

Supporting Information

Co-Catalyzed Direct Regio- and Enantioselective Intermolecular γ -Amination of *N*-Acylpyrazoles

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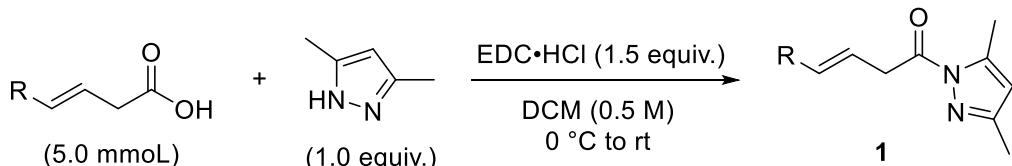
1. Reagents

All commercial materials were used as received unless otherwise noted. Flash chromatography was performed using 200-300 mesh SiliaFlash 60[®] silica gel (Silicycle Inc.). Co(OAc)₂·4H₂O (99%, Adamas), Pybox (>98%, 98% ee, Daicel), DBAD (98%, Adamas), DEAD (98%, Adamas), and DIAD (98%, Adamas) were used in the catalyzed reactions.

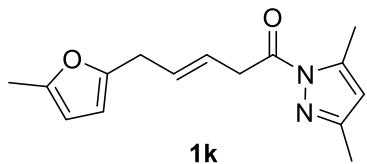
2. Instruments

¹H NMR and ¹³C NMR spectra were acquired on a Bruker AVANCE III HD 400 spectrometer and Bruker AVANCE III HD 500 spectrometer, and calibrated using residual solvent peaks as internal reference. Enantiomeric excesses were measured on an Agilent HPLC. Optical rotations were measured on a Rudolph Research Analytical (Autopol VI). High resolution mass spectra (HRMS) were operated on a Bruker Daltonics SolariX 7.0 Tesla Fourier Transform Ion Cyclotron Resonance (FT-ICR) Mass Spectrometer using the electrospray ionization (ESI) technique. X-ray diffraction data were collected on a Bruker D8 Venture or a Bruker APEX-II CCD diffractometer. Multiplicities are recorded as: s = singlet, d = doublet, t = triplet, dd = doublet of doublets, m = multiplet, br = broad.

3. Preparation of *N*-acylpyrazoles

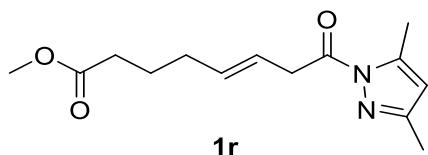


To the mixture of carboxylic acid^[1] (5.0 mmol, 1.0 equiv.) and pyrazole (5.0 mmol, 1.0 equiv.) in dry DCM (10 mL, 0.5 M) was added EDC·HCl (1.438 g, 7.5 mmol, 1.5 equiv.) at 0 °C. The resulting mixture was allowed to warm up to room temperature. The reaction was checked by TLC. After that, the reaction was quenched by saturated brine. The organic layer was separated and the aqueous phase was extracted with DCM (10 mL×3). The combined organic layers were dried over Na₂SO₄. After removal of the solvent in vacuo, the residue was purified by silica gel column (petroleum ether/ethyl acetate) to afford the pure product.^[2]



(E)-1-(3,5-dimethyl-1H-pyrazol-1-yl)-5-(5-methylfuran-2-yl)pent-3-en-1-one

Compound **1k** (800 mg, yellow oil, 62% yield). Flash silica gel chromatography (petroleum ether/ethyl acetate = 120/1). **1H NMR** (CDCl_3 , 500 MHz, ppm) δ 5.94 (s, 1H), 5.87-5.73 (m, 4H), 3.86 (d, J = 7.0 Hz, 2H), 3.36 (d, J = 6.0 Hz, 2H), 2.52 (s, 3H), 2.23 (d, J = 6.5 Hz, 6H); **13C NMR** (CDCl_3 , 126 MHz, ppm) δ 172.1, 152.1, 152.0, 150.6, 144.1, 130.4, 124.0, 111.1, 106.1, 106.0, 38.9, 31.5, 14.5, 13.8, 13.5; **HRMS**: calculated for $\text{C}_{15}\text{H}_{18}\text{N}_2\text{O}_2\text{Na}^+$ [$\text{M}+\text{Na}$]⁺: 281.1260; **found**: 281.1266.

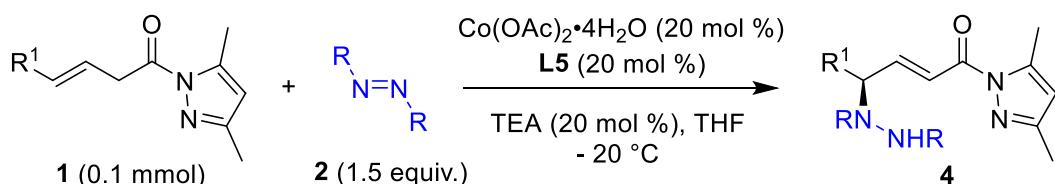


methyl (E)-8-(3,5-dimethyl-1H-pyrazol-1-yl)-8-oxooct-5-enoate

Compound **1r** (686 mg, colorless oil, 52% yield). Flash silica gel chromatography (petroleum ether/ethyl acetate = 25/1). **1H NMR** (CDCl_3 , 500 MHz, ppm) δ 5.96 (s, 1H), 5.71-5.59 (m, 2H), 3.82 (d, J = 6.5 Hz, 2H), 3.66 (s, 3H), 2.53 (s, 3H), 2.32 (t, J = 7.5 Hz, 2H), 2.24 (s, 3H), 2.11 (q, J = 7.0 Hz, 2H), 1.76-1.70 (m, 2H); **13C NMR** (CDCl_3 , 126 MHz, ppm) δ 174.0, 172.3, 151.9, 144.1, 133.8, 122.7, 111.1, 51.4, 39.0, 33.3, 31.9, 24.3, 14.4, 13.8; **HRMS**: calculated for $\text{C}_{14}\text{H}_{20}\text{N}_2\text{O}_3\text{Na}^+$ [$\text{M}+\text{Na}$]⁺: 287.1366; **found**: 287.1370.

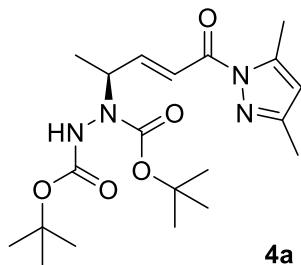
4. General procedure for Co-catalyzed γ -amination reactions

4.1 General procedure



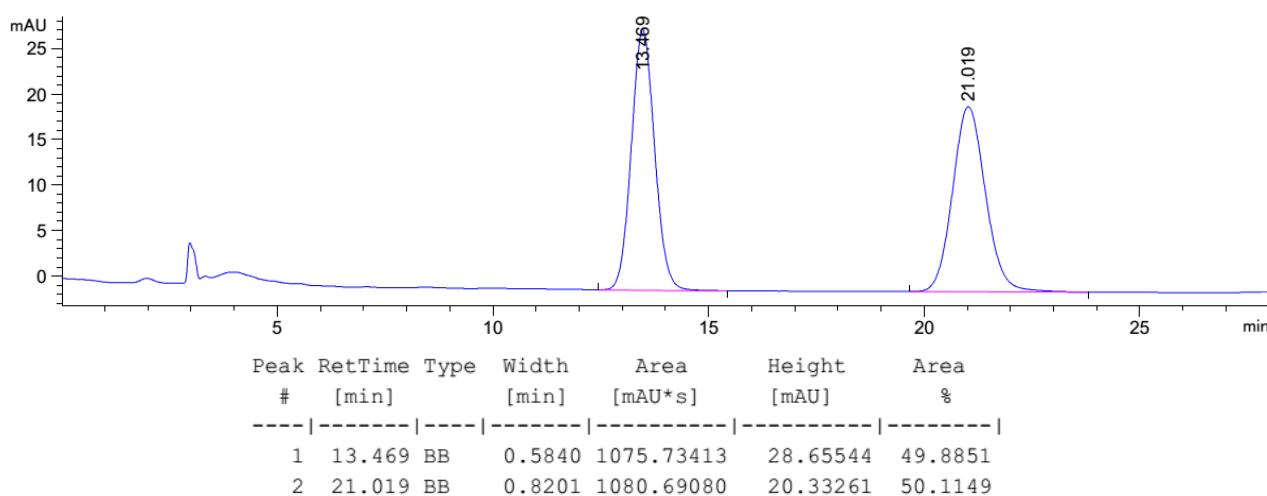
A dried 10 mL schlenk tube equipped with a magnetic stirring bar was charged with $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (4.98 mg, 0.02 mmol) and (*S,S*)-*i*Pr-Pybox (6.02 mg, 0.02 mmol). Anhydrous THF (0.5 mL) was added via syringe. The mixture was stirred for 30 minutes to give pink catalyst solution at rt to -20 °C. Then Azodicarboxylate **2** (0.15 mmol, 1.5 equiv.), *N*-

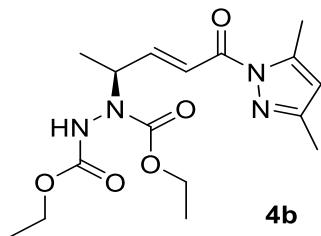
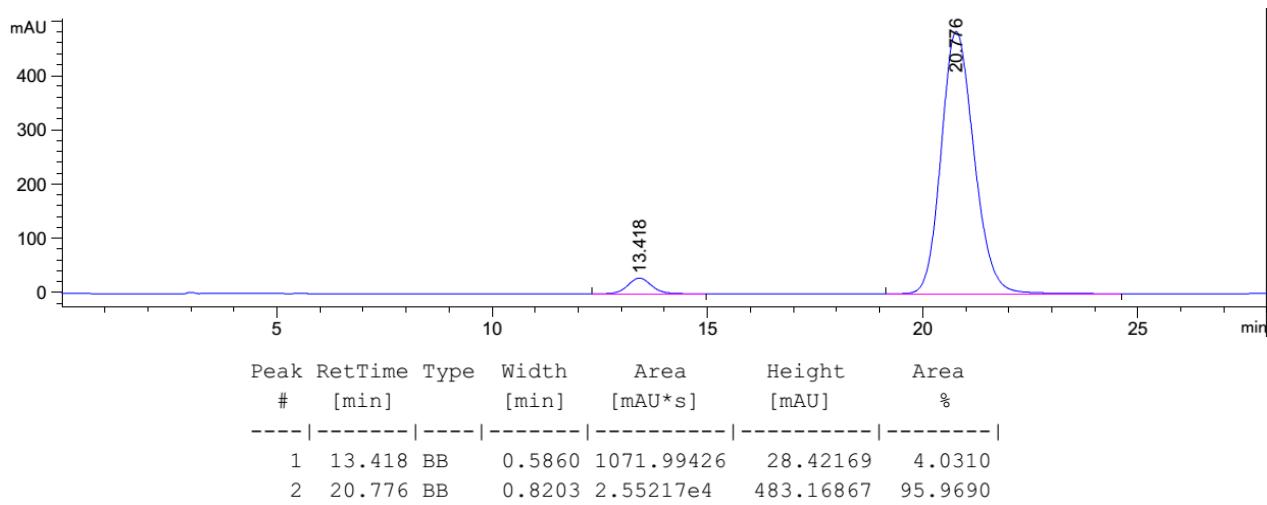
acylpyrazoles **1** (0.1 mmol, 1.0 equiv.), anhydrous THF (0.5 mL) and TEA (0.02 mmol, 0.2 equiv.) were added. The reaction mixture was stirred for 12h-60h at -20 °C. After reaction was completed, the reaction solvent was removed in *vacuo* and the resulting residue was purified by silica gel flash chromatography to give the products **4**.



Di-*tert*-butyl (*S,E*)-1-(5-(3,5-dimethyl-1*H*-pyrazol-1-yl)-5-oxopent-3-en-2-yl)hydrazine-1,2-dicarboxylate

Compound **4a** (36 mg, colorless oil, 88% yield). Flash silica gel chromatography (petroleum ether/ethyl acetate = 8/1). **1H NMR** (CDCl_3 , 400 MHz, ppm) δ 7.34 (d, J = 15.6 Hz, 1H), 7.12 (d, J = 11.2 Hz, 1H), 6.31-6.12 (m, 1H), 5.98 (s, 1H), 5.10-4.87 (m, 1H), 2.56 (s, 3H), 2.25 (s, 3H), 1.47 (s, 18H), 1.39 (d, J = 6.8 Hz, 3H); **13C NMR** (CDCl_3 , 101 MHz, ppm) δ 164.8, 155.7, 154.5, 152.0, 149.0, 144.4, 121.3, 111.5, 81.5, 81.1, 53.2, 28.2, 28.1, 16.6, 14.6, 13.8; **HRMS**: calculated for $\text{C}_{20}\text{H}_{32}\text{N}_4\text{O}_5\text{Na}^+$ [$\text{M}+\text{Na}$]⁺: 431.2265; **found**: 431.2268. **Optical rotation**: $[\alpha]_D^{20} = -4.2$ (c = 1.0, CHCl_3). **HPLC**: DAICEL CHIRALPAK AD, hexane/*i*-PrOH = 90/10, flow rate: 1.0 mL/min, λ = 254 nm, t_R (minor) = 13.4 min, t_R (major) = 20.8 min, ee = 92%.

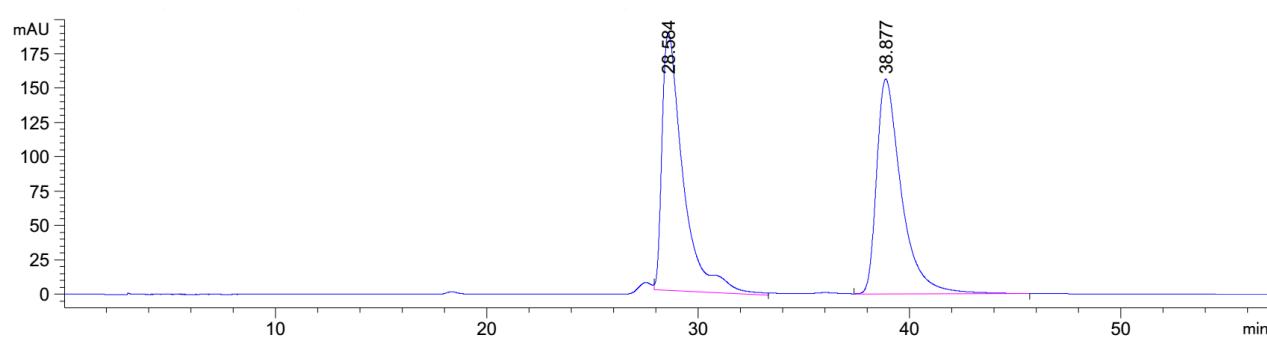


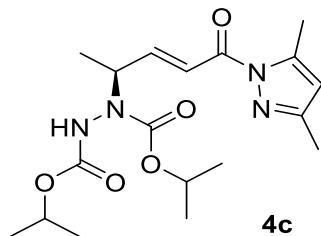
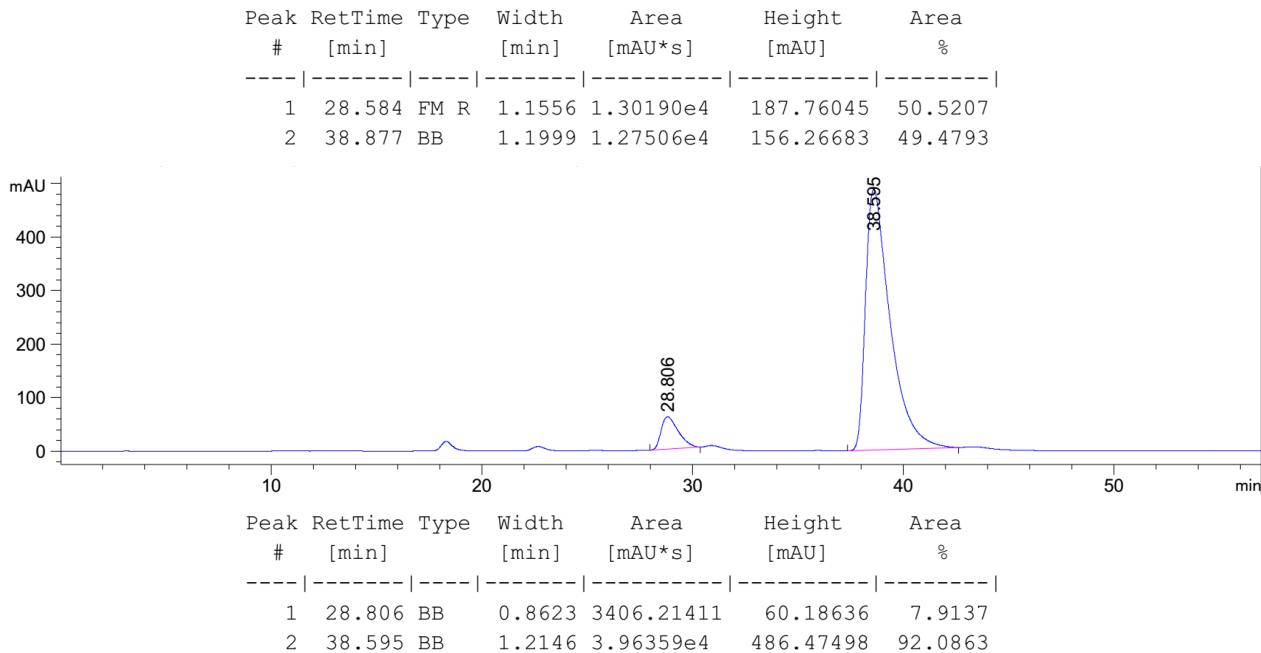


Diethyl (S,E)-1-(5-(3,5-dimethyl-1*H*-pyrazol-1-yl)-5-oxopent-3-en-2-yl)hydrazine-1,2-dicarboxylate

Compound **4b** (20 mg, colorless oil, 57% yield). Flash silica gel chromatography (petroleum ether/ethyl acetate = 3/1). **1H NMR** (CDCl_3 , 400 MHz, ppm) δ 7.35 (d, J = 16.0 Hz, 1H), 7.14-7.10 (m, 1H), 6.55-6.37 (m, 1H), 5.99 (s, 1H), 5.07 (br, 1H), 4.22-4.17 (m, 4H), 2.57 (s, 3H), 2.25 (s, 3H), 1.42 (d, J = 6.8 Hz, 3H), 1.27 (t, J = 7.2 Hz, 6H); **13C NMR** (CDCl_3 , 101 MHz, ppm) δ 164.7, 156.8, 155.6, 152.1, 148.3, 144.5, 121.6, 111.6, 62.8, 62.2, 54.6, 16.6, 14.6, 14.5, 14.4, 13.8; **HRMS**: calculated for $\text{C}_{16}\text{H}_{24}\text{N}_4\text{O}_5\text{Na}^+$ [$\text{M}+\text{Na}$]⁺: 375.1639; **found**: 375.1644.

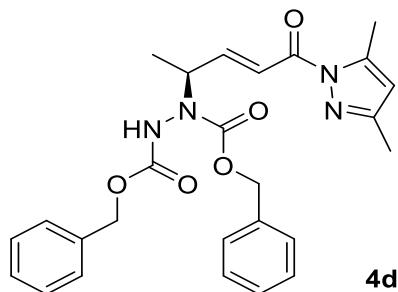
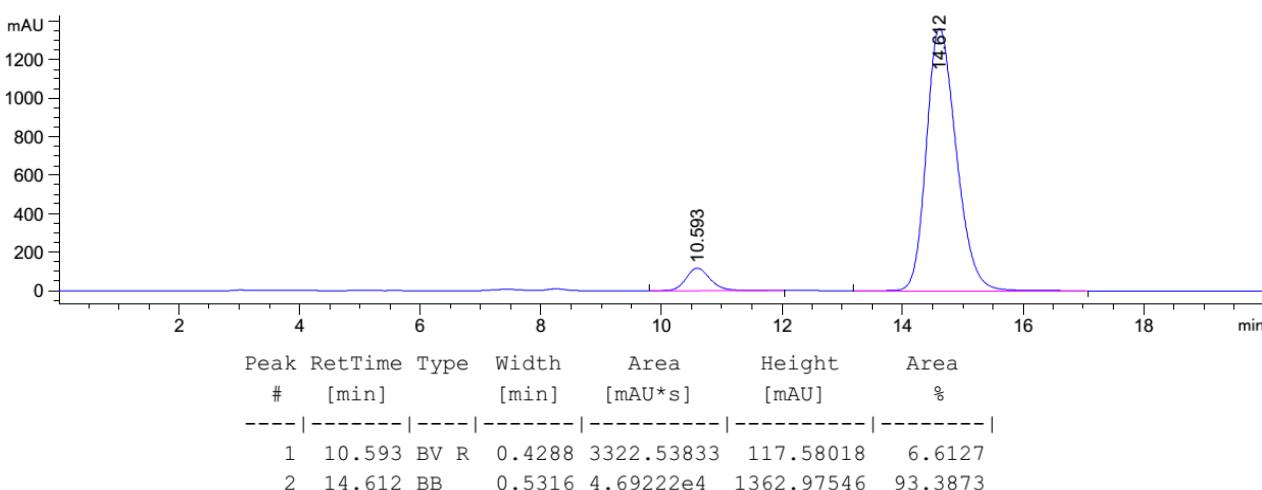
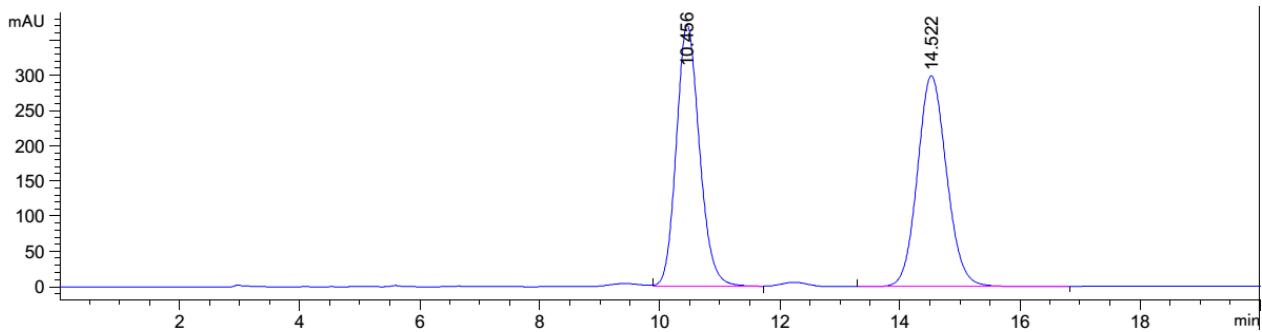
Optical rotation: $[\alpha]_D^{20} = +1.7$ ($c = 1.0$, CHCl_3). **HPLC:** DAICEL CHIRALPAK AD-H, hexane/*i*-PrOH = 96/4, flow rate: 1.0 mL/min, $\lambda = 254$ nm, $t_R(\text{minor}) = 28.8$ min, $t_R(\text{major}) = 38.6$ min, ee = 84%.





Diisopropyl (S,E)-1-(5-(3,5-dimethyl-1H-pyrazol-1-yl)-5-oxopent-3-en-2-yl)hydrazine-1,2-dicarboxylate

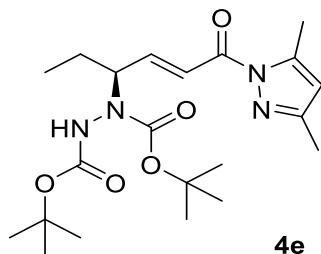
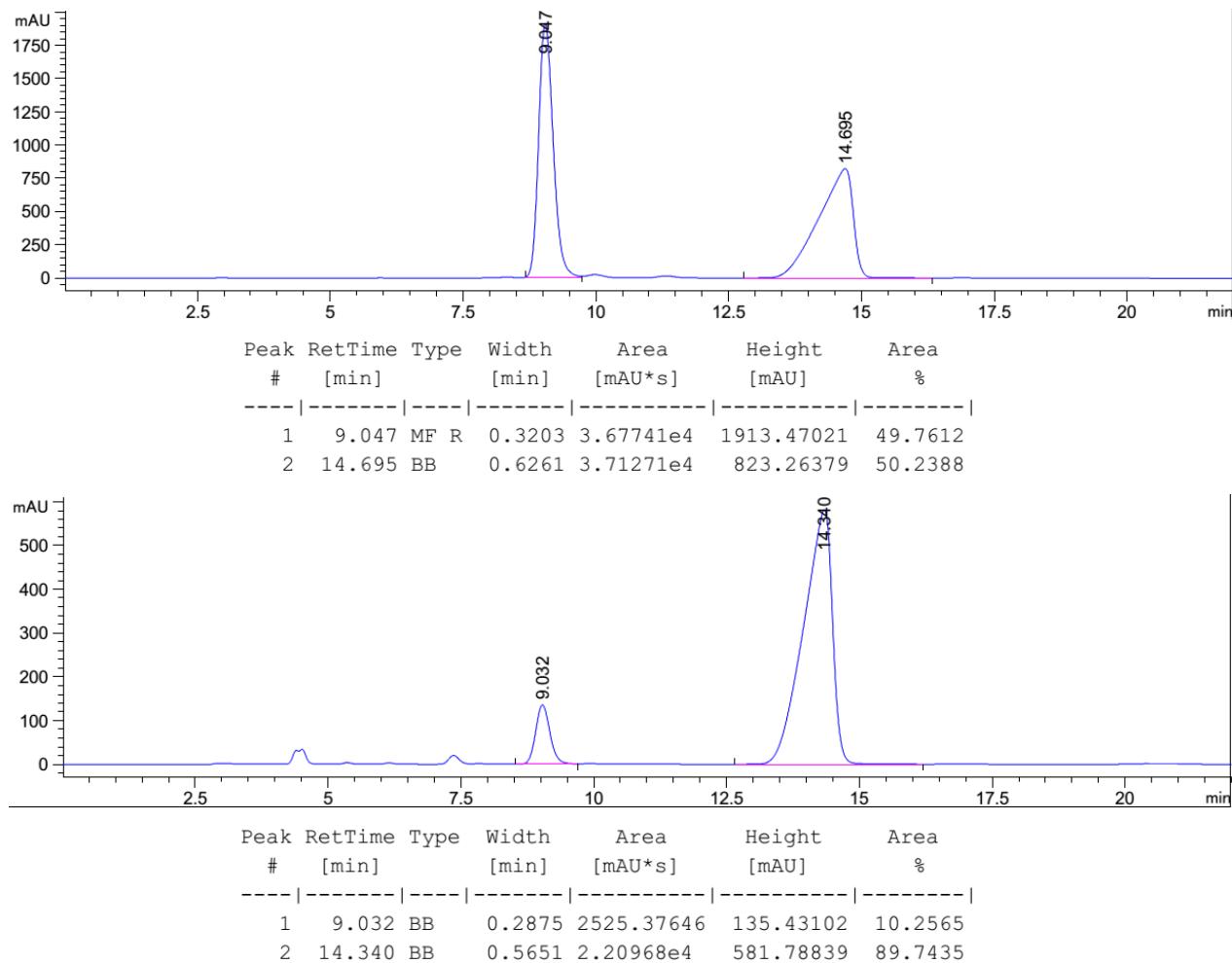
Compound **4c** (30 mg, white solid, 79% yield). Flash silica gel chromatography (petroleum ether/ethyl acetate = 5/1). **¹H NMR** (CDCl_3 , 400 MHz, ppm) δ 7.35 (d, J = 15.6 Hz, 1H), 7.13-7.10 (m, 1H), 6.36-6.20 (m, 1H), 5.99 (s, 1H), 4.98-4.95 (m, 3H), 2.57 (s, 3H), 2.25 (s, 3H), 1.41 (d, J = 6.8 Hz, 3H), 1.26 (d, J = 6.0 Hz, 12H); **¹³C NMR** (CDCl_3 , 101 MHz, ppm) δ 164.8, 156.5, 155.1, 152.1, 148.5, 144.4, 121.5, 111.5, 70.4, 69.9, 53.9, 22.1, 22.0, 21.9, 21.7, 14.6, 13.8; **HRMS**: calculated for $\text{C}_{18}\text{H}_{28}\text{N}_4\text{O}_5\text{Na}^+$ [$\text{M}+\text{Na}]^+$: 403.1952; **found**: 403.1943. **Optical rotation**: $[\alpha]_D^{20} = -1.1$ (c = 1.0, CHCl_3). **HPLC**: DAICEL CHIRALPAK AD, hexane/*i*-PrOH = 90/10, flow rate: 1.0 mL/min, λ = 254 nm, t_R (minor) = 10.6 min, t_R (major) = 14.6 min, ee = 86%.



Dibenzyl (*S,E*-1-(5-(3,5-dimethyl-1*H*-pyrazol-1-yl)-5-oxopent-3-en-2-yl)hydrazine-1,2-dicarboxylate

Compound **4d** (22 mg, colorless oil, 46% yield). Flash silica gel chromatography (petroleum ether/ethyl acetate = 4/1). **1H NMR** (CDCl_3 , 400 MHz, ppm) δ 7.30 (br, 13H), 7.13-7.10 (m, 1H), 6.82-6.67 (m, 1H), 5.97 (s, 1H), 5.15 (br, 4H), 2.54 (s, 3H), 2.23 (s, 3H), 1.42-1.34 (m, 3H); **13C NMR** (CDCl_3 , 101 MHz, ppm) δ 164.6, 156.7, 155.4, 152.1, 148.0, 144.5, 135.7, 135.6, 134.7, 128.6, 128.5, 128.4, 128.3, 128.2, 128.0, 121.9, 111.6, 69.6, 67.9, 54.5, 16.7, 14.6, 13.8; **HRMS**: calculated for $\text{C}_{26}\text{H}_{28}\text{N}_4\text{O}_5\text{Na}^+$ [$\text{M}+\text{Na}$]⁺: 499.1952; **found**: 499.1947. **Optical rotation**: $[\alpha]_D^{20} = +2.8$ ($c = 1.0$, CHCl_3). **HPLC**: DAICEL CHIRALPAK AD, hexane/*i*-PrOH =

80/20, flow rate: 1.0 mL/min, $\lambda = 254$ nm, $t_R(\text{minor}) = 9.0$ min, $t_R(\text{major}) = 14.3$ min, ee = 80%.

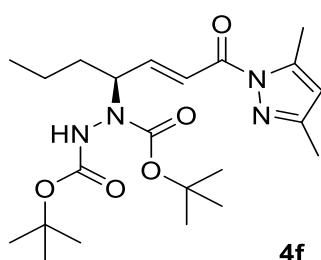
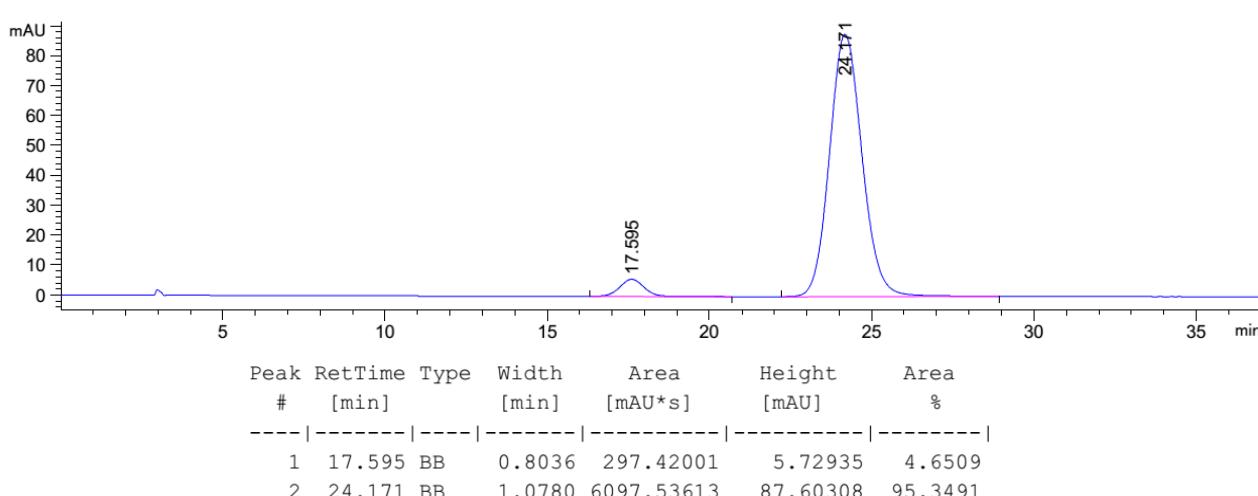
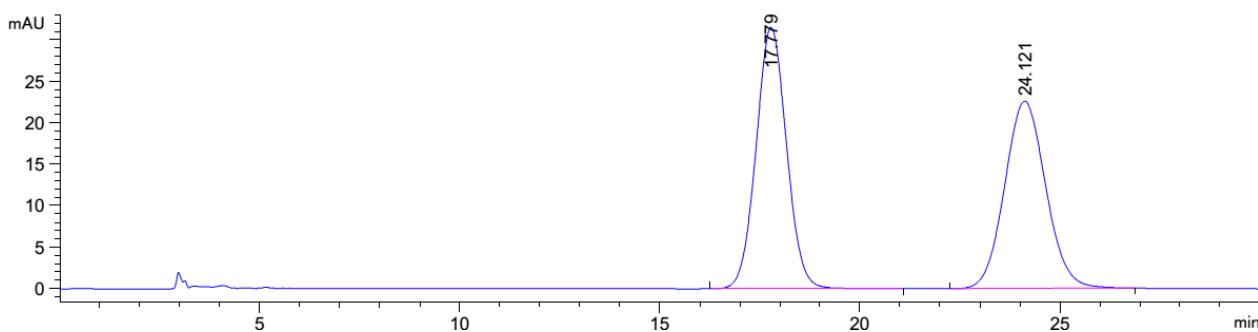


Di-*tert*-butyl (*S,E*)-1-(6-(3,5-dimethyl-1*H*-pyrazol-1-yl)-6-oxohex-4-en-3-yl)hydrazine-1,2-dicarboxylate

Compound **4e** (37 mg, colorless oil, 88% yield). Flash silica gel chromatography (petroleum ether/ethyl acetate = 12/1). **1H NMR** (CDCl_3 , 400 MHz, ppm) δ 7.38 (d, $J = 15.6$ Hz, 1H), 7.12-7.08 (m, 1H), 6.23-6.03 (m, 1H), 5.98 (s, 1H), 4.82-4.58 (m, 1H), 2.57 (s, 3H), 2.25 (s, 3H), 1.82-1.63 (m, 2H), 1.47 (s, 18H), 1.00 (br, 3H); **13C NMR** (CDCl_3 , 101 MHz, ppm) δ 164.8, 156.1, 154.8, 152.0, 147.3, 144.4, 122.3, 111.5, 81.5, 81.1, 59.5, 28.2, 28.1, 24.6, 14.6, 13.8, 10.9; **HRMS**: calculated for $\text{C}_{21}\text{H}_{34}\text{N}_4\text{O}_5\text{Na}^+$ [$\text{M}+\text{Na}$]⁺: 445.2421; **found**: 445.2431.

Optical rotation: $[\alpha]_D^{20} = +8.5$ ($c = 1.0$, CHCl_3). **HPLC:** DAICEL CHIRALPAK AD, hexane/*i*-

$\text{PrOH} = 90/10$, flow rate: 1.0 mL/min, $\lambda = 254 \text{ nm}$, $t_{\text{R}}(\text{minor}) = 17.6 \text{ min}$, $t_{\text{R}}(\text{major}) = 24.2 \text{ min}$, ee = 90%.

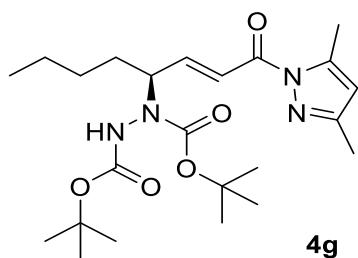
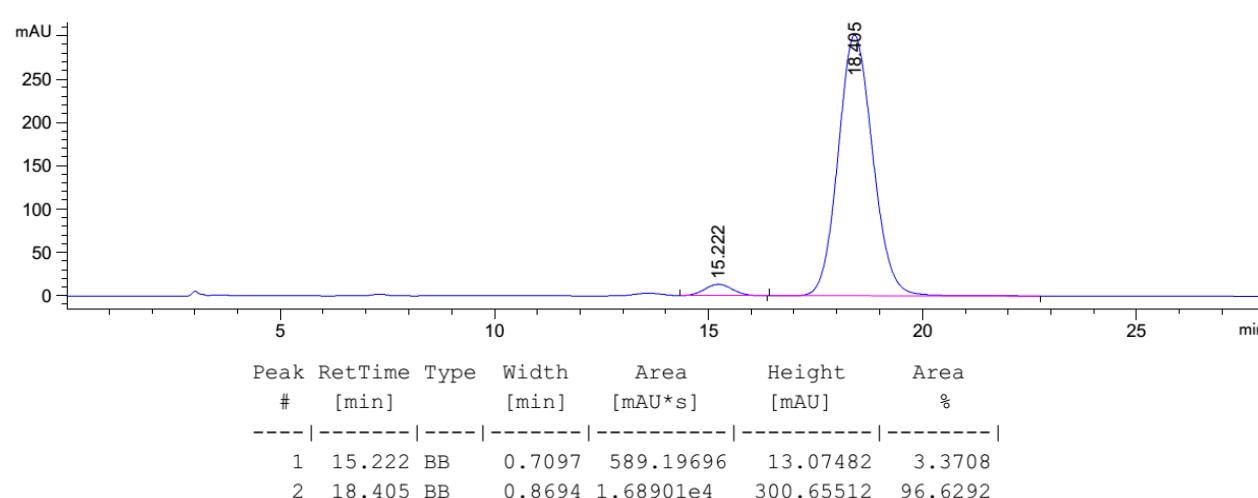
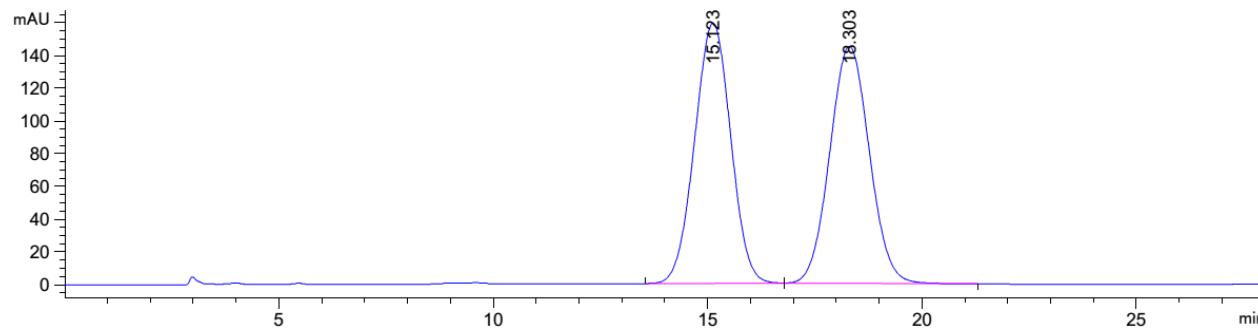


Di-*tert*-butyl (*S,E*)-1-(1-(3,5-dimethyl-1*H*-pyrazol-1-yl)-1-oxohept-2-en-4-yl)hydrazine-1,2-dicarboxylate

Compound **4f** (40 mg, colorless oil, 92% yield). Flash silica gel chromatography (petroleum ether/ethyl acetate = 14/1). **¹H NMR** (CDCl_3 , 400 MHz, ppm) δ 7.37 (d, $J = 15.6 \text{ Hz}$, 1H), 7.12-7.08 (m, 1H), 6.24-6.06 (m, 1H), 5.99 (s, 1H), 4.92-4.70 (m, 1H), 2.57 (s, 3H), 2.25 (s, 3H), 1.79 (br, 2H), 1.47 (s, 20H), 0.95 (t, $J = 7.2 \text{ Hz}$, 3H); **¹³C NMR** (CDCl_3 , 101 MHz, ppm) δ 164.8, 155.7, 154.7, 152.0, 147.6, 144.4, 122.1, 111.4, 81.6, 81.1, 57.7, 33.3, 28.2, 28.1, 19.3,

14.6, 13.9, 13.8; **HRMS**: calculated for $C_{22}H_{36}N_4O_5Na^+$ [M+Na]⁺: 459.2578; **found**: 459.2576.

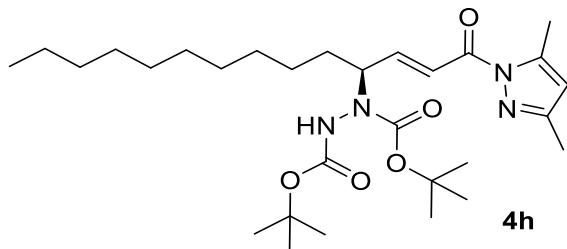
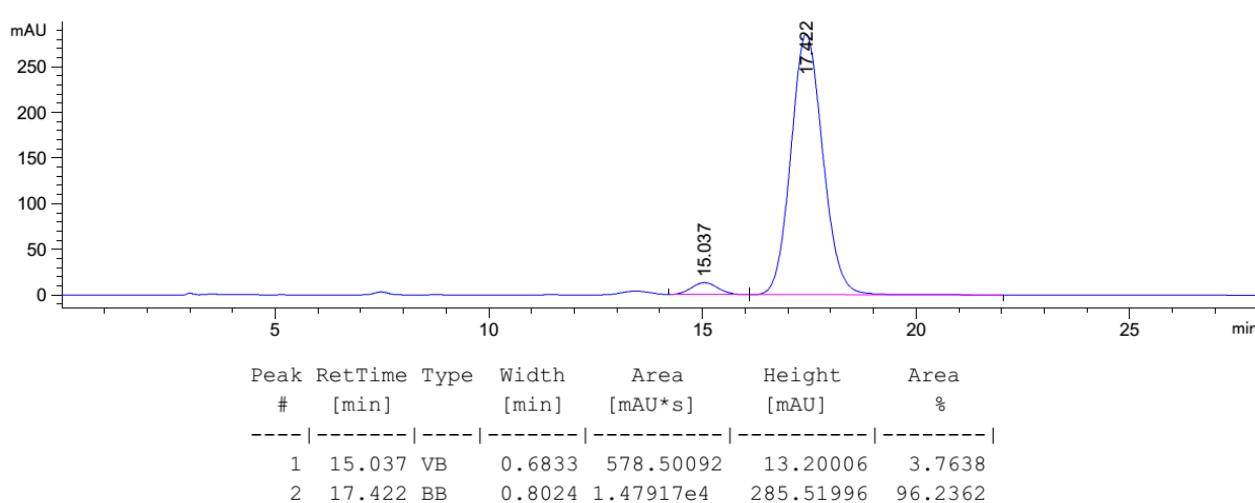
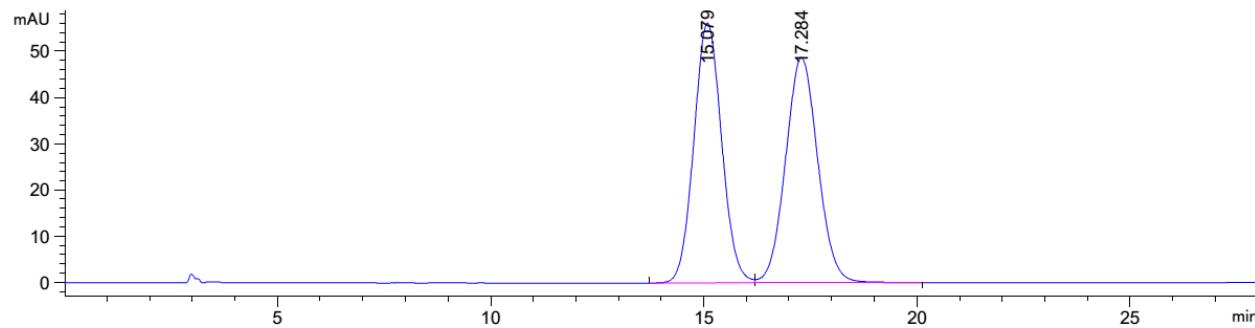
Optical rotation: $[\alpha]^{20}_D = +4.8$ ($c = 1.0$, CHCl₃). **HPLC:** DAICEL CHIRALPAK AD, hexane/*i*-PrOH = 90/10, flow rate: 1.0 mL/min, $\lambda = 254$ nm, $t_R(\text{minor}) = 15.2$ min, $t_R(\text{major}) = 18.4$ min, ee = 94%.



Di-*tert*-butyl (*S,E*)-1-(1-(3,5-dimethyl-1*H*-pyrazol-1-yl)-1-oxooct-2-en-4-yl)hydrazine-1,2-dicarboxylate

Compound **4g** (41 mg, colorless oil, 91% yield). Flash silica gel chromatography (petroleum ether/ethyl acetate = 14/1). **¹H NMR** (CDCl₃, 400 MHz, ppm) δ 7.37 (d, $J = 15.6$ Hz, 1H), 7.12-7.08 (m, 1H), 6.21-6.02 (m, 1H), 5.98 (s, 1H), 4.89-4.67 (m, 1H), 2.57 (s, 3H), 2.25 (s, 3H), 1.80-1.63 (m, 2H), 1.47 (s, 18H), 1.37-1.34 (m, 4H), 0.91 (t, $J = 5.2$ Hz, 3H); **¹³C NMR**

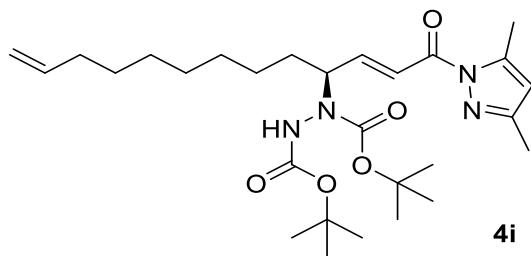
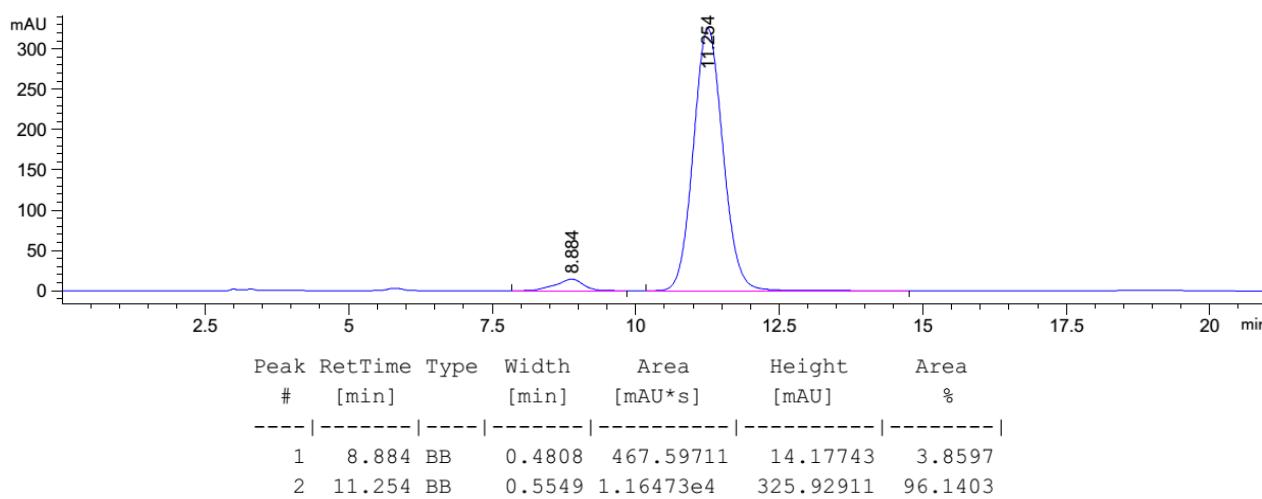
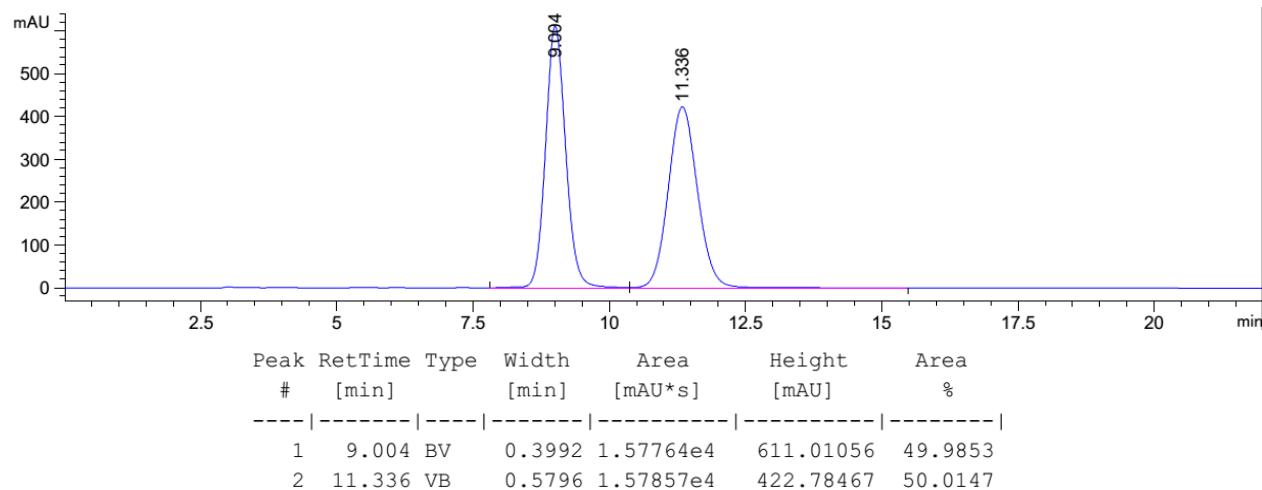
(CDCl₃, 101 MHz, ppm) δ 164.9, 155.9, 154.7, 152.0, 147.6, 144.4, 122.1, 111.4, 81.5, 81.1, 58.2, 30.9, 28.2, 28.1, 22.5, 14.6, 14.0, 13.8; **HRMS**: calculated for C₂₃H₃₈N₄O₅Na⁺ [M+Na]⁺: 473.2734; **found**: 473.2735. **Optical rotation**: [α]_D²⁰ = +3.8 (c = 1.0, CHCl₃). **HPLC**: DAICEL CHIRALPAK AD, hexane/*i*-PrOH = 90/10, flow rate: 1.0 mL/min, λ = 254 nm, t_R(minor) = 15.0 min, t_R(major) = 17.4 min, ee = 92%.



Di-*tert*-butyl (*S,E*)-1-(1-(3,5-dimethyl-1*H*-pyrazol-1-yl)-1-oxotetradec-2-en-4-yl)hydrazine-1,2-dicarboxylate

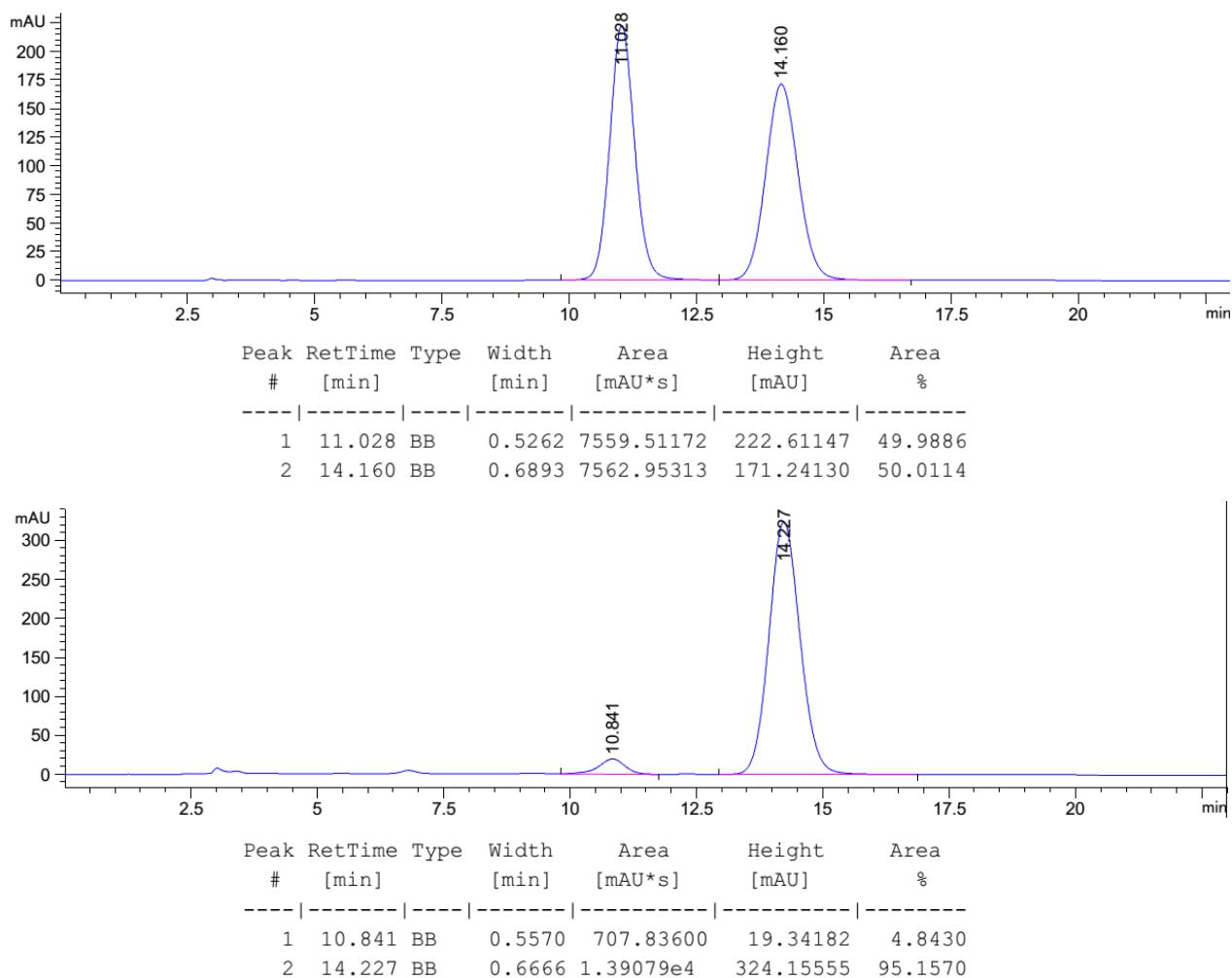
Compound **4h** (45 mg, colorless oil, 84% yield). Flash silica gel chromatography (petroleum ether/ethyl acetate = 16/1). **1H NMR** (CDCl₃, 400 MHz, ppm) δ 7.36 (d, *J* = 15.6 Hz, 1H), 7.12

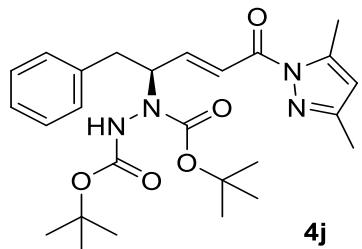
(br, 1H), 6.17 (br, 1H), 5.98 (s, 1H), 4.89-4.67 (m, 1H), 2.57 (s, 3H), 2.25 (s, 3H), 1.85-1.80 (m, 2H), 1.47 (s, 18H), 1.25 (s, 16H), 0.88 (t, $J = 6.8$ Hz, 3H); ^{13}C NMR (CDCl_3 , 101 MHz, ppm) δ 164.8, 155.9, 154.7, 152.0, 147.7, 144.4, 122.1, 111.4, 81.5, 81.0, 58.1, 31.9, 31.3, 29.6, 29.5, 29.4, 29.3, 28.2, 28.1, 26.1, 22.7, 14.6, 14.1, 13.8; HRMS: calculated for $\text{C}_{29}\text{H}_{50}\text{N}_4\text{O}_5\text{Na}^+$ $[\text{M}+\text{Na}]^+$: 557.3673; found: 557.3676. Optical rotation: $[\alpha]_D^{20} = +1.7$ ($c = 1.0$, CHCl_3). HPLC: DAICEL CHIRALPAK AD, hexane/*i*-PrOH = 90/10, flow rate: 1.0 mL/min, $\lambda = 254$ nm, $t_{\text{R}}(\text{minor}) = 8.9$ min, $t_{\text{R}}(\text{major}) = 11.3$ min, ee = 92%.



Di-*tert*-butyl (S,E)-1-(1-(3,5-dimethyl-1*H*-pyrazol-1-yl)-1-oxotrideca-2,12-dien-4-yl)hydrazine-1,2-dicarboxylate

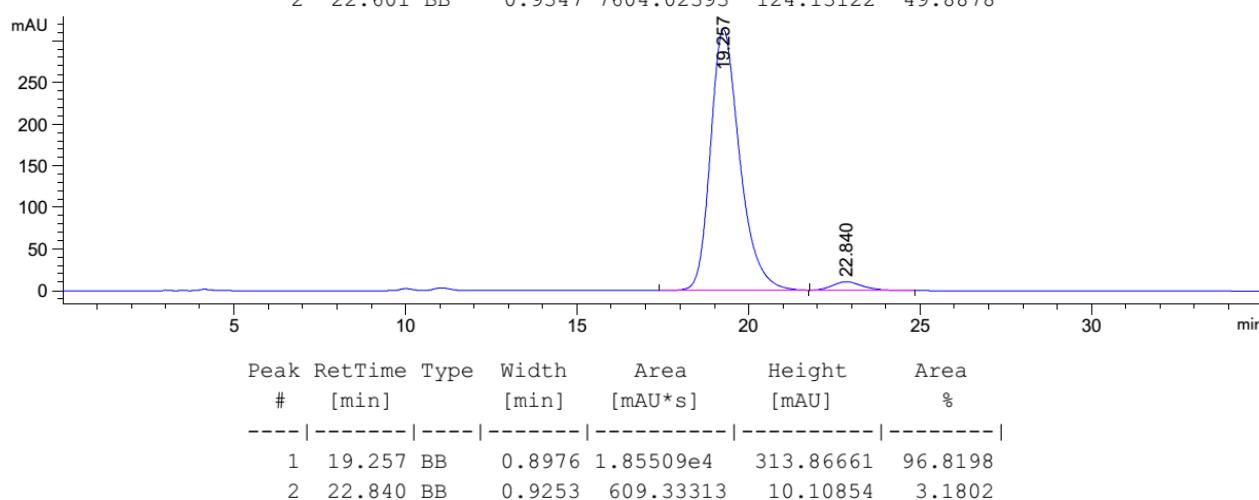
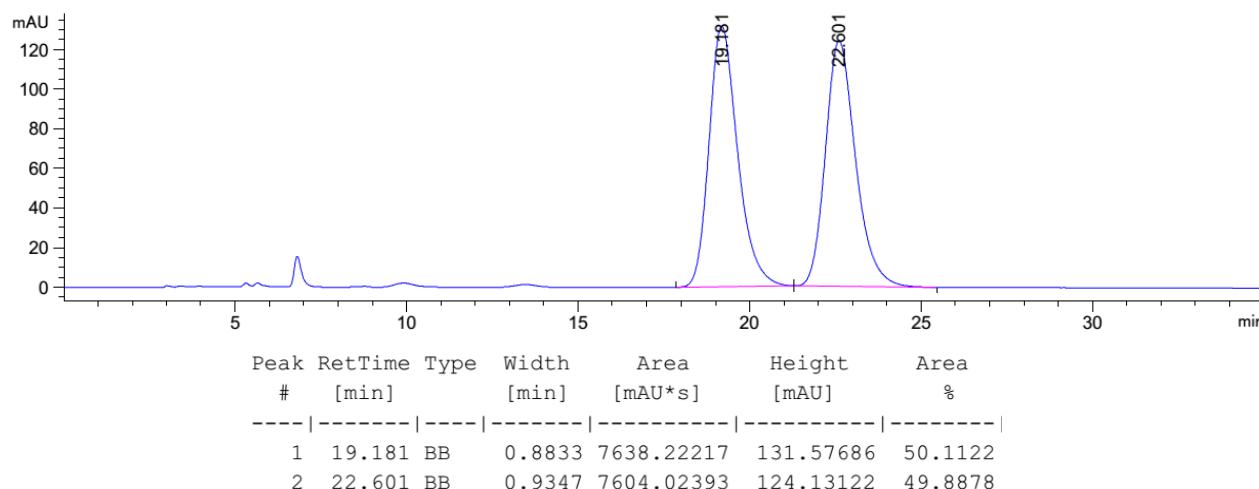
Compound **4i** (40 mg, colorless oil, 77% yield). Flash silica gel chromatography (petroleum ether/ethyl acetate = 16/1). **¹H NMR** (CDCl_3 , 400 MHz, ppm) δ 7.36 (d, J = 16.0 Hz, 1H), 7.12-7.08 (m, 1H), 6.21 (br, 1H), 5.98 (s, 1H), 5.86-5.75 (m, 1H), 5.01-4.67 (m, 3H), 2.57 (s, 3H), 2.25 (s, 3H), 2.03 (dd, J = 6.8 Hz, J = 14.0 Hz, 2H), 1.97-1.62 (m, 3H), 1.47 (s, 18H), 1.38-1.30 (m, 9H); **¹³C NMR** (CDCl_3 , 101 MHz, ppm) δ 164.8, 155.8, 154.8, 152.0, 147.6, 144.4, 139.2, 122.1, 114.2, 111.4, 81.8, 81.1, 58.1, 33.8, 31.2, 29.3, 29.1, 28.9, 28.2, 28.1, 26.1, 14.6, 13.8; **HRMS**: calculated for $\text{C}_{28}\text{H}_{46}\text{N}_4\text{O}_5\text{Na}^+$ [$\text{M}+\text{Na}$]⁺: 541.3360; **found**: 541.3362. **Optical rotation**: $[\alpha]_D^{20} = +2.3$ (c = 1.0, CHCl_3). **HPLC**: DAICEL CHIRALPAK AD, hexane/*i*-PrOH = 90/10, flow rate: 1.0 mL/min, λ = 254 nm, t_R (minor) = 10.8 min, t_R (major) = 14.2 min, ee = 90%.

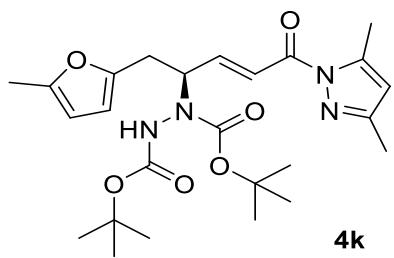




Di-*tert*-butyl (S,E)-1-(5-(3,5-dimethyl-1*H*-pyrazol-1-yl)-5-oxo-1-phenylpent-3-en-2-yl)hydrazine-1,2-dicarboxylate

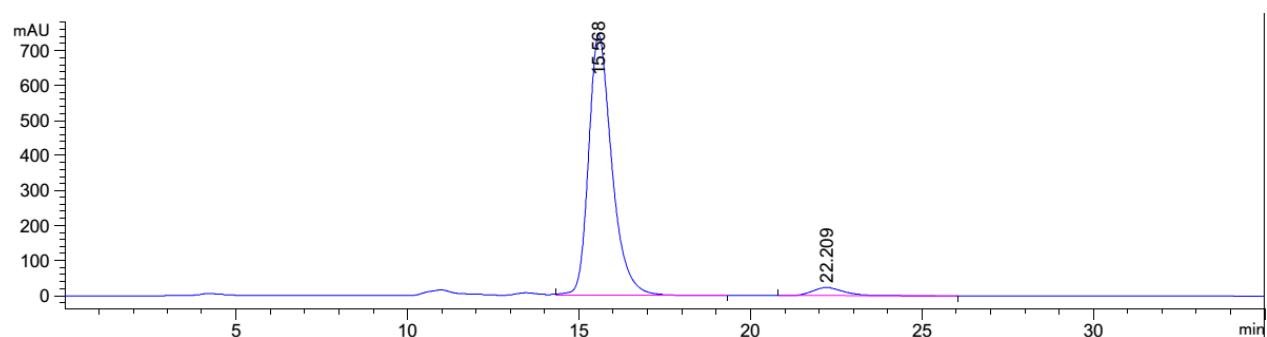
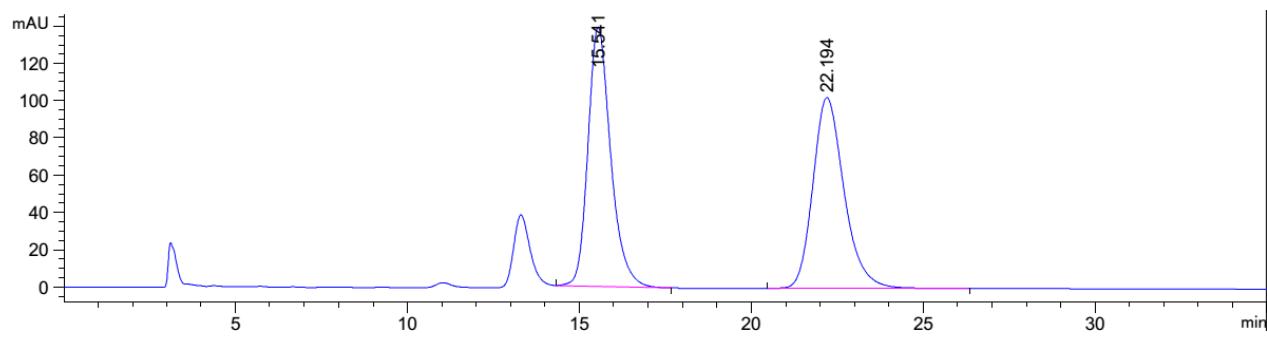
Compound **4j** (43 mg, colorless oil, 89% yield). Flash silica gel chromatography (petroleum ether/ethyl acetate = 12/1). **¹H NMR** (CDCl_3 , 400 MHz, ppm) δ 7.31-7.21 (m, 7H), 6.13 (br, 1H), 5.97 (s, 1H), 5.38-5.00 (m, 1H), 3.16-2.99 (m, 2H), 2.56 (s, 3H), 2.24 (s, 3H), 1.51-1.32 (m, 18H); **¹³C NMR** (CDCl_3 , 101 MHz, ppm) δ 164.6, 155.7, 154.4, 151.9, 146.7, 144.4, 137.4, 129.2, 128.7, 126.7, 122.2, 111.5, 82.2, 81.3, 37.9, 28.1, 14.6, 13.8; **HRMS**: calculated for $\text{C}_{26}\text{H}_{36}\text{N}_4\text{O}_5\text{Na}^+$ [$\text{M}+\text{Na}]^+$: 507.2578; **found**: 507.2578. **Optical rotation**: $[\alpha]_D^{20} = +9.8$ ($c = 1.0$, CHCl_3). **HPLC**: DAICEL CHIRALPAK IA, hexane/*i*-PrOH = 90/10, flow rate: 1.0 mL/min, $\lambda = 254$ nm, $t_R(\text{major}) = 19.3$ min, $t_R(\text{minor}) = 22.8$ min, ee = 94%.



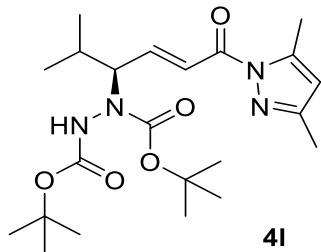


Di-*tert*-butyl (*S,E*)-1-(5-(3,5-dimethyl-1*H*-pyrazol-1-yl)-1-(5-methylfuran-2-yl)-5-oxopent-3-en-2-yl)hydrazine-1,2-dicarboxylate

Compound **4k** (36 mg, colorless oil, 74% yield). Flash silica gel chromatography (petroleum ether/ethyl acetate = 10/1). **¹H NMR** (CDCl_3 , 500 MHz, ppm) δ 7.40 (d, J = 15.0 Hz, 1H), 7.20 (s, 1H), 6.25-6.01 (m, 1H), 5.98 (s, 2H), 5.84 (s, 1H), 5.27-2.04 (m, 1H), 3.13-2.93 (m, 2H), 2.56 (s, 3H), 2.24 (s, 6H), 1.47-1.43 (m, 18H); **¹³C NMR** (CDCl_3 , 126 MHz, ppm) δ 164.6, 155.8, 154.3, 151.9, 151.2, 149.5, 146.8, 144.3, 122.1, 111.4, 107.9, 106.2, 82.0, 81.3, 30.3, 28.1, 14.6, 13.8, 13.5; **HRMS**: calculated for $\text{C}_{25}\text{H}_{36}\text{N}_4\text{O}_6\text{Na}^+$ [$\text{M}+\text{Na}]^+$: 511.2527; **found**: 511.2523. **Optical rotation**: $[\alpha]_D^{20} = +19.3$ ($c = 1.0$, CHCl_3). **HPLC**: DAICEL CHIRALPAK IA, hexane/*i*-PrOH = 90/10, flow rate: 1.0 mL/min, λ = 254 nm, $t_R(\text{major}) = 15.6$ min, $t_R(\text{minor}) = 22.2$ min, ee = 92%.

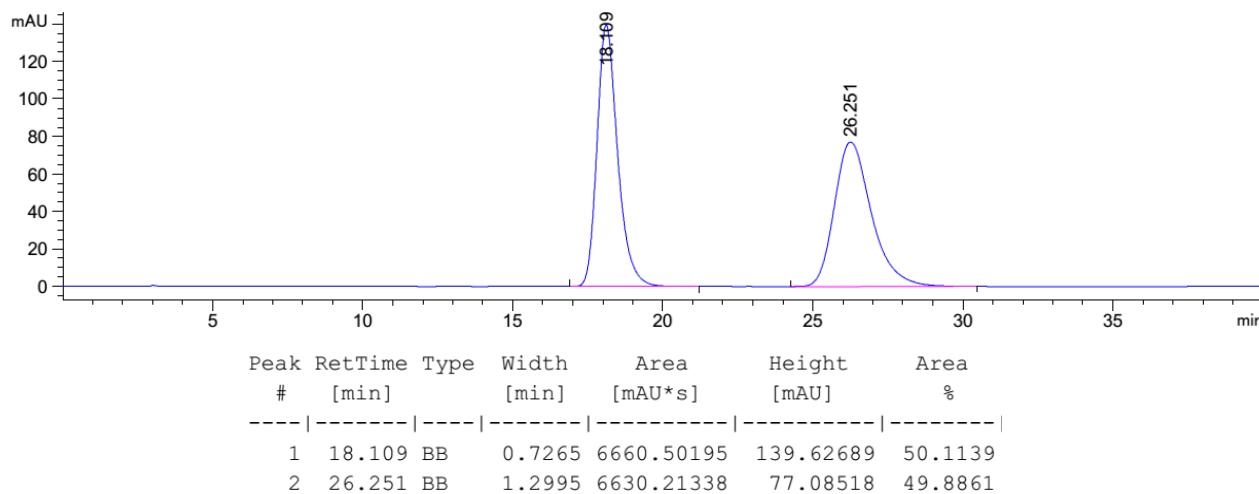


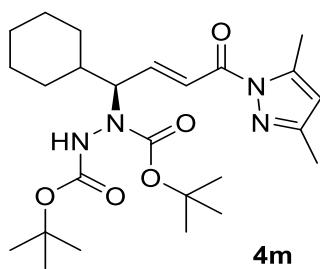
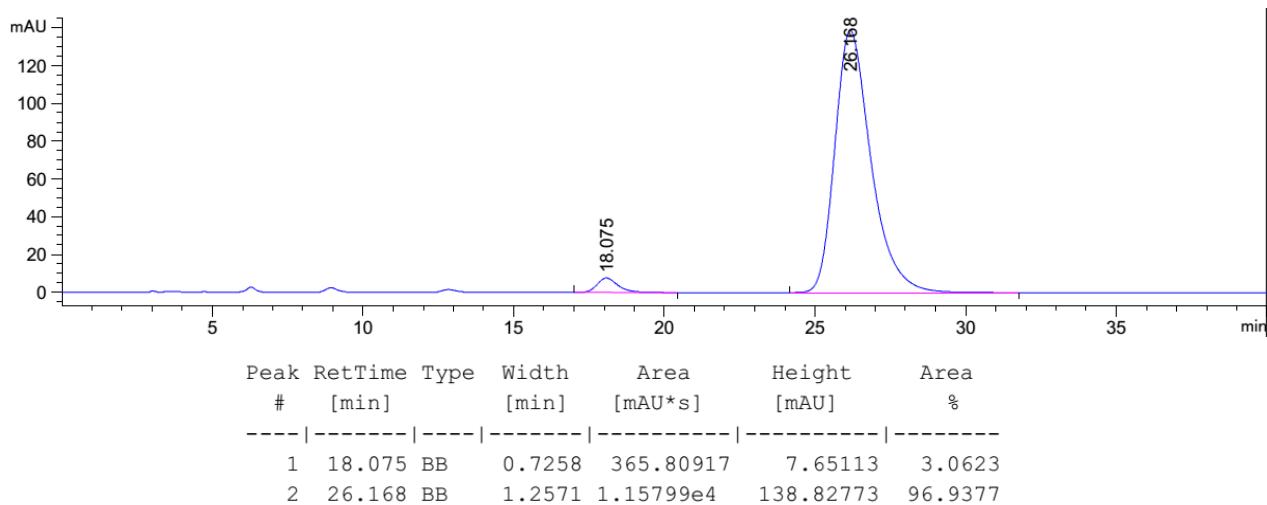
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.568	FM R	0.7848	3.51180e4	745.78461	96.0133
2	22.209	BB	0.9670	1458.17151	23.08390	3.9867



Di-tert-butyl (S,E)-1-(6-(3,5-dimethyl-1*H*-pyrazol-1-yl)-2-methyl-6-oxohex-4-en-3-yl)hydrazine-1,2-dicarboxylate

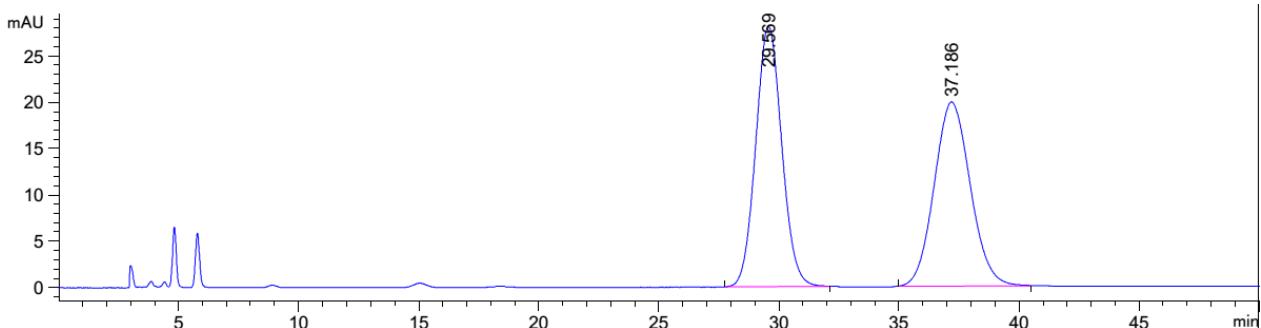
Compound **4l** (33 mg, colorless oil, 76% yield). Flash silica gel chromatography (petroleum ether/ethyl acetate = 12/1). **1H NMR** (CDCl_3 , 400 MHz, ppm) δ 7.42 (d, J = 15.2 Hz, 1H), 7.11-7.05 (m, 1H), 6.18-6.03 (m, 1H), 5.98 (s, 1H), 4.50-4.25 (m, 1H), 2.57 (s, 3H), 2.25 (s, 3H), 2.01 (br, 1H), 1.47 (s, 18H), 1.06 (br, 3H), 0.90 (d, J = 6.8 Hz, 3H); **13C NMR** (CDCl_3 , 101 MHz, ppm) δ 164.7, 154.8, 151.9, 146.0, 144.3, 123.4, 111.4, 81.9, 81.1, 64.3, 29.8, 28.2, 20.1, 19.6, 14.6, 13.8; **HRMS**: calculated for $\text{C}_{22}\text{H}_{36}\text{N}_4\text{O}_5\text{Na}^+$ [$\text{M}+\text{Na}$]⁺: 459.2578; **found**: 459.2574. **Optical rotation**: $[\alpha]_D^{20} = +32.5$ (c = 1.0, CHCl_3). **HPLC**: DAICEL CHIRALPAK IA, hexane/*i*-PrOH = 90/10, flow rate: 1.0 mL/min, λ = 254 nm, t_R (minor) = 18.0 min, t_R (major) = 26.2 min, ee = 94%.

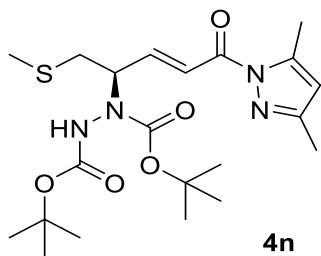
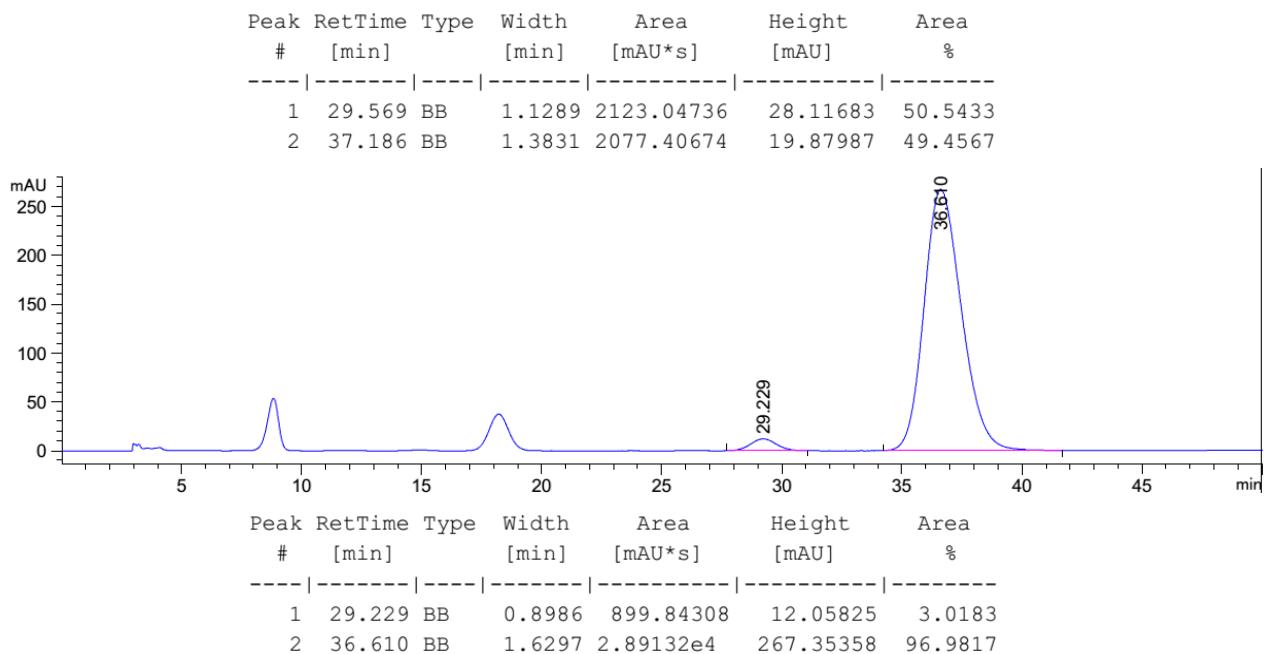




Di-*tert*-butyl (S,E)-1-(1-cyclohexyl-4-(3,5-dimethyl-1*H*-pyrazol-1-yl)-4-oxobut-2-en-1-yl)hydrazine-1,2-dicarboxylate

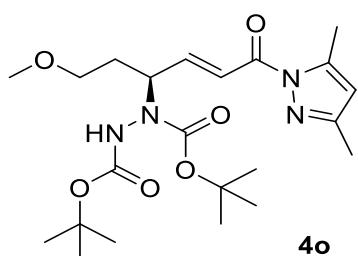
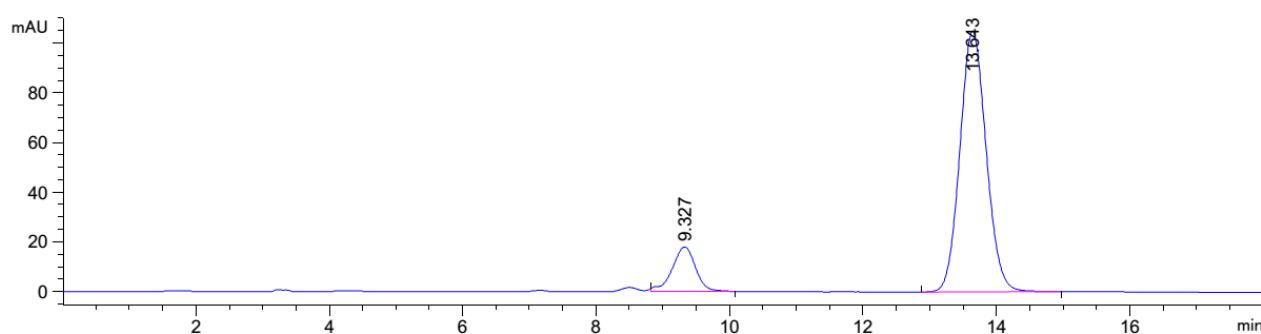
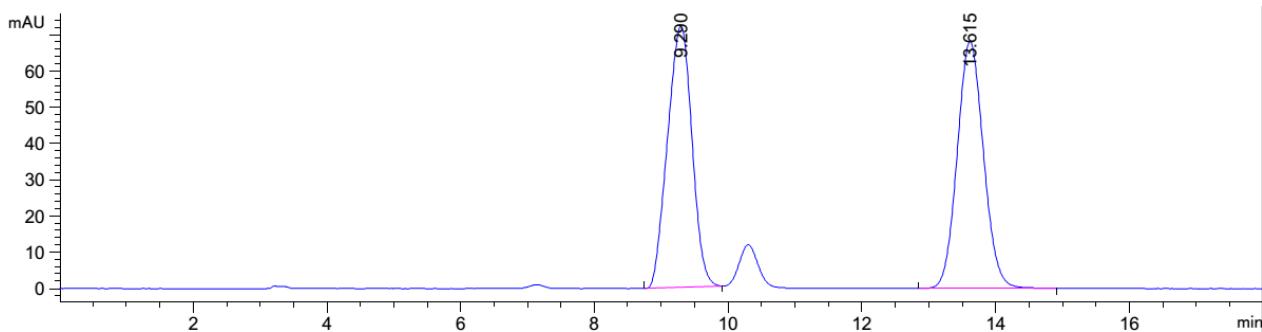
Compound **4m** (26 mg, colorless oil, 55% yield). Flash silica gel chromatography (petroleum ether/ethyl acetate = 12/1). **¹H NMR** (CDCl_3 , 500 MHz, ppm) δ 7.40 (br, 1H), 7.06 (br, 1H), 6.20-6.11 (m, 1H), 5.98 (s, 1H), 4.58-4.30 (m, 1H), 2.57 (s, 3H), 2.25 (s, 3H), 1.77-1.60 (m, 6H), 1.47 (s, 18H), 1.26-1.14 (m, 3H), 1.02-0.88 (m, 2H); **¹³C NMR** (CDCl_3 , 126 MHz, ppm) δ 164.7, 156.1, 154.8, 151.9, 145.9, 144.3, 123.4, 111.4, 81.9, 81.1, 63.3, 38.7, 38.1, 30.2, 30.0, 29.7, 28.2, 28.1, 26.9, 26.3, 25.9, 14.6, 13.8; **HRMS**: calculated for $\text{C}_{25}\text{H}_{40}\text{N}_4\text{O}_5\text{Na}^+$ [$\text{M}+\text{Na}$]⁺: 499.2891; **found**: 499.2887. **Optical rotation**: $[\alpha]_D^{20} = +25.5$ ($c = 1.0$, CHCl_3). **HPLC**: DAICEL CHIRALPAK AD, hexane/*i*-PrOH = 95/5, flow rate: 1.0 mL/min, $\lambda = 254$ nm, $t_R(\text{minor}) = 29.2$ min, $t_R(\text{major}) = 36.6$ min, ee = 94%.





Di-*tert*-butyl (*R,E*)-1-(5-(3,5-dimethyl-1*H*-pyrazol-1-yl)-1-(methylthio)-5-oxopent-3-en-2-yl)hydrazine-1,2-dicarboxylate

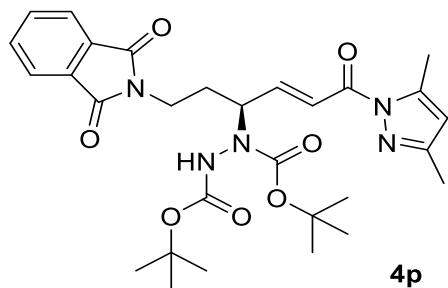
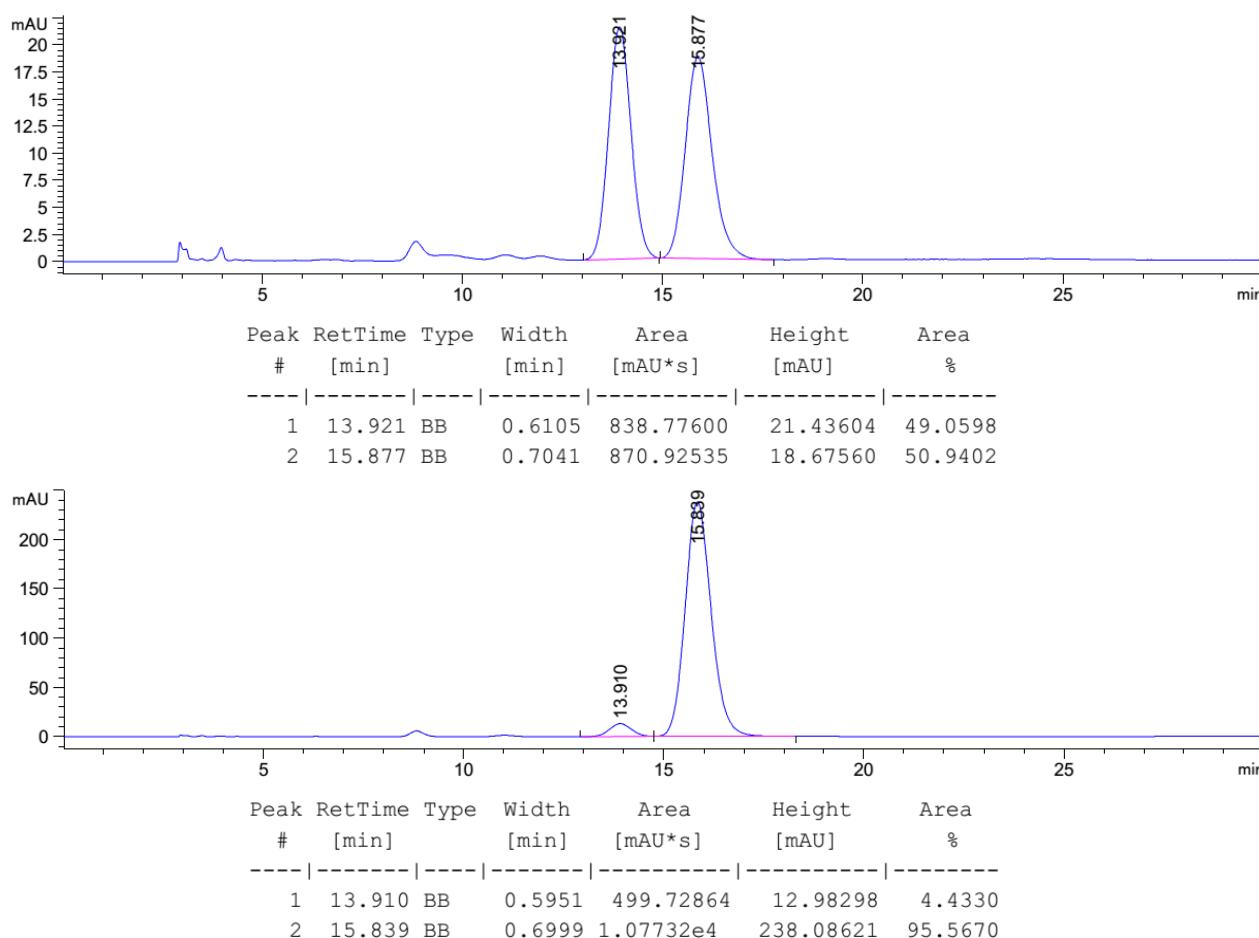
Compound **4n** (41 mg, colorless oil, 90% yield). Flash silica gel chromatography (petroleum ether/ethyl acetate = 4/1). **¹H NMR** (CDCl₃, 500 MHz, ppm) δ 7.45 (d, *J* = 13.0 Hz, 1H), 7.20-7.15 (m, 1H), 6.28-6.04 (m, 1H), 5.98 (s, 1H), 5.12-4.86 (m, 1H), 2.94-2.72 (m, 2H), 2.57 (s, 3H), 2.25 (s, 3H), 2.14 (s, 3H), 1.47 (s, 18H); **¹³C NMR** (CDCl₃, 126 MHz, ppm) δ 164.5, 155.6, 154.5, 152.0, 145.8, 144.4, 123.0, 111.5, 81.7, 81.4, 35.5, 28.2, 15.4, 14.6, 13.8; **HRMS**: calculated for C₂₁H₃₄N₄O₅SNa⁺ [M+Na]⁺: 477.2142; **found**: 477.2147. **Optical rotation**: [α]_D²⁰ = +13.4 (*c* = 1.0, CHCl₃). **HPLC**: DAICEL CHIRALPAK IC, hexane/*i*-PrOH = 90/10, flow rate: 1.0 mL/min, λ = 254 nm, t_R(minor) = 9.3 min, t_R(major) = 13.6 min, ee = 74%.



Di-*tert*-butyl (S,E)-1-(6-(3,5-dimethyl-1*H*-pyrazol-1-yl)-1-methoxy-6-oxohex-4-en-3-yl)hydrazine-1,2-dicarboxylate

Compound **4o** (36 mg, colorless oil, 80% yield). Flash silica gel chromatography (petroleum ether/ethyl acetate = 6/1). **¹H NMR** (CDCl₃, 500 MHz, ppm) δ 7.40 (d, *J* = 16.0 Hz, 1H), 7.14 (m, 1H), 6.41-6.32 (m, 1H), 5.98 (s, 1H), 5.14-4.97 (m, 1H), 3.55-3.44 (m, 2H), 3.34 (s, 3H), 2.56 (s, 3H), 2.24 (s, 3H), 2.08 (s, 1H), 1.87 (s, 1H), 1.47 (s, 18H); **¹³C NMR** (CDCl₃, 126 MHz, ppm) δ 164.8, 155.8, 154.8, 151.9, 147.3, 144.3, 122.1, 111.4, 81.4, 81.1, 69.3, 58.7, 55.9, 31.3, 28.2, 28.1, 28.0, 14.6, 13.7; **HRMS**: calculated for C₂₂H₃₆N₄O₆Na⁺ [M+Na]⁺: 475.2527; **found**: 475.2530. **Optical rotation**: [α]_D²⁰ = +1.3 (*c* = 1.0, CHCl₃). **HPLC**: DAICEL CHIRALPAK AD, hexane/*i*-PrOH = 90/10, flow rate: 1.0 mL/min, λ = 254 nm, t_R(minor) = 13.9 min, t_R(major) =

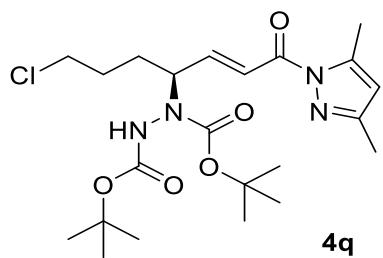
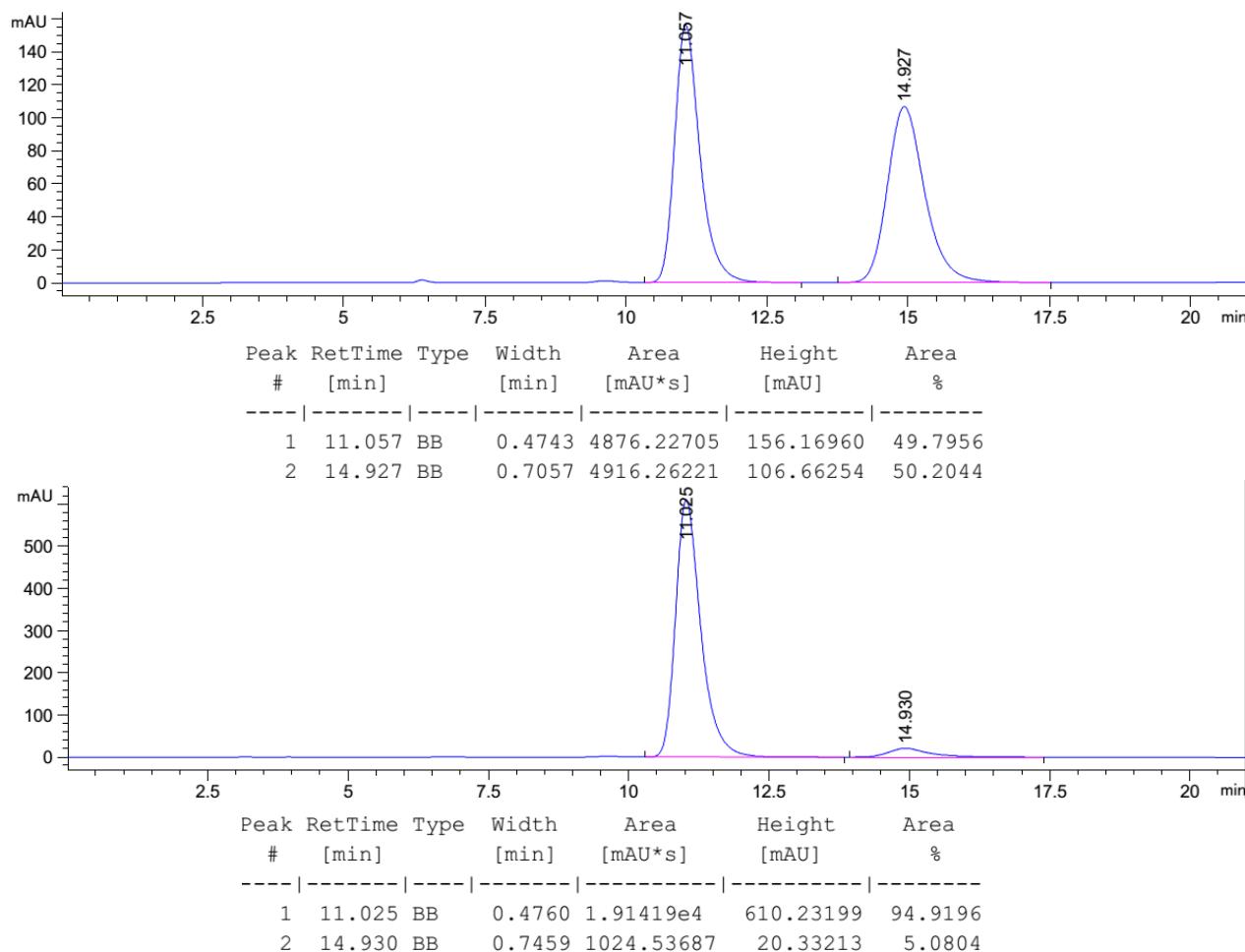
15.8 min, ee = 92%.



Di-*tert*-butyl (S,E)-1-(6-(3,5-dimethyl-1*H*-pyrazol-1-yl)-1-(1,3-dioxoisindolin-2-yl)-6-oxohex-4-en-3-yl)hydrazine-1,2-dicarboxylate

Compound **4p** (44 mg, colorless oil, 78% yield). Flash silica gel chromatography (petroleum ether/ethyl acetate = 4/1). **¹H NMR** (CDCl_3 , 500 MHz, ppm) δ 7.84 (s, 2H), 7.72 (s, 2H), 7.40 (d, J = 15.5 Hz, 1H), 7.14 (s, 1H), 6.56-6.44 (m, 1H), 5.97 (s, 1H), 5.01-4.74 (m, 1H), 3.87-3.56 (m, 2H), 2.54 (s, 3H), 2.23 (s, 3H), 2.10-2.05 (m, 2H), 1.48 (s, 18H); **¹³C NMR** (CDCl_3 , 126 MHz, ppm) δ 168.2, 164.5, 155.7, 155.6, 154.6, 151.9, 146.2, 144.3, 134.0, 132.1, 123.2, 122.5, 111.4, 81.7, 81.2, 56.0, 35.0, 29.7, 28.1, 28.0, 14.5, 13.8; **HRMS:** calculated for $\text{C}_{29}\text{H}_{37}\text{N}_5\text{O}_7\text{Na}^+$ $[\text{M}+\text{Na}]^+$: 590.2585; **found:** 590.2593. **Optical rotation:** $[\alpha]_D^{20}$ = -4.0 (c = 1.0,

CHCl_3). **HPLC:** DAICEL CHIRALPAK IA, hexane/*i*-PrOH = 70/30, flow rate: 1.0 mL/min, λ = 254 nm, $t_R(\text{major}) = 11.0 \text{ min}$, $t_R(\text{minor}) = 14.9 \text{ min}$, ee = 90%.

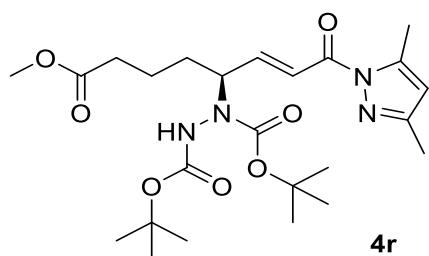
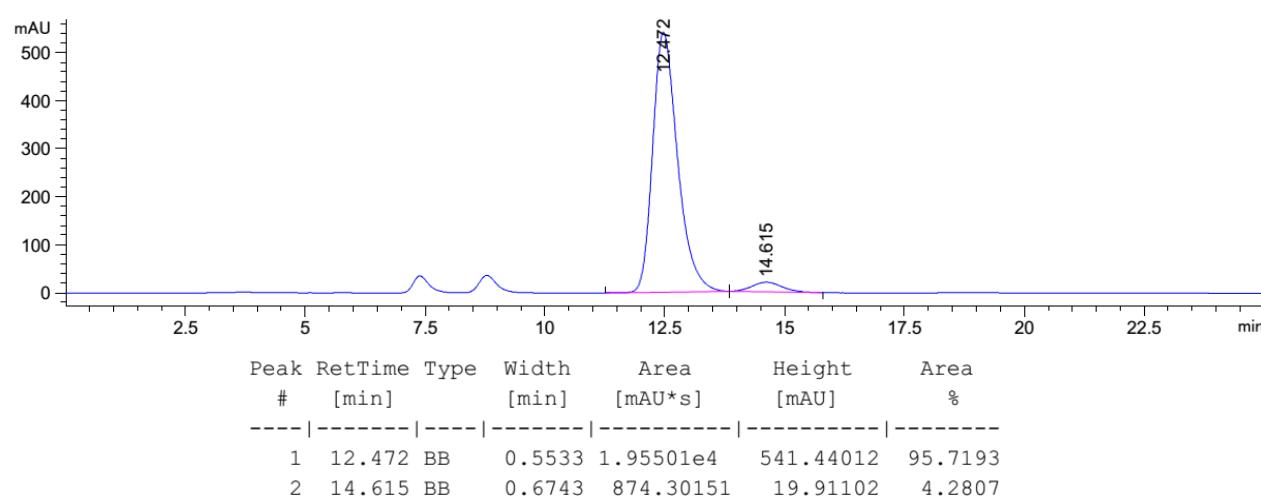
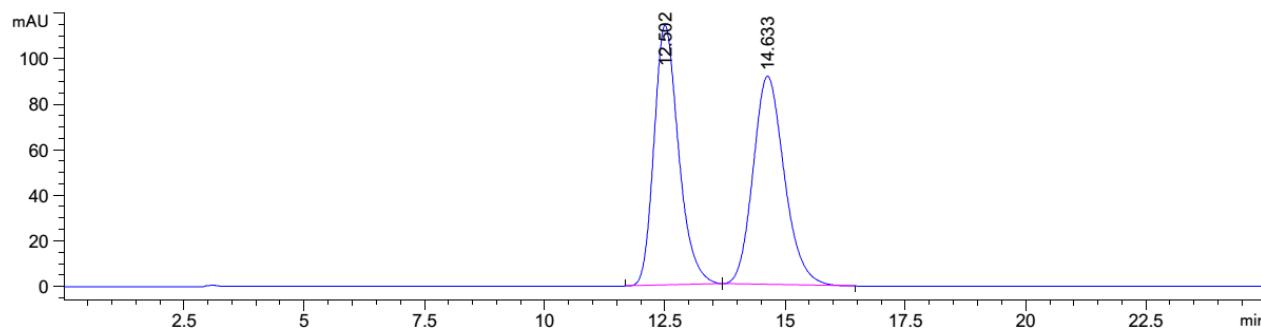


Di-*tert*-butyl (*S,E*)-1-(7-chloro-1-(3,5-dimethyl-1*H*-pyrazol-1-yl)-1-oxohept-2-en-4-yl)hydrazine-1,2-dicarboxylate

Compound **4q** (33 mg, colorless oil, 70% yield). Flash silica gel chromatography (petroleum ether/ethyl acetate = 4/1). **¹H NMR** (CDCl_3 , 500 MHz, ppm) δ 7.39 (d, J = 16.0 Hz, 1H), 7.09-7.08 (m, 1H), 6.34-6.17 (m, 1H), 5.99 (s, 1H), 4.95-4.72 (m, 1H), 3.62-3.57 (m, 2H), 2.57 (s, 3H), 2.25 (s, 3H), 2.12-1.83 (m, 4H), 1.47 (s, 19H); **¹³C NMR** (CDCl_3 , 126 MHz, ppm) δ 164.6, 155.6, 154.7, 152.1, 146.8, 144.4, 122.5, 111.6, 81.7, 81.2, 57.0, 45.0, 29.1, 28.7, 28.2, 28.1,

14.6, 13.8; **HRMS**: calculated for $C_{22}H_{35}N_4O_5ClNa^+$ [M+Na]⁺: 493.2188; **found**: 493.2179.

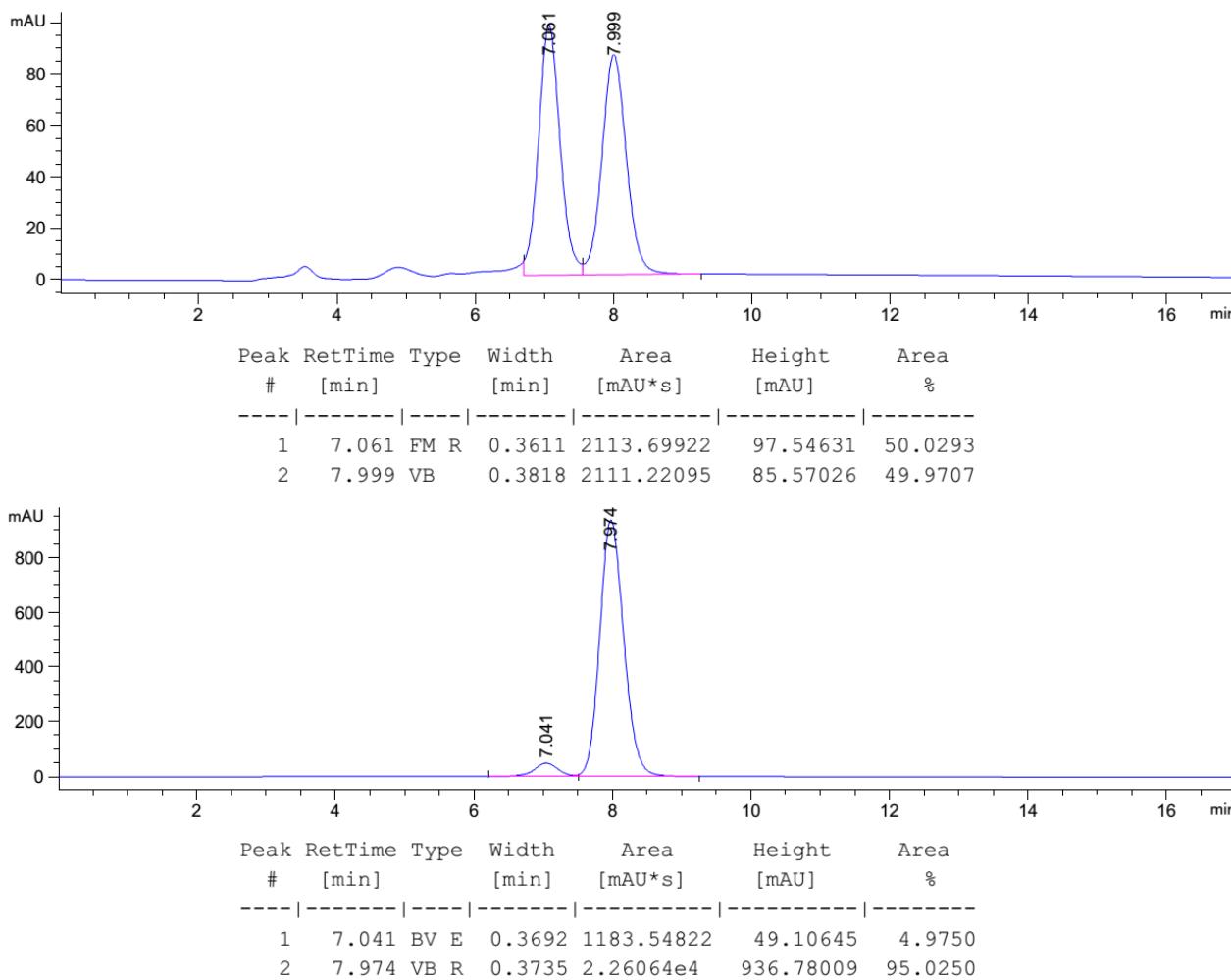
Optical rotation: $[\alpha]^{20}_D = +0.5$ ($c = 1.0$, CHCl₃). **HPLC:** DAICEL CHIRALPAK IA, hexane/*i*-PrOH = 90/10, flow rate: 1.0 mL/min, $\lambda = 254$ nm, t_R (major) = 12.5 min, t_R (minor) = 14.6 min, ee = 92%.



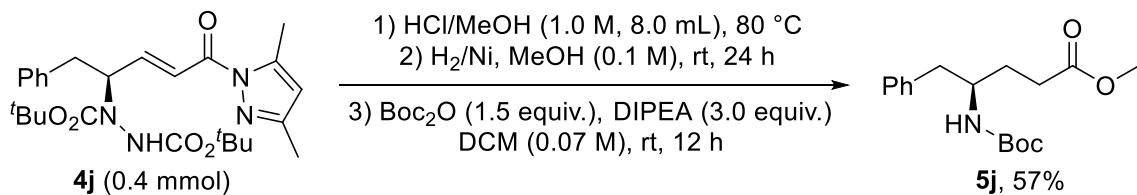
Di-*tert*-butyl (S,E)-1-(1-(3,5-dimethyl-1*H*-pyrazol-1-yl)-8-methoxy-1,8-dioxooct-2-en-4-yl)hydrazine-1,2-dicarboxylate

Compound **4r** (43 mg, colorless oil, 87% yield). Flash silica gel chromatography (petroleum ether/ethyl acetate = 4/1). **¹H NMR** (CDCl₃, 500 MHz, ppm) δ 7.38 (d, $J = 15.5$ Hz, 1H), 7.10 (br, 1H), 6.39 (br, 1H), 5.99 (s, 1H), 4.93-4.69 (m, 1H), 3.68 (s, 3H), 2.56 (s, 3H), 2.37 (s, 2H),

2.25 (s, 3H), 1.81-1.67 (m, 4H), 1.47 (s, 18H); **¹³C NMR** (CDCl_3 , 126 MHz, ppm) δ 173.8, 164.6, 155.8, 154.7, 152.0, 147.0, 144.3, 122.4, 111.4, 81.9, 81.0, 57.4, 51.5, 33.6, 30.6, 28.2, 28.0, 21.4, 14.5, 13.7; **HRMS**: calculated for $\text{C}_{24}\text{H}_{38}\text{N}_4\text{O}_7\text{Na}^+$ [M+Na]⁺: 517.2633; **found**: 517.2639. **Optical rotation**: $[\alpha]_D^{20} = -5.3$ ($c = 1.0$, CHCl_3). **HPLC**: DAICEL CHIRALPAK AD, hexane/*i*-PrOH = 70/30, flow rate: 1.0 mL/min, $\lambda = 254$ nm, $t_{\text{R}}(\text{minor}) = 7.0$ min, $t_{\text{R}}(\text{major}) = 8.0$ min, ee = 90%.

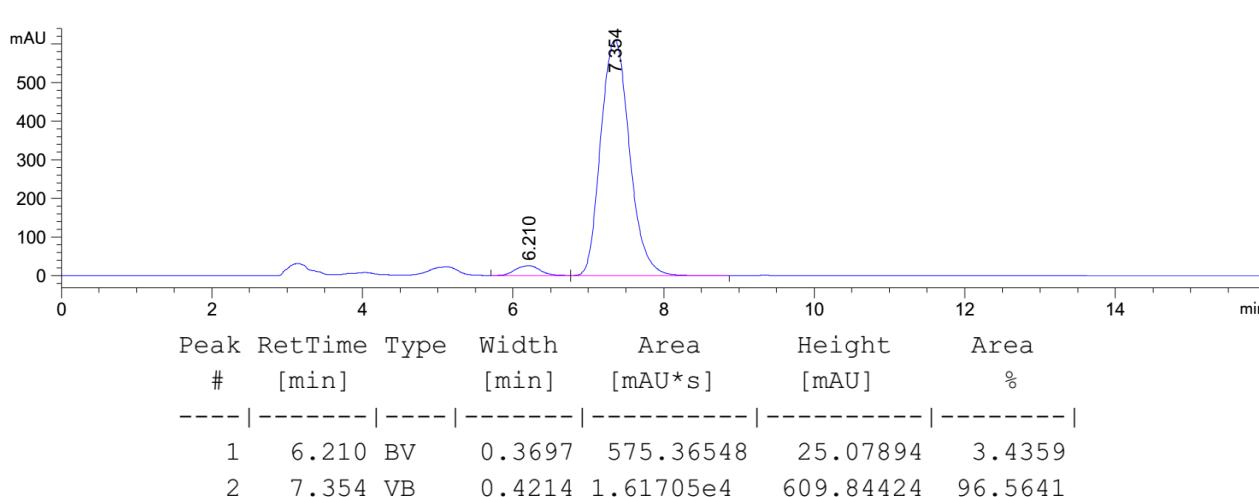
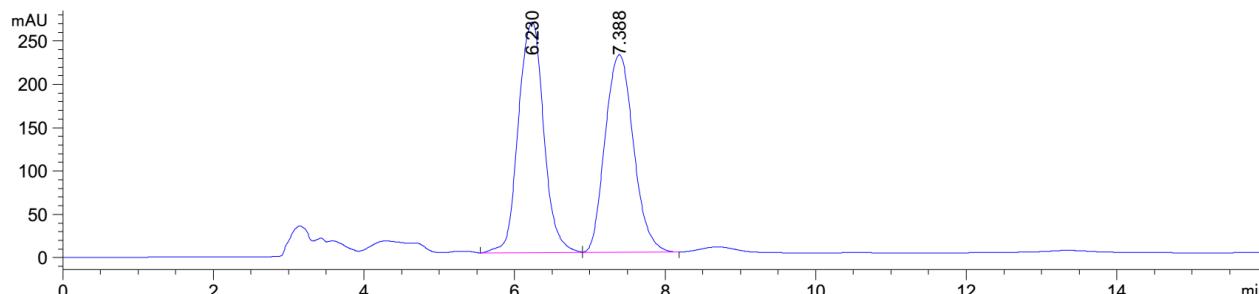


5. Transformation of γ -amination product **4j**



The **4j** (197 mg, 0.4 mmol, 1.0 equiv.) was dissolved in HCl/MeOH (1.0 M, 8.0 mL) solution at 80 °C. After 10 hours, the solvent was removed in vacuo and the crude product was dissolved in MeOH (4.0 mL). The reaction solution was treated with Raney-Ni (400 mg) and stirred under H_2

(3 atm) atmosphere for 24 h. The reaction mixture was filtered over celite and concentrated to give crude amino. The crude amino was dissolved in DCM (6.0 mL). DIPEA (200 μ L, 1.2 mmol, 3 equiv.) and Boc₂O (140 μ L, 0.6 mmol, 1.5 equiv.) were added. After the reaction mixture was stirred overnight. The solvent was removed in vacuo and the crude product was directly loaded onto silica gel column, followed by gradient elution with petroleum ether/ethyl acetate (12/1 to 6/1). After removing the solvent, product **5j** (70 mg) was obtained as white solid in 57% yield. ¹H NMR (CDCl₃, 500 MHz, ppm) δ 7.30-7.27 (m, 2H), 7.22-7.17 (m, 3H), 4.40-4.19 (m, 1H), 3.83 (br, 1H), 3.65 (s, 3H), 2.84-2.72 (m, 2H), 2.37 (dd, *J* = 13.5 Hz, *J* = 6.0 Hz, 2H), 1.89-1.80 (m, 1H), 1.65-1.58 (m, 1H), 1.39 (s, 9H); ¹³C NMR (CDCl₃, 126 MHz, ppm) δ 174.0, 155.5, 137.8, 129.4, 128.4, 126.4, 79.2, 51.7, 51.4, 41.8, 31.0, 29.3, 28.4; HRMS: calculated for C₁₇H₂₅NO₄Na⁺ [M+Na]⁺: 330.1676; found: 330.1671. Optical rotation: $[\alpha]_D^{20}$ = +4.3 (*c* = 1.0, CHCl₃), (lit $[\alpha]_D^{20}$ = +3.7 (*c* = 1.0, CHCl₃, (*R*))^[3]. HPLC: DAICEL CHIRALPAK IA, hexane/*i*-PrOH = 90/10, flow rate: 1.0 mL/min, *λ* = 210 nm, t_R(minor) = 6.2 min, t_R(major) = 7.4 min, ee = 94%.



6. DFT Calculation

Cartesian coordinates, electronic energies and free energies of all stationary points. Numbers (and values) of imaginary frequencies of all transition structures.

Rea1

B3LYP/6-31G(d,p)(lanl2dz)(gas) Energy =	-1923.835455
B3LYP/6-31G(d,p)(lanl2dz) (gas) Free Energy=	-1923.259291
M06-L/6-311+G(2d,p)(sdd)/SMD (THF) Energy =	-1924.748416
B3LYP/6-31G(d,p) (lanl2dz)(gas) Geometry	
C 0.76725 -2.64568 -0.92574	C 1.70418 3.96345 0.05299
C 1.37652 -3.71188 -1.59166	H 0.92437 3.20355 0.03516
C 2.59541 -3.4904 -2.22702	H 1.60096 4.54319 0.97529
C 3.16353 -2.21918 -2.18601	H 1.53847 4.64447 -0.79074
C 2.47752 -1.20392 -1.51573	H 2.76746 2.90167 -2.12186
H 0.89502 -4.68156 -1.58909	Co 0.36765 0.04943 0.06619
H 3.09842 -4.29919 -2.74656	O -0.7561 0.33894 -1.47375
H 4.11096 -1.99699 -2.66036	C -1.88115 0.90345 -1.16411
C -0.48199 -2.79428 -0.169	C -3.09431 0.69602 -1.75439
O -1.04262 -4.03064 -0.12824	H -3.97344 1.19664 -1.37246
C -2.32105 -3.8187 0.54063	C -3.24981 -0.23769 -2.84346
C -2.16337 -2.43989 1.22384	H -2.3343 -0.72523 -3.17604
H -3.09757 -3.8121 -0.23241	C -4.41203 -0.55192 -3.44767
H -2.48566 -4.65033 1.22562	H -5.32875 -0.06124 -3.11659
N -1.02786 -1.84602 0.48317	C -4.54866 -1.54425 -4.56368
C -3.41825 -1.55607 1.20299	H -5.22675 -2.36817 -4.29971
H -3.55382 -1.21785 0.16786	H -4.96244 -1.08503 -5.47245
C -3.21473 -0.33631 2.10815	H -3.57886 -1.98123 -4.82401
H -2.22651 0.09613 1.96907	C -2.47888 2.8402 0.45301
H -3.97535 0.42608 1.91144	C -0.75988 2.36549 1.81865
H -3.29162 -0.62833 3.16185	C -1.85692 3.22781 1.63249
C -4.66157 -2.3434 1.63959	H -2.15359 4.04636 2.27141
H -4.90218 -3.16958 0.96226	N -0.70942 1.50066 0.80027
H -4.52862 -2.75685 2.64687	N -1.76315 1.7837 -0.0249
H -5.53397 -1.68317 1.66886	C 0.23042 2.3364 2.93348
H -1.81957 -2.54761 2.26073	H 0.21425 3.28208 3.48044
N 1.30906 -1.41826 -0.89503	H -0.00623 1.51868 3.6205
C 2.97807 0.17707 -1.45968	H 1.23467 2.15335 2.54629
O 4.24793 0.38353 -1.89867	C -3.66105 3.43791 -0.23252
C 4.53926 1.76197 -1.5382	H -3.51426 3.47275 -1.3154
C 3.14841 2.36881 -1.23773	H -4.57614 2.86546 -0.04275
H 5.18486 1.74317 -0.65285	H -3.8198 4.45267 0.13943
H 5.06825 2.22755 -2.36991	O 1.59053 -0.1976 1.52227
N 2.29791 1.17419 -1.04906	C 1.21251 -0.68316 2.66642
C 3.09382 3.32782 -0.04194	C 2.37478 -0.89038 3.63692
H 3.27437 2.7236 0.8575	H 3.21689 -1.37657 3.13669
C 4.17906 4.40725 -0.15044	H 2.72564 0.08618 3.98984
H 4.10819 5.10396 0.69021	H 2.05143 -1.48084 4.49549
H 5.1917 3.99056 -0.14576	O 0.05405 -0.92924 3.01655
H 4.05723 4.98948 -1.0719	

Rea2

B3LYP/6-31G(d,p)(lanl2dz)(gas) Energy =	-802.291551
B3LYP/6-31G(d,p)(lanl2dz) (gas) Free Energy=	-802.05809
M06-L/6-311+G(2d,p)(sdd)/SMD (THF) Energy =	-802.434766
B3LYP/6-31G(d,p) (lanl2dz)(gas) Geometry	
N 0.2998 0.27996 0.46826	C -1.64756 -0.68989 -0.11575
N -0.29982 -0.27995 -0.46844	C 1.64755 0.68988 0.11558

O	-2.46357	0.35216	-0.18359	H	-3.73121	0.33669	2.16525
O	2.46358	-0.35215	0.18364	H	-5.28112	-0.31904	1.60998
O	1.89326	1.85289	-0.0979	H	-3.82404	-1.33204	1.55733
O	-1.89329	-1.85293	0.09757	C	4.43781	-1.62774	0.16838
C	3.93147	-0.19653	-0.00963	H	5.52445	-1.65523	0.04499
C	-3.93146	0.19653	0.00975	H	4.1916	-2.00446	1.16499
C	-4.43779	1.62778	-0.16802	H	3.98645	-2.2924	-0.57329
H	-4.19163	2.00465	-1.16459	C	4.49113	0.73067	1.07157
H	-5.52441	1.65528	-0.04456	H	4.11184	1.74699	0.95833
H	-3.98636	2.29232	0.57372	H	4.22741	0.36048	2.06695
C	-4.49121	-0.73048	-1.07157	H	5.58289	0.75489	0.99688
H	-4.22754	-0.36015	-2.0669	C	4.20225	0.31734	-1.42547
H	-4.11193	-1.74683	-0.9585	H	3.73135	-0.33701	-2.16513
H	-5.58296	-0.75469	-0.99681	H	3.82412	1.33181	-1.55746
C	-4.20216	-0.31755	1.42552	H	5.28123	0.31882	-1.60987

Com

B3LYP/6-31G(d,p)(lanl2dz)(gas) Energy =	-2725.951038						
B3LYP/6-31G(d,p)(lanl2dz) (gas) Free Energy=	-2725.122139						
M06-L/6-311+G(2d,p)(sdd)/SMD (THF) Energy =	-2727.205182						
B3LYP/6-31G(d,p) (lanl2dz)(gas) Geometry							
C	-3.12221	1.61896	-1.69334	H	-1.8602	-6.22189	0.50757
C	-3.55977	2.04137	-2.95267	C	-3.05123	-3.93796	1.5855
C	-3.68244	1.09488	-3.96572	H	-3.30731	-2.87771	1.61712
C	-3.37593	-0.23717	-3.69387	H	-3.73186	-4.48203	2.2497
C	-2.96825	-0.57661	-2.40386	H	-2.03533	-4.05444	1.98267
H	-3.7882	3.08766	-3.11338	H	-1.15775	-3.96955	-0.48922
H	-4.01494	1.39041	-4.95564	Co	-2.17719	-0.2419	0.3591
H	-3.46189	-1.01096	-4.44656	O	-0.37593	-0.18906	-0.35093
C	-2.94432	2.55222	-0.5666	C	0.53749	-0.74237	0.36912
O	-3.43109	3.80664	-0.73809	C	1.75311	-1.21141	-0.09253
C	-3.05169	4.52993	0.46388	C	2.10852	-1.16824	-1.48243
C	-2.48903	3.4359	1.41484	H	1.40342	-0.67615	-2.15036
H	-2.29395	5.2694	0.18191	C	3.25991	-1.66063	-1.99653
H	-3.93768	5.04416	0.8402	C	3.64419	-1.58683	-3.44438
N	-2.38757	2.24743	0.54035	H	3.80138	-2.58456	-3.87846
C	-1.16452	3.82989	2.09673	H	2.87351	-1.08241	-4.03707
H	-0.43788	4.04866	1.30241	H	4.5839	-1.03544	-3.58239
C	-0.6005	2.68999	2.94929	C	0.85457	-1.12864	2.91367
H	-0.41006	1.80443	2.34443	C	-1.34652	-0.91923	3.32058
H	0.34599	2.99243	3.40663	C	-0.09268	-1.15674	3.92037
H	-1.29801	2.42059	3.75233	H	0.10446	-1.30926	4.97163
C	-1.36397	5.0983	2.94351	N	-1.18228	-0.75504	2.00509
H	-1.71103	5.95418	2.35324	N	0.16422	-0.89029	1.75105
H	-2.0955	4.92438	3.74249	C	-2.68144	-0.83537	3.99055
H	-0.42177	5.39016	3.41717	H	-2.95366	-1.80433	4.42517
H	-3.21839	3.19065	2.20058	H	-2.64678	-0.11143	4.81235
N	-2.8418	0.336	-1.42893	H	-3.44619	-0.54126	3.27165
C	-2.67427	-1.96174	-2.00291	C	2.33509	-1.2746	3.03427
O	-2.71749	-2.90677	-2.96907	H	2.68726	-2.24537	2.66901
C	-2.39838	-4.15906	-2.30231	H	2.8686	-0.50505	2.47019
C	-2.18916	-3.76784	-0.80764	H	2.60654	-1.20001	4.09019
H	-3.2427	-4.83686	-2.45536	O	-3.91645	-0.3124	1.19804
H	-1.50762	-4.57444	-2.77968	C	-5.05879	-0.57935	0.62965
N	-2.38499	-2.30683	-0.80991	C	-6.22456	-0.59196	1.62201
C	-3.14849	-4.49492	0.16015	H	-7.16929	-0.73231	1.09466
H	-4.16871	-4.31701	-0.20958	H	-6.08761	-1.40451	2.34377
C	-2.87302	-6.00719	0.14519	H	-6.25093	0.34297	2.19048
H	-3.5761	-6.5307	0.80049	O	-5.25364	-0.81343	-0.56506
H	-2.96993	-6.44682	-0.85386	N	3.6421	0.83712	0.56943

C	2.77535	1.87983	0.04138	O	5.05115	-1.4226	1.03693
O	2.05789	2.48706	0.81027	O	6.67501	-0.25226	-0.06612
O	2.89937	2.06607	-1.27074	C	7.79553	-1.13469	0.31334
C	2.15438	3.12254	-1.97959	C	8.98895	-0.46509	-0.3716
C	2.55072	4.49423	-1.42334	H	9.90383	-1.02917	-0.16715
H	3.63563	4.62786	-1.47726	H	8.83901	-0.4247	-1.45414
H	2.08107	5.28104	-2.02278	H	9.12055	0.55666	-0.00449
H	2.23232	4.6055	-0.38626	C	7.56051	-2.54095	-0.2474
C	2.64206	2.95742	-3.42075	H	6.70647	-3.01946	0.2327
H	2.16127	3.69786	-4.06754	H	7.38294	-2.49504	-1.32629
H	3.72559	3.09314	-3.47828	H	8.45045	-3.15501	-0.07513
H	2.40188	1.95806	-3.79371	C	7.96693	-1.13468	1.8358
C	0.65024	2.85951	-1.87549	H	8.08325	-0.11125	2.20566
H	0.41353	1.84948	-2.21913	H	7.11041	-1.59451	2.32981
H	0.30281	2.95053	-0.84692	H	8.8685	-1.69627	2.1008
H	0.11292	3.58022	-2.5021	H	3.95136	-2.17542	-1.33149
N	4.59002	0.54002	-0.20937	H	2.43852	-1.68946	0.59068
C	5.43019	-0.48988	0.3573				

TS-R

B3LYP/6-31G(d,p)(lanl2dz)(gas) Energy = -2725.925174
 B3LYP/6-31G(d,p)(lanl2dz) (gas) Free Energy= -2725.092932
 M06-L/6-311+G(2d,p)(sdd)/SMD (THF) Energy = -2727.180335

Number of Imaginary Frequencies = 1(-291.59)

B3LYP/6-31G(d,p) (lanl2dz)(gas) Geometry							
C	3.29956	0.5838	2.94716	N	3.48478	-2.16968	-0.1169
C	3.63386	0.26006	4.26414	C	4.36481	-3.27265	-2.23202
C	4.00439	-1.05139	4.55351	H	5.36923	-2.92752	-1.95757
C	4.03741	-1.99061	3.52643	C	4.46414	-4.63891	-2.93192
C	3.69799	-1.58217	2.23259	H	5.04267	-4.54878	-3.85639
H	3.59394	1.02747	5.02724	H	4.9559	-5.39991	-2.31541
H	4.26518	-1.33715	5.56742	H	3.47008	-5.01746	-3.20134
H	4.32316	-3.02072	3.69867	C	3.74908	-2.22256	-3.16433
C	2.87369	1.93973	2.55665	H	3.78049	-1.24356	-2.69515
O	3.0785	2.92356	3.46115	H	4.31433	-2.17509	-4.10106
C	2.57102	4.13616	2.83689	H	2.71086	-2.47981	-3.41492
C	2.08832	3.67889	1.42729	H	2.5227	-3.67134	-1.19259
H	1.75836	4.51457	3.4639	Co	2.93056	0.26012	0.07958
H	3.38379	4.86509	2.81672	O	1.12045	-0.42132	0.18134
N	2.344	2.22428	1.43197	C	0.40539	-0.35074	-0.86737
C	0.61541	4.04108	1.14113	C	-0.89635	-0.86224	-0.99034
H	0.01947	3.648	1.97781	C	-1.54994	-1.42584	0.09491
C	0.1047	3.39622	-0.15124	H	-1.00291	-1.46901	1.03605
H	0.14577	2.30865	-0.08695	C	-2.8908	-1.88383	0.10039
H	-0.9339	3.687	-0.33696	C	-3.33505	-2.75884	1.23969
H	0.703	3.71344	-1.01408	H	-3.89522	-3.62728	0.88273
C	0.44717	5.56853	1.09648	H	-2.48753	-3.11016	1.83761
H	0.76944	6.05765	2.02265	H	-3.99649	-2.18405	1.90768
H	1.02652	6.00047	0.2713	C	0.61057	0.73596	-3.20944
H	-0.60265	5.832	0.9375	C	2.70337	1.45041	-2.78659
H	2.71187	4.1174	0.63633	C	1.66492	1.44667	-3.74461
N	3.33491	-0.31995	1.95399	H	1.68528	1.91271	-4.71878
C	3.73088	-2.50741	1.08721	N	2.30991	0.77102	-1.71042
O	4.03739	-3.79848	1.3667	N	1.02798	0.32589	-1.96003
C	4.1423	-4.44563	0.06859	C	4.05478	2.07602	-2.90414
C	3.55795	-3.40784	-0.92781	H	4.82486	1.30298	-2.98585
H	5.20327	-4.64733	-0.11584	H	4.09468	2.71663	-3.78804
H	3.59344	-5.38716	0.11636	H	4.28587	2.66817	-2.01573

C	-0.71433	0.45531	-3.84144	C	-4.79107	2.60551	-2.79832
H	-0.86029	-0.61494	-4.02219	H	-4.38672	3.34471	-2.09913
H	-1.55761	0.79834	-3.2355	H	-3.97153	2.00286	-3.18991
H	-0.7495	0.96536	-4.80649	H	-5.26382	3.14297	-3.62772
O	4.67176	1.06325	0.06871	N	-4.80297	-0.29703	1.32211
C	5.71315	0.57088	-0.53896	C	-5.98965	-0.93686	0.94009
C	7.00555	1.31713	-0.20492	O	-6.20227	-1.53849	-0.10978
H	7.86017	0.81443	-0.65982	O	-6.87518	-0.82346	1.96013
H	6.94765	2.34386	-0.58258	C	-8.19123	-1.45025	1.89338
H	7.14222	1.38146	0.87883	C	-8.81465	-1.06565	3.23952
O	5.71715	-0.37214	-1.33385	H	-9.82321	-1.48231	3.32559
N	-3.91223	-0.19381	0.34848	H	-8.20717	-1.44699	4.06545
C	-4.26762	0.20669	-0.94582	H	-8.87649	0.02227	3.33586
O	-3.66037	-0.08214	-1.97391	C	-8.05134	-2.97422	1.78128
O	-5.25202	1.13669	-0.88045	H	-7.58826	-3.25145	0.83398
C	-5.826	1.71978	-2.09428	H	-7.43668	-3.35751	2.60222
C	-6.37367	0.62042	-3.01233	H	-9.03871	-3.44419	1.84653
H	-7.01149	-0.05761	-2.43908	C	-9.01083	-0.86433	0.73629
H	-6.96815	1.07222	-3.81398	H	-9.04758	0.22701	0.81668
H	-5.56478	0.03829	-3.4539	H	-8.57189	-1.13415	-0.22433
C	-6.97005	2.57349	-1.53649	H	-10.0376	-1.24394	0.77824
H	-7.48532	3.09462	-2.34955	H	-3.33549	-2.07406	-0.86987
H	-7.69355	1.94504	-1.00989	H	-1.44353	-0.76368	-1.91172
H	-6.58593	3.317	-0.83198				

TS-S

B3LYP/6-31G(d,p)(lanl2dz)(gas) Energy = -2725.931863
 B3LYP/6-31G(d,p)(lanl2dz) (gas) Free Energy= -2725.097275
 M06-L/6-311+G(2d,p)(sdd)/SMD (THF) Energy = -2727.184211

Number of Imaginary Frequencies = 1(-265.99)

B3LYP/6-31G(d,p) (lanl2dz)(gas) Geometry							
C	-3.96102	-1.57408	1.1688	C	-2.89311	1.74992	2.13343
C	-4.678	-2.06463	2.26043	O	-2.88279	2.53545	3.23271
C	-4.80817	-1.25337	3.38624	C	-2.17304	3.74544	2.83905
C	-4.22531	0.01236	3.39037	C	-1.83602	3.53042	1.33209
C	-3.5307	0.42656	2.25106	H	-2.84296	4.59139	3.01564
H	-5.11786	-3.05305	2.21075	H	-1.29363	3.83794	3.48043
H	-5.35895	-1.60441	4.25296	N	-2.35292	2.17631	1.05854
H	-4.29947	0.67632	4.24281	C	-2.44901	4.59922	0.40072
C	-3.72882	-2.34518	-0.06401	H	-3.52035	4.65927	0.64557
O	-4.4468	-3.46945	-0.2415	C	-1.80788	5.9689	0.67518
C	-4.11485	-3.92528	-1.58331	H	-2.27125	6.7404	0.0526
C	-2.91005	-3.03399	-2.00534	H	-1.91344	6.28477	1.71934
H	-3.87663	-4.98942	-1.52074	H	-0.73719	5.95107	0.43881
H	-5.00123	-3.78186	-2.20642	C	-2.31695	4.21312	-1.07786
N	-2.87267	-2.00383	-0.94898	H	-2.84211	3.2807	-1.29574
C	-1.57859	-3.81248	-2.1189	H	-2.73119	5.0057	-1.71082
H	-1.47376	-4.40001	-1.19421	H	-1.2632	4.08561	-1.35445
C	-0.37029	-2.87549	-2.22581	H	-0.75017	3.51107	1.17207
H	-0.29713	-2.227	-1.35121	Co	-2.36269	0.25331	-0.42867
H	0.5553	-3.45501	-2.30508	O	-0.69235	-0.21661	0.50901
H	-0.44227	-2.23927	-3.11606	C	0.33448	0.38785	0.05017
C	-1.62816	-4.78274	-3.30957	C	1.41582	0.77742	0.8512
H	-2.46715	-5.48501	-3.24948	C	2.34427	1.80213	0.62488
H	-1.72093	-4.23326	-4.2543	H	2.2898	2.40745	-0.27618
H	-0.70935	-5.37493	-3.36063	C	3.40849	1.99926	1.51318
H	-3.1072	-2.53578	-2.96272	C	4.22156	3.26203	1.56854
N	-3.4053	-0.35562	1.16956	H	5.25018	3.04127	1.87043

H	4.25038	3.78384	0.61159	H	8.99229	1.55354	-1.96396
H	3.79969	3.93186	2.33071	H	7.59121	2.37985	-1.24699
C	1.16425	0.70248	-2.3706	C	8.09682	-1.03964	-1.62132
C	-0.93275	0.94617	-3.15114	H	8.90258	-0.99647	-2.36066
C	0.42904	0.89136	-3.52559	H	8.53743	-1.20034	-0.63342
H	0.82737	0.94942	-4.52815	H	7.45451	-1.8941	-1.85216
N	-1.03666	0.80052	-1.83005	C	6.62035	0.45825	-3.00943
N	0.24846	0.69561	-1.34271	H	5.95479	-0.38285	-3.22799
C	-2.12805	1.11821	-4.03335	H	6.04503	1.38379	-3.03463
H	-2.05688	2.05756	-4.59247	H	7.38686	0.4972	-3.79069
H	-2.18266	0.30762	-4.76892	N	4.12206	-0.67933	0.73278
H	-3.03624	1.12801	-3.43056	C	3.72356	-1.21125	1.96254
C	2.6256	0.43664	-2.22415	O	3.69967	-0.65198	3.05466
H	3.20309	1.34515	-2.03557	O	3.32077	-2.48659	1.73926
H	2.83586	-0.25646	-1.4015	C	2.81473	-3.31947	2.82703
H	2.99126	0.00025	-3.15745	C	2.47955	-4.63322	2.1128
O	-3.873	0.98199	-1.3953	H	2.09353	-5.36698	2.82737
C	-5.11763	0.59693	-1.39362	H	1.72339	-4.46666	1.33979
C	-6.022	1.50283	-2.23089	H	3.37194	-5.04746	1.63477
H	-7.06603	1.2113	-2.10786	C	1.54762	-2.70119	3.43396
H	-5.88774	2.54896	-1.94044	H	1.78115	-1.77823	3.96507
H	-5.74968	1.42472	-3.28936	H	0.81902	-2.48205	2.64631
O	-5.58692	-0.38763	-0.81538	H	1.09207	-3.40847	4.13577
N	4.64163	0.52206	0.8535	C	3.90752	-3.54282	3.88045
C	5.35306	0.94755	-0.29682	H	4.80528	-3.95721	3.41074
O	5.23577	2.03275	-0.8442	H	4.16832	-2.60618	4.37371
O	6.27451	0.01711	-0.60819	H	3.55651	-4.25612	4.63401
C	7.28891	0.26106	-1.64432	H	3.33883	1.4677	2.45778
C	8.16712	1.45403	-1.25094	H	1.39962	0.31632	1.83373
H	8.59468	1.29722	-0.25572				

TS-R'

B3LYP/6-31G(d,p)(lanl2dz)(gas) Energy = -2725.92561
 B3LYP/6-31G(d,p)(lanl2dz) (gas) Free Energy= -2725.090877
 M06-L/6-311+G(2d,p)(sdd)/SMD (THF) Energy = -2727.184039
 Number of Imaginary Frequencies = 1(-219.09)

B3LYP/6-31G(d,p) (lanl2dz)(gas) Geometry							
C	-3.32722	1.0634	-2.46204	C	-0.95795	5.98152	0.19623
C	-3.88086	0.98442	-3.74249	H	-1.21835	6.50913	-0.7282
C	-4.22995	-0.26806	-4.24109	H	-1.70162	6.24977	0.95696
C	-4.01777	-1.3952	-3.45237	H	0.00894	6.36945	0.53026
C	-3.46046	-1.23015	-2.18024	H	-2.97406	4.07026	0.34369
H	-4.02293	1.89178	-4.31611	N	-3.12772	-0.02206	-1.69658
H	-4.66033	-0.36445	-5.23267	C	-3.20084	-2.37747	-1.29378
H	-4.27155	-2.39103	-3.79326	O	-3.48934	-3.60198	-1.80284
C	-2.93513	2.34973	-1.86138	C	-3.26836	-4.52384	-0.70063
O	-3.36138	3.46438	-2.50426	C	-2.52213	-3.67718	0.36457
C	-2.75224	4.56654	-1.7785	H	-4.24979	-4.86204	-0.34943
C	-2.24367	3.91874	-0.46568	H	-2.70215	-5.37488	-1.08149
H	-1.93331	4.95906	-2.39286	N	-2.71131	-2.28902	-0.12048
H	-3.51013	5.33858	-1.64158	C	-3.	-3.92612	1.80646
N	-2.27001	2.47037	-0.77931	H	-4.05613	-3.63282	1.85388
C	-0.88478	4.45549	0.01323	C	-2.86608	-5.41902	2.15327
H	-0.1479	4.23039	-0.77057	H	-3.20796	-5.60115	3.17675
C	-0.43837	3.77461	1.31081	H	-3.45703	-6.06571	1.4947
H	-0.26027	2.7106	1.16246	H	-1.82021	-5.74545	2.09263
H	0.49366	4.21829	1.67344	C	-2.2289	-3.0625	2.80835
H	-1.19534	3.90264	2.09503	H	-2.41946	-2.00811	2.61527

H	-2.55556	-3.28611	3.82958	C	2.93288	1.18784	-0.14838
H	-1.15041	-3.25943	2.75282	O	2.08313	1.57113	0.64976
H	-1.44031	-3.87587	0.3217	O	4.06123	1.87181	-0.45743
Co	-2.3256	0.1866	0.12818	C	4.4221	3.1112	0.23384
O	-0.5945	-0.33433	-0.57065	C	4.53703	2.87403	1.74431
C	0.32001	-0.56806	0.26867	H	5.17218	2.00424	1.93614
C	1.53162	-1.23952	-0.07941	H	4.99258	3.74873	2.22102
C	1.45116	-2.23796	-1.13026	H	3.55814	2.69674	2.18988
H	0.64856	-2.12805	-1.85567	C	5.79513	3.43353	-0.36489
C	2.37939	-3.1979	-1.29184	H	6.17853	4.37096	0.05025
C	2.41339	-4.1721	-2.43018	H	6.50783	2.63493	-0.14047
H	2.42538	-5.21247	-2.0782	H	5.7249	3.53428	-1.45161
H	1.5527	-4.04464	-3.0945	C	3.41183	4.2113	-0.10949
H	3.3222	-4.03103	-3.02929	H	3.3481	4.34079	-1.19461
C	0.69563	-0.20024	2.7971	H	2.42449	3.9554	0.27526
C	-1.38822	0.60846	3.06745	H	3.73147	5.16222	0.33067
C	-0.17533	0.31851	3.732	N	3.80007	-0.53868	-1.52562
H	0.03693	0.46856	4.78029	C	4.78234	-0.86687	-0.58848
N	-1.27122	0.29022	1.78068	O	4.67315	-0.83327	0.63972
N	0.00654	-0.20581	1.6034	O	5.87747	-1.3075	-1.24739
C	-2.64978	1.15123	3.65441	C	7.05771	-1.78653	-0.53278
H	-3.38377	0.34854	3.77738	C	8.0091	-2.16373	-1.67325
H	-2.44709	1.60199	4.62883	H	8.95273	-2.54607	-1.27148
H	-3.09415	1.89754	2.99271	H	7.56105	-2.93468	-2.30679
C	2.08758	-0.69138	3.02193	H	8.22281	-1.29145	-2.2976
H	2.1566	-1.77625	2.88363	C	6.70918	-3.02215	0.30737
H	2.81153	-0.22266	2.35347	H	6.01988	-2.76248	1.11119
H	2.36754	-0.4707	4.05457	H	6.24796	-3.78905	-0.32351
O	-4.0403	0.77701	0.74935	H	7.62104	-3.44441	0.74326
C	-4.85436	0.0687	1.47755	C	7.66174	-0.66448	0.32126
C	-6.22572	0.72575	1.64496	H	7.85767	0.2158	-0.29942
H	-6.88909	0.07536	2.21687	H	6.98498	-0.38473	1.12887
H	-6.11769	1.68364	2.16499	H	8.61265	-0.99626	0.75202
H	-6.66716	0.94021	0.66665	H	3.17924	-3.28245	-0.55718
O	-4.6016	-1.0083	2.02324	H	2.23275	-1.44277	0.71567
N	2.77206	0.10927	-1.02538				

TS-S'

B3LYP/6-31G(d,p)(lanl2dz)(gas) Energy = -2725.924034
 B3LYP/6-31G(d,p)(lanl2dz) (gas) Free Energy= -2725.089077
 M06-L/6-311+G(2d,p)(sdd)/SMD (THF) Energy = -2727.177067
 Number of Imaginary Frequencies = 1(-214.76)

B3LYP/6-31G(d,p) (lanl2dz)(gas) Geometry							
C	-3.40613	1.39352	-1.85795	C	-1.38051	3.91392	1.66302
C	-3.88535	1.73309	-3.12375	H	-0.80256	4.22231	0.7807
C	-4.00091	0.7289	-4.08249	C	-0.55833	2.87106	2.42528
C	-3.63465	-0.57438	-3.75418	H	-0.25354	2.05776	1.76815
C	-3.16606	-0.82754	-2.4626	H	0.34957	3.32911	2.83119
H	-4.15947	2.75989	-3.33133	H	-1.1294	2.46039	3.26715
H	-4.37133	0.95974	-5.07609	C	-1.64269	5.14965	2.5409
H	-3.70448	-1.38759	-4.46597	H	-2.19313	5.93766	2.01461
C	-3.23631	2.37611	-0.77474	H	-2.22047	4.87864	3.43329
O	-3.81763	3.57833	-0.95061	H	-0.69713	5.58375	2.87969
C	-3.49978	4.34065	0.24439	H	-3.32448	3.0541	2.02102
C	-2.71838	3.34351	1.15088	N	-3.06024	0.13949	-1.53915
H	-2.89274	5.19809	-0.06289	C	-2.76104	-2.17024	-2.01101
H	-4.43911	4.69382	0.67372	O	-2.76019	-3.15831	-2.93379
N	-2.58477	2.14254	0.29854	C	-2.29332	-4.34581	-2.2327

C	-2.09026	-3.87687	-0.75994	C	-6.23496	-0.69413	1.7894
H	-3.06328	-5.11479	-2.3391	H	-7.21659	-0.34234	1.46917
H	-1.3753	-4.6811	-2.72098	H	-6.20351	-1.78757	1.76556
N	-2.40806	-2.43752	-0.81392	H	-6.06405	-0.38879	2.82764
C	-2.96419	-4.63996	0.25968	O	-5.42955	0.72307	0.02534
H	-3.99853	-4.59993	-0.11407	N	3.17008	0.50744	-0.09089
C	-2.52796	-6.11184	0.3335	C	2.57091	1.70385	-0.48532
H	-3.17437	-6.66909	1.01839	O	1.40557	1.99138	-0.22497
H	-2.57056	-6.61594	-0.63867	O	3.46504	2.54763	-1.04354
H	-1.50019	-6.19429	0.70718	C	3.10448	3.92664	-1.38082
C	-2.93069	-3.98276	1.64497	C	2.73223	4.70184	-0.11154
H	-3.31717	-2.96191	1.60988	H	3.54303	4.63784	0.62087
H	-3.53474	-4.56325	2.35096	H	2.57481	5.75818	-0.35483
H	-1.90604	-3.94972	2.03577	H	1.82244	4.29978	0.33506
H	-1.0395	-3.97788	-0.4577	C	4.40558	4.46863	-1.98129
Co	-2.29183	-0.23566	0.26141	H	4.27647	5.51167	-2.28724
O	-0.52837	-0.17267	-0.54689	H	5.21624	4.41624	-1.24916
C	0.45415	-0.53882	0.14863	H	4.6975	3.87982	-2.8553
C	1.71632	-0.84844	-0.47887	C	1.98084	3.94601	-2.42442
C	2.38114	-2.11422	-0.25838	H	2.26746	3.34921	-3.29612
H	2.22132	-2.64743	0.67511	H	1.05703	3.54221	-2.00951
C	3.27597	-2.591	-1.1508	H	1.80503	4.97429	-2.75872
C	4.10083	-3.82622	-0.96778	N	4.25698	0.11916	-0.74098
H	5.1665	-3.56956	-1.00253	C	5.18925	-0.44191	0.13013
H	3.89884	-4.31742	-0.01055	O	5.1639	-0.49072	1.35596
H	3.92493	-4.55268	-1.77252	O	6.23601	-0.8971	-0.62164
C	0.94929	-0.82673	2.67704	C	7.52057	-1.20383	-0.00133
C	-1.24602	-0.71883	3.17811	C	8.40475	-1.54399	-1.20625
C	0.0537	-0.85047	3.72166	H	9.41794	-1.79615	-0.87725
H	0.31008	-0.93081	4.76792	H	7.99534	-2.39818	-1.75413
N	-1.16709	-0.62039	1.85585	H	8.46042	-0.69422	-1.89262
N	0.18044	-0.70368	1.52821	C	7.41389	-2.41015	0.94208
C	-2.541	-0.66416	3.92201	H	6.74646	-2.18803	1.7742
H	-2.64611	-1.54628	4.56265	H	7.03229	-3.28457	0.40505
H	-2.56132	0.21493	4.5764	H	8.4061	-2.66245	1.33274
H	-3.37555	-0.62013	3.22301	C	8.06384	0.03384	0.72655
C	2.43662	-0.87929	2.75743	H	8.09745	0.88768	0.04237
H	2.81727	-1.89497	2.61476	H	7.4338	0.29008	1.57898
H	2.93429	-0.24882	2.01677	H	9.08123	-0.15976	1.08311
H	2.73578	-0.55899	3.75841	H	3.42556	-2.04124	-2.077
O	-3.95987	-0.58319	1.15738	H	1.64794	-0.56188	-1.52338
C	-5.14578	-0.11035	0.88824				

Int-R

B3LYP/6-31G(d,p)(lanl2dz)(gas) Energy =
B3LYP/6-31G(d,p)(lanl2dz) (gas) Free Energy=
M06-L/6-311+G(2d,p)(sdd)/SMD (THF) Energy =
B3LYP/6-31G(d,p) (lanl2dz)(gas) Geometry

C	1.65835	-3.01056	0.06374
C	1.75771	-4.35544	-0.30738
C	2.91861	-4.79102	-0.94089
C	3.93021	-3.87363	-1.21795
C	3.7384	-2.54061	-0.84852
H	0.93587	-5.02484	-0.08623
H	3.02993	-5.83247	-1.22523
H	4.84462	-4.15941	-1.72312
C	0.48154	-2.49088	0.78576

-2725.95712
-2725.115677
-2727.208044

O	-0.56053	-3.33513	0.9031
C	-1.63821	-2.50335	1.46089
C	-0.8694	-1.32075	2.08316
H	-2.29249	-2.18873	0.6387
H	-2.18636	-3.11703	2.17459
N	0.41543	-1.3284	1.31719
C	-1.63623	0.00699	2.07679
H	-1.81447	0.28227	1.03149
C	-0.83854	1.10716	2.78642

H	0.16526	1.21321	2.36878	C	-0.14126	4.35003	-0.58299
H	-1.35436	2.06936	2.70155	H	0.13914	4.52355	-1.6277
H	-0.73062	0.88279	3.8555	H	-1.15098	3.92227	-0.57504
C	-3.01282	-0.18346	2.73263	H	-0.17443	5.32044	-0.08383
H	-3.64891	-0.84847	2.14302	O	3.40525	-0.66203	1.9782
H	-2.91556	-0.57877	3.75293	C	4.66613	-0.52225	2.25911
H	-3.52951	0.77746	2.79001	C	5.05426	-1.17778	3.58323
H	-0.59238	-1.54982	3.12545	H	6.11865	-1.03888	3.77691
N	2.6378	-2.12955	-0.19649	H	4.47061	-0.74139	4.40008
C	4.69184	-1.47792	-1.20816	H	4.81696	-2.24582	3.55801
O	5.92751	-1.86678	-1.59522	O	5.50747	0.08048	1.58221
C	6.6827	-0.62015	-1.67518	N	-3.43597	0.70252	-1.50066
C	5.58496	0.4581	-1.78524	C	-3.63512	1.93064	-0.94328
H	7.25853	-0.52633	-0.74893	O	-3.22277	2.98579	-1.45068
H	7.34801	-0.68663	-2.53608	O	-4.32253	1.86326	0.21902
N	4.39855	-0.23449	-1.21173	C	-5.33337	2.88993	0.51151
C	5.9219	1.80877	-1.13531	C	-6.22572	3.09196	-0.71927
H	5.96263	1.6318	-0.05635	H	-6.56917	2.11812	-1.08072
C	7.28892	2.31719	-1.62295	H	-7.09281	3.70525	-0.45275
H	7.51119	3.29267	-1.17892	H	-5.68056	3.59464	-1.52114
H	8.10836	1.64427	-1.34907	C	-6.13852	2.26165	1.65169
H	7.30322	2.4426	-2.7133	H	-6.94696	2.9341	1.95623
C	4.83043	2.84233	-1.44166	H	-6.56978	1.31184	1.32648
H	3.84694	2.47949	-1.13837	H	-5.50177	2.07474	2.52164
H	5.02684	3.7807	-0.91222	C	-4.65545	4.18755	0.96495
H	4.79476	3.06925	-2.51495	H	-3.99216	3.99249	1.81461
H	5.34899	0.63891	-2.84684	H	-4.07027	4.61692	0.15126
Co	2.48676	-0.23034	0.36999	H	-5.41211	4.91291	1.28442
O	1.27963	0.13329	-1.12107	N	-3.58653	-0.51348	-0.78732
C	0.71134	1.24636	-1.12719	C	-4.86634	-0.92808	-0.82262
C	-0.43525	1.52818	-1.95491	O	-5.85776	-0.43629	-1.37991
C	-1.2504	0.49252	-2.2674	O	-4.94471	-2.09412	-0.05941
H	-0.96154	-0.51035	-1.96378	C	-6.17574	-2.85416	0.00365
C	-2.66027	0.65406	-2.75733	C	-5.79738	-4.05224	0.8846
C	-3.14548	-0.46904	-3.66685	H	-6.65335	-4.72317	1.0117
H	-4.21422	-0.34408	-3.85641	H	-4.97702	-4.61726	0.43084
H	-2.60254	-0.44716	-4.61785	H	-5.47434	-3.71311	1.87418
H	-2.99878	-1.44035	-3.18953	C	-6.59072	-3.33795	-1.39428
C	0.85976	3.4953	0.12349	H	-6.83276	-2.48678	-2.03079
C	2.42858	2.67804	1.52527	H	-5.77256	-3.90301	-1.85409
C	1.64839	3.81925	1.20105	H	-7.46343	-3.99725	-1.32442
H	1.66222	4.7706	1.71196	C	-7.29317	-2.03962	0.67302
N	2.14908	1.69473	0.67875	H	-6.95961	-1.68164	1.65318
N	1.18918	2.1846	-0.196	H	-7.55368	-1.18141	0.05414
C	3.40969	2.52788	2.63979	H	-8.18136	-2.66449	0.82264
H	4.34257	2.08655	2.28037	H	-2.78512	1.62626	-3.23645
H	3.613	3.5002	3.09348	H	-0.75297	2.54218	-2.1427
H	3.007	1.86082	3.40853				

Int-S

B3LYP/6-31G(d,p)(lanl2dz)(gas) Energy = -2725.963452
 B3LYP/6-31G(d,p)(lanl2dz) (gas) Free Energy= -2725.125174
 M06-L/6-311+G(2d,p)(sdd)/SMD (THF) Energy = -2727.21277

B3LYP/6-31G(d,p) (lanl2dz)(gas) Geometry

C	3.82992	-2.37863	0.91341	C	1.67197	-2.88175	0.24323
C	4.04049	-3.67743	1.37857	H	4.9965	-3.94254	1.81313
C	2.99701	-4.59515	1.27211	H	3.12402	-5.61235	1.62817
C	1.78944	-4.19347	0.7067	H	0.94868	-4.86812	0.6034

C	4.84616	-1.31755	1.00694	N	2.08522	1.80313	-0.72819
O	6.10365	-1.69198	1.3252	N	1.17425	2.32695	0.17633
C	6.88499	-0.46584	1.34568	C	3.25106	2.57646	-2.77403
C	5.87127	0.65147	0.95491	H	3.62784	1.55396	-2.79641
H	7.28501	-0.34623	2.35698	H	2.73739	2.79774	-3.71549
H	7.71107	-0.58531	0.6417	H	4.08558	3.2819	-2.68692
N	4.59967	-0.08126	0.79321	C	-0.1521	4.50649	0.5361
C	5.7899	1.79006	1.99393	H	0.16243	4.70617	1.56629
H	5.59364	1.31986	2.96907	H	-0.19144	5.46325	0.01134
C	4.64344	2.76134	1.69243	H	-1.16508	4.08558	0.56634
H	3.68228	2.24516	1.69214	O	3.38872	-0.41042	-1.98993
H	4.61113	3.55783	2.44314	C	3.54746	-1.5315	-2.64966
H	4.77509	3.23251	0.71108	C	4.24206	-1.32526	-3.99598
C	7.13162	2.53607	2.07214	H	3.60304	-0.72622	-4.65339
H	7.96761	1.87567	2.32734	H	5.1792	-0.77542	-3.86404
H	7.36626	3.01694	1.11481	H	4.44025	-2.28913	-4.46623
H	7.09136	3.31974	2.83474	O	3.19826	-2.65164	-2.28522
H	6.12583	1.09066	-0.01921	N	-3.32699	0.83048	1.52504
N	2.67439	-1.99888	0.34978	C	-3.49916	1.98734	0.828
C	0.45126	-2.36879	-0.40114	O	-3.13479	3.09827	1.24593
O	-0.62115	-3.16872	-0.39558	O	-4.09475	1.78147	-0.36864
C	-1.68768	-2.40647	-1.0593	C	-5.0601	2.76786	-0.873
C	-1.02081	-1.04885	-1.41442	C	-5.76657	2.00598	-1.99731
H	-1.98776	-2.98683	-1.93631	H	-6.24557	1.10797	-1.59956
H	-2.51782	-2.29126	-0.36021	H	-6.52956	2.63984	-2.46053
N	0.37368	-1.20337	-0.92628	H	-5.05309	1.70548	-2.77065
C	-1.10725	-0.68244	-2.90908	C	-6.05532	3.12294	0.23822
H	-0.69916	-1.53029	-3.47945	H	-6.88778	3.69927	-0.17891
C	-2.58034	-0.48015	-3.29992	H	-6.4414	2.20296	0.68708
H	-2.66444	-0.20206	-4.35584	H	-5.5767	3.72031	1.01714
H	-3.17864	-1.38417	-3.14708	C	-4.32677	3.99777	-1.41977
H	-3.03248	0.31215	-2.69376	H	-3.817	4.52782	-0.6148
C	-0.27558	0.56108	-3.24658	H	-3.58833	3.69682	-2.17069
H	0.78327	0.40262	-3.02949	H	-5.04142	4.67635	-1.89884
H	-0.37701	0.80904	-4.30905	N	-3.4794	-0.45443	0.95094
H	-0.62119	1.429	-2.67108	C	-4.7679	-0.84229	1.00997
H	-1.50602	-0.25827	-0.82795	O	-5.76151	-0.25919	1.46698
Co	2.43937	-0.15015	-0.35202	O	-4.8509	-2.10373	0.42444
O	1.39379	0.35605	1.25394	C	-6.10831	-2.82069	0.38232
C	0.77763	1.44097	1.19486	C	-5.73276	-4.13691	-0.31105
C	-0.36451	1.74704	2.02253	H	-6.60904	-4.78683	-0.40439
H	-0.70336	2.7644	2.13917	H	-5.33729	-3.94302	-1.31325
C	-1.17517	0.72497	2.38508	H	-4.96603	-4.66694	0.26262
H	-0.87578	-0.29475	2.15632	C	-7.14638	-2.06018	-0.45686
C	-2.60336	0.91489	2.81211	H	-7.4059	-1.11962	0.02854
C	-3.11488	-0.1176	3.80974	H	-6.73879	-1.84576	-1.45088
H	-4.19164	0.01186	3.94268	H	-8.05085	-2.66654	-0.58277
H	-2.93921	-1.13024	3.44082	C	-6.62492	-3.10051	1.80184
H	-2.61179	0.00895	4.77435	H	-5.8611	-3.63087	2.3809
C	0.81638	3.62309	-0.18027	H	-6.86336	-2.16438	2.30668
C	2.31187	2.75234	-1.62644	H	-7.52125	-3.73007	1.76251
C	1.5416	3.90464	-1.31055	H	-2.75379	1.92816	3.18794
H	1.52027	4.83422	-1.86026				

Int-R'

B3LYP/6-31G(d,p)(lanl2dz)(gas) Energy = -2725.949156
B3LYP/6-31G(d,p)(lanl2dz) (gas) Free Energy= -2725.111049
M06-L/6-311+G(2d,p)(sdd)/SMD (THF) Energy = -2727.206974
B3LYP/6-31G(d,p) (lanl2dz)(gas) Geometry
C 3.33256 1.22149 2.22846 C 3.8976 1.27781 3.50509

C	4.11083	0.0855	4.19278	C	-0.04742	0.10239	-3.74139
C	3.76739	-1.11987	3.58615	H	-0.27547	0.2189	-4.79058
C	3.21245	-1.09027	2.30338	N	1.11808	0.03081	-1.82918
H	4.1551	2.24007	3.92986	N	-0.21321	-0.26506	-1.58031
H	4.54306	0.09548	5.18814	C	2.52604	0.54925	-3.80094
H	3.92189	-2.07385	4.07456	H	3.15693	-0.3447	-3.82453
C	3.0913	2.43182	1.42381	H	2.3537	0.89519	-4.8225
O	3.72716	3.55493	1.83422	H	3.07172	1.31357	-3.24323
C	3.27877	4.59407	0.92207	C	-2.41679	-0.45502	-2.89225
C	2.55657	3.82002	-0.21249	H	-2.639	-1.52839	-2.86581
H	2.599	5.25276	1.4747	H	-3.03241	0.01399	-2.11902
H	4.15472	5.15903	0.60111	H	-2.73206	-0.08279	-3.86992
N	2.38262	2.46555	0.3634	O	3.93156	0.39522	-0.88653
C	1.26141	4.49783	-0.69051	C	4.66499	-0.46732	-1.53221
H	0.59983	4.58709	0.18252	C	6.09112	0.03026	-1.7711
C	0.5432	3.66901	-1.7597	H	6.673	-0.72992	-2.29397
H	0.21684	2.70778	-1.36432	H	6.07133	0.94941	-2.36612
H	-0.34463	4.20101	-2.1168	H	6.57168	0.27531	-0.81864
H	1.19759	3.49799	-2.62354	O	4.30107	-1.5674	-1.95221
C	1.57374	5.91115	-1.21248	N	-2.71622	-0.089	0.93261
H	2.03564	6.55248	-0.45344	C	-2.58744	1.20769	0.58074
H	2.25182	5.86935	-2.07385	O	-1.63808	1.59487	-0.13996
H	0.65491	6.40611	-1.54067	O	-3.50969	2.00292	1.12628
H	3.22143	3.69943	-1.08097	C	-3.71993	3.37569	0.65884
N	2.99719	0.06007	1.64407	C	-3.94911	3.38732	-0.85682
C	2.84102	-2.3191	1.58208	H	-4.68187	2.61966	-1.12104
O	3.01621	-3.48488	2.24921	H	-4.33156	4.36618	-1.16488
C	2.72312	-4.51979	1.26908	H	-3.02421	3.18428	-1.39863
C	2.04843	-3.75927	0.09741	C	-4.9982	3.77905	1.39967
H	3.67548	-4.97614	0.97652	H	-5.25916	4.81584	1.16516
H	2.08963	-5.26695	1.7485	H	-5.82837	3.13102	1.10684
N	2.36498	-2.34062	0.39902	H	-4.85836	3.68821	2.4805
C	2.48735	-4.24216	-1.29677	C	-2.54031	4.255	1.08669
H	3.56	-4.03448	-1.39358	H	-2.40903	4.2109	2.17259
C	2.24379	-5.75591	-1.42764	H	-1.6212	3.91715	0.60663
H	2.55049	-6.10288	-2.4191	H	-2.72981	5.29697	0.80634
H	2.80302	-6.34481	-0.69191	N	-3.90399	-0.63477	1.46726
H	1.17951	-5.99617	-1.31033	C	-4.83377	-0.65388	0.49556
C	1.75912	-3.47931	-2.40716	O	-4.7454	-0.25774	-0.69152
H	2.01791	-2.42277	-2.36594	O	-5.99261	-1.20575	0.99405
H	2.05771	-3.86422	-3.38804	C	-7.17393	-1.3496	0.17159
H	0.67131	-3.59701	-2.3194	C	-8.18313	-1.98757	1.13542
H	0.9543	-3.84645	0.16411	H	-9.14137	-2.15849	0.63353
Co	2.18559	0.054	-0.18179	H	-7.80504	-2.94598	1.50383
O	0.39494	-0.19759	0.58902	H	-8.35073	-1.33545	1.99775
C	-0.54613	-0.35825	-0.21284	C	-6.9068	-2.29168	-1.01265
C	-1.8404	-1.03686	0.22809	H	-6.17026	-1.85158	-1.685
C	-1.50973	-2.20822	1.12325	H	-6.52559	-3.25161	-0.6477
H	-1.01843	-1.96201	2.06127	H	-7.83458	-2.48113	-1.56472
C	-1.84196	-3.46643	0.82774	C	-7.68854	0.01901	-0.30015
C	-1.60598	-4.65095	1.71925	H	-7.83689	0.67818	0.56189
H	-1.03826	-5.43789	1.20523	H	-6.97028	0.48051	-0.97766
H	-1.06442	-4.37014	2.62766	H	-8.65064	-0.0936	-0.81329
H	-2.55987	-5.10042	2.02153	H	-2.36805	-3.66501	-0.10687
C	-0.95117	-0.20694	-2.75004	H	-2.37772	-1.4062	-0.6488
C	1.22515	0.24131	-3.13601				

Int-S'

B3LYP/6-31G(d,p)(lanl2dz)(gas)	Energy =	-2725.949245					
B3LYP/6-31G(d,p)(lanl2dz) (gas)	Free Energy=	-2725.111638					
M06-L/6-311+G(2d,p)(sdd)/SMD (THF)	Energy =	-2727.204955					
B3LYP/6-31G(d,p) (lanl2dz)(gas)	Geometry						
C	-3.414	0.82667	-2.30794	C	2.09501	-4.57695	-0.68968
C	-3.91567	0.75729	-3.60822	H	2.40137	-5.07115	-1.62023
C	-4.02311	-0.49241	-4.21463	H	2.93416	-4.62469	0.00982
C	-3.62445	-1.62735	-3.51261	H	1.27251	-5.17466	-0.27312
C	-3.13053	-1.4674	-2.21552	C	1.15059	-0.3556	2.50756
H	-4.21424	1.66784	-4.11245	C	-0.98453	0.11349	3.06294
H	-4.41167	-0.58074	-5.22397	C	0.32139	-0.09383	3.57167
H	-3.68675	-2.61976	-3.94165	H	0.6201	-0.06677	4.6093
C	-3.27307	2.09376	-1.57302	N	-0.97445	-0.0154	1.74321
O	-3.88991	3.16884	-2.10352	N	0.33983	-0.30478	1.38002
C	-3.53467	4.2765	-1.23375	C	-2.21764	0.44874	3.83634
C	-2.87576	3.59998	-0.00249	H	-2.33904	-0.24595	4.67377
H	-2.83535	4.91856	-1.78162	H	-2.12769	1.45586	4.25937
H	-4.44551	4.83319	-1.01082	H	-3.09346	0.39882	3.19024
N	-2.63333	2.21529	-0.47335	C	2.59152	-0.72785	2.56731
C	-1.63163	4.34185	0.51504	H	2.69811	-1.81741	2.51658
H	-0.90102	4.36693	-0.30551	H	3.22899	-0.32248	1.7757
C	-0.99452	3.62115	1.70654	H	2.98642	-0.40752	3.53435
H	-0.62691	2.63618	1.42213	O	-3.79898	-0.1505	1.22578
H	-0.14694	4.19834	2.08952	C	-5.01776	0.15208	0.86664
H	-1.71863	3.51021	2.52388	C	-6.03905	-0.09012	1.97844
C	-2.00115	5.78783	0.8896	H	-7.04843	0.09133	1.60706
H	-2.40434	6.35634	0.04425	H	-5.95782	-1.11457	2.35393
H	-2.74886	5.8055	1.69223	H	-5.83909	0.57988	2.82183
H	-1.11833	6.3242	1.25031	O	-5.37364	0.59569	-0.22615
H	-3.59868	3.52508	0.82372	N	2.97078	0.2606	-0.53758
N	-3.03513	-0.26441	-1.6296	C	2.65014	1.54993	-0.27277
C	-2.68343	-2.60184	-1.38901	O	1.49488	1.88027	0.06908
O	-2.69485	-3.82532	-1.96136	O	3.69245	2.37947	-0.38336
C	-2.17738	-4.73495	-0.94864	C	3.5894	3.80278	-0.05323
C	-1.94368	-3.83624	0.30329	C	3.23465	3.97423	1.42805
H	-2.93006	-5.51137	-0.78943	H	3.96027	3.44326	2.05191
H	-1.26588	-5.18922	-1.34458	H	3.26602	5.03567	1.69634
N	-2.28214	-2.48331	-0.18237	H	2.23762	3.58513	1.63758
C	-2.78302	-4.26077	1.5288	C	5.00918	4.30529	-0.33127
H	-3.82629	-4.34288	1.18841	H	5.07782	5.37762	-0.12308
C	-2.32246	-5.63883	2.03062	H	5.73112	3.77771	0.29787
H	-2.94415	-5.96805	2.86872	H	5.27771	4.1313	-1.3767
H	-2.38023	-6.41366	1.25783	C	2.5814	4.491	-0.98091
H	-1.28522	-5.59676	2.38425	H	2.84864	4.30969	-2.02654
C	-2.72694	-3.21866	2.65191	H	1.57254	4.11584	-0.80589
H	-3.12913	-2.25812	2.32289	H	2.59727	5.57222	-0.80662
H	-3.30688	-3.56511	3.51437	N	4.11966	-0.08162	-1.29734
H	-1.6943	-3.06414	2.98869	C	5.07971	-0.55764	-0.48661
H	-0.88495	-3.83145	0.59252	O	5.06218	-0.75712	0.74731
Co	-2.19793	-0.07185	0.17142	O	6.18915	-0.84641	-1.25363
O	-0.46154	-0.16036	-0.71386	C	7.39898	-1.36681	-0.65451
C	0.56179	-0.26803	-0.00767	C	8.33692	-1.51714	-1.85958
C	1.8527	-0.66065	-0.72785	H	9.31045	-1.90762	-1.54466
C	2.26951	-2.08676	-0.41164	H	7.90617	-2.20304	-2.59539
H	3.12093	-2.18534	0.2552	H	8.48879	-0.54933	-2.34669
C	1.67809	-3.15729	-0.9486	C	7.14877	-2.73818	-0.00764

H	6.47204	-2.6373	0.84073	H	7.31114	-0.23618	1.19595
H	6.70188	-3.41989	-0.73954	H	8.95952	-0.72006	0.71465
H	8.09461	-3.17567	0.33235	H	0.85919	-3.01257	-1.65617
C	7.98783	-0.36578	0.35134	H	1.54757	-0.61809	-1.78178
H	8.13759	0.60485	-0.13322				
Pro-R							
B3LYP/6-31G(d,p)(lanl2dz)(gas) Energy =				-2726.550564			
B3LYP/6-31G(d,p)(lanl2dz) (gas) Free Energy=				-2725.706594			
M06-L/6-311+G(2d,p)(sdd)/SMD (THF) Energy =				-2727.797359			
B3LYP/6-31G(d,p) (lanl2dz)(gas) Geometry							
C	-2.48098	0.63272	3.01729	C	1.54991	1.08968	-1.37058
C	-2.59904	1.45921	4.13635	H	1.21959	1.59526	-0.46564
C	-3.0638	2.75722	3.95715	C	2.90518	1.44621	-1.92827
C	-3.41792	3.16949	2.67432	C	3.18177	2.94967	-1.90607
C	-3.26922	2.28659	1.59788	H	4.19157	3.15892	-2.26748
H	-2.33659	1.07098	5.11337	H	2.45607	3.46041	-2.54552
H	-3.16778	3.43035	4.80224	H	3.08526	3.35459	-0.89465
H	-3.83745	4.15103	2.49052	C	-1.15555	-2.15498	-2.96676
C	-2.0494	-0.75856	3.11956	C	-3.06209	-2.53989	-1.82221
O	-2.15718	-1.36899	4.32812	C	-2.2712	-2.96474	-2.91197
C	-1.68604	-2.72453	4.12005	H	-2.50262	-3.76628	-3.59914
C	-1.46371	-2.83304	2.5843	N	-2.46719	-1.50299	-1.21847
H	-0.75723	-2.85003	4.68894	N	-1.29105	-1.26222	-1.9149
H	-2.44321	-3.40622	4.51203	C	-4.39191	-3.0694	-1.39315
N	-1.63625	-1.44413	2.11396	H	-5.18022	-2.34191	-1.61579
C	-0.10037	-3.44401	2.2073	H	-4.61311	-3.99931	-1.92361
H	0.66913	-2.85795	2.73236	H	-4.41899	-3.24556	-0.3158
C	0.17157	-3.34877	0.7021	C	-0.02734	-2.19732	-3.94553
H	0.18944	-2.30822	0.37427	H	0.05917	-1.26944	-4.52286
H	1.13637	-3.80667	0.45712	H	0.94267	-2.38457	-3.47116
H	-0.6022	-3.87017	0.12657	H	-0.21442	-3.0088	-4.65253
C	-0.01645	-4.90053	2.6918	O	-4.31619	-1.08993	0.96618
H	-0.16049	-4.99214	3.77428	C	-5.44641	-0.60587	0.54958
H	-0.77769	-5.51849	2.20032	C	-6.66154	-1.20295	1.26409
H	0.96168	-5.33089	2.45465	H	-7.57578	-0.70058	0.9441
H	-2.2561	-3.4331	2.11529	H	-6.73864	-2.27209	1.0366
N	-2.80006	1.03445	1.75998	H	-6.54765	-1.11345	2.34891
C	-3.75697	2.70693	0.26108	O	-5.59898	0.23676	-0.343
O	-4.9502	3.37112	0.31685	N	3.97734	0.70808	-1.20746
C	-5.3836	3.4616	-1.06428	C	4.32565	-0.56139	-1.63078
C	-4.11754	3.08452	-1.87941	O	3.88394	-1.06313	-2.65398
H	-6.18867	2.7333	-1.19655	O	5.18909	-1.13362	-0.76715
H	-5.75197	4.47487	-1.23986	C	5.79883	-2.44285	-1.0642
N	-3.20058	2.52211	-0.86525	C	6.60326	-2.35975	-2.36508
C	-4.38126	2.09047	-3.02656	H	7.32447	-1.53852	-2.3116
H	-4.7922	1.18817	-2.55813	H	7.1567	-3.2927	-2.51325
C	-5.40852	2.66049	-4.01715	H	5.94838	-2.19889	-3.2217
H	-5.59768	1.9482	-4.82722	C	6.72548	-2.65335	0.13592
H	-6.37212	2.87483	-3.54226	H	7.2485	-3.60969	0.0426
H	-5.04429	3.58989	-4.47428	H	7.47015	-1.85421	0.19217
C	-3.07735	1.72605	-3.74696	H	6.15457	-2.66067	1.06917
H	-2.33999	1.34087	-3.04034	C	4.71587	-3.5255	-1.11312
H	-3.25912	0.96495	-4.51406	H	4.13293	-3.52228	-0.18632
H	-2.64406	2.60323	-4.24559	H	4.04265	-3.3661	-1.95535
H	-3.63855	3.9825	-2.30126	H	5.18548	-4.50925	-1.21526
Co	-2.62484	-0.40046	0.35632	N	4.40326	1.18607	0.01671
O	-1.02608	0.35087	-0.37021	C	5.68585	1.72131	0.10589
C	-0.51901	-0.22585	-1.37171	O	6.34649	2.09083	-0.84211
C	0.76173	0.14414	-1.92903	O	6.01237	1.78851	1.41298

C	7.27437	2.41511	1.84647	H	8.18613	4.37367	1.83861
C	7.20122	2.29004	3.37001	C	8.46374	1.62632	1.28927
H	8.0968	2.72316	3.82512	H	8.38841	0.57284	1.5773
H	6.32512	2.81656	3.75945	H	8.50313	1.69484	0.20187
H	7.13411	1.23987	3.66882	H	9.39533	2.0257	1.70312
C	7.30022	3.88605	1.41925	H	2.97701	1.07758	-2.95304
H	7.32967	3.97836	0.33321	H	1.10931	-0.36177	-2.8186
H	6.41499	4.40745	1.79679	H	4.08598	0.67764	0.83388
Pro-S							
B3LYP/6-31G(d,p)(lanl2dz)(gas) Energy = -2726.548638							
B3LYP/6-31G(d,p)(lanl2dz) (gas) Free Energy= -2725.706165							
M06-L/6-311+G(2d,p)(sdd)/SMD (THF) Energy = -2727.792679							
B3LYP/6-31G(d,p) (lanl2dz)(gas) Geometry							
C	3.27081	1.13953	2.42347	H	-0.13295	-3.47202	0.07441
C	3.22809	1.45054	3.78943	Co	2.60811	-0.4057	-0.02375
C	2.48949	0.64655	4.6485	O	1.02587	0.62692	-0.25554
C	1.82954	-0.46119	4.12376	C	0.51322	0.66389	-1.41159
C	1.93699	-0.72009	2.75772	C	-0.78173	1.24154	-1.67642
H	3.77732	2.31241	4.14682	H	-1.14013	1.27303	-2.69564
H	2.43568	0.87279	5.70863	C	-1.57748	1.73293	-0.69763
H	1.25708	-1.13703	4.74638	H	-1.24247	1.69084	0.33654
C	4.06034	2.00311	1.51921	C	-2.94678	2.29995	-0.9756
O	5.09921	2.6582	2.12968	C	-3.25344	3.54988	-0.14969
C	5.63932	3.54185	1.118	H	-4.27233	3.89586	-0.34007
C	4.938	3.09051	-0.19148	H	-3.15118	3.3502	0.92094
H	5.38706	4.57333	1.39545	H	-2.54734	4.34214	-0.41497
H	6.7248	3.42669	1.11226	C	1.18261	-0.04066	-3.80071
N	3.86249	2.19849	0.27728	C	3.11056	-0.94456	-3.05856
C	4.40882	4.24444	-1.06254	C	2.32298	-0.70066	-4.20558
H	3.72569	4.83363	-0.43257	H	2.57202	-0.96131	-5.22464
C	3.61731	3.71319	-2.26431	N	2.48879	-0.45664	-1.97657
H	2.79611	3.07247	-1.93709	N	1.29942	0.10119	-2.4268
H	3.20788	4.54123	-2.85323	C	4.45109	-1.60416	-2.99234
H	4.26263	3.12065	-2.92435	H	4.8701	-1.48889	-1.992
C	5.55971	5.15539	-1.51754	H	4.37365	-2.67362	-3.22262
H	6.10787	5.59055	-0.67427	H	5.12813	-1.16155	-3.7318
H	6.2781	4.59873	-2.13173	C	0.04991	0.44775	-4.64431
H	5.1803	5.98436	-2.1236	H	-0.07417	1.53563	-4.58944
H	5.61799	2.48206	-0.80658	H	0.26025	0.19187	-5.68531
N	2.63634	0.06566	1.91201	H	-0.90966	-0.00877	-4.37636
C	1.31351	-1.91323	2.1668	O	4.39308	-1.15693	0.05697
O	0.73292	-2.77953	3.03504	C	4.84671	-1.98325	0.95158
C	0.20569	-3.85402	2.21833	C	6.31496	-2.36112	0.72697
C	0.70704	-3.53298	0.77933	H	6.41571	-2.92172	-0.2093
H	0.59666	-4.79245	2.61776	H	6.92963	-1.46075	0.62995
H	-0.88492	-3.84819	2.31326	H	6.68073	-2.97368	1.5527
N	1.30105	-2.18835	0.92137	O	4.2234	-2.46646	1.90393
C	1.72268	-4.56556	0.23717	N	-3.99896	1.26872	-0.76341
H	2.53759	-4.62228	0.97116	C	-4.34324	0.42847	-1.80619
C	1.0624	-5.94661	0.09668	O	-3.92673	0.58001	-2.94516
H	1.79157	-6.683	-0.25569	O	-5.17299	-0.54636	-1.38103
H	0.65151	-6.32369	1.03968	C	-5.77788	-1.49334	-2.33586
H	0.24491	-5.91616	-0.6349	C	-6.66325	-2.35285	-1.42999
C	2.32054	-4.11911	-1.10147	H	-7.41415	-1.73622	-0.92771
H	2.85617	-3.17576	-0.99594	H	-7.17885	-3.1141	-2.02285
H	3.01905	-4.87628	-1.47485	H	-6.06259	-2.85683	-0.66699
H	1.53677	-3.98762	-1.85875	C	-6.62463	-0.73045	-3.35929

H	-7.17347	-1.44259	-3.98403	H	-7.98002	0.07708	4.6302
H	-7.35171	-0.09242	-2.84768	H	-7.00957	-1.05052	3.66171
H	-5.99922	-0.10881	-4.0004	H	-6.21206	0.23388	4.59062
C	-4.68606	-2.3424	-2.99475	C	-8.4145	0.5516	1.91843
H	-4.04128	-1.72926	-3.62424	H	-8.48731	1.20701	1.05022
H	-4.07414	-2.83446	-2.23189	H	-8.32151	-0.48406	1.5761
H	-5.14885	-3.11978	-3.61138	H	-9.33648	0.63447	2.503
N	-4.39124	0.98388	0.53057	C	-7.26736	2.39244	3.24961
C	-5.67503	1.35007	0.92639	H	-6.37552	2.64051	3.8337
O	-6.36796	2.16487	0.35399	H	-7.33095	3.06744	2.39567
O	-5.96199	0.6778	2.06052	H	-8.14416	2.54643	3.88678
C	-7.2155	0.93084	2.79354	H	-3.02631	2.53683	-2.03802
C	-7.09495	-0.01161	3.99337	H	-4.04561	0.11692	0.92532

Pro-R'

B3LYP/6-31G(d,p)(lanl2dz)(gas) Energy =	-2726.539292						
B3LYP/6-31G(d,p)(lanl2dz) (gas) Free Energy=	-2725.695526						
M06-L/6-311+G(2d,p)(sdd)/SMD (THF) Energy =	-2727.787576						
B3LYP/6-31G(d,p) (lanl2dz)(gas) Geometry							
C	-1.67214	0.62631	-2.90668	C	-2.22988	-3.09379	2.50801
C	-1.51787	0.40046	-4.27651	H	-2.11085	-2.07795	2.12851
C	-1.26941	-0.89449	-4.71228	H	-3.01996	-3.09059	3.26755
C	-1.21309	-1.91715	-3.76611	H	-1.29622	-3.39348	3.00253
C	-1.39837	-1.62447	-2.41005	H	-0.56915	-4.52166	0.76384
H	-1.59155	1.23642	-4.96217	Co	-1.95776	0.27318	-0.10455
H	-1.13367	-1.11023	-5.76725	O	-0.1166	-0.00132	0.40947
H	-1.06591	-2.94838	-4.05977	C	0.16797	0.20551	1.61013
C	-1.91853	1.96183	-2.37281	C	1.57647	-0.10036	2.10562
O	-2.49194	2.87911	-3.19851	C	1.68727	-1.58115	2.3942
C	-2.58046	4.09436	-2.41454	H	1.26239	-2.24428	1.64447
C	-2.22613	3.65192	-0.96877	C	2.24936	-2.06656	3.50456
H	-1.85728	4.81375	-2.81921	C	2.37997	-3.52403	3.83379
H	-3.58925	4.49477	-2.52836	H	1.8933	-3.75951	4.78857
N	-1.67236	2.294	-1.15406	H	1.93412	-4.15325	3.05827
C	-1.26951	4.61873	-0.24756	H	3.43487	-3.80591	3.94007
H	-0.37971	4.72752	-0.88587	C	-0.98047	1.01621	3.75341
C	-0.81918	4.07243	1.11191	C	-2.985	1.06184	2.71176
H	-0.26467	3.13949	1.00087	C	-2.31011	1.31595	3.93185
H	-0.16904	4.79321	1.61913	H	-2.75642	1.68079	4.8462
H	-1.6798	3.88044	1.7635	N	-2.11541	0.6118	1.79886
C	-1.9265	6.00036	-0.09271	N	-0.87268	0.57906	2.43523
H	-2.2112	6.44047	-1.05511	C	-4.44468	1.20423	2.42658
H	-2.83082	5.93452	0.52464	H	-4.98605	0.29411	2.71537
H	-1.2425	6.70033	0.39751	H	-4.8655	2.0353	3.00097
H	-3.13668	3.54543	-0.36162	H	-4.60805	1.3553	1.35854
N	-1.62317	-0.36407	-1.97585	C	0.15813	1.1656	4.70777
C	-1.44206	-2.75498	-1.45303	H	0.65857	0.21272	4.91318
O	-1.83979	-3.9278	-2.03553	H	0.9083	1.8753	4.33993
C	-1.86695	-4.90595	-0.97448	H	-0.22999	1.54757	5.65469
C	-1.47307	-4.10216	0.29831	O	-3.83889	0.40326	-0.48952
H	-2.87878	-5.3171	-0.92888	C	-4.57917	-0.62791	-0.77846
H	-1.1636	-5.70682	-1.22566	C	-6.03897	-0.25794	-1.05918
N	-1.1529	-2.75622	-0.21345	H	-6.59346	-1.13407	-1.39919
C	-2.58765	-4.05506	1.36878	H	-6.50701	0.13174	-0.14796
H	-3.48432	-3.66786	0.86808	H	-6.09477	0.5334	-1.81328
C	-2.86996	-5.46348	1.9147	O	-4.21385	-1.8057	-0.83143
H	-3.68579	-5.4358	2.64441	N	2.53796	0.33306	1.07898
H	-3.16033	-6.17188	1.13083	C	2.89589	1.67227	1.05168
H	-1.98678	-5.87244	2.42267	O	2.57534	2.44253	1.94708

O	3.61957	1.95946	-0.03821	O	4.02329	-1.67358	-1.37341
C	4.27632	3.27181	-0.19041	C	5.21007	-2.40569	-1.84039
C	5.2548	3.49469	0.9667	C	4.7553	-2.94597	-3.19856
H	5.94572	2.64973	1.04348	H	5.56127	-3.52191	-3.66307
H	5.83919	4.40194	0.78245	H	3.88478	-3.59807	-3.08243
H	4.72486	3.60521	1.91339	H	4.48417	-2.12532	-3.86914
C	5.02578	3.10953	-1.5149	C	5.53005	-3.55338	-0.87667
H	5.56887	4.02892	-1.75309	H	5.82986	-3.17081	0.09933
H	5.74337	2.28671	-1.45176	H	4.6549	-4.19895	-0.75202
H	4.32736	2.89806	-2.32988	H	6.34488	-4.16028	-1.28478
C	3.22162	4.37789	-0.28991	C	6.38932	-1.4407	-2.00505
H	2.51301	4.15514	-1.09407	H	6.11033	-0.61053	-2.66187
H	2.67299	4.48034	0.64637	H	6.70235	-1.04003	-1.04061
H	3.7112	5.32961	-0.52133	H	7.23419	-1.96649	-2.46181
N	2.7719	-0.49643	0.01005	H	2.66928	-1.36982	4.23177
C	4.02473	-1.04596	-0.17501	H	1.81503	0.47446	2.99533
O	4.93999	-0.97376	0.61955	H	2.10561	-0.47531	-0.75168

Pro-S'

B3LYP/6-31G(d,p)(lanl2dz)(gas) Energy =	-2726.523302						
B3LYP/6-31G(d,p)(lanl2dz) (gas) Free Energy=	-2725.679605						
M06-L/6-311+G(2d,p)(sdd)/SMD (THF) Energy =	-2727.771778						
B3LYP/6-31G(d,p) (lanl2dz)(gas) Geometry							
C	-3.22487	1.21058	-2.2307	H	-4.61685	-3.9045	0.68029
C	-3.63387	1.30371	-3.56013	C	-3.73073	-5.74604	1.36422
C	-3.77785	0.13492	-4.30065	H	-4.43487	-5.87928	2.19167
C	-3.53568	-1.08254	-3.67164	H	-4.07753	-6.37335	0.53476
C	-3.14543	-1.10402	-2.32652	H	-2.75858	-6.13535	1.69196
H	-3.83473	2.28137	-3.98113	C	-3.15167	-3.41302	2.16939
H	-4.08483	0.16874	-5.34108	H	-3.19303	-2.34812	1.93217
H	-3.6673	-2.02245	-4.1918	H	-3.78683	-3.60426	3.042
C	-3.05567	2.41085	-1.40813	H	-2.12067	-3.66663	2.44734
O	-3.73268	3.51737	-1.80076	H	-1.73801	-4.58126	-0.02009
C	-3.39045	4.53736	-0.83502	Co	-2.18426	0.1674	0.21297
C	-2.60068	3.77884	0.26581	O	-0.48431	-0.28035	-0.53916
H	-2.77979	5.29507	-1.34284	C	0.4895	-0.43955	0.23521
H	-4.31751	4.99376	-0.48448	C	1.758	-1.01413	-0.38153
N	-2.32865	2.46466	-0.35422	C	2.11633	-2.38515	0.16002
C	-1.34237	4.52273	0.74621	H	2.87124	-2.41773	0.94
H	-0.70738	4.68553	-0.13777	C	1.54039	-3.50723	-0.27779
C	-0.54817	3.69791	1.76407	C	1.83298	-4.88053	0.25114
H	-0.22132	2.75008	1.33727	H	2.17531	-5.54868	-0.54932
H	0.33862	4.25012	2.09583	H	2.60111	-4.85835	1.02975
H	-1.15766	3.48733	2.65135	H	0.93135	-5.33866	0.67728
C	-1.72178	5.89325	1.33216	C	0.95825	-0.25254	2.76358
H	-2.23815	6.5337	0.60839	C	-1.20585	0.24949	3.15928
H	-2.37985	5.77547	2.20195	C	0.06488	0.08086	3.75531
H	-0.82823	6.43091	1.666	H	0.30124	0.1823	4.80522
H	-3.24851	3.58922	1.13399	N	-1.12107	0.0228	1.84493
N	-2.97671	0.03301	-1.60838	N	0.21635	-0.2887	1.58741
C	-3.00462	-2.41469	-1.65709	C	-2.48738	0.63195	3.82702
O	-3.59207	-3.45425	-2.34052	H	-2.59066	0.10813	4.78307
C	-3.30148	-4.64137	-1.57002	H	-2.50976	1.70833	4.04079
C	-2.69536	-4.09345	-0.24827	H	-3.32693	0.38792	3.17547
H	-4.23724	-5.18961	-1.43287	C	2.40913	-0.56824	2.91606
H	-2.6042	-5.26298	-2.14347	H	2.58741	-1.64896	2.96584
N	-2.43755	-2.67465	-0.54529	H	3.03799	-0.17663	2.11688
C	-3.62053	-4.26215	0.98083	H	2.75648	-0.14112	3.86031

O	-3.87781	0.00206	1.14135	H	2.17067	3.87135	-1.12072
C	-5.01444	0.54854	0.83779	H	3.40867	5.08674	-1.50646
C	-6.16676	0.07081	1.72948	N	4.06881	-0.70418	-0.98272
H	-7.11649	0.47283	1.37249	C	5.20336	-0.93727	-0.2146
H	-6.2063	-1.0228	1.74568	O	5.21836	-0.97103	1.00019
H	-6.0028	0.40122	2.76168	O	6.23175	-1.15757	-1.05412
O	-5.22891	1.38364	-0.04902	C	7.56313	-1.54188	-0.54432
N	2.96231	-0.13562	-0.3726	C	8.37419	-1.70884	-1.83106
C	2.87137	1.25183	-0.29597	H	9.40201	-1.99587	-1.59071
O	1.88824	1.82751	0.13252	H	7.9371	-2.48478	-2.46602
O	4.00877	1.82396	-0.73061	H	8.39932	-0.7729	-2.39661
C	4.20821	3.28694	-0.62426	C	7.46579	-2.86698	0.21756
C	4.13982	3.71438	0.8445	H	6.87173	-2.75569	1.12511
H	4.84339	3.12816	1.44372	H	7.01106	-3.63662	-0.41389
H	4.41778	4.76984	0.92864	H	8.46998	-3.20404	0.4937
H	3.13545	3.58365	1.24799	C	8.13209	-0.41233	0.3197
C	5.62366	3.46285	-1.17864	H	8.14473	0.52664	-0.24287
H	5.90221	4.52049	-1.16125	H	7.54088	-0.27559	1.22553
H	6.34659	2.90386	-0.57747	H	9.16205	-0.65161	0.60313
H	5.68258	3.10717	-2.21148	H	0.78888	-3.4404	-1.06559
C	3.18318	4.01548	-1.49808	H	1.44473	-1.13074	-1.42539
H	3.23349	3.6513	-2.52916	H	4.23984	-0.44199	-1.94715

7. Crystal structure information for compound 4c

Single crystals of **4c** were obtained by recrystallization from PE/EA (10/1) at 25 °C. (very slow evaporation in air).

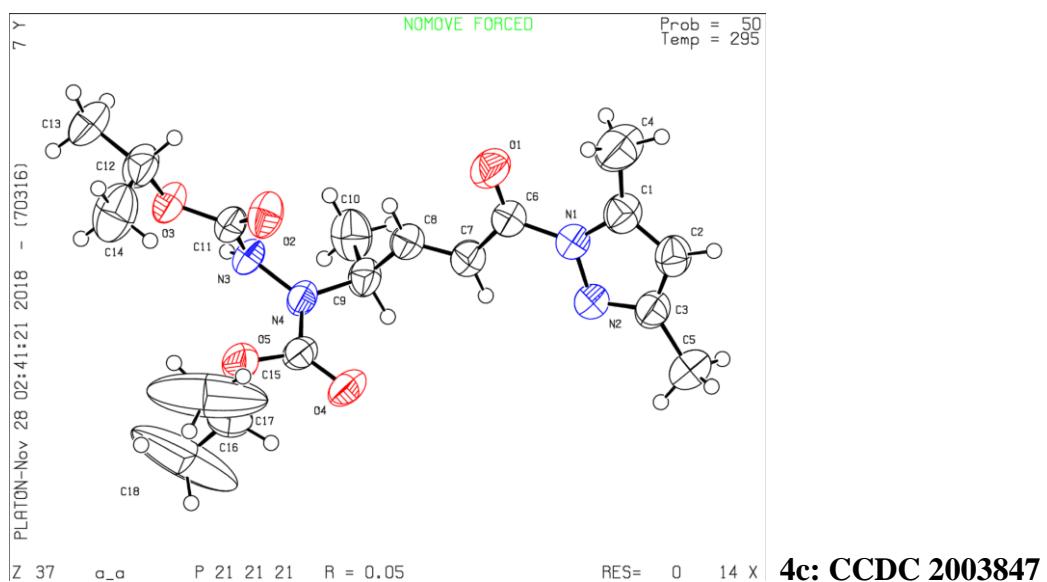


Table SI-1. Crystal Data and Structure Refinement for 4c

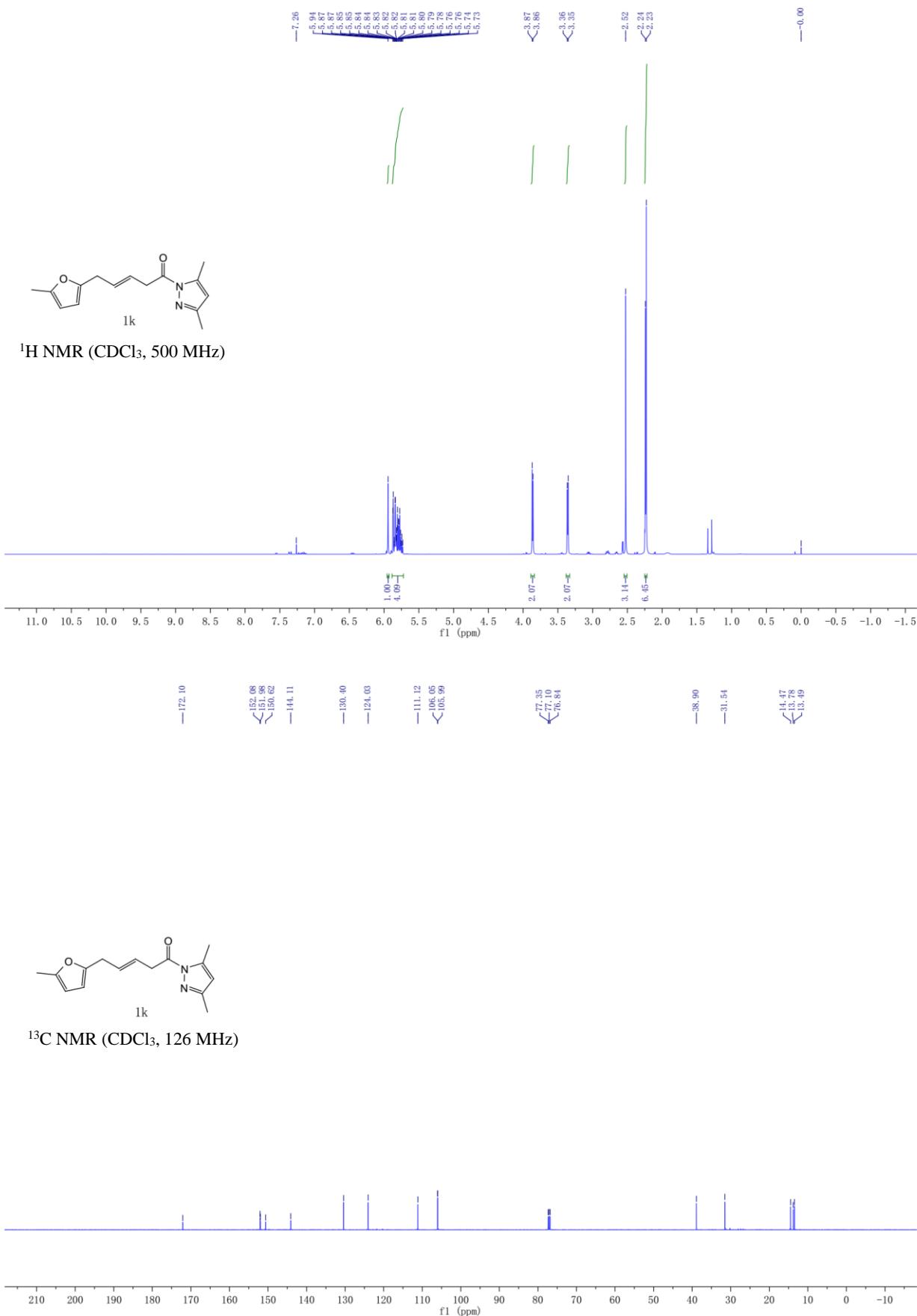
Identification code	4c
Empirical formula	C ₁₈ H ₂₈ N ₄ O ₅

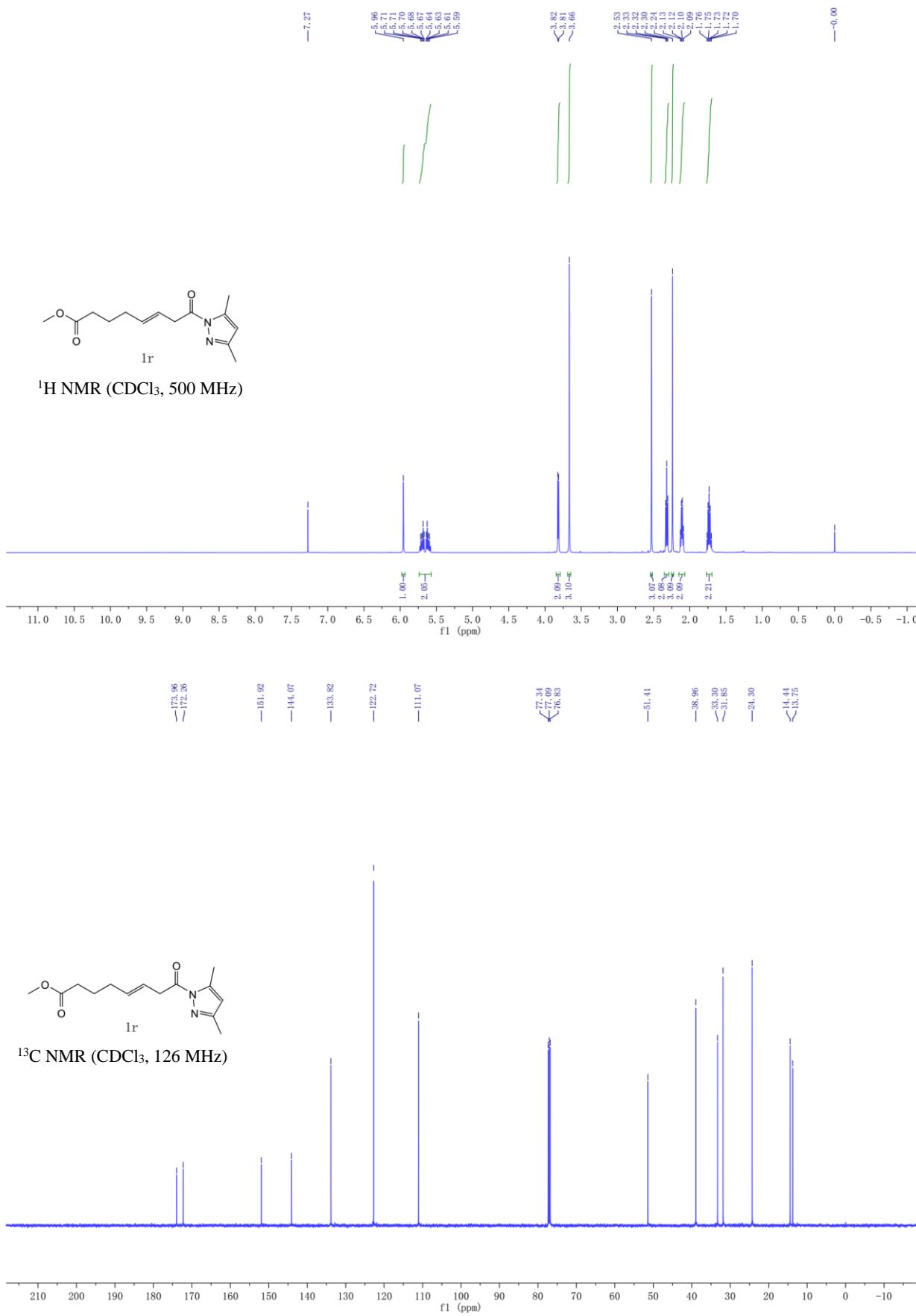
Formula weight	380.44	
Temperature	295(2) K	
Wavelength	1.54178 Å	
Crystal system, space group	Orthorhombic, P2(1)2(1)2(1)	
Unit cell dimensions	a = 10.2559(3) Å b = 10.4990(4) Å c = 19.8970(7) Å	alpha = 90 deg. beta = 90 deg. gamma = 90 deg.
Volume	2142.44(13) Å ³	
Z, Calculated density	4, 1.179 Mg/m ³	
Absorption coefficient	0.719 mm ⁻¹	
F(000)	816	
Crystal size	0.240 x 0.220 x 0.200 mm	
Theta range for data collection	4.444 to 68.460 deg.	
Limiting indices	-12<=h<=12, -12<=k<=12, -24<=l<=23	
Reflections collected / unique	33991 / 3925 [R(int) = 0.0456]	
Completeness to theta = 67.679°	99.8 %	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	3925 / 0 / 251	
Goodness-of-fit on F ²	1.035	
Final R indices [I>2sigma(I)]	R1 = 0.0510, wR2 = 0.1426	
R indices (all data)	R1 = 0.0574, wR2 = 0.1531	
Absolute structure parameter	0.08(7)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.340 and -0.283 e. Å ⁻³	

8. References

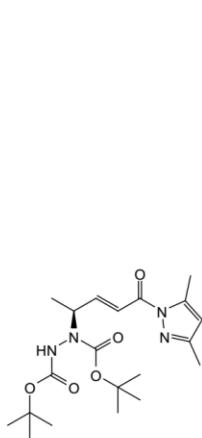
1. Wang, J., Chen, J., Kee, C. W., Tan, C. H. *Angew. Chem. Int. Ed.*, **2012**, *51*, 2382-2386.
2. Zhang, H. J., Shi, C. Y., Zhong, F., Yin, L. *J. Am. Chem. Soc.*, **2017**, *139*, 2196-2199.
3. Moutevvelis-Minakakis, P., Sinanoglou, C., Loukas, V., Kokotos, G. *Synthesis* **2005**, 933-938.

9. ¹H and ¹³C NMR Spectra of Compounds



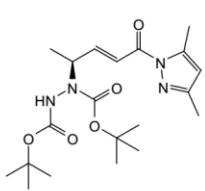
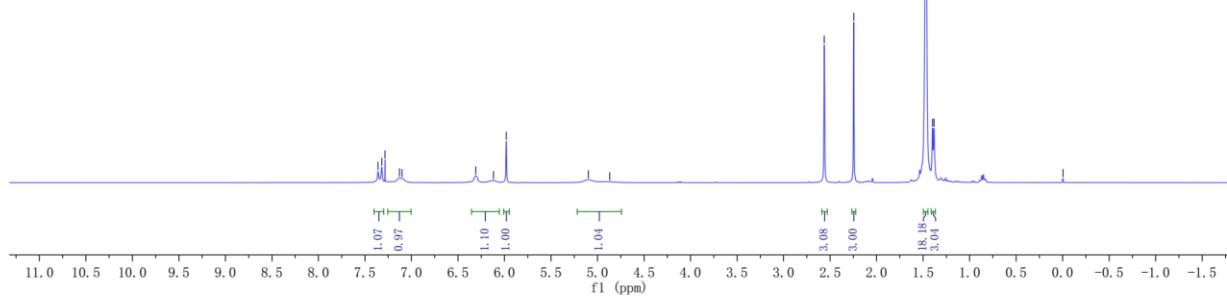


4a



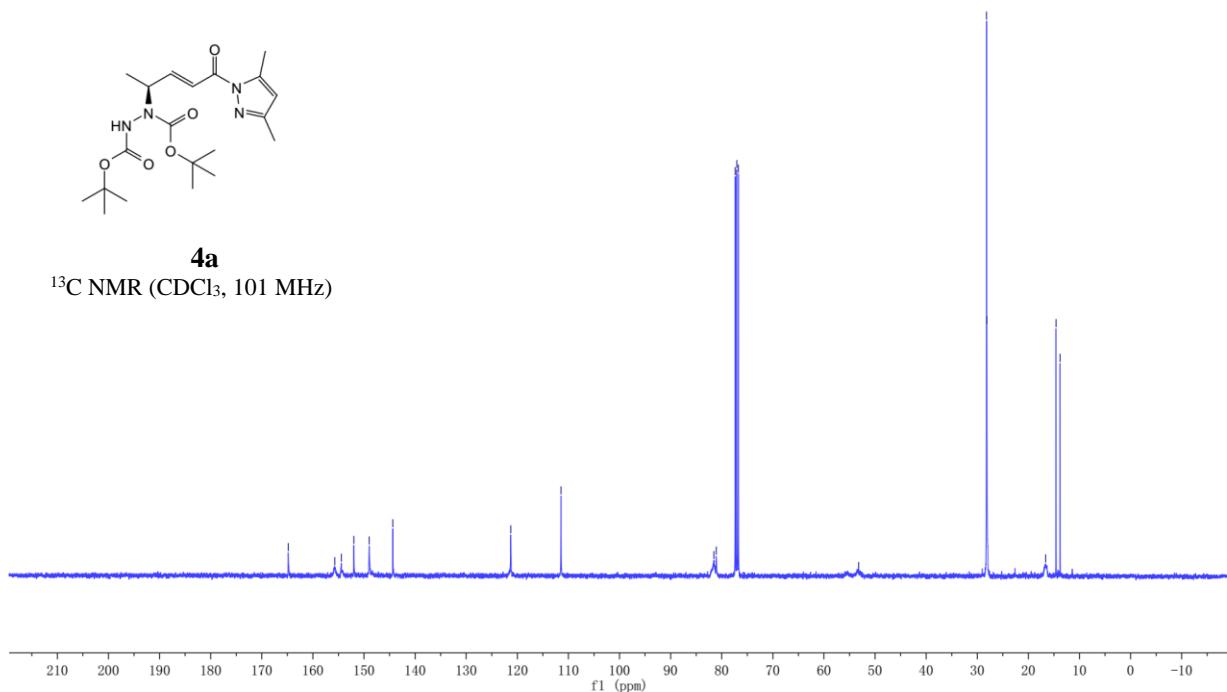
4a

^1H NMR (CDCl_3 , 400 MHz)

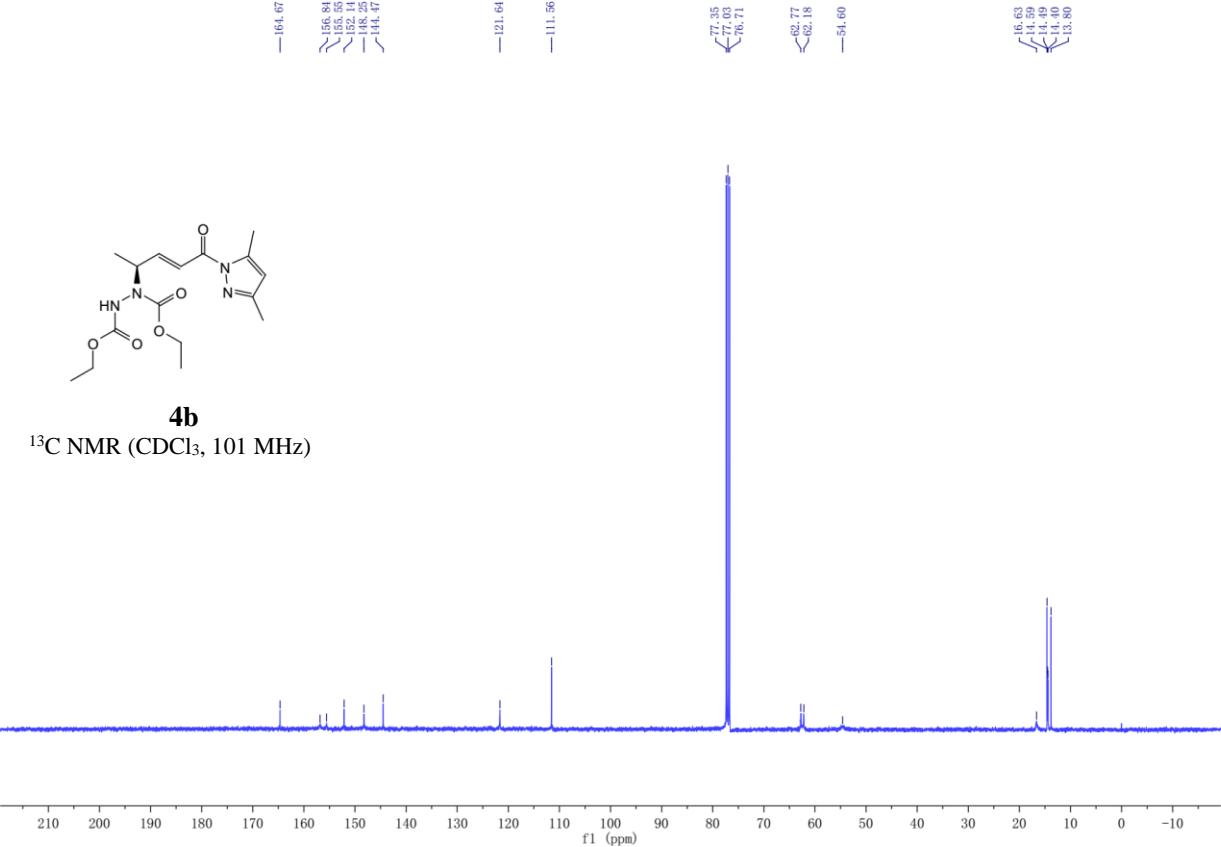
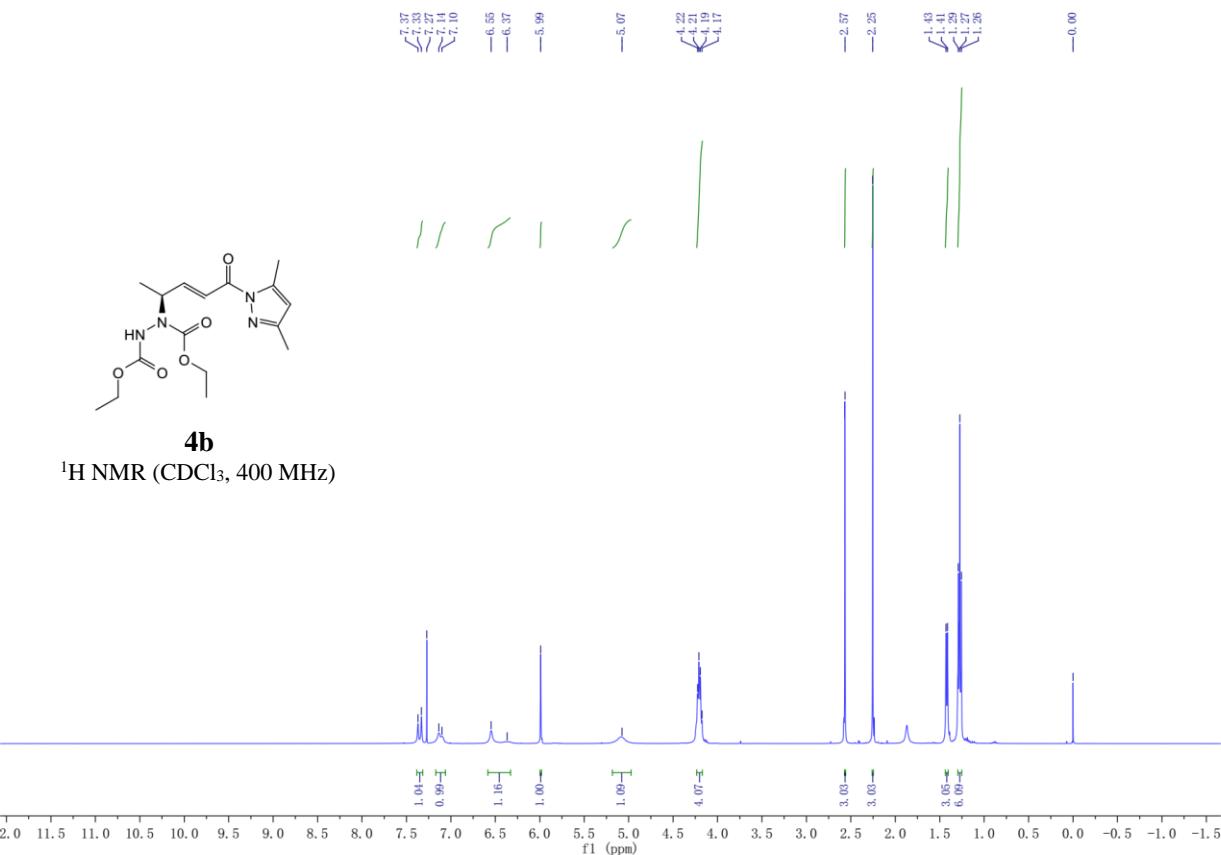


4a

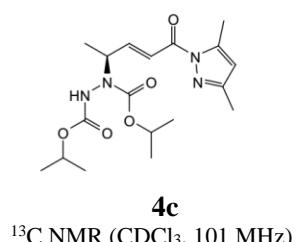
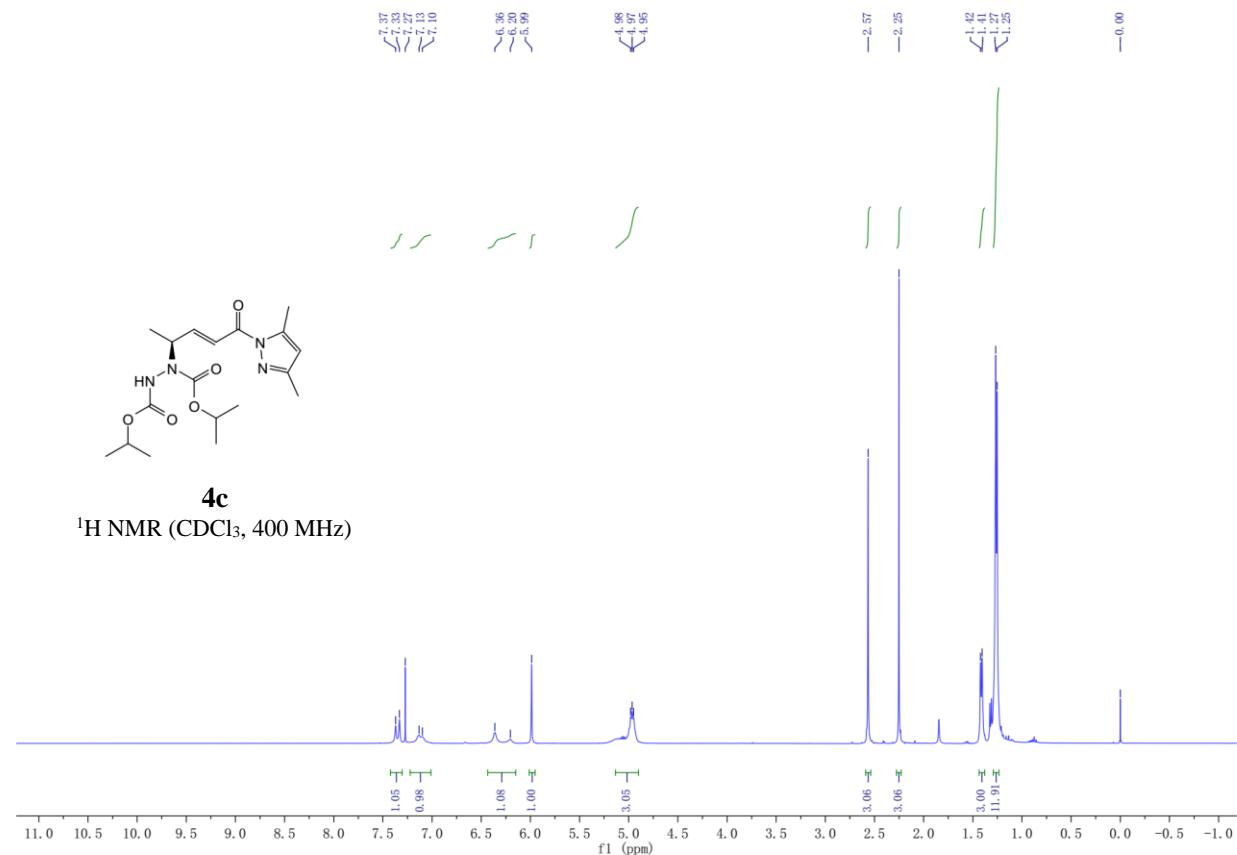
^{13}C NMR (CDCl_3 , 101 MHz)



4b

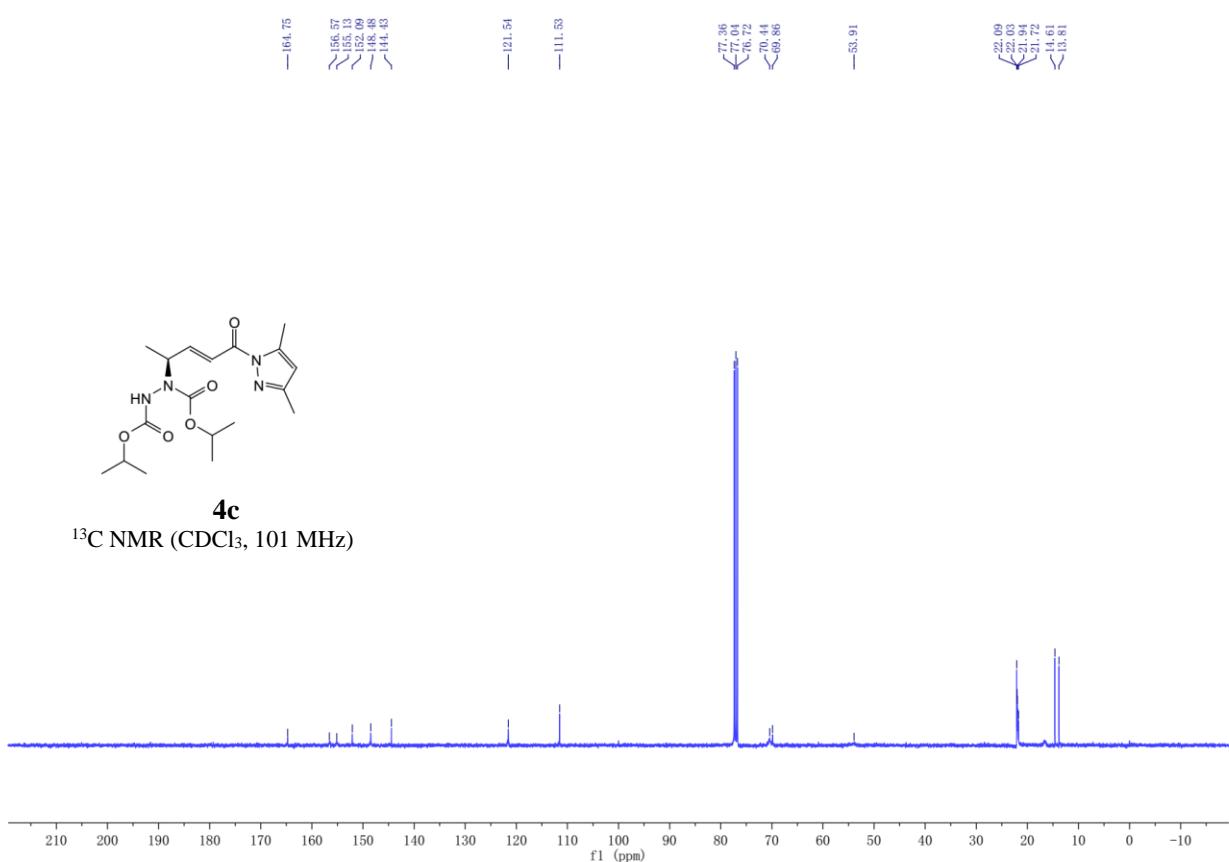


4c

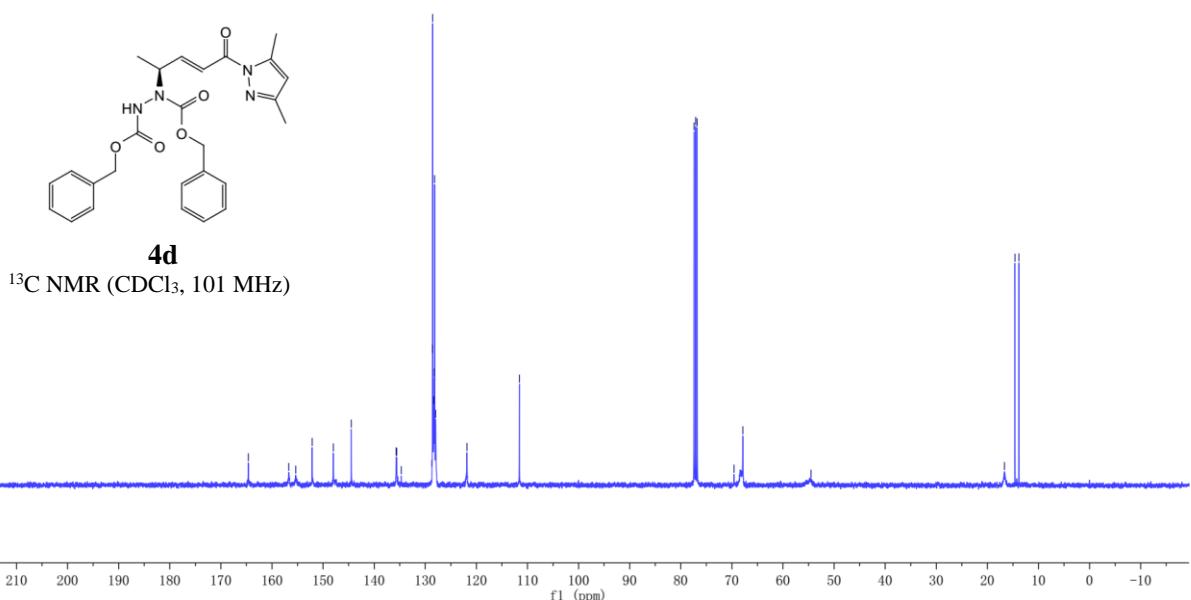
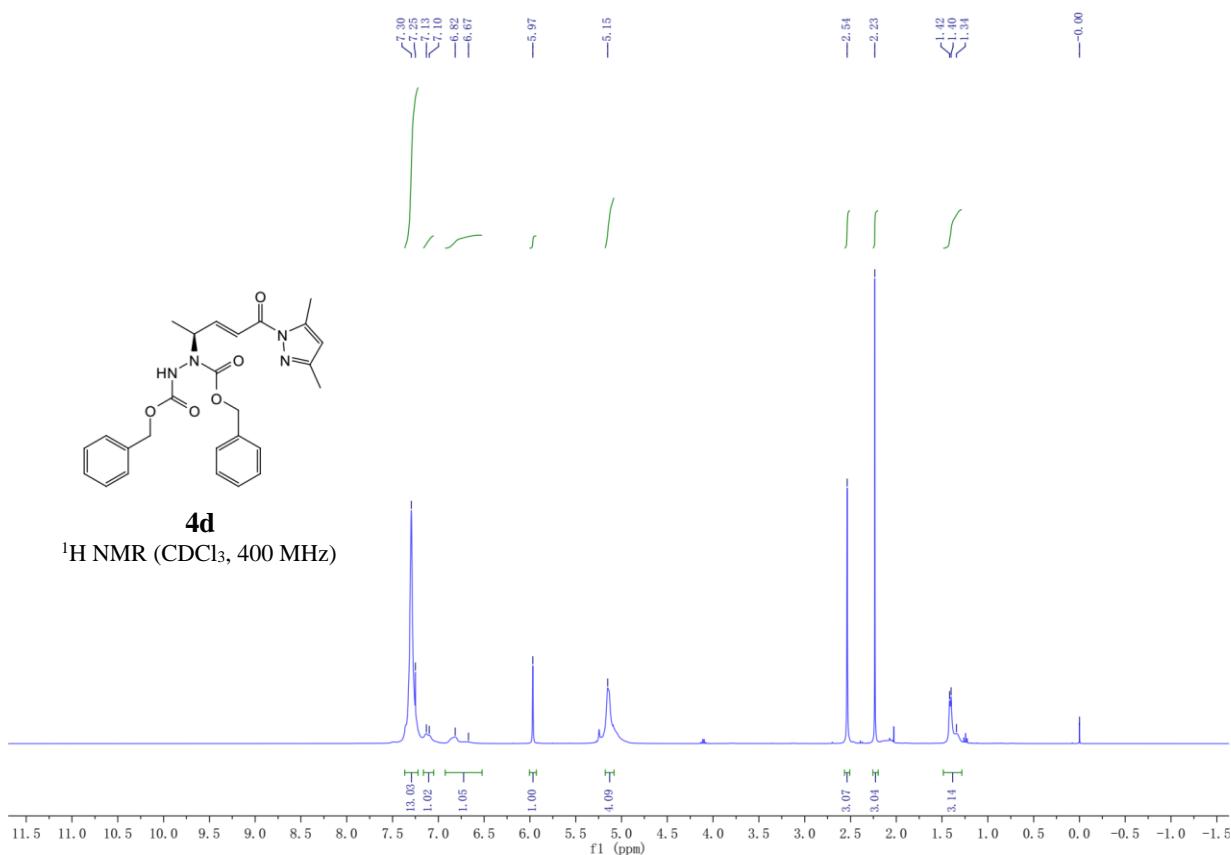


4c

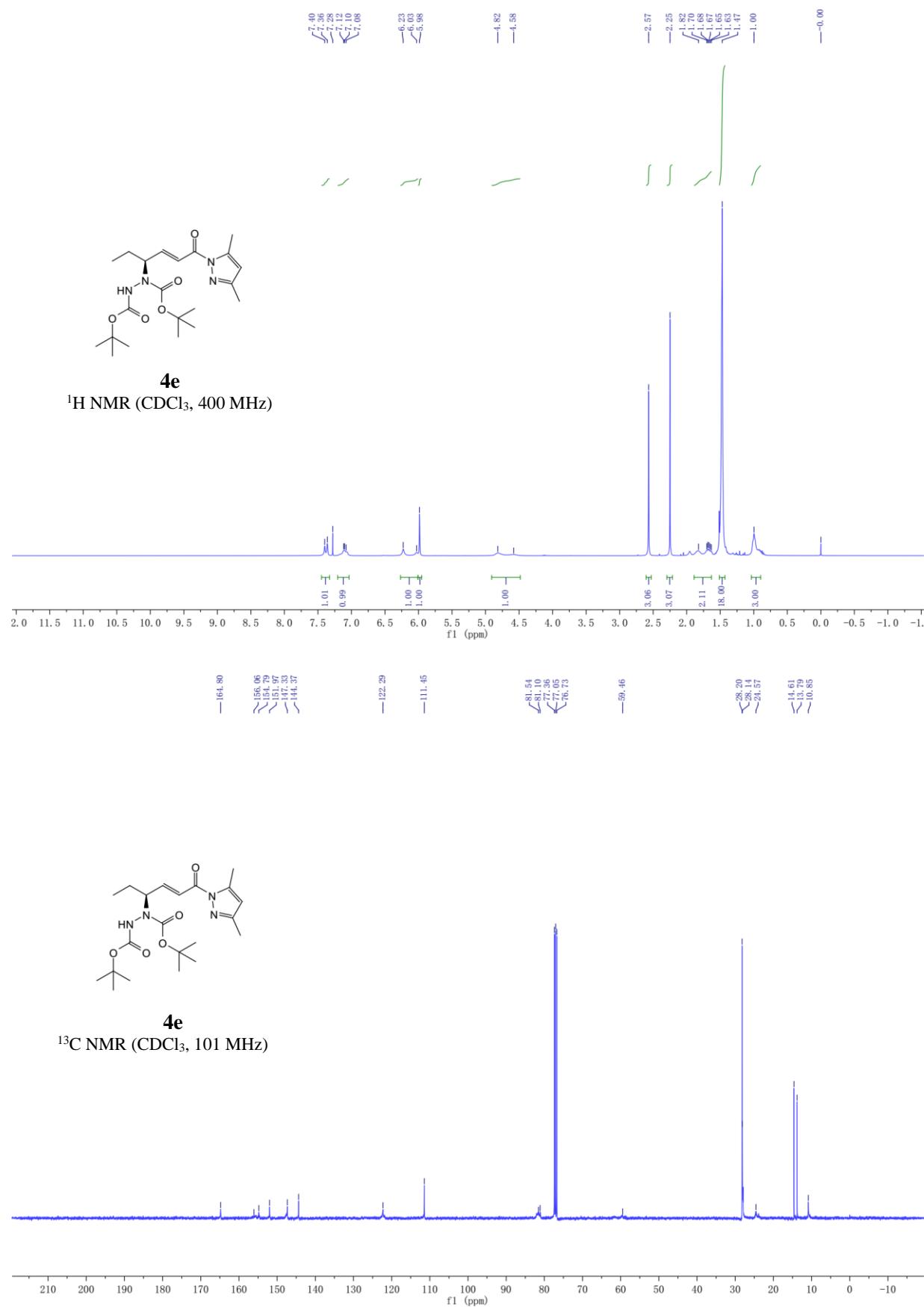
^{13}C NMR (CDCl_3 , 101 MHz)



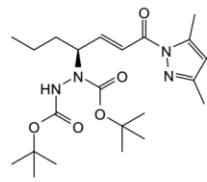
4d



4e

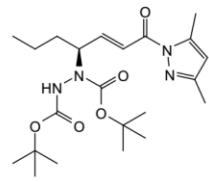
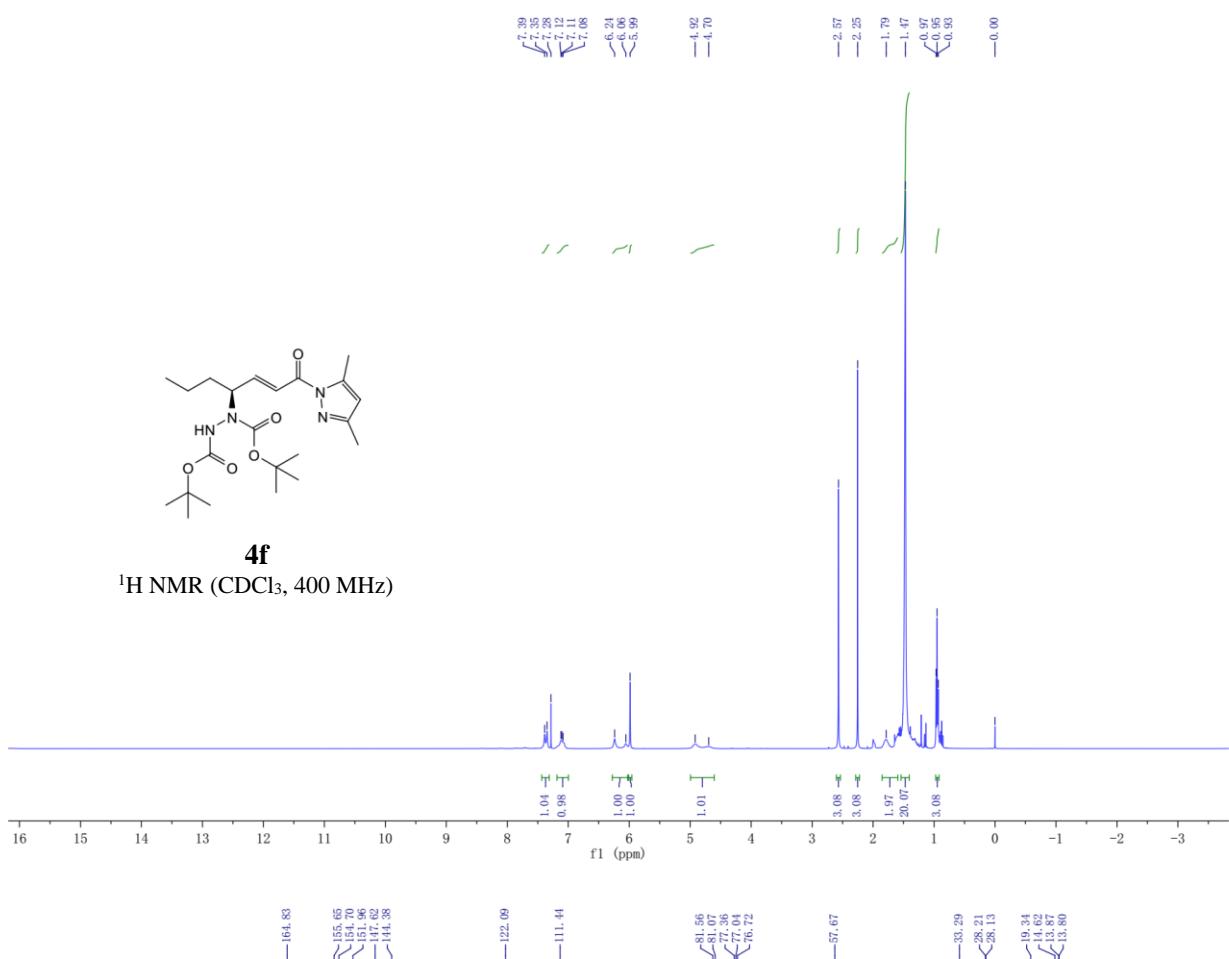


4f



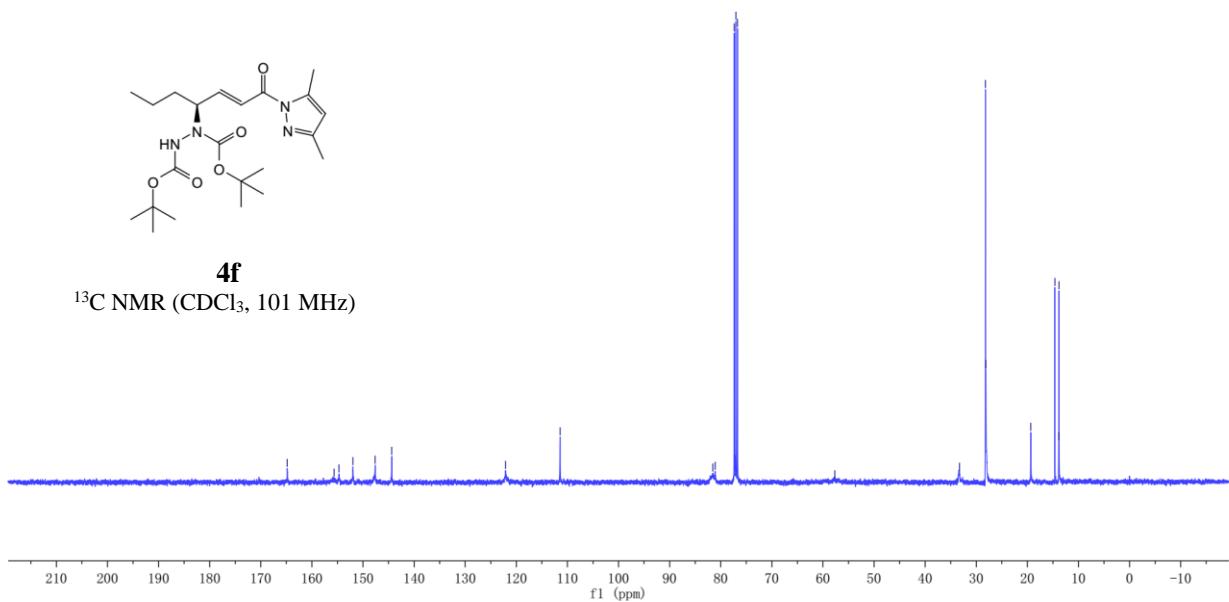
4f

¹H NMR (CDCl₃, 400 MHz)

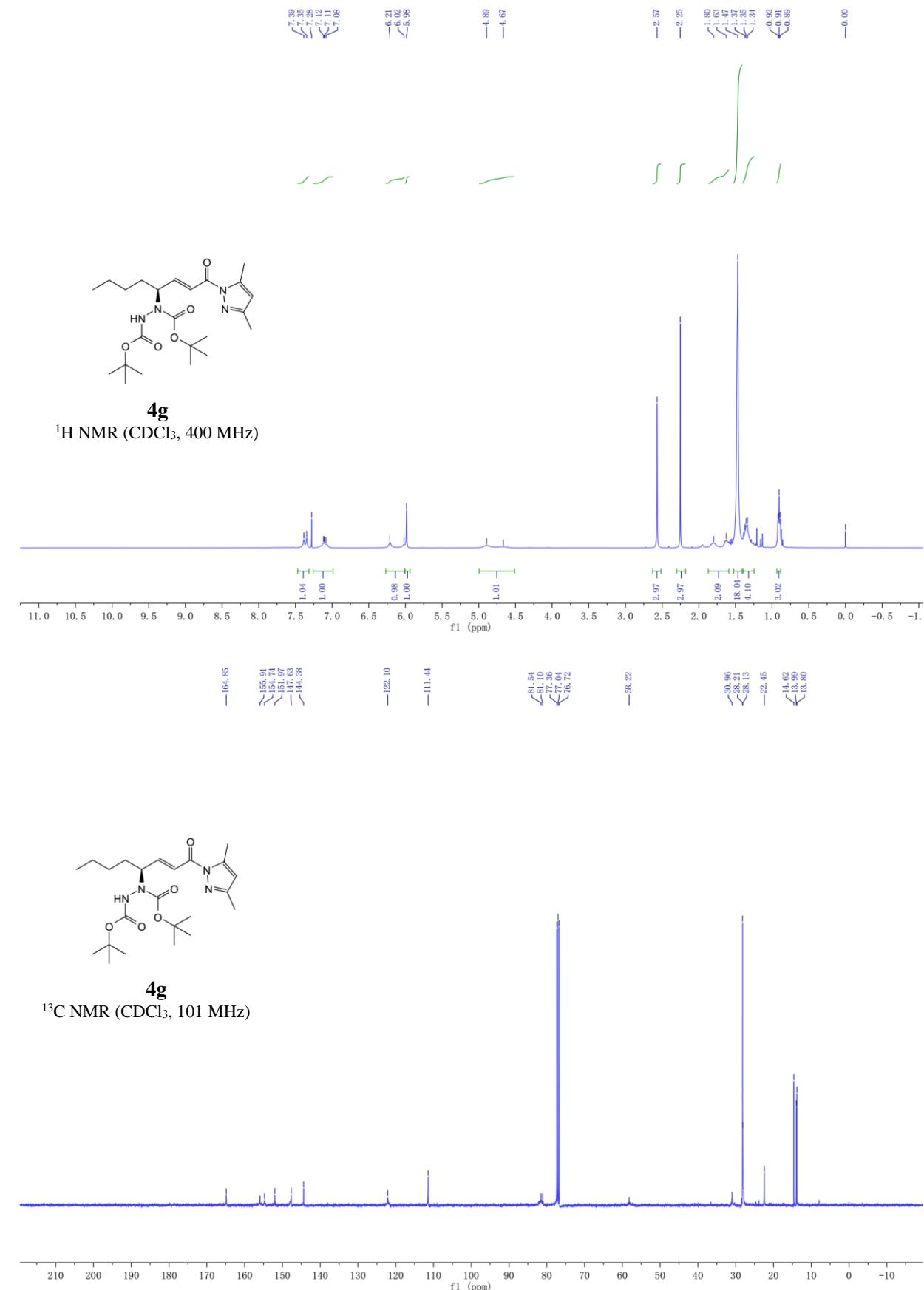


4f

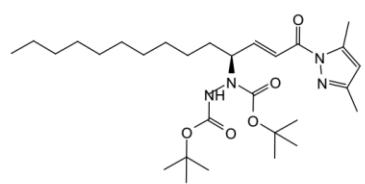
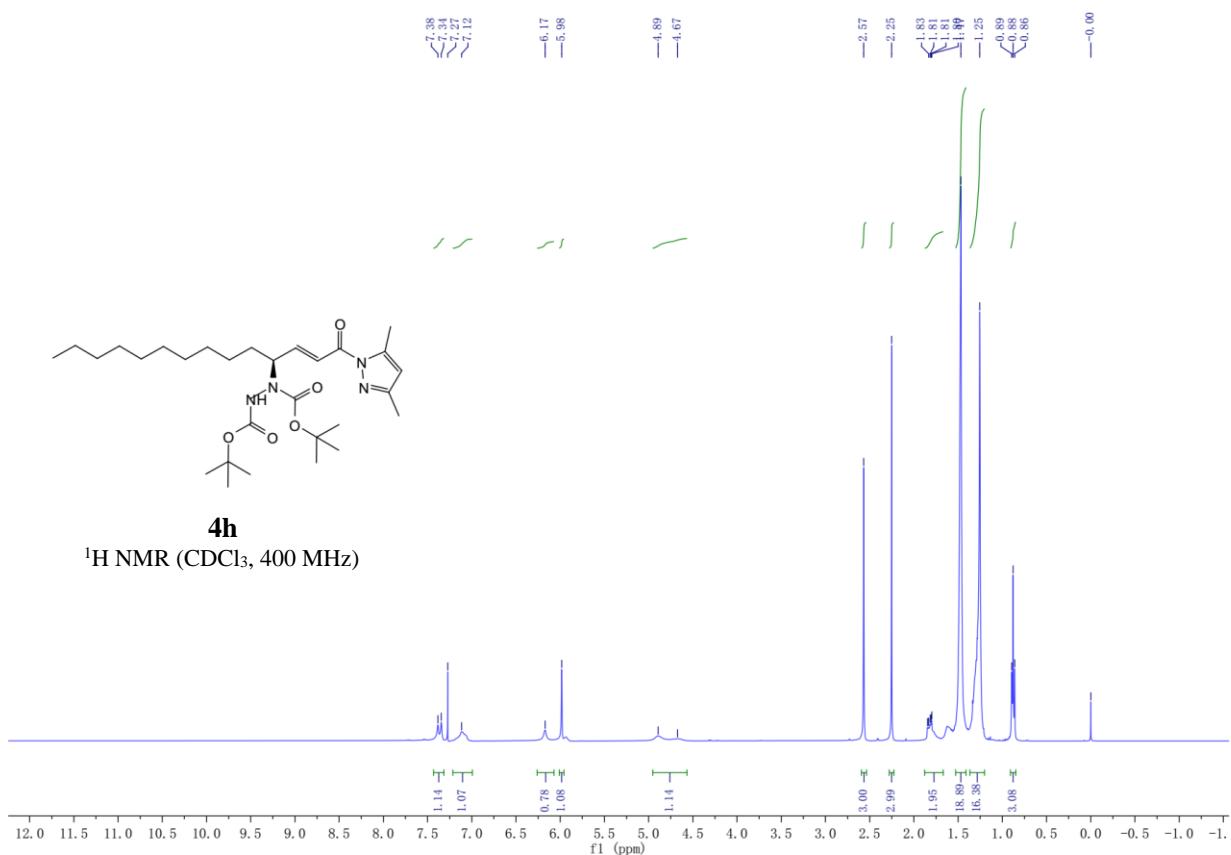
¹³C NMR (CDCl₃, 101 MHz)



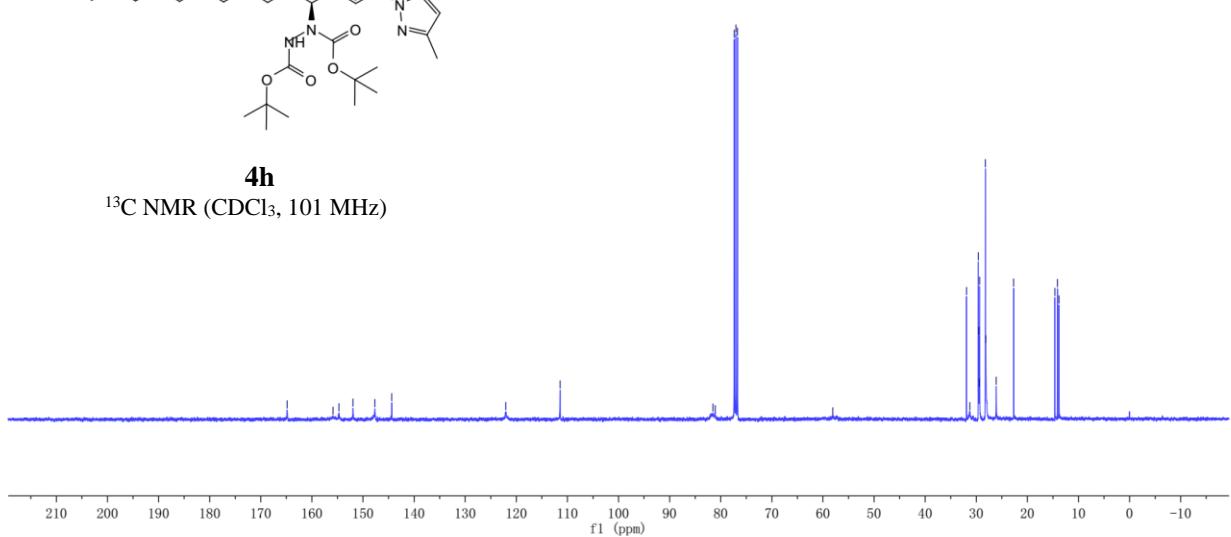
4g



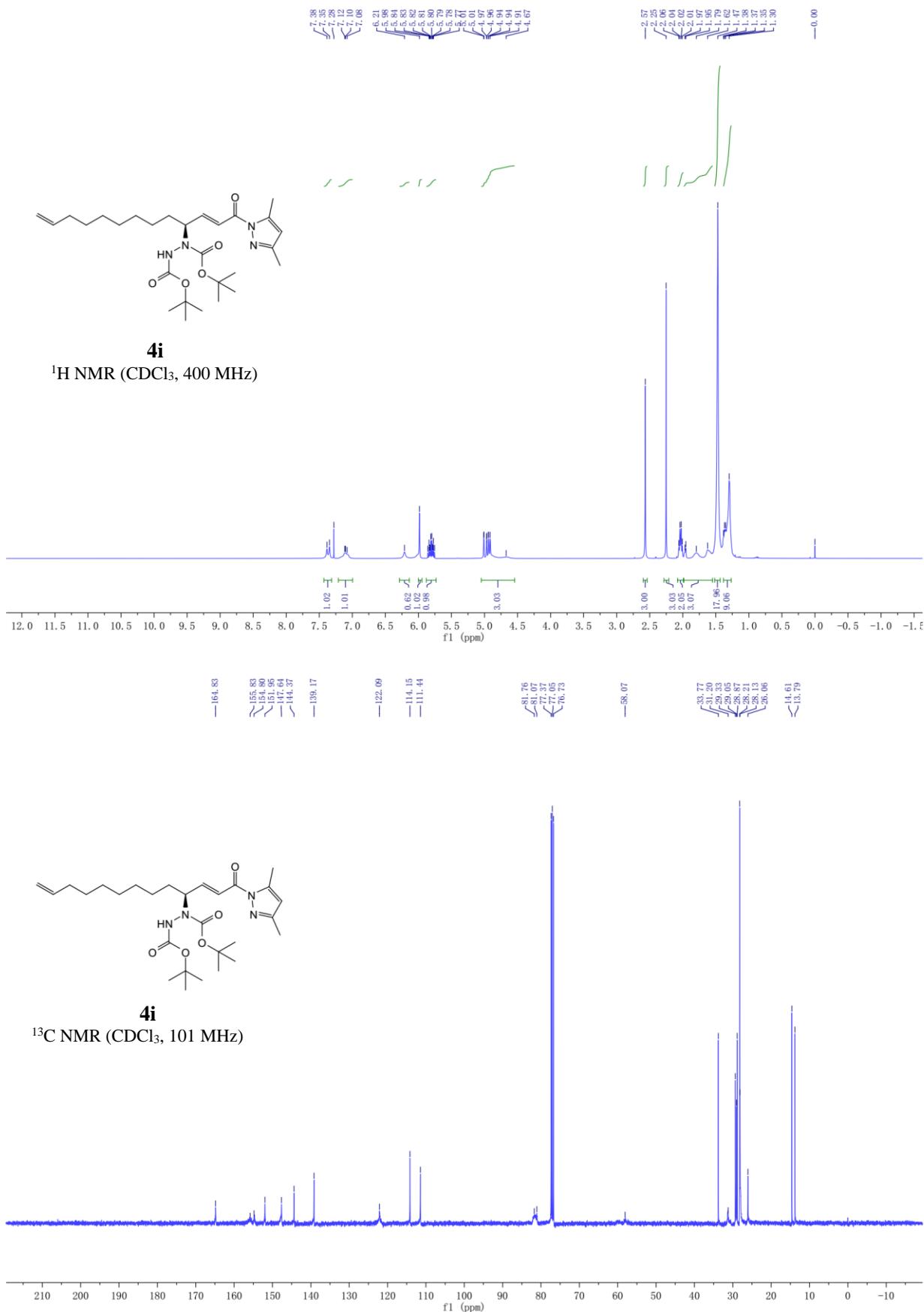
4h



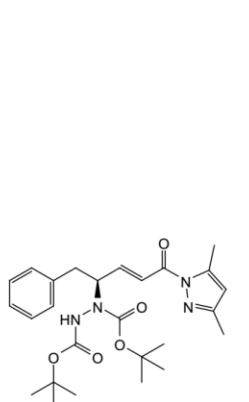
4h
 ^{13}C NMR (CDCl_3 , 101 MHz)



4i

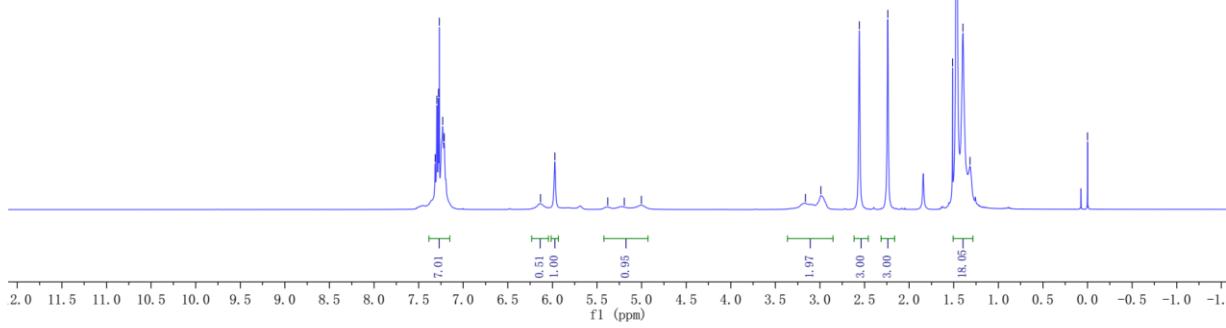


4j

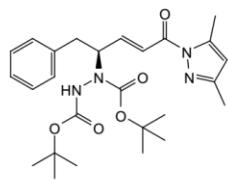


4j

^1H NMR (CDCl_3 , 400 MHz)

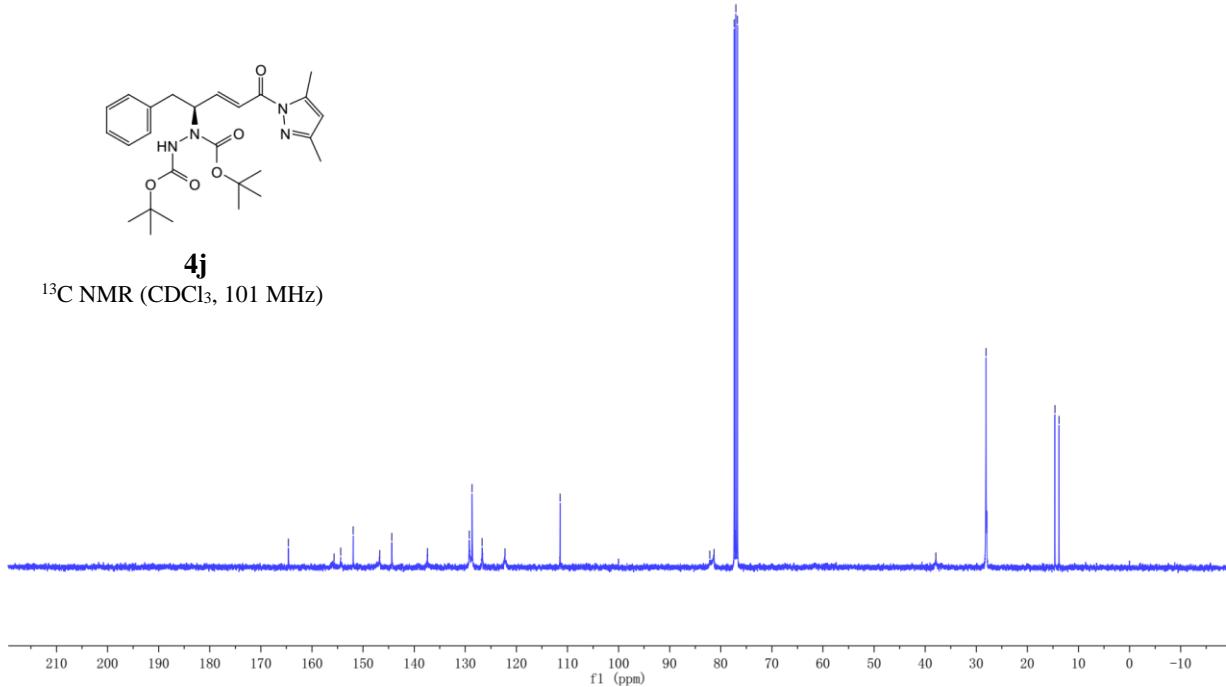


—164.62
—155.67
—154.38
—151.94
—146.72
—144.38
—137.39
—129.23
—128.65
—126.70
—122.22
—111.45
—37.92
—28.11
—14.61
—13.80

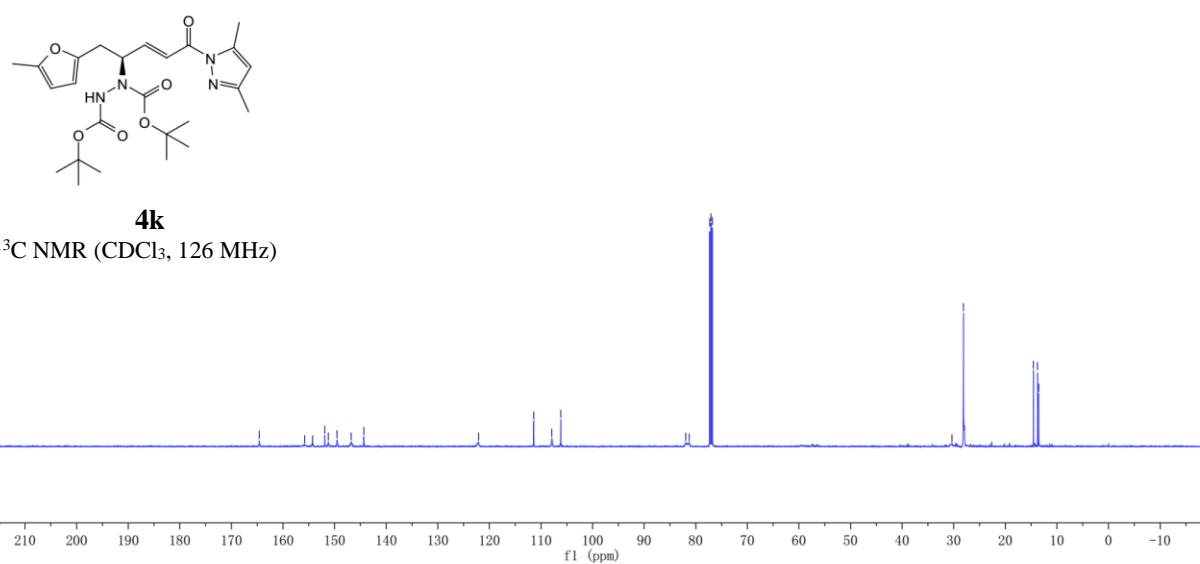
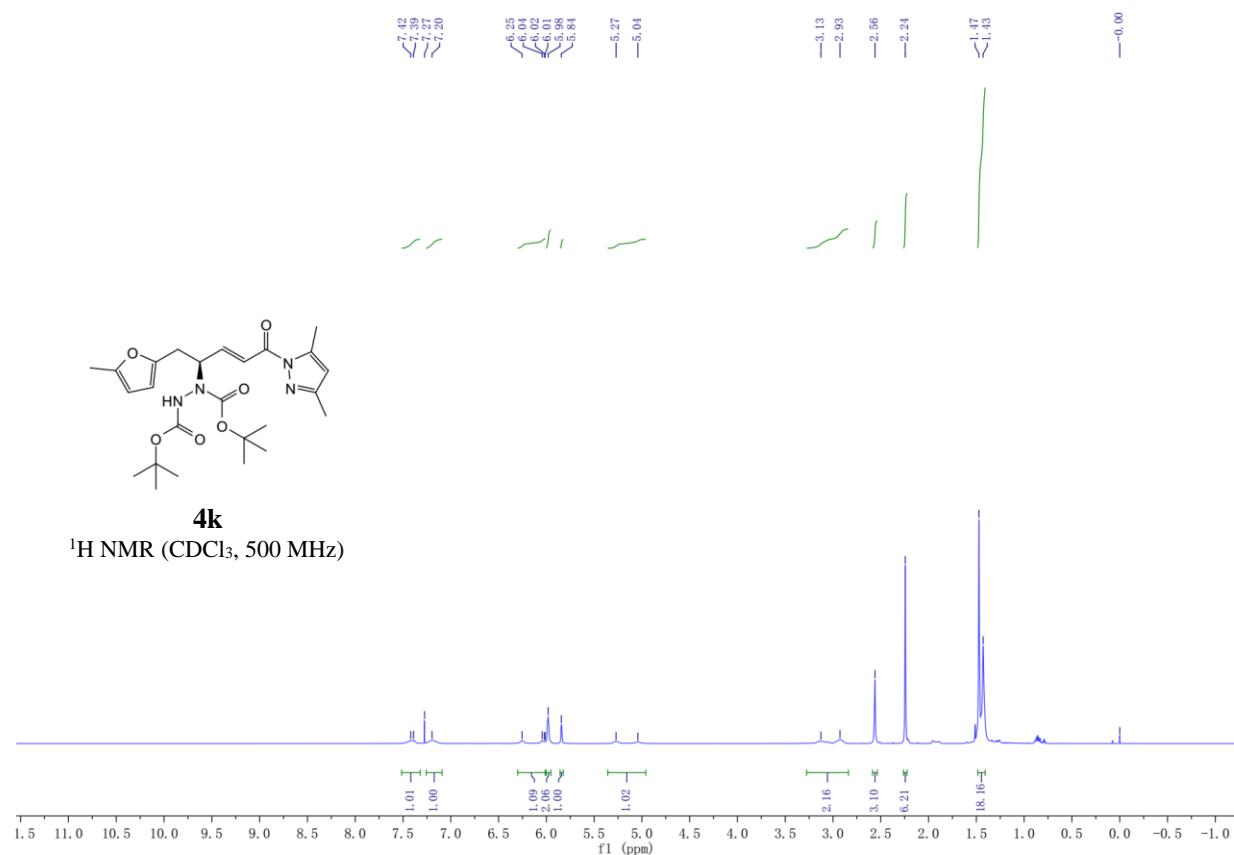


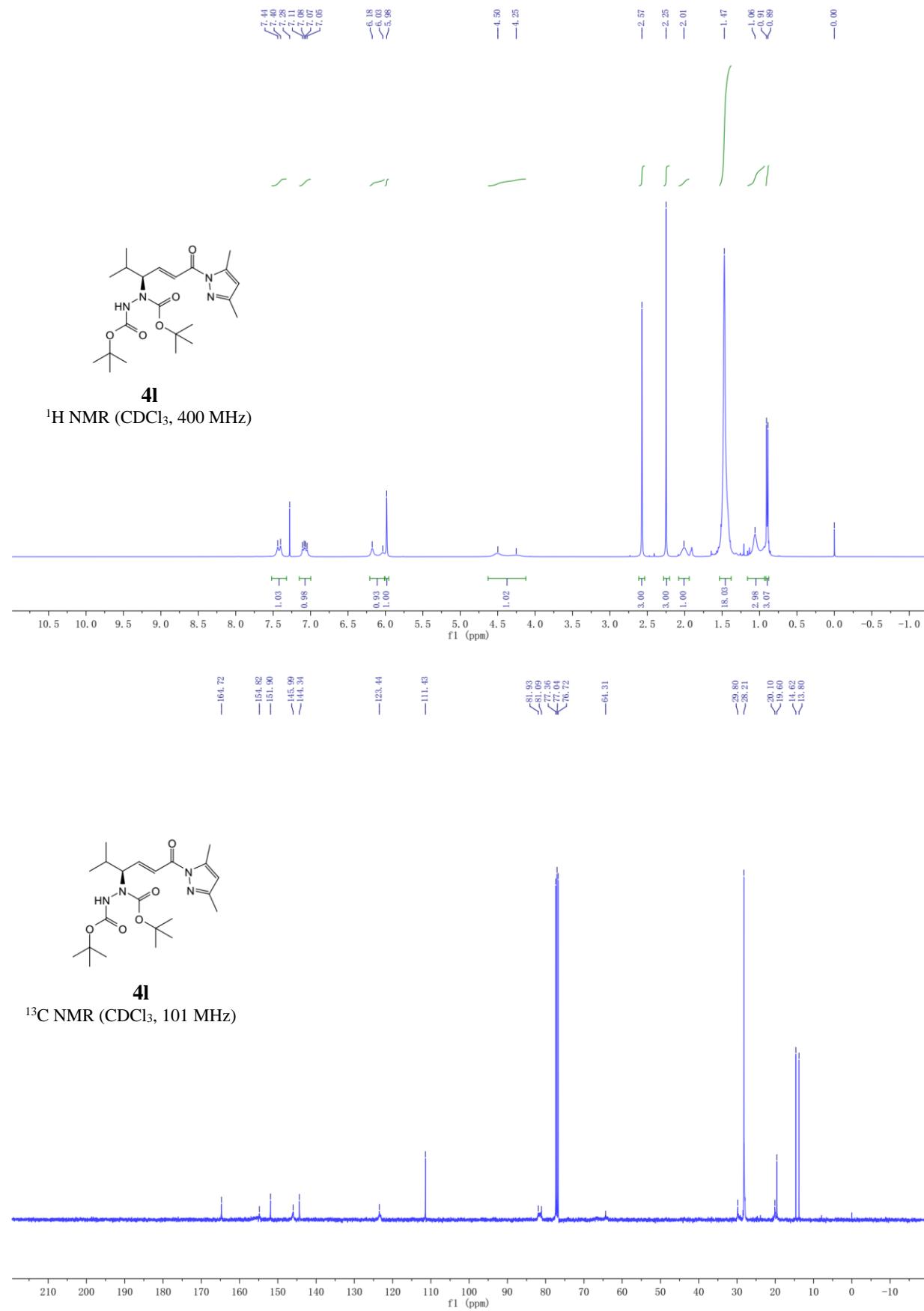
4j

^{13}C NMR (CDCl_3 , 101 MHz)

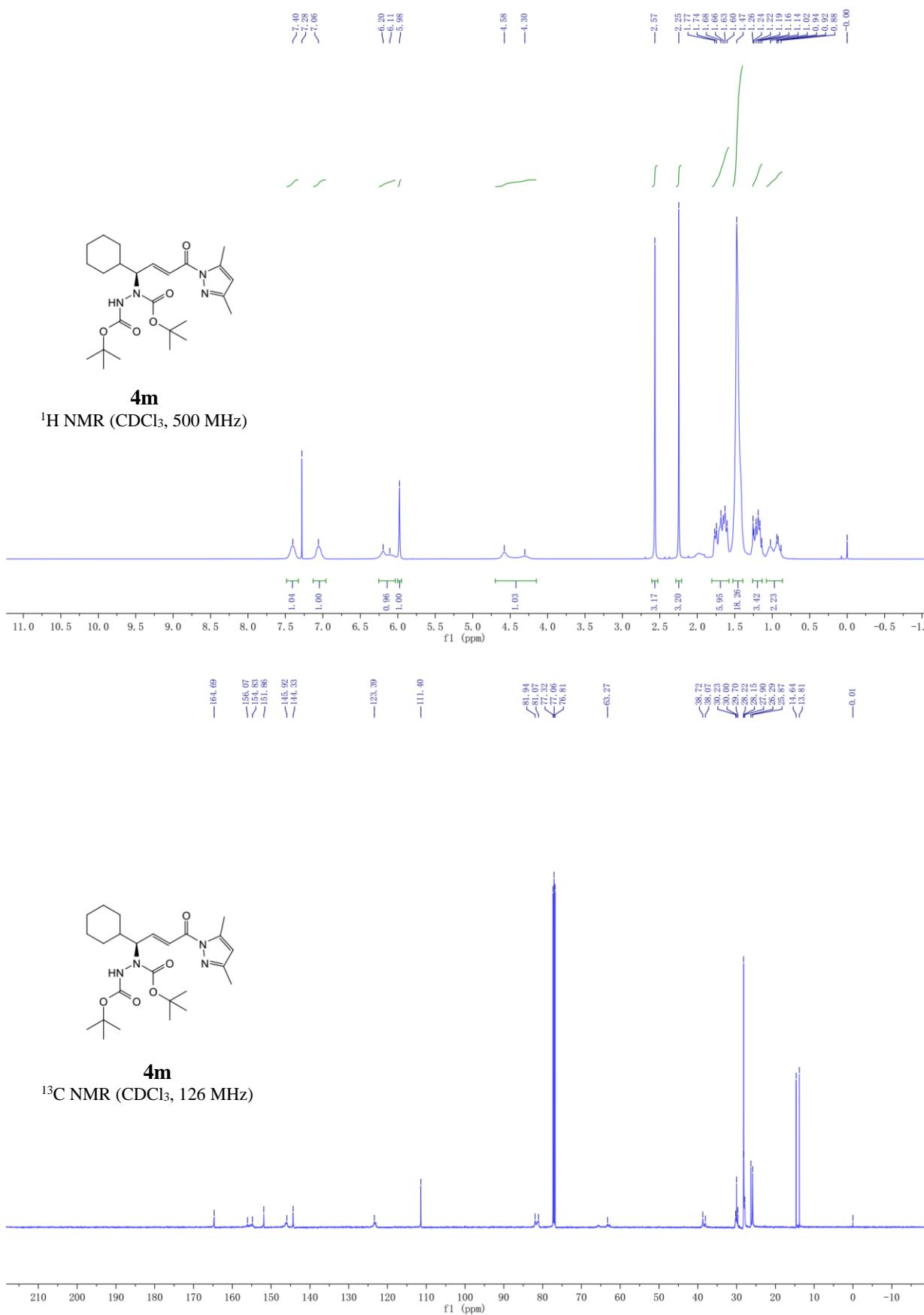


4k

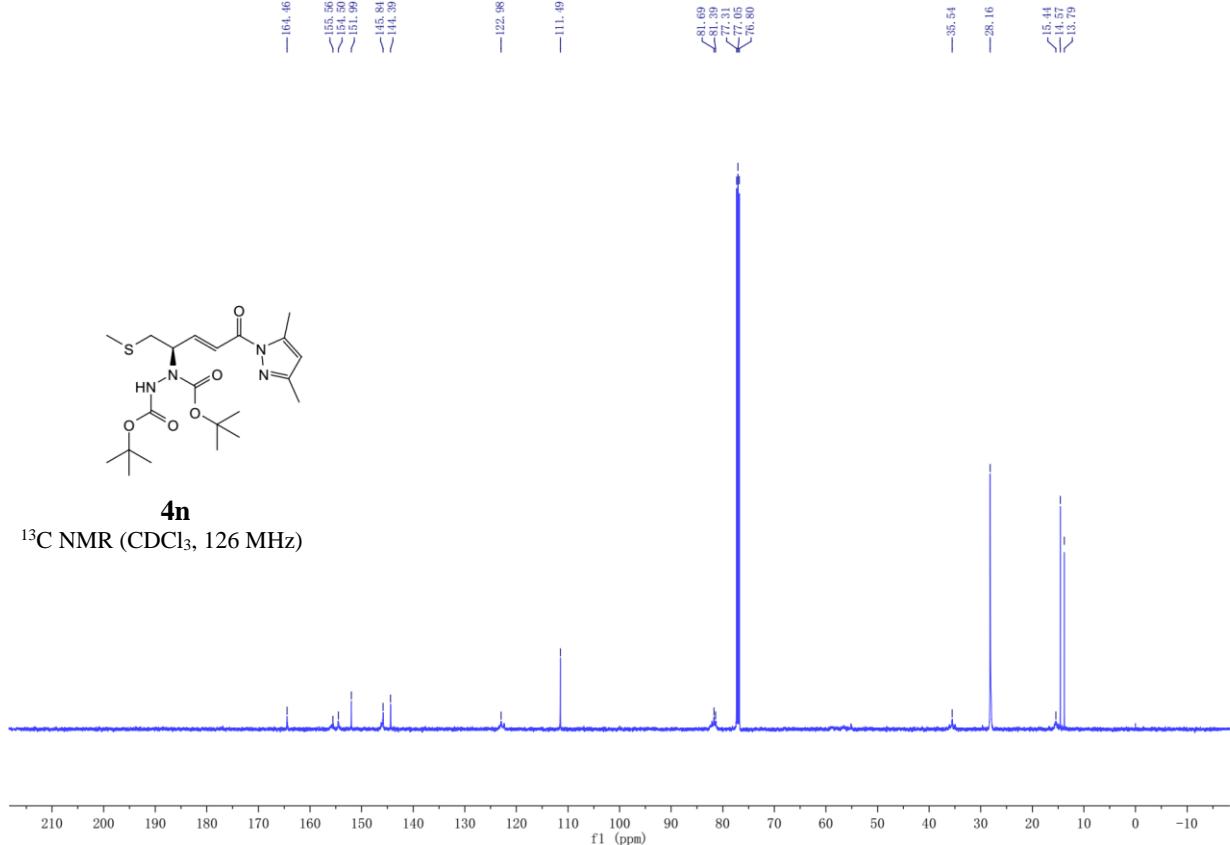
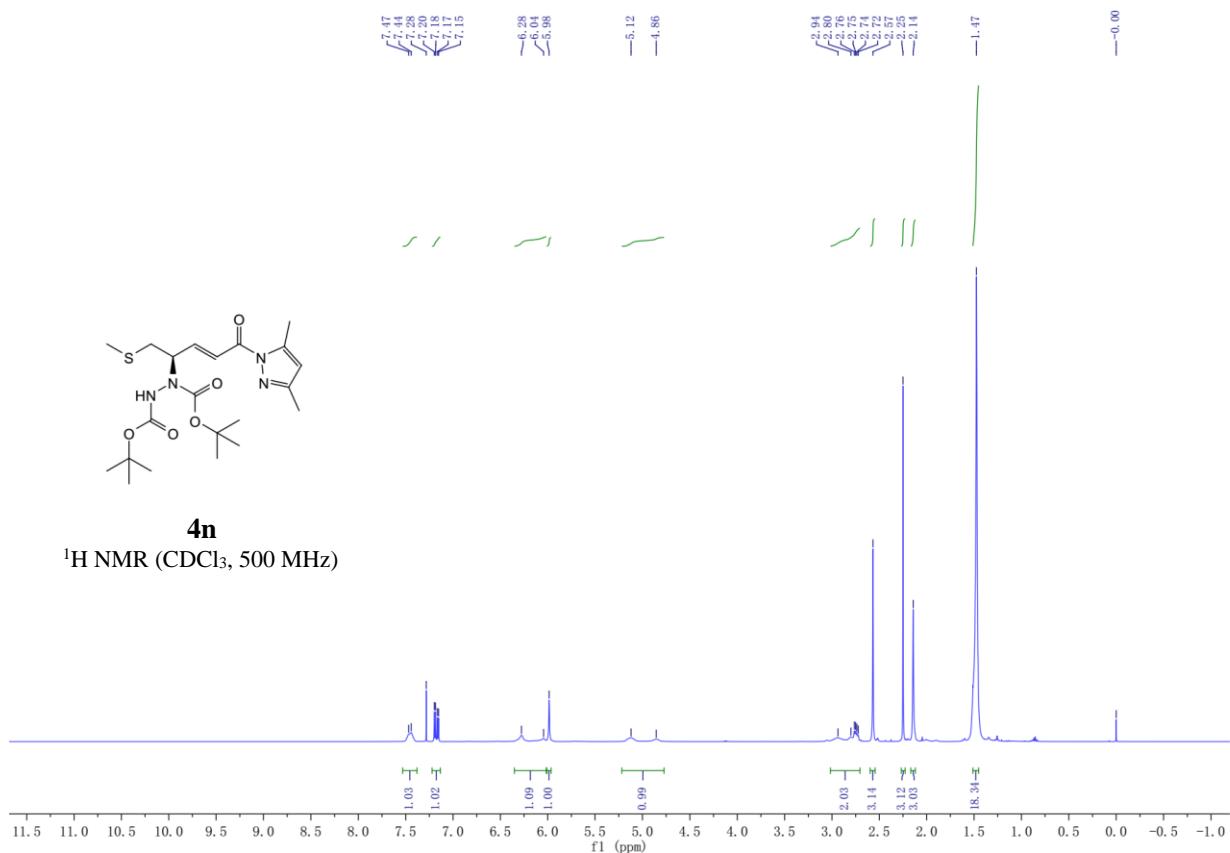


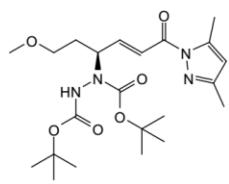


4m



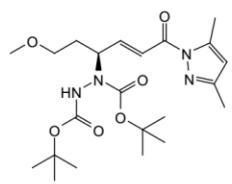
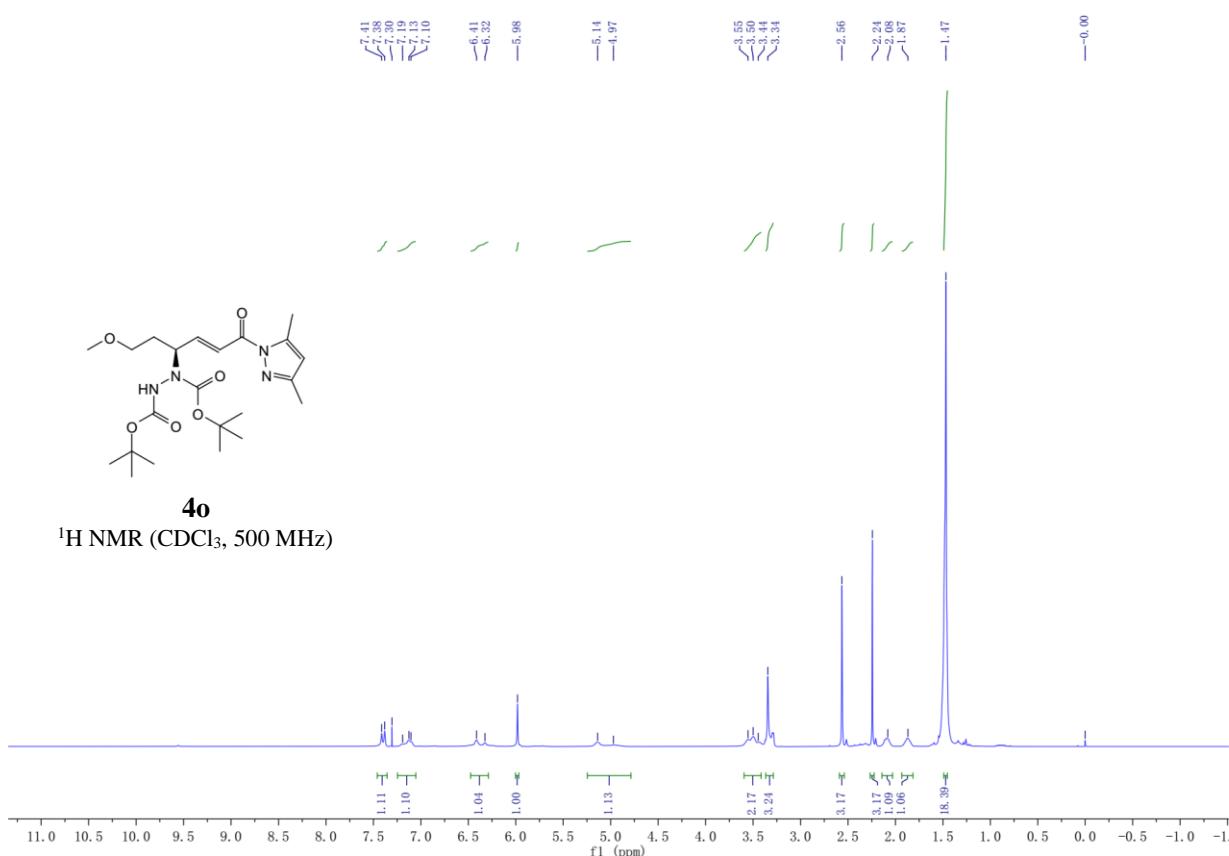
4n





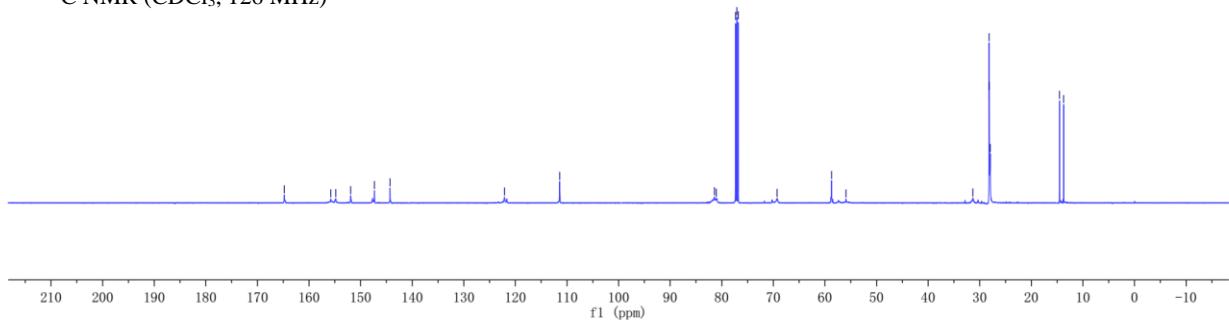
40

¹H NMR (CDCl₃, 500 MHz)

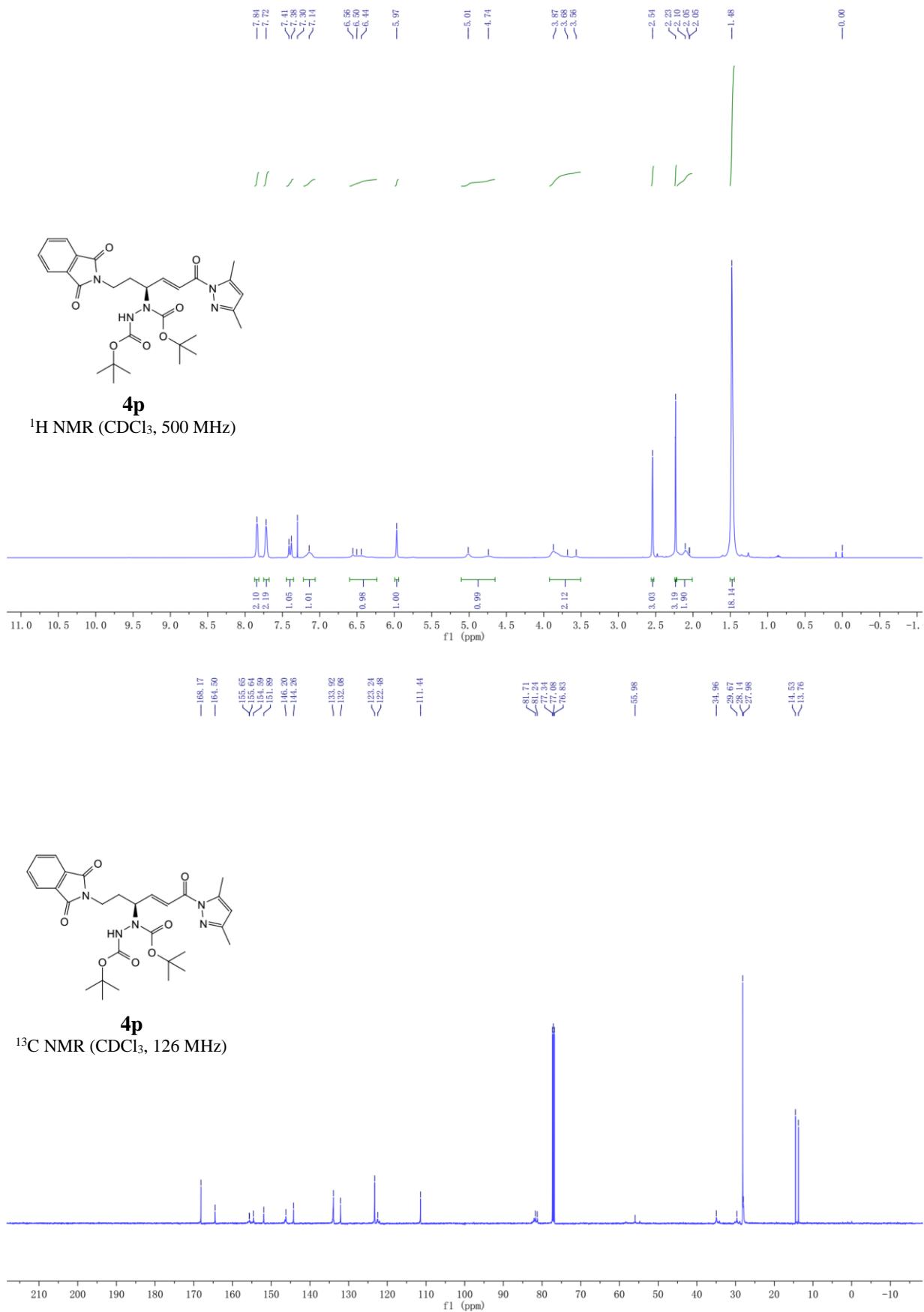


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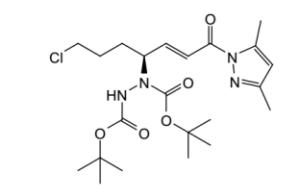
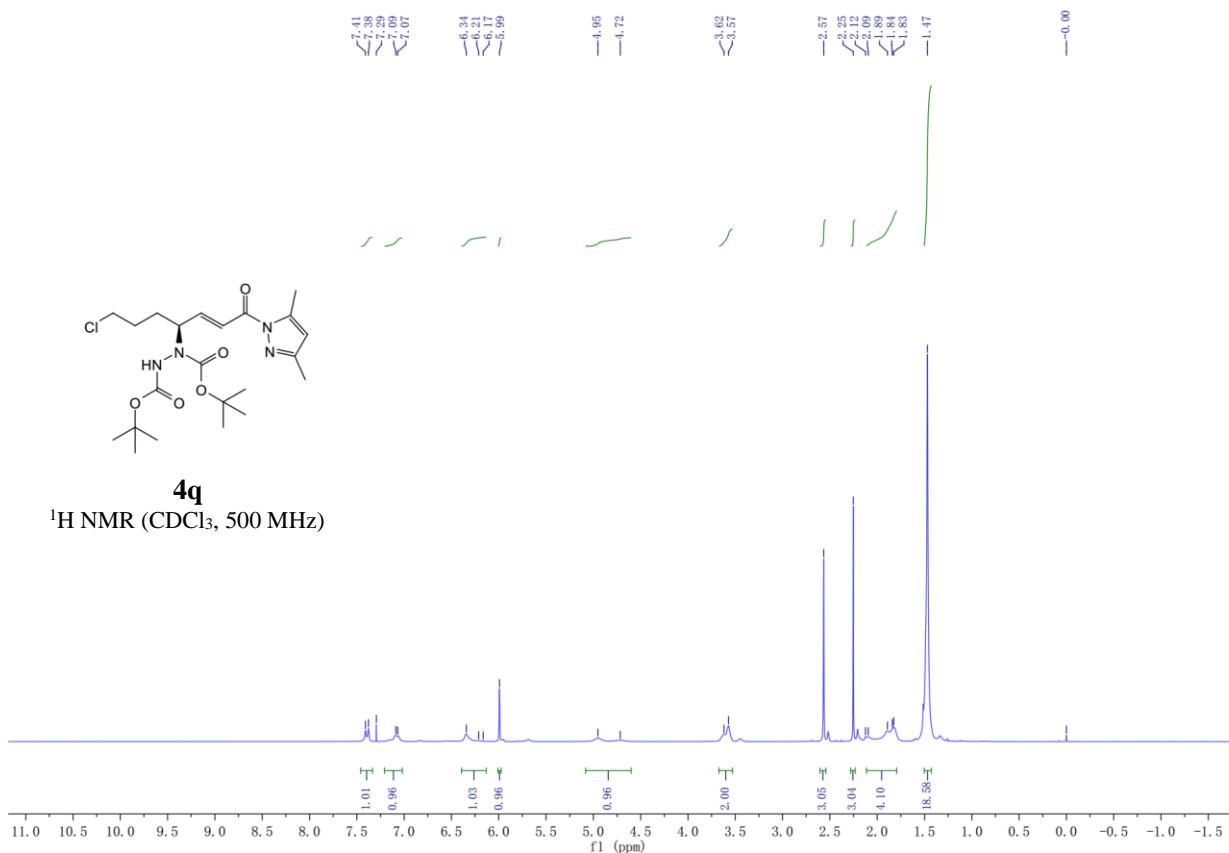
¹³C NMR (CDCl₃, 126 MHz)



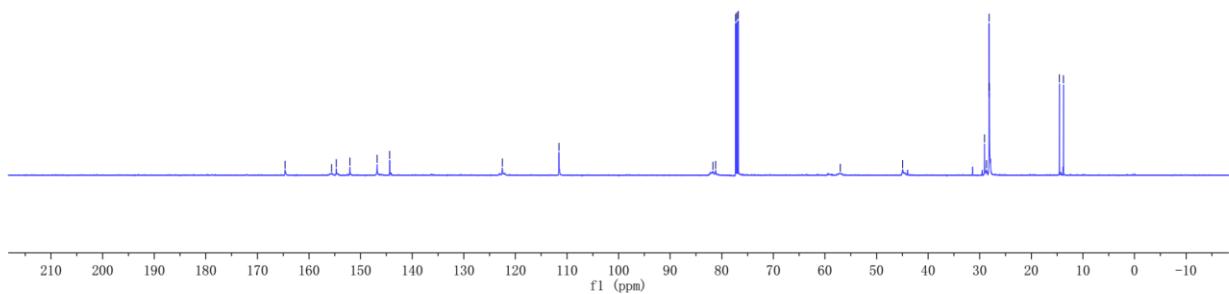
4p



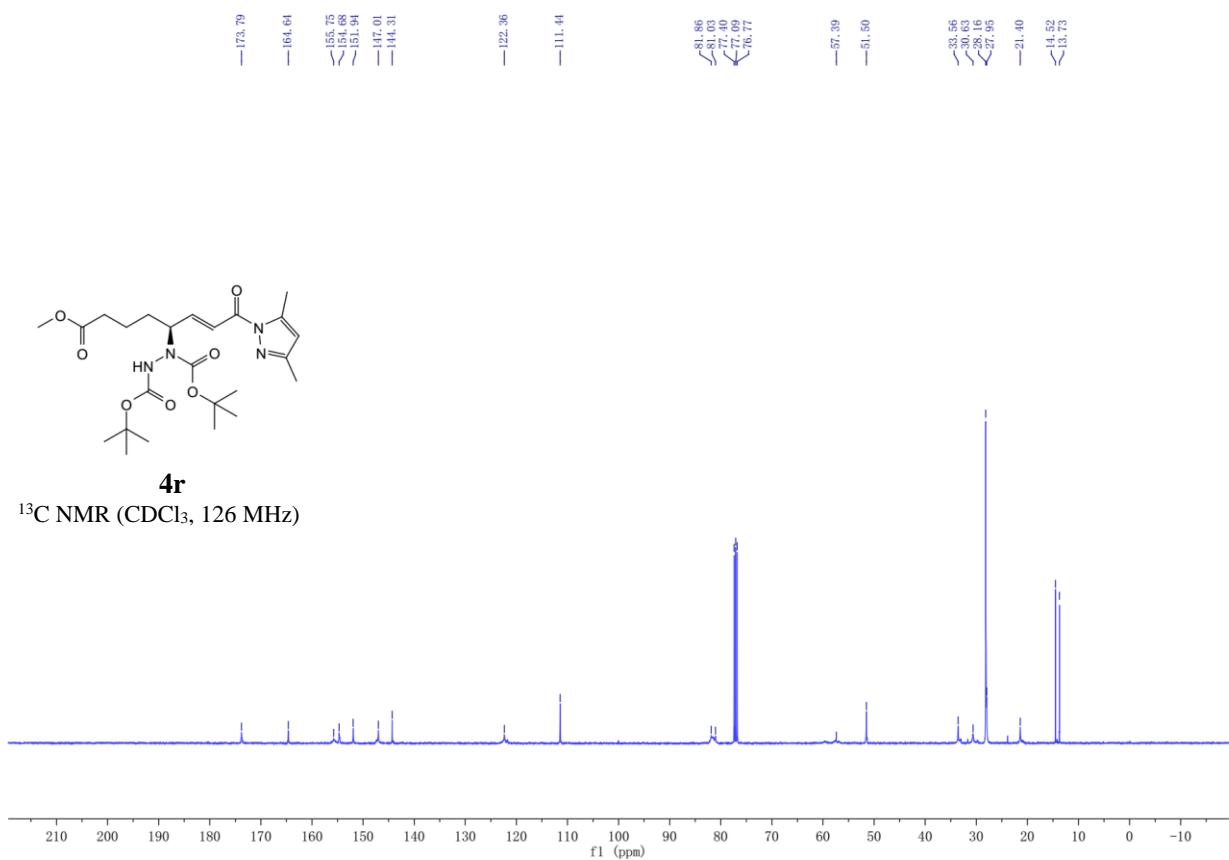
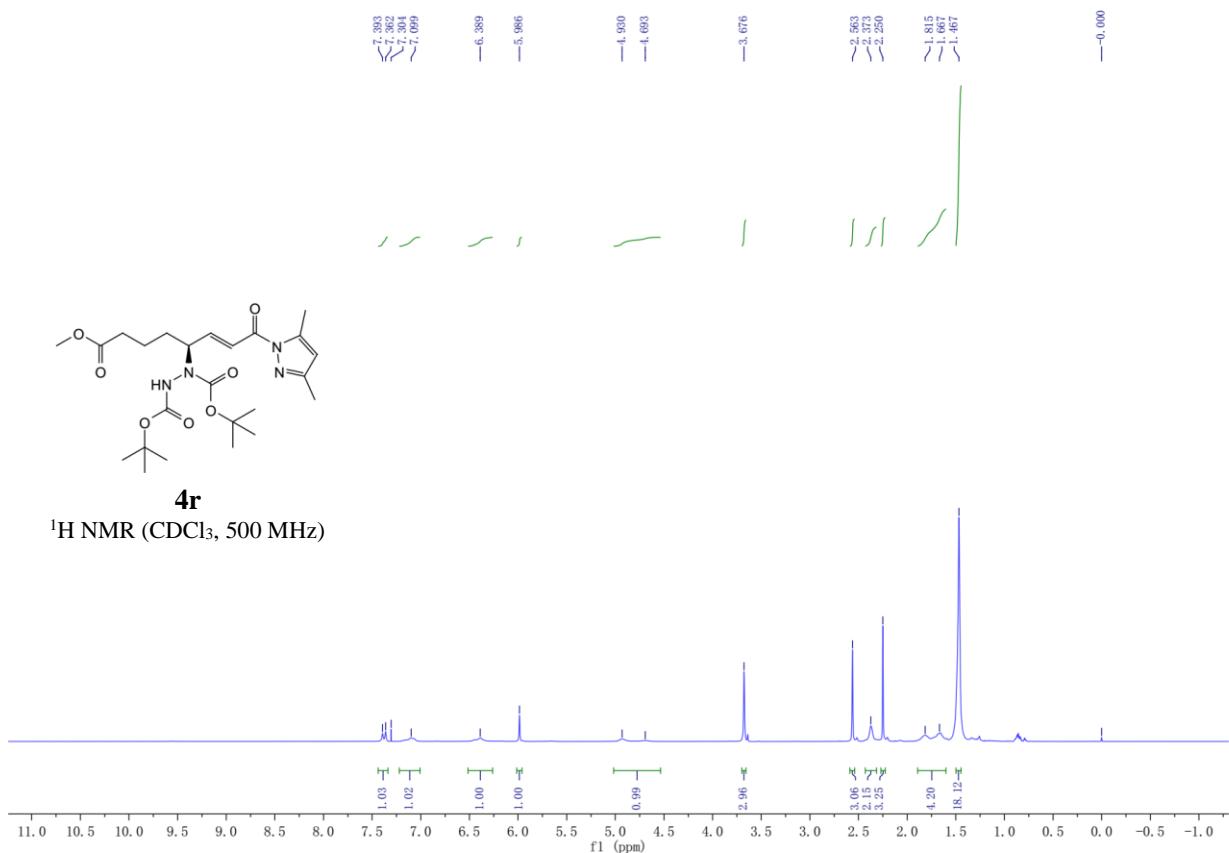
4q



4q
 ^{13}C NMR (CDCl_3 , 126 MHz)



4r



5j

