Supporting information for Rh_2(*S*-biTISP)$_2$-Catalyzed Asymmetric Functionalization of Indoles and Pyrroles with Vinylcarbenoids

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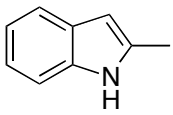
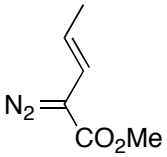
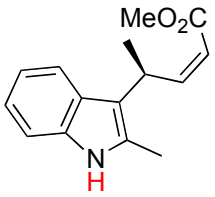
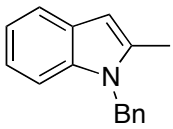
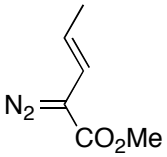
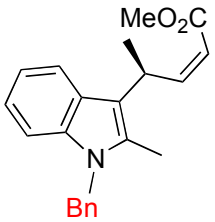
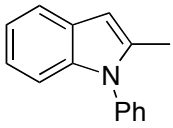
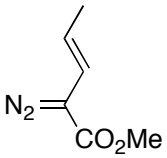
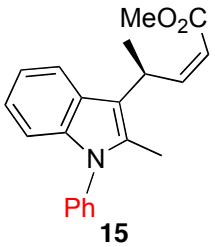
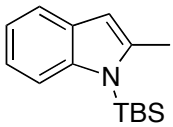
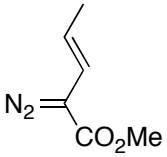
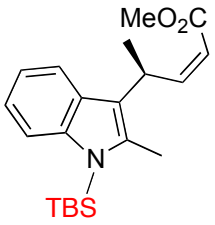
Supporting Information

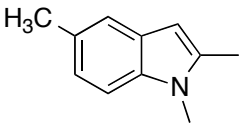
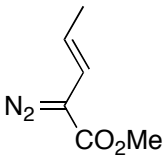
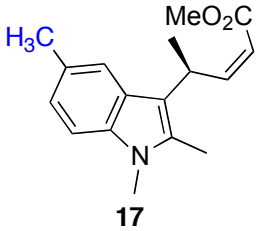
Reaction Equations for Table 3:

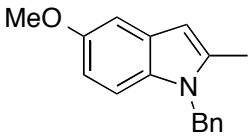
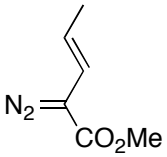
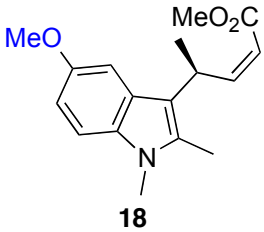
1)  **S-1** +  $Rh_2(S\text{-biTISP})_2$, DCM, -45 °C, yield: 67%, ee: 82% →  **13**

2)  **S-2** +  $Rh_2(S\text{-biTISP})_2$, DCM, -45 °C, yield: 74%, ee: 90% →  **14**

3)  **S-3** +  $Rh_2(S\text{-biTISP})_2$, DCM, -45 °C, yield: 81%, ee: 95% →  **15**

4)  **S-4** +  $Rh_2(S\text{-biTISP})_2$, DCM, -45 °C, yield: 83%, ee: 94% →  **16**

5)  **S-5** +  $Rh_2(S\text{-biTISP})_2$, DCM, -45 °C, yield: 70%, ee: 88% →  **17**

6)  **S-6** +  $Rh_2(S\text{-biTISP})_2$, DCM, -45 °C, yield: 72%, ee: 86% →  **18**

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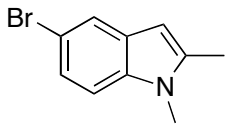

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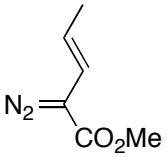
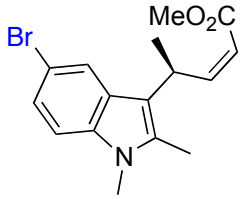


Rh_2(*S*-biTISP)$_2$

DCM, -45 °C

yield: 81%

ee: 88%



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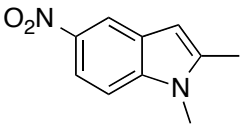

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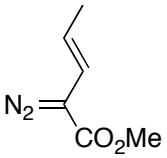
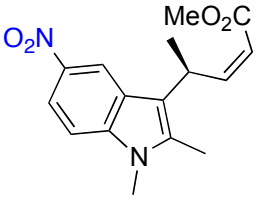


Rh_2(*S*-biTISP)$_2$

DCM, -20 °C

yield: 48%

ee: 87%



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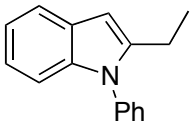

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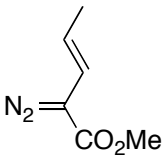
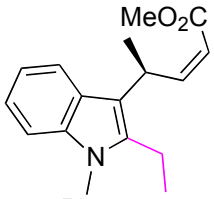


Rh_2(*S*-biTISP)$_2$

DCM, -45 °C

yield: 86%

ee: 94%



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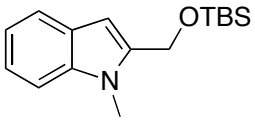

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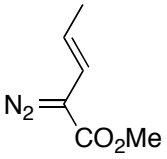
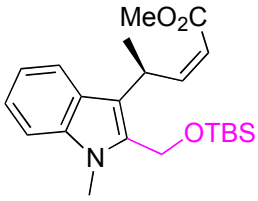


Rh_2(*S*-biTISP)$_2$

DCM, -45 °C

yield: 64%

ee: 91%



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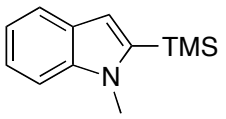
11)



S-11

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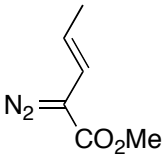
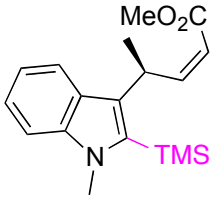


Rh_2(*S*-biTISP)$_2$

DCM, -45 °C

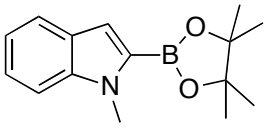
yield: 74%

ee: 92%



23

12)



S-12

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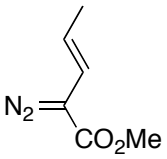
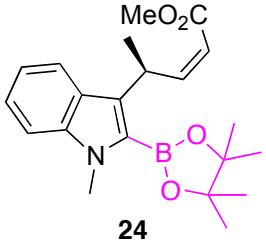


Rh_2(*S*-biTISP)$_2$

DCM, -20 °C

yield: 82%

ee: 94%



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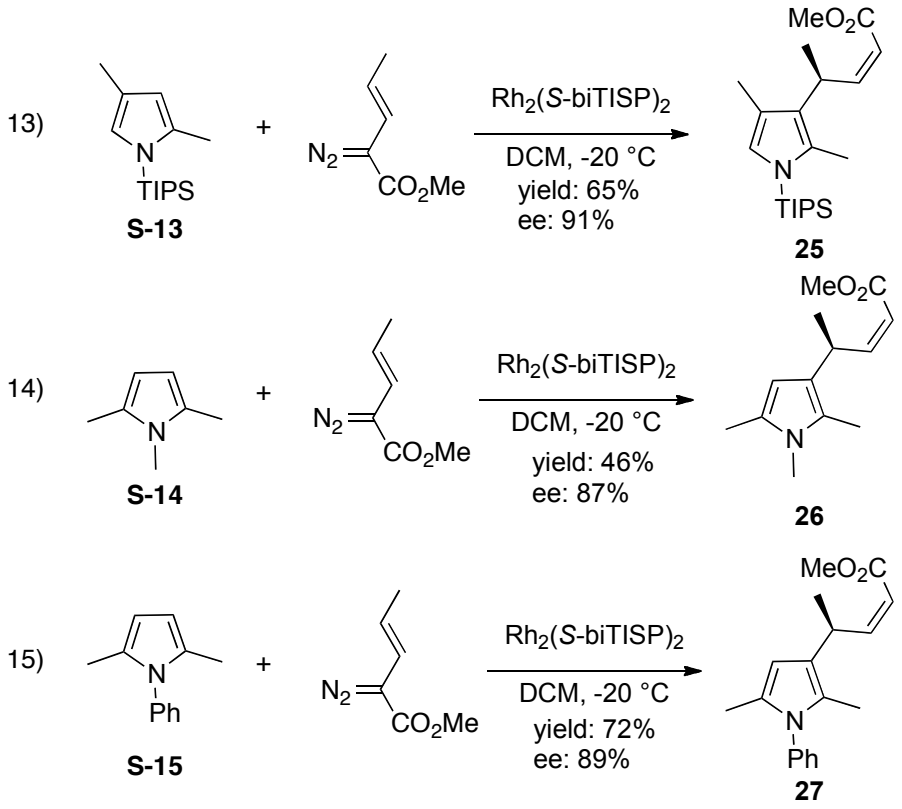
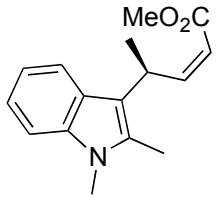
Reaction Equations for Table 4:



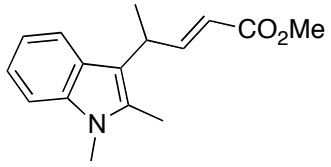
General Methods: All experiments were performed under anhydrous conditions in an atmosphere of argon except where stated, using flame-dried glassware. THF and methylenechloride were dried by a solvent purification system (passed through activated alumina columns). Unless otherwise noted, all other reagents were obtained from commercial sources and used as received. ^{1}H Nuclear Magnetic Resonance (NMR) spectra were recorded at 400 or 600 MHz. Data are presented as follows: chemical shift (in ppm on the δ scale relative to δH 7.26 for the residual protons in $CDCl_3$), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), coupling constant (*J*/Hz), integration. Coupling constants were taken directly from the spectra and are uncorrected. ^{13}C NMR spectra were recorded at 100 or 150 MHz, and all chemical shift values are reported in ppm on the δ scale, with an internal reference of δC 77.0 for $CDCl_3$. Mass spectral determinations were carried out by using APCI as ionization source. Melting points are uncorrected. Infrared spectral data are reported in units of cm^{-1}. Analytical TLC was performed on silica gel plates using UV light or potassium permanganate stain if stated. Flash column chromatography was performed on silica gel 60A (230-400 mesh).



(*S*,*Z*)-Methyl 4-(1,2-dimethyl-1*H*-indol-3-yl)pent-2-enoate (6):

To a flame-dried 25 mL flask containing Rh_2(*S*-biTISP)$_2$ (5.6 mg, 0.02 equiv.) and 1,2-dimethylindole (**5**) (130.6 mg, 0.90 mmol, 6.0 equiv.) in 6 mL dried CH_2Cl_2 under argon atmosphere was added a solution of fresh purified *trans*-methyl vinyldiazoacetate (**1b**) (21.0 mg, 0.15 mmol, 1.0 equiv.) in 6 mL dried CH_2Cl_2 by syringe pump over 3 h at -45 °C. The solution was warmed up to room temperature over night. The mixture was concentrated under reduced pressure and purified by flash chromatography on silica gel (85/15 pentane/Et_2O, R_f: 0.45) to provide the corresponding product **6** as colorless gel powder (25.5 mg, 66% yield).

Spectroscopic data on the purified products was consistent with reported value.[1] HPLC: (OD-H, 1% isopropanol in hexane, 0.7 mL/min) retention times of 18.5 (major) and 21.3 (minor), 89% ee; $[\alpha]^{25}_D$ 317.0 (*c* = 0.89, $CHCl_3$).



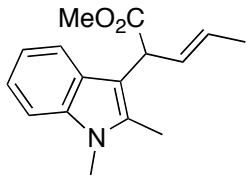
(*E*)-methyl 4-(1,2-dimethyl-1*H*-indol-3-yl)pent-2-enoate (11)

Derived from 1,2-dimethylindole (**5**) (130.6 mg, 0.90 mmol, 6.0 equiv.) and *trans*-methyl vinyldiazoacetate (**1b**) (21 mg, 0.15 mmol, 1.0 equiv.) in the presence of Rh_2(*S*-DOSP)$_4$ (5.6 mg, 0.02 equiv.) and purified by flash chromatography on silica gel (85/15 pentane/Et_2O, R_f: 0.28 for product **11** and 0.33 for product **12**) to provide product **11** as a colorless viscous oil (13.1 mg, 34% yield) and product **12** as a colorless powder (12.3 mg, 32% yield).

^{1}H NMR (400 MHz, $CDCl_3$): 7.51 (d, *J* = 7.8 Hz, 1H), 7.28 (dd, *J* = 15.9, 5.5 Hz, 1H), 7.25 (d, *J* = 8.3 Hz, 1H), 7.14 (t, *J* = 7.7 Hz, 1H), 7.03 (t, *J* = 7.8 Hz, 1H), 5.84 (dd, *J* = 1.9, 15.9 Hz, 1H), 3.85-3.93 (m, 1H), 3.69 (s, 3H), 3.64 (s, 3H), 2.34 (s, 3H), 1.55 (d, *J* =

[1] Lian, Y.; Davies, H. M. L. *Org. Lett.* **2010**, *12*, 924.

7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 167.4, 153.3, 136.7, 132.6, 126.1, 120.6, 119.0, 118.9, 118.7, 111.8, 108.7, 51.4, 33.6, 29.5, 19.4, 10.5; IR (neat): 2921, 1718, 1471, 1408, 1272, 908, 730 cm^{-1}; HRMS (EI) calc for $C_{16}H_{20}O_2N$ $(M+H)^+$ 258.1489 found 258.1490.

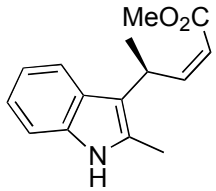


(*E*)-methyl 2-(1,2-dimethyl-1*H*-indol-3-yl)pent-3-enoate (12):

^{1}H NMR (400 MHz, $CDCl_3$): 7.60 (d, J = 7.8 Hz, 1H), 7.24 (d, J = 7.4 Hz, 1H), 7.14-7.19 (m, 1H), 7.06-7.11 (m, 1H), 6.04 (qq, J = 7.4, 1.6 Hz, 1H), 5.47-5.56 (m, 1H), 4.53-4.57 (m, 1H), 3.67 (s, 3H), 3.66 (s, 3H), 2.41 (s, 3H), 1.67-1.70 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 174.1, 136.5, 133.6, 127.8, 127.2, 126.2, 120.8, 119.1, 118.9, 108.7, 108.1, 52.0, 45.7, 29.6, 17.9, 10.6; IR (neat): 2917, 1731, 1471, 1409, 1158, 963, 738 cm^{-1}; HRMS (EI) calc for $C_{16}H_{20}O_2N$ $(M+H)^+$ 258.1489 found 258.1490; M. P. 70-72 °C.

General procedure for the reaction between indoles and methyl vinyldiazoacetate:

To a flame-dried 25 mL flask containing Rh_2(*S*-biTISP)$_2$ (5.5 mg, 0.02 equiv.) and indoles (0.90 mmol, 6.0 equiv.) in 6 mL dried CH_2Cl_2 under argon atmosphere was added a solution of fresh purified *trans*-methyl vinyldiazoacetate (**1b**) (21.0 mg, 0.15 mmol, 1.0 equiv.) in 6 mL dried CH_2Cl_2 by syringe pump over 3 h at -45 °C. The solution was warmed up to room temperature over night. The mixture was concentrated under reduced pressure and purified by flash chromatography on silica gel (pentane/Et_2O) to provide the corresponding products as colorless oil or powder.

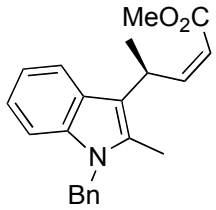


(*S*,*Z*)-methyl 4-(2-methyl-1*H*-indol-3-yl)pent-2-enoate (13):

Derived from 2-methylindole (**S-1**) (118.0 mg, 0.90 mmol, 6.0 equiv.) and *trans*-methyl vinyldiazoacetate **(1b)** (21 mg, 0.15 mmol, 1.0 equiv.), and purified by flash

chromatography on silica gel (7/3 pentane/Et_2O, R_f: 0.41) to provide product **13** as a colorless powder (24.6 mg, 67% yield).

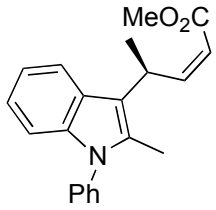
Spectroscopic data on the purified products was consistent with reported value.[1] HPLC: (AD-H, 3% isopropanol in hexane, 0.7 mL/min) retention times of 26.4 (major) and 30.4 (minor), 82% ee; $[\alpha]^{25}_D$ 324.6 (*c* = 0.30, $CHCl_3$).



(*S*,*Z*)-methyl 4-(1-benzyl-2-methyl-1*H*-indol-3-yl)pent-2-enoate (14):

Derived from 1-benzyl-2-methyl-1H-indole (**S-2**) (199 mg, 0.90 mmol, 6.0 equiv.) and *trans*-methyl vinyldiazoacetate (**1b)** (21 mg, 0.15 mmol, 1.0 equiv.), and purified by flash chromatography on silica gel (9/1 pentane/Et_2O, R_f: 0.42) to provide product **14** as colorless oil (37.0 mg, 74% yield).

Spectroscopic data on the purified products was consistent with reported value.[1] HPLC: (AD-H, 1% isopropanol in hexane, 0.7 mL/min) retention times of 8.9 (major) and 13.1 (minor), 90% ee; $[\alpha]^{25}_D$ 305.5 (*c* = 0.73, $CHCl_3$).

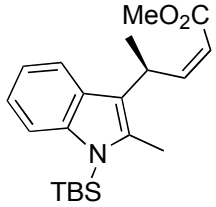


(*S*,*Z*)-methyl 4-(2-methyl-1-phenyl-1*H*-indol-3-yl)pent-2-enoate (15):

Derived from 1-phenyl-2-methyl-1H-indole (**S-3**) (187 mg, 0.90 mmol, 6.0 equiv.) and *trans*-methyl vinyldiazoacetate (**1b)** (21 mg, 0.15 mmol, 1.0 equiv.), and purified by flash chromatography on silica gel (10/1 pentane/Et_2O, R_f: 0.44) to provide product **15** as colorless oil (38.6 mg, 81% yield).

^{1}H NMR (400 MHz, $CDCl_3$): 7.72-7.76 (m, 1H), 7.49-7.55 (m, 2H), 7.41-7.47 (m, 1H), 7.31-7.34 (m, 1H), 7.05-7.14 (m, 3H), 6.84 (t, *J* = 11.0 Hz, 1H), 5.74 (dm, *J* = 11.0 Hz,

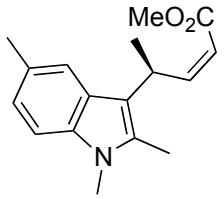
1H), 5.20-5.28 (m, 1H), 3.74 (s, 3H), 2.30 (s, 3H), 1.61 (d, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 166.8, 153.8, 138.0, 137.8, 133.1, 129.4, 128.3, 127.6, 126.2, 120.9, 119.4, 119.0, 116.5, 114.6, 110.3, 51.1, 30.6, 20.8, 11.3; IR (neat): 1717, 1500, 1368, 1175, 823, 739, 699 cm^{-1}; HRMS (APCI) calc for $C_{21}H_{22}O_2N$ $(M+H)^+$ 320.1645 found 320.1649; HPLC: (OD-H, 0.5% isopropanol in hexane, 0.5 mL/min) retention times of 10.2 (major) and 10.9 (minor), 94% ee; $[\alpha]^{25}_D$ 246.4 (c = 1.22, $CHCl_3$).



(*S*,*Z*)-methyl 4-(1-(*tert*-butyldimethylsilyl)-2-methyl-1*H*-indol-3-yl)pent-2-enoate (16):

Derived from 1-(*tert*-butyldimethylsilyl)-2-methyl-1*H*-indole (**S-4**) (221 mg, 0.90 mmol, 6.0 equiv.) and *trans*-methyl vinyldiazoacetate (**1b)** (21 mg, 0.15 mmol, 1.0 equiv.), and purified by flash chromatography on silica gel (20/1 pentane/Et_2O, R_f: 0.38) to provide product **16** as colorless oil (44.6 mg, 83% yield).

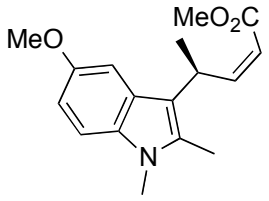
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65-7.71 (m, 1H), 7.50-7.55 (m, 1H), 7.06-7.10 (m, 2H), 6.83 (dd, J = 11.3, 10.4 Hz, 1H), 5.72 (dd, J = 11.3, 1.2 Hz, 1H), 5.14-5.22 (m, 1H), 3.74 (s, 3H), 2.49 (s, 3H), 1.57 (d, J = 7.0 Hz, 3H), 0.99 (s, 9H), 0.67 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.7, 153.8, 141.9, 137.8, 129.4, 120.0, 119.0, 118.7, 117.8, 116.6, 114.4, 51.0, 30.5, 26.8, 20.6, 20.5, 14.7, 0.0; IR (neat): 2952, 2930, 1720, 1472, 1272, 1193, 1174, 1001, 821, 785, 736 cm^{-1}; HRMS (APCI) calc. for $C_{21}H_{32}O_2NSi$ $(M+H)^+$ 358.2197 found 358.2196. HPLC: (OA-2000, hexane, 0.5 mL/min) retention times of 14.4 (major) and 15.3 (minor), 94% ee; $[\alpha]^{25}_D$ 247.5 (c = 0.82, $CHCl_3$).



(*S*,*Z*)-methyl 4-(1,2,5-trimethyl-1*H*-indol-3-yl)pent-2-enoate (17):

Derived from 1,2,5-trimethyl-1*H*-indole (**S-5**) (143 mg, 0.90 mmol, 6.0 equiv.) and *trans*-methyl vinyldiazoacetate (**1b)** (21 mg, 0.15 mmol, 1.0 equiv.), and purified by flash chromatography on silica gel (85/15 pentane/Et_2O, R_f: 0.49) to provide product **17** as colorless oil (28.6 mg, 70% yield).

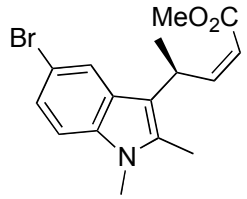
^{1}H NMR (400 MHz, $CDCl_3$): 7.46 (s, 1H), 7.15 (d, *J* = 8.2 Hz, 1H), 6.97 (d, *J* = 8.2 Hz, 1H), 6.80 (t, *J* = 11.4 Hz, 1H), 5.68 (d, *J* = 11.4 Hz, 1H), 5.10-5.18 (m, 1H), 3.74 (s, 3H), 3.61 (s, 3H), 2.46 (s, 3H), 2.42 (s, 3H), 1.55 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 165.8, 154.3, 135.3, 132.9, 127.7, 125.9, 121.8, 116.0, 112.7, 108.6, 51.0, 30.6, 29.5, 21.6, 21.0, 10.5; IR (neat): 1715, 1644, 1436, 1370, 1197, 1181, 1111, 822, 800 cm^{-1}; HRMS (APCI) calc for $C_{17}H_{22}O_2N$ $(M+H)^+$ 272.1645 found 272.1646; HPLC: (AD-H, 1% isopropanol in hexane, 0.7 mL/min) retention times of 7.9 (major) and 10.5 (minor), 88 % ee; $[\alpha]^{25}_D$ 354.1 (*c* = 1.13, $CHCl_3$).



(*S*,*Z*)-Methyl 4-(5-methoxy-1,2-dimethyl-1*H*-indol-3-yl)pent-2-enoate (18):

Derived from 5-methoxy-1,2-dimethyl-1H-indole (**S-6**) (158 mg, 0.90 mmol, 6.0 equiv.) and *trans*-methyl vinyldiazoacetate **(1b)** (21 mg, 0.15 mmol, 1.0 equiv.), and purified by flash chromatography on silica gel (85/15 pentane/Et_2O, R_f: 0.28) to provide product **18** as a colorless powder (31.0 mg, 72% yield).

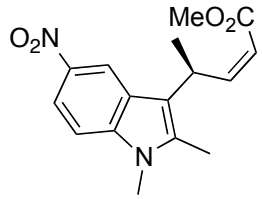
Spectroscopic data on the purified products was consistent with reported value.[1] HPLC: (AD-H, 1% isopropanol in hexane, 0.7 mL/min) retention times of 15.4 (major) and 22.1 (minor), 86 % ee; $[\alpha]^{25}_D$ 377.6 (*c* = 0.52, $CHCl_3$).



(*S*,*Z*)-methyl 4-(5-bromo-1,2-dimethyl-1*H*-indol-3-yl)pent-2-enoate (19):

Derived from 5-bromo-1,2-dimethyl-1H-indole (**S-7**) (202 mg, 0.90 mmol, 6.0 equiv.) and *trans*-methyl vinyldiazoacetate **(1b)** (21 mg, 0.15 mmol, 1.0 equiv.), and purified by flash chromatography on silica gel (85/15 pentane/Et_2O, R_f: 0.34) to provide product **19** as a colorless powder (40.8 mg, 81% yield).

^{1}H NMR (400 MHz, $CDCl_3$): 7.78 (d, *J* = 1.8 Hz, 1H), 7.21 (dd, *J* = 8.8, 1.8 Hz, 1H), 7.10 (d, *J* = 8.6 Hz, 1H), 6.70 (dd, *J* = 11.6, 10.7 Hz, 1H), 5.70 (dd, *J* = 11.3, 0.9 Hz, 1H), 5.09-5.18 (m, 1H), 3.73 (s, 3H), 3.61 (s, 3H), 2.43 (s, 3H), 1.52 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 166.7, 153.5, 135.6, 134.3, 127.5, 123.0, 121.5, 116.6, 113.2, 111.9, 110.3, 51.1, 30.3, 29.6, 20.9, 10.6; IR (neat): 2948, 1716, 1473, 1435, 1174, 825, 789 cm^{-1}; HRMS (APCI) calc for $C_{16}H_{19}O_2NBr$ $(M+H)^+$ 336.0594 found 336.0598; M. P.: 103-105 °C; HPLC: (OJ, 3% isopropanol in hexane, 1.0 mL/min) retention times of 11.9 (major) and 15.8 (minor), 88% ee; $[\alpha]^{25}_D$ 299.3 (*c* = 0.97, $CHCl_3$).

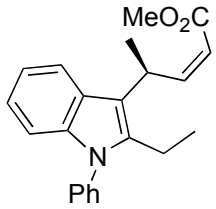


(*S*,*Z*)-methyl 4-(1,2-dimethyl-5-nitro-1*H*-indol-3-yl)pent-2-enoate (20):

Derived from 5-nitro-1,2-dimethyl-1H-indole (**S-8**) (171 mg, 0.90 mmol, 6.0 equiv.) and *trans*-methyl vinyldiazoacetate **(1b)** (21 mg, 0.15 mmol, 1.0 equiv.) at -20 °C, and purified by flash chromatography on silica gel (7/3 pentane/Et_2O, R_f: 0.22) to provide product **20** as a yellowish powder (21.6 mg, 48% yield).

^{1}H NMR (400 MHz, $CDCl_3$): 8.60 (d, *J* = 2.1 Hz, 1H), 8.04 (dd, *J* = 9.2, 2.2 Hz, 1H), 7.25 (d, *J* = 2.2 Hz, 1H), 6.72 (dd, *J* = 11.3, 10.7 Hz, 1H), 5.75 (dd, *J* = 11.3, 0.9 Hz, 1H), 5.14-5.21 (m, 1H), 3.73 (s, 3H), 3.69 (s, 3H), 2.48 (s, 3H), 1.55 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 166.6, 152.8, 140.8, 139.8, 136.6, 125.1, 117.3, 116.4, 116.3,

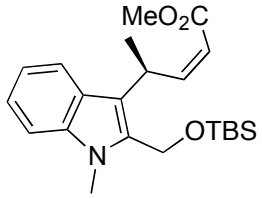
116.2, 108.5, 51.2, 30.2, 30.1, 21.1, 10.8; IR (neat): 2950, 1716, 1512, 1485, 1329, 1195, 1176, 825, 740 cm^{-1}; HRMS (APCI) calc for $C_{16}H_{19}O_4N_2$ $(M+H)^+$ 303.1339 found 303.1339; M. P.: 134-136 °C; HPLC: (AD-H, 10% isopropanol in hexane, 1.0 mL/min) retention times of 14.9 (major) and 15.7 (minor), 87% ee; $[\alpha]^{25}_D$ 287.6 (*c* = 1.56, $CHCl_3$).



(*S*,*Z*)-methyl 4-(2-ethyl-1-phenyl-1*H*-indol-3-yl)pent-2-enoate (21):

Derived from 1-phenyl-2-ethyl-1H-indole (**S-9**) (199 mg, 0.90 mmol, 6.0 equiv.) and *trans*-methyl vinyldiazoacetate (**1b)** (21 mg, 0.15 mmol, 1.0 equiv.), and purified by flash chromatography on silica gel (10/1 pentane/Et_2O, R_f: 0.50) to provide product **21** as colorless oil (43.1 mg, 86% yield).

^{1}H NMR (400 MHz, $CDCl_3$): 7.74-7.78 (m, 1H), 7.50-7.56 (m, 2H), 7.43-7.49 (m, 1H), 7.33-7.39 (m, 1H), 7.05-7.15 (m, 2H), 6.99-7.04 (m, 1H), 6.90 (t, *J* = 10.5 Hz, 1H), 5.74 (dd, *J* = 11.3, 0.8 Hz, 1H), 5.21-5.29 (m, 1H), 3.75 (s, 3H), 2.65-2.85 (m, 2H), 1.64 (d, *J* = 7.0 Hz, 3H), 0.96 (t, *J* = 7.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 166.8, 154.0, 139.5, 138.2, 138.0, 129.4, 128.6, 127.9, 126.0, 120.9, 119.3, 119.2, 116.4, 113.9, 110.4, 51.1, 30.6, 21.1, 18.0, 14.9; IR (neat): 2968, 1719, 1597, 1499, 1458, 1370, 1177, 824, 742, 700 cm^{-1}; HRMS (APCI) calc for $C_{22}H_{24}O_2N$ $(M+H)^+$ 334.1802 found 334.1801; HPLC: (AD-H, hexane, 1.0 mL/min) retention times of 9.0 (major) and 9.7 (minor), 94% ee; $[\alpha]^{25}_D$ 276.2 (*c* = 1.36, $CHCl_3$).

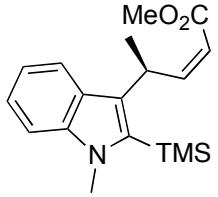


(*S*,*Z*)-methyl 4-(2-(((*tert*-butyldimethylsilyl)oxy)methyl)-1-methyl-1*H*-indol-3-yl)pent-2-enoate (22):

Derived from 2-((*tert*-butyldimethylsilyloxy)methyl)-1-methyl-1H-indole (**S-10**) (248

mg, 0.90 mmol, 6.0 equiv.) and *trans*-methyl vinyldiazoacetate **(1b)** (21 mg, 0.15 mmol, 1.0 equiv.), and purified by flash chromatography in silica gel (30/1 pentane/Et_2O, R_f: 0.35) to provide product **22** as a colorless powder (37.2 mg, 64% yield).

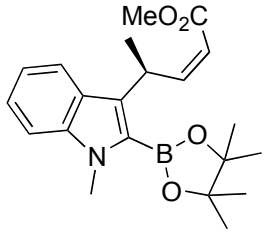
Spectroscopic data on the purified products was consistent with reported value.[1] HPLC: (OD, 0.5% isopropanol in hexane, 0.7 mL/min) retention times of 13.9 (minor) and 16.2 (major), 91% ee; $[\alpha]^{25}_D$ 237.3 (*c* = 0.76, $CHCl_3$).



(*S*,*Z*)-methyl 4-(1-methyl-2-(trimethylsilyl)-1*H*-indol-3-yl)pent-2-enoate (23):

Derived from 1-methyl-2-(trimethylsilyl)-1*H*-indole (**S-11**) (199 mg, 0.90 mmol, 6.0 equiv.) and *trans*-methyl vinyldiazoacetate (**1b**) (21 mg, 0.15 mmol, 1.0 equiv.), and purified by flash chromatography on silica gel (20/1 pentane/Et_2O, R_f: 0.46) to provide product **23** as colorless oil (34.8 mg, 74% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77 (d, *J* = 8.2 Hz, 1H), 7.33 (d, *J* = 8.4 Hz, 1H), 7.23 (t, *J* = 7.6 Hz, 1H), 7.08 (t, *J* = 7.9 Hz, 1H), 7.00 (dd, *J* = 11.4, 9.8 Hz, 1H), 5.74 (dd, *J* = 11.4, 0.8 Hz, 1H), 5.15-5.24 (m, 1H), 3.81 (s, 3H), 3.76 (s, 3H), 1.61 (d, *J* = 7.0 Hz, 3H), 0.48 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.4, 154.4, 140.5, 136.1, 127.6, 125.7, 122.0, 120.4, 118.4, 117.1, 109.6, 51.1, 33.3, 32.1, 22.1, 1.6; IR (neat): 2950, 1719, 1405, 1250, 1193, 1174, 839, 738 cm^{-1}; HRMS (APCI) calc. for $C_{18}H_{26}O_2NSi$ $(M+H)^+$ 316.1727 found 316.1728; HPLC: (OD-H, hexane, 1.0 mL/min) retention times of 4.9 (major) and 6.1 (minor), 92% ee; $[\alpha]^{25}_D$ 189.9 (*c* = 0.91, $CHCl_3$).



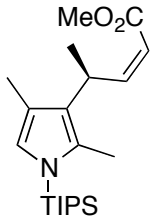
(*S*,*Z*)-methyl 4-(1-methyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-indol-3-yl)pent-2-enoate (23):

Derived from 1-methyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-indole (**S-12**) (231 mg, 0.90 mmol, 6.0 equiv.) and *trans*-methyl vinyldiazoacetate (**1b)** (21 mg, 0.15 mmol, 1.0 equiv.) at -20 °C, and purified by flash chromatography on silica gel (10/1 pentane/Et_2O, R_f: 0.39) to provide product **23** as colorless oil (45.6 mg, 82% yield).

^1H NMR (400 MHz, $CDCl_3$): δ 7.84 (d, *J* = 8.2 Hz, 1H), 7.32 (d, *J* = 8.4 Hz, 1H), 7.26 (t, *J* = 7.4 Hz, 1H), 7.09 (t, *J* = 7.4 Hz, 1H), 6.93 (dd, *J* = 11.4, 10.2 Hz, 1H), 5.69 (d, *J* = 11.4 Hz, 1H), 5.51-5.61 (m, 1H), 3.93 (s, 3H), 3.74 (s, 3H), 1.61 (d, *J* = 7.4 Hz, 3H), 1.39 (s, 6H), 1.38 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.5, 154.7, 140.1, 131.1, 126.1, 123.1, 120.9, 118.6, 116.6, 109.9, 83.5, 50.9, 32.2, 31.3, 24.83, 24.79, 21.8; IR (neat): 2976, 1723, 1525, 1391, 1299, 1260, 1172, 1138, 847, 823, 742 cm^{-1}; HRMS (APCI) calc. for $C_{21}H_{29}O_4NB$ $(M+H)^+$ 370.2184 found 370.2185; HPLC: (AD-H, 3% isopropanol in hexane, 1.0 mL/min) retention times of 9.3 (major) and 12.4 (minor), 94% ee; $[\alpha]^{25}_D$ 172.0 (*c* = 1.60, $CHCl_3$).

General procedure for the reaction between pyrroles and methyl vinyldiazoacetate:

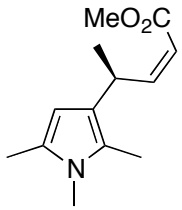
To a flame-dried 25 mL flask containing Rh_2(*S*-biTISP)$_2$ (5.5 mg, 0.02 equiv.) and indoles (0.90 mmol, 6.0 equiv.) in 6 mL dried CH_2Cl_2 under argon atmosphere was added a solution of fresh purified *trans*-methyl vinyldiazoacetate (**1b**) (21.0 mg, 0.15 mmol, 1.0 equiv.) in 6 mL dried CH_2Cl_2 by syringe pump over 3 h at -20 °C. The solution was warmed up to room temperature over night. The mixture was concentrated under reduced pressure and purified by flash chromatography on silica gel (pentane/Et_2O with 0.5% Et_3N) to provide the corresponding products as colorless oil or powder.



(*S*,*Z*)-Methyl 4-(2,4-dimethyl-1-(triisopropylsilyl)-1*H*-pyrrol-3-yl)pent-2-enoate (25):

Derived from 1-triisopropylsilyl-2,4-dimethylpyrrole (**S-13**) (226 mg, 0.90 mmol, 6.0 equiv.) and *trans*-methyl vinyldiazoacetate **(1b)** (21 mg, 0.15 mmol, 1.0 equiv.), and purified by flash chromatography on silica gel (40/1 pentane/Et_2O, R_f: 0.38) to provide product **25** as a colorless oil (35.6 mg, 65% yield).

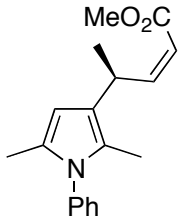
Spectroscopic data on the purified products was consistent with reported value.[1] HPLC: (OD, 0.2% isopropanol in hexane, 0.7 mL/min) retention times of 16.9 (minor) and 25.3 (major), 91% ee; $[\alpha]^{25}_D$ 194.6 (*c* = 1.63, $CHCl_3$).



(*S*,*Z*)-Methyl 4-(1,2,5-trimethyl-1*H*-pyrrol-3-yl)pent-2-enoate (26):

Derived from 1,2,5-trimethylpyrrole (**S-14**) (98.2 mg, 0.90 mmol, 6.0 equiv.) and *trans*-methyl vinyldiazoacetate (**1b**) (21 mg, 0.15 mmol, 1.0 equiv.), and purified by flash chromatography in silica gel (9/1 pentane/Et_2O, containing 0.5% Et_3N, R_f: 0.45) to provide **26** as a colorless oil (15.3 mg, 46% yield).

Spectroscopic data on the purified products was consistent with reported value.[1] HPLC: (OD-H, 2% isopropanol in hexane, 0.7 mL/min) retention times of 9.8 (minor) and 16.4 (major), 87% ee; $[\alpha]^{25}_D$ 286.1 (*c* = 0.61, $CHCl_3$).

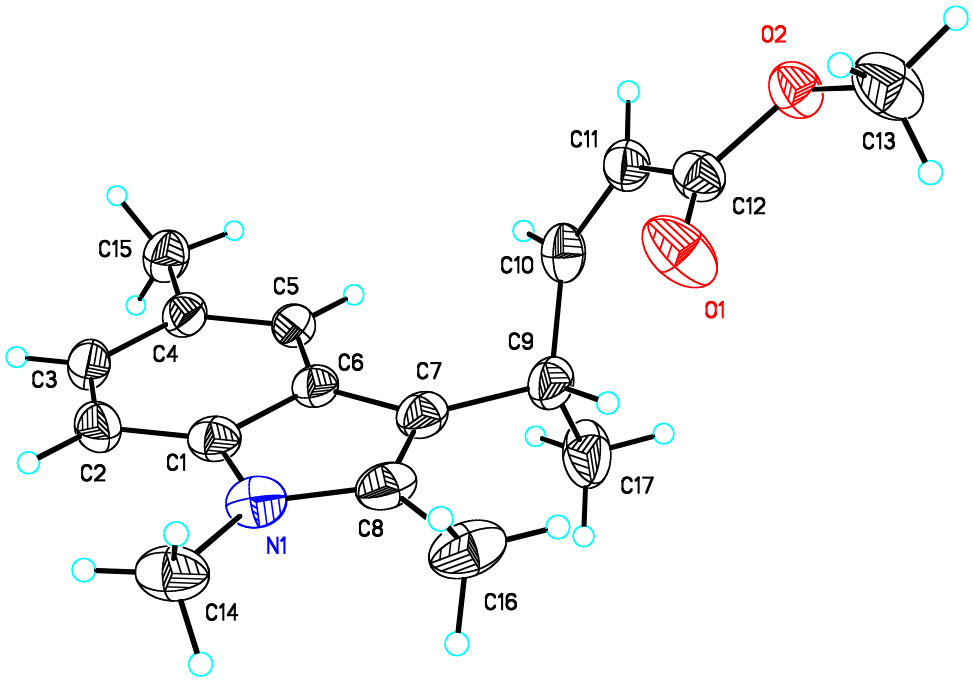


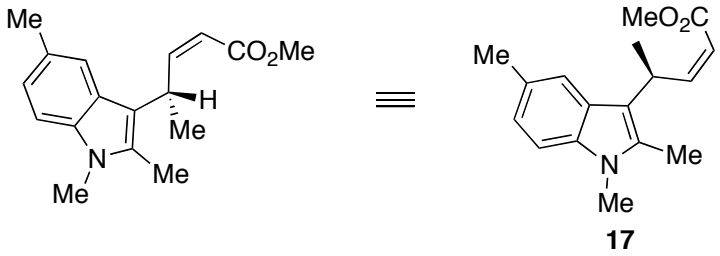
(*S*,*Z*)-methyl 4-(2,5-dimethyl-1-phenyl-1*H*-pyrrol-3-yl)pent-2-enoate (27):

Derived from 2,5-dimethyl-1-phenyl-1*H*-pyrrole (**S-15**) (154 mg, 0.90 mmol, 6.0 equiv.) and *trans*-methyl vinyldiazoacetate (**1b**) (21 mg, 0.15 mmol, 1.0 equiv.), and purified by flash chromatography in silica gel (10/1 pentane/Et_2O, containing 0.5% Et_3N, R_f: 0.55) to provide **27** as a colorless oil (30.8 mg, 72% yield).

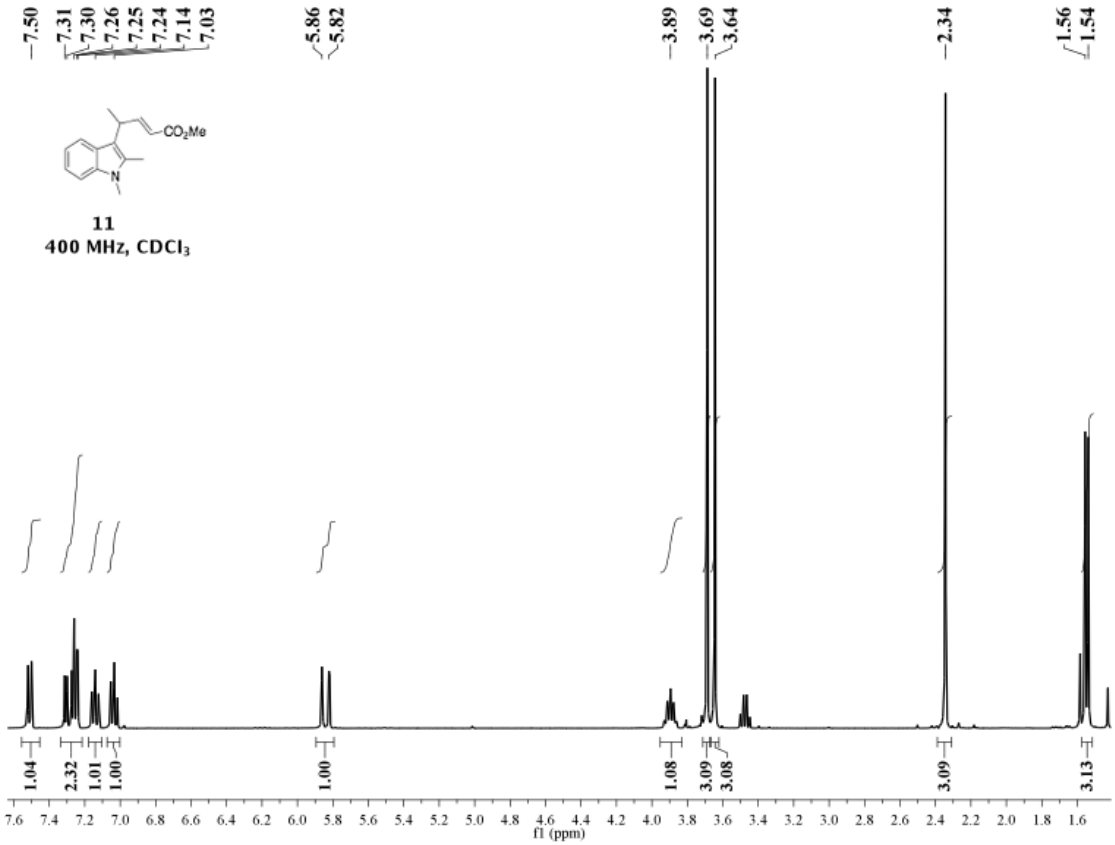
^{1}H NMR (400 MHz, $CDCl_3$): 7.82-7.87 (m, 2H), 7.36-7.41 (m, 1H), 7.19-7.23 (m, 2H), 6.30 (t, J = 11.0 Hz, 1H), 5.92 (s, 1H), 5.67 (dd, J = 11.0, 0.8 Hz, 1H), 4.82-4.91 (m, 1H), 3.73 (s, 3H), 2.04 (s, 3H), 1.97 (s, 3H), 1.37 (d, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 167.0, 155.4, 138.9, 128.9, 128.3, 127.9, 127.5, 125.1, 121.5, 115.1, 103.5, 51.0, 29.8, 21.1, 12.9, 10.7; IR (neat): 2921, 1718, 1499, 1404, 1193, 1174, 1008, 826, 766, 699 cm^{-1}; HRMS (APCI) calc for $C_{18}H_{22}O_2N$ $(M+H)^+$ 284.1645 found 284.1648; HPLC: (OJ, 1% isopropanol in hexane, 0.7 mL/min) retention times of 16.8 (major) and 18.8 (major), 89% ee; $[\alpha]^{25}_D$ 287.2 (c = 1.71, $CHCl_3$).

Crystal Structure of 17





17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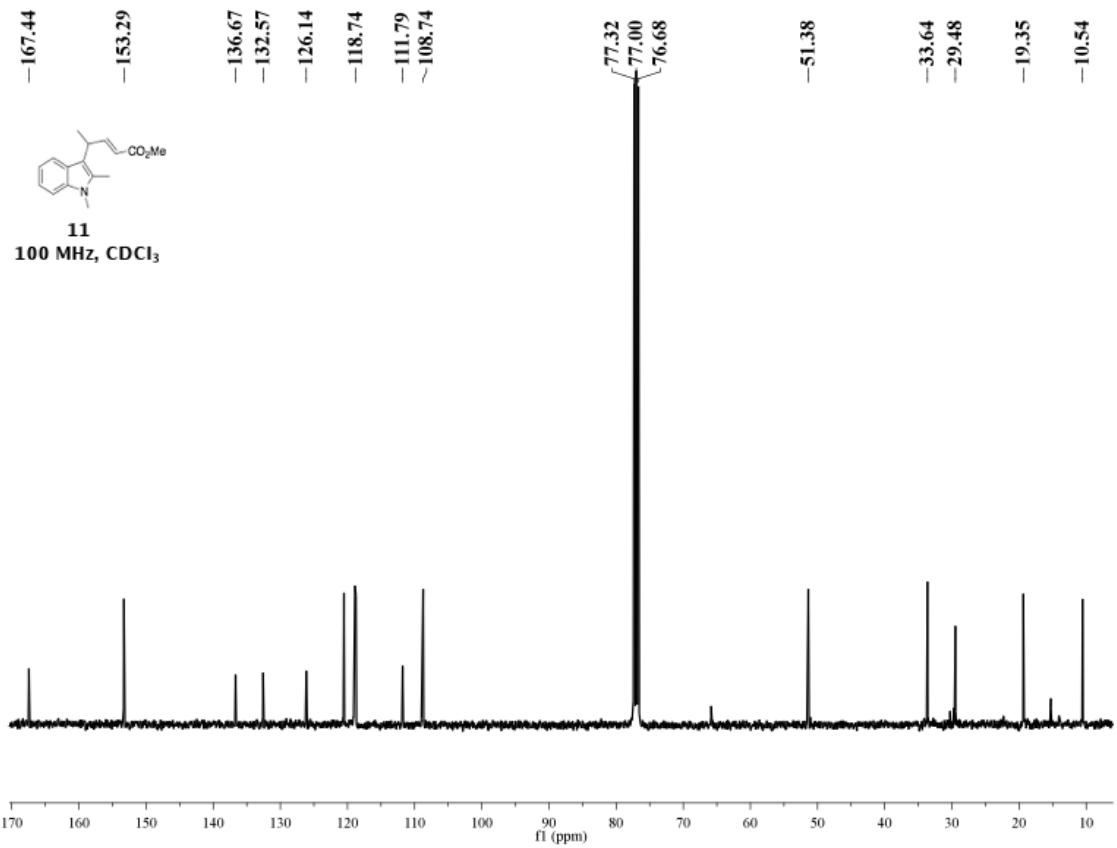
7.31
7.30
7.26
7.25
7.24
7.14
7.03
5.86
5.82
3.89
3.69
3.64
2.34
1.56
1.54
CO2Me
N
11
400 MHz, CDCl3
1.04
2.32
1.01
1.00
1.00
1.08
3.09
3.08
3.09
3.13
f1 (ppm)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153.29
136.67
132.57
126.14
118.74
111.79
108.74
77.32
77.00
76.68
51.38
33.64
29.48
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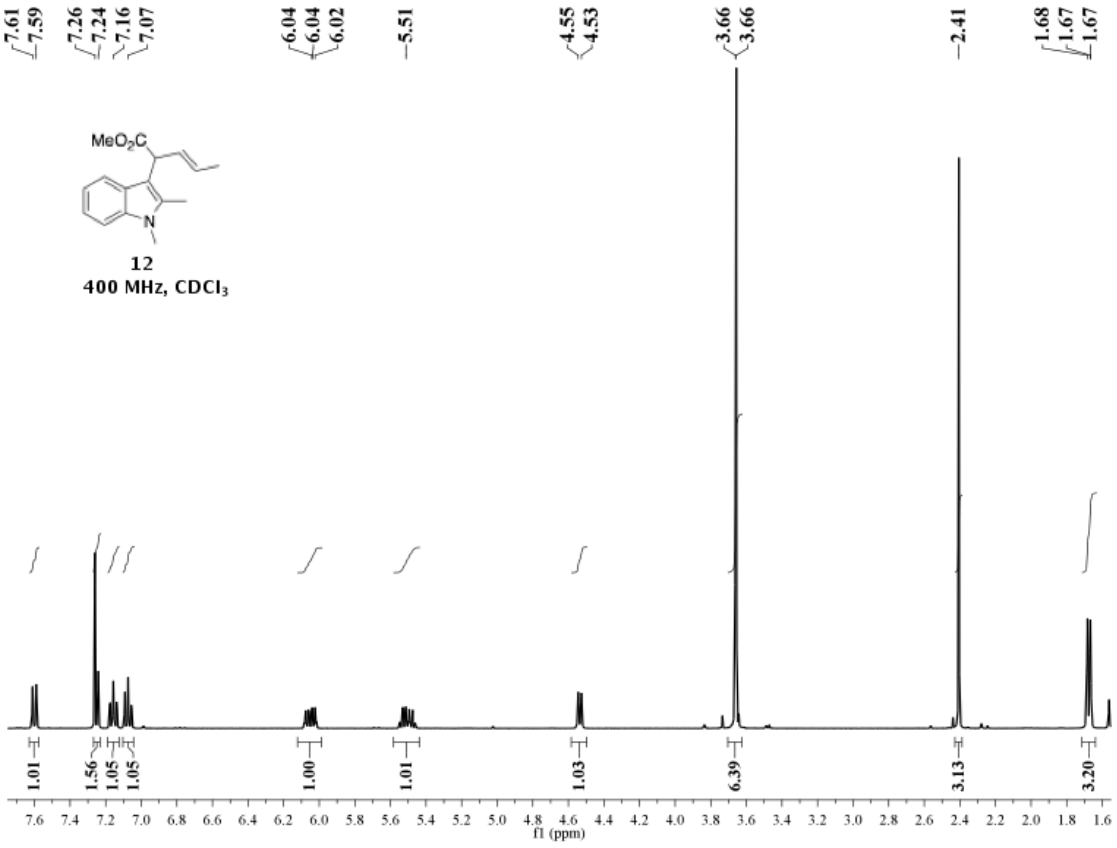
CO2Me
N
11
100 MHz, CDCl3
f1 (ppm)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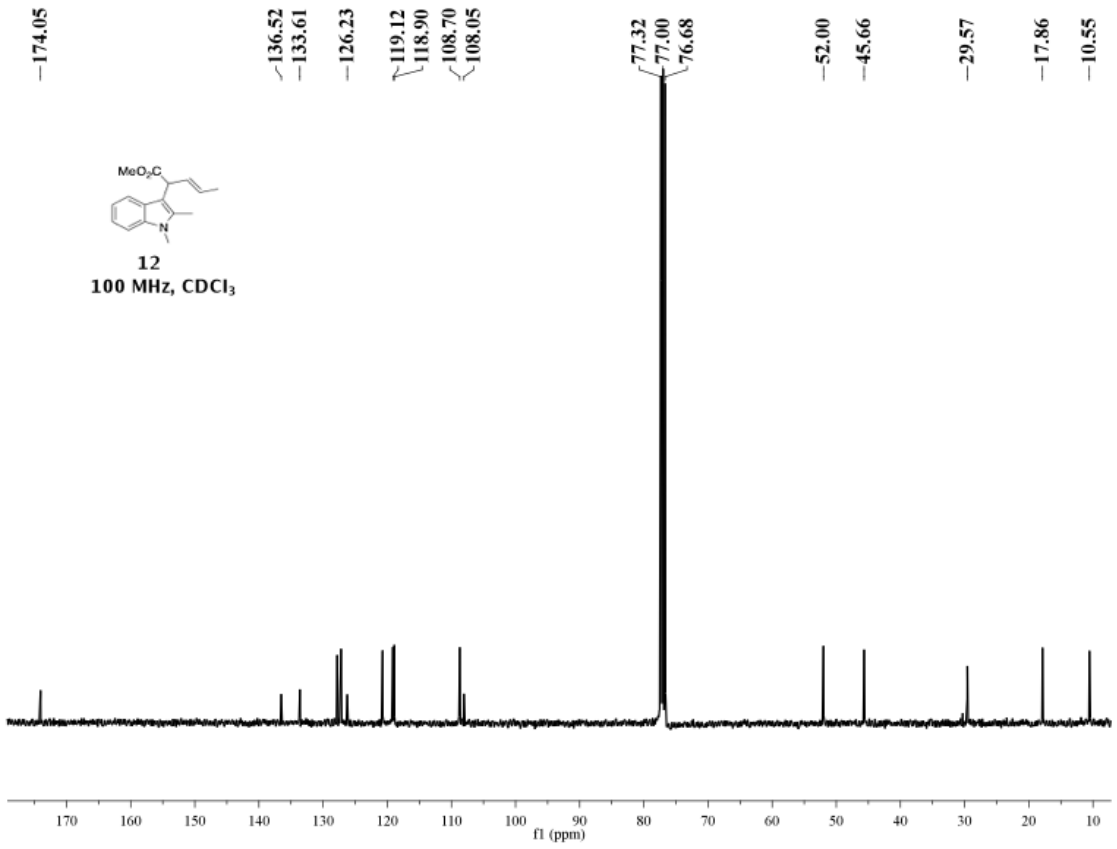
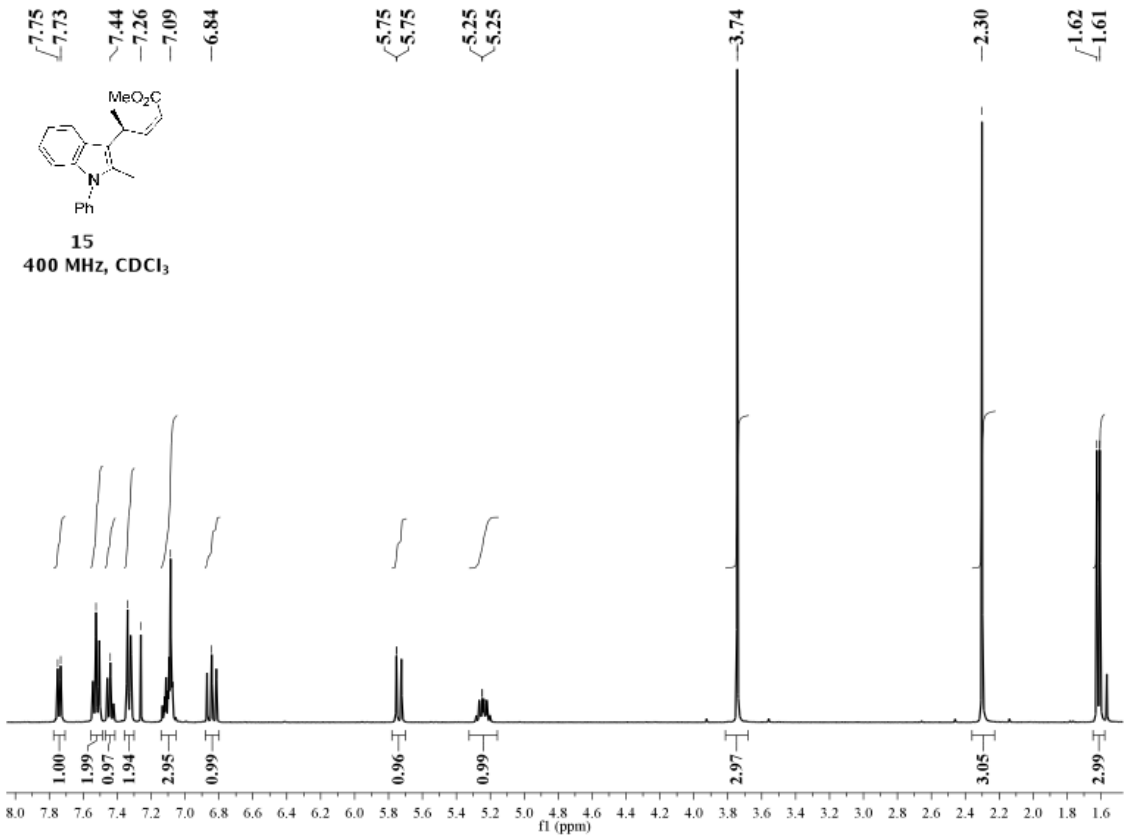
7.59
7.26
7.24
7.16
7.07
6.04
6.04
6.02
5.51
4.55
4.53
3.66
3.66
2.41
1.68
1.67
1.67
MeO2C
N
12
400 MHz, CDCl3
1.01
1.56
1.05
1.05
1.00
1.01
1.03
6.39
3.13
3.20
f1 (ppm)


174.05
136.52
133.61
126.23
119.12
118.90
108.70
108.05
77.32
77.00
76.68
52.00
45.66
29.57
17.86
10.55
MeO2C
N
12
100 MHz, CDCl3
f1 (ppm)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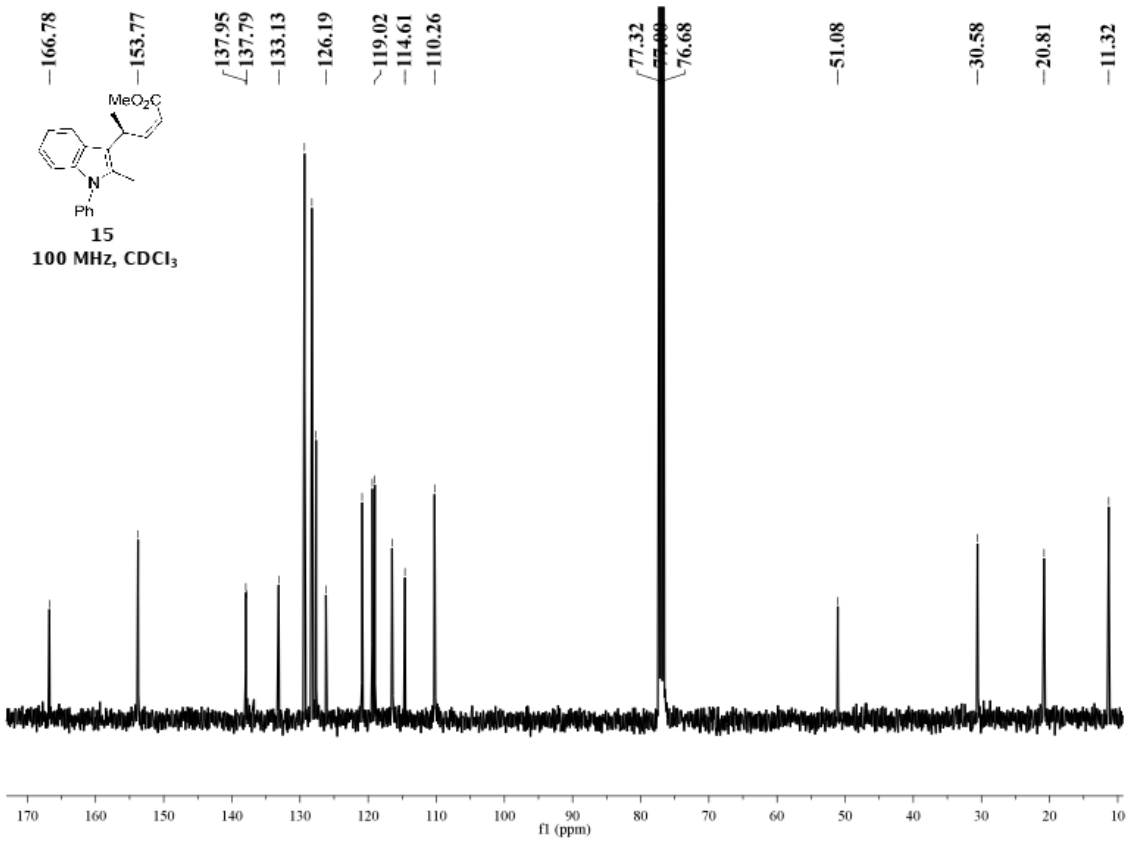
7.73
7.44
7.26
7.09
6.84
5.75
5.75
5.25
5.25
3.74
2.30
1.62
1.61
MeO2C
N
Ph
15
400 MHz, CDCl3
1.00
1.99
0.97
1.94
2.95
0.99
0.96
0.99
2.97
3.05
2.99
8.0 7.8 7.6 7.4 7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6
f1 (ppm)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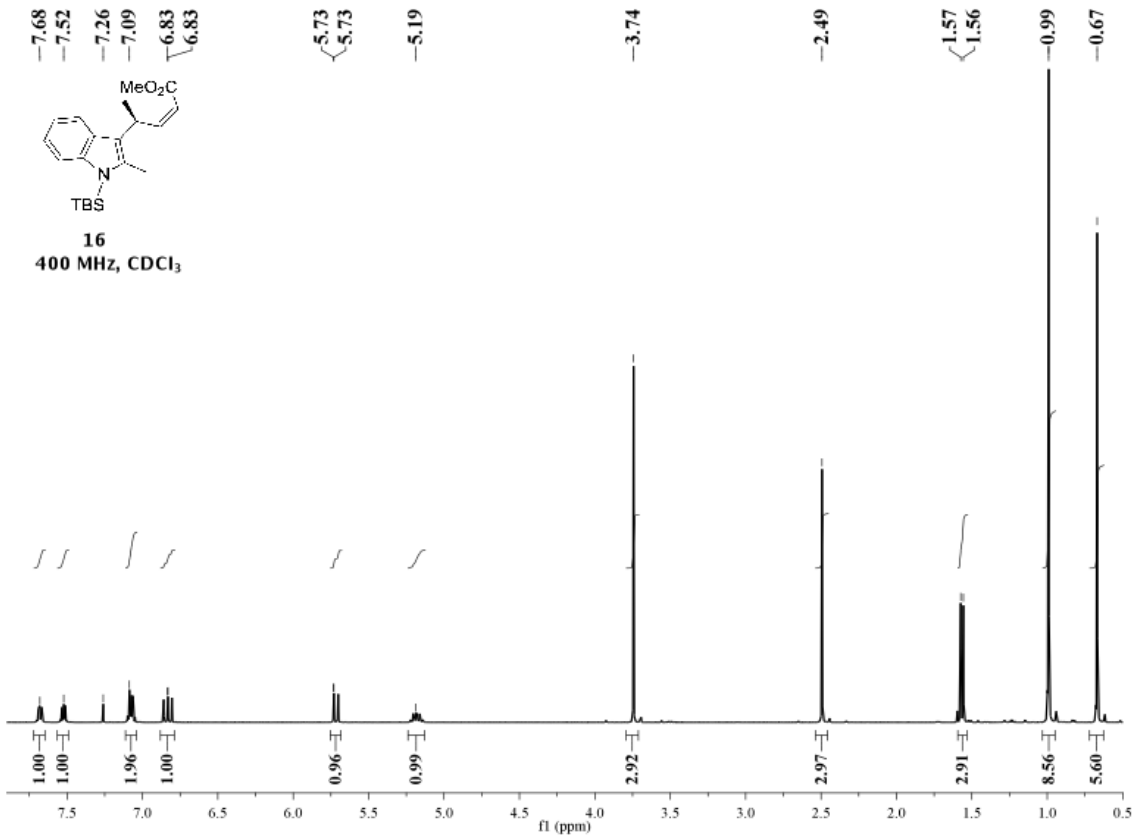
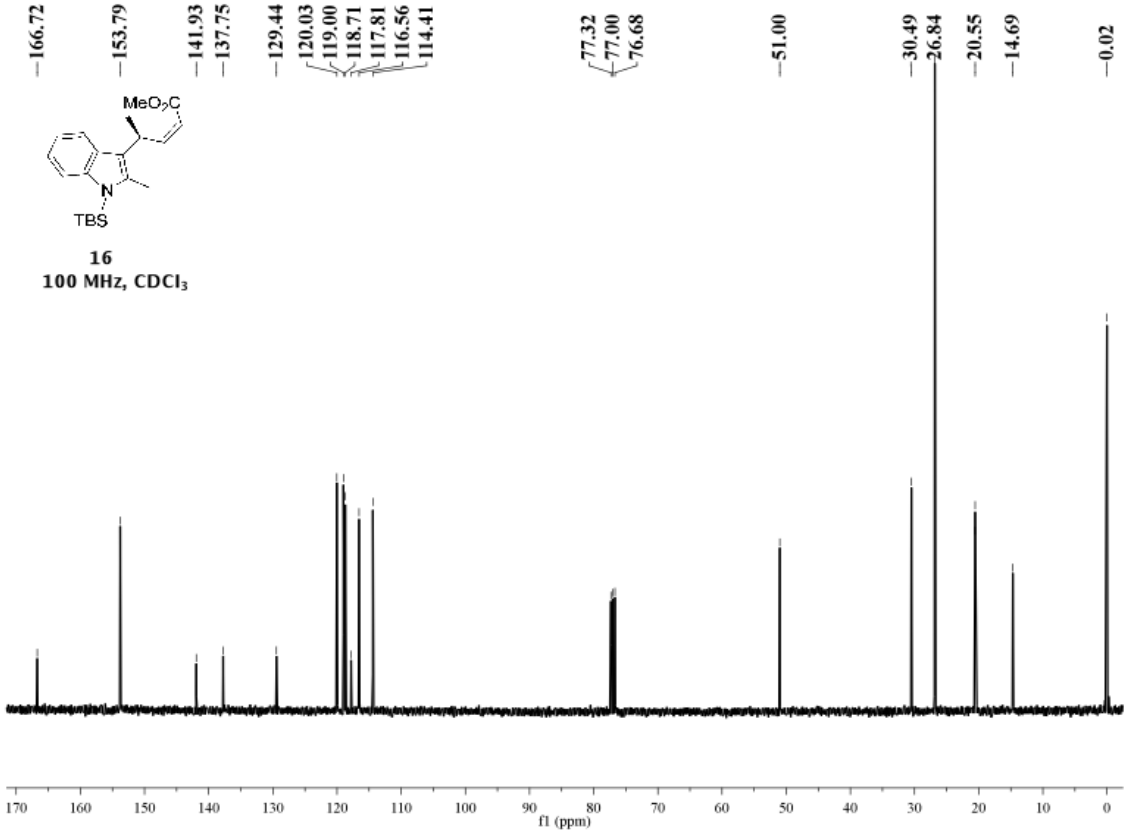
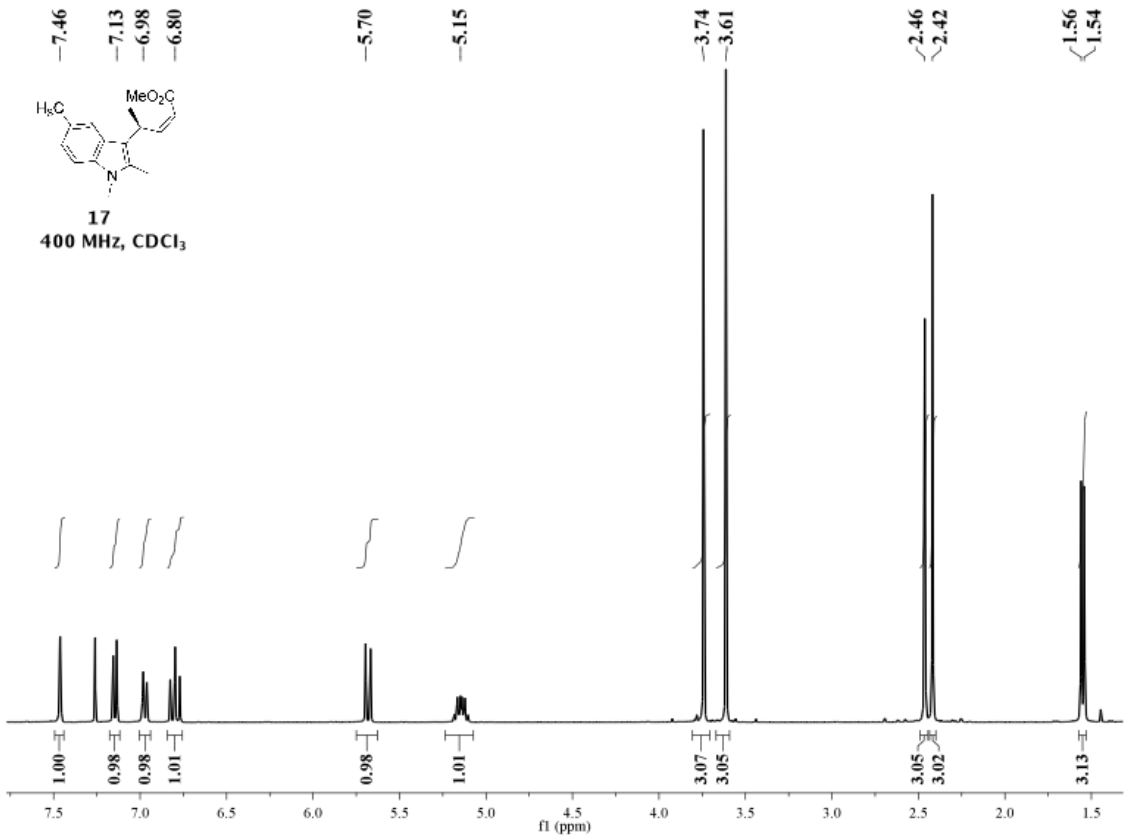
153.77
137.95
137.79
133.13
126.19
119.02
114.61
110.26
77.32
76.68
51.08
30.58
20.81
11.32
MeO2C
N
Ph
15
100 MHz, CDCl3
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

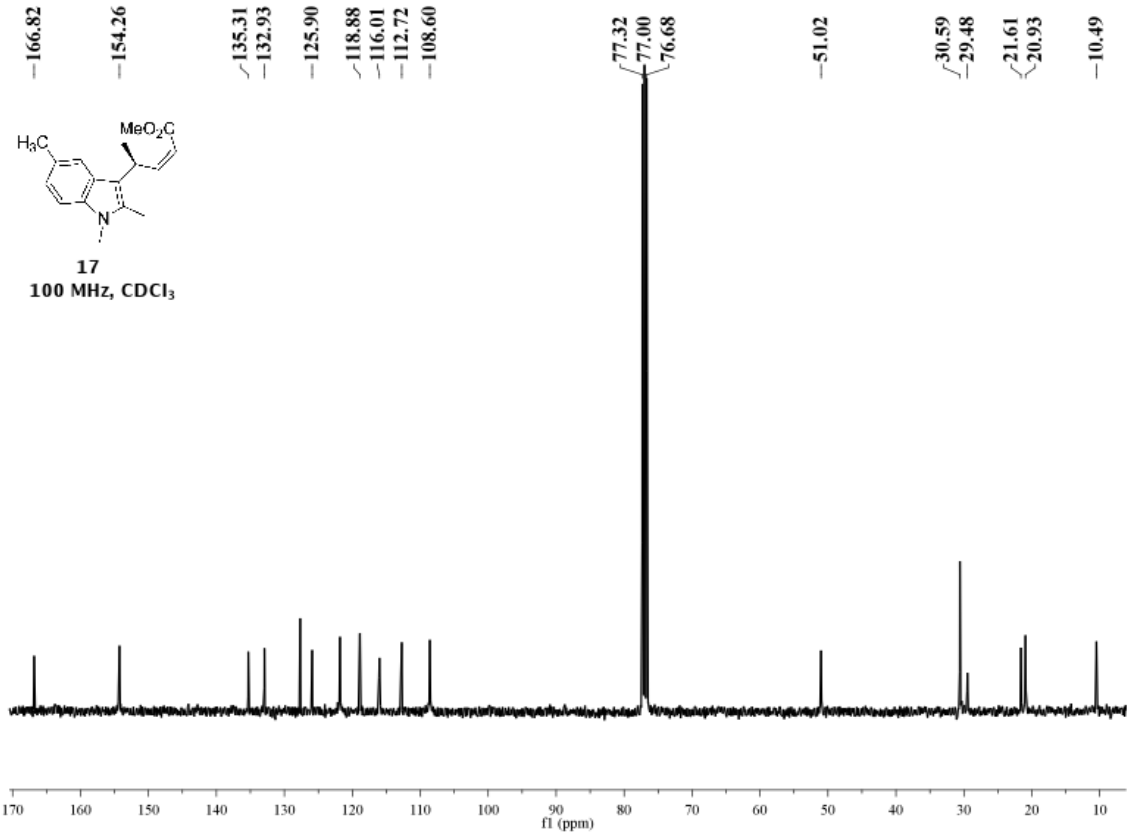


16
400 MHz, $CDCl_3$



16
100 MHz, $CDCl_3$


7.46
7.13
6.98
6.80
5.70
5.15
3.74
3.61
2.46
2.42
1.56
1.54
MeO2C
H3C
N
17
400 MHz, CDCl3
1.00
0.98
0.98
1.01
0.98
1.01
3.07
3.05
3.05
3.02
3.13
f1 (ppm)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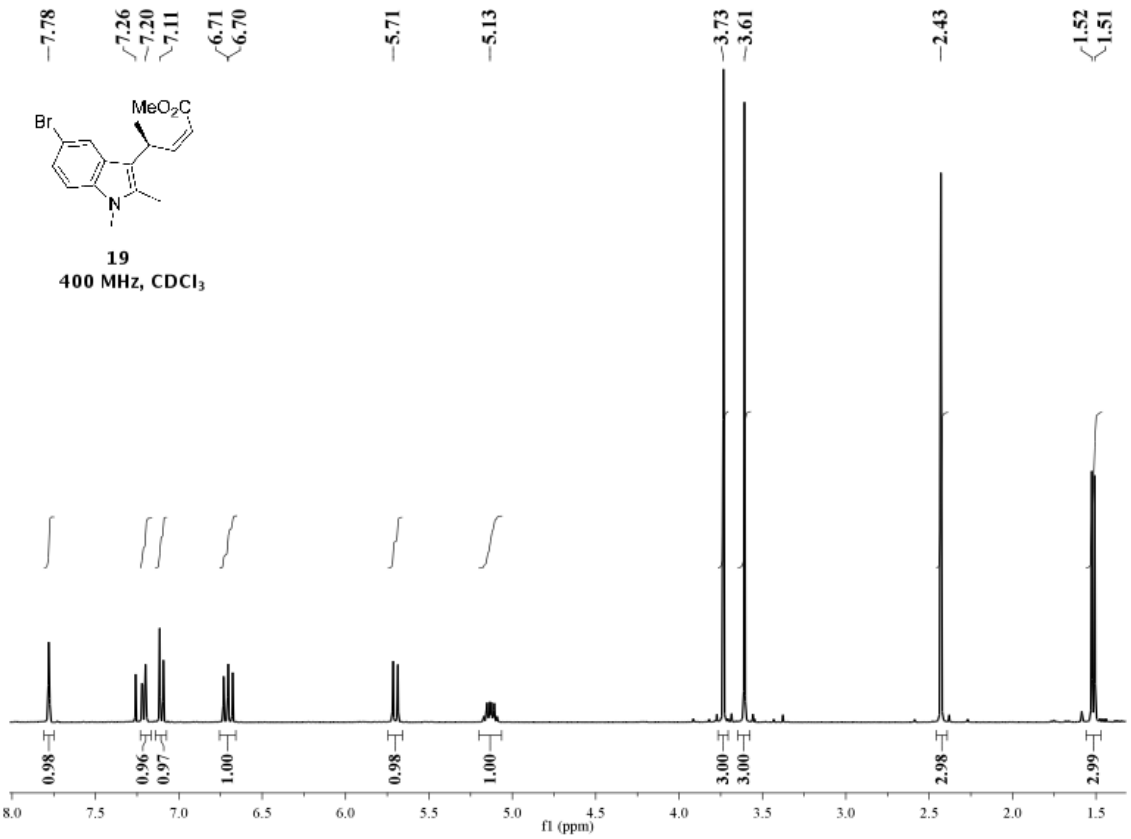
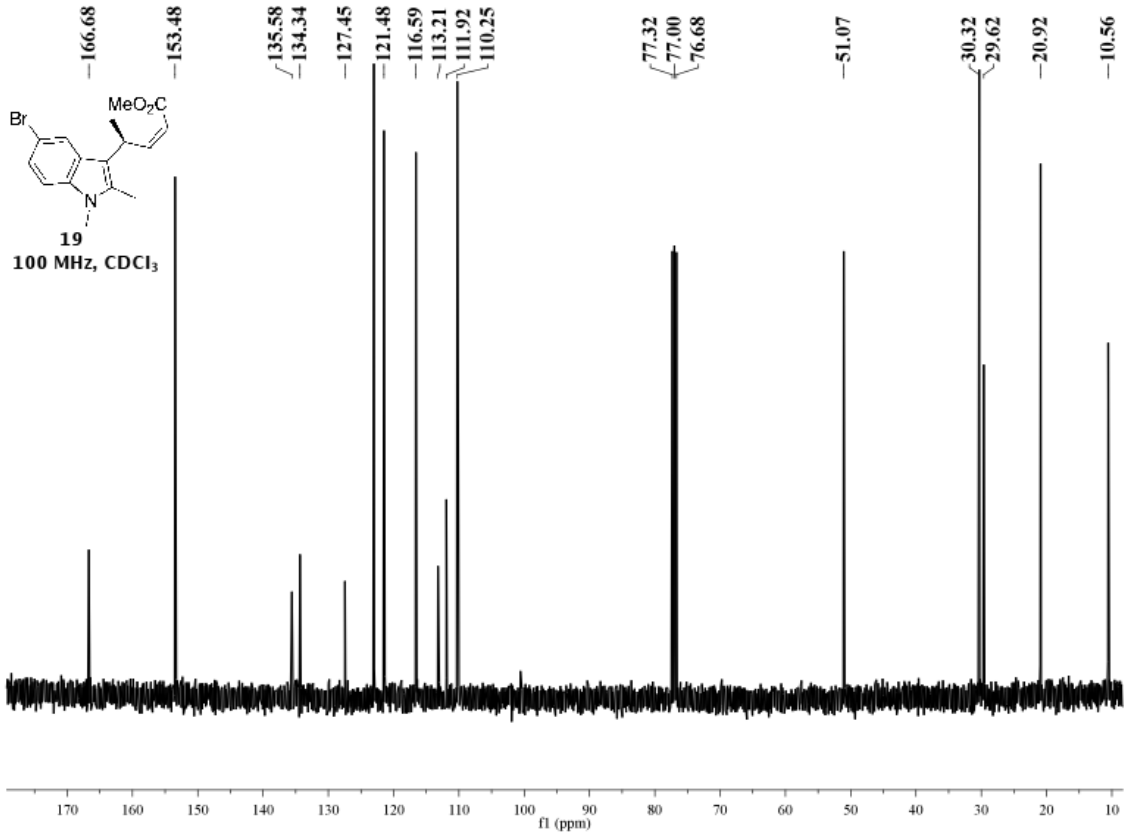
125.90
118.88
116.01
112.72
108.60
77.32
77.00
76.68
51.02
30.59
29.48
21.61
20.93
10.49
MeO2C
H3C
N
17
100 MHz, CDCl3
f1 (ppm)


7.78
7.26
7.20
7.11
6.71
6.70
5.71
5.13
3.73
3.61
2.43
1.52
1.51
Br
MeO2C
N
19
400 MHz, CDCl3
0.98
0.96
0.97
1.00
0.98
1.00
3.00
3.00
2.98
2.99
fl (ppm)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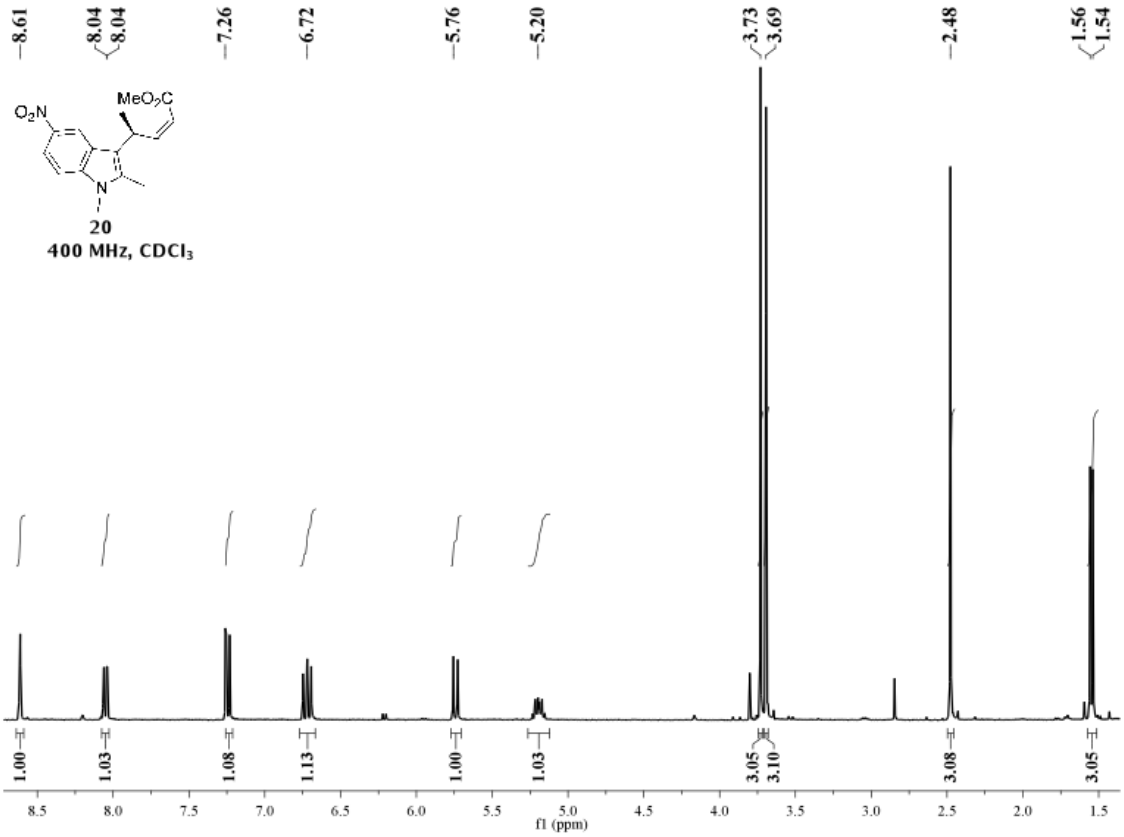
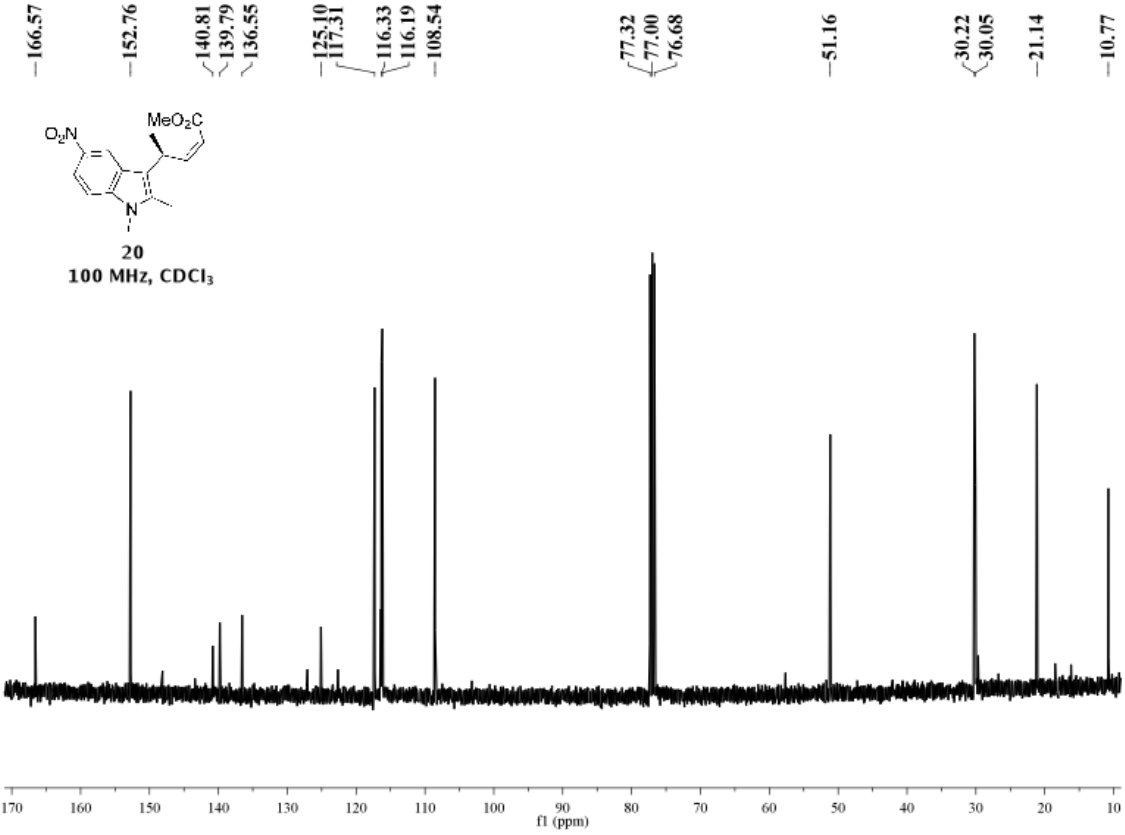
153.48
135.58
134.34
127.45
121.48
116.59
113.21
111.92
110.25
77.32
77.00
76.68
51.07
30.32
29.62
20.92
10.56
Br
MeO2C
N
19
100 MHz, CDCl3
fl (ppm)


8.61
8.04
8.04
7.26
6.72
5.76
5.20
3.73
3.69
2.48
1.56
1.54
MeO2C
O2N
N
20
400 MHz, CDCl3
1.00
1.03
1.08
1.13
1.00
1.03
3.05
3.10
3.08
3.05
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
f1 (ppm)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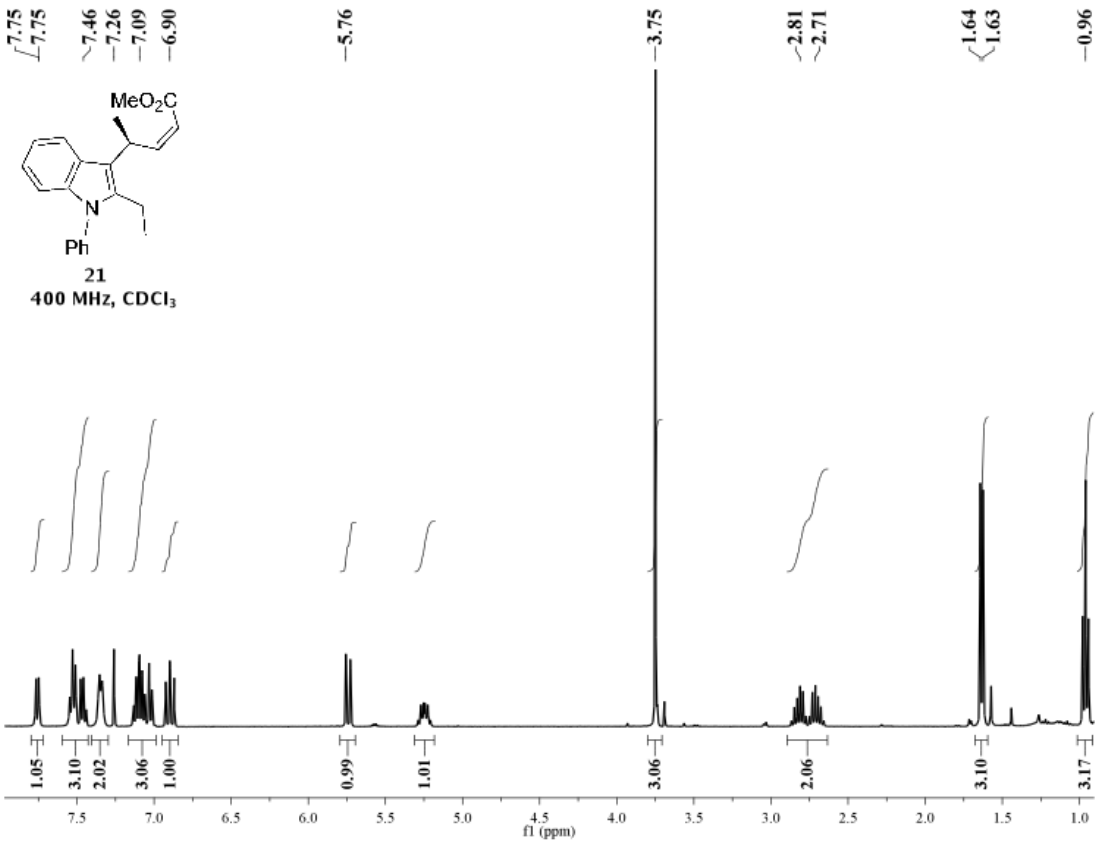
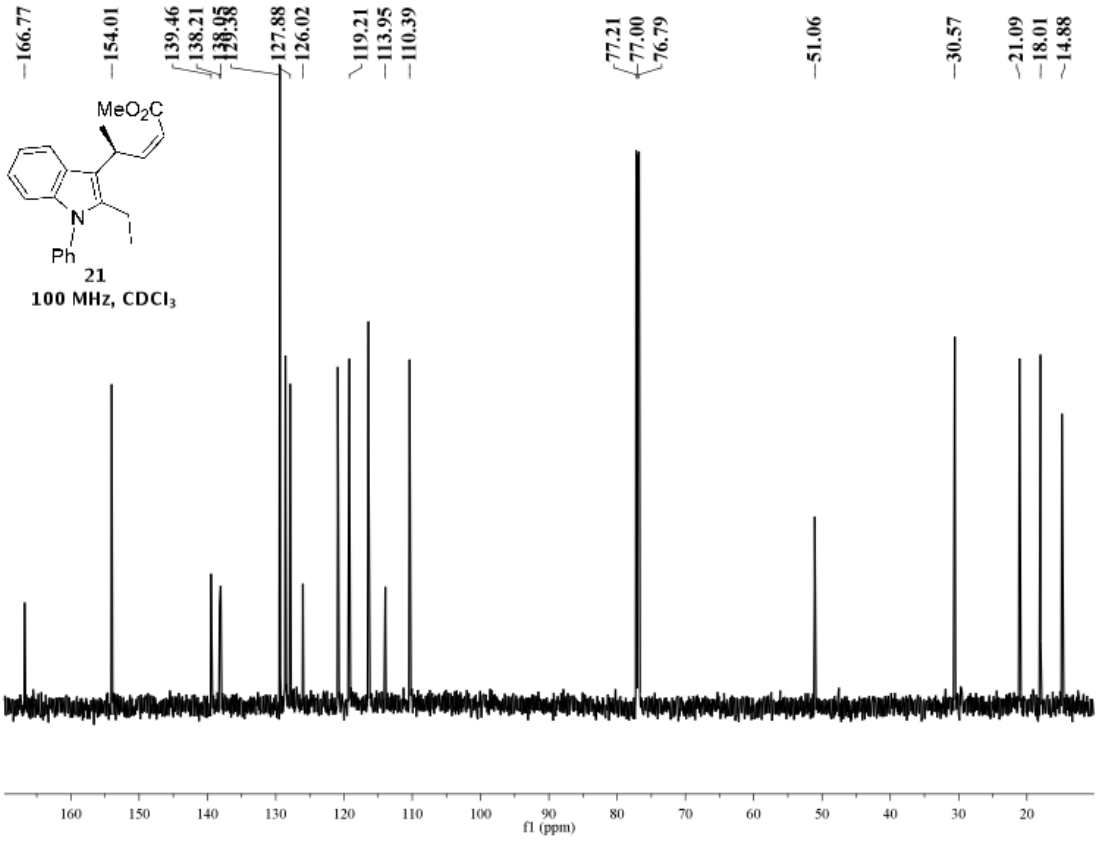
139.79
136.55
125.10
117.31
116.33
116.19
108.54
77.32
77.00
76.68
51.16
30.22
30.05
21.14
10.77
MeO2C
O2N
N
20
100 MHz, CDCl3
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


7.75
7.75
7.46
7.26
7.09
6.90
5.76
3.75
2.81
2.71
1.64
1.63
0.96
MeO2C
N
Ph
21
400 MHz, CDCl3
1.05
3.10
2.02
3.06
1.00
0.99
1.01
3.06
2.06
3.10
3.17
f1 (ppm)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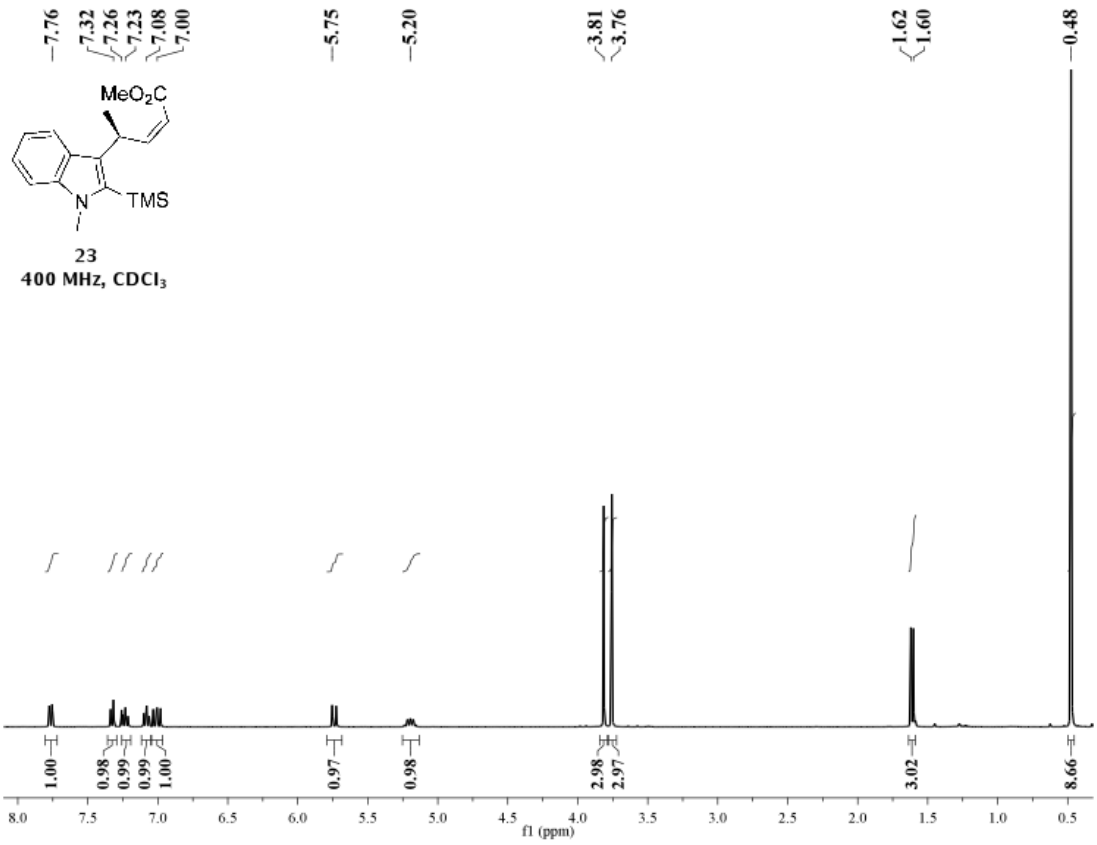
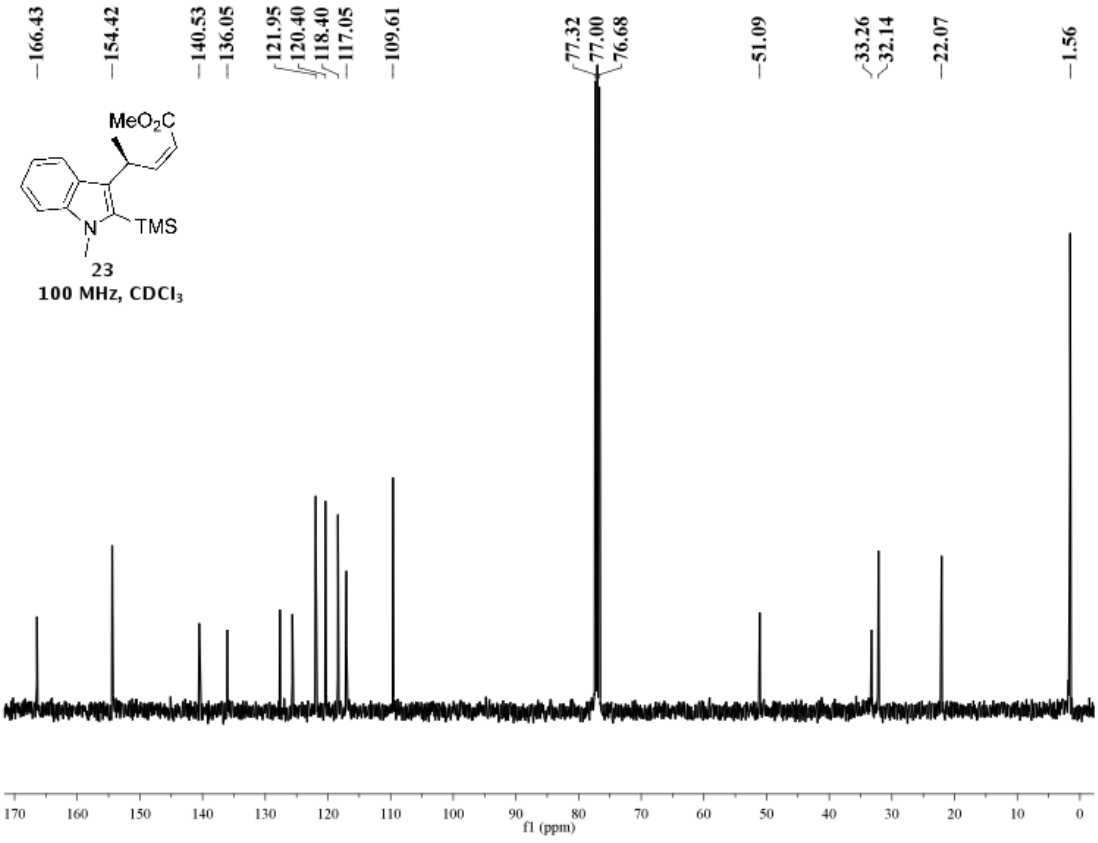
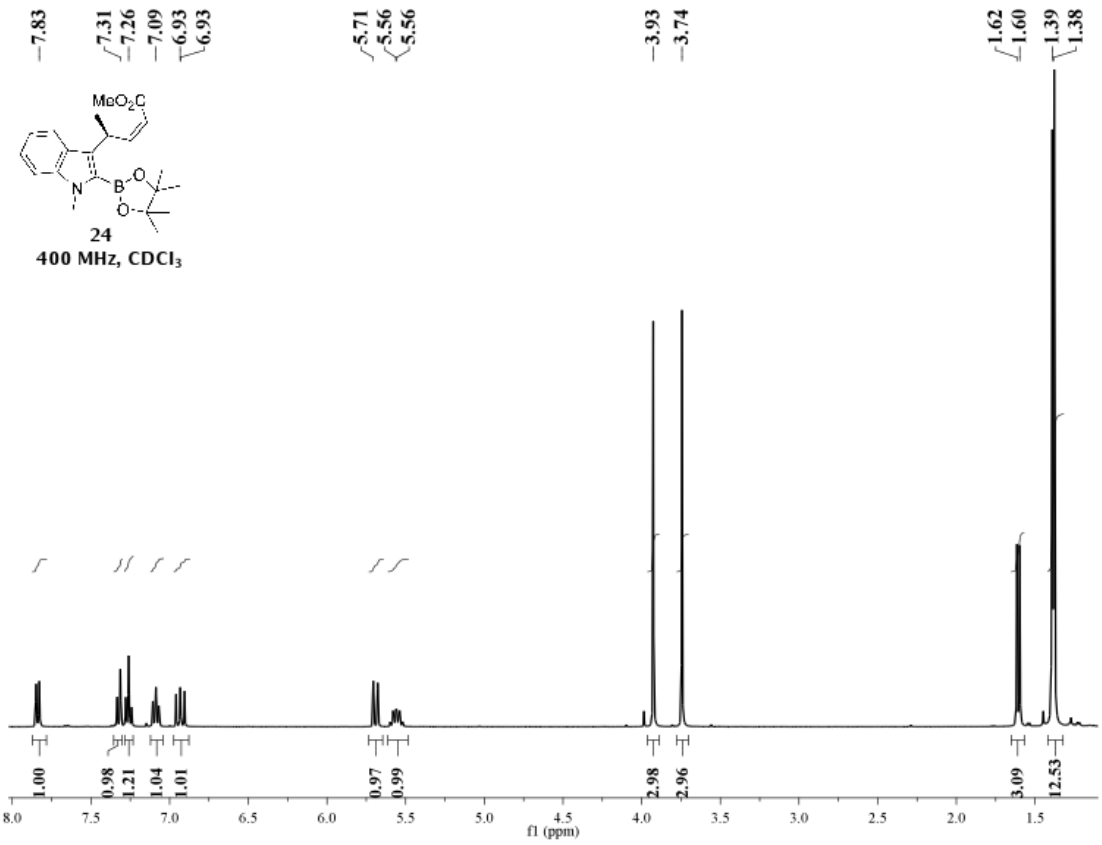
154.01
139.46
138.21
127.88
126.02
119.21
113.95
110.39
77.21
77.00
76.79
51.06
30.57
21.09
18.01
14.88
MeO2C
N
Ph
21
100 MHz, CDCl3
f1 (ppm)

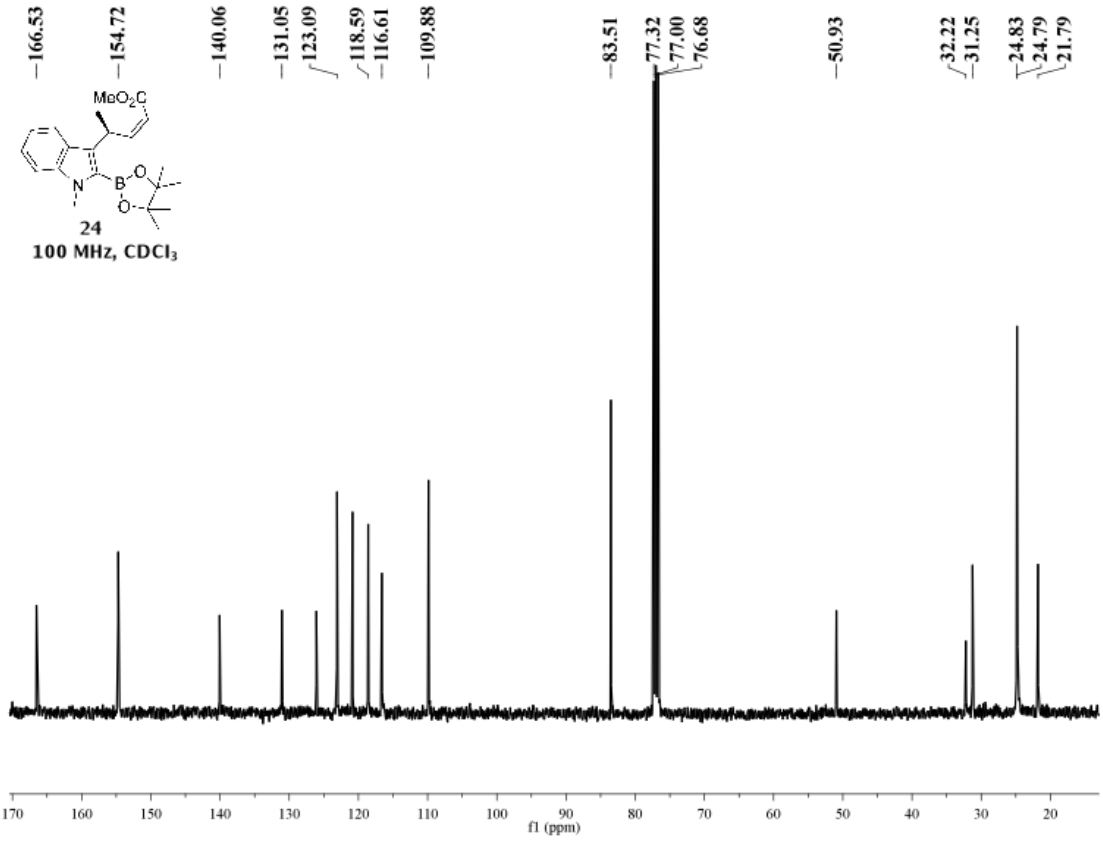


23
400 MHz, $CDCl_3$



23
100 MHz, $CDCl_3$


7.83
7.31
7.26
7.09
6.93
6.93
5.71
5.56
5.56
3.93
3.74
1.62
1.60
1.39
1.38
MeO2C
24
400 MHz, CDCl3
1.00
0.98
1.21
1.04
1.01
0.97
0.99
2.98
2.96
3.09
12.53
f1 (ppm)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140.06
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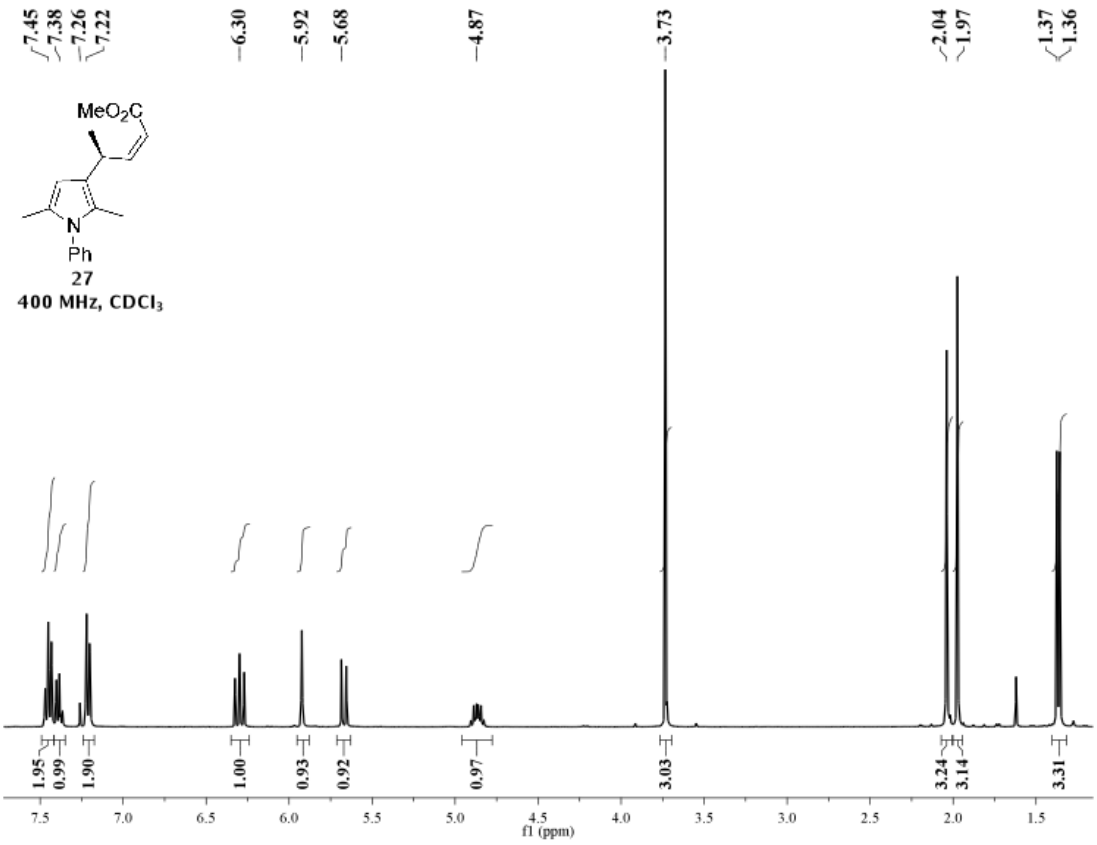
118.59
116.61
109.88
83.51
77.32
77.00
76.68
50.93
32.22
31.25
24.83
24.79
21.79
MeO2C
24
100 MHz, CDCl3
f1 (ppm)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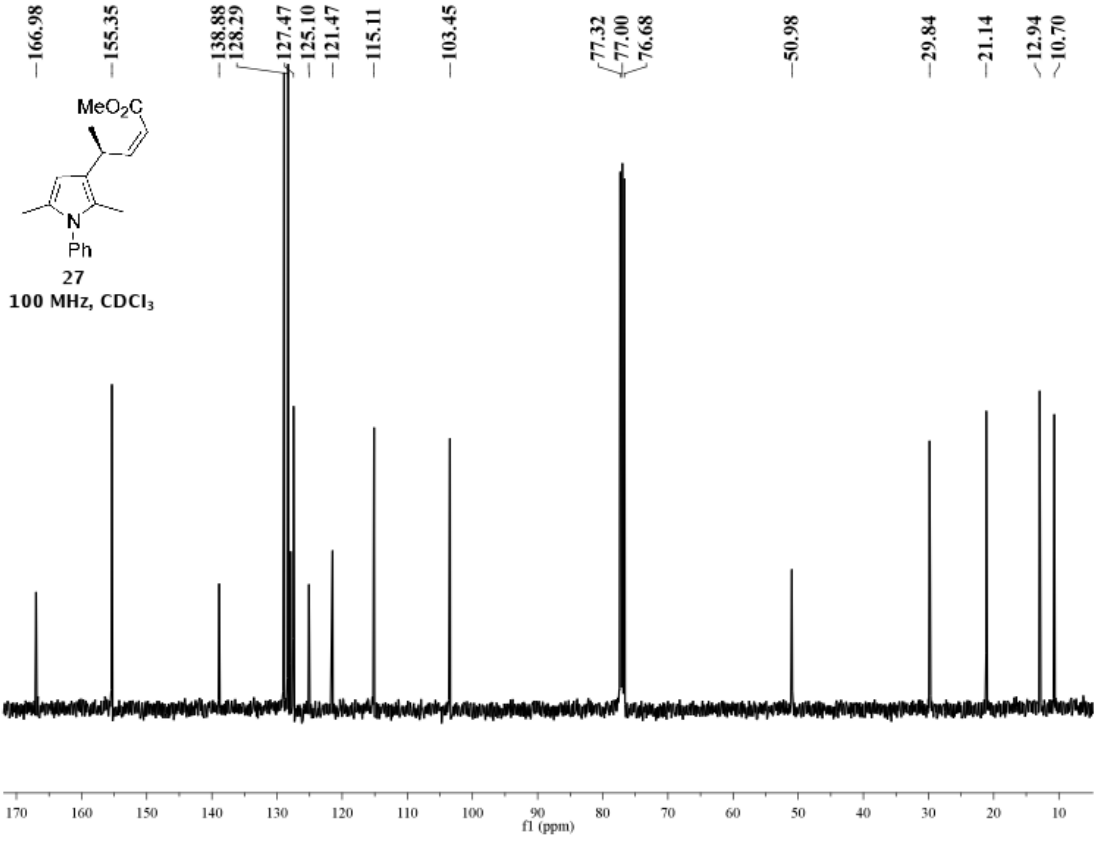
5.92
5.68
4.87
3.73
2.04
1.97
1.37
1.36
MeO2C
N
Ph
27
400 MHz, CDCl3
1.95
0.99
1.90
1.00
0.93
0.92
0.97
3.03
3.24
3.14
3.31
f1 (ppm)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128.29
127.47
125.10
121.47
115.11
103.45
77.32
77.00
76.68
50.98
29.84
21.14
12.94
10.70
MeO2C
N
Ph
27
100 MHz, CDCl3
f1 (ppm)