## **Supporting Information**

Oxidative Palladium(II) Catalysis: A Highly Efficient and Chemoselective

Cross Coupling Method for Carbon-Carbon Bond Formation under Base
Free and Nitrogenous-Ligand Conditions

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General Experimental Conditions. DMF, DMA, THF, acetonitrle, and toluene were used in anhydrous forms, which were purchased from Aldrich chemical. <sup>1</sup>H NMR spectra were recorded at 250, 300, and 400 MHz. <sup>13</sup>C NMR spectra were recorded at 63, 75.5, and 100 MHz. Thin-layer chromatography (TLC) was performed using commercially prepared 60 mesh silica gel plates visualized with short-wavelength UV light (254 nm). Silica gel 60 (9385, 230-400 mesh) was used for column chromatography. The reported yields are isolated yields and are the average of two runs. All commercially available reagents such as boronic acids and olefins were used as received from Aldrich and Acros chemical. In addition, the use of oxygen in conjunction with metals can lead to explosive mixtures, and care should be exercised especially when scaling up although we have not encountered any dangerous incidents during the oxidative palladium(II) catalysis reactions.

(*IE*)-2-Hex-1-enyl-4,4,5,5-tetramethyl-[1,3,2]dioxaborolane (1): To a stirred solution of 1-hexyne (1 g, 12.2 mmol), was cautiously added catechol borane (1.4 ml, 13.4 mmol) under a  $N_2$  atmosphere, and the resulting mixture was maintained at 70 °C for 2 hours with stirring. After cooled to room temperature, the reaction was diluted with THF (30 mL) prior to the addition of pinacol (1.7 g, 14.6 mmol). The resulting reaction mixture was stirred for 3 hours at room temperature, diluted with EtOAc (30 mL) and washed with water followed by saturated brine. The separated organic layer was dried over anhydrous  $Na_2SO_4$ , filtered and reduced *in vacuo* to give an oil, which was column chromatographed eluting with 10% EtOAc in hexanes to afford 1 (78%) as colorless oil:  $^1H$  NMR (250 MHz, CDCl<sub>3</sub>)  $\delta$ =6.61 (dt, J = 6.5, 17.9 Hz, 1 H), 5.40 (d, J = 17.9 Hz, 1 H), 2.13 (dt, J = 6.5, 6.6 Hz, 2 H), 1.27-1.41 (m, 4 H), 1.24 (s, 12 H), 0.86 (t, J = 6.9 Hz, 3 H).

General procedure A for the coupling reaction with pinacolboronic ester and olefin in the absence of base (Base Free Conditions): To a solution of olefin (1.5 mmol) in *N,N*-dimethylacetamide (2.5 mL, C = 0.2 M), was added pinacolboronic ester (0.5 mmol) followed by a single addition of Pd(OAc)<sub>2</sub> (0.025 mmol). The reaction flask was fitted with an oxygen balloon. The resulting reaction was stirred for 6 hours at 50 °C, diluted with ethyl acetate (20 mL), and washed with water (2 X 10 mL). The separated organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and filtered. The filtrate was concentrated *in vacuo*, and subjected to flash chromatography affording a cross-coupling compound.

(2*E*,4*E*)-Nona-2,4-dienoic acid *tert*-butyl ester (2): Following the general procedure **A**, cross coupling reaction of boronic ester **1** with *tert*-butyl acrylate afforded diene **2** (95%):  $^{1}$ H NMR (250 MHz, CDCl<sub>3</sub>)  $\delta$ = 7.13 (dd, J = 25.4, 15.4 Hz, 1 H), 6.10 (m, 2 H), 5.68 (d, J = 15.4 Hz, 1 H), 2.12 (m, 2 H), 1.45 (s, 9 H), 1.32 (m, 4 H), 0.87 (t, J = 6.9 Hz, 3 H);  $^{13}$ C NMR (63 MHz, CDCl<sub>3</sub>)  $\delta$  = 166.7, 144.1, 144.0, 128.3, 121.0, 80.0, 32.6, 30.8, 28.1, 22.2, 13.8;;Anal. calcd for C<sub>13</sub>H<sub>22</sub>O<sub>2</sub>: C 74.24, H 10.54, found: C 74.23, H 10.54.

(*IE*, *3E*)-Octa-1,3-dienyl-benzene (9): Following the general procedure **A**, cross coupling reaction of boronic ester **1** with styrene afforded diene **9** (88%):  $^{1}$ H NMR (250 MHz, CDCl<sub>3</sub>)  $\delta = 7.27$  (m, 5 H, Ph), 6.73 (dd, J = 15.6, 10.3 Hz, 1 H), 6.41 (d, J = 15.6 Hz, 1 H), 6.18 (dd, J = 15.1, 10.3 Hz, 1 H), 5.80 (dt, J = 15.1, 7.5 Hz, 1 H), 2.12 (m, 2 H), 1.34 (m, 4 H), 0.88 (t, J = 6.9 Hz, 3 H);  $^{13}$ C NMR (63 MHz, CDCl<sub>3</sub>)  $\delta = 137.6$ , 136.0, 130.4, 129.9, 129.4, 128.5, 127.0, 126.1, 32.6, 31.4, 22.3, 14.0; Anal. calcd for  $C_{14}H_{18}$ : C 90.26, H 9.74, found: C 90.25, H 9.75.

(2*E*,4*E*)-Nona-2,4-dienyloxymethyl-benzene (10): Following the general procedure **A**, cross coupling reaction of boronic ester **1** with allyl benzyl ether afforded diene **10** (87%):  $^{1}$ H NMR (250 MHz, CDCl<sub>3</sub>)  $\delta$  = 7.28 (m, 5 H, Ph), 6.21 (dd, J = 15.2, 10.5 Hz, 1 H), 6.03 (dd, J = 15.2, 10.2 Hz, 1 H), 5.68 (m, 2 H), 4.48 (s, 2 H), 4.02 (d, J = 6.3 Hz, 2 H), 2.11 (m, 2 H), 1.31 (m, 4 H), 0.87 (t, J = 6.8 Hz, 3 H);  $^{13}$ C NMR (63 MHz, CDCl<sub>3</sub>)  $\delta$  = 138.3, 135.7, 133.5, 129.4, 128.3, 127.8, 127.5, 126.8, 71.9, 70.6, 32.3, 31.3, 22.2, 13.9; Anal. calcd for C<sub>16</sub>H<sub>22</sub>O: C 83.43, H 9.65, found: C 83.39, H 9.67.

(2*E*,4*E*)- and (2*Z*,4*E*)-Nona-2,4-dienenitrile (11): Following the general procedure **A**, cross coupling reaction of boronic ester **1** with acrylonitrile afforded an inseparable mixture of (2*E*,4*E*)- and (2*Z*,4*E*)-diene **10** (78%, 2*E*,4*E*:2*Z*,4*E*=3:2). For (2*E*,4*E*):  $^{1}$ H NMR (250 MHz, CDCl<sub>3</sub>)  $\delta$  = 6.84 (m, 1 H), 6.04-6.21 (m, 2 H), 5.21 (d, *J* = 16.0 Hz, 1 H), 2.18 (m, 2 H), 1.34 (m, 4 H), 0.88 (t, *J* = 7.0 Hz, 3 H). For (2*Z*,4*E*):  $^{1}$ H NMR (250 MHz, CDCl<sub>3</sub>)  $\delta$  = 6.77 (dd, *J* = 10.9, 10.9 Hz, 1 H), 6.47-6.58 (m, 1 H), 6.04-6.21 (m, 1 H), 5.07 (d, *J* = 10.9 Hz, 1 H), 2.18 (m, 2 H), 1.34 (m, 4 H), 0.89 (t, *J* = 7.0 Hz, 3 H); Anal. calcd for C<sub>9</sub>H<sub>13</sub>N: C 79.95, H 9.69, N 10.36, found: C 79.95, H 9.70, N 10.35

(2*E*,4*E*)-2-Methyl-nona-2,4-dienoic acid *tert*-butyl ester (12): Following the general procedure **A**, cross coupling reaction of boronic ester **1** with *tert*-butyl methacrylate afforded diene **12** (90%):  $^{1}$ H NMR (250 MHz, CDCl<sub>3</sub>)  $\delta$  = 7.04 (d, *J* = 11.3 Hz, 1 H), 6.29 (dd, *J* = 14.8, 11.4 Hz, 1 H), 5.92 (m, 1 H), 2.18 (m, 2 H), 1.85 (s, 3 H), 1.46 (s, 9 H), 1.33 (m, 4 H), 0.88 (t, *J* = 7.0 Hz,3 H);  $^{13}$ C NMR (63 MHz, CDCl<sub>3</sub>)  $\delta$  = 167.9, 142.5, 137.8, 126.5, 126.1, 79.9, 32.9, 31.1, 28.1, 22.2, 13.8, 12.5; Anal. calcd for  $C_{14}H_{24}O_2$ : C 74.95, H 10.78, found: C 74.89, H 10.68

(2*E*,4*E*)-3-Methyl-nona-2,4-dienoic acid ethyl ester (13): Following the general procedure **A**, cross coupling reaction of boronic ester **1** with ethyl crotonate afforded diene **12** (89%):  $^{1}$ H NMR (250 MHz, CDCl<sub>3</sub>)  $\delta$  = 6.08 (m, 1 H), 5.66 (s, 1 H), 4.13 (q, 2 H, J = 7.2 Hz), 2.24 (s, 3 H), 2.15 (m, 2 H), 1.31 (m, 4 H), 1.25 (t, J = 7.2 Hz, 3 H), 0.87 (t, J = 7.0 Hz, 3 H);  $^{13}$ C NMR (63 MHz, CDCl<sub>3</sub>)  $\delta$  = 167.9, 142.5, 137.8, 126.5, 126.1, 79.9, 32.9, 31.1, 22.2, 14.3, 13.9, 13.8; Anal. calcd for  $C_{12}H_{20}O_2$ : C 73.43, H 10.27, found: C 73.41, H 10.28.

(1*E*,3*E*)-(1-Methyl-octa-1,3-dienyl)-benzene and (3*E*)-(1-Methylene-oct-3-enyl)-benzene (14): Following the general procedure **A**, cross coupling reaction of boronic ester **1** with amethylstyrene afforded an inseparable mixture of dienes **14** (50%, 14*a*(1*E*,3*E*) : 14*b*(3*E*) = 1 : 2.8). <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>)  $\delta$  = 7.21- 7.45 (m, 5 H, Ph), 6.42 (for 14*a*, m), 5.84 (for 14*a*, m), 5.49 (for 14*b*, m), 5.34 (for 14*b*, br s), 5.07 (for 14*b*, d, J = 1.4 Hz), 2.14 (for 14*a*, s), 1.99 (m, 2 H), 1.29 (m, 4 H), 0.88 (m, 3 H).

(*IE*,3*E*)- and (*IZ*,3*E*)-(2-Methyl-octa-1,3-dienyl)-benzene (15): Following the general procedure **A**, cross coupling reaction of boronic ester **1** with *trans*-b-methylstyrene afforded an inseparable mixture of dienes **15** (52%, (*IE*,3*E*):(*IZ*,3*E*) = 6:1):  $^{1}$ H NMR (250 MHz, CDCl<sub>3</sub>)  $\delta$  = 7.24 (m, 5 H, Ph), 6.57 (for (*IZ*,3*E*), d, J = 15.7 Hz) and 6.22 (for (*IE*,3*E*), dd, J = 15.5, 1.1 Hz), 6.40 (for (*IE*,3*E*), s) and 6.33 (for (*IZ*,3*E*), s), 5.77 (dt, J = 15.5, 7.1 Hz, 2 H), 2.15 (m, 2 H), 1.97 (d, J = 1.1 Hz, 3 H), 1.35 (m, 4 H), 0.89 (t, J = 7.0 Hz, 3 H).

(2E,4E)-6-(tert-Butyl-diphenyl-silanyloxy)-hexa-2,4-dienoic acid tert-butyl ester (18): Following the general procedure A, cross coupling reaction of boronic ester 17, prepared from propargyl alcohol through TBDPS protection, hydroboration with catechol borane, and pinacol esterification, with tert-butyl acrylate afforded diene 18 (92%): <sup>1</sup>H NMR (250 MHz,

CDCl<sub>3</sub>)  $\delta = 7.65-7.34$  (m, 10 H, Ph), 7.19 (dd, J = 15.3, 11.4 Hz, 1 H), 6.46 (dd, 15.2, 11.4 Hz, 1 H), 6.10 (dt, J = 15.2, 2.4 Hz, 1 H), 4.29 (d, J = 2.4 Hz, 2 H), 1.47 (s, 9 H), 1.04 (s, 9 H); <sup>13</sup>C NMR (63 MHz, CDCl<sub>3</sub>)  $\delta = 166.5$ , 143.0, 140.6, 135.4, 133.2, 129.7, 127.7, 126.8, 122.7, 80.2, 63.6, 28.1, 26.7, 19.2.

(2*E*,4*E*)-7-Hydroxy-octa-2,4-dienoic acid *tert*-butyl ester (20): Following the general procedure **A**, cross coupling reaction of boronic ester 19, prepared from 4-pentyn-2-ol through TMS protection, hydroboration with catechol borane, and pinacol esterification, with *tert*-butyl acrylate afforded diene 20 (81%):  $^{1}$ H NMR (250 MHz, CDCl<sub>3</sub>)  $\delta$  = 7.14 (dd, *J* = 15.3, 10.5 Hz, 1 H), 6.20 (dd, *J* = 15.1, 10.5 Hz, 1 H), 6.06 (dt, *J* = 15.1, 7.0 Hz, 1 H), 5.73 (d, *J* = 15.3 Hz, 1 H), 3.88 (m, 1 H), 2.30 (m, 2 H), 1.46 (s, 9 H), 1.20 (d, *J* = 6.2 Hz, 3 H);  $^{13}$ C NMR (63 MHz, CDCl<sub>3</sub>)  $\delta$  = 166.4, 143.2, 138.8, 131.1, 122.2, 80.2, 67.1, 42.6, 28.1, 23.0; Anal. calcd for  $C_{12}H_{20}O_3$ : C 67.89, H 9.50, found: C 67.71, H 9.54

**2-Isopropenyl pinacol boronic ester (21)**: Following the known procedure, <sup>25</sup> isopropenyl bromide was converted to 2-isopropenyl boronic acid, which was treated pinacol affording a corresponding pinacol boronic ester **21**: <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>)  $\delta$  = 5.7 (br s, 1 H), 5.61 (br s, 1 H), 1.79 (dd, J = 1.31, 1.26 Hz, 3 H), 1.25 (s, 12 H).

(2*E*)-4-Methyl-penta-2,4-dienoic acid *tert*-butyl ester (22): Following the general procedure **A**, cross coupling reaction of boronic ester 21 with *tert*-butyl acrylate afforded diene 22 (86%):  $^{1}$ H NMR (250 MHz, CDCl<sub>3</sub>)  $\delta$  = 7.24 (d, J = 15.7 Hz, 1 H), 5.78 (d, J = 15.7 Hz, 1 H), 5.28 (m, 2 H), 1.85 (s, 3 H), 1.48 (s, 9 H);  $^{13}$ C NMR (63 MHz, CDCl<sub>3</sub>)  $\delta$  = 166.5, 145.9, 140.5, 123.6, 120.6, 80.3, 46.3, 30.9, 28.1, 18.1; Anal. calcd for C<sub>10</sub>H<sub>16</sub>O<sub>2</sub>: C 71.39, H 9.59, found: C 71.41, H 9.62

trans-2-phenyvinyl pinacol boronic ester (23): Pinacol was added to a solution of commercially available trans-2-phenyl boronic acid in THF at room temperature. After stirred for 3 hours, the reaction mixture was concentrated *in vacuo* and chromatographed on silica gel to afford pinacol boronic ester compound 23 as colorless oil in quantitative yield: <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>)  $\delta = 7.24-7.49$  (m, 6 H), 6.15 (d, J = 18.4 Hz, 1 H), 1.30 (s, 12 H); <sup>13</sup>C-NMR (63 MHz, CDCl<sub>3</sub>)  $\delta = 149.5$ , 137.4, 128.9, 127.1, 83.4, 24.8.

(2*E*,4*E*)-5-Phenyl-penta-2,4-dienoic acid *tert*-butyl ester (24): Following the general procedure **A**, cross coupling reaction of boronic ester 23 with *tert*-butyl acrylate afforded diene 24 (81%):  $^{1}$ H NMR (250 MHz, CDCl<sub>3</sub>)  $\delta$  = 7.21-7.39 (m, 6 H), 6.77 (m, 2 H), 5.85 (d, J = 15.2 Hz, 1 H), 1.44 (s, 9 H);  $^{13}$ C NMR (63 MHz, CDCl<sub>3</sub>)  $\delta$  = 166.4, 143.5, 139.7, 136.1, 128.9, 128.8, 127.1, 126.3, 123.3, 80.3, 28.2; Anal. calcd for C<sub>15</sub>H<sub>19</sub>O<sub>2</sub>: C 78.23, H 7.88, found: C 78.34, H 7.82

(*IZ*)-2-Hex-1-enyl-4,4,5,5-tetramethyl-[1,3,2]dioxaborolane (25): $^{25}$  A two neck flask was charged with [Rh(cod)Cl<sub>2</sub>]<sub>2</sub> (43 mg, 0.015 eq) and then flushed with nitrogen. Cyclohexane, P(*i*-Pr)<sub>3</sub> (67 mL. 0.06 eq.), TEA (0.82 mL, 1 eq.), and catechol borane (0.65 mL, 5.8 mmol) were successively added and the mixture was stirred for 30 minutes at room temperature. 1-Hexyne (0.58 g, 1.2 eq.) was added and the reaction mixture was stirred for 4 hours at room temperature. After addition of pinacol (1.0 g, 1.5 eq.), the resulting reaction mixture was stirred for additional 12 hours, concentrated *in vacuo* and chromatographed on silica gel to give *cis*-pinacol boronic ester **25** as colorless oil; <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>)  $\delta$  = 6.40 (dt, J = 13.4, 6.6 Hz, 1 H), 5.30 (dt, J = 13.4, 1.1 Hz, 1 H), 2.38 (m, 2 H), 1.31 (m, 4 H), 1.24 (s, 12 H), 0.87 (t, J = 7.0 Hz, 3 H).

(2*E*,4*Z*)-Nona-2,4-dienoic acid *tert*-butyl ester (26): Following the general procedure **A**, cross coupling reaction of boronic ester 25 with *tert*-butyl acrylate afforded diene 26 (91%):  $^{1}$ H NMR (250 MHz, CDCl<sub>3</sub>)  $\delta$  = 7.50 (ddd, J = 15.3, 11.5, 0.7 Hz, 1 H), 6.06 (dd, J = 11.0, 10.9 Hz, 1 H), 5.79 (m, 1 H), 5.77 (d, J = 15.3 Hz, 1 H), 2.25 (m, 2 H), 1.46 (s, 9 H), 1.34 (m, 4 H), 0.89 (t, J = 7.0 Hz, 3 H);  $^{13}$ C NMR (63 MHz, CDCl<sub>3</sub>)  $\delta$  = 166.8, 141.0, 138.5, 126.3, 122.9, 80.1, 31.5, 28.1, 27.9, 22.3, 13.9.

General procedure B for the coupling reaction with pinacolboronic ester and olefin in the presence of 1,10-phenanthroline as a ligand: To a premixed solution of palladium acetate (0.025 mole) and 1,10-phenanthroline as a ligand (0.028 mmol) in DMF (2.5 mL) for 30 minutes, were added olefin (1.5 mmol) and pinacolboronic ester (0.5 mmol). The reaction flask was fitted with an oxygen balloon and the reaction mixture was stirred at room temperature for 12 hours, then diluted with ethyl acetate (20 mL), and washed with water and brine (2 X 10 mL). The separated organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and filtered. The filtrate was concentrated *in vacuo* and the residue was chromatographed on silica gel to give a cross-coupled product.

(3*E*,5*E*)-Deca-3,5-dien-2-one (27): Following the general procedure **B**, cross coupling reaction of boronic ester **1** with methyl vinyl ketone afforded diene **27** (88%). <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>) δ= 7.01 (m, 1 H), 6.10 (m, 2 H), 5.96 (d, J = 15.5 Hz, 1 H), 2.17 (s, 3H), 2.11 (m, 2 H), 1.30 (m, 4 H), 0.82 (t, J = 7.0 Hz, 3 H); <sup>13</sup>C NMR (63 MHz, CDCl<sub>3</sub>) δ = 198.9, 145.8, 144.1, 128.8, 128.7, 32.8, 30.7, 27.1, 22.2, 13.8; Anal. calcd for C<sub>10</sub>H<sub>16</sub>O: C 78.90, H 10.59, found: C 78.89, H 10.60.

(*E*)-tert-Butyl 3-phenylpropenoate (28): Following the general procedure **B**, cross coupling reaction of phenylboronic acid with *tert*-butyl acrylate afforded 28 (87%):  $^{1}$ H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  = 7.58 (d, J = 16.0 Hz, 1 H), 7.50 (m, 2H), 7.37 (m, 3H), 6.37 (d, J = 16.0 Hz, 1 H), 1.54 (s, 9 H);  $^{13}$ C NMR (63 MHz, CDCl<sub>3</sub>)  $\delta$  = 166.3, 143.5, 134.6, 129.9, 128.7, 127.9, 120.1, 80.4, 28.1; Anal. calcd for C<sub>13</sub>H<sub>16</sub>O<sub>2</sub>: C 76.44, H 7.90, found: C 76.43, H 7.92

(*E*)-4-Phenylbut-3-en-2-one (33): Following the general procedure **B**, cross coupling reaction of phenylboronic acid with methyl vinyl ketone afforded 33 (71%):  $^{1}$ H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta = 7.54$  (m, 2 H), 7.50 (d, J = 10.3 Hz, 1 H), 7.40 (m, 3 H), 6.72 (d, J = 10.2 Hz, 1 H), 2.39 (s, 3 H);  $^{13}$ C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta = 198.7$ , 143.7, 134.6, 130.7, 129.2, 128.5, 127.4, 27.7; Anal. calcd for C<sub>10</sub>H<sub>10</sub>O: C 82.16, H 6.89, found: C 82.08, H 6.92

(*E*)-Cinnamamide (34): Following the general procedure **B**, cross coupling reaction of phenylboronic acid with acrylamide afforded 34 (64%):  $^{1}$ H NMR 300 MHz, CDCl<sub>3</sub>)  $\delta = 7.64$  (d, J = 15.7 Hz, 1 H), 7.52 (m, 2 H), 7.38 (m, 3 H), 6.46 (d, J = 15.7 Hz, 1 H), 5.57 (br, 2 H);  $^{13}$ C NMR (75.5 MHz, CDCl<sub>3</sub>)  $\delta = 167.8$ , 142.5, 134.4, 129.9, 128.8, 127.9, 119.4; Anal. calcd for C<sub>9</sub>H<sub>9</sub>NO: C 73.45, H 6.16, N 9.52, found: C 73.37, H 6.18, N 9.49.

(*E*)-1,2-Diphenylethene (35): Following the general procedure **B**, cross coupling reaction of phenylboronic acid with styren afforded 35 (85%):  $^{1}$ H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 7.51 (d, J = 4.75 Hz, 4 H), 7.35 (t, J = 5.0 Hz, 4 H), 7.24 (m, 2 H), 7.10 (s, 2 H);  $^{13}$ C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  = 137.5, 128.9, 128.8, 127.8, 126.7; Anal. calcd for C<sub>14</sub>H<sub>12</sub>: C 93.29, H 6.71, found: C 92.97, H 6.85

**Cinnamonitrile** (**36**): Following the general procedure **B**, cross coupling reaction of phenylboronic acid with acrylnitrile afforded **36** (84%):  $^{1}$ H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 7.41 (m, 6 H), 5.86 (d, J = 10.5 Hz, 1 H);  $^{13}$ C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  = 150.8, 133.7, 131.4, 129.3, 127.5, 118.3, 96.5; Anal. calcd for C<sub>9</sub>H<sub>7</sub>N: C 83.69, H 5.46, N 10.84, found: C 83.65, H 5.52, N 10.82

**1-[(Cinnamyl-oxy) methyl] benzene** (**37):** Following the general procedure **B**, cross coupling reaction of phenylboronic acid with allylic benzyl ether afforded **37** (78%):  $^{1}$ H NMR (250 MHz, CDCl<sub>3</sub>)  $\delta$  = 4.21 (d, J = 4.2 Hz, 2H), 4.58 (s, 2H), 6.35 (td, J = 4.5 Hz, 12.0 Hz, 1H), 6.64 (d, J = 12.0 Hz, 1H), 7.25 - 7.35 (m, 10H);  $^{13}$ C NMR (63 MHz, CDCl<sub>3</sub>)  $\delta$  = 70.6, 72.1, 126.5, 126.7, 128.1, 128.6, 132.4, 136.7, 138.5

tert-Butyl 2-benzylacrlate (38): Following the general procedure **B**, cross coupling reaction of phenylboronic acid with tert-butyl methacrylate afforded 38 (85%; coupled:migrated = 1:1.4):  ${}^{1}$ H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 7.35 (m, 2 H), 7.22 (m, 3 H), 6.14 (s, 1 H), 5.34 (d, J = 0.75 Hz, 1 H), 3.57 (s, 2 H), 1.41 (s, 9 H).

(*E*)-Ethyl 3-phenylbut-2-enoate (39): Following the general procedure **B**, cross coupling reaction of phenylboronic acid with ethyl crotonate afforded 39 (82%):  $^{1}$ H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta = 7.49$  (m, 2 H), 7.37 (m, 3 H), 6.13 (q, J = 1.25 Hz, 1 H), 4.21 (q, J = 7.25 Hz, 2 H), 2.57 (d, J = 1.5 Hz, 3 H), 1.31 (t, J = 7.25 Hz, 3 H);  $^{13}$ C NMR (63 MHz, CDCl<sub>3</sub>)  $\delta = 166.8$ , 155.4, 142.2, 128.9, 128.4, 126.2, 117.1, 59.8, 17.9, 14.3; Anal. calcd for C<sub>12</sub>H<sub>14</sub>O<sub>2</sub>: C 75.76, H 7.42, found: C 75.77, H 7.45

General procedure C for the coupling reaction with arylboronic acid and olefin in the presence of 2,9-dimethyl-phenanthroline as a ligand: To a premixed solution of palladium acetate (0.025 mole) and 2,9-dimethyl-phenanthroline as a ligand (0.028 mmol) in DMF (2.5 mL) for 30 minutes, were added olefin (1.5 mmol) and arylboronic acid (0.5 mmol). The reaction flask was fitted with an oxygen balloon and the reaction mixture was stirred at room temperature for 12 hours, then diluted with ethyl acetate (20 mL), and washed with water and brine (2 X 10 mL). The separated organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and filtered. The filtrate was concentrated *in vacuo* and the residue was chromatographed on silica gel to give a cross-coupled product.

(*E*)-tert-Butyl 3-(4-methoxyphenyl) acrylate (31): Following the general procedure C, cross coupling reaction of 4-methoxyphenyl boronic acid with *tert*-butyl acrylate afforded 31 (61%):  $^{1}$ H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 7.52 (d, J = 16.0 Hz, 1 H), 7.43 (d, J = 8.4 Hz, 1 H), 6.86 (d, J = 8.4 Hz, 1 H), 6.22 (d, J = 16.0 Hz, 1 H), 3.81 (s, 3 H), 1.51 (s, 9 H);  $^{13}$ C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  = 166.9, 161.3, 143.4, 129.7, 127.6, 117.9, 114.4, 80.4, 55.5, 28.4; Anal. calcd for  $C_{14}H_{18}O_3$ : C 71.77, H 7.74, found: C 71.78, H 7.74

(*E*)-*tert*-**Butyl 3-(3-acetylphenyl) acrylate (32):** Following the general procedure **C**, cross coupling reaction of 3-acetyl phenylboronic acid with *tert*-butyl acrylate afforded **32** (72%):  ${}^{1}$ H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta = 8.05$  (s, 1 H), 7.91 (d, J = 7.6 Hz, 1 H), 7.66 (d, J = 7.6 Hz, 1 H), 7.52 (d, J = 16.4 Hz, 1 H), 7.45 (t, J = 8Hz, 1 H), 6.42 (d, J = 16 Hz, 1 H), 2.60 (s, 3 H), 1.51 (s, 9 H);  ${}^{13}$ C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta = 197.7$ , 166.1, 142.5, 137.8, 135.4, 132.3, 129.7, 129.3, 127.7, 121.8, 81.0, 28.3, 26.8; Anal. calcd for C<sub>15</sub>H<sub>18</sub>O<sub>3</sub>: C 73.15, H 7.37, found: C 73.13, H 7.39

(*E*)-tert-Butyl 3-(4-dimethylamino phenyl) acrylate (40): Following the general procedure C, cross coupling reaction of 4-(dimethylamino)phenylboronic acid with tert-butyl acrylate afforded phenyl olefin 40 (94%): <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 7.50 (d, *J* = 16.0 Hz, 1 H), 7.38 (d, *J* = 8.8 Hz, 2 H), 6.64 (d, *J* = 8.8 Hz, 2 H), 6.13 (d, *J* = 16.0 Hz, 1 H), 2.98 (s, 6 H), 1.50 (s, 9 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  = 167.5, 151.7, 144.2, 129.7, 122.7, 114.8, 112.0, 79.9, 40.3, 28.5; Anal. calcd for C<sub>15</sub>H<sub>21</sub>NO<sub>2</sub>: C 72.84, H 8.56, N 5.66, found: C 72.85, H 8.54, N 5.67.

(*E*)-*tert*-Butyl 3-(4-acetylphenyl) acrylate (41): Following the general procedure C, cross coupling reaction of 4-acetylphenyl boronic acid with *tert*-butyl acrylate afforded 41 (71%):  $^{1}$ H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 7.95 (d, J = 8.5 Hz, 2 H), 7.59 (d, J = 16.0 Hz, 1 H), 7.57 (d, J = 8.5 Hz, 2 H), 6.45 (d, J = 16.0 Hz, 1 H), 2.60 (s, 3 H), 1.53 (s, 9 H);  $^{13}$ C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  = 197.3, 165.7, 141.9, 139.0, 137.7, 128.7, 127.9, 122.7, 80.9, 28.1, 26.6; Anal. calcd for C<sub>15</sub>H<sub>18</sub>O<sub>3</sub>: C 73.15, H 7.37, found: C 73.14, H 7.38

(*E*)-tert-Butyl 3-(4-nitrophenyl) acrylate (42): Following the general procedure C, cross coupling reaction of 4-nitrophenyl boronic acid with *tert*-butyl acrylate afforded 42 (57%):  $^{1}$ H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 8.23 (d, J = 9.0 Hz, 2 H), 7.65 (d, J = 8.5 Hz, 2 H), 7.59 (d, J = 16.0 Hz, 1 H), 6.48 (d, J = 16.0 Hz, 1 H), 1.54 (s, 9 H);  $^{13}$ C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  = 164.8, 140.9, 140.5, 130.0, 128.4, 124.5, 124.1, 81.3, 28.1; Anal. calcd for C<sub>13</sub>H<sub>15</sub>NO<sub>4</sub>: C 62.64, H 6.07, N 5.62, found: C 62.63, H 6.09, N 5.62.

(*E*)-tert-Butyl 3-(4-cyanophenyl) acrylate (43): Following the general procedure C, cross coupling reaction of 4-cyanophenyl boronic acid with *tert*-butyl acrylate afforded 43 (69%):  $^{1}$ H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta = 7.65$  (d, J = 8.2 Hz, 2 H), 7.58 (d, J = 8.2 Hz, 2 H), 7.56 (d,

J = 15.8 Hz, 1 H), 6.44 (d, J = 16.0 Hz, 1 H), 1.53 (s, 9 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  = 165.3, 141.0, 139.0, 132.5, 131.6, 128.2, 123.8, 113.0, 81.2, 28.1; Anal. calcd for C<sub>14</sub>H<sub>15</sub>NO<sub>2</sub>: C 73.34, H 6.59, N 6.11, found: C 73.33, H 6.60, N 6.10

(*E*)-tert-Butyl 3-o-tolylacrylate (44): Following the general procedure **C**, cross coupling reaction of *o*-toludylboronic acid with *tert*-butyl acrylate afforded 44 (84%):  $^{1}$ H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 7.87 (d, J = 16.0 Hz, 1 H), 7.52 (d, J = 7.2 Hz, 1 H), 7.22 (m, 3 H), 6.27 (d, J = 15.6 Hz, 1 H), 2.41 (s, 3 H), 1.52 (s, 9 H);  $^{13}$ C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  = 166.8, 141.4, 137.7, 133.7, 130.9, 129.9, 126.5, 126.4, 121.3, 80.7, 28.4, 13.9; Anal. calcd for C<sub>14</sub>H<sub>18</sub>O<sub>2</sub>: C 77.03, H 8.31, O 14.66, found: C 77.01, H 8.31

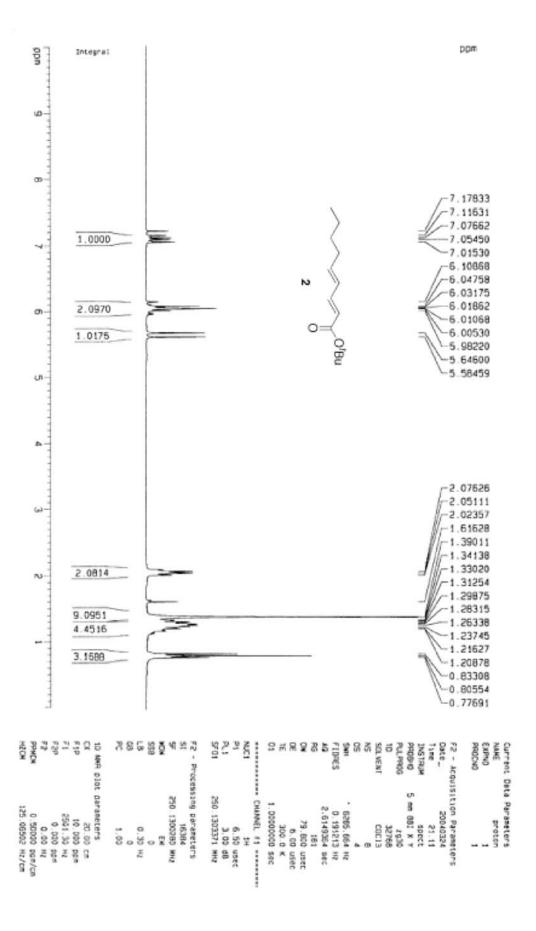
(2*E*)-2-Propenoic acid, 3-[1-(phenylsulfonyl)-1H-indol-3-yl]-1,1-dimethylethyl ester (45): Following the general procedure **C**, cross coupling reaction of 1-(Phenylsolfonyl)-3-indoleboronic acid with *tert*-butyl acrylate afforded phenyl olefin **45** (63%):  $^{1}$ H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 7.99 (d, *J* = 8.4 Hz, 1 H), 7.89 (d, *J* = 7.6 Hz, 2 H), 7.80 (s, 1 H), 7.79 (d, *J* = 8.8 Hz, 1 H), 7.66 (d, *J* = 16.0 Hz, 1 H), 7.55 (t, *J* = 7.6 Hz, 1 H), 7.45 (t, 8.0 Hz, 2 H), 7.36 (t, *J* = 7.6 Hz, 1 H), 7.31 (t, *J* = 7.6 Hz, 1 H), 6.44 (d, *J* = 16.0 Hz, 1 H), 1.52 (s, 9 H).

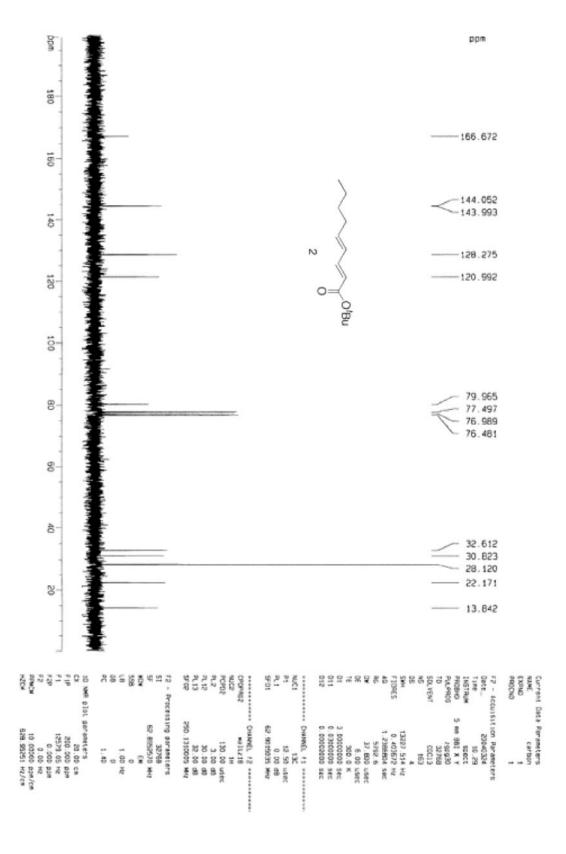
(2*E*)-2-Propenoic acid, 3-[1-(phenylsulfonyl)-1H-indol-2-yl]-1,1-dimethylethyl ester (46): Following the general procedure **C**, cross coupling reaction of 1-(phenylsulfonyl)-2-indolboronic acid with *tert*-butyl acrylate afforded phenyl olefin **46** (49%) at room temperature under molecular oxygen.;  $^{1}$ H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 8.24 (d, J = 16.0 Hz, 1H), 8.21 (d, J = 8.4 Hz, 1H), 7.74 (d, J = 7.2 Hz, 2H), 7.52 – 7.25 (m, 6H), 6.93 (s, 1H), 6.28 (d, J = 16.0 Hz, 1H), 1.55 (s, 9H).

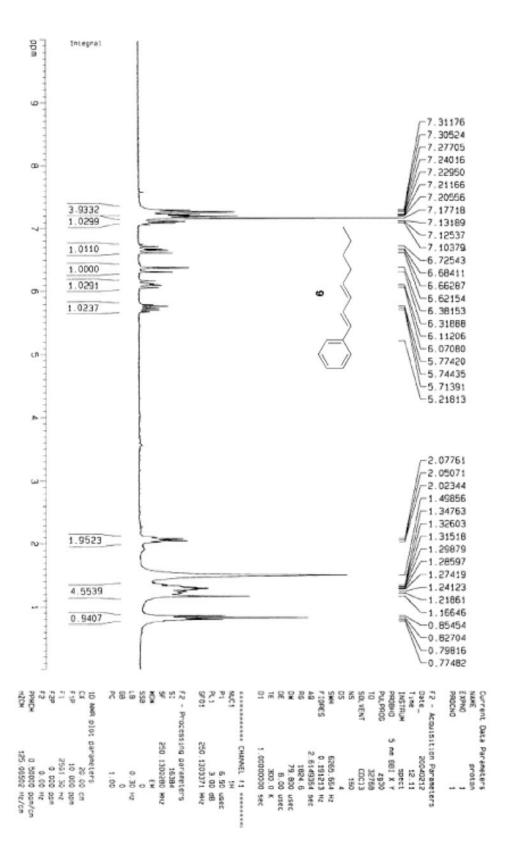
(*1E*)-3-Hex-1-enyl-cyclohex-2-enone (47): Following the general procedure **A**, cross coupling reaction of boronic ester **1** with cyclohexenone afforded diene **44** (37%). Following the general procedure **B**, cross coupling reaction of boronic ester **1** with cyclohexenone afforded diene **47** for 2 hours (82%):  $^{1}$ H NMR (250 MHz, CDCl<sub>3</sub>)  $\delta = 6.19$  (m, 2 H), 5.85 (s, 1 H), 2.41 (m, 4 H), 2.16 (m, 2 H), 2.00 (m, 2 H), 1.35 (m, 4 H), 0.89 (t, J = 7.0 Hz, 3 H);  $^{13}$ C NMR (63 MHz, CDCl<sub>3</sub>)  $\delta = 200.5$ , 157.7, 139.2, 131.3, 126.4, 37.7, 32.9, 31.0, 25.0, 22.3, 22.2, 13.9; Anal. calcd for  $C_{12}H_{18}O$ : C 80.85, H 10.18, found: C 80.82, H 10.19

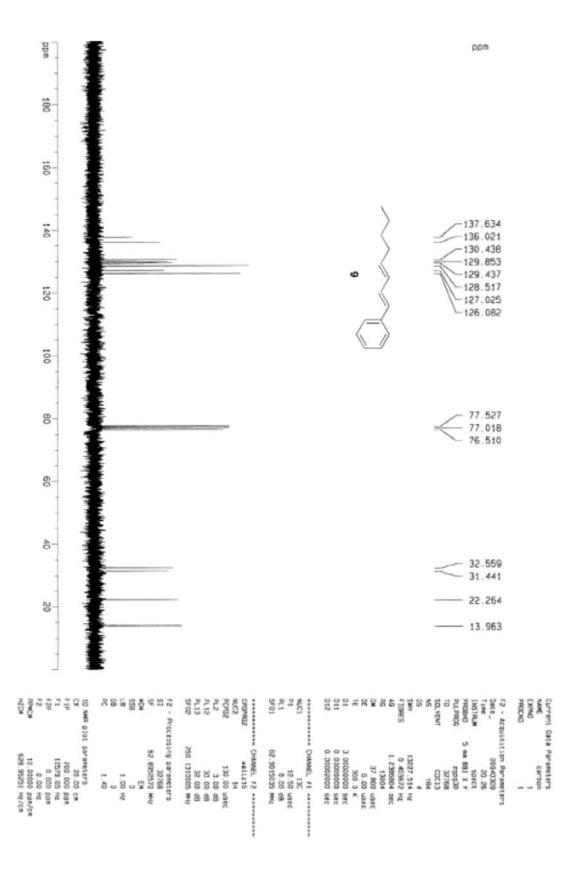
(1*E*)-3-Phenyl-cyclohex-2-enone (48): Following the general procedure **B**, cross coupling reaction of phenylboronic acid with cyclohexenone afforded 48 (81%): <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  = 2.14 (q, J = 6.8 Hz, 2 H), 2.47 (t, J = 6.8 Hz, 2 H), 2.76 (t, J = 5.6 Hz, 2H), 6.40 (s, 1H), 7.39 (m, 3H), 7.52 (m, 2H); <sup>13</sup>C NMR (75.5 MHz, CDCl<sub>3</sub>)  $\delta$  = 199.9, 159.8, 138.6, 130.0, 128.7, 126.0, 125.3, 115.4, 37.1, 28.0, 22.7; Anal. calcd for C<sub>12</sub>H<sub>12</sub>O: C 83.69, H 7.02, found: C 83.69, H 7.05

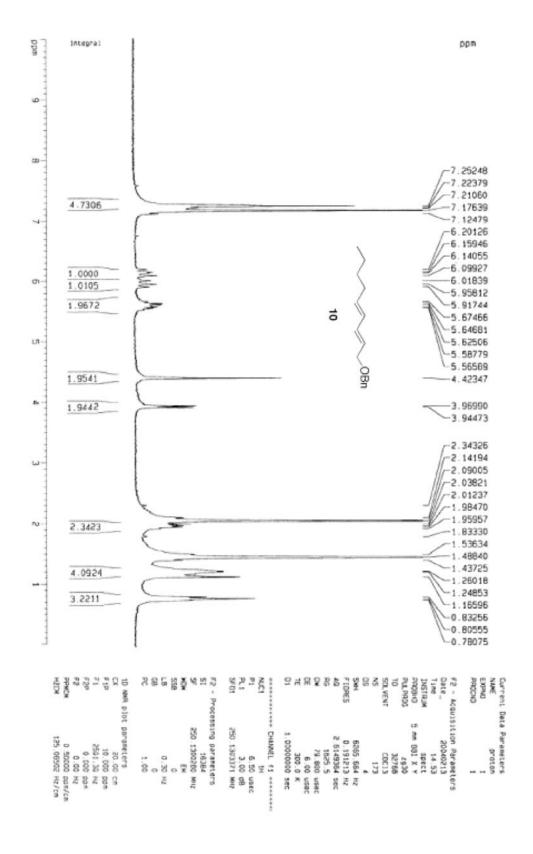
(*E*)-tert-Butyl 3-(4-iodophenyl) acrylate (51): Following the general procedure **C**, cross coupling reaction of 4-iodophenylboronic acid with *tert*-butyl acrylate afforded phenyl olefin 51 (81%):  $^{1}$ H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 7.70 (d, J = 8.2 Hz, 2 H), 7.48 (d, J = 16.0 Hz, 1 H), 7.22 (d, J = 8.2 Hz, 2 H), 6.35 (d, J = 16.0 Hz, 1 H), 1.52 (s, 9 H);  $^{13}$ C NMR (75.5 MHz, CDCl<sub>3</sub>)  $\delta$  = 166.0, 142.2, 138.0, 134.1, 129.4, 120.9, 96.0, 80.1, 28.1; Anal. calcd for  $C_{13}H_{15}IO_2$ : C 47.29, H 4.58, I 38.44, found: C 47.32, H 4.59, I 38.35.

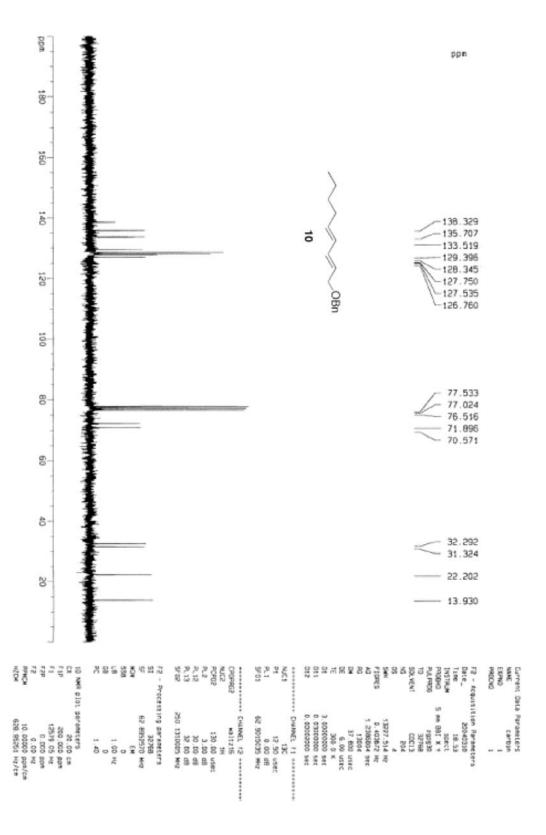


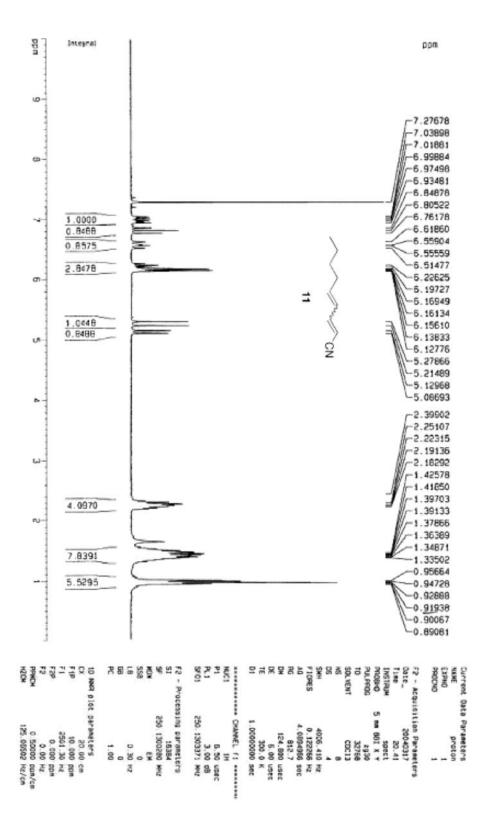


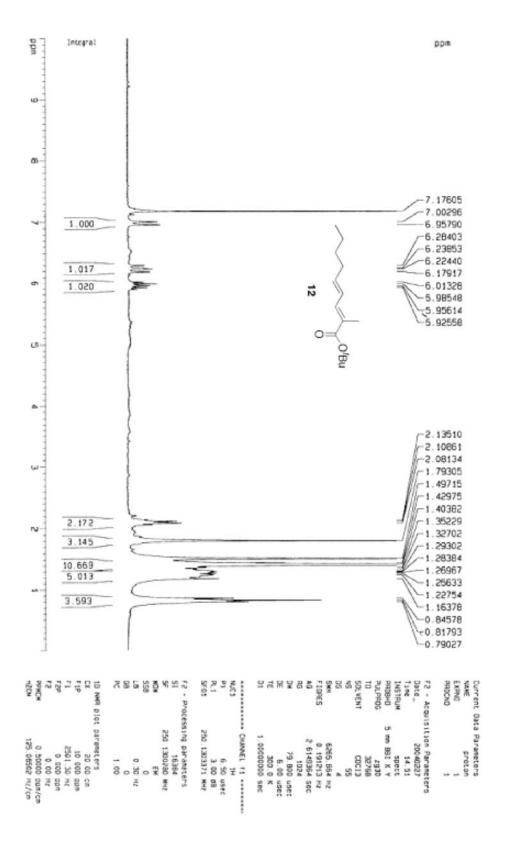


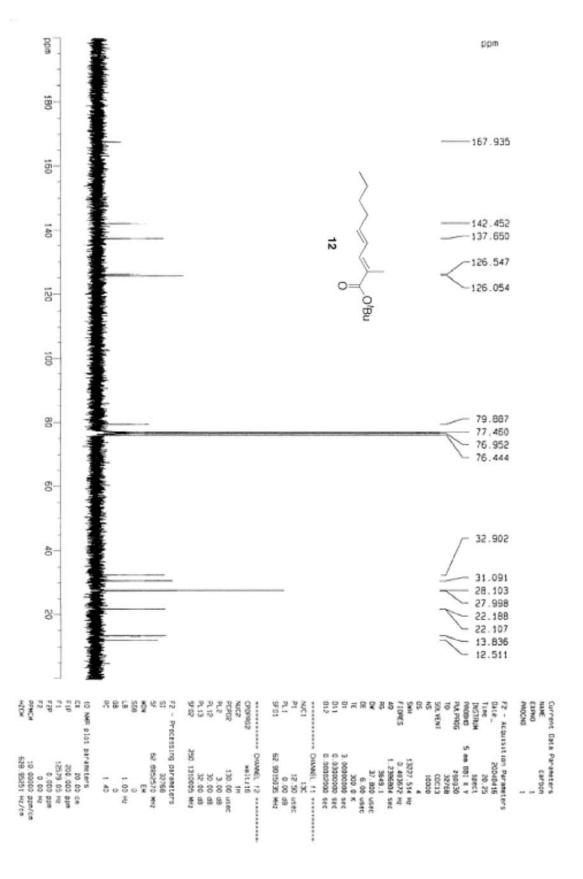


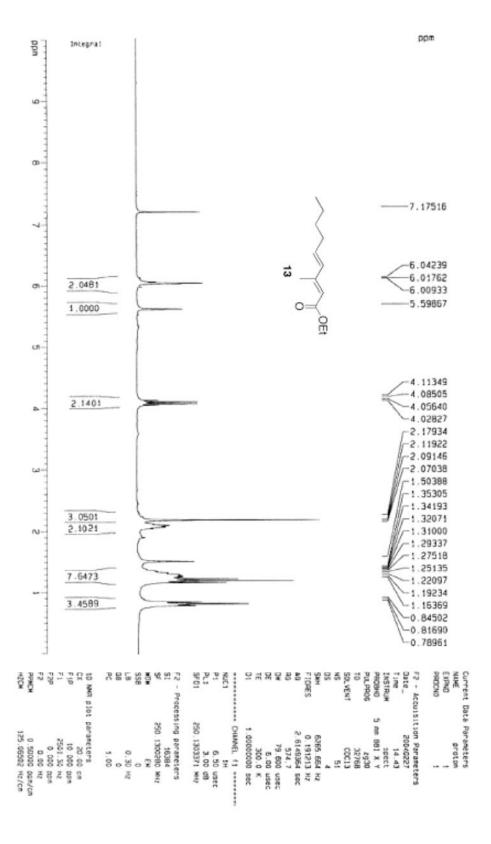


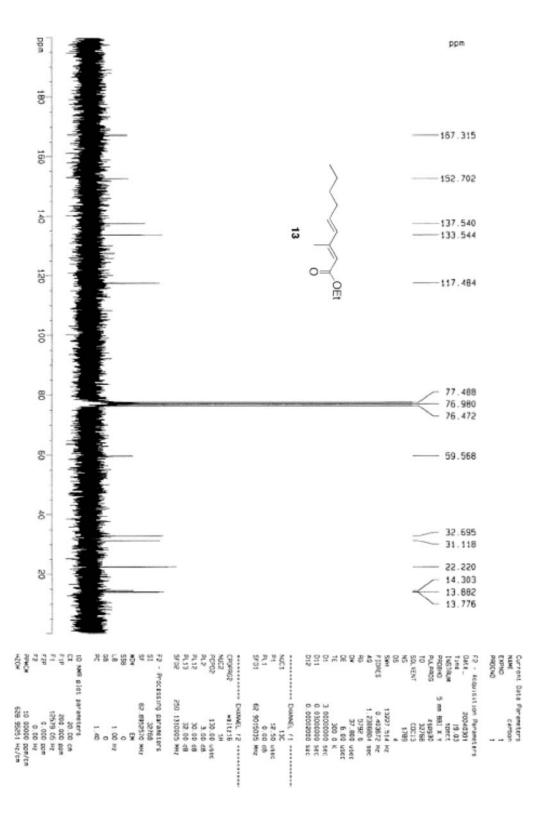


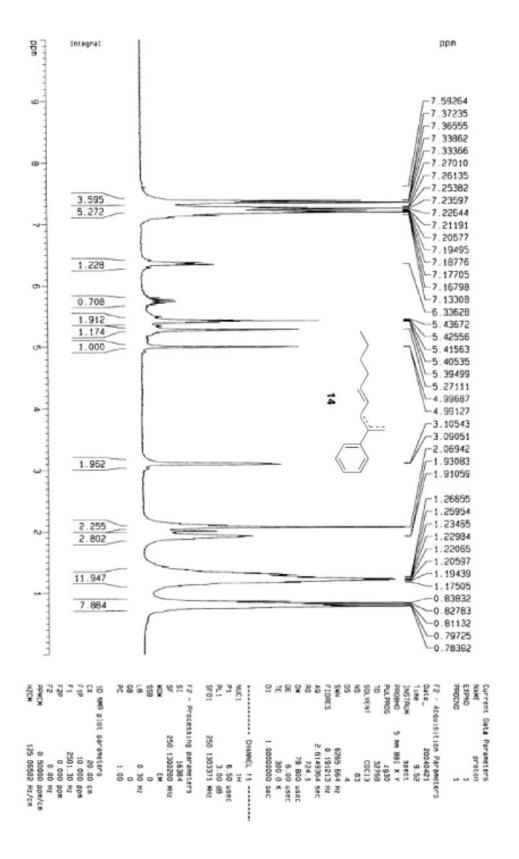


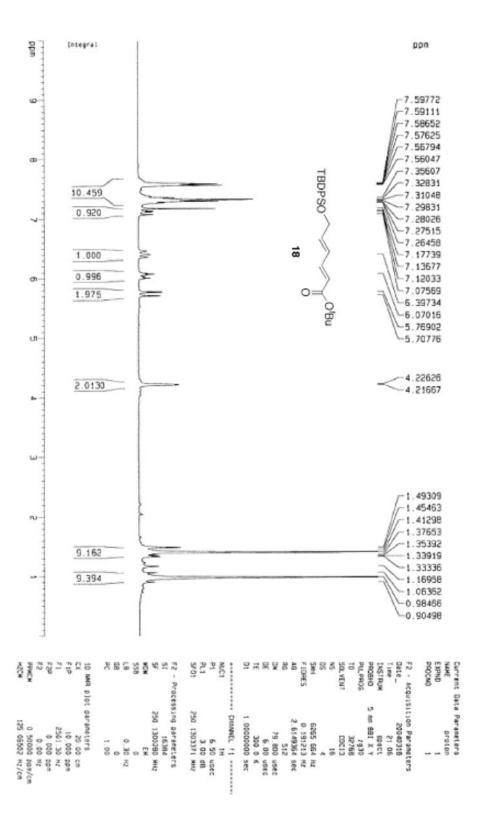


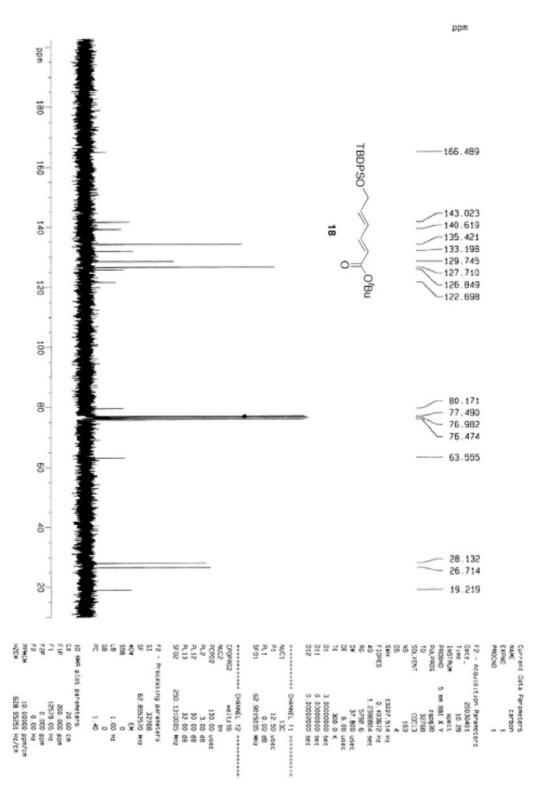


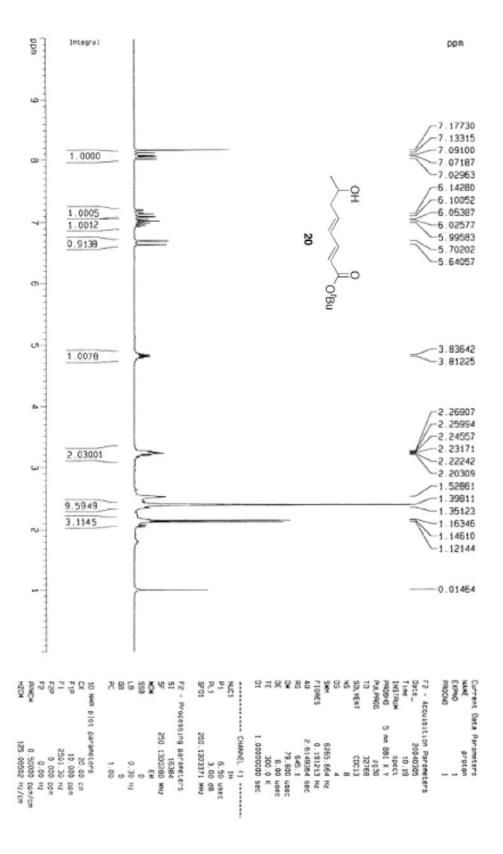


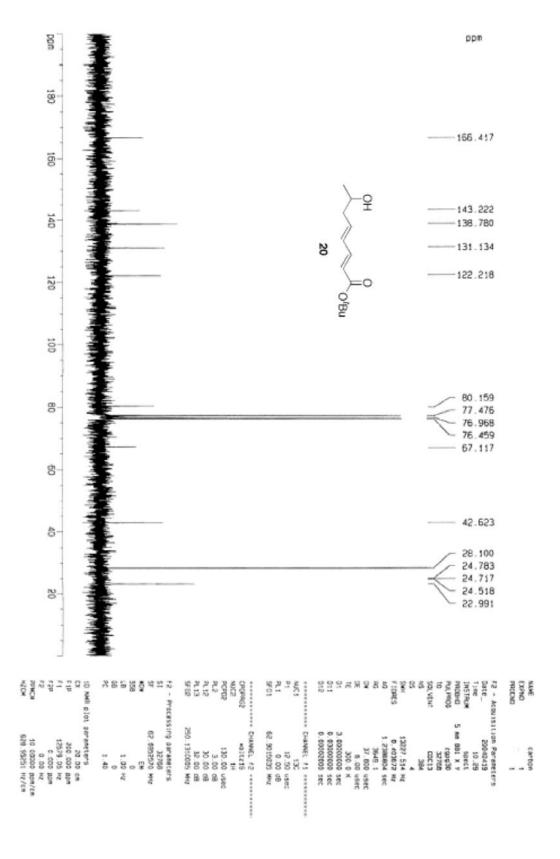


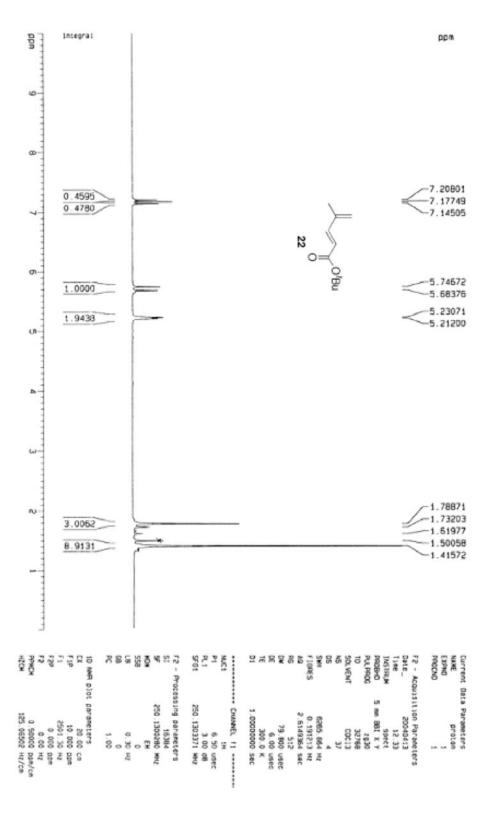


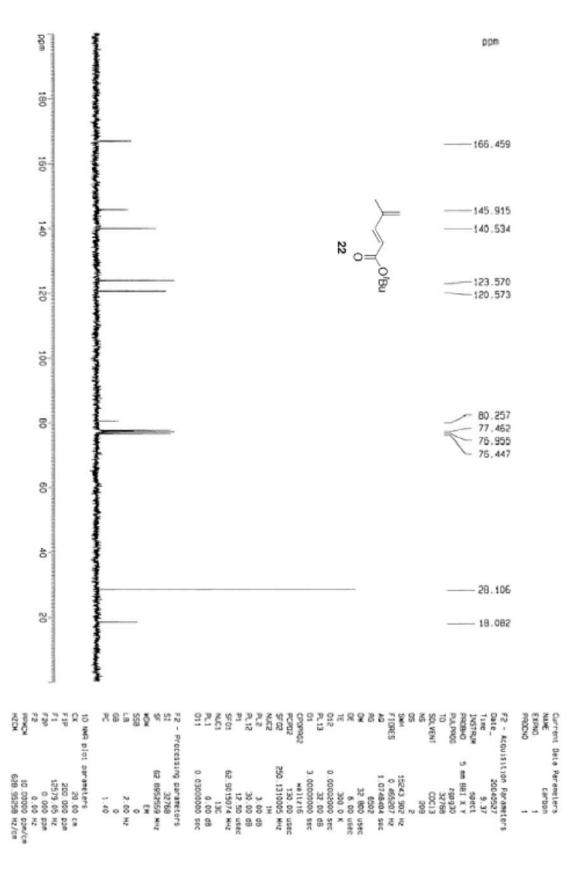


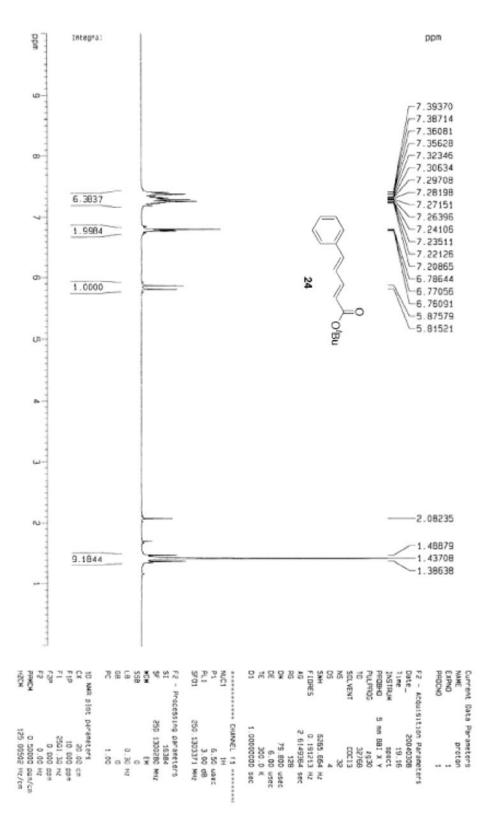


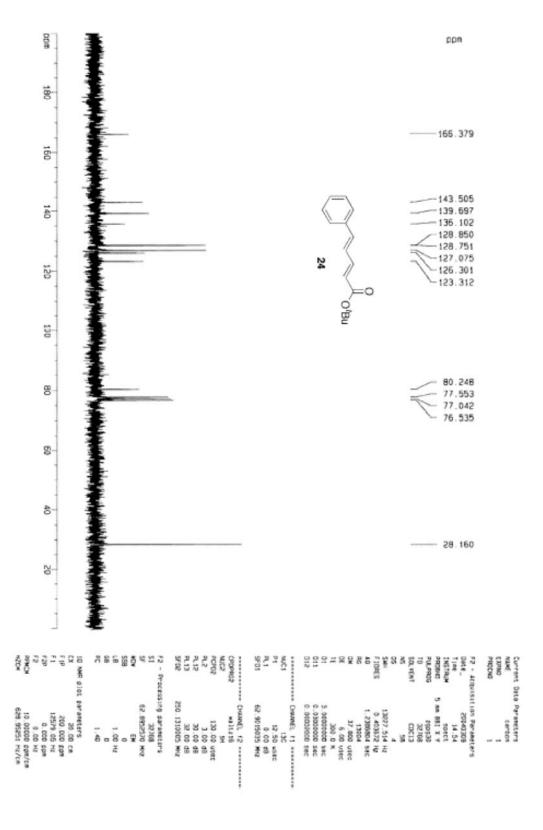


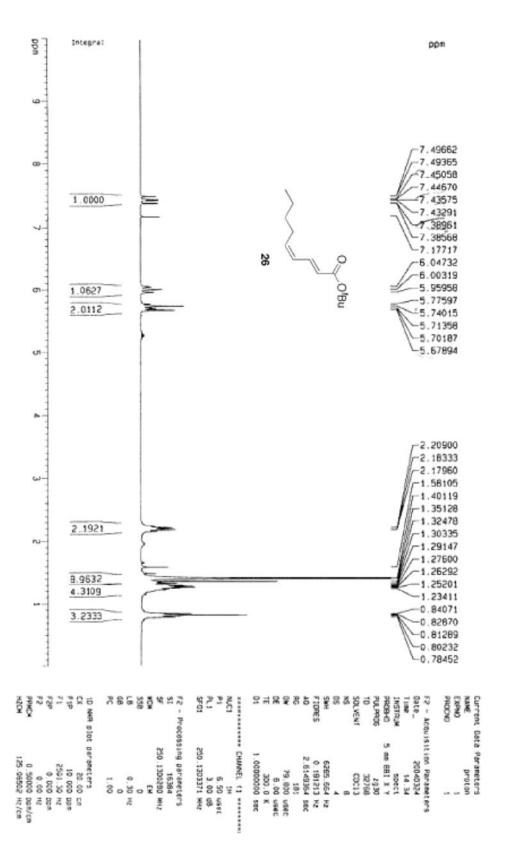


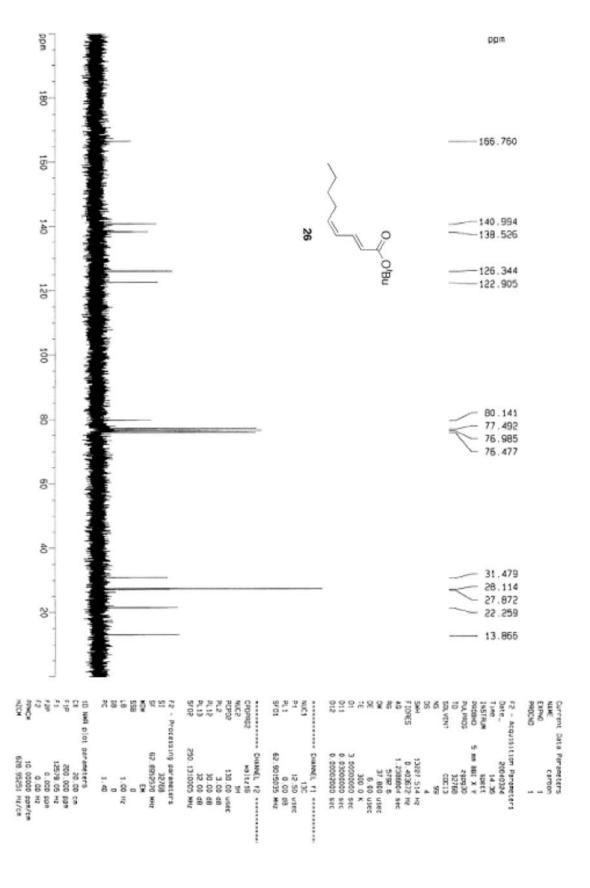


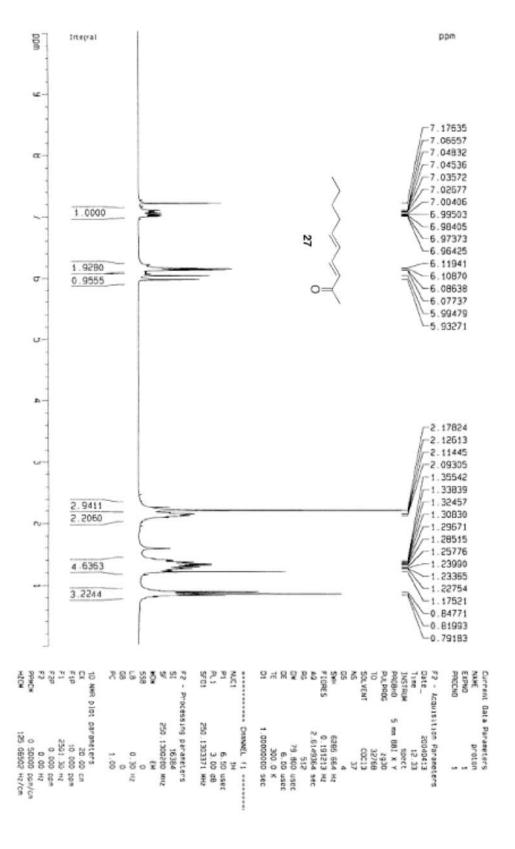


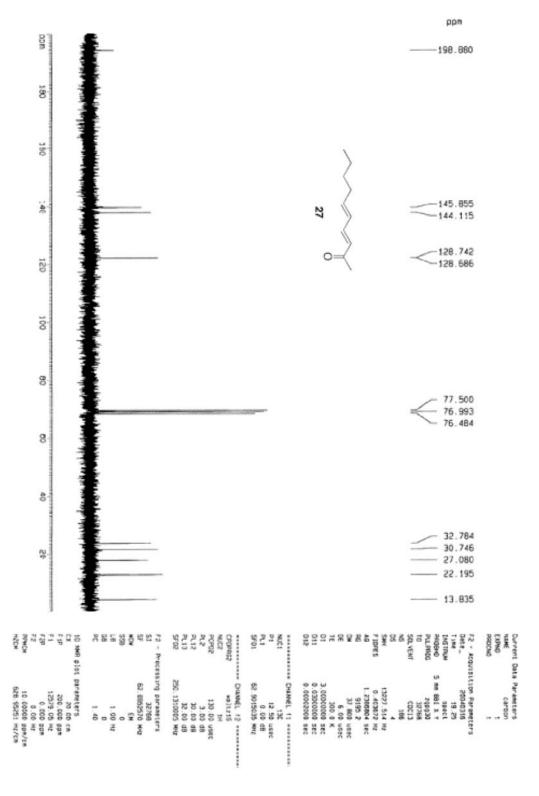


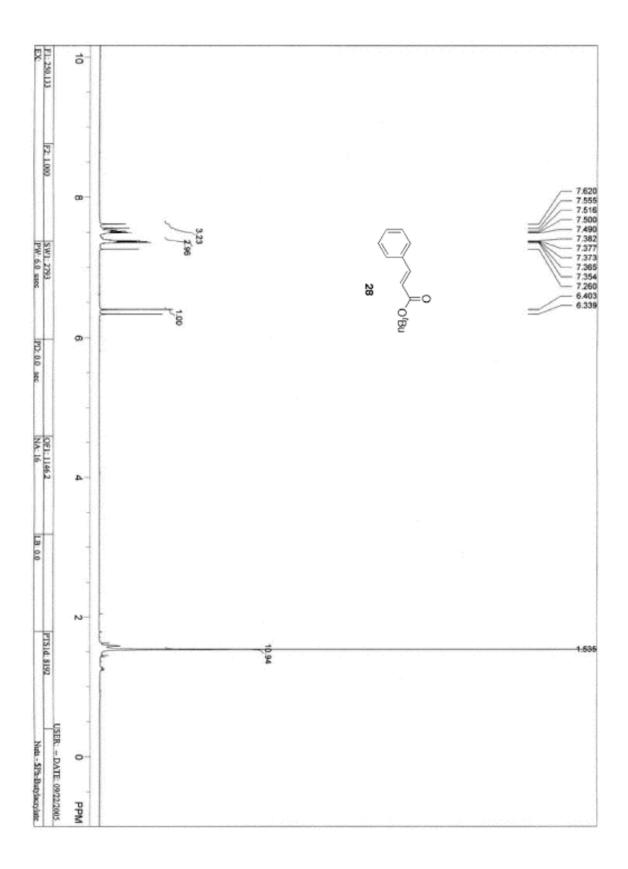


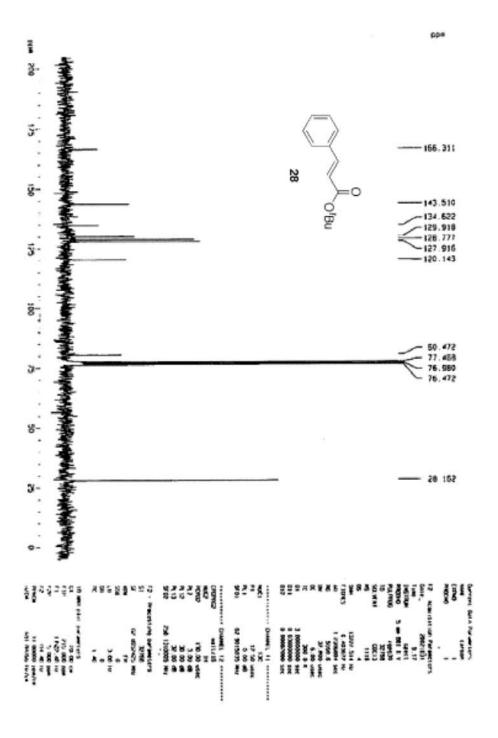


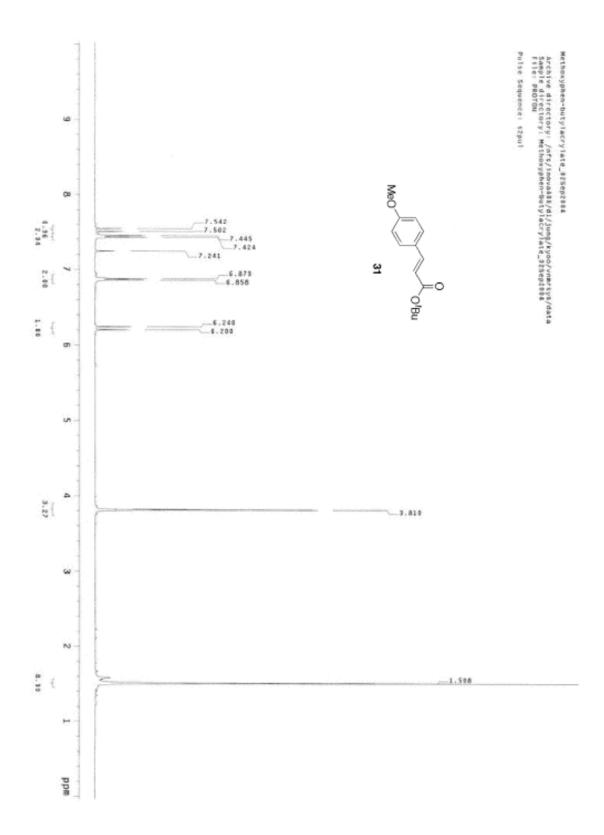


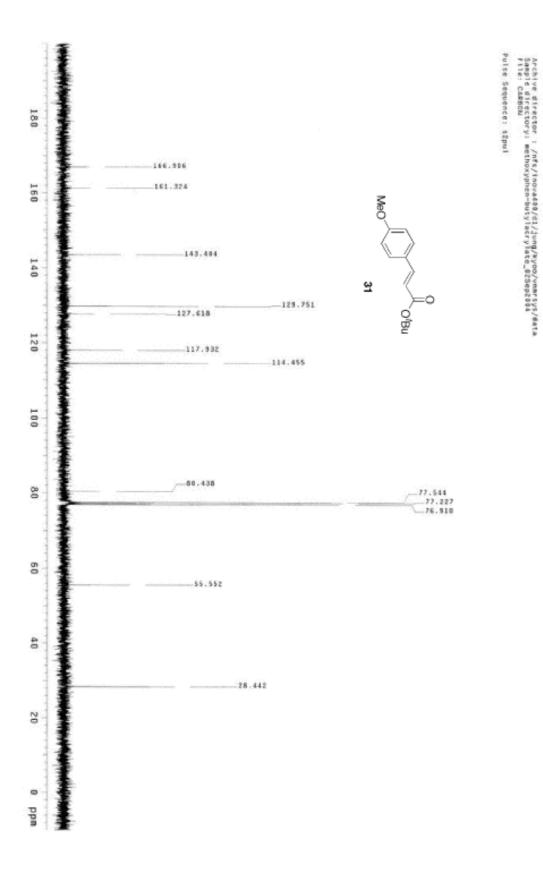




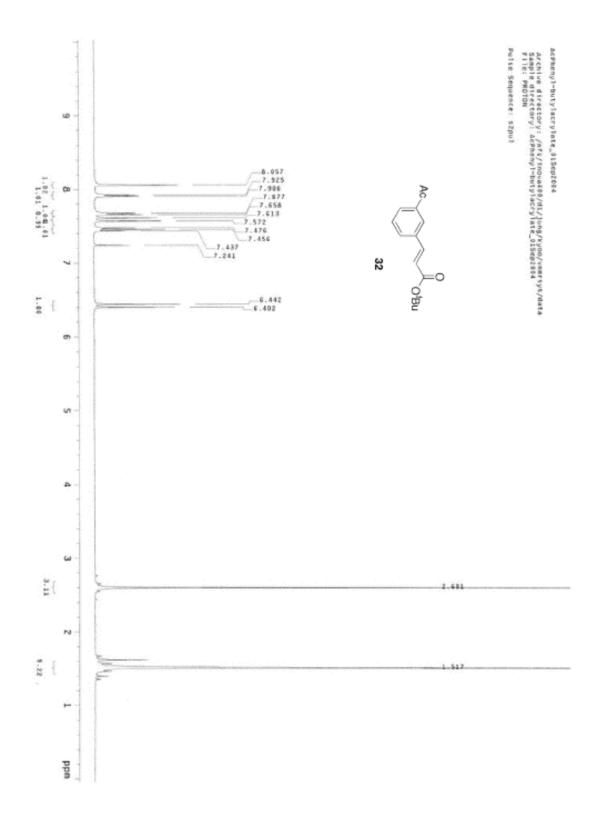


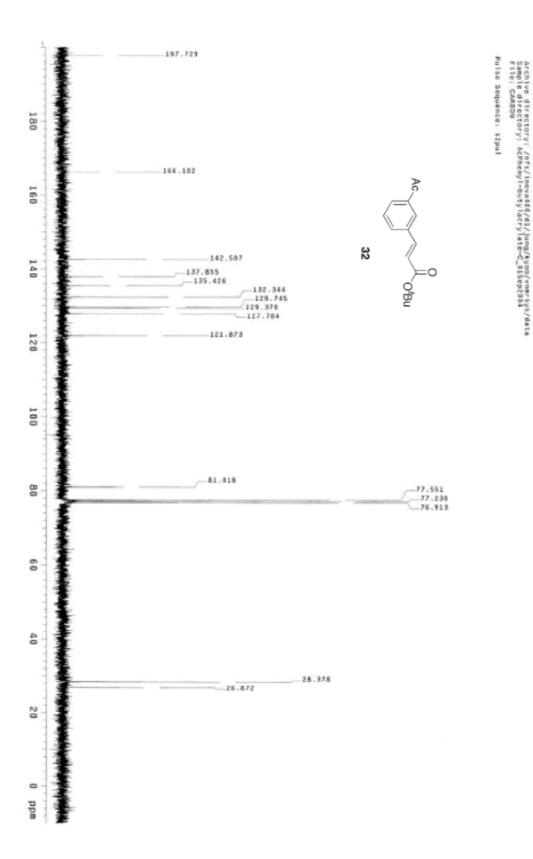




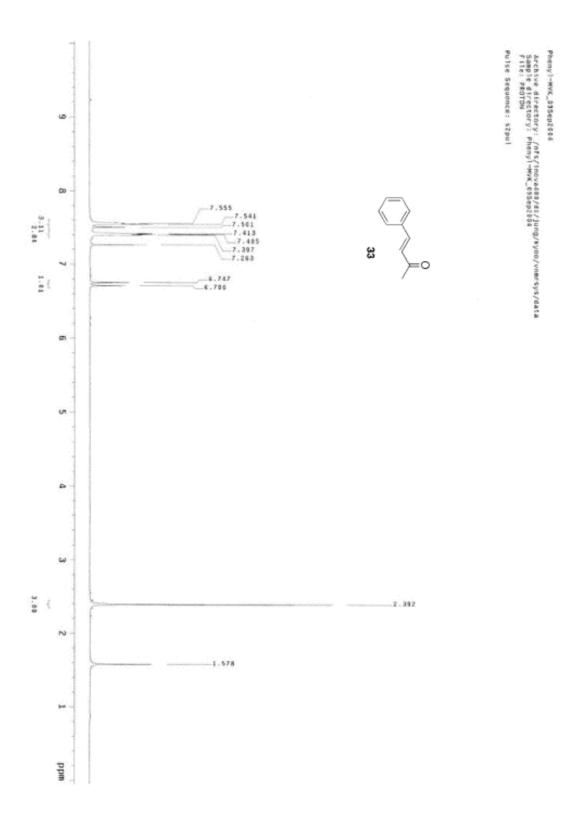


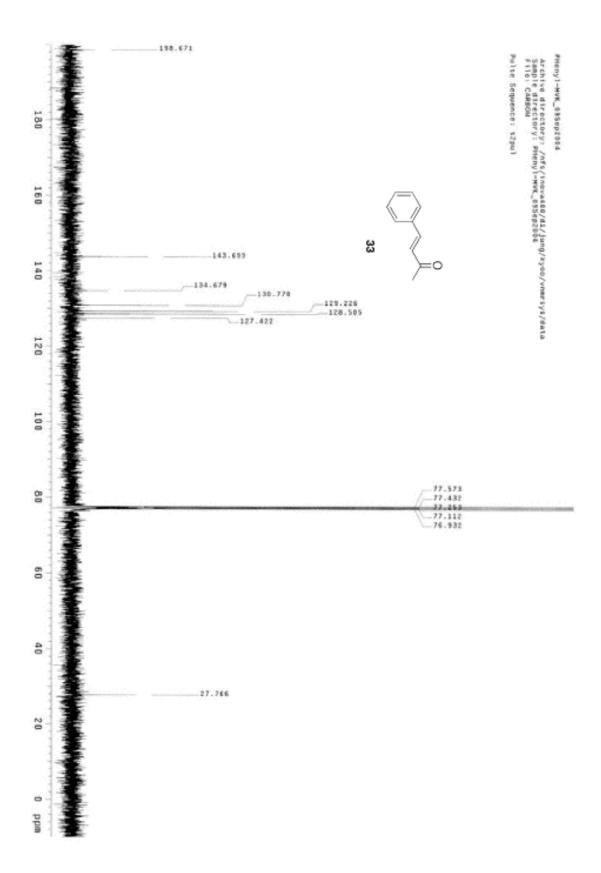
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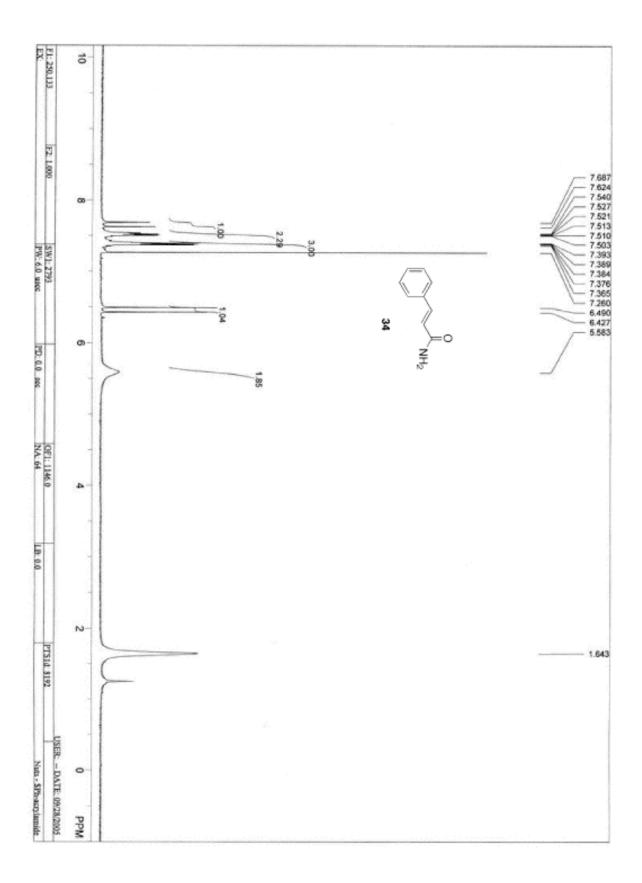


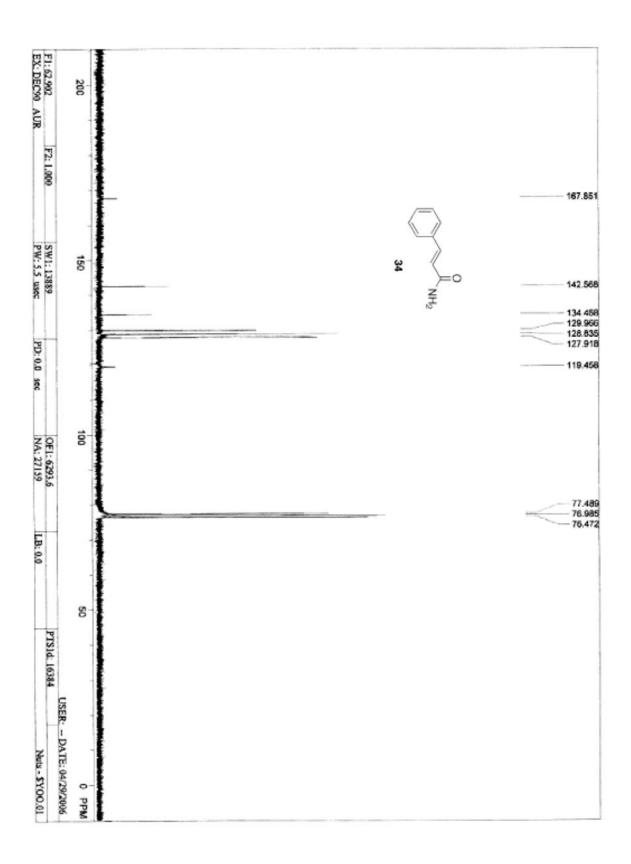


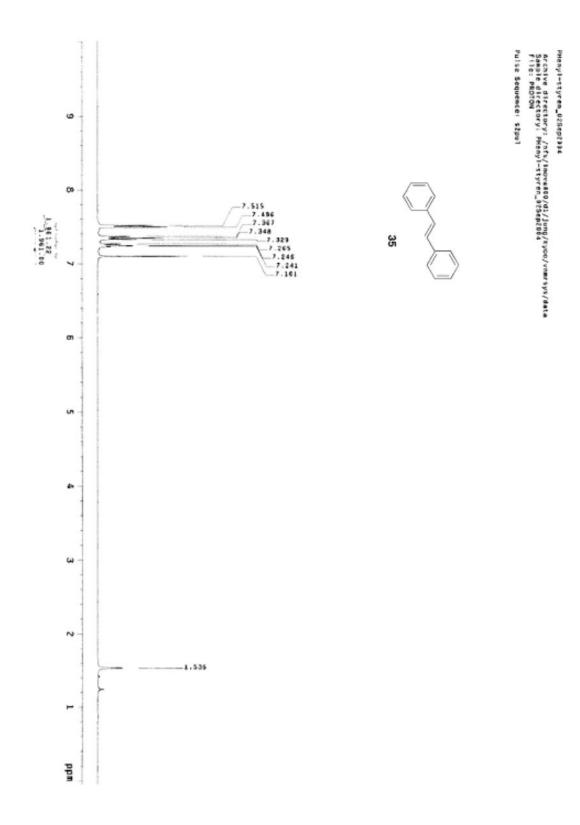
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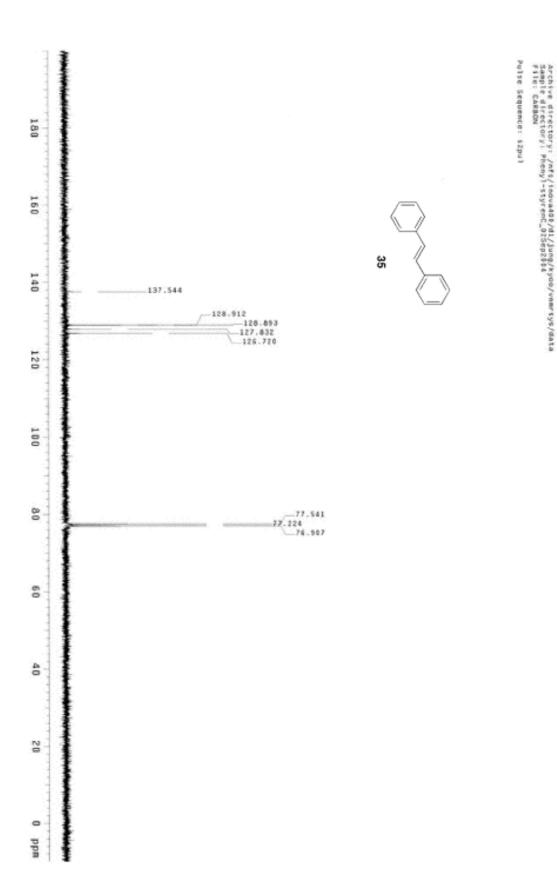




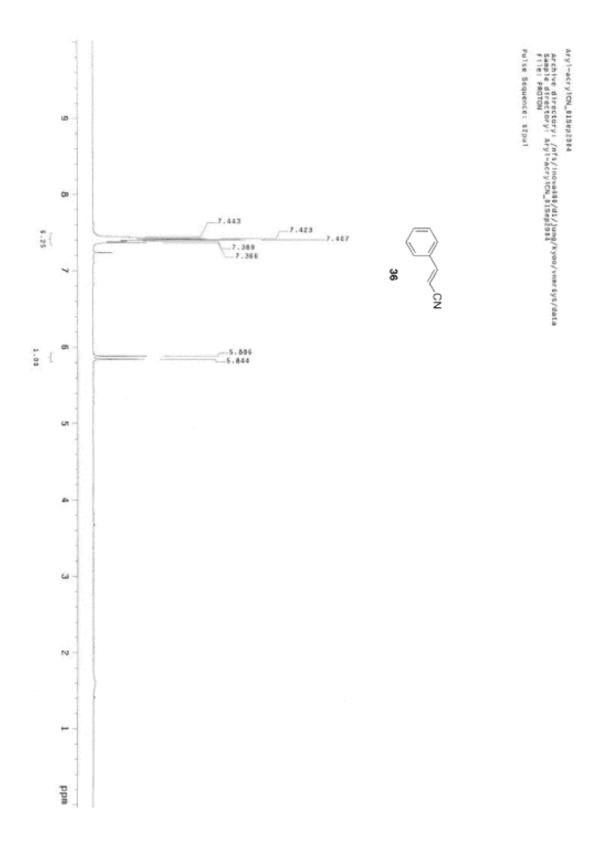


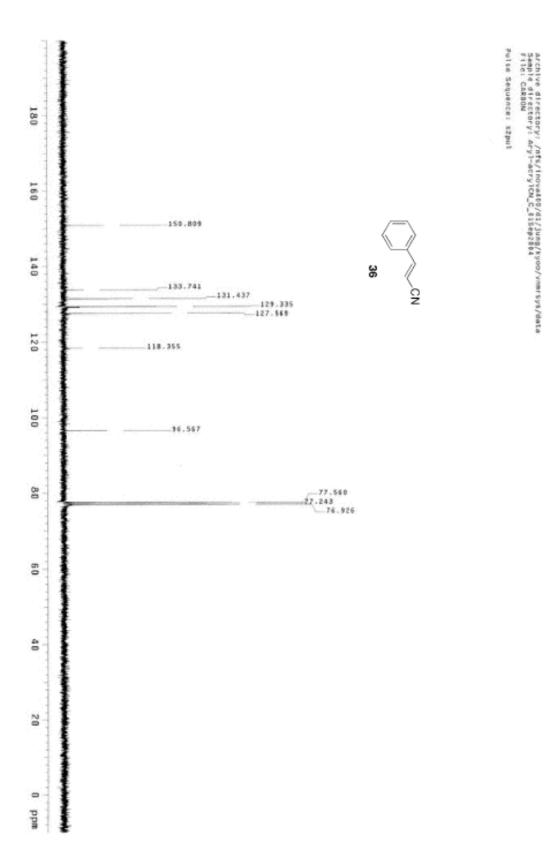






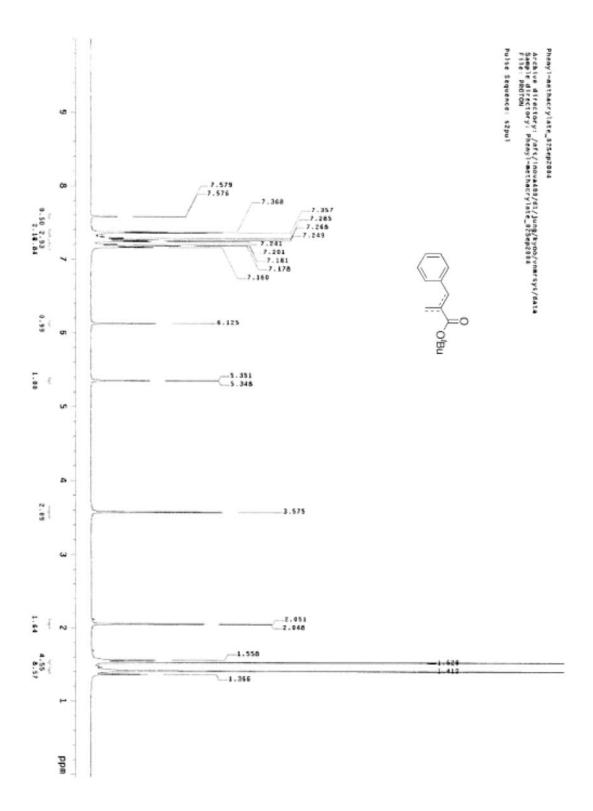
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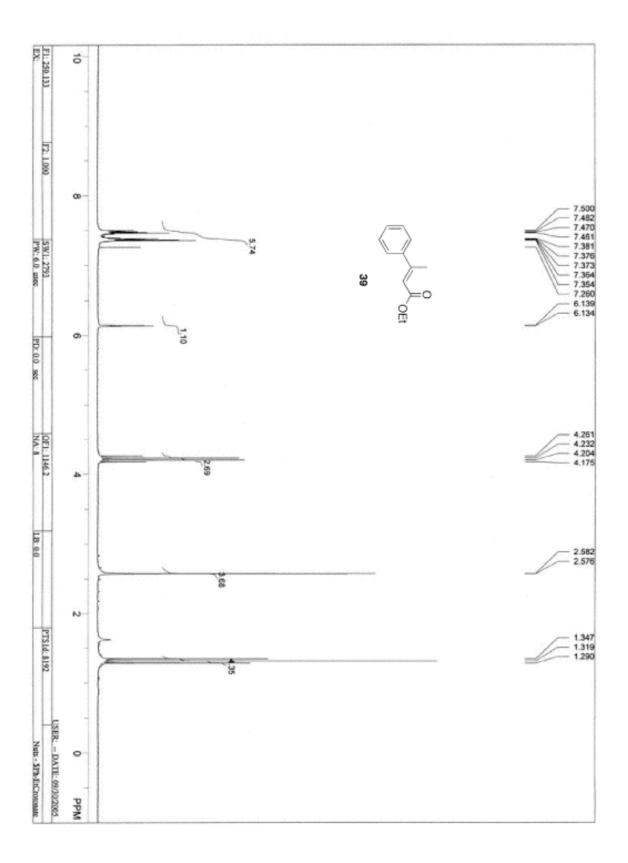


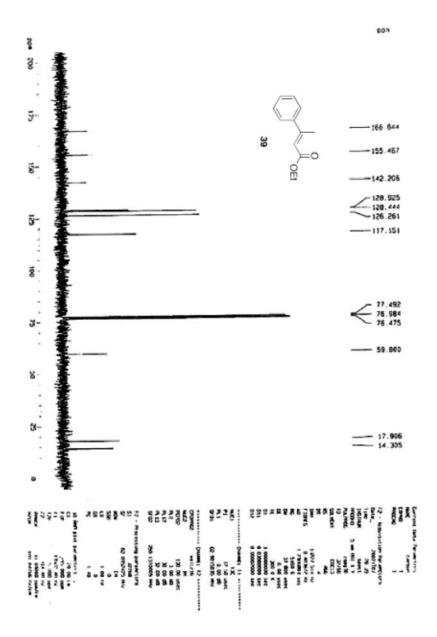


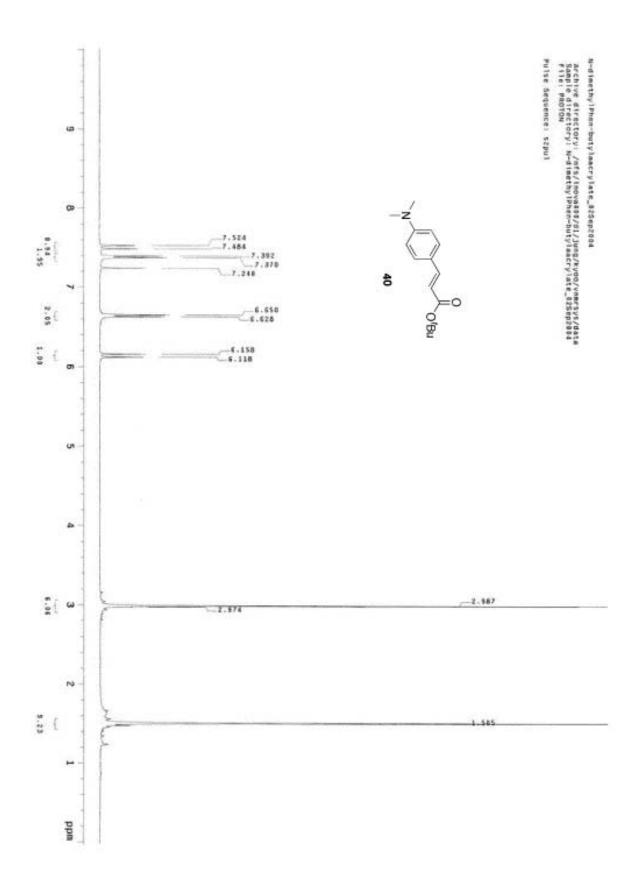
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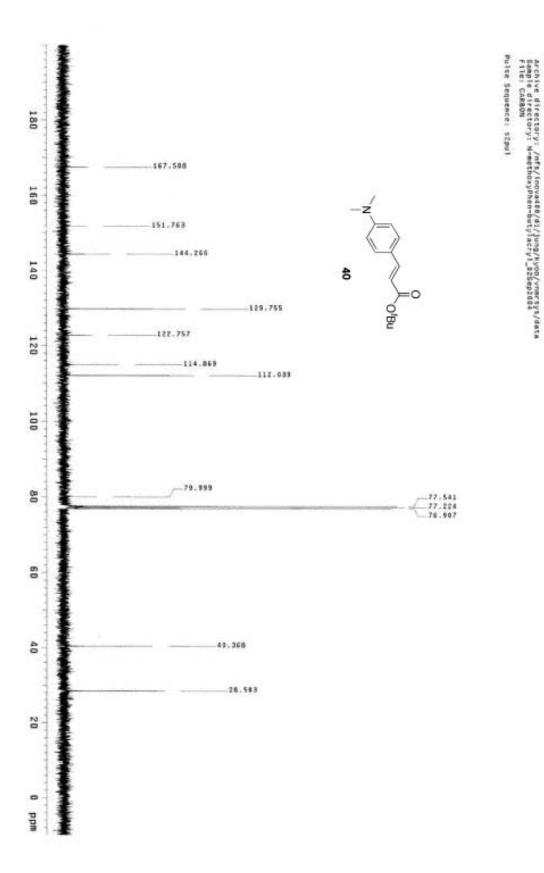
S-52



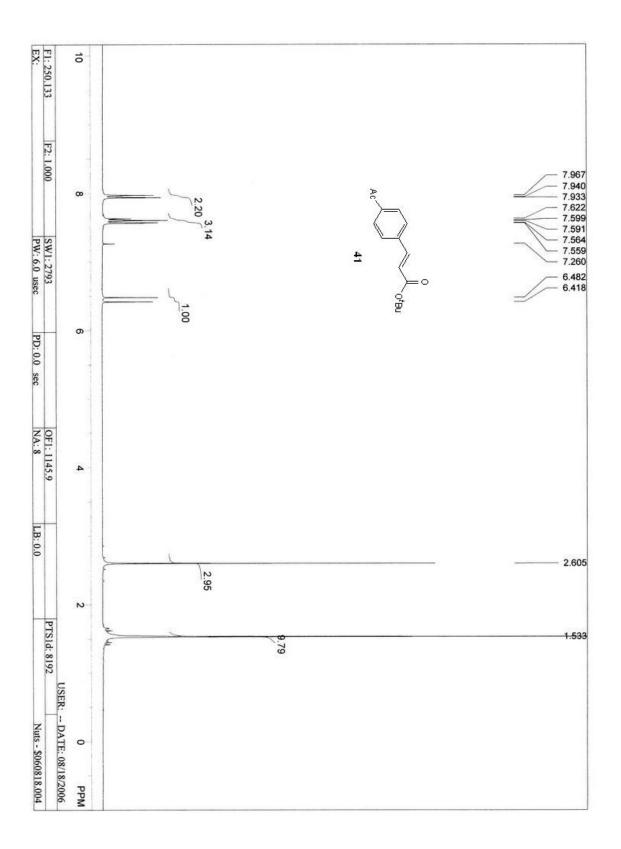


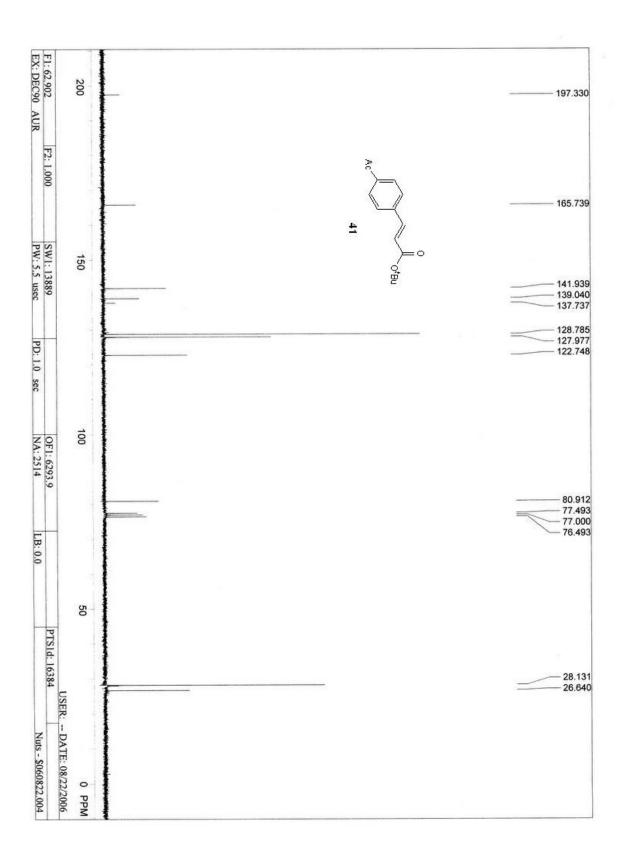


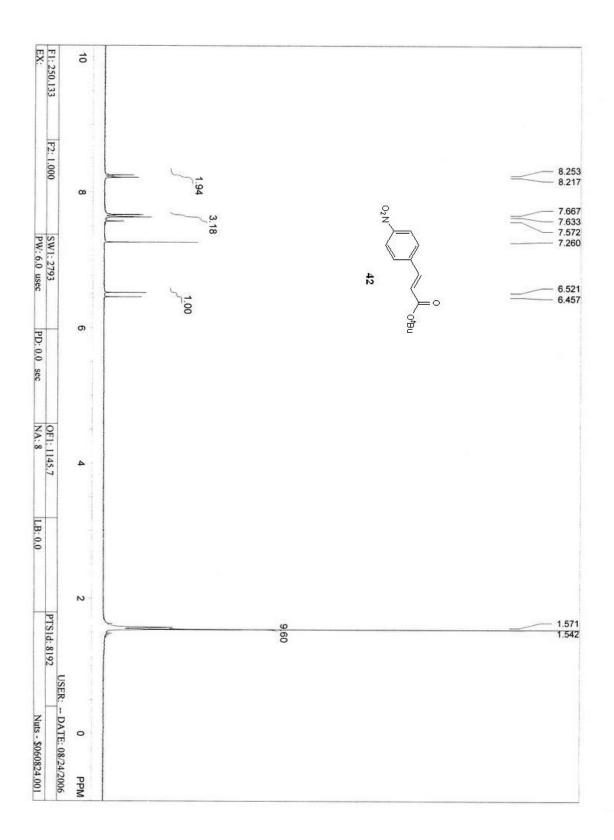


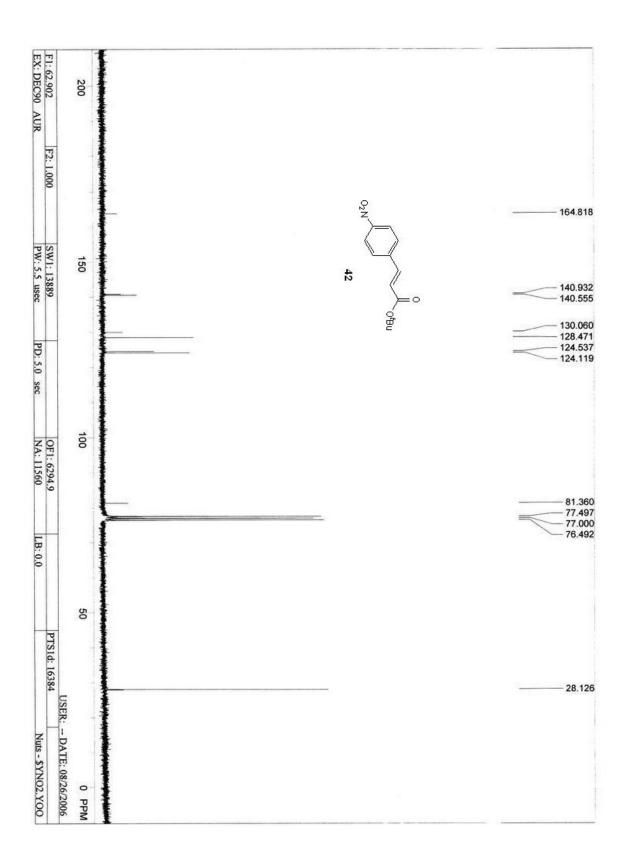


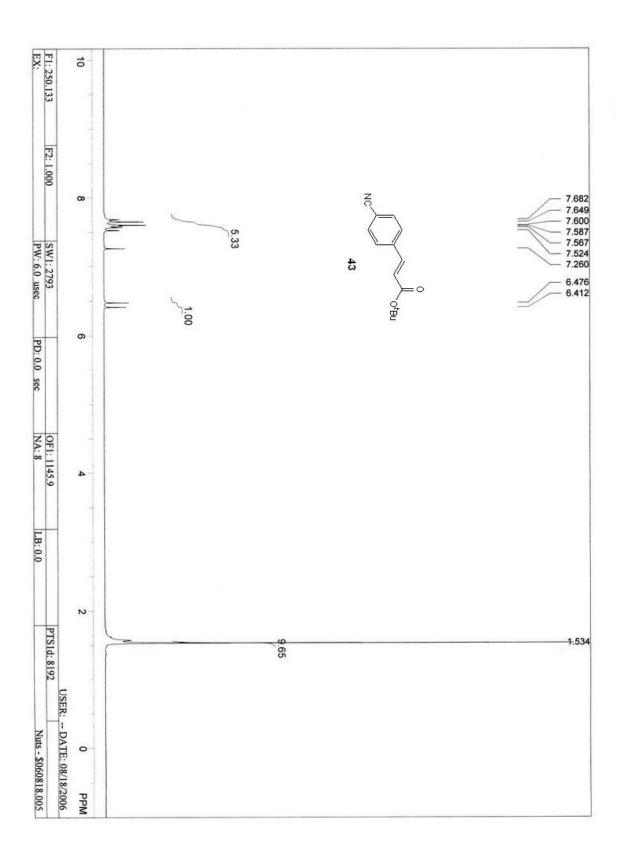
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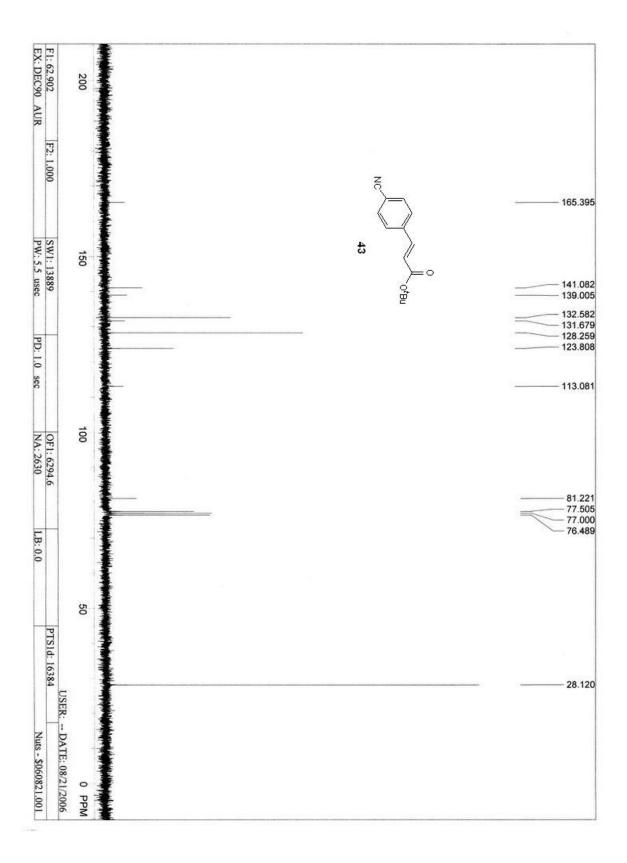


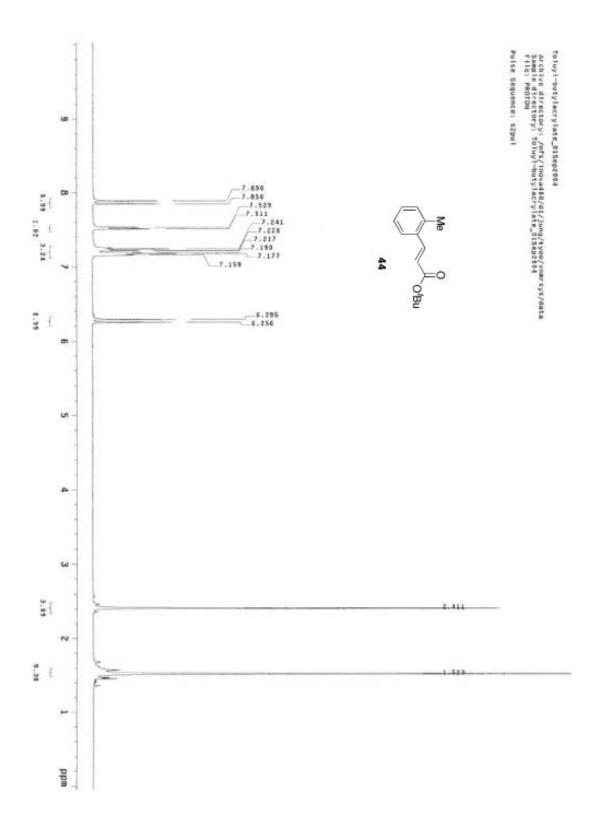


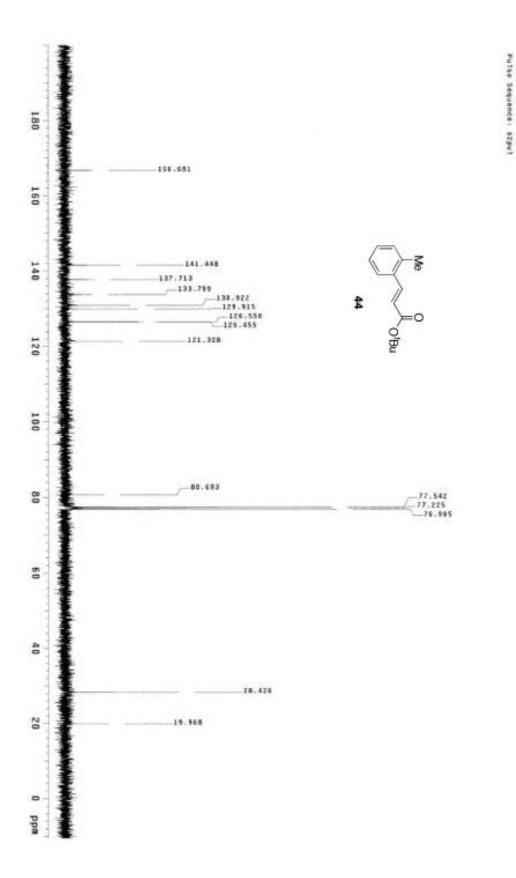












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