Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Semiconductors as Heterogeneous Visible Light Photoredox Catalysts in Combined Dual Metal Catalyzed C-H Functionalizations

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1 General information

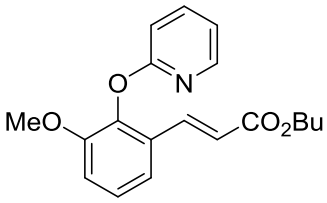
All commercially available chemicals were used as provided by the suppliers without further treatment. All solvents were dried and distilled under argon prior to use. Solvents for chromatography were technical grade and distilled prior to use. Analytical thin-layer chromatography (TLC) was performed on Macherey-Nagel ALUGRAM Xtra SIL G/UV254 aluminum plates with F-254 indicator, visualized by UV irradiation. Macherey-Nagel silica gel 60 (particle size 0.063 – 0.2 mm) was used for column chromatography. Solvent mixtures are understood as volume/volume. An 11 W fluorescent bulb, warm white, was used for irradiation with light. All reactions concerning the scope were repeated at least twice. 1H NMR, 13C NMR and 19F NMR spectra were recorded on VNMRS-400, VNMRS-600 or Mercury 300 spectrometer in CDCl3. Chemical shifts (δ) are reported in ppm and multiplicities are indicated: s (singlet), d (doublet), dd (doublet of doublet, t (triplet), dt (doublet of triplet), td (triplet of doublet), q, (quartet), quint (quintet) m (multiplet); coupling constants (J) are in Hertz (Hz). Mass spectra (MS-EI: 70 eV were conducted on a Finnigan MET SSQ 7000 system, LCMS spectra on a LTQ Orbitrap XL spectrometer and HRMS spectra on a Thermo Scientific LTQ Orbitrap XL spectrometer. IR spectra (ATR) were recorded on a Perkin Elmer spectrometer and wave numbers are given in reciprocal centimeters (cm-1).Starting materials were synthesized according to literature-known procedures, products compared to literature known compounds.[1-3]

2 General procedure for the Ru-catalyzed ortho-selective olefination of diaryl ether

The respective diaryl ether (1 equiv.) and acrylate (2 equiv.), Ru-catalyst (5 mol%), AgSbF6 (0.2 equiv.) and photoredox catalyst (10 mol% or 1 equiv.) were dissolved in DMA (0.1 M). A 4 mL vial equipped with a Teflon-coated magnetic stirring bar served as reaction vessel. The mixture was irradiated by an 11 W lamp (distance ca. 3 cm) after placing it on an aluminium block heated at 120 °C. The reaction was quenched with 2 mL of 10% aqueous LiCl solution, after complete consumption of substrate (followed by TLC). The aqueous layer was then extracted with DCM (5x20 mL) and the combined organic layer dried

over MgSO4. After removal of solvents, the crude product was purified by flash column chromatography (SiO2, *n*-pentane/EtOAc 5:1 -> 1:1).

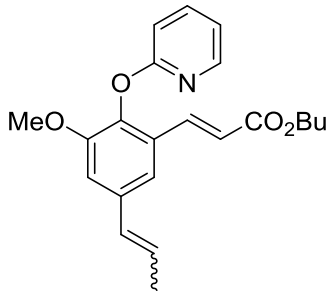
Butyl (*E*)-3-(3-methoxy-2-(pyridin-2-yloxy)phenyl)acrylate 2a



According to general procedure and starting from 2-(2-methoxyphenoxy)pyridine (40 mg, 0.20 mmol) the product was obtained as brown oil (50 mg, 0.17 mmol, 84%).

^{1}H-NMR (600 MHz; CDCl$_3$): 8.08 (dt, *J* = 4.9, 0.9 Hz, 1H), 7.82 (d, *J* = 16.1 Hz, 1H), 7.68 (dd, *J* = 8.3, 7.2, 1H), 7.28 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.22 (t, *J* = 8.0 Hz, 1H), 7.02-6.98 (m, 2H), 6.95 (dd, *J* = 7.1, 5.0 Hz, 1H), 6.45 (d, *J* = 16.1 Hz, 1H), 4.13 (t, *J* = 6.7 Hz, 2H), 3.72 (s, 3H), 1.62 (dd, *J* = 9.9, 5.2 Hz, 2H), 1.37 (t, *J* = 7.5 Hz, 2H), 0.91 (t, *J* = 7.4 Hz, 3H).**^{13}C-NMR (151 MHz; CDCl$_3$):** 166.9, 163.3, 152.4, 147.4, 141.5, 139.3, 138.7, 129.2, 125.8, 120.2, 119.1, 118.2, 114.0, 110.5, 64.3, 56.1, 30.7, 19.1, 13.7.

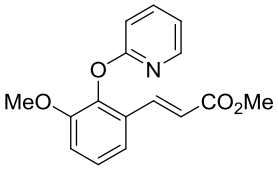
Butyl (2*E*)-3-(3-methoxy-5-(prop-1-en-1-yl)-2-(pyridin-2-yloxy)phenyl)acrylate 2b, mixture of isomers



According to general procedure and starting from 2-(2-methoxyphenoxy)pyridine (40 mg, 0.20 mmol) the product w<as obtained as brown oil (50 mg, 0.17 mmol, 84%; mixture of isomers).

^{1}H-NMR (600 MHz; CDCl$_3$): 8.10-8.08 (m, 1H), 7.79 (d, *J* = 16.1 Hz, 1H), 7.68-7.66 (m, 1H), 7.20 (d, *J* = 1.7 Hz, 2H), 6.99-6.97 (m, 3H), 6.94 (ddd, *J* = 7.1, 5.0, 0.8 Hz, 2H), 6.47 (s, 1H), 6.40-6.37 (m, 2H), 6.23 (t, *J* = 11.1 Hz, 1H), 4.14 (d, *J* = 6.7 Hz, 2H), 3.73 (s, 3H), 1.90 (dd, *J* = 6.6, 1.6 Hz, 4H), 1.62 (t, *J* = 7.5 Hz, 2H), 1.38 (t, *J* = 7.5 Hz, 2H), 0.92 (t, *J* = 7.4 Hz, 3H); **^{13}C-NMR (151 MHz; CDCl$_3$):** 166.9, 152.3, 147.5, 139.3, 138.9, 135.9, 130.2, 128.9, 126.5, 120.1, 118.2, 116.9, 111.2, 110.4, 110.1, 83.5, 64.3, 56.0, 30.7, 19.1, 18.5, 13.7.

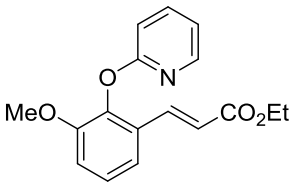
Methyl (*E*)-3-(3-methoxy-2-(pyridin-2-yloxy)phenyl)acrylate 2c



According to general procedure and starting from 2-(o-tolyloxy)pyridine (40 mg, 0.20 mmol) the product was obtained as colourless solid (36 mg, 0.13 mmol, 63%); mp: 108-110 °C.

^{1}H-NMR (400 MHz; CDCl$_3$): 8.06 (dd, *J* = 5.0, 1.4 Hz, 1H), 7.82 (d, *J* = 16.2 Hz, 1H), 7.66 (ddd, *J* = 8.3, 7.2, 1.9 Hz, 1H), 7.25 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.19 (t, *J* = 8.0 Hz, 1H), 7.00-6.91 (m, 3H), 6.44 (d, *J* = 16.1 Hz, 1H), 3.71 (s, 3H), 3.69 (s, 3H); **^{13}C-NMR (101 MHz; CDCl$_3$):** 167.2, 163.3, 152.4, 147.4, 141.5, 139.3, 139.0, 129.1, 125.8, 119.8, 119.2, 118.2, 114.1, 110.4, 56.0, 51.6; **MS (ESI):** *m/z* (%) = 396.1 (85), 286.1 ([M+H]$^+$, 40), 254.1 (28), 210.1 (20), 196.1 (100); **HRMS (ESI)** for $C_{16}H_{16}O_4N$: calculated for [M+H]$^+$ 286.10730, found 286.10738; **IR (ATR):** ν = 3395, 3039, 2981, 2943, 1704, 1637, 1577, 1463, 1428, 1266, 1179, 1071, 994, 880, 770, 734.

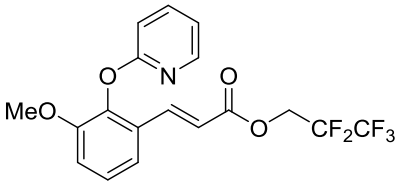
Ethyl (E)-3-(3-methoxy-2-(pyridin-2-yloxy)phenyl)acrylate 2d



According to general procedure and starting from 2-(o-tolyloxy)pyridine (40 mg, 0.20 mmol) the product was obtained as brown oil (39 mg, 0.13 mmol, 65%).

^{1}H-NMR (400 MHz; $CDCl_3$): 8.07 (dd, *J* = 4.9, 1.4 Hz, 1H), 7.82 (d, *J* = 16.1 Hz, 1H), 7.66 (m, *J* = 1.7 Hz, 1H), 7.26 (dd, *J* = 8.2, 1.5 Hz, 1H), 7.19 (t, *J* = 8.0 Hz, 1H), 7.00-6.96 (m, 2H), 6.93 (dd, *J* = 6.8, 5.4 Hz, 1H), 6.44 (d, *J* = 16.1 Hz, 1H), 4.17 (q, *J* = 7.1 Hz, 2H), 3.69 (s, 3H), 1.25 (t, *J* = 7.1 Hz, 3H); **^{13}C-NMR (101 MHz; $CDCl_3$):** 166.8, 163.3, 152.4, 147.4, 141.5, 139.3, 138.8, 129.2, 125.8, 120.2, 119.2, 118.2, 114.0, 110.4, 60.4, 56.0, 14.2.

2,2,3,3,3-pentafluoropropyl (*E*)-3-(3-methoxy-2-(pyridin-2-yloxy)phenyl)acrylate 2e



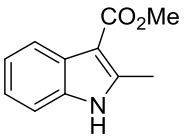
According to general procedure and starting from 2-(*o*-tolyloxy)pyridine (40 mg, 0.20 mmol) the product was obtained as colourless oil (55 mg, 0.11 mmol, 55%), mp: 120-122 °C

^{1}H-NMR (400 MHz; $CDCl_3$): 8.06 (dd, *J* = 4.9, 1.4 Hz, 1H), 7.91 (d, *J* = 16.2 Hz, 1H), 7.70-7.66 (m, 1H), 7.28 (dd, *J* = 7.9, 1.1 Hz, 1H), 7.22 (t, *J* = 8.1 Hz, 1H), 7.05-6.98 (m, 2H), 6.94 (dd, *J* = 6.7, 5.3 Hz, 1H), 6.47 (d, *J* = 16.1 Hz, 1H), 4.57 (t, *J* = 12.8 Hz, 2H), 3.71 (s, 3H); **^{13}C{^{19}F}-NMR (101 MHz; $CDCl_3$):** 164.9, 163.2, 152.5, 147.4, 141.9, 141.5, 139.3, 128.6, 125.9, 119.2, 118.42, 118.30, 117.6, 114.7, 112.1, 110.4, 59.2, 56.1; **^{19}F-NMR (376 MHz; $CDCl_3$):** -83.9, -123.4 (t, *J* = 12.9 Hz); **MS (ESI):** *m/z* (%) = 396.1 (85), 286.1 ([M+H]$^+$, 40), 254.1 (28), 210.1 (20), 196.1 (100); **HRMS (ESI)** for $C_{18}H_{15}O_4NF_5$: calculated for [M+H]$^+$ 404.09125, found 404.09158; **IR (ATR):** ν = 3395, 3039, 2981, 2943, 1704, 1637, 1577, 1463, 1428, 1266, 1179, 1071, 994, 880, 770, 734.

3 General procedure for the Pd-catalysed indole synthesis

In a 4 mL vial equipped with a Teflon-coated magnetic stirring bar, the appropriate *N*-aryl enamide (1 equiv.), $Pd(OAc)_2$ (10 mol%), K_2CO_3 (3 equiv.) and photoredox catalyst (10 mol%, 1 equiv.) were dissolved in DMF (0.1 M) and the reaction mixture placed in front of an 11 W household lamp (distance ca. 3 cm) on an aluminium block heated at 120 °C. After complete consumption of starting material (followed by TLC), the reaction was quenched with 2 mL of 10% aqueous LiCl solution, the aqueous layer extracted with DCM (5x20 mL) and the combined organic layer dried over $MgSO_4$. After removal of solvents, the crude product was purified by flash column chromatography (SiO_2, *n*-pentane/EtOAc 5:1 → 1:1).

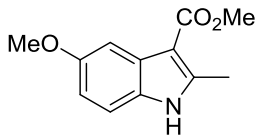
Methyl 2-methyl-1*H*-indole-3-carboxylate 4a



According to general procedure and starting from methyl (*Z*)-3-(phenylamino)but-2-enoate (38 mg, 0.20 mmol) the product was obtained as colorless solid (32 mg, 0.17 mmol, 85%).

^{1}H-NMR (600 MHz; $CDCl_3$): 8.43 (s, 1H), 8.09 (d, *J* = 7.7 Hz, 1H), 7.30 (d, *J* = 7.4 Hz, 1H), 7.21 (ddd, *J* = 11.1, 7.6, 1.3 Hz, 2H), 3.94 (s, 3H), 2.74 (s, 3H); **^{13}C-NMR (101 MHz; $CDCl_3$):** 166.5, 144.0, 134.4, 127.1, 122.4, 121.7, 121.2, 110.5, 104.5, 50.8, 14.2.

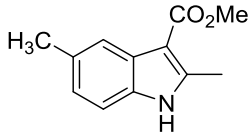
Methyl 5-methoxy-2-methyl-1*H*-indole-3-carboxylate 4b



According to general procedure and starting from methyl (*Z*)-3-((4-methoxyphenyl)amino)but-2-enoate (44 mg, 0.20 mmol) the product was obtained as colorless solid (36 mg, 0.16 mmol, 82%).

^{1}H-NMR (600 MHz; $CDCl_3$): 8.32 (s, 1H), 7.60 (d, *J* = 2.5 Hz, 1H), 7.18 (d, *J* = 8.8 Hz, 1H), 6.83 (dd, *J* = 8.7, 2.5 Hz, 1H), 3.93 (d, *J* = 11.6 Hz, 3H), 3.88 (s, 3H), 2.71 (s, 3H); **^{13}C-NMR (151 MHz; $CDCl_3$):** 166.5, 155.6, 144.1, 129.3, 128.1, 112.1, 111.1, 104.3, 103.4, 55.8, 50.8, 14.5.

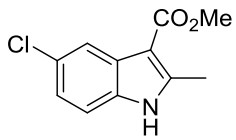
Methyl 2,5-dimethyl-1*H*-indole-3-carboxylate 4c



According to general procedure and starting from methyl (*Z*)-3-(*p*-tolylamino)but-2-enoate (41 mg, 0.20 mmol) the product was obtained as colorless solid (28 mg, 0.14 mmol, 69%).

^{1}H-NMR (600 MHz; $CDCl_3$): 8.32 (s, 1H), 7.88 (s, 1H), 7.18 (d, *J* = 8.2 Hz, 1H), 7.01 (dd, *J* = 8.2, 1.0 Hz, 1H), 3.93 (s, 3H), 2.72 (s, 3H), 2.47 (d, *J* = 6.7 Hz, 3H); **^{13}C-NMR (151 MHz; $CDCl_3$):** 166.5, 143.9, 132.7, 131.1, 127.3, 123.8, 121.0, 110.1, 104.0, 50.7, 21.6, 14.3

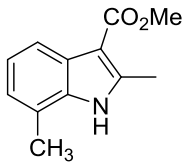
Methyl 5-chloro-2-methyl-1*H*-indole-3-carboxylate 4d



According to general procedure and starting from methyl (*Z*)-3-((4-chlorophenyl)amino)but-2-enoate (45 mg, 0.20 mmol) the product was obtained as yellow solid (37 mg, 0.17 mmol, 83%).

^{1}H-NMR (600 MHz; $CDCl_3$): 8.62 (s, 1H), 8.05 (d, *J* = 2.0 Hz, 1H), 7.20 (d, *J* = 8.5 Hz, 1H), 7.14 (dd, *J* = 8.5, 2.0 Hz, 1H), 3.93 (s, 3H), 2.73 (d, *J* = 7.3 Hz, 3H); **^{13}C-NMR (151 MHz; $CDCl_3$):** 166.0, 145.3, 132.8, 128.2, 127.5, 122.6, 120.9, 111.5, 104.3, 50.9, 14.2.

Methyl 2,7-dimethyl-1*H*-indole-3-carboxylate 4e

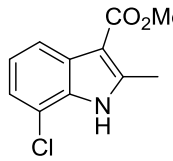


According to general procedure and starting from methyl (*Z*)-3-(*o*-tolylamino)but-2-enoate (44 mg, 0.20 mmol) the product was obtained as colorless solid (29 mg, 0.14 mmol, 71%).

^{1}H-NMR (400 MHz; $CDCl_3$): 8.33 (s, 1H), 7.93 (d, *J* = 8.0 Hz, 1H), 7.13 (t, *J* = 7.6 Hz, 1H), 6.99 (d, *J* = 7.2 Hz, 1H), 3.98 (s, 3H), 2.76 (s, 3H), 2.48 (s, 3H);

^{13}C-NMR (101 MHz; $CDCl_3$): 166.5, 143.9, 133.9, 126.5, 123.0, 121.1, 119.5, 118.8, 104.2, 50.5, 16.2, 14.2.

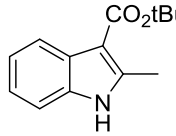
Methyl 7-chloro-2-methyl-1*H*-indole-3-carboxylate 4f



According to general procedure and starting from methyl (*Z*)-3-((2-chlorophenyl)amino)but-2-enoate **1h** (45 mg, 0.20 mmol) the product was obtained as yellow solid (27 mg, 0.12 mmol, 60%).

^{1}H-NMR (400 MHz; $CDCl_3$): 8.36 (s, 1H), 8.10-8.08 (m, 1H), 7.30 (dd, *J* = 7.0, 1.2 Hz, 1H), 7.23-7.18 (m, 2H), 3.96-3.93 (m, 3H), 2.78 (s, 3H); **^{13}C-NMR (101 MHz; $CDCl_3$):** 166.4, 143.9, 134.4, 127.1, 122.4, 121.7, 121.3, 110.4, 104.6, 50.7, 14.2

***Tert*-butyl 2-methyl-1*H*-indole-3-carboxylate 4g**



According to general procedure and starting from *tert*-butyl (*Z*)-3-(phenylamino)but-2-enoate **1n** (47 mg, 0.20 mmol) the product was obtained as colorless solid (37 mg, 0.16 mmol, 80%).

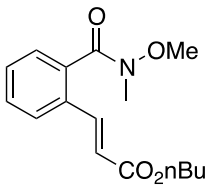
^{1}H-NMR (600 MHz; $CDCl_3$): 8.32 (s, 1H), 8.08 (d, *J* = 7.5 Hz, 1H), 7.27 (dd, *J* = 8.6, 7.7 Hz, 1H), 7.21-7.15 (m, 2H), 2.73 (s, 3H), 1.66 (s, 9H); **^{13}C-NMR (151 MHz; $CDCl_3$):** 165.4, 143.3, 134.4, 127.2, 122.1, 121.47, 121.27, 110.3, 106.0, 79.8, 28.7, 14.2

4 General procedure for the Rh-catalysed ortho olefination

A 4 mL vial was equipped with the corresponding Weinreb amide (1 equiv.), $[RhCp^*Cl_2]_2$ (1.0/2.5 mol%) and photoredox catalyst (10 mol%, 1 equiv.) and a teflon-coated magnetic stirring bar. After addition of $AgSbF_6$ (5/10 mol%) in chlorobenzene (0.01 mM) the corresponding electrophile (2 equiv.) was added and the reaction mixture placed in a preheated aluminum block (100 °C, actual vial temperature ~80 °C) under light irradiation from ca. 3 cm distance. After the indicated time, the reaction mixture was directly absorbed on SiO_2 and the product purified by flash column chromatography.

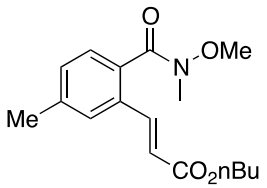
Butyl (*E*)-3-(2-(methoxy(methyl)carbamoyl)phenyl)acrylate 6a

Starting from *N*-methoxy-*N*-methylbenzamide (33 mg, 0.2 mmol) the product was isolated as colorless oil after flash chromatography (*n*-pentane/ethyl acetate 5:1) 49 mg (0.17 mmol, 84% yield).



^{1}H-NMR (600 MHz; $CDCl_3$): 7.72 (d, *J* = 15.9 Hz, 1H), 7.66-7.64 (m, 1H), 7.43-7.37 (m, 3H), 6.42 (d, *J* = 15.9 Hz, 1H), 4.18 (t, *J* = 6.7 Hz, 2H), 3.39-3.35 (m, 6H), 1.68-1.65 (m, 2H), 1.42 (q, *J* = 7.5 Hz, 2H), 0.95 (t, *J* = 7.4 Hz, 3H); **^{1}H-^{13}C-NMR (151 MHz; $CDCl_3$):** 166.5, 141.3, 136.0, 131.7, 130.5, 129.6, 128.11, 127.98, 127.2, 120.4, 83.5, 64.5, 61.1, 30.7, 19.2, 13.7.

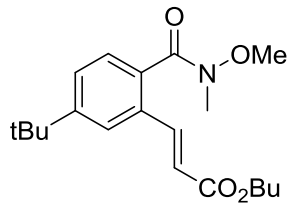
Butyl (*E*)-3-(2-(methoxy(methyl)carbamoyl)-5-methylphenyl)acrylate 6b



Starting from *N*-methoxy-*N*,4-dimethylbenzamide (36 mg, 0.2 mmol) the product was isolated as colorless oil after flash chromatography (*n*-pentane/ethyl acetate 5:1) 39 mg (0.13 mmol, 64% yield).

^{1}H-NMR (600 MHz; CDCl$_3$): 7.71 (d, *J* = 15.9 Hz, 1H), 7.45 (s, 1H), 7.27 (d, *J* = 7.8 Hz, 1H), 7.21-7.20 (m, 1H), 6.40 (d, *J* = 15.9 Hz, 1H), 4.18 (t, *J* = 6.7 Hz, 2H), 3.42-3.33 (m, 6H), 2.38 (s, 3H), 1.68-1.63 (m, 2H), 1.41 (dq, *J* = 15.0, 7.5 Hz, 2H), 0.94 (t, *J* = 7.4 Hz, 3H); **^{13}C-NMR (151 MHz; CDCl$_3$):** 166.6, 141.4, 139.6, 133.2, 131.6, 130.4, 127.2, 126.9, 120.2, 83.5, 64.4, 61.1, 30.7, 21.3, 19.2, 13.7

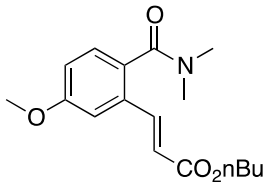
Butyl (E)-3-(5-(tert-butyl)-2-(methoxy(methyl)carbamoyl)phenyl)acrylate 6c



Starting from 4-(tert-butyl)-N-methoxy-N-methylbenzamide (44 mg, 0.2 mmol) the product was isolated as colorless oil after flash chromatography (*n*-pentane/ethyl acetate 5:1) 46 mg (0.13 mmol, 66% yield).

^{1}H-NMR (600 MHz; CDCl$_3$): 7.74 (d, *J* = 15.9 Hz, 1H), 7.63 (d, *J* = 1.7 Hz, 1H), 7.43 (dd, *J* = 8.1, 1.8 Hz, 1H), 7.31 (d, *J* = 8.1 Hz, 1H), 6.42 (d, *J* = 15.9 Hz, 1H), 4.18 (t, *J* = 6.7 Hz, 2H), 3.41 (s, 6H), 1.66 (dd, *J* = 14.8, 7.0 Hz, 2H), 1.42 (dd, *J* = 15.0, 7.5 Hz, 2H), 1.33 (s, 9H), 0.95 (t, *J* = 7.4 Hz, 3H); **^{13}C-NMR (151 MHz; CDCl$_3$):** 166.7, 153.1, 152.7, 141.9, 133.1, 131.3, 127.0, 123.3, 120.0, 64.4, 61.1, 34.8, 31.1, 30.7, 19.2, 13.7.

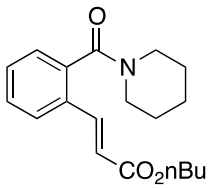
Butyl (*E*)-3-(2-(dimethylcarbamoyl)-5-methoxyphenyl)acrylate 6d



Starting from 4-methoxy-*N,N*-dimethylbenzamide (36 mg, 0.2 mmol) the product was isolated as colorless oil after flash chromatography (*n*-pentane/ethyl acetate 1:1) 44 mg (0.14 mmol. 72% yield).

^{1}H-NMR (600 MHz; CDCl$_3$): 7.63 (d, *J* = 15.9 Hz, 1H), 7.23 (d, *J* = 8.4 Hz, 1H), 7.11 (d, *J* = 2.5 Hz, 1H), 6.94 (dd, *J* = 8.5, 2.5 Hz, 1H), 6.40 (d, *J* = 15.9 Hz, 1H), 4.18 (t, *J* = 6.7 Hz, 2H), 3.84 (s, 3H), 3.13 (s, 3H), 2.79 (s, 3H), 1.67 (t, *J* = 7.5 Hz, 2H), 1.42 (dd, *J* = 15.0, 7.5 Hz, 2H), 0.95 (t, *J* = 7.4 Hz, 3H); **^{13}C-NMR (151 MHz; CDCl$_3$):** 170.2, 166.5, 160.0, 141.0, 132.7, 130.0, 128.5, 120.8, 116.2, 111.2, 64.5, 55.4, 38.8, 35.0, 30.7, 19.2, 13.7.

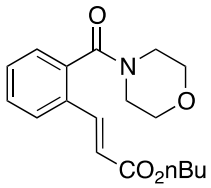
Butyl (*E*)-3-(2-(piperidin-1-carbonyl)phenyl)acrylate 6e



Starting from phenyl (piperidin-1-yl)methanone (38 mg, 0.2 mmol) the product was isolated as colorless oil after flash chromatography (*n*-pentane/ethyl acetate 10:1) 45 mg (0.14 mmol, 71% yield).

^{1}H-NMR (400 MHz; CDCl$_3$): 7.69 (d, *J* = 16.0 Hz, 1H), 7.26 (s, 1H), 6.42 (d, *J* = 16.0 Hz, 1H), 3.69 (s, 2H), 3.32 (s, 2H), 1.66 (s, 7H), 1.49 (s, 2H), 1.42 (d, *J* = 7.5 Hz, 2H), 0.94 (t, *J* = 7.4 Hz, 3H); **^{13}C-NMR (101 MHz; CDCl$_3$):** 170.2, 141.0, 136.5, 130.2, 129.3, 128.3, 126.74, 126.70, 126.51, 120.5, 64.4, 48.1, 42.6, 30.7, 25.6, 24.6, 19.2, 13.7

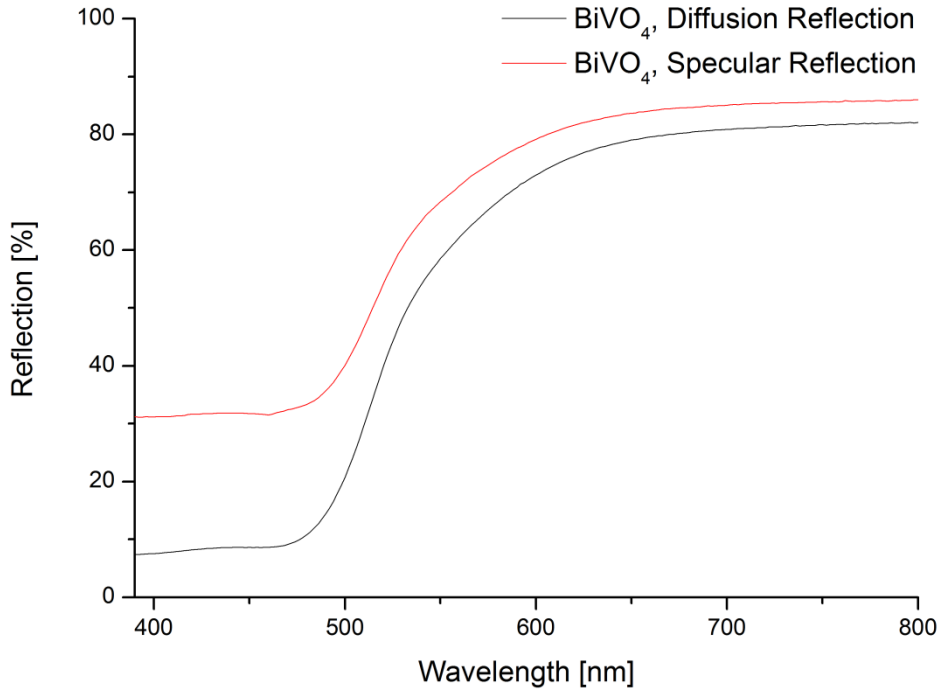
Butyl (*E*)-3-(2-(morpholin-4-carbonyl)phenyl)acrylate 4f

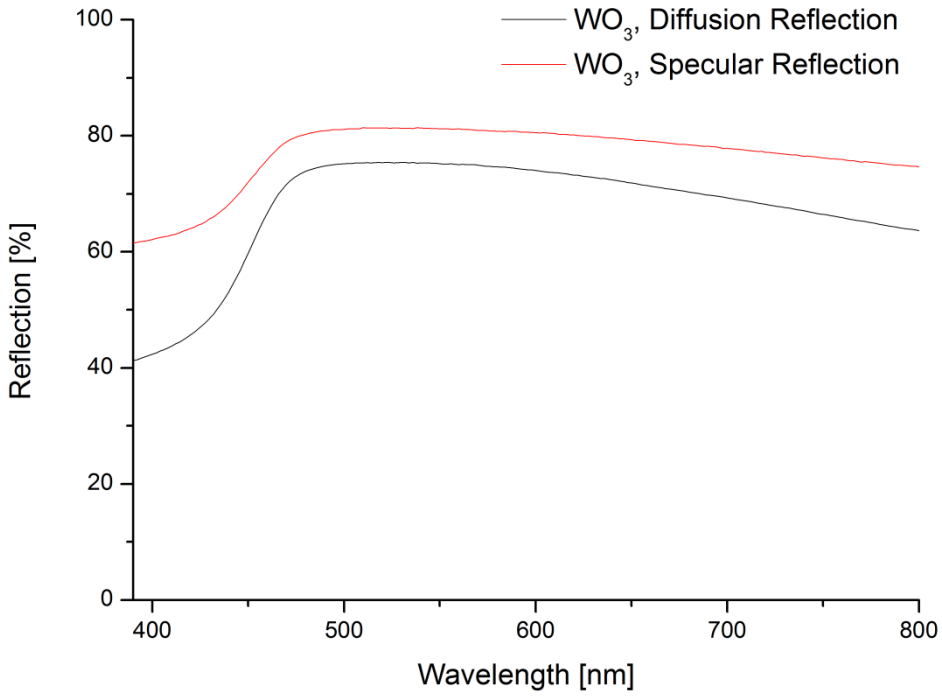


Starting from morpholin(phenyl)methanone (38 mg, 0.2 mmol) the product was isolated as colorless oil after flash chromatography (*n*-pentane/ethyl acetate 10:1) 43 mg (0.14 mmol, 68% yield).

^{1}H-NMR (600 MHz; $CDCl_3$): 7.69 (d, *J* = 16.0 Hz, 1H), 7.64-7.63 (m, 1H), 7.41-7.39 (m, 2H), 7.29-7.28 (m, 1H), 6.42 (d, *J* = 16.0 Hz, 1H), 4.18 (s, 2H), 3.76 (d, *J* = 5.0 Hz, 2H), 3.53 (t, *J* = 4.6 Hz, 2H), 3.15 (t, *J* = 4.7 Hz, 2H), 1.68-1.64 (m, 2H), 1.41 (q, *J* = 7.5 Hz, 2H), 0.94 (t, *J* = 7.4 Hz, 3H); **^{13}C-NMR (151 MHz; $CDCl_3$):** 172.7, 168.6, 140.6, 136.4, 130.3, 129.5, 126.7, 126.1, 121.0, 66.8, 64.6, 47.4, 42.2, 30.7, 19.1, 13.7

Solid State UV-Vis Reflectance spectra





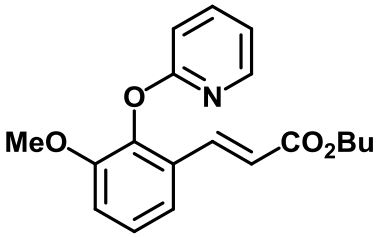
References:

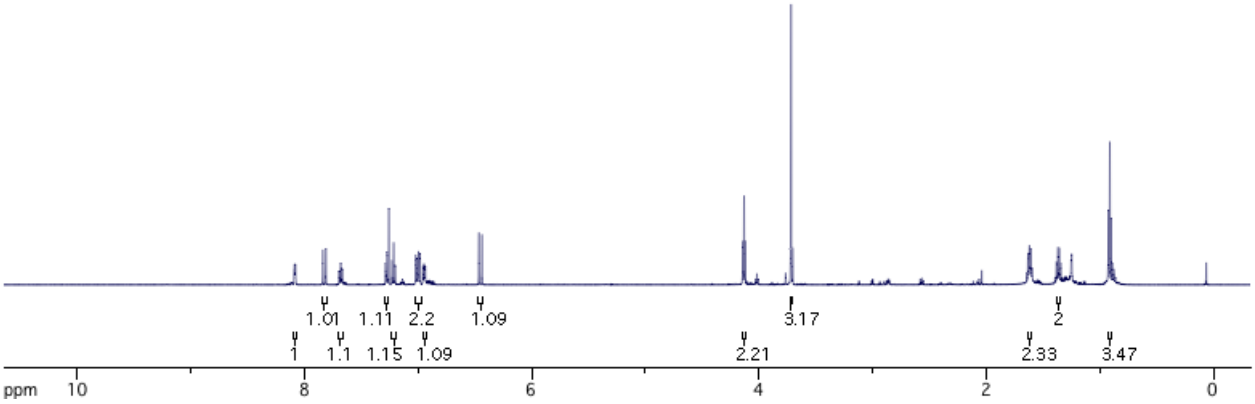
[1] D. C. Fabry, M. A. Ronge, J. Zoller, M. Rueping, *Angew. Chem. Int. Ed.* **2015**, *54*, 2801–2805.

[2] J. Zoller, D. C. Fabry, M. A. Ronge, M. Rueping, *Angew. Chem. Int. Ed.* **2014**, *53*, 13264–13268.

[3] D. C. Fabry, J. Zoller, S. Raja, M. Rueping, *Angew. Chem. Int. Ed.* **2014**, *53*, 10228–10231.

Pulse Sequence: s2pul
Spectrometer Freq.: 599.86 MHz
Solvent: $CDCl_3$
Temperature: 299.15 K
Spectral Width: 27.06 ppm
Number of Scans: 4
Relaxation Delay: 1.000 s





Pulse Sequence: s2pul
Spectrometer Freq.: 150.85 MHz
Solvent: $CDCl_3$
Temperature: 299.15 K
Spectral Width: 267.30 ppm
Number of Scans: 384
Relaxation Delay: 0.500 s

166.928
163.325
152.433
147.449
141.477
139.297
138.721
129.186
125.848
120.186
119.111
118.189
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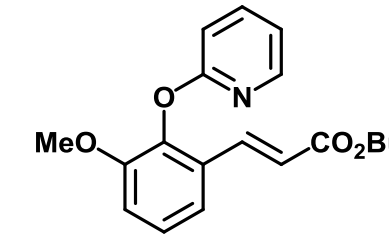
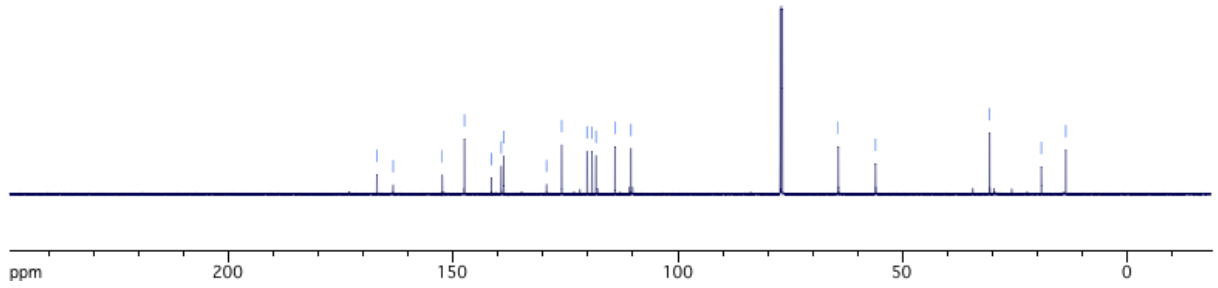
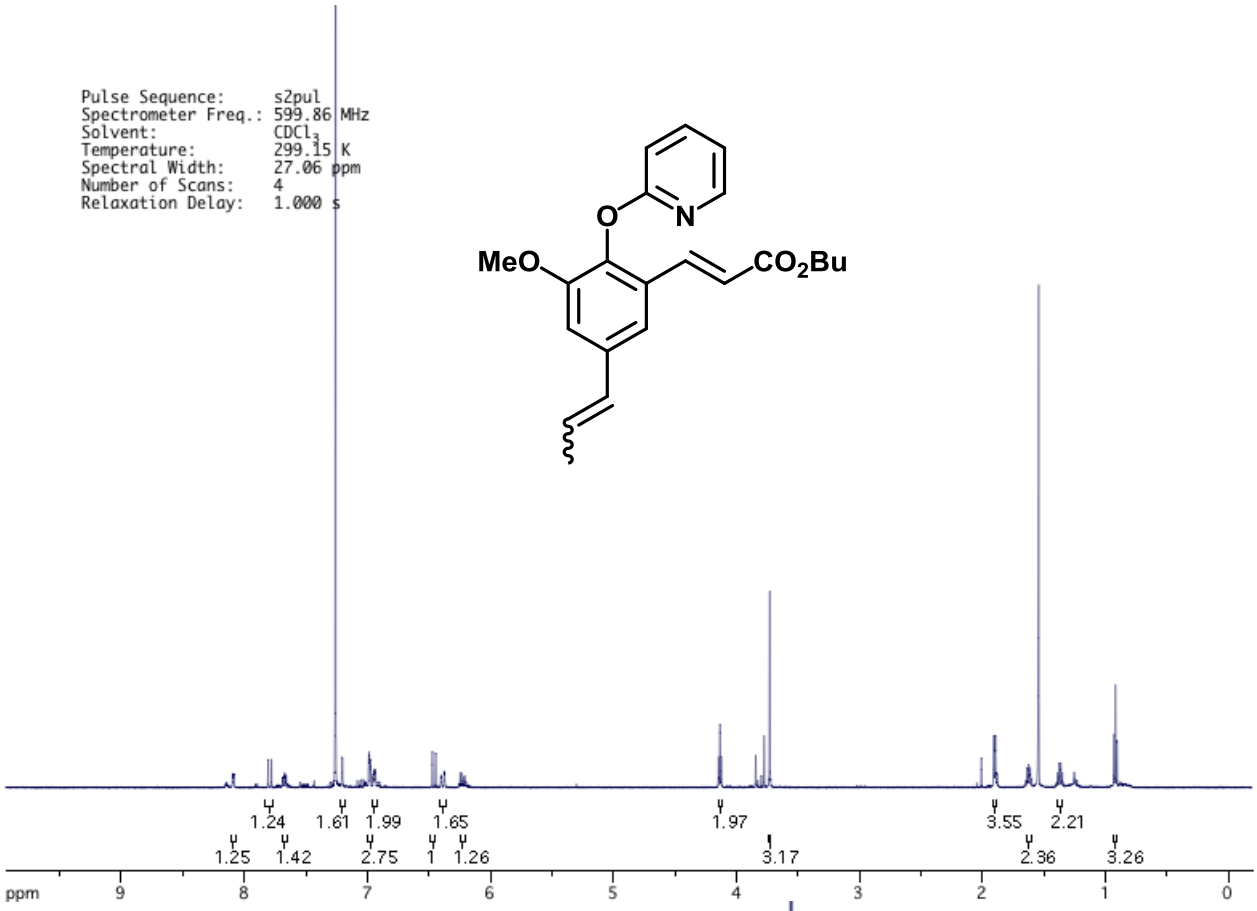
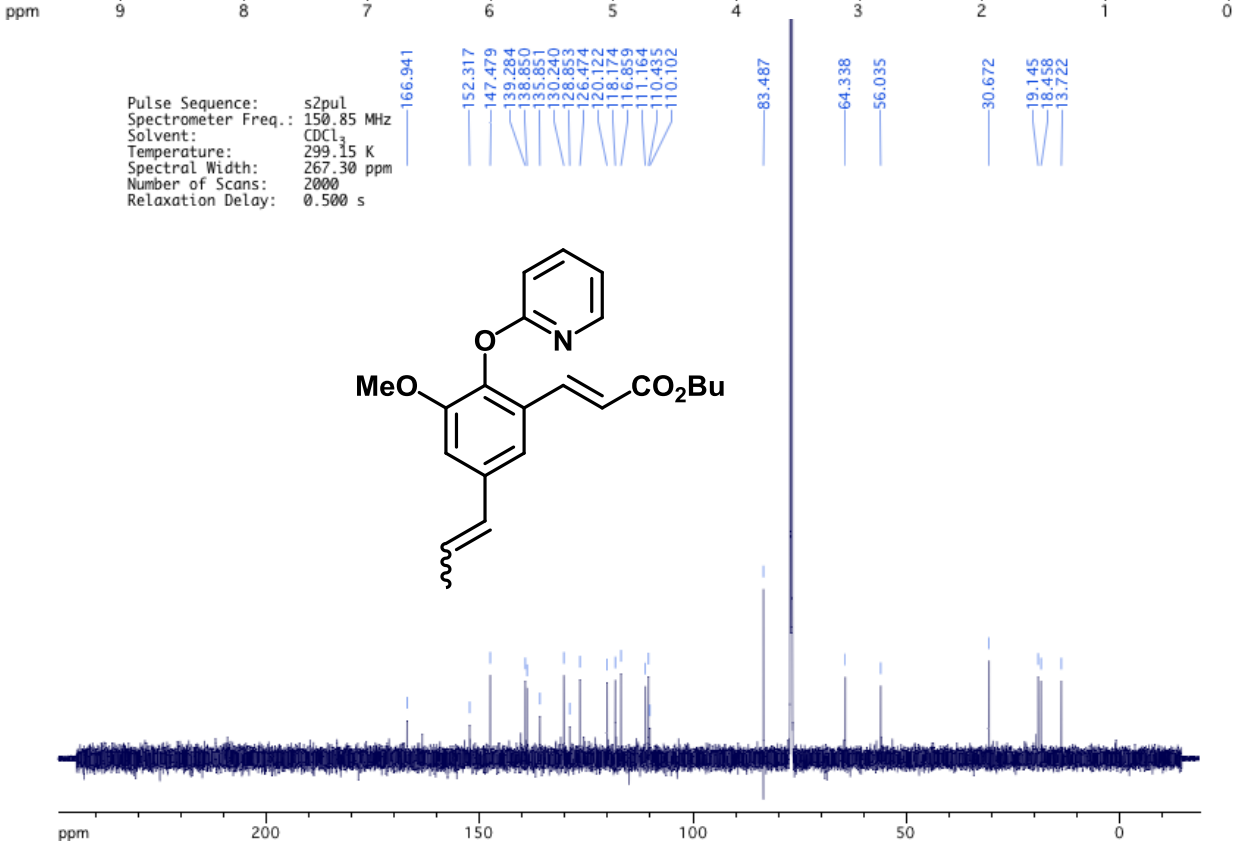
110.455
64.341
56.063
30.668
19.139
13.717






Pulse Sequence: s2pul
Spectrometer Freq.: 599.86 MHz
Solvent: CDCl3
Temperature: 299.15 K
Spectral Width: 27.06 ppm
Number of Scans: 4
Relaxation Delay: 1.000 s
MeO
CO2Bu
1.24
1.61
1.99
1.65
1.97
3.55
2.21
1.25
1.42
2.75
1
1.26
3.17
2.36
3.26
ppm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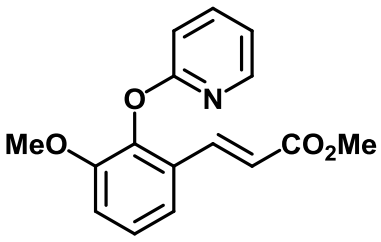
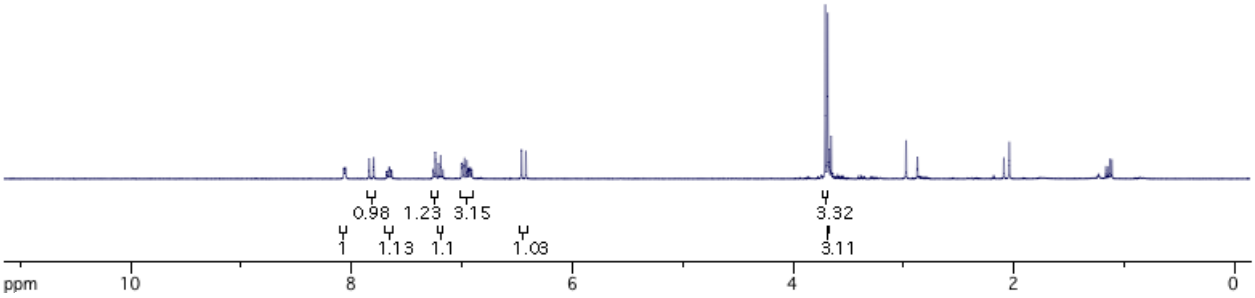
Spectrometer Freq.: 150.85 MHz
Solvent: CDCl3
Temperature: 299.15 K
Spectral Width: 267.30 ppm
Number of Scans: 2000
Relaxation Delay: 0.500 s
166.941
152.317
147.479
139.284
138.850
135.851
130.240
128.653
126.474
120.122
118.174
116.859
111.164
110.435
110.102
83.487
64.338
56.035
30.672
19.145
18.458
13.722
MeO
CO2Bu
ppm

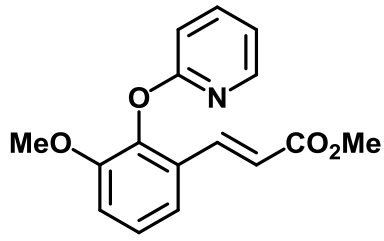
Pulse Sequence: s2pul
Spectrometer Freq.: 399.97 MHz
Solvent: $CDCl_3$
Temperature: 298.15 K
Spectral Width: 26.94 ppm
Number of Scans: 16
Relaxation Delay: 1.000 s

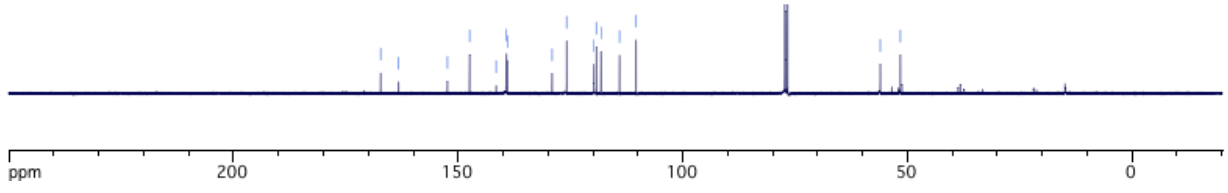




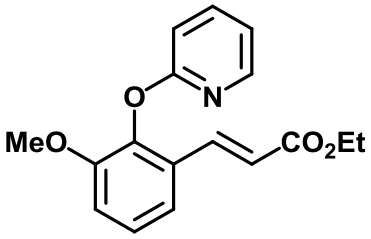
Pulse Sequence: s2pul
Spectrometer Freq.: 100.58 MHz
Solvent: $CDCl_3$
Temperature: 298.15 K
Spectral Width: 270.16 ppm
Number of Scans: 512
Relaxation Delay: 0.500 s

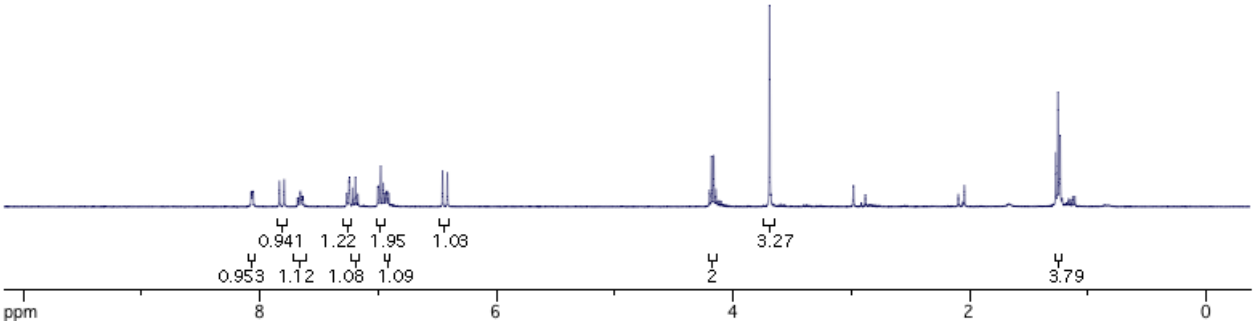
167.230
163.290
152.408
147.428
141.533
139.282
139.035
129.098
125.833
119.769
119.212
118.200
114.063
110.432
56.037
51.582





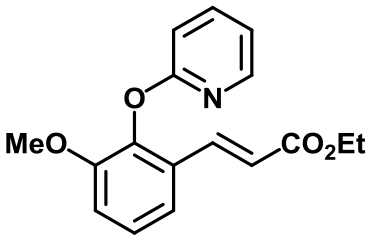
Pulse Sequence: s2pul
Spectrometer Freq.: 399.97 MHz
Solvent: $CDCl_3$
Temperature: 298.15 K
Spectral Width: 26.94 ppm
Number of Scans: 16
Relaxation Delay: 1.000 s

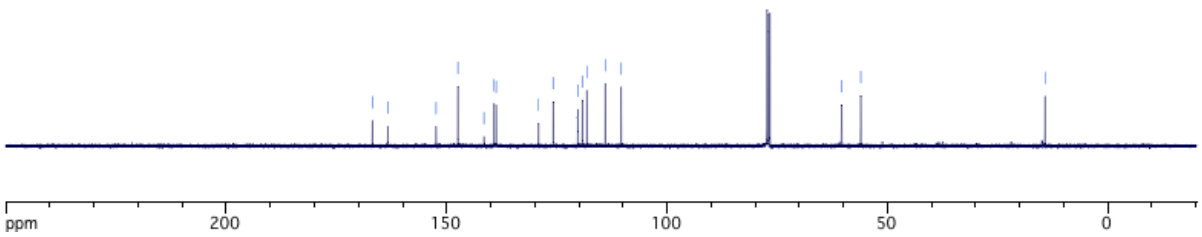




Pulse Sequence: s2pul
Spectrometer Freq.: 100.58 MHz
Solvent: $CDCl_3$
Temperature: 298.15 K
Spectral Width: 270.16 ppm
Number of Scans: 512
Relaxation Delay: 0.500 s

166.808
163.321
152.413
147.425
141.524
139.261
138.759
129.171
125.803
120.207
119.176
118.174
113.993
110.440
60.385
56.042
14.226





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Temperature: 298.15 K
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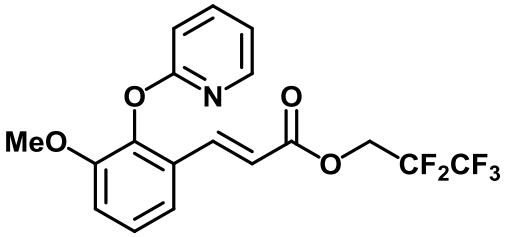
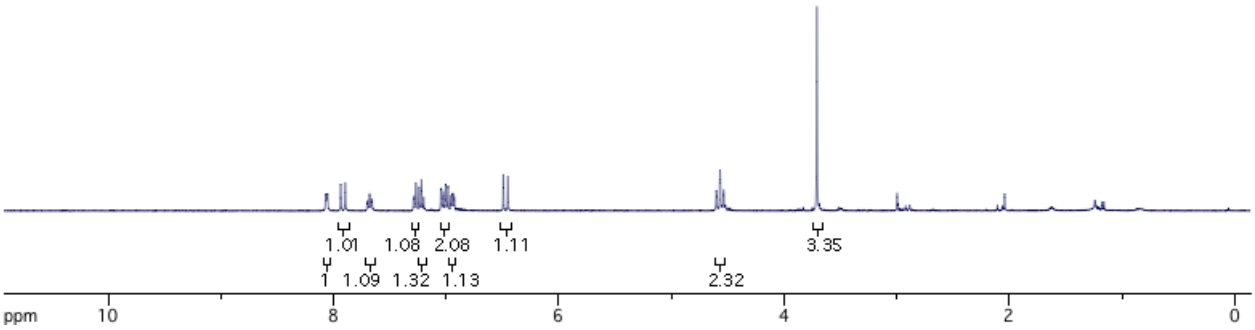
Number of Scans: 16
Relaxation Delay: 1.000 s





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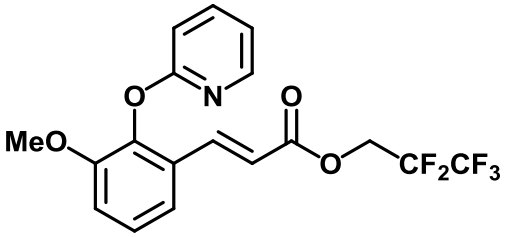
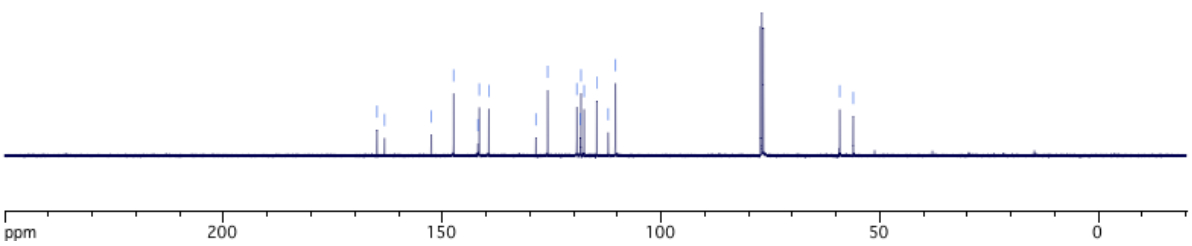
Spectrometer Freq.: 100.58 MHz
Solvent: $CDCl_3$
Temperature: 298.15 K
Spectral Width: 270.16 ppm
Number of Scans: 1000
Relaxation Delay: 0.500 s

164.929
163.224
152.530
147.393
141.851
141.541
139.344
128.574
125.915
119.231
118.419
118.298
117.579
114.679
112.097
110.448
59.162
56.061





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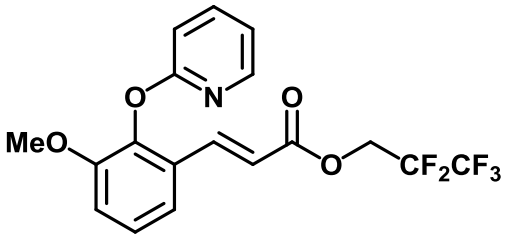
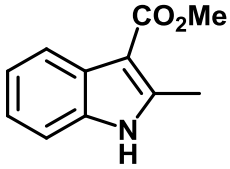
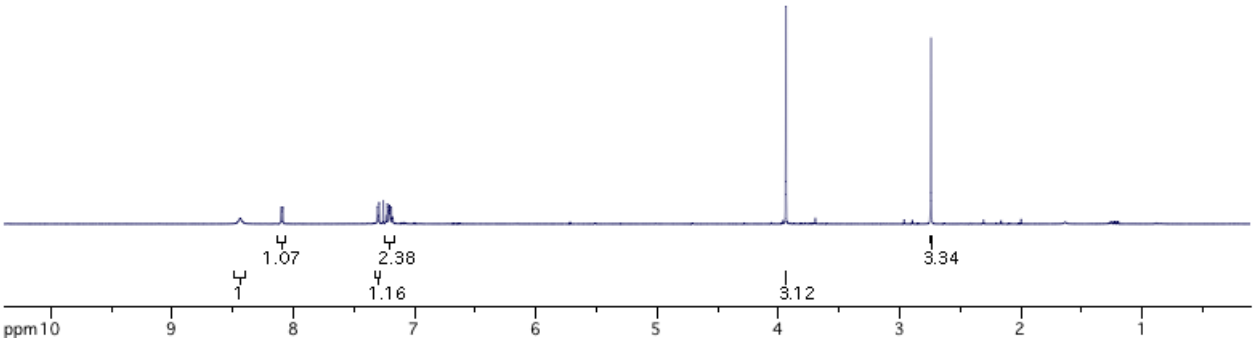
Solvent: $CDCl_3$
Temperature: 298.15 K
Spectral Width: 316.34 ppm
Number of Scans: 64
Relaxation Delay: 1.000 s



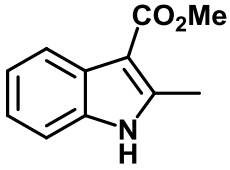
Pulse Sequence: s2pul
Spectrometer Freq.: 599.86 MHz
Solvent: $CDCl_3$
Temperature: 299.15 K
Spectral Width: 27.06 ppm
Number of Scans: 4
Relaxation Delay: 1.000 s

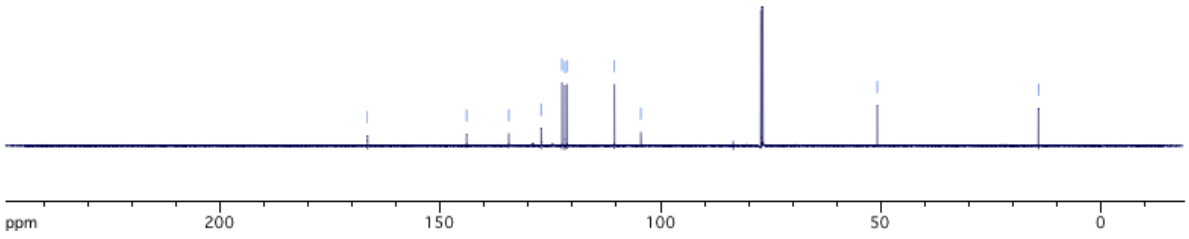




Pulse Sequence: s2pul
Spectrometer Freq.: 150.85 MHz
Solvent: $CDCl_3$
Temperature: 299.15 K
Spectral Width: 267.30 ppm
Number of Scans: 384
Relaxation Delay: 0.500 s

166.507
143.995
134.438
127.090
122.359
121.708
121.248
110.480
104.482
50.799
14.223





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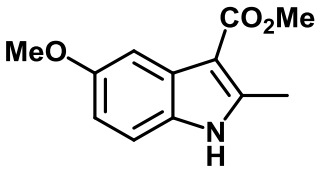
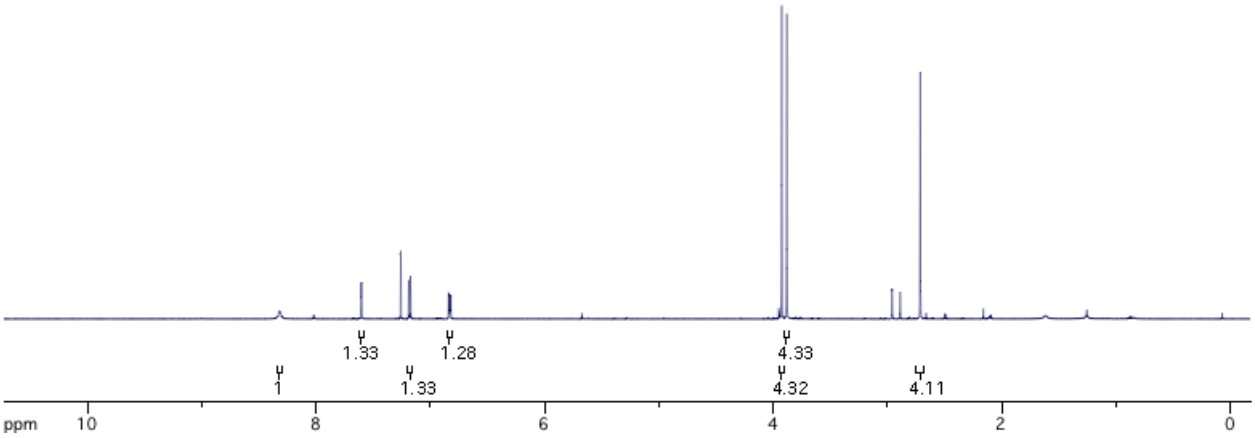
Spectral Width: 27.06 ppm
Number of Scans: 4
Relaxation Delay: 1.000 s





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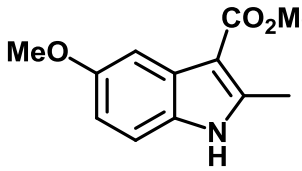
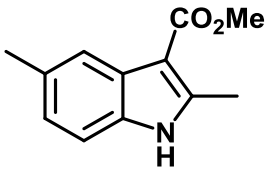
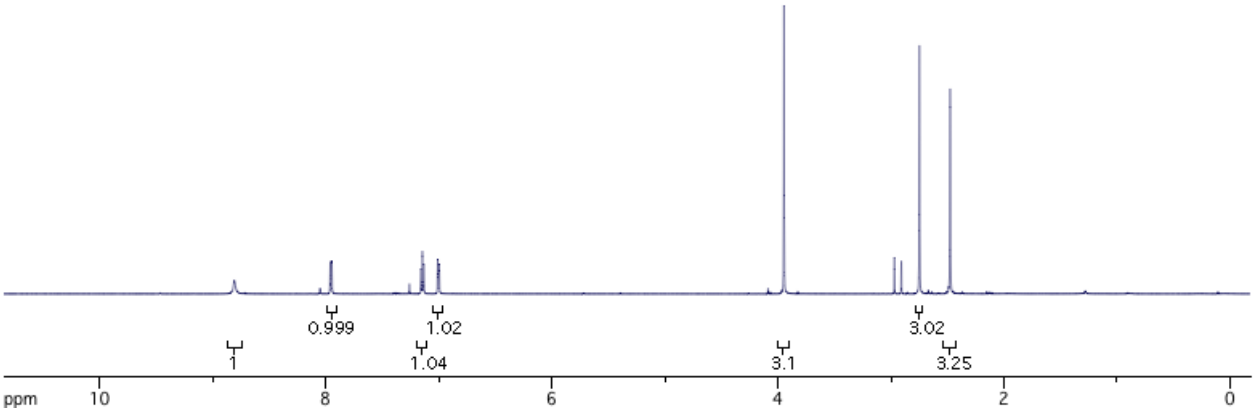
Spectrometer Freq.: 150.85 MHz
Solvent: $CDCl_3$
Temperature: 299.15 K
Spectral Width: 267.30 ppm
Number of Scans: 384
Relaxation Delay: 0.500 s

166.471, 155.565, 144.144, 129.283, 128.051, 112.119, 112.074, 111.131, 104.345, 103.384, 83.529, 55.783, 50.759, 14.459



Pulse Sequence: s2pul
Spectrometer Freq.: 599.86 MHz
Solvent: $CDCl_3$
Temperature: 299.15 K
Spectral Width: 27.06 ppm
Number of Scans: 4
Relaxation Delay: 1.000 s





Pulse Sequence: s2pul
Spectrometer Freq.: 150.85 MHz
Solvent: $CDCl_3$
Temperature: 299.15 K
Spectral Width: 267.30 ppm
Number of Scans: 384
Relaxation Delay: 0.500 s

166.817
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126.736
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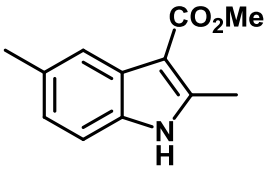
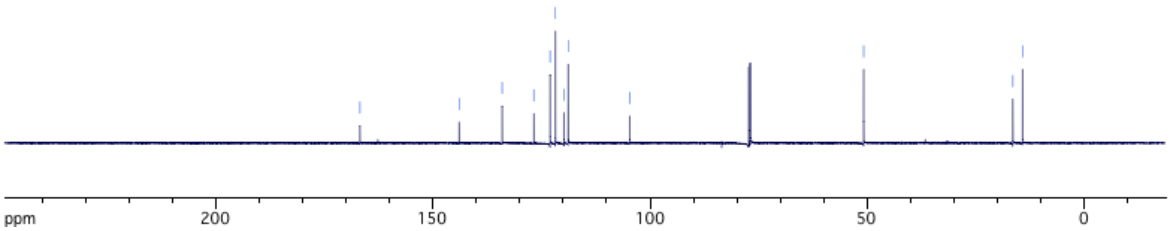
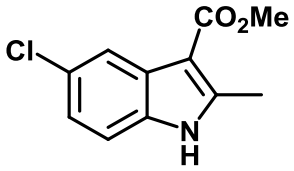
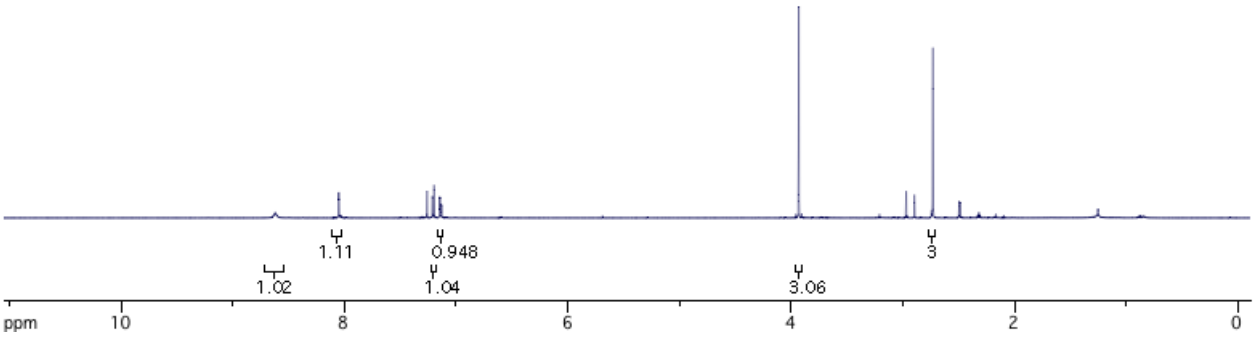
121.809
119.820
118.850
104.671
50.824
16.508
14.221





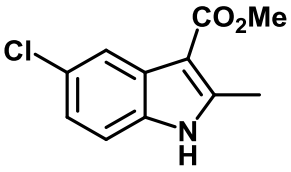
Pulse Sequence: s2pul
Spectrometer Freq.: 599.86 MHz
Solvent: $CDCl_3$
Temperature: 299.15 K
Spectral Width: 27.06 ppm
Number of Scans: 4
Relaxation Delay: 1.000 s

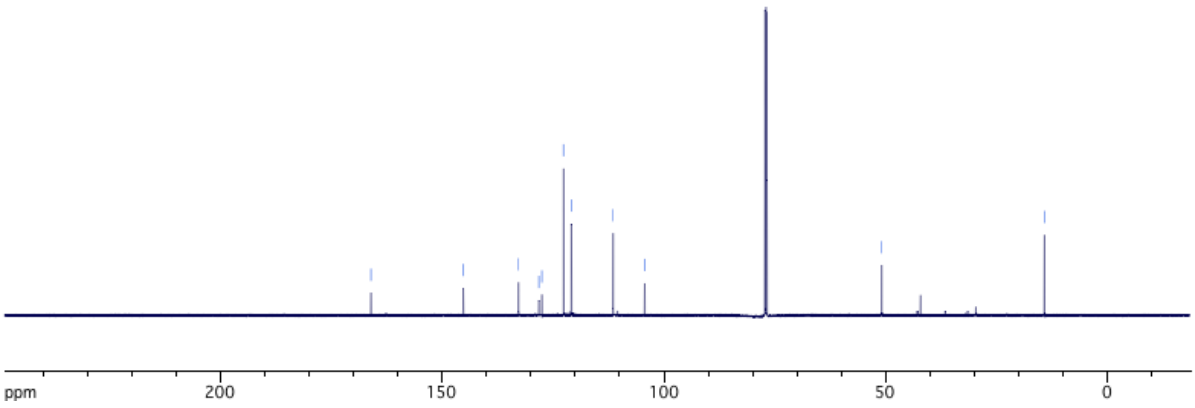




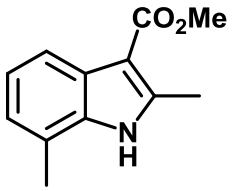
Pulse Sequence: s2pul
Spectrometer Freq.: 150.85 MHz
Solvent: $CDCl_3$
Temperature: 299.15 K
Spectral Width: 267.30 ppm
Number of Scans: 384
Relaxation Delay: 0.500 s

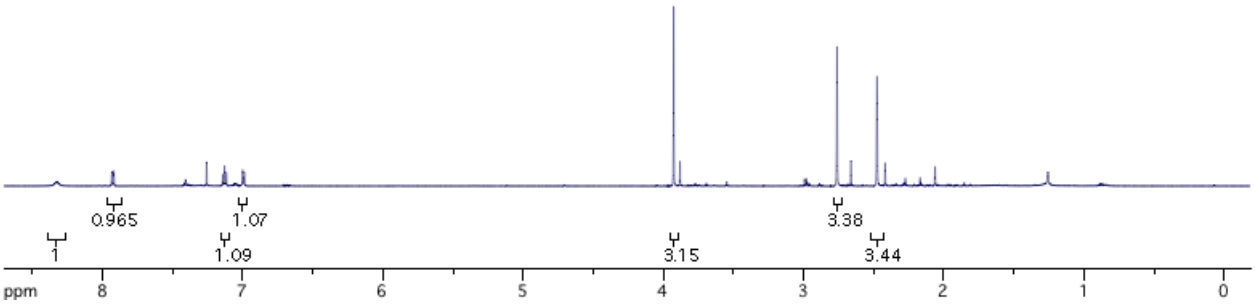
166.040
145.254
132.798
128.178
127.515
122.618
120.871
111.468
104.329
50.932
14.222





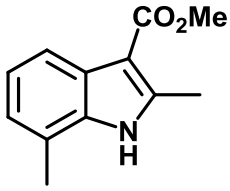
Pulse Sequence: s2pul
Spectrometer Freq.: 599.86 MHz
Solvent: $CDCl_3$
Temperature: 299.15 K
Spectral Width: 27.06 ppm
Number of Scans: 16
Relaxation Delay: 1.000 s

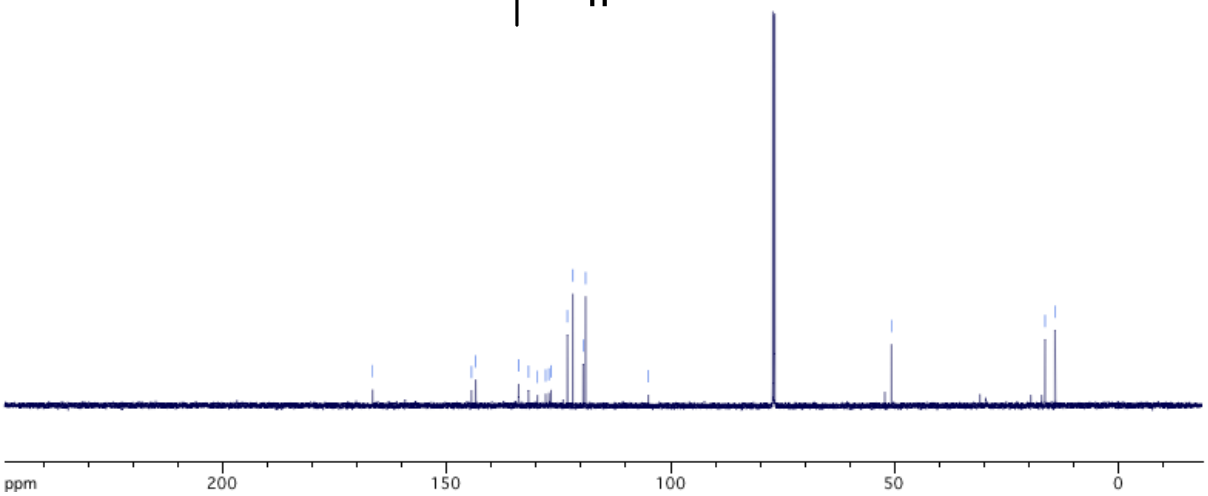


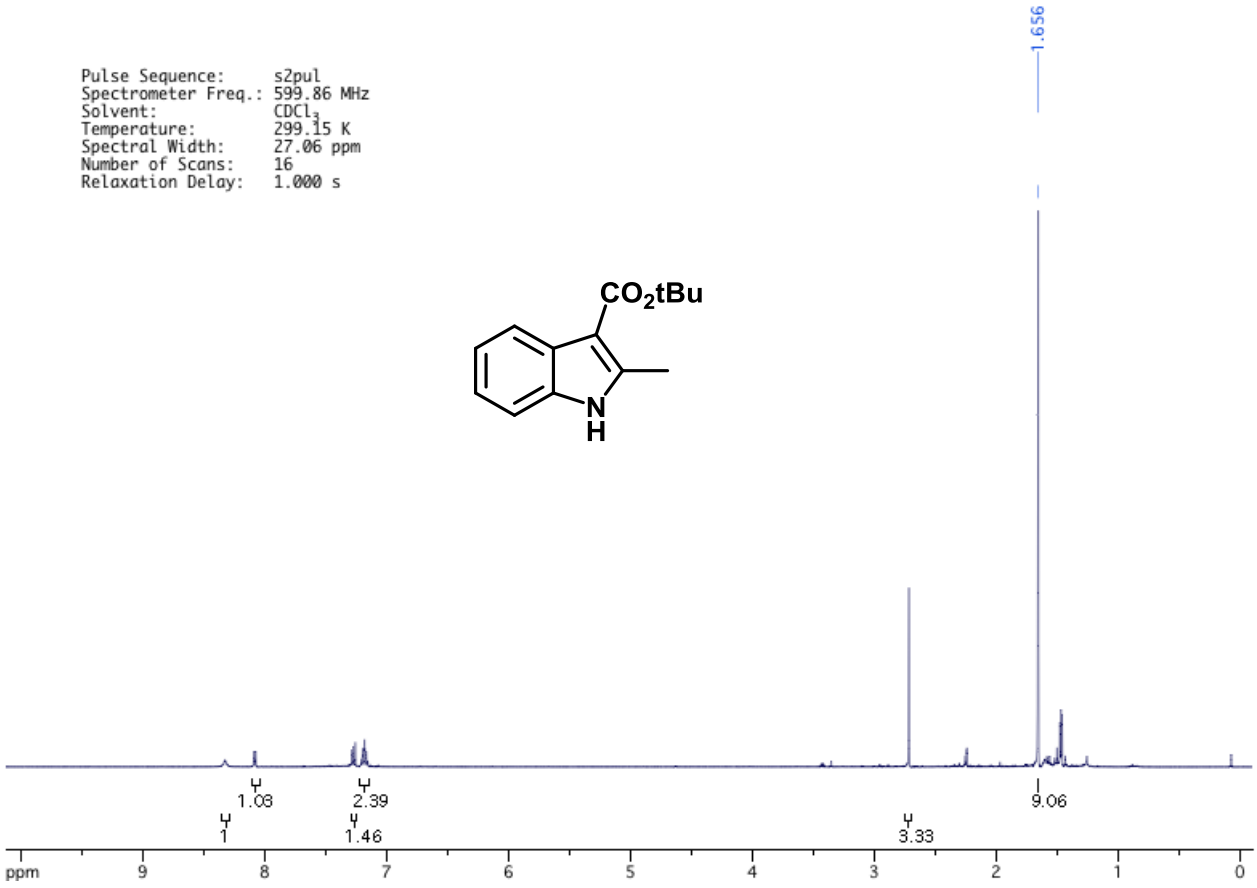


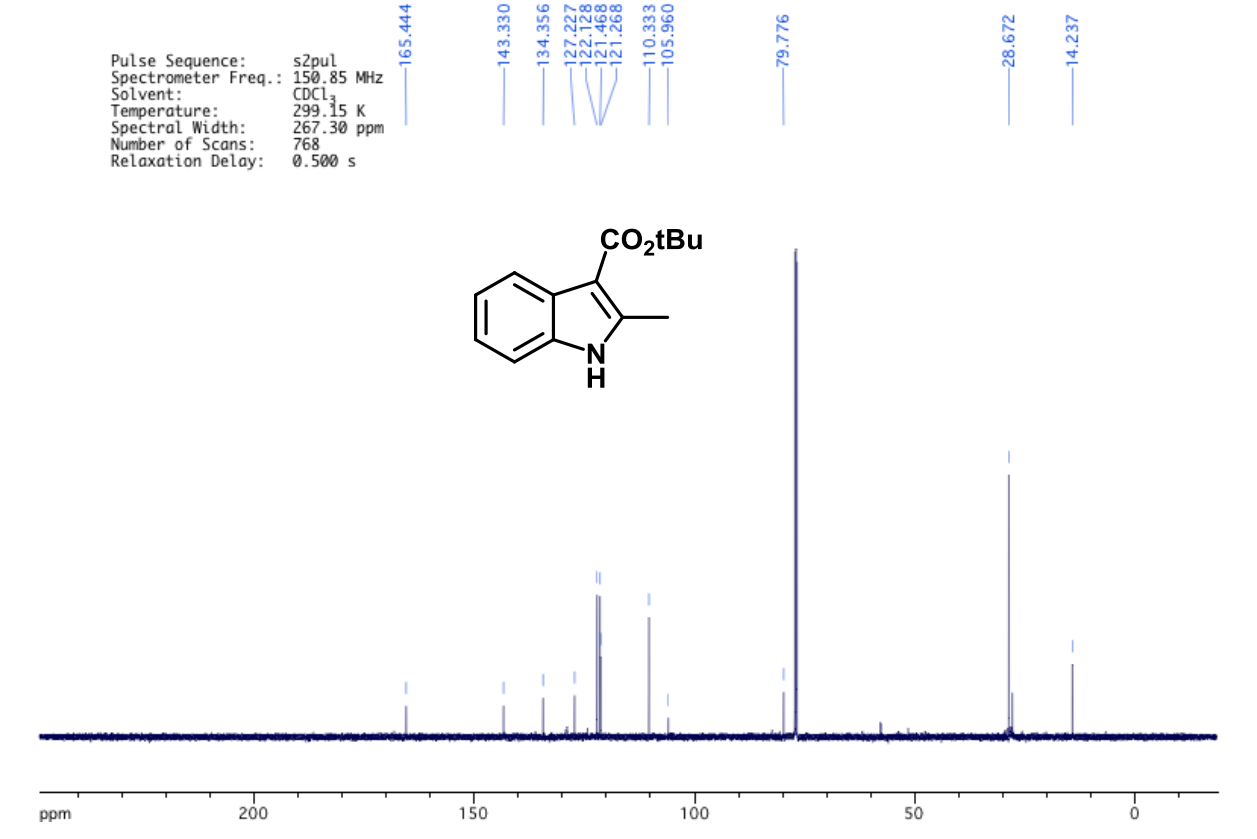
Pulse Sequence: s2pul
Spectrometer Freq.: 150.85 MHz
Solvent: $CDCl_3$
Temperature: 299.15 K
Spectral Width: 267.30 ppm
Number of Scans: 768
Relaxation Delay: 0.500 s

166.519
144.457
143.509
133.907
131.731
129.727
127.897
127.146
126.692
123.035
121.835
119.518
118.980
104.976
50.717
16.433
14.230

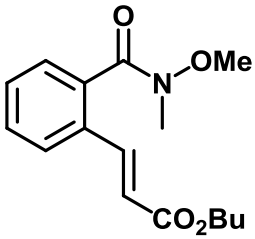


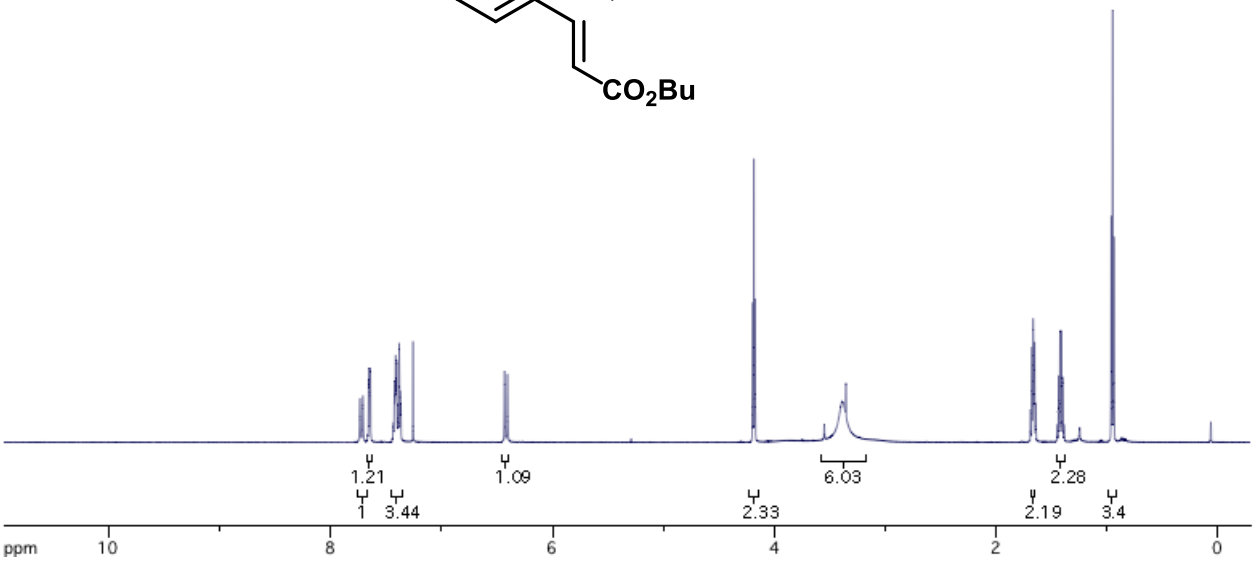



Pulse Sequence: s2pul
Spectrometer Freq.: 599.86 MHz
Solvent: CDCl3
Temperature: 299.15 K
Spectral Width: 27.06 ppm
Number of Scans: 16
Relaxation Delay: 1.000 s
1.656
CO2tBu
N
H
1.08
2.39
1
1.46
3.33
9.06
ppm

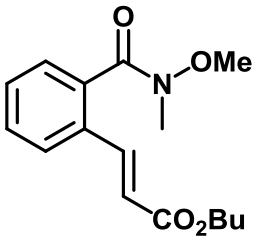

Pulse Sequence: s2pul
Spectrometer Freq.: 150.85 MHz
Solvent: CDCl3
Temperature: 299.15 K
Spectral Width: 267.30 ppm
Number of Scans: 768
Relaxation Delay: 0.500 s
165.444
143.330
134.356
127.227
122.128
121.468
121.268
110.333
105.960
79.776
28.672
14.237
CO2tBu
N
H
ppm

Pulse Sequence: s2pul
Spectrometer Freq.: 599.86 MHz
Solvent: $CDCl_3$
Temperature: 299.15 K
Spectral Width: 27.06 ppm
Number of Scans: 4
Relaxation Delay: 1.000 s

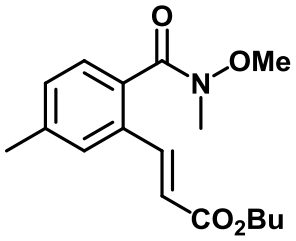


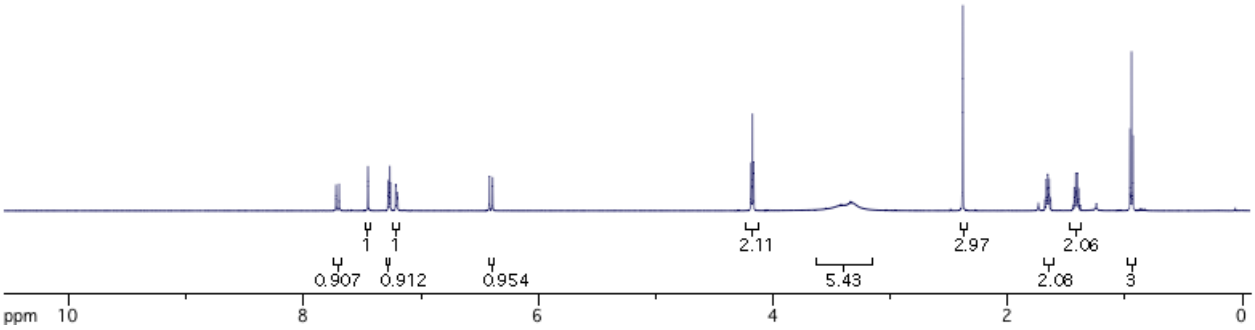


Pulse Sequence: s2pul
Spectrometer Freq.: 150.85 MHz
Solvent: $CDCl_3$
Temperature: 299.15 K
Spectral Width: 267.30 ppm
Number of Scans: 384
Relaxation Delay: 0.500 s



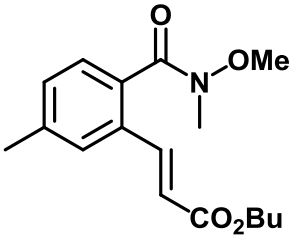
Pulse Sequence: s2pul
Spectrometer Freq.: 599.86 MHz
Solvent: $CDCl_3$
Temperature: 299.15 K
Spectral Width: 27.06 ppm
Number of Scans: 4
Relaxation Delay: 1.000 s

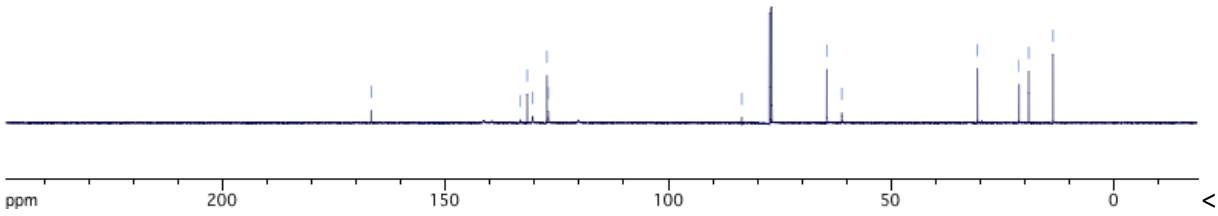




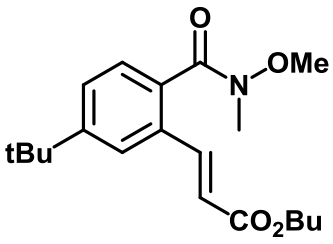
Pulse Sequence: s2pul
Spectrometer Freq.: 150.85 MHz
Solvent: $CDCl_3$
Temperature: 299.15 K
Spectral Width: 267.30 ppm
Number of Scans: 384
Relaxation Delay: 0.500 s

166.617
133.176
131.640
130.431
127.244
126.908
83.529
64.431
61.082
30.689
21.344
19.172
13.724



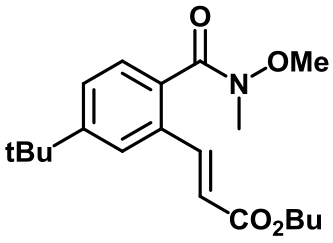


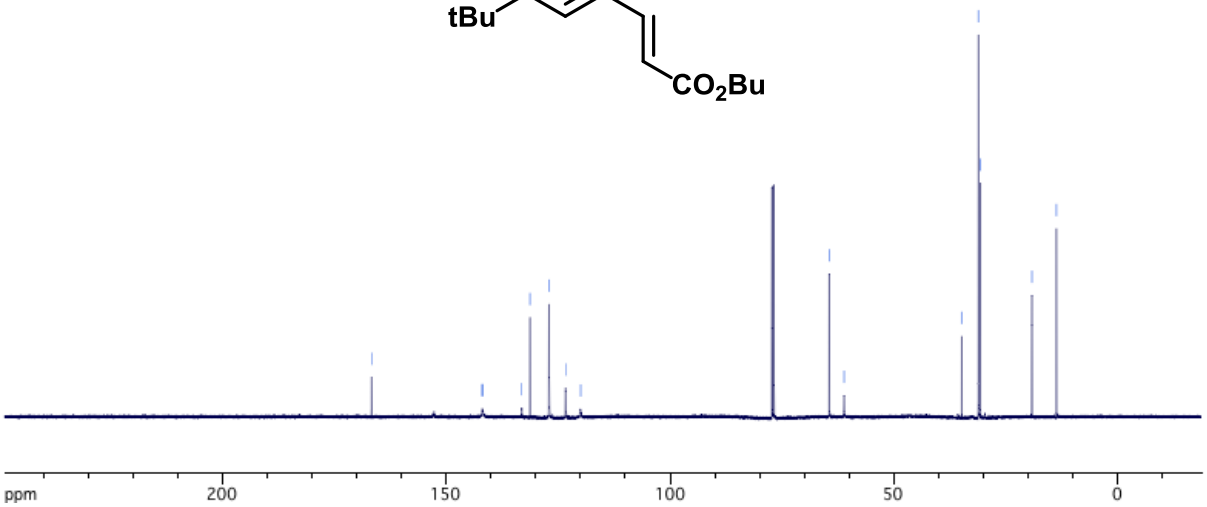
Pulse Sequence: s2pul
Spectrometer Freq.: 599.86 MHz
Solvent: $CDCl_3$
Temperature: 299.15 K
Spectral Width: 27.06 ppm
Number of Scans: 4
Relaxation Delay: 1.000 s



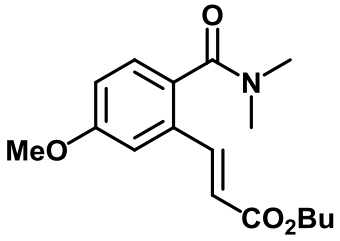
Pulse Sequence: s2pul
Spectrometer Freq.: 150.85 MHz
Solvent: $CDCl_3$
Temperature: 299.15 K
Spectral Width: 267.30 ppm
Number of Scans: 384
Relaxation Delay: 0.500 s

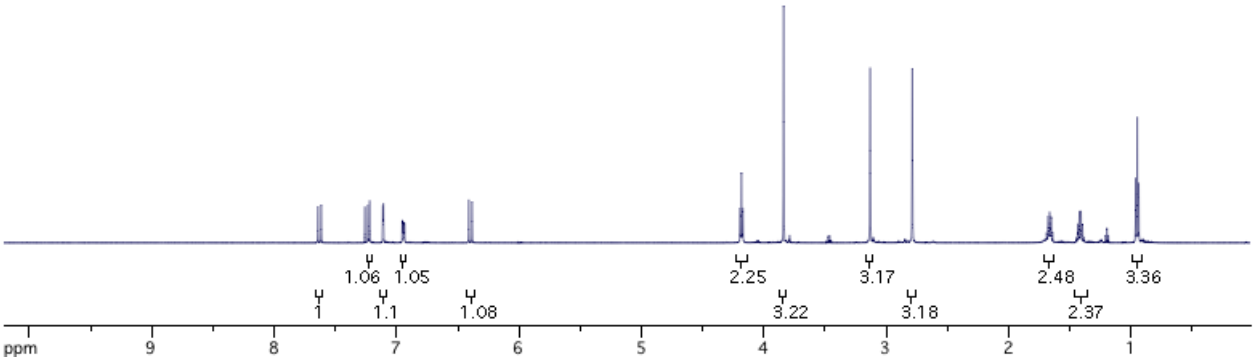
166.659
141.942
141.928
133.145
131.289
127.039
123.329
119.967
64.447
61.126
34.844
31.113
30.708
19.171
13.724





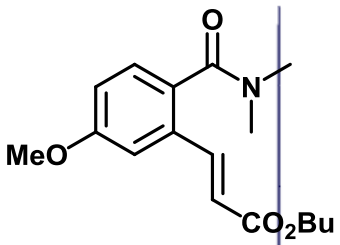
Pulse Sequence: s2pul
Spectrometer Freq.: 599.86 MHz
Solvent: $CDCl_3$
Temperature: 299.15 K
Spectral Width: 27.06 ppm
Number of Scans: 4
Relaxation Delay: 1.000 s

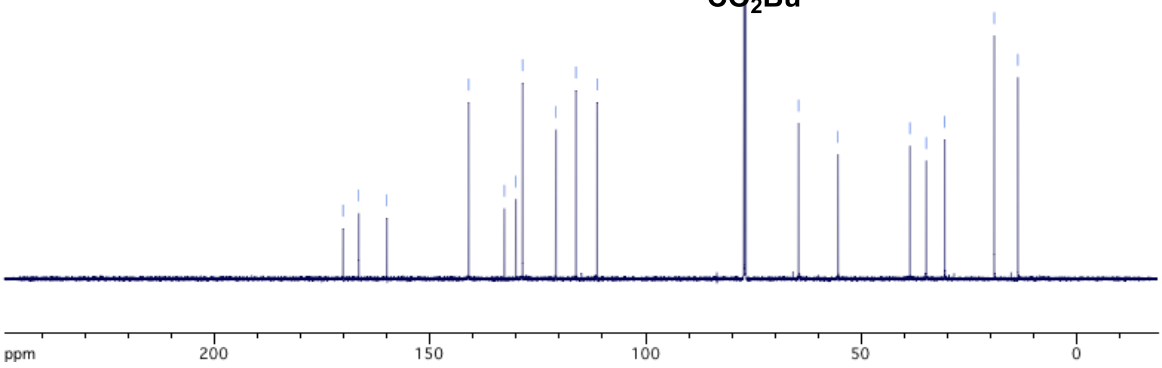




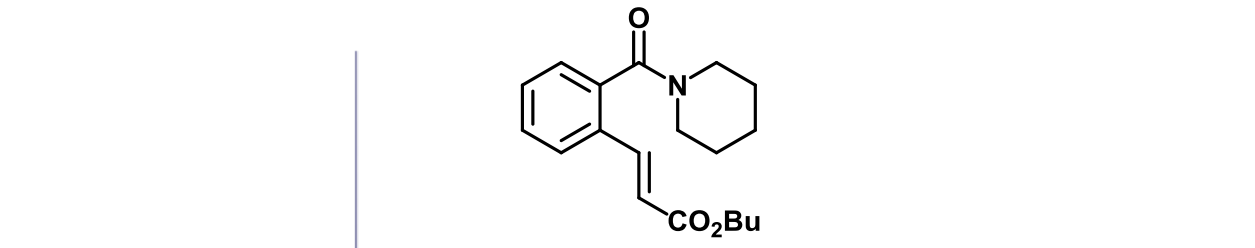
Pulse Sequence: s2pul
Spectrometer Freq.: 150.85 MHz
Solvent: $CDCl_3$
Temperature: 299.15 K
Spectral Width: 267.30 ppm
Number of Scans: 384
Relaxation Delay: 0.500 s

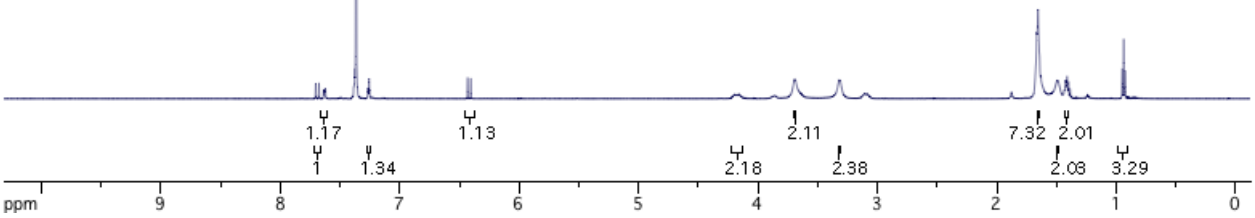
170.134
166.505
159.978
141.037
132.750
130.090
128.499
120.784
116.158
111.246
64.535
55.423
38.735
34.942
30.670
19.174
13.724

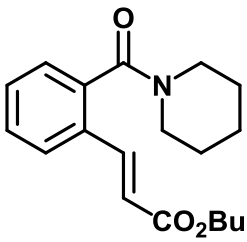


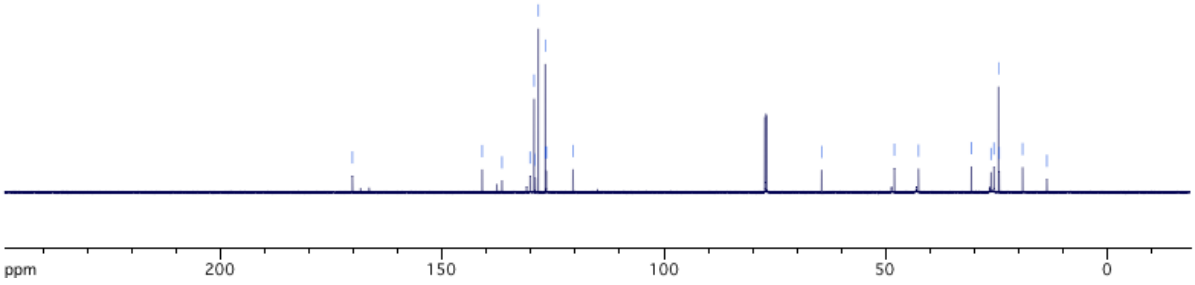


Pulse Sequence: s2pul
Spectrometer Freq.: 599.86 MHz
Solvent: $CDCl_3$
Temperature: 299.15 K
Spectral Width: 27.06 ppm
Number of Scans: 16
Relaxation Delay: 1.000 s









Pulse Sequence: s2pul
Spectrometer Freq.: 599.86 MHz
Solvent: $CDCl_3$
Temperature: 299.15 K
Spectral Width: 27.06 ppm
Number of Scans: 16
Relaxation Delay: 1.000 s