

Supporting information for
Rhodium Carbenoid Approach for Introduction of 4-
Substituted (Z)-Pent-2-enoates into Sterically
Encumbered Pyrroles and Indoles

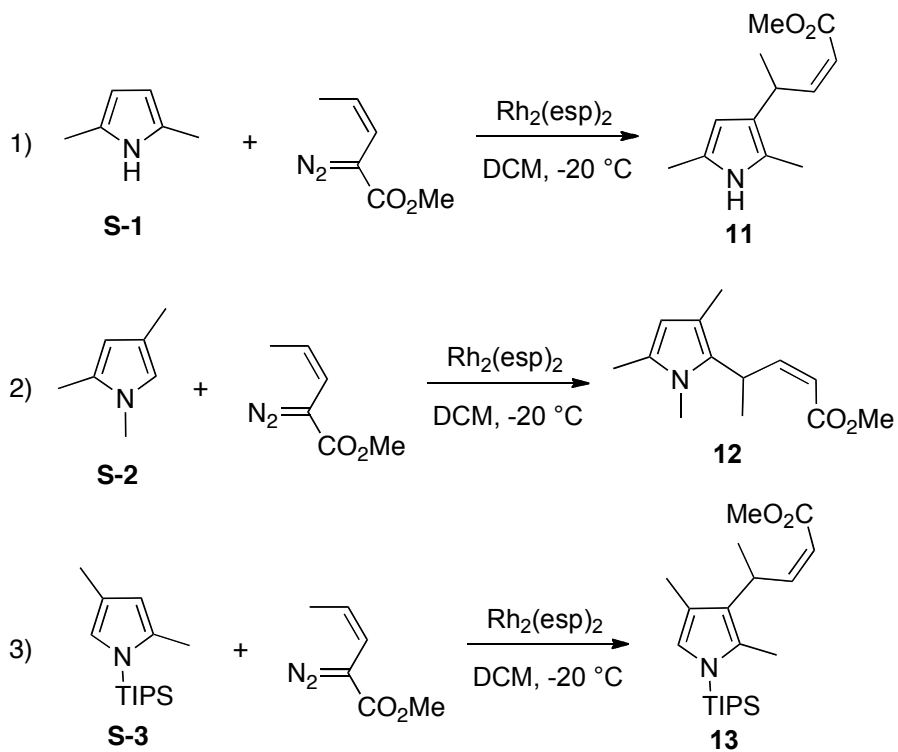
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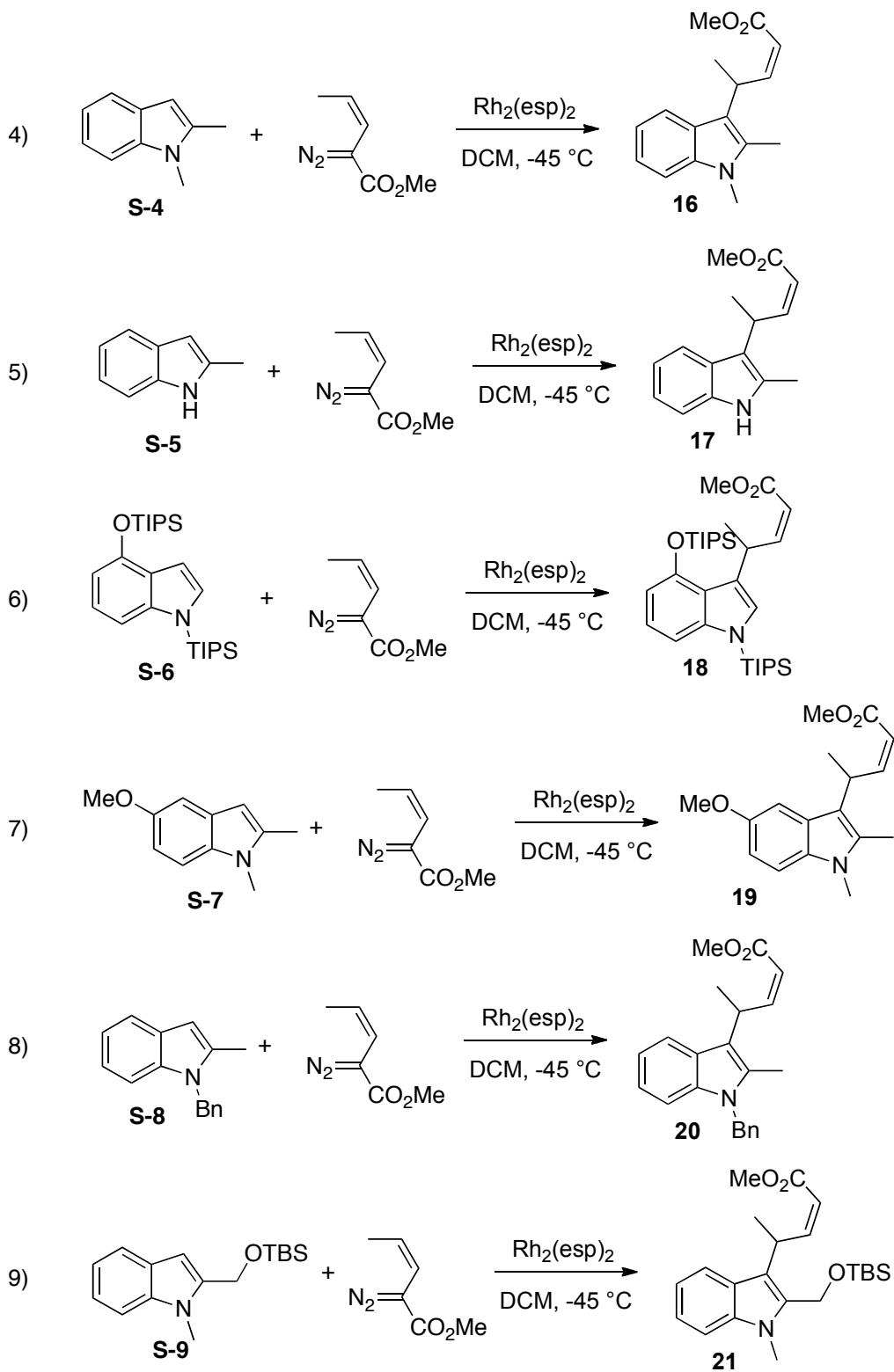
Supporting Information

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Reaction Equations for Table 1:

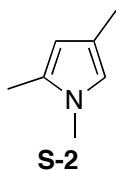


Reaction Equations for Table 2:



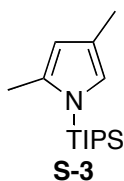
General Methods: All experiments were performed under anhydrous conditions in an atmosphere of argon except where stated, using flame-dried glassware. THF and methylenechloride were dried by a solvent purification system (passed through activated alumina columns). Unless otherwise noted, all other reagents were obtained from commercial sources and used as received. ¹H 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 δ H 7.26 for the residual protons in CDCl₃), 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. ¹³C 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 δ C 77.0 for CDCl₃. 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).

Procedure of making the pyrrole or indole derivatives:



1,2,4-Trimethyl-1*H*-pyrrole (S-2):

Pyrrole **S-2** was prepared in accordance with reported procedure¹ from the corresponding pyrrole and spectroscopic data on the purified products was consistent with reported value.

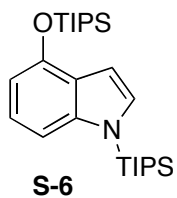


2,4-Dimethyl-1-(triisopropylsilyl)-1*H*-pyrrole (S-3):

To a solution containing 2,4-dimethylpyrrole (0.95 g, 10 mmol, 1.0 equiv.) in 10 ml dried THF was added 2.5M n-BuLi solution in hexane (4.4 mL, 12 mmol, 1.2 equiv.) at -78 °C. After stirring for 30 min, TIPSCl (2.31 g, 12 mmol, 1.2 equiv.) was added slowly and the solution was warmed up to room temperature slowly. The mixture was quenched by sodium bicarbonate solution and extracted by pentane (50 mL × 3). The organic layer was dried (MgSO₄) and concentrated under reduced pressure. The crude mixture was purified by flash chromatography on silica gel (pentane/Et₂O, R_f: 0.44) to provide product **S-3** as colorless oil (1.84 g, 73% yield).

¹H NMR (400 MHz, CDCl₃): δ 6.46 (s, 1H), 5.86 (s, 1H), 2.28 (d, *J* = 0.6 Hz, 3H), 2.06 (d, *J* = 0.6 Hz, 3H), 1.43-1.55 (m, 3H), 1.12 (d, *J* = 7.3 Hz, 18H); ¹³C NMR (100 MHz, CDCl₃): δ 133.4, 122.4, 119.4, 112.9, 18.2, 15.5, 12.8, 11.9; IR (neat): 2946, 2893, 2867, 1704, 1464, 1306, 1138, 1070, 883, 684 cm⁻¹; HRMS (APCI) calc. for C₁₅H₂₈NSi (M+H)⁺ 250.1986 found 250.1982.

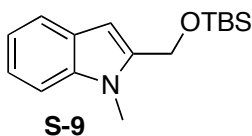
¹ Zinic, M.; Kuflinec, J.; Hofman, H.; Kajfez, F. *J. Org. Chem.* **1985**, *50*, 697.



1-(Triisopropylsilyl)-4-((triisopropylsilyl)oxy)-1H-indole (S-6):

Following the procedure described in the synthesis of **S-3**, the product **S-6** was derived from 4-((triisopropylsilyl)oxy)-1H-indole (2.89 g, 10 mmol, 1.0 equiv.), n-BuLi solution in hexane (4.4 mL, 12 mmol, 1.2 equiv.), TIPSCl (2.31 g, 12 mmol, 1.2 equiv.). The crude mixture was purified by flash chromatography on silica gel (pentane, R_f : 0.41) to provide product **22** as reddish oil (2.27 g, 51% yield).

^1H NMR (400 MHz, CDCl_3): δ 7.14 (d, $J = 3.4$ Hz, 1H), 7.11 (d, $J = 8.0$ Hz, 1H), 6.96 (t, $J = 7.9$ Hz, 1H), 6.72 (d, $J = 3.1$ Hz, 1H), 6.54 (d, $J = 7.6$ Hz, 1H), 1.62-1.74 (m, 3H), 1.28-1.43 (m, 3H), 1.14 (d, $J = 7.3$ Hz, 36H); ^{13}C NMR (100 MHz, CDCl_3): δ 149.2, 142.7, 129.3, 124.9, 121.7, 108.1, 107.4, 102.3, 18.15, 18.08, 12.9, 12.8; IR (neat): 2944, 2864, 1485, 1259, 1125, 1034, 882, 799, 732 cm^{-1} ; M.p. 84-86 $^\circ\text{C}$; HRMS (APCI) calc. for $\text{C}_{26}\text{H}_{48}\text{NSi}_2$ ($\text{M}+\text{H}$) $^+$ 446.3269 found 446.3263.



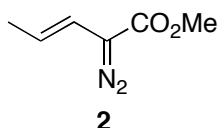
2-(((tert-Butyldimethylsilyl)oxy)methyl)-1-methyl-1H-indole (S-9):

To a solution containing 1-methyl-1H-indole-2-carbaldehyde (1.59 g, 10 mmol, 1.0 equiv.) in 10 mL dried THF was added 1M LiAlH_4 (4 mL, 5.0 mmol, 0.5 equiv.) at 0 $^\circ\text{C}$. The mixture was stirred for 30 min and was quenched by NH_4Cl solution. 1M HCl solution was added until all precipitate was dissolved and was extracted by Et_2O (50 mL \times 3). The organic layer was dried (MgSO_4) and concentrated under reduced pressure. The crude powder was dissolved in 20 mL dried CH_2Cl_2 , imidazole (1.36 g, 20 mmol, 2.0 equiv.) and TBSCl (2.11 g, 14 mmol, 1.4 equiv.) was added in sequence. After stirring at room temperature for 3h, the mixture was quenched by sodium bicarbonate solution, and then was extracted by Et_2O (50 mL \times 3). The organic layer was dried (MgSO_4) and concentrated under reduced pressure. The crude mixture was then purified by flash

chromatography on silica gel (pentane to 20/1 pentane/Et₂O, R_f: 0.62) to provide the product **S-9** as a colorless powder (2.23 g, 81% yield).

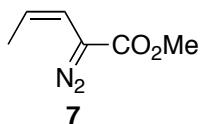
¹H NMR (400 MHz, CDCl₃): δ 7.58 (d, *J* = 7.9 Hz, 1H), 7.31 (d, *J* = 8.2 Hz, 1H), 7.21 (tm, *J* = 7.6 Hz, 1H), 7.09 (tm, *J* = 7.6 Hz, 1H), 6.38 (s, 1H), 4.84 (s, 2H), 3.79 (s, 3H), 0.91 (s, 9H), 0.07 (s, 6H); ¹³C NMR (100 MHz, CDCl₃): δ 138.9, 137.9, 127.3, 121.4, 120.6, 119.3, 109.0, 100.7, 58.1, 29.9, 25.8, 18.2, -5.3; IR (neat): 2930, 2855, 1469, 1379, 1245, 1054, 837, 771, 734 cm⁻¹; M.p. 65-67 °C; HRMS (APCI) calc. for C₁₆H₂₆ONSi (M+H)⁺ 276.1778 found 276.1775.

Procedure for making diazoacetates:



(*E*)-Methyl 2-diazopent-3-enoate (**2**):

Diazoacetate **2** was prepared by following the reported procedure² and the spectroscopic data on the purified products was consistent with reported value.



(*Z*)-Methyl 2-diazopent-3-enoate (**7**):

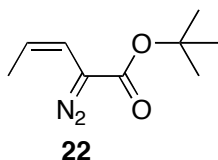
The de-conjugation process was followed by a modified procedure reported by Ukaji and Inomata.³ To a solution of containing LiHMDS (20.1 g, 120 mmol, 1.5 equiv.) and HMPA (83.5 mL, 480 mmol, 6.0 equiv.) in 300 mL dried THF was added a solution of methyl pent-2-enoate (9.12 g, 80 mmol, 1.0 equiv.) in 20 mL dried THF at -78 °C. After stirring for 30 min, the solution was quenched by methanol. The mixture was poured into saturated NH₄Cl solution and extracted by pentane (200 ml × 3). The organic layers were combined and washed with H₂O twice and then brine solution. The solvent was removed under reduced pressure and the residue was dissolved in 200 mL dried CH₃CN. After

² Doyle, M. P.; Ming, Y.; Hu, W.; Gronenberg, L. S. *J. Am. Chem. Soc.* **2003**, *125*, 4692.

³ Guha, S. K.; Shibayama, A.; Abe, D.; Ukaji, Y.; Inomata, K. *Chem. Lett.* **2003**, *32*, 778.

addition of *p*-ABSA (*p*-acetamidobenzenesulfonyl azide) (28.8 g, 120 mmol, 1.5 equiv.), the solution was cooled down to 0 °C and then DBU (24 mL, 160 mmol, 2.0 equiv.) was added quickly. The solution was warmed up to room temperature overnight and quenched by sodium bicarbonate solution and extracted by pentane (200 mL × 2). The organic layer was dried (MgSO₄) and concentrated under reduced pressure. The crude mixture was purified by flash chromatography on silica gel (30/1 pentane/Et₂O, R_f: 0.45) to provide product **7** as reddish oil (7.62 g, 68% yield).

¹H NMR (400 MHz, CDCl₃): δ 5.57-5.67 (m, 2H), 3.80 (s, 3H), 1.63-1.73 (m, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 166.8, 123.6, 112.0, 52.1, 13.5; IR (neat): 2078, 1694, 1435, 1289, 1220, 1109, 702 cm⁻¹.



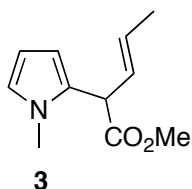
(Z)-tert-Butyl 2-diazopent-3-enoate (22):

Following the general procedure of making the methyl vinyl diazoacetate **7**, the product was derived from LiHMDS (4.1 g, 24 mmol, 1.5 equiv.), HMPA (17 mL, 96 mmol, 6.0 equiv.), *tert*-butyl pent-2-enoate (2.5 g, 16 mmol, 1.0 equiv.), *p*-ABSA (*p*-acetamidobenzenesulfonyl azide) (5.76 g, 24 mmol, 1.5 equiv.) and DBU (4.8 mL, 32 mmol, 2.0 equiv.). The crude mixture was purified by flash chromatography on silica gel (40/1 pentane/Et₂O, R_f: 0.51) to provide product **22** as reddish oil (1.48 g, 51% yield).

¹H NMR (400 MHz, CDCl₃): δ 5.49-5.60 (m, 2H), 1.63-1.70 (m, 3H), 1.47 (s, 9H); ¹³C NMR (100 MHz, CDCl₃): δ 165.6, 122.7, 112.6, 81.7, 28.2, 13.4; IR (neat): 2978, 2077, 1698, 1368, 1294, 1167, 1106, 701 cm⁻¹.

General procedure for the reactions between pyrroles and methyl vinyl diazoacetate:

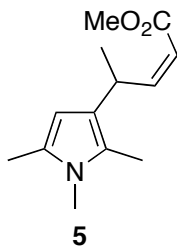
To a flame-dried 25 mL flask containing $\text{Rh}_2(\text{esp})_2$ (2.3 mg, 0.02 equiv.) and pyrroles (0.90 mmol, 6.0 equiv.) in 6 mL dried CH_2Cl_2 under argon atmosphere was added a solution of fresh purified methyl vinyl diazoacetate (21 mg, 0.15 mmol, 1.0 equiv.) in 6 mL dried CH_2Cl_2 by syringe pump over 3 h at -20°C . The solution was warmed up to room temperature over 2 h. The mixture was concentrated under reduced pressure and purified by flash chromatography on silica gel (85/15 pentane/ Et_2O , containing 0.5% Et_3N) to provide the corresponding products as colorless oils.



(E)-Methyl 2-(1-methyl-1H-pyrrol-2-yl)pent-3-enoate (3):

Derived from *N*-methylpyrrole (**1**) (73 mg, 0.90 mmol, 6.0 equiv.) and *trans*-methyl vinyl diazoacetate **2** (21 mg, 0.15 mmol, 1.0 equiv.), and purified by flash chromatography on silica gel (85/15 pentane/ Et_2O , containing 0.5% Et_3N , R_f : 0.46) to provide **3** as a colorless oil (15.5 mg, 53% yield).

^1H NMR (400 MHz, CDCl_3): δ 6.57 (dd, $J = 2.2, 2.0$ Hz, 1H), 6.08 (dd, $J = 3.0, 2.8$ Hz, 1H), 6.03-6.06 (m, 1H), 5.75 (ddq, $J = 15.3, 7.8, 1.6$ Hz, 1H), 5.51-5.62 (m, 1H), 4.32 (d, $J = 7.8$ Hz, 1H), 3.71 (s, 3H), 3.54 (s, 3H), 1.72 (ddd, $J = 6.3, 1.6, 0.8$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 172.4, 129.0, 128.7, 126.8, 122.5, 107.3, 170.0, 52.3, 47.0, 34.0, 17.8; IR (neat): 2919, 1733, 1434, 1298, 1225, 1192, 1163, 989, 966, 707 cm^{-1} ; HRMS (APCI) calc. for $\text{C}_{11}\text{H}_{16}\text{O}_2\text{N}$ ($\text{M}+\text{H}$) $^+$ 194.1176 found 194.1177.

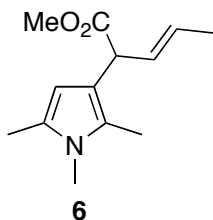


(Z)-Methyl 4-(1,2,5-trimethyl-1H-pyrrol-3-yl)pent-2-enoate (5):

Derived from 1,2,5-trimethylpyrrole (**4**) (49.1 mg, 0.45 mmol, 3.0 equiv.) and *trans*-

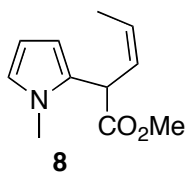
methyl vinyldiazoacetate **2** (21 mg, 0.15 mmol, 1.0 equiv.), and purified by flash chromatography on silica gel (9/1 pentane/Et₂O, containing 0.5% Et₃N, R_f: 0.45) to provide **5** as a colorless oil (9.2 mg, 28% yield) and **6** (16.6 mg, 50% yield).

¹H NMR (400 MHz, CDCl₃): δ 6.21 (dd, *J* = 11.4, 10.8 Hz, 1H), 5.78 (br, 1H), 5.61 (dd, *J* = 11.4, 1.0 Hz, 1H), 4.77-4.86 (m, 1H), 3.73 (s, 3H), 3.35 (s, 3H), 2.20 (s, 3H), 2.15 (s, 3H), 1.29 (d, *J* = 7.0 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 167.0, 155.6, 127.2, 124.2, 120.9, 114.9, 102.3, 51.0, 30.1, 29.7, 21.3, 12.5, 10.0; IR (neat): 2925, 1719, 1634, 1435, 1397, 1193, 1173, 826 cm⁻¹; HRMS (APCI) calc. for C₁₃H₂₀O₂N (M+H)⁺ 222.1489 found 222.1488.



(E)-Methyl 2-(1,2,5-trimethyl-1H-pyrrol-3-yl)pent-3-enoate (6):

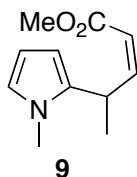
¹H NMR (400 MHz, CDCl₃): δ 5.76-5.84 (m, 2H), 5.50-5.59 (m, 1H), 4.15 (d, *J* = 8.8 Hz, 1H), 3.68 (s, 3H), 3.35 (s, 3H), 2.18 (s, 3H), 2.15 (s, 3H), 1.69 (dd, *J* = 6.0, 1.6 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 174.3, 129.2, 127.4, 126.6, 124.1, 115.2, 104.2, 51.9, 46.9, 30.2, 17.9, 12.4, 10.1; IR (neat): 2917, 1732, 1433, 1238, 1155, 992, 964, 769 cm⁻¹; HRMS (APCI) calc. for C₁₃H₂₀O₂N (M+H)⁺ 222.1489 found 222.1489.



(Z)-Methyl 2-(1-methyl-1H-pyrrol-2-yl)pent-3-enoate (8):

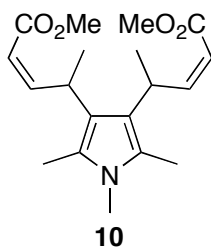
Derived from 1-methylpyrrole (**1**) (73 mg, 0.90 mmol, 6.0 equiv.) and *cis*-methyl vinyldiazoacetate **7** (21 mg, 0.15 mmol, 1.0 equiv.), and purified by flash chromatography on silica gel (85/15 pentane/Et₂O, containing 0.5% Et₃N, R_f: 0.39) to provide **8** as a colorless oil (14.6 mg, 50% yield) and **9** as a colorless oil (1.4 mg, 5% yield).

^1H NMR (400 MHz, CDCl_3): δ 6.57 (t, $J = 2.2$ Hz, 1H), 6.06-6.09 (m, 2H), 5.77-5.83 (m, 1H), 5.66-5.74 (m, 1H), 4.65 (d, $J = 9.2$ Hz, 1H), 3.71 (s, 3H), 3.58 (s, 3H), 1.70 (dd, $J = 6.7, 1.6$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 172.3, 129.2, 127.0, 126.1, 122.5, 107.1, 107.0, 52.4, 41.7, 34.0, 13.1; IR (neat): 2920, 1733, 1490, 1434, 1302, 1164, 766, 708 cm^{-1} ; HRMS (APCI) calc. for $\text{C}_{11}\text{H}_{16}\text{O}_2\text{N}$ ($\text{M}+\text{H}$) $^+$ 194.1175 found 194.1174.



(Z)-Methyl 4-(1-methyl-1H-pyrrol-2-yl)pent-2-enoate (9):

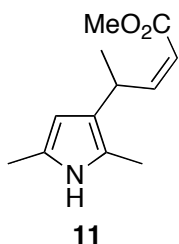
^1H NMR (400MHz, CDCl_3): δ 6.55 (t, $J = 2.4$ Hz, 1H), 6.06-6.12 (m, 2H), 5.97-5.99 (m, 1H), 5.74 (dd, $J = 11.2, 1.0$ Hz, 1H), 4.92-5.01 (m, 1H), 3.75 (s, 3H), 3.53 (s, 3H), 1.38 (d, $J = 7.2$ Hz, 3H); ^{13}C NMR (100MHz, CDCl_3): δ 166.8, 153.7, 135.5, 121.9, 116.8, 106.8, 104.2, 51.2, 33.7, 30.0, 19.5; IR (neat): 1717, 1637, 1436, 1195, 1176, 826, 705 cm^{-1} ; HRMS (APCI) calc. for $\text{C}_{11}\text{H}_{16}\text{O}_2\text{N}$ ($\text{M}+\text{H}$) $^+$ 194.1176 found 194.1175.



(2Z,2'Z)-Dimethyl 4,4'-(1,2,5-trimethyl-1H-pyrrole-3,4-diyl)bis(pent-2-enoate) (10):

To a flame-dried 25 mL flask containing $\text{Rh}_2(\text{esp})_2$ (5.7 mg, 0.05 equiv.) and 1,2,5-trimethylpyrrole (**4**) (16.4 mg, 0.15 mmol, 1.0 equiv.) in 6 mL dried CH_2Cl_2 under argon atmosphere was added a solution of fresh purified *cis*-methyl vinyl diazoacetate **7** (105 mg, 0.75 mmol, 5.0 equiv.) in 6 mL dried CH_2Cl_2 by syringe pump over 3 h at -20 $^\circ\text{C}$. The solution was stirred at -20 $^\circ\text{C}$ over-night and warmed up to room temperature over 2 h. The mixture was concentrated under reduced pressure and purified by flash chromatography on silica gel (85/15 pentane/ Et_2O containing 0.5% Et_3N , R_f : 0.34) to provide **10** as a mixture of two inseparable diastereomers in a ratio of 1/1 (43.2 mg, 86% combined yield).

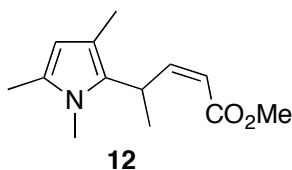
^1H NMR (400 MHz, CDCl_3): δ 6.65 (dd, $J = 11.4, 10.2$ Hz, 2H), 6.57 (t, $J = 10.8$ Hz, 2H), 5.70 (dd, $J = 11.4, 1.0$ Hz, 2H), 5.63 (dd, $J = 11.4, 1.0$ Hz, 2H), 4.90-5.05 (m, 4H), 3.73 (s, 6H), 3.72 (s, 6H), 3.35 (s, 3H), 3.34 (s, 3H), 2.26 (s, 6H), 2.25 (s, 6H), 1.42 (d, $J = 7.3$ Hz, 6H), 1.35 (d, $J = 7.3$ Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3): δ 166.7, 166.6, 155.0, 154.7, 123.2, 119.3, 119.2, 116.6, 116.3, 50.99, 50.95, 30.11, 30.05, 30.00, 29.86, 21.6, 21.5, 11.4, 11.2; IR (neat): 2950, 1716, 1634, 1435, 1369, 1192, 1171, 1003, 821 cm^{-1} ; HRMS (APCI) calc. for $\text{C}_{19}\text{H}_{28}\text{O}_4\text{N}$ ($\text{M}+\text{H}$) $^+$ 334.2013 found 334.2010.



(Z)-Methyl 4-(2,5-dimethyl-1H-pyrrol-3-yl)pent-2-enoate (11):

Derived from 2,5-dimethylpyrrole (**S-1**) (85.6 mg, 0.90 mmol, 6.0 equiv.) and *cis*-methyl vinyl diazoacetate **7** (21 mg, 0.15 mmol, 1.0 equiv.), and purified by flash chromatography on silica gel (7/3 pentane/ Et_2O , containing 1% Et_3N , R_f : 0.42) to provide **11** as a yellowish oil (18.4 mg, 59% yield).

^1H NMR (400 MHz, CDCl_3): δ 7.45 (br, 1H), 6.21 (t, $J = 11.4$ Hz, 1H), 5.75 (d, $J = 2.8$ Hz, 1H), 5.62 (d, $J = 11.4$ Hz, 1H), 4.73-4.81 (m, 1H), 3.72 (s, 3H), 2.22 (s, 3H), 2.17 (s, 3H), 1.29 (d, $J = 6.8$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 167.2, 155.5, 125.6, 122.5, 122.0, 115.3, 103.7, 51.2, 29.9, 21.4, 13.2, 11.2; IR (neat): 3380, 2922, 1705, 1634, 1436, 1403, 1195, 1175, 826, 782 cm^{-1} ; HRMS (APCI) calc. for $\text{C}_{12}\text{H}_{18}\text{O}_2\text{N}$ ($\text{M}+\text{H}$) $^+$ 208.1332 found 208.1331.

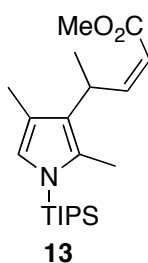


(Z)-Methyl 4-(1,3,5-trimethyl-1H-pyrrol-2-yl)pent-2-enoate (12):

Derived from 1,2,4-trimethylpyrrole (**S-2**) (98 mg, 0.90 mmol, 6.0 equiv.) and *cis*-methyl vinyl diazoacetate **7** (21 mg, 0.15 mmol, 1.0 equiv.), and purified by flash

chromatography on silica gel (10/1 pentane/Et₂O, containing 0.5% Et₃N, R_f: 0.49) to provide product **12** as a colorless oil (24.8 mg, 75% yield).

¹H NMR (400 MHz, CDCl₃): δ 6.44 (dd, *J* = 11.4, 10.2 Hz, 1H), 5.70 (dd, *J* = 11.4, 1.0 Hz, 1H), 5.65 (s, 1H), 5.01-5.11 (m, 1H), 3.72 (s, 3H), 3.43 (s, 3H), 2.15 (d, *J* = 0.8 Hz, 3H), 2.13 (s, 3H), 1.43 (d, *J* = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 166.9, 152.8, 129.2, 127.3, 116.7, 113.6, 108.8, 51.3, 30.7, 30.6, 20.1, 12.8, 12.7; IR (neat): 2926, 1717, 1637, 1435, 1396, 1194, 1174, 1010, 824, 773 cm⁻¹; HRMS (APCI) calc. for C₁₃H₂₀O₂N (M+H)⁺ 222.1489 found 222.1492.



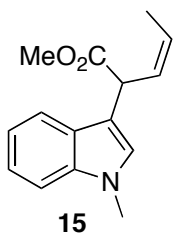
(Z)-Methyl 4-(2,4-dimethyl-1-(triisopropylsilyl)-1H-pyrrol-3-yl)pent-2-enoate (13):

Derived from 1-triisopropylsilyl-2,4-dimethylpyrrole (**S-3**) (226 mg, 0.90 mmol, 6.0 equiv.) and *cis*-methyl vinyl diazoacetate **7** (21 mg, 0.15 mmol, 1.0 equiv.), and purified by flash chromatography on silica gel (40/1 pentane/Et₂O, R_f: 0.38) to provide product **13** as a colorless oil (47.6 mg, 87% yield).

¹H NMR (400 MHz, CDCl₃): δ 6.51 (dd, *J* = 11.2, 10.0 Hz, 1H), 6.39 (s, 1H), 5.64 (dd, *J* = 11.2, 1.0 Hz, 1H), 4.80-4.88 (m, 1H), 3.70 (s, 3H), 2.24 (s, 3H), 2.11 (d, *J* = 0.8 Hz, 3H), 1.45 (hept., *J* = 7.6 Hz, 3H), 1.35 (d, *J* = 7.2 Hz, 3H), 1.10 (d, *J* = 7.6 Hz, 18H); ¹³C NMR (100 MHz, CDCl₃): δ 166.8, 154.7, 129.4, 124.1, 122.0, 117.9, 115.8, 50.9, 30.5, 20.6, 18.4, 13.3, 13.1, 12.4; IR (neat): 2948, 2868, 1722, 1463, 1436, 1313, 1192, 1173, 1017, 882, 824, 685 cm⁻¹; HRMS (APCI) calc. for C₂₁H₃₈O₂NSi (M+H)⁺ 364.2666 found 364.2672.

General procedure for the reaction between pyrroles and methyl vinyl diazoacetate:

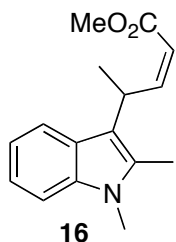
To a flame-dried 25 mL flask containing $\text{Rh}_2(\text{esp})_2$ (2.3 mg, 0.02 equiv.) and indoles (0.90 mmol, 6.0 equiv.) in 6 mL dried CH_2Cl_2 under argon atmosphere was added a solution of fresh purified methyl vinyl diazoacetate (21.0 mg, 0.15 mmol, 1.0 equiv.) in 6 mL dried CH_2Cl_2 by syringe pump over 3 h at -45°C . The solution was warmed up to room temperature over 2 h. 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.



(Z)-Methyl 2-(1-methyl-1H-indol-3-yl)pent-3-enoate (15):

Derived from *N*-methylindole (**14**) (118.0 mg, 0.90 mmol, 6.0 equiv.) and *cis*-methyl vinyl diazoacetate **7** (21 mg, 0.15 mmol, 1.0 equiv.), and purified by flash chromatography on silica gel (85/15 pentane/ Et_2O , R_f : 0.29) to provide product **15** as a colorless oil (28.6 mg, 78% yield).

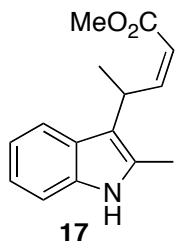
^1H NMR (500 MHz, CDCl_3): δ 7.66 (d, $J = 7.8$ Hz, 1H), 7.30 (d, $J = 8.2$ Hz, 1H), 7.24 (td, $J = 8.2, 1.2$ Hz, 1H), 7.13 (td, $J = 7.8, 1.2$ Hz, 1H), 7.03 (s, 1H), 5.93-6.00 (m, 1H), 5.66-5.74 (m, 1H), 4.91 (d, $J = 9.4$ Hz, 1H), 3.76 (s, 3H), 3.71 (s, 3H), 1.76 (dd, $J = 6.7, 1.6$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3): δ 173.8, 137.0, 127.6, 126.7, 126.6, 126.4, 121.8, 119.2 (2C), 112.0, 109.3, 52.2, 41.0, 32.8, 13.1; IR (neat): 2949, 1732, 1472, 1433, 1330, 1310, 1192, 1152, 1014, 776, 739 cm^{-1} ; HRMS (APCI) calc. for $\text{C}_{15}\text{H}_{18}\text{O}_2\text{N}$ ($\text{M}+\text{H}$) $^+$ 244.1332 found 244.1330.



(Z)-Methyl 4-(1,2-dimethyl-1H-indol-3-yl)pent-2-enoate (16):

Derived from 1,2-dimethylindole (**S-4**) (65.3 mg, 0.45 mmol, 3.0 equiv.) and *cis*-methyl vinyldiazoacetate **7** (21 mg, 0.15 mmol, 1.0 equiv.), and purified by flash chromatography on silica gel (85/15 pentane/Et₂O, R_f: 0.45) to provide product **16** as a colorless gel powder (34.7 mg, 90% yield).

¹H NMR (400 MHz, CDCl₃): δ 7.70 (d, *J* = 7.9 Hz, 1H), 7.26 (d, *J* = 8.3 Hz, 1H), 7.16 (td, *J* = 7.9, 1.0 Hz, 1H), 7.07 (td, *J* = 7.6, 1.0 Hz, 1H), 6.79 (t, *J* = 11.4 Hz, 1H), 5.69 (d, *J* = 11.4 Hz, 1H), 5.15-5.22 (m, 1H), 3.74 (s, 3H), 3.65 (s, 3H), 2.45 (s, 3H), 1.56 (d, *J* = 7.3 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 166.8, 154.1, 136.9, 132.9, 125.8, 120.4, 119.1, 118.6, 116.2, 113.3, 108.9, 51.0, 30.5, 29.5, 20.9, 10.5; IR (neat): 2994, 1716, 1637, 1471, 1435, 1368, 1193, 1173, 824, 737 cm⁻¹; HRMS (APCI) calc. for C₁₆H₁₉O₂N (M+H)⁺ 258.1489 found 258.1488.

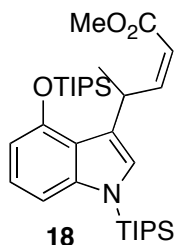


(Z)-Methyl 4-(2-methyl-1H-indol-3-yl)pent-2-enoate (17):

Derived from 2-methylindole (**S-5**) (118.0 mg, 0.90 mmol, 6.0 equiv.) and *cis*-methyl vinyldiazoacetate **7** (21 mg, 0.15 mmol, 1.0 equiv.), and purified by flash chromatography on silica gel (7/3 pentane/Et₂O, R_f: 0.41) to provide product **17** as a colorless powder (26.8 mg, 73% yield).

¹H NMR (400 MHz, CDCl₃): δ 7.74 (br, 1H), 7.68 (d, *J* = 7.6 Hz, 1H), 7.26-7.28 (m, 1H), 7.05-7.13 (m, 2H), 6.76 (t, *J* = 11.2, 10.4 Hz, 1H), 5.71 (dd, *J* = 11.2, 1.0 Hz, 1H), 5.11-5.19 (m, 1H), 3.74 (s, 3H), 2.45 (s, 3H), 1.55 (d, *J* = 6.8 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 166.8, 153.9, 135.4, 130.9, 126.9, 120.8, 119.06, 119.03, 116.4, 114.0,

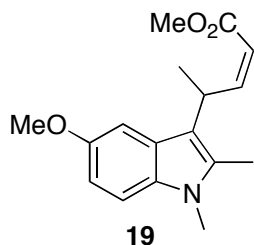
110.5, 51.1, 30.2, 20.7, 12.1; IR (neat): 3399(br), 2950, 1717, 1703, 1639, 1460, 1435, 1301, 1196, 1176, 824, 741 cm^{-1} ; M.p. 59-61 $^{\circ}\text{C}$; HRMS (APCI) calc. for $\text{C}_{15}\text{H}_{18}\text{O}_2\text{N}$ ($\text{M}+\text{H}$) $^{+}$ 244.1332 found 244.1330.



(Z)-Methyl 4-(1-(triisopropylsilyl)-4-((triisopropylsilyl)oxy)-1H-indol-3-yl)pent-2-enoate (18):

Derived from 1,5-bistriisopropylsilylindole (**S-6**) (400.8 mg, 0.90 mmol, 6.0 equiv.) and *cis*-methyl vinyl diazoacetate **7** (21 mg, 0.15 mmol, 1.0 equiv.), and purified by flash chromatography on silica gel (30/1 pentane/ Et_2O , R_f : 0.54) to provide product **18** as a colorless oil (44.6 mg, 53% yield).

^1H NMR (400 MHz, CDCl_3): δ 7.03 (d, $J = 8.3$ Hz, 1H), 6.90 (t, $J = 7.9$ Hz, 1H), 6.86 (s, 1H), 6.68 (dd, $J = 11.4, 9.5$ Hz, 1H), 6.49 (d, $J = 7.9$ Hz, 1H), 5.76 (dd, $J = 11.4, 0.6$ Hz, 1H), 5.06-5.13 (m, 1H), 3.67 (s, 3H), 1.65 (hept., $J = 7.6$ Hz, 3H), 1.49 (d, $J = 7.0$ Hz, 3H), 1.47 (hept., $J = 7.6$ Hz, 3H), 1.17 (dd, $J = 7.6, 1.6$ Hz, 18H), 1.14 (dd, $J = 7.6, 1.0$ Hz, 18H); ^{13}C NMR (100 MHz, CDCl_3): δ 166.5, 155.3, 150.2, 144.0, 125.4, 122.7, 121.5, 121.4, 117.2, 107.6, 107.1, 51.0, 31.7, 24.2, 18.3, 18.2, 13.7, 12.9; IR (neat): 2945, 2867, 1730, 1489, 1461, 1264, 1172, 1128, 1098, 882, 782, 687 cm^{-1} ; HRMS (APCI) calc. for $\text{C}_{32}\text{H}_{56}\text{O}_3\text{NSi}_2$ ($\text{M}+\text{H}$) $^{+}$ 558.3793 found 558.3799.

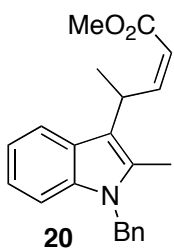


(Z)-Methyl 4-(5-methoxy-1,2-dimethyl-1H-indol-3-yl)pent-2-enoate (19):

Derived from 5-methoxy-1,2-dimethyl-1H-indole (**S-7**) (158 mg, 0.90 mmol, 6.0 equiv.)

and *cis*-methyl vinyl diazoacetate **7** (21 mg, 0.15 mmol, 1.0 equiv.), and purified by flash chromatography on silica gel (85/15 pentane/Et₂O, R_f: 0.28) to provide product **19** as a colorless powder (39.6 mg, 92% yield).

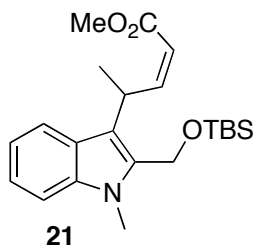
¹H NMR (400 MHz, CDCl₃): δ 7.14-7.17 (m, 2H), 6.82 (dd, *J* = 8.9, 2.5 Hz, 1H), 6.75 (dd, *J* = 11.1, 10.5 Hz, 1H), 5.69 (dd, *J* = 11.4, 1.0 Hz, 1H), 5.12-5.20 (m, 1H), 3.88 (s, 3H), 3.74 (s, 3H), 3.61 (s, 3H), 2.42 (s, 3H), 1.55 (d, *J* = 7.3 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 166.8, 153.9, 153.3, 133.7, 132.4, 126.1, 116.2, 112.8, 109.5, 109.4, 102.2, 56.1, 51.0, 30.4, 29.6, 20.7, 10.6; IR (neat): 2948, 1716, 1486, 1435, 1406, 1227, 1194, 1175, 1033, 824, 793 cm⁻¹; M.p. 91-93 °C; HRMS (APCI) calc. for C₁₇H₂₂O₃N (M+H)⁺ 288.1594 found 288.1591.



(Z)-Methyl 4-(1-benzyl-2-methyl-1H-indol-3-yl)pent-2-enoate (20):

Derived from 1-benzyl-2-methyl-1H-indole (**S-8**) (199 mg, 0.90 mmol, 6.0 equiv.) and *cis*-methyl vinyl diazoacetate **7** (21 mg, 0.15 mmol, 1.0 equiv.), and purified by flash chromatography on silica gel (9/1 pentane/Et₂O, R_f: 0.42) to provide product **20** as colorless oil (45.5 mg, 91% yield).

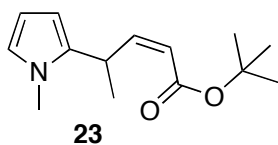
¹H NMR (400 MHz, CDCl₃): δ 7.72-7.76 (m, 1H), 7.19-7.30 (m, 4H), 7.07-7.13 (m, 2H), 6.97 (d, *J* = 7.3 Hz, 2H), 6.82 (t, *J* = 10.8 Hz, 1H), 5.71 (dm, *J* = 11.2 Hz, 1H), 5.30 (s, 2H), 5.15-5.26 (m, 1H), 3.73 (s, 3H), 2.38 (s, 3H), 1.59 (d, *J* = 7.3 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 166.8, 154.0, 137.9, 136.8, 132.8, 128.7, 127.2, 126.1, 126.0, 120.6, 119.2, 118.9, 116.3, 114.0, 109.4, 51.0, 46.5, 30.6, 21.0, 10.5; IR (neat): 1716, 1637, 1466, 1452, 1435, 1339, 1194, 1174, 823, 730, 695 cm⁻¹; HRMS (APCI) calc. for C₂₂H₂₄O₂N (M+H)⁺ 334.1802 found 334.1797.



(Z)-Methyl 4-(2-(((*tert*-butyldimethylsilyl)oxy)methyl)-1-methyl-1*H*-indol-3-yl)pent-2-enoate (21):

Derived from 2-(((*tert*-butyldimethylsilyloxy)methyl)-1-methyl-1*H*-indole (**S-9**) (248 mg, 0.90 mmol, 6.0 equiv.) and *cis*-methyl vinyldiazoacetate **7** (21 mg, 0.15 mmol, 1.0 equiv.), and purified by flash chromatography on silica gel (30/1 pentane/Et₂O, R_f: 0.35) to provide product **21** as a colorless powder (25.6 mg, 44% yield).

¹H NMR (400 MHz, CDCl₃): δ 7.75 (d, *J* = 8.2 Hz, 1H), 7.31 (d, *J* = 8.2 Hz, 1H), 7.22 (td, *J* = 7.0, 0.8 Hz, 1H), 7.08 (td, *J* = 7.0, 0.8 Hz, 1H), 6.80 (t, *J* = 11.2 Hz, 1H), 5.68 (d, *J* = 11.2 Hz, 1H), 5.16-5.27 (m, 1H), 4.98 (d, *J* = 12.9 Hz, 1H), 4.85 (d, *J* = 12.9 Hz, 1H), 3.77 (s, 3H), 3.74 (s, 3H), 1.59 (d, *J* = 7.0 Hz, 3H), 0.90 (s, 9H), 0.11 (s, 3H), 0.09 (s, 3H); ¹³C NMR (100MHz, CDCl₃): δ 166.6, 154.1, 137.5, 134.8, 125.2, 121.5, 120.2, 118.7, 116.4, 114.8, 109.3, 55.0, 51.0, 30.4, 29.9, 25.8, 21.2, 18.2; IR (neat): 2951, 2929, 1720, 1471, 1436, 1405, 1254, 1195, 1177, 1058, 836, 776, 738 cm⁻¹; M.p. 78-80 °C; HRMS (APCI) calc. for C₂₂H₃₃O₃NSi (M)⁺ 387.2242 found 387.2241.

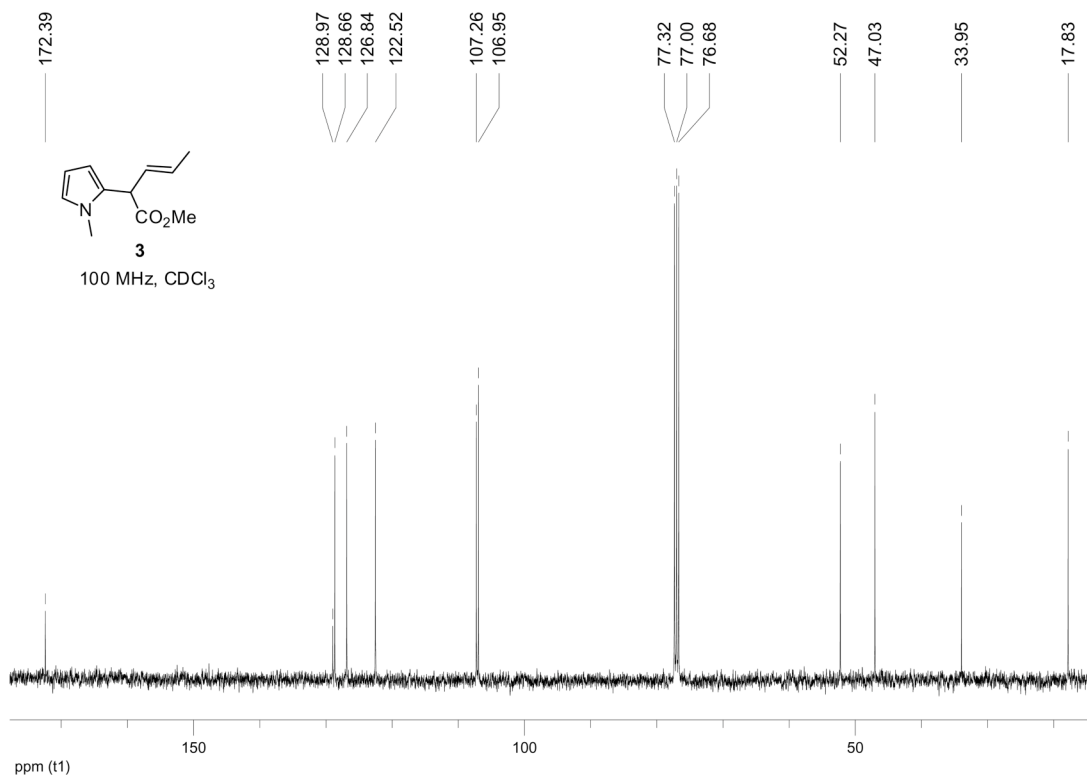
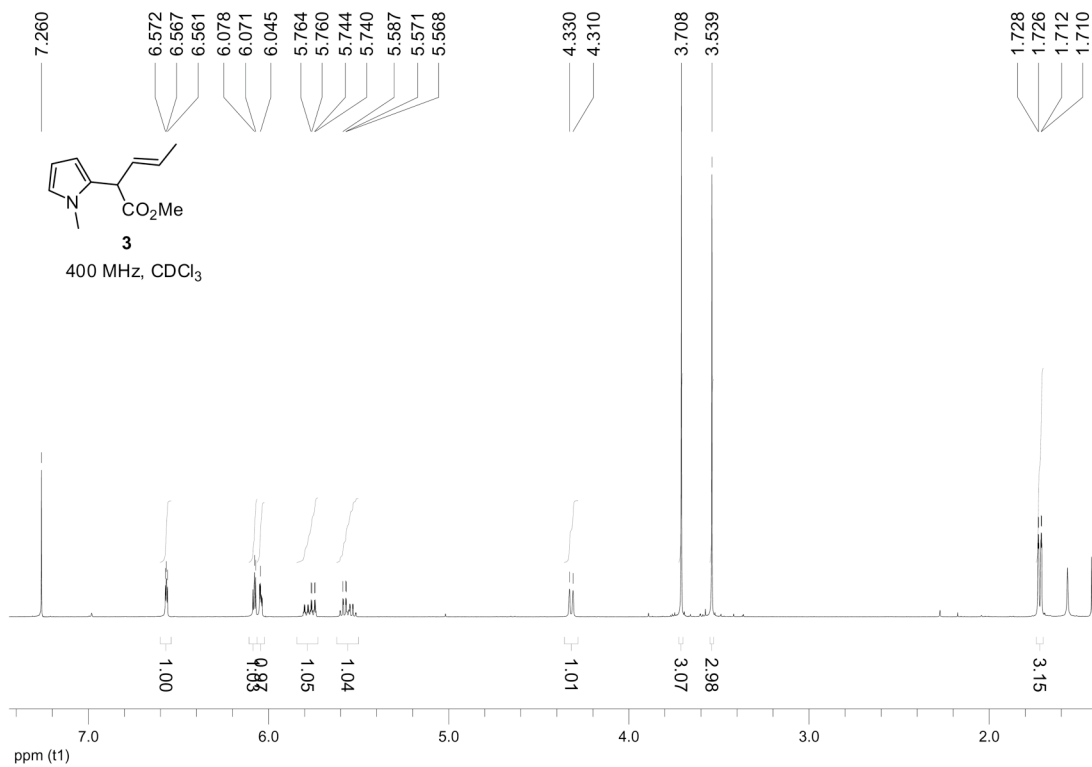


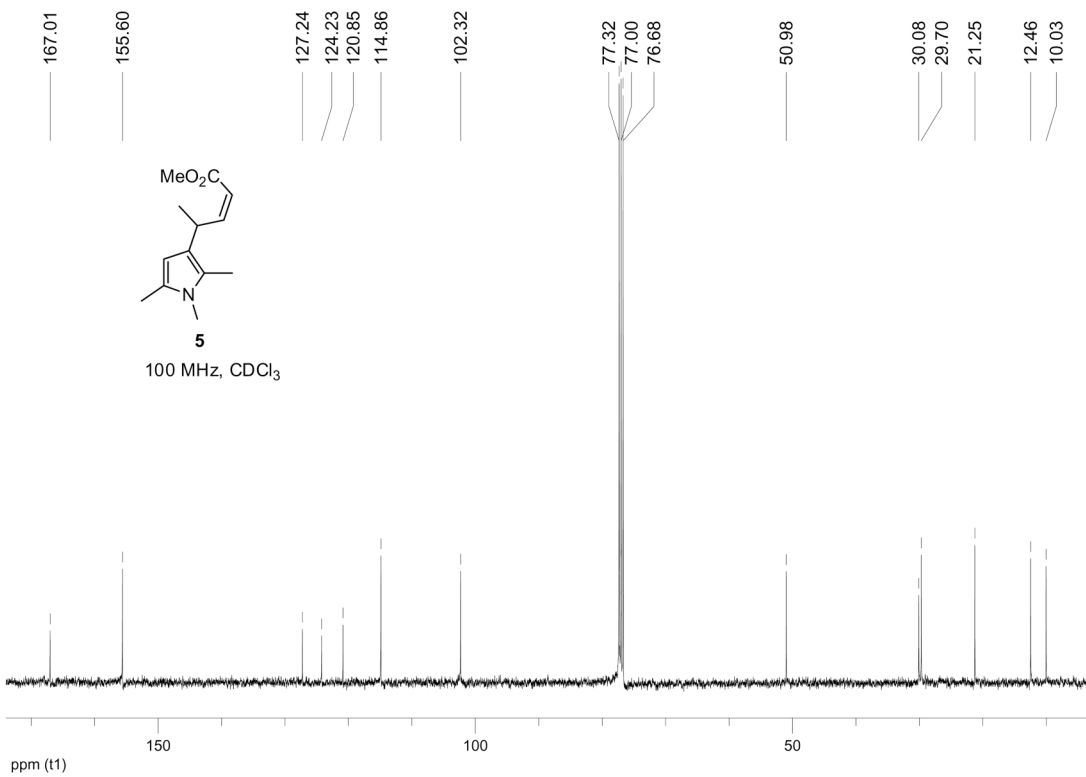
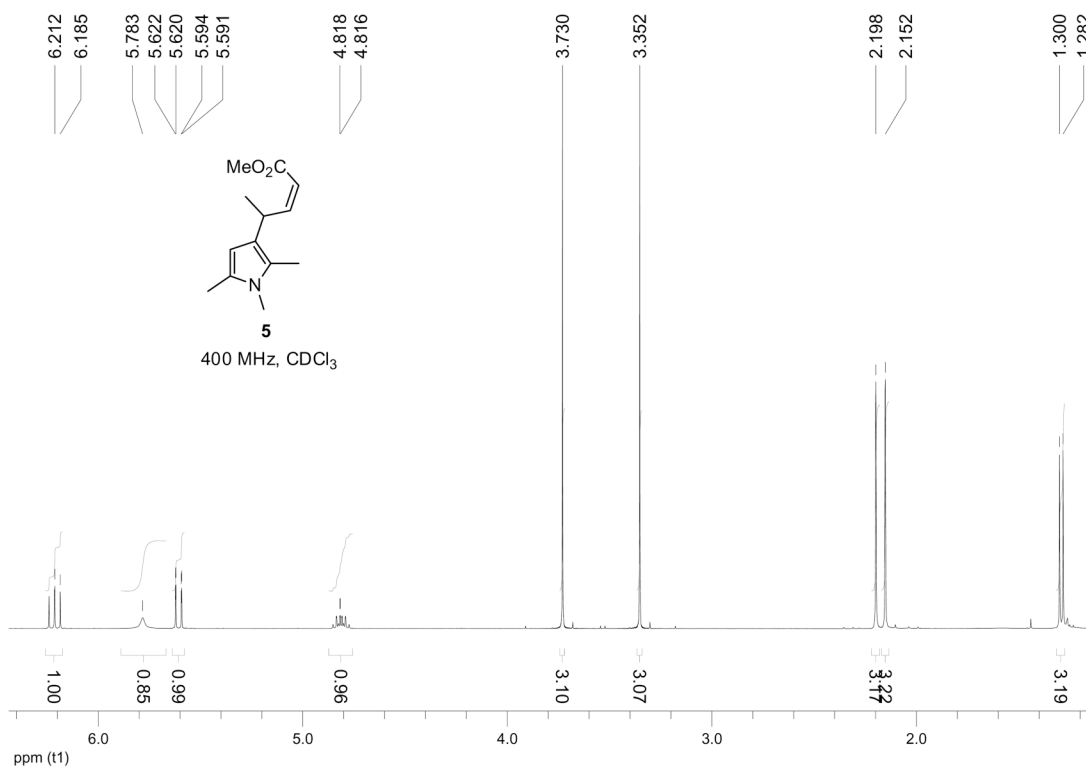
(Z)-*tert*-Butyl 4-(1-methyl-1*H*-pyrrol-2-yl)pent-2-enoate (23):

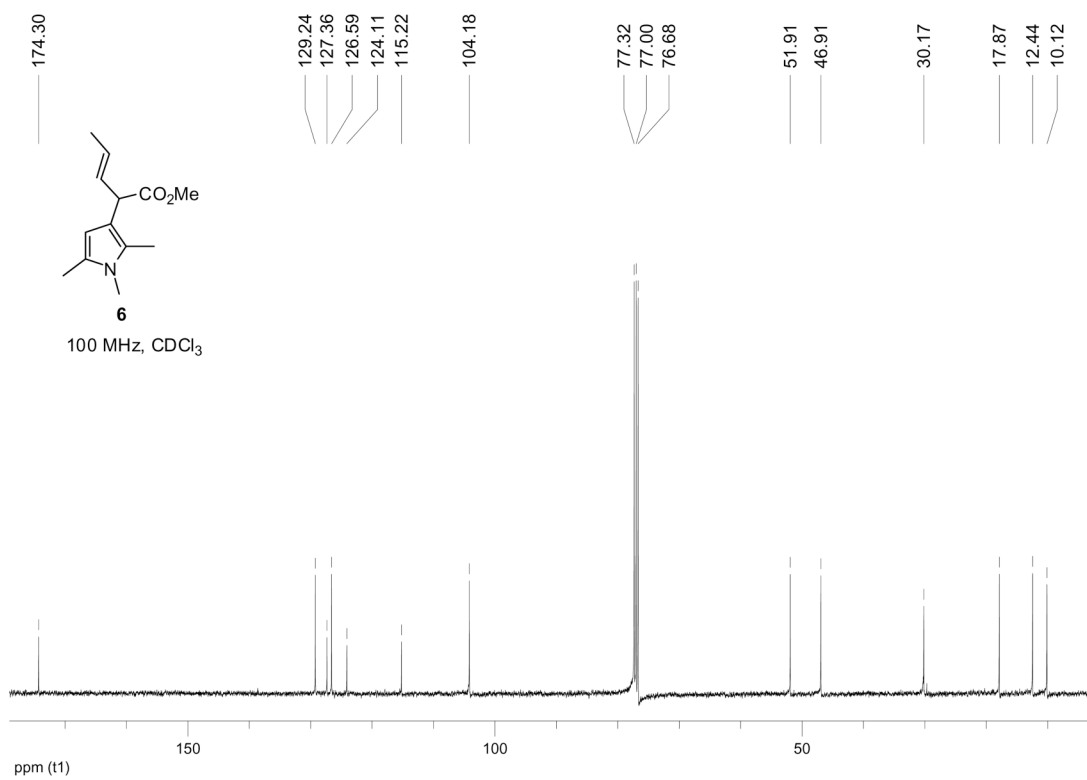
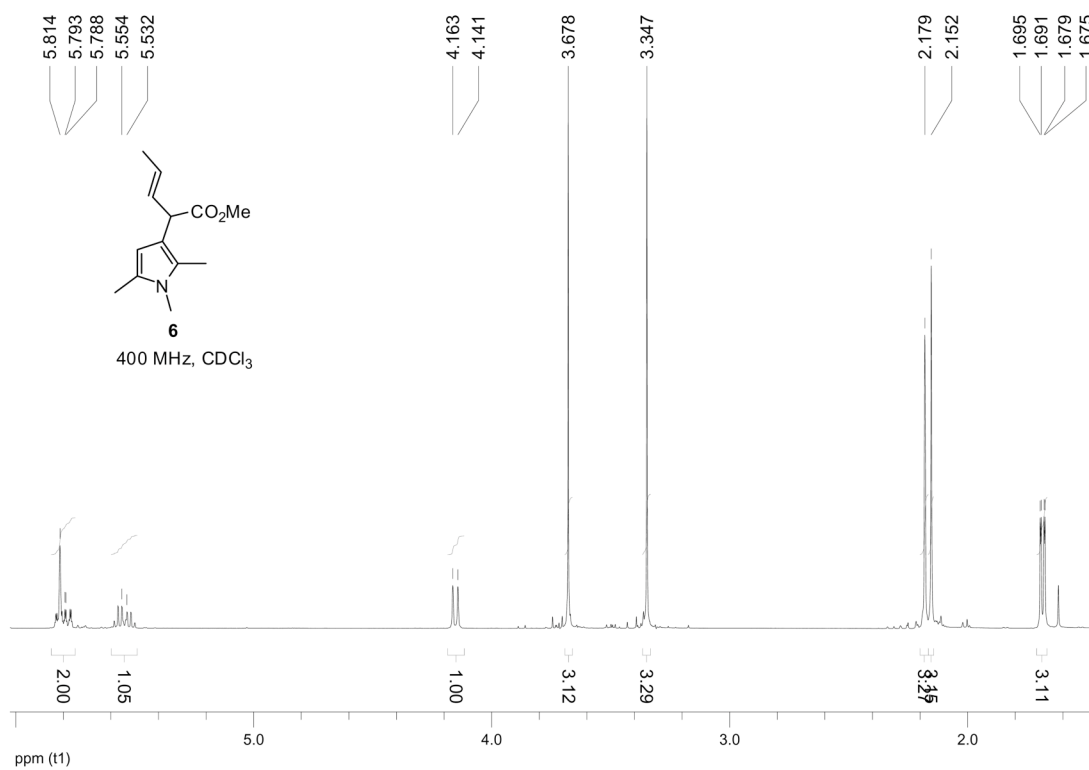
To a flame-dried 25 mL flask containing Rh₂(esp)₂ (2.3 mg, 0.02 equiv.) and 1-methylpyrrole (**1**) (73 mg, 0.90 mmol, 6.0 equiv.) in 6 mL dried CH₂Cl₂ under argon atmosphere was added a solution of *tert*-butyl vinyldiazoacetate **22** (27.4 mg, 0.15 mmol, 1.0 equiv.) in 6 mL dried CH₂Cl₂ by syringe pump over 3 h at -20 °C. The solution was stirred at -20 °C over-night and warmed up to room temperature over 2 h. The mixture was concentrated under reduced pressure and purified by flash chromatography on silica gel (10/1 pentane/Et₂O, R_f: 0.65) to provide product **23** as colorless oil (17.6 mg, 50%

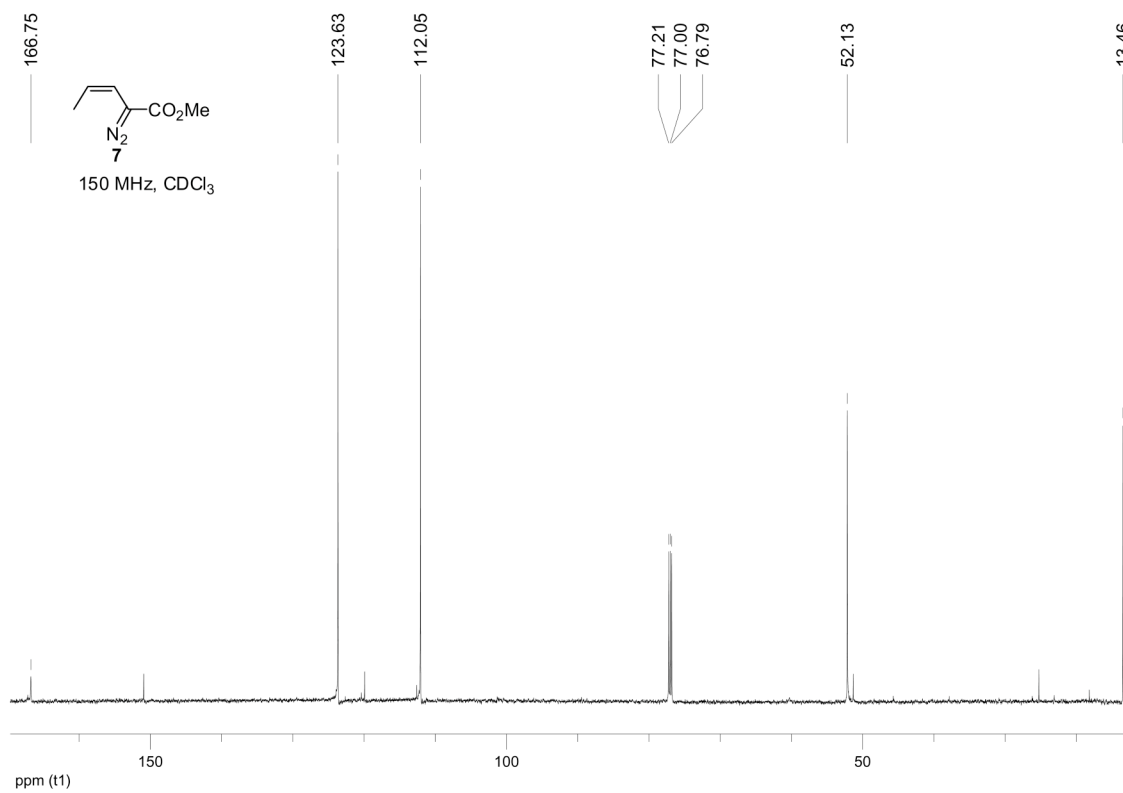
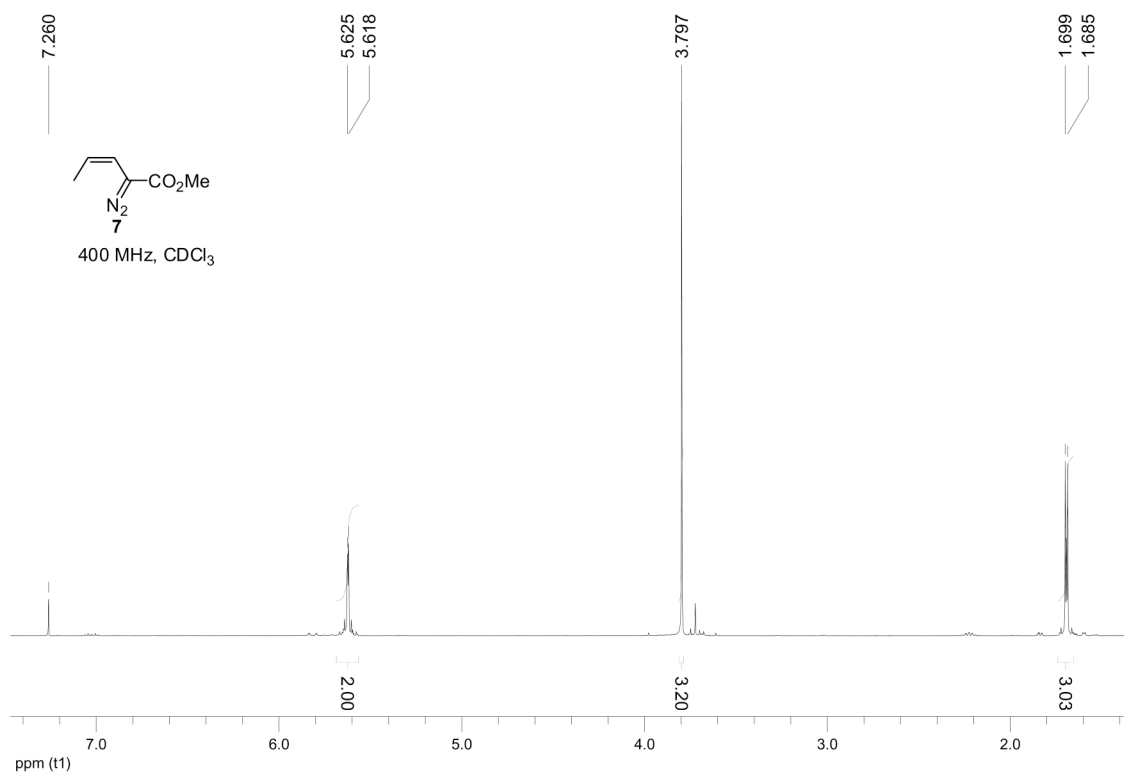
yield).

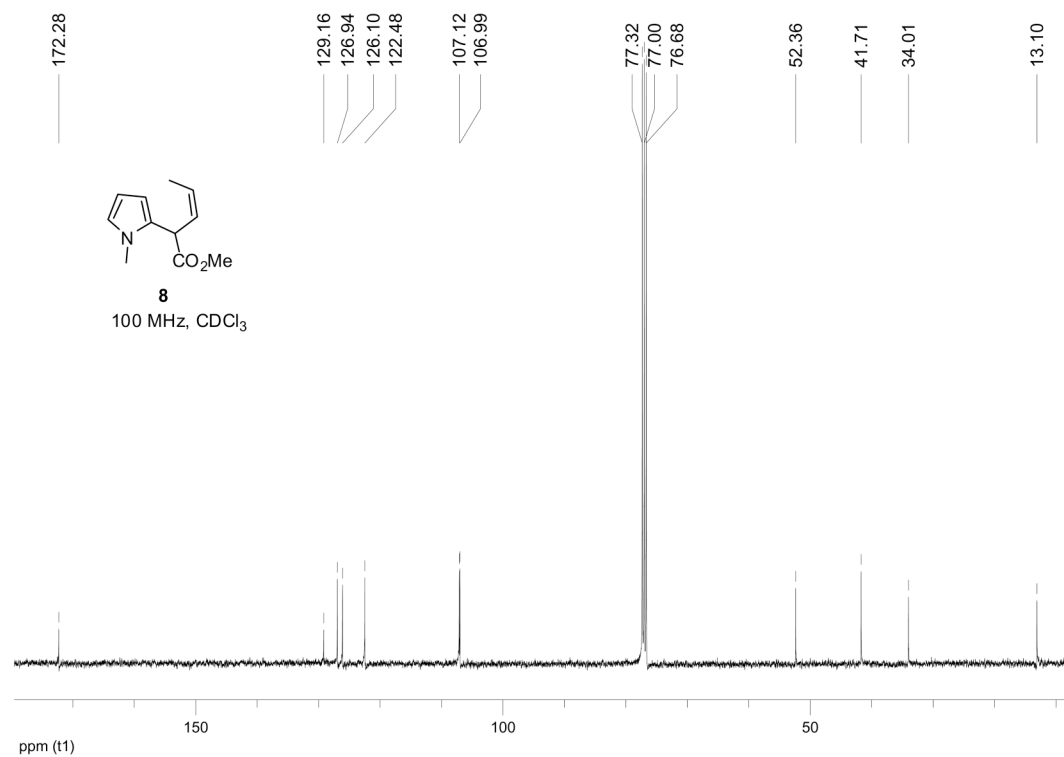
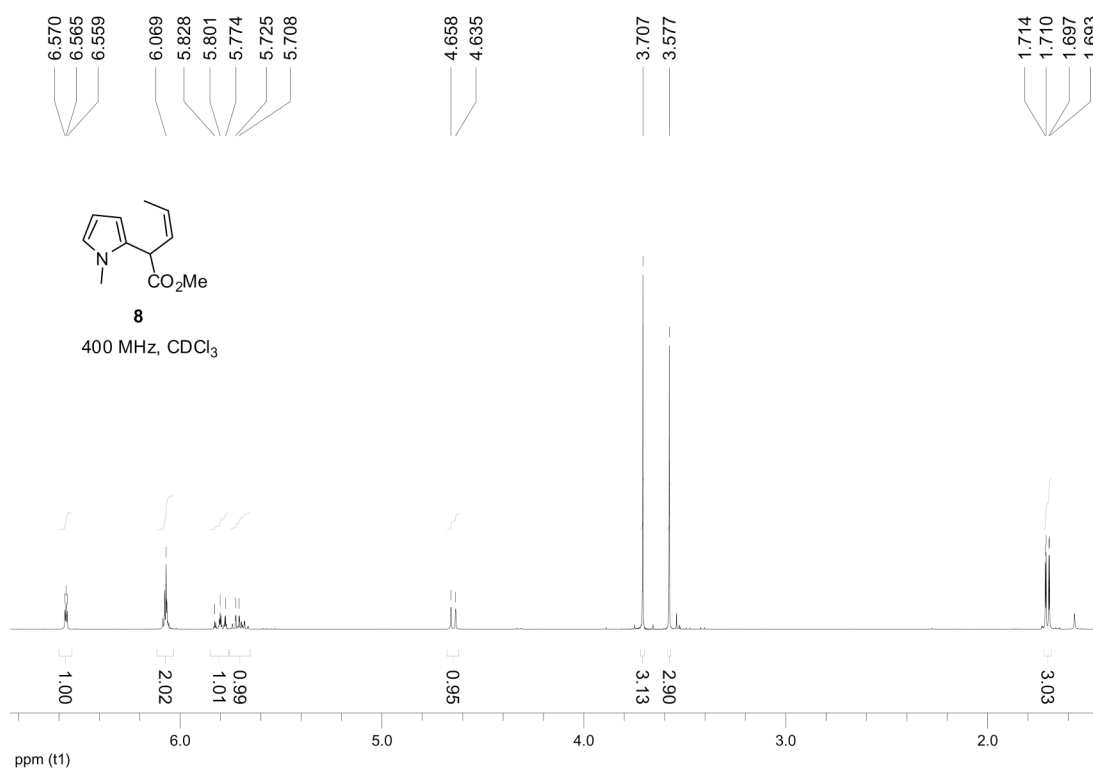
^1H NMR (400 MHz, CDCl_3): δ 6.55 (t, $J = 2.3$ Hz, 1H), 6.09 (t, $J = 3.1$ Hz, 1H), 5.93-5.99 (m, 2H), 5.64 (d, $J = 11.6$ Hz, 1H), 4.84-4.93 (m, 1H), 3.52 (s, 3H), 1.51 (s, 9H), 1.38 (d, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 165.9, 151.4, 135.9, 121.9, 119.2, 106.7, 104.0, 80.4, 33.6, 29.9, 28.2, 19.3; IR (neat): 2976, 1711, 1406, 1367, 1241, 1214, 1151, 828, 705 cm^{-1} ; HRMS (APCI) calc. for $\text{C}_{14}\text{H}_{22}\text{O}_2\text{N}$ ($\text{M}+\text{H}$) $^+$ 236.1645 found 236.1648.

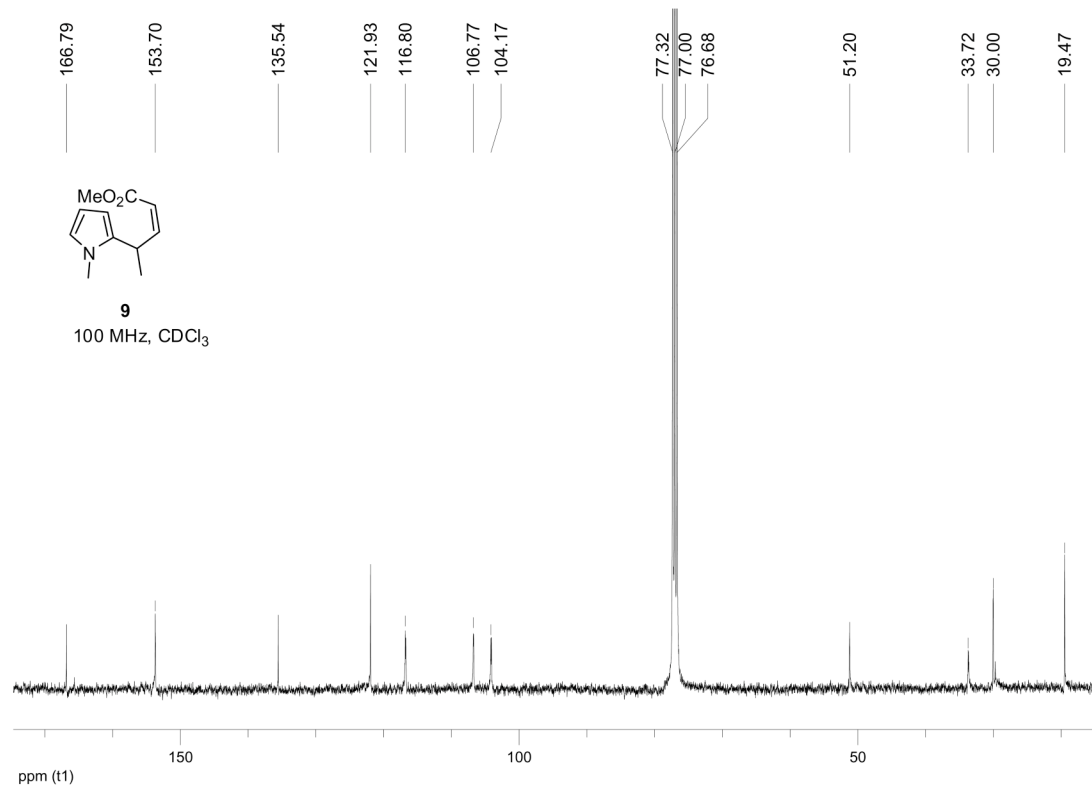
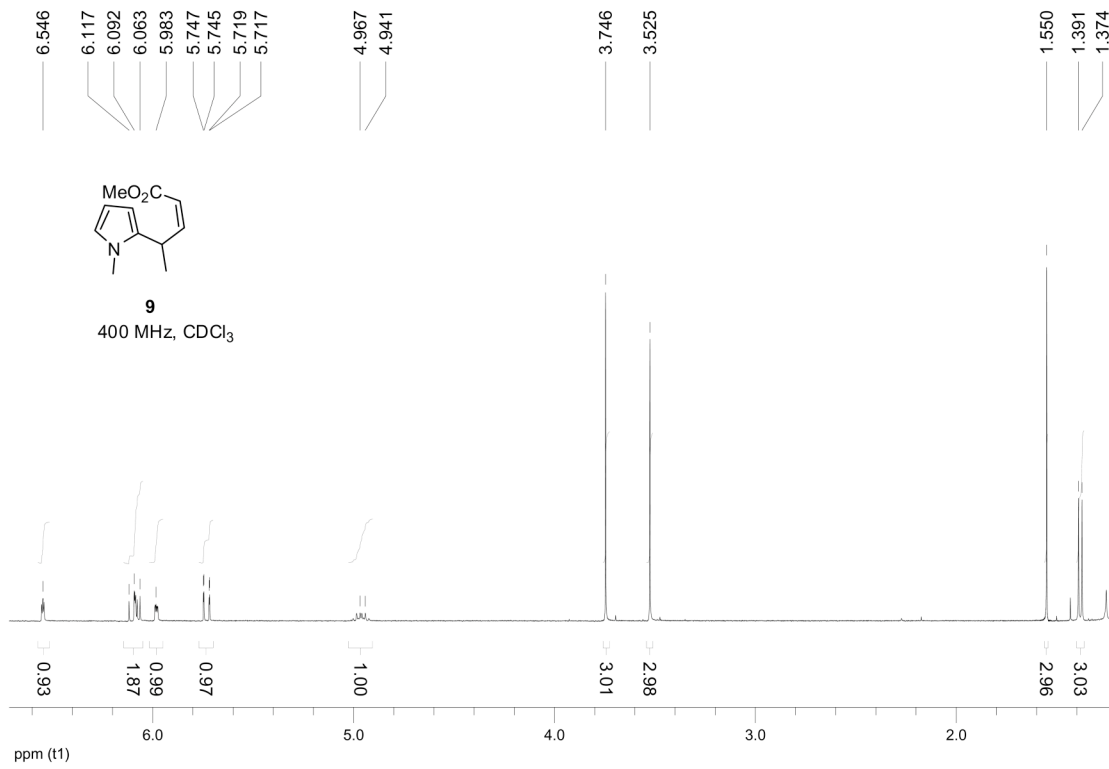


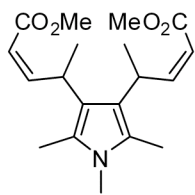












10
400 MHz, CDCl₃

