0 (m), 150.0 – 149.7 (m), 149.5 – 149.3 (m), 147.8 (td,  $J$  = 12.7, 11.2, 5.0 Hz), 147.5 – 147.3 (m), 145.4 (dd,  $J$  = 12.7, 3.3 Hz), 143.3 (q,  $J$  = 39.9 Hz), 136.5, 136.3, 134.2, 133.9, 129.3, 129.0, 128.7, 128.7, 128.5, 127.8, 127.7, 125.4, 125.1, 124.8, 121.3 – 120.7 (m), 119.0 (dd,  $J$  = 18.4, 5.1 Hz), 118.1 (q,  $J$  = 269 Hz), 105.4 (ddd,  $J$  = 27.6, 20.5, 6.6 Hz). 68.4, 68.4, 57.6, 56.7, 54.8, 53.6, 43.4, 43.0, 42.3, 41.8, 39.3, 38.0, 35.6, 35.0, 31.3, 31.1.  $^{19}\text{F}$  NMR (471 MHz,  $\text{CDCl}_3$ ):  $\delta$  = -62.54 – -63.17 (m, 3 F), -118.46 – -119.09 (m, 1 F), -135.16 – -135.85 (m, 1 F), -142.46 – -142.95 (m, 1F). IR (KBr): 2996, 2920, 2834, 1765, 1712, 1661, 1516, 1439, 1376, 1239, 1155, 1098, 1054, 970, 915, 849, 748, 660  $\text{cm}^{-1}$ . HRMS-ESI ( $m/z$ ): calcd for  $\text{C}_{32}\text{H}_{27}\text{F}_6\text{IN}_5\text{O}_3$  [ $\text{M} + \text{H}$ ] $^+$ : 770.1057; found: 770.1042.

**(Z)-2-Iodo-1-phenylvinyl (1*S*,5*R*)-8-oxo-1,5,6,8-tetrahydro-2*H*-1,5-methanopyrido[1,2-*a*][1,5] diazocine-3(4*H*)-carboxylate ((Z)-3aea)**



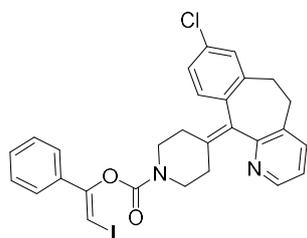
Pale yellow solid (21.3 mg, 46%). mp: 140 – 142  $^{\circ}\text{C}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.38 – 7.25 (m, 5 H), 7.10 (d,  $J$  = 7.3 Hz, 1 H), 6.63 – 6.44 (m, 2 H), 6.19 (d,  $J$  = 6.8 Hz, 0.45 H), 6.10 (d,  $J$  = 7.2 Hz, 0.55 H), 4.59 (d,  $J$  = 13.2 Hz, 0.5 H), 4.52 – 4.41 (m, 1 H), 4.36 (d,  $J$  = 13.2 Hz, 0.5 H), 4.29 (d,  $J$  = 12.8 Hz, 0.5 H), 4.18 – 4.11 (m, 0.5

H), 4.04 – 3.92 (m, 1 H), 3.43 (t,  $J$  = 12.0 Hz, 1 H), 3.27 – 3.08 (m, 2 H), 2.60 (s, 1 H), 2.13 – 2.00 (m, 2 H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 163.3, 163.1, 154.4, 154.4, 151.1, 151.0, 148.9, 148.3, 139.0, 138.9, 133.7, 133.5, 129.0, 128.6, 124.7, 124.5, 117.3, 117.3, 105.7, 105.5, 68.5, 68.1, 51.3, 51.0, 50.5, 50.0, 49.3, 48.7, 34.2, 29.5, 27.0, 26.9, 25.5, 25.4. IR (KBr): 3078, 2996, 2930, 2858,

1766, 1721, 1652, 1550, 1429, 1369, 1232, 1162, 1103, 1050, 978, 915, 848, 799, 744  $\text{cm}^{-1}$ .

HRMS-ESI ( $m/z$ ): calcd for  $\text{C}_{20}\text{H}_{20}\text{IN}_2\text{O}_3$  [ $\text{M} + \text{H}$ ] $^+$ : 463.0513; found: 463.0511.

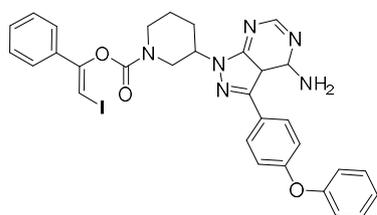
**(Z)-2-Iodo-1-phenylvinyl 4-(8-chloro-5,6-dihydro-11H-benzo[5,6]cyclohepta[1,2-b]pyridin-11-ylidene) piperidine-1-carboxylate ((Z)-3afa)**



Yellow oil (34.9 mg, 60%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 8.51 – 8.34 (m, 1 H), 7.50 – 7.41 (m, 3 H), 7.38 – 7.30 (m, 3 H), 7.22 – 7.08 (m, 4 H), 6.56 (s, 1 H), 4.17 – 4.02 (m, 1 H), 3.96 – 3.81 (m, 1 H), 3.48 – 3.33 (m, 3 H), 3.29 – 3.17 (m, 1 H), 2.95 – 2.80 (m, 2 H), 2.79 – 2.67 (m, 1 H), 2.64 – 2.56 (m, 1 H), 2.52 – 2.38 (m, 2 H).  $^{13}\text{C}$

NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 156.6, 155.0, 151.3, 146.4, 139.5, 139.4, 137.8, 137.4, 137.0, 134.4, 133.5, 133.4, 134.2, 133.0, 130.4, 129.2, 129.0, 128.6, 126.2, 125.1, 122.4, 68.2, 45.8, 45.3, 31.6, 31.5, 31.1, 31.0, 30.6, 30.4. IR (KBr): 3082, 2987, 2921, 2854, 1723, 1566, 1512, 1430, 1375, 1324, 1218, 1095, 1055, 996, 916, 830, 745, 698, 649  $\text{cm}^{-1}$ . HRMS-ESI ( $m/z$ ): calcd for  $\text{C}_{28}\text{H}_{25}\text{ClIN}_2\text{O}_2$  [ $\text{M} + \text{H}$ ] $^+$ : 583.0644; found: 583.0642.

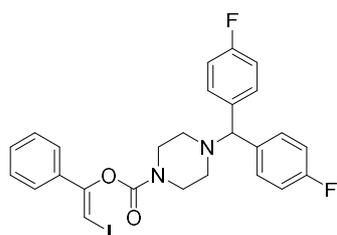
**(Z)-2-Iodo-1-phenylvinyl 3-(4-amino-3-(4-phenoxyphenyl)-3a,4-dihydro-1H-pyrazolo[3,4-d]pyrimidin-1-yl)piperidine-1-carboxylate ((Z)-3aga)**



Yellow oil (46.1 mg, 70%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 8.34 (d,  $J$  = 18.4 Hz, 1 H), 7.75 – 7.55 (m, 2 H), 7.50 – 7.27 (m, 7 H), 7.22 – 7.05 (m, 5 H), 6.56 (d,  $J$  = 5.6 Hz, 1 H), 6.09 (s, 2 H), 5.21 – 4.92 (m, 1 H), 4.70 – 4.18 (m, 2 H), 3.82 (t,  $J$  =

11.8 Hz, 0.5 H), 3.62 (t,  $J$  = 11.6 Hz, 0.5 H), 3.20 (t,  $J$  = 11.4 Hz, 0.5 H), 2.99 (t,  $J$  = 12.0 Hz, 0.5 H), 2.42 – 2.25 (m, 2 H), 2.07 – 1.77 (m, 2 H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 158.4, 157.9, 156.2, 155.4, 155.3, 154.9, 154.2, 154.0, 151.3, 144.0, 134.1, 129.9, 129.1, 128.6, 127.6, 125.1, 123.9, 119.4, 119.0, 98.4, 68.4, 53.0, 52.6, 48.7, 47.9, 44.8, 44.2, 30.1, 29.6, 29.2, 24.8, 24.2. IR (KBr): 3082, 2995, 2935, 2858, 1726, 1624, 1574, 1521, 1482, 1429, 1375, 1237, 1147, 1106, 1059, 979, 936, 852, 799, 749, 693  $\text{cm}^{-1}$ . HRMS-ESI ( $m/z$ ): calcd for  $\text{C}_{31}\text{H}_{28}\text{IN}_6\text{O}_3$  [ $\text{M} + \text{H}$ ] $^+$ : 659.1262; found: 659.1256.

**(Z)-2-Iodo-1-phenylvinyl 4-(bis(4-fluorophenyl)methyl)piperazine-1-carboxylate ((Z)-3aha)**

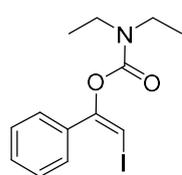


Pale yellow oil (31.9 mg, 57%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ = 7.46 – 7.31 (m, 9 H), 7.00 (t, *J* = 8.6 Hz, 4 H), 6.55 (s, 1 H), 4.30 (s, 1 H), 3.77 (s, 2 H), 3.56 (s, 2 H), 2.47 (d, *J* = 23.2 Hz, 4 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 161.9 (d, *J* = 244.4 Hz), 155.0, 151.3, 137.6, 134.2, 129.2 (d, *J* = 9.5 Hz), 129.2, 128.6, 125.1, 115.6 (d, *J* = 26.4 Hz), 74.3, 68.1, 51.7, 51.4, 45.0, 44.3. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>): δ = -115.04 – -115.21 (m). IR (KBr): 3087, 2995, 2909, 2812, 1727, 1602, 1552, 1506, 1428, 1229, 1155, 1070, 998, 915, 833, 745, 654 cm<sup>-1</sup>. HRMS-ESI (*m/z*): calcd for C<sub>26</sub>H<sub>24</sub>F<sub>2</sub>IN<sub>2</sub>O<sub>2</sub> [M + H]<sup>+</sup>: 561.0845; found: 561.0838.

**C. General procedure for the preparation of (*E*)-β-iodoenol carbamates**

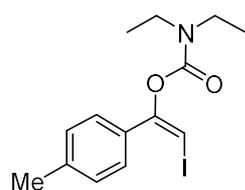
A 25 mL oven-dried Schlenk tube equipped with a magnetic stirring bar was charged with alkynylbenziodoxole **1** (0.1 mmol) and tris(2-phenylpyridine)iridium (0.001 mmol). The tube was then evacuated, refilled with CO<sub>2</sub> (1 atm) three times, and charged further with amine **2** (0.3 mmol), 1,8-diazabicyclo[5.4.0]undec-7-ene (0.2 mmol) and ethyl acetate (1 mL) via a syringe. The reaction mixture was stirred at room temperature for 14 h under 30 W green LEDs irradiation. After the reaction was completed, the reaction mixture was diluted with dichloromethane (10 mL). The solvent was removed under reduced pressure and the crude residue was separated by column chromatography on a silica gel column using petroleum ether/ethyl acetate (20:1-10:1) as the eluent to give the desired product (*E*)-**3**.

**(*E*)-2-Iodo-1-phenylvinyl diethylcarbamate ((*E*)-3aa)**



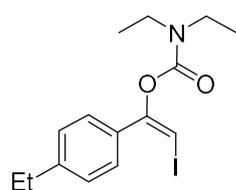
Yellow oil (*E/Z* = 82:18, 23.5 mg, 68%). Spectroscopic data for *E*-isomer: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.65 – 7.58 (m, 2 H), 7.43 – 7.31 (m, 3 H), 6.32 (s, 1 H), 3.36 (q, *J* = 7.1 Hz, 2 H), 3.26 (q, *J* = 7.2 Hz, 2 H), 1.19 (t, *J* = 7.0 Hz, 3 H), 1.10 (t, *J* = 7.2 Hz, 3 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 152.9, 151.5, 134.9, 129.1, 128.7, 127.9, 66.1, 42.0, 41.7, 14.2, 13.1. IR (KBr): 3063, 2980, 2931, 1717, 1634, 1468, 1420, 1376, 1315, 1262, 1150, 1066, 1015, 953, 924, 846, 752, 694 cm<sup>-1</sup>. HRMS-ESI (*m/z*): calcd for C<sub>13</sub>H<sub>17</sub>INO<sub>2</sub> [M + H]<sup>+</sup>: 346.0298; found: 346.0293.

**(E)-2-Iodo-1-(p-tolyl)vinyl diethylcarbamate ((E)-3ba)**



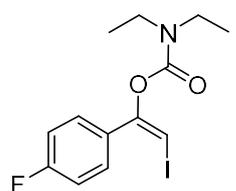
Pale yellow oil (*E/Z* = 84:16, 22.3 mg, 62%). Spectroscopic data for *E*-isomer: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.51 (d, *J* = 7.6 Hz, 2 H), 7.19 (d, *J* = 8.0 Hz, 2 H), 6.26 (s, 1 H), 3.36 (q, *J* = 7.2 Hz, 2 H), 3.26 (q, *J* = 7.2 Hz, 2 H), 2.36 (s, 3 H), 1.19 (t, *J* = 7.2 Hz, 3 H), 1.10 (t, *J* = 7.2 Hz, 3 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 153.1, 151.7, 139.2, 132.1, 128.8, 128.7, 65.6, 42.1, 41.7, 21.4, 14.2, 13.2. IR (KBr): 2986, 2925, 1766, 1713, 1554, 1517, 1465, 1379, 1313, 1247, 1147, 1060, 916, 816, 750, 656 cm<sup>-1</sup>. HRMS-ESI (*m/z*): calcd for C<sub>14</sub>H<sub>19</sub>INO<sub>2</sub> [M + H]<sup>+</sup>: 360.0455; found: 360.0448.

**(E)-1-(4-Ethylphenyl)-2-iodovinyl diethylcarbamate ((E)-3sa)**



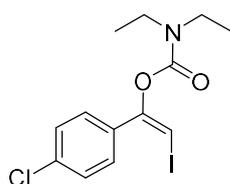
Pale yellow oil (*E/Z* = 86:14, 22.8 mg, 61%). Spectroscopic data for *E*-isomer: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.57 – 7.51 (m, 2 H), 7.24 – 7.18 (m, 2 H), 6.27 (s, 1 H), 3.37 (q, *J* = 6.9 Hz, 2 H), 3.27 (q, *J* = 7.2 Hz, 2 H), 2.67 (q, *J* = 7.7 Hz, 2 H), 1.25 (t, *J* = 7.6 Hz, 3 H), 1.20 (t, *J* = 7.0 Hz, 3 H), 1.11 (t, *J* = 7.0 Hz, 3 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 153.1, 151.7, 145.3, 132.2, 128.7, 127.5, 65.5, 42.1, 41.8, 28.7, 15.1, 14.2, 13.2. IR (KBr): 3068, 2973, 2929, 1769, 1719, 1622, 1511, 1464, 1418, 1377, 1313, 1259, 1149, 1066, 1016, 923, 832, 754, 693 cm<sup>-1</sup>. HRMS-ESI (*m/z*): calcd for C<sub>15</sub>H<sub>21</sub>INO<sub>2</sub> [M + H]<sup>+</sup>: 374.0611; found: 374.0609.

**(E)-1-(4-Fluorophenyl)-2-iodovinyl diethylcarbamate ((E)-3ca)**



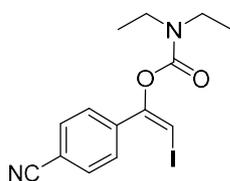
Pale yellow oil (*E/Z* = 80:20, 23.2 mg, 64%). Spectroscopic data for *E*-isomer: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.63 – 7.55 (m, 2 H), 7.10 – 7.02 (m, 2 H), 6.31 (s, 1 H), 3.35 (q, *J* = 7.1 Hz, 2 H), 3.26 (q, *J* = 7.1 Hz, 2 H), 1.18 (t, *J* = 7.0 Hz, 3 H), 1.10 (t, *J* = 7.2 Hz, 3 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 162.8 (d, *J* = 247.9 Hz), 153.0, 150.9, 131.1 (d, *J* = 3.5 Hz), 130.5 (d, *J* = 8.4 Hz), 115.1 (d, *J* = 21.6 Hz), 66.6, 42.2, 41.8, 14.2, 13.2. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>): δ = -110.93 – -111.03 (m). IR (KBr): 3068, 2973, 2929, 1769, 1719, 1622, 1511, 1464, 1418, 1377, 1313, 1259, 1149, 1066, 1016, 923, 832, 754, 693 cm<sup>-1</sup>. HRMS-ESI (*m/z*): calcd for C<sub>13</sub>H<sub>16</sub>FINO<sub>2</sub> [M + H]<sup>+</sup>: 364.0204; found: 364.0198.

**(E)-1-(4-Chlorophenyl)-2-iodovinyl diethylcarbamate ((E)-3da)**



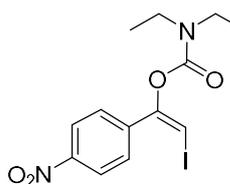
Pale yellow oil (*E/Z* = 84:16, 25.4 mg, 67%). Spectroscopic data for *E*-isomer: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.58 – 7.52 (m, 2 H), 7.38 – 7.32 (m, 2 H), 6.34 (s, 1 H), 3.35 (q, *J* = 7.2 Hz, 2 H), 3.26 (q, *J* = 7.2 Hz, 2 H), 1.19 (t, *J* = 7.2 Hz, 3 H), 1.10 (t, *J* = 7.2 Hz, 3 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 152.9, 150.7, 135.0, 133.5, 130.2, 128.4, 67.0, 42.2, 41.8, 14.2, 13.2. IR (KBr): 3066, 2979, 2930, 1769, 1719, 1629, 1553, 1477, 1418, 1380, 1310, 1259, 1149, 1066, 1013, 922, 828, 753, 659 cm<sup>-1</sup>. HRMS-ESI (*m/z*): calcd for C<sub>13</sub>H<sub>16</sub>ClINO<sub>2</sub> [M + H]<sup>+</sup>: 379.9909; found: 379.9902.

**(E)-1-(4-Cyanophenyl)-2-iodovinyl diethylcarbamate ((E)-3ea)**



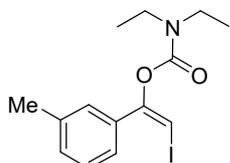
Pale yellow oil (*E/Z* = 71:29, 15.5 mg, 42%). Spectroscopic data for *E*-isomer: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.80 – 7.64 (m, 4 H), 6.47 (s, 1 H), 3.36 (q, *J* = 7.1 Hz, 2 H), 3.25 (q, *J* = 7.1 Hz, 2 H), 1.20 (t, *J* = 7.2 Hz, 3 H), 1.10 (t, *J* = 7.0 Hz, 3 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 152.7, 150.0, 139.6, 132.0, 129.6, 118.4, 112.7, 68.7, 42.3, 41.9, 14.3, 13.2. IR (KBr): 3124, 2989, 2919, 2836, 2225, 1768, 1711, 1551, 1514, 1465, 1410, 1384, 1311, 1251, 1148, 1061, 1016, 919, 834, 751, 662 cm<sup>-1</sup>. HRMS-ESI (*m/z*): calcd for C<sub>14</sub>H<sub>16</sub>IN<sub>2</sub>O<sub>2</sub> [M + H]<sup>+</sup>: 371.0251; found: 371.0247.

**(E)-2-Iodo-1-(4-nitrophenyl)vinyl diethylcarbamate ((E)-3fa)**



Pale yellow oil (*E/Z* = 61:39, 26.5 mg, 68%). Spectroscopic data for *E*-isomer: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 8.24 (d, *J* = 8.4 Hz, 2 H), 7.78 (d, *J* = 8.8 Hz, 2 H), 6.51 (s, 1 H), 3.37 (q, *J* = 7.2 Hz, 2 H), 3.25 (q, *J* = 7.2 Hz, 2 H), 1.21 (t, *J* = 7.2 Hz, 3 H), 1.10 (t, *J* = 7.0 Hz, 3 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 152.7, 149.7, 147.7, 141.5, 129.9, 123.4, 69.2, 42.3, 41.9, 14.3, 13.1. IR (KBr): 3118, 2994, 2894, 2825, 1838, 1767, 1693, 1519, 1390, 1338, 1245, 1151, 1056, 916, 849, 790, 749, 661 cm<sup>-1</sup>. HRMS-ESI (*m/z*): calcd for C<sub>13</sub>H<sub>16</sub>IN<sub>2</sub>O<sub>4</sub> [M + H]<sup>+</sup>: 391.0149; found: 391.0141.

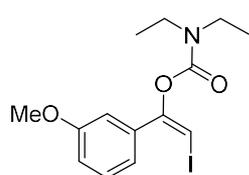
**(E)-2-Iodo-1-(*m*-tolyl)vinyl diethylcarbamate ((E)-3ia)**



Pale yellow oil (*E/Z* = 84:16, 22.3 mg, 62%). Spectroscopic data for *E*-isomer: <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ = 7.42 – 7.34 (m, 2 H), 7.25 –

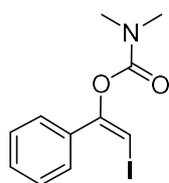
7.21 (m, 1 H), 7.14 (d,  $J = 7.5$  Hz, 1 H), 6.27 (s, 1 H), 3.34 (q,  $J = 7.2$  Hz, 2 H), 3.24 (q,  $J = 7.2$  Hz, 2 H), 2.35 (s, 3 H), 1.17 (t,  $J = 7.0$  Hz, 3 H), 1.08 (t,  $J = 7.0$  Hz, 3 H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta = 153.1, 151.8, 137.6, 134.8, 130.0, 129.4, 127.9, 125.9, 66.0, 42.1, 41.8, 21.4, 14.2, 13.2$ . IR (KBr): 2989, 1766, 1716, 1551, 1523, 1468, 1413, 1378, 1312, 1245, 1148, 1061, 915, 841, 787, 748, 663  $\text{cm}^{-1}$ . HRMS-ESI ( $m/z$ ): calcd for  $\text{C}_{14}\text{H}_{19}\text{INO}_2$  [ $\text{M} + \text{H}$ ] $^+$ : 360.0455; found: 360.0446.

**(*E*)-2-Iodo-1-(3-methoxyphenyl)vinyl diethylcarbamate ((*E*)-3ka)**



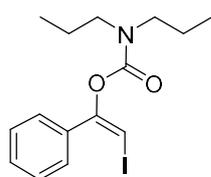
Pale yellow oil ( $E/Z = 82:18$ , 24.4 mg, 65%). Spectroscopic data for *E*-isomer:  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.32 - 7.26$  (m, 1 H), 7.21 - 7.15 (m, 2 H), 6.93 - 6.87 (m, 1 H), 6.32 (s, 1 H), 3.82 (s, 3 H), 3.36 (q,  $J = 7.1$  Hz, 2 H), 3.27 (q,  $J = 7.2$  Hz, 2 H), 1.20 (t,  $J = 7.2$  Hz, 3 H), 1.11 (t,  $J = 6.8$  Hz, 3 H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 159.1, 153.0, 151.4, 136.1, 129.1, 121.1, 115.2, 114.3, 66.2, 55.3, 42.2, 41.8, 14.3, 13.2$ . IR (KBr): 3068, 2991, 2922, 2835, 1922, 1840, 1767, 1708, 1573, 1469, 1382, 1245, 1147, 1055, 923, 849, 754, 666  $\text{cm}^{-1}$ . HRMS-ESI ( $m/z$ ): calcd for  $\text{C}_{14}\text{H}_{19}\text{INO}_3$  [ $\text{M} + \text{H}$ ] $^+$ : 376.0404; found: 376.0399.

**(*E*)-2-Iodo-1-phenylvinyl dimethylcarbamate ((*E*)-3ab)**



Pale yellow oil ( $E/Z = 84:16$ , 19.7 mg, 62%). Spectroscopic data for *E*-isomer:  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.69 - 7.55$  (m, 2 H), 7.43 - 7.32 (m, 3 H), 6.32 (s, 1 H), 3.02 (s, 3 H), 2.89 (s, 3 H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 153.7, 151.6, 134.8, 129.2, 128.8, 128.0, 66.3, 36.6, 36.3$ . IR (KBr): 3065, 2997, 2902, 2832, 1765, 1716, 1517, 1384, 1246, 1152, 1057, 981, 916, 858, 753, 688  $\text{cm}^{-1}$ . HRMS-ESI ( $m/z$ ): calcd for  $\text{C}_{11}\text{H}_{13}\text{INO}_2$  [ $\text{M} + \text{H}$ ] $^+$ : 317.9985; found: 317.9979.

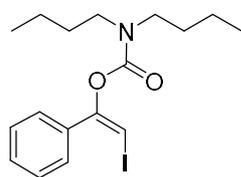
**(*E*)-2-Iodo-1-phenylvinyl dipropylcarbamate ((*E*)-3ac)**



Pale yellow oil ( $E/Z = 82:18$ , 23.9 mg, 64%). Spectroscopic data for *E*-isomer:  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.63 - 7.57$  (m, 2 H), 7.41 - 7.32 (m, 3 H), 6.30 (s, 1 H), 3.26 (t,  $J = 7.4$  Hz, 2 H), 3.16 (t,  $J = 7.6$  Hz, 2 H), 1.68 - 1.58 (m, 2 H), 1.57 - 1.45 (m, 2 H), 0.92 (t,  $J = 7.4$  Hz, 3 H), 0.83 (t,  $J = 7.4$  Hz, 3 H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 153.5, 151.7, 134.9, 129.1, 128.8, 128.0, 66.1, 49.4, 49.1, 22.0, 21.0, 11.2, 11.1$ . IR (KBr): 3067, 2964, 2931, 2875, 1721, 1631, 1462, 1417,

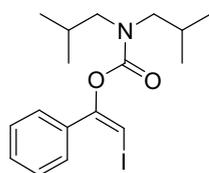
1377, 1238, 1150, 1073, 910, 857, 750, 694  $\text{cm}^{-1}$ . HRMS-ESI ( $m/z$ ): calcd for  $\text{C}_{15}\text{H}_{21}\text{INO}_2$  [ $\text{M} + \text{H}$ ] $^+$ : 374.0611; found: 374.0602.

**(E)-2-Iodo-1-phenylvinyl dibutylcarbamate ((E)-3ad)**



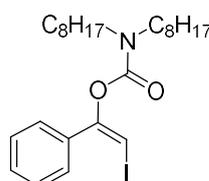
Pale yellow oil ( $E/Z = 81:19$ , 27.7 mg, 69%). Spectroscopic data for *E*-isomer:  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.60$  (d,  $J = 7.2$  Hz, 2 H), 7.42 – 7.32 (m, 3 H), 6.30 (s, 1 H), 3.28 (t,  $J = 7.6$  Hz, 2 H), 3.18 (t,  $J = 7.6$  Hz, 2 H), 1.60 – 1.52 (m, 2 H), 1.52 – 1.43 (m, 2 H), 1.38 – 1.30 (m, 2 H), 1.28 – 1.20 (m, 2 H), 0.95 (t,  $J = 7.2$  Hz, 3 H), 0.88 (t,  $J = 7.4$  Hz, 3 H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 153.5$ , 151.7, 135.0, 129.2, 128.8, 128.0, 66.2, 47.5, 47.2, 30.9, 29.9, 20.0, 19.9, 13.8, 13.8. IR (KBr): 3124, 3000, 2953, 1921, 1838, 1767, 1719, 1548, 1465, 1411, 1381, 1243, 1149, 1066, 976, 916, 865, 761, 664  $\text{cm}^{-1}$ . HRMS-ESI ( $m/z$ ): calcd for  $\text{C}_{17}\text{H}_{25}\text{INO}_2$  [ $\text{M} + \text{H}$ ] $^+$ : 402.0924; found: 402.0918.

**(E)-2-Iodo-1-phenylvinyl diisobutylcarbamate ((E)-3ae)**



Pale yellow oil ( $E/Z = 78:22$ , 27.3 mg, 68%). Spectroscopic data for *E*-isomer:  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.63 - 7.57$  (m, 2 H), 7.41 – 7.32 (m, 3 H), 6.29 (s, 1 H), 3.15 (d,  $J = 7.6$  Hz, 2 H), 3.05 (d,  $J = 7.6$  Hz, 2 H), 2.07 – 1.87 (m, 2 H), 0.92 (d,  $J = 6.4$  Hz, 6 H), 0.82 (d,  $J = 6.8$  Hz, 6 H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 154.0$ , 151.8, 134.9, 129.1, 128.8, 128.0, 66.0, 55.1, 55.0, 27.4, 26.6, 20.1, 19.9. IR (KBr): 3067, 2960, 2876, 1766, 1721, 1463, 1416, 1380, 1242, 1151, 1071, 1011, 915, 857, 749, 694  $\text{cm}^{-1}$ . HRMS-ESI ( $m/z$ ): calcd for  $\text{C}_{17}\text{H}_{25}\text{INO}_2$  [ $\text{M} + \text{H}$ ] $^+$ : 402.0924; found: 402.0917.

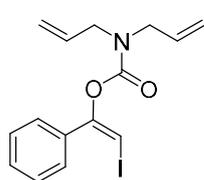
**(E)-2-Iodo-1-phenylvinyl dioctylcarbamate ((E)-3af)**



Pale yellow oil ( $E/Z = 72:28$ , 33.3 mg, 65%). Spectroscopic data for *E*-isomer:  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.60$  (d,  $J = 6.8$  Hz, 2 H), 7.41 – 7.32 (m, 3 H), 6.30 (s, 1 H), 3.27 (t,  $J = 7.4$  Hz, 2 H), 3.17 (t,  $J = 7.6$  Hz, 2 H), 1.61 – 1.53 (m, 2 H), 1.53 – 1.45 (m, 2 H), 1.34 – 1.26 (m, 12 H), 1.25 – 1.18 (m, 8 H), 0.92 – 0.84 (m, 6 H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 153.4$ , 151.7, 135.0, 129.2, 128.8, 128.0, 66.2, 47.7, 47.4, 31.8, 31.7, 29.3, 29.3, 29.2, 29.2, 28.8, 27.8, 26.8, 26.7, 22.6, 22.6, 14.1. IR (KBr): 2992, 2927, 2854, 1762, 1729, 1553, 1464, 1378, 1243, 1151, 1056, 916, 855, 743, 656

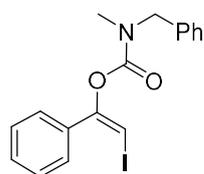
cm<sup>-1</sup>. HRMS-ESI (*m/z*): calcd for C<sub>25</sub>H<sub>41</sub>INO<sub>2</sub> [M + H]<sup>+</sup>: 514.2176; found: 514.2168.

**(*E*)-2-Iodo-1-phenylvinyl diallylcarbamate ((*E*)-3ah)**



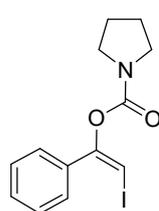
Pale yellow oil (*E/Z* = 75:25, 26.9 mg, 73%). Spectroscopic data for *E*-isomer: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.67 – 7.54 (m, 2 H), 7.44 – 7.31 (m, 3 H), 6.33 (s, 1 H), 5.88 – 5.67 (m, 2 H), 5.26 – 5.07 (m, 4 H), 3.94 (d, *J* = 5.6 Hz), 3.85 (d, *J* = 5.6 Hz). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 153.4, 151.5, 134.6, 133.0, 132.7, 129.3, 128.9, 128.0, 117.8, 117.0, 66.5, 49.4, 48.8. IR (KBr): 3070, 2966, 1766, 1718, 1549, 1458, 1402, 1239, 1149, 1067, 916, 857, 749, 688 cm<sup>-1</sup>. HRMS-ESI (*m/z*): calcd for C<sub>15</sub>H<sub>17</sub>INO<sub>2</sub> [M + H]<sup>+</sup>: 370.0298; found: 370.0292.

**(*E*)-2-Iodo-1-phenylvinyl benzyl(methyl)carbamate ((*E*)-3ak)**



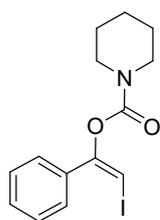
Pale yellow oil (*E/Z* = 80:20, 22.8 mg, 58%). Spectroscopic data for *E*-isomer: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.70 – 7.62 (m, 1 H), 7.59 – 7.53 (m, 1 H), 7.45 – 7.28 (m, 6 H), 7.25 – 7.14 (m, 2 H), 6.40 (s, 0.5 H), 6.35 (s, 1 H), 4.58 (s, 1 H), 4.44 (s, 1 H), 2.96 (s, 1.5 H), 2.90 (s, 1.5 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 154.5, 153.6, 151.5, 136.8, 136.7, 134.7, 134.6, 129.3, 128.9, 128.8, 128.7, 128.6, 128.1, 128.0, 127.9, 127.6, 127.1, 66.6, 66.3, 52.8, 52.7, 34.8, 34.0. IR (KBr): 3069, 2987, 2928, 2853, 1731, 1632, 1454, 1390, 1243, 1121, 1056, 996, 915, 862, 741, 696 cm<sup>-1</sup>. HRMS-ESI (*m/z*): calcd for C<sub>17</sub>H<sub>17</sub>INO<sub>2</sub> [M + H]<sup>+</sup>: 394.0298; found: 394.0292.

**(*E*)-2-Iodo-1-phenylvinyl pyrrolidine-1-carboxylate ((*E*)-3ao)**



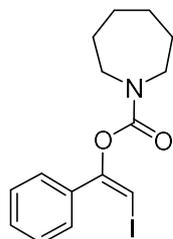
Pale yellow oil (*E/Z* = 83:17, 16.5 mg, 48%). Spectroscopic data for *E*-isomer: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.62 (d, *J* = 7.2 Hz, 2 H), 7.45 – 7.31 (m, 3 H), 6.34 (s, 1 H), 3.48 (t, *J* = 6.6 Hz, 2 H), 3.36 (t, *J* = 6.6 Hz, 2 H), 1.98 – 1.80 (m, 4 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 152.0, 151.5, 135.0, 129.2, 128.9, 128.0, 66.3, 46.4, 46.3, 25.8, 24.8. IR (KBr): 3121, 2996, 2889, 2834, 1768, 1709, 1546, 1391, 1243, 1155, 1067, 914, 859, 787, 748, 672 cm<sup>-1</sup>. HRMS-ESI (*m/z*): calcd for C<sub>13</sub>H<sub>15</sub>INO<sub>2</sub> [M + H]<sup>+</sup>: 344.0142; found: 344.0135.

**(E)-2-Iodo-1-phenylvinyl piperidine-1-carboxylate ((E)-3ap)**



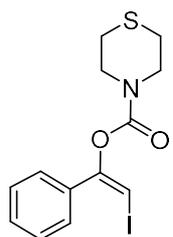
Pale yellow oil (*E/Z* = 85:15, 22.5 mg, 63%). Spectroscopic data for *E*-isomer:  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.69 – 7.58 (m, 2 H), 7.43 – 7.32 (m, 3 H), 6.31 (s, 1 H), 3.53 (s, 2 H), 3.38 (s, 2 H), 1.64 – 1.48 (m, 6 H).  $^{13}\text{C}$  NMR (100MHz,  $\text{CDCl}_3$ ):  $\delta$  = 152.5, 151.6, 134.8, 129.2, 128.8, 128.0, 66.0, 45.5, 45.0, 25.9, 25.4, 24.1. IR (KBr): 3065, 3004, 2931, 2854, 1769, 1712, 1629, 1558, 1420, 1232, 1141, 1068, 1019, 961, 911, 851, 749, 689  $\text{cm}^{-1}$ . HRMS-ESI (*m/z*): calcd for  $\text{C}_{14}\text{H}_{17}\text{INO}_2$  [ $\text{M} + \text{H}$ ] $^+$ : 358.0298; found: 358.0289.

**(E)-2-Iodo-1-phenylvinyl azepane-1-carboxylate ((E)-3aq)**



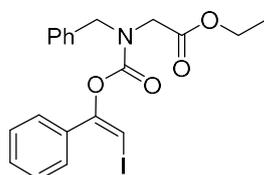
Pale yellow oil (*E/Z* = 83:17, 20.8 mg, 56%). Spectroscopic data for *E*-isomer:  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.62 (d,  $J$  = 6.8 Hz, 2 H), 7.48 – 7.32 (m, 3 H), 6.31 (s, 1 H), 3.50 (t,  $J$  = 6.0 Hz, 2 H), 3.39 (t,  $J$  = 6.2 Hz, 2 H), 1.77 – 1.71 (m, 2 H), 1.70 – 1.63 (m, 2 H), 1.61 – 1.50 (m, 4 H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 153.4, 151.7, 134.9, 129.2, 128.8, 128.0, 66.2, 47.4, 47.2, 28.6, 27.9, 27.2, 26.8. IR (KBr): 3122, 2997, 2921, 2844, 1769, 1709, 1544, 1468, 1404, 1248, 1158, 1064, 1001, 915, 849, 750, 683  $\text{cm}^{-1}$ . HRMS-ESI (*m/z*): calcd for  $\text{C}_{15}\text{H}_{19}\text{INO}_2$  [ $\text{M} + \text{H}$ ] $^+$ : 372.0455; found: 372.0448.

**(E)-2-Iodo-1-phenylvinyl thiomorpholine-4-carboxylate ((E)-3ar)**



Pale yellow oil (*E/Z* = 86:14, 23.3 mg, 62%). Spectroscopic data for *E*-isomer:  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.66 – 7.56 (m, 2 H), 7.47 – 7.32 (m, 3 H), 6.34 (s, 1 H), 3.85 (s, 2 H), 3.71 (s, 2 H), 2.62 (br, 4H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 152.3, 151.3, 134.5, 129.4, 128.7, 128.2, 66.6, 47.2, 47.5, 27.5, 27.1. IR (KBr): 2996, 2902, 2840, 1766, 1706, 1551, 1389, 1289, 1243, 1190, 1147, 1065, 950, 915, 845, 784, 746, 680  $\text{cm}^{-1}$ . HRMS-ESI (*m/z*): calcd for  $\text{C}_{13}\text{H}_{15}\text{INO}_2\text{S}$  [ $\text{M} + \text{H}$ ] $^+$ : 375.9863; found: 375.9855.

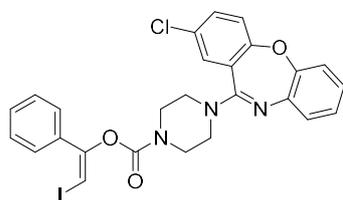
**Ethyl (E)-N-benzyl-N-(((2-iodo-1-phenylvinyl)oxy)carbonyl)glycinate ((E)-3ay)**



Pale yellow oil (*E/Z* = 80:20, 28.4 mg, 61%). Spectroscopic data for *E*-isomer:  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.67 – 7.61 (m, 1 H), 7.60 –

7.53 (m, 1 H), 7.44 – 7.35 (m, 4 H), 7.34 – 7.28 (m, 2 H), 7.25 – 7.19 (m, 2 H), 6.40 (d,  $J = 7.6$  Hz, 1 H), 4.68 (s, 1 H), 4.54 (s, 1 H), 4.15 (p,  $J = 7.1$  Hz, 2 H), 3.94 (d,  $J = 9.6$  Hz, 2 H), 1.22 (q,  $J = 7.5$  Hz, 3 H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 169.0, 168.9, 154.0, 153.8, 151.1, 151.1, 136.2, 136.0, 134.4, 134.3, 129.4, 129.4, 128.9, 128.9, 128.8, 128.7, 128.3, 128.1, 127.9, 127.8, 127.5, 67.0, 66.8, 61.4, 61.3, 51.8, 51.7, 48.2, 47.8, 14.1, 14.1$ . IR (KBr): 3121, 2995, 2896, 2826, 1758, 1711, 1548, 1450, 1390, 1240, 1156, 1096, 1058, 964, 916, 747, 681  $\text{cm}^{-1}$ . HRMS-ESI ( $m/z$ ): calcd for  $\text{C}_{20}\text{H}_{21}\text{INO}_4$  [ $\text{M} + \text{H}$ ] $^+$ : 466.0510; found: 466.0500.

**(*E*)-2-Iodo-1-phenylvinyl 4-(2-chlorodibenzo[*b,f*][1,4]oxazepin-11-yl)piperazine-1-carboxylate ((*E*)-3aca)**



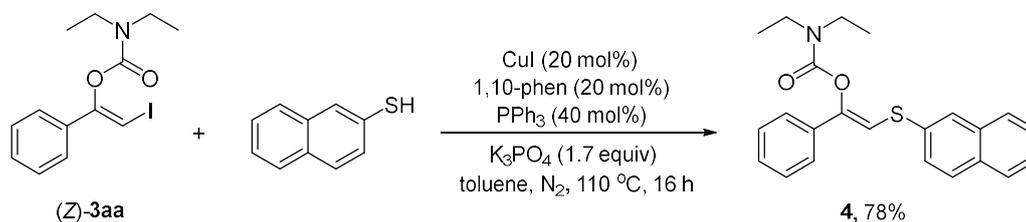
Pale yellow solid ( $E/Z = 78:22$ , 31.0 mg, 53%). mp: 185 – 186 °C.

Spectroscopic data for *E*-isomer:  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.67 - 7.58$  (m, 2 H), 7.44 – 7.36 (m, 4 H), 7.31 (d,  $J = 2.8$  Hz, 1 H), 7.22 – 7.15 (m, 2 H), 7.13 – 7.08 (m, 2 H), 7.06 – 6.99 (m,

1 H), 6.38 (s, 1 H), 3.80 – 3.45 (m, 8 H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 159.3, 158.7, 152.5, 151.7, 151.2, 134.5, 132.9, 130.4, 129.4, 128.8, 128.7, 128.2, 127.1, 125.8, 125.1, 124.7, 122.8, 120.1, 66.6, 47.3, 44.2, 43.6$ . IR (KBr): 3066, 2997, 2922, 2852, 1722, 1596, 1465, 1410, 1292, 1232, 1150, 1074, 1013, 913, 841, 783, 746, 688  $\text{cm}^{-1}$ . HRMS-ESI ( $m/z$ ): calcd for  $\text{C}_{26}\text{H}_{22}\text{ClIN}_3\text{O}_3$  [ $\text{M} + \text{H}$ ] $^+$ : 586.0389; found: 586.0380.

**D. Procedure for the synthesis of compound 4-12**

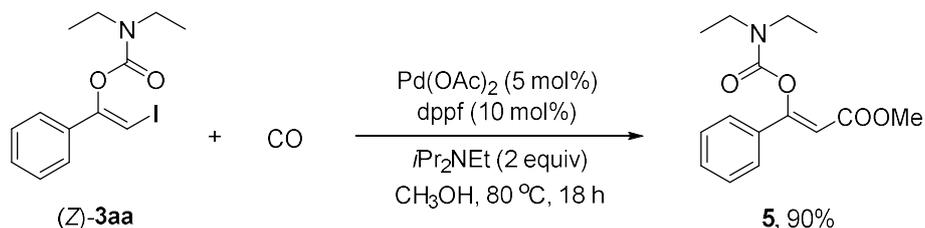
**Procedure for the synthesis of compound 4:**



To a solution of (*Z*)-2-iodo-1-phenylvinyl diethylcarbamate ((*Z*)-3aa, 0.2 mmol) in toluene (2 ml) was added the mixture of naphthalene-2-thiol (0.38 mmol), copper(I) iodide (0.04 mmol), 1,10-phenanthroline (0.04 mmol), triphenylphosphine (0.08 mmol) and tripotassium phosphate (0.34 mmol) successively. The resulting mixture was stirred at 110 °C for 16 h under an

atmosphere of N<sub>2</sub>. After the reaction was completed, the reaction mixture was cooled to room temperature, washed with water and then extracted with ethyl acetate (10 mL×3). The combined organic phase was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and then filtered. After removing the solvent under vacuum, the crude product was purified by column chromatography on silica gel using petroleum ether/ethyl acetate (20:1) as the eluent to give the desired product (*Z*)-2-(naphthalen-2-ylthio)-1-phenylvinyl diethylcarbamate (**4**) as brown oil (58.8 mg, 78%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ = 7.90 (s, 1 H), 7.77 (q, *J* = 7.7 Hz, 3 H), 7.53 (d, *J* = 8.5 Hz, 1 H), 7.49 – 7.41 (m, 4 H), 7.34 (t, *J* = 7.5 Hz, 2 H), 7.30 – 7.22 (m, 1 H), 6.68 (s, 1 H), 3.52 (q, *J* = 7.0 Hz, 2 H), 3.39 (q, *J* = 7.0 Hz, 2 H), 1.34 (t, *J* = 7.0 Hz, 3 H), 1.19 (t, *J* = 7.3 Hz, 3 H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ = 152.7, 147.0, 134.8, 133.7, 132.6, 132.1, 128.7, 128.5, 128.2, 128.1, 127.7, 127.5, 127.3, 126.7, 126.0, 124.3, 113.0, 42.3, 14.4, 13.3. IR (KBr): 3055, 2985, 2927, 1765, 1718, 1502, 1420, 1376, 1310, 1244, 1150, 1057, 914, 808, 744, 638 cm<sup>-1</sup>. HRMS-ESI (*m/z*): calcd for C<sub>23</sub>H<sub>24</sub>NO<sub>2</sub>S [M + H]<sup>+</sup>: 378.1522; found: 378.1520.

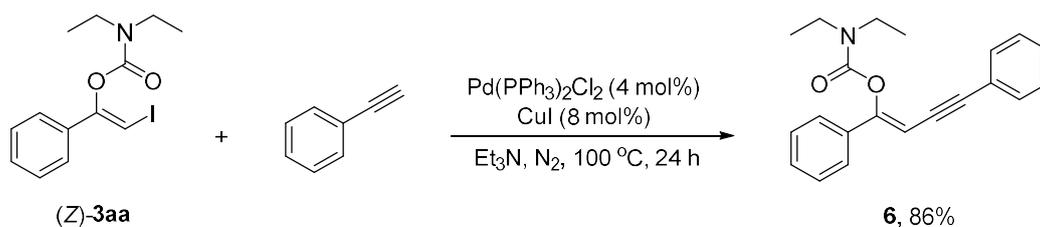
#### Procedure for the synthesis of compound **5**:



To a solution of (*Z*)-2-iodo-1-phenylvinyl diethylcarbamate ((*Z*)-**3aa**, 0.2 mmol) in methanol (2 ml) was added the mixture of palladium acetate (0.01 mmol), 1,1'-ferrocenediyl-bis(diphenylphosphine) (dpfp) (0.02 mmol) and *N,N*-diisopropylethylamine (0.4 mmol) successively. The tube was then evacuated, refilled with CO (1 atm) three times. The resulting mixture was stirred at 80 °C for 18 h. After the reaction was completed, the reaction mixture was cooled to room temperature, diluted with ethyl acetate (10 mL) and filtrated through a small pad of silica gel. The solvent was removed under reduced pressure and the crude product was purified by column chromatography on silica gel using petroleum ether/ethyl acetate (20:1) as the eluent to give the desired product methyl (*Z*)-3-((diethylcarbamoyl)oxy)-3-phenylacrylate (**5**) as pale yellow oil (49.9 mg, 90%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ = 7.61 – 7.55 (m, 2 H), 7.43 – 7.35 (m, 3 H), 6.22 (s, 1 H), 3.72 (s, 3 H), 3.51 (q, *J* = 7.2 Hz, 2 H), 3.38 (q, *J* = 7.2 Hz, 2 H), 1.31

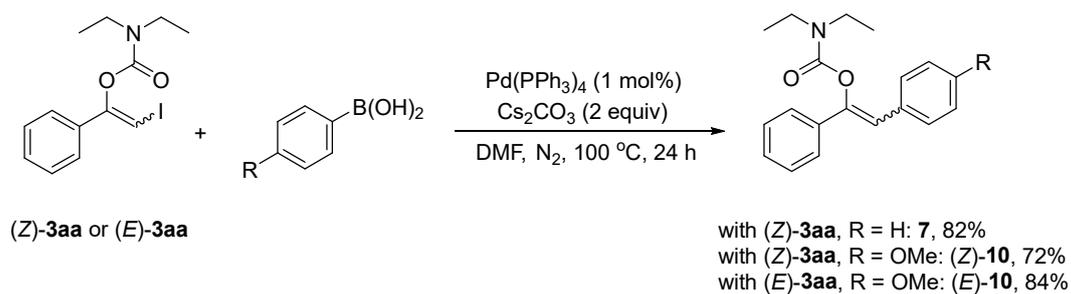
(t,  $J = 7.0$  Hz, 3 H), 1.21 (t,  $J = 7.0$  Hz, 3 H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta = 164.6, 158.4, 152.5, 134.4, 130.5, 128.6, 125.9, 106.0, 51.2, 42.3, 42.0, 14.1, 13.2$ . IR (KBr): 2993, 2895, 2828, 1835, 1767, 1712, 1641, 1518, 1382, 1244, 1154, 1056, 993, 915, 749, 661  $\text{cm}^{-1}$ . HRMS-ESI ( $m/z$ ): calcd for  $\text{C}_{15}\text{H}_{20}\text{NO}_4$  [ $\text{M} + \text{H}$ ] $^+$ : 278.1387; found: 278.1385.

### Procedure for the synthesis of compound 6:



To a solution of (*Z*)-2-iodo-1-phenylvinyl diethylcarbamate ((*Z*)-**3aa**, 0.2 mmol) in triethylamine (2 ml) was added the mixture of phenylacetylene (0.24 mmol), bis(triphenylphosphine)palladium(II) chloride (0.008 mmol) and copper(I) iodide (0.016 mmol) successively. The resulting mixture was stirred at 100 °C for 24 h under an atmosphere of  $\text{N}_2$ . After the reaction was completed, the reaction mixture was cooled to room temperature, diluted with ethyl acetate (10 mL) and filtrated through a small pad of silica gel. The solvent was removed under reduced pressure and the crude product was purified by column chromatography on silica gel using petroleum ether/ethyl acetate (20:1) as the eluent to give the desired product (*Z*)-1,4-diphenylbut-1-en-3-yn-1-yl diethylcarbamate (**6**) as brown oil (54.9 mg, 86%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.55 - 7.50$  (m, 2 H), 7.46 – 7.41 (m, 2 H), 7.40 – 7.34 (m, 3 H), 7.34 – 7.29 (m, 3 H), 6.15 (s, 1 H), 3.56 (q,  $J = 7.1$  Hz, 2 H), 3.41 (q,  $J = 7.2$  Hz, 2 H), 1.35 (t,  $J = 7.2$  Hz, 3 H), 1.18 (t,  $J = 7.2$  Hz, 3 H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 156.3, 152.8, 134.5, 131.4, 129.3, 128.6, 128.2, 128.1, 124.6, 123.5, 97.5, 96.2, 84.6, 42.3, 42.1, 14.3, 13.4$ . IR (KBr): 3056, 2975, 2928, 1721, 1585, 1476, 1422, 1377, 1311, 1247, 1149, 1067, 996, 917, 836, 751, 687  $\text{cm}^{-1}$ . HRMS-ESI ( $m/z$ ): calcd for  $\text{C}_{21}\text{H}_{22}\text{NO}_2$  [ $\text{M} + \text{H}$ ] $^+$ : 320.1645; found: 320.1644.

## Procedure for the synthesis of compound 7 and 10:



To a solution of 2-iodo-1-phenylvinyl diethylcarbamate (**3aa**, 0.2 mmol) in *N,N*-dimethylformamide (2 ml) was added the mixture of arylboronic acid (0.4 mmol), tetrakis(triphenylphosphine)palladium (0.002 mmol) and cesium carbonate (0.4 mmol) successively. The resulting mixture was stirred at 100 °C for 24 h under an atmosphere of N<sub>2</sub>. After the reaction was completed, the reaction mixture was cooled to room temperature, washed with water and then extracted with ethyl acetate (10 mL×3). The combined organic phase was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and then filtered. After removing the solvent under vacuum, the crude product was purified by column chromatography on silica gel using petroleum ether/ethyl acetate (20:1) as the eluent to give the desired product **7** or **10**.

### (Z)-1,2-Diphenylvinyl diethylcarbamate (**7**)

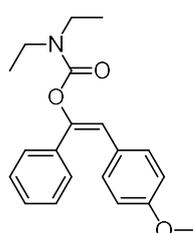
Pale yellow solid (48.4 mg, 82%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.61 – 7.52 (m, 4 H), 7.43 – 7.32 (m, 5 H), 7.30 – 7.24 (m, 1 H), 6.70 (s, 1 H), 3.59 (q, *J* = 7.1 Hz, 2 H), 3.38 (q, *J* = 7.1 Hz, 2 H), 1.34 (t, *J* = 7.2 Hz, 3 H), 1.18 (t, *J* = 7.2 Hz, 3 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 153.1, 147.0, 136.6, 134.7, 128.7, 128.5, 128.3, 127.3, 124.8, 116.7, 41.9, 41.7, 14.4, 13.2. IR (KBr): 2981, 2924, 2847, 1766, 1711, 1560, 1462, 1417, 1378, 1310, 1248, 1150, 1101, 1056, 1009, 959, 915, 859, 750, 687 cm<sup>-1</sup>. HRMS-ESI (*m/z*): calcd for C<sub>19</sub>H<sub>22</sub>NO<sub>2</sub> [M + H]<sup>+</sup>: 296.1645; found: 296.1641.

### (Z)-2-(4-Methoxyphenyl)-1-phenylvinyl diethylcarbamate ((Z)-**10**)

Pale yellow oil (46.8 mg, 72%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.56 – 7.51 (m, 2 H), 7.49 – 7.44 (m, 2 H), 7.40 – 7.35 (m, 2 H), 7.32 – 7.26 (m, 1 H), 6.92 – 6.86 (m, 2 H), 6.63 (s, 1 H), 3.82 (s, 3 H), 3.58 (q, *J* = 7.1 Hz, 2 H), 3.37 (q, *J* = 7.1 Hz, 2 H), 1.33 (t, *J* = 7.2 Hz, 3 H), 1.17 (t, *J* = 7.2 Hz, 3 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 158.8, 153.1, 145.4, 136.7, 129.9, 128.4, 127.9,

127.3, 124.5, 116.3, 113.7, 55.1, 41.9, 41.6, 14.4, 13.2. IR (KBr): 2981, 2838, 1714, 1599, 1508, 1421, 1375, 1307, 1247, 1149, 1050, 19, 821, 748, 690, 635  $\text{cm}^{-1}$ . HRMS-ESI ( $m/z$ ): calcd for  $\text{C}_{20}\text{H}_{24}\text{NO}_3$  [ $\text{M} + \text{H}$ ] $^+$ : 326.1751; found: 326.1749.

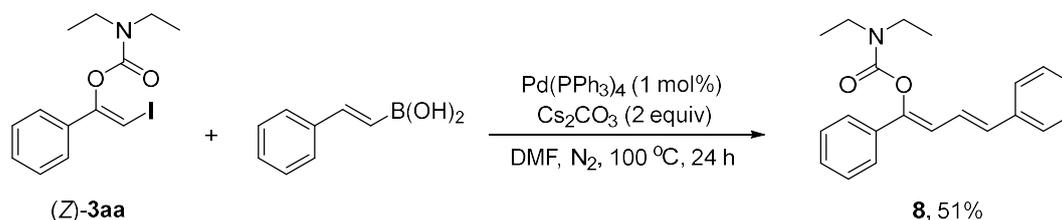
**(E)-2-(4-Methoxyphenyl)-1-phenylvinyl diethylcarbamate ((E)-10)**



Pale yellow oil (54.6 mg, 84%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.42 – 7.37 (m, 2 H), 7.31 – 7.26 (m, 3 H), 7.07 – 7.02 (m, 2 H), 6.73 – 6.68 (m, 2 H), 6.43 (s, 1 H), 3.75 (s, 3 H), 3.41 (q,  $J$  = 7.3 Hz, 2 H), 3.30 (q,  $J$  = 7.2 Hz, 2 H), 1.24 (t,  $J$  = 6.0 Hz, 3 H), 1.13 (t,  $J$  = 6.8 Hz, 3 H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 158.5, 154.2, 146.7, 135.4, 130.1, 128.8, 128.4, 128.3, 127.1,

119.0, 113.5, 55.1, 41.9, 41.7, 14.3, 13.3. IR (KBr): 2983, 2837, 1765, 1713, 1604, 1510, 1465, 1419, 1372, 1245, 1156, 1062, 951, 879, 833, 756, 696  $\text{cm}^{-1}$ . HRMS-ESI ( $m/z$ ): calcd for  $\text{C}_{20}\text{H}_{24}\text{NO}_3$  [ $\text{M} + \text{H}$ ] $^+$ : 326.1751; found: 326.1749.

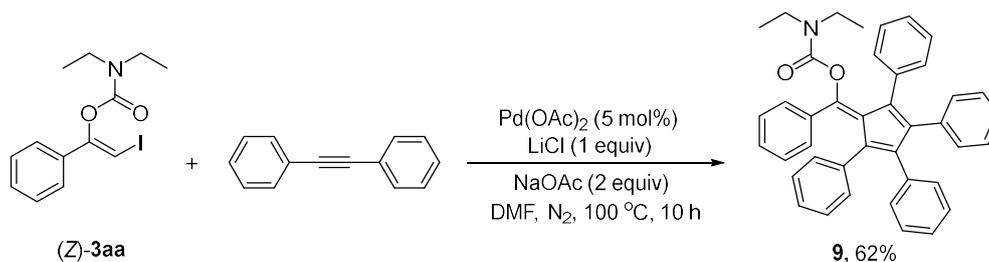
**Procedure for the synthesis of compound 8:**



To a solution of (*Z*)-2-iodo-1-phenylvinyl diethylcarbamate ((*Z*)-**3aa**, 0.2 mmol) in *N,N*-dimethylformamide (2 ml) was added the mixture of (*E*)-styrylboronic acid (0.4 mmol), tetrakis(triphenylphosphine)platinum (0.002 mmol), cesium carbonate (0.4 mmol) successively. The resulting mixture was stirred at 100 °C for 24 h under an atmosphere of  $\text{N}_2$ . After the reaction was completed, the reaction mixture was cooled to room temperature, washed with water and then extracted with ethyl acetate (10 mL $\times$ 3). The combined organic phase was dried over anhydrous  $\text{Na}_2\text{SO}_4$ , and then filtered. After removing the solvent under vacuum, the crude product was purified by column chromatography on silica gel using petroleum ether/ethyl acetate (20:1) as the eluent to give the desired product (1*Z*,3*E*)-1,4-diphenylbuta-1,3-dien-1-yl diethylcarbamate (**8**) as brown oil (32.7 mg, 51%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.53 (d,  $J$  = 7.6 Hz, 2 H), 7.45 (d,  $J$  = 7.6 Hz, 2 H), 7.41 – 7.33 (m, 4 H), 7.32 – 7.24 (m, 2 H), 7.03 (dd,  $J$  = 15.6, 10.8 Hz, 1 H), 6.75 (d,

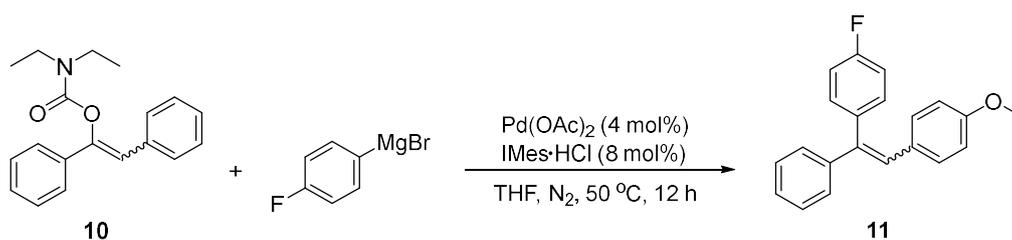
$J = 16.0$  Hz, 1 H), 6.65 (d,  $J = 11.2$  Hz, 1 H), 3.63 (q,  $J = 7.1$  Hz, 2 H), 3.44 (q,  $J = 7.2$  Hz, 2 H), 1.42 (t,  $J = 7.2$  Hz, 3 H), 1.25 (t,  $J = 7.2$  Hz, 3 H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 153.5, 147.0, 137.4, 135.5, 133.5, 128.6, 128.5, 128.3, 127.7, 126.5, 124.4, 122.4, 117.3, 42.2, 41.9, 14.6, 13.4$ . IR (KBr): 2989, 2924, 1765, 1716, 1556, 1377, 1314, 1244, 1153, 1055, 914, 853, 745, 684  $\text{cm}^{-1}$ . HRMS-ESI ( $m/z$ ): calcd for  $\text{C}_{21}\text{H}_{24}\text{NO}_2$  [ $\text{M} + \text{H}$ ] $^+$ : 322.1802; found: 322.1800.

### Procedure for the synthesis of compound 9:



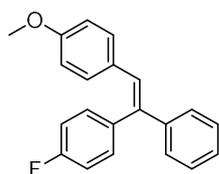
To a solution of (*Z*)-2-iodo-1-phenylvinyl diethylcarbamate ((*Z*)-**3aa**, 0.2 mmol) in *N,N*-dimethylformamide (2 ml) was added the mixture of 1,2-diphenylethyne (0.4 mmol), palladium acetate (0.01 mmol), lithium chloride (0.2 mmol), sodium acetate (0.4 mmol) successively. The resulting mixture was stirred at 100 °C for 10 h under an atmosphere of  $\text{N}_2$ . After the reaction was completed, the reaction mixture was cooled to room temperature, washed with water and then extracted with ethyl acetate (10 mL $\times$ 3). The combined organic phase was dried over anhydrous  $\text{Na}_2\text{SO}_4$ , and then filtered. After removing the solvent under vacuum, the crude product was purified by column chromatography on silica gel using petroleum ether/ethyl acetate (20:1) as the eluent to give the desired product phenyl(2,3,4,5-tetraphenylcyclopenta-2,4-dien-1-ylidene)methyl diethylcarbamate (**9**) as brown solid (71.1 mg, 62%). mp: 180 – 181 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.29 - 7.24$  (m, 2 H), 7.19 – 7.08 (m, 5 H), 7.02 – 6.90 (m, 7 H), 6.86 (t,  $J = 7.6$  Hz, 2 H), 6.79 – 6.70 (m, 7 H), 6.68 (d,  $J = 7.2$  Hz, 2 H), 3.01 (q,  $J = 7.3$  Hz, 2 H), 2.54 (q,  $J = 7.2$  Hz, 2 H), 0.94 (t,  $J = 7.0$  Hz, 3 H), 0.82 (t,  $J = 7.2$  Hz, 3 H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 156.8, 152.0, 144.0, 143.2, 138.7, 136.7, 135.7, 135.4, 135.2, 133.4, 133.2, 133.0, 131.2, 130.6, 130.5, 130.2, 129.2, 127.6, 126.9, 126.9, 126.8, 125.9, 125.9, 125.5, 124.9, 41.9, 41.0, 13.9, 12.9$ . IR (KBr): 3058, 2987, 2925, 2839, 1767, 1725, 1595, 1538, 1486, 1418, 1383, 1247, 1137, 1076, 917, 752, 698, 652  $\text{cm}^{-1}$ . HRMS-ESI ( $m/z$ ): calcd for  $\text{C}_{41}\text{H}_{36}\text{NO}_2$  [ $\text{M} + \text{H}$ ] $^+$ : 574.2741; found: 574.2739.

### Procedure for the synthesis of compound 11:



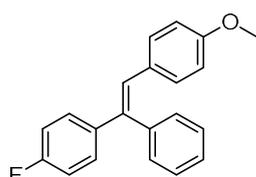
A 10 mL oven-dried Schlenk tube containing a magnetic stirring bar was charged with palladium acetate (0.008 mmol) and 1,3-bis(2,4,6-trimethylphenyl)imidazolium chloride (0.016 mmol). The tube was then evacuated, refilled with N<sub>2</sub> three times, and charged further with 1,2-diphenylvinyl diethylcarbamate (**10**, 0.2 mmol), (4-fluorophenyl)magnesium bromide (0.4 mmol, in THF) and freshly distilled tetrahydrofuran (1 mL) via a syringe. The reaction mixture was stirred at 50 °C for 12 h. After the reaction was completed, the reaction mixture was cooled to room temperature, diluted with H<sub>2</sub>O (20 mL) and extracted with ethyl acetate (15 mL×3). The combined organic layers were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and then filtered. The volatile compounds were removed under vacuum and the crude residue was separated by column chromatography on a silica gel column using petroleum ether as eluent to give the desired product **11**.

#### (*Z*)-1-Fluoro-4-(2-(4-methoxyphenyl)-1-phenylvinyl)benzene (**(Z)-11**)<sup>9</sup>



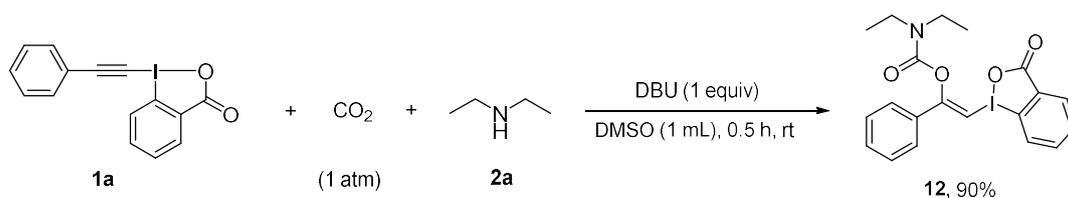
White solid (*Z/E* = 94:6, 45.6 mg, 75%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.36 – 7.28 (m, 5 H), 7.25 – 7.18 (m, 2 H), 7.10 – 7.03 (m, 2 H), 7.02 – 6.96 (m, 2 H), 6.94 (s, 1 H), 6.76 – 6.68 (m, 2 H), 3.79 (s, 3 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 162.1 (d, *J* = 244.7 Hz), 158.5, 143.4, 139.6, 136.5 (d, *J* = 3.6 Hz), 132.1 (d, *J* = 7.8 Hz), 130.8, 129.9, 128.2, 128.0, 127.4, 127.3, 115.7 (d, *J* = 21.2 Hz), 113.5, 55.2. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>): δ = -114.73 – -114.85 (m).

#### (*E*)-1-Fluoro-4-(2-(4-methoxyphenyl)-1-phenylvinyl)benzene (**(E)-11**)<sup>10</sup>



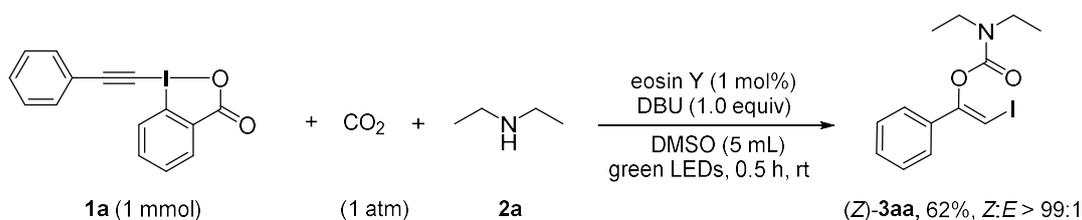
White solid (*Z/E* = 4:96, 48.6 mg, 80%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.29 – 7.24 (m, 3 H), 7.23 – 7.15 (m, 3 H), 7.14 – 7.09 (m, 2 H), 6.93 – 6.85 (m, 4 H), 6.77 (s, 1 H), 6.63 – 6.56 (m, 2H), 3.67 (s, 3 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 162.2 (d, *J* = 245.2 Hz), 158.4, 140.5, 139.7 (d, *J* = 3.2 Hz), 139.6, 130.7, 130.3, 129.9, 129.0, 128.9, 128.8, 127.5 (d, *J* = 1.7 Hz), 127.4, 115.0 (d, *J* = 21.3 Hz), 113.4, 55.1. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>): δ = -115.38 – -115.47 (m).

## Procedure for the synthesis of compound **12**:



To a 10 mL oven-dried Schlenk tube containing a magnetic stirring bar was added ethynylbenziodoxole **1a** (0.1 mmol). The tube was then evacuated, refilled with CO<sub>2</sub> (1 atm) three times, and charged further with diethylamine **2a** (3.0 equiv), 1,8-diazabicyclo[5.4.0]undec-7-ene (1.0 equiv) and dimethyl sulfoxide (1 mL) via a syringe. The reaction mixture was stirred at room temperature for 30 min. After the reaction was completed, the reaction mixture was diluted with H<sub>2</sub>O (20 mL) and extracted with ethyl acetate (15 mL×3). The combined organic layers were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and then filtered. The volatile compounds were removed under vacuum and the obtained solid was recrystallized in EtOAc to afford the vinylbenziodoxolone (*Z*)-2-(3-oxo-1λ<sup>3</sup>-benzo[*d*][1,2]iodaoxol-1(3*H*)-yl)-1-phenylvinyl diethylcarbamate (**12**) as pale yellow solid (41.9 mg, 90%). mp: 169 – 170 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 8.40 (dd, *J* = 6.9, 2.2 Hz, 1H), 7.67 – 7.54 (m, 5 H), 7.51 – 7.40 (m, 3 H), 6.94 (s, 1 H), 3.35 (q, *J* = 7.1 Hz, 2 H), 3.27 (q, *J* = 7.2 Hz, 2 H), 1.13 (t, *J* = 7.2 Hz, 3 H), 1.07 (t, *J* = 7.2 Hz, 3 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 166.7, 161.4, 151.9, 133.6, 133.3, 132.7, 132.5, 131.3, 130.7, 129.1, 126.3, 126.2, 114.7, 90.6, 42.7, 42.2, 14.3, 13.0. IR (KBr): 3058, 2987, 2925, 2839, 1767, 1725, 1595, 1538, 1486, 1418, 1383, 1247, 1137, 1076, 917, 752, 698, 652 cm<sup>-1</sup>. HRMS-ESI (*m/z*): calcd for C<sub>20</sub>H<sub>21</sub>INO<sub>4</sub> [M + H]<sup>+</sup>: 466.0510; found: 466.0506.

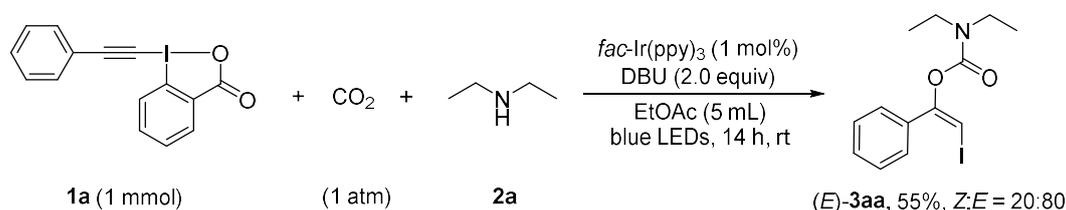
## E. Procedure for the synthesis (*Z*)-**3aa** in a larger scale



A 50 mL oven-dried Schlenk tube containing a magnetic stirring bar was charged with ethynylbenziodoxole **1a** (1 mmol) and eosin Y (0.01 mmol). The tube was then evacuated, refilled with CO<sub>2</sub> (1 atm) three times, and charged further with diethylamine **2a** (3 mmol),

1,8-diazabicyclo[5.4.0]undec-7-ene (1 mmol) and dimethyl sulfoxide (5 mL) via a syringe. The reaction mixture was stirred at room temperature for 0.5 h under 30 W green LEDs irradiation. After the reaction was completed, the reaction mixture was diluted with H<sub>2</sub>O (40 mL) and extracted with ethyl acetate (30 mL×3). The combined organic layers were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and then filtered. The volatile compounds were removed under vacuum and the crude residue was separated by column chromatography on a silica gel column using petroleum ether/ethyl acetate (20:1) as eluent to give the desired product (*Z*)-**3aa** in 62% yield.

## F. Procedure for the synthesis (*E*)-**3aa** in a larger scale



A 50 mL oven-dried Schlenk tube containing a magnetic stirring bar was charged with ethynylbenziodoxole **1a** (1 mmol) and tris(2-phenylpyridine)iridium (0.01 mmol). The tube was then evacuated, refilled with CO<sub>2</sub> (1 atm) three times, and charged further with diethylamine **2a** (3 mmol), 1,8-diazabicyclo[5.4.0]undec-7-ene (2 mmol) and ethyl acetate (5 mL) via a syringe. The reaction mixture was stirred at room temperature for 14 h under 30 W green LEDs irradiation. After the reaction was completed, the reaction mixture was diluted with dichloromethane (20 mL). The solvent was removed under reduced pressure and the crude residue was separated by column chromatography on a silica gel column using petroleum ether/ethyl acetate (20:1) as the eluent to give the desired product (*E*)-**3aa**.

## G. Mechanistic studies

### i. UV-Vis absorption spectra of (Z)-3aa and (E)-3aa

Solutions of (Z)-3aa and (E)-3aa (0.1 M, 0.05 M, 0.01 M, 0.001 M) in 200  $\mu$ L DMSO were recorded in 1 mm path quartz cuvettes using a Shimadzu UV-2600 spectrophotometer.

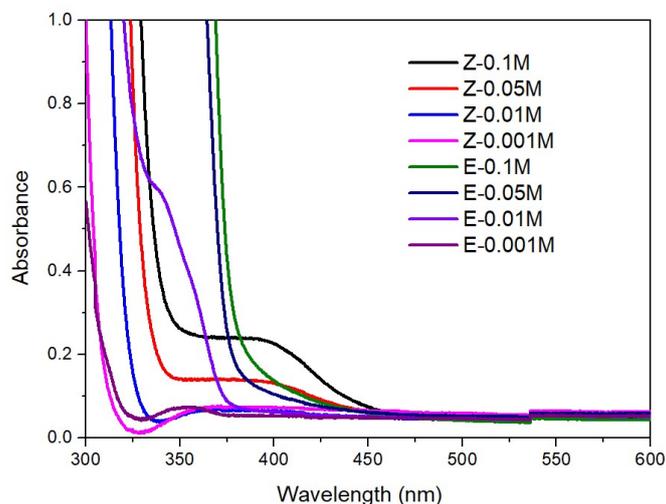
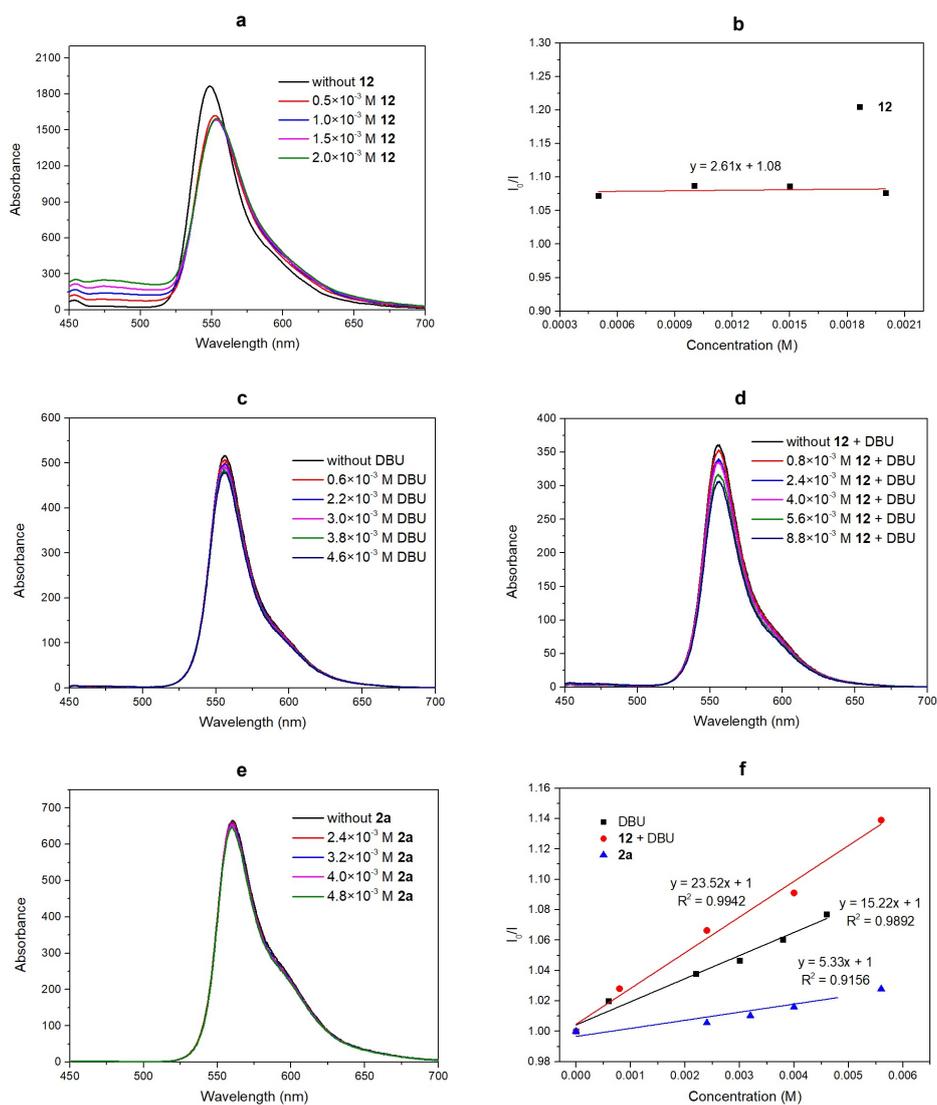


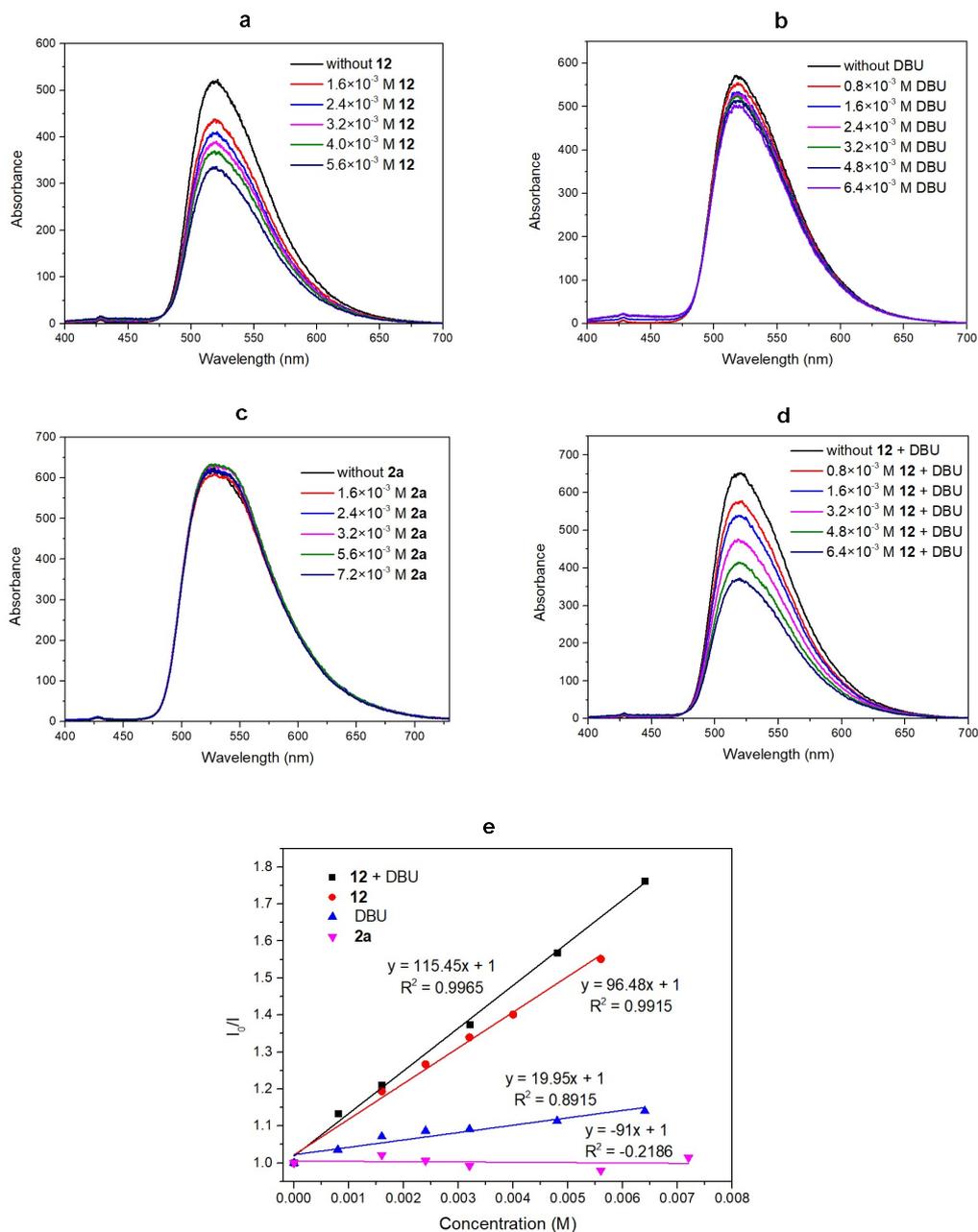
Figure S1. UV-Vis absorption spectra of (Z)-3aa and (E)-3aa.

### ii. Stern-Volmer fluorescence quenching experiments

Fluorescence spectra were collected on Horiba Fluoromax-4 spectrofluorometer. Samples for the quenching experiments were prepared in a 4 mL glass cuvette with a septum screw cap. Eosin Y was irradiated at 400 nm and the emission intensity at 555 nm was observed. *fac*-Ir(ppy)<sub>3</sub> was irradiated at 380 nm and the emission intensity at 518 nm was observed. In a typical experiment, the emission spectrum of a  $5.0 \times 10^{-5}$  M solution of eosin Y or *fac*-Ir(ppy)<sub>3</sub> in DMSO was collected. Then, appropriate amount of quencher was added to the measured solution and the emission spectrum of the sample was collected. Here  $I_0$  and  $I$  represent the intensities of the emission in the absence and presence of the quencher.



**Figure S2.** The emission quenching of eosin Y. a) Steady-state Stern–Volmer experiment of **12**. b) Stern–Volmer fluorescence quenching experiments using eosin Y with **12**. c) Steady-state Stern–Volmer experiment of DBU. d) Steady-state Stern–Volmer experiment of **12** + DBU. e) Steady-state Stern–Volmer experiment of **2a**. f) Stern–Volmer fluorescence quenching experiments using eosin Y with DBU, **12** + DBU and **2a**.



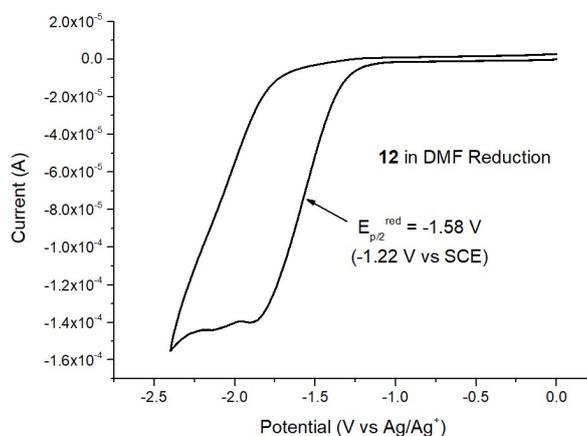
**Figure S3.** The emission quenching of *fac*-Ir(ppy)<sub>3</sub>. a) Steady-state Stern–Volmer experiment of 12. b) Steady-state Stern–Volmer experiment of DBU. c) Steady-state Stern–Volmer experiment of 2a. d) Steady-state Stern–Volmer experiment of 12+DBU. e) Stern–Volmer fluorescence quenching experiments using *fac*-Ir(ppy)<sub>3</sub> with 12, DBU, 2a and 12+DBU.

### iii. Cyclic voltammetry test

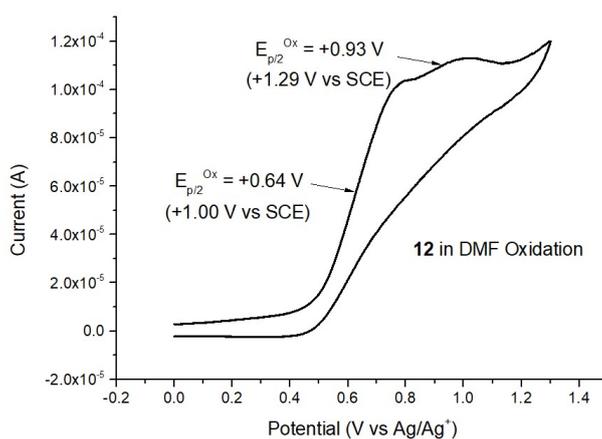
Cyclic voltammetry test was performed in a three-electrode cell under nitrogen at room temperature. All cyclic voltammograms were measured using Ag/Ag<sup>+</sup> (0.01 M AgNO<sub>3</sub> in MeCN) reference electrode, a platinum (Pt) wire counter electrode and a glassy carbon working electrode. The conditions of the experiments were as follows: testing compounds are in solution of 0.1 M

tetrabutylammonium tetrafluoroborate ( $n\text{Bu}_4\text{NBF}_4$ ) in DMF at a scan rate of 100 mV/s; Prior to each measurement, solutions were purged with nitrogen ( $\text{N}_2$ ) for 5 minutes to ensure the oxygen-free conditions.

Measuring the  $\text{Fc}/\text{Fc}^+$  redox couple afforded  $E_{1/2} = +0.06 \text{ V}$  vs  $\text{Ag}/\text{Ag}^+$  under our experimental conditions. The obtained value was referenced to  $\text{Ag}/\text{Ag}^+$  and converted to SCE by adding 0.36 V, providing a value of +0.42 V for the  $\text{Fc}/\text{Fc}^+$  couple.<sup>4</sup> The oxidation and reduction half-peak potential of **12** in DMF was measured as +0.64 V, +0.93 V and  $-1.58 \text{ V}$  (vs  $\text{Ag}/\text{Ag}^+$ ), and calculated to +1.00 V, +1.29 V and  $-1.22 \text{ V}$  (vs SCE), respectively.

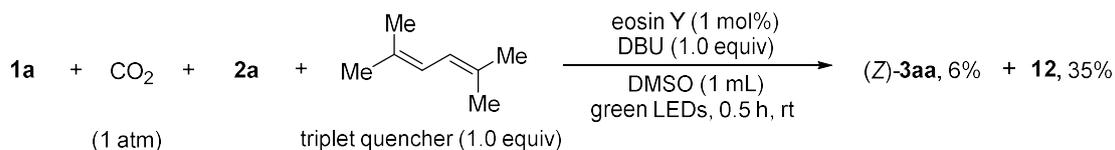


**Figure S4.** Cyclic voltammetry of **12** (0.01 M) in DMF (vs  $\text{Ag}/\text{Ag}^+$ ) with  $n\text{Bu}_4\text{NBF}_4$  (0.1 M) under nitrogen at a glassy carbon electrode at a scan rate of 100 mV/s.



**Figure S5.** Cyclic voltammetry of **12** (0.01 M) in DMF (vs  $\text{Ag}/\text{Ag}^+$ ) with  $n\text{Bu}_4\text{NBF}_4$  (0.1 M) under nitrogen at a glassy carbon electrode at a scan rate of 100 mV/s.

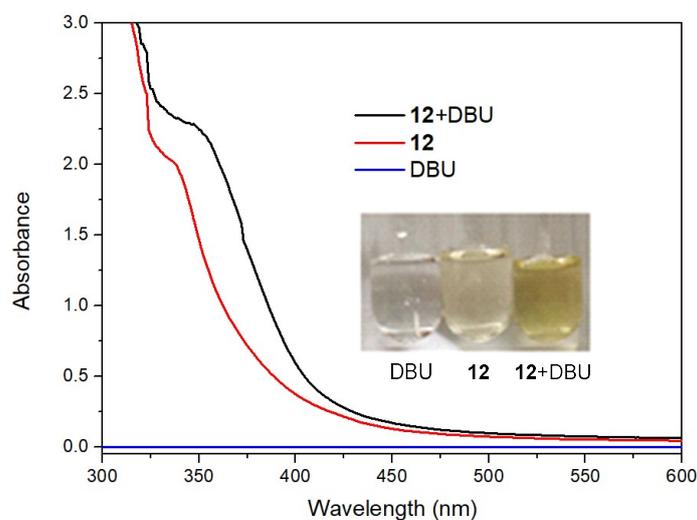
#### iv. Control experiment using triplet quencher



A 25 mL oven-dried Schlenk tube containing a magnetic stirring bar was charged with ethynylbenziodoxole **1a** (0.1 mmol) and eosin Y (0.001 mmol). The tube was then evacuated, refilled with CO<sub>2</sub> (1 atm) three times, and charged further with diethylamine **2a** (0.3 mmol), 1,8-diazabicyclo[5.4.0]undec-7-ene (0.1 mmol), 2,5-dimethylhexa-2,4-diene (a triplet quencher,<sup>5,6</sup> 0.1 mmol) and dimethyl sulfoxide (1 mL) via a syringe. The reaction mixture was stirred at room temperature for 0.5 h under 30 W green LEDs irradiation. After the reaction was completed, the reaction mixture was diluted with H<sub>2</sub>O (20 mL) and extracted with ethyl acetate (15 mL×3). The combined organic layers were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and then filtered. The volatile compounds were removed under vacuum and the crude residue was analyzed by <sup>1</sup>H NMR with CH<sub>2</sub>Br<sub>2</sub> as internal standard. The model reaction was significantly inhibited in the presence of 1.0 equivalent of 2,5-dimethylhexa-2,4-diene.

#### v. UV-vis absorption spectra of the charge-transfer complex

Solutions of **12** and DBU (0.1 M) in 2 mL DMSO were recorded in 1 cm path quartz cuvettes using a Shimadzu UV-2600 spectrophotometer.



**Figure S6.** UV-visible absorption spectra (DMSO, *c* = 0.1 M).

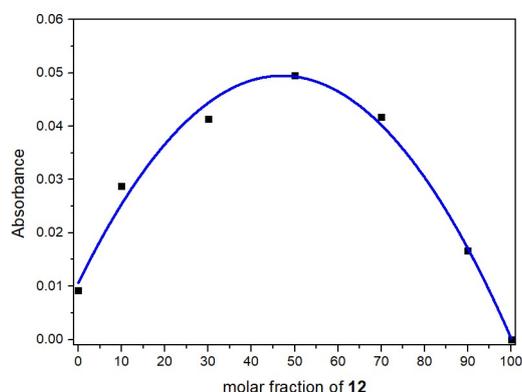
## vi. Determination of the Stoichiometry of the charge-transfer complex

The stoichiometry of the EDA complex formed between **12** and DBU in DMSO was determined using the Job's plot method. The Job's plot was constructed by measuring the absorption at 425 nm of DMSO solutions of different ratios of **12** and DBU, where the total concentration of the two components remained constant at 0.1 M (Figure S7). The absorbance values were corrected with respect to the molar fraction of **12** and plotted against the molar fraction **12** (Table S1).

**Table S1.** Absorbance of 0.1 M DMSO solutions of different molar ratios of **12** and DBU.<sup>a</sup>

entry	<b>12</b> : DBU ratio	Molar fraction of <b>12</b> (%)	Absorbance at 425 nm	Absorbance corrected for molar fraction of <b>12</b>
1	1.0 : 0.0	100	0.185	0
2	0.9 : 0.1	90	0.167	0.0167
3	0.7 : 0.3	70	0.139	0.0417
4	0.5 : 0.5	50	0.099	0.0495
5	0.3 : 0.7	30	0.059	0.0413
6	0.1 : 0.9	10	0.032	0.0288
7	0.0 : 1.0	0	0.009	0.0009

<sup>a</sup>All the absorption spectra were recorded in quartz cuvettes with a path length of 1.0 mm.



**Figure S7.** Job's plot of **12** and DBU in DMSO.

## vii. The *Z* to *E* isomerization of (*Z*)-**3aa**

To a oven-dried 25 mL reaction vial containing a magnetic stirring bar was added tris(2-phenylpyridine)iridium (0.001 mmol). The vial was capped. After evacuated and backfilled N<sub>2</sub> three times, (*Z*)-**3aa** (0.1 mmol) and ethyl acetate (1 mL) were added via a syringe. The reaction mixture was stirred at room temperature for 14 h under 30 W green LEDs irradiation. After the reaction was completed, the reaction mixture was diluted with dichloromethane (10 mL). The solvent was removed under reduced pressure and the crude residue was analyzed by <sup>1</sup>H NMR

with CH<sub>2</sub>Br<sub>2</sub> as internal standard.

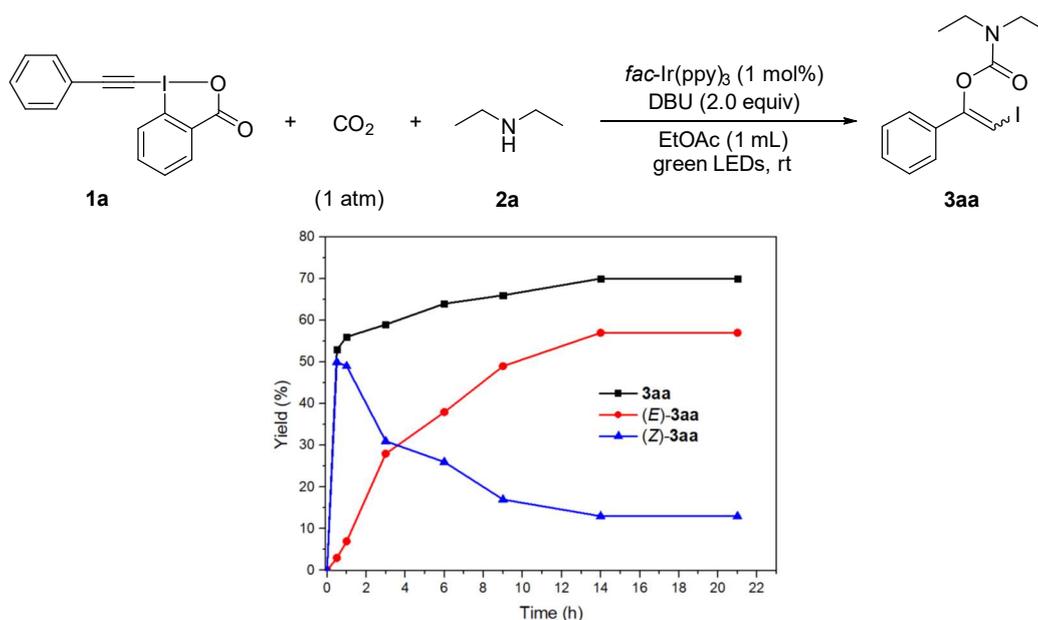
**Table S2.** Isomerizations of *Z* and *E*-isomers.<sup>a</sup>

entry	substrate	Deviation from standard conditions	yield	Z/E
1	( <i>Z</i> )- <b>3aa</b>	none	>99%	18:82
2	( <i>Z</i> )- <b>3aa</b>	without <i>fac</i> -Ir(ppy) <sub>3</sub>	>99%	100:0
3	( <i>Z</i> )- <b>3aa</b>	in the dark	>99%	100:0
4	( <i>Z</i> )- <b>3aa</b>	Blue LEDs without <i>fac</i> -Ir(ppy) <sub>3</sub>	>99%	41:59

<sup>a</sup>Standard reaction conditions: (*Z*)-**3aa** (0.1 mmol), *fac*-Ir(ppy)<sub>3</sub> (1 mol %), EtOAc (1 mL), green LEDs, N<sub>2</sub>, 14 h, rt.

### viii. Time course studies of the reaction catalyzed by *fac*-Ir(ppy)<sub>3</sub>

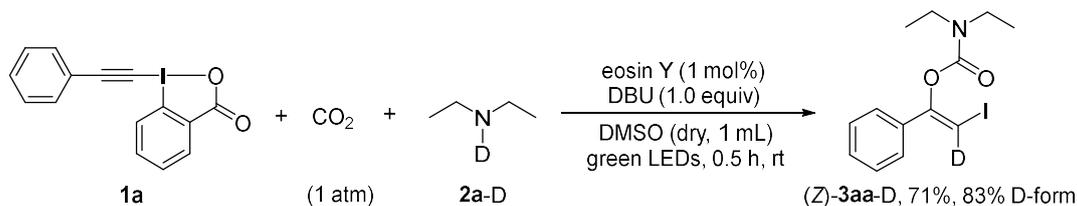
A 25 mL oven-dried Schlenk tube containing a magnetic stirring bar was charged with ethynylbenziodoxole **1a** (0.1 mmol) and tris(2-phenylpyridine)iridium (0.001 mmol). The tube was then evacuated, refilled with CO<sub>2</sub> (1 atm) three times, and charged further with diethylamine **2a** (0.3 mmol), 1,8-diazabicyclo[5.4.0]undec-7-ene (0.2 mmol) and ethyl acetate (1 mL) via a syringe. The reaction mixture was stirred at room temperature under 30 W green LEDs irradiation for 30 min, 1 h, 3 h, 6 h, 9 h, 14 h, 21 h, respectively. After the reaction was stopped, the reaction mixture was diluted with dichloromethane (10 mL). The solvent was removed under reduced pressure and the crude residue was analyzed by <sup>1</sup>H NMR with CH<sub>2</sub>Br<sub>2</sub> as internal standard.



**Figure S8.** Time course studies.

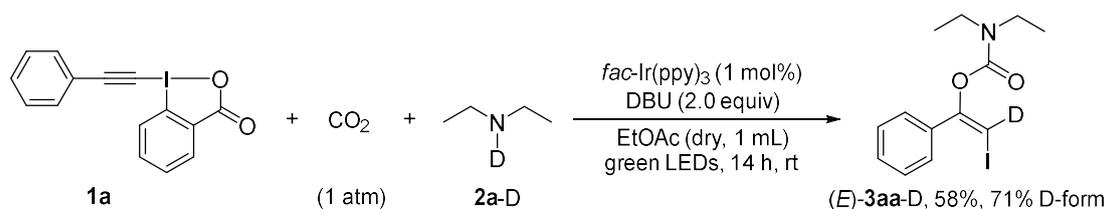
## ix. Isotope-labelling studies

### Synthesis of (*Z*)-3aa-D:



A 25 mL oven-dried Schlenk tube containing a magnetic stirring bar was charged with ethynylbenziodoxole **1a** (0.1 mmol) and eosin Y (0.001 mmol). The tube was then evacuated, refilled with CO<sub>2</sub> (1 atm) three times, and charged further with diethylamine-N-D1 (**2a-D**) (0.3 mmol), 1,8-diazabicyclo[5.4.0]undec-7-ene (0.1 mmol) and anhydrous dimethyl sulfoxide (1 mL) (Note that anhydrous condition is important) via a syringe. The reaction mixture was stirred at room temperature for 0.5 h under 30 W green LEDs irradiation. After the reaction was completed, the reaction mixture was diluted with H<sub>2</sub>O (20 mL) and extracted with ethyl acetate (15 mL×3). The combined organic layers were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and then filtered. The volatile compounds were removed under vacuum and the crude residue was separated by column chromatography on a silica gel column using petroleum ether/ethyl acetate (20:1) as eluent to give the desired product (*Z*)-2-iodo-1-phenylvinyl-2-*d* diethylcarbamate ((*Z*)-**3aa-D**) in 71% yield with 83% of D-form as pale yellow oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.51 – 7.39 (m, 2 H), 7.38 – 7.27 (m, 3 H), 6.55 (d, *J* = 2.0 Hz, 0.17 H), 3.53 (q, *J* = 7.1 Hz, 2 H), 3.37 (q, *J* = 7.2 Hz, 2 H), 1.36 (t, *J* = 7.0 Hz, 3 H), 1.20 (t, *J* = 6.8 Hz, 3 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 155.2, 151.9, 134.6, 129.0, 128.6, 125.1, 68.0, 42.3, 42.1, 14.5, 13.3. IR (KBr): 3056, 2968, 2926, 1794, 1717, 1590, 1473, 1418, 1316, 1244, 1147, 1075, 1010, 953, 860, 749, 682, 608 cm<sup>-1</sup>. HRMS-ESI (*m/z*): calcd for C<sub>13</sub>H<sub>16</sub>DINO<sub>2</sub> [M + H]<sup>+</sup>: 347.0361; found: 347.0359.

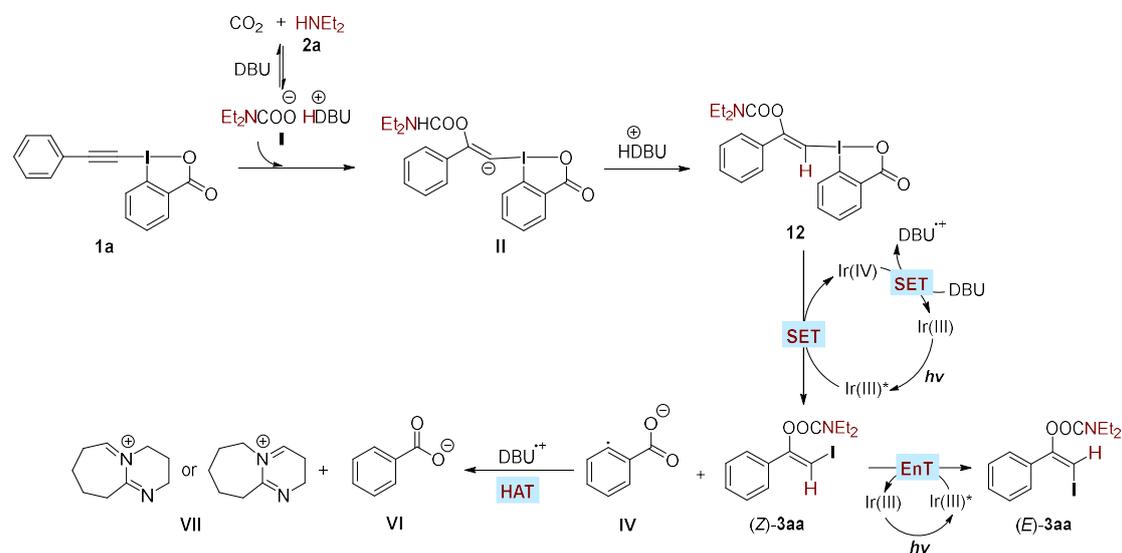
### Synthesis of (*E*)-3aa-D:



A 25 mL oven-dried Schlenk tube containing a magnetic stirring bar was charged with ethynylbenziodoxole **1a** (0.1 mmol) and tris(2-phenylpyridine)iridium (0.001 mmol). The tube was

then evacuated, refilled with CO<sub>2</sub> (1 atm) three times, and charged further with diethylamine-N-D1 **2a-D** (0.3 mmol), 1,8-diazabicyclo[5.4.0]undec-7-ene (0.2 mmol) and anhydrous ethyl acetate (1 mL) (Note that anhydrous condition is important) via a syringe. The reaction mixture was stirred at room temperature for 14 h under 30 W green LEDs irradiation. After the reaction was completed, the reaction mixture was diluted with dichloromethane (10 mL). The solvent was removed under reduced pressure and the crude residue was separated by column chromatography on a silica gel column using petroleum ether/ethyl acetate (20:1) as the eluent to give the desired product (*E*)-2-iodo-1-phenylvinyl-2-*d* diethylcarbamate ((*E*)-**3aa-D**) in 58% yield with 71% of D-form as yellow oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.66 – 7.54 (m, 2 H), 7.44 – 7.32 (m, 3 H), 6.32 (s, 0.29 H) 3.36 (q, *J* = 7.1 Hz, 2 H), 3.26 (q, *J* = 7.1 Hz, 2 H), 1.19 (t, *J* = 7.0 Hz, 3 H), 1.10 (t, *J* = 7.0 Hz, 3 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 153.1, 151.7, 151.6, 135.0, 129.2, 128.8, 128.0, 66.2, 42.2, 41.8, 14.2, 13.2. IR (KBr): 3062, 2957, 2855, 1717, 1579, 1419, 1249, 1150, 1064, 949, 904, 845, 756, 687 cm<sup>-1</sup>. HRMS-ESI (*m/z*): calcd for C<sub>13</sub>H<sub>16</sub>DINO<sub>2</sub> [M + H]<sup>+</sup>: 347.0361; found: 347.0358.

**x. An alternative mechanism for the reaction catalyzed by *fac*-Ir(ppy)<sub>3</sub>**



**Figure S9.** Proposed mechanism.

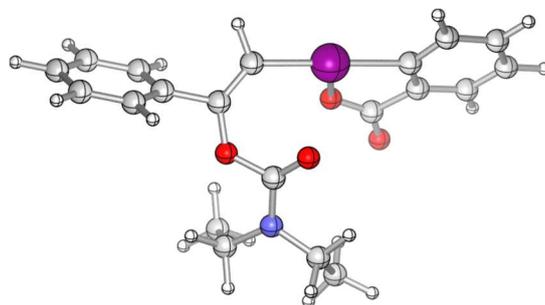
On the basis of the above-mentioned investigations and previous reports,<sup>7,8</sup> we proposed an alternative mechanism for the reaction catalyzed by photocatalyst *fac*-Ir(ppy)<sub>3</sub> under green LEDs irradiation. Initially, the vinylbenziodoxolone intermediate **12** is formed through the three-component coupling reaction of EBX (**1a**), CO<sub>2</sub> and amine in the presence of DBU.

Subsequent single-electron reduction of **12** by the excited photocatalyst Ir(III)\* will give (*Z*)-**3aa** and aryl radical **IV**. Then, hydrogen atom transfer (HAT) from the ammonium radical cation to **IV** will produce stable benzoate **VI** and **VII**. Single-electron transfer between the oxidized Ir(IV) species and DBU will regenerate the ground-state Ir(III) catalyst. Finally, a photoinduced *Z*→*E* isomerization of (*Z*)-**3aa** will occur via an energy transfer process to deliver the product (*E*)-**3aa**.

## H. Details of DFT calculations

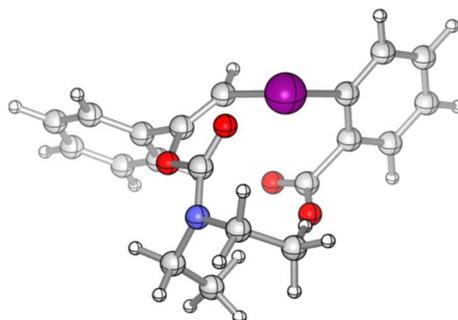
The adiabatic S<sub>0</sub>–T<sub>1</sub> gap for **12** and **12**+DBU were determined via the energy difference of the optimized singlet ground state structure and the first excited triplet structure. Density functional theory (DFT) calculations at B3LYP /BSI level using Gaussian 09 software. BSI denotes that LANL2DZ basis set is used for the Iodine center, and 6-31++G(d,p) basis sets are used for all the other atoms. SMD polarizable continuum model in EtOAc solvent was employed 3D geometries were prepared using CYLView software. Structures were confirmed to be a minimum on the potential energy surface via harmonic frequency calculations.

Optimized structure of **12** for S<sub>0</sub>:



Gibbs free energy (B3LYP/6-31++G(d,p)): -1135.199322 a.u.

Optimized structure of **12** for T<sub>1</sub>:



Gibbs free energy (B3LYP/6-31++G(d,p)): -1135.056376 a.u.

S<sub>0</sub>–T<sub>1</sub> gibbs free energy barrier (B3LYP/6-31++G(d,p)): 0.142946 a.u. (89.7 kcal/mol)

**Table S3. 12** standard orientation S0 (coordinates)

	Coordinates (Angstroms)		
	X	Y	Z
C	2.47306	-4.99684	-4.42078
C	1.16335	-5.44956	-4.26666
C	0.32621	-4.84685	-3.33527
C	0.79926	-3.78038	-2.56831
C	2.11431	-3.33327	-2.70616
C	2.94728	-3.94759	-3.63822
H	3.12626	-5.46965	-5.14841
H	0.79587	-6.27274	-4.87201
H	-0.69501	-5.19416	-3.20699
H	2.47939	-2.54888	-2.04701
H	3.97349	-3.60944	-3.74415
C	-0.08547	-3.12994	-1.56162
O	-0.31078	-3.96515	-0.53678
C	-1.28866	-3.81423	0.42696
N	-1.00625	-4.60205	1.47454
C	-1.89082	-4.5575	2.63356
H	-2.38333	-5.53326	2.74159
H	-2.66391	-3.81988	2.41411
C	-1.15155	-4.19058	3.91719
H	-0.56915	-3.27861	3.76592
H	-1.8736	-4.02422	4.72351
H	-0.47164	-4.98708	4.2361
C	0.15919	-5.49662	1.50734
H	-0.08857	-6.27735	2.23511
H	0.24073	-5.98654	0.53408
C	1.48145	-4.82629	1.86788
H	2.27108	-5.58663	1.87751
H	1.75121	-4.04228	1.15664
H	1.43634	-4.36447	2.85736
O	-2.28269	-3.13259	0.25376
C	-0.46971	-1.87033	-1.80706
H	-0.15344	-1.40886	-2.732
I	-1.43788	-0.47725	-0.58397
C	-2.42945	0.94949	0.66867
C	-1.8849	1.18949	1.91968
C	-3.52621	1.62407	0.14563
C	-2.51908	2.17479	2.68422
C	-4.16025	2.56243	0.95369
H	-3.87291	1.43937	-0.86594
C	-3.65312	2.83228	2.22476
H	-2.08028	2.41369	3.64782

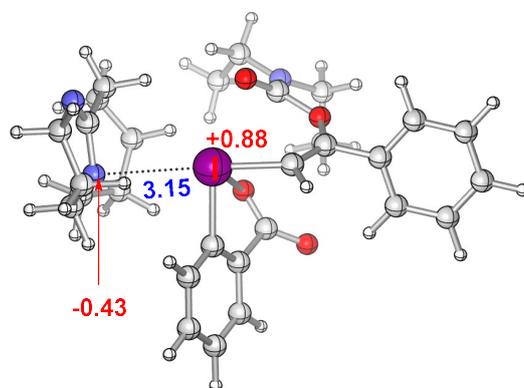
H	-5.0293	3.09467	0.57962
H	-4.13488	3.5788	2.84914
O	0.01019	-0.21392	1.67329
C	-0.63057	0.47646	2.49478
O	-0.42205	0.70065	3.69853

**Table S4. 12** standard orientation T1 (coordinates)

	Coordinates (Angstroms)		
	X	Y	Z
C	6.26906	1.97897	-1.35919
C	5.84567	1.05143	-2.31022
C	4.5902	0.46609	-2.1973
C	3.75395	0.82222	-1.13748
C	4.17835	1.7377	-0.1731
C	5.44057	2.31449	-0.29184
H	7.2509	2.4347	-1.44839
H	6.49488	0.78441	-3.13867
H	4.25274	-0.25894	-2.93243
H	3.53688	1.94389	0.68074
H	5.77925	3.02107	0.45963
C	2.40859	0.19725	-1.00091
O	2.53194	-1.09613	-0.66835
C	1.52888	-2.04381	-0.72855
N	1.88198	-3.1123	0.00049
C	0.93618	-4.21699	0.11415
H	1.36526	-5.10286	-0.37315
H	0.04542	-3.93058	-0.44658
C	0.57696	-4.52985	1.56395
H	0.26069	-3.61807	2.07619
H	-0.24061	-5.25785	1.5921
H	1.4245	-4.95744	2.10915
C	3.17279	-3.21102	0.69592
H	3.35444	-4.28322	0.82998
H	3.95121	-2.84036	0.02466
C	3.24586	-2.48238	2.03437
H	4.2414	-2.63744	2.46631
H	3.06742	-1.40994	1.92784
H	2.5022	-2.86626	2.73721
O	0.54373	-1.9145	-1.43244
C	1.344	0.98846	-1.18839
H	1.51392	2.01963	-1.46462
I	-0.68729	0.65052	-0.82283
C	-0.71171	2.03247	0.81348
C	0.15942	1.79487	1.86411

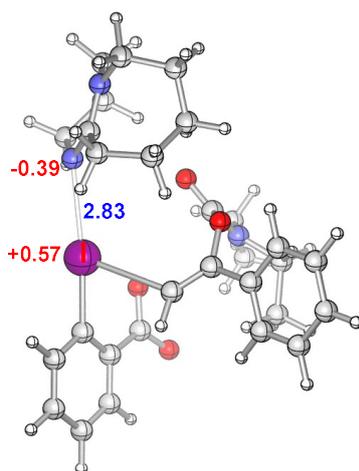
C	-1.54195	3.14274	0.71579
C	0.16398	2.75295	2.88372
C	-1.54562	4.04868	1.77161
H	-2.15947	3.31067	-0.16059
C	-0.69126	3.84713	2.85561
H	0.87352	2.61247	3.69302
H	-2.19494	4.91775	1.73227
H	-0.67837	4.56386	3.6713
O	0.64058	-0.51248	1.60669
C	1.12662	0.58336	1.96021
O	2.26576	0.86946	2.36427

Optimized structure of **12**+DBU for S0:



Gibbs free energy (B3LYP/6-31++G(d,p)): -1602.52928 a.u.

Optimized structure of **12**+DBU for T1:



Gibbs free energy (B3LYP/6-31++G(d,p)): -1602.595574 a.u.

S0–T1 gibbs free energy barrier (B3LYP/6-31++G(d,p)): 0.066294 a.u. (41.6 kcal/mol)

**Table S5.** 12+DBU standard orientation S0 (coordinates)

	Coordinates (Angstroms)		
	X	Y	Z
C	6.26906	1.97897	-1.35919
C	5.84567	1.05143	-2.31022
C	4.5902	0.46609	-2.1973
C	3.75395	0.82222	-1.13748
C	4.17835	1.7377	-0.1731
C	5.44057	2.31449	-0.29184
H	7.2509	2.4347	-1.44839
H	6.49488	0.78441	-3.13867
H	4.25274	-0.25894	-2.93243
H	3.53688	1.94389	0.68074
H	5.77925	3.02107	0.45963
C	2.40859	0.19725	-1.00091
O	2.53194	-1.09613	-0.66835
C	1.52888	-2.04381	-0.72855
N	1.88198	-3.1123	0.00049
C	0.93618	-4.21699	0.11415
H	1.36526	-5.10286	-0.37315
H	0.04542	-3.93058	-0.44658
C	0.57696	-4.52985	1.56395
H	0.26069	-3.61807	2.07619
H	-0.24061	-5.25785	1.5921
H	1.4245	-4.95744	2.10915
C	3.17279	-3.21102	0.69592
H	3.35444	-4.28322	0.82998
H	3.95121	-2.84036	0.02466
C	3.24586	-2.48238	2.03437
H	4.2414	-2.63744	2.46631
H	3.06742	-1.40994	1.92784
H	2.5022	-2.86626	2.73721
O	0.54373	-1.9145	-1.43244
C	1.344	0.98846	-1.18839
H	1.51392	2.01963	-1.46462
I	-0.68729	0.65052	-0.82283
C	-0.71171	2.03247	0.81348
C	0.15942	1.79487	1.86411
C	-1.54195	3.14274	0.71579
C	0.16398	2.75295	2.88372
C	-1.54562	4.04868	1.77161
H	-2.15947	3.31067	-0.16059
C	-0.69126	3.84713	2.85561
H	0.87352	2.61247	3.69302

H	-2.19494	4.91775	1.73227
H	-0.67837	4.56386	3.6713
O	0.64058	-0.51248	1.60669
C	1.12662	0.58336	1.96021
O	2.26576	0.86946	2.36427
C	-3.84341	-0.82965	-1.11608
C	-3.18655	-2.19811	-0.98577
C	-3.85816	-0.34293	1.32322
C	-3.14735	-2.94822	0.34872
C	-2.6598	-1.01253	1.98512
C	-2.18145	-2.33325	1.35884
H	-2.14639	-2.08963	-1.32533
H	-4.15402	-3.05871	0.77248
H	-4.75189	-0.97979	1.4004
H	-2.96885	-1.18709	3.02346
H	-3.68564	-2.80523	-1.74415
H	-4.07899	0.55646	1.90607
H	-2.80743	-3.96621	0.12061
H	-1.81544	-0.31903	2.03308
H	-1.98684	-3.05614	2.15796
H	-1.21874	-2.15707	0.86587
N	-3.70498	0.11919	-0.07313
N	-4.36653	-0.60237	-2.26189
C	-4.91426	0.69745	-2.59887
H	-4.68392	0.89542	-3.65191
H	-6.0097	0.63884	-2.53162
C	-4.39829	1.8237	-1.71053
H	-4.98333	2.74013	-1.84177
H	-3.35808	2.05777	-1.97161
C	-4.47553	1.35402	-0.27052
H	-5.53135	1.18773	0.00131
H	-4.07826	2.10577	0.419

**Table S6.** 12+DBU standard orientation T1 (coordinates)

	Coordinates (Angstroms)		
	X	Y	Z
C	1.79669	-5.63047	-1.80163
C	0.49589	-5.36868	-1.38018
C	0.14953	-4.10326	-0.91722
C	1.10243	-3.08038	-0.87913
C	2.40929	-3.35261	-1.29376
C	2.75295	-4.61904	-1.75358
H	2.06618	-6.61973	-2.15937
H	-0.25528	-6.15232	-1.4104

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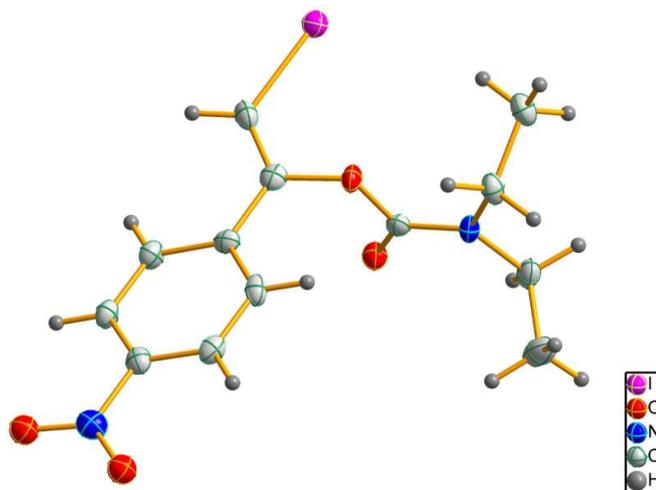
H	-0.86228	-3.8998	-0.58252
H	3.16405	-2.57396	-1.23795
H	3.77385	-4.81833	-2.06538
C	0.70729	-1.72195	-0.40916
O	-0.36536	-1.78011	0.46647
C	-0.42983	-1.00716	1.60496
N	0.56035	-1.21005	2.51485
C	0.41142	-0.46378	3.77034
H	-0.31483	-0.98622	4.41103
H	-0.02595	0.49951	3.51064
C	1.71398	-0.24803	4.52866
H	2.46005	0.24052	3.89981
H	1.51157	0.3971	5.38945
H	2.13416	-1.1833	4.91405
C	1.39759	-2.41178	2.50684
H	1.32583	-2.86777	3.50232
H	0.95974	-3.12976	1.81161
C	2.86281	-2.17554	2.1433
H	3.37194	-3.14049	2.04517
H	2.94137	-1.64559	1.19167
H	3.38382	-1.58483	2.89854
O	-1.38628	-0.28044	1.76492
C	1.25509	-0.59894	-0.83134
H	2.03742	-0.4764	-1.56667
I	0.11187	2.00424	-0.81794
C	2.21227	2.24542	-1.15696
C	3.18905	2.07534	-0.17226
C	2.61003	2.54216	-2.45409
C	4.53807	2.19366	-0.49933
C	3.96313	2.665	-2.77485
H	1.86389	2.67114	-3.23089
C	4.9331	2.48678	-1.79935
H	5.2741	2.06014	0.28722
H	4.24871	2.89761	-3.79649
H	5.98639	2.58388	-2.04073
O	1.72745	1.86877	1.76712
C	2.88923	1.77002	1.25556
O	3.74185	1.41007	2.07361
C	-3.50708	1.05432	-0.8333
C	-3.13346	0.24338	-2.05425
C	-5.54605	-0.32232	-0.77584
C	-2.8628	-1.25868	-1.77304
C	-5.01672	-1.7192	-0.40748
C	-3.48981	-1.81196	-0.48866

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H	-2.24326	0.70779	-2.48163
H	-3.19314	-1.84655	-2.63903
H	-5.6326	-0.22836	-1.8618
H	-5.49049	-2.45255	-1.07321
H	-3.92301	0.35489	-2.80623
H	-6.55884	-0.18043	-0.38378
H	-1.78074	-1.39724	-1.69113
H	-5.32706	-1.97508	0.61353
H	-3.19189	-2.86176	-0.37764
H	-3.04628	-1.28454	0.36182
N	-4.72593	0.76504	-0.26472
N	-2.69269	1.96155	-0.4183
C	-3.08206	2.72441	0.75697
H	-2.17523	3.12089	1.22499
H	-3.68585	3.59085	0.44466
C	-3.86199	1.87224	1.75344
H	-4.18425	2.4655	2.61557
H	-3.20584	1.07276	2.10731
C	-5.07809	1.28126	1.05589
H	-5.87044	2.0369	0.95151
H	-5.48993	0.45742	1.65188

## I. X-ray crystal structure and data for compound (**Z**)-**3fa**

Single-crystal X-ray diffraction data for (**Z**)-**3fa** was collected on an X-ray diffractometer operated at 90 kV and 50 mA using MoK $\alpha$  radiation ( $\lambda = 0.71073$  Å) at 100 K. All empirical absorption corrections were performed using the CrystalClear program. The structure was solved by a direct method and refined on  $F^2$  by the full-matrix least squares technique using the SHELXTL-97 program package. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms attached to carbon were placed in geometrically idealized positions and refined using a riding model. The X-ray crystal structure of compound (**Z**)-**3fa** is shown in **Figure S10**, and the crystallographic data for compound (**Z**)-**3fa** is given in **Table S7**.



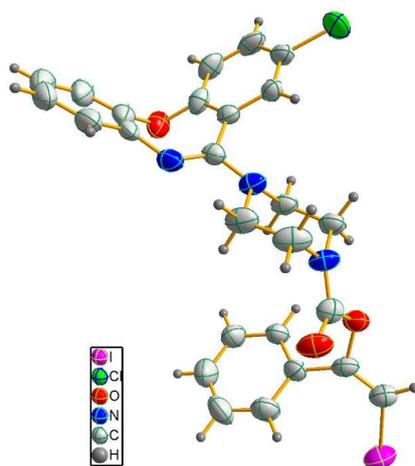
**Figure S10.** X-ray crystal structures of compound (**Z**)-**3fa**. Ellipses are drawn at the 50% probability level.

**Table S7.** Crystal data and structure refinements for (**Z**)-**3fa**

Compound	( <b>Z</b> )- <b>3fa</b>
Empirical formula	C <sub>13</sub> H <sub>15</sub> IN <sub>2</sub> O <sub>4</sub>
Formula weight	390.17
Temperature (K)	100.00(10)
Wavelength (Å)	0.71073
Crystal system	monoclinic
Space group	P2 <sub>1</sub> /c
	$a = 13.0208(5)\text{Å}$ $\alpha = 90^\circ$
	$b = 12.6688(5)\text{Å}$ $\beta = 95.3680(10)^\circ$
	$c = 8.9165(3)\text{Å}$ $\gamma = 90^\circ$
Volume (Å <sup>3</sup> )	1464.40(9)
Z	4
Density (calcd g cm <sup>-3</sup> )	1.770
Absorption coeff. (mm <sup>-1</sup> )	2.201
$F(000)$	768.0
Crystal size (mm <sup>3</sup> )	0.12 × 0.08 × 0.05
2 $\theta$ range for data collection	4.496 to 54.968
Limiting indices	-16 ≤ h ≤ 16, -16 ≤ k ≤ 16, -11 ≤ l ≤ 10
Reflections collected	14030
Unique	3357 [R <sub>int</sub> = 0.0638, R <sub>sigma</sub> = 0.0562]
Refinement method	Full-matrix least-squares on $F^2$
Data/restraints/parameters	3357/0/2183
Goodness-of-fit on $F^2$	1.037
Final R indexes [ $I > 2\sigma(I)$ ]	$R_1 = 0.0368$ , $wR_2 = 0.0610$
R indexes (all data)	$R_1 = 0.0696$ , $wR_2 = 0.1209$

## J. X-ray crystal structure and data for compound (*E*)-3aca

Single-crystal X-ray diffraction data for (*E*)-3aca was collected on an X-ray diffractometer operated at 90 kV and 50 mA using MoK $\alpha$  radiation ( $\lambda = 0.71073$  Å) at 293(2) K. All empirical absorption corrections were performed using the CrystalClear program. The structure was solved by a direct method and refined on  $F^2$  by the full-matrix least squares technique using the SHELXTL-97 program package. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms attached to carbon were placed in geometrically idealized positions and refined using a riding model. The X-ray crystal structure of compound (*E*)-3aca is shown in **Figure S11**, and the crystallographic data for compound (*E*)-3aca is given in **Table S8**.



**Figure S11.** X-ray crystal structures of compound (*E*)-3aca. Ellipses are drawn at the 50% probability level.

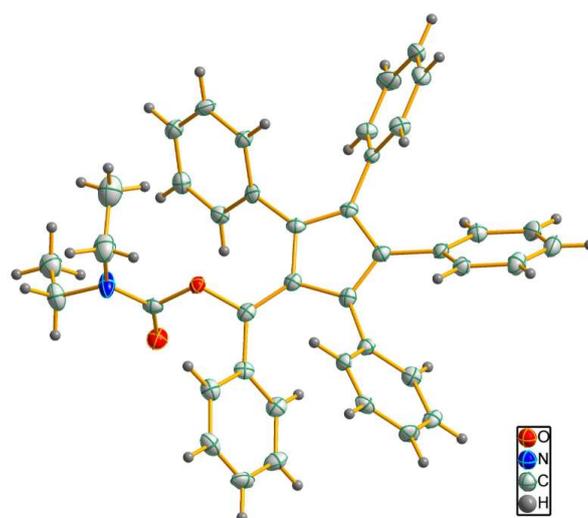
**Table S8.** Crystal data and structure refinements for (*E*)-3aca

Compound	( <i>E</i> )-3aca
Empirical formula	C <sub>26</sub> H <sub>21</sub> ClIN <sub>3</sub> O <sub>3</sub>
Formula weight	585.81
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	monoclinic
Space group	Cc
	$a = 12.6059(14)$ Å $\alpha = 90^\circ$
	$b = 17.029(2)$ Å $\beta = 97.402(13)^\circ$
	$c = 11.5334(16)$ Å $\gamma = 90^\circ$
Volume (Å <sup>3</sup> )	2455.2(5)
Z	4

Density (calcd g cm <sup>-3</sup> )	1.585
Absorption coeff. (mm <sup>-1</sup> )	1.446
<i>F</i> (000)	1168.0
Crystal size (mm <sup>3</sup> )	0.14 × 0.13 × 0.12
2 $\theta$ range for data collection	4.042 to 49.992
Limiting indices	-14 ≤ <i>h</i> ≤ 14, -20 ≤ <i>k</i> ≤ 17, -11 ≤ <i>l</i> ≤ 13
Reflections collected	5688
Unique	3480 [ <i>R</i> <sub>int</sub> = 0.0234, <i>R</i> <sub>sigma</sub> = 0.0359]
Refinement method	Full-matrix least-squares on <i>F</i> <sup>2</sup>
Data/restraints/parameters	3480/2/307
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.044
Final <i>R</i> indexes [ <i>I</i> ≥ 2 $\sigma$ ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0287, <i>wR</i> <sub>2</sub> = 0.0624
<i>R</i> indexes (all data)	<i>R</i> <sub>1</sub> = 0.0318, <i>wR</i> <sub>2</sub> = 0.0645

## K. X-ray crystal structure and data for compound **9**

Single-crystal X-ray diffraction data for **9** was collected on an X-ray diffractometer operated at 90 kV and 50 mA using MoK $\alpha$  radiation ( $\lambda$  = 0.71073 Å) at 100.01(11) K. All empirical absorption corrections were performed using the CrystalClear program. The structure was solved by a direct method and refined on *F*<sup>2</sup> by the full-matrix least squares technique using the SHELXTL-97 program package. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms attached to carbon were placed in geometrically idealized positions and refined using a riding model. The X-ray crystal structure of compound **9** is shown in **Figure S12**, and the crystallographic data for compound **9** is given in **Table S9**.



**Figure S12.** X-ray crystal structures of compound **9**. Ellipses are drawn at the 50% probability level.

**Table S9.** Crystal data and structure refinements for **9**

Compound	<b>9</b>
Empirical formula	C <sub>41</sub> H <sub>36</sub> NO <sub>2</sub>
Formula weight	573.27
Temperature (K)	100.01(11)
Wavelength (Å)	0.71073
Crystal system	orthorhombic
Space group	Pca2 <sub>1</sub>
	$a = 24.5244(15)\text{Å}$ $\alpha = 90^\circ$ $b = 25.6507(14)\text{Å}$ $\beta = 90^\circ$ $c = 10.3465(6)\text{Å}$ $\gamma = 90^\circ$
Volume (Å <sup>3</sup> )	6508.7(7)
Z	8
Density (calcd g cm <sup>-3</sup> )	1.258
Absorption coeff. (mm <sup>-1</sup> )	0.155
<i>F</i> (000)	2600.0
Crystal size (mm)	0.13 × 0.12 × 0.11
2 $\theta$ range for data collection	4.558 to 59.174
Limiting indices	-30 ≤ <i>h</i> ≤ 21, -23 ≤ <i>k</i> ≤ 35, -8 ≤ <i>l</i> ≤ 13
Reflections collected	25236
Unique	12508 [ <i>R</i> <sub>int</sub> = 0.0698, <i>R</i> <sub>sigma</sub> = 0.0929]
Refinement method	Full-matrix least-squares on <i>F</i> <sup>2</sup>
Data/restraints/parameters	12508/16/824
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.034
Final <i>R</i> indexes [ <i>I</i> ≥ 2 $\sigma$ ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0816, <i>wR</i> <sub>2</sub> = 0.1976
<i>R</i> indexes (all data)	<i>R</i> <sub>1</sub> = 0.1080, <i>wR</i> <sub>2</sub> = 0.2232

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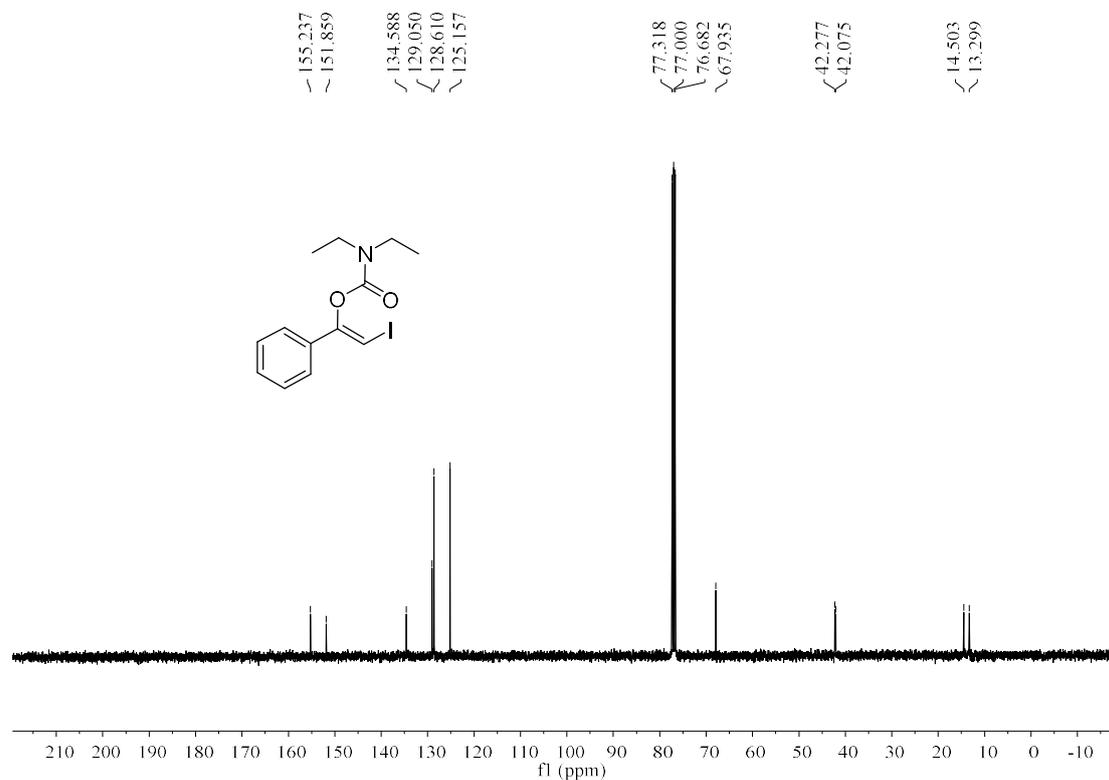
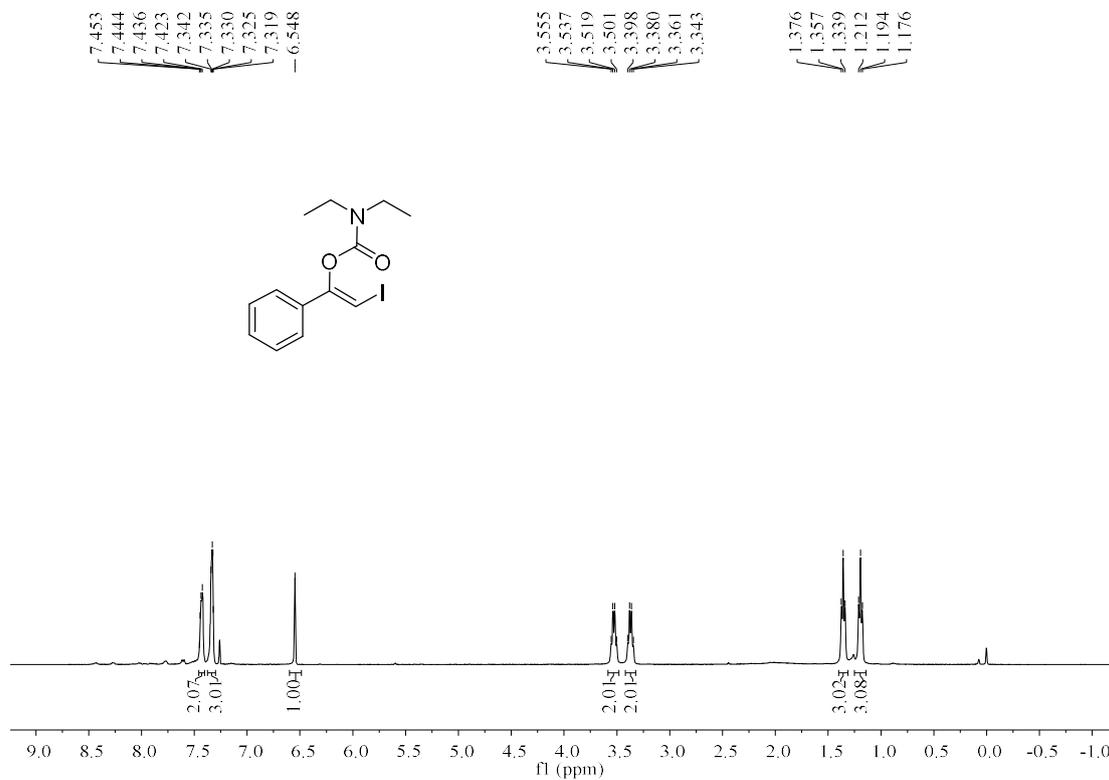
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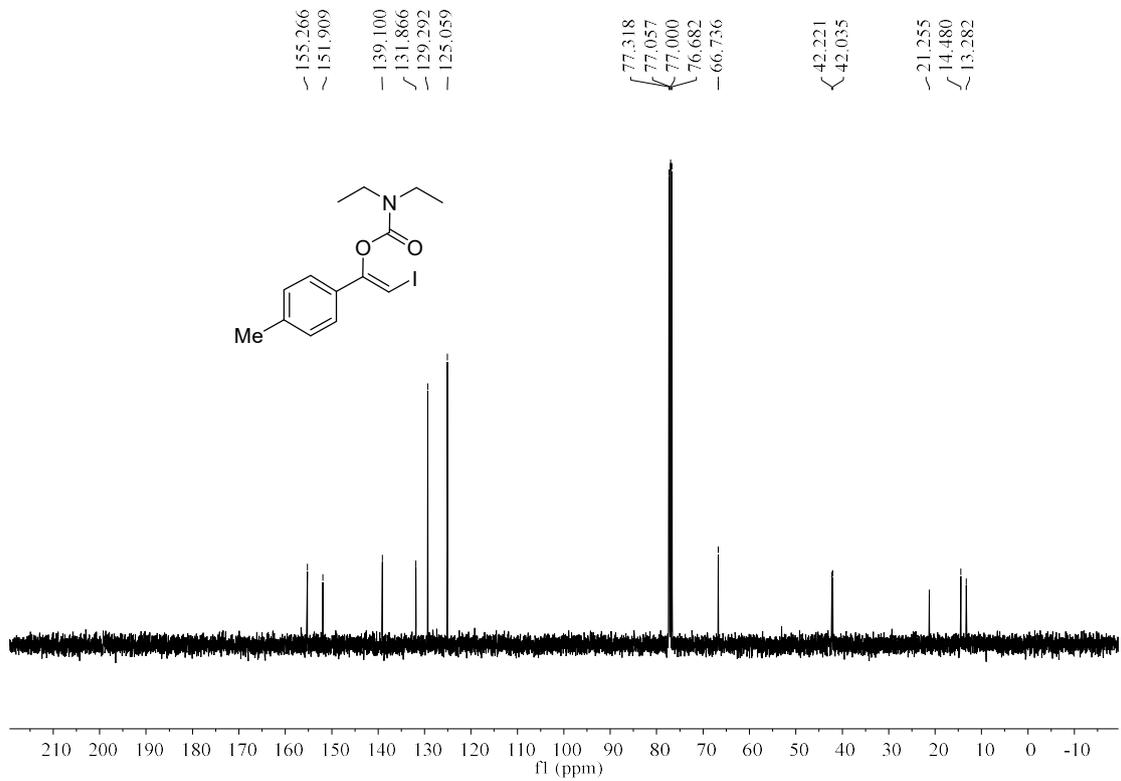
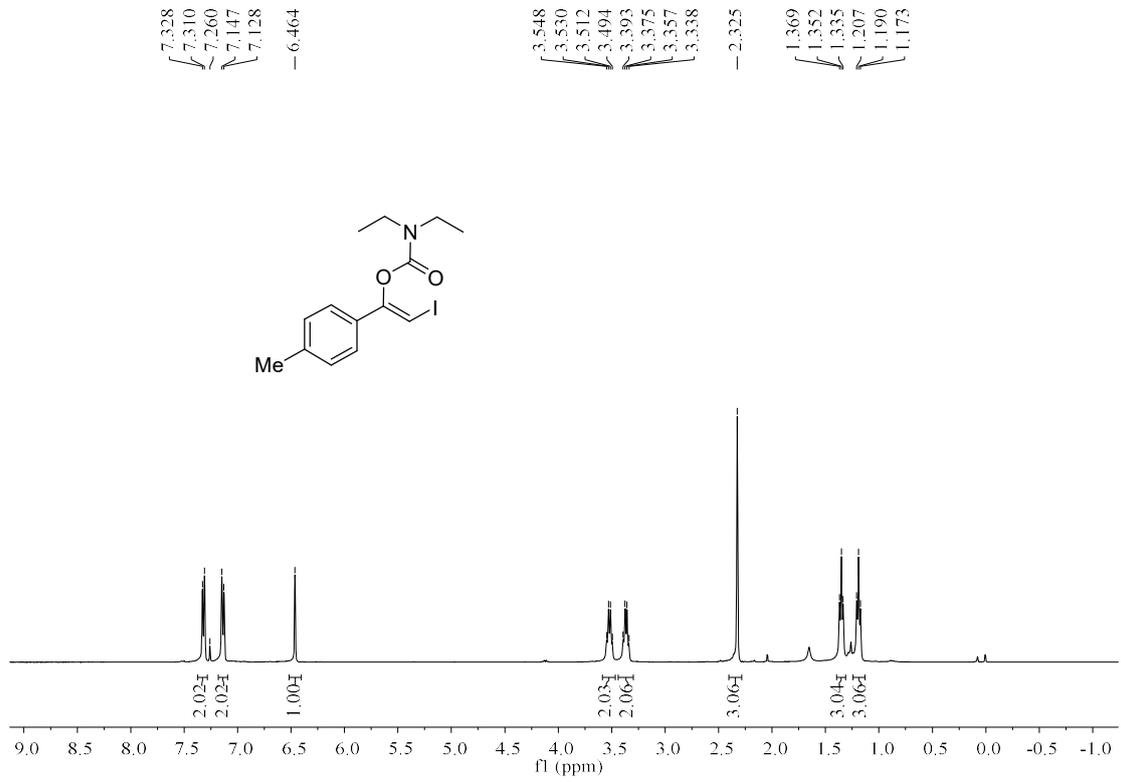
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## M. NMR Spectra

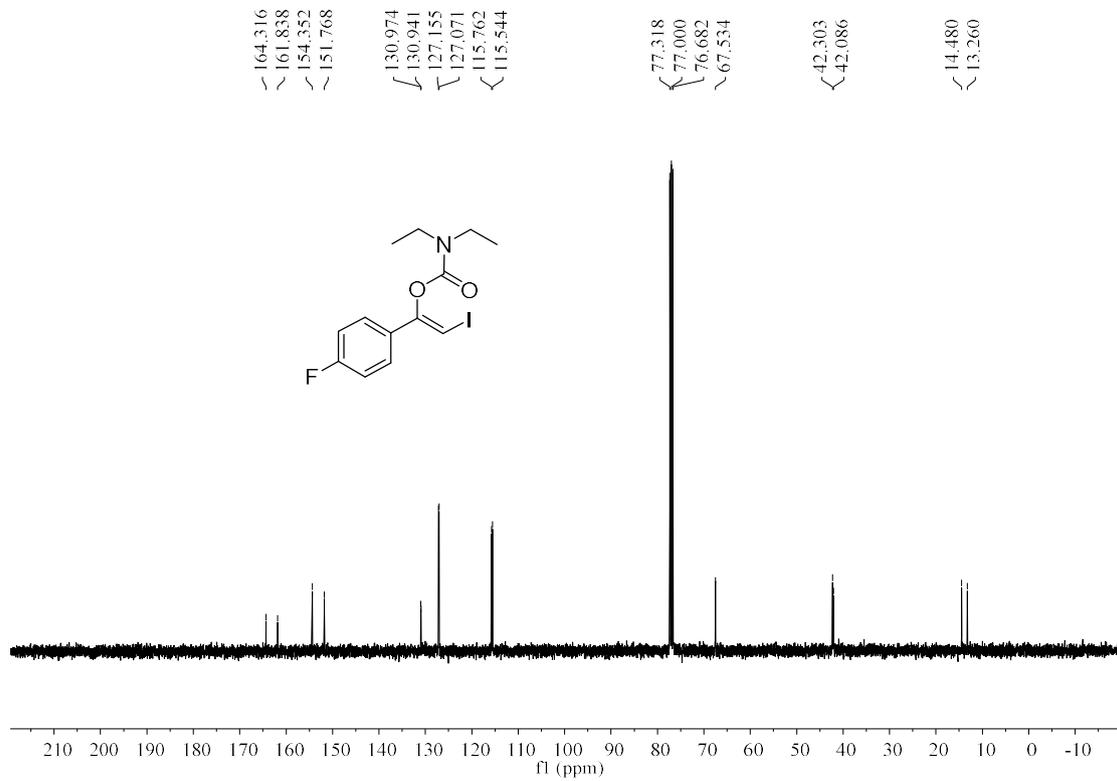
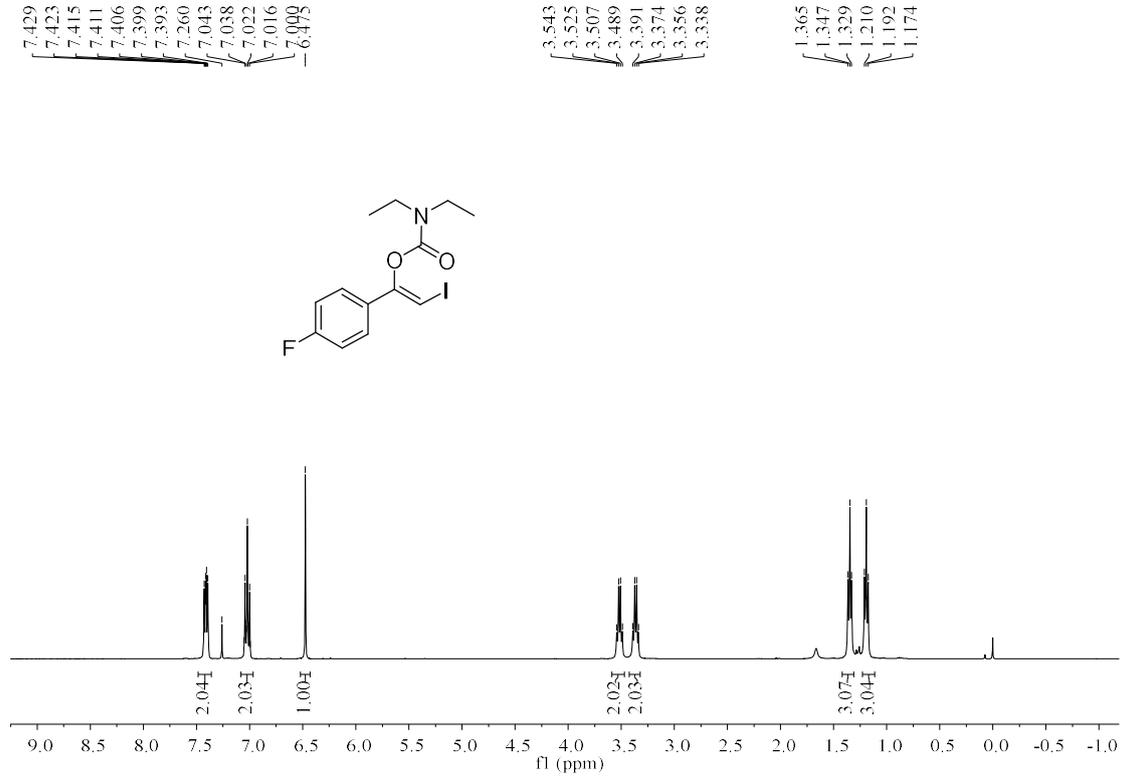
### (Z)-2-Iodo-1-phenylvinyl diethylcarbamate ((Z)-3aa)

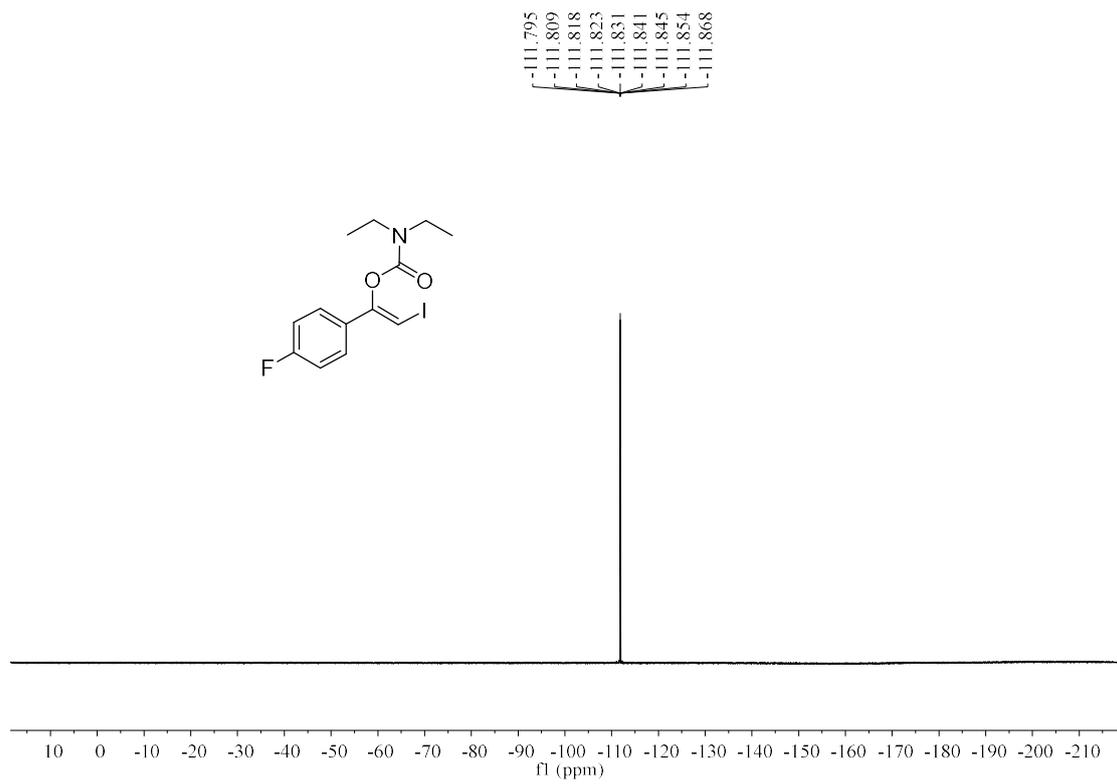


**(Z)-2-Iodo-1-(p-tolyl)vinyl diethylcarbamate ((Z)-3ba)**

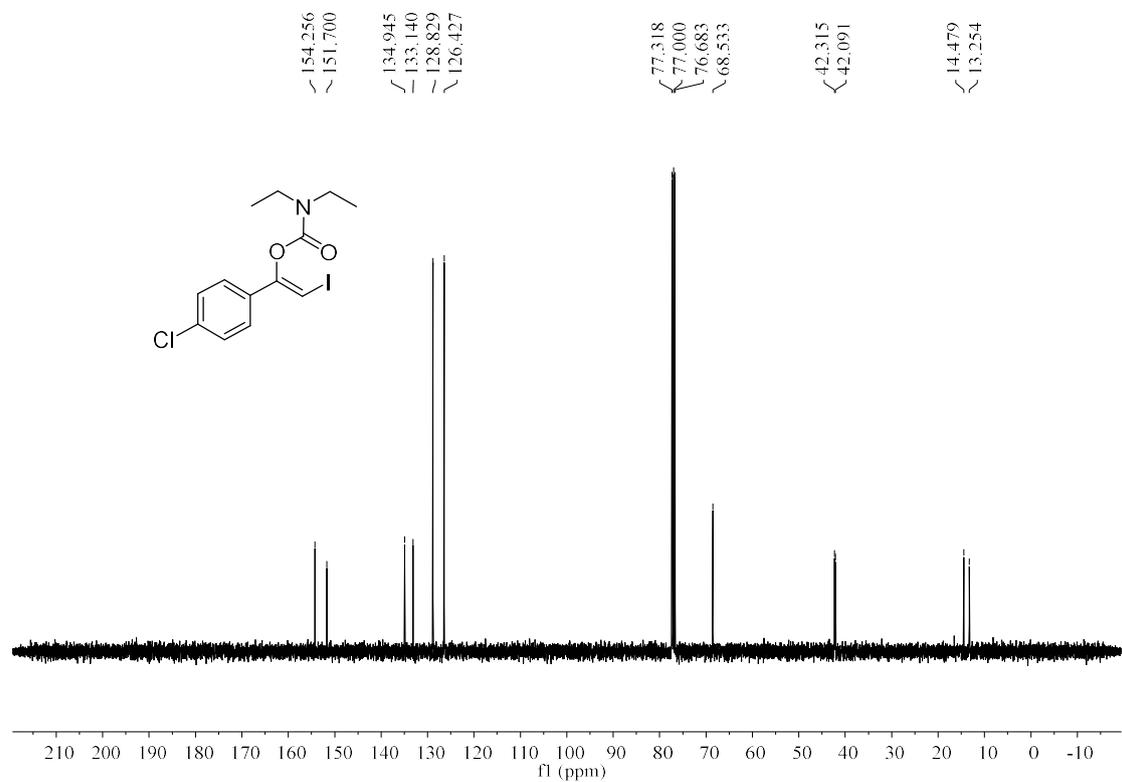
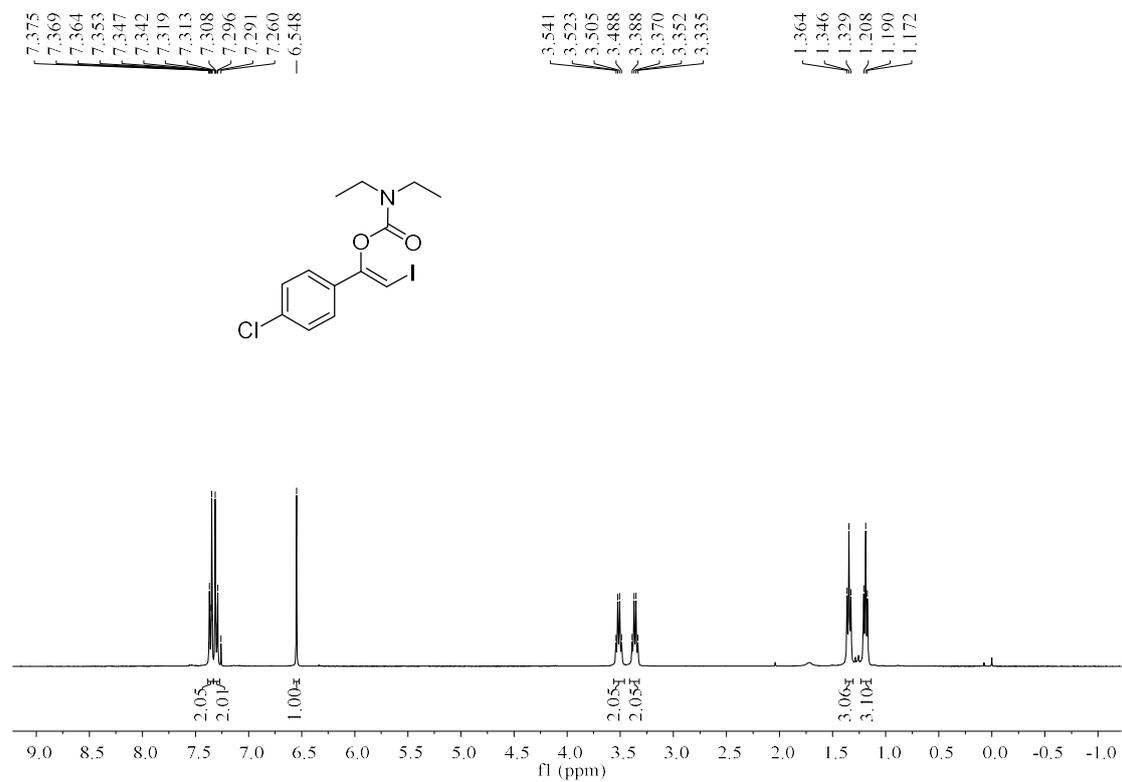


**(Z)-1-(4-Fluorophenyl)-2-iodovinyl diethylcarbamate ((Z)-3ca)**

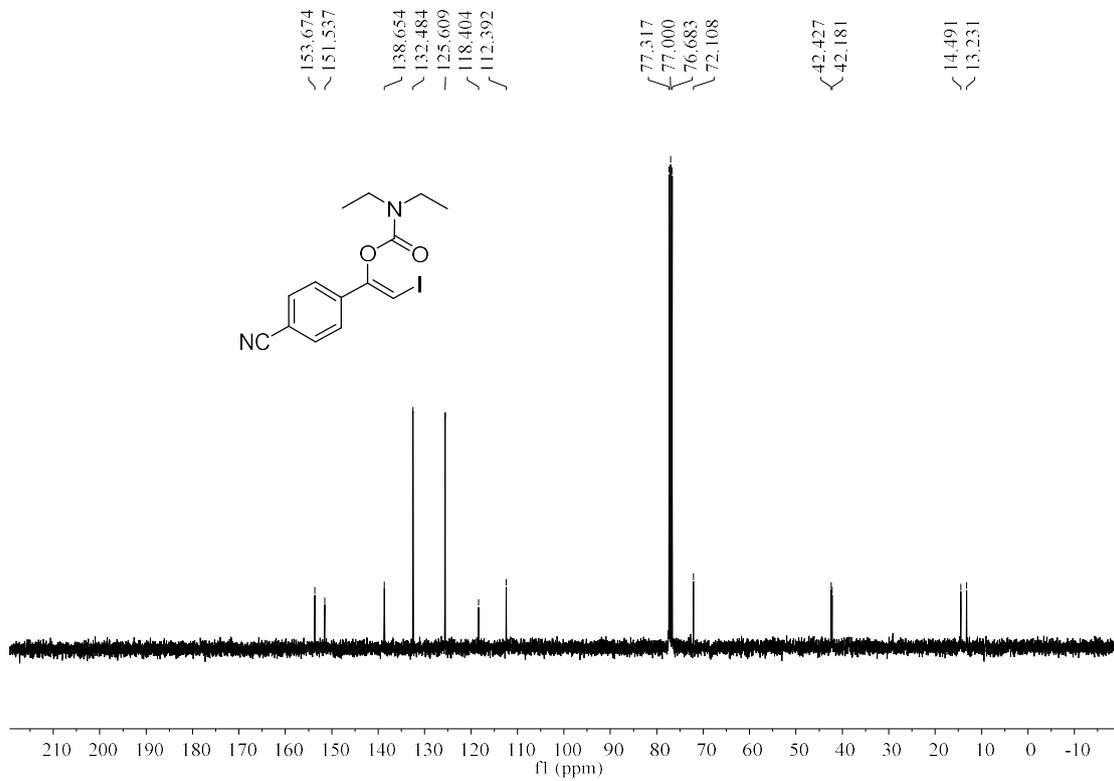
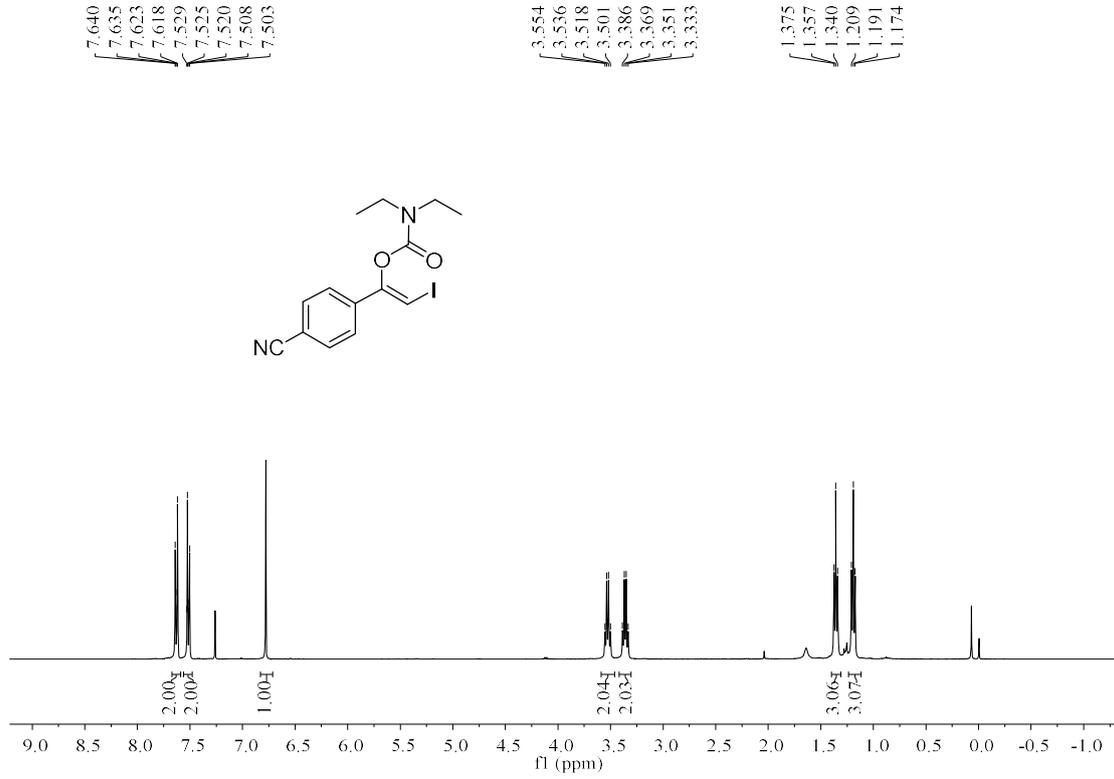




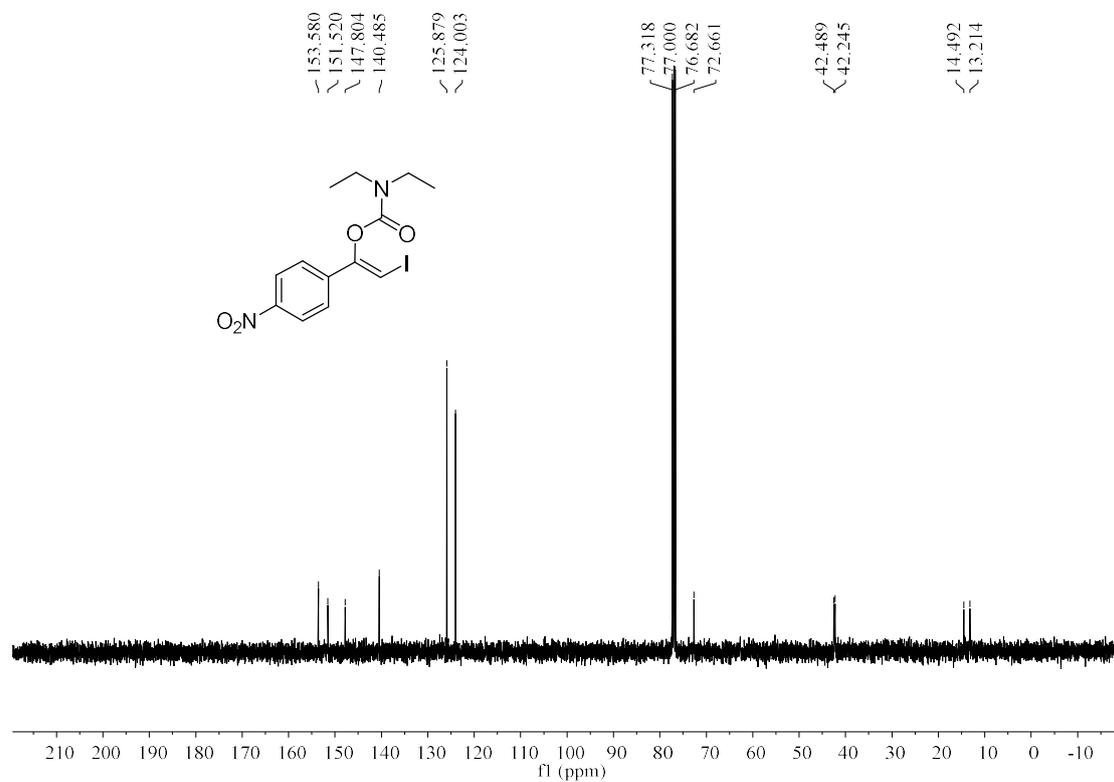
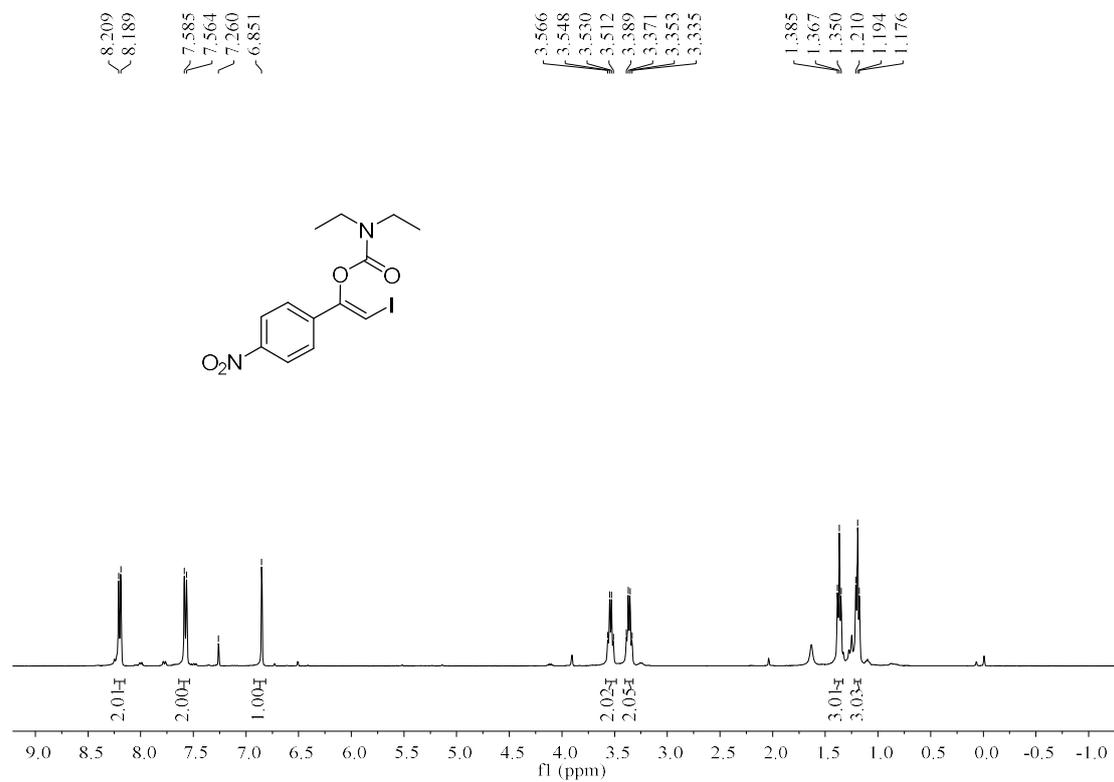
**(Z)-1-(4-Chlorophenyl)-2-iodovinyl diethylcarbamate ((Z)-3da)**



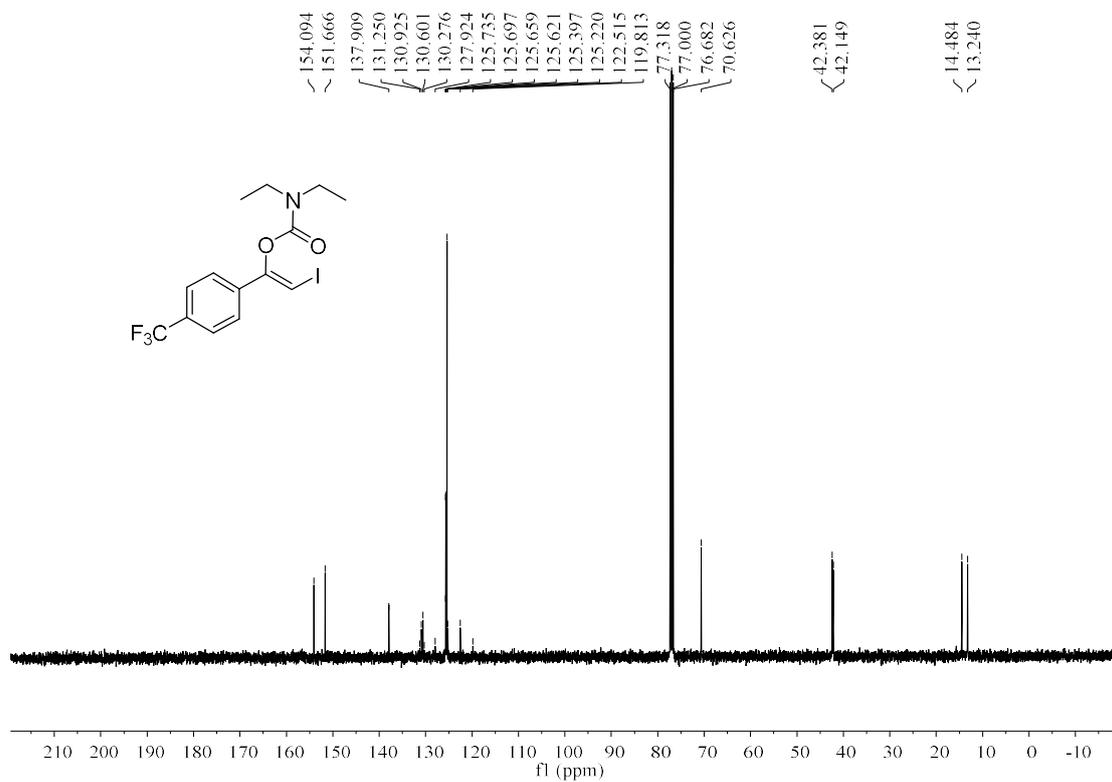
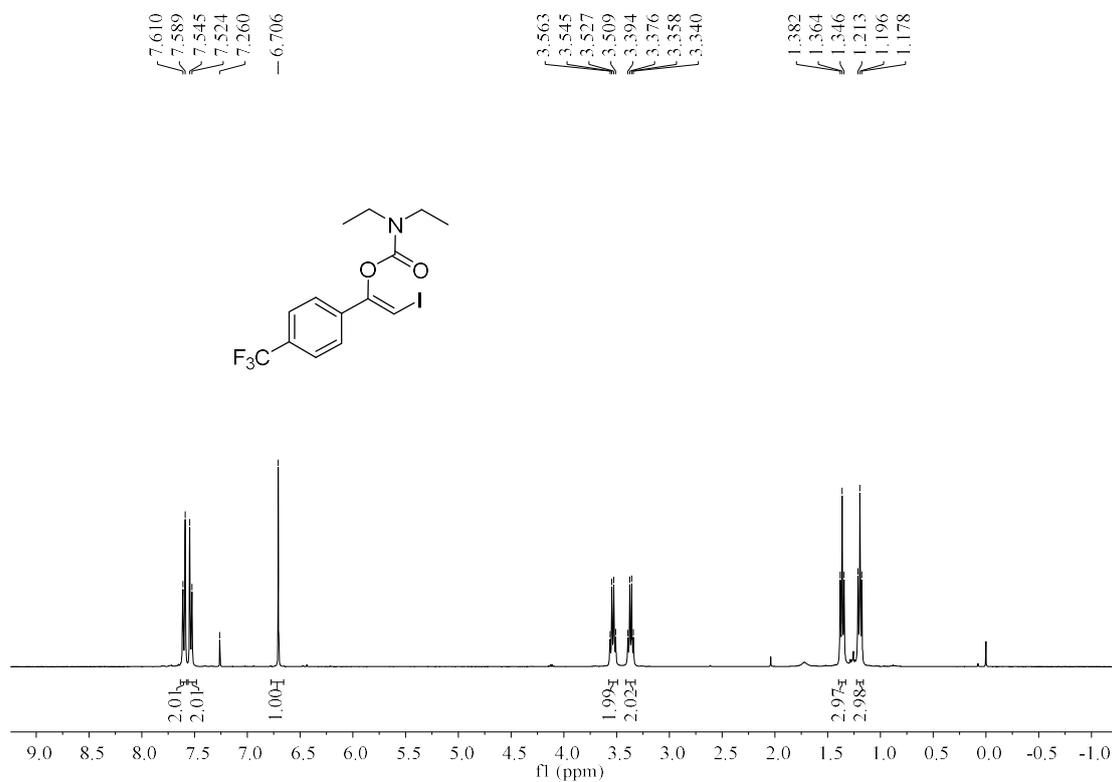
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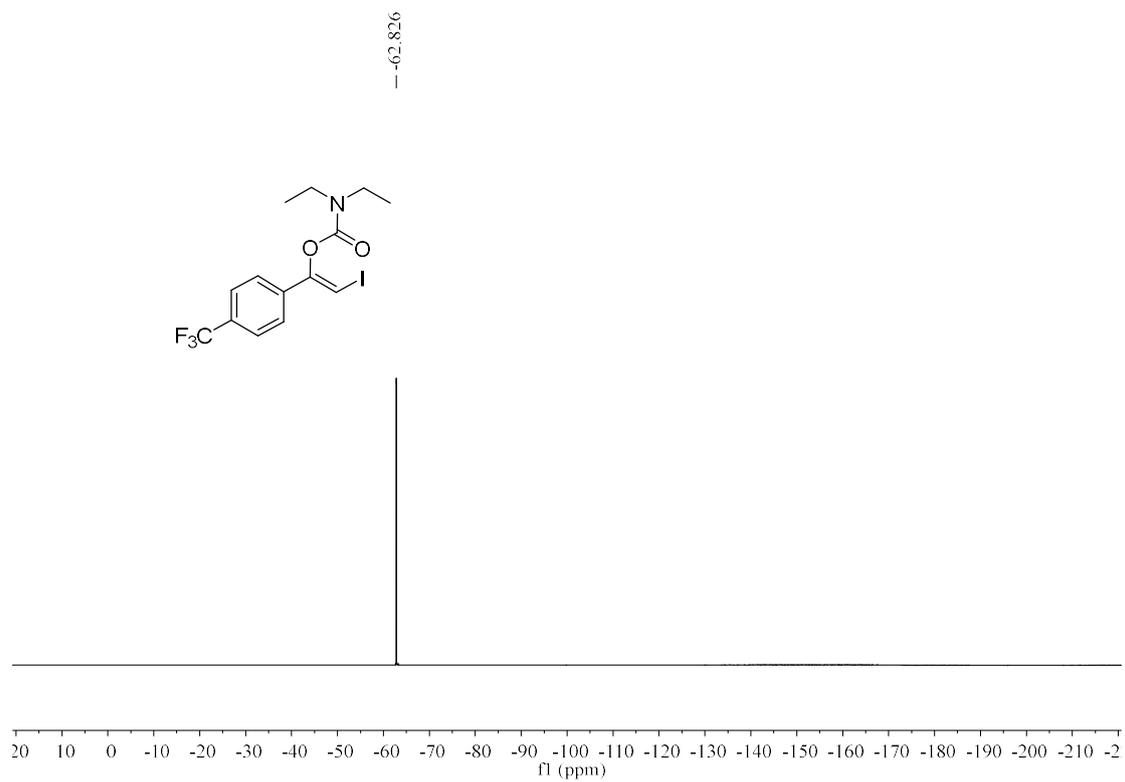


**(Z)-2-Iodo-1-(4-nitrophenyl)vinyl diethylcarbamate ((Z)-3fa)**

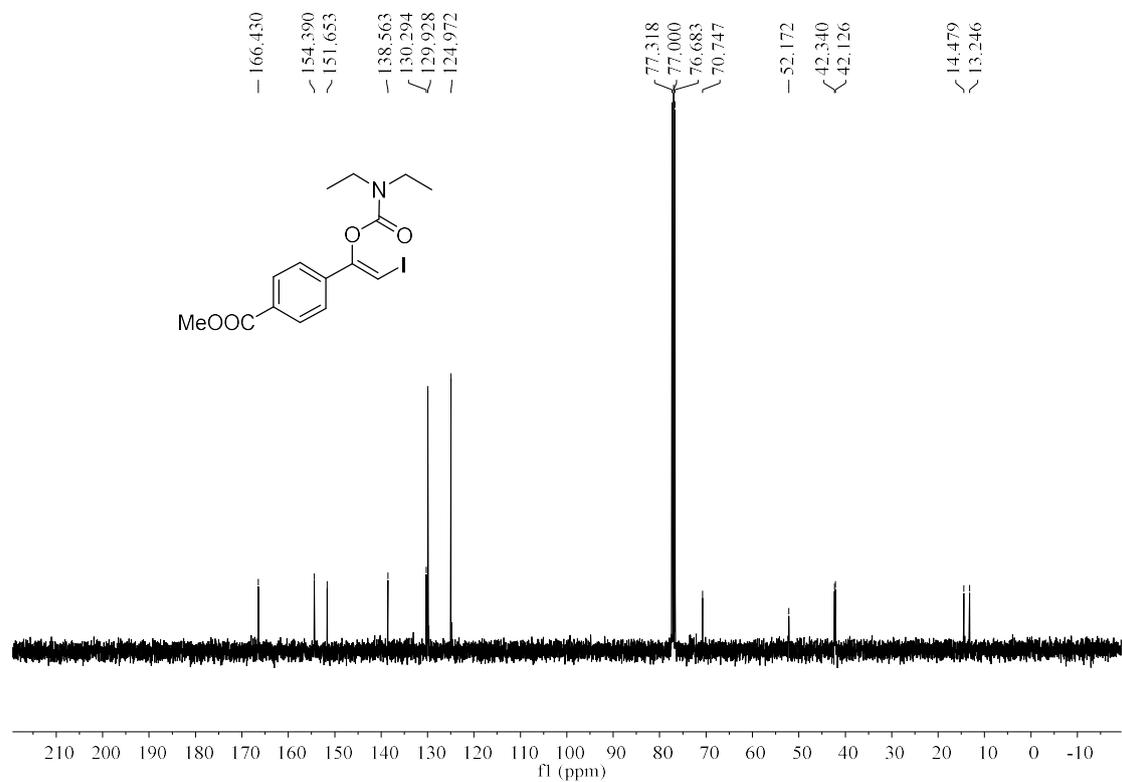
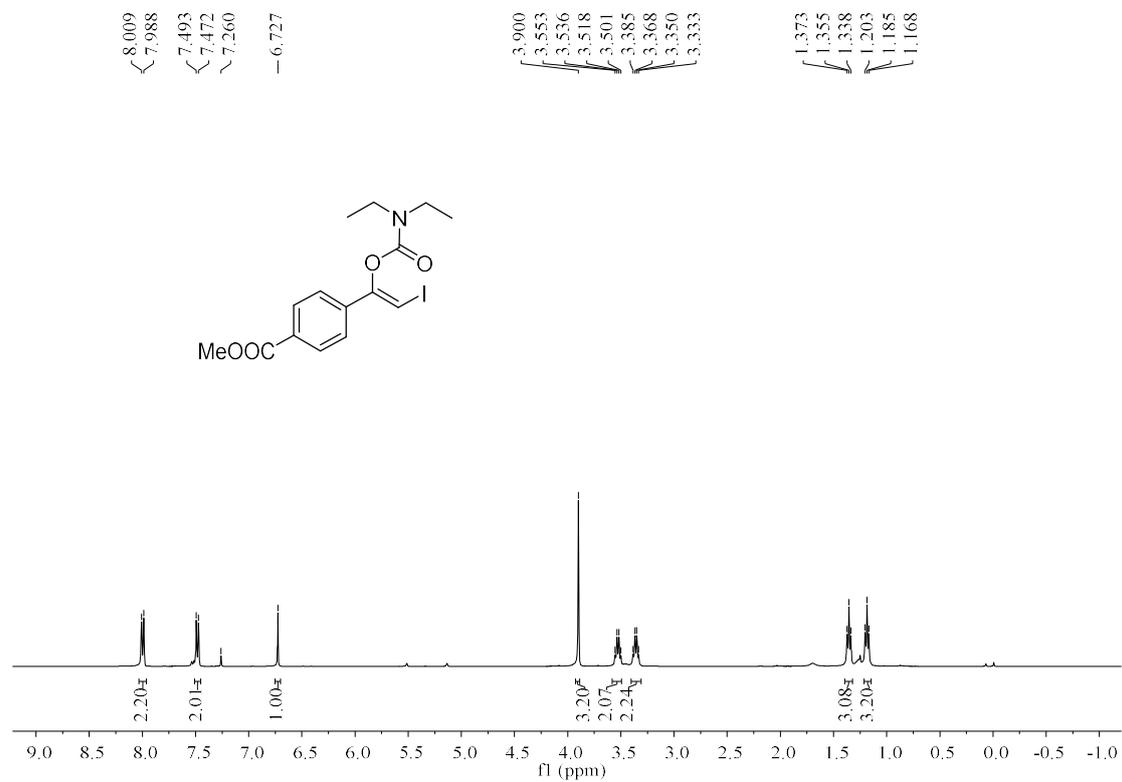


**(Z)-2-Iodo-1-(4-(trifluoromethyl)phenyl)vinyl diethylcarbamate ((Z)-3ga)**

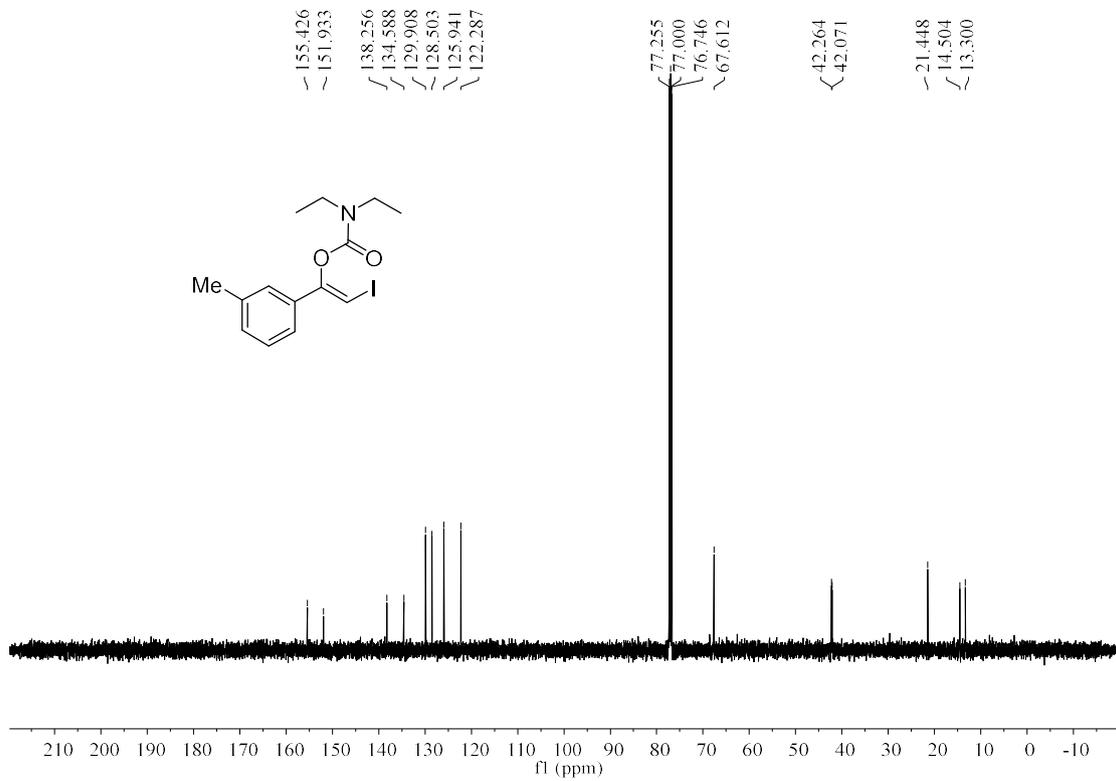
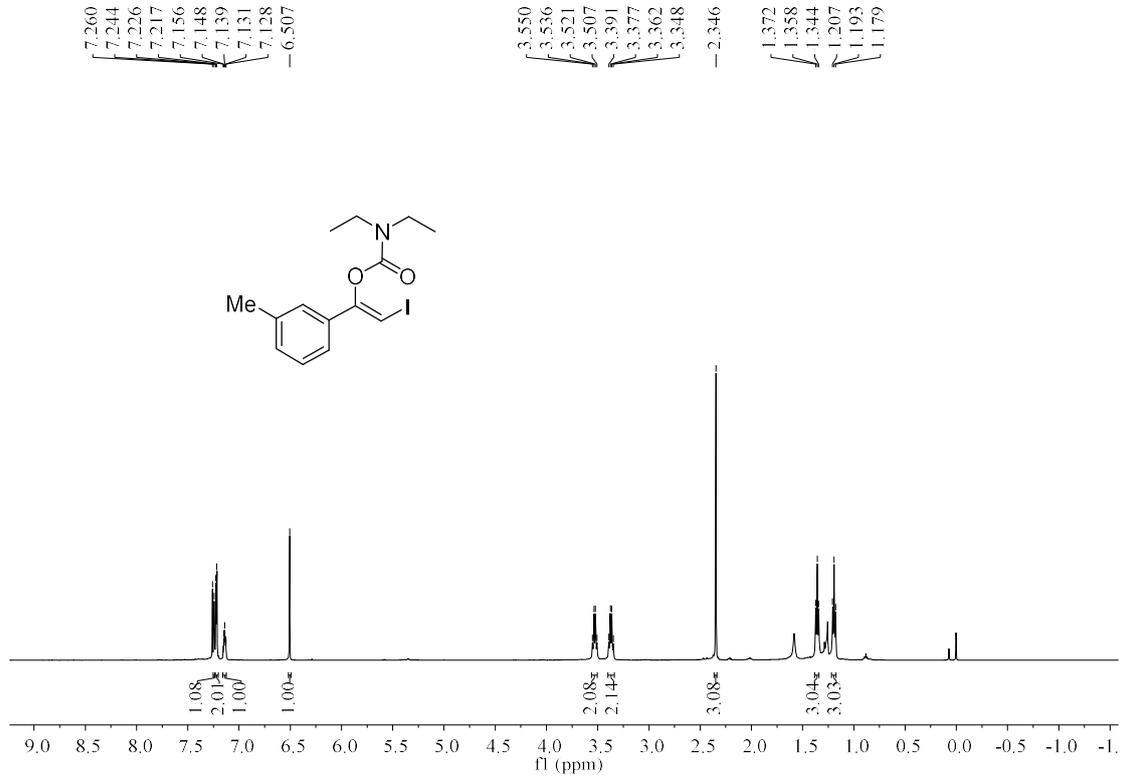




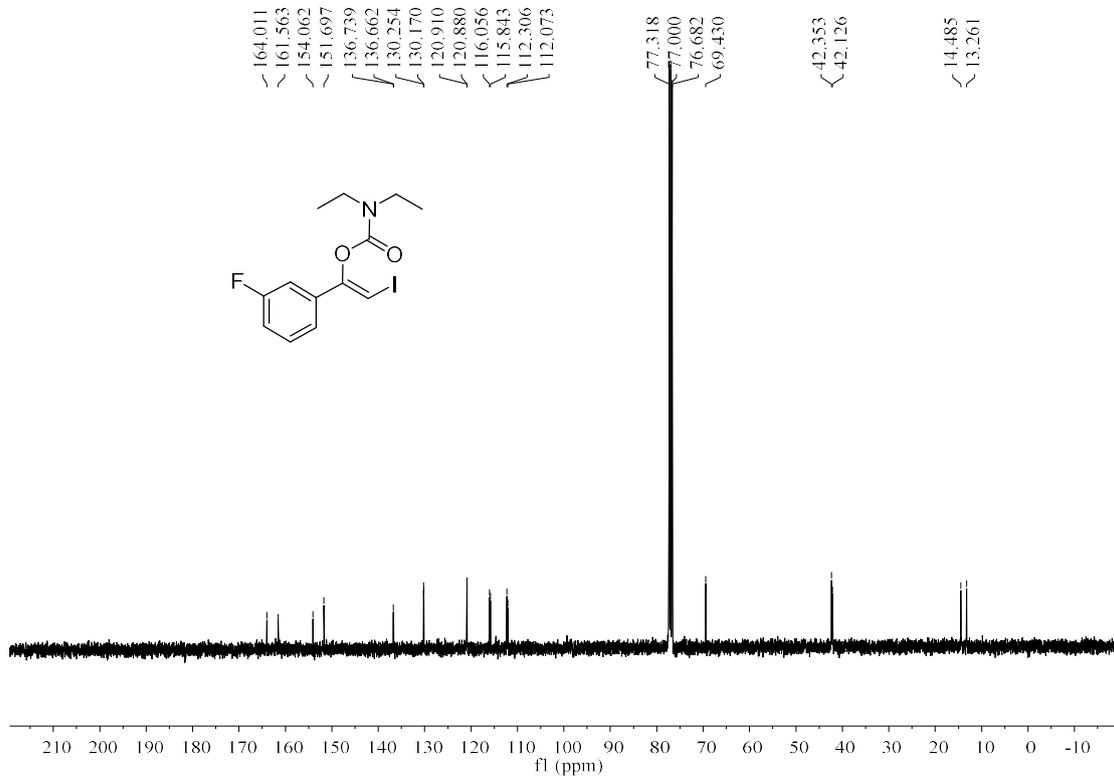
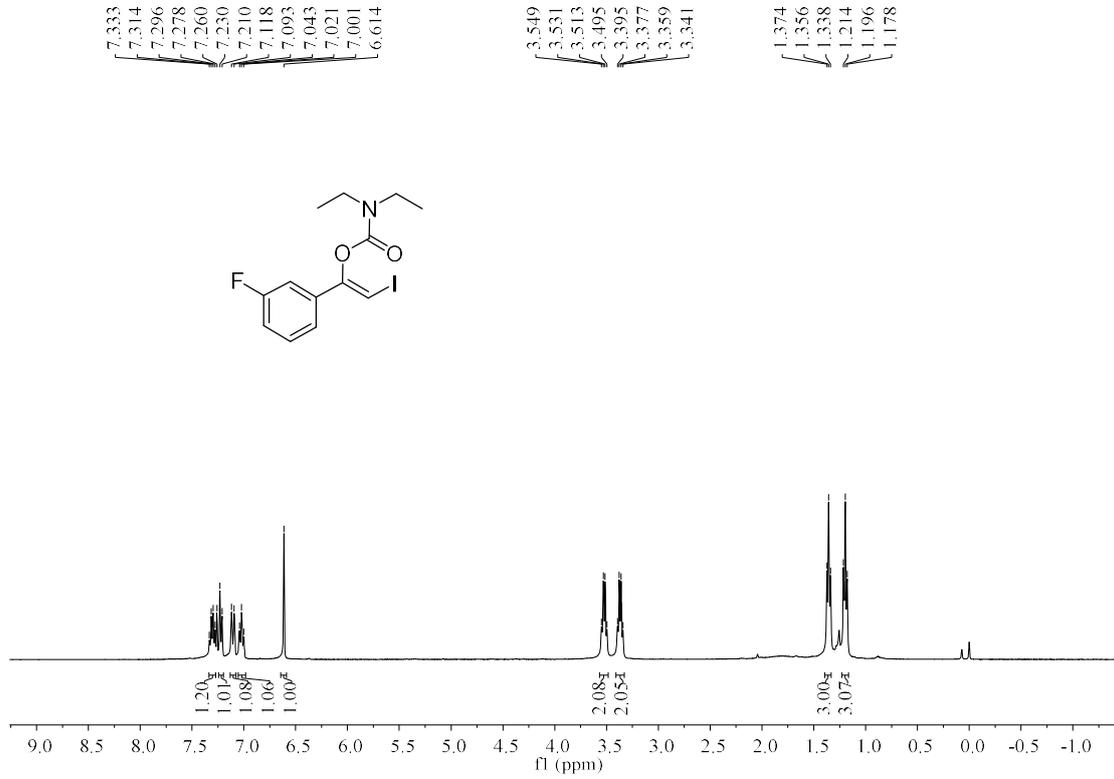
Methyl (Z)-4-(1-((diethylcarbamoyloxy)-2-iodovinyl)benzoate ((Z)-3ha)

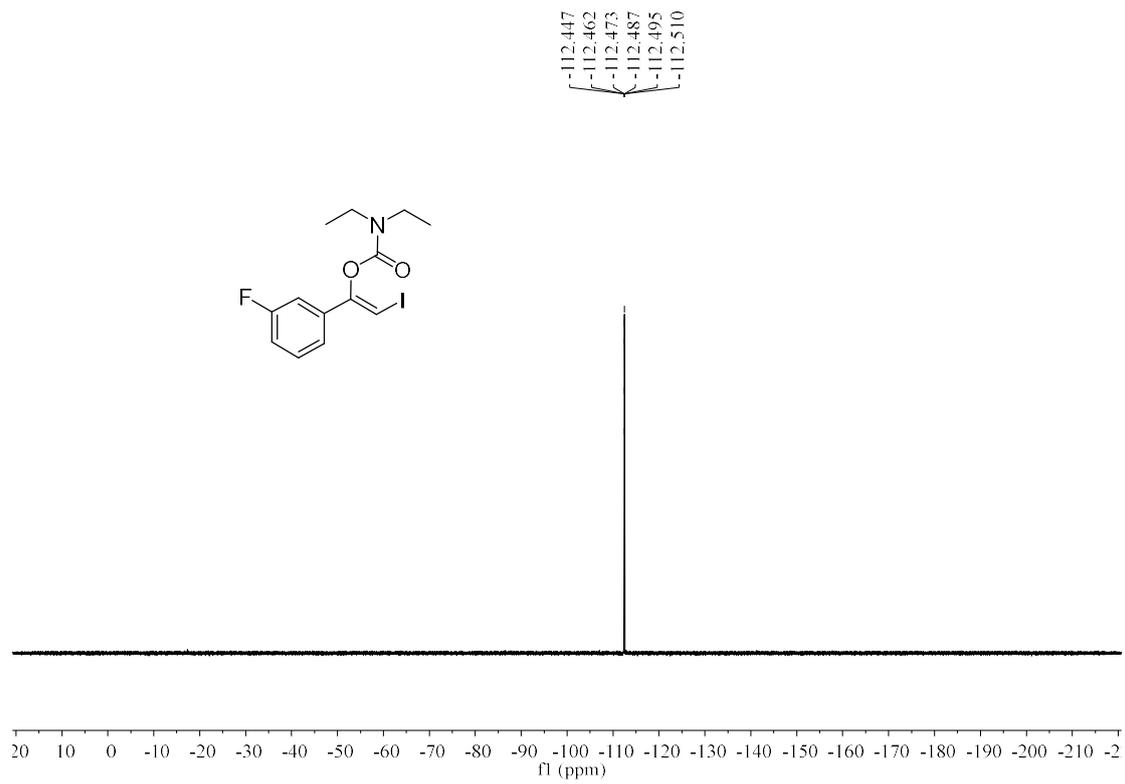


**(Z)-2-Iodo-1-(*m*-tolyl)vinyl diethylcarbamate ((Z)-3ia)**

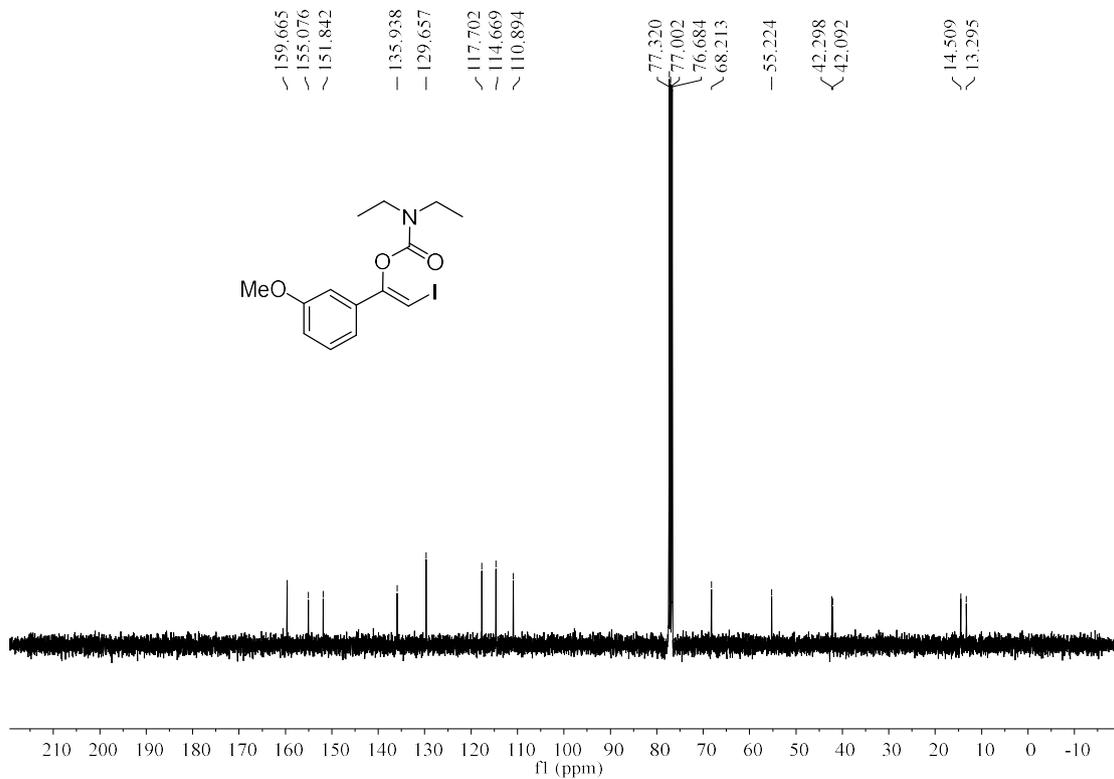
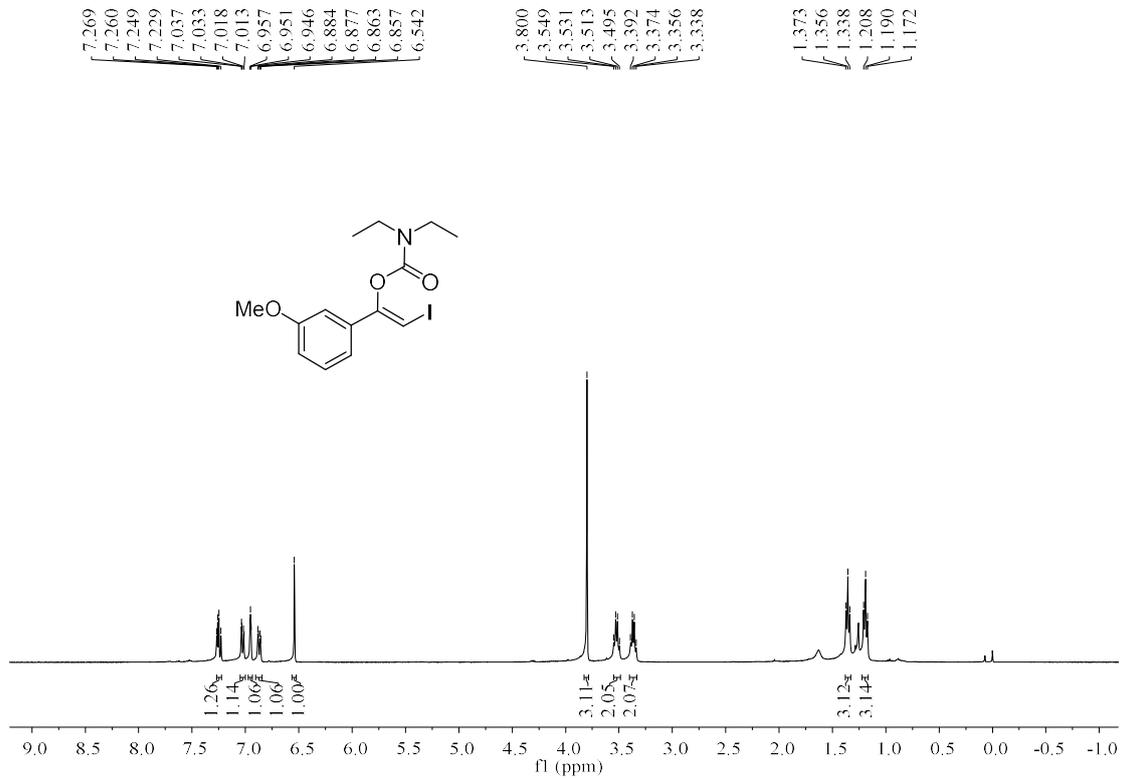


**(Z)-1-(3-Fluorophenyl)-2-iodovinyl diethylcarbamate ((Z)-3ja)**

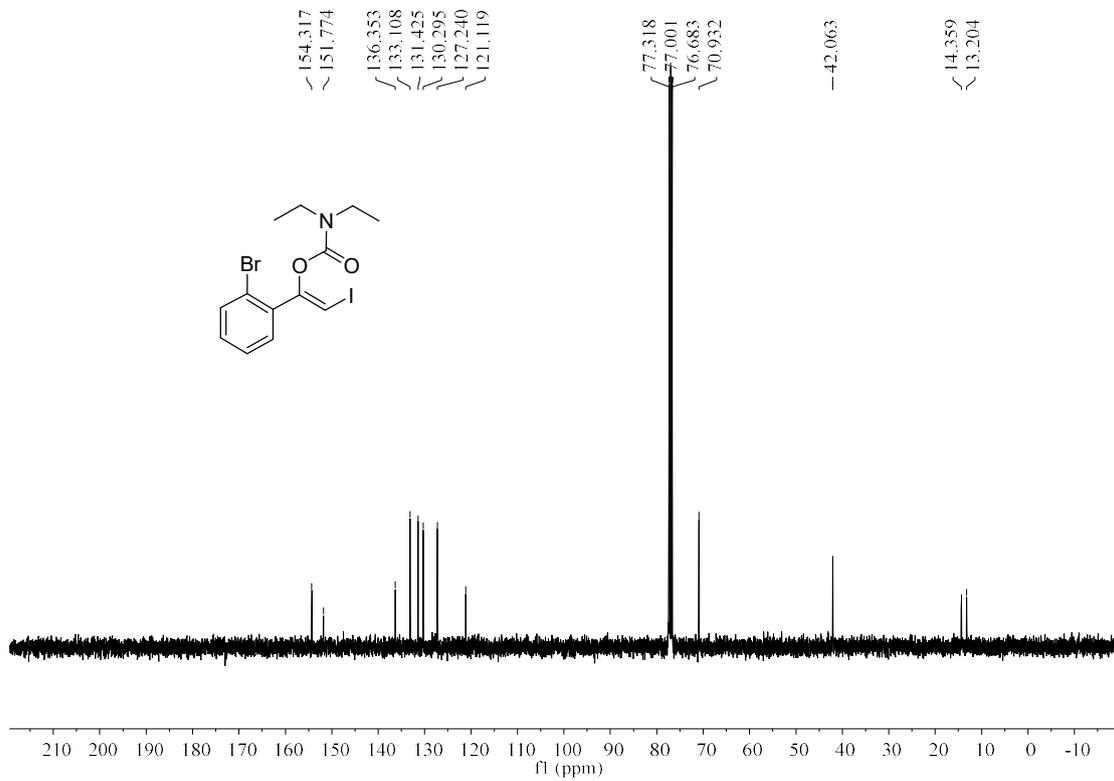
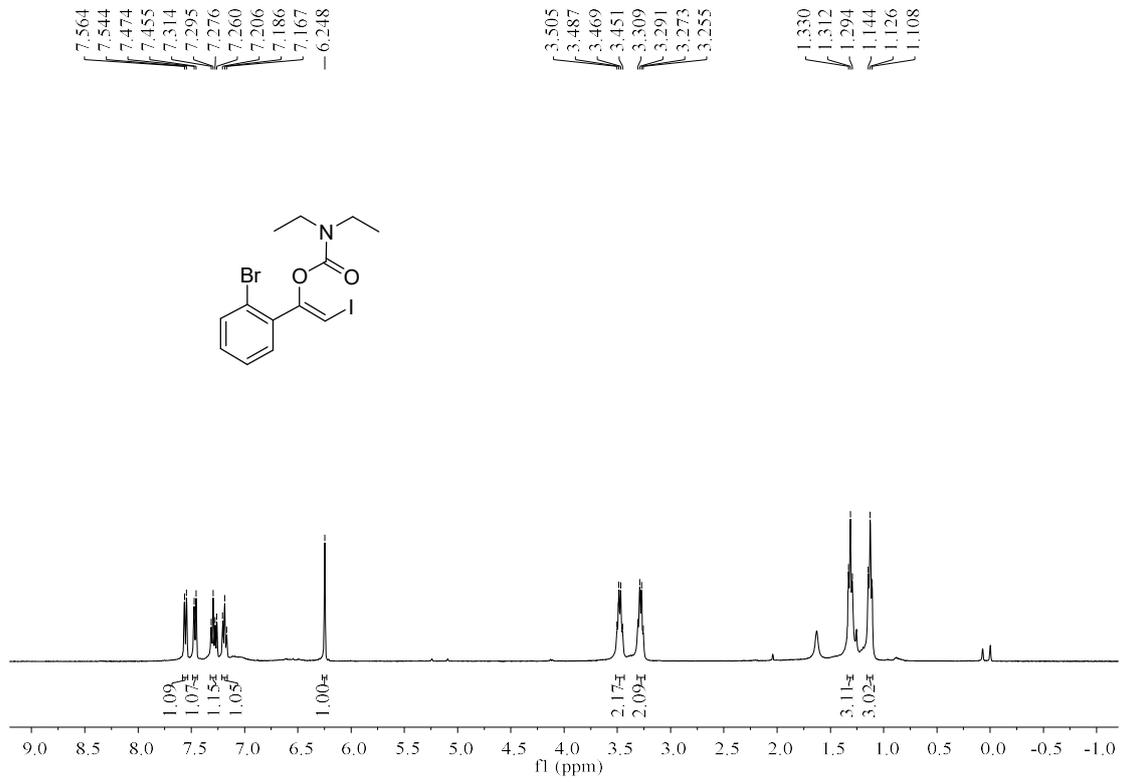




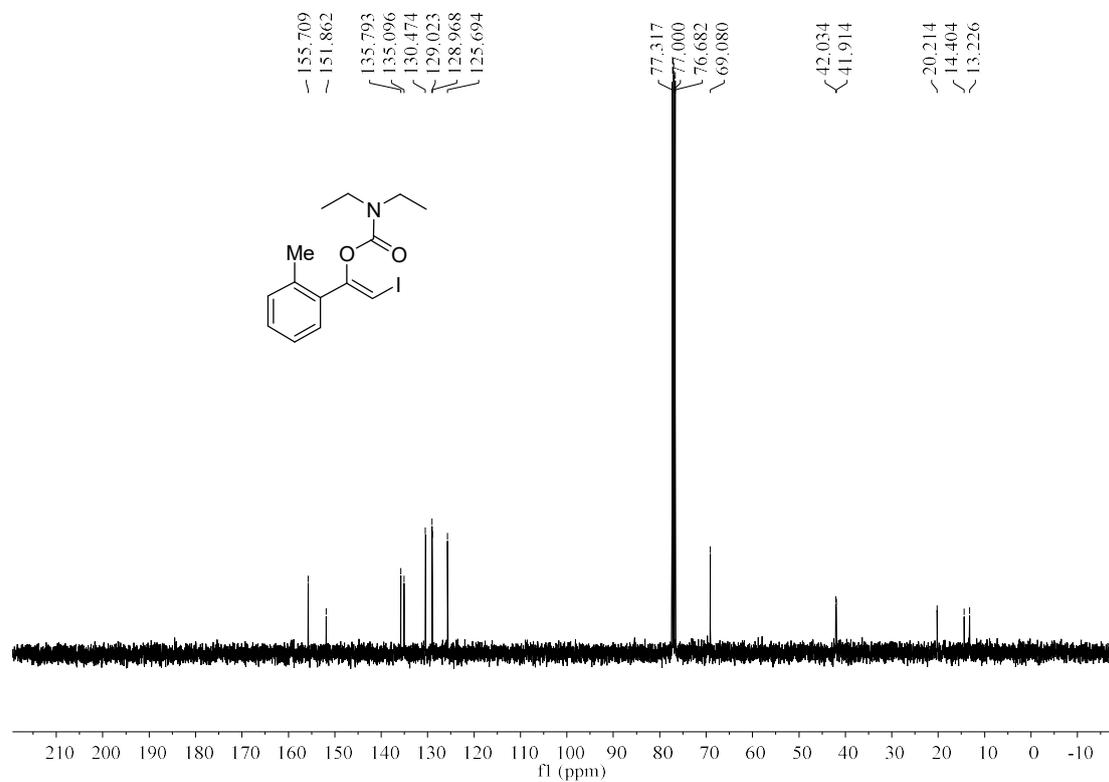
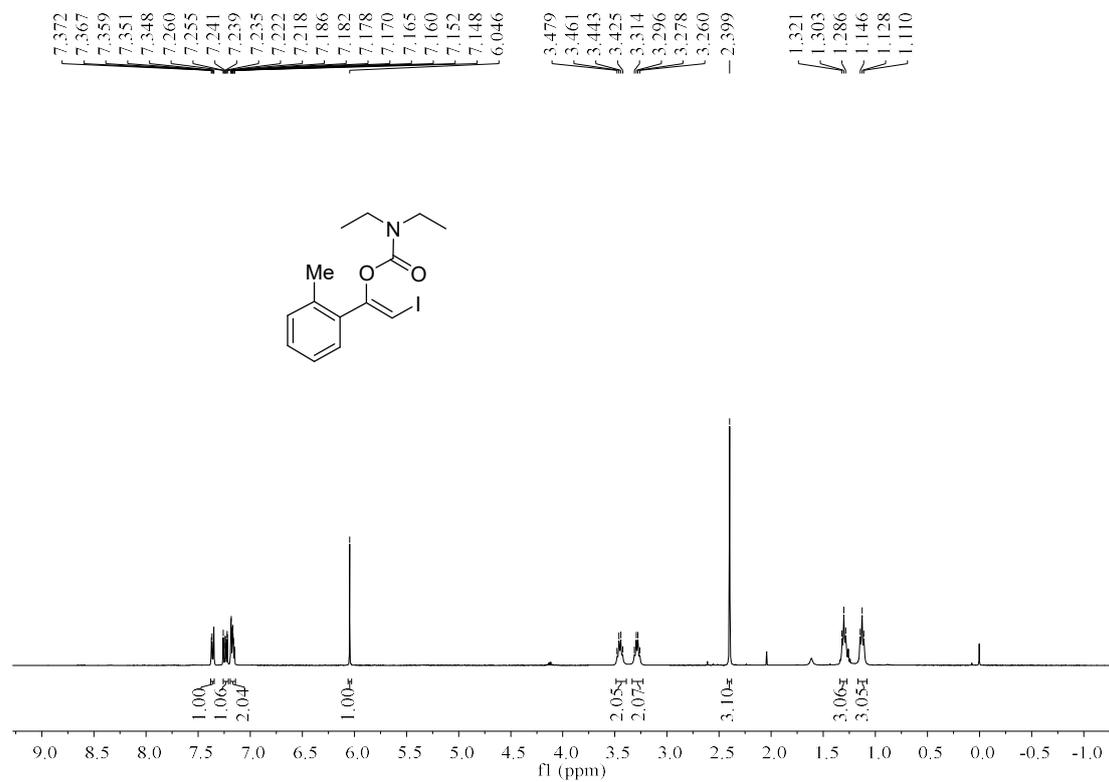
**(Z)-2-Iodo-1-(3-methoxyphenyl)vinyl diethylcarbamate ((Z)-3ka)**



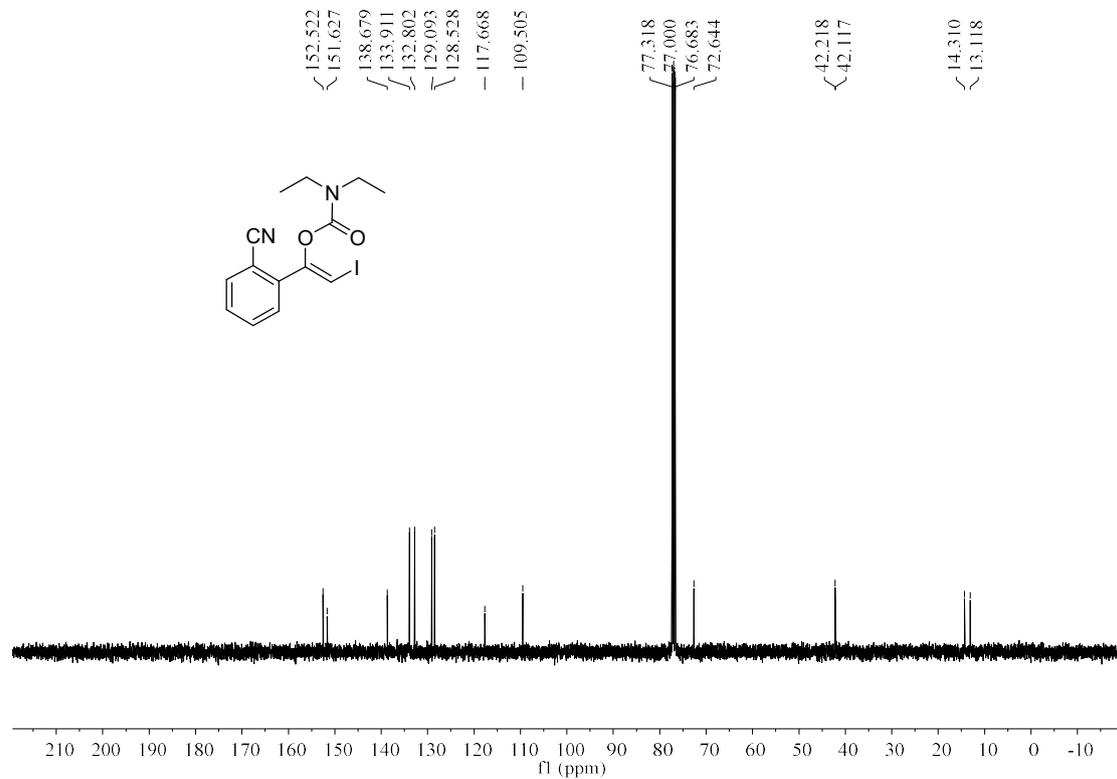
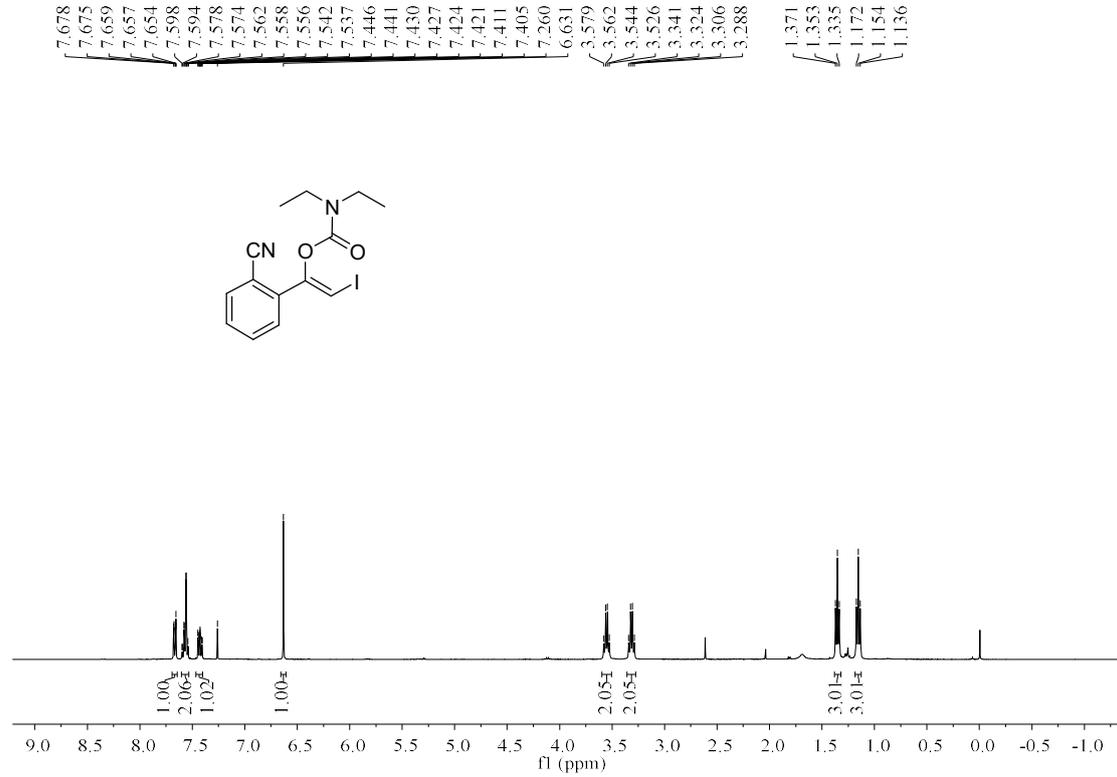
**(Z)-1-(2-Bromophenyl)-2-iodovinyl diethylcarbamate ((Z)-3la)**



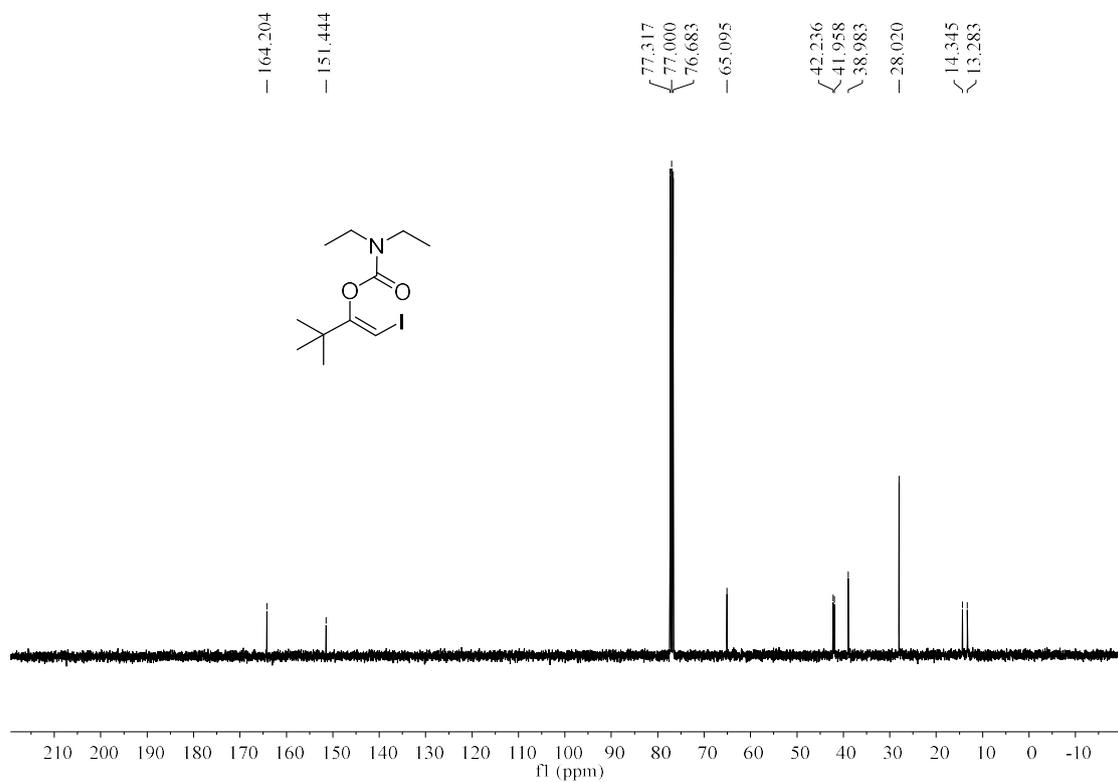
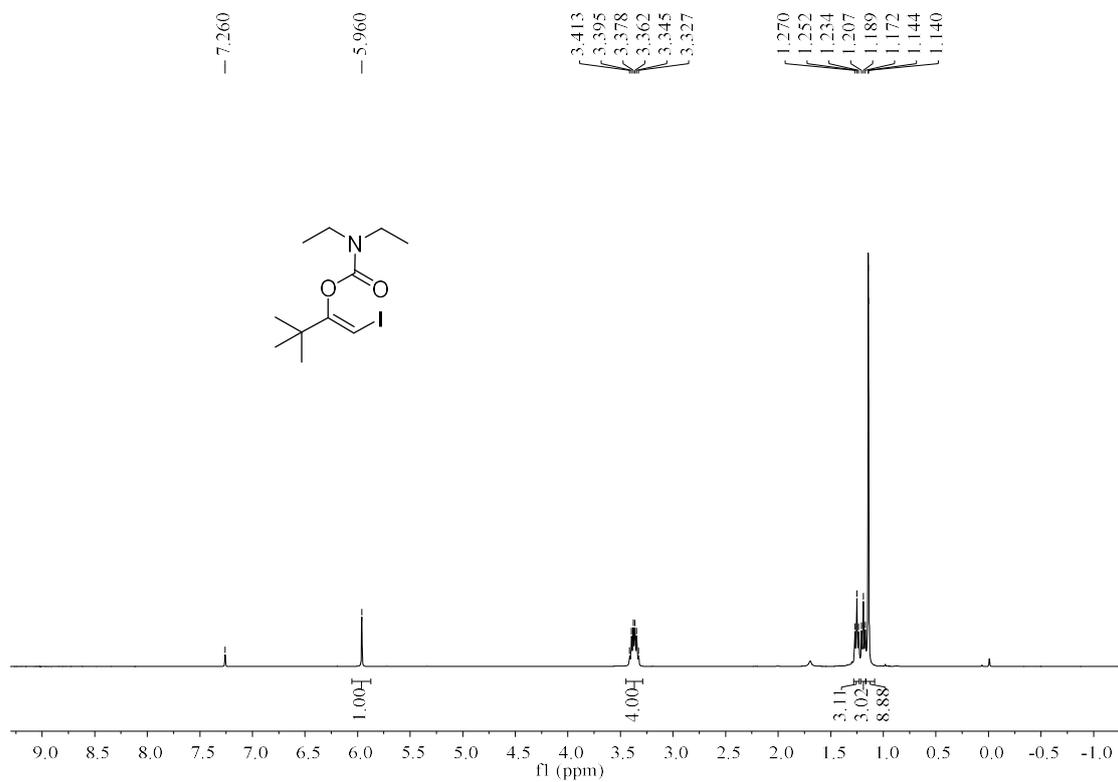
**(Z)-2-Iodo-1-(*o*-tolyl)vinyl diethylcarbamate ((Z)-3ma)**



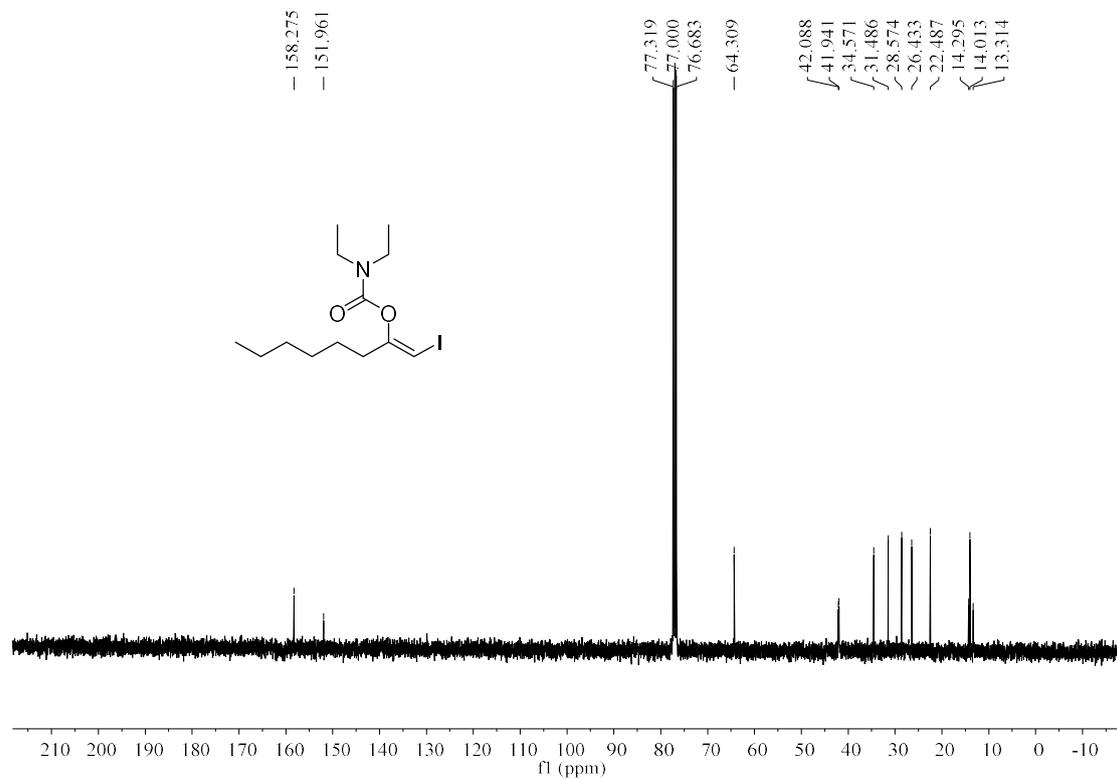
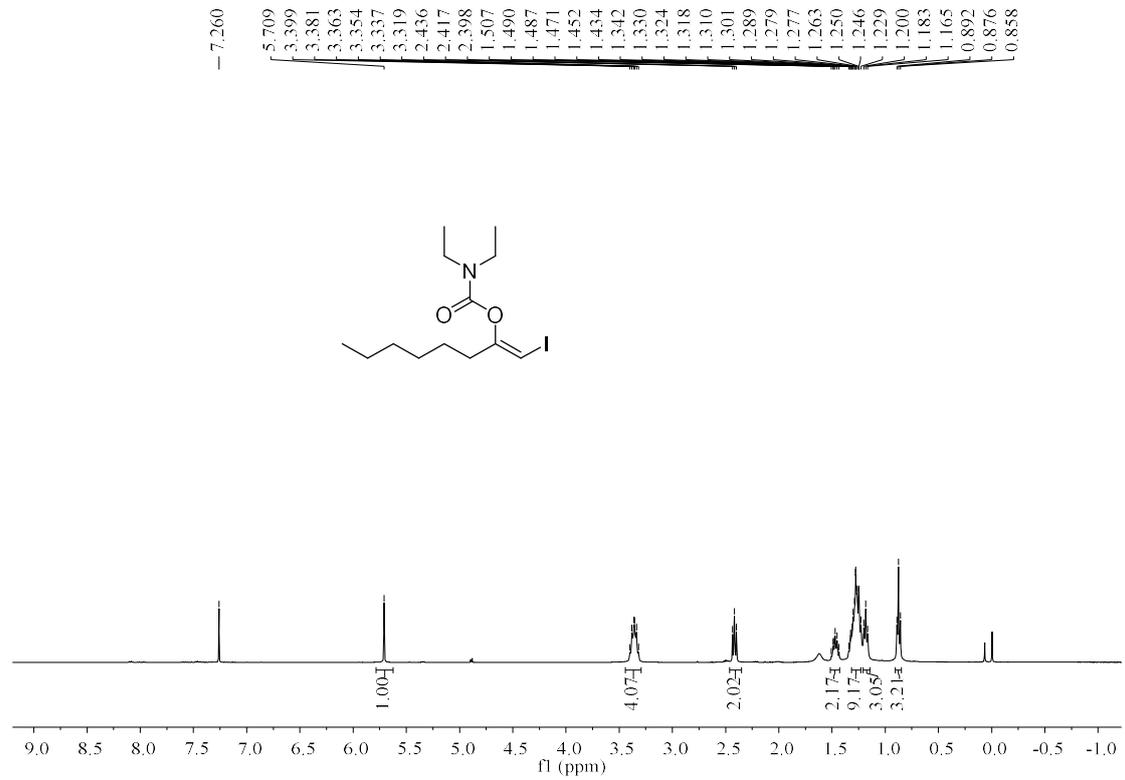
**(Z)-1-(2-Cyanophenyl)-2-iodovinyl diethylcarbamate ((Z)-3na)**



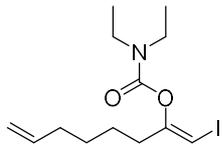
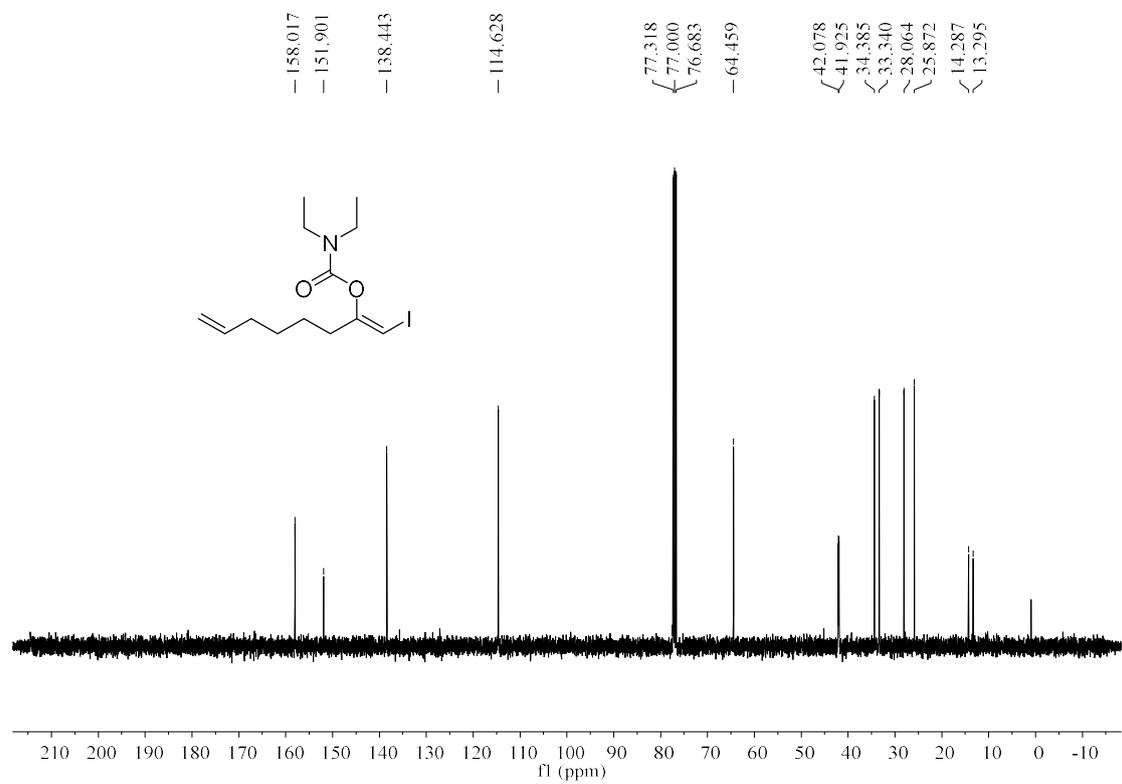
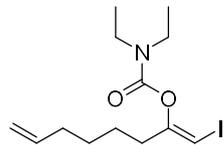
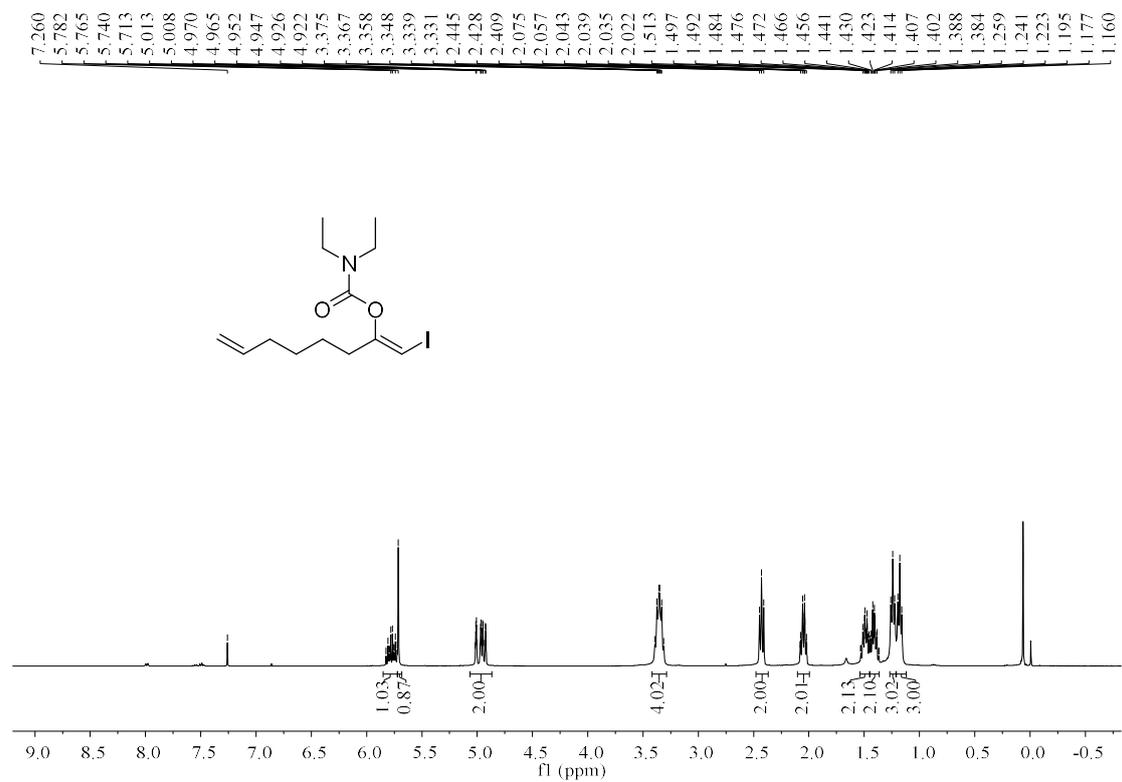
**(Z)-1-Iodo-3,3-dimethylbut-1-en-2-yl diethylcarbamate ((Z)-30a)**



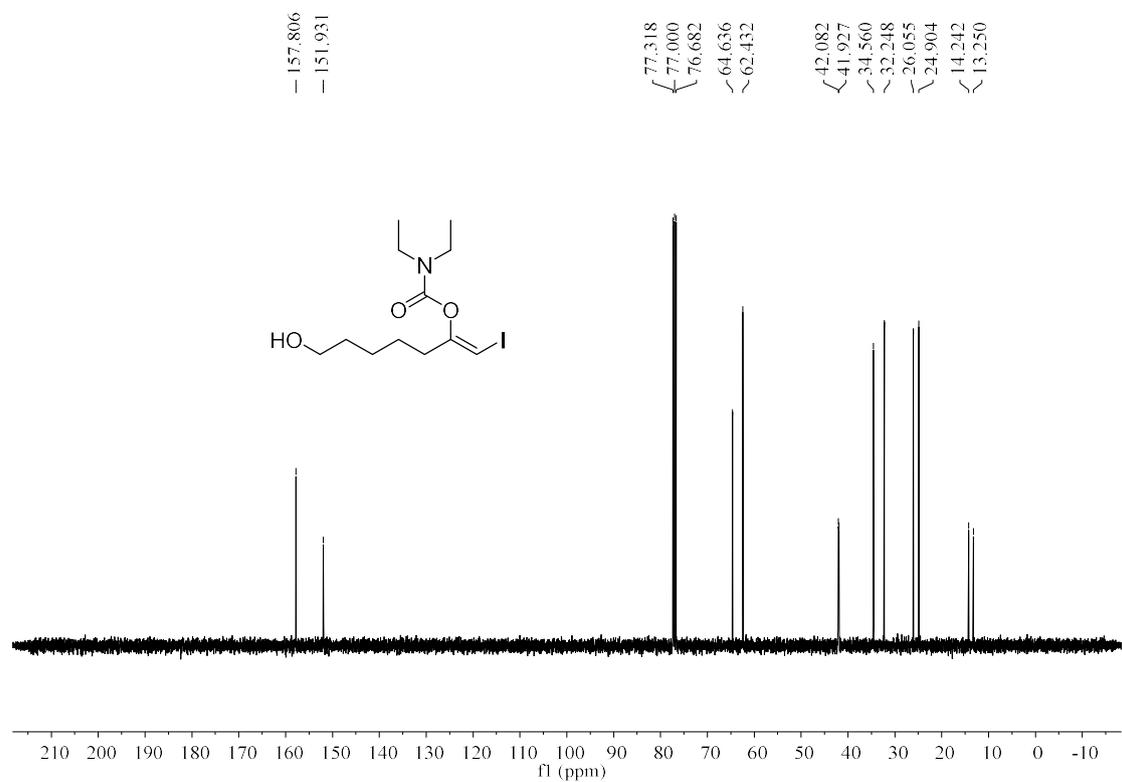
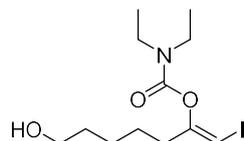
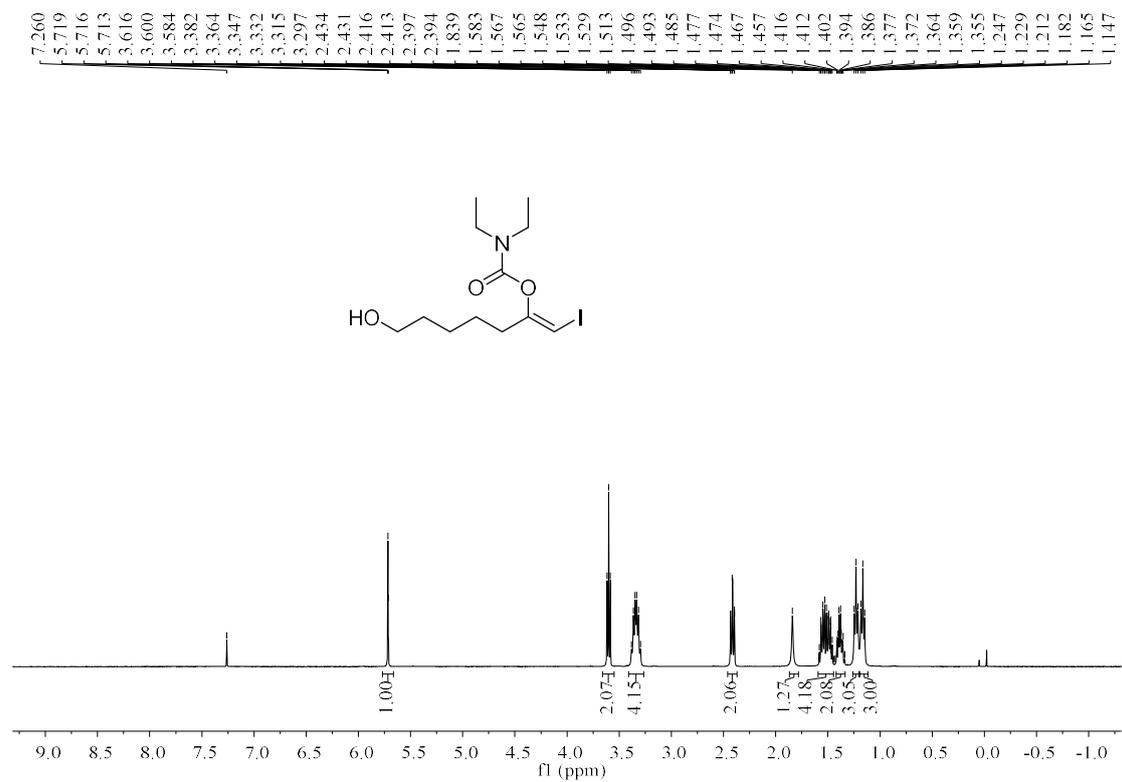
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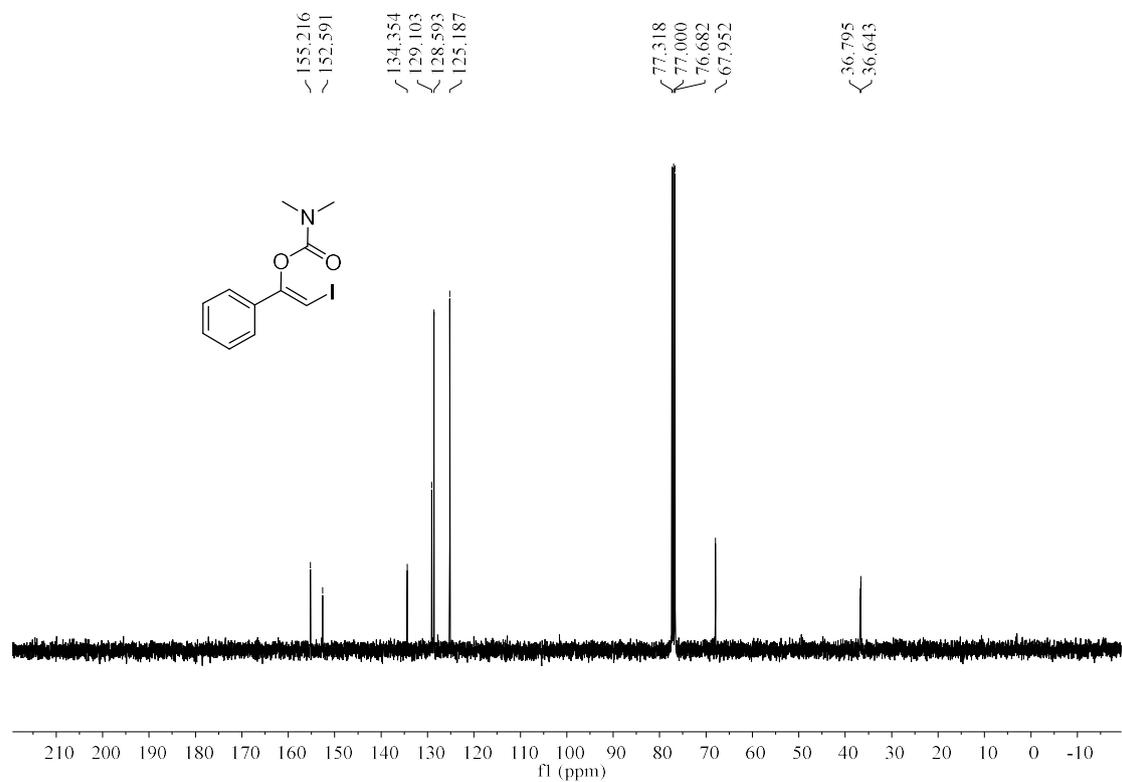
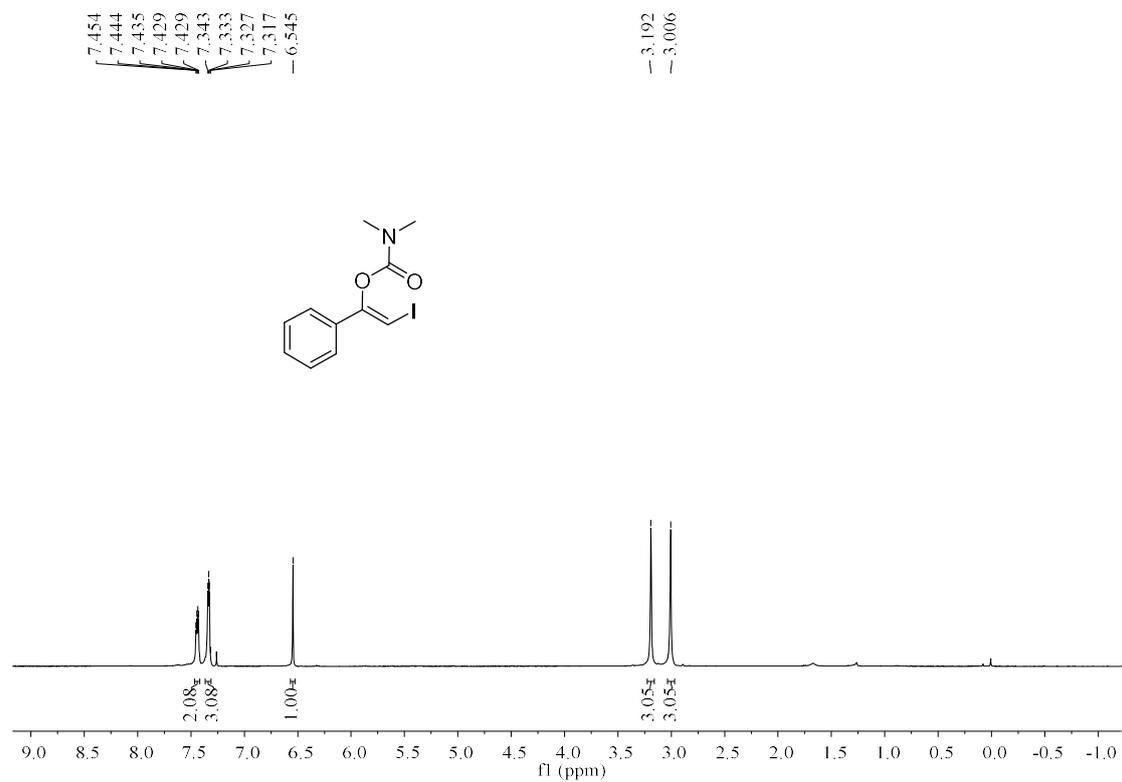
**(Z)-1-Iodoocta-1,7-dien-2-yl diethylcarbamate ((Z)-3qa)**



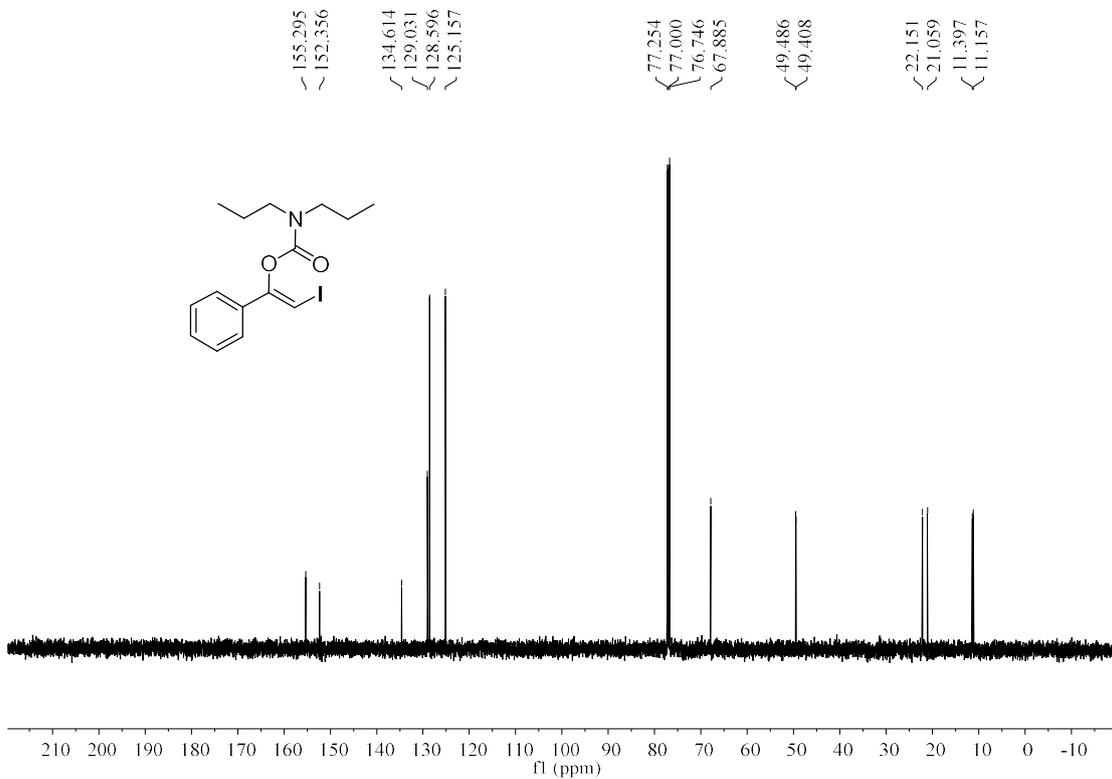
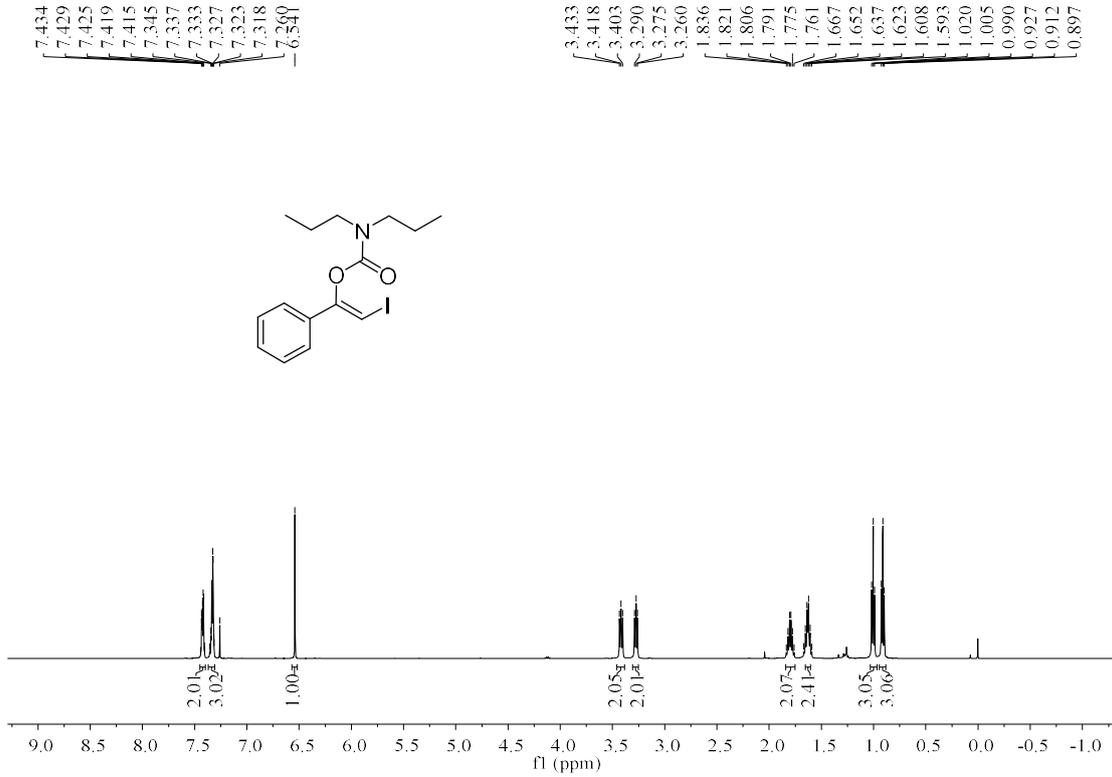
**(Z)-7-Hydroxy-1-iodohept-1-en-2-yl diethylcarbamate ((Z)-3ra)**



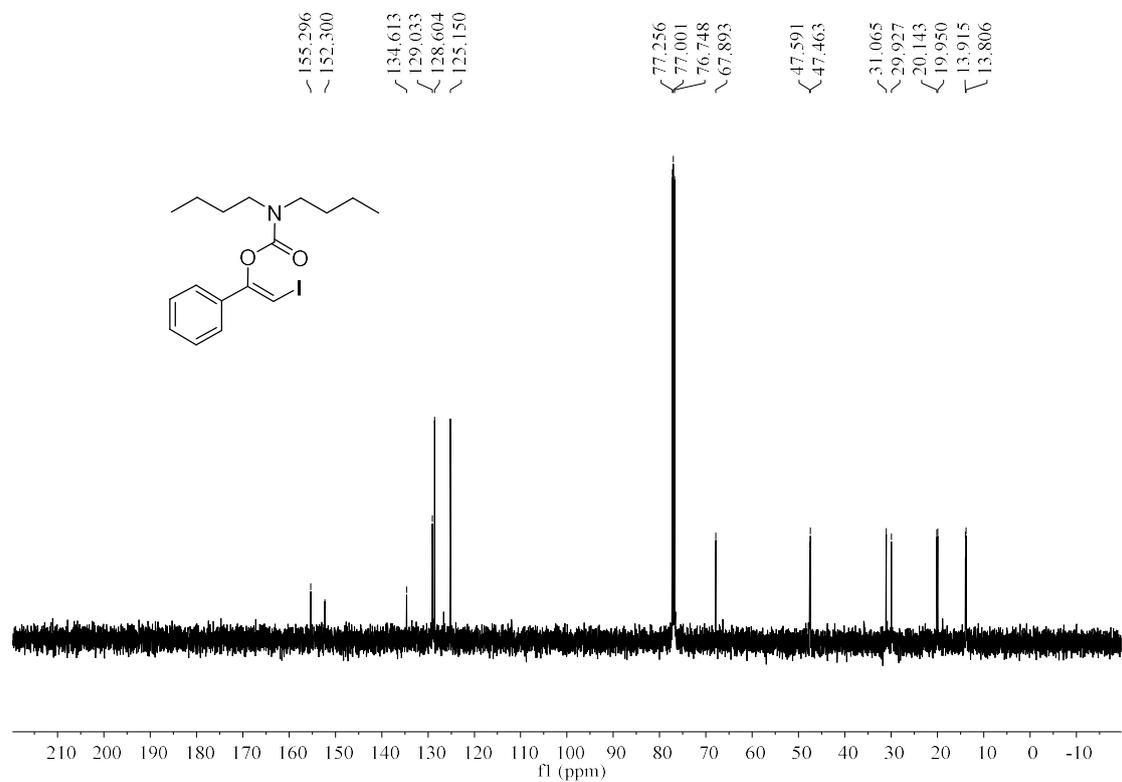
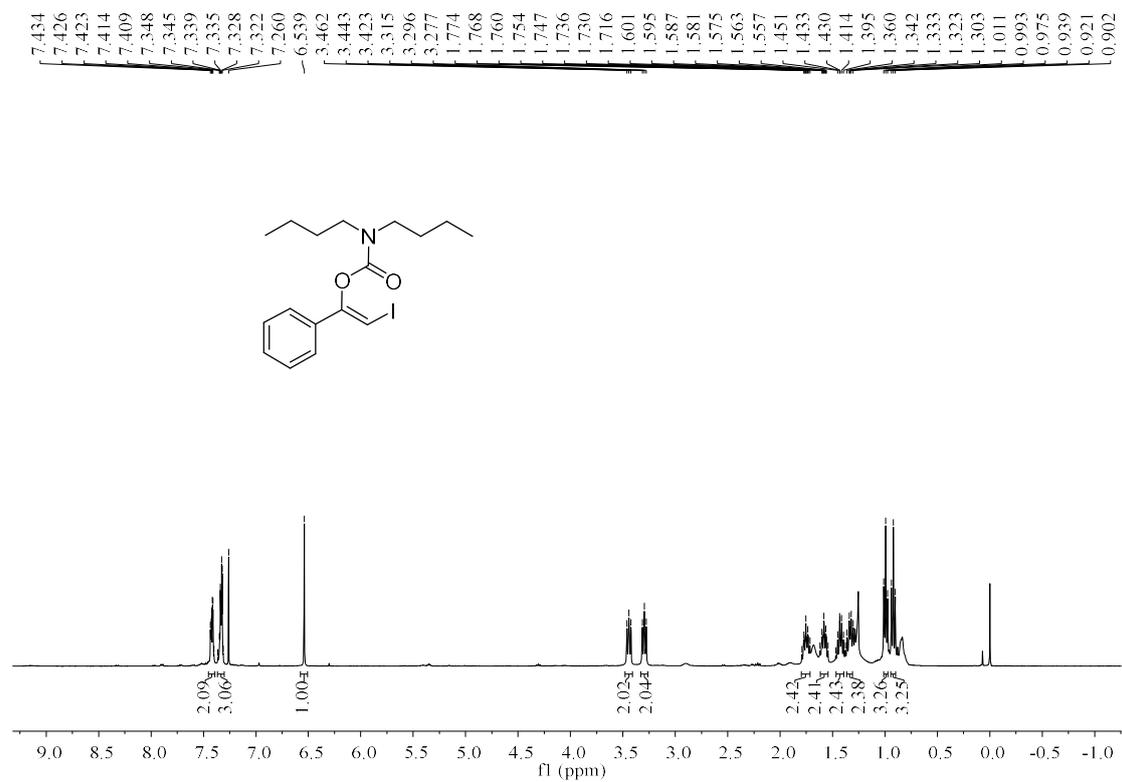
**(Z)-2-Iodo-1-phenylvinyl dimethylcarbamate ((Z)-3ab)**



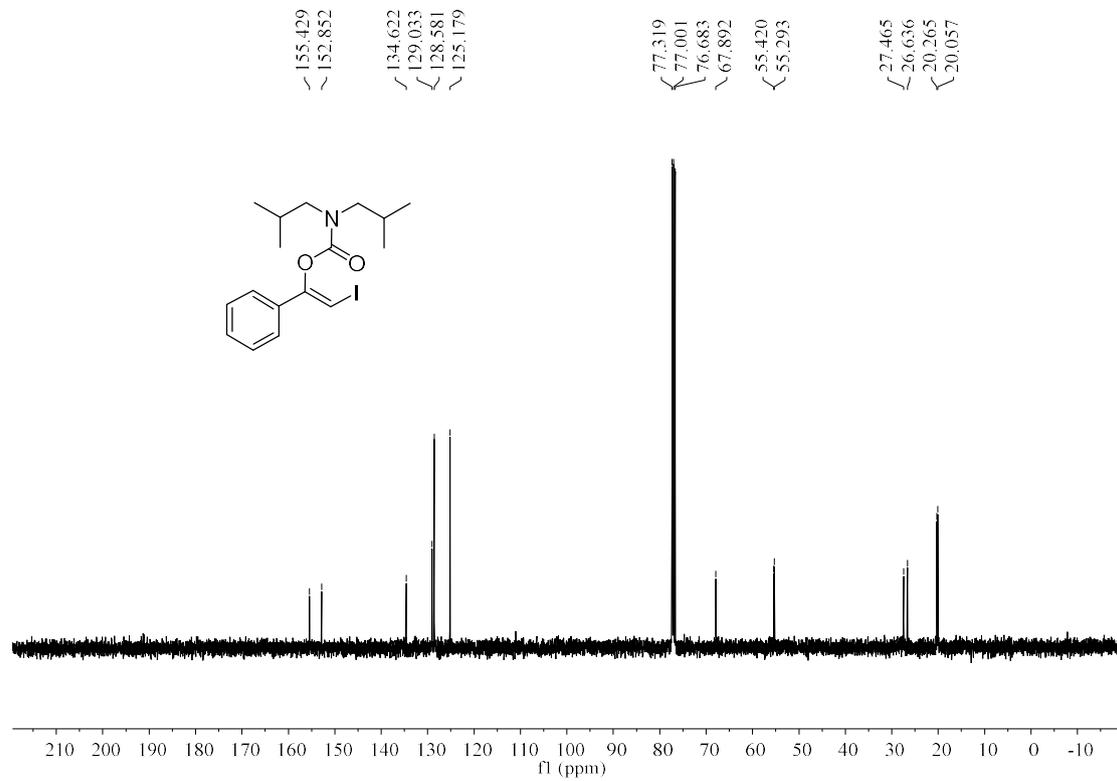
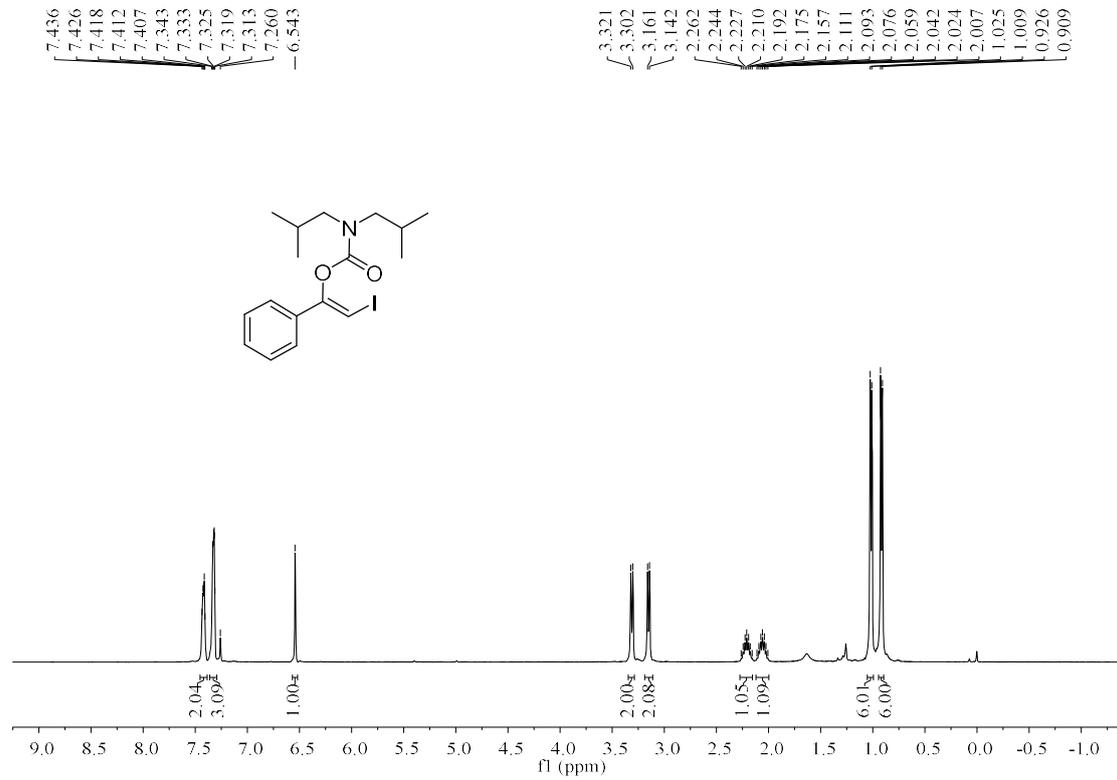
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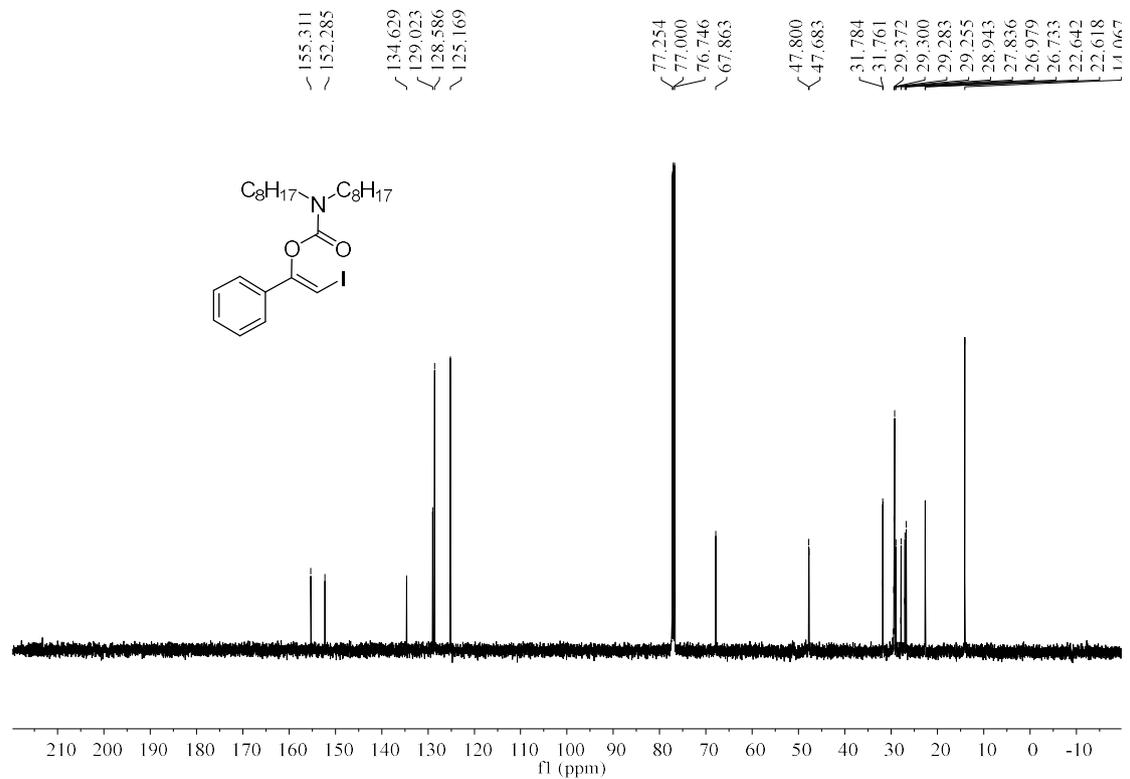
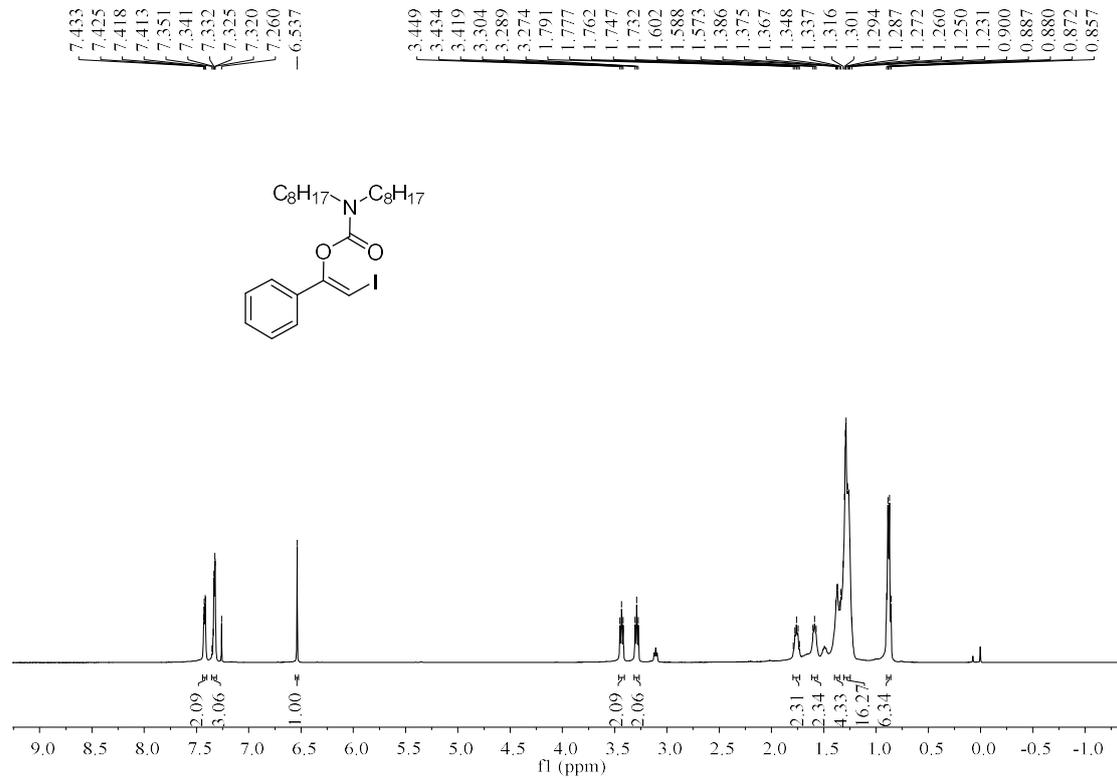
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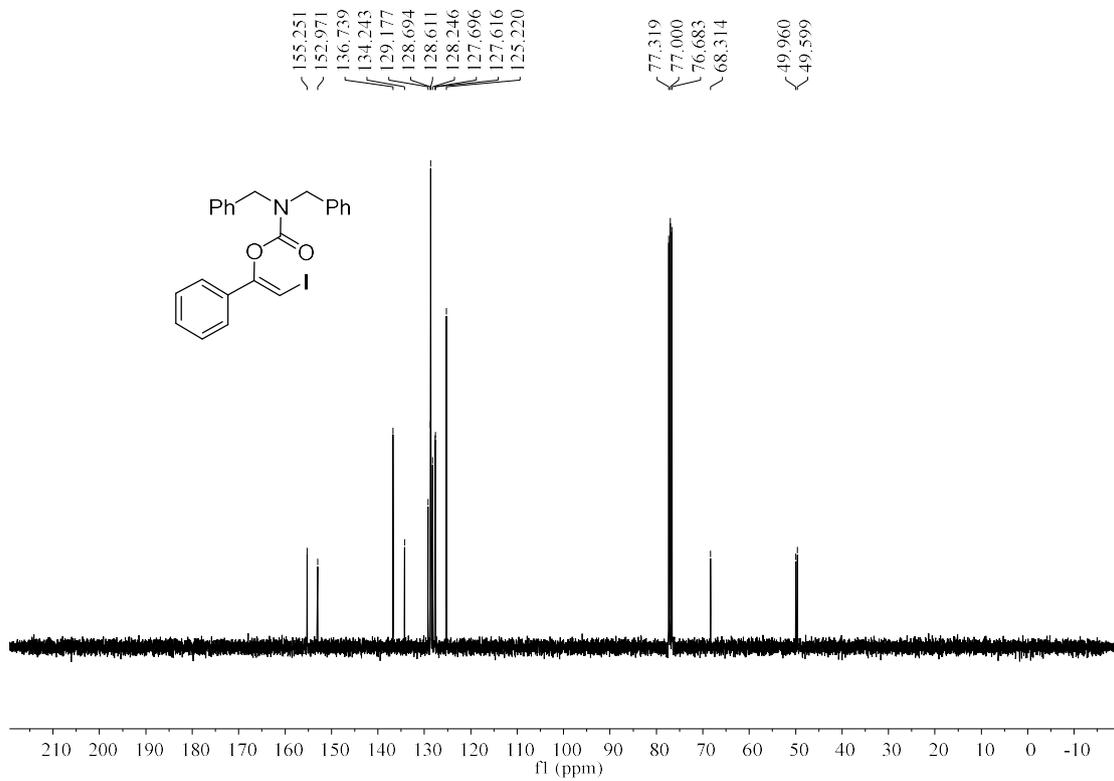
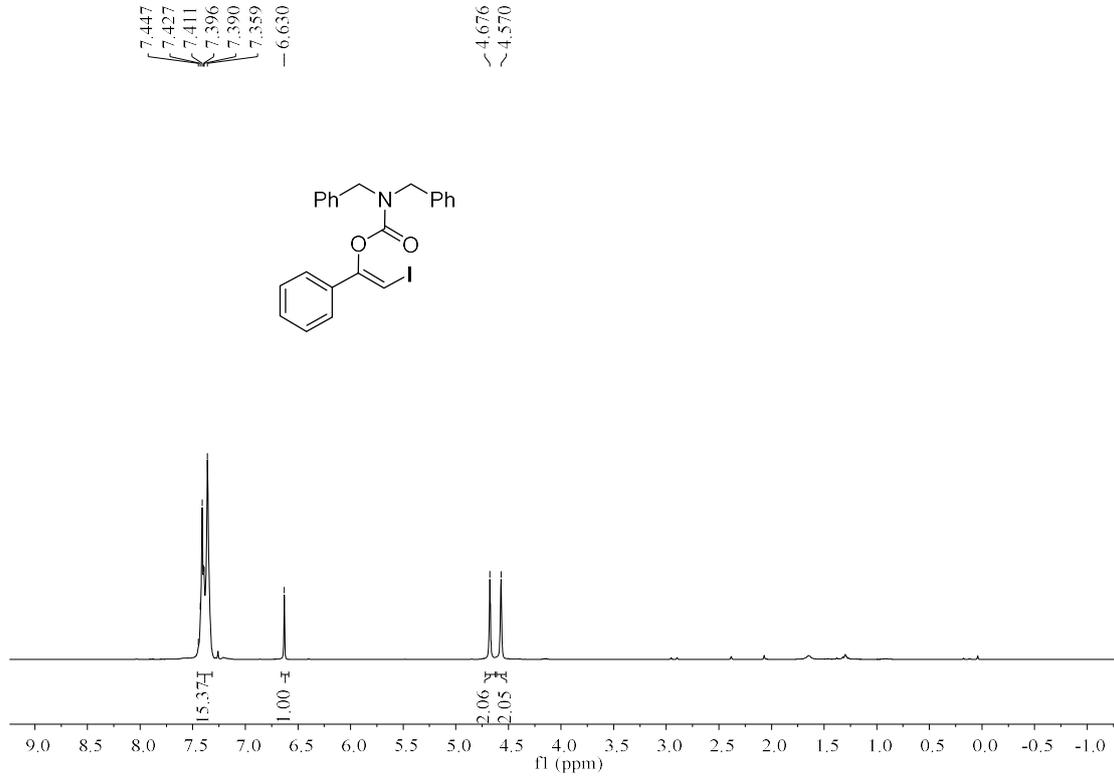
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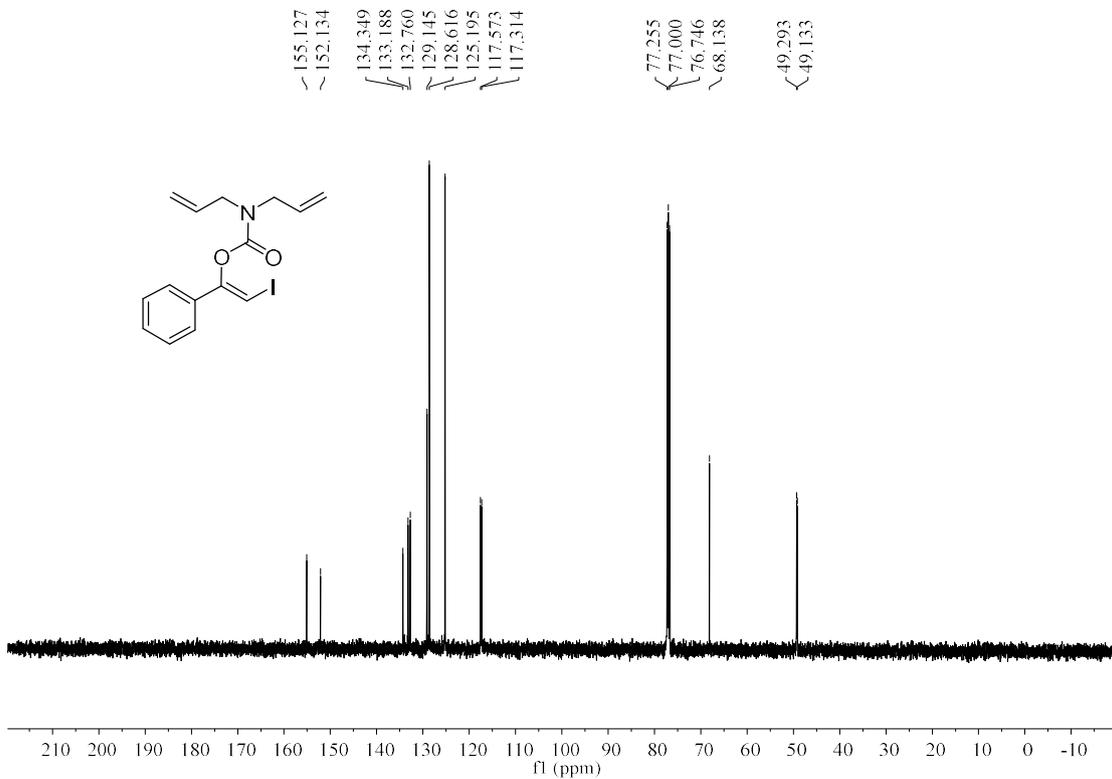
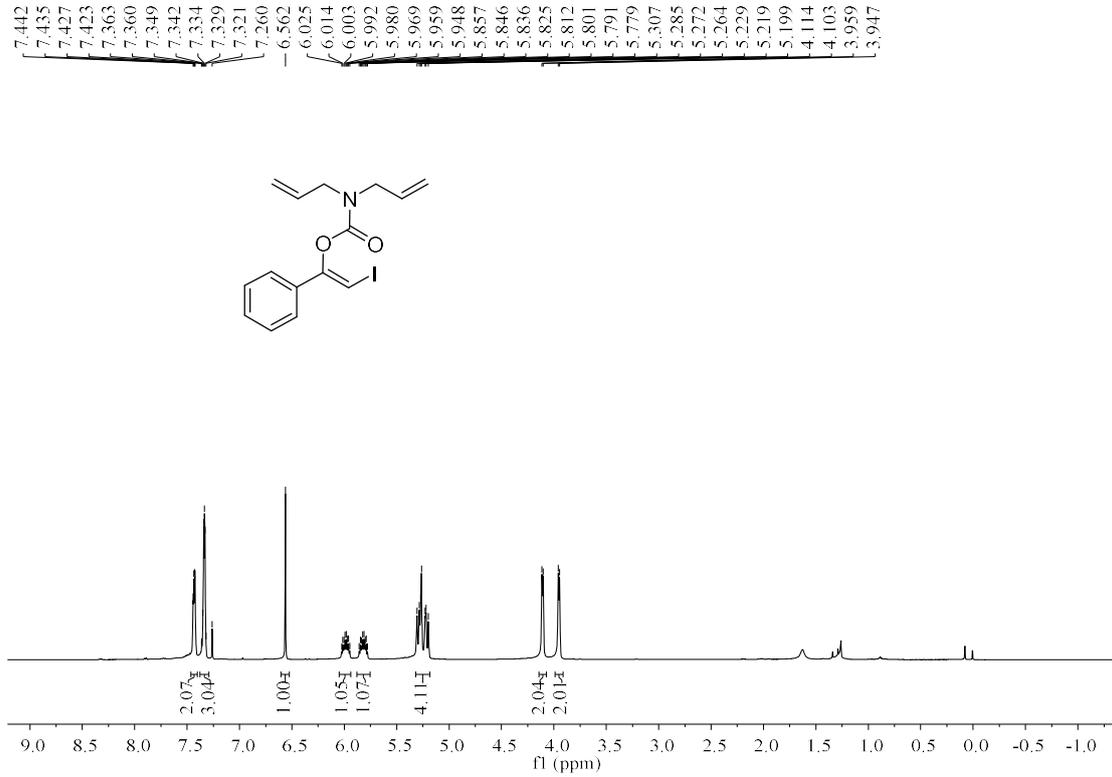
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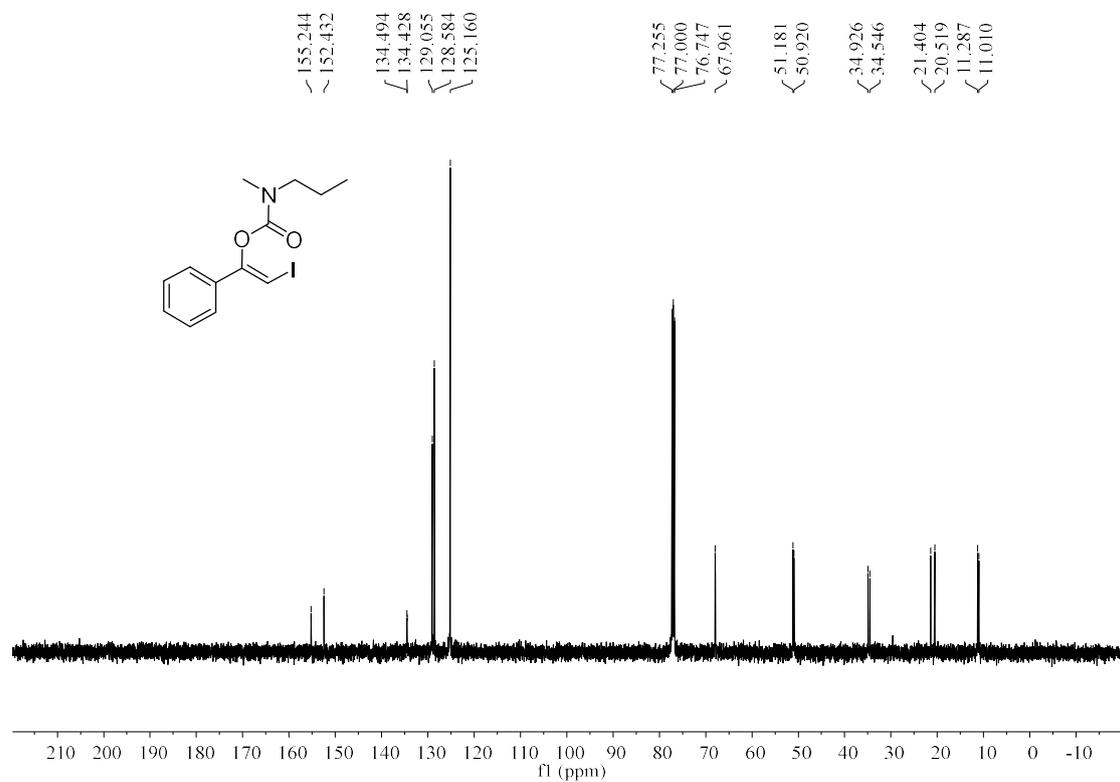
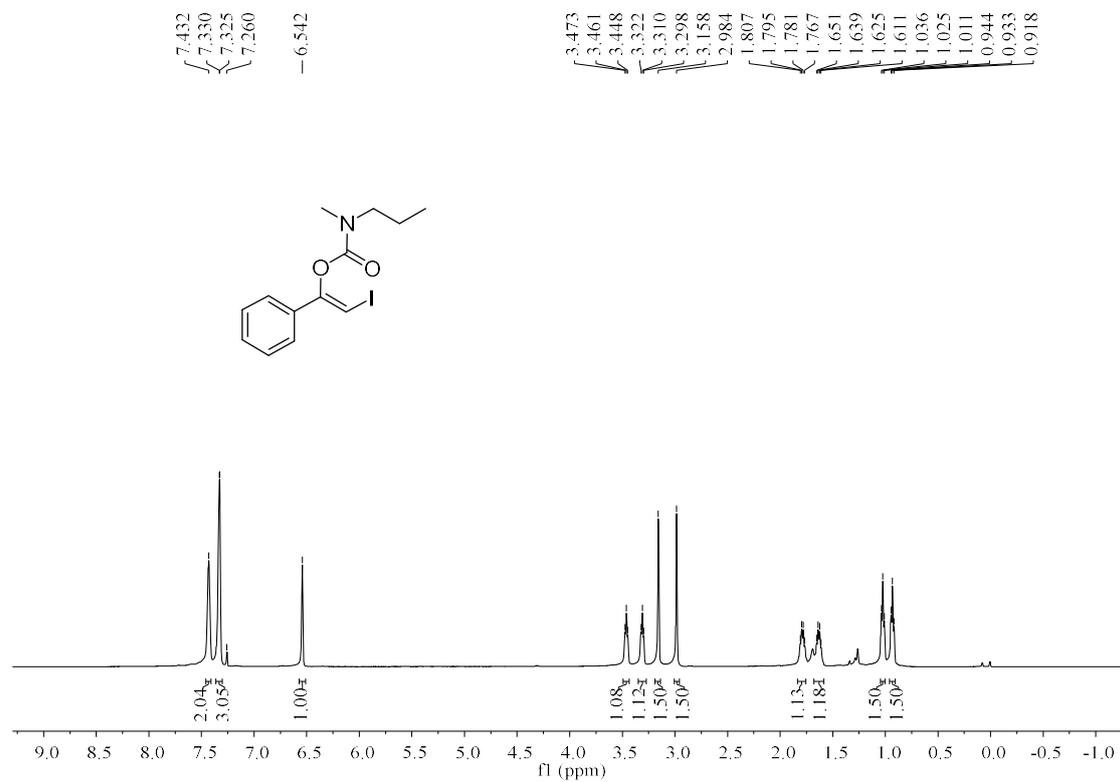
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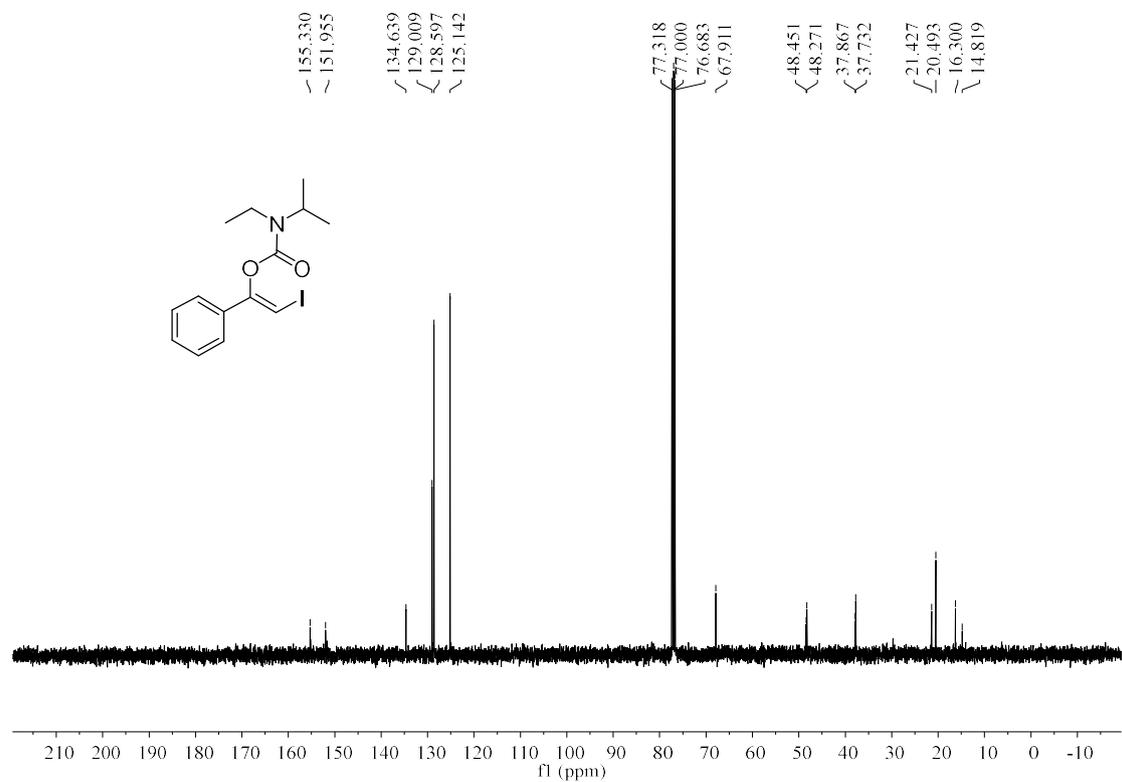
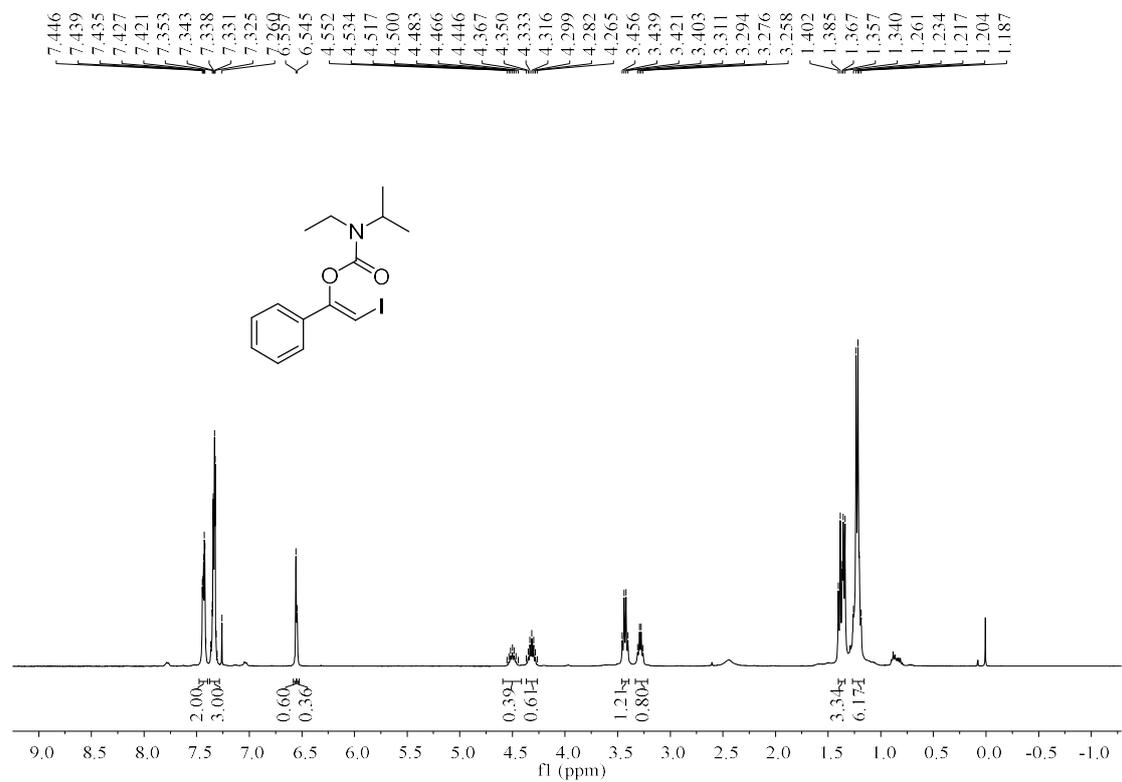
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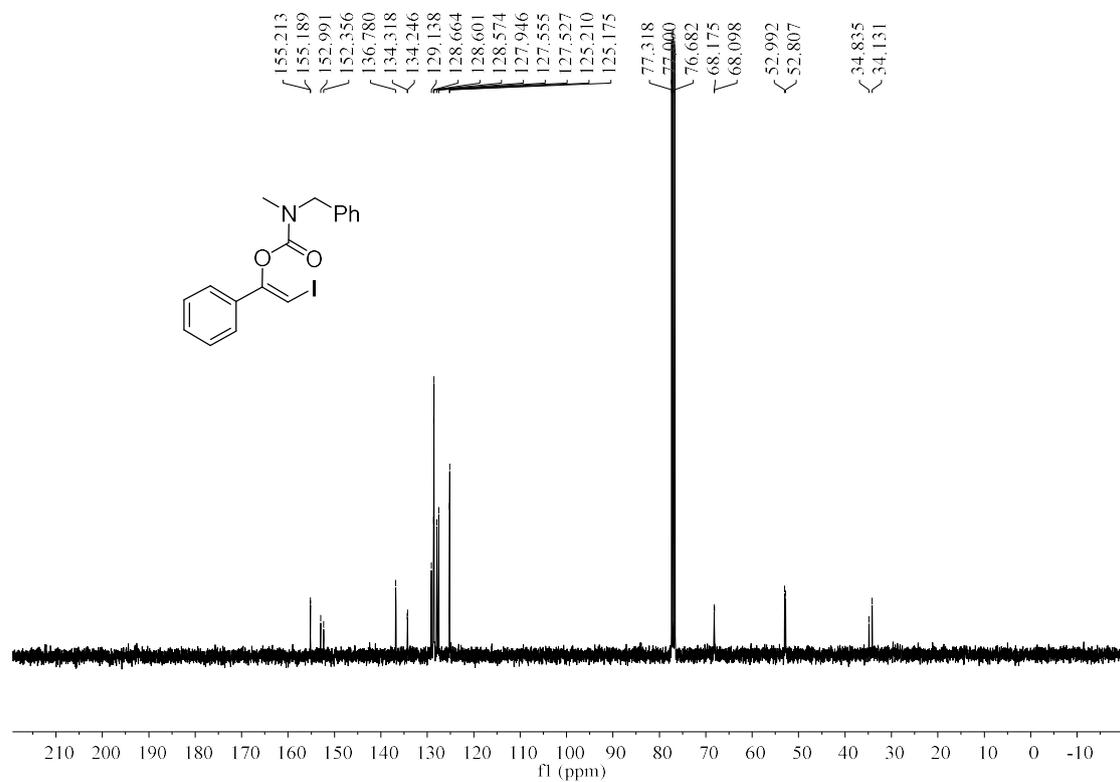
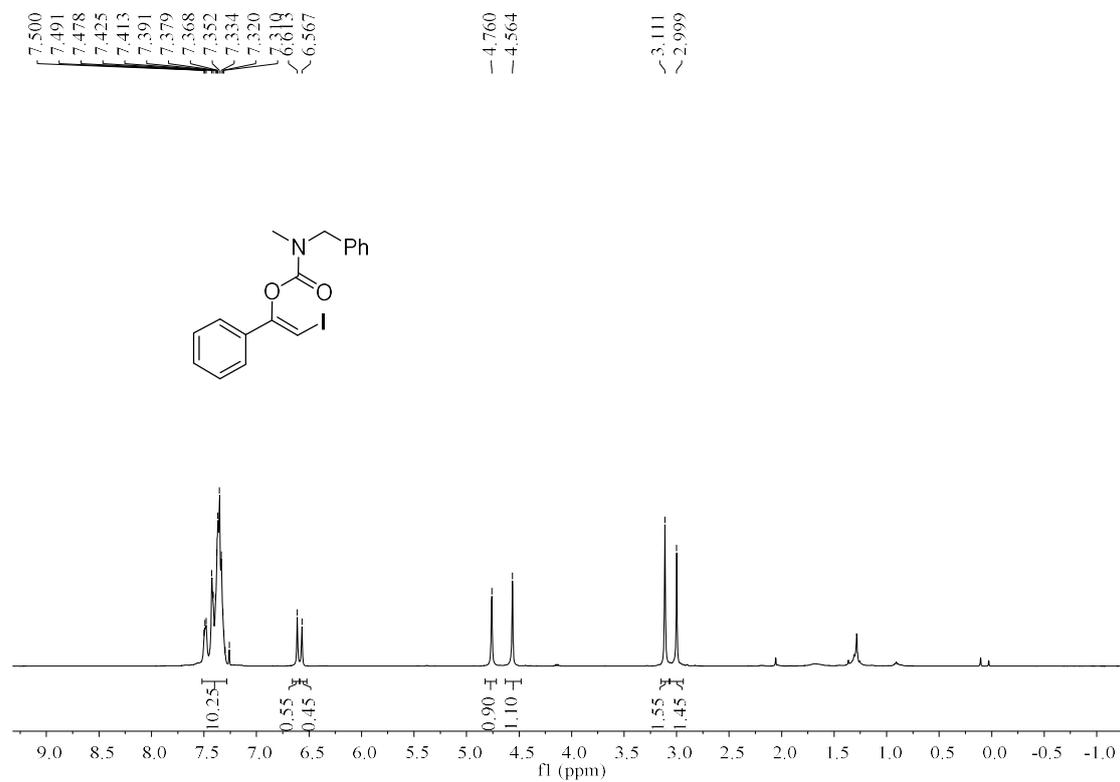
**(Z)-2-Iodo-1-phenylvinyl methyl(propyl)carbamate ((Z)-3ai)**



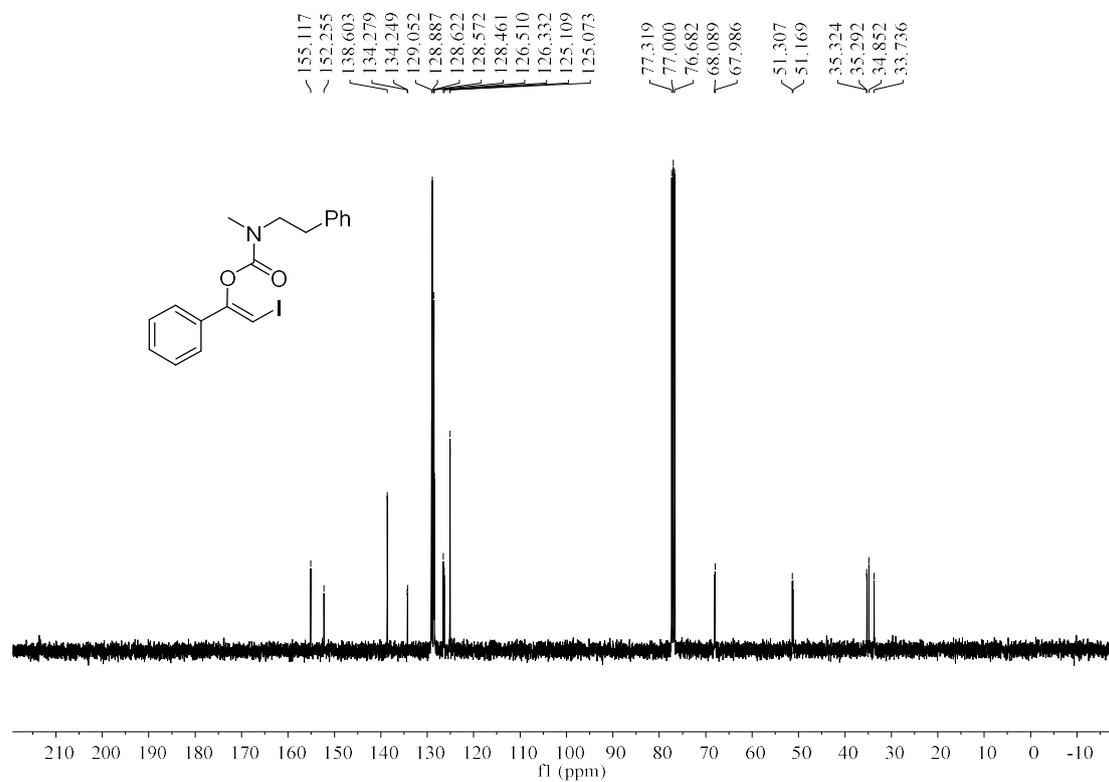
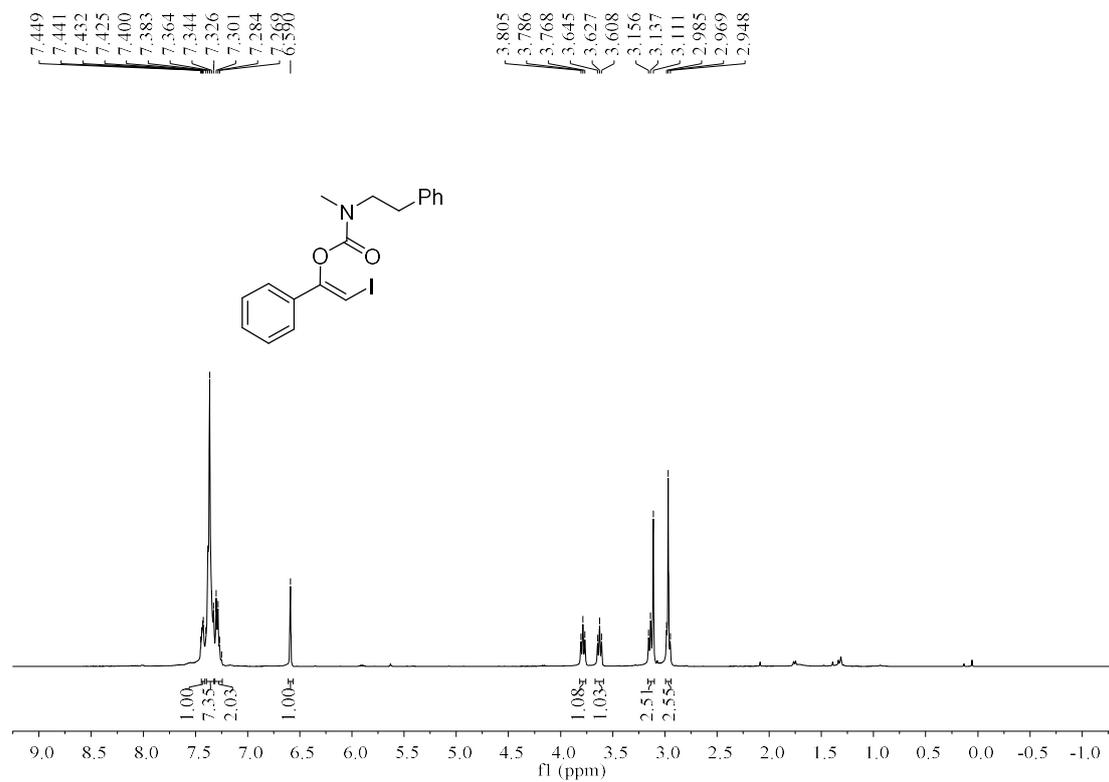
**(Z)-2-Iodo-1-phenylvinyl ethyl(isopropyl)carbamate ((Z)-3aj)**



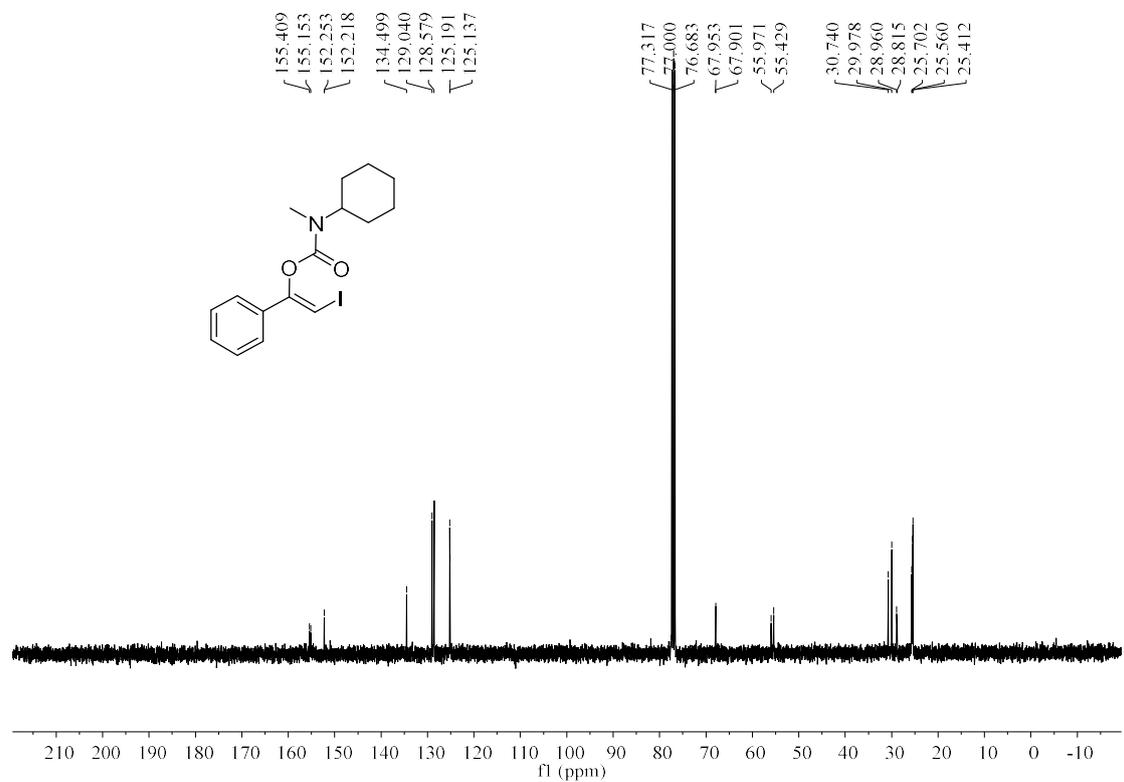
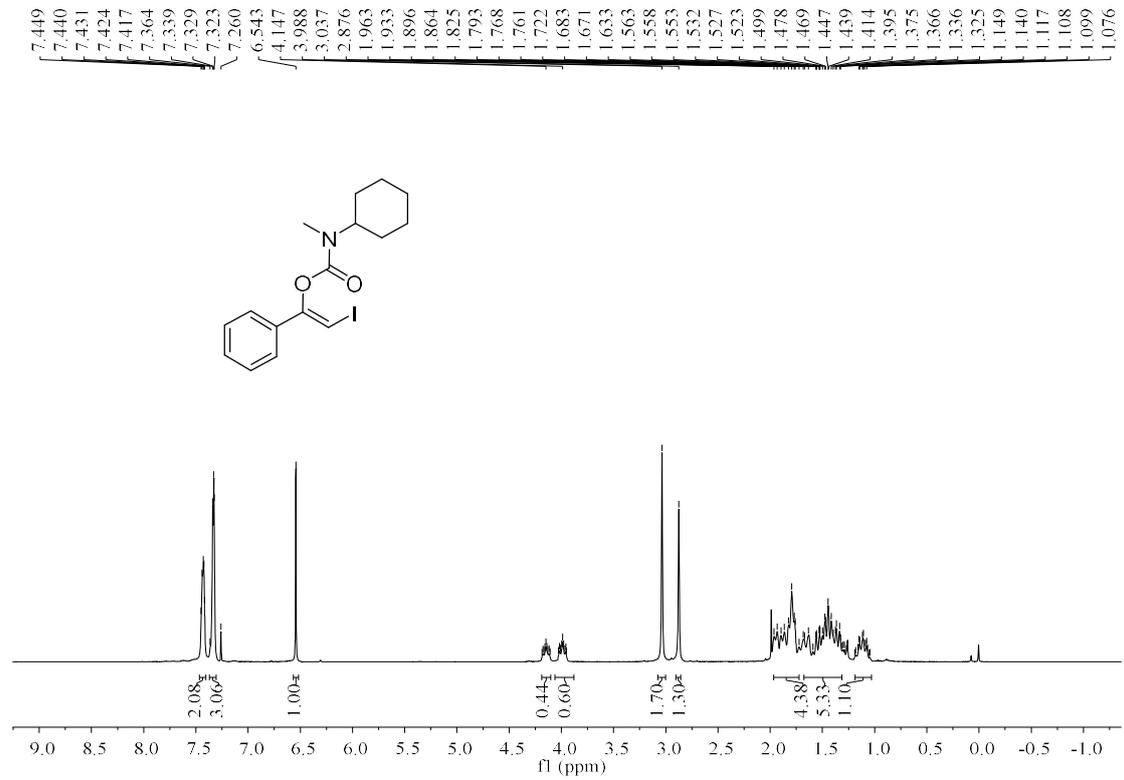
**(Z)-2-Iodo-1-phenylvinyl benzyl(methyl)carbamate ((Z)-3ak)**



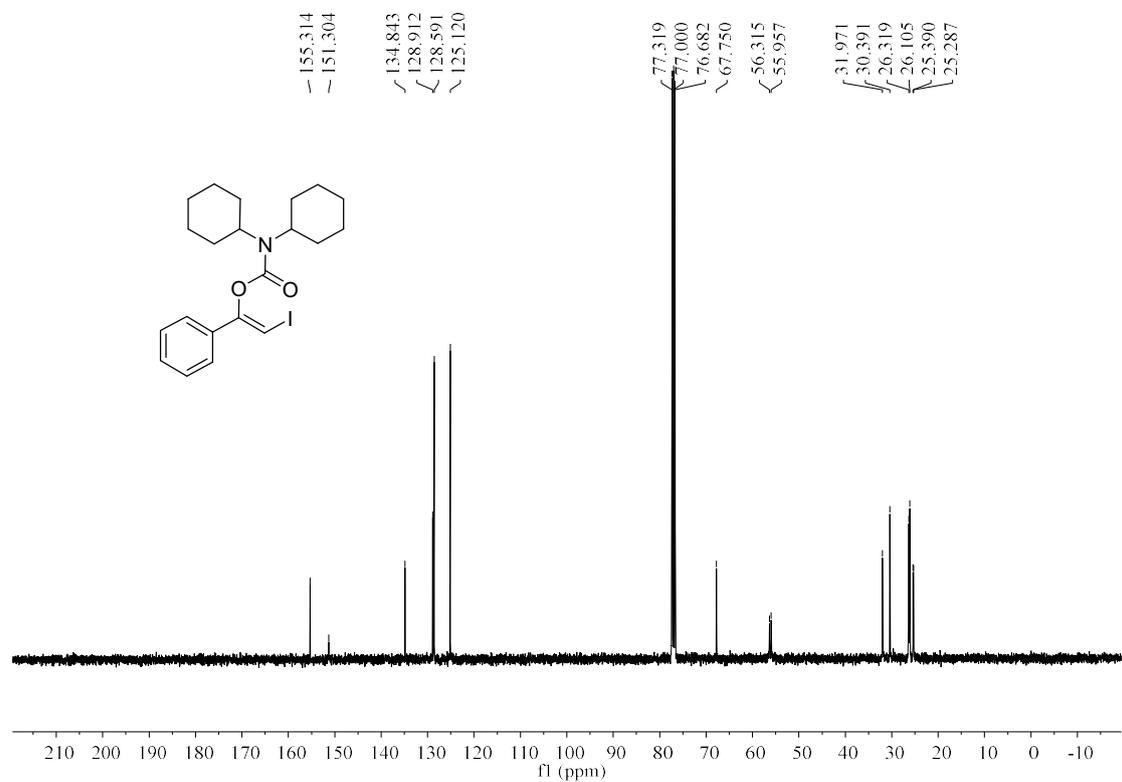
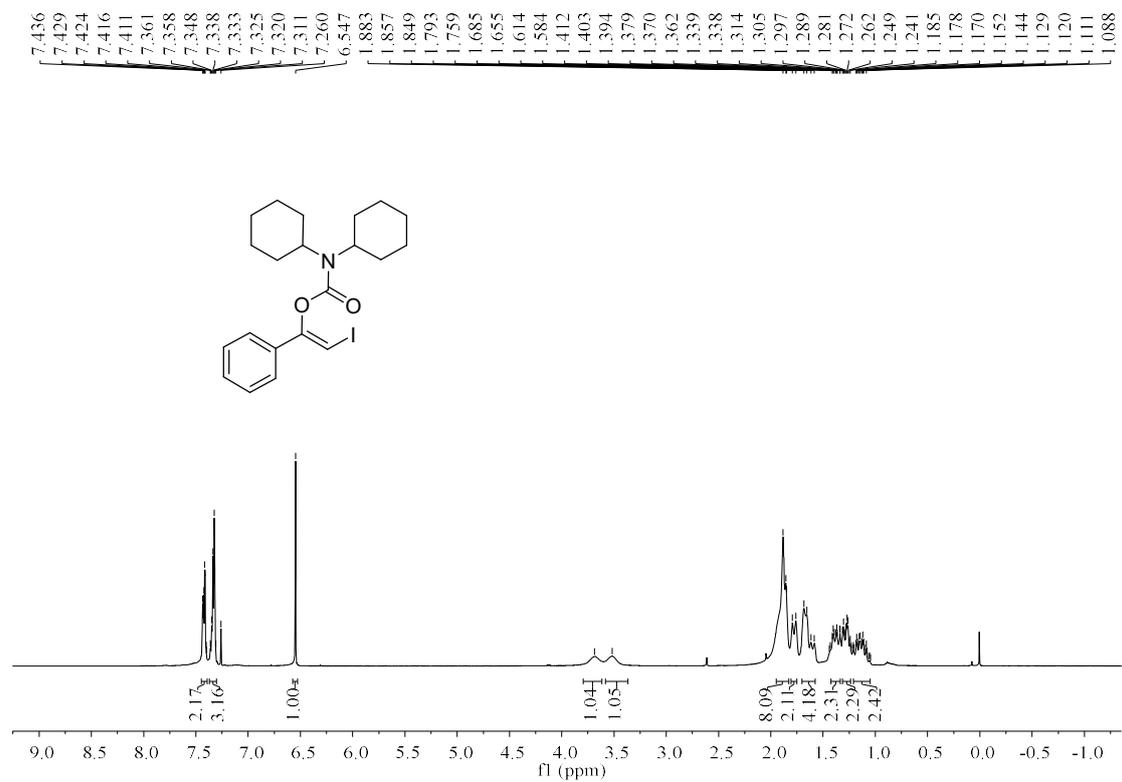
**(Z)-2-Iodo-1-phenylvinyl methyl(phenethyl)carbamate ((Z)-3al)**



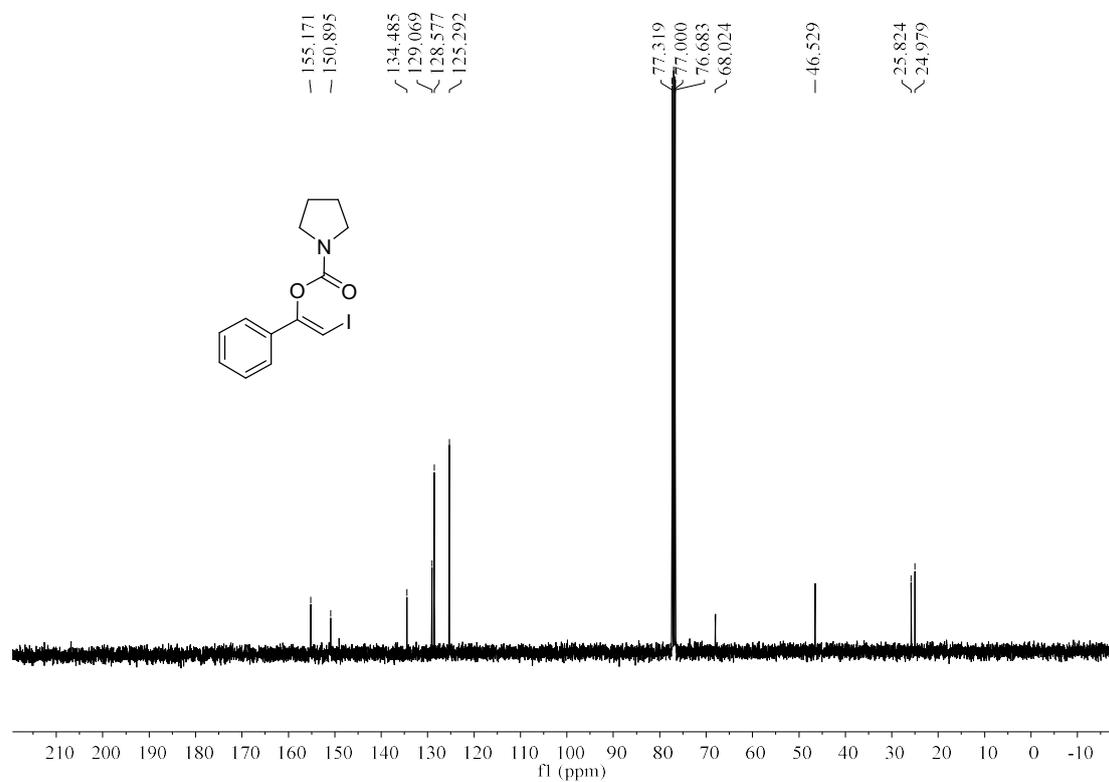
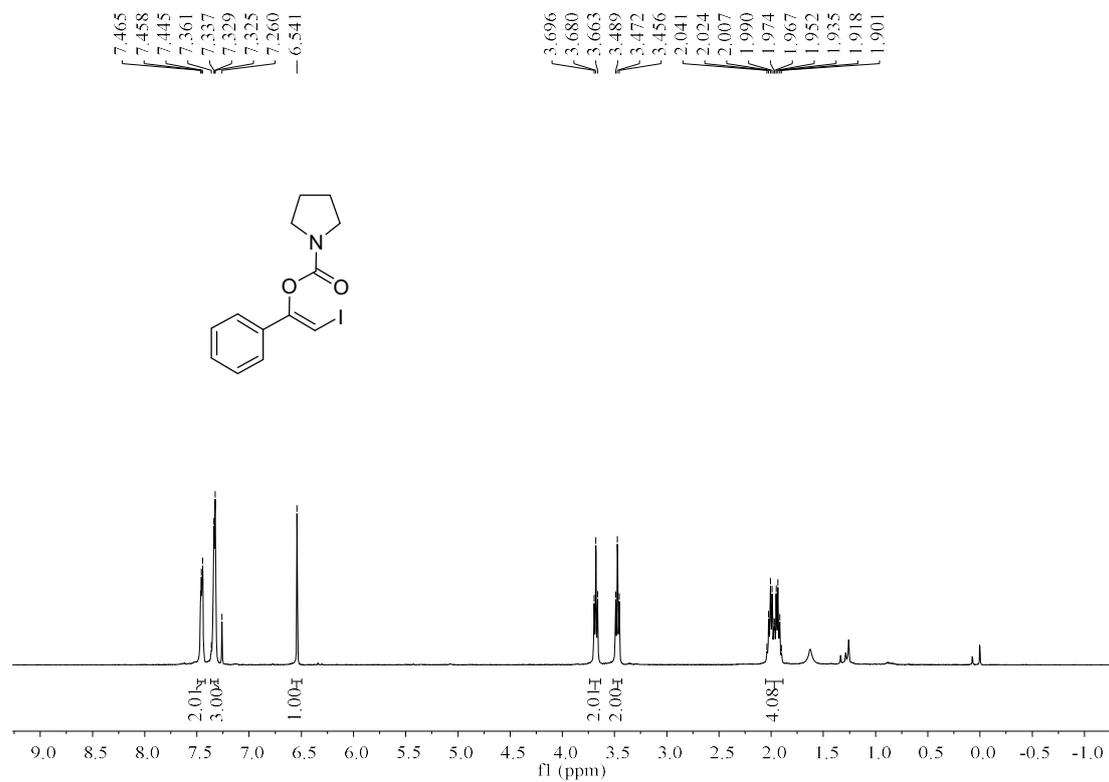
**(Z)-2-Iodo-1-phenylvinyl cyclohexyl(methyl)carbamate ((Z)-3am)**



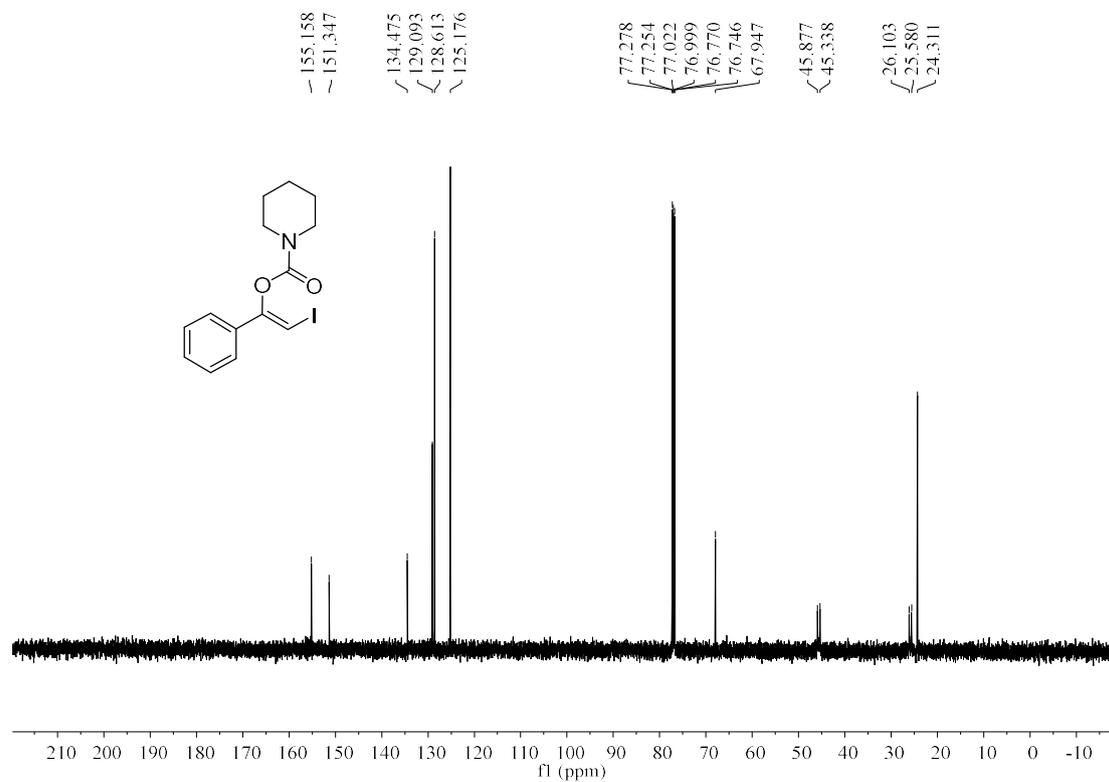
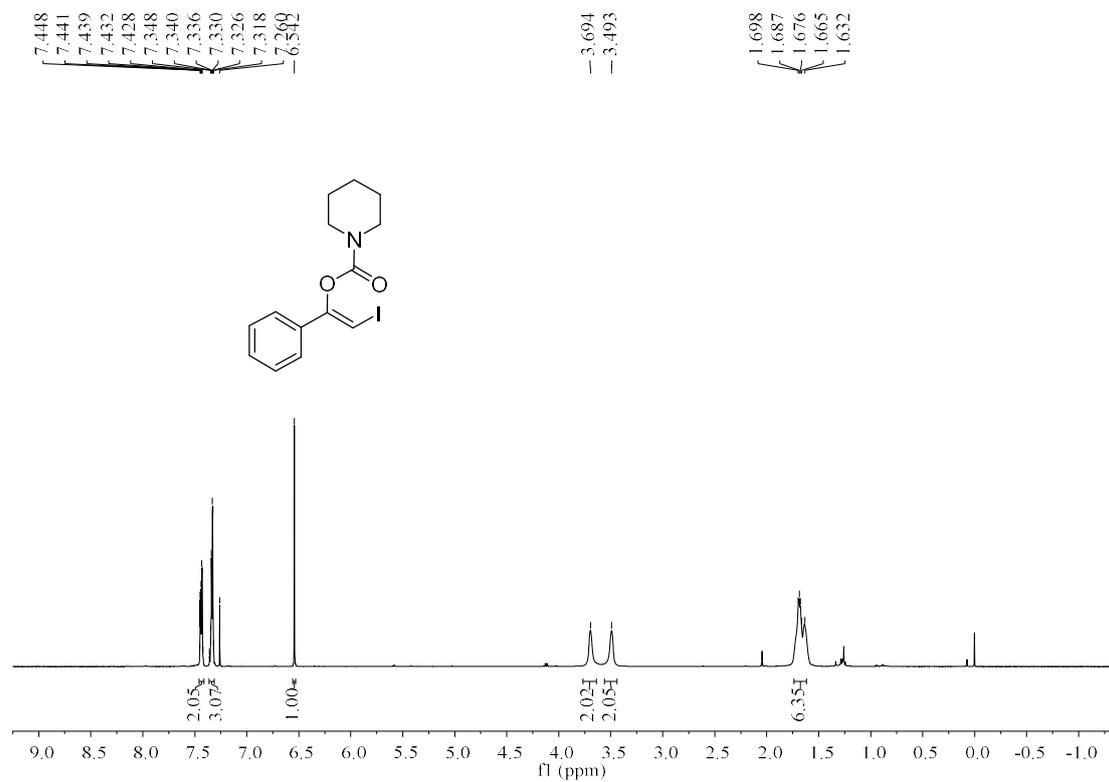
**(Z)-2-Iodo-1-phenylvinyl dicyclohexylcarbamate ((Z)-3an)**



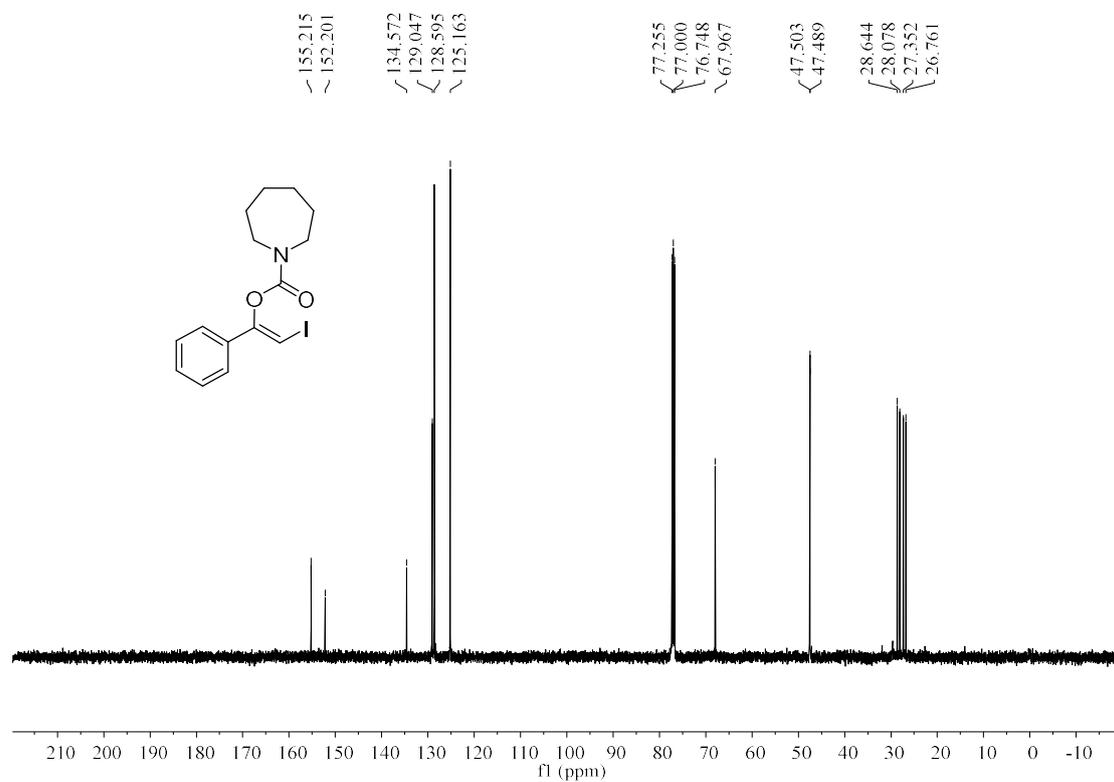
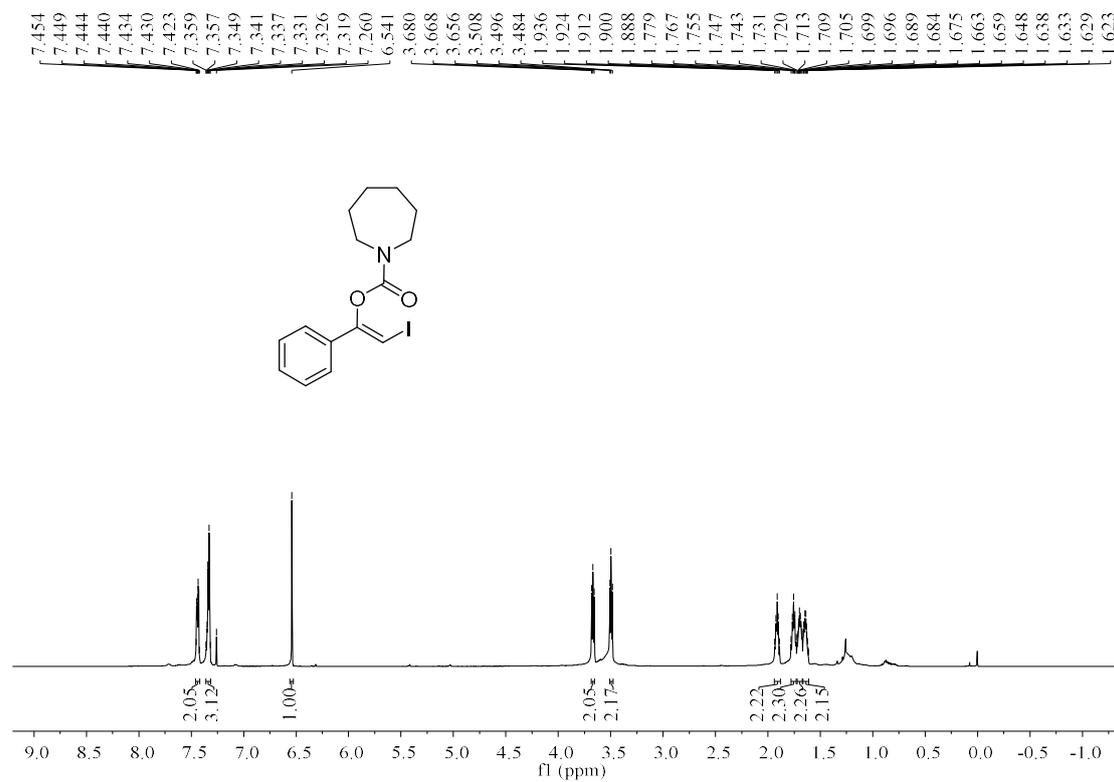
**(Z)-2-Iodo-1-phenylvinyl pyrrolidine-1-carboxylate ((Z)-3ao)**



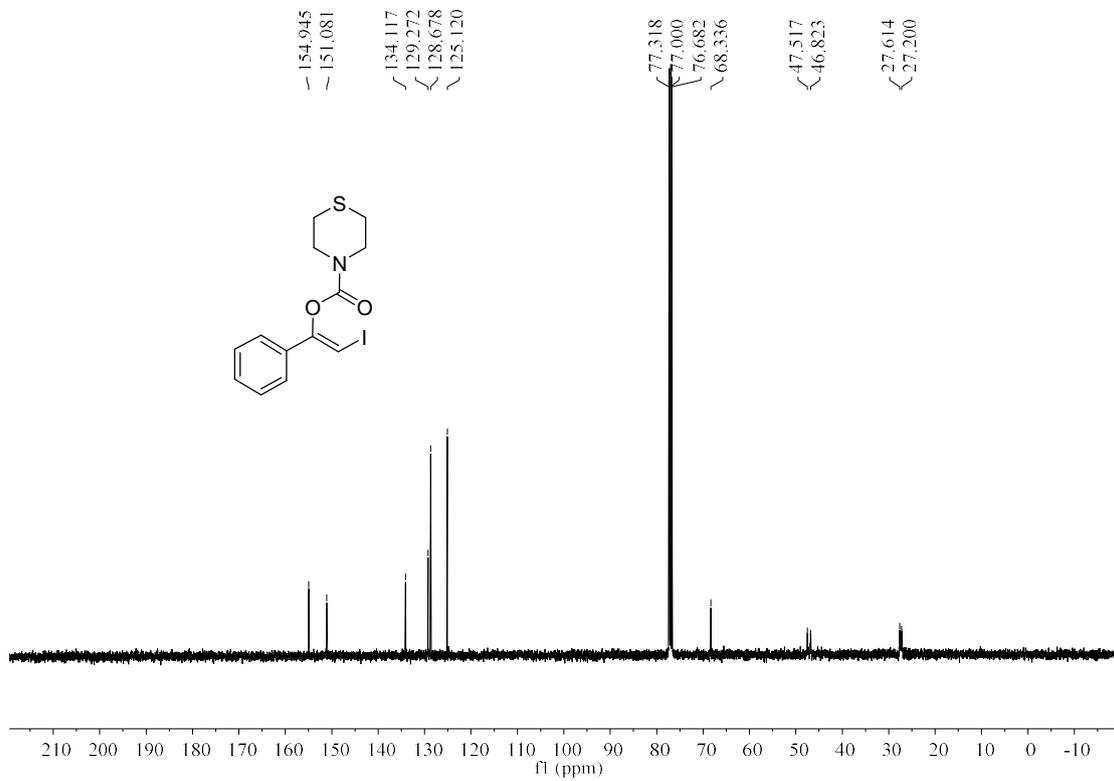
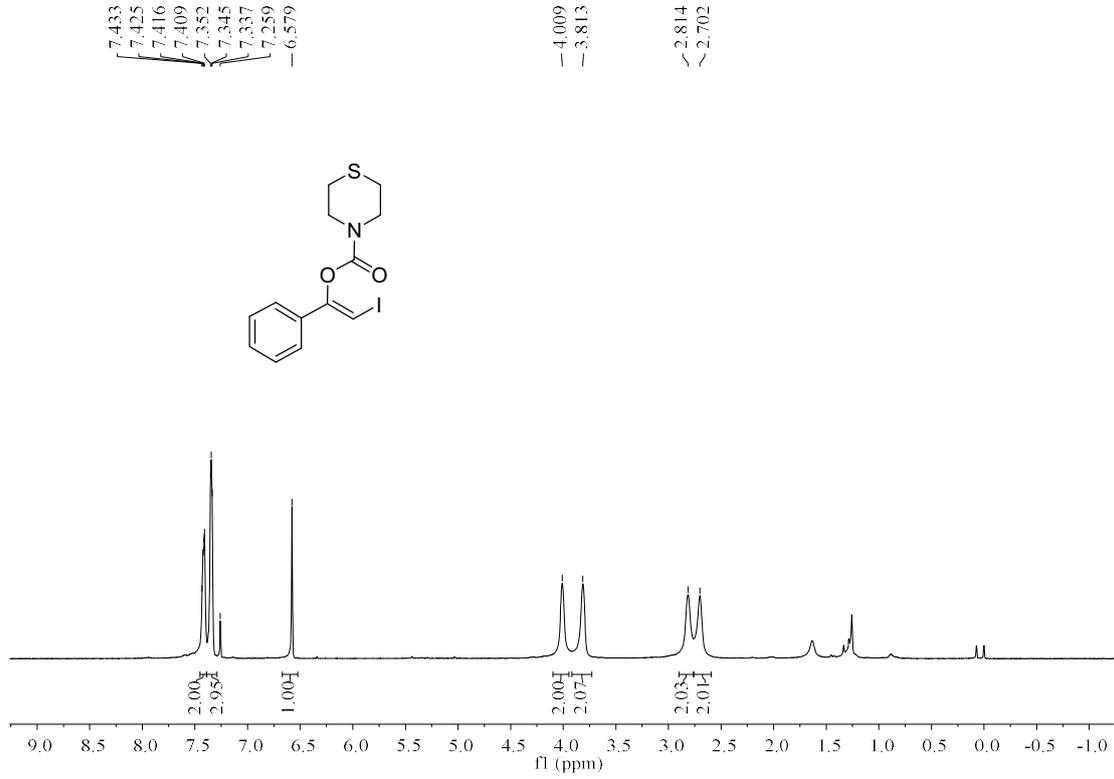
**(Z)-2-Iodo-1-phenylvinyl piperidine-1-carboxylate ((Z)-3ap)**



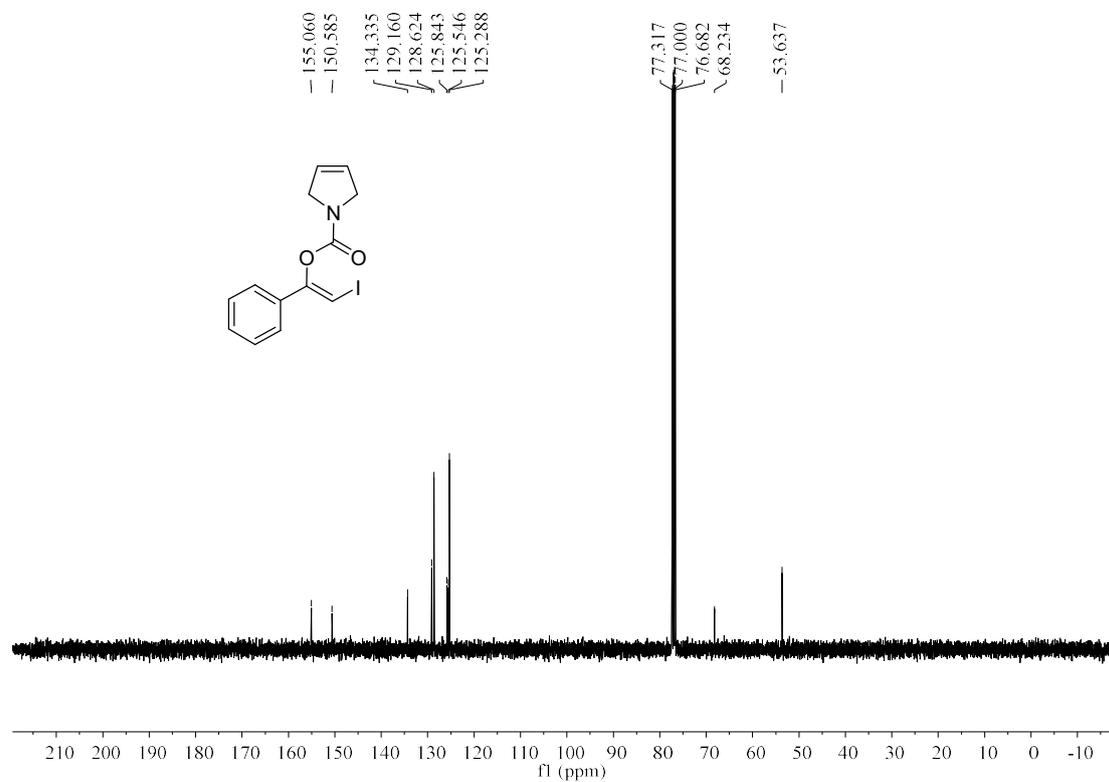
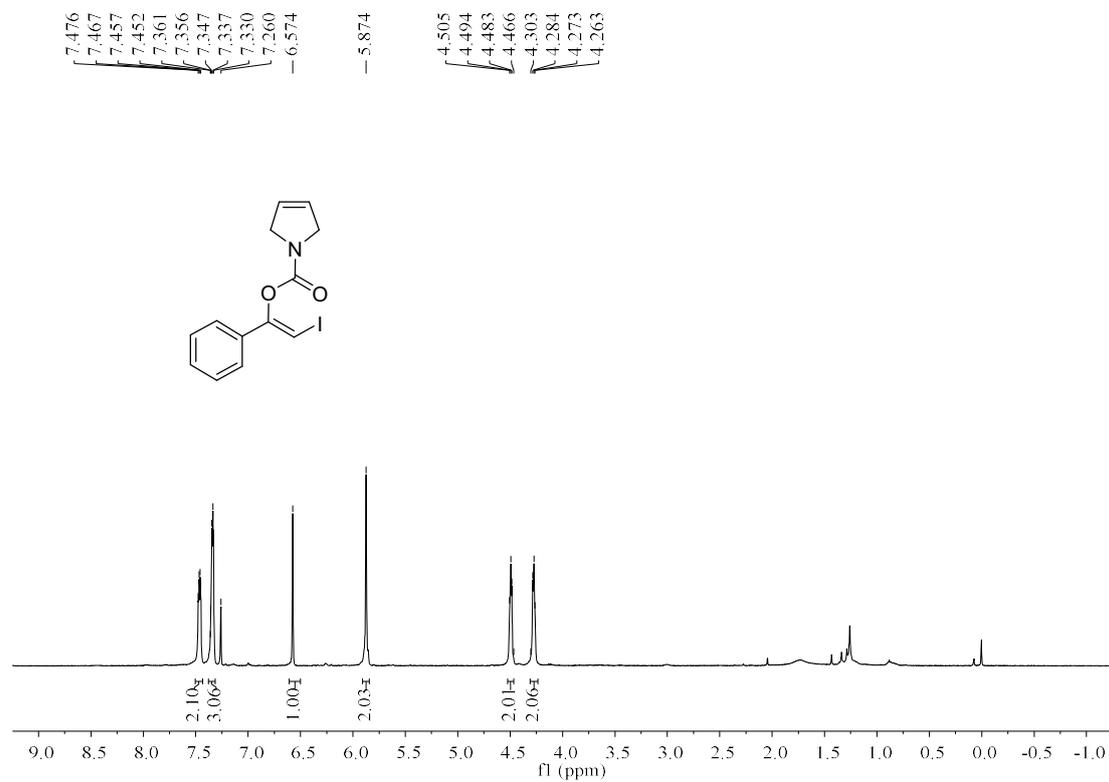
**(Z)-2-Iodo-1-phenylvinyl azepane-1-carboxylate ((Z)-3aq)**



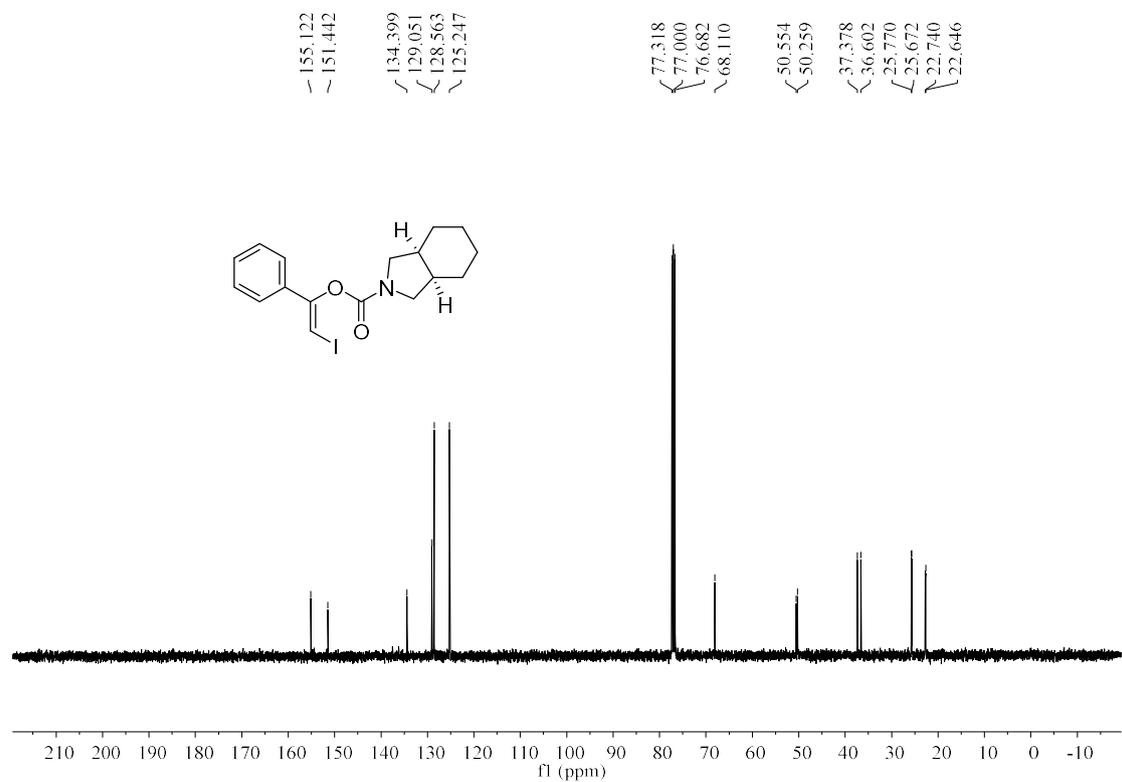
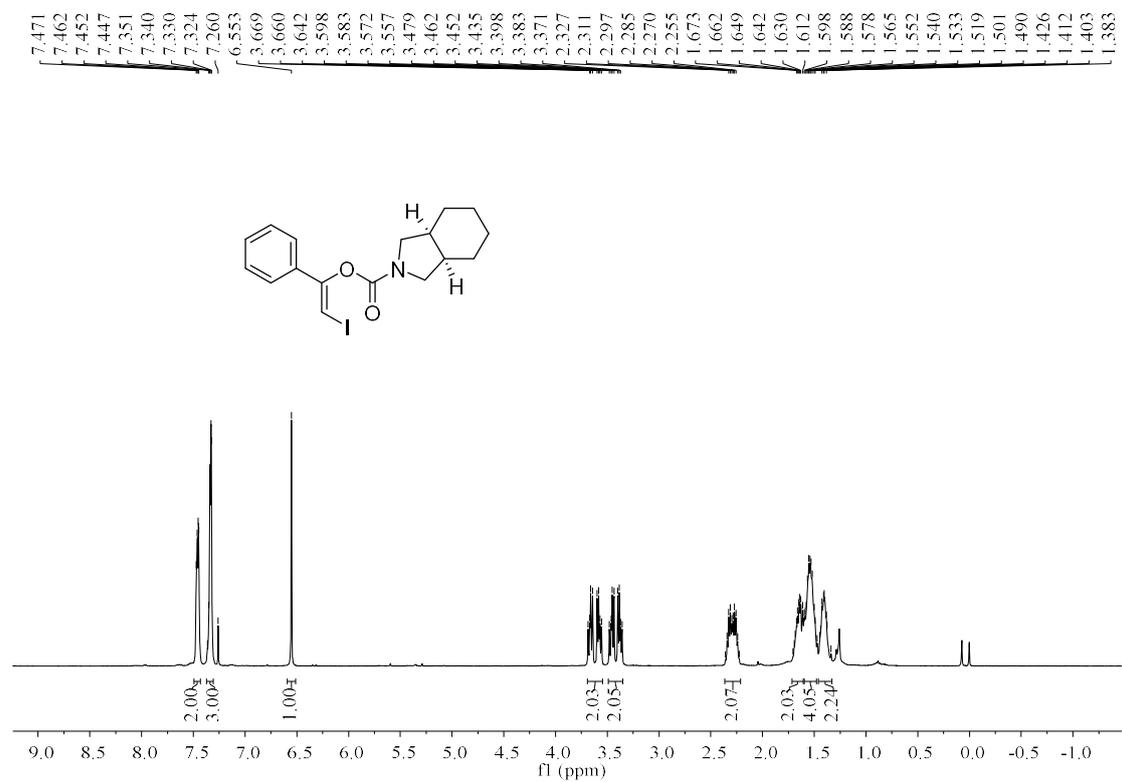
**(Z)-2-Iodo-1-phenylvinyl thiomorpholine-4-carboxylate ((Z)-3ar)**



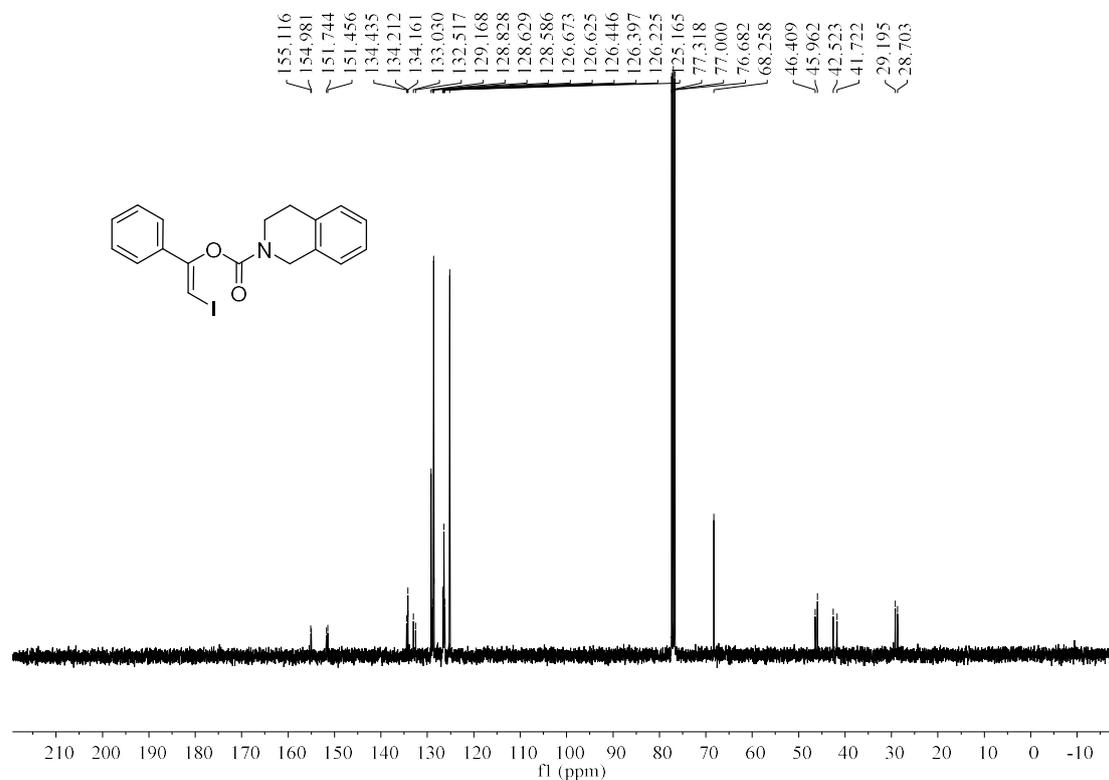
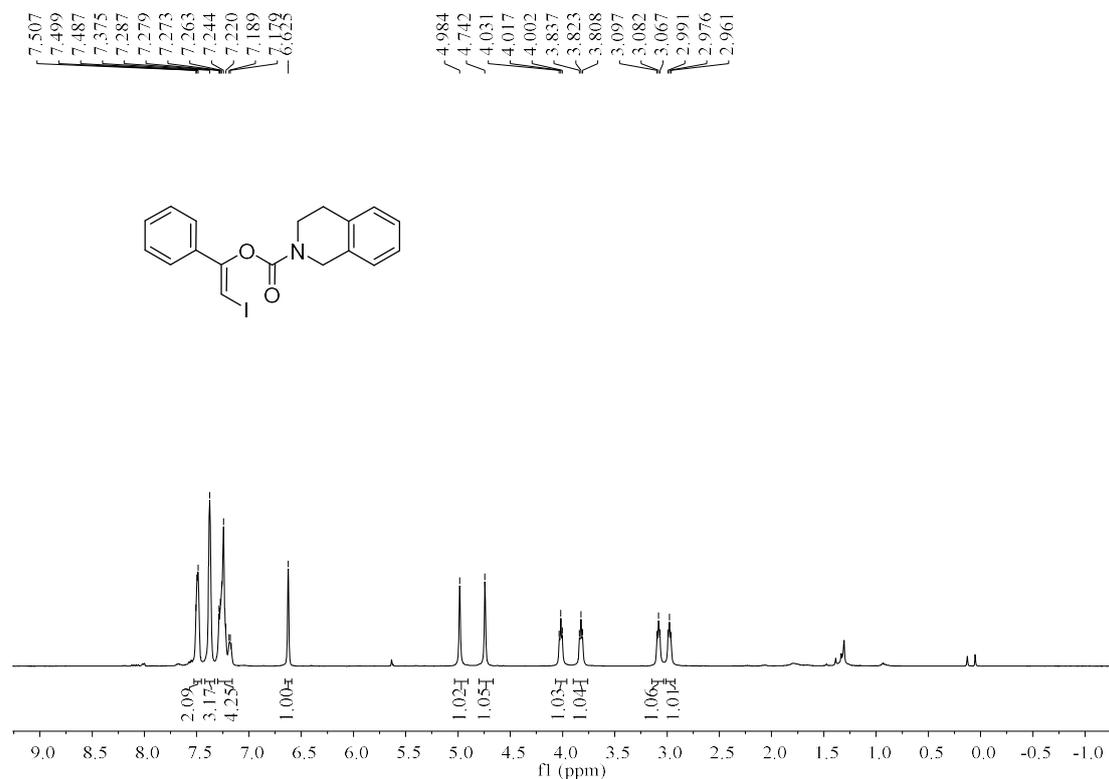
**(Z)-2-Iodo-1-phenylvinyl 2,5-dihydro-1H-pyrrole-1-carboxylate ((Z)-3as)**



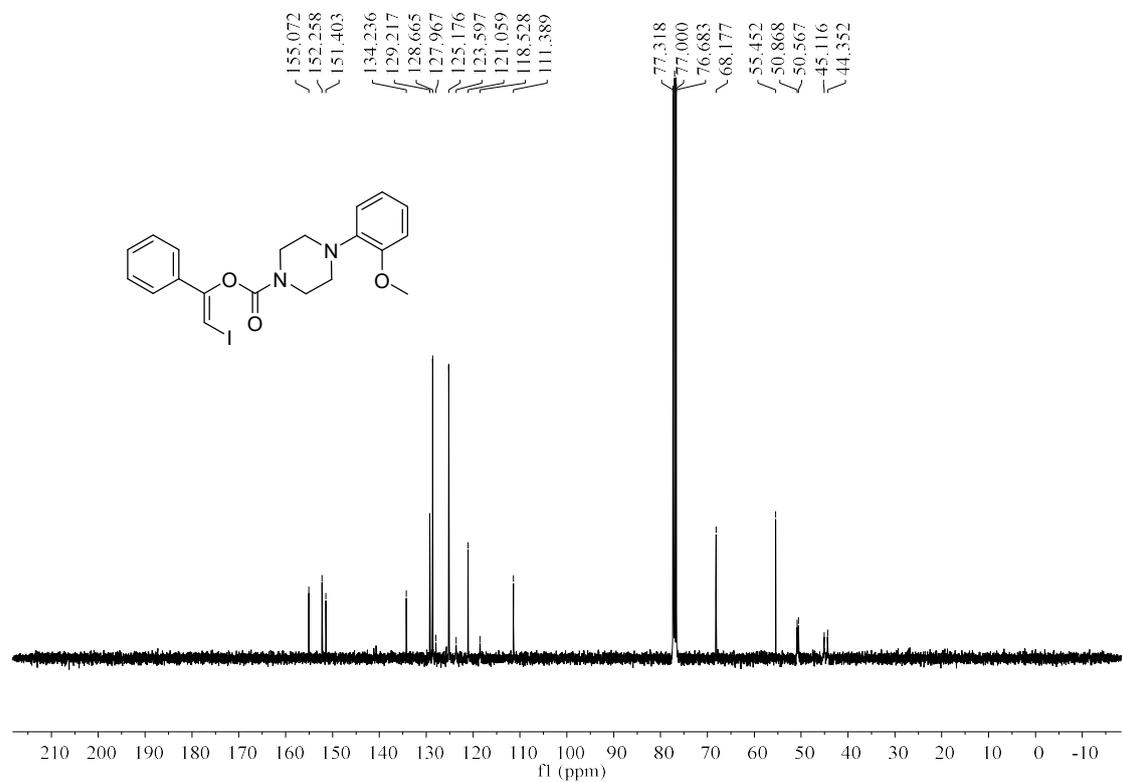
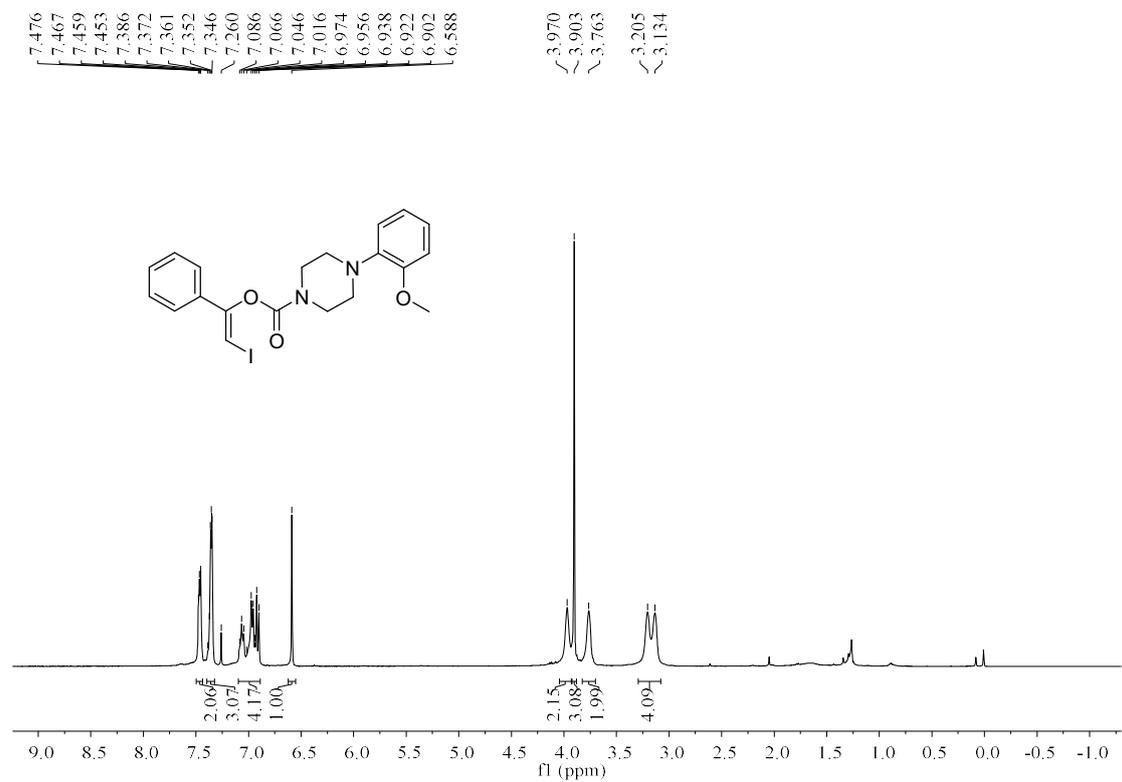
**(Z)-2-Iodo-1-phenylvinyl (3aR,7aS)-octahydro-2H-isoindole-2-carboxylate ((Z)-3at)**



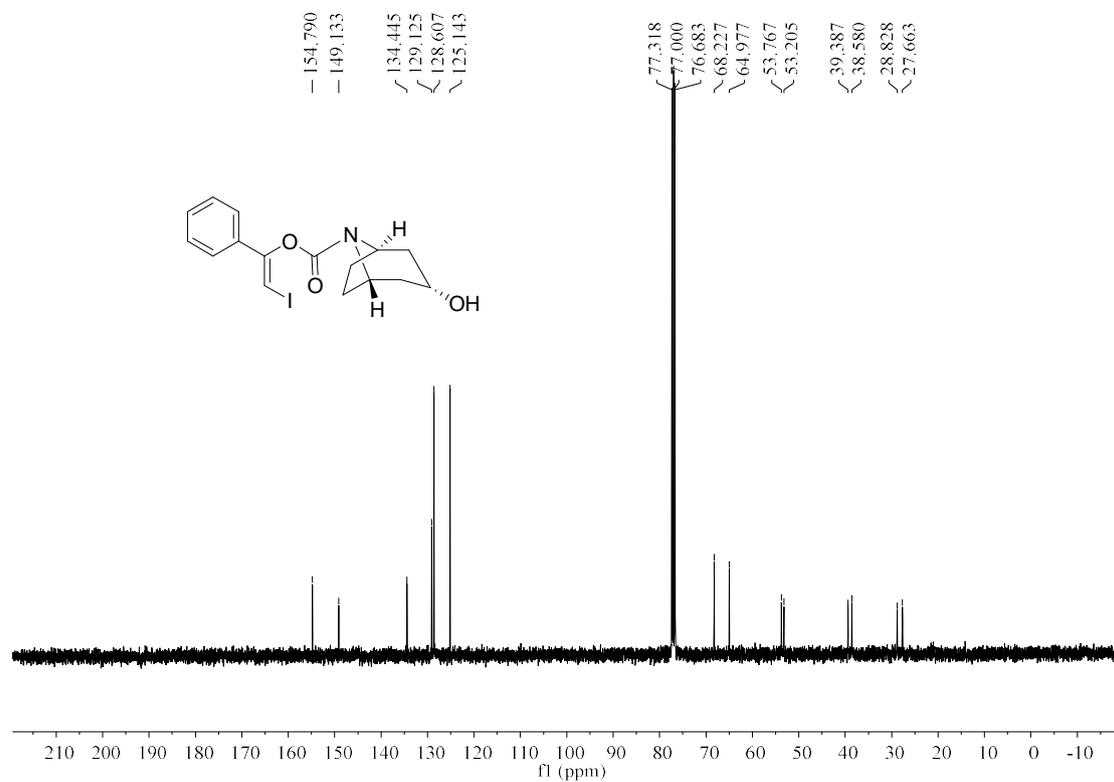
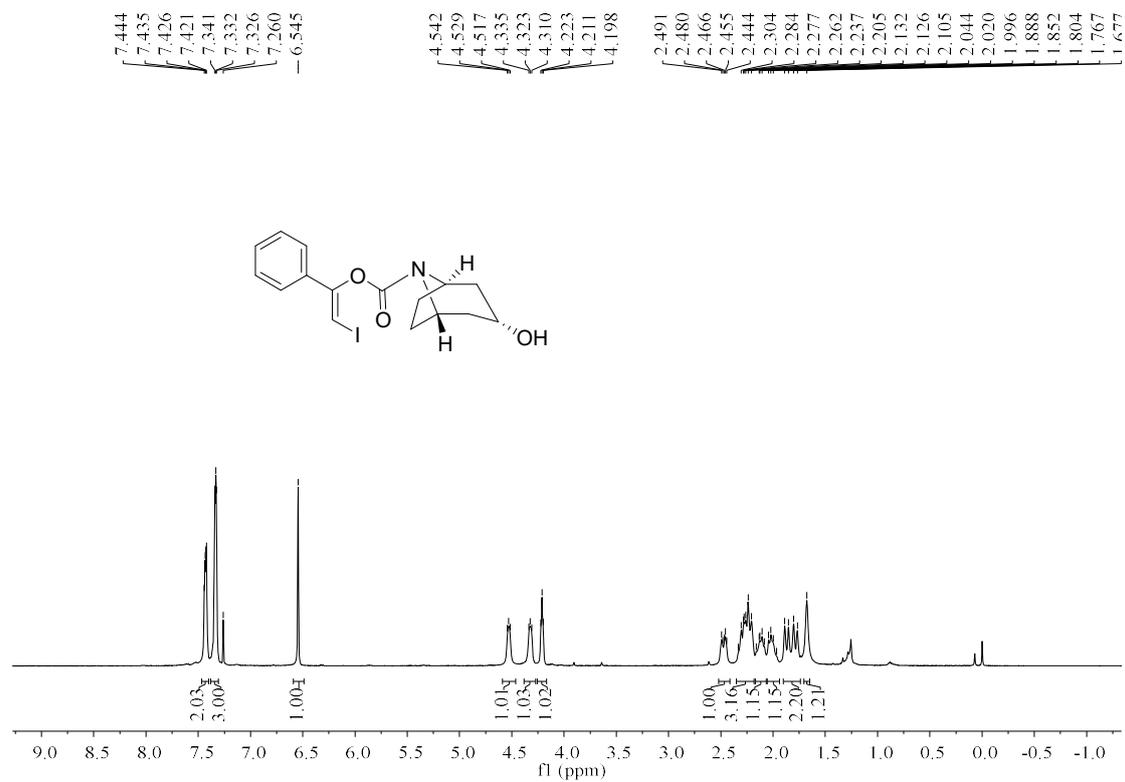
**(Z)-2-Iodo-1-phenylvinyl 3,4-dihydroisoquinoline-2(1H)-carboxylate ((Z)-3au)**



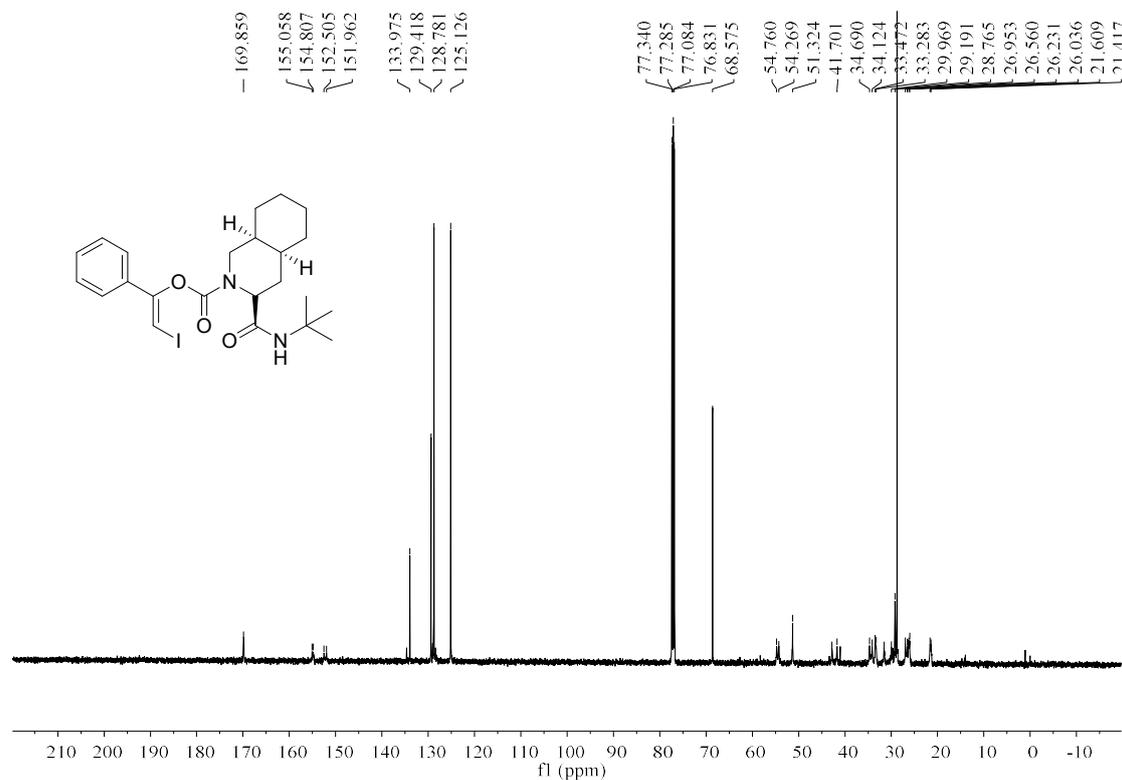
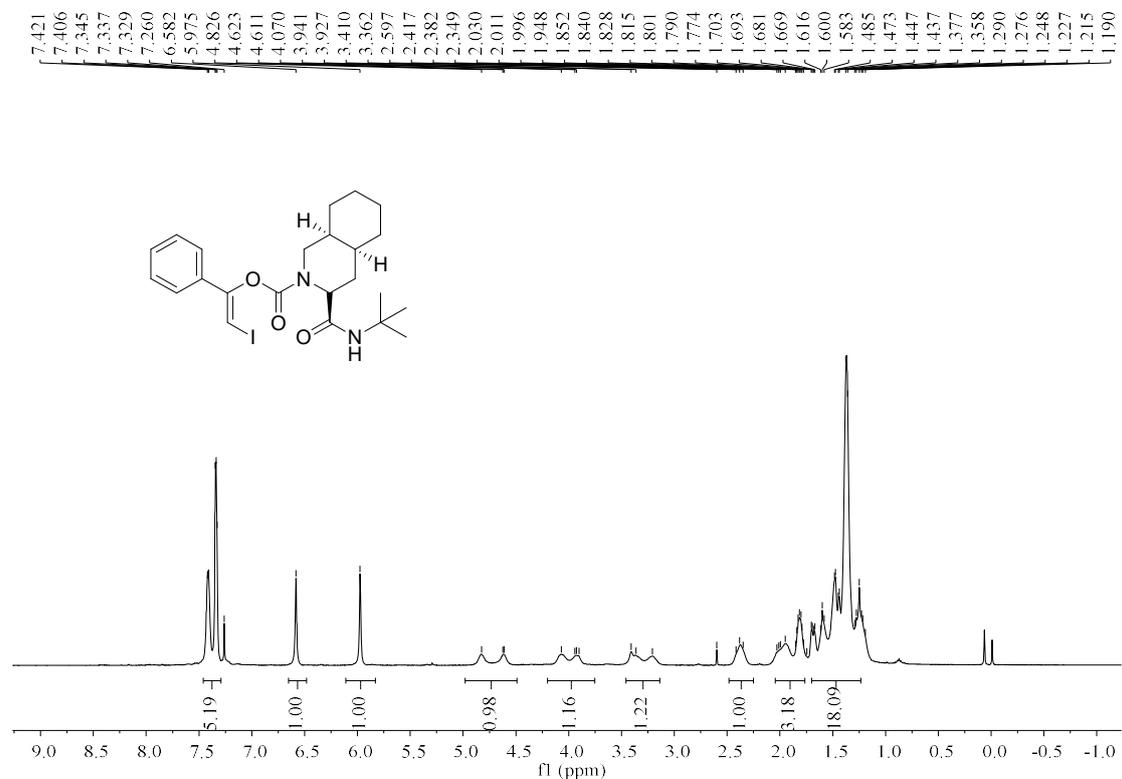
**(Z)-2-Iodo-1-phenylvinyl 4-(2-methoxyphenyl)piperazine-1-carboxylate ((Z)-3av)**



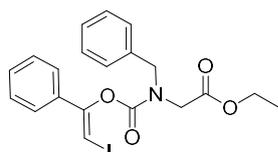
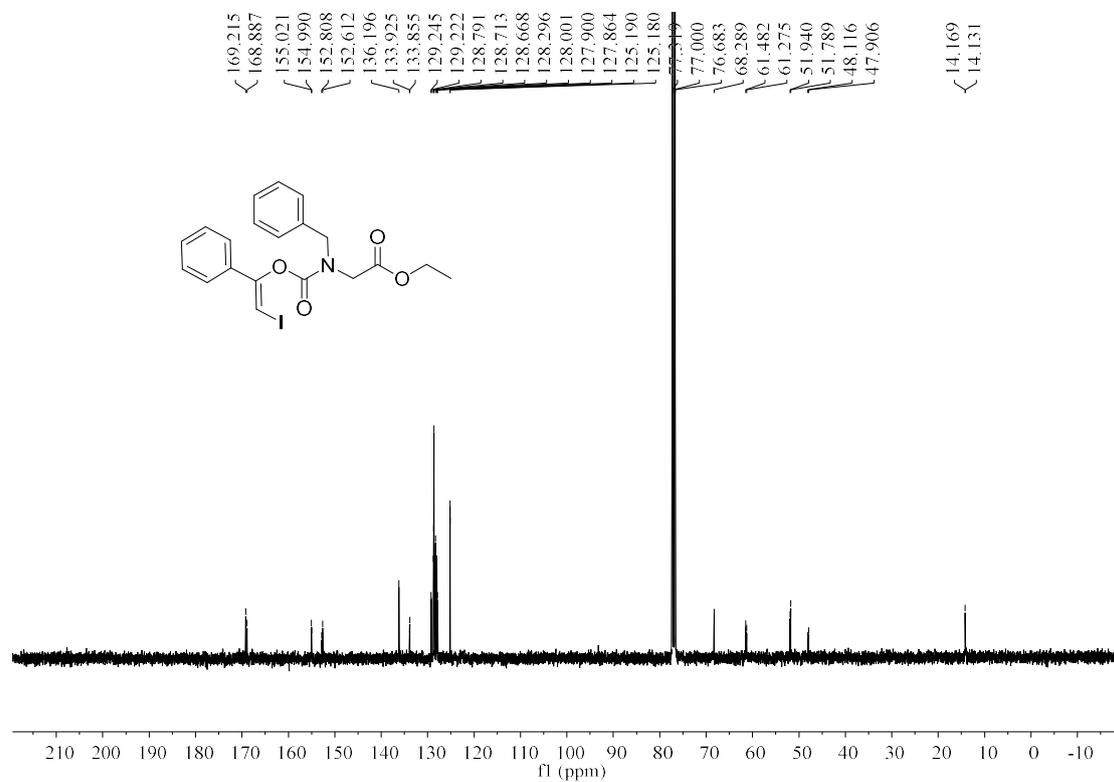
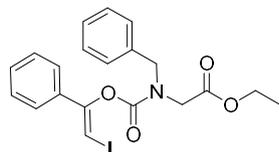
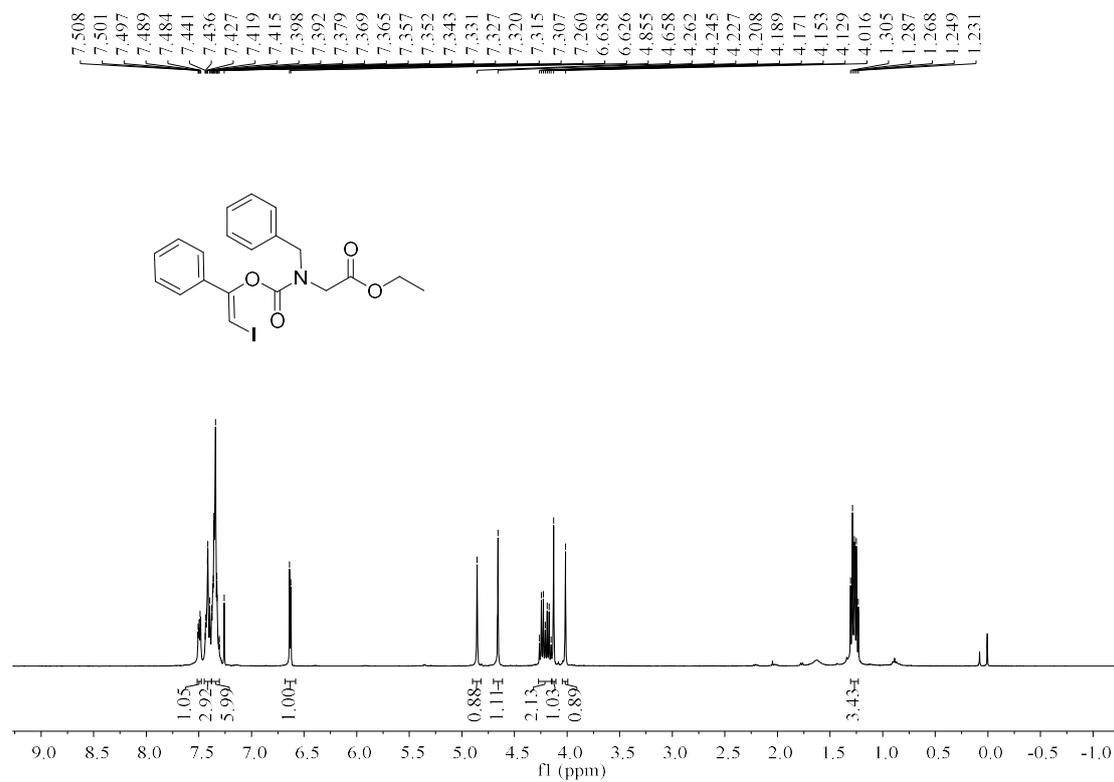
**(Z)-2-Iodo-1-phenylvinyl (1R,3r,5S)-3-hydroxy-8-azabicyclo[3.2.1]octane-8-carboxylate ((Z)-3aw)**



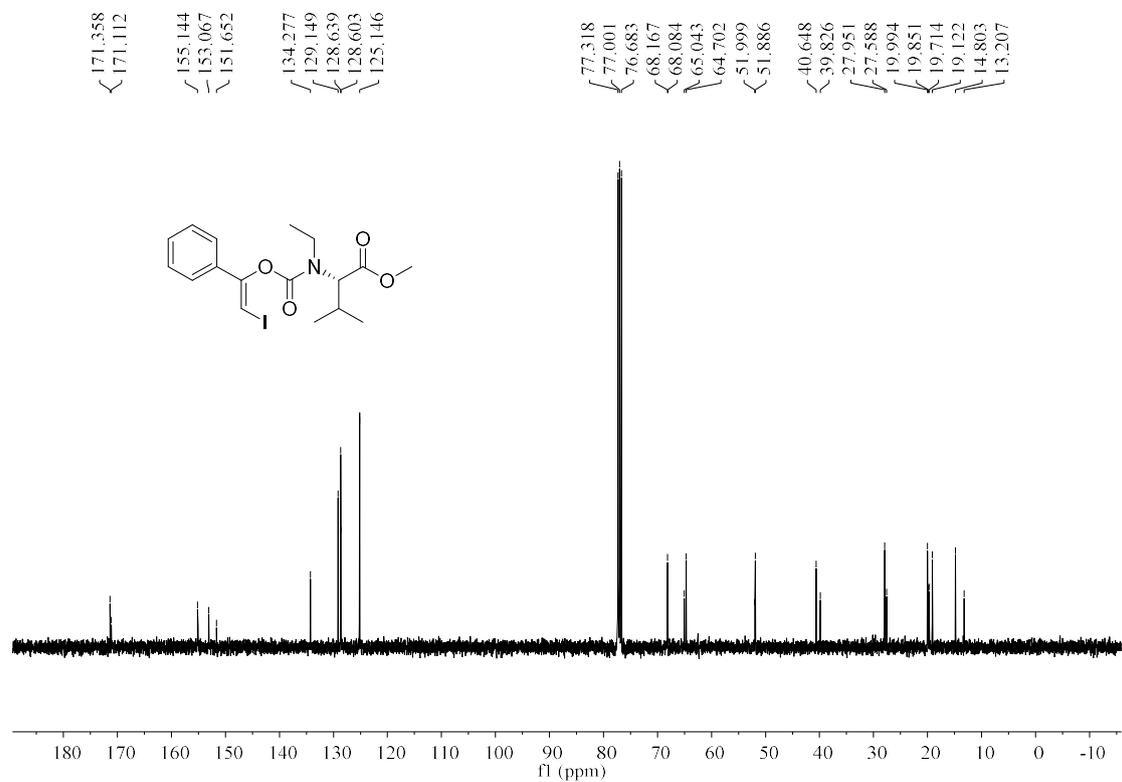
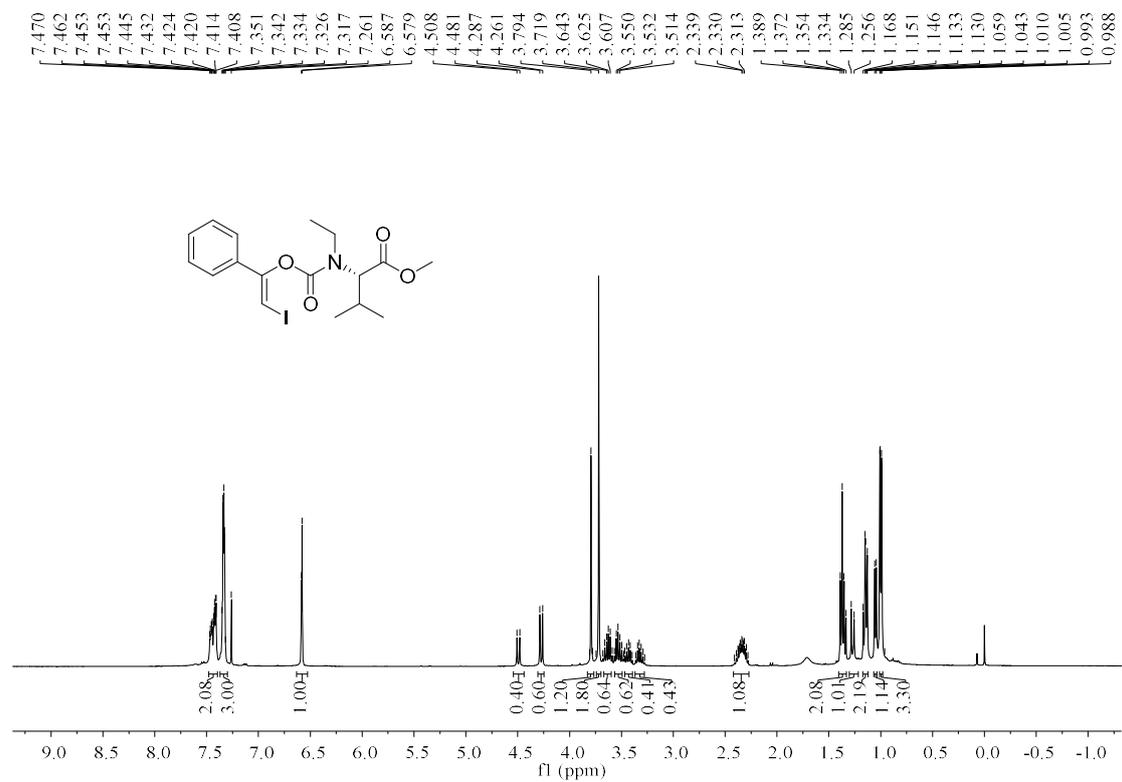
**(Z)-2-Iodo-1-phenylvinyl (3R,4aS,8aS)-3-(tert-butylcarbamoyl)octahydroisoquinoline-2(1H)-carboxylate ((Z)-3ax)**



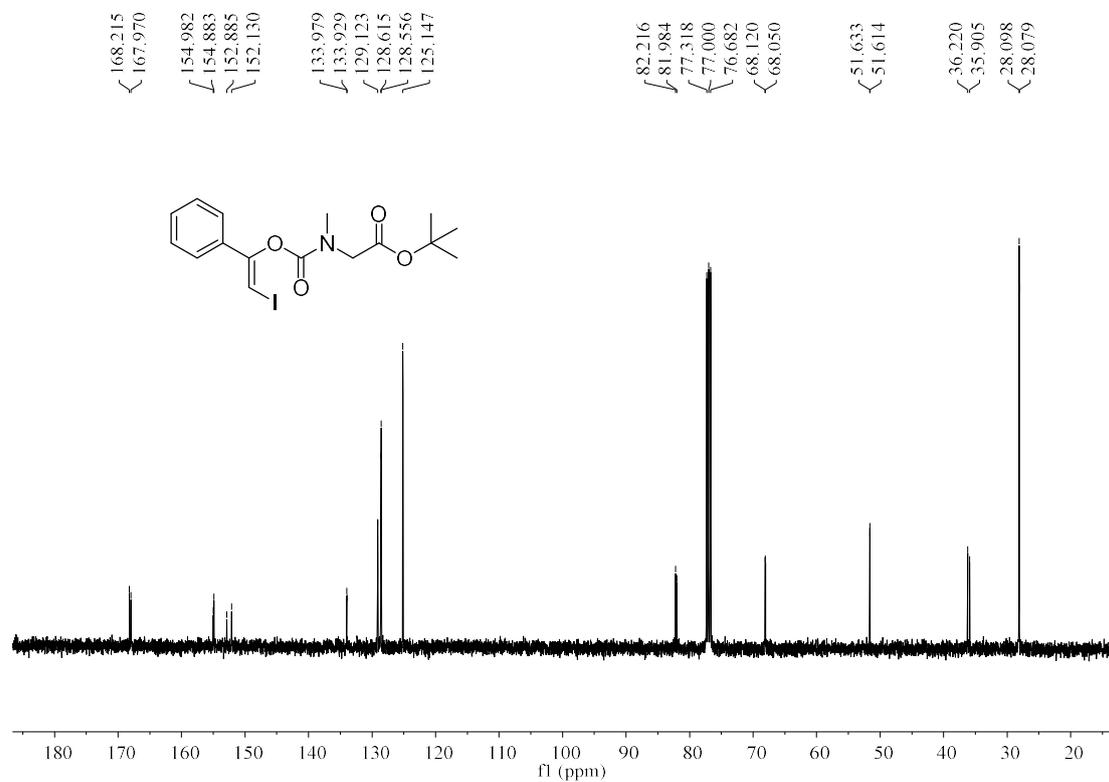
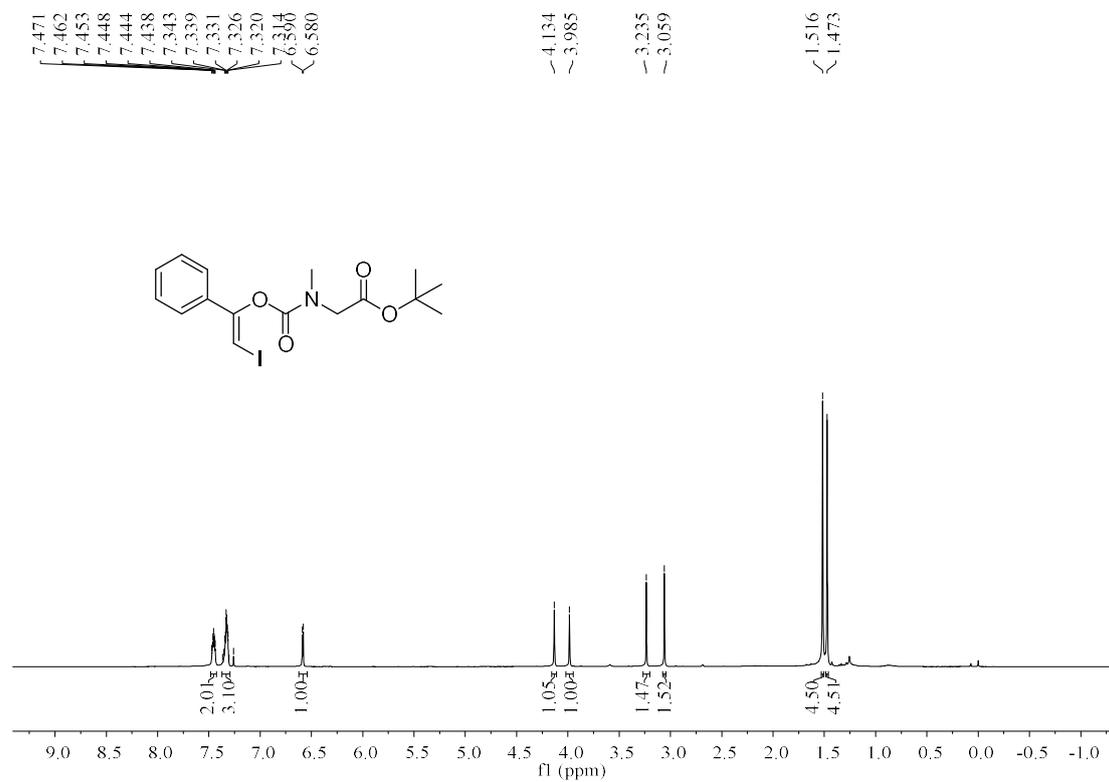
**Ethyl (Z)-N-benzyl-N-((2-iodo-1-phenylvinyl)oxy)carbonyl)glycinate ((Z)-3ay)**



Methyl (*Z*)-*N*-ethyl-*N*-(((2-iodo-1-phenylvinyl)oxy)carbonyl)-*L*-valinate ((*Z*)-3az)

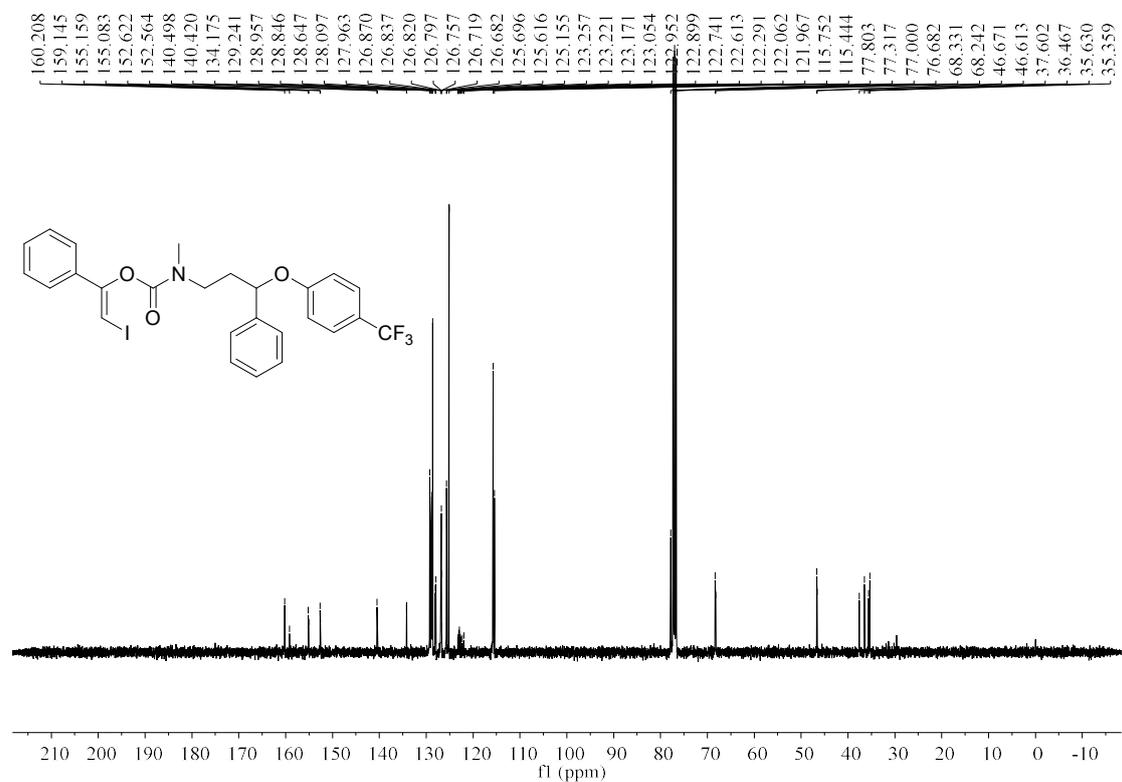
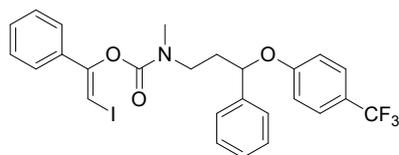
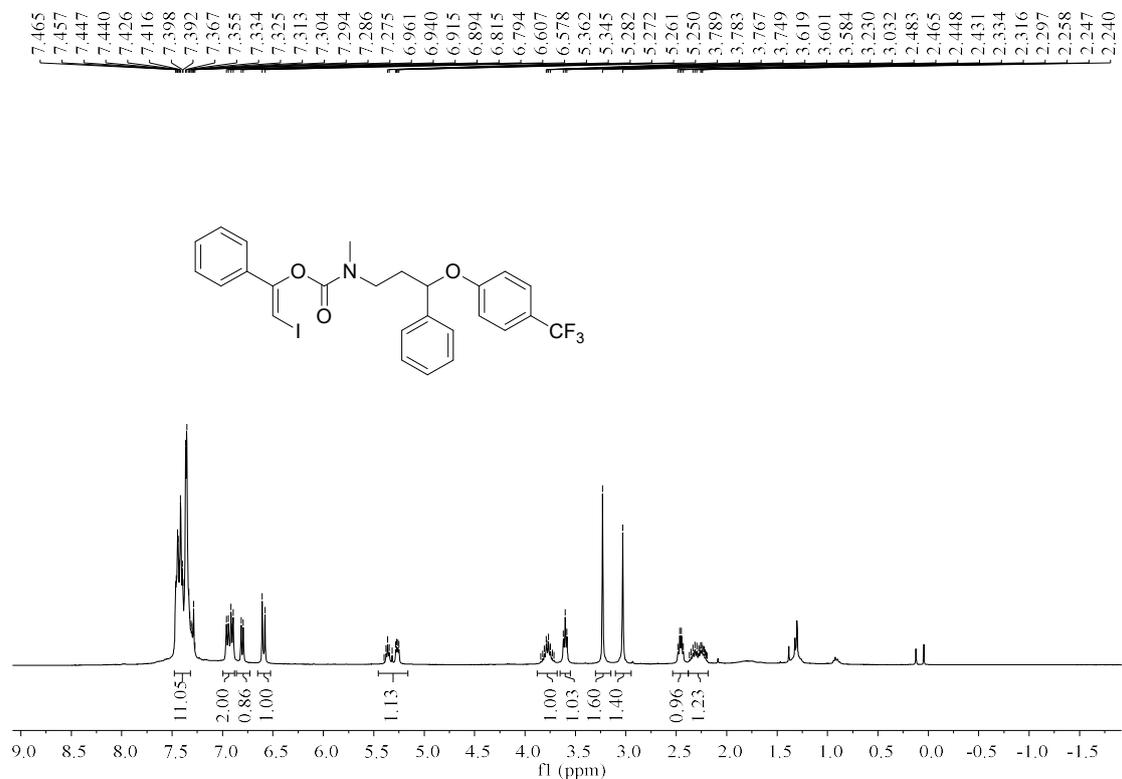


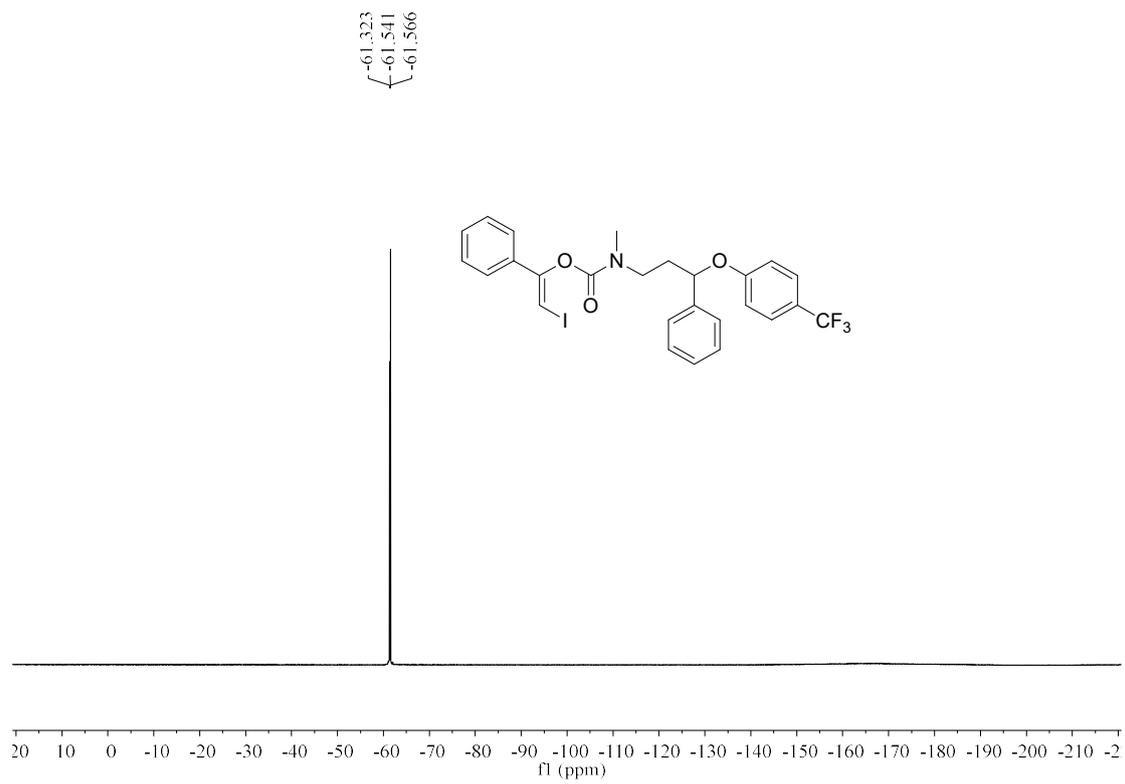
***tert*-Butyl (*Z*)-*N*-(((2-iodo-1-phenylvinyl)oxy)carbonyl)-*N*-methylglycinate ((*Z*)-3aaa)**



**(Z)-2-Iodo-1-phenylvinyl methyl(3-phenyl-3-(4-(trifluoromethyl)phenoxy)propyl)carbamate**

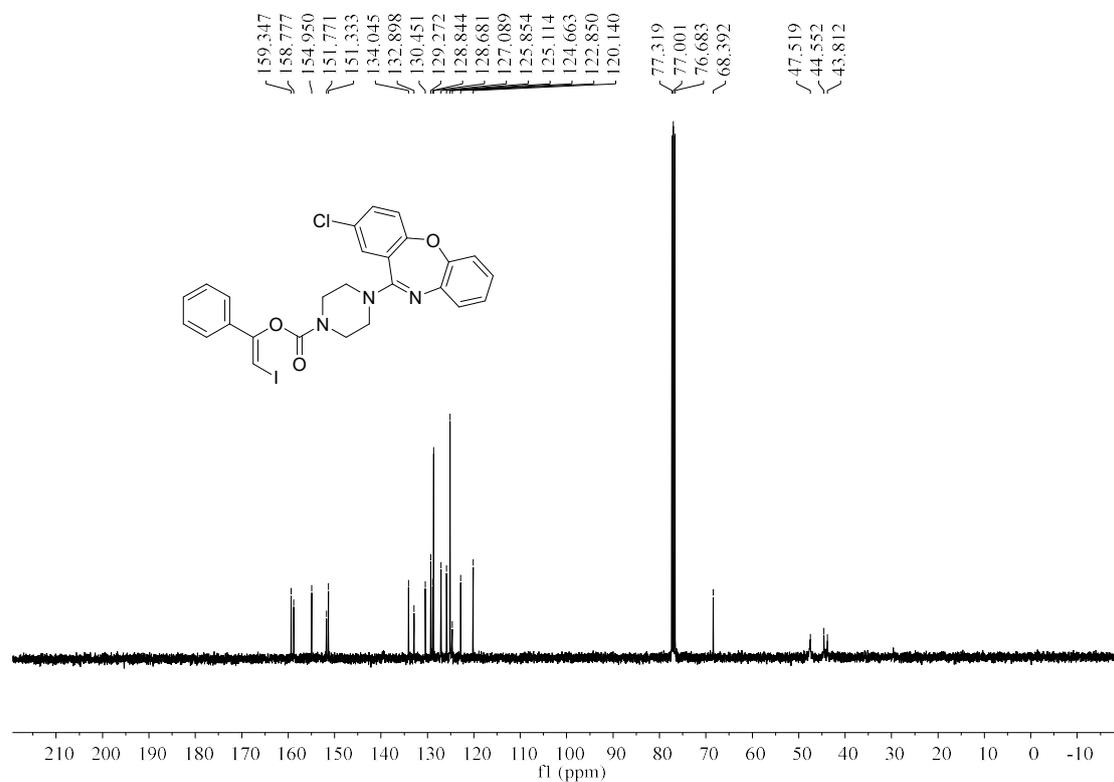
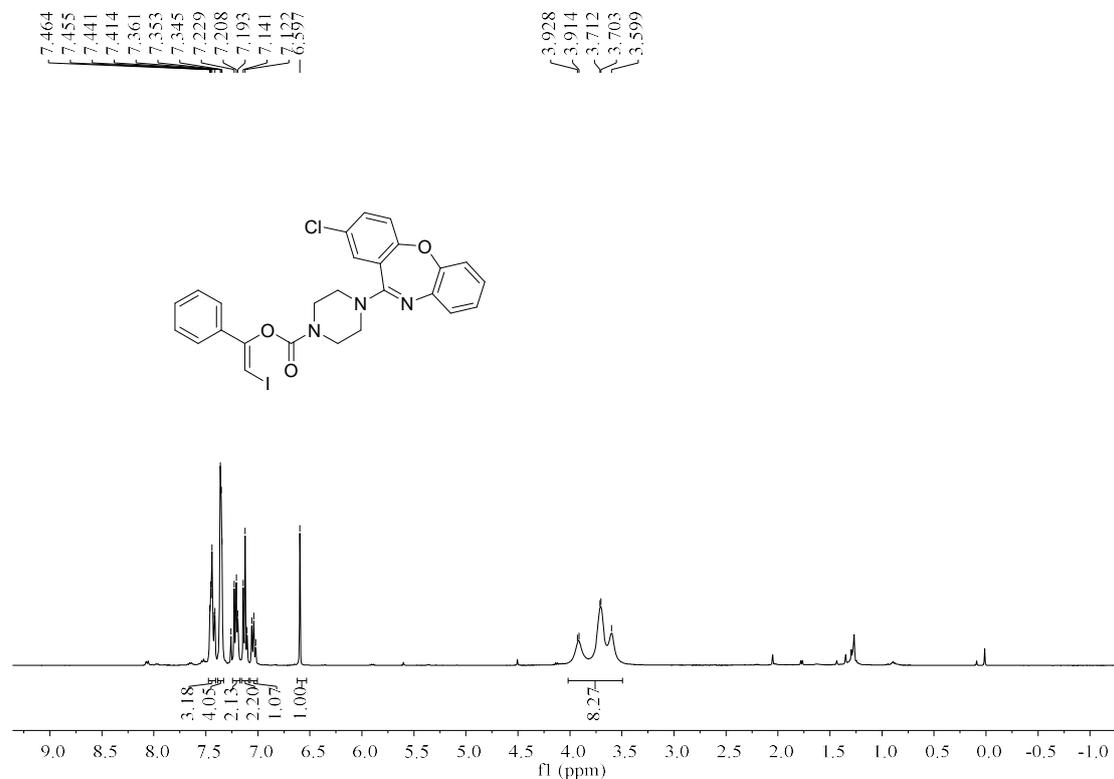
**((Z)-3aba)**



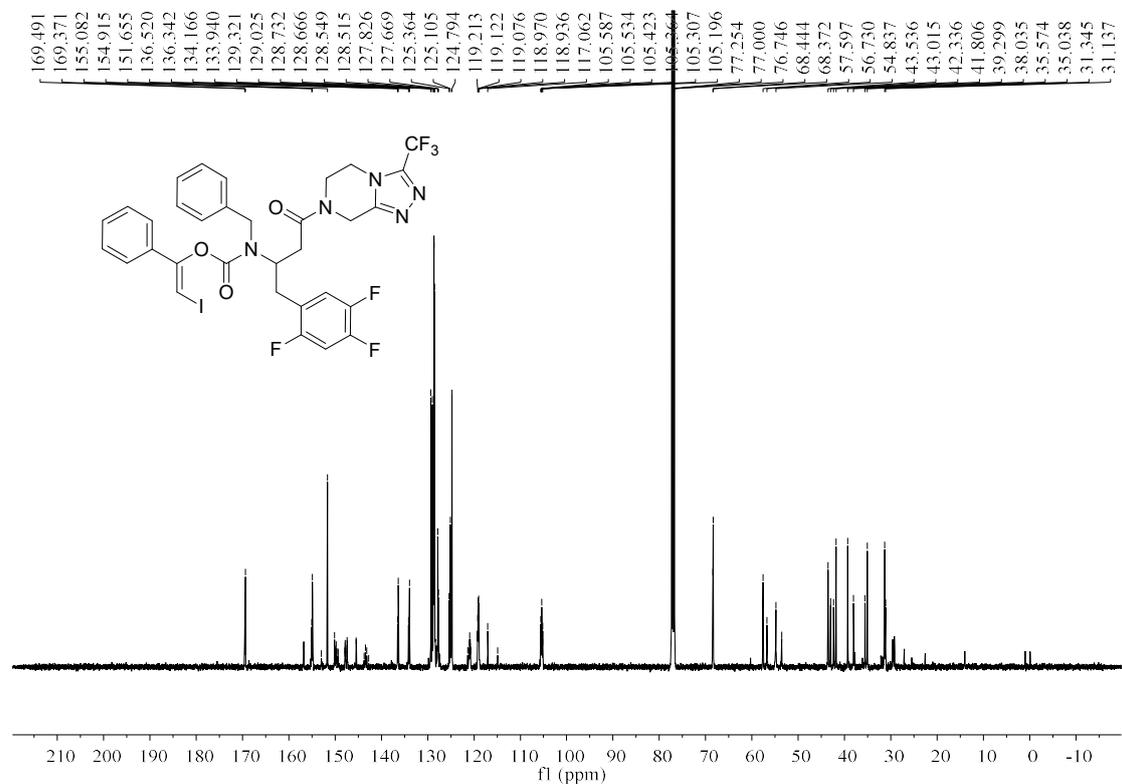
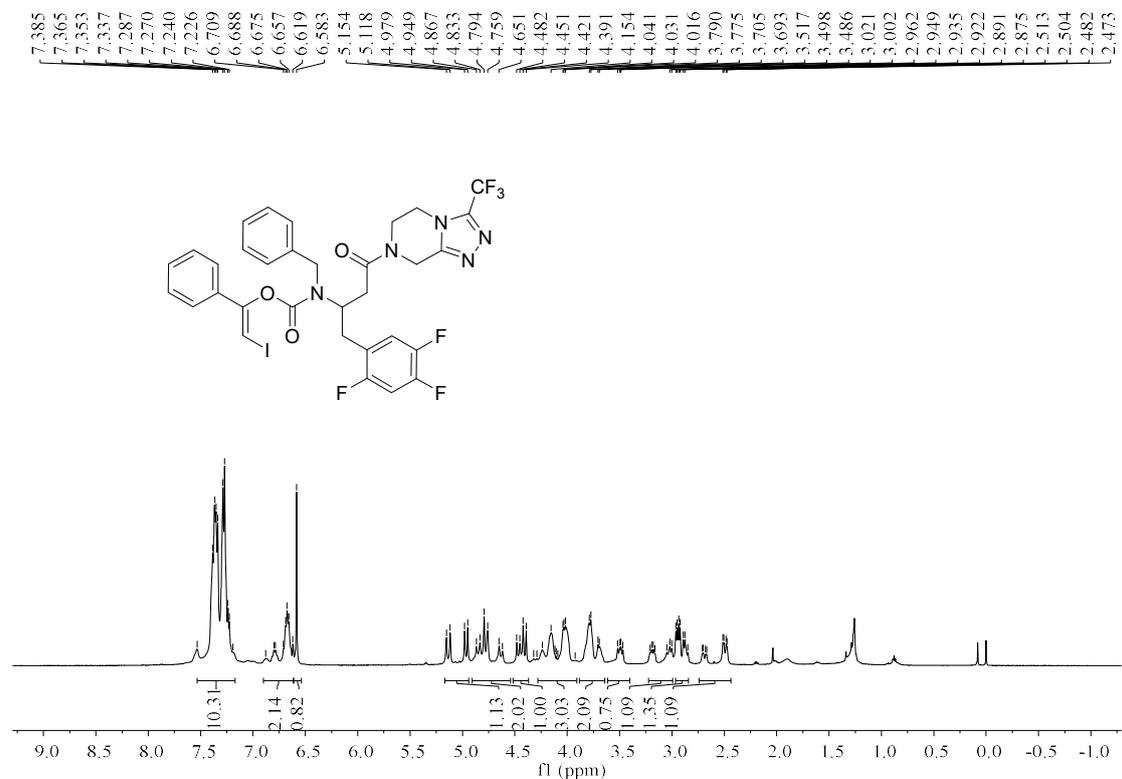


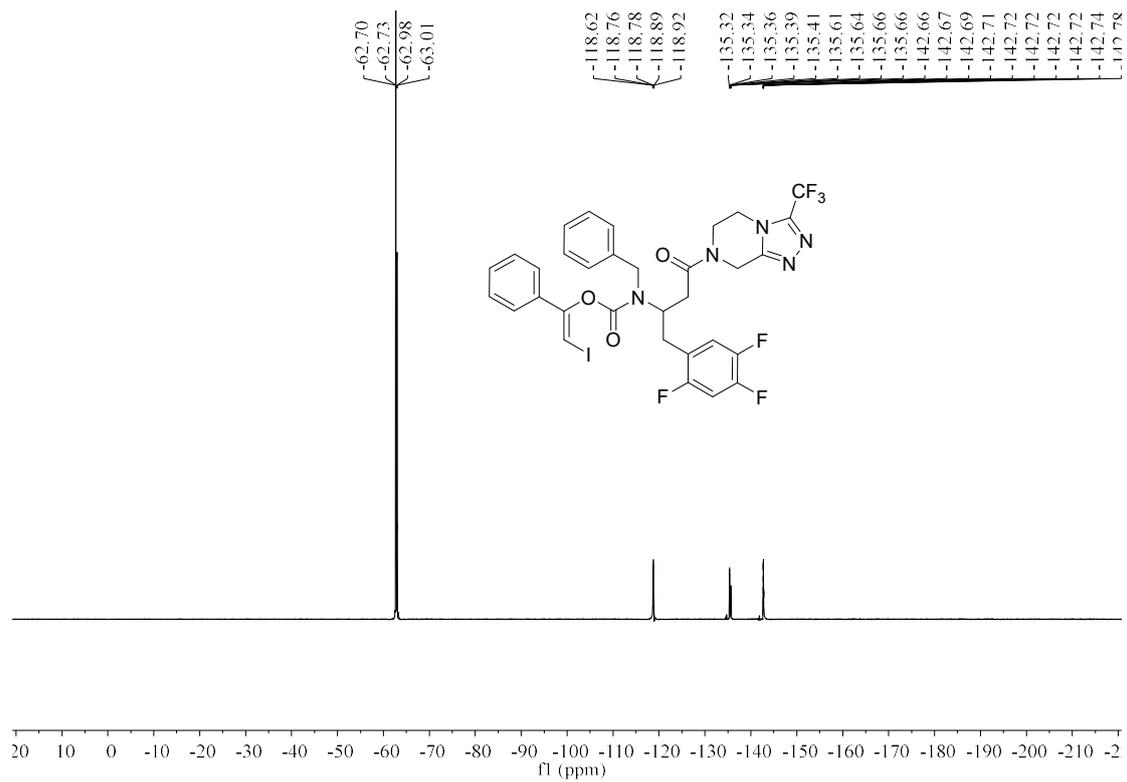
**(Z)-2-Iodo-1-phenylvinyl 4-(2-chlorodibenzo[*b,f*][1,4]oxazepin-11-yl)piperazine-1-carboxylate**

**((Z)-3aca)**

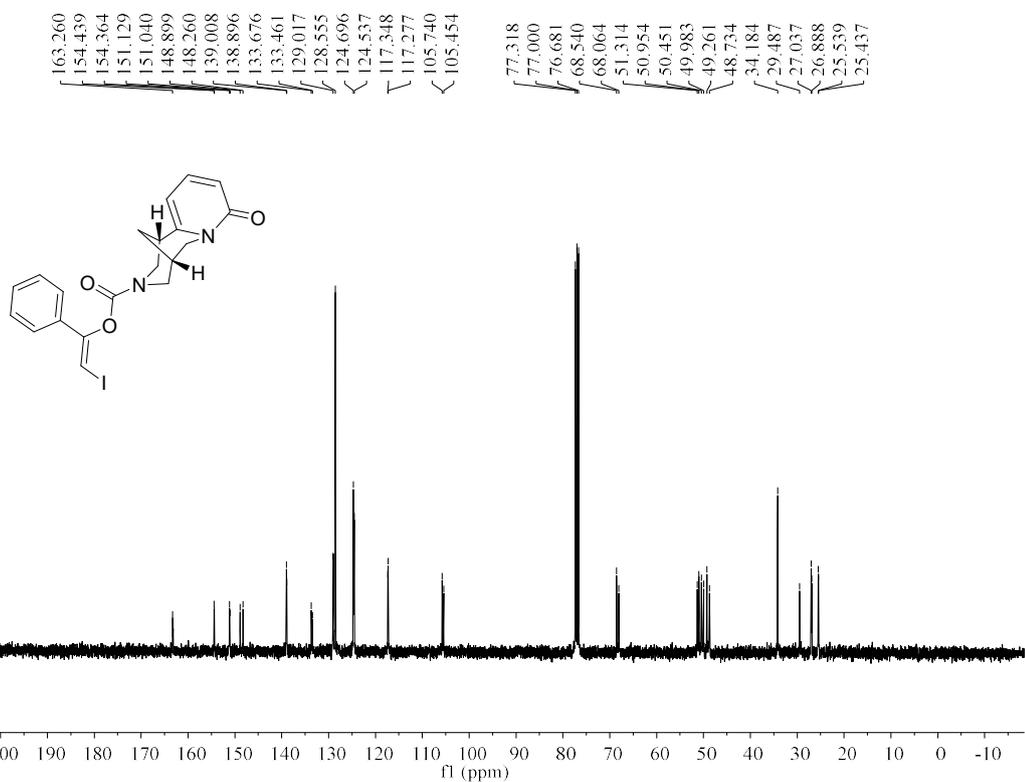
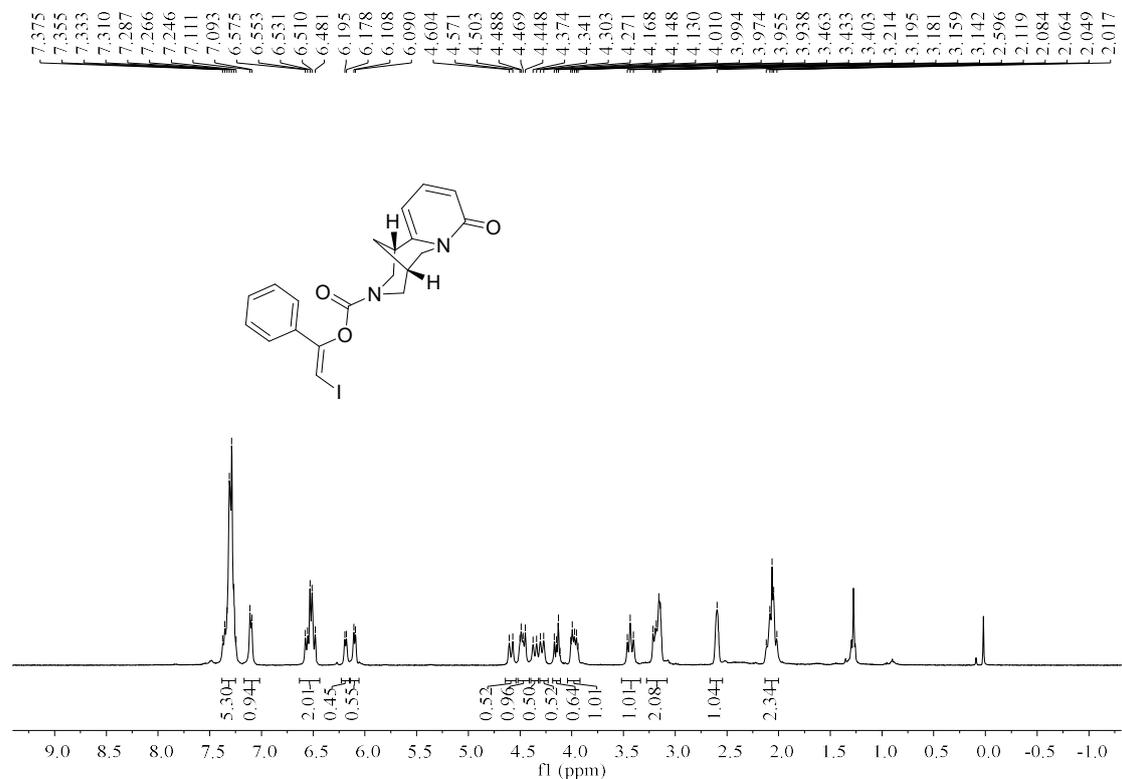


**(Z)-2-Iodo-1-phenylvinyl benzyl(4-oxo-4-(3-(trifluoromethyl)-5,6-dihydro-[1,2,4]triazolo[4,3-a]pyrazin-7(8H)-yl)-1-(2,4,5-trifluorophenyl)butan-2-yl)carbamate ((Z)-3ada)**

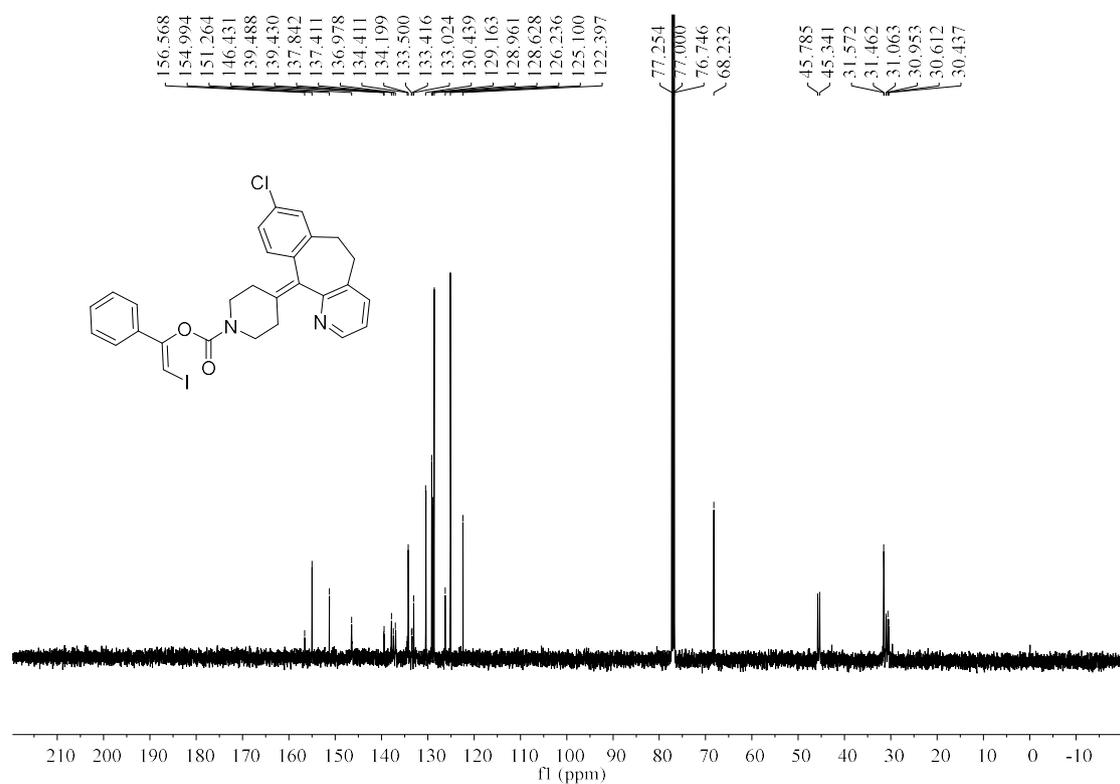
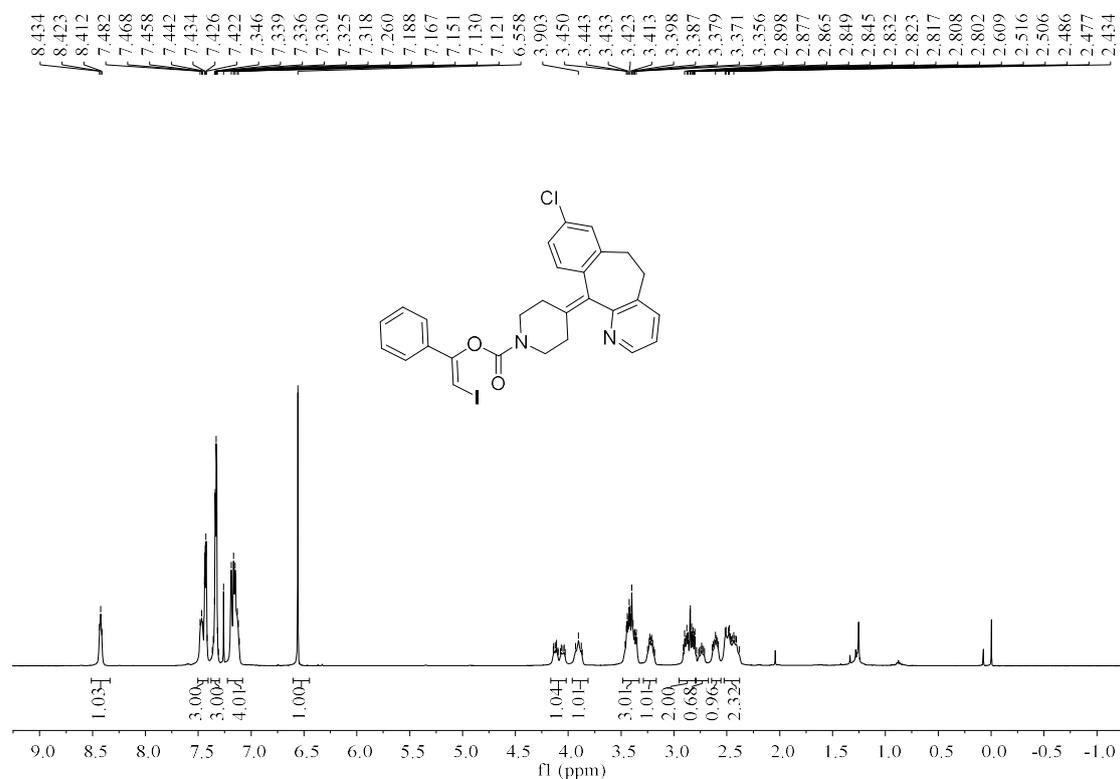




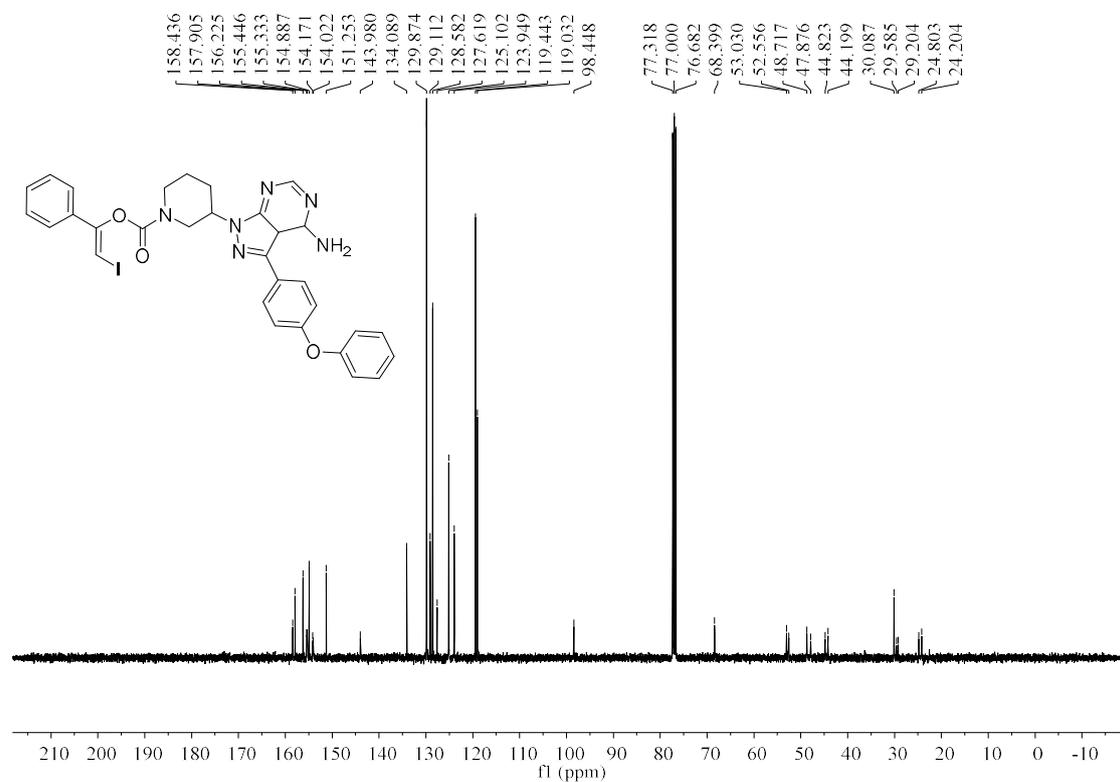
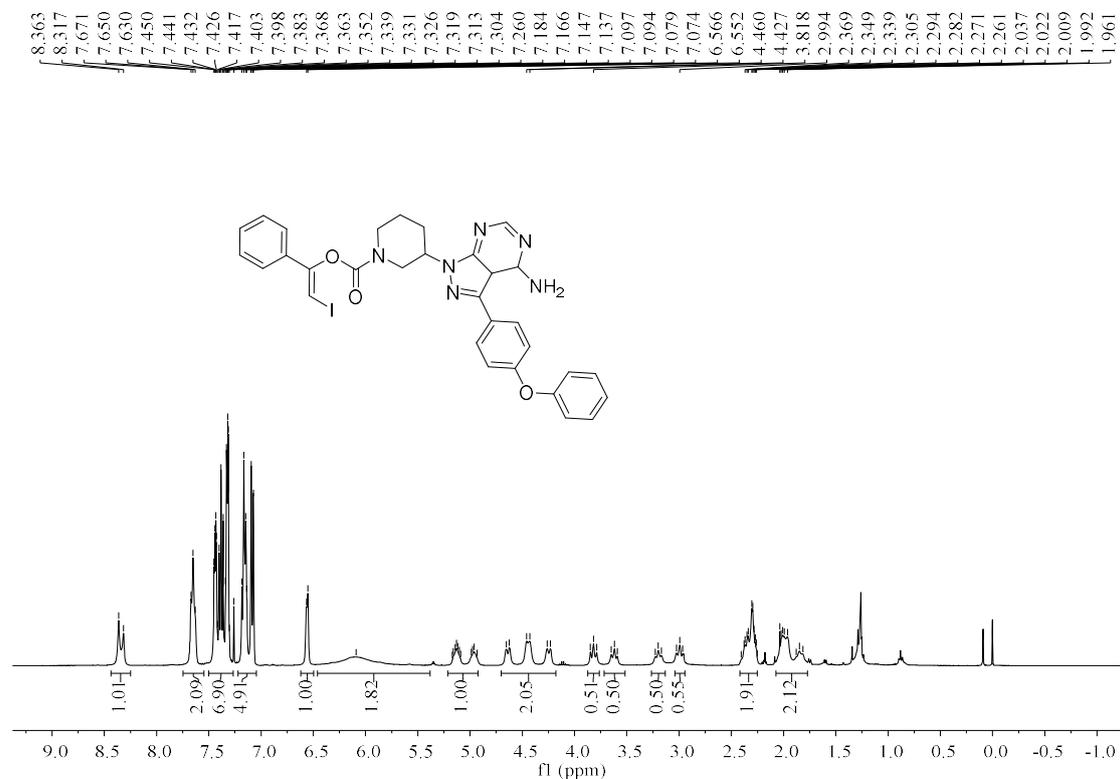
**(Z)-2-Iodo-1-phenylvinyl (1S,5R)-8-oxo-1,5,6,8-tetrahydro-2H-1,5-methanopyrido[1,2-a][1,5]diazocine-3(4H)-carboxylate ((Z)-3aea)**



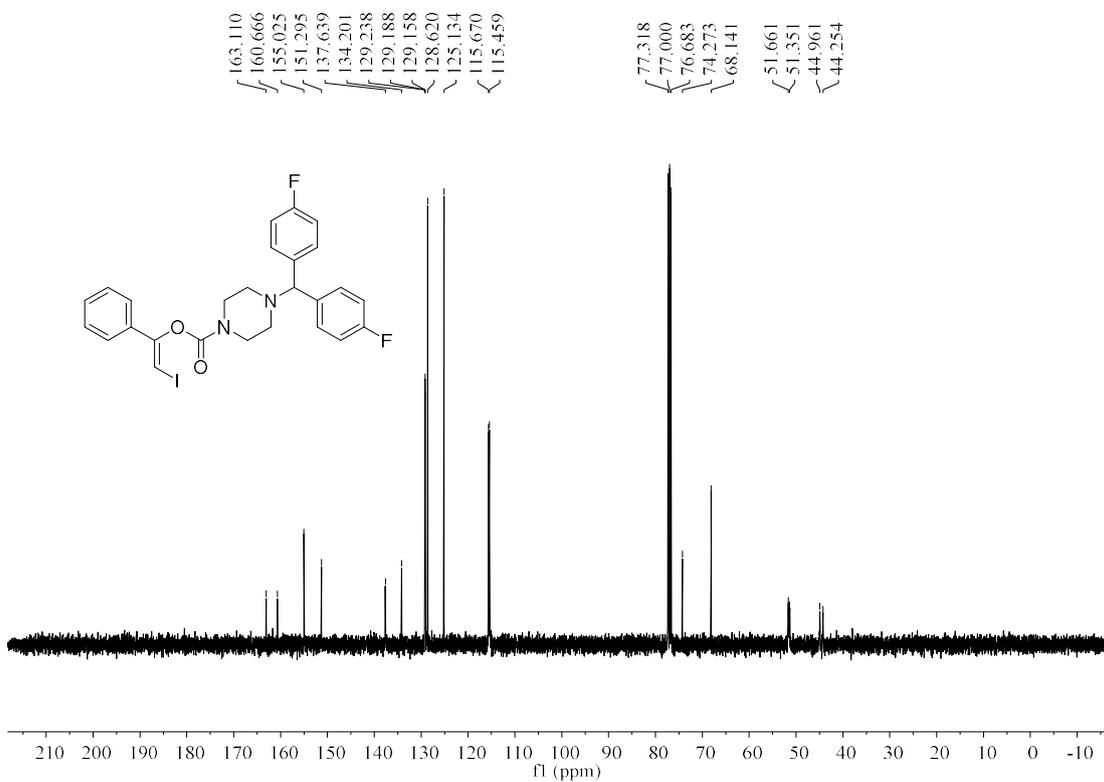
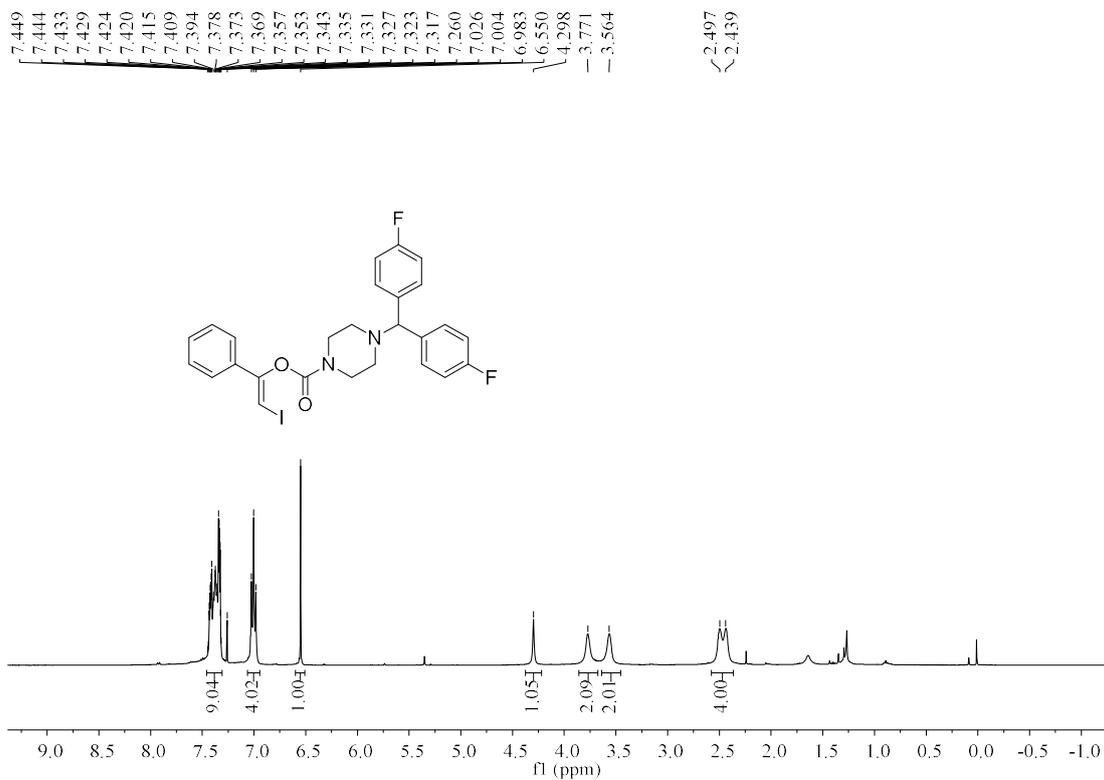
**(Z)-2-Iodo-1-phenylvinyl 4-(8-chloro-5,6-dihydro-11H-benzo[5,6]cyclohepta[1,2-b]pyridin-11-ylidene) piperidine-1-carboxylate ((Z)-3afa)**

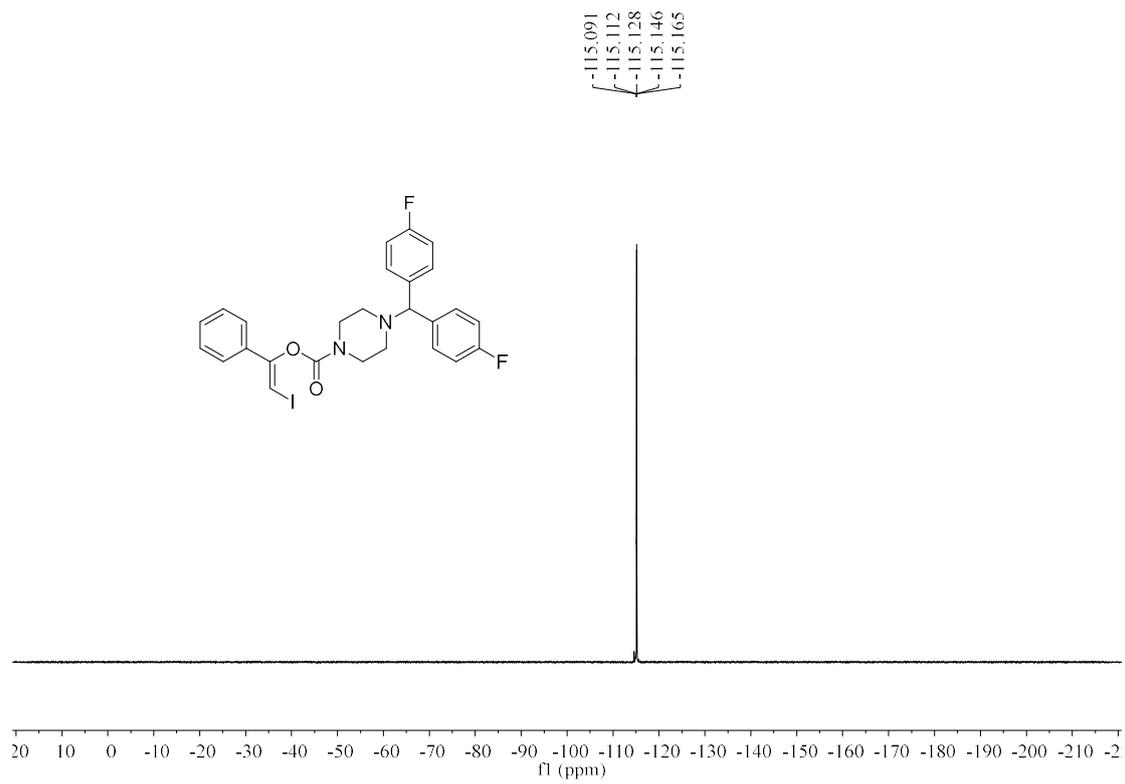


**(Z)-2-Iodo-1-phenylvinyl 3-(4-amino-3-(4-phenoxyphenyl)-3a,4-dihydro-1H-pyrazolo[3,4-d]pyrimidin-1-yl)piperidine-1-carboxylate ((Z)-3aga)**

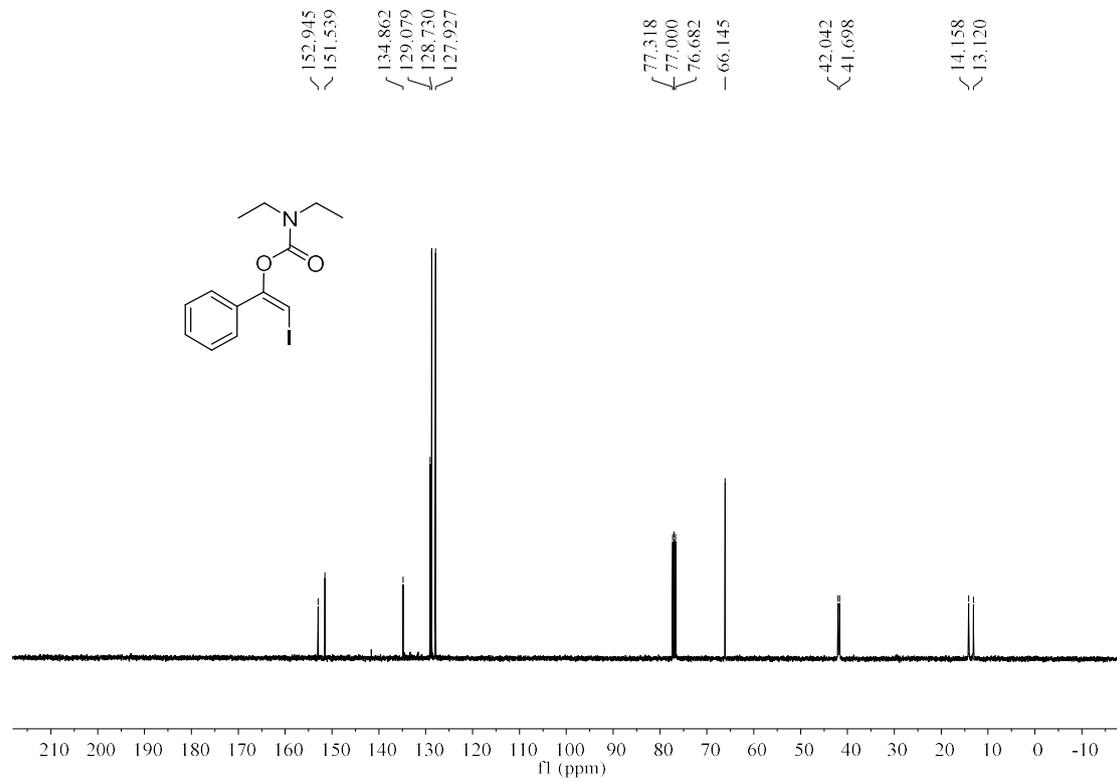
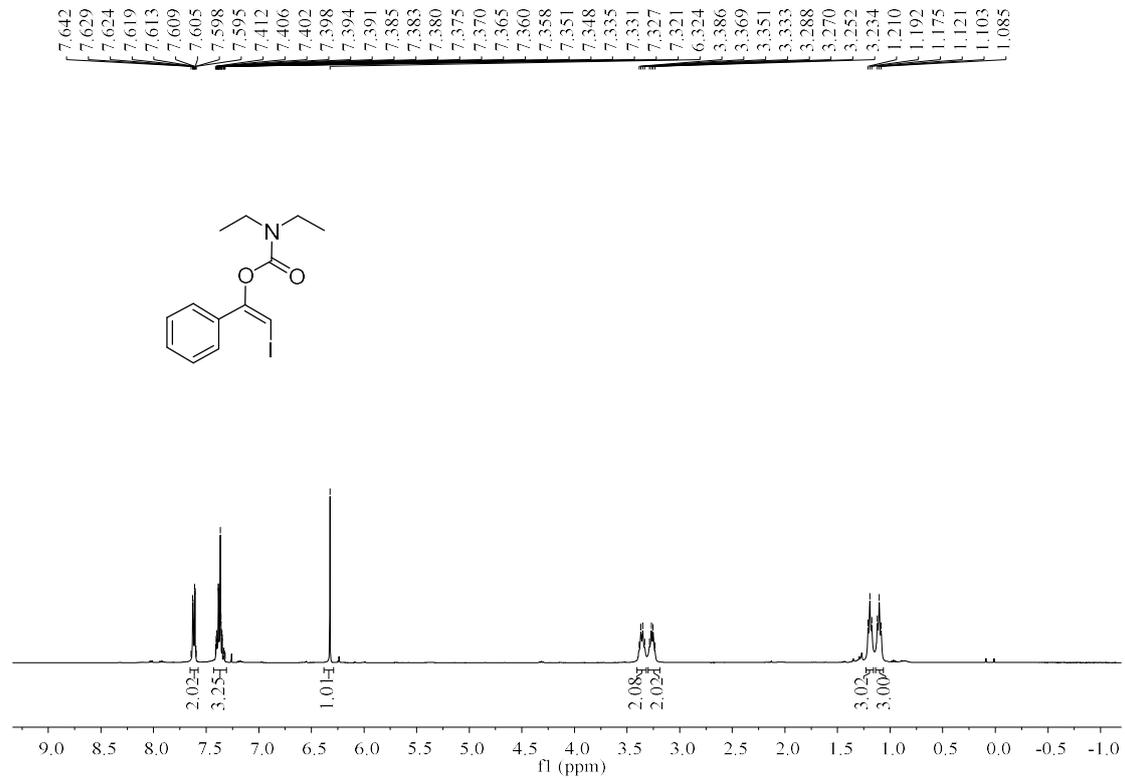


**(Z)-2-Iodo-1-phenylvinyl 4-(bis(4-fluorophenyl)methyl)piperazine-1-carboxylate ((Z)-3aha)**

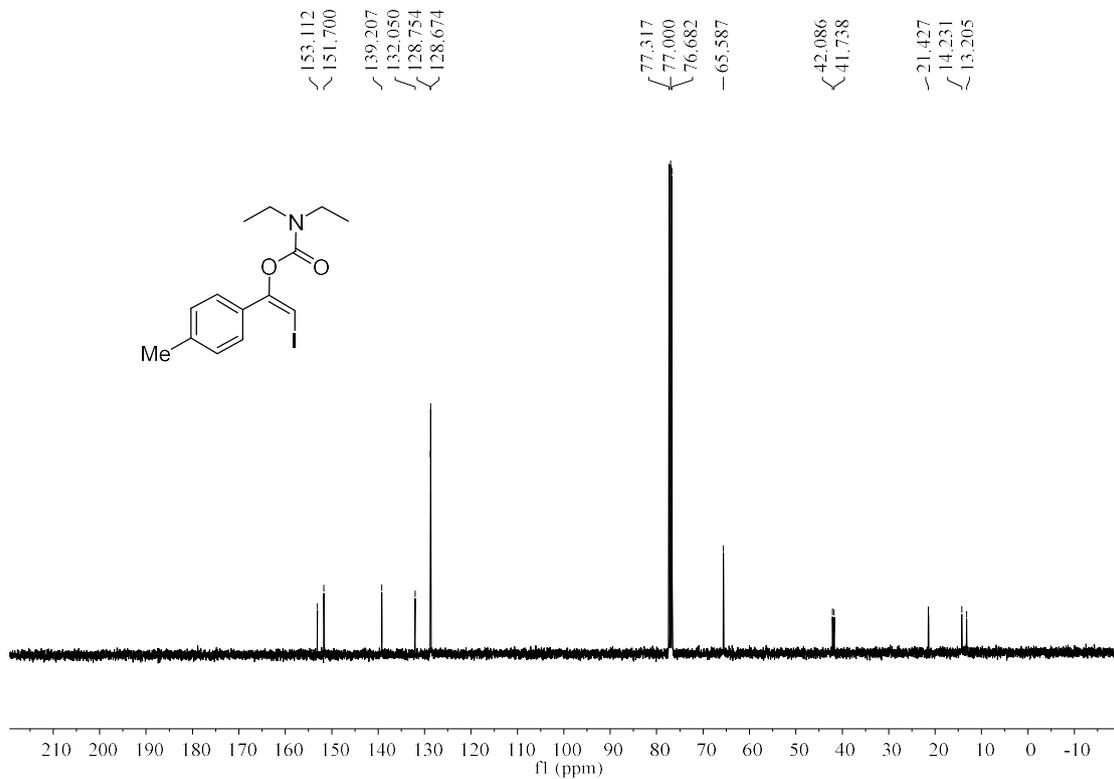
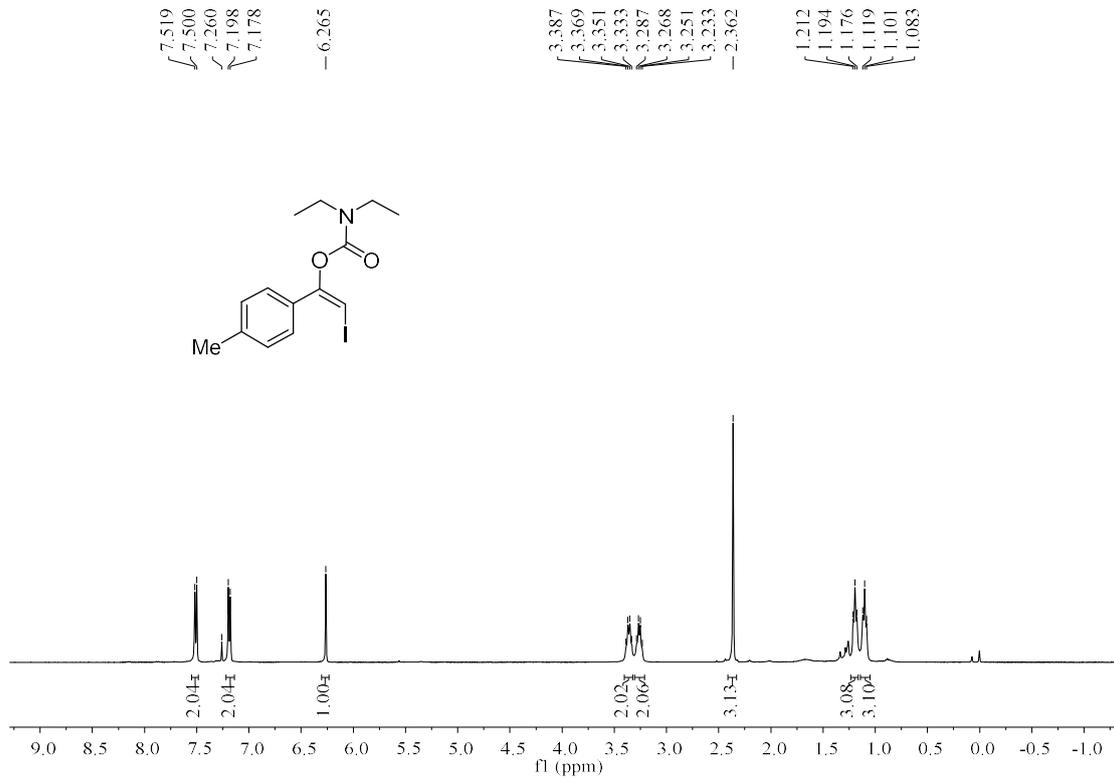




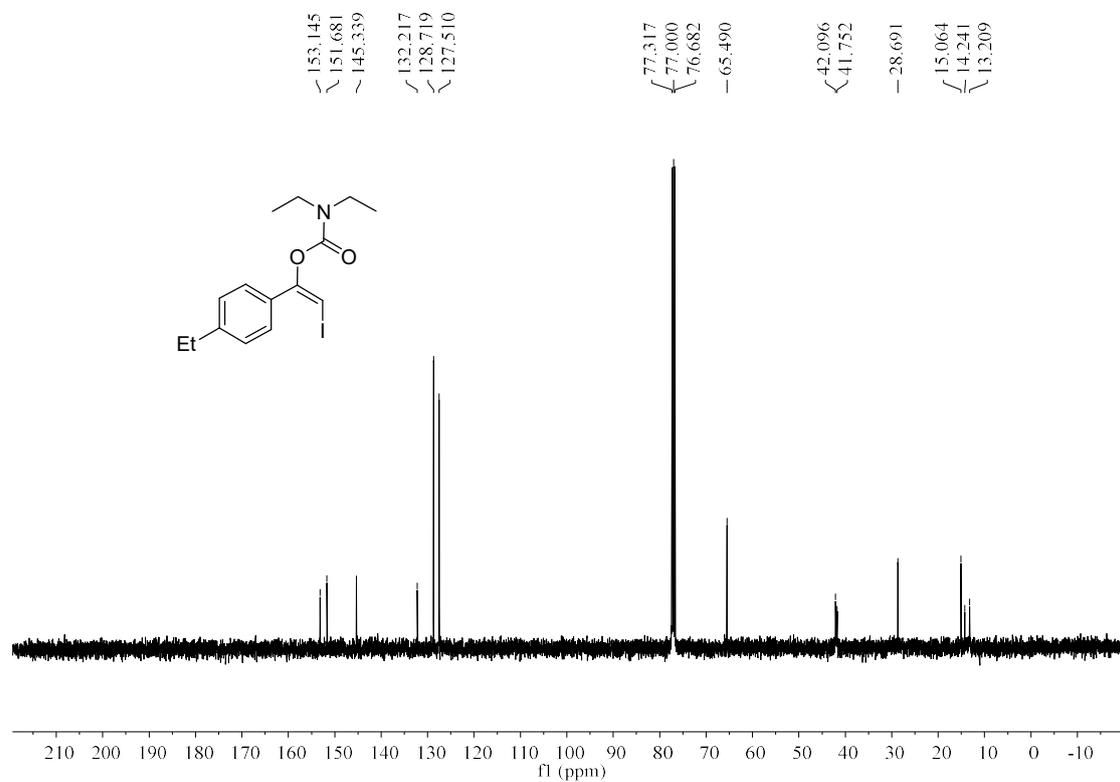
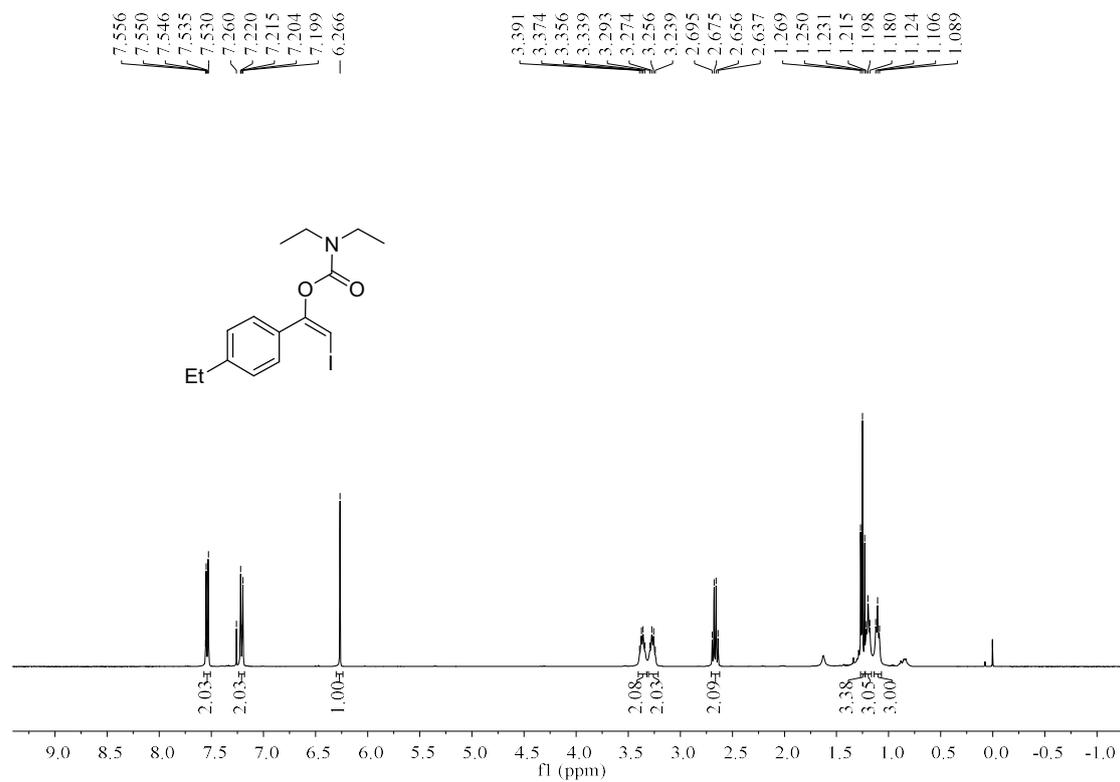
**(E)-2-Iodo-1-phenylvinyl diethylcarbamate ((E)-3aa)**



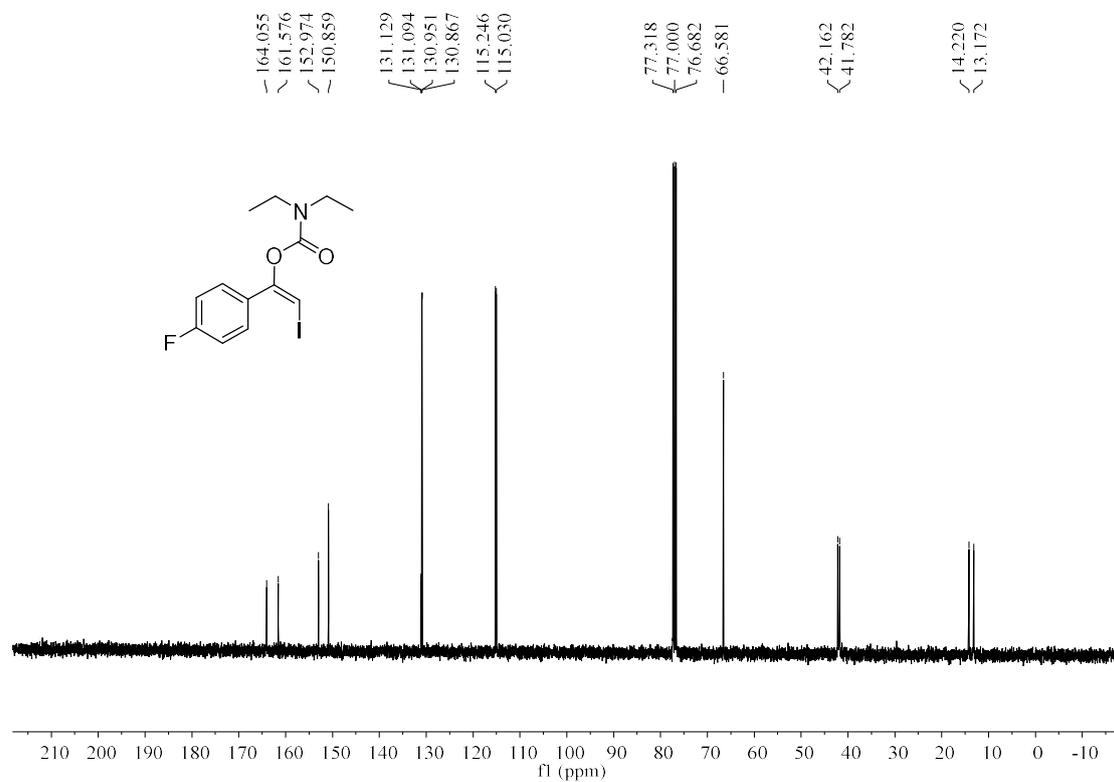
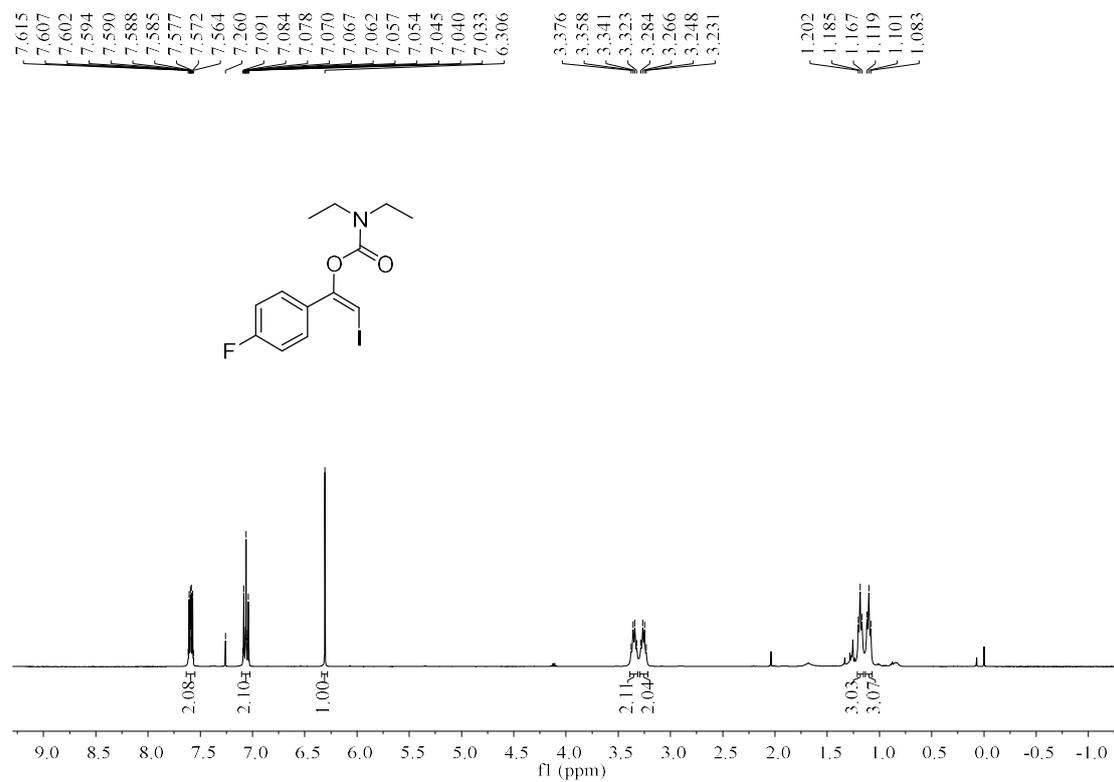
**(E)-2-Iodo-1-(p-tolyl)vinyl diethylcarbamate ((E)-3ba)**

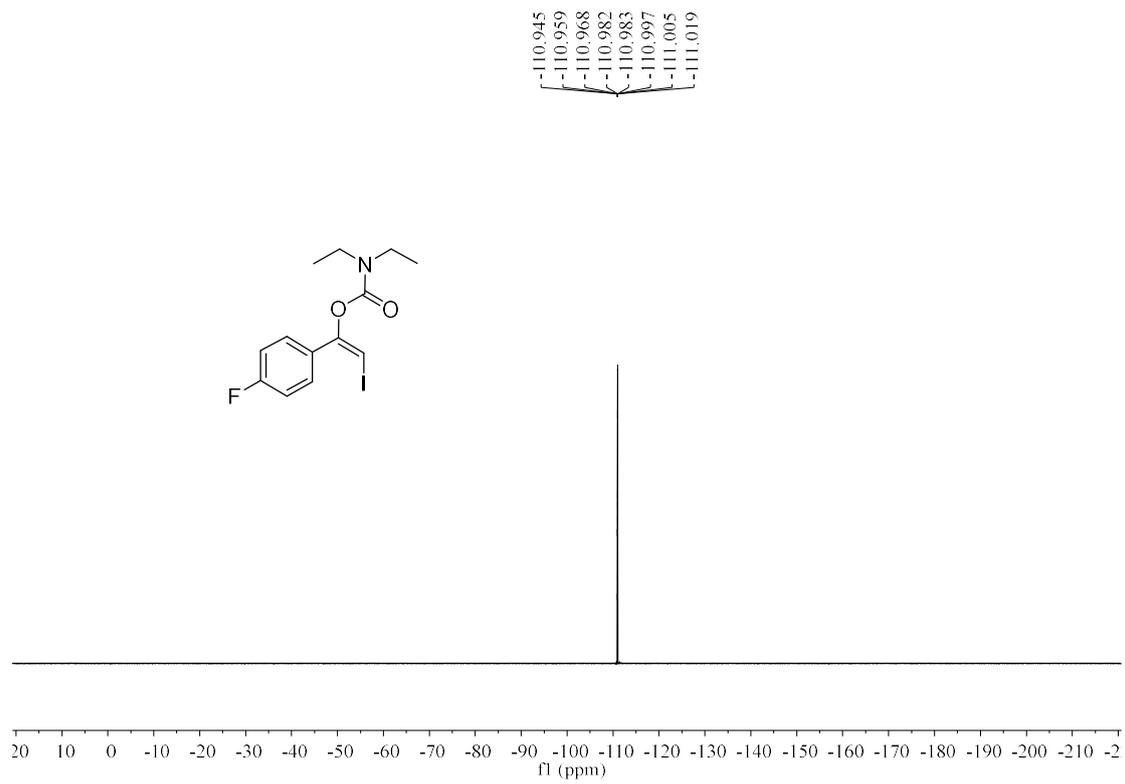


**(E)-1-(4-Ethylphenyl)-2-iodovinyl diethylcarbamate ((E)-3sa)**

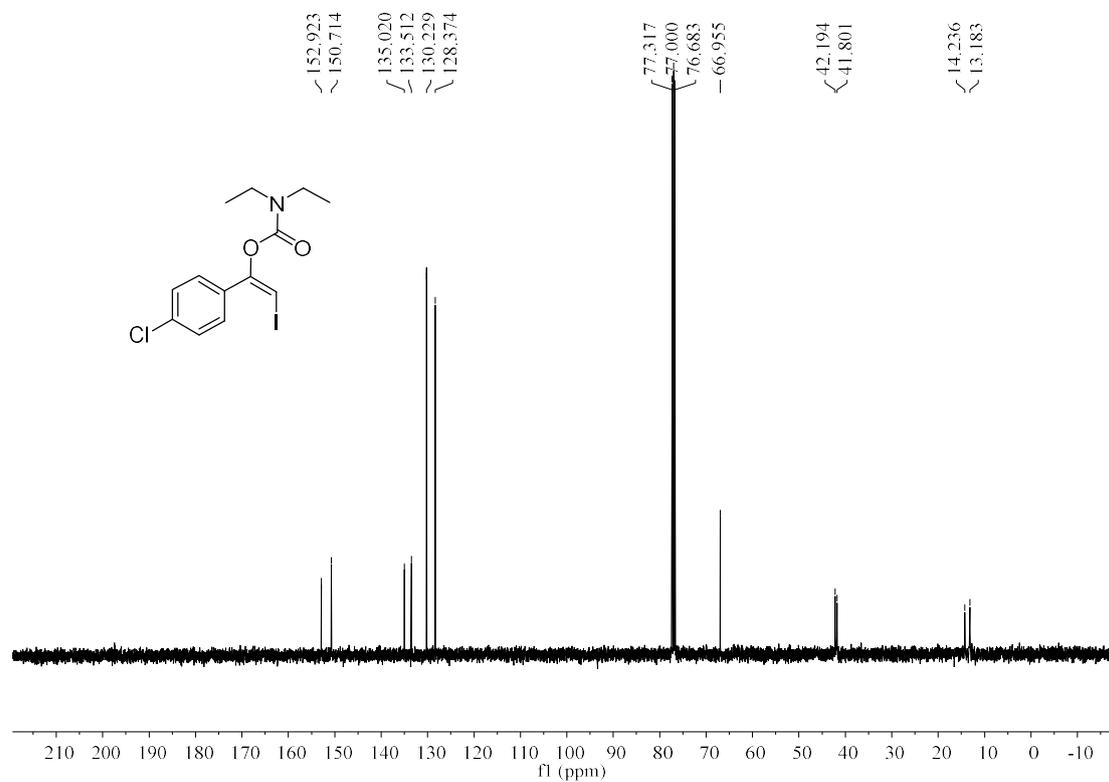
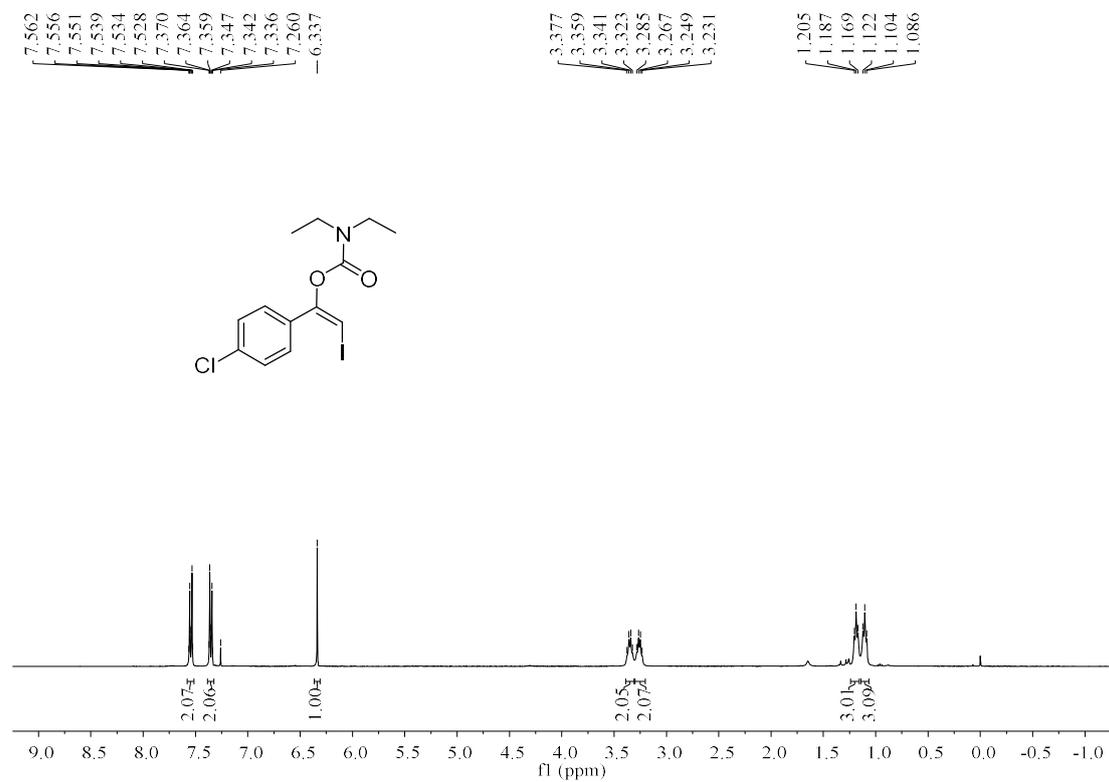


**(E)-1-(4-Fluorophenyl)-2-iodovinyl diethylcarbamate ((E)-3ca)**

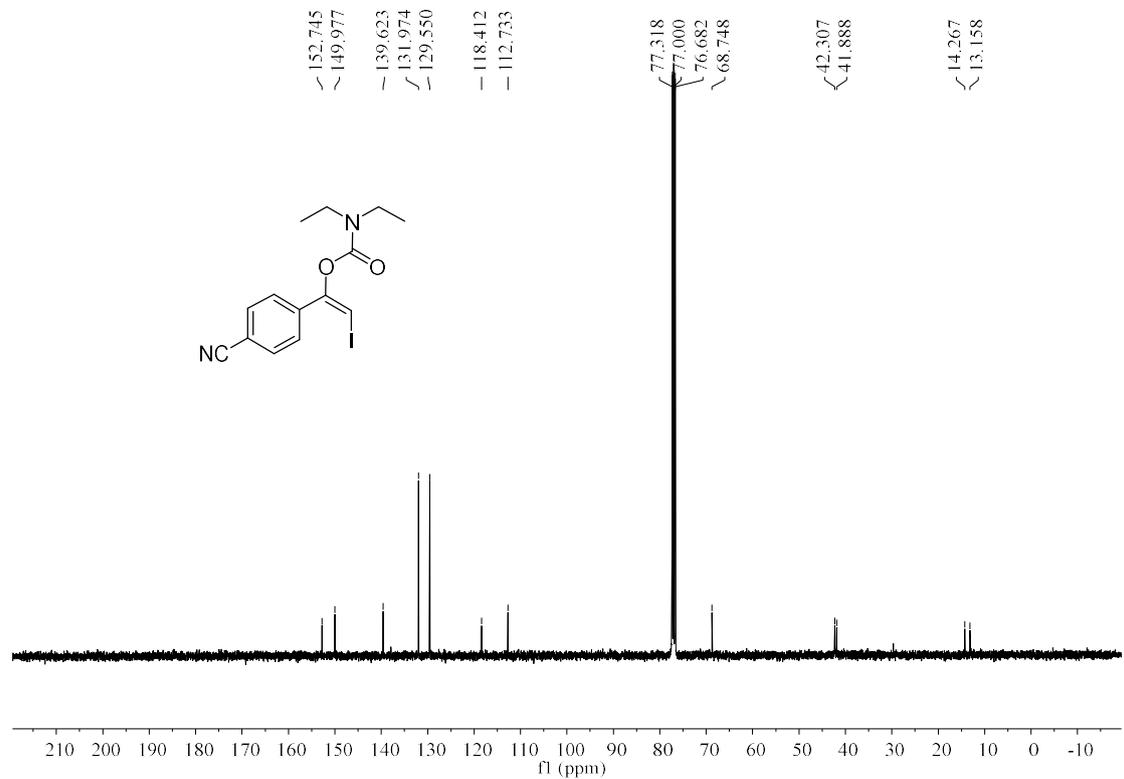
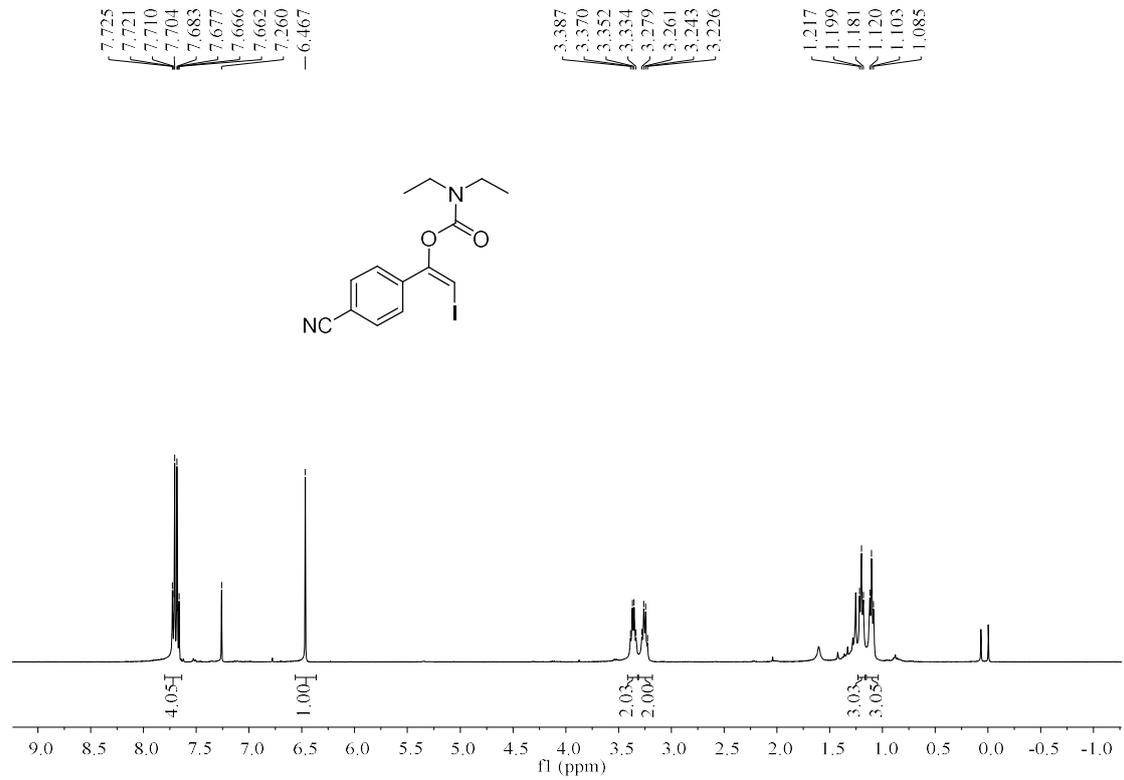




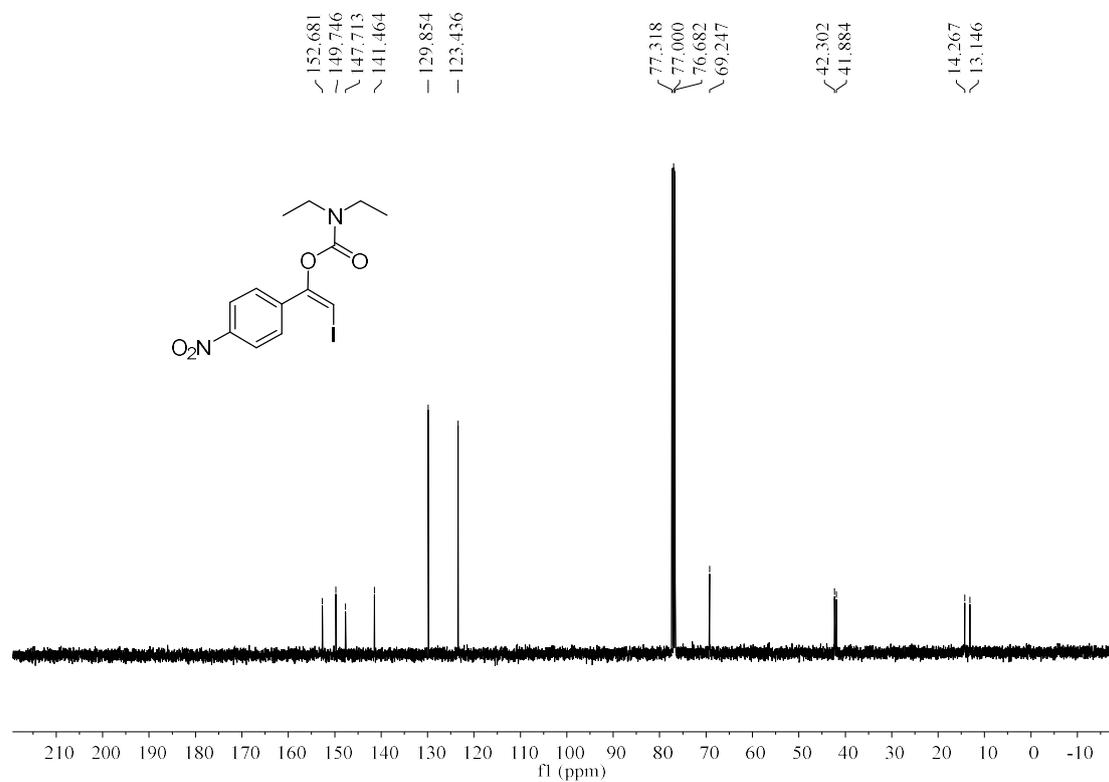
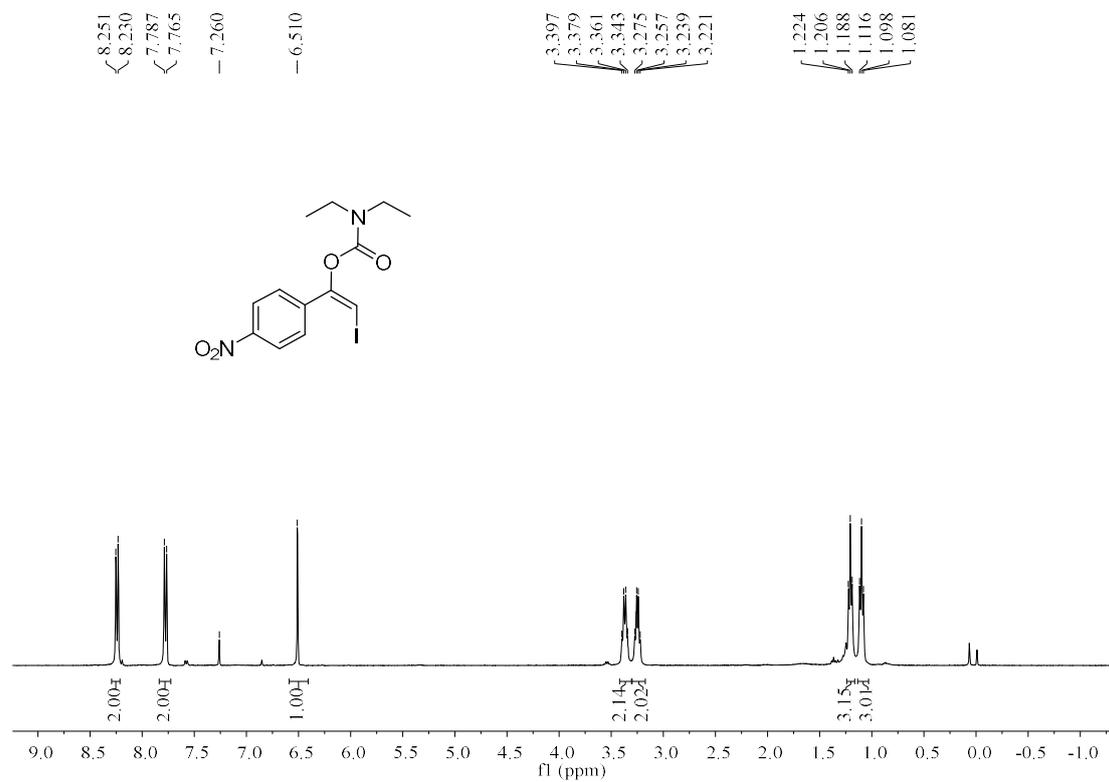
**(E)-1-(4-Chlorophenyl)-2-iodovinyl diethylcarbamate ((E)-3da)**



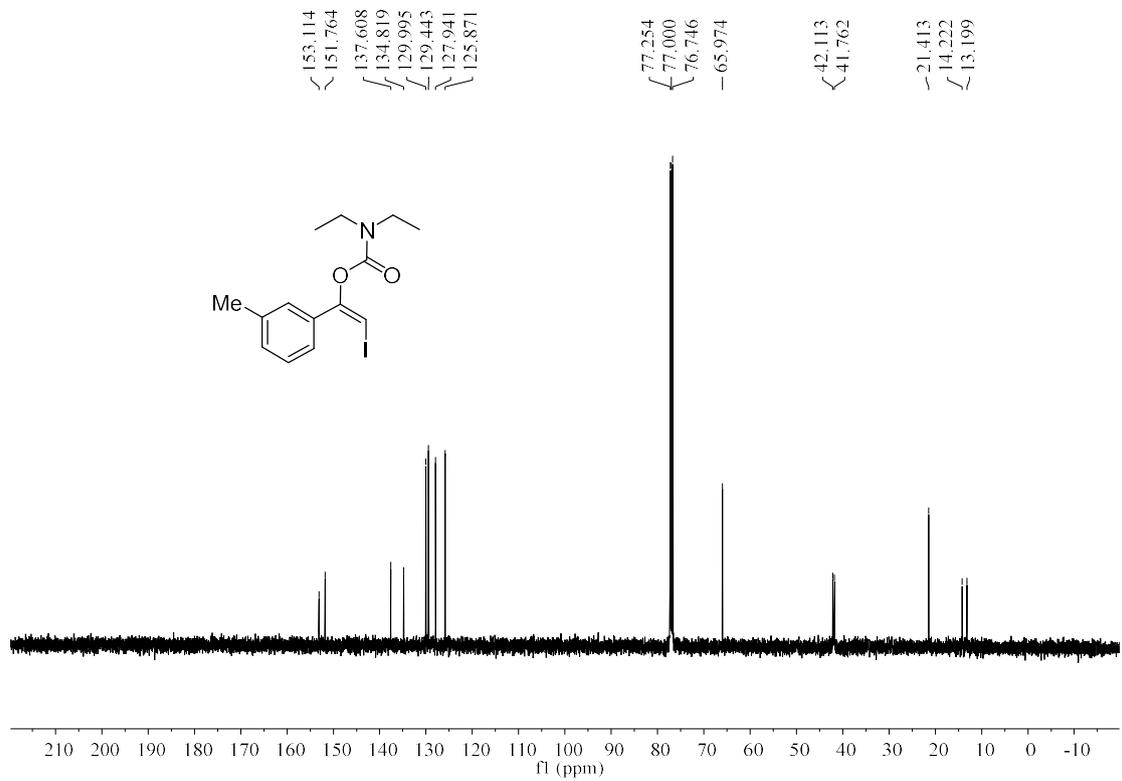
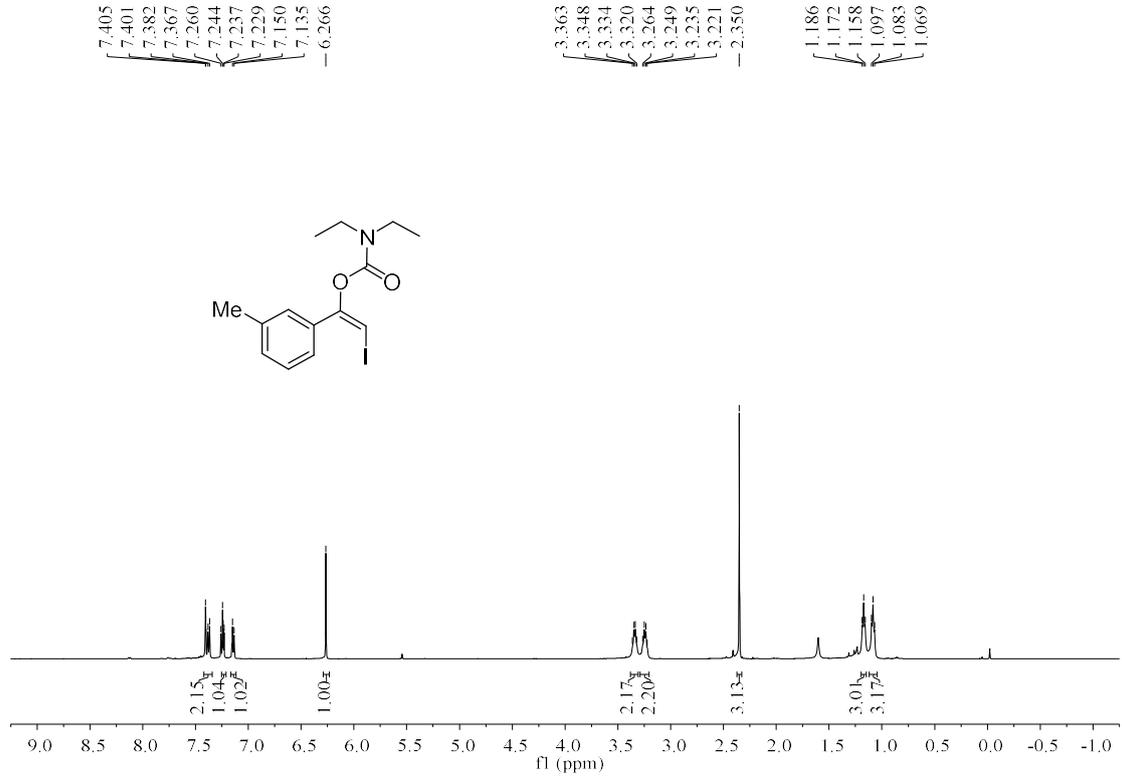
**(E)-1-(4-Cyanophenyl)-2-iodovinyl diethylcarbamate ((E)-3ea)**



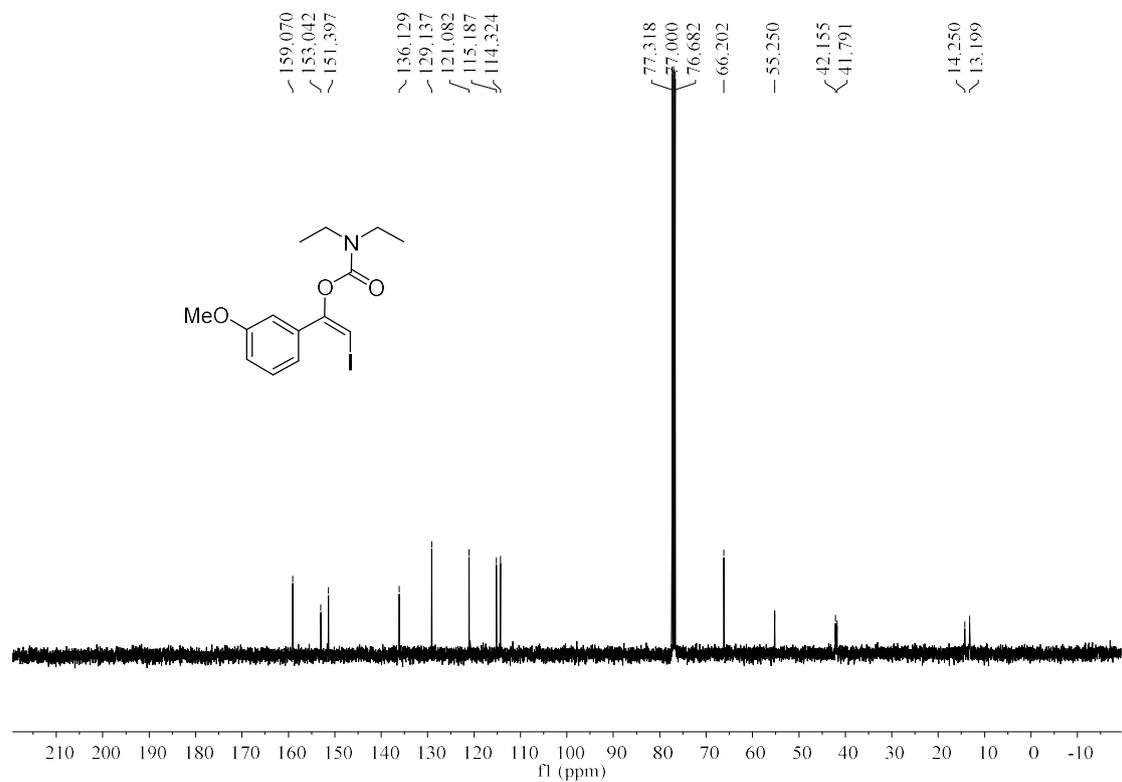
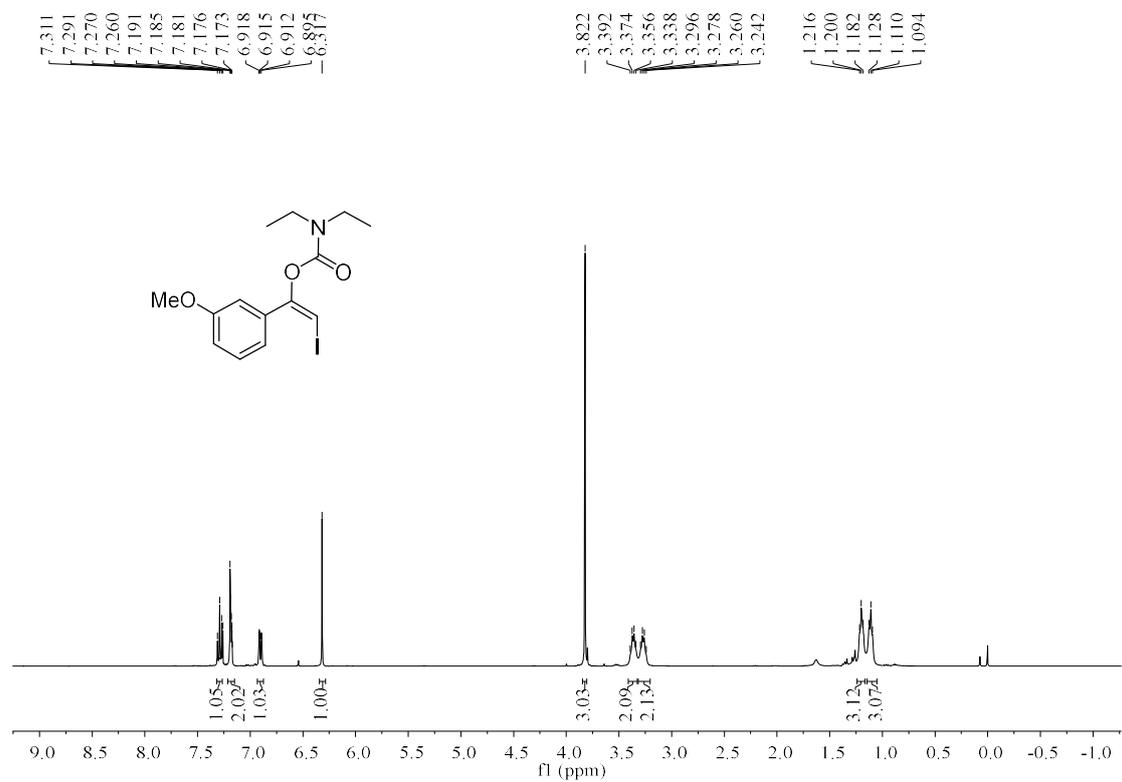
**(E)-2-Iodo-1-(4-nitrophenyl)vinyl diethylcarbamate ((E)-3fa)**



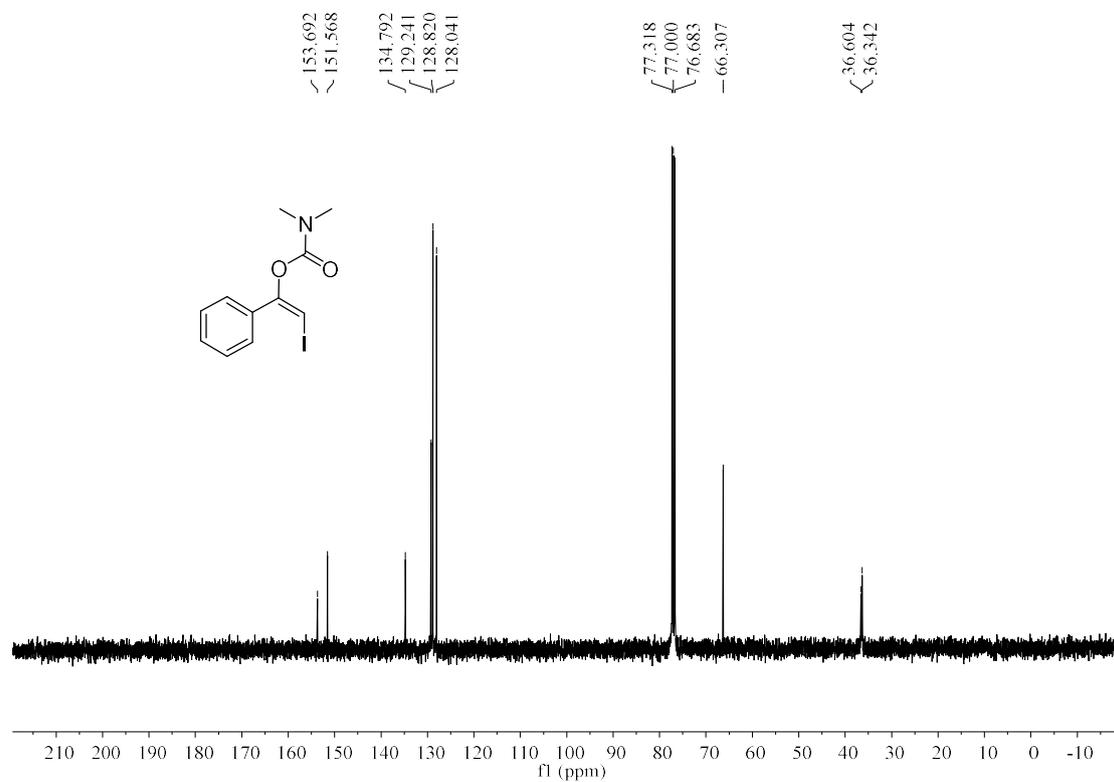
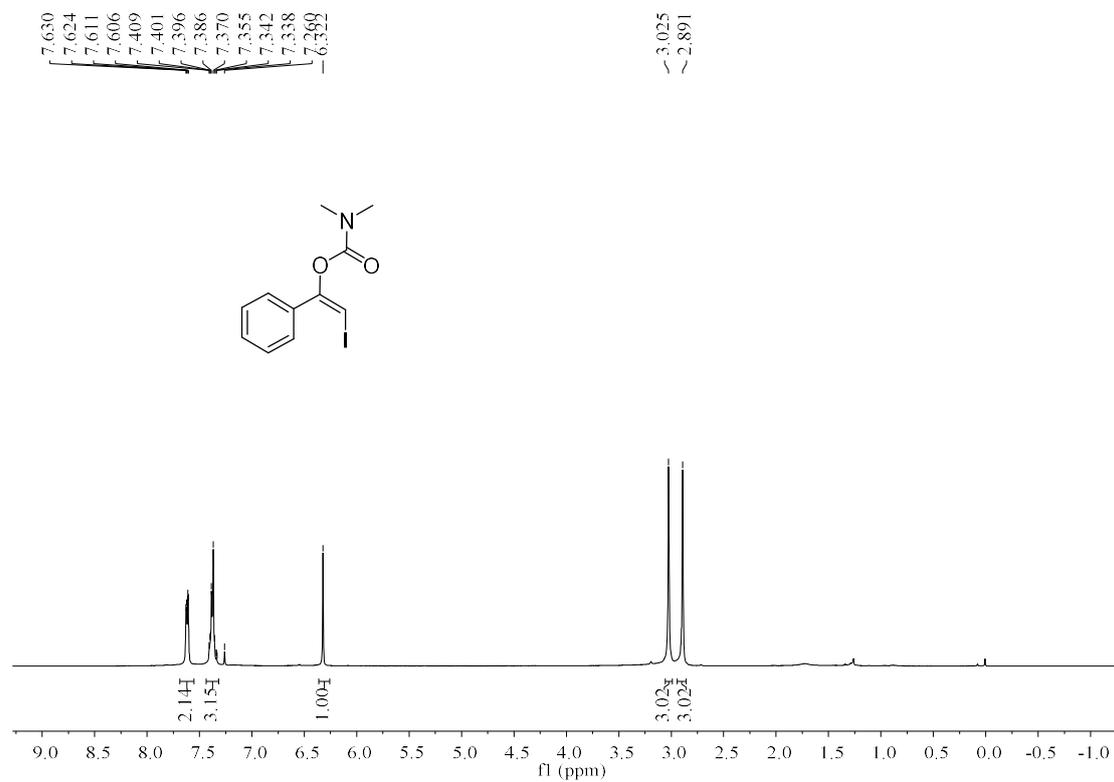
**(E)-2-Iodo-1-(m-tolyl)vinyl diethylcarbamate ((E)-3ia)**



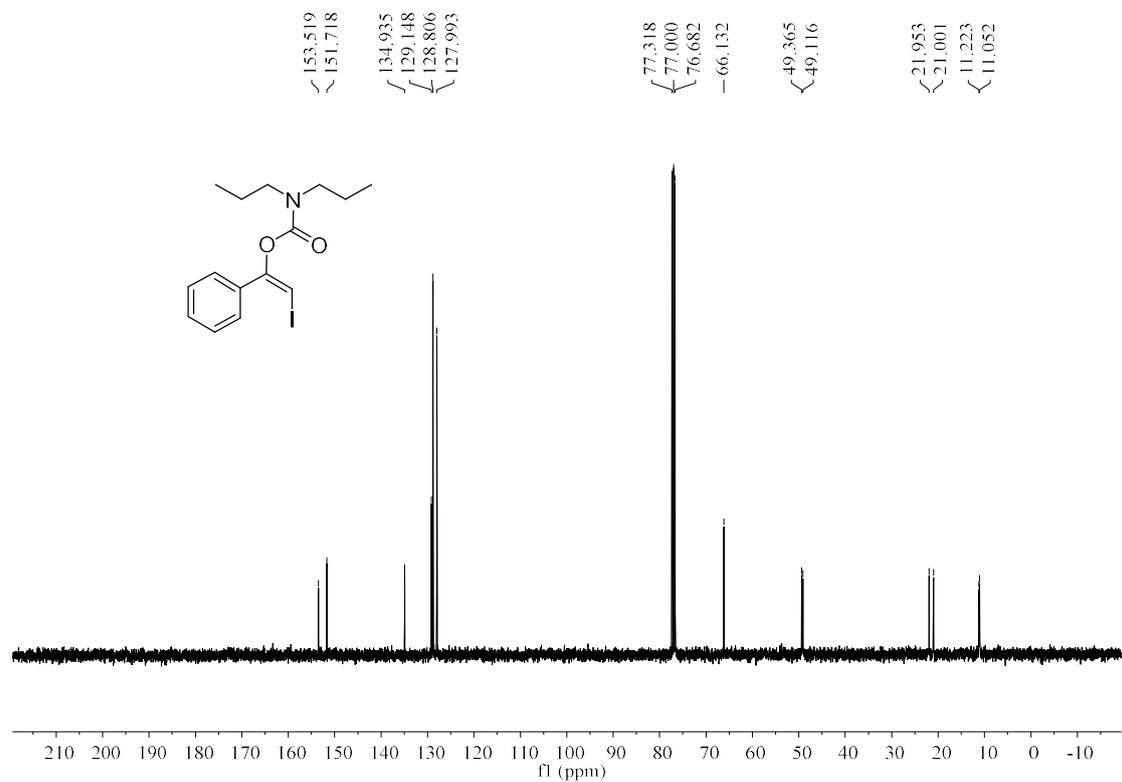
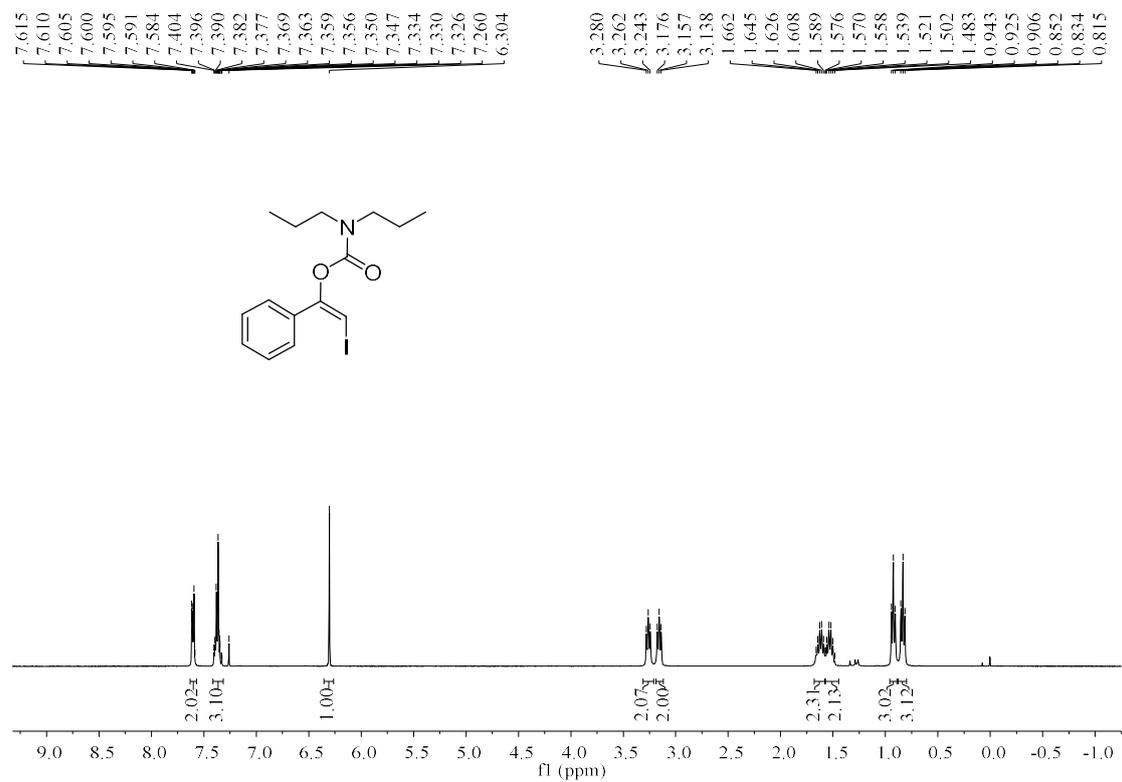
**(E)-2-Iodo-1-(3-methoxyphenyl)vinyl diethylcarbamate ((E)-3ka)**



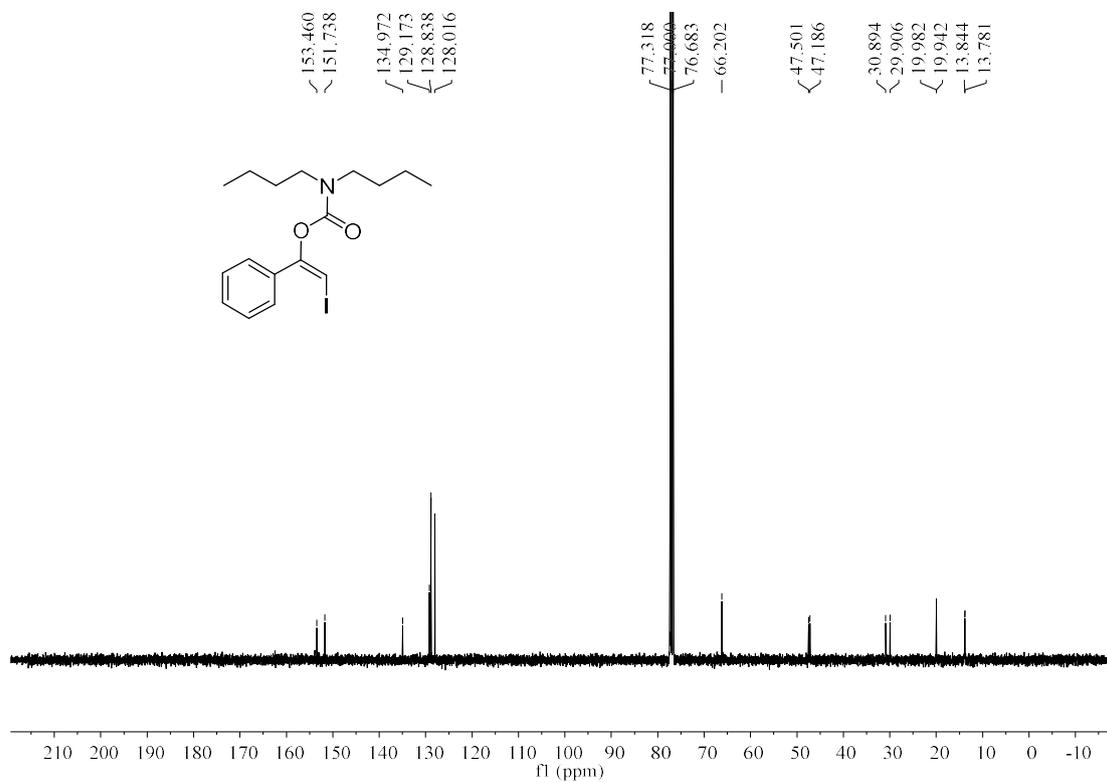
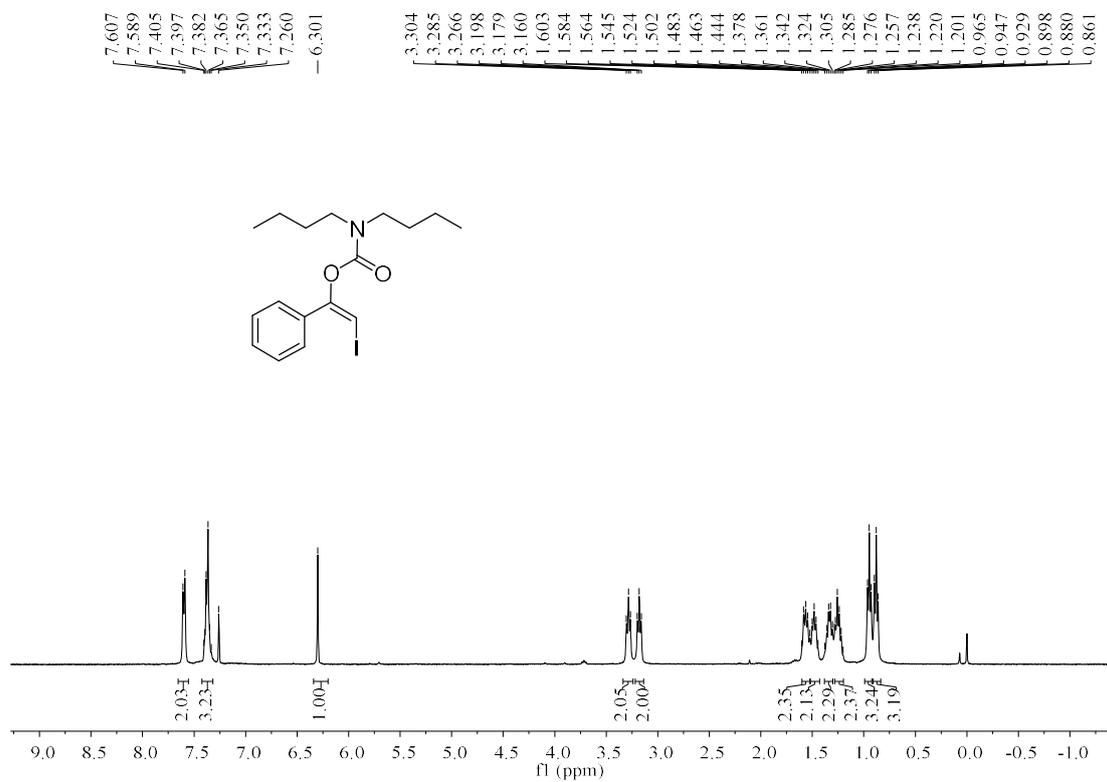
**(E)-2-Iodo-1-phenylvinyl dimethylcarbamate ((E)-3ab)**



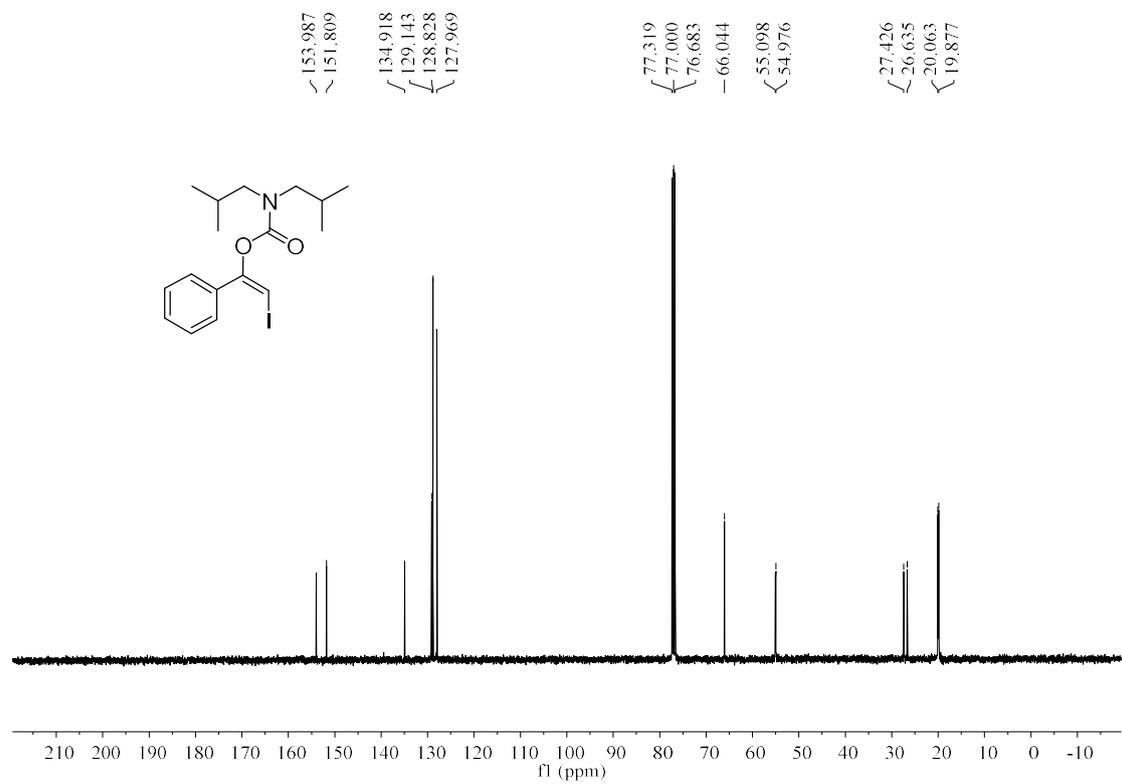
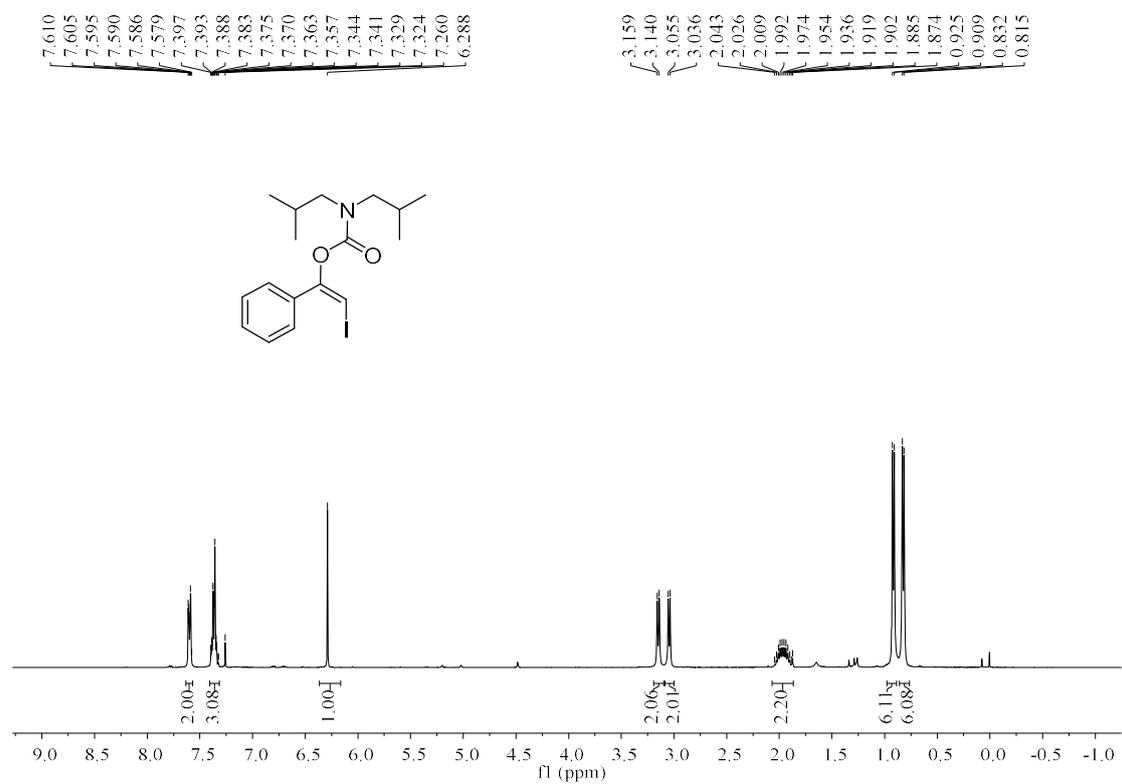
**(E)-2-Iodo-1-phenylvinyl dipropylcarbamate ((E)-3ac)**



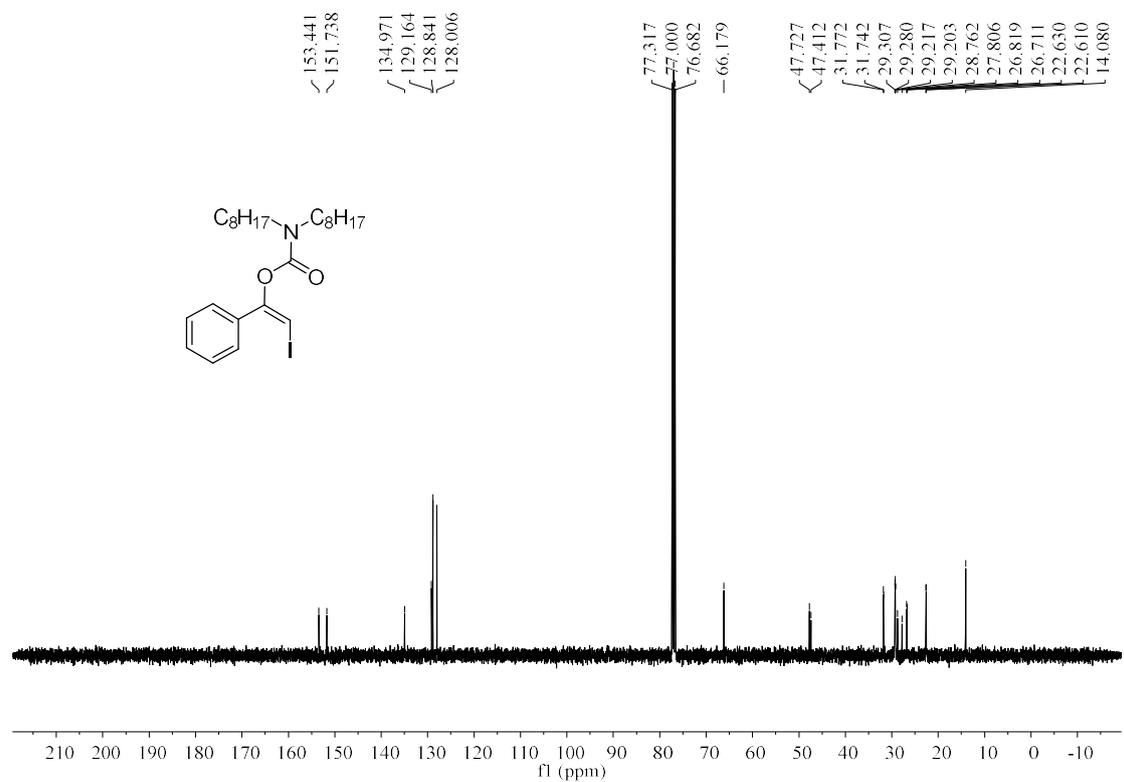
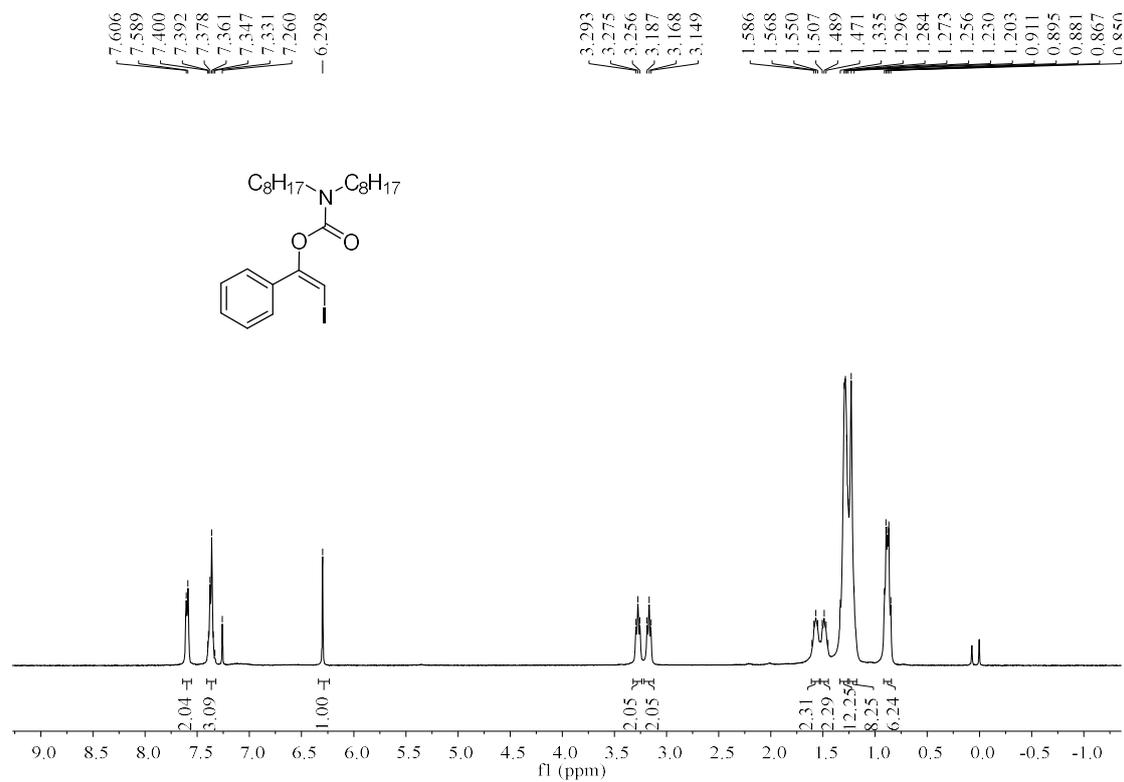
**(E)-2-Iodo-1-phenylvinyl dibutylcarbamate ((E)-3ad)**



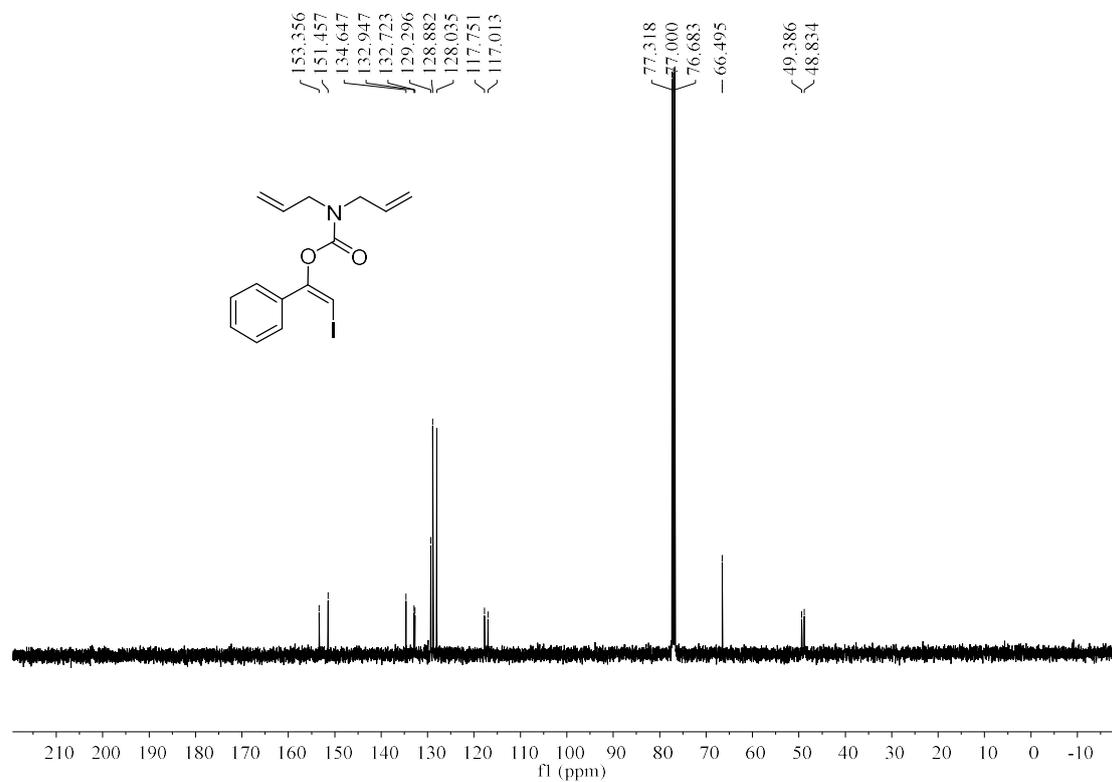
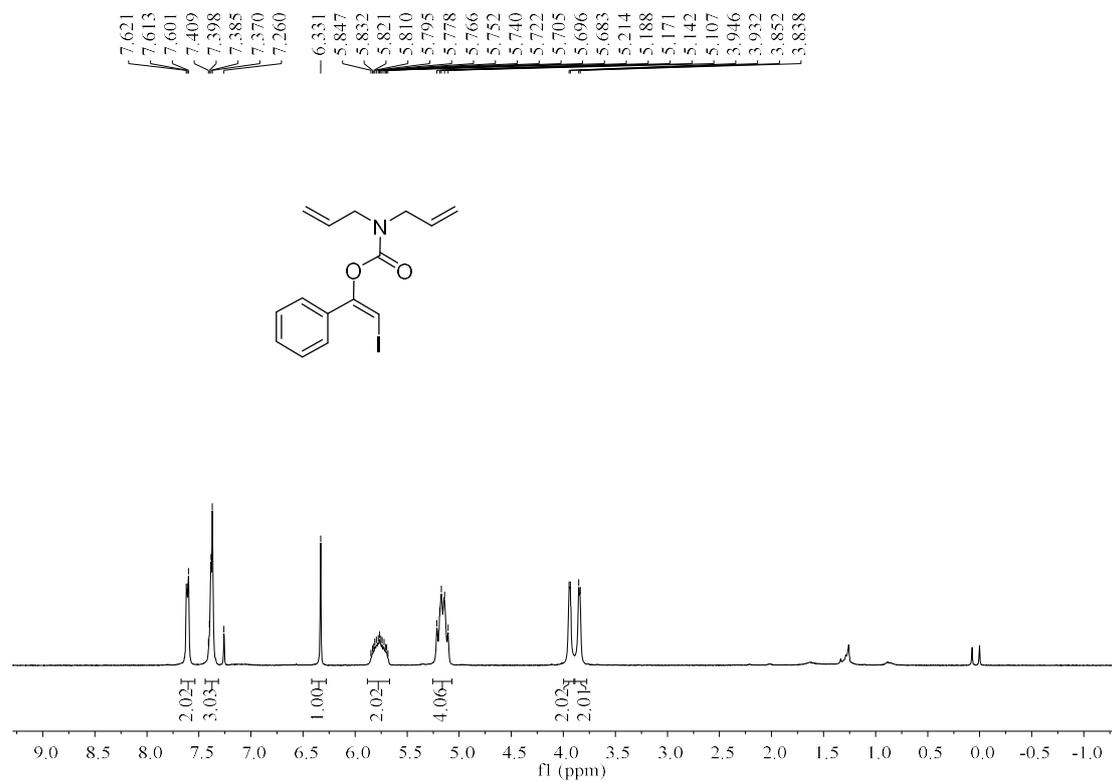
**(E)-2-Iodo-1-phenylvinyl diisobutylcarbamate ((E)-3ae)**



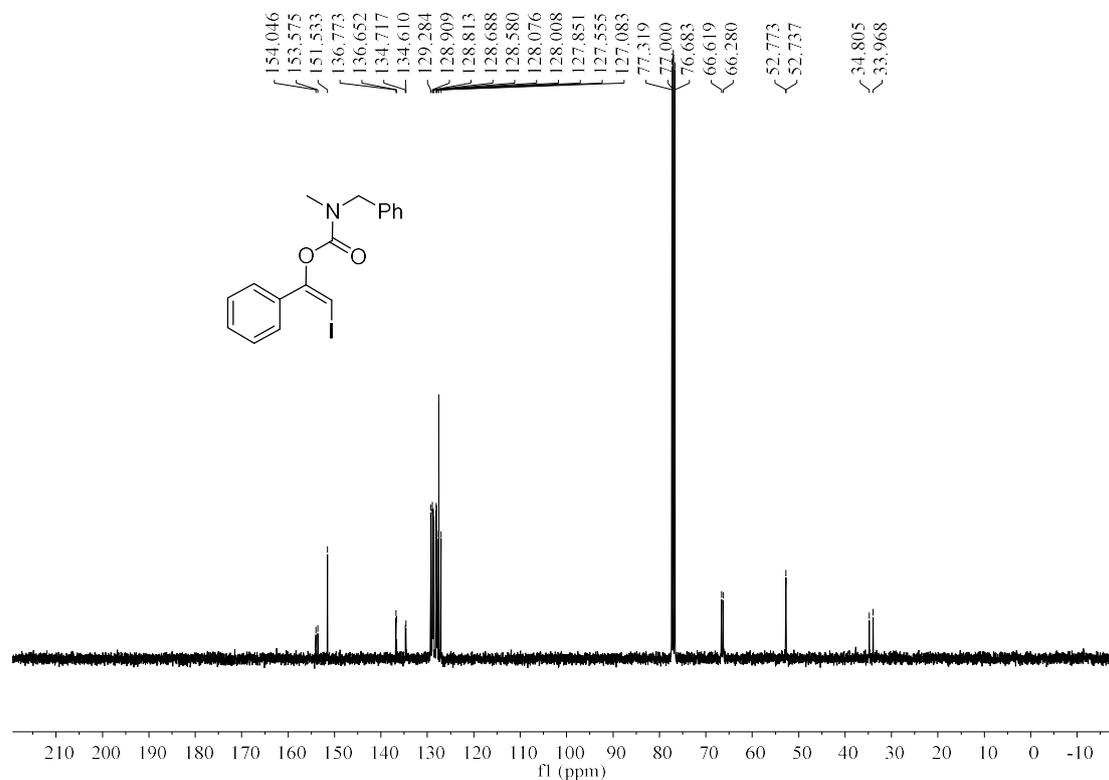
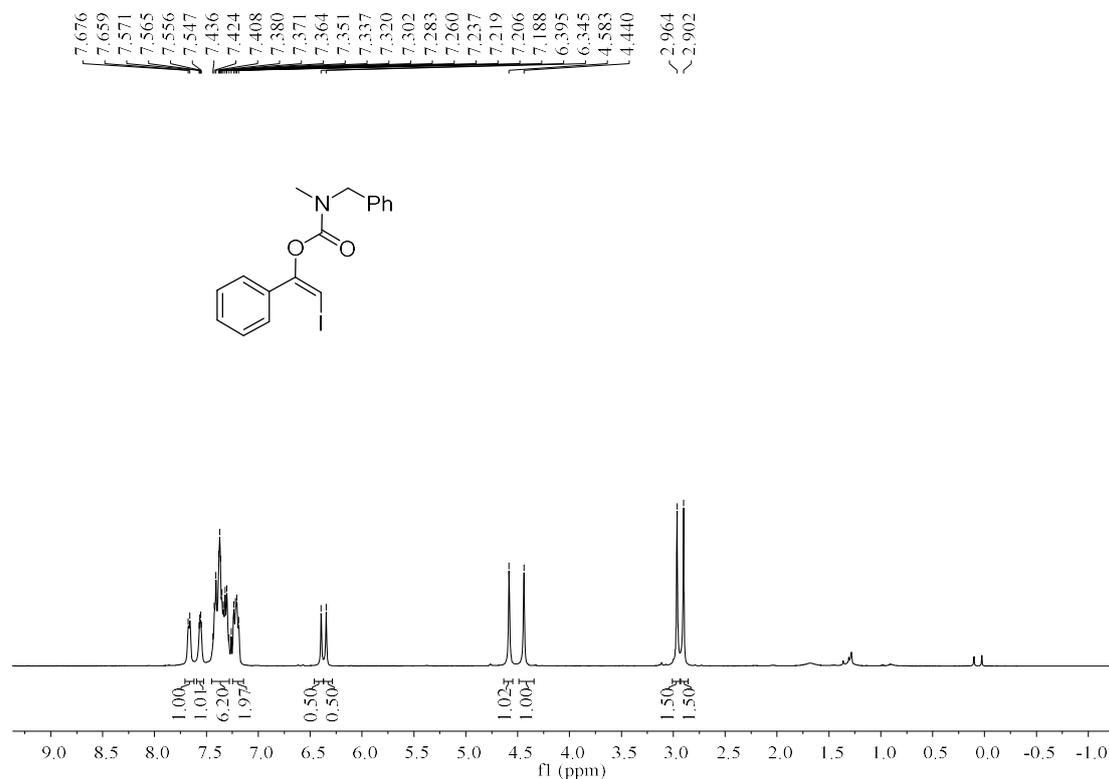
**(E)-2-Iodo-1-phenylvinyl dioctylcarbamate ((E)-3af)**



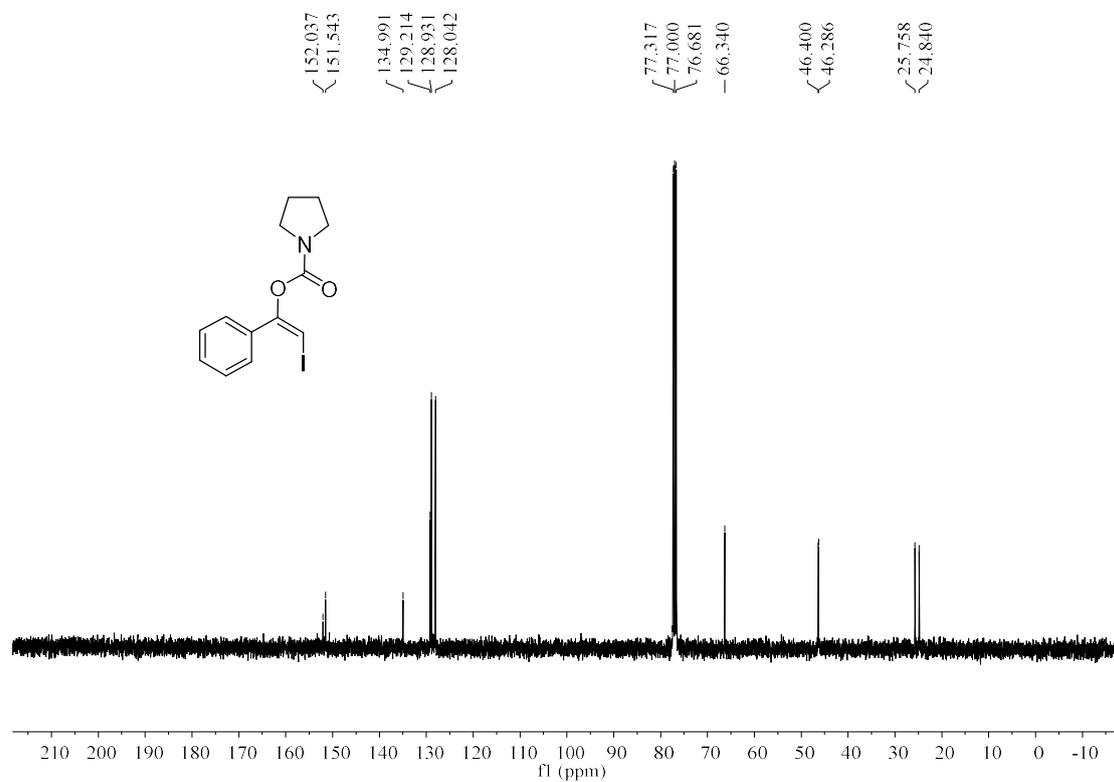
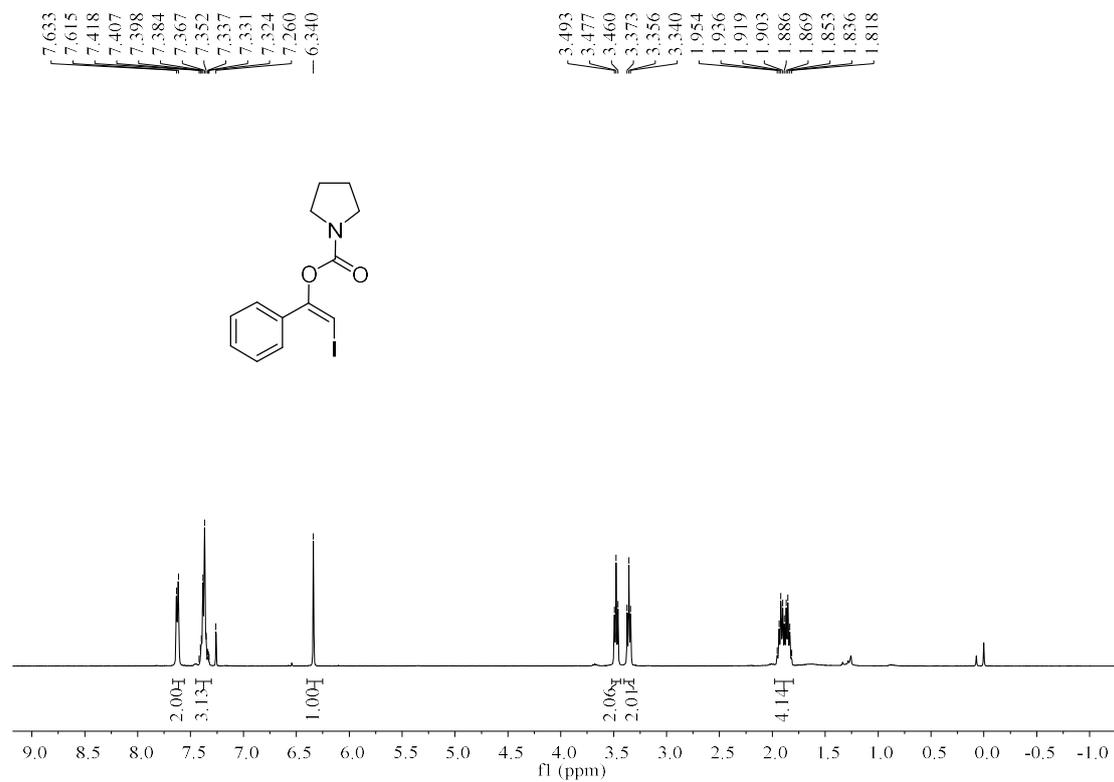
**(E)-2-Iodo-1-phenylvinyl diallylcarbamate ((E)-3ah)**



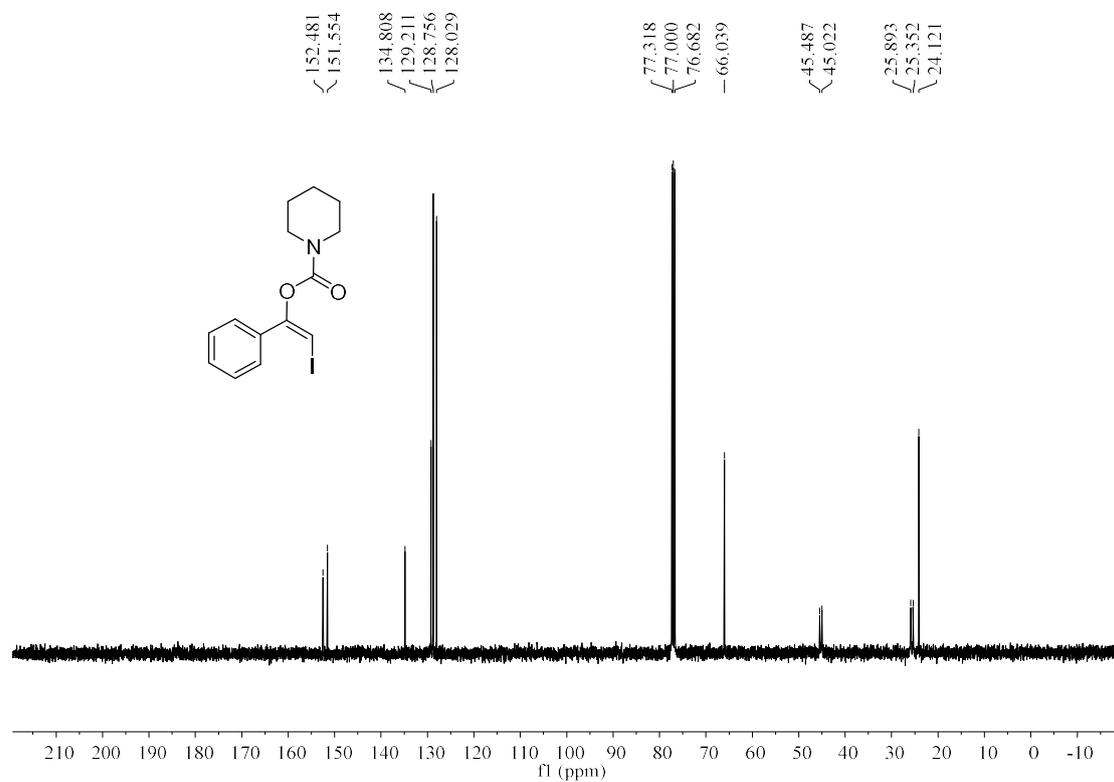
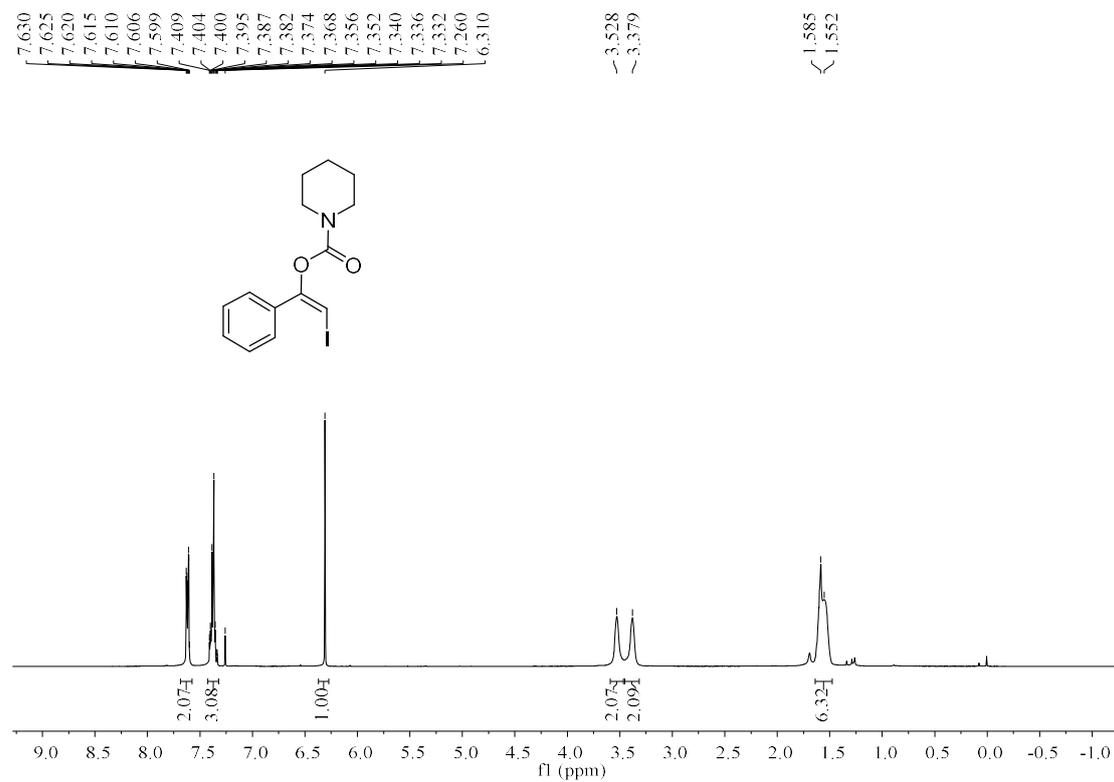
**(E)-2-Iodo-1-phenylvinyl benzyl(methyl)carbamate ((E)-3ak)**



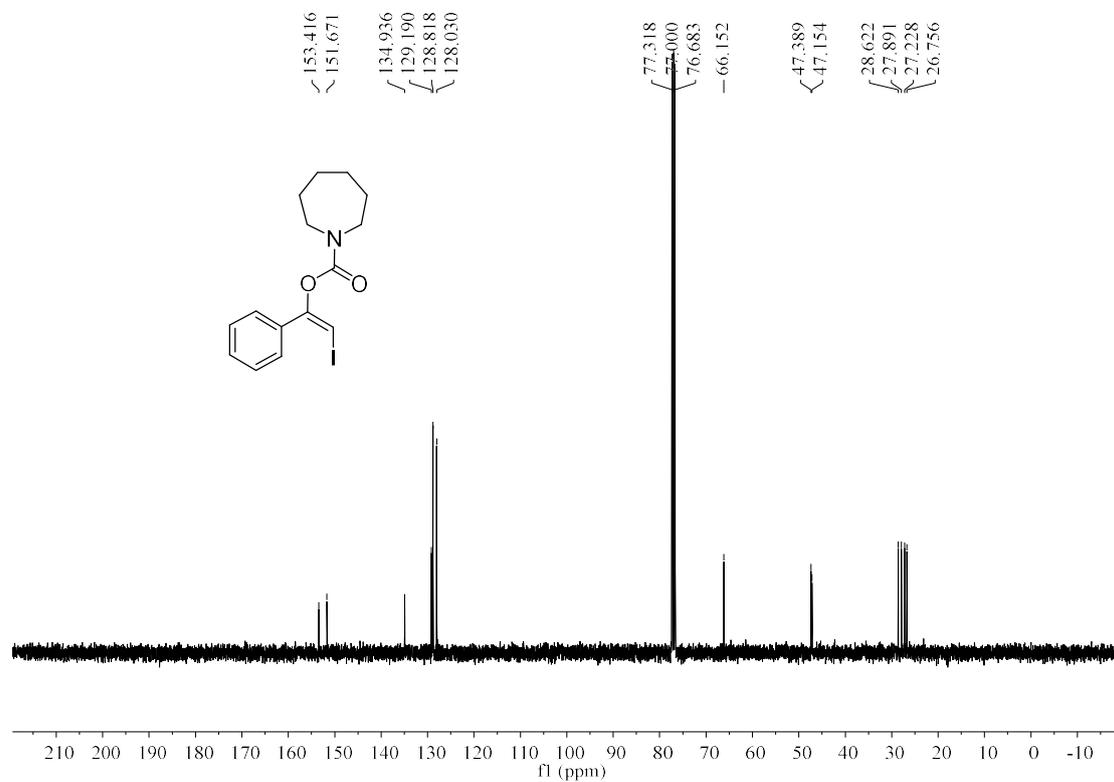
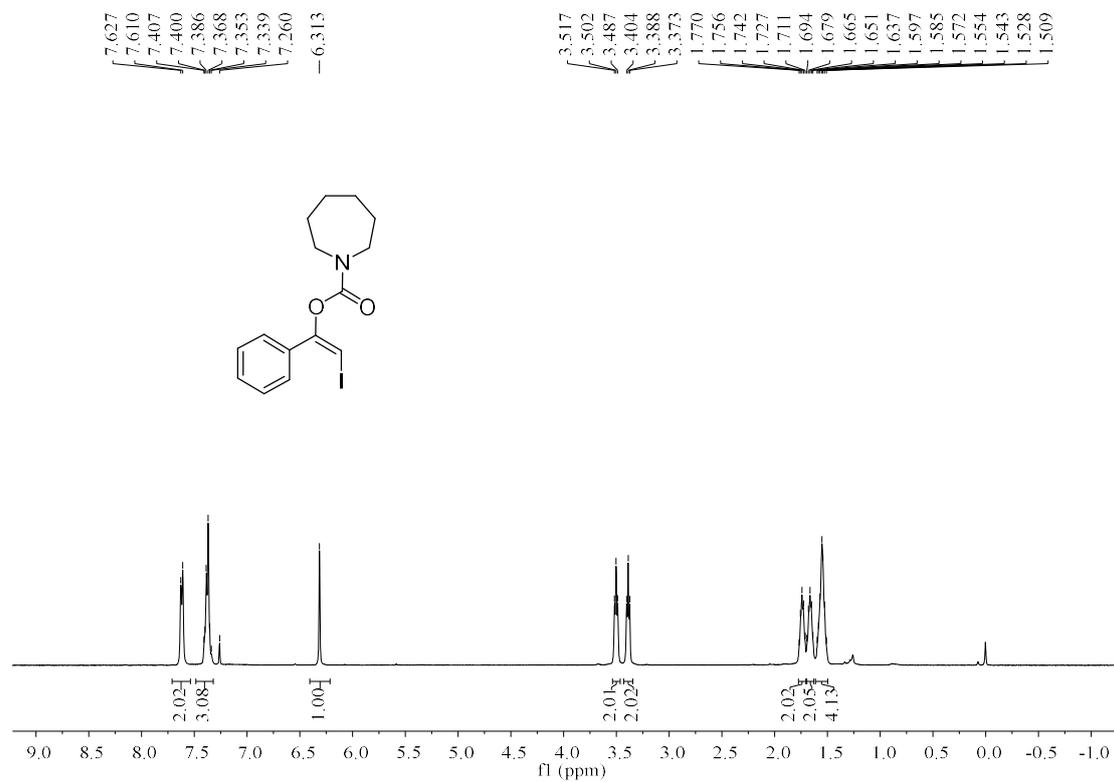
**(E)-2-Iodo-1-phenylvinyl pyrrolidine-1-carboxylate ((E)-3ao)**



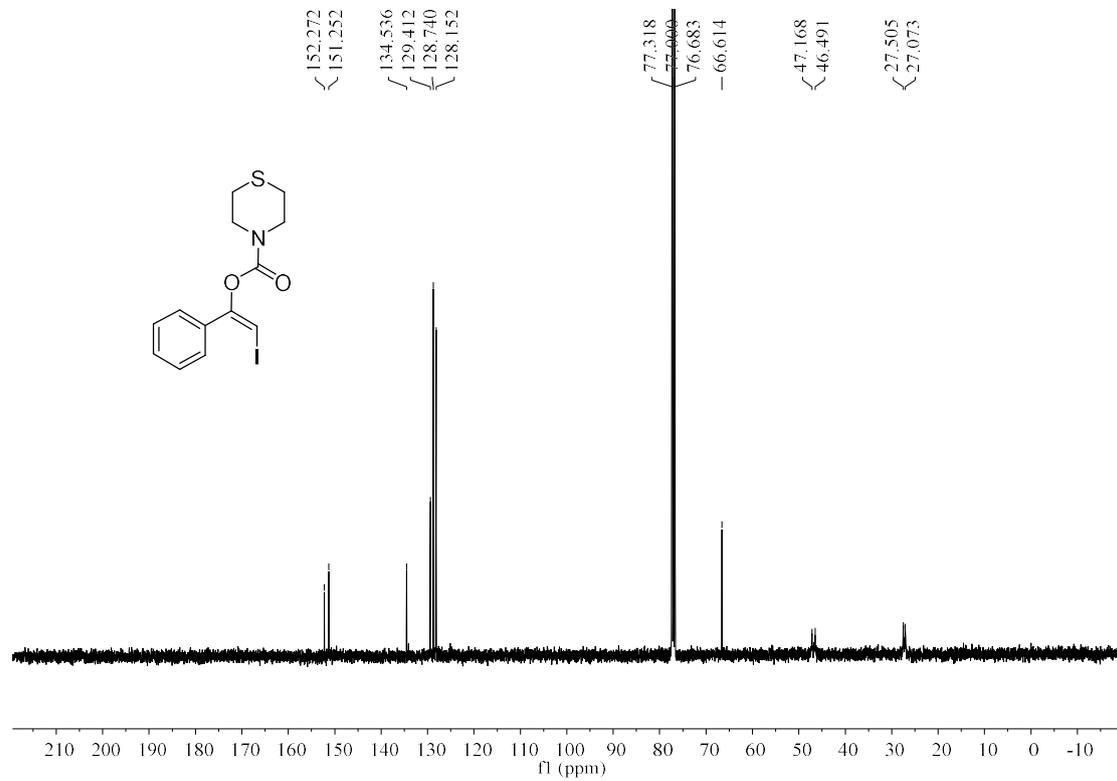
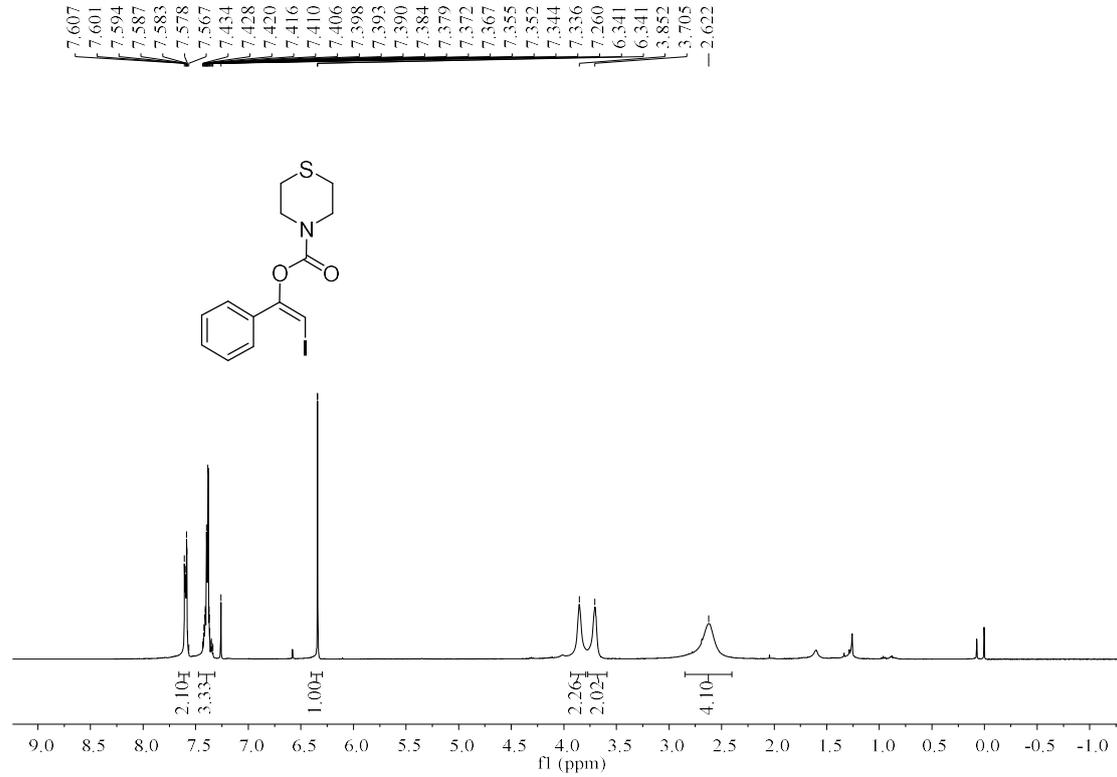
**(E)-2-Iodo-1-phenylvinyl piperidine-1-carboxylate ((E)-3ap)**



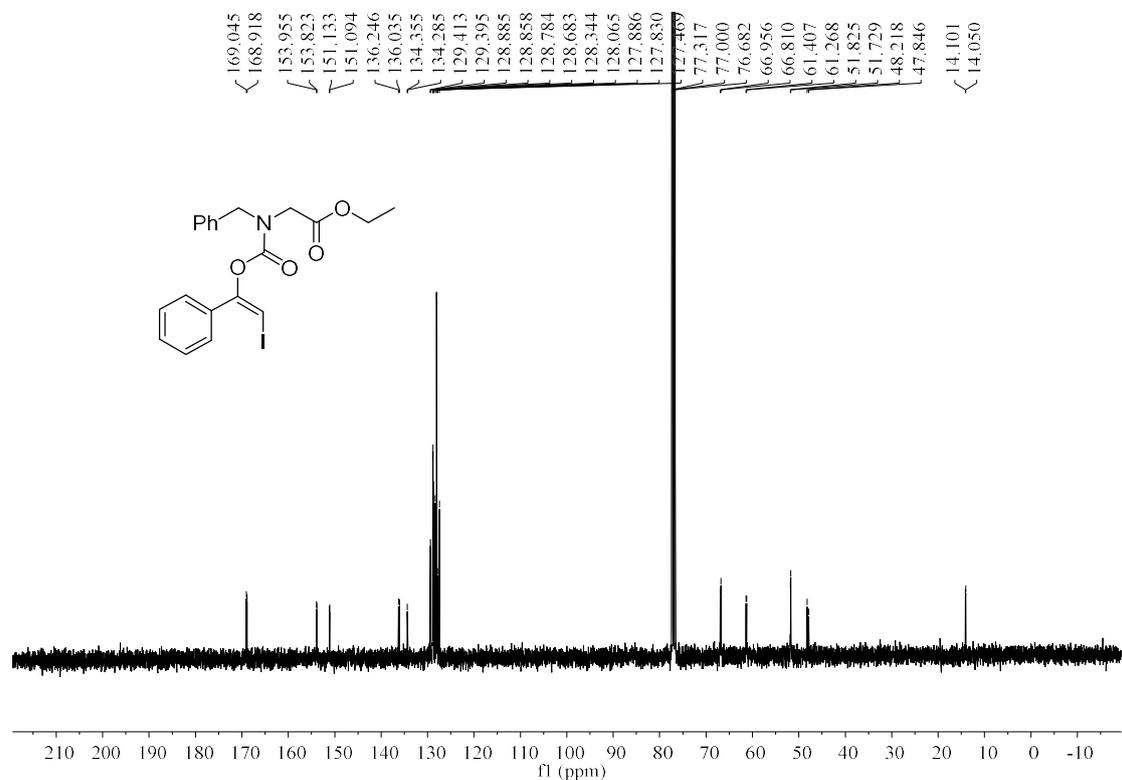
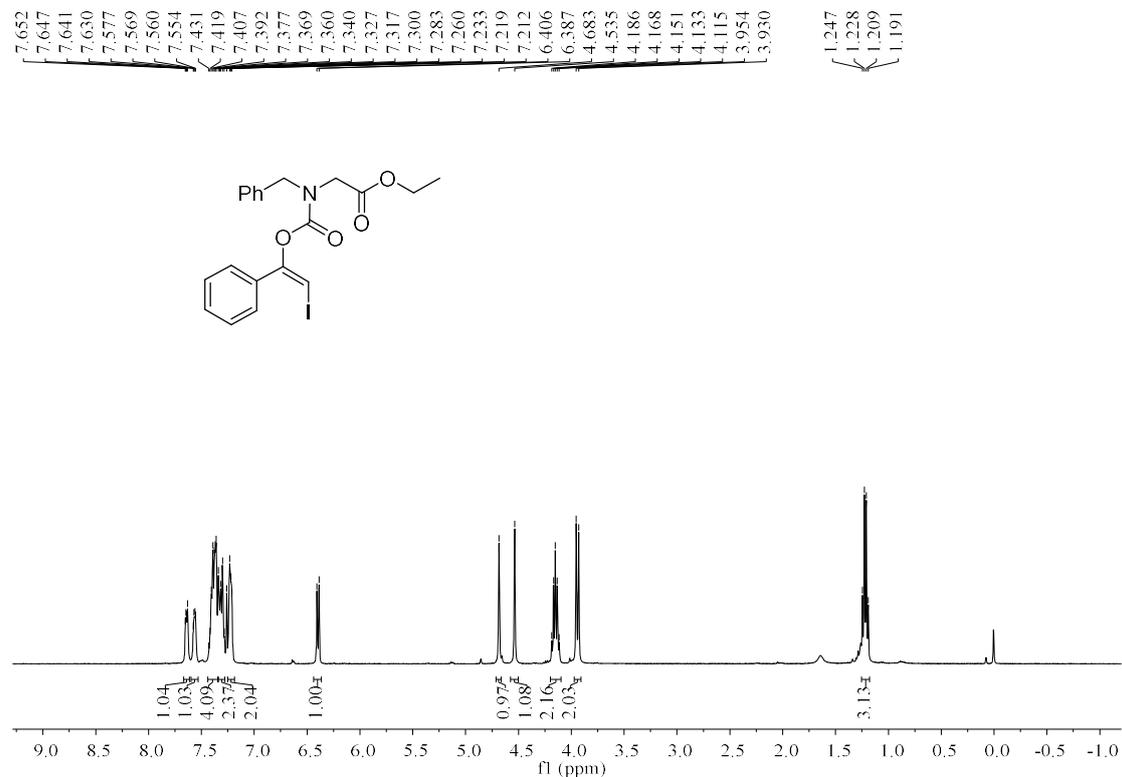
**(E)-2-Iodo-1-phenylvinyl azepane-1-carboxylate ((E)-3aq)**



**(E)-2-Iodo-1-phenylvinyl thiomorpholine-4-carboxylate ((E)-3ar)**

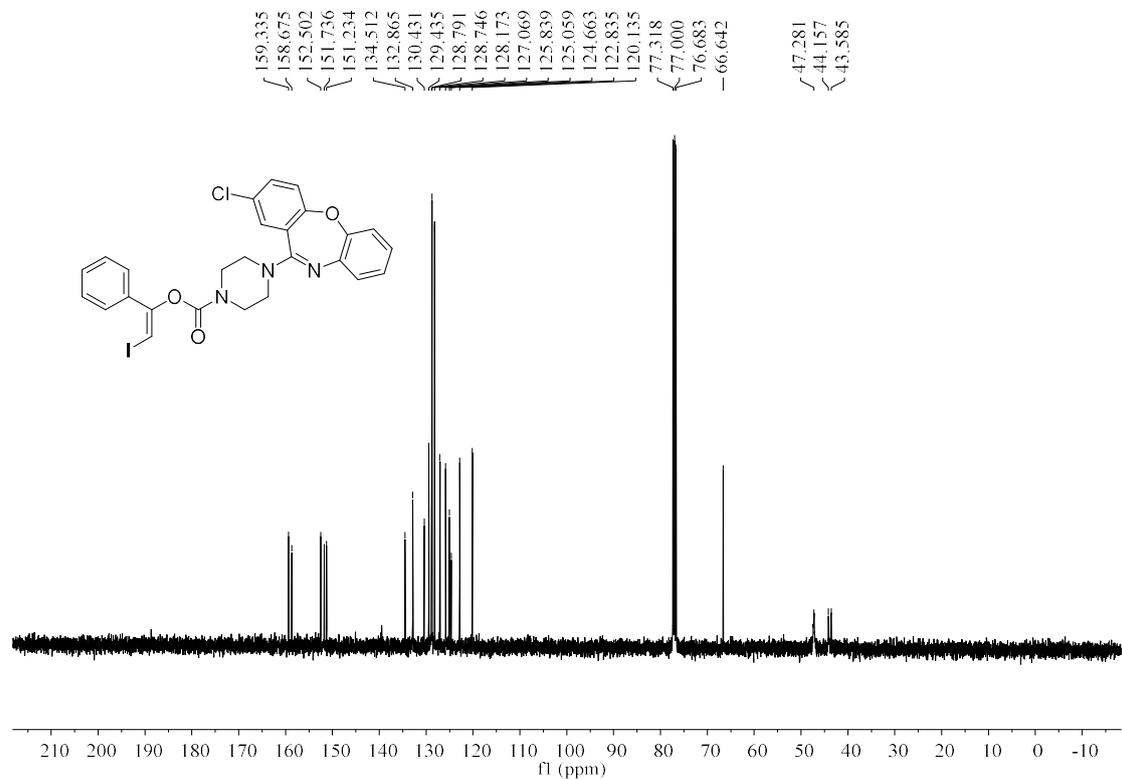
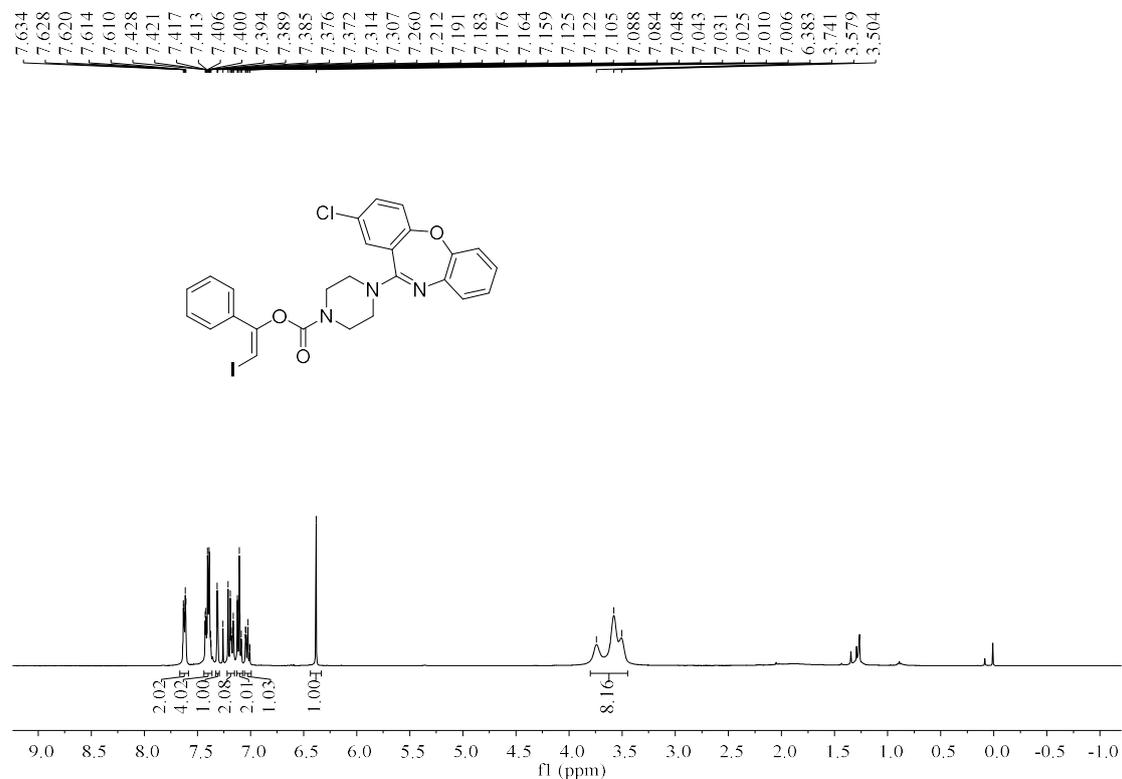


**Ethyl (E)-N-benzyl-N-(((2-iodo-1-phenylvinyl)oxy)carbonyl)glycinate ((E)-3ay)**

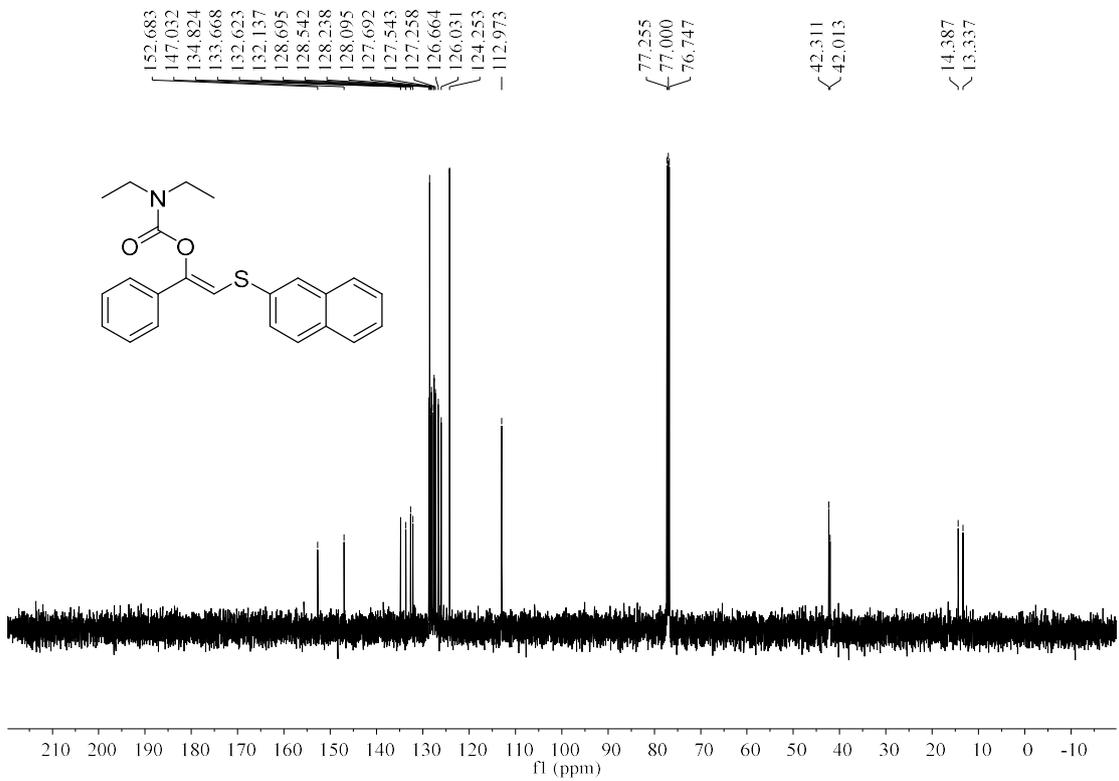
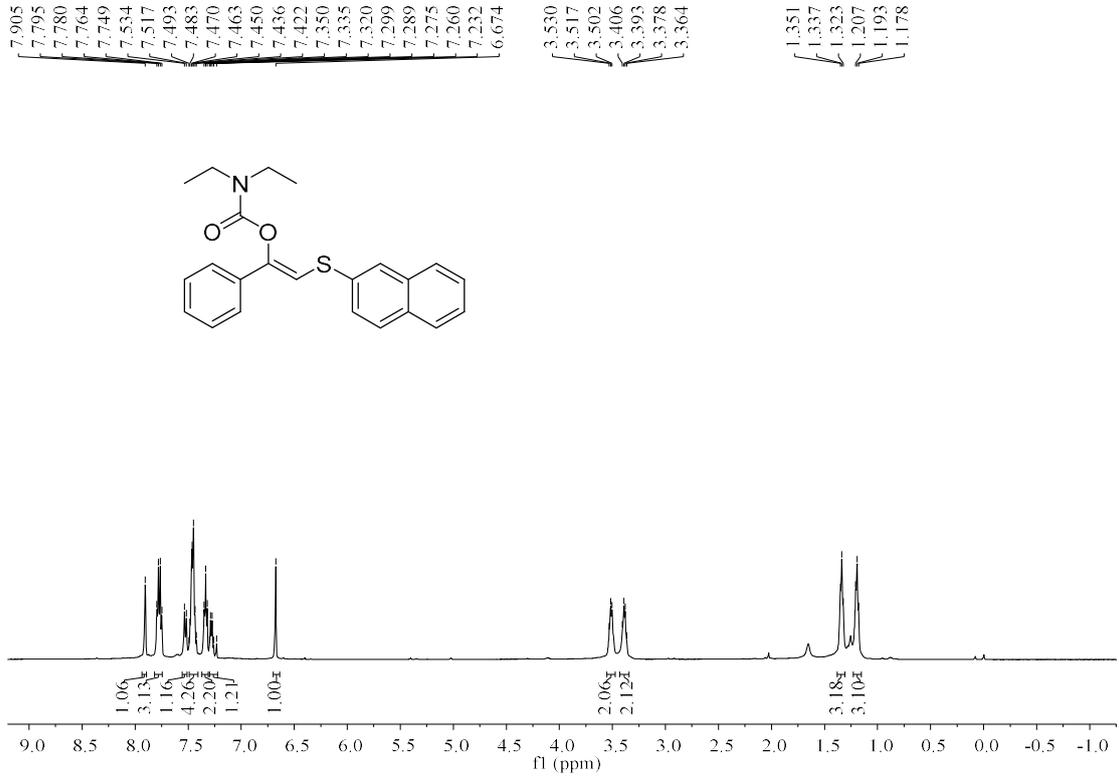


**(E)-2-Iodo-1-phenylvinyl 4-(2-chlorodibenzo[b,f][1,4]oxazepin-11-yl)piperazine-1-carboxylate**

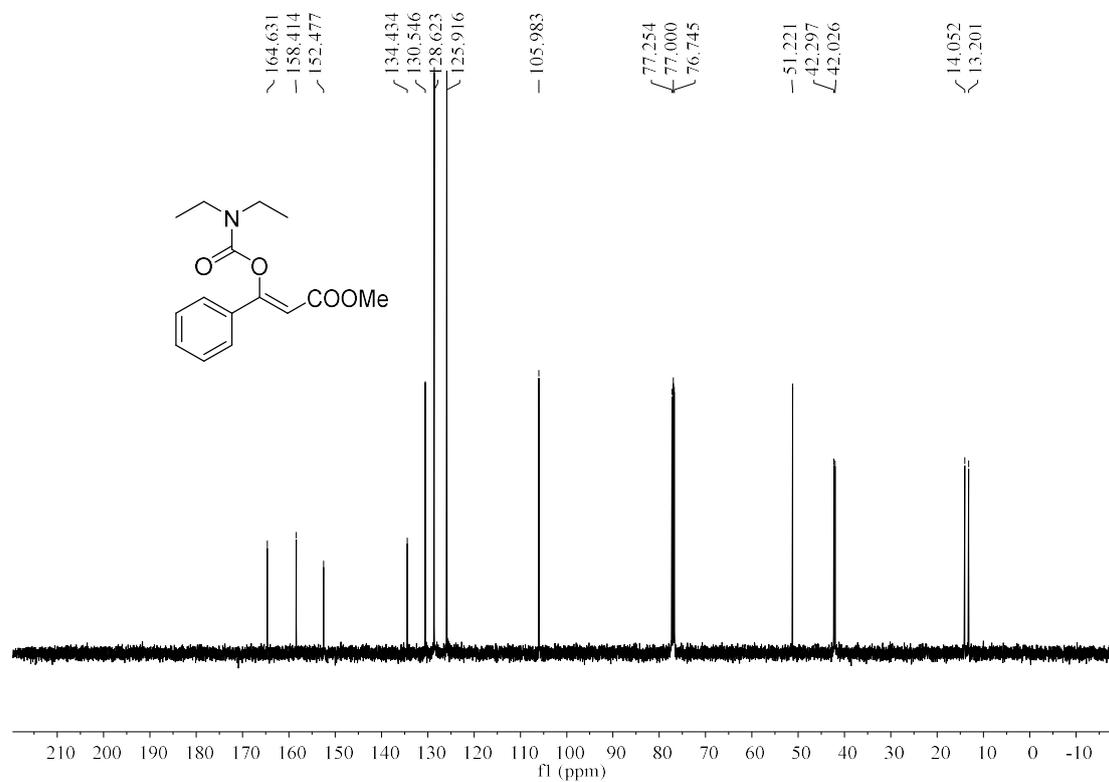
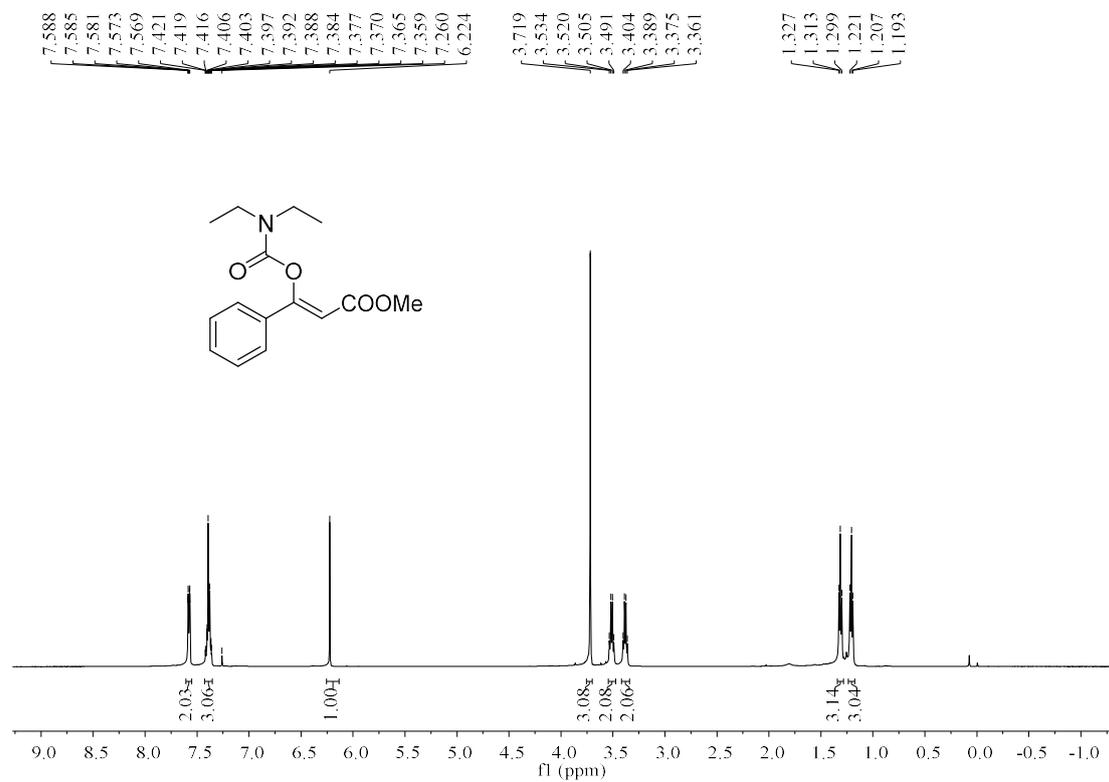
**((E)-3aca)**



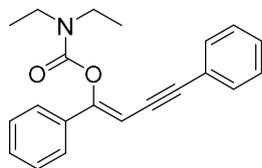
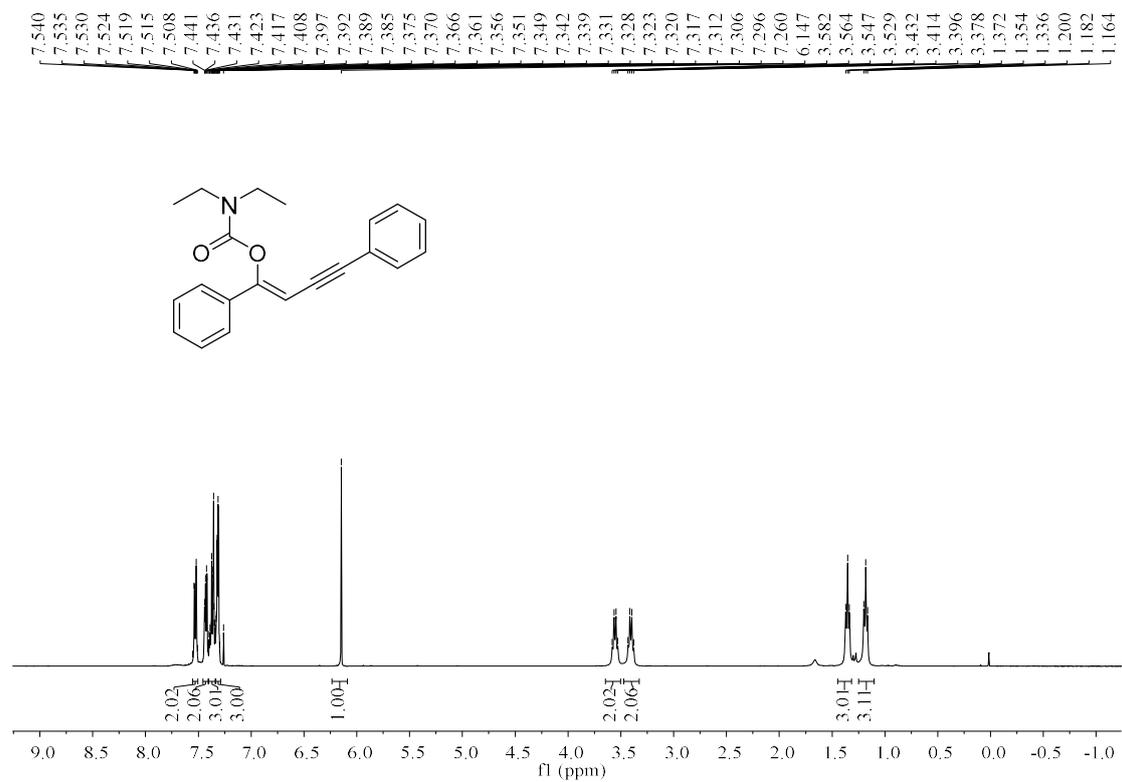
(Z)-2-(Naphthalen-2-ylthio)-1-phenylvinyl diethylcarbamate (4)



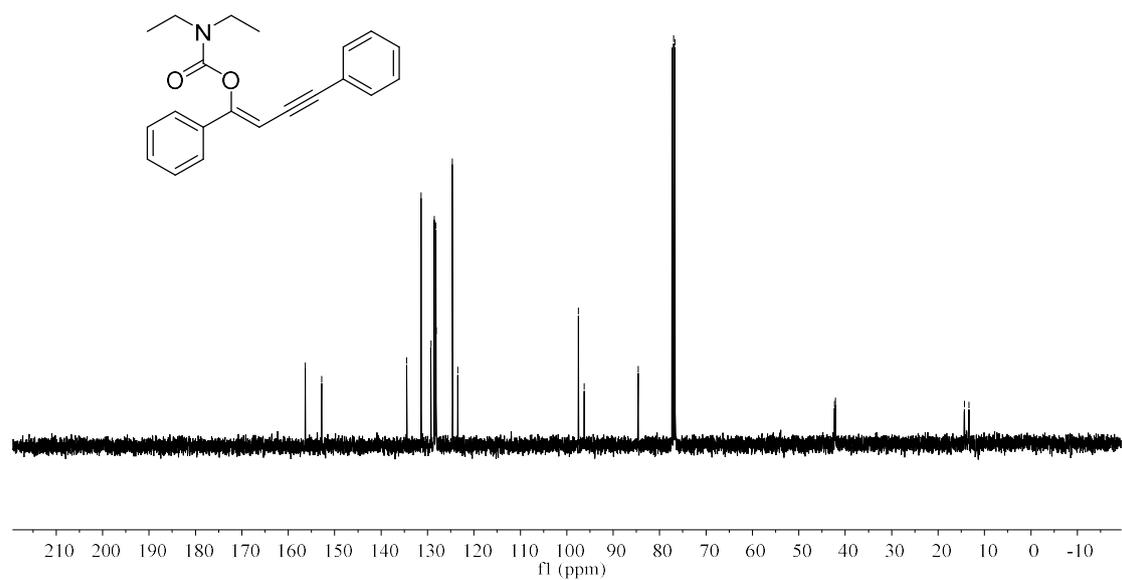
**Methyl (Z)-3-((diethylcarbamoyl)oxy)-3-phenylacrylate (5)**



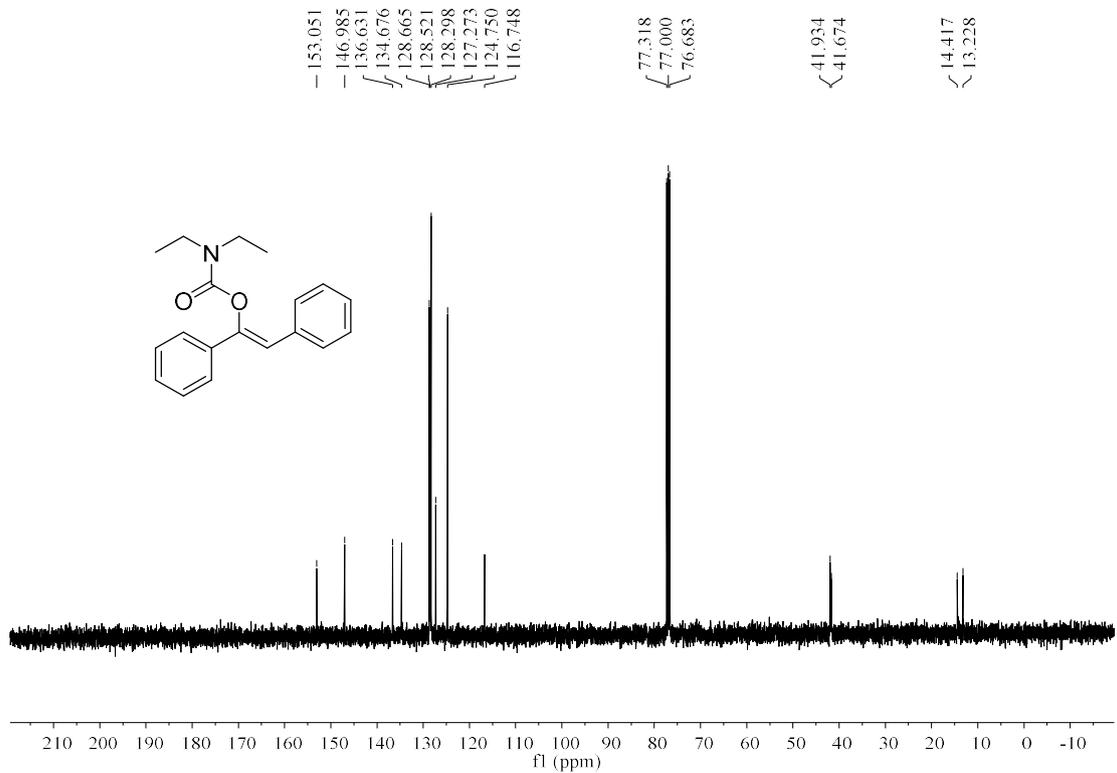
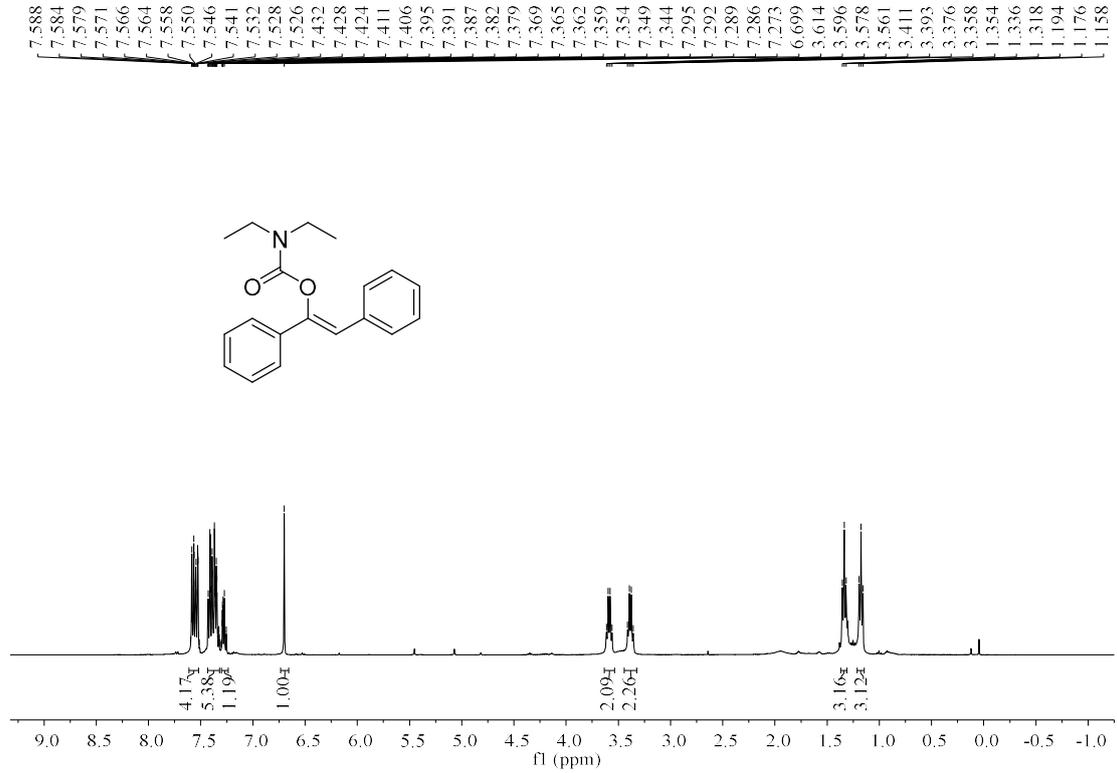
**(Z)-1,4-Diphenylbut-1-en-3-yn-1-yl diethylcarbamate (6)**



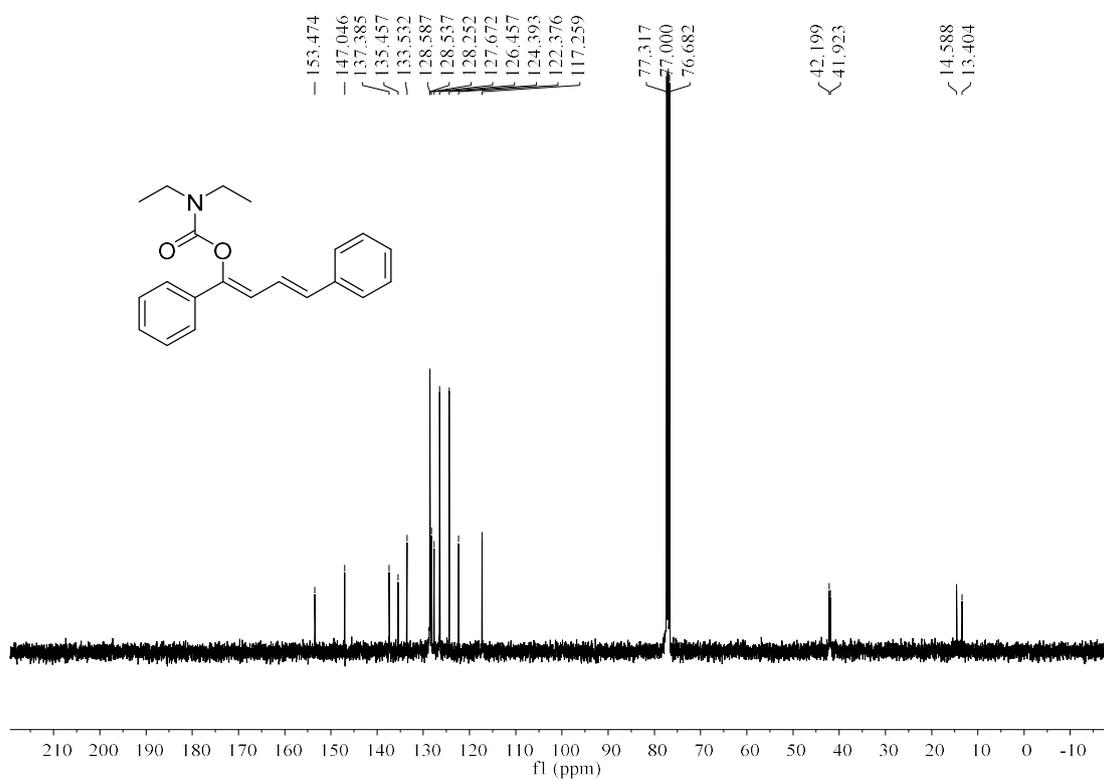
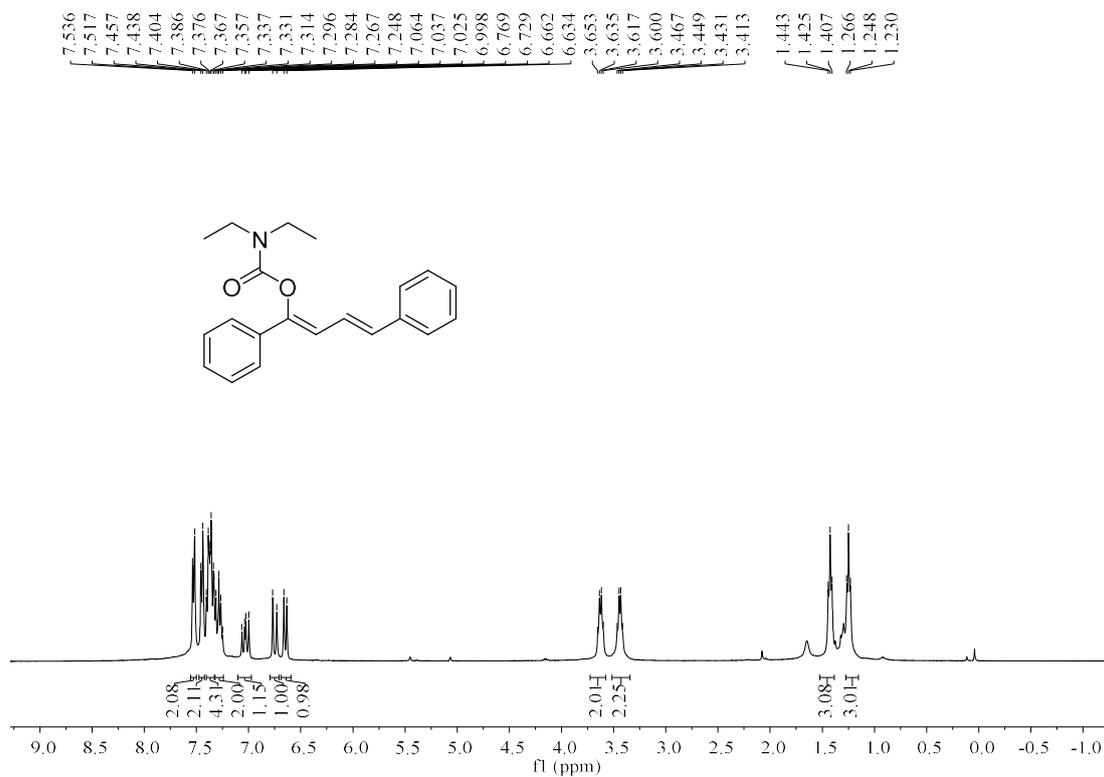
156.303, 152.818, 134.492, 131.357, 129.271, 128.574, 128.216, 128.149, 124.649, 123.511, 97.481, 96.238, 84.613, 77.318, 77.000, 76.683, 42.327, 42.105, 14.335, 13.352



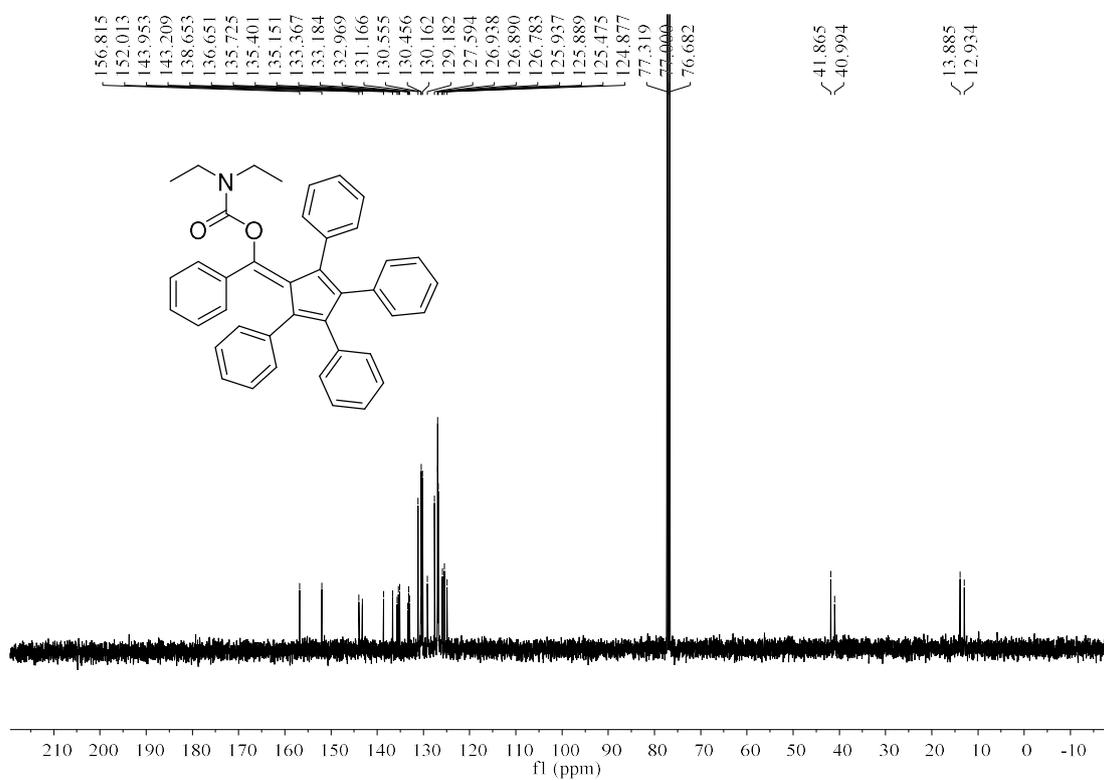
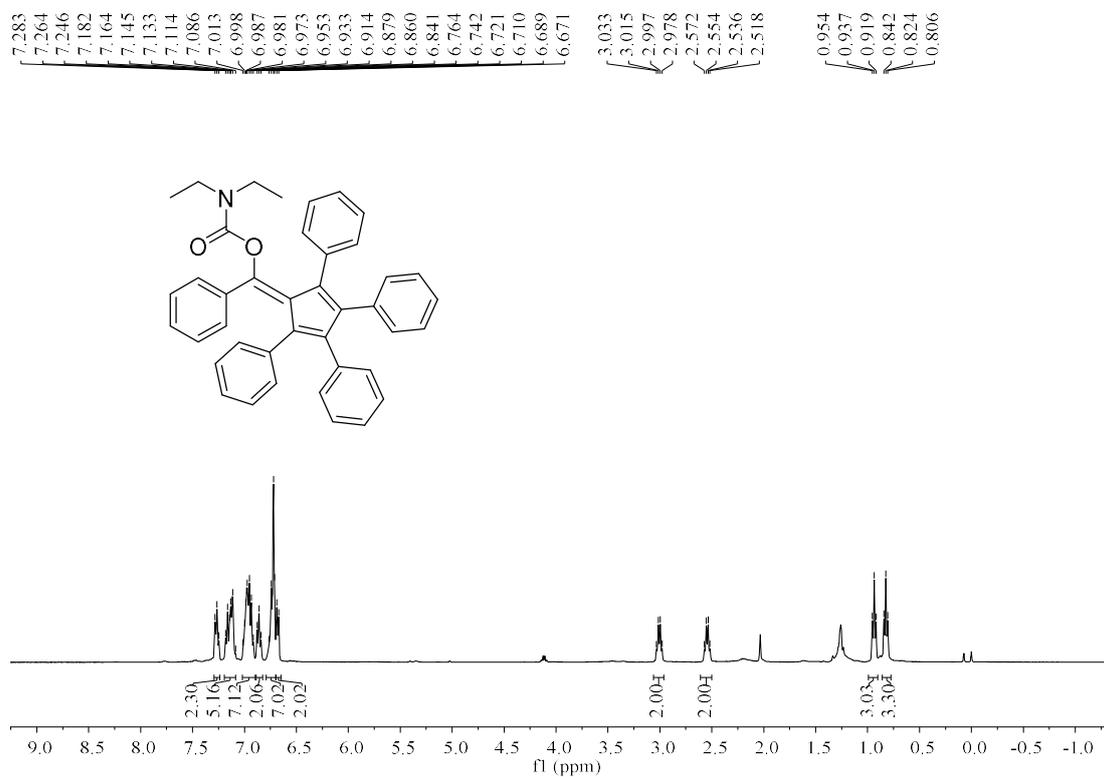
(Z)-1,2-Diphenylvinyl diethylcarbamate (7)



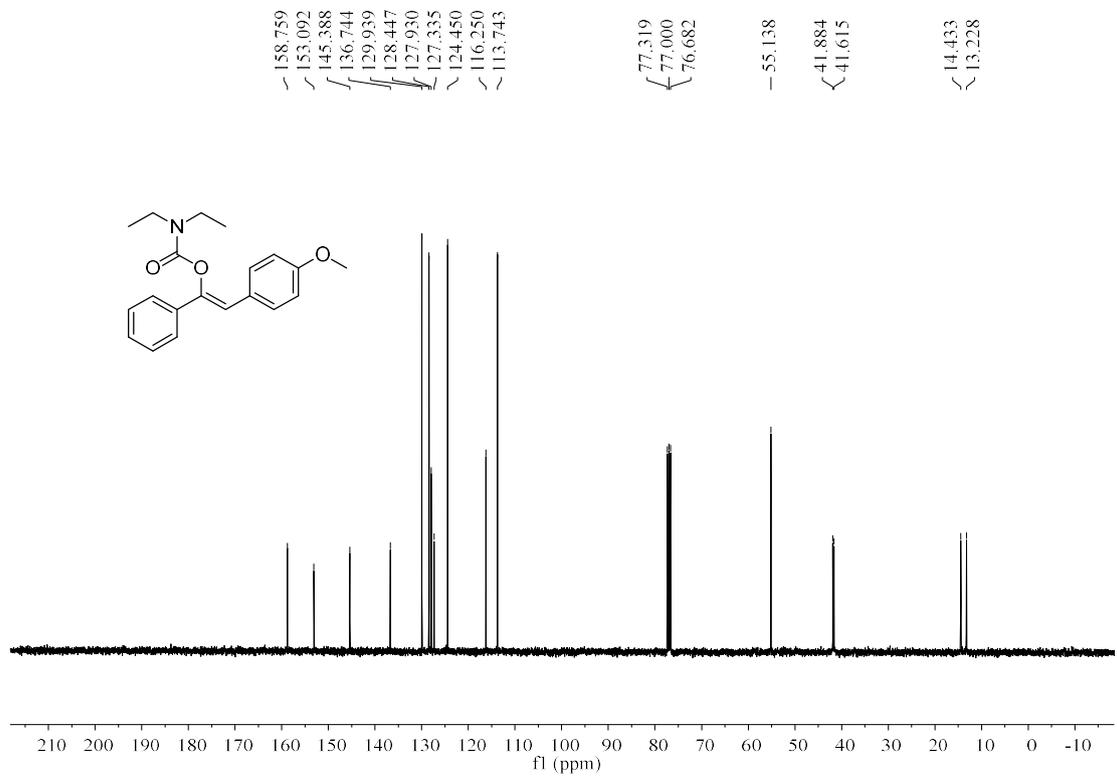
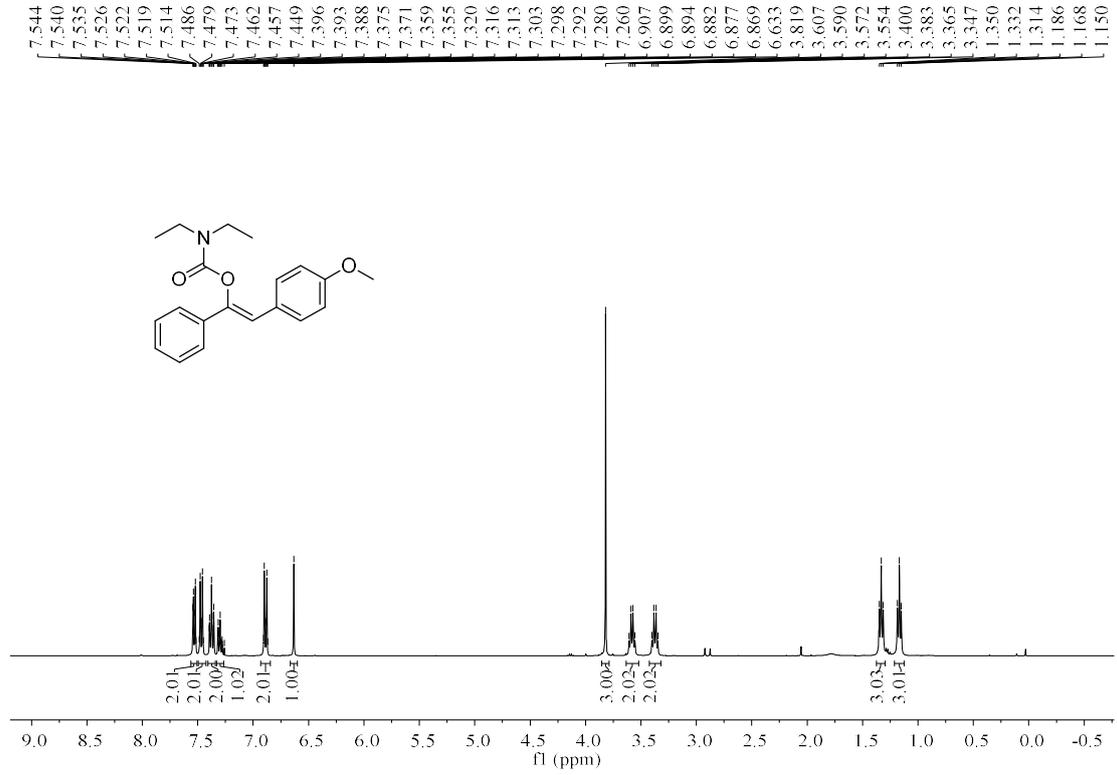
(1Z,3E)-1,4-Diphenylbuta-1,3-dien-1-yl diethylcarbamate (8)



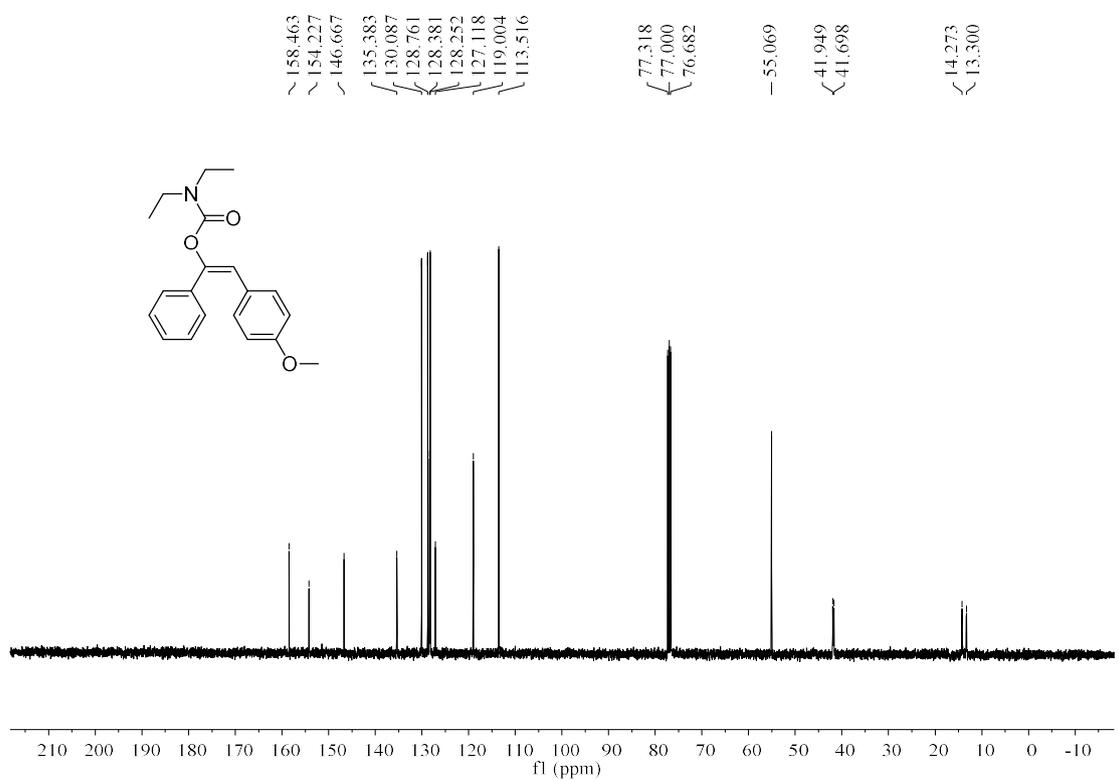
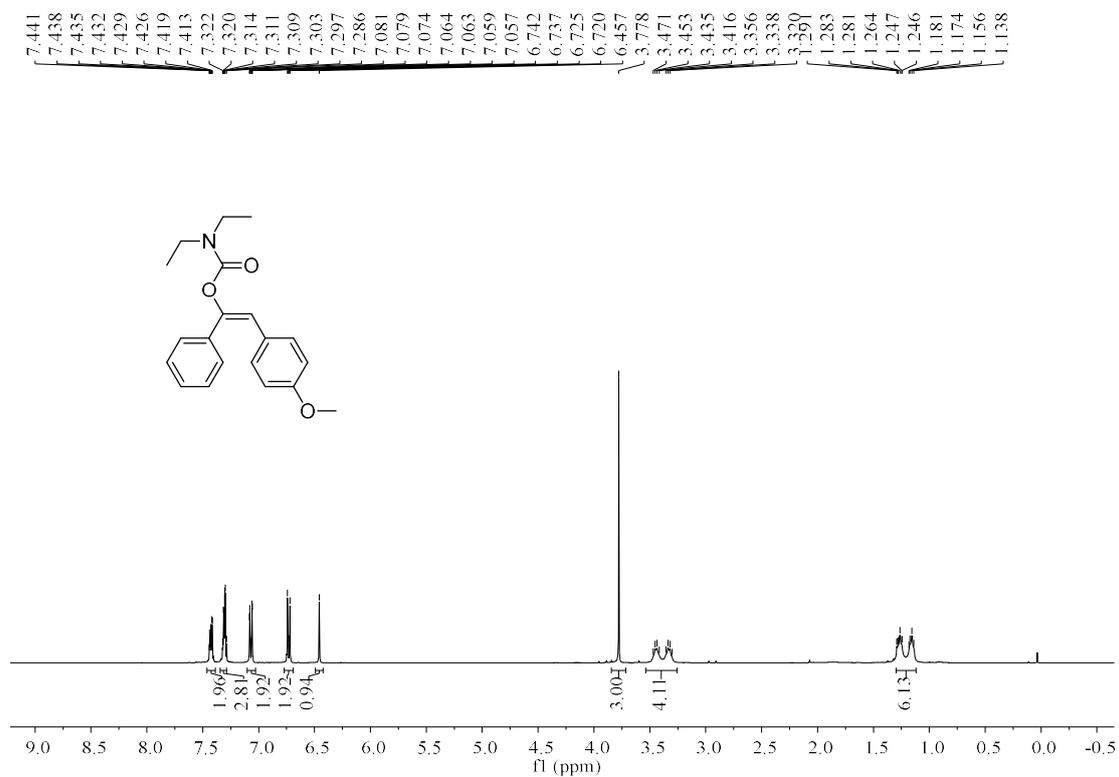
Phenyl(2,3,4,5-tetraphenylcyclopenta-2,4-dien-1-ylidene)methyl diethylcarbamate (9)



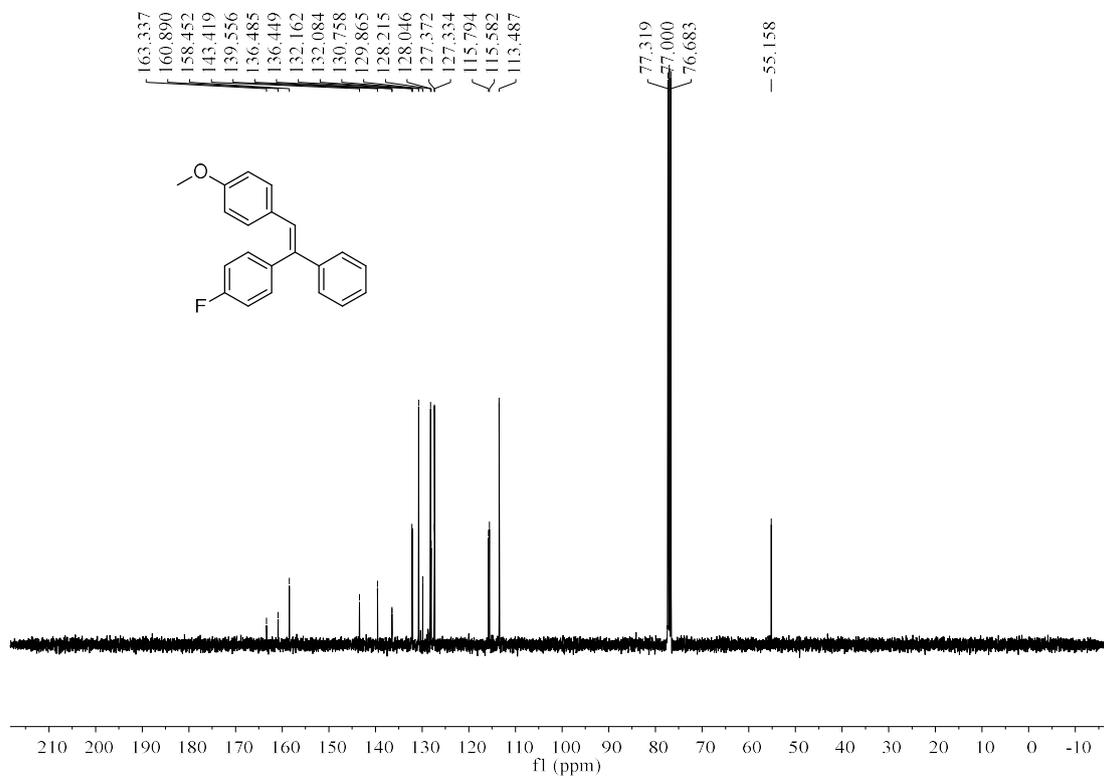
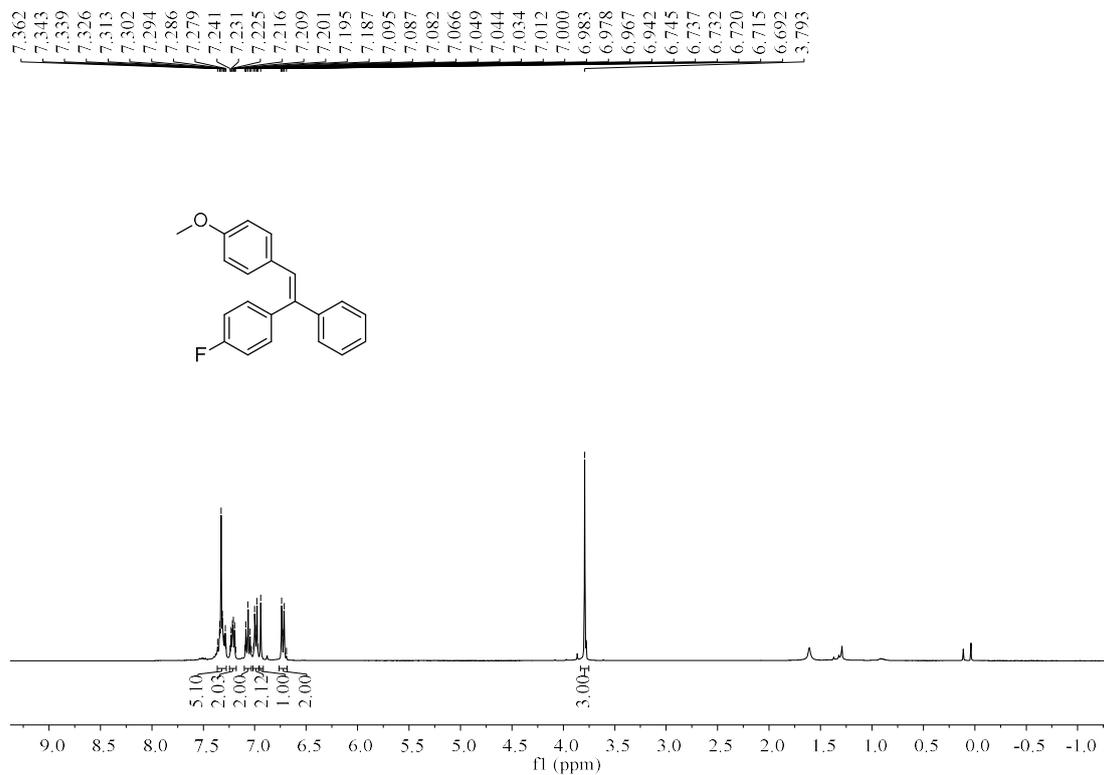
**(Z)-2-(4-Methoxyphenyl)-1-phenylvinyl diethylcarbamate ((Z)-10)**

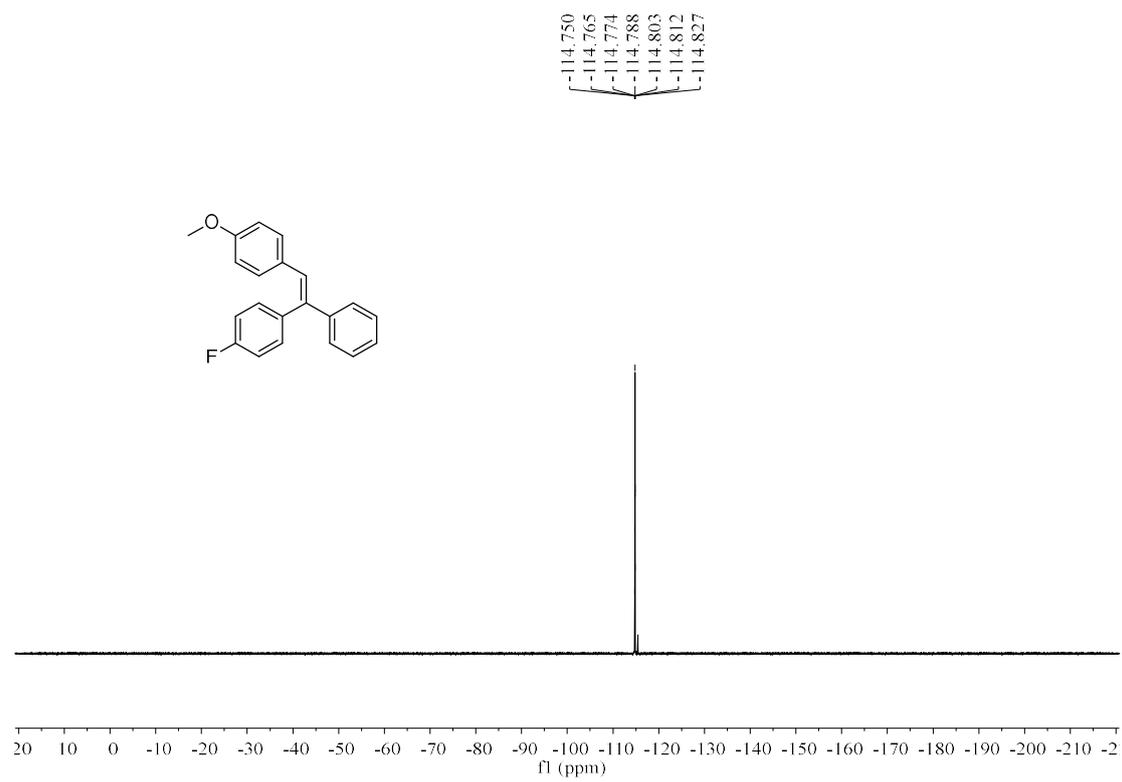


**(E)-2-(4-Methoxyphenyl)-1-phenylvinyl diethylcarbamate ((E)-10)**

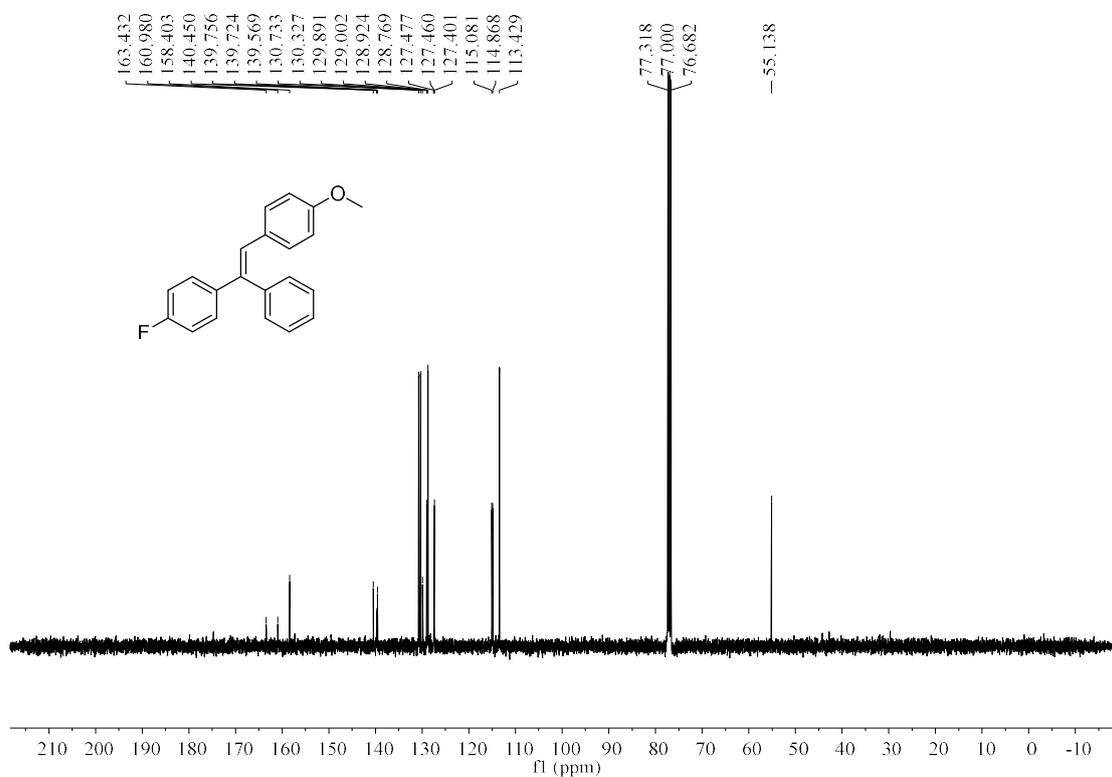
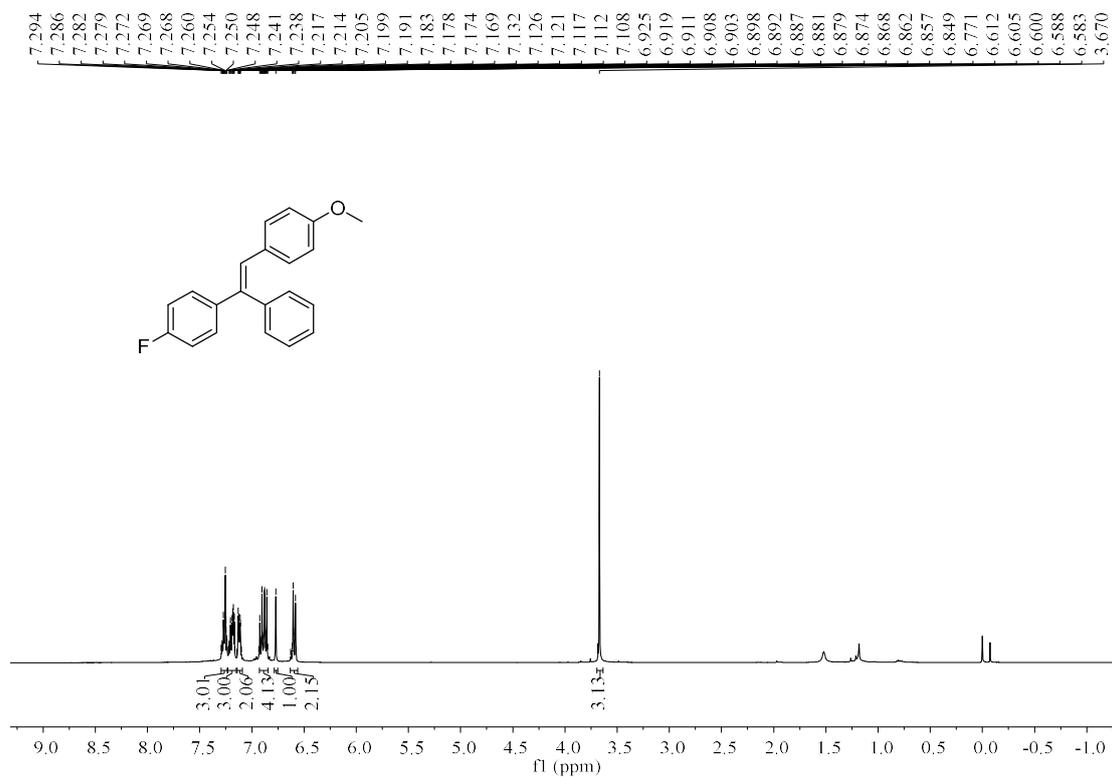


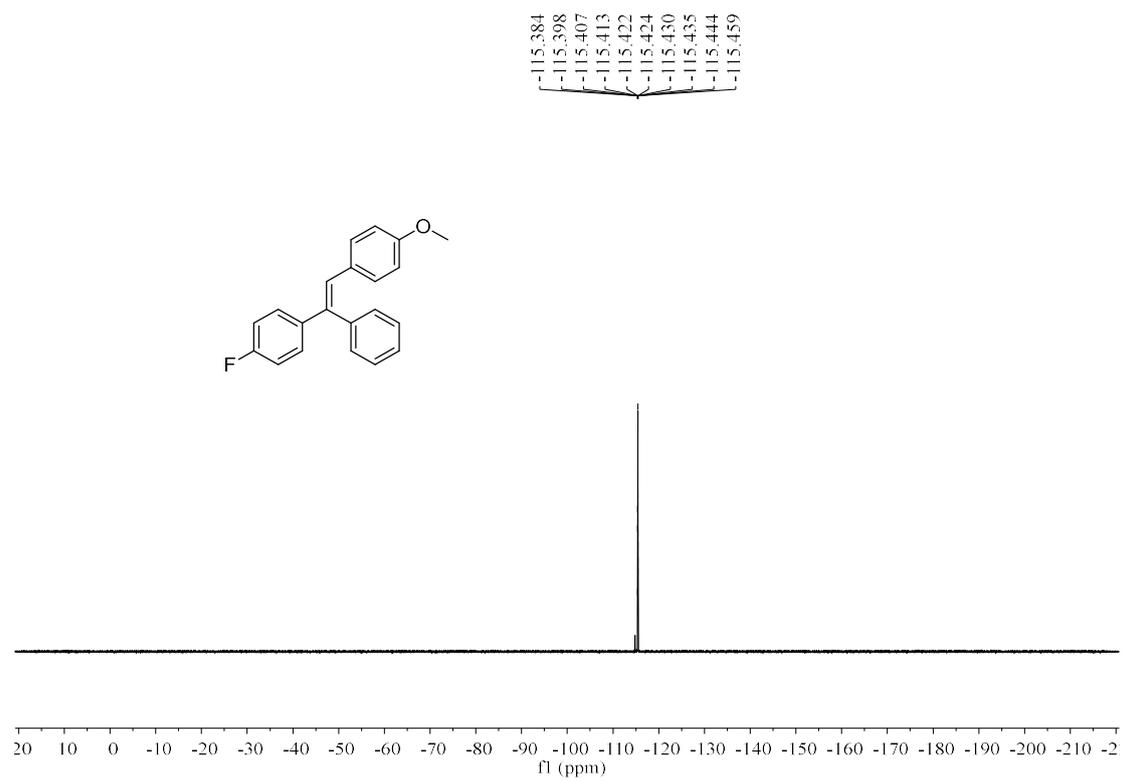
**(Z)-1-Fluoro-4-(2-(4-methoxyphenyl)-1-phenylvinyl)benzene ((Z)-11)**



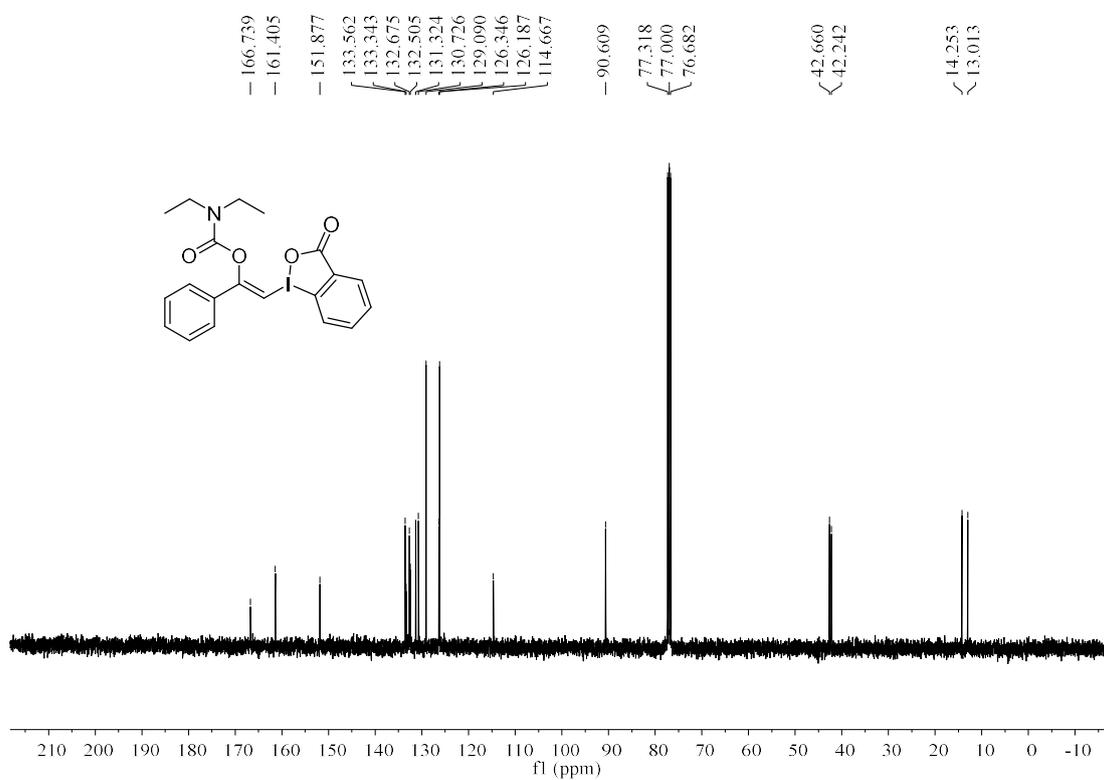
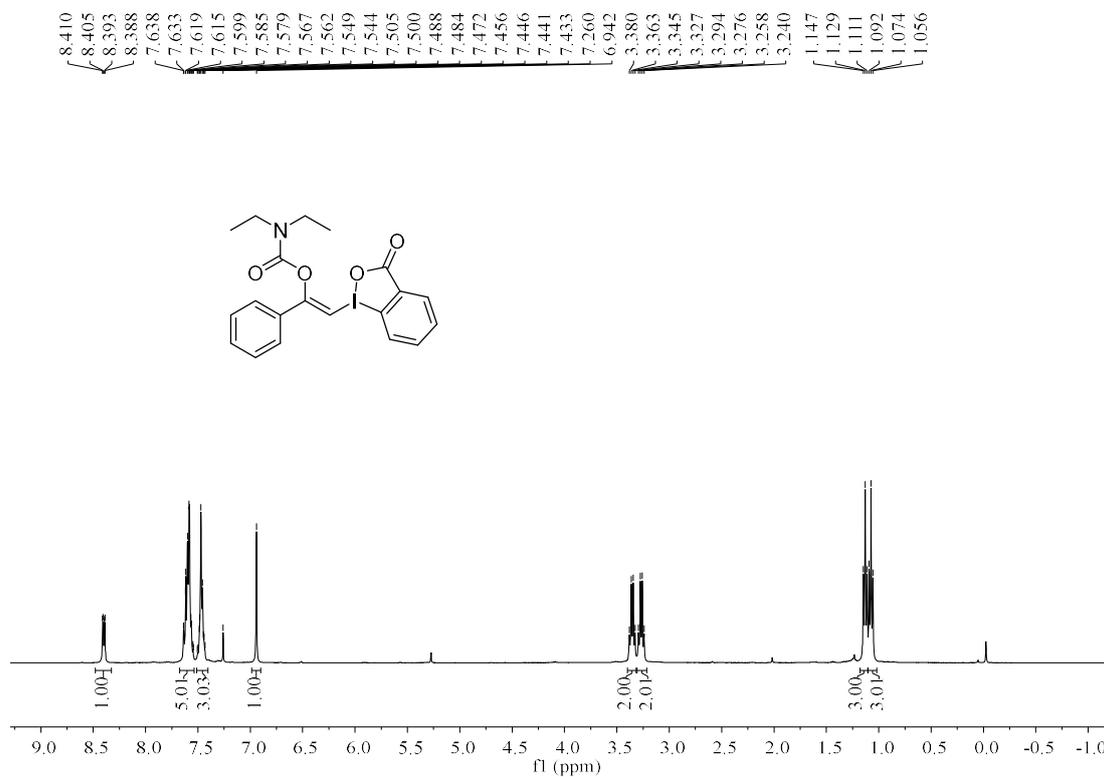


**(E)-1-Fluoro-4-(2-(4-methoxyphenyl)-1-phenylvinyl)benzene ((E)-11)**

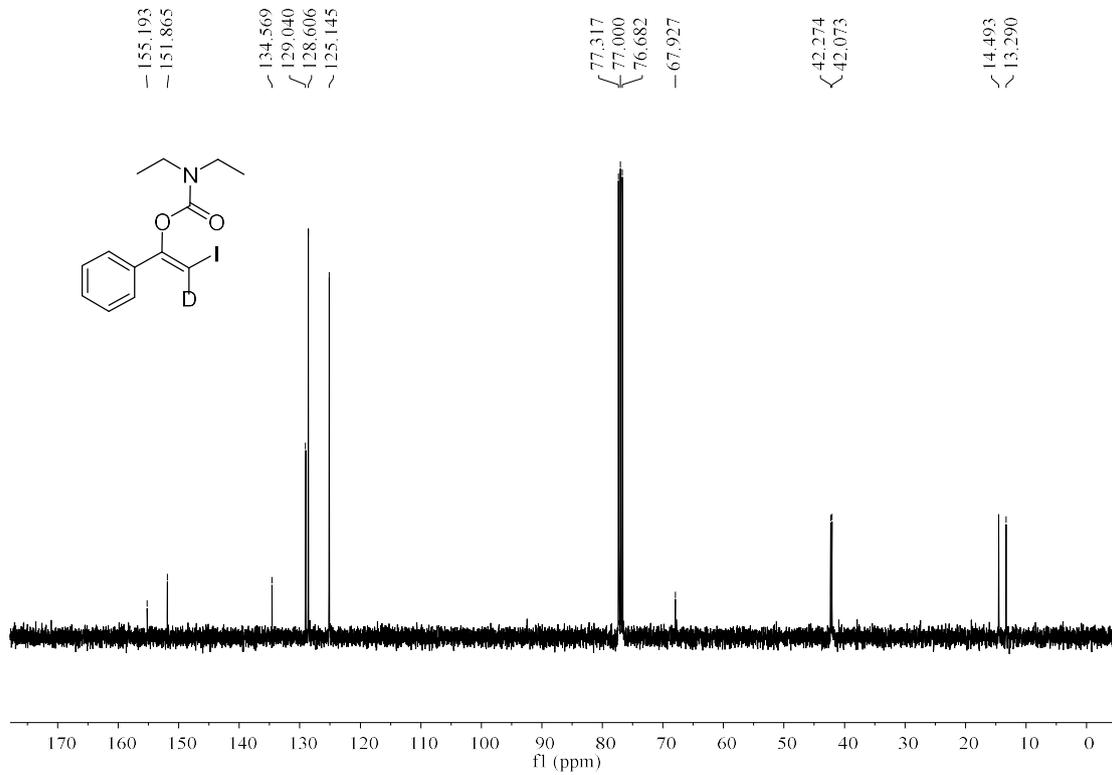
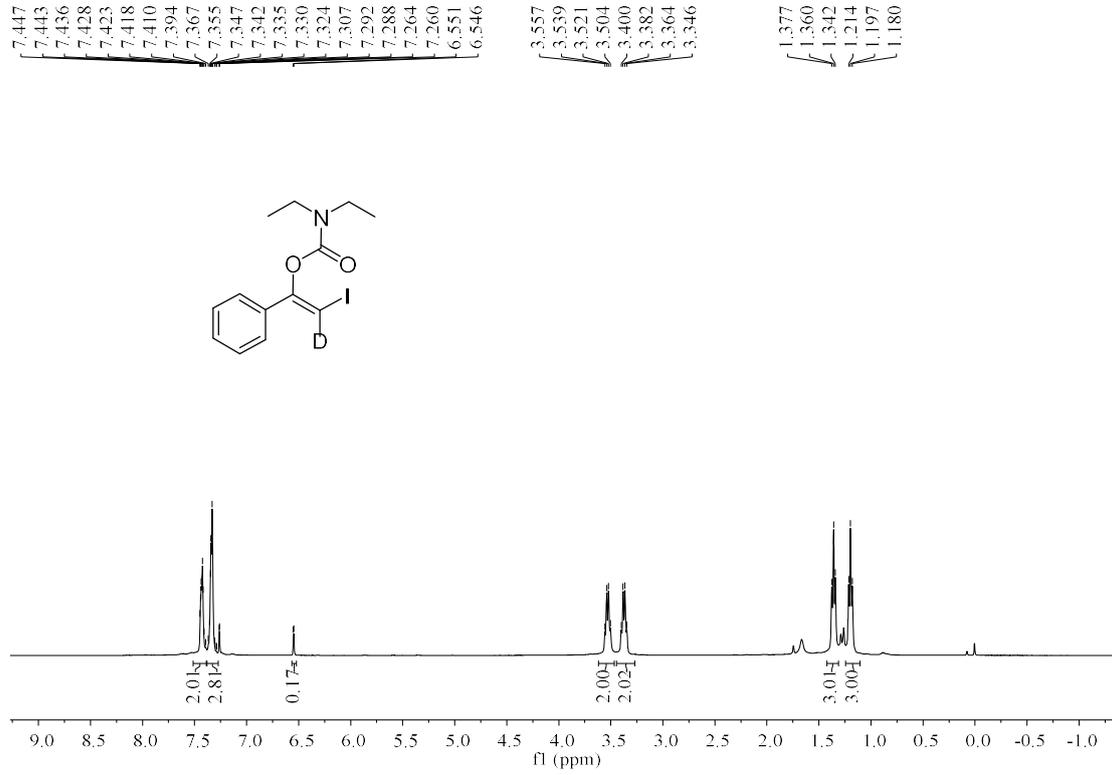




**(Z)-2-(3-Oxo-1 $\lambda^3$ -benzo[d][1,2]iodaoxol-1(3H)-yl)-1-phenylvinyl diethylcarbamate (12)**



**(Z)-2-Iodo-1-phenylvinyl-2-*d* diethylcarbamate ((Z)-3aa-D)**



**(E)-2-Iodo-1-phenylvinyl-2-d diethylcarbamate ((E)-3aa-D)**

