

Diaza [1,4] Wittig-type rearrangement of *N*-allylic-*N*-Boc-hydrazines into γ -amino-*N*-Boc-enamines

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Electronic Supplementary Information

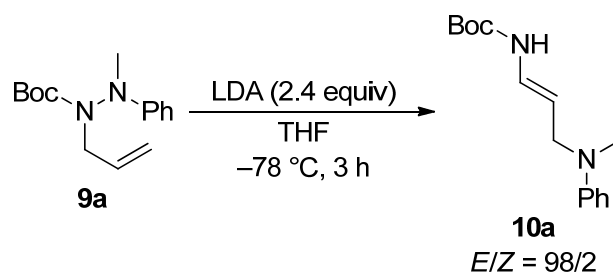
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1. Experimental details and products characterizations

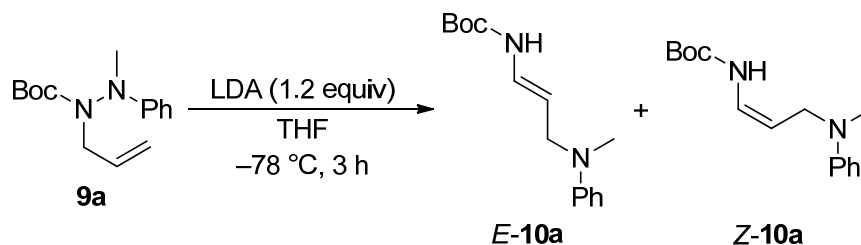
General: Infrared spectra were recorded on a Perkin Elmer Spectrum GX FT-IR spectrometer. ^1H and ^{13}C NMR spectra were measured on a Varian or a Bruker 400 MHz spectrometers (^1H : 400 MHz, ^{13}C : 100 MHz). The splitting patterns are denoted as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; and br, broad peak. High-resolution mass spectra were measured on a Thermo Fisher Scientific LC/FT-MS spectrometer. Reactions involving air- or moisture-sensitive compounds were conducted in appropriate round-bottomed flasks with a magnetic stirring bar under an argon atmosphere. Reactions under lower temperature were carried out using a Constant Temp. Bath with Magnetic Stirrer (PSL-1400 and PSL-1800, EYELA, Japan) and a Ultra-Cooling Reactor (UCR-150, Techno Sigma Co., Ltd., Japan). Tetrahydrofuran (THF) and diethyl ether were purchased from KANTO Chemical Co., Inc., Japan as an anhydrous solvent. For thin layer chromatography (TLC) analysis throughout this work, Merck TLC plates (silica gel 60 F₂₅₄) were used. The products were purified by preparative column chromatography on silica gel (silica gel 60N, spherical neutral, KANTO Chemical Co., Inc., Japan).

Representative procedure for the reaction of **9a** into **10a** (Table 1, Entry 3)



A solution of **9a** (100 mg, 0.381 mmol) in THF (3.4 mL) was treated with a ca. 0.7 M LDA solution in THF-*n*-hexane¹ (1.30 mL, 0.91 mmol) at $-78\text{ }^\circ\text{C}$ and stirred for 3 h at the same temperature. The resulting mixture was poured into saturated aqueous ammonium chloride and extracted with ethyl acetate. The combined extracts were washed with brine, dried over sodium sulfate, and concentrated. The residue was purified by chromatography on silica gel (*n*-hexane/EtOAc = 6/1 to 4/1 as the eluent) to obtain **10a** (80.8 mg, 81% yield) as colorless crystals. The *E/Z* ratio was determined to be 98/2 by ^1H NMR analysis.

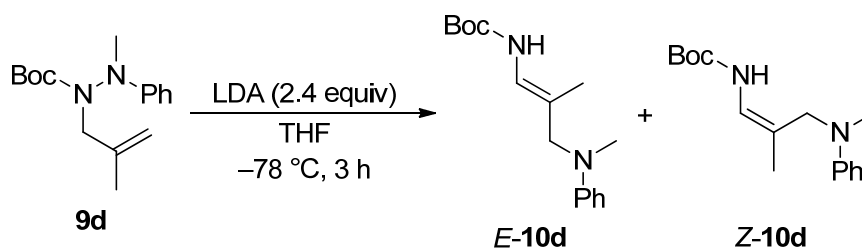
tert-Butyl (3-(methyl(phenyl)amino)prop-1-en-1-yl)carbamate (**10a**) (Table 1, Entry 5)



¹ Tayama, E.; Saito, S. *Tetrahedron* **2016**, 72, 599–604.

A solution of **9a** (101 mg, 0.385 mmol) in THF (3.5 mL) was treated with a ca. 0.7 M LDA solution in THF-*n*-hexane (0.66 mL, 0.46 mmol) at $-78\text{ }^{\circ}\text{C}$ and stirred for 3 h at the same temperature. The resulting mixture was poured into saturated aqueous ammonium chloride and extracted with ethyl acetate. Extractive workup and purification of the residue by careful chromatography on silica gel (*n*-hexane/EtOAc = 8/1 to 5/1 as the eluent) to obtain *E*-**10a** (74.5 mg, 74% yield) as colorless crystals and *Z*-**10a** (2.1 mg, 2% yield) as colorless crystals. *E*-**10a**: colorless crystals; mp 100–102 $^{\circ}\text{C}$; IR (KBr) 3366, 3051, 3011, 2986, 2975, 2935, 2873, 2824, 1697, 1673, 1605, 1593, 1570, 1512, 1471, 1457, 1443, 1426, 1392, 1368, 1354, 1343, 1305, 1294, 1245, 1225, 1199, 1162, 1120, 1085, 1037, 1018, 989, 950, 920, 860, 809, 772, 741, 689 cm^{-1} ; ^1H NMR (400 MHz, DMSO-*d*₆) δ 9.09 (1H, d, $J = 10.4$ Hz, NH), 7.15 (2H, dddd, $J = 8.8, 7.2, 1.6, 1.6$ Hz, Ph), 6.70 (2H, dd, $J = 8.8, 1.6$ Hz, Ph), 6.60 (1H, dt, $J = 7.2, 1.6$ Hz, Ph), 6.49 (1H, dd, $J = 14.0, 10.4$ Hz, 1-H), 5.01 (1H, dt, $J = 14.0, 6.4$ Hz, 2-H), 3.85 (2H, d, $J = 6.4$ Hz, 3-H), 2.80 (3H, s, NCH₃), 1.40 (9H, s, *t*-Bu); ^{13}C NMR (100 MHz, CDCl₃) δ 152.7, 149.4, 129.1, 126.2, 116.6, 112.9, 104.1, 80.5, 52.4, 37.4, 28.2; HRMS-ESI (m/z): [M+H]⁺ calcd for C₁₅H₂₃N₂O₂: 263.1754. Found: 263.1746. *Z*-**10a**: colorless crystals; mp 58–60 $^{\circ}\text{C}$; IR (KBr) 3246, 3137, 3086, 3061, 3022, 2999, 2980, 2931, 1701, 1667, 1600, 1505, 1476, 1456, 1376, 1366, 1328, 1281, 1241, 1199, 1164, 1111, 1058, 1034, 984, 965, 921, 860, 779, 743, 689 cm^{-1} ; ^1H NMR (400 MHz, DMSO-*d*₆) δ 9.04 (1H, d, $J = 10.4$ Hz, NH), 7.14 (2H, dd, $J = 8.5, 7.2$ Hz, Ph), 6.68 (2H, d, $J = 8.5$ Hz, Ph), 6.61 (1H, t, $J = 7.2$ Hz, Ph), 6.39 (1H, dd, $J = 10.4, 9.0$ Hz, 1-H), 4.42 (1H, dt, $J = 9.0, 6.6$ Hz, 2-H), 3.99 (2H, d, $J = 6.6$ Hz, 3-H), 2.81 (3H, s, NCH₃), 1.45 (9H, s, *t*-Bu); ^{13}C NMR (100 MHz, CDCl₃) δ 152.7, 150.3, 129.1, 125.2, 118.5, 114.8, 103.0, 80.5, 50.5, 38.6, 28.2; HRMS-ESI (m/z): [M+H]⁺ calcd for C₁₅H₂₃N₂O₂: 263.1754. Found: 263.1747.

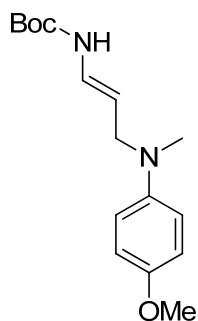
tert-Butyl (2-methyl-3-(methyl(phenyl)amino)prop-1-en-1-yl)carbamate (10d) (Table 1, Entry 11)



A solution of **9d** (157 mg, 0.568 mmol) in THF (5.1 mL) was treated with a ca. 0.7 M LDA solution in THF-*n*-hexane (1.95 mL, 1.36 mmol) at $-78\text{ }^{\circ}\text{C}$ and stirred for 3 h at the same temperature. The resulting mixture was poured into saturated aqueous ammonium chloride and extracted with ethyl acetate. Extractive workup and purification of the residue by careful chromatography on silica gel (*n*-hexane/EtOAc = 15/1 to 10/1 as the eluent) to obtain *E*-**10d** (110.8 mg, 71% yield) as colorless crystals and *Z*-**10d** (5.5 mg, 4% yield) as a colorless oil. *E*-**10d**: colorless crystals; mp 117–119 $^{\circ}\text{C}$; IR (KBr) 3256, 3131, 3088, 2973, 2938, 2915, 2872, 2803, 1692, 1597, 1571, 1505, 1475, 1446, 1389, 1365, 1354, 1332, 1224, 1192, 1160, 1102, 1046, 1028, 1013, 990, 965, 925, 860, 829, 778, 754, 745, 694 cm^{-1} ; ^1H NMR (400 MHz, DMSO-*d*₆) δ 8.59 (1H, d, $J = 10.2$ Hz, NH), 7.14 (2H, dd, $J = 8.4, 7.2$ Hz, Ph), 6.68 (2H, d, $J = 8.4$ Hz, Ph), 6.59 (1H, t, $J = 7.2$ Hz, Ph), 6.19 (1H, d, $J = 10.2$ Hz, 1-H), 3.76 (2H, s, 3-H), 2.82 (3H, s, NCH₃), 1.53 (3H, s, 2-CH₃), 1.41 (9H, s, *t*-Bu); ^{13}C NMR (100 MHz, CDCl₃) δ 152.8, 150.1, 129.0, 119.9, 116.5, 112.6, 111.9, 80.4, 58.0, 37.2, 28.3, 12.7;

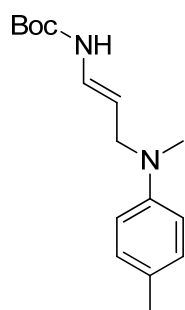
HRMS–ESI (m/z): $[M+H]^+$ calcd for $C_{16}H_{25}N_2O_2$: 277.1911. Found: 277.1907. **Z-10d**: colorless oil; IR (film) 3329, 3085, 3061, 3025, 2976, 2930, 2817, 1719, 1701, 1685, 1599, 1508, 1499, 1491, 1480, 1449, 1390, 1365, 1338, 1246, 1160, 1106, 1048, 1022, 992, 974, 923, 864, 749, 692 cm^{-1} ; 1H NMR (400 MHz, $DMSO-d_6$) δ 8.79 (1H, d, $J = 9.6$ Hz, NH), 7.13 (2H, dd, $J = 8.3, 7.2$ Hz, Ph), 6.65 (2H, d, $J = 8.3$ Hz, Ph), 6.59 (1H, t, $J = 7.2$ Hz, Ph), 6.24 (1H, d, $J = 9.6$ Hz, 1-H), 3.94 (2H, s, 3-H), 2.82 (3H, s, NCH_3), 1.44 (12H, s, 2- CH_3 and *t*-Bu); ^{13}C NMR (100 MHz, $DMSO-d_6$) δ 153.4, 149.5, 128.8, 120.8, 115.6, 113.1, 112.0, 79.0, 50.9, 38.0, 28.1, 18.4; HRMS–ESI (m/z): $[M+H]^+$ calcd for $C_{16}H_{25}N_2O_2$: 277.1911. Found: 277.1904.

(E)-tert-Butyl (3-((4-methoxyphenyl)(methyl)amino)prop-1-en-1-yl)carbamate (10e) (Table 2, Entry 1)



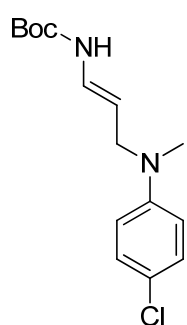
The reaction was carried out analogously to the representative procedure employing **9e** (100 mg, 0.342 mmol). Chromatographic purification on silica gel (*n*-hexane/EtOAc = 3/1 to 2/1 as the eluent) gave **10e** (67.6 mg, 68% yield) as colorless crystals; mp 96–99 °C; IR (KBr) 3368, 3048, 3012, 2978, 2936, 2901, 2871, 2836, 2806, 1698, 1673, 1516, 1461, 1448, 1428, 1393, 1368, 1349, 1299, 1246, 1224, 1193, 1163, 1116, 1087, 1041, 1020, 955, 921, 863, 811, 798, 784, 772, 752, 699 cm^{-1} ; 1H NMR (400 MHz, $DMSO-d_6$) δ 9.08 (1H, d, $J = 10.4$ Hz, NH), 6.78 (2H, ddd, $J = 9.2, 3.0, 3.0$ Hz, ArH), 6.69 (2H, ddd, $J = 9.2, 3.0, 3.0$ Hz, ArH), 6.47 (1H, dd, $J = 14.2, 10.4$ Hz, 1-H), 4.99 (1H, dt, $J = 14.2, 6.8$ Hz, 2-H), 3.76 (2H, d, $J = 6.8$ Hz, 3-H), 3.66 (3H, s, OCH_3), 2.71 (3H, s, NCH_3), 1.40 (9H, s, *t*-Bu); ^{13}C NMR (100 MHz, $DMSO-d_6$) δ 152.8, 151.0, 144.0, 127.0, 114.55, 114.46, 103.5, 78.9, 55.2, 52.6, 37.8, 28.1; HRMS–ESI (m/z): $[M+H]^+$ calcd for $C_{16}H_{25}N_2O_3$: 293.1860. Found: 293.1851.

(E)-tert-Butyl (3-(methyl(*p*-tolyl)amino)prop-1-en-1-yl)carbamate (10f) (Table 2, Entry 2)



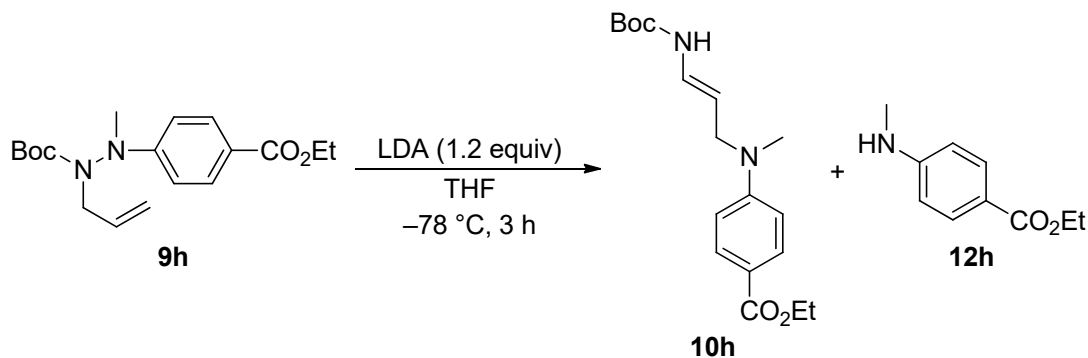
The reaction was carried out analogously to the representative procedure employing **9f** (127 mg, 0.460 mmol). Chromatographic purification on silica gel (*n*-hexane/EtOAc = 15/1 to 5/1 as the eluent) gave **10f** (89.0 mg, 70% yield) as colorless crystals; mp 122–125 °C; IR (KBr) 3357, 3012, 2980, 2934, 2909, 2814, 1697, 1673, 1616, 1522, 1464, 1445, 1426, 1390, 1368, 1352, 1298, 1245, 1225, 1192, 1162, 1117, 1086, 1042, 1018, 955, 922, 863, 801, 775, 764, 752, 702 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$) δ 7.03 (2H, ddd, $J = 8.6, 2.5, 2.5$ Hz, ArH), 6.67 (2H, ddd, $J = 8.6, 2.5, 2.5$ Hz, ArH), 6.60 (1H, br d, $J = 13.8$ Hz, 1-H), 6.17 (1H, br d, $J = 9.6$ Hz, NH), 4.98 (1H, dt, $J = 13.8, 6.8$ Hz, 2-H), 3.82 (2H, dd, $J = 6.8, 0.8$ Hz, 3-H), 2.82 (3H, s, NCH_3), 2.24 (3H, s, $ArCH_3$), 1.45 (9H, s, *t*-Bu); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.6, 147.5, 129.6, 126.2, 126.1, 113.5, 104.3, 80.5, 52.9, 37.7, 28.2, 20.2; HRMS–ESI (m/z): $[M+H]^+$ calcd for $C_{16}H_{25}N_2O_2$: 277.1911. Found: 277.1903.

(E)-tert-Butyl (3-((4-chlorophenyl)(methyl)amino)prop-1-en-1-yl)carbamate (10g) (Table 2, Entry 3)



The reaction was carried out analogously to the representative procedure employing **9g** (139 mg, 0.468 mmol). Chromatographic purification on silica gel (*n*-hexane/EtOAc = 10/1 as the eluent) gave **10g** (109 mg, 78% yield) as colorless crystals; mp 129–133 °C; IR (KBr) 3353, 3014, 2981, 2936, 2874, 2816, 1694, 1671, 1596, 1509, 1459, 1446, 1427, 1391, 1370, 1352, 1302, 1244, 1227, 1199, 1157, 1119, 1086, 1043, 1019, 958, 922, 857, 804, 778, 760 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.15 (2H, ddd, $J = 9.0, 2.9, 2.9$ Hz, ArH), 6.67–6.56 (1H, br m, 1-H), 6.63 (2H, ddd, $J = 9.0, 2.9, 2.9$ Hz, ArH), 6.22 (1H, br d, $J = 10.4$ Hz, NH), 4.95 (1H, dt, $J = 14.4, 6.4$ Hz, 2-H), 3.83 (2H, dd, $J = 6.4, 1.2$ Hz, 3-H), 2.85 (3H, s, NCH_3), 1.46 (9H, s, *t*-Bu); ^{13}C NMR (100 MHz, CDCl_3) δ 152.6, 148.0, 128.9, 126.4, 121.4, 114.0, 103.5, 80.6, 52.5, 37.6, 28.2; HRMS–ESI (m/z): $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{15}\text{H}_{22}\text{ClN}_2\text{O}_2$: 297.1364. Found: 297.1360.

(E)-Ethyl 4-((3-((tert-butoxycarbonyl)amino)allyl)(methyl)amino)benzoate (10h) (Table 2, Entry 5)

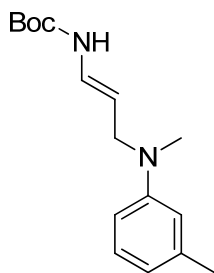


A solution of **9h** (121 mg, 0.362 mmol) in THF (3.3 mL) was treated with a ca. 0.7 M LDA solution in THF–*n*-hexane (0.62 mL, 0.43 mmol) at -78 °C and stirred for 3 h at the same temperature. The resulting mixture was poured into saturated aqueous ammonium chloride and extracted with ethyl acetate. Extractive workup and purification of the residue by chromatography on silica gel (*n*-hexane/EtOAc = 5/1 to 2/1 as the eluent) to obtain **10h** (44.3 mg, 37% yield) as colorless crystals and ethyl 4-(methylamino)benzoate (**12h**)² (6.3 mg, 10% yield) as colorless crystals. **10h**: colorless crystals; mp 106–108 °C; IR (KBr) 3331, 2978, 2930, 2894, 1725, 1718, 1677, 1609, 1514, 1478, 1455, 1389, 1367, 1353, 1317, 1286, 1251, 1228, 1188, 1170, 1125, 1042, 1016, 961, 921, 865, 829, 771, 700 cm^{-1} ; ^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ 9.15 (1H, d, $J = 10.2$ Hz, NH), 7.75 (2H, d, $J = 8.8$ Hz, ArH), 6.73 (2H, d, $J = 8.8$ Hz, ArH), 6.51 (1H, dd, $J = 14.0, 10.2$ Hz, 1-H), 5.01 (1H, dt, $J = 14.0, 6.4$ Hz, 2-H), 4.22 (2H, q, $J = 7.0$ Hz, OCH_2CH_3), 3.95 (2H, d, $J = 6.4$ Hz, 3-H), 2.92 (3H, s, NCH_3), 1.40 (9H, s, *t*-Bu), 1.28 (3H, t, $J = 7.0$ Hz, OCH_2CH_3); ^{13}C NMR (100 MHz, CDCl_3) δ 167.0, 152.6, 152.3, 131.3, 126.6, 117.5, 110.9, 103.0, 80.7, 60.1, 51.8, 37.4, 28.2, 14.5; HRMS–ESI (m/z): $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{18}\text{H}_{26}\text{N}_2\text{O}_4\text{Na}$: 357.1785. Found: 357.1777. **12h**: colorless crystals; IR (KBr) 3383, 2986, 2936, 2902, 2824, 1681, 1604, 1578, 1538, 1475, 1449, 1416, 1391, 1366, 1347, 1310, 1277, 1175, 1128, 1116, 1104, 1068, 1023, 943, 921, 835, 771, 700 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.88 (2H, ddd, $J = 8.8, 2.4, 2.4$ Hz, ArH), 6.55 (2H, ddd, $J = 8.8, 2.4, 2.4$ Hz, ArH), 4.32 (2H, q, $J = 7.2$ Hz, OCH_2CH_3), 4.17 (1H, br, NH), 2.89

² Sun, N.; Wang, S.; Mo, W.; Hu, B.; Shen, Z.; Hu, X. *Tetrahedron* **2010**, *66*, 7142–7148.

(3H, s, NCH₃), 1.36 (3H, t, $J = 7.2$ Hz, OCH₂CH₃); ¹³C NMR (100 MHz, CDCl₃) δ 166.9, 152.8, 131.4, 118.6, 111.0, 60.2, 30.2, 14.5; HRMS–ESI (m/z): [M+H]⁺ calcd for C₁₀H₁₄NO₂: 180.1019. Found: 180.1017.

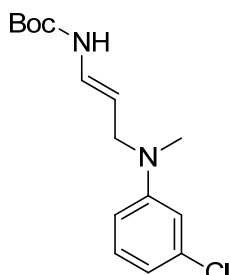
(*E*)-*tert*-Butyl (3-(methyl(*m*-tolyl)amino)prop-1-en-1-yl)carbamate (10i) (Table 2, Entry 6)



The reaction was carried out analogously to the representative procedure employing **9i** (132 mg, 0.478 mmol). Chromatographic purification on silica gel (*n*-hexane/EtOAc = 15/1 to 5/1 as the eluent) gave **10i** (81.3 mg, 62% yield) as colorless crystals; mp 58–61 °C; IR (KBr) 3354, 3068, 2984, 2935, 2907, 2870, 2812, 1695, 1672, 1599, 1560, 1510, 1458, 1423, 1390, 1368, 1353, 1300, 1248, 1227, 1204, 1158, 1121, 1100, 1043, 1019, 987, 953, 925, 859, 826, 791, 775, 750 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.17–7.02 (1H, m, ArH), 6.69–6.50 (4H, m, 1-H and ArH), 6.25 (1H, br d, $J = 10.4$ Hz, NH), 4.97 (1H, dt, $J = 14.0, 6.4$ Hz, 2-H), 3.83 (2H, dd, $J = 6.4, 1.2$ Hz, 3-H), 2.83 (3H, s, NCH₃), 2.30 (3H, s, ArCH₃), 1.45 (9H, s, *t*-Bu); ¹³C NMR (100 MHz, CDCl₃) δ 152.7, 149.5, 138.7, 128.9, 126.2, 117.6, 113.7, 110.2, 104.2, 80.4, 52.4, 37.4, 28.2, 21.9;

HRMS–ESI (m/z): [M+H]⁺ calcd for C₁₆H₂₅N₂O₂: 277.1911. Found: 277.1906.

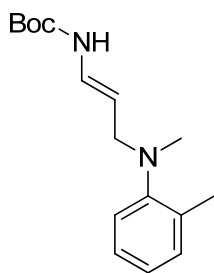
(*E*)-*tert*-Butyl (3-((3-chlorophenyl)(methyl)amino)prop-1-en-1-yl)carbamate (10j) (Table 2, Entry 7)



The reaction was carried out analogously to the representative procedure employing **9j** (136 mg, 0.458 mmol). Chromatographic purification on silica gel (*n*-hexane/EtOAc = 12/1 to 5/1 as the eluent) gave **10j** (108 mg, 79% yield) as colorless crystals; mp 77–79 °C; IR (KBr) 3354, 3067, 2983, 2935, 2907, 2870, 2812, 1695, 1672, 1598, 1560, 1510, 1457, 1423, 1368, 1353, 1299, 1248, 1227, 1203, 1158, 1120, 1099, 1043, 1019, 986, 952, 924, 858, 824, 791, 774, 749 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.10 (1H, dd, $J = 8.2, 8.2$ Hz, ArH), 6.70–6.54 (4H, m, 1-H and ArH), 6.26 (1H, br d, $J = 10.4$ Hz, NH), 4.96 (1H, dt, $J = 14.4, 6.2$ Hz, 2-H), 3.84 (2H, dd, $J = 6.2, 1.2$ Hz, 3-H), 2.85 (3H, s, NCH₃), 1.45 (9H, s, *t*-Bu); ¹³C NMR (100 MHz, CDCl₃) δ 152.6, 150.4, 135.0, 130.0, 126.4, 116.2, 112.5, 110.8, 103.4, 80.6, 52.1, 37.4, 28.2;

HRMS–ESI (m/z): [M+H]⁺ calcd for C₁₅H₂₂ClN₂O₂: 297.1364. Found: 297.1357.

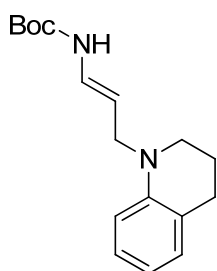
(*E*)-*tert*-Butyl (3-(methyl(*o*-tolyl)amino)prop-1-en-1-yl)carbamate (10k) (Table 2, Entry 8)



The reaction was carried out analogously to the representative procedure employing **9k** (134 mg, 0.485 mmol). Chromatographic purification on silica gel (*n*-hexane/EtOAc = 30/1 to 5/1 as the eluent) gave **10k** (19.2 mg, 14% yield) as a pale yellow oil; IR (film) 3318, 3064, 2977, 2932, 2870, 2790, 1704, 1675, 1597, 1577, 1494, 1452, 1416, 1390, 1366, 1283, 1242, 1164, 1130, 1103, 1048, 1018, 953, 922, 864, 820, 764, 724 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.19–7.11 (2H, m, ArH), 7.00 (1H, d, $J = 7.5$ Hz, ArH), 6.95

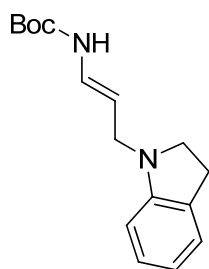
(1H, ddd, $J = 7.5, 7.5, 0.8$ Hz, ArH), 6.64 (1H, br dd, $J = 14.4, 10.4$ Hz, 1-H), 6.22 (1H, br d, $J = 10.4$ Hz, NH), 4.99 (1H, dt, $J = 14.4, 6.8$ Hz, 2-H), 3.40 (2H, d, $J = 6.8$ Hz, 3-H), 2.64 (3H, s, NCH₃), 2.30 (3H, s, ArCH₃), 1.47 (9H, s, *t*-Bu); ¹³C NMR (100 MHz, CDCl₃) δ 152.7, 151.9, 132.6, 131.0, 126.4, 126.2, 122.7, 119.7, 105.8, 80.5, 56.4, 40.2, 28.2, 18.3; HRMS–ESI (m/z): [M+H]⁺ calcd for C₁₆H₂₅N₂O₂: 277.1911. Found: 277.1907.

(E)-tert-Butyl (3-(3',4'-dihydroquinolin-1'(2'H)-yl)prop-1-en-1-yl)carbamate (10l) (Table 2, Entry 9)



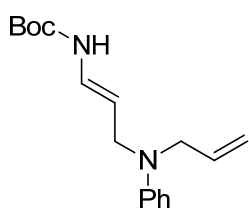
The reaction was carried out analogously to the representative procedure employing **9l** (100 mg, 0.347 mmol). Chromatographic purification on silica gel (*n*-hexane/EtOAc = 10/1 as the eluent) gave **10l** (56.8 mg, 57% yield) as colorless crystals; mp 101–104 °C; IR (KBr) 3360, 3014, 2986, 2969, 2949, 2928, 2844, 1698, 1672, 1601, 1572, 1508, 1458, 1391, 1372, 1365, 1352, 1307, 1282, 1243, 1227, 1203, 1190, 1163, 1149, 1118, 1090, 1058, 1047, 1016, 952, 920, 868, 860, 811, 773, 737 cm⁻¹; ¹H NMR (400 MHz, DMSO-*d*₆) δ 9.09 (1H, d, *J* = 10.4 Hz, NH), 6.93 (1H, ddd, *J* = 8.8, 7.4, 1.4 Hz, ArH), 6.84 (1H, dd, *J* = 7.2, 1.4 Hz, ArH), 6.58 (1H, d, *J* = 8.8 Hz, ArH), 6.49 (1H, dd, *J* = 14.0, 10.0 Hz, 1-H), 6.45 (1H, ddd, *J* = 7.4, 7.2, 1.2 Hz, ArH), 5.03 (1H, dt, *J* = 14.0, 6.4 Hz, 2-H), 3.78 (2H, d, *J* = 6.4 Hz, 3-H), 3.16 (2H, t, *J* = 5.6 Hz, 2'-H), 2.65 (2H, t, *J* = 6.2 Hz, 4'-H), 1.84 (2H, tt, *J* = 6.2, 5.6 Hz, 3'-H), 1.40 (9H, s, *t*-Bu); ¹³C NMR (100 MHz, CDCl₃) δ 152.7, 145.2, 129.1, 127.0, 126.1, 122.8, 115.9, 111.1, 103.9, 80.4, 50.8, 48.4, 28.2, 28.0, 22.2; HRMS–ESI (*m/z*): [M+H]⁺ calcd for C₁₇H₂₅N₂O₂: 289.1911. Found: 289.1903.

(E)-tert-Butyl (3-(indolin-1-yl)prop-1-en-1-yl)carbamate (10m) (Table 2, Entry 10)



The reaction was carried out analogously to the representative procedure employing **9m** (110 mg, 0.401 mmol). Chromatographic purification on silica gel (*n*-hexane/EtOAc = 10/1 to 5/1 as the eluent) gave **10m** (51.0 mg, 46% yield) as pale brown crystals; mp 109–112 °C; IR (KBr) 3347, 2986, 2935, 2878, 1697, 1676, 1605, 1512, 1470, 1402, 1390, 1365, 1352, 1314, 1300, 1281, 1245, 1228, 1204, 1163, 1100, 1081, 1021, 948, 861, 775, 749, 734, 707 cm⁻¹; ¹H NMR (400 MHz, DMSO-*d*₆) δ 9.13 (1H, d, *J* = 10.0 Hz, NH), 7.00 (1H, dd, *J* = 7.6, 1.0 Hz, ArH), 6.96 (1H, ddd, *J* = 7.6, 7.6, 1.0 Hz, ArH), 6.61–6.49 (3H, m, 1-H and ArH), 5.04 (1H, dt, *J* = 14.4, 7.0 Hz, 2-H), 3.63 (2H, dd, *J* = 7.0, 0.6 Hz, 3-H), 3.21 (2H, t, *J* = 8.4 Hz, indoline-CH₂), 2.83 (2H, t, *J* = 8.4 Hz, indoline-CH₂), 1.41 (9H, s, *t*-Bu); ¹³C NMR (100 MHz, DMSO-*d*₆) δ 152.8, 151.9, 130.0, 127.7, 127.0, 124.2, 117.0, 107.3, 103.2, 79.0, 51.8, 47.9, 28.0, 27.8; HRMS–ESI (*m/z*): [M+H]⁺ calcd for C₁₆H₂₃N₂O₂: 275.1754. Found: 275.1746.

(E)-tert-Butyl (3-(allyl(phenyl)amino)prop-1-en-1-yl)carbamate (10n) (Table 2, Entry 11)

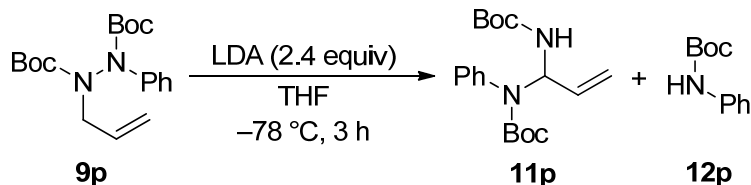


The reaction was carried out analogously to the representative procedure employing **9n** (101 mg, 0.350 mmol). Chromatographic purification on silica gel (*n*-hexane/EtOAc = 8/1 as the eluent) gave **10n** (65.5 mg, 65% yield) as colorless oil; IR (film) 3313, 3060, 3005, 2978, 2931, 1721, 1704, 1673, 1643, 1598, 1573, 1504, 1454, 1391, 1367, 1348, 1290, 1252, 1232, 1162, 1126, 1101, 1042, 1013, 988, 950, 862, 747, 692 cm⁻¹; ¹H NMR (400 MHz, CD₃OD) δ 7.13 (2H, dddd, *J* = 9.0, 7.3, 2.2, 2.2 Hz, Ph), 6.72 (2H, dd, *J* = 9.0, 1.0 Hz, Ph), 6.61 (1H, tt, *J* = 7.3, 1.0 Hz, Ph), 6.53 (1H, d, *J* = 14.2 Hz, 1-H), 5.85 (1H, ddt, *J* = 17.2, 10.4, 5.0 Hz, CH₂CH=CH₂), 5.15 (1H, ddt, *J* = 17.2, 1.8, 1.8 Hz, CH₂CH=CH₂), 5.13 (1H, ddt, *J* = 10.4, 1.8, 1.8 Hz, CH₂CH=CH₂), 5.09 (1H, dt, *J* = 14.2, 6.4 Hz, 2-H), 3.89 (2H, ddd, *J* = 5.0, 1.8, 1.8 Hz, CH₂CH=CH₂), 3.86 (2H, dd, *J* = 6.4, 1.0 Hz, 3-H), 1.45 (9H, s, *t*-Bu); ¹³C NMR (100 MHz, DMSO-*d*₆) δ 152.8, 148.1, 134.6, 128.9, 126.7, 115.7, 115.6, 112.1, 103.9, 78.9, 51.7, 49.5, 28.0; HRMS–ESI (*m/z*): [M+H]⁺ calcd for C₁₇H₂₅N₂O₂: 289.1911. Found: 289.1901.

(E)-tert-Butyl (3-(diphenylamino)prop-1-en-1-yl)carbamate (10o) (Table 2, Entry 12)

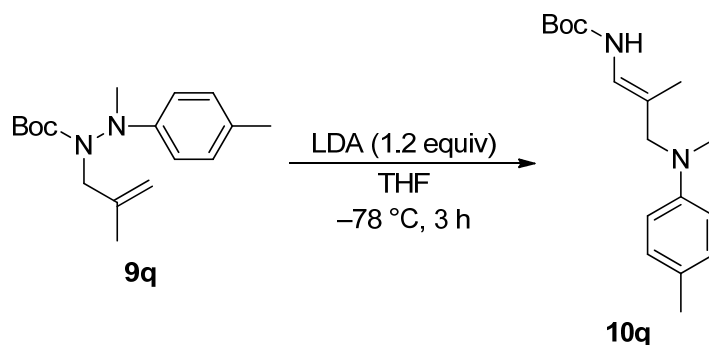
The reaction was carried out analogously to the representative procedure employing **9o** (105 mg, 0.324 mmol). Chromatographic purification on silica gel (*n*-hexane/EtOAc = 15/1 to 7/1 as the eluent) gave **10o** (50.2mg, 48% yield) as colorless crystals; mp 119–121 °C; IR (KBr) 3392, 3271, 3054, 3021, 2981, 2927, 1719, 1672, 1589, 1493, 1449, 1390, 1375, 1366, 1353, 1296, 1230, 1200, 1159, 1102, 1074, 1062, 1029, 1009, 952, 864, 805, 768, 754, 726, 698 cm⁻¹; ¹H NMR (400 MHz, DMSO-*d*₆) δ 9.10 (1H, d, *J* = 10.4 Hz, NH), 7.25 (4H, dddd, *J* = 8.8, 7.4, 1.4, 1.4 Hz, Ph), 6.97 (4H, dd, *J* = 8.8, 1.4 Hz, Ph), 6.91 (2H, tt, *J* = 7.4, 1.4 Hz, Ph), 6.49 (1H, dd, *J* = 14.0, 10.4 Hz, 1-H), 5.11 (1H, dt, *J* = 14.0, 6.0 Hz, 2-H), 4.28 (2H, d, *J* = 6.0 Hz, 3-H), 1.38 (9H, s, *t*-Bu); ¹³C NMR (100 MHz, CDCl₃) δ 152.5, 147.7, 129.2, 126.1, 121.2, 120.9, 104.8, 80.5, 51.9, 28.2; HRMS–ESI (*m/z*): [M+Na]⁺ calcd for C₂₀H₂₄N₂O₂Na: 347.1730. Found: 347.1722.

tert-Butyl (1-((tert-butoxycarbonyl)amino)allyl)(phenyl)carbamate (11p) (Table 2, Entry 13)



A solution of **9p** (104 mg, 0.298 mmol) in THF (2.7 mL) was treated with a ca. 0.7 M LDA solution in THF–*n*-hexane (1.02 mL, 0.72 mmol) at –78 °C and stirred for 3 h at the same temperature. The resulting mixture was poured into saturated aqueous ammonium chloride and extracted with ethyl acetate. Extractive workup and purification of the residue by chromatography on silica gel (*n*-hexane/EtOAc = 20/1 to 5/1 as the eluent) to obtain **11p** (7.8 mg, 8% yield) as colorless crystals, *tert*-butyl phenylcarbamate (**12p**) (34.8 mg, 60% yield) as colorless crystals, and the recovery of **9p** (29.6 mg, 28% yield) as a colorless oil. **11p**: colorless crystals; mp 63–65 °C; IR (KBr) 3373, 3065, 2984, 2931, 1708, 1686, 1597, 1516, 1497, 1455, 1407, 1390, 1366, 1337, 1325, 1314, 1296, 1280, 1246, 1167, 1076, 1044, 1017, 996, 987, 946, 924, 910, 881, 839, 784, 769, 753, 700 cm⁻¹; ¹H NMR (400 MHz, DMSO-*d*₆) δ 7.35 (2H, dddd, *J* = 7.5, 7.5, 1.4, 1.4 Hz, Ph), 7.31–7.22 (1H, br, NH), 7.27 (1H, tt, *J* = 7.5, 1.4 Hz, Ph), 7.04 (2H, d, *J* = 7.5 Hz, Ph), 6.05 (1H, br dd, *J* = 6.8, 6.4 Hz, CHCH=CH₂), 5.87 (1H, ddd, *J* = 17.2, 10.4, 6.4 Hz, CHCH=CH₂), 5.30 (1H, d, *J* = 17.2 Hz, CHCH=CH₂), 5.18 (1H, d, *J* = 10.4 Hz, CHCH=CH₂), 1.38 (9H, s, *t*-Bu), 1.33 (9H, s, *t*-Bu); ¹³C NMR (100 MHz, DMSO-*d*₆) δ 154.4, 153.3, 138.6, 135.0, 129.3, 128.4, 126.9, 116.9, 79.5, 78.4, 66.1, 28.1, 28.0; HRMS–ESI (*m/z*): [M+H]⁺ calcd for C₁₉H₂₉N₂O₄: 349.2122. Found: 349.2109.

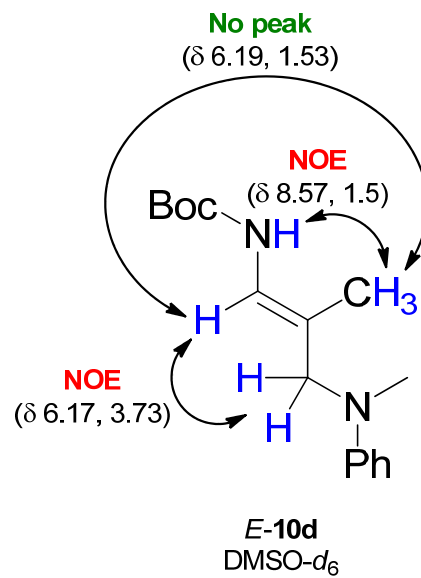
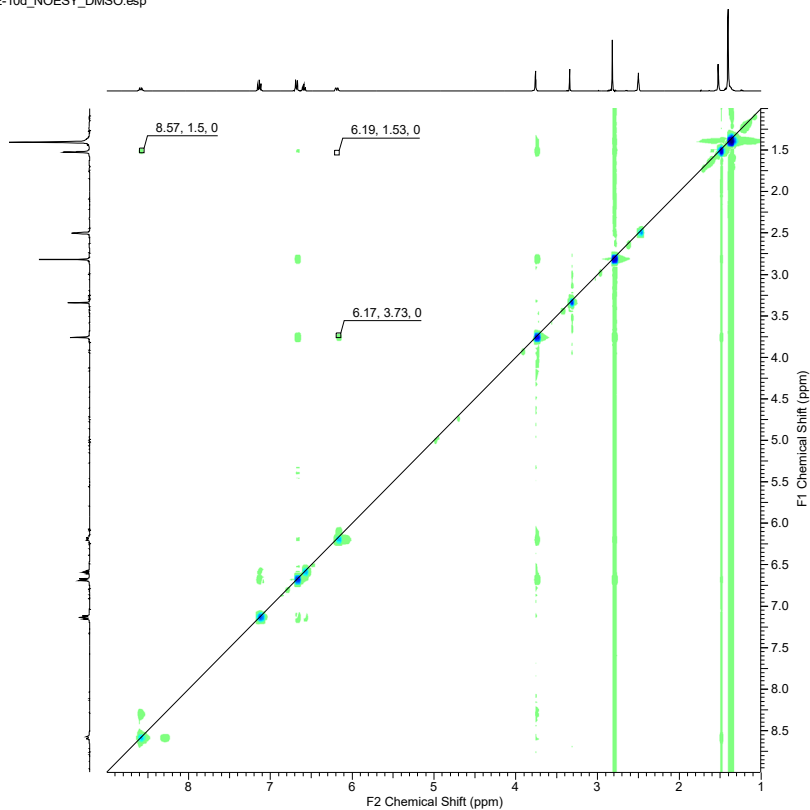
(*E*)-tert-Butyl (2-methyl-3-(methyl(*p*-tolyl)amino)prop-1-en-1-yl)carbamate (10q**)**



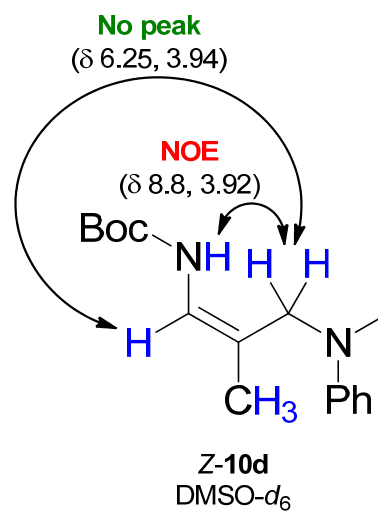
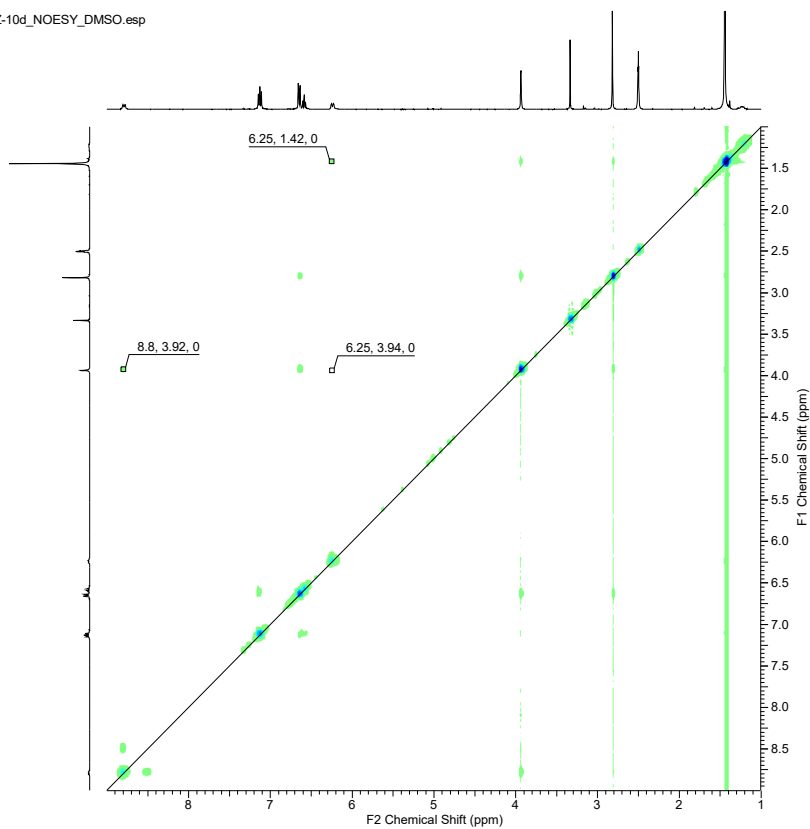
This compound was prepared separately to determine the ratio of products in the crossover experiment (Scheme 2). The reaction was carried out analogously to the representative procedure employing **9q** (193 mg, 0.665 mmol) with 1.2 equivalents of LDA. Chromatographic purification on silica gel (*n*-hexane/EtOAc = 20/1 to 5/1 as the eluent) gave **10q** (101 mg, 52% yield) as colorless crystals; mp 78–80 °C; IR (KBr) 3271, 3004, 2977, 2920, 2860, 1715, 1680, 1618, 1523, 1478, 1448, 1391, 1365, 1350, 1328, 1272, 1252, 1242, 1172, 1109, 1054, 1024, 974, 931, 875, 834, 796, 778, 743, 712 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.02 (2H, d, *J* = 8.4 Hz, ArH), 6.68 (2H, ddd, *J* = 8.4, 2.5, 2.5 Hz, ArH), 6.45 (1H, d, *J* = 10.4 Hz, 1-H), 6.04 (1H, br d, *J* = 10.4 Hz, NH), 3.74 (2H, s, 3-H), 2.80 (3H, s, NCH₃), 2.24 (3H, s, ArCH₃), 1.54 (3H, s, 2-CH₃), 1.47 (9H, s, *t*-Bu); ¹³C NMR (100 MHz, CDCl₃) δ 152.8, 148.3, 129.5, 125.8, 120.0, 113.2, 112.2, 80.4, 58.5, 37.4, 28.3, 20.2, 12.8; HRMS–ESI (*m/z*): [M+H]⁺ calcd for C₁₇H₂₇N₂O₂: 291.2067. Found: 291.2061.

2. Determination of *E/Z* stereochemistry of 10d by NOESY

E-10d_NOESY_DMSO.esp

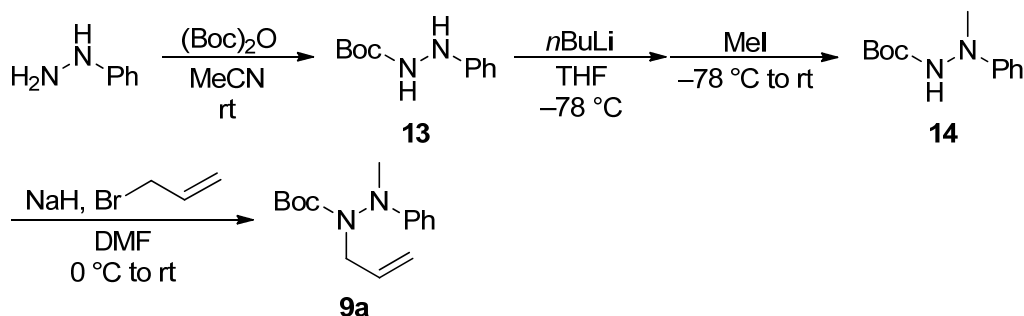


Z-10d_NOESY_DMSO.esp



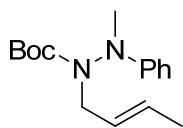
3. Preparation of substrates

tert-Butyl 1-allyl-2-methyl-2-phenylhydrazinecarboxylate (**9a**)



(Step 1) A solution of phenylhydrazine (1.08 g, 10.0 mmol) and di-*tert*-butyl dicarbonate (2.3 mL, 10 mmol) in acetonitrile (4 mL) was stirred for 15 h at room temperature. The resulting solution was evaporated and the residue was purified by chromatography on silica gel (*n*-hexane/EtOAc = 5/1 to 3/1 as the eluent) to obtain *tert*-butyl 2-phenylhydrazinecarboxylate (**13**) (2.02 g, 97% yield) as pale yellow crystals. (Step 2) A solution of **13** (627 mg, 3.01 mmol) in THF (15 mL) was treated with a 1.64 M *n*-butyllithium hexane solution (3.67 mL, 6.02 mmol) at $-78\text{ }^\circ\text{C}$ under an argon atmosphere and the mixture was stirred for 30 min at the same temperature. Iodomethane (187 μL , 3.01 mmol) was added to the mixture and allowed to warm to room temperature. After stirring for 2 h at room temperature, the resulting mixture was quenched with saturated aqueous ammonium chloride and extracted with ethyl acetate. The combined extracts were washed with brine, dried over sodium sulfate, and concentrated. Purification of the residue by chromatography on silica gel (*n*-hexane/EtOAc = 9/1 to 6/1 as the eluent) afforded *tert*-butyl 2-methyl-2-phenylhydrazinecarboxylate (**14**) (592 mg, 88% yield) as pale yellow crystals. (Step 3) A solution of **14** (446 mg, 2.01 mmol) and allyl bromide (190 μL , 2.20 mmol) in DMF (4 mL) was treated with sodium hydride (60 wt.% in oil, 96 mg, 2.4 mmol) at $0\text{ }^\circ\text{C}$ and the mixture was stirred for 1 h at room temperature. The resulting mixture was quenched with saturated aqueous ammonium chloride at $0\text{ }^\circ\text{C}$ and extracted with ethyl acetate. The combined extracts were washed with brine, dried over sodium sulfate, and concentrated. Purification of the residue by chromatography on silica gel (*n*-hexane/EtOAc = 30/1 to 15/1 as the eluent) afforded **9a** (486 mg, 92% yield) as colorless crystals; mp $30\text{--}31\text{ }^\circ\text{C}$; IR (KBr) 3081, 2972, 2928, 2818, 1698, 1642, 1599, 1500, 1454, 1427, 1378, 1320, 1280, 1239, 1159, 1113, 1083, 1054, 1033, 992, 932, 876, 857, 750, 693 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.23 (2H, dddd, $J = 8.4, 7.2, 2.0, 2.0$ Hz, Ph), 6.80 (1H, t, $J = 7.2$ Hz, Ph), 6.66 (2H, d, $J = 8.4$ Hz, Ph), 5.99 (1H, dddd, $J = 17.0, 10.3, 6.4, 6.4$ Hz, $\text{CH}=\text{CH}_2$), 5.23 (1H, d, $J = 17.0$ Hz, $\text{CH}=\text{CH}_2$), 5.16 (1H, dd, $J = 10.3, 1.4$ Hz, $\text{CH}=\text{CH}_2$), 4.33 (1H, br, CH_2), 3.90 (1H, br, CH_2), 3.10 (3H, s, NCH_3), 1.65–1.05 (9H, br, *t*-Bu); ^{13}C NMR (100 MHz, CDCl_3) δ 155.4, 149.3, 133.6, 128.9, 118.5, 111.7, 80.6, 51.6, 39.7, 28.2; HRMS–ESI (m/z): $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{15}\text{H}_{23}\text{N}_2\text{O}_2$: 263.1754. Found: 263.1746.

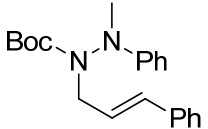
(*E*)-*tert*-Butyl 1-(but-2-en-1-yl)-2-methyl-2-phenylhydrazinecarboxylate (**9b**)



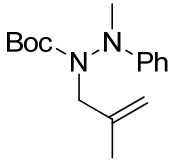
Prepared by the same procedure with **9a** (90% yield from **13**) using *trans*-crotyl chloride instead of allyl bromide; colorless oil; IR (KBr) 3064, 3004, 2974, 2930, 2878, 2813, 1703, 1600, 1500, 1476, 1454, 1382, 1366, 1311, 1256, 1231, 1170, 1135, 1112, 1084, 1050, 1031,

991, 968, 881, 859, 748, 692 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.22 (2H, dddd, $J = 8.4, 7.2, 1.8, 1.8$ Hz, Ph), 6.79 (1H, tt, $J = 7.2, 1.8$ Hz, Ph), 6.65 (2H, d, $J = 8.4$ Hz, Ph), 5.72-5.55 (2H, m, $\text{CH}=\text{CHCH}_3$), 4.40-4.15 (1H, br, CH_2), 3.95-3.65 (1H, br, CH_2), 3.08 (3H, s, NCH_3), 1.75-1.62 (3H, m, $\text{CH}=\text{CHCH}_3$), 1.60-1.10 (9H, br, $t\text{-Bu}$); ^{13}C NMR (100 MHz, CDCl_3) δ 155.4, 149.3, 129.7, 128.9, 126.2, 118.3, 111.7, 80.4, 50.6, 39.7, 28.2, 17.8; HRMS-ESI (m/z): $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{16}\text{H}_{25}\text{N}_2\text{O}_2$: 277.1911. Found: 277.1902.

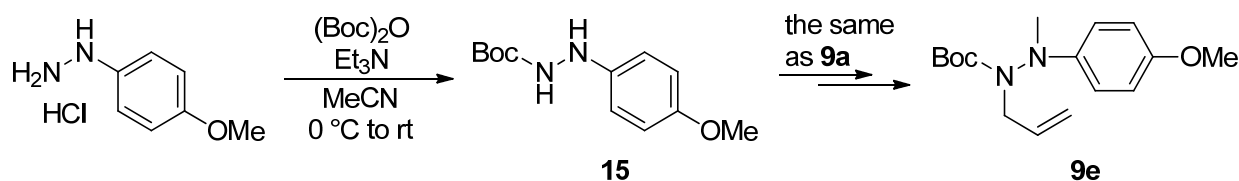
(E)-tert-Butyl 1-cinnamyl-2-methyl-2-phenylhydrazinecarboxylate (9c)

 Prepared by the same procedure with **9a** (87% yield from **13**) using cinnamyl bromide instead of allyl bromide; colorless crystals; mp 45–47 °C; IR (KBr) 3059, 3023, 3009, 2974, 2931, 2895, 1693, 1597, 1493, 1466, 1451, 1421, 1376, 1347, 1307, 1284, 1261, 1217, 1165, 1117, 1079, 1045, 1025, 986, 974, 945, 883, 861, 774, 759, 749, 739, 690 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.39-7.33 (2H, m, Ph), 7.30 (2H, dd, $J = 7.4$ Hz, Ph), 7.27-7.19 (3H, m, Ph), 6.80 (1H, tt, $J = 7.4, 1.0$ Hz, Ph), 6.68 (2H, d, $J = 8.4$ Hz, Ph), 6.55 (1H, d, $J = 15.8$ Hz, $\text{CH}=\text{CHPh}$), 6.35 (1H, ddd, $J = 15.8, 7.4, 6.6$ Hz, $\text{CH}=\text{CHPh}$), 4.65-4.35 (1H, br, CH_2), 4.02 (1H, dd, $J = 13.4, 7.4$ Hz, CH_2), 3.10 (3H, s, NCH_3), 1.75-1.05 (9H, br, $t\text{-Bu}$); ^{13}C NMR (100 MHz, CDCl_3) δ 155.4, 149.2, 136.7, 133.6, 129.0, 128.5, 127.6, 126.4, 124.7, 118.5, 111.8, 80.7, 50.9, 39.9, 28.2; HRMS-ESI (m/z): $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{21}\text{H}_{27}\text{N}_2\text{O}_2$: 339.2067. Found: 339.2057.

tert-Butyl 2-methyl-1-(2-methylallyl)-2-phenylhydrazinecarboxylate (9d)

 Prepared by the same procedure with **9a** (91% yield from **13**) using 3-chloro-2-methyl-1-propene instead of allyl bromide; colorless crystals; mp 31–32 °C; IR (KBr) 3076, 3006, 2979, 2924, 2817, 1697, 1654, 1599, 1500, 1463, 1454, 1422, 1375, 1339, 1314, 1287, 1271, 1228, 1168, 1121, 1091, 1069, 1028, 1014, 990, 966, 938, 908, 883, 861, 819, 767, 750, 694 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.23 (2H, dddd, $J = 8.4, 7.4, 1.6, 1.6$ Hz, Ph), 6.80 (1H, tt, $J = 7.4, 1.6$ Hz, Ph), 6.63 (2H, d, $J = 8.4$ Hz, Ph), 4.94-4.86 (2H, m, $\text{C}(\text{CH}_3)=\text{CH}_2$), 4.42 (1H, br, CH_2), 3.65 (1H, d, $J = 15.2$ Hz, CH_2), 3.11 (3H, s, NCH_3), 1.83 (3H, s, $\text{C}(\text{CH}_3)=\text{CH}_2$), 1.65-1.05 (9H, br, $t\text{-Bu}$); ^{13}C NMR (100 MHz, CDCl_3) δ 155.9, 148.9, 141.5, 129.0, 118.4, 114.1, 111.6, 80.6, 55.1, 39.7, 28.1, 20.6; HRMS-ESI (m/z): $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{16}\text{H}_{25}\text{N}_2\text{O}_2$: 277.1911. Found: 277.1902.

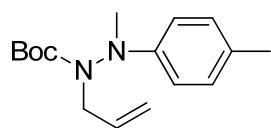
tert-Butyl 1-allyl-2-(4-methoxyphenyl)-2-methylhydrazinecarboxylate (9e)



A mixture of 4-methoxyphenylhydrazine hydrochloride (1.75 g, 10.0 mmol) in acetonitrile (5 mL) was treated with triethylamine (1.39 mL, 10.0 mmol) followed by di-*tert*-butyl dicarbonate (2.3 mL, 10 mmol) at 0 °C and stirred for 4 h at room temperature. The resulting mixture was diluted with saturated aqueous ammonium chloride and extracted with ethyl acetate. The combined extracts were washed with brine, dried over sodium sulfate, and concentrated. Purification of the residue by chromatography on silica gel (*n*-hexane/EtOAc = 4/1 to 2/1 as the eluent) afforded *tert*-butyl 2-(4-methoxyphenyl)hydrazinecarboxylate (**15**) (2.13 g, 89% yield) as yellow crystals. The following procedures are the same as **9a**. **9e** was obtained in

66% overall yield from **15**; pale yellow oil; IR (film) 3077, 3043, 2975, 2932, 2899, 2832, 1701, 1642, 1617, 1585, 1509, 1458, 1439, 1374, 1365, 1279, 1244, 1176, 1158, 1112, 1038, 993, 924, 878, 859, 820, 802, 763, 725, 691 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 6.81 (2H, ddd, $J = 9.0, 3.0, 3.0$ Hz, ArH), 6.61 (2H, d, $J = 9.0$ Hz, ArH), 5.98 (1H, dddd, $J = 17.0, 10.2, 6.4, 6.4$ Hz, $\text{CH}=\text{CH}_2$), 5.23 (1H, d, $J = 17.0$ Hz, $\text{CH}=\text{CH}_2$), 5.16 (1H, dd, $J = 10.2, 1.2$ Hz, $\text{CH}=\text{CH}_2$), 4.29 (1H, br, CH_2), 3.93 (1H, br, CH_2), 3.75 (3H, s, OCH_3), 3.06 (3H, s, NCH_3), 1.65-1.05 (9H, br, $t\text{-Bu}$); ^{13}C NMR (100 MHz, CDCl_3) δ 155.5, 152.7, 143.8, 133.7, 118.2, 114.3, 113.0, 80.5, 55.6, 51.8, 39.9, 28.2; HRMS-ESI (m/z): $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{16}\text{H}_{25}\text{N}_2\text{O}_3$: 293.1860. Found: 293.1848.

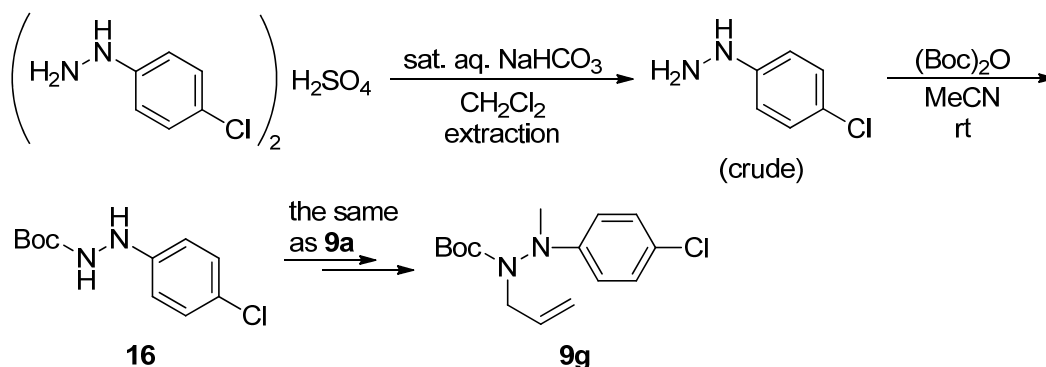
tert-Butyl 1-allyl-2-methyl-2-(*p*-tolyl)hydrazinecarboxylate (9f)



Prepared by the same procedure with **9e** (53% overall yield) using *p*-tolylhydrazine hydrochloride as a starting material; colorless crystals; mp 52–54 °C; IR (KBr) 3077, 2978, 2919, 2812, 1696, 1614, 1516, 1459, 1429, 1379, 1364, 1314, 1278, 1238, 1162,

1144, 1111, 1056, 989, 950, 930, 914, 877, 858, 804, 762 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.03 (2H, d, $J = 8.0$ Hz, ArH), 6.56 (2H, d, $J = 8.0$ Hz, ArH), 5.98 (1H, dddd, $J = 17.1, 10.3, 6.8, 6.8$ Hz, $\text{CH}=\text{CH}_2$), 5.22 (1H, d, $J = 17.1$ Hz, $\text{CH}=\text{CH}_2$), 5.15 (1H, dddd, $J = 10.3, 1.6, 1.0, 1.0$ Hz, $\text{CH}=\text{CH}_2$), 4.31 (1H, br, CH_2), 3.89 (1H, br, CH_2), 3.08 (3H, s, NCH_3), 2.26 (3H, s, ArCH_3), 1.65-1.05 (9H, br, $t\text{-Bu}$); ^{13}C NMR (100 MHz, CDCl_3) δ 155.6, 147.0, 133.8, 129.5, 127.6, 118.2, 111.8, 80.6, 51.6, 39.8, 28.2, 20.3; HRMS-ESI (m/z): $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{16}\text{H}_{25}\text{N}_2\text{O}_2$: 277.1911. Found: 277.1907.

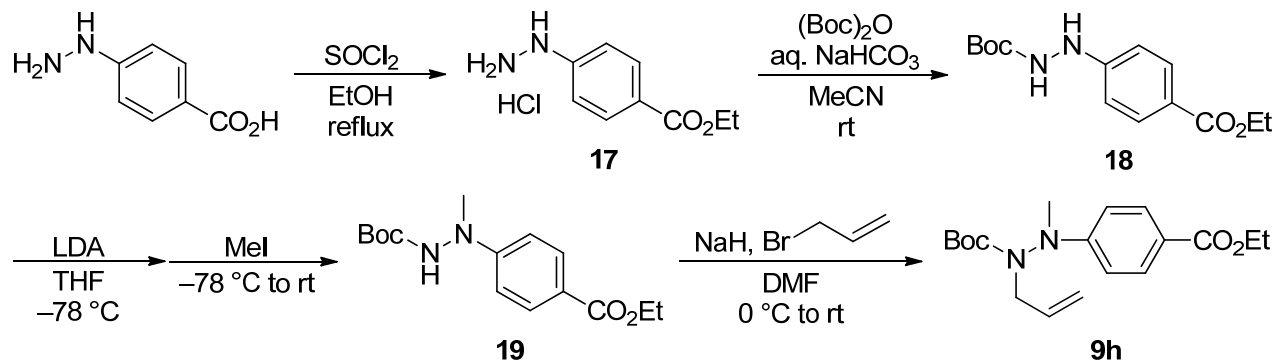
tert-Butyl 1-allyl-2-(4-chlorophenyl)-2-methylhydrazinecarboxylate (9g)



A suspension of 4-chlorophenylhydrazine sulfate (1.38 g, 3.60 mmol) in dichloromethane was washed with saturated aqueous sodium hydrogen carbonate until most of the salts were dissolved. The organic layer was washed with brine, dried over sodium sulfate, and concentrated. The residue was dissolved in acetonitrile (4.8 mL) and the solution was treated with di-*tert*-butyl dicarbonate (1.47 mL, 6.40 mmol) at 0 °C and stirred for 1 h at room temperature. The resulting mixture was concentrated and the residue was purified by chromatography on silica gel (*n*-hexane/EtOAc = 5/1 to 3/1 as the eluent) to obtain *tert*-butyl 2-(4-chlorophenyl)hydrazinecarboxylate (**16**) (1.52 g, 87% yield) as colorless crystals. The following procedures are the same as **9a**. **9g** was obtained in 70% overall yield from **16**; pale yellow crystals; mp 47–49 °C; IR (KBr) 3073, 2980, 2912, 2822, 1702, 1641, 1594, 1494, 1459, 1428, 1378, 1365, 1319, 1280, 1238, 1162, 1146, 1113, 1097, 1054, 996, 950, 931, 915, 878, 858, 814, 762 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.17 (2H, ddd, $J = 9.2, 2.9, 2.9$ Hz, ArH), 6.58 (2H, d, $J = 9.2$ Hz, ArH), 5.96 (1H, dddd, $J = 16.8, 10.4, 6.8, 6.8$ Hz,

$CH=CH_2$), 5.23 (1H, d, $J = 16.8$ Hz, $CH=CH_2$), 5.17 (1H, dddd, $J = 10.4, 1.6, 1.0, 1.0$ Hz, $CH=CH_2$), 4.27 (1H, br, CH_2), 3.92 (1H, br, CH_2), 3.08 (3H, s, NCH_3), 1.65-1.05 (9H, br, t -Bu); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.1, 148.0, 133.3, 128.8, 123.3, 118.7, 113.0, 80.9, 51.4, 39.6, 28.2; HRMS-ESI (m/z): $[M+Na]^+$ calcd for $C_{15}H_{21}ClN_2O_2Na$: 319.1184. Found: 319.1183.

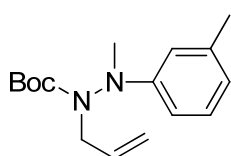
***tert*-Butyl 1-allyl-2-(4-(ethoxycarbonyl)phenyl)-2-methylhydrazinecarboxylate (**9h**)**



(Step 1) A mixture of 4-hydrazinobenzoic acid (1.52 g, 10.0 mmol) in ethanol (50 mL) was treated with thionyl chloride (0.80 mL, 11 mmol) and refluxed for 15 h. The resulting mixture was cooled to room temperature and filtered. The filtrate was washed with diethyl ether and dried under reduced pressure to obtain ethyl 4-hydrazinylbenzoate hydrochloride (**17**) (1.43 g, 66%) as pale brown crystals. (Step 2) A solution of **17** (1.43 g, 6.60 mmol) in acetonitrile (6.6 mL) and saturated aqueous sodium hydrogen carbonate (6.6 mL) was treated with di-*tert*-butyl dicarbonate (1.59 mL, 6.92 mmol) at room temperature and stirred for 4 h at the same temperature. The resulting mixture was diluted with water and extracted with ethyl acetate. The combined extracts were washed with brine, dried over sodium sulfate, and concentrated. Purification of the residue by chromatography on silica gel (n -hexane/EtOAc = 4/1 to 2/1 as the eluent) afforded *tert*-butyl 2-(4-(ethoxycarbonyl)phenyl)hydrazinecarboxylate (**18**) (1.82 g, 98% yield) as a pale yellow solid. (Step 3) A solution of **18** (1.12 g, 4.00 mmol) in THF (15 mL) was treated with a ca. 0.7 M LDA THF/ n -hexane solution (11.4 mL, 8.0 mmol) at $-78^\circ C$ under an argon atmosphere and the mixture was stirred for 10 min at the same temperature. Iodomethane (249 μ L, 4.00 mmol) was added to the mixture and allowed to warm to room temperature. After stirring for 2 h at room temperature, the resulting mixture was quenched with saturated aqueous ammonium chloride and extracted with ethyl acetate. The combined extracts were washed with brine, dried over sodium sulfate, and concentrated. Purification of the residue by chromatography on silica gel (n -hexane/EtOAc = 4/1 to 2/1 as the eluent) afforded *tert*-butyl 2-(4-(ethoxycarbonyl)phenyl)-2-methylhydrazinecarboxylate (**19**) (1.03 g, 87% yield) as a pale yellow solid. (Step 4) A solution of **19** (589 mg, 2.00 mmol) and allyl bromide (190 μ L, 2.20 mmol) in DMF (4 mL) was treated with sodium hydride (60 wt.% in oil, 96 mg, 2.4 mmol) at $0^\circ C$ and the mixture was stirred for 1 h at room temperature. The resulting mixture was quenched with saturated aqueous ammonium chloride at $0^\circ C$ and extracted with ethyl acetate. The combined extracts were washed with brine, dried over sodium sulfate, and concentrated. Purification of the residue by chromatography on silica gel (n -hexane/EtOAc = 8/1 to 5/1 as the eluent) afforded **9h** (619 mg, 93% yield) as a pale yellow oil; IR (film) 3081, 2978, 2932, 2904, 2820, 1706, 1644, 1605, 1570, 1515, 1456, 1428, 1366, 1341, 1312, 1276, 1240, 1180, 1157, 1142, 1107, 1053, 1023, 994, 926, 879, 857, 839, 769, 698

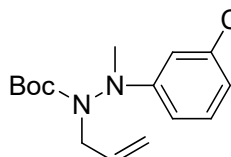
cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.93 (2H, ddd, *J* = 9.0, 2.4, 2.4 Hz, ArH), 6.64 (2H, ddd, *J* = 9.0, 2.4, 2.4 Hz, ArH), 5.96 (1H, dddd, *J* = 17.1, 10.0, 7.2, 6.1 Hz, CH=CH₂), 5.23 (1H, dd, *J* = 17.1, 1.2 Hz, CH=CH₂), 5.17 (1H, dddd, *J* = 10.0, 1.2, 1.2, 1.2 Hz, CH=CH₂), 4.40-4.25 (1H, br, NCH₂), 4.33 (2H, q, *J* = 7.0 Hz, OCH₂CH₃), 3.94 (1H, br, NCH₂), 3.16 (3H, s, NCH₃), 1.70-1.10 (9H, br, *t*-Bu), 1.37 (3H, t, *J* = 7.0 Hz, OCH₂CH₃); ¹³C NMR (100 MHz, CDCl₃) δ 166.5, 154.7, 152.5, 132.9, 131.0, 120.0, 118.9, 110.6, 81.0, 60.2, 51.0, 39.4, 28.0, 14.3; HRMS-ESI (*m/z*): [M+Na]⁺ calcd for C₁₈H₂₆N₂O₄Na: 357.1785. Found: 357.1771.

***tert*-Butyl 1-allyl-2-methyl-2-(*m*-tolyl)hydrazinecarboxylate (9i)**



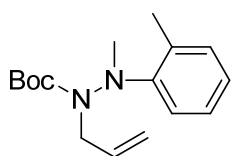
Prepared by the same procedure with **9e** (75% overall yield) using *m*-tolylhydrazine hydrochloride as a starting material; pale yellow crystals; mp 26–28 °C; IR (film) 3079, 3037, 2976, 2927, 2812, 1703, 1642, 1604, 1586, 1493, 1473, 1453, 1432, 1368, 1337, 1316, 1278, 1243, 1157, 1113, 1060, 993, 926, 861, 768, 692 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.15-7.06 (1H, m, ArH), 6.62 (1H, d, *J* = 7.6 Hz, ArH), 6.46 (2H, s, ArH), 5.98 (1H, dddd, *J* = 16.7, 10.1, 6.8, 6.8 Hz, CH=CH₂), 5.22 (1H, d, *J* = 16.7 Hz, CH=CH₂), 5.15 (1H, dddd, *J* = 10.1, 1.6, 1.1, 1.1 Hz, CH=CH₂), 4.35 (1H, br, CH₂), 3.87 (1H, br, CH₂), 3.09 (3H, s, NCH₃), 2.30 (3H, s, ArCH₃), 1.65-1.05 (9H, br, *t*-Bu); ¹³C NMR (100 MHz, CDCl₃) δ 155.4, 149.2, 138.6, 133.6, 128.8, 119.3, 118.3, 112.4, 109.0, 80.5, 51.6, 39.8, 28.2, 21.8; HRMS-ESI (*m/z*): [M+H]⁺ calcd for C₁₆H₂₅N₂O₂: 277.1911. Found: 277.1906.

***tert*-Butyl 1-allyl-2-(3-chlorophenyl)-2-methylhydrazinecarboxylate (9j)**



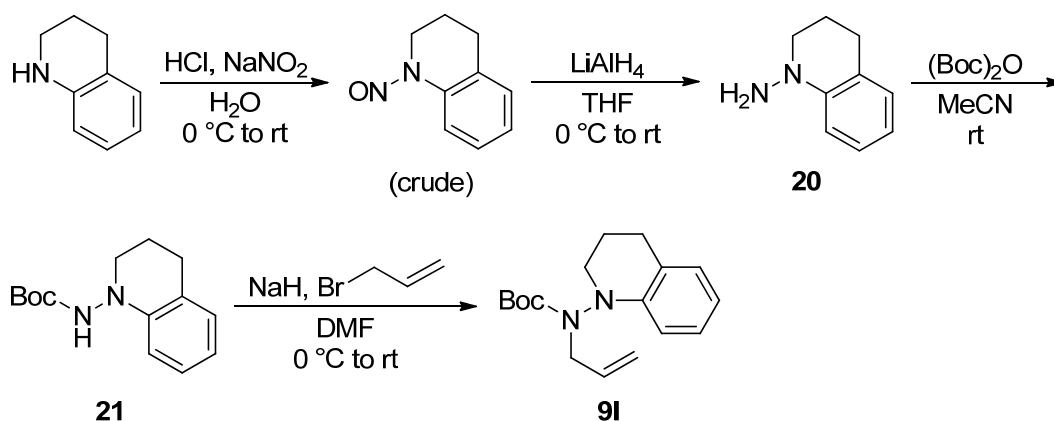
Prepared by the same procedure with **9e** (94% overall yield) using 3-chlorophenylhydrazine hydrochloride as a starting material; pale yellow crystals; mp 35–37 °C; IR (KBr) 3066, 2999, 2969, 2931, 2814, 1696, 1595, 1567, 1484, 1453, 1434, 1417, 1367, 1335, 1320, 1299, 1264, 1234, 1159, 1139, 1104, 1079, 1059, 997, 986, 926, 890, 859, 842, 797, 779, 763 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.13 (1H, dd, *J* = 8.1, 8.0 Hz, ArH), 6.77 (1H, ddd, *J* = 8.0, 2.0, 0.8 Hz, ArH), 6.64 (1H, dd, *J* = 2.0, 2.0 Hz, ArH), 6.53 (1H, dd, *J* = 8.1, 2.0 Hz, ArH), 5.96 (1H, dddd, *J* = 16.8, 10.3, 7.2, 6.2 Hz, CH=CH₂), 5.23 (1H, d, *J* = 16.8 Hz, CH=CH₂), 5.18 (1H, dddd, *J* = 10.3, 1.2, 1.2, 1.2 Hz, CH=CH₂), 4.29 (1H, br, CH₂), 3.91 (1H, br, CH₂), 3.09 (3H, s, NCH₃), 1.65-1.05 (9H, br, *t*-Bu); ¹³C NMR (100 MHz, CDCl₃) δ 155.0, 150.4, 134.9, 133.3, 130.0, 118.8, 118.4, 111.8, 110.0, 81.1, 51.4, 39.6, 28.2; HRMS-ESI (*m/z*): [M+Na]⁺ calcd for C₁₅H₂₁ClN₂O₂Na: 319.1184. Found: 319.1177.

***tert*-Butyl 1-allyl-2-methyl-2-(*o*-tolyl)hydrazinecarboxylate (9k)**



Prepared by the same procedure with **9e** (98% overall yield) using *o*-tolylhydrazine hydrochloride as a starting material; pale yellow oil; IR (film) 3076, 2976, 2930, 2800, 1719, 1695, 1641, 1600, 1579, 1493, 1467, 1451, 1432, 1390, 1366, 1332, 1304, 1276, 1247, 1176, 1154, 1130, 1096, 1054, 992, 923, 876, 858, 807, 762, 720 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.14-7.06 (2H, m, ArH), 6.99-6.88 (1H, br, ArH), 6.92 (1H, ddd, *J* = 7.5, 7.5, 1.0 Hz, ArH), 5.78 (1H, br, CH=CH₂), 5.06-4.95 (2H, m, CH=CH₂), 4.40-3.30 (2H, br, CH₂), 3.06 (3H, s, NCH₃), 2.20 (3H, s, ArCH₃), 1.45 (9H, br, *t*-Bu); ¹³C NMR (100 MHz, CDCl₃) δ 154.9, 147.0, 134.6, 131.5, 130.6, 126.0, 122.7, 117.9, 117.1, 80.4, 49.9, 40.3, 28.4, 19.2; HRMS-ESI (*m/z*): [M+H]⁺ calcd for C₁₆H₂₅N₂O₂: 277.1911. Found: 277.1906.

***tert*-Butyl allyl(3',4'-dihydroquinolin-1'(2*H*)-yl)carbamate (**9I**)**

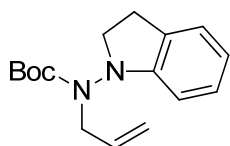


(Step 1)³ A mixture of 1,2,3,4-tetrahydroquinoline (0.63 mL, 5.0 mmol) and concentrated hydrochloric acid (0.83 mL) in water (2 mL) was treated with a solution of sodium nitrite (0.41 g, 5.9 mmol) in water (1.5 mL) at 0 °C and stirred for 1 h at room temperature. The resulting mixture was diluted with water and extracted with toluene. The combined extracts were washed with water, dried over sodium sulfate, and concentrated. The residue was dissolved in THF (5 mL) and the solution was added to a suspension of lithium aluminum hydride (0.38 g, 10 mmol) in THF (10 mL) at 0 °C under an argon atmosphere. After stirring for 30 min at room temperature, the resulting mixture was quenched with water at 0 °C and filtered through a pad of Celite. The precipitate was washed with dichloromethane and the filtrate was extracted with dichloromethane. The combined extracts were washed with water, dried over sodium sulfate, and concentrated. Purification of the residue by chromatography on silica gel (*n*-hexane/EtOAc = 4/1 to 2/1 as the eluent) gave 3,4-dihydroquinolin-1(2*H*)-amine (**20**) (576 mg, 78% yield) as a yellow oil. (Step 2) A solution of **20** (568 mg, 3.83 mmol) and di-*tert*-butyl dicarbonate (0.88 mL, 3.8 mmol) in acetonitrile (1.5 mL) was stirred for 13 h at room temperature. The resulting solution was evaporated and the residue was purified by chromatography on silica gel (*n*-hexane/EtOAc = 5/1 to 3/1 as the eluent) to obtain *tert*-butyl (3,4-dihydroquinolin-1(2*H*)-yl)carbamate (**21**) (863 mg, 91% yield) as a yellow oil. (Step 3) A solution of **21** (857 mg, 3.45 mmol) and allyl bromide (0.33 mL, 3.8 mmol) in DMF (7 mL) was treated with sodium hydride (60 wt.% in oil, 0.16 g, 4.0 mmol) at 0 °C and the mixture was stirred for 2 h at room temperature. The resulting mixture was quenched with saturated aqueous ammonium chloride at 0 °C and extracted with ethyl acetate. The combined extracts were washed with brine, dried over sodium sulfate, and concentrated. Purification of the residue by chromatography on silica gel (*n*-hexane/EtOAc = 20/1 to 15/1 as the eluent) afforded **9I** (803 mg, 81% yield) as a colorless oil; IR (film) 3076, 2973, 2931, 2861, 1701, 1642, 1603, 1579, 1491, 1458, 1431, 1365, 1340, 1304, 1248, 1170, 1149, 1117, 1077, 1039, 1024, 992, 970, 924, 863, 798, 746, 714 cm⁻¹; ¹H NMR (400 MHz, DMSO-*d*₆) δ 6.98 (1H, dd, *J* = 8.1, 7.2 Hz, ArH), 6.93 (1H, d, *J* = 7.4 Hz, ArH), 6.60 (1H, ddd, *J* = 7.4, 7.2, 1.0 Hz, ArH), 6.45 (1H, dd, *J* = 8.1, 1.0 Hz, ArH), 5.94 (1H, dddd, *J* = 17.0, 10.2, 6.2, 6.2 Hz, CH₂CH=CH₂), 5.23 (1H, dddd, *J* = 17.0, 1.6, 1.6, 1.6 Hz, CH₂CH=CH₂), 5.14 (1H, dddd, *J* = 10.2, 1.6, 1.0, 1.0 Hz, CH₂CH=CH₂), 4.21 (1H, dd,

³ Paris, D.; Cottin, M.; Demonchaux, P.; Augert, G.; Dupassieux, P.; Lenoir, P.; Peck, M. J.; Jasserand, D. *J. Med. Chem.* **1995**, *38*, 669–685.

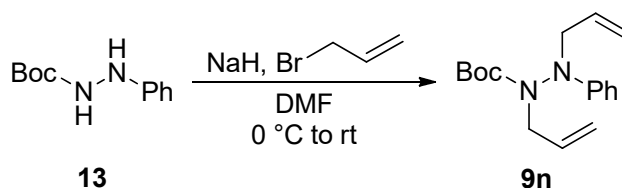
$J = 14.5, 6.2$ Hz, $\text{CH}_2\text{CH}=\text{CH}_2$), 3.85 (1H, dd, $J = 14.5, 6.2$ Hz, $\text{CH}_2\text{CH}=\text{CH}_2$), 3.38 (2H, br, 2'- CH_2), 2.69 (1H, ddd, $J = 16.0, 7.6, 7.6$ Hz, 4'- CH_2), 2.60 (1H, ddd, $J = 16.0, 5.2, 5.2$ Hz, 4'- CH_2), 1.98-1.83 (2H, m, 3'- CH_2), 1.60-1.00 (9H, br, *t*-Bu); ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$) δ 154.4, 144.9, 133.9, 128.8, 126.6, 121.8, 118.2, 117.7, 110.5, 79.7, 50.5, 49.8, 27.8, 26.7, 21.8; HRMS-ESI (m/z): $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{17}\text{H}_{25}\text{N}_2\text{O}_2$: 289.1911. Found: 289.1901.

***tert*-Butyl allyl(indolin-1-yl)carbamate (9m)**



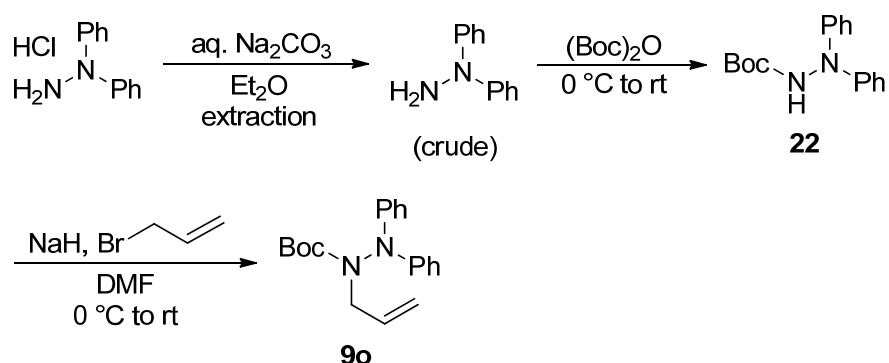
Prepared by the same procedure with **9l** (46% overall yield) using indoline as a starting material; colorless oil; IR (film) 3079, 3050, 3028, 2974, 2929, 2882, 1701, 1643, 1609, 1598, 1483, 1459, 1433, 1366, 1284, 1251, 1150, 1085, 1056, 1044, 1018, 993, 922, 860, 747, 720 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.07-7.01 (2H, m, ArH), 6.73 (1H, ddd, $J = 7.3, 7.3, 1.0$ Hz, ArH), 6.47 (1H, dd, $J = 8.2, 1.0$ Hz, ArH), 5.98 (1H, dddd, $J = 16.8, 10.2, 6.4, 6.0$ Hz, $\text{CH}_2\text{CH}=\text{CH}_2$), 5.25 (1H, d, $J = 16.8$ Hz, $\text{CH}_2\text{CH}=\text{CH}_2$), 5.17 (1H, dddd, $J = 10.2, 1.2, 1.2, 1.2$ Hz, $\text{CH}_2\text{CH}=\text{CH}_2$), 4.19 (1H, dd, $J = 15.0, 6.0$ Hz, $\text{CH}_2\text{CH}=\text{CH}_2$), 4.06 (1H, br, $\text{CH}_2\text{CH}=\text{CH}_2$), 3.66 (2H, br, indoline- CH_2), 3.07-2.86 (2H, m, indoline- CH_2), 1.21 (9H, br, *t*-Bu); ^{13}C NMR (100 MHz, CDCl_3) δ 154.5, 151.1, 134.2, 126.8, 126.5, 124.6, 119.4, 117.6, 108.1, 80.6, 53.0, 52.1, 28.0, 27.6; HRMS-ESI (m/z): $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{16}\text{H}_{23}\text{N}_2\text{O}_2$: 275.1754. Found: 275.1746.

***tert*-Butyl 1,2-diallyl-2-phenylhydrazinecarboxylate (9n)**



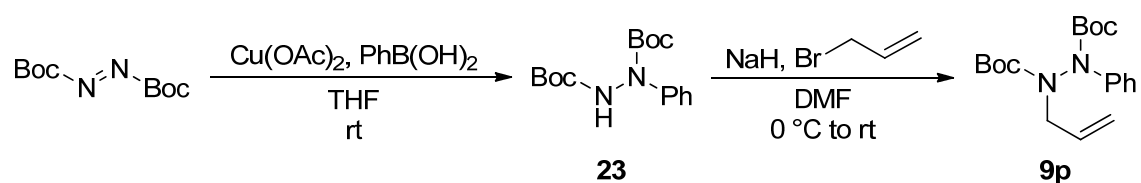
A solution of **13** (0.52 g, 2.5 mmol) and allyl bromide (0.52 mL, 6.0 mmol) in DMF (4.5 mL) was treated with sodium hydride (60 wt.% in oil, 0.22 g, 5.5 mmol) at 0 °C and the mixture was stirred for 2.5 h at room temperature. The resulting mixture was quenched with saturated aqueous ammonium chloride at 0 °C and extracted with ethyl acetate. The combined extracts were washed with brine, dried over sodium sulfate, and concentrated. Purification of the residue by chromatography on silica gel (*n*-hexane/EtOAc = 20/1 as the eluent) afforded **9n** (0.54 g, 75% yield) as a yellow oil; IR (film) 3079, 3041, 3027, 3005, 2977, 2929, 1704, 1644, 1598, 1499, 1455, 1433, 1418, 1378, 1366, 1276, 1241, 1151, 1084, 1054, 1036, 991, 921, 875, 858, 748, 692 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.19 (2H, dd, $J = 8.2, 7.4$ Hz, Ph), 6.75 (1H, t, $J = 7.4$ Hz, Ph), 6.64 (2H, d, $J = 8.2$ Hz, Ph), 6.02-5.86 (2H, m, $\text{CH}_2\text{CH}=\text{CH}_2$), 5.37-5.07 (4H, m, $\text{CH}_2\text{CH}=\text{CH}_2$), 4.26-4.07 (2H, m, $\text{CH}_2\text{CH}=\text{CH}_2$), 4.04-3.82 (2H, m, $\text{CH}_2\text{CH}=\text{CH}_2$), 1.65-1.00 (9H, br, *t*-Bu); ^{13}C NMR (100 MHz, CDCl_3 , 65/35 mix of rotamers) δ 154.6, 153.8, 148.4, 134.7, 133.9, 128.7, 118.4, 118.2, 117.0, 112.1, 80.3, 79.8, 56.4, 55.9, 54.0, 52.0, 27.8; HRMS-ESI (m/z): $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{17}\text{H}_{25}\text{N}_2\text{O}_2$: 289.1911. Found: 289.1901.

tert-Butyl 1-allyl-2,2-diphenylhydrazinecarboxylate (**9o**)



(Step 1) A suspension of diphenylhydrazine hydrochloride (0.66 g, 3.0 mmol) in diethyl ether was washed with saturated aqueous sodium carbonate until most of the salts were dissolved. The organic layer was washed with brine, dried over sodium sulfate, and concentrated. Di-*tert*-butyl dicarbonate (0.69 mL, 3.0 mmol) was added to the residue at 0 °C and stirred for 1 h at room temperature. The resulting mixture was purified by chromatography on silica gel (*n*-hexane/EtOAc = 9/1 to 5/1 as the eluent) to obtain *tert*-butyl 2,2-diphenylhydrazinecarboxylate (**22**) (682 mg, 80% yield) as colorless crystals. (Step 2) A solution of **22** (682 mg, 2.40 mmol) and allyl bromide (0.23 mL, 2.7 mmol) in DMF (5 mL) was treated with sodium hydride (60 wt.% in oil, 0.12 g, 3.0 mmol) at 0 °C and the mixture was stirred for 1 h at room temperature. The resulting mixture was quenched with saturated aqueous ammonium chloride at 0 °C and extracted with ethyl acetate. The combined extracts were washed with brine, dried over sodium sulfate, and concentrated. Purification of the residue by chromatography on silica gel (*n*-hexane/EtOAc = 10/1 as the eluent) afforded **9o** (706 mg, 91% yield) as colorless crystals; mp 47–49 °C; IR (KBr) 3068, 2994, 2981, 2966, 2915, 1693, 1642, 1590, 1498, 1459, 1432, 1380, 1365, 1330, 1298, 1275, 1250, 1148, 1110, 1082, 1034, 992, 945, 928, 855, 778, 770, 750, 695 cm⁻¹; ¹H NMR (400 MHz, CDCl₃, 8/2 mix of rotamers) δ 7.25 (4H, dddd, *J* = 8.4, 7.2, 2.0, 2.0 Hz, Ph), 7.09 (4H, d, *J* = 8.4 Hz, Ph), 6.97 (2H, tt, *J* = 7.2, 1.6 Hz, Ph), 6.03–5.81 (0.2H, br, CH=CH₂), 5.95 (0.8H, ddt, *J* = 17.0, 10.0, 6.8 Hz, CH=CH₂), 5.16 (1H, d, *J* = 17.0 Hz, CH=CH₂), 5.11 (1H, d, *J* = 10.0 Hz, CH=CH₂), 4.25–4.10 (0.4H, br, CH₂), 4.20 (1.6H, d, *J* = 6.8 Hz, CH₂), 1.50 (1.8H, s, *t*-Bu), 1.24 (7.2H, s, *t*-Bu); ¹³C NMR (100 MHz, CDCl₃, 8/2 mix of rotamers) δ 155.4, 154.5, 145.0, 144.9, 133.6, 133.1, 129.0, 128.8, 122.4, 122.1, 119.2, 119.0, 118.9, 118.1, 81.3, 81.0, 53.6, 51.7, 28.3, 28.0; HRMS–ESI (*m/z*): [M+H]⁺ calcd for C₂₀H₂₅N₂O₂: 325.1911. Found: 325.1899.

Di-*tert*-butyl 1-allyl-2-phenylhydrazine-1,2-dicarboxylate (**9p**)

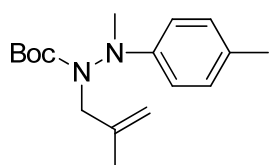


(Step 1)⁴ A mixture of di-*tert*-butyl azodicarboxylate (115 mg, 0.50 mmol) and phenylboronic acid (122 mg, 1.00 mmol) and copper(II) acetate (9 mg, 0.05 mmol) in THF (1.0 mL) was stirred for 45 h at room temperature

⁴ Uemura, T.; Chatani, N. *J. Org. Chem.* **2005**, *70*, 8631–8634.

under an argon atmosphere. The resulting mixture was concentrated and the residue was purified by chromatography on silica gel (*n*-hexane/EtOAc = 8/1 to 5/1 as the eluent) to give di-*tert*-butyl 1-phenylhydrazine-1,2-dicarboxylate (**23**) (131 mg, 85% yield) as colorless crystals. (Step 2) A solution of **23** (662 mg, 2.15 mmol) and allyl bromide (0.21 mL, 2.4 mmol) in DMF (4.3 mL) was treated with sodium hydride (60 wt.% in oil, 0.10 g, 2.5 mmol) at 0 °C and the mixture was stirred for 1 h at room temperature. The resulting mixture was quenched with saturated aqueous ammonium chloride at 0 °C and extracted with ethyl acetate. The combined extracts were washed with brine, dried over sodium sulfate, and concentrated. Purification of the residue by chromatography on silica gel (*n*-hexane/EtOAc = 20/1 to 10/1 as the eluent) afforded **9p** (735 mg, 98% yield) as a pale yellow oil; IR (film) 3077, 2978, 2931, 1719, 1644, 1597, 1492, 1477, 1455, 1434, 1420, 1391, 1367, 1339, 1318, 1280, 1253, 1149, 1078, 1052, 1023, 992, 970, 923, 855, 824, 756, 732, 691 cm⁻¹; ¹H NMR (400 MHz, CDCl₃, 7/3 mix of rotamers) δ 7.45-7.26 (4H, m, Ph), 7.19-7.10 (1H, m, Ph), 5.92-5.78 (1H, m, CH=CH₂), 5.18-5.06 (2H, m, CH=CH₂), 4.19 (0.7H, dd, *J* = 15.0, 6.6 Hz, CH₂), 4.09 (0.3H, dd, *J* = 15.2, 6.4 Hz, CH₂), 4.06-3.88 (1H, br, CH₂), 1.53 (2.7H, s, *t*-Bu), 1.51 (6.3H, s, *t*-Bu), 1.49 (9H, s, *t*-Bu); ¹³C NMR (100 MHz, CDCl₃, 7/3 mix of rotamers) δ 154.9, 154.6, 153.3, 152.8, 140.9, 133.3, 132.8, 128.3, 125.4, 125.3, 123.1, 118.5, 117.8, 81.8, 81.7, 81.4, 81.3, 53.8, 51.8, 28.2, 28.1; HRMS–ESI (*m/z*): [M+H]⁺ calcd for C₁₉H₂₉N₂O₄: 349.2122. Found: 349.2107.

***tert*-Butyl 2-methyl-1-(2-methylallyl)-2(*p*-tolyl)hydrazinecarboxylate (**9q**)**

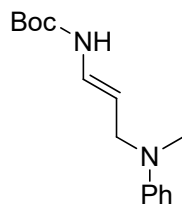


Prepared by the same procedure with **9g** (48% overall yield) using *p*-tolylhydrazine hydrochloride as a starting material and 3-chloro-2-methyl-1-propene instead of allyl bromide; pale yellow oil; IR (film) 3076, 2974, 2926, 2811, 1702, 1656, 1617, 1578, 1516, 1454, 1425, 1366, 1314, 1289, 1256, 1232, 1167, 1116, 1077, 1039, 1015, 973,

939, 899, 885, 860, 806, 787, 763 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.03 (2H, d, *J* = 8.6 Hz, ArH), 6.53 (2H, d, *J* = 8.6 Hz, ArH), 4.90 (1H, s, C(CH₃)=CH₂), 4.88 (1H, s, C(CH₃)=CH₂), 4.39 (1H, br, CH₂), 3.64 (1H, d, *J* = 15.2 Hz, CH₂), 3.09 (3H, s, NCH₃), 2.25 (3H, s, ArCH₃), 1.82 (3H, s, C(CH₃)=CH₂), 1.30 (9H, br, *t*-Bu); ¹³C NMR (100 MHz, CDCl₃) δ 155.9, 146.6, 141.6, 129.5, 127.5, 113.9, 111.7, 80.5, 55.1, 39.7, 28.2, 20.5, 20.2; HRMS–ESI (*m/z*): [M+H]⁺ calcd for C₁₇H₂₇N₂O₂: 291.2067. Found: 291.2057.

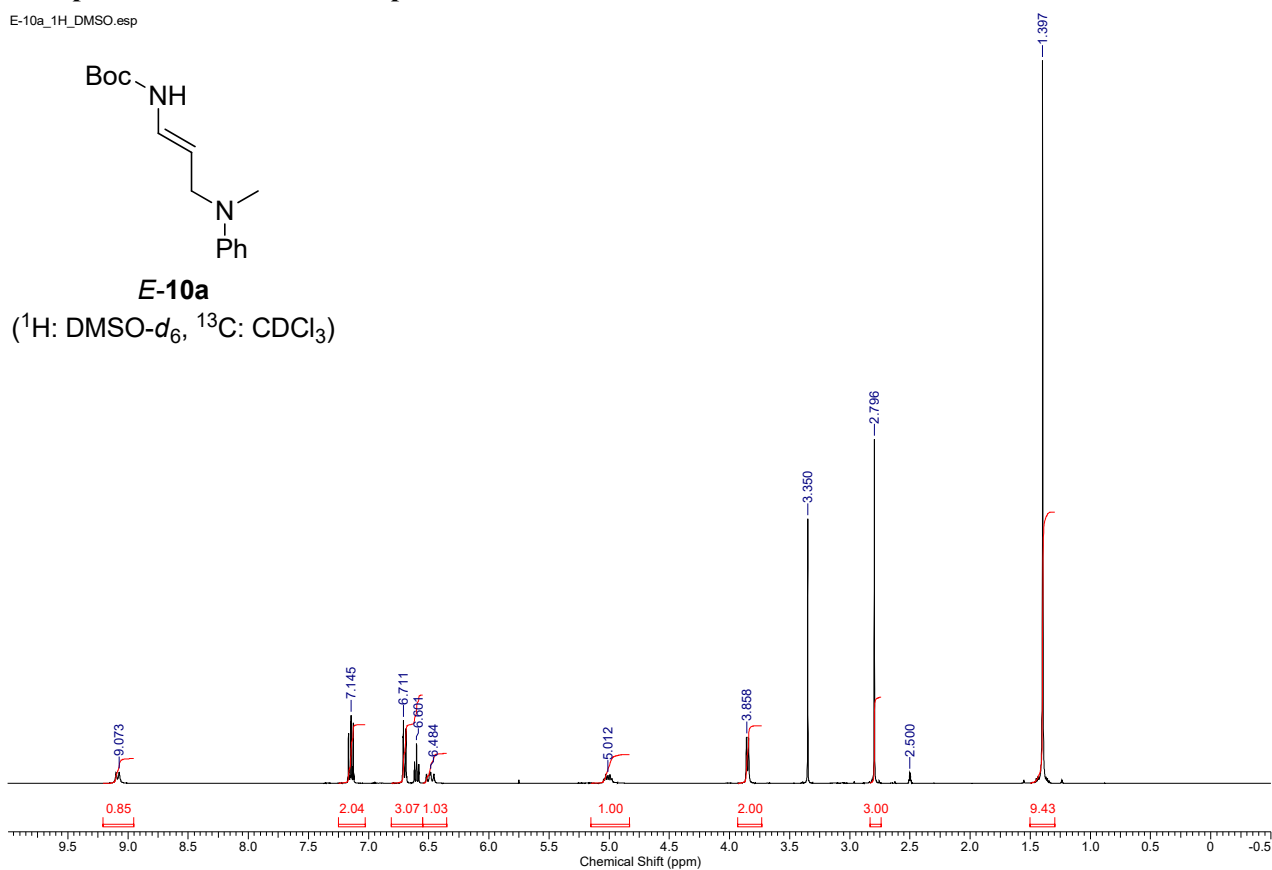
4. Copies of ^1H and ^{13}C NMR spectra of 10 and 11

E-10a_1H_DMSO.esp

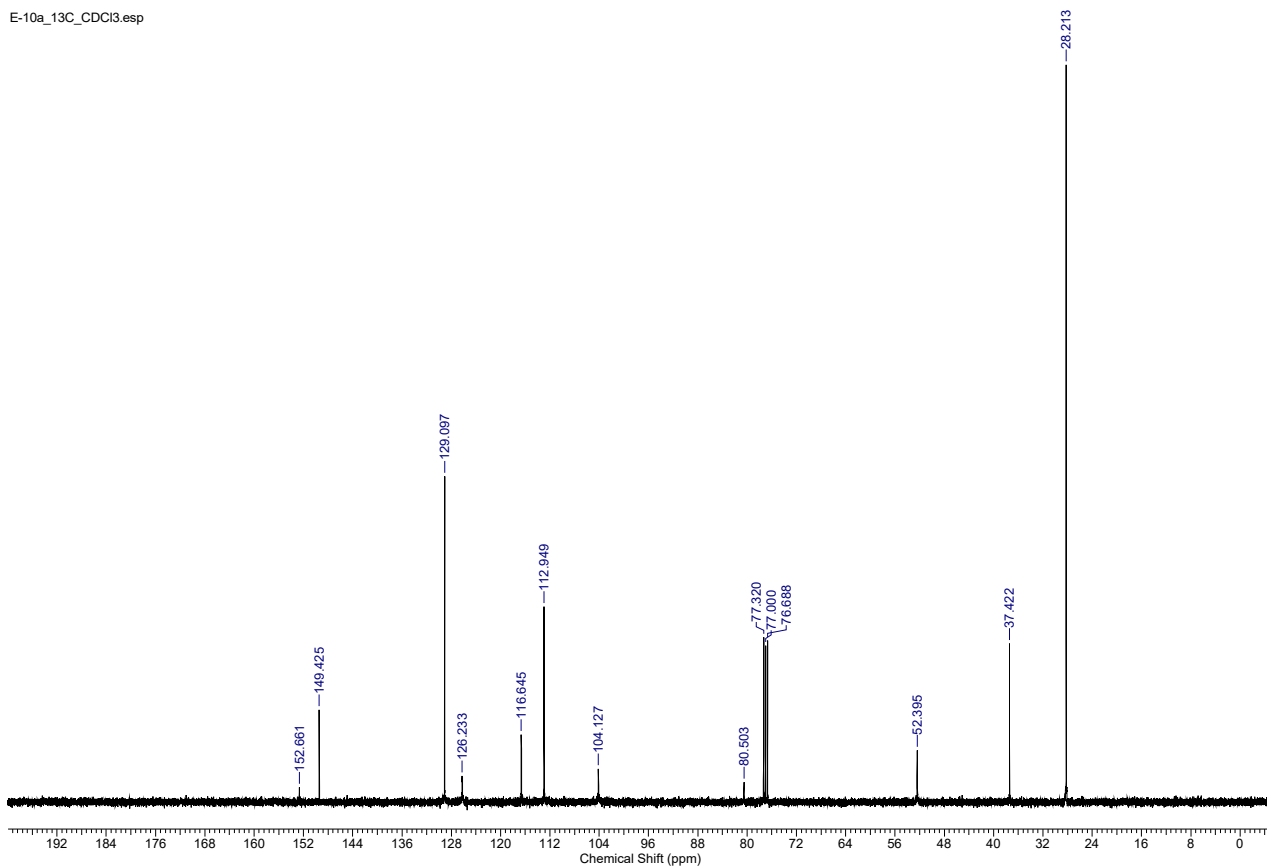


E-10a

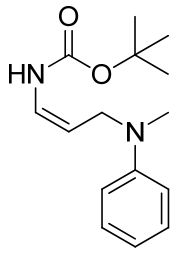
(^1H : DMSO- d_6 , ^{13}C : CDCl $_3$)



E-10a_13C_CDCl3.esp

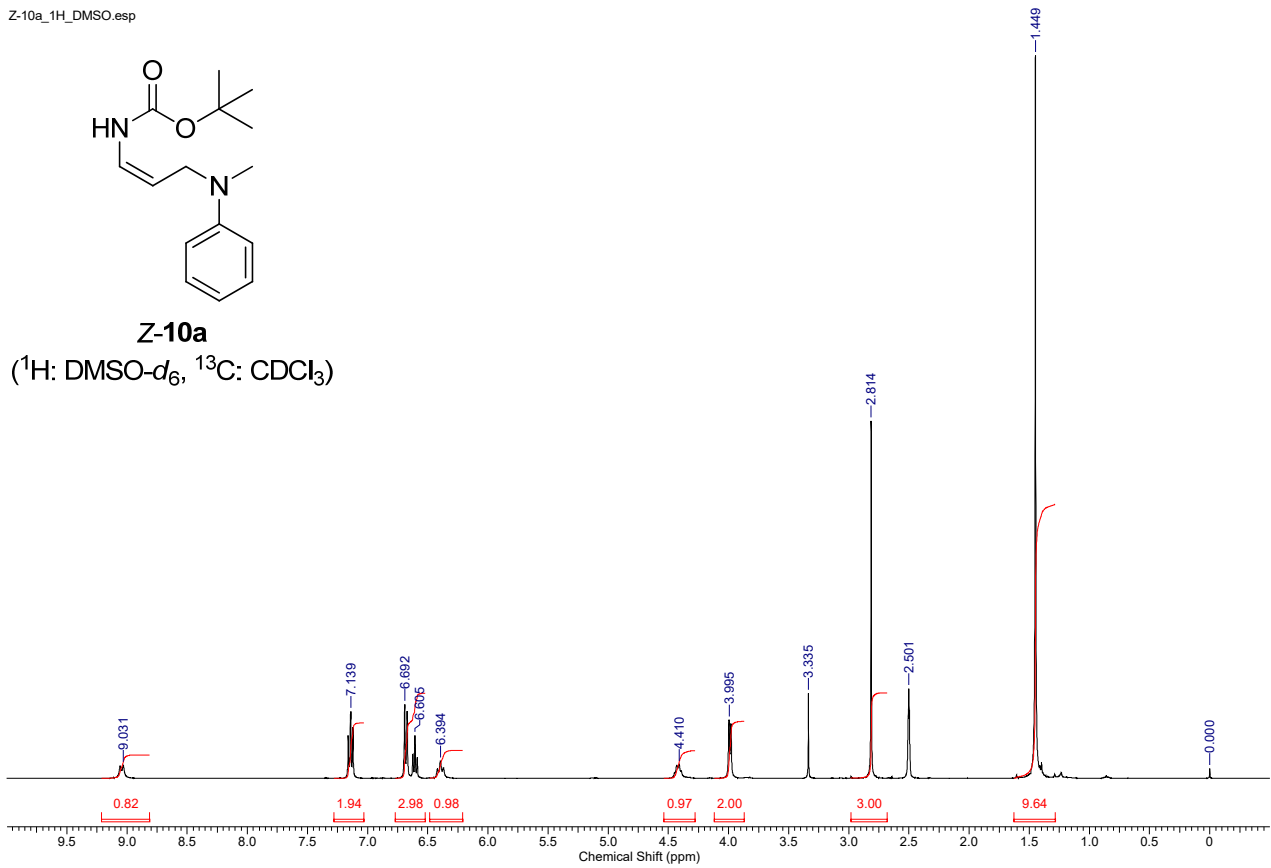


Z-10a_1H_DMSO.esp

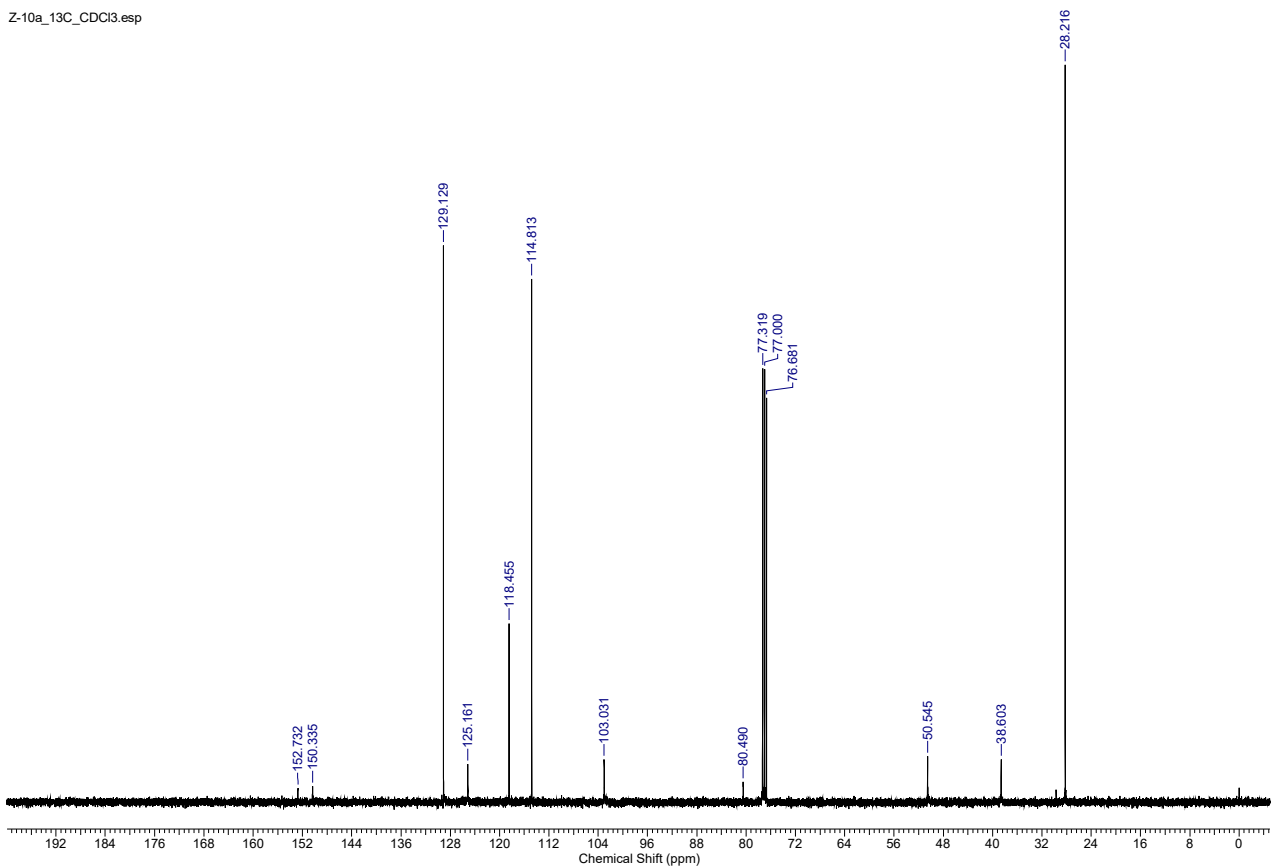


Z-10a

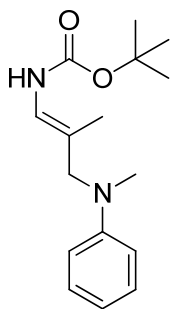
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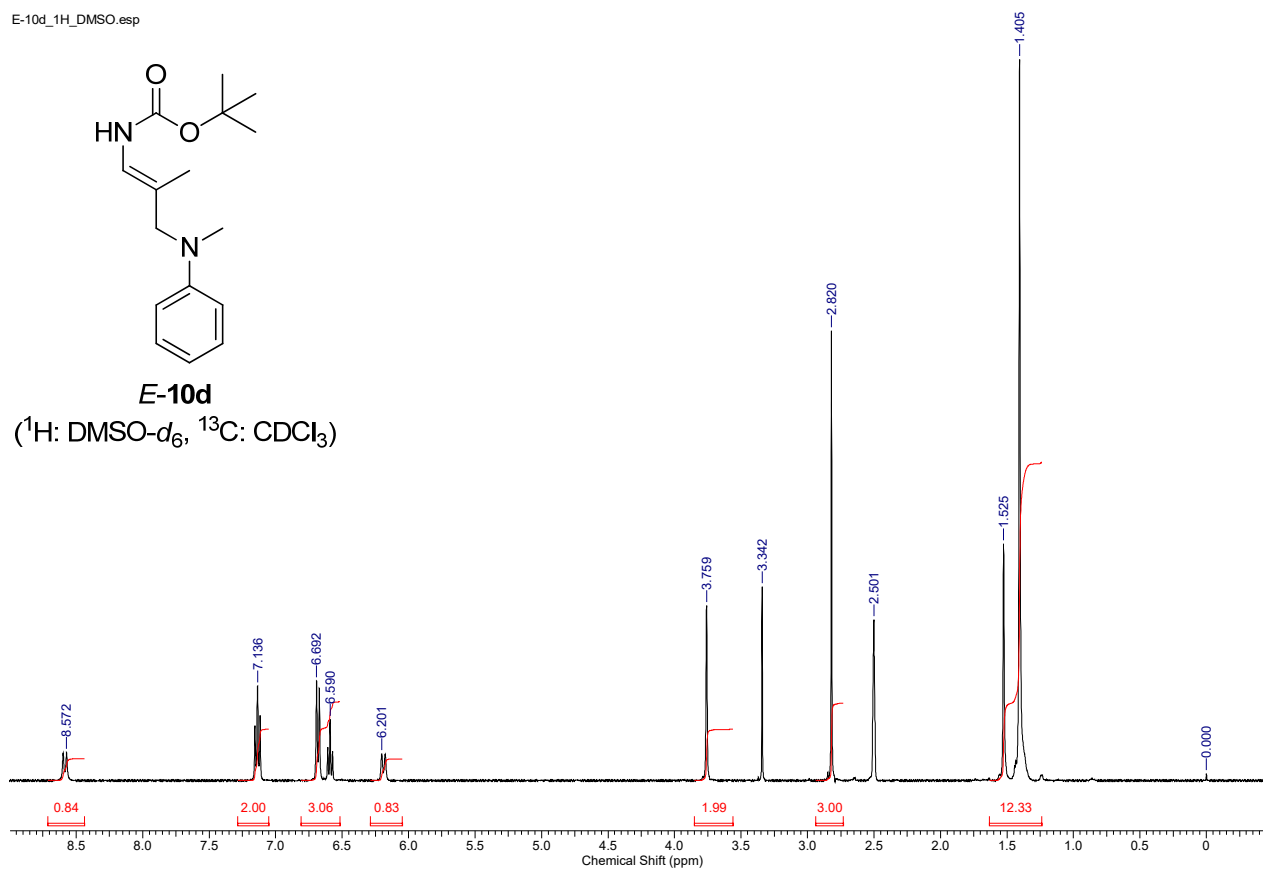


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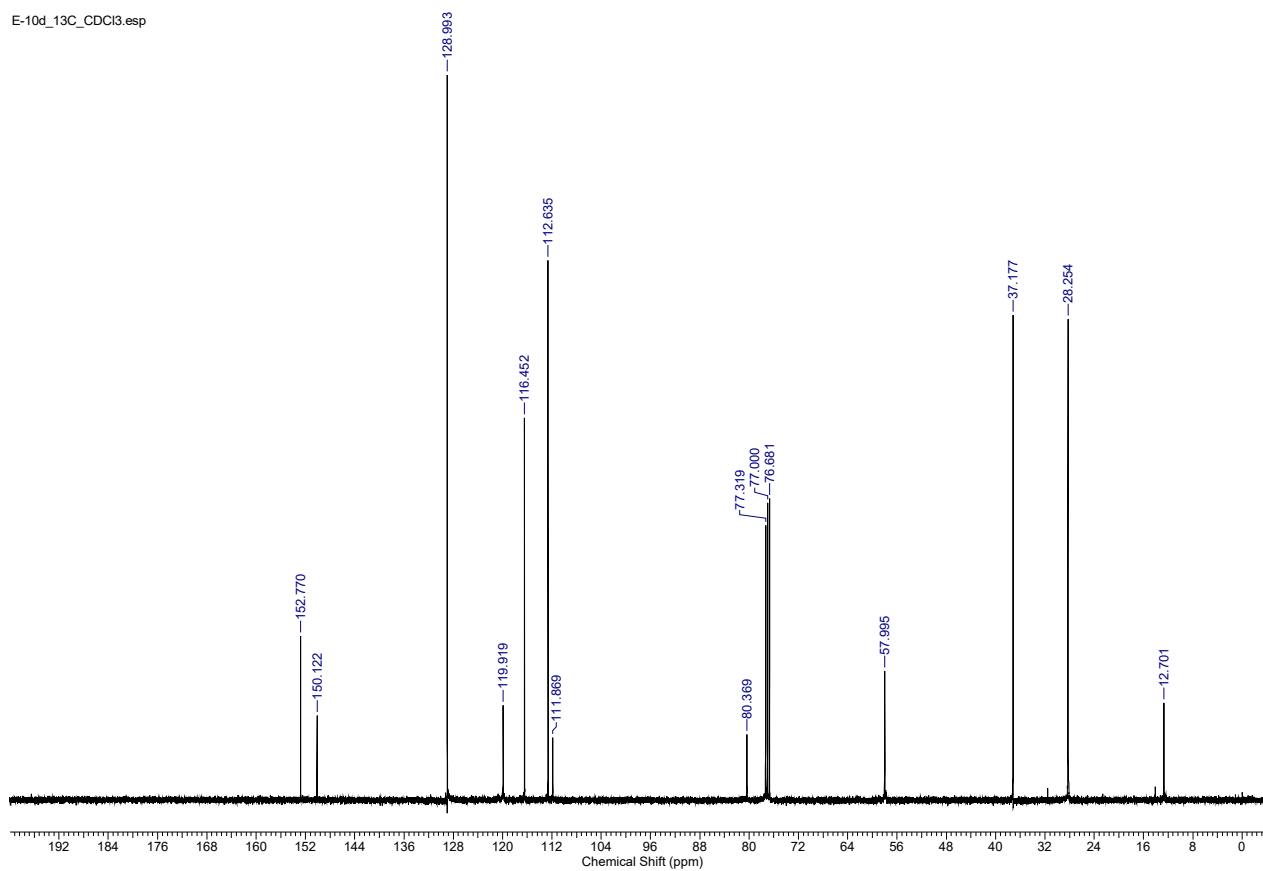


E-10d

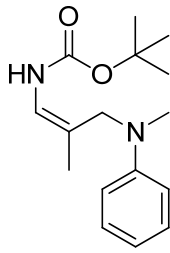
(¹H: DMSO-d₆, ¹³C: CDCl₃)



E-10d_13C_CDCl3.esp

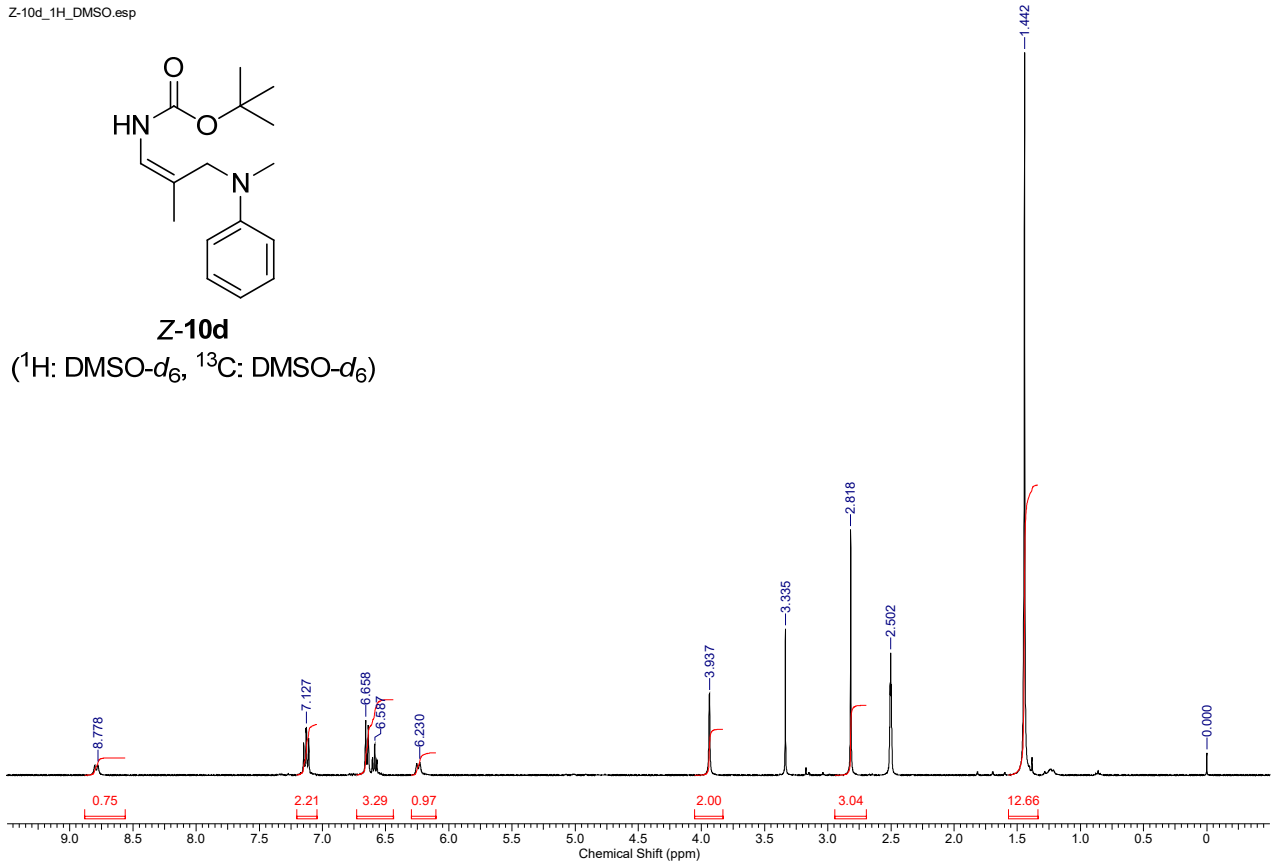


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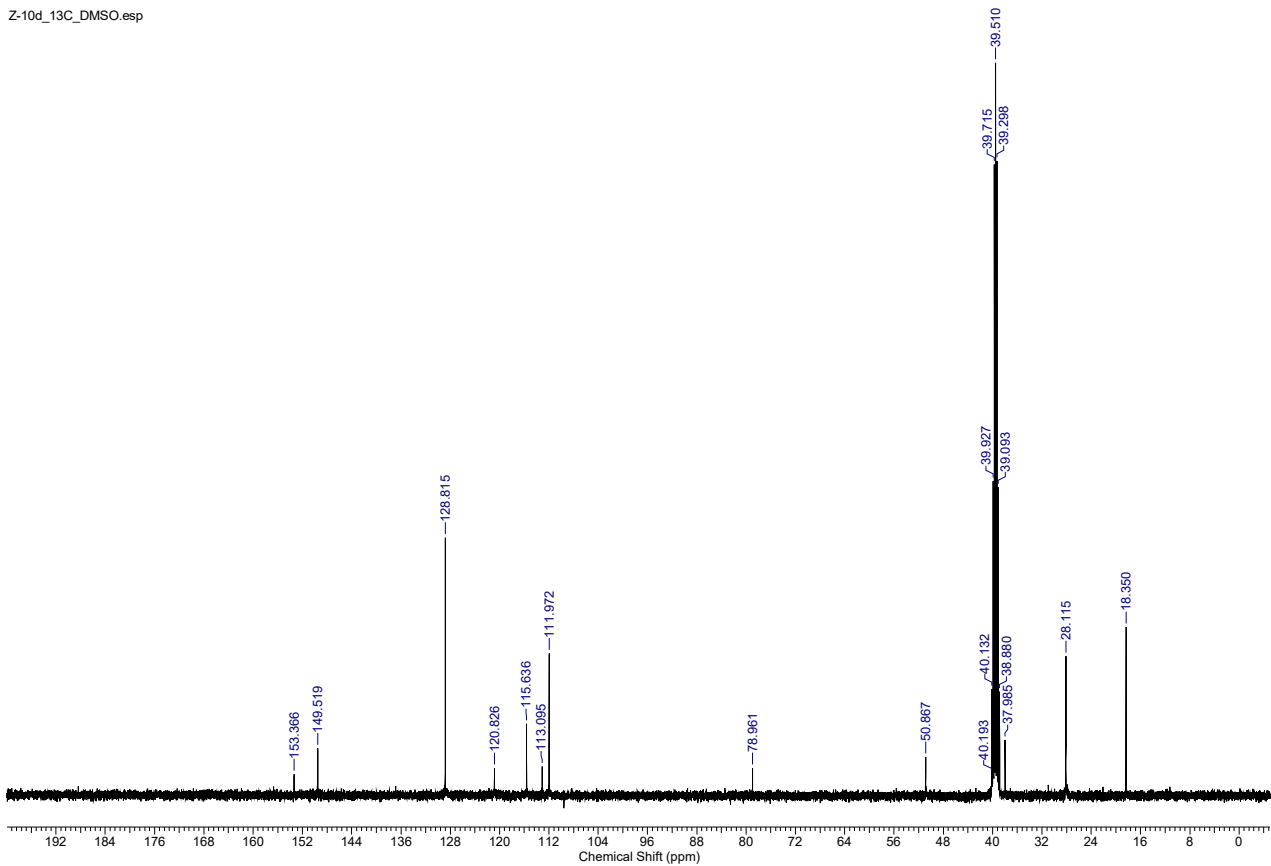


Z-10d

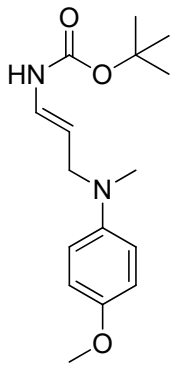
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Z-10d_13C_DMSO.esp

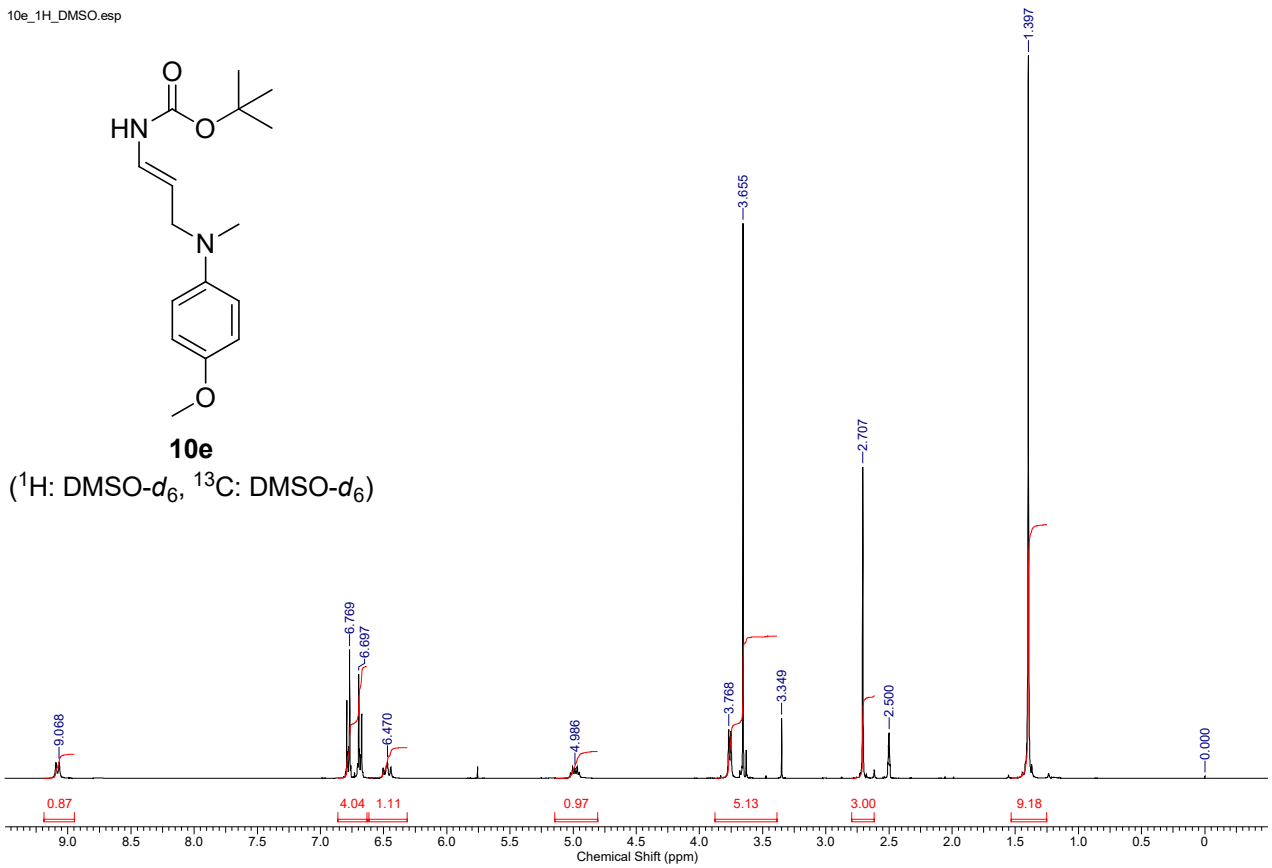


10e_1H_DMSO.esp

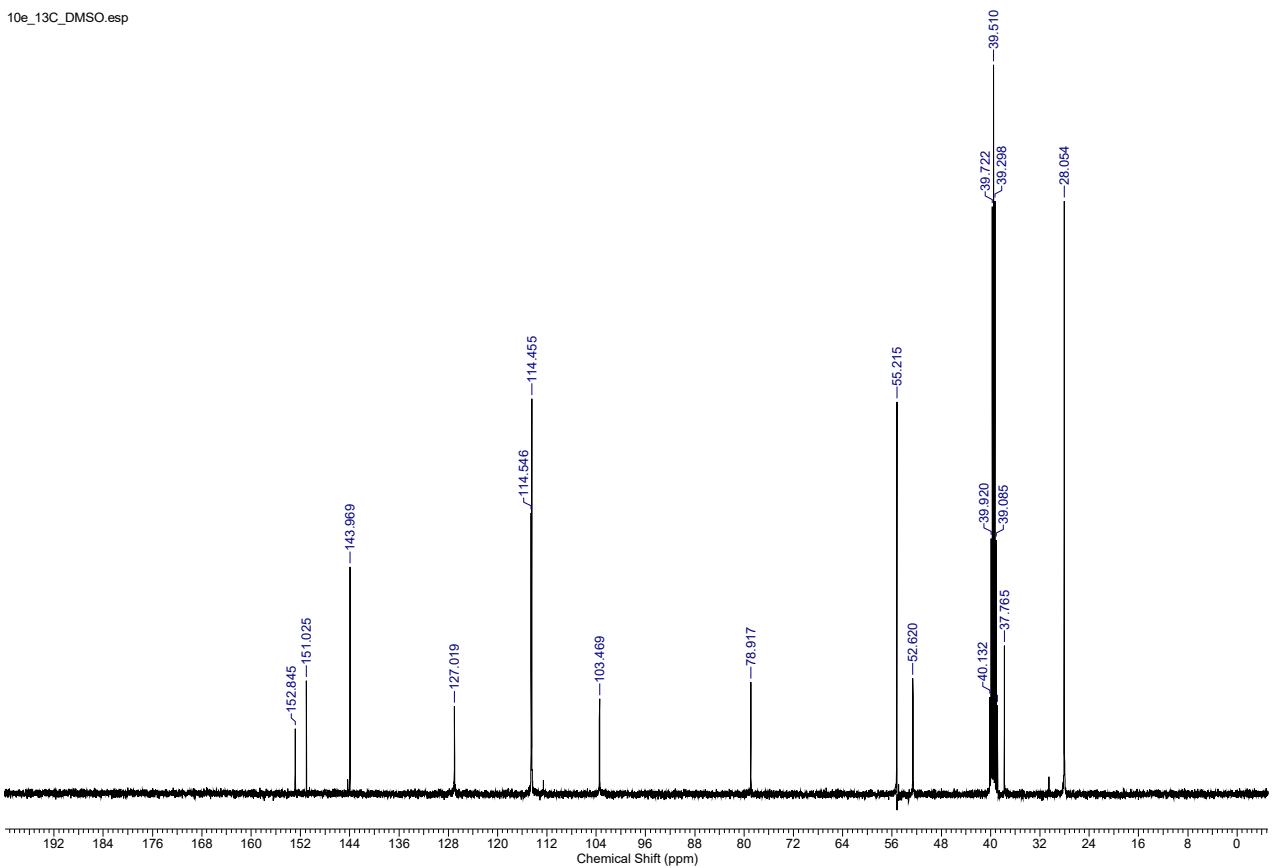


10e

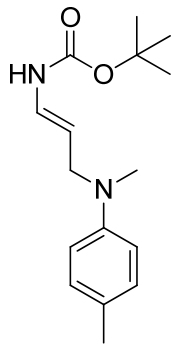
(¹H: DMSO-*d*₆, ¹³C: DMSO-*d*₆)



10e_13C_DMSO.esp

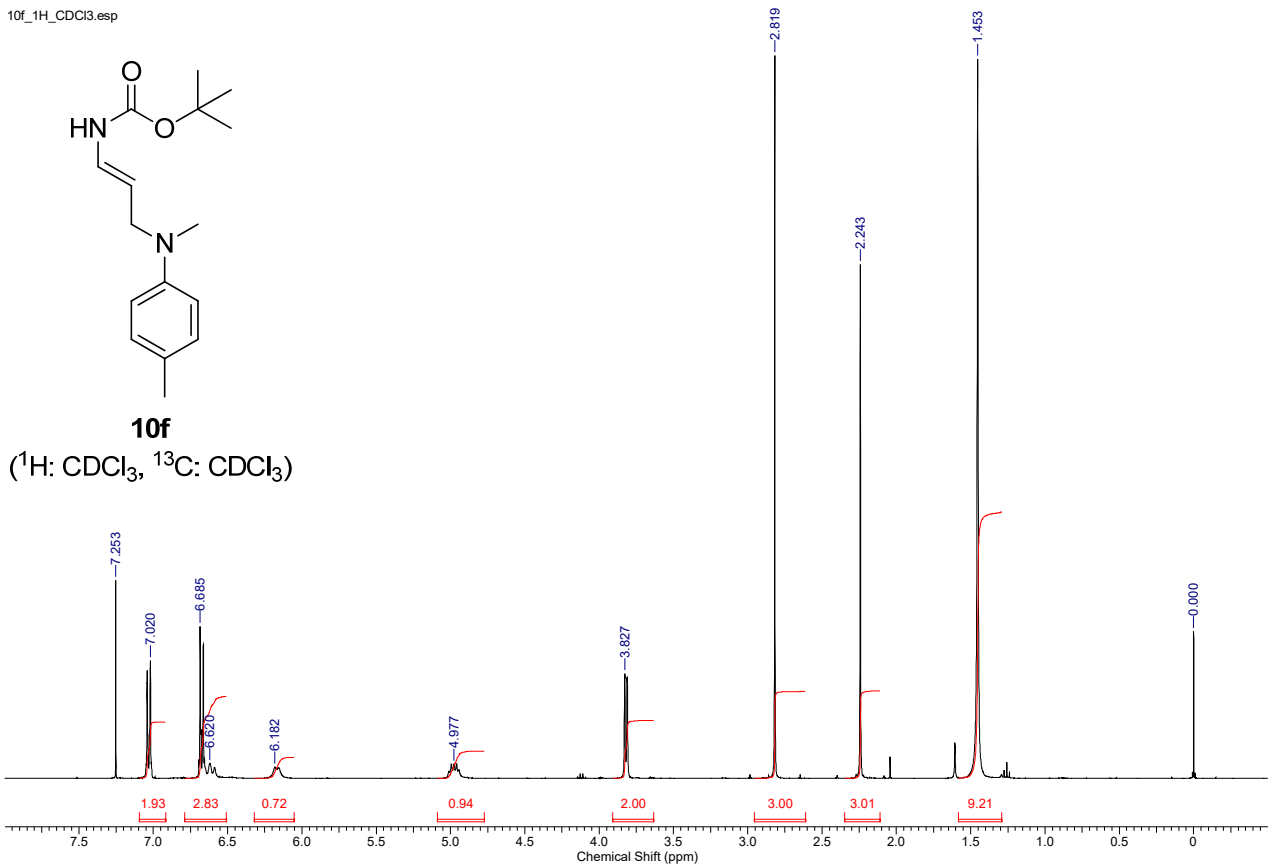


10f_1H_CDCl3.esp

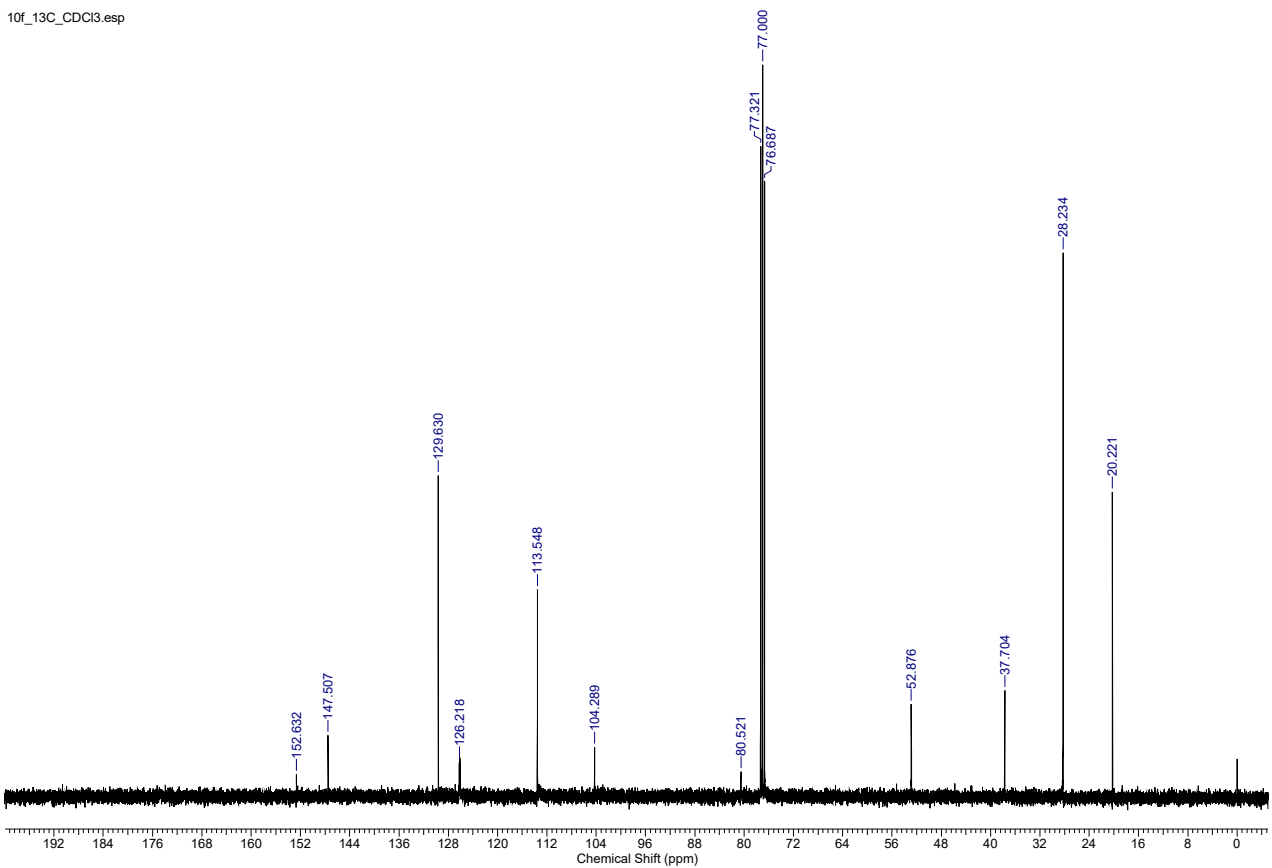


10f

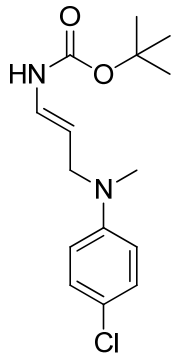
(¹H: CDCl₃, ¹³C: CDCl₃)



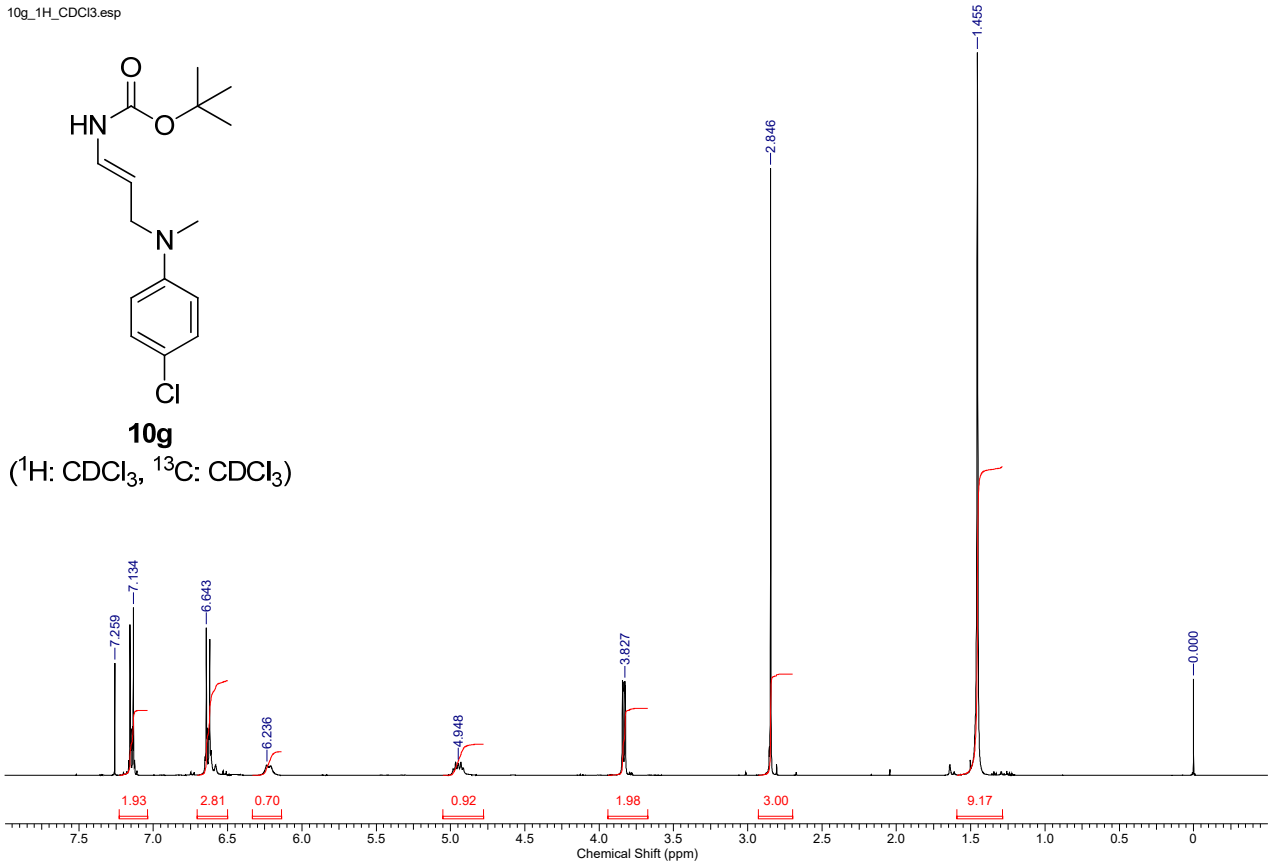
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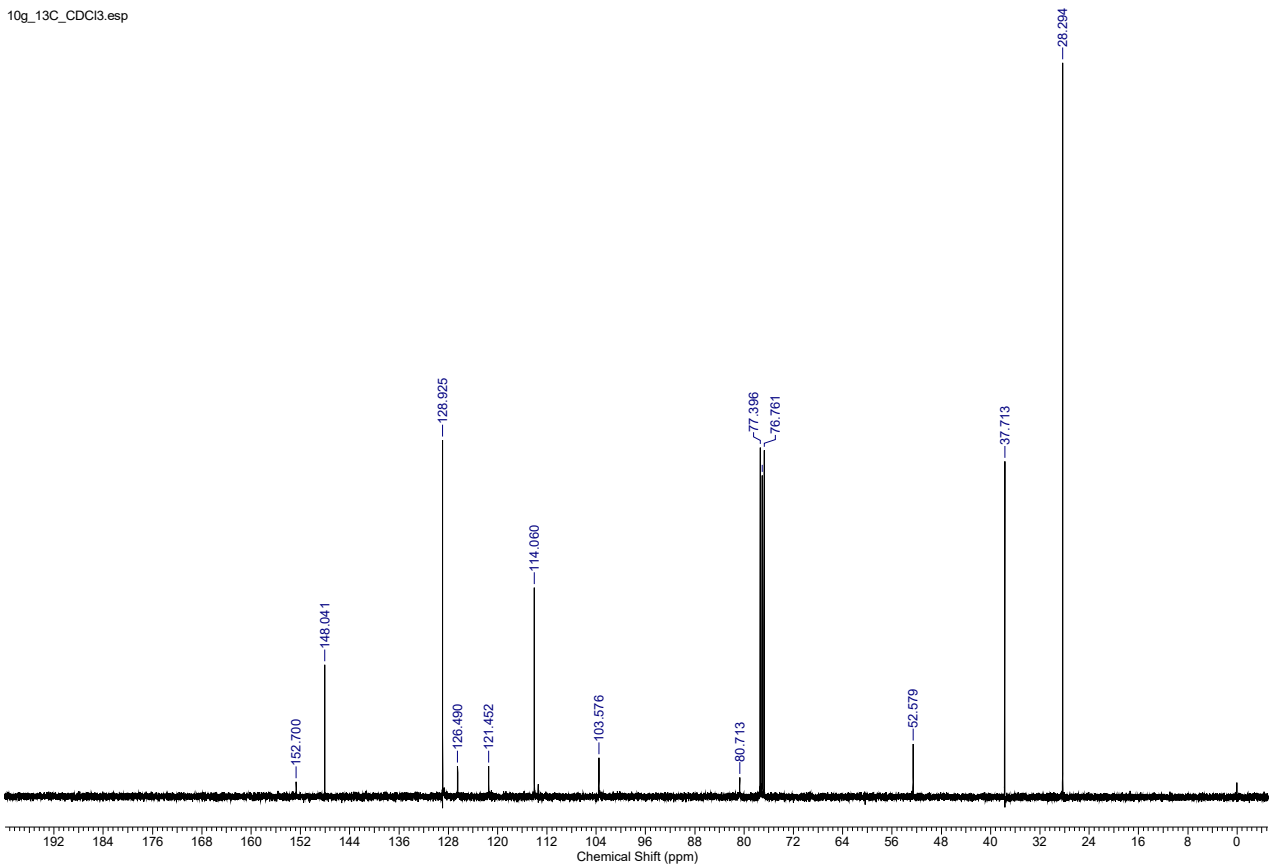
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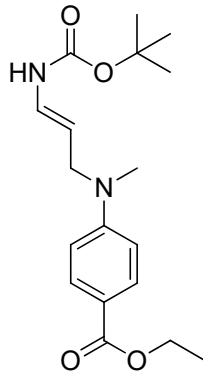
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(¹H: CDCl₃, ¹³C: CDCl₃)



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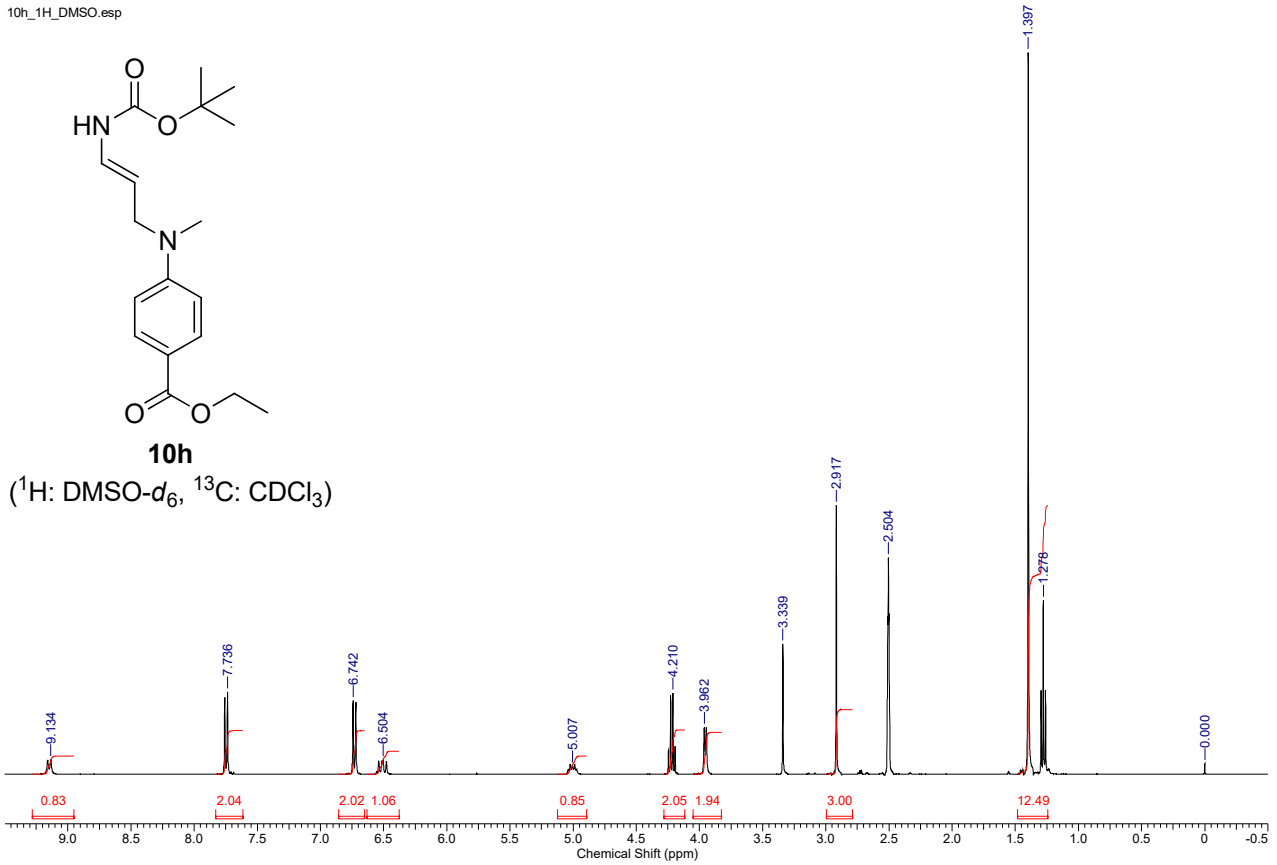


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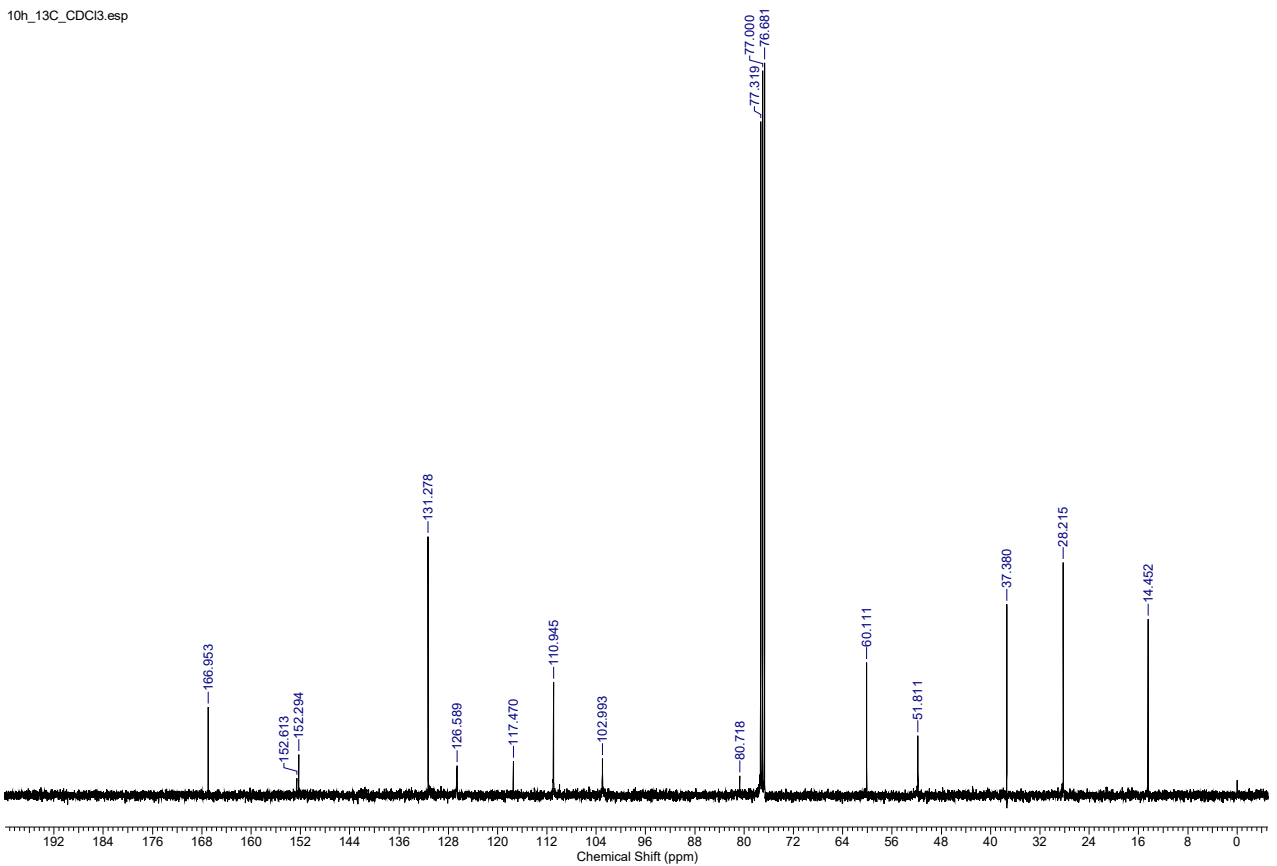


10h

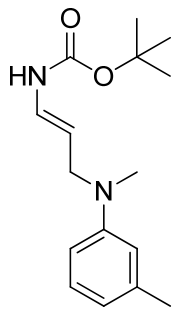
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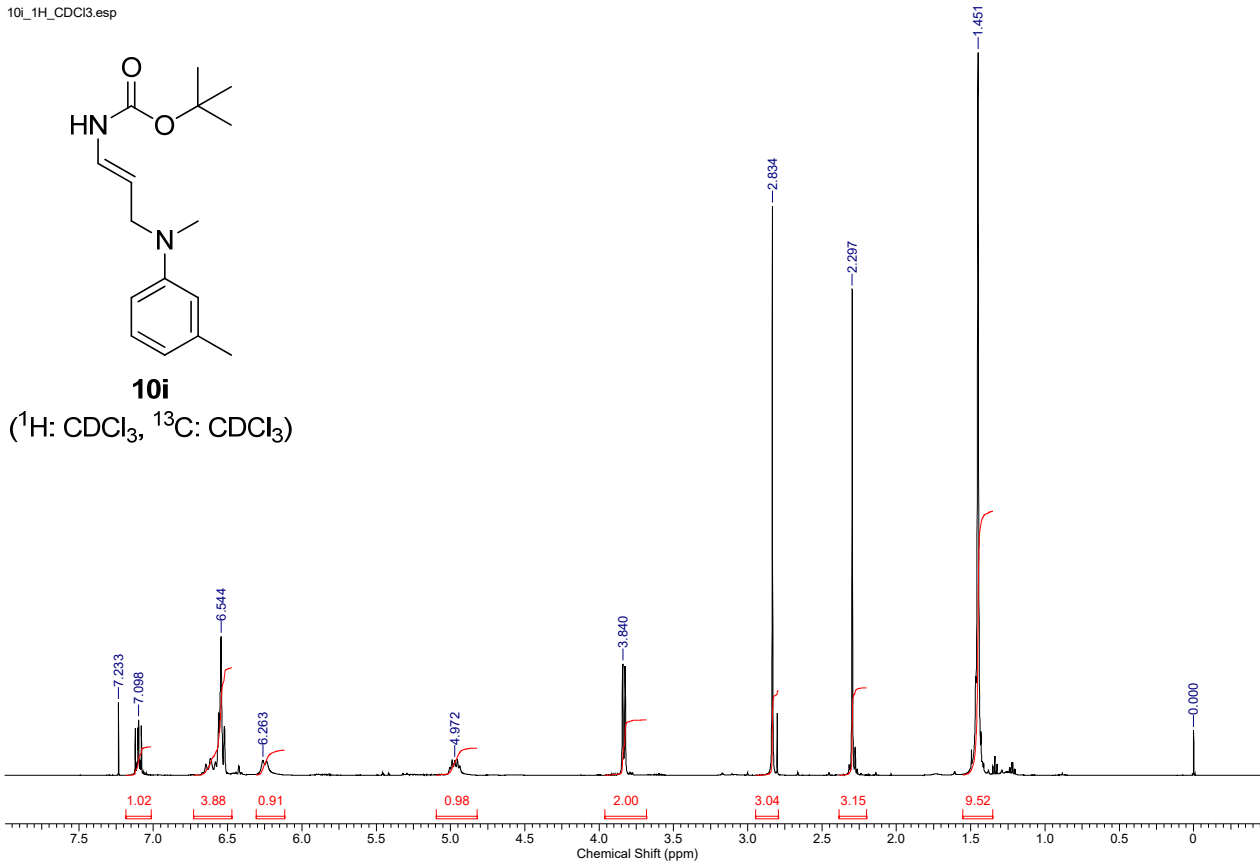


10i_1H_CDCl3.esp

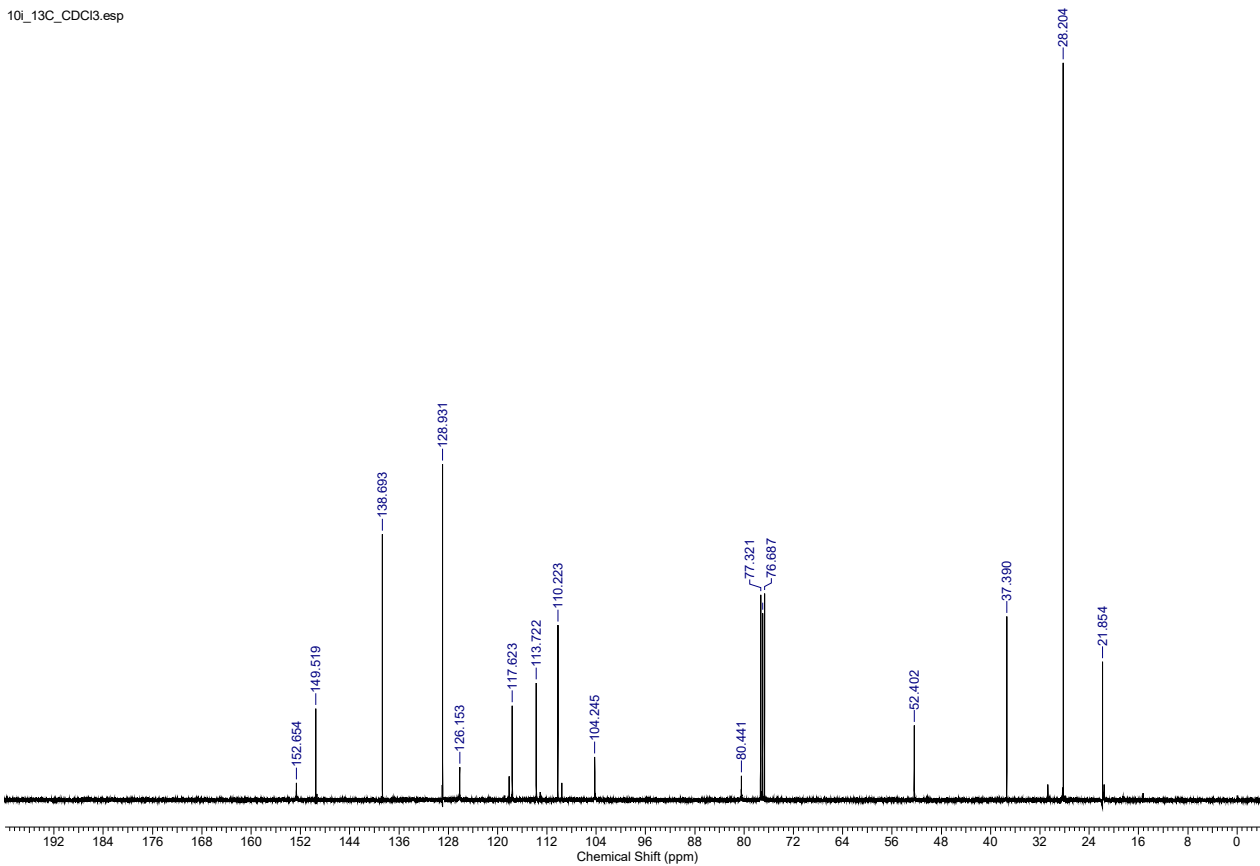


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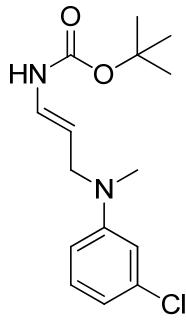
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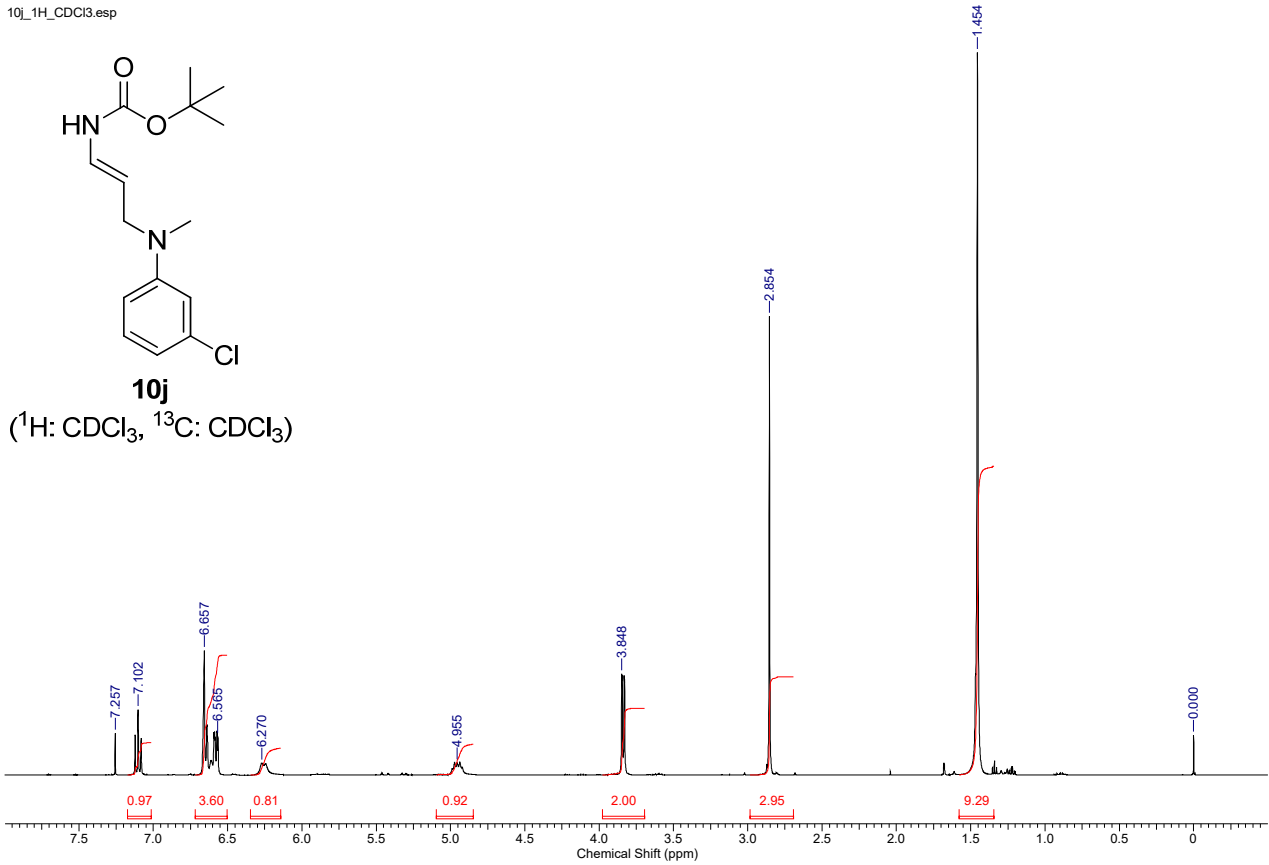


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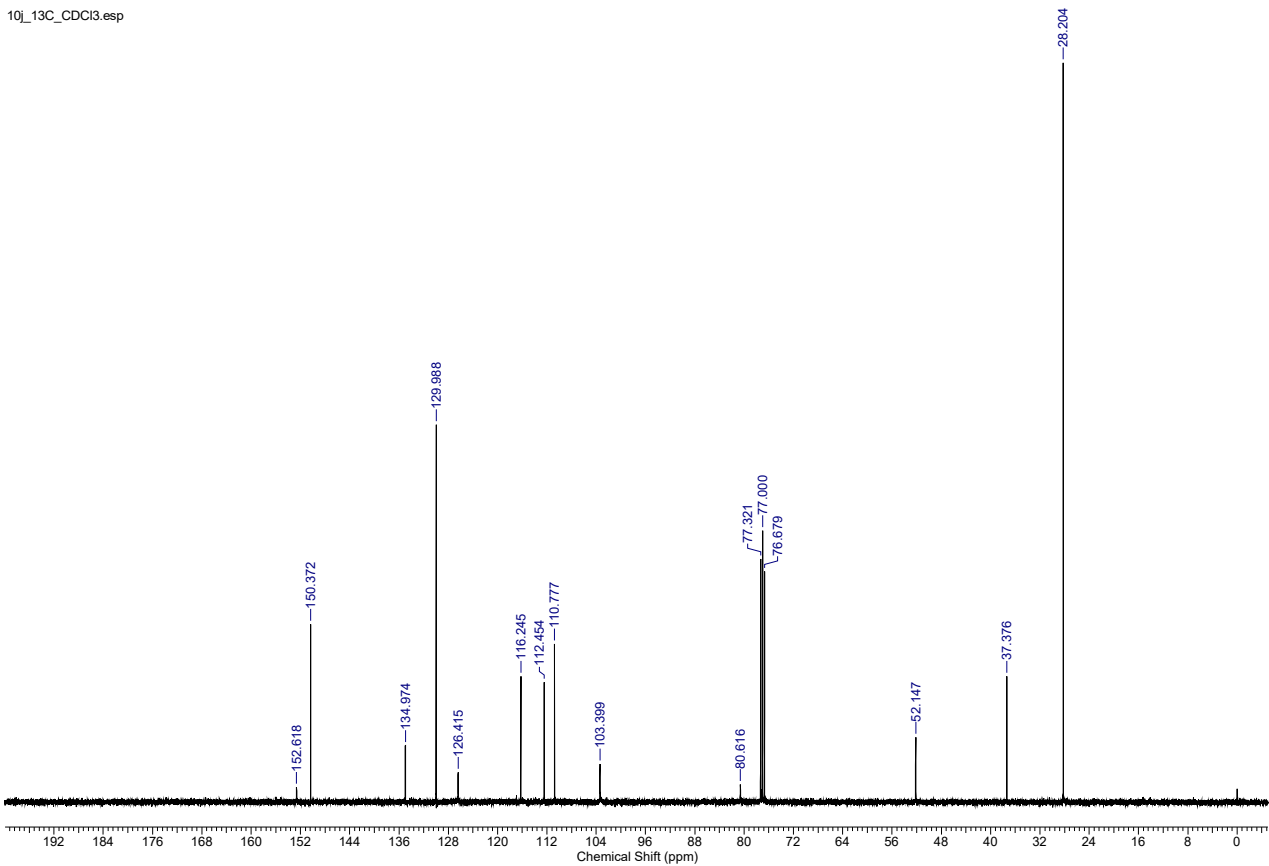


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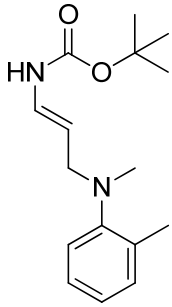
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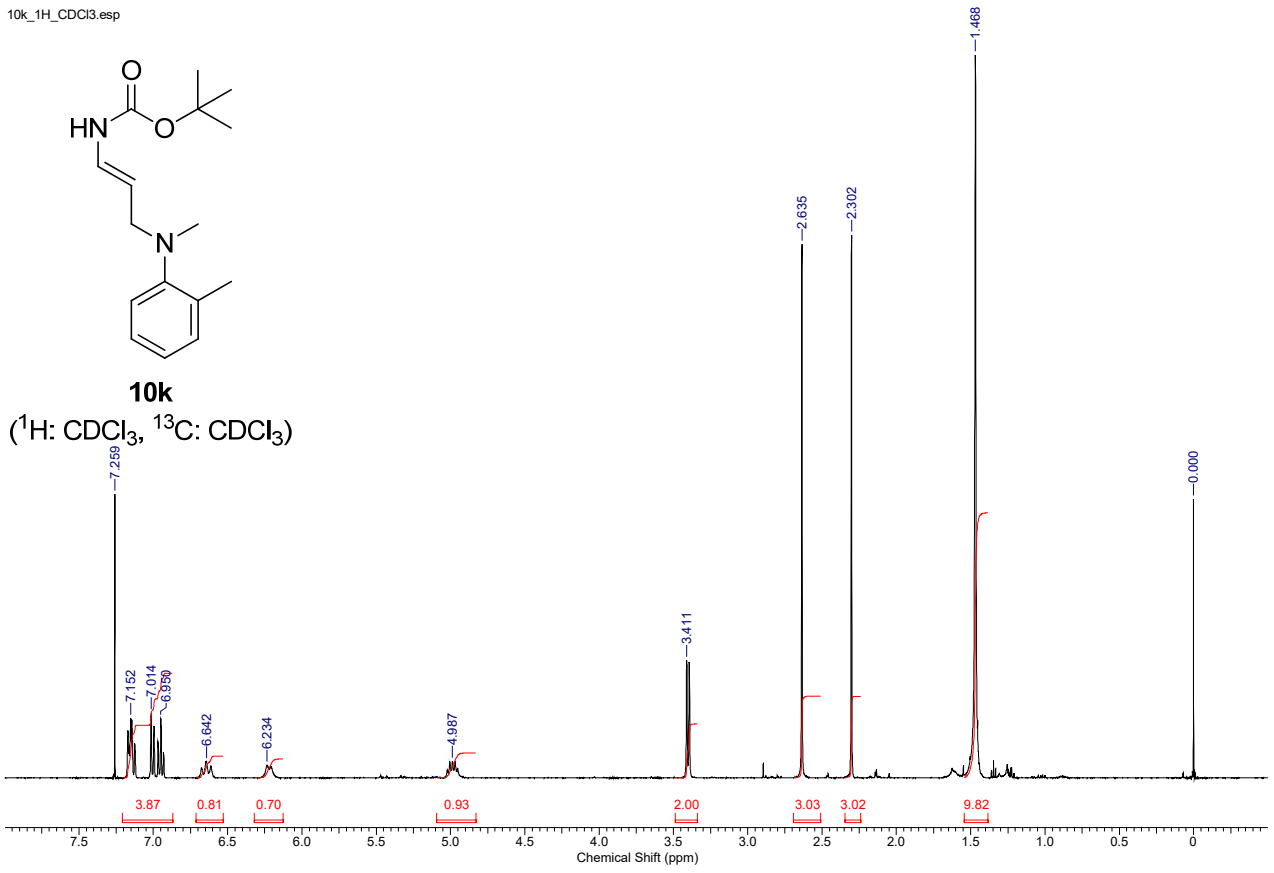
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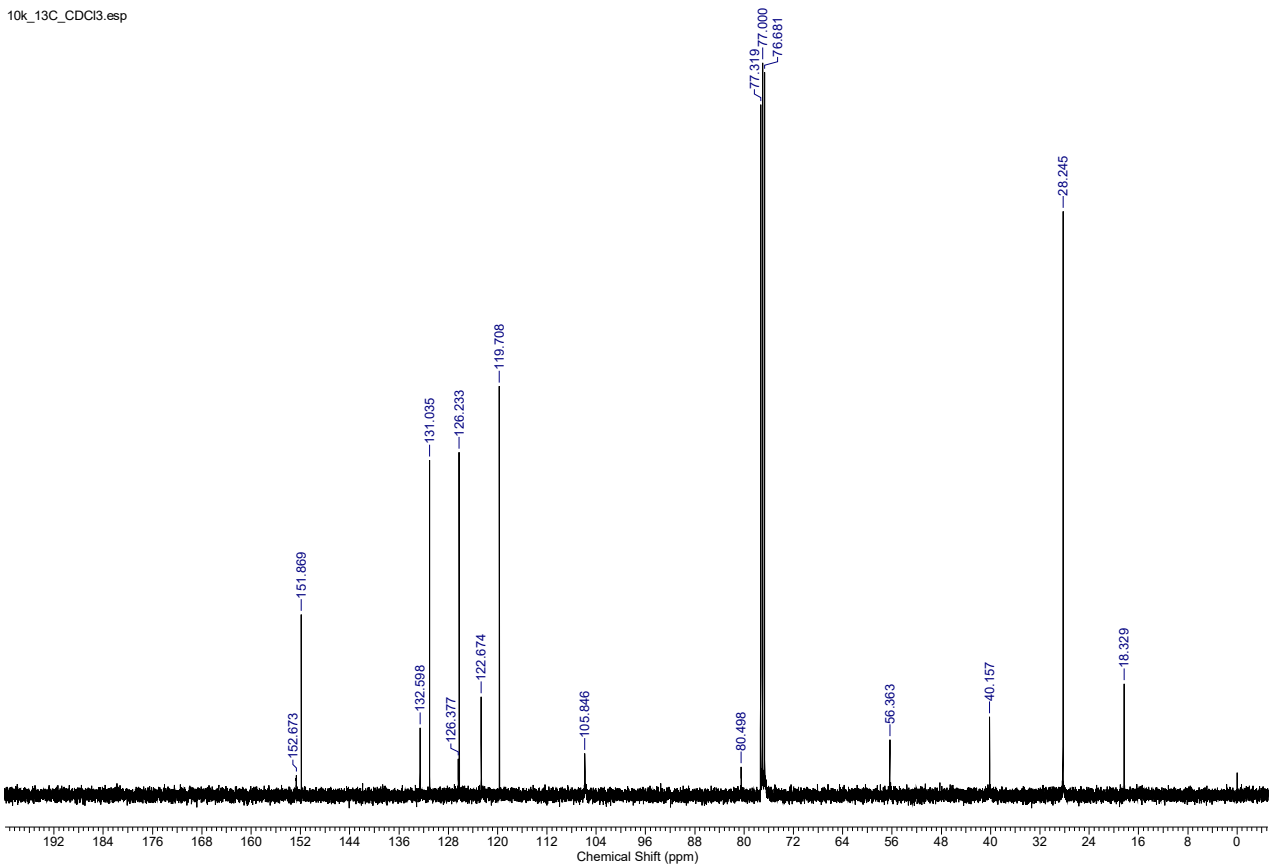
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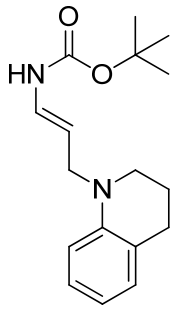
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(¹H: CDCl₃, ¹³C: CDCl₃)



10k_13C_CDCl3.esp

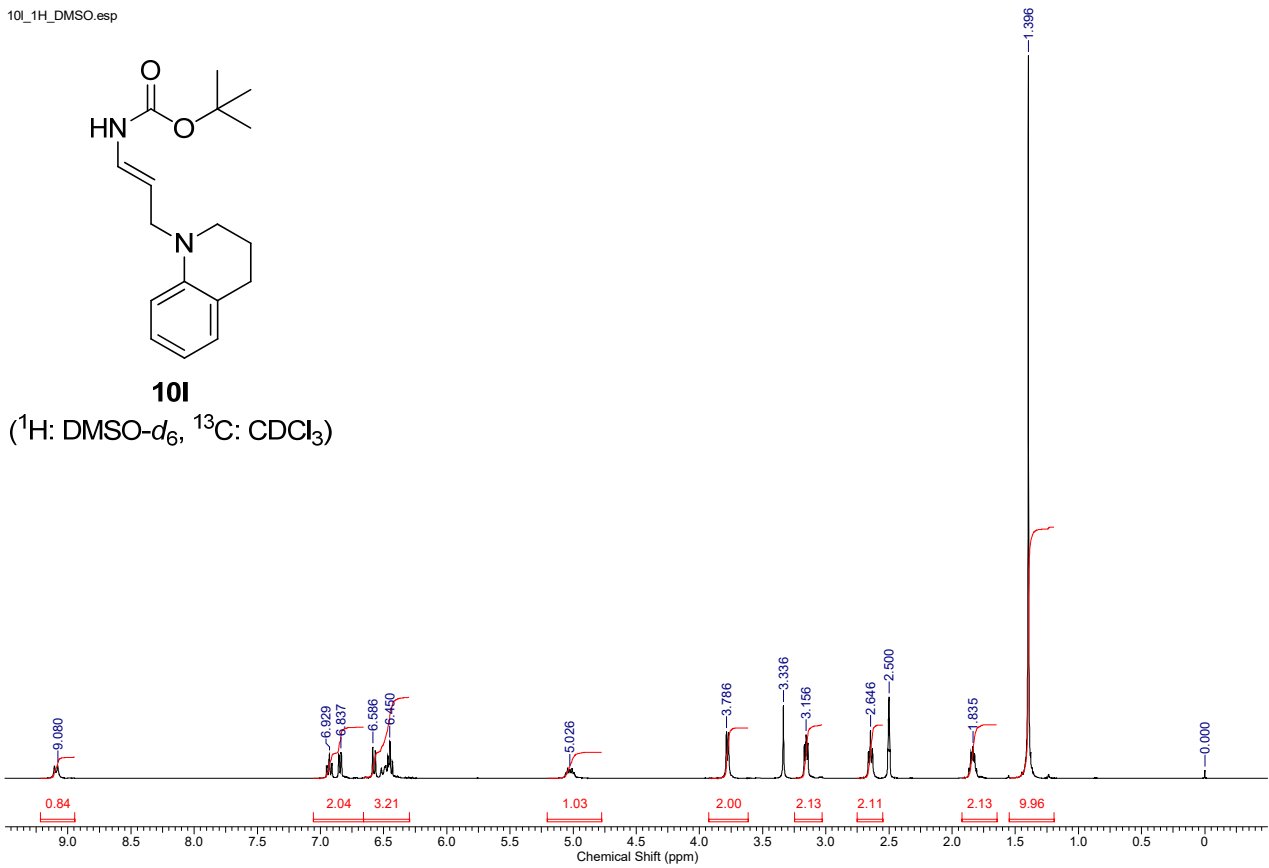


10I_1H_DMSO.esp

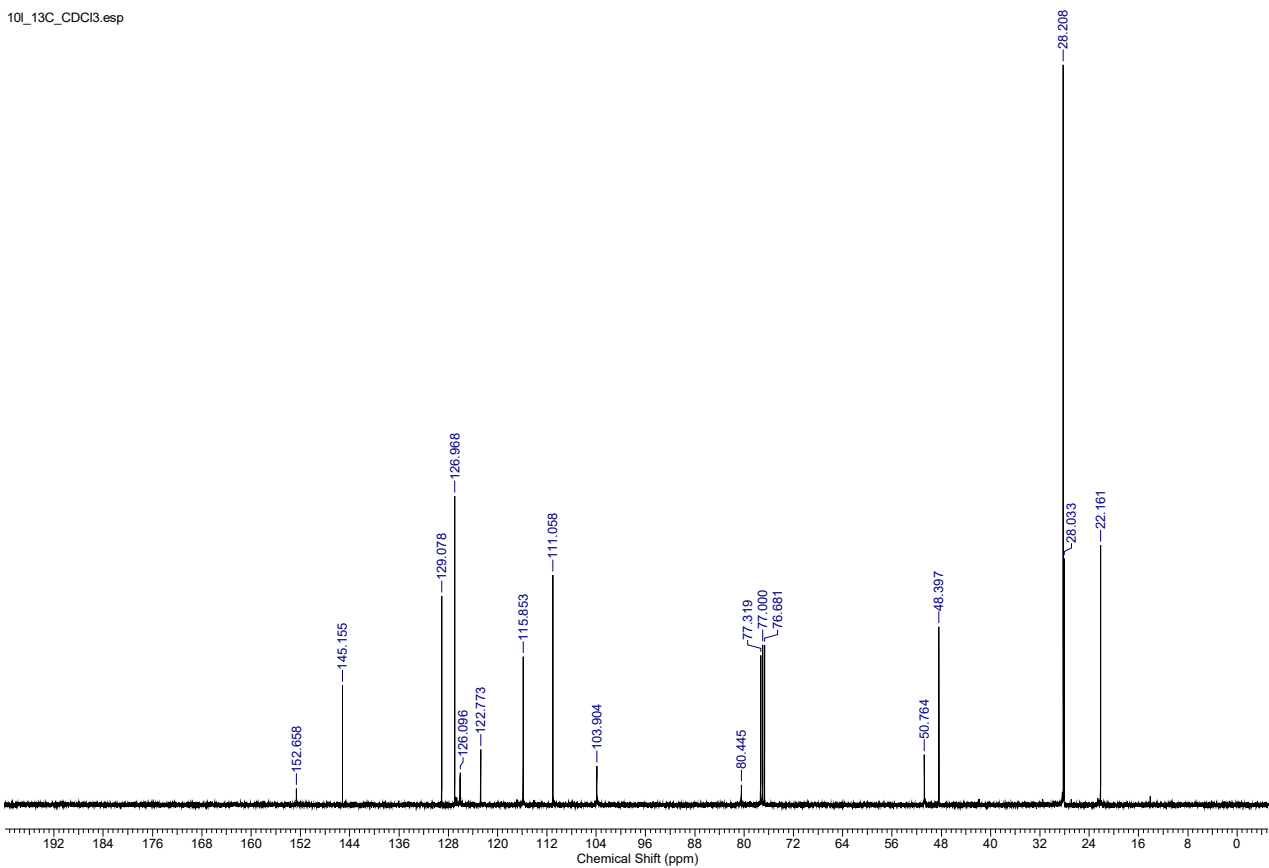


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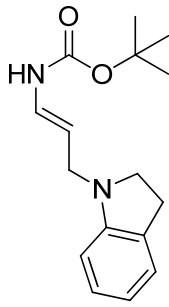
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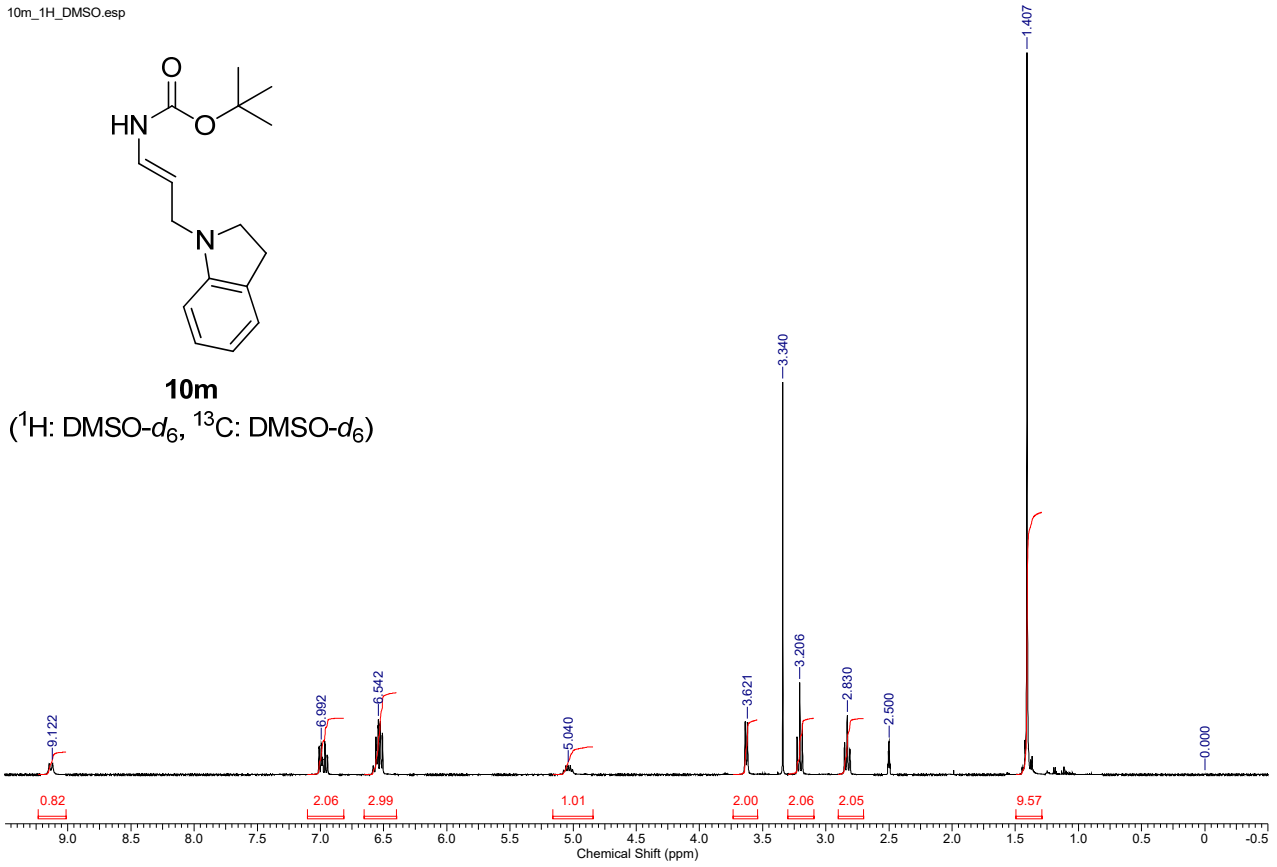
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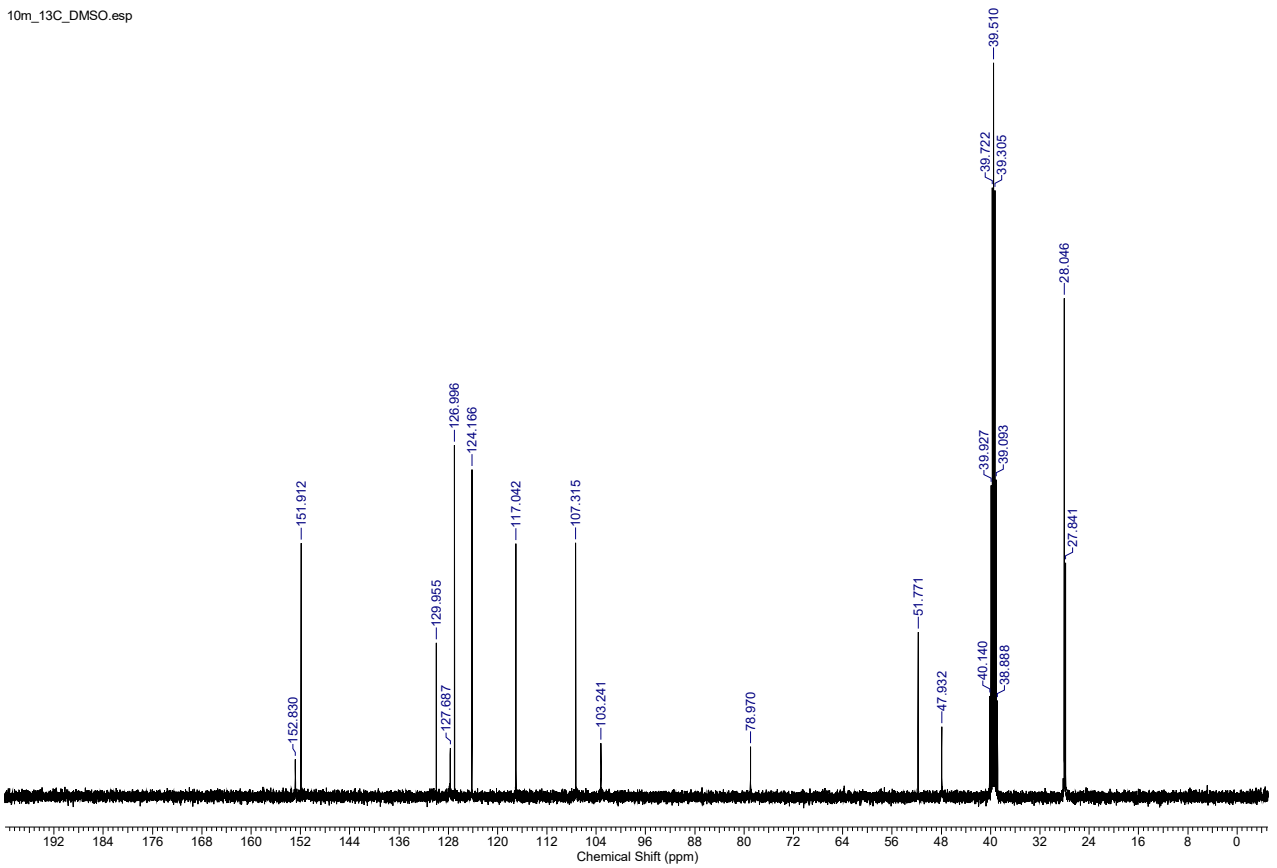
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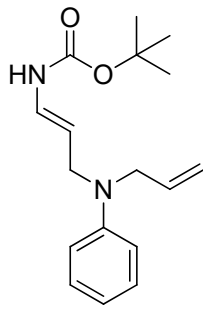
10m
(¹H: DMSO-d₆, ¹³C: DMSO-d₆)



10m_13C_DMSO.esp

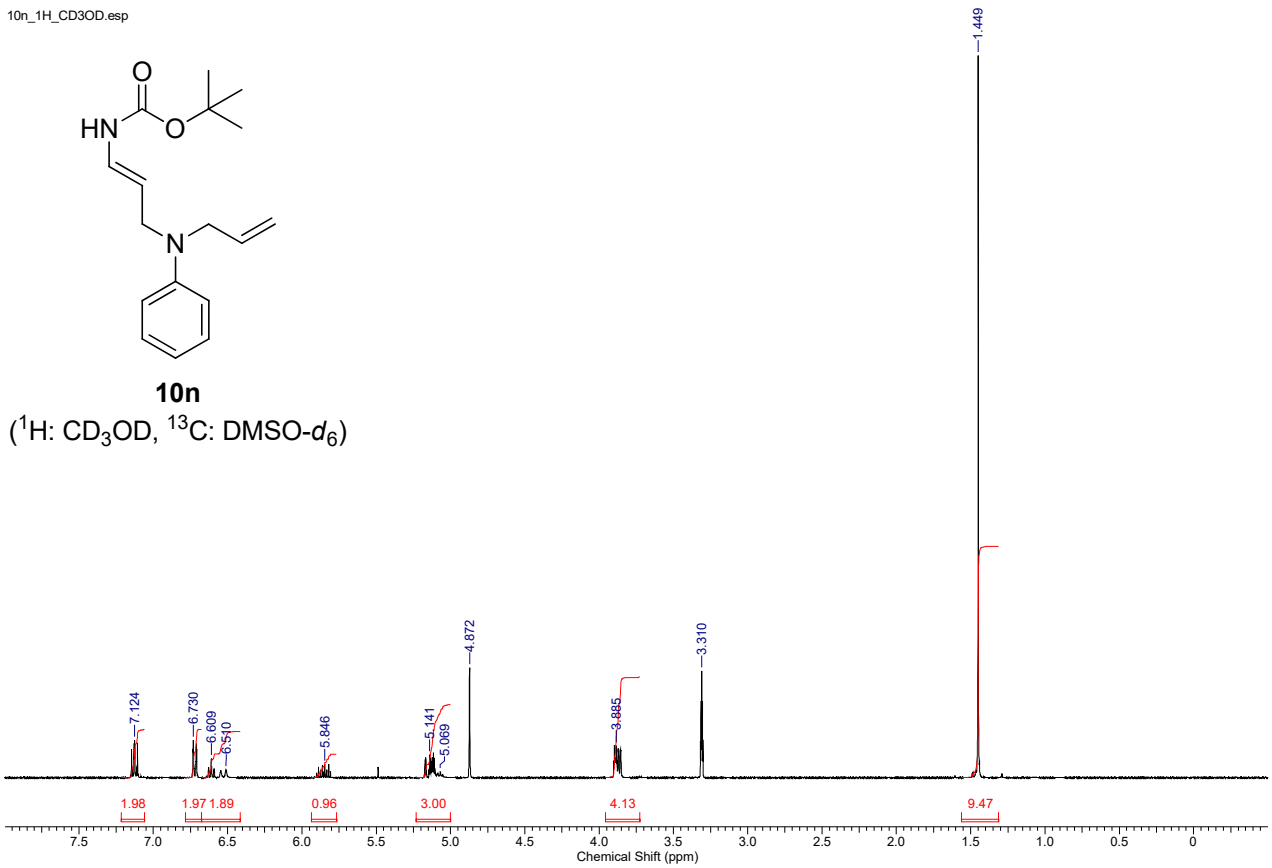


10n_1H_CD3OD.esp

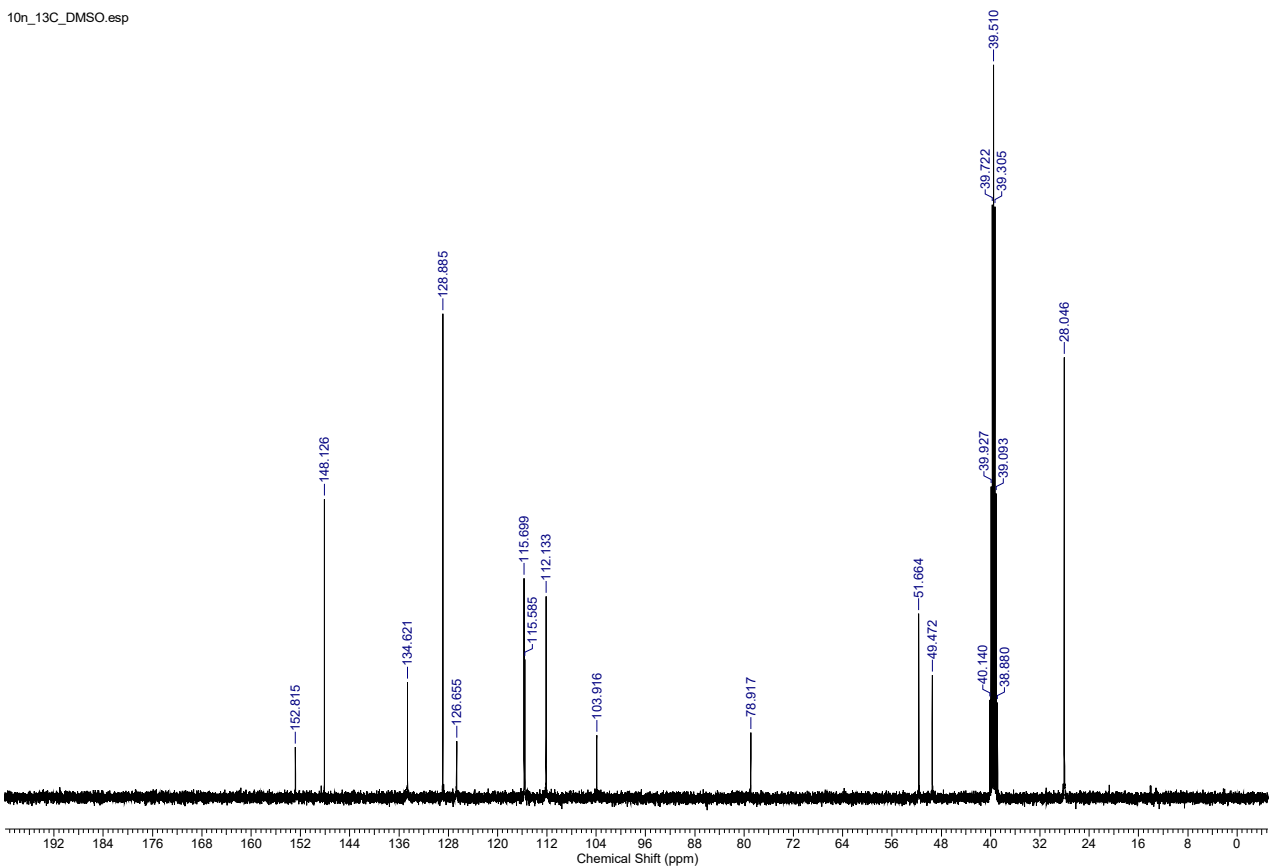


10n

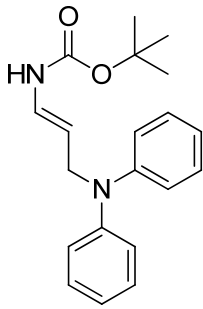
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10n_13C_DMSO.esp

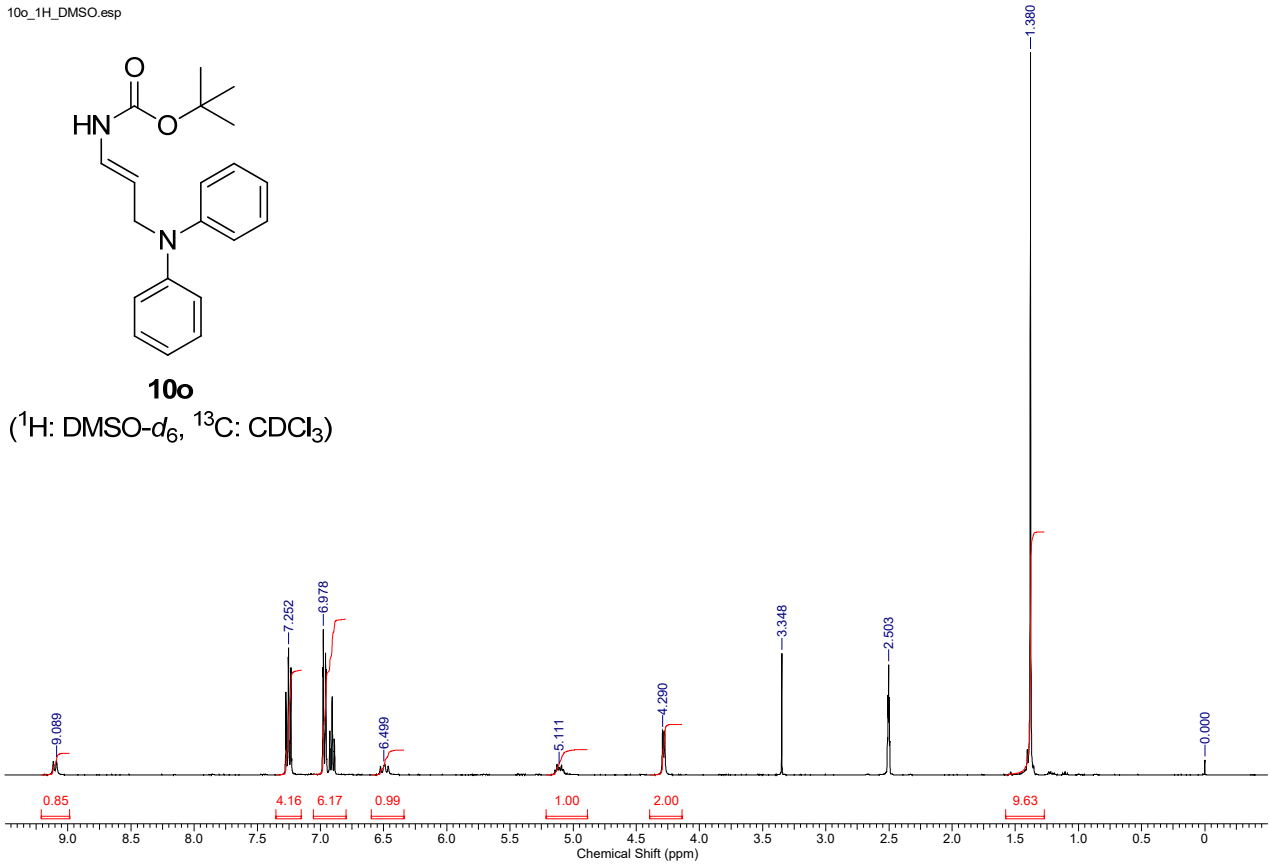


10o_1H_DMSO.esp

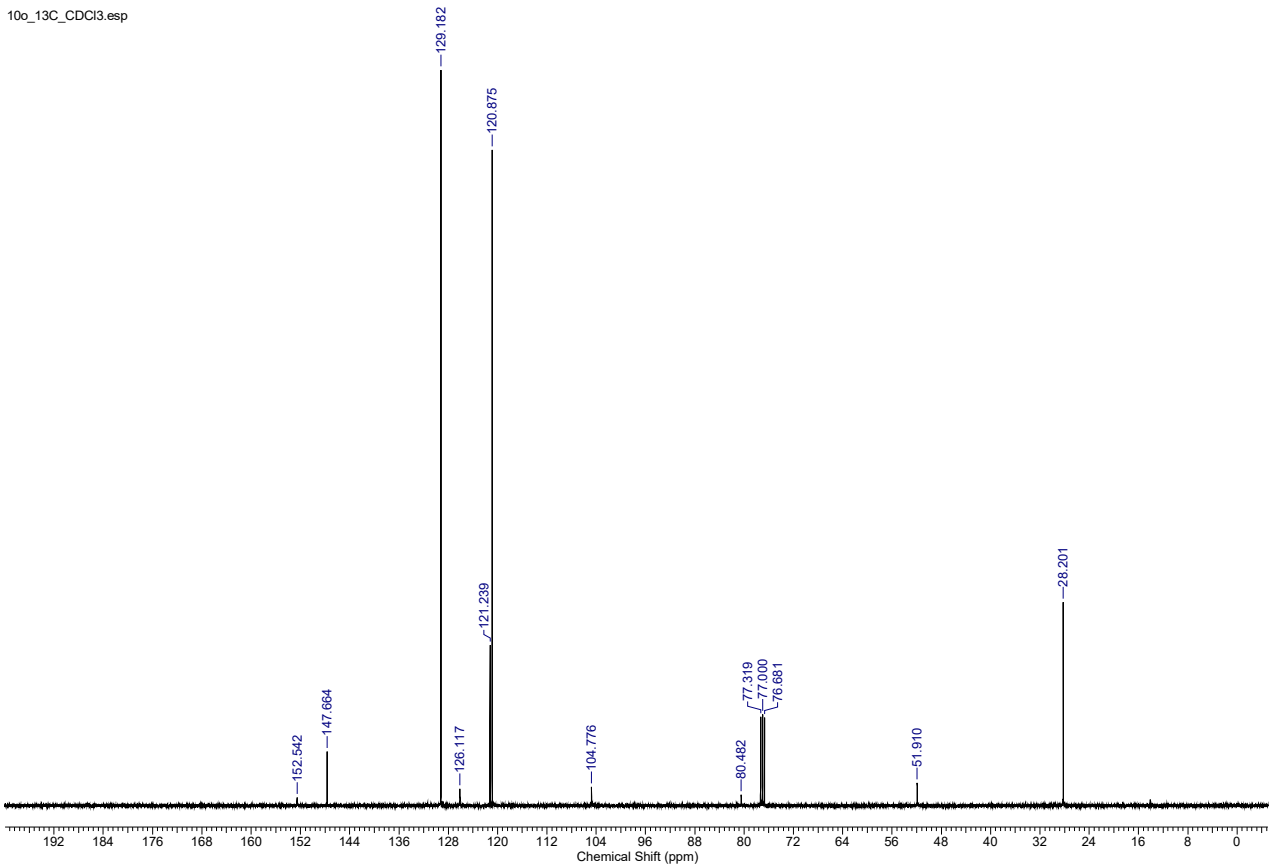


10o

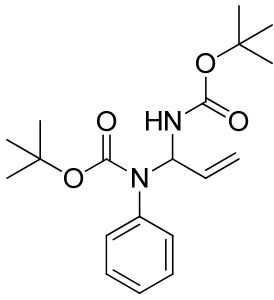
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10o_13C_CDCl3.esp

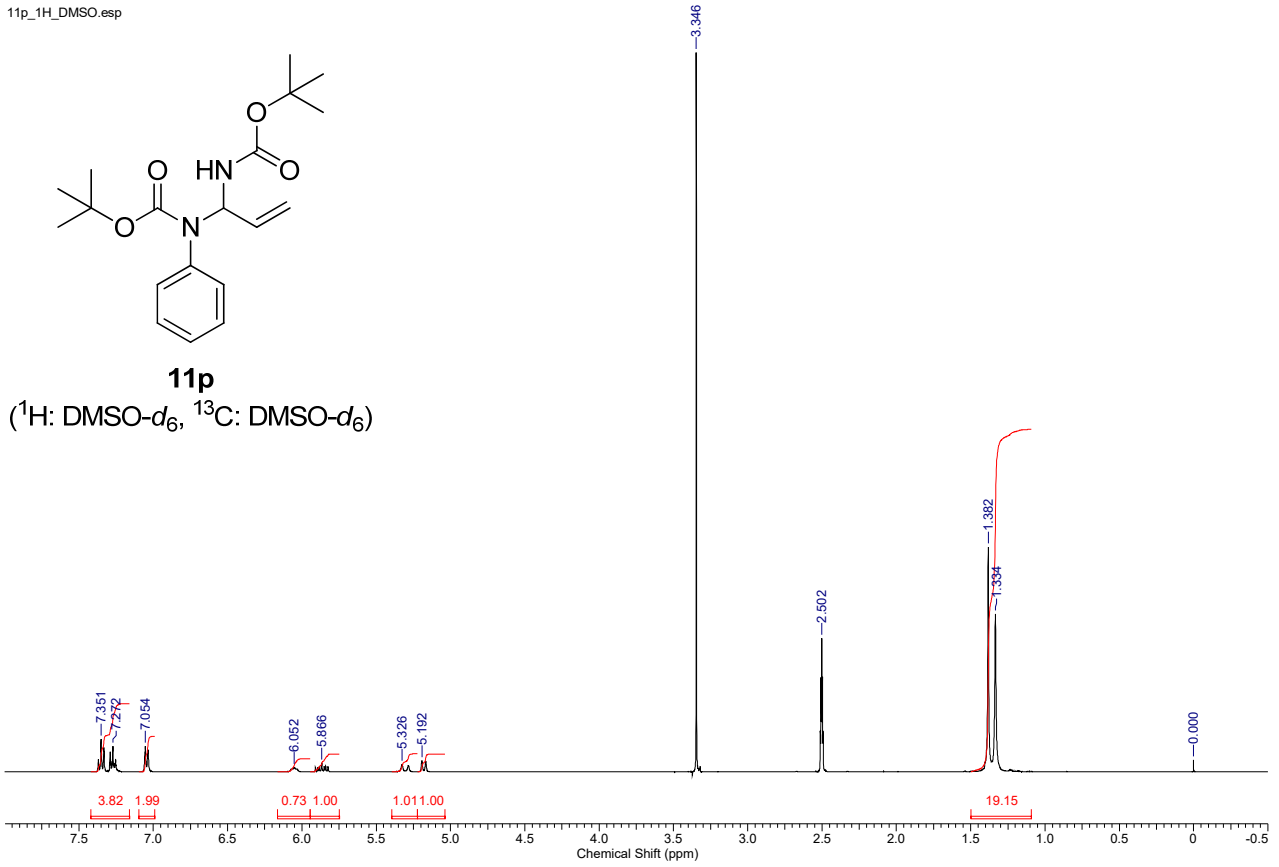


11p_1H_DMSO.esp

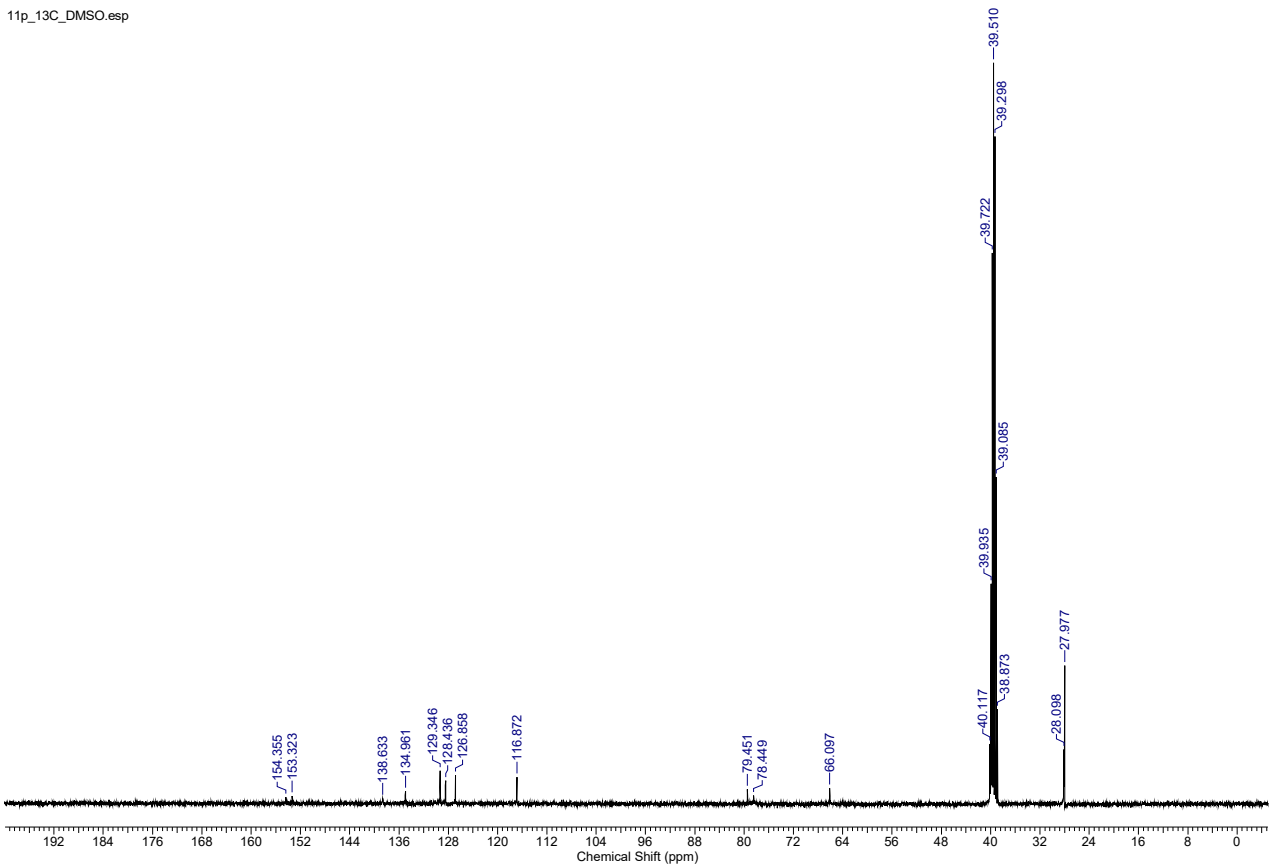


11p

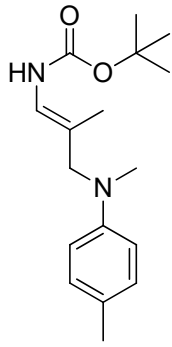
(¹H: DMSO-d₆, ¹³C: DMSO-d₆)



11p_13C_DMSO.esp

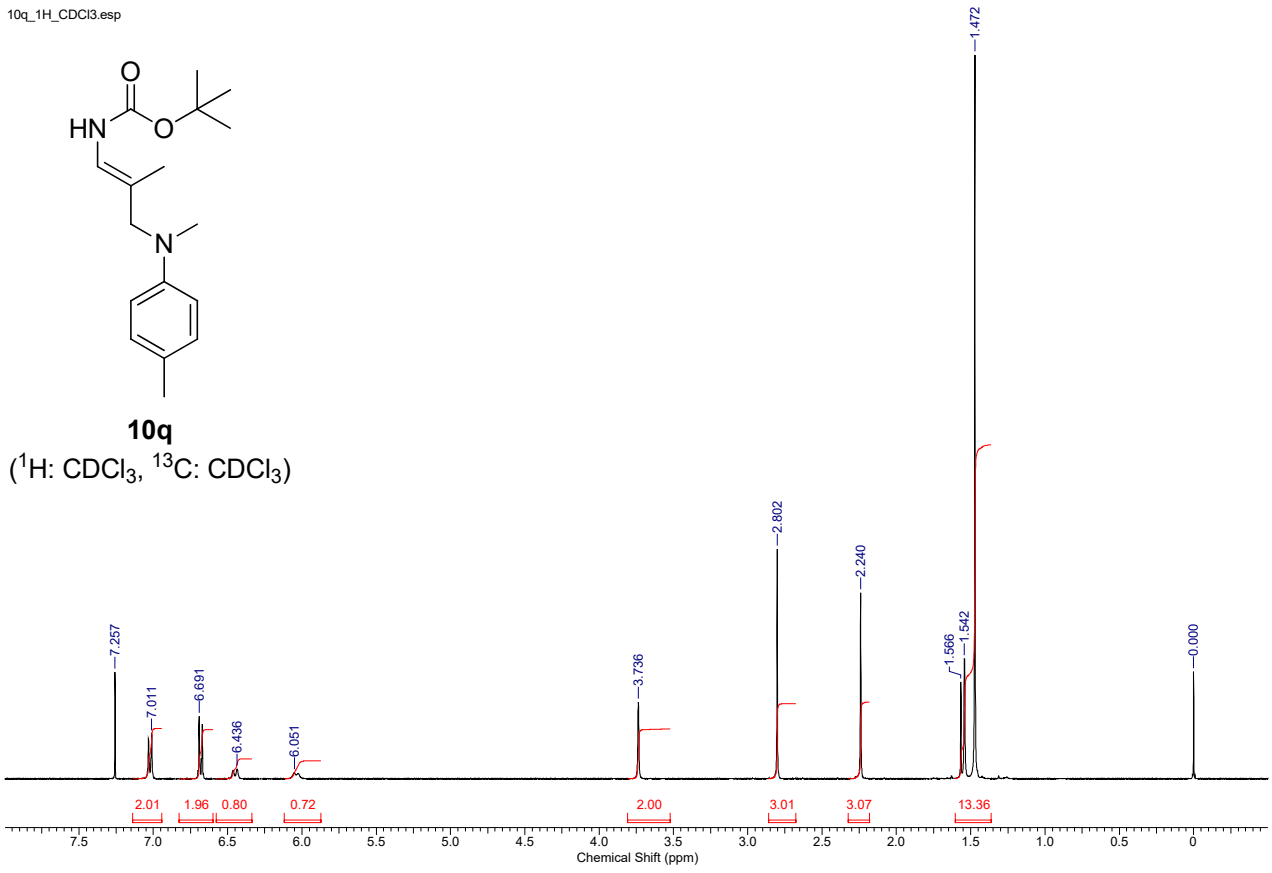


10q_1H_CDCl3.esp



10q

(¹H: CDCl₃, ¹³C: CDCl₃)



10q_13C_CDCl3.esp

