Supporting information

Positional Isomerization of *N*-Allyl Compounds with a Practical Low-Valent Cobalt Catalyst System

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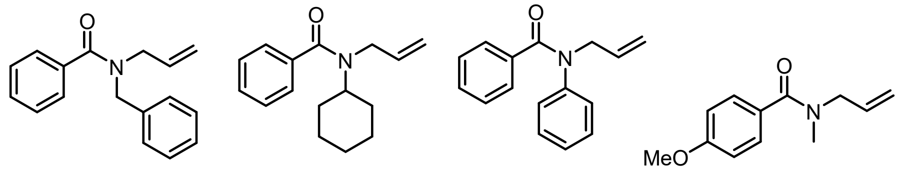
1. Experimental Section

Materials and Methods

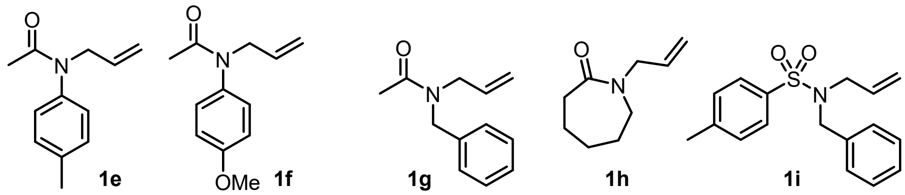
General. Prior to use, all glassware was washed with aqua regia (3:1 (v/v) concentrated HCl/concentrated HNO_3). Dry-flash chromatography was performed on SiO_2 with a particle size of 0.018–0.032 mm, while gravity column chromatography was carried out on SiO_2 with a particle size of 0.063–0.200 mm. IR spectra were recorded on a Thermo-Scientific Nicolet 6700 FT-IR Diamond Crystal instrument. Melting points were determined on a Boetius PMHK apparatus and are not corrected. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Ultrashield Avance III spectrometer (at 500 and 126 MHz, respectively) and Varian spectrometer (at 400 and 101 MHz, respectively) using $CDCl_3$ as the solvent. Chemical shifts are expressed in parts per million (ppm) on the (δ) scale. Chemical shifts were calibrated relative to those of the solvent or TMS.

Materials. Unless stated otherwise, all solvents and reagents were obtained from commercial sources and used without further purification. Zinc powder (-100 mesh, 99.9% (metals basis)) was purchased from Thermo Fisher Scientific. $CoBr_2$ (99%) was purchased from Merck. MeCN was distilled over CaH_2 and stored over molecular sieves (4Å) and under argon. Prior to use, MeCN was degassed by bubbling argon for 5 min.

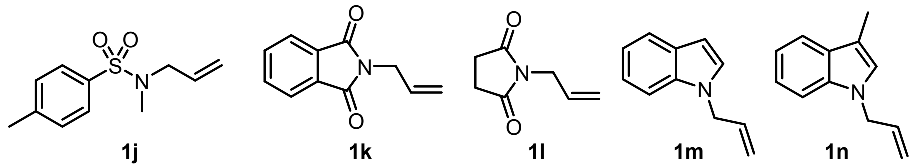
Preparation of Starting Materials



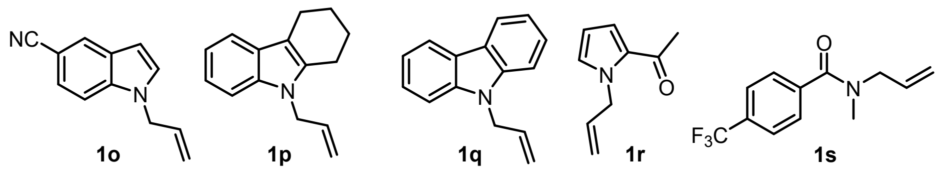
1a **1b** **1c** **1d**



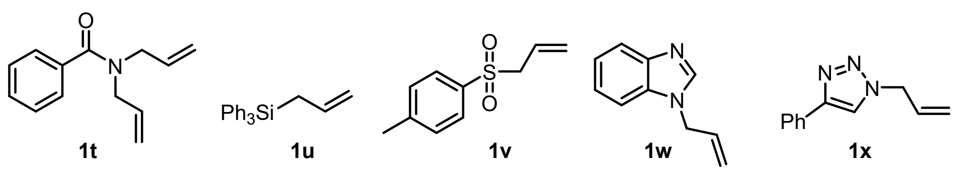
1e **1f** **1g** **1h** **1i**



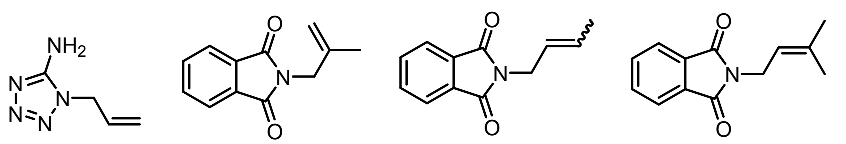
1j **1k** **1l** **1m** **1n**



1o **1p** **1q** **1r** **1s**



1t **1u** **1v** **1w** **1x**



1y **1z** **1aa** **1ab**

Compounds **1a**,[1] **1b**,[2] **1c**[3], **1d-1g**,[1] **1h**,[4] **1i**,[1] **1j**,[1] **1k**,[5] **1l**,[6] **1m**,[7] **1n**,[8] **1o**,[8] **1p**,[9] **1q**,[10] **1r**,[11] **1s**,[1] **1t**,[12] **1u**,[13] **1v**,[14] **1w**,[15] **1x**,[16] **1y**[17], **1z**,[18] **1aa**[19] and **1ab**[20] were synthesized according to the previously reported procedures.

Procedure for Zn activation

Zinc powder was freshly activated before use. Activation process comprised stirring in 5% HCl for 7 minutes, washing with water and acetone and drying *in vacuo*.

General procedure A

An oven-dried 5 mL vial with a stirring bar was charged sequentially with $CoBr_2$ (4.9 mg, 0.022 mmol, 0.1 eq), dppe (17.8 mg, 0.045 mmol, 0.2 eq), acetonitrile (0.5 mL), ZnI_2 (71.3 mg, 0.223 mmol, 1 eq (for **1a**-**1f**, **1i**-**1k** and **1s**) or 21.4 mg, 0.067 mmol, 0.3 eq (for **1m**-**1q**)) and activated zinc powder (4.4 mg, 0.067 mmol, 0.3 eq). The resulting mixture was bubbled with argon for 2 minutes, capped and stirred at room temperature for 10 min. A solution of compound **1** (0.223 mmol, 1 eq) in acetonitrile (1.7 mL) was then added. The mixture was purged with argon for an additional 2 min, sealed, and stirred at 80 °C in an oil bath for 16 h. Upon cooling to room temperature, the reaction mixture was diluted with CH_2Cl_2 (15 mL), filtered through a short pad of silica gel and the pad was washed with EtOAc (30 mL). The organic solution was concentrated under reduced pressure, and the residue was purified by chromatography on silica gel to afford the desired product **2**.

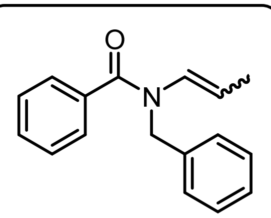
General procedure B

An oven-dried 5 mL vial with a stirring bar was charged sequentially with $CoBr_2$ (4.9 mg, 0.022 mmol, 0.1 eq), dppe (17.8 mg, 0.045 mmol, 0.2 eq), acetonitrile (0.5 mL), ZnI_2 (71.3 mg, 0.223 mmol, 1 eq (for **1g**, **1h** and **1l**) or 21.4 mg, 0.067 mmol, 0.3 eq (for **1r**)) and activated zinc powder (4.4 mg, 0.067 mmol, 0.3 eq). The resulting mixture was bubbled with argon for 2 minutes, capped and stirred at room temperature for 10 min. A solution of compound **1** (0.223 mmol, 1 eq) in acetonitrile (1.7 mL) was then added. The mixture was purged with argon for an additional 2 min, sealed, and stirred at 80 °C in an oil bath for 16 h. Upon cooling to room temperature, the reaction mixture was diluted with CH_2Cl_2 (15 mL) and washed with brine (2 x 30 mL). The combined aqueous layers were extracted with CH_2Cl_2 (10 mL), and the combined organic layers were washed with brine (20 mL). The organic phase was dried over anhydrous Na_2SO_4, concentrated under reduced pressure, and the residue was purified by chromatography on silica gel to afford the desired product **2**.

Representative 1 mmol scale

Following the general procedure A, reaction was performed using **1a** (251.3 mg, 1.0 mmol), $CoBr_2$ (21.9 mg, 0.1 mmol), dppe (79.7 mg, 0.2 mmol), Zn (19.6 mg, 0.3 mmol), ZnI_2 (319.2 mg, 1.0 mmol) and 9.8 mL of CH_3CN in oven-dried 18 mL ace pressure tube at 80 °C for 16 h, followed by dry-flash column chromatography (Hexane/EtOAc = 7/3) to afford **2a** (246.3 mg, 98%) as inseparable mixture of (*E*)-**2a** and (*Z*)-**2a** (colorless oil). The *E*/*Z* ratio (89/11) was determined by integration of well-resolved signals in the ^{1}H NMR spectrum.

***N*-benzyl-*N*-(1-propenyl)benzamide (2a).**[2,21]


2a

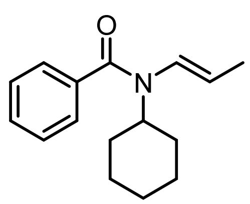
Following the general procedure A, reaction was performed using **1a** (56.1 mg, 0.223 mmol), $CoBr_2$ (4.9 mg, 0.022 mmol), dppe (17.8 mg, 0.045 mmol), Zn (4.4 mg, 0.067 mmol) and ZnI_2 (71.3 mg, 0.223 mmol) in the 2.2 mL of CH_3CN at 80 °C for 16 h, followed by dry-flash column chromatography (Hexane/EtOAc = 7/3) to afford **2a** (55.6 mg, 99%) as inseparable mixture of (*E*)-**2a** and (*Z*)-**2a** (colorless oil). The *E*/*Z* ratio (*E*/*Z* = 89/11) was determined by integration of well-resolved signals in the ^{1}H NMR spectrum. A slightly different ratio (*E*/*Z* = 91/9) was obtained from GC–MS analysis.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.63 – 7.06 (m, 10H (*E*)-**2a** and 10H (*Z*)-**2a**), 6.47 (d, *J* = 13.5 Hz, 1H (*E*)-**2a**), 6.00 (d, *J* = 8.0 Hz, 1H (*Z*)-**2a**), 5.21 – 4.63 (m, 3H (*E*)-**2a** and 3H (*Z*)-**2a**), 1.78 – 1.43 (m, 3H (*E*)-**2a** and 3H (*Z*)-**2a**) ppm.

^{13}C NMR (126 MHz, Chloroform-*d*) δ 170.4, 137.4, 135.8, 130.3, 130.0, 128.8, 128.5, 128.2, 127.2, 127.0, 107.6, 47.4, 15.5 ppm.

IR (ATR): 3062, 3031, 2922, 2855, 1644, 1603, 1578, 1496, 1446, 1400, 1375, 1321, 1286, 1237, 1218, 1150, 1096, 1077, 1029, 975, 942, 788, 731, 699, 659, 621 cm^{-1}.

***N*-cyclohexyl-*N*-(1-propenyl)benzamide (2b).**[2]



2b

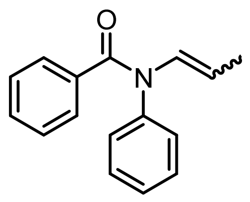
Following the general procedure A, reaction was performed using **1b** (54.4 mg, 0.223 mmol), $CoBr_2$ (4.9 mg, 0.022 mmol), dppe (17.8 mg, 0.045 mmol), Zn (4.4 mg, 0.067 mmol) and ZnI_2 (71.3 mg, 0.223 mmol) in the 2.2 mL of CH_3CN at 80 °C for 16 h, followed by dry-flash column chromatography (Hexane/EtOAc = 7/3) to afford (*E*)-**2b** (51.1 mg, 94%) as colorless oil (*E*/*Z* > 95/5).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.49 – 7.44 (m, 1H), 7.43 – 7.37 (m, 1H), 7.36 – 7.24 (m, 3H), 6.06 – 5.92 (m, 1H), 5.36 – 5.07 (m, 1H), 4.58 – 4.26 (m, 1H), 1.93 – 1.75 (m, 4H), 1.72 – 1.02 (m, 9H) ppm.

^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.6, 170.4, 137.7, 137.5, 129.5, 129.3, 128.3, 128.1, 127.9, 127.5 (127.51), 127.5 (127.46), 127.0, 125.6, 55.2, 54.9, 30.6, 30.3, 25.9, 25.8, 25.7, 15.3, 12.7 ppm.

IR (ATR): 3029, 2931, 2856, 1637, 1580, 1493, 1448, 1399, 1357, 1314, 1265, 1212, 1178, 1155, 1135, 1075, 1029, 952, 925, 894, 804, 785, 747, 720, 698, 631 cm^{-1}.

***N*-phenyl-*N*-(1-propenyl)benzamide (2c).**[2]



2c

Following the general procedure A, reaction was performed using **1c** (53.0 mg, 0.223 mmol), $CoBr_2$ (4.9 mg, 0.022 mmol), dppe (17.8 mg, 0.045 mmol), Zn (4.4 mg, 0.067 mmol) and ZnI_2 (71.3 mg, 0.223 mmol) in the 2.2 mL of CH_3CN at 80 °C for 16 h, followed by dry-flash column chromatography (Hexane/EtOAc = 9/1) to afford (*E*)-**2c** (42.9 mg, 78%) as colorless solid (m.p. = 79 – 81 °C) and a mixture of (*Z*)-**2c** and inseparable impurities. The yield of (*Z*)-**2c** (3.2 mg, 6%) was determined by quantitative ^{1}H NMR analysis of the isolated mixture using methyl benzoate as an internal standard. The identity of (*Z*)-**2c** was further confirmed by GC-MS analysis ($[M]^+$ = 237). Overall yield of isomerization: 87%, *E*/*Z* ratio = 93/7.

<u>(*E*)-**2c**</u>

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.42 – 7.15 (m, 9H), 7.13 – 7.07 (m, 2H), 4.79 – 4.69 (m, 1H), 1.68 (dd, *J* = 6.8, 1.7 Hz, 3H) ppm.

^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.8, 140.4, 135.9, 130.4, 129.9, 129.4, 129.3, 128.7, 127.9, 127.7, 111.3, 15.3 ppm.

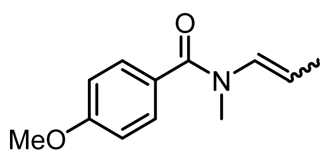
IR (ATR): 3268, 3076, 3056, 2964, 2943, 2921, 2881, 2856, 1642, 1599, 1578, 1493, 1448, 1386, 1360, 1319, 1298, 1267, 1161, 1116, 1077, 1027, 1000, 949, 926, 876, 849, 793, 780, 731, 702, 655, 636 cm^{-1}.

(*Z*)-**2c**

Characteristic peaks:

^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.40 (dd, *J* = 8.4, 1.8 Hz, 1H), 5.36 – 5.27 (m, 1H), 1.33 (dd, *J* = 7.1, 1.8 Hz, 3H) ppm.

4-methoxy-*N*-methyl-*N*-(1-propenyl)benzamide (2d).[1,2]


2d

Following the general procedure A, reaction was performed using **1d** (45.9 mg, 0.223 mmol), $CoBr_2$ (4.9 mg, 0.022 mmol), dppe (17.8 mg, 0.045 mmol), Zn (4.4 mg, 0.067 mmol) and ZnI_2 (71.3 mg, 0.223 mmol) in the 2.2 mL of CH_3CN at 80 °C for 16 h, followed by dry-flash column chromatography (Hexane/EtOAc = 7/3) to afford **2d** (29.3 mg, 64%) as inseparable mixture of (*E*)-**2d** and (*Z*)-**2d** (colorless oil). The *E*/*Z* ratio (*E*/*Z* = 91/9) was determined by integration of well-resolved signals in the ^{1}H NMR spectrum.

(*E*)-**2d**:

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.45 – 7.40 (m, 2H), 6.93 – 6.88 (m, 2H), 6.60 (s, 1H), 5.08 – 4.94 (m, 1H), 3.83 (s, 3H), 1.65 (s, 3H) ppm.

^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.9, 161.1, 130.1 (130.13), 130.1 (130.13), 127.9, 113.7, 105.6, 55.4 (55.45), 55.4 (55.38), 15.5 ppm.

(*Z*)-**2d**:

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.54 – 7.47 (m, 2H), 6.85 – 6.81 (m, 2H), 6.13 (d, *J* = 8.1 Hz, 1H), 5.14 – 5.08 (m, 1H), 3.80 (s, 3H), 1.53 (d, *J* = 6.9 Hz, 3H) ppm.

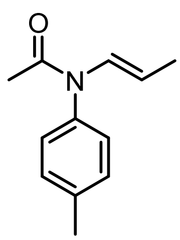
^{13}C NMR (101 MHz, Chloroform-*d*) δ 113.1, 12.6 ppm. (only those two peaks are observed in the spectrum)

Unresolved signals:

^{1}H NMR (400 MHz, Chloroform-*d*) δ 3.18 (s, 3H (*E*)-**2d** and 3H (*Z*)-**2d**) ppm.

IR (ATR): 3494, 3077, 2935, 2839, 1634, 1608, 1576, 1513, 1458, 1417, 1391, 1369, 1303, 1280, 1254, 1173, 1111, 1097, 1070, 1030, 942, 842, 804, 764, 752, 709, 633, 609, 591, 507 cm^{-1}.

***N*-(4-methylphenyl)-*N*-(1-propenyl)acetamide (2e).**[1]



2e

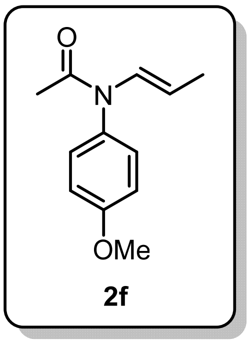
Following the general procedure A, reaction was performed using **1e** (42.3 mg, 0.223 mmol), $CoBr_2$ (4.9 mg, 0.022 mmol), dppe (17.8 mg, 0.045 mmol), Zn (4.4 mg, 0.067 mmol) and ZnI_2 (71.3 mg, 0.223 mmol) in the 2.2 mL of CH_3CN at 80 °C for 16 h, followed by dry-flash column chromatography (Hexane/EtOAc = 7/3) to afford (*E*)-**2e** (34.3 mg, 81%) as colorless solid (m.p. = 66 – 68 °C) (*E*/*Z* > 95/5).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.44 (d, *J* = 14.3 Hz, 1H), 7.29 – 7.22 (m, 2H), 7.06 – 7.01 (m, 2H), 4.41 (dq, *J* = 13.6, 6.7 Hz, 1H), 2.40 (s, 3H), 1.83 (s, 3H), 1.61 (dd, *J* = 6.7, 1.6 Hz, 3H) ppm.

^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.5, 138.5, 137.6, 130.6, 129.1, 128.7, 109.2, 23.2, 21.2, 15.1 ppm.

IR (ATR): 3325, 3074, 3033, 2922, 2886, 1679, 1513, 1434, 1388, 1371, 1353, 1313, 1292, 1212, 1176, 1122, 1022, 954, 829, 804, 733, 598, 511, 416 cm^{-1}.

***N*-(4-methoxyphenyl)-*N*-(1-propenyl)acetamide (2f).**[1]



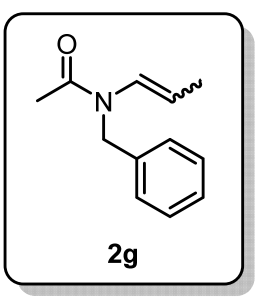
Following the general procedure A, reaction was performed using **1f** (45.9 mg, 0.223 mmol), $CoBr_2$ (4.9 mg, 0.022 mmol), dppe (17.8 mg, 0.045 mmol), Zn (4.4 mg, 0.067 mmol) and ZnI_2 (71.3 mg, 0.223 mmol) in the 2.2 mL of CH_3CN at 80 °C for 16 h, followed by dry-flash column chromatography (Hexane/EtOAc = 7/3) to afford (*E*)-**2f** (36.3 mg, 79%) as colorless oil (*E*/*Z* > 95/5).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.42 (d, *J* = 14.2 Hz, 1H), 7.06 – 7.02 (m, 2H), 6.98 – 6.92 (m, 2H), 4.39 (dq, *J* = 13.6, 6.7 Hz, 1H), 3.82 (s, 3H), 1.81 (s, 3H), 1.59 (d, *J* = 6.5 Hz, 3H) ppm.

^{13}C NMR (126 MHz, Chloroform-*d*) δ 168.8, 159.4, 132.8, 129.9, 129.2, 115.1, 109.1, 55.6, 23.2, 15.1 ppm.

IR (ATR): 3500, 3074, 3006, 2959, 2934, 2840, 1673, 1609, 1584, 1512, 1463, 1443, 1388, 1372, 1314, 1293, 1271, 1248, 1182, 1170, 1123, 1106, 1034, 954, 841, 807, 743, 699, 599, 530 cm^{-1}.

***N*-benzyl-*N*-(1-propenyl)acetamide (2g).**[1]



Following the general procedure B, reaction was performed using **1g** (42.3 mg, 0.223 mmol), $CoBr_2$ (4.9 mg, 0.022 mmol), dppe (17.8 mg, 0.045 mmol), Zn (4.4 mg, 0.067 mmol) and ZnI_2 (71.3 mg, 0.223 mmol) in the 2.2 mL of CH_3CN at 80 °C for 16 h, followed by gravity column chromatography (Hexane/EtOAc = 8/2) to afford (*E*)-**2g** (30.0 mg, 71%) as colorless oil, (*Z*)-**2g** (3.4 mg, 8%) as colorless oil and recovered starting material **1g** (1.3 mg, 3%). The identity of (*Z*)-**2c** was further confirmed by GC-MS analysis ($[M]^+$ = 189). Overall yield of isomerization: 79%, *E*/*Z* ratio = 90/10, recovery of **1g**: 3%.

(*E*)-**2g** (exists as a mixture of two rotamers in the ratio 1:0.47)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.39 – 7.12 (m, 5H major rotamer and 6H minor rotamer), 6.54 (dq, *J* = 13.8, 1.6 Hz, 1H major rotamer), 5.06 – 4.88 (m, 1H major rotamer and 1H minor rotamer), 4.84 (s, 2H major rotamer), 4.74 (s, 2H minor rotamer), 2.29 (s, 3H major rotamer), 2.13 (s, 3H minor rotamer), 1.68 – 1.62 (m, 3H major rotamer and 3H minor rotamer) ppm.

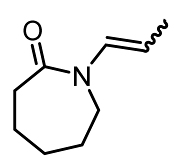
^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.4, 169.3, 137.5, 136.5, 129.0, 128.6, 128.5, 127.4, 127.0, 126.9, 125.7, 109.2, 107.3, 49.8, 46.9, 22.4, 22.3, 15.7, 15.5 ppm.

IR (ATR): 3064, 3032, 2927, 1675, 1653, 1496, 1454, 1405, 1378, 1360, 1318, 1281, 1215, 1056, 1030, 990, 933, 733, 698 cm^{-1}.

(*Z*)-**2g**:

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.31 – 7.21 (m, 5H), 5.99 (dq, *J* = 7.8, 1.9 Hz, 1H), 5.49 (dq, *J* = 7.8, 7.0 Hz, 1H), 4.63 (s, 2H), 2.05 (s, 3H), 1.44 (dd, *J* = 7.0, 1.8 Hz, 3H) ppm.

***N*-(1-propenyl)caprolactam (2h).**[22,23]



2h

Following the general procedure B, reaction was performed using **1h** (34.2 mg, 0.223 mmol), $CoBr_2$ (4.9 mg, 0.022 mmol), dppe (17.8 mg, 0.045 mmol), Zn (4.4 mg, 0.067 mmol) and ZnI_2 (71.3 mg, 0.223 mmol) in the 2.2 mL of CH_3CN at 80 °C for 16 h, followed by dry-flash column chromatography (Hexane/EtOAc = 8/2 – Hexane/EtOAc = 1/1) to afford (*E*)-**2h** (17.8 mg, 52%) as colorless oil and 3.6 mg of inseparable mixture of (*Z*)-**2h** and recovery of the substrate **1h**. The molar ratio of (*Z*)-**2h** and recovered starting material **1h** ((*Z*)-**2h**/**1h** = 1/2.3) was determined by integration of well-resolved signals in the ^{1}H NMR spectrum. GC–MS analysis of the mixture revealed two peaks with identical molecular ions $[M]^+$=153, observed in the same ratio (1:2.3) as determined by ^1H NMR. Overall yield of isomerization: 55%, *E*/*Z* ratio = 95/5, recovery of **1h**: 7%.

(*E*)-**2h**:

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.08 (dq, *J* = 14.5, 1.7 Hz, 1H), 5.02 (dq, *J* = 14.6, 6.6 Hz, 1H), 3.56 – 3.51 (m, 2H), 2.59 – 2.55 (m, 2H), 1.74 – 1.59 (m, 9H) ppm.

^{13}C NMR (126 MHz, Chloroform-*d*) δ 173.9, 127.6, 105.9, 45.7, 37.3, 29.6, 27.5, 23.6, 15.4 ppm.

IR (ATR): 3495, 3069, 2930, 2857, 1651, 1477, 1441, 1409, 1379, 1365, 1353, 1328, 1315, 1262, 1214, 1192, 1153, 1080, 1039, 976, 957, 893, 841, 787, 709, 574 cm^{-1}.

(*Z*)-**2h**:

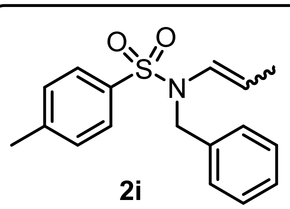
Resolved signals:

^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.25 (d, *J* = 8.4 Hz, 1H), 5.28 – 5.19 (m, 1H), 3.54 – 3.47 (m, 2H), 2.61 – 2.56 (m, 2H) ppm.

Unresolved signals:

^{1}H NMR (400 MHz, Chloroform-*d*) δ 1.80 – 1.56 (m, 9H (*Z*)-**2h** and 9H **1h**) ppm.

***N*-benzyl-4-methyl-*N*-(1-propenyl)benzenesulfonamide (2i).**[1]



2i

Following the general procedure A, reaction was performed using **1i** (67.3 mg, 0.223 mmol), $CoBr_2$ (4.9 mg, 0.022 mmol), dppe (17.8 mg, 0.045 mmol), Zn (4.4 mg, 0.067 mmol) and ZnI_2 (71.3 mg, 0.223 mmol) in the 2.2 mL of CH_3CN at 80 °C for 16 h, followed by dry-flash column chromatography (Hexane/EtOAc = 8/2) to afford 61.1 mg of inseparable mixture of

(*E*)-**2i**, (*Z*)-**2i** and recovery of the substrate **1i**. The molar ratio of (*E*)-**2i**, (*Z*)-**2i** and recovery of the substrate **1i** ((*E*)-**2i**/(*Z*)-**2i**/**1i** = 1/0.40/0.78) was determined by integration of well-resolved signals in the ^{1}H NMR spectrum. Overall yield of isomerization: 58%, *E*/*Z* ratio = 71/29, recovery of **1i**: 33%.

<u>(*E*)-**2i**:</u>

Resolved signals:

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.70 – 7.66 (m, 2H), 6.59 (dq, *J* = 14.1, 1.5 Hz, 1H), 4.77 – 4.67 (m, 1H), 4.47 (s, 2H), 2.42 (s, 3H) ppm.

^{13}C NMR (101 MHz, Chloroform-*d*) δ 143.7, 136.3, 136.0, 129.9, 128.6, 127.7, 127.4, 127.1 (127.11), 126.5, 108.7, 49.8, 21.6, 15.5 ppm.

<u>(*Z*)-**2i**:</u>

Resolved signals:

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.72 – 7.70 (m, 2H), 5.25 (dq, *J* = 7.5, 1.8 Hz, 1H), 4.22 (s, 2H) ppm.

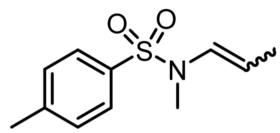
Visible peaks:

^{13}C NMR (101 MHz, Chloroform-*d*) δ 143.6, 135.4, 131.9, 129.7, 128.8, 128.4, 127.8, 127.1 (127.09), 126.0, 54.6, 13.1 ppm.

Unresolved signals:

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.34 – 7.20 (m, 7H (*E*)-**2i**, 7H (*Z*)-**2i** and 7H **1i**), 5.60 – 5.41 (m, 1H (*Z*)-**2i** and 1H **1i**), 2.45 – 2.43 (m, 3H (*Z*)-**2i** and 3H **1i**), 1.56 – 1.51 (m, 3H (*E*)-**2i** and 3H (*Z*)-**2i**) ppm.

N,4-dimethyl-N-(1-propenyl)benzenesulfonamide (2j).[1,24]



2j

Following the general procedure A, reaction was performed using **1j** (50.3 mg, 0.223 mmol), $CoBr_2$ (4.9 mg, 0.022 mmol), dppe (17.8 mg, 0.045 mmol), Zn (4.4 mg, 0.067 mmol) and ZnI_2 (71.3 mg, 0.223 mmol) in the 2.2 mL of CH_3CN at 80 °C for 16 h, followed by gravity column chromatography (Hexane/EtOAc = 9/1) to afford (*E*)-**2j** (27.7 mg, 55%) as colorless solid (m.p. = 43 – 44 °C). Attempts to isolate pure (*Z*)-**2j** were unsuccessful, and its yield (3.8 mg, 8%) and recovery of the starting material **1j** (16.1 mg, 32%) was determined by quantitative ^{1}H NMR analysis of the crude reaction mixture, based on integration of characteristic signals. Overall yield of isomerization: 63%, *E*/*Z* ratio = 88/12, recovery of **1j**: 32%.

(*E*)-**2j**:

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.65 – 7.60 (m, 2H), 7.31 – 7.27 (m, 2H), 6.70 (dq, J = 14.0, 1.5 Hz, 1H), 4.71 (dq, J = 13.4, 6.6 Hz, 1H), 2.82 (s, 3H), 2.42 (s, 3H), 1.67 (dd, J = 6.6, 1.5 Hz, 3H) ppm.

^{13}C NMR (101 MHz, Chloroform-*d*) δ 143.7, 134.8, 129.8, 128.4, 127.2, 106.5, 32.4, 21.7, 15.3 ppm.

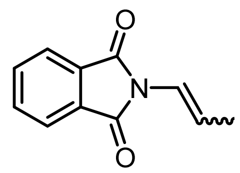
IR (ATR): 3072, 2924, 1659, 1598, 1495, 1454, 1355, 1330, 1306, 1242, 1199, 1161, 1120, 1091, 1019, 993, 945, 921, 815, 772, 663, 582, 549 cm^{-1}.

(*Z*)-**2j**:

Characteristic signals:

^{1}H NMR (400 MHz, Chloroform-*d*) δ 5.53 – 5.43 (m, 2H), 1.76 – 1.73 (m, 3H).

***N*-(1-propenyl)phthalimide (2k).**[25,26]


2k

Following the general procedure A, reaction was performed using **1k** (41.8 mg, 0.223 mmol), $CoBr_2$ (4.9 mg, 0.022 mmol), dppe (17.8 mg, 0.045 mmol), Zn (4.4 mg, 0.067 mmol) and ZnI_2 (71.3 mg, 0.223 mmol) in the 2.2 mL of CH_3CN at 80 °C for 16 h, followed by dry-flash column chromatography (Hexane/EtOAc = 98/2 – Hexane/EtOAc = 95/5) to afford (*E*)-**2k** (30.5 mg, 73%) as yellow solid (m.p. = 150 – 151 °C) and 9.6 mg of inseparable mixture of (*Z*)-**2k** and recovery of the substrate **1k**. The molar ratio of (*Z*)-**2k** and recovered starting material **1k** ((*Z*)-**2k/1k = 1**/0.9) was determined by integration of well-resolved signals in the ^{1}H NMR spectrum. GC–MS analysis of the mixture revealed two peaks with identical molecular ions $[M]^+$=187, observed in the same ratio (1:0.9) as determined by ^{1}H NMR. Overall yield of isomerization: 85%, *E*/*Z* ratio = 86/14, recovery of **1k**: 11%.

(*E*)-**2k**:

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.87 – 7.80 (m, 2H), 7.74 – 7.68 (m, 2H), 6.63 – 6.50 (m, 2H), 1.83 (d, *J* = 5.2 Hz, 3H) ppm.

^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.8, 134.3, 131.8, 123.5, 118.5, 118.1, 16.4 ppm.

IR (ATR): 3462, 3086, 3058, 2957, 2917, 2885, 2852, 1798, 1772, 1705, 1610, 1467, 1452, 1436, 1396, 1380, 1324, 1204, 1174, 1143, 1088, 1063, 1017, 997, 950, 921, 878, 801, 785, 714, 627, 564, 532 cm^{-1}.

(*Z*)-**2k**:

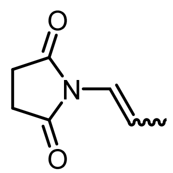
Resolved signals:

^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.14 (dq, *J* = 8.3, 1.8 Hz, 1H), 1.69 (dd, *J* = 7.0, 1.8 Hz, 3H) ppm.

Unresolved signals:

¹H NMR (400 MHz, Chloroform-*d*) δ 7.92 – 7.82 (m, 2H (*Z*)-**2k** and 2H **1k**), 7.78 – 7.68 (m, 2H (*Z*)-**2k** and 2H **1k**), 5.95 – 5.82 (m, 1H (*Z*)-**2k** and 1H **1k**) ppm.

_N_-(1-propenyl)succinimide (2l).[23]



2l

Following the general procedure B, reaction was performed using **1l** (31.1 mg, 0.223 mmol), $CoBr_2$ (4.9 mg, 0.022 mmol), dppe (17.8 mg, 0.045 mmol), Zn (4.4 mg, 0.067 mmol) and ZnI_2 (71.3 mg, 0.223 mmol) in the 2.2 mL of CH_3CN at 80 °C for 16 h, followed by dry-flash column chromatography (Hexane/EtOAc = 9/1 – Hexane/EtOAc = 7/3) to afford (*E*)-**2l** (13.7 mg, 44%) as colorless solid (m.p. = 54 – 55 °C) and 9.4 mg of inseparable mixture of (*Z*)-**2l** and recovery of the substrate **1l**. The molar ratio of (*Z*)-**2l** and recovered starting material **1l** ((*Z*)-**2l/1l =** 1/1.7) was determined by integration of well-resolved signals in the ^{1}H NMR spectrum. GC–MS analysis of the mixture revealed two peaks with identical molecular ions $[M]^+$=139, observed in the same ratio (1:1.7) as determined by ^{1}H NMR. Overall yield of isomerization: 55%, *E*/*Z* ratio = 80/20, recovery of **1l**: 19%.

<u>(*E*)-**2l**</u>

¹H NMR (500 MHz, Chloroform-*d*) δ 6.56 (dq, *J* = 14.7, 6.8 Hz, 1H), 6.41 (dq, *J* = 14.6, 1.7 Hz, 1H), 2.70 (s, 4H), 1.77 (dd, *J* = 6.8, 1.7 Hz, 3H) ppm.

¹³C NMR (126 MHz, Chloroform-*d*) δ 175.6, 120.1, 118.9, 27.9, 16.3 ppm.

IR (ATR): 2943, 1770, 1704, 1432, 1392, 1376, 1329, 1296, 1259, 1192, 1116, 1010, 957, 821, 754, 664, 624, 462 cm^{-1}.

(*Z*)-**2l**

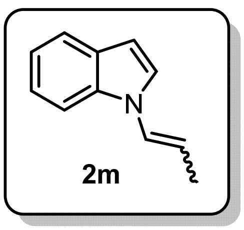
Resolved signals:

^{1}H NMR (500 MHz, Chloroform-*d*) δ 5.92 (dq, *J* = 8.5, 1.8 Hz, 1H), 2.78 (s, 4H), 1.58 (dd, *J* = 7.0, 1.7 Hz, 3H) ppm.

Unresolved signals:

^{1}H NMR (500 MHz, Chloroform-*d*) δ 5.86 – 5.72 (m, 1H (*Z*)-**2l** and 1H **1l**) ppm.

1-(1-propenyl)-1*H*-indole (2m).[24]



Following the general procedure A, reaction was performed using **1m** (35.1 mg, 0.223 mmol), $CoBr_2$ (4.9 mg, 0.022 mmol), dppe (17.8 mg, 0.045 mmol), Zn (4.4 mg, 0.067 mmol) and ZnI_2 (21.4 mg, 0.067 mmol) in the 2.2 mL of CH_3CN at 80 °C for 16 h, followed by gravity column chromatography (Hexane) to afford **2m** (23.5 mg, 67%) as inseparable mixture of (*E*)-**2m** and (*Z*)-**2m** (colorless oil). The *E*/*Z* ratio (*E*/*Z* = 87/13) was determined by integration of well-resolved signals in the ^{1}H NMR spectrum. Recovered starting material **1m** was also isolated (10.5 mg, 30%).

(*E*)-**2m**:

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.43 (d, *J* = 8.2 Hz, 1H), 6.97 (dd, *J* = 14.0, 1.6 Hz, 1H), 6.56 (d, *J* = 3.3 Hz, 1H), 5.75 (dqd, *J* = 13.6, 6.8, 1.2 Hz, 1H), 1.87 (dt, *J* = 6.7, 1.4 Hz, 3H) ppm.

^{13}C NMR (101 MHz, Chloroform-*d*) δ 135.4, 128.9, 124.9, 124.4, 122.4, 121.1, 120.4, 111.0, 109.7, 103.8, 15.5 ppm.

(*Z*)-**2m**:

^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.83 – 6.78 (m, 1H), 6.58 (d, *J* = 3.3 Hz, 1H), 5.52 (dqd, *J* = 8.4, 7.1, 1.1 Hz, 1H), 1.81 (dt, *J* = 7.1, 1.5 Hz, 3H) ppm.

In ^{13}C NMR spectrum, signal at 136.4 ppm is not visible.

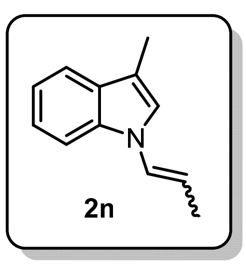
^{13}C NMR (101 MHz, Chloroform-*d*) δ 128.3, 127.6, 124.7, 122.2, 120.9, 120.3, 118.3, 110.2, 102.9, 13.1 ppm.

Unresolved signals:

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.65 – 7.57 (m, 1H (*Z*)-**2m** and 1H (*E*)-**2m**), 7.34 – 7.28 (m, 1H (*Z*)-**2m** and 1H (*E*)-**2m**), 7.26 – 7.19 (m, 2H (*Z*)-**2m** and 1H (*E*)-**2m**), 7.17 – 7.08 (m, 1H (*Z*)-**2m** and 1H (*E*)-**2m**) ppm.

IR (ATR): 3053, 2963, 2920, 2885, 2854, 1674, 1611, 1576, 1519, 1475, 1463, 1352, 1326, 1279, 1232, 1202, 1157, 1125, 1092, 1015, 932, 884, 763, 741, 718, 424 cm^{-1}.

3-methyl-1-(1-propenyl)-1*H*-indole (2n).[27]



Following the general procedure A, reaction was performed using **1n** (38.3 mg, 0.223 mmol), $CoBr_2$ (4.9 mg, 0.022 mmol), dppe (17.8 mg, 0.045 mmol), Zn (4.4 mg, 0.067 mmol) and ZnI_2 (21.4 mg, 0.067 mmol) in the 2.2 mL of CH_3CN at 80 °C for 16 h, followed by gravity column chromatography (Hexane) to afford **2n** (32.6 mg, 85%) as inseparable mixture of (*E*)-**2n** and (*Z*)-**2n** (pale yellow oil). The *E*/*Z* ratio (*E*/*Z* = 88/12) was determined by integration of well-resolved signals in the ^{1}H NMR spectrum. Recovered starting material **1n** was also isolated (5.0 mg, 13%).

(*E*)-**2n**:

^{1}**H NMR** (400 MHz, Chloroform-*d*) δ 7.38 (dt, *J* = 8.2, 1.0 Hz, 1H), 6.92 (dq, *J* = 14.0, 1.7 Hz, 1H), 5.63 (dq, *J* = 13.6, 6.7 Hz, 1H), 2.32 (d, *J* = 1.2 Hz, 3H) ppm.

^{13}**C NMR** (101 MHz, Chloroform-*d*) δ 135.7, 129.3, 124.8, 122.4, 121.8, 119.8, 119.2, 113.3, 109.4, 109.0, 15.5, 9.8 ppm.

(*Z*)-**2n**:

^{1}**H NMR** (400 MHz, Chloroform-*d*) δ 7.26 (dt, *J* = 8.1, 1.1 Hz, 1H), 7.05 – 7.04 (m, 1H), 6.76 (dq, *J* = 8.6, 1.8 Hz, 1H), 5.40 (dq, *J* = 8.6, 7.1 Hz, 1H), 2.34 (d, *J* = 1.1 Hz, 3H) ppm.

Visible peaks:

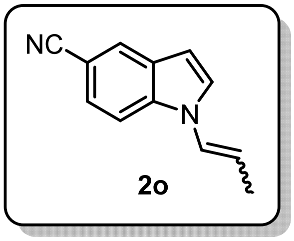
^{13}**C NMR** (101 MHz, Chloroform-*d*) δ 128.6, 125.0, 124.6, 122.2, 119.0, 116.3, 112.2, 110.1, 13.2, 9.8 ppm.

Unresolved signals:

^{1}**H NMR** (400 MHz, Chloroform-*d*) δ 7.57 – 7.51 (m, 1H (*Z*)-**2n** and 1H (*E*)-**2n**), 7.24 – 7.18 (m, 1H (*Z*)-**2n** and 1H (*E*)-**2n**), 7.17 – 7.09 (m, 1H (*Z*)-**2n** and 2H (*E*)-**2n**), 1.86 – 1.81 (m, 3H (*Z*)-**2n** and 3H (*E*)-**2n**) ppm.

IR (ATR): 3049, 2917, 2885, 2858, 1672, 1612, 1564, 1464, 1412, 1390, 1363, 1333, 1284, 1231, 1206, 1159, 1127, 1113, 1090, 1040, 1016, 929, 783, 738, 672, 585, 547, 424 cm^{-1}.

1-(1-propenyl)-1*H*-indole-5-carbonitrile (2o).[27]



Following the general procedure A, reaction was performed using **1o** (40.7 mg, 0.223 mmol), $CoBr_2$ (4.9 mg, 0.022 mmol), dppe (17.8 mg, 0.045 mmol), Zn (4.4 mg, 0.067 mmol) and ZnI_2 (21.4 mg, 0.067 mmol) in the 2.2 mL of CH_3CN at 80 °C for 16 h, followed by gravity column chromatography (Hexane/EtOAc = 9/1) to afford **2o** (17.5 mg, 43%) as inseparable mixture of (*E*)-**2o** and (*Z*)-**2o** (colorless solid, m.p. = 72 – 73 °C). The *E*/*Z* ratio (*E*/*Z* = 83/17) was determined by integration of well-resolved signals in the ^{1}H NMR spectrum. Recovered starting material **1o** was also isolated (18.7 mg, 46%).

(*E*)-**2o**:

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.95 – 7.93 (m, 1H), 6.95 (dq, *J* = 14.0, 1.7 Hz, 1H), 6.64 (d, *J* = 3.4 Hz, 1H), 5.87 (dq, *J* = 13.7, 6.8 Hz, 1H), 1.91 (dd, *J* = 6.8, 1.7 Hz, 3H) ppm.

^{13}C NMR (101 MHz, Chloroform-*d*) δ 136.8, 128.6, 127.0, 126.6, 125.3, 124.2, 120.7, 114.4, 110.6, 104.4, 103.4, 15.4 ppm.

(*Z*)-**2o**:

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.97 (dd, *J* = 1.6, 0.7 Hz, 1H), 7.34 – 7.30 (m, 2H), 6.78 (dq, *J* = 8.4, 1.8 Hz, 1H), 6.66 (dd, *J* = 3.3, 0.9 Hz, 1H), 5.72 (dq, *J* = 8.4, 7.1 Hz, 1H), 1.77 (dd, *J* = 7.1, 1.8 Hz, 3H) ppm.

Visible peaks:

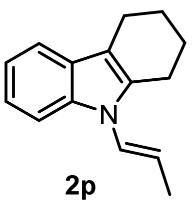
^{13}C NMR (101 MHz, Chloroform-*d*) δ 130.0, 128.0, 126.5, 125.2, 124.0, 122.1, 120.8, 111.2, 103.6, 13.0 ppm.

Unresolved signals:

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.51 – 7.41 (m, 1H (*Z*)-**2o** and 3H (*E*)-**2o**) ppm.

IR (ATR): 3111, 3047, 2921, 2886, 2856, 2220, 1720, 1674, 1610, 1515, 1478, 1451, 1382, 1360, 1342, 1326, 1291, 1240, 1218, 1129, 1095, 933, 889, 804, 763, 725, 624, 493, 420 cm^{-1}.

9-(1-propenyl)-2,3,4,9-tetrahydro-1*H*-carbazole (2p).[28]



2p

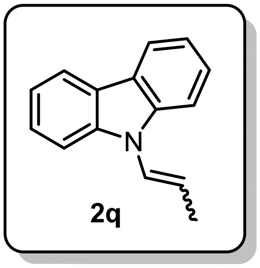
Following the general procedure A, reaction was performed using **1p** (47.2 mg, 0.223 mmol), $CoBr_2$ (4.9 mg, 0.022 mmol), dppe (17.8 mg, 0.045 mmol), Zn (4.4 mg, 0.067 mmol) and ZnI_2 (21.4 mg, 0.067 mmol) in the 2.2 mL of CH_3CN at 80 °C for 16 h, followed by gravity column chromatography (Hexane) to afford (*E*)-**2p** (27.8 mg, 59%) as pale yellow oil. Traces of (*Z*)-**2p** are barely detectable in ^{1}H NMR spectrum (*E*/*Z* > 95/5). Recovered starting material **1p** was also isolated (15.1 mg, 32%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.47 (t, *J* = 7.1 Hz, 2H), 7.17 (t, *J* = 7.5 Hz, 1H), 7.10 (t, *J* = 7.4 Hz, 1H), 6.73 (dq, *J* = 14.1, 1.7 Hz, 1H), 5.83 (dq, *J* = 13.6, 6.7 Hz, 1H), 2.77 – 2.70 (m, 4H), 1.99 – 1.81 (m, 7H) ppm.

^{13}C NMR (101 MHz, Chloroform-*d*) δ 135.9, 135.2, 128.1, 124.5, 121.4, 119.7, 117.9, 116.5, 111.2, 110.3, 23.5, 23.4, 23.1, 21.2, 15.9 ppm.

IR (ATR): 3412, 3048, 2932, 2853, 1669, 1614, 1596, 1571, 1478, 1462, 1419, 1373, 1344, 1316, 1280, 1253, 1236, 1224, 1178, 1163, 1147, 1069, 1039, 1017, 989, 946, 931, 843, 824, 739, 679, 661, 626, 596, 559, 523, 433 cm^{-1}.

9-(1-propenyl)-9*H*-carbazole (2q).[27]



Following the general procedure A, reaction was performed using **1q** (46.3 mg, 0.223 mmol), $CoBr_2$ (4.9 mg, 0.022 mmol), dppe (17.8 mg, 0.045 mmol), Zn (4.4 mg, 0.067 mmol) and ZnI_2 (21.4 mg, 0.067 mmol) in the 2.2 mL of CH_3CN at 80 °C for 16 h, followed by gravity column chromatography (Hexane) to afford **2q** (18.5 mg, 40%) as inseparable mixture of (*E*)-**2q** and (*Z*)-**2q** (sticky colorless oil). The *E*/*Z* ratio (*E*/*Z* = 96/4) was determined by integration of well-resolved signals in the ^{1}H NMR spectrum. Recovered starting material **1q** was also isolated (13.4 mg, 29%).

<u>(*E*)-**2q**:</u>

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.07 (d, *J* = 7.7 Hz, 2H), 7.57 (d, *J* = 8.3 Hz, 2H), 7.49 – 7.41 (m, 2H), 7.28 – 7.23 (m, 2H), 6.93 (dd, *J* = 14.1, 1.7 Hz, 1H), 6.12 (dq, *J* = 13.8, 6.8 Hz, 1H), 2.00 (dd, *J* = 6.7, 1.6 Hz, 3H) ppm.

^{13}C NMR (101 MHz, Chloroform-*d*) δ 139.9, 126.1, 124.2, 123.5, 120.3, 120.1, 119.0, 110.2, 15.9 ppm.

<u>(*Z*)-**2q**:</u>

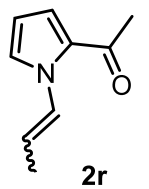
The (*Z*)-isomer is barely detectable in the spectrum. Characteristic peaks:

^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.72 (d, *J* = 8.4 Hz, 1H), 6.02 – 5.91 (m, 1H), 1.64 (dd, *J* = 6.9, 1.7 Hz, 3H) ppm.

^{13}C NMR (101 MHz, Chloroform-*d*) δ 125.9, 119.7, 110.7 ppm.

IR (ATR): 3418, 3047, 2968, 2917, 2881, 2853, 1669, 1624, 1596, 1490, 1481, 1454, 1365, 1346, 1335, 1323, 1238, 1225, 1156, 1121, 1076, 1029, 1004, 951, 931, 844, 750, 723, 660, 617, 566, 528, 423 cm^{-1}.

1-(1-(1-propenyl)-1*H*-pyrrol-2-yl)ethan-1-one (2r).[27]



2r

Following the general procedure B, reaction was performed using **1r** (33.3 mg, 0.223 mmol), $CoBr_2$ (4.9 mg, 0.022 mmol), dppe (17.8 mg, 0.045 mmol), Zn (4.4 mg, 0.067 mmol) and ZnI_2 (21.4 mg, 0.067 mmol) in the 2.2 mL of CH_3CN at 80 °C for 16 h, followed by dry-flash column chromatography (Hexane/EtOAc = 8/2) to afford 29.3 mg of inseparable mixture of (*E*)-**2r**, (*Z*)-**2r** and recovery of the substrate **1r**. The molar ratio of (*E*)-**2r**, (*Z*)-**2r** and recovered starting material **1r** ((*E*)-**2r**/(*Z*)-**2r**/**1r** = 1/0.4/0.6) was determined by integration of well-resolved signals in the ^{1}H NMR spectrum. GC–MS analysis of the mixture revealed three peaks with identical molecular ions $[M]^+$=149, observed in the same ratio (1/0.4/0.6) as determined by ^{1}H NMR. Overall yield of isomerization: 62%, *E*/*Z* ratio = 70/30, recovery of **1r**: 26%.

(*E*)-**2r**:

Resolved signals:

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.63 (dq, *J* = 14.0, 1.8 Hz, 1H), 6.17 (dd, *J* = 4.0, 2.7 Hz, 1H), 5.70 (dq, *J* = 13.7, 6.8 Hz, 1H), 1.81 (dd, *J* = 6.8, 1.8 Hz, 3H) ppm.

^{13}C NMR (126 MHz, Chloroform-*d*) δ 188.7, 130.2, 128.7, 126.3, 120.6, 115.6, 109.4, 27.4, 15.1 ppm.

(*Z*)-**2r**:

Resolved signals:

^{1}H NMR (500 MHz, Chloroform-*d*) δ 6.92 (t, *J* = 2.1 Hz, 1H), 6.22 (dd, *J* = 4.0, 2.6 Hz, 1H), 5.50 (dq, *J* = 8.6, 7.1 Hz, 1H), 1.70 (dd, *J* = 7.1, 1.9 Hz, 3H) ppm.

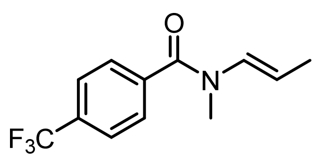
Visible peaks:

^{13}C NMR (126 MHz, Chloroform-*d*) δ 188.2, 129.8, 128.6, 119.7, 118.5, 108.7, 27.1, 12.3 ppm.

Unresolved signals:

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.15 – 7.08 (m, 1H (*E*)-**2r** and 1H (*Z*)-**2r**), 7.00 – 6.95 (m, 1H (*E*)-**2r**, 1H (*Z*)-**2r** and 1H **1r**), 2.43 (s, 3H (*E*)-**2r**, 3H (*Z*)-**2r** and 3H **1r**) ppm.

***N*-methyl-*N*-(1-propenyl)-4-(trifluoromethyl)benzamide (2s).**[1]



2s

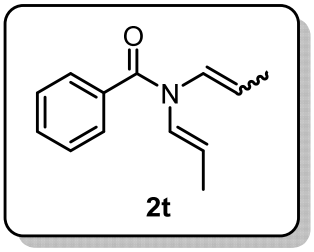
Following the general procedure A, reaction was performed using **1s** (54.3 mg, 0.223 mmol), $CoBr_2$ (4.9 mg, 0.022 mmol), dppe (17.8 mg, 0.045 mmol), Zn (4.4 mg, 0.067 mmol) and ZnI_2 (71.3 mg, 0.223 mmol) in the 2.2 mL of CH_3CN at 80 °C for 16 h, followed by dry-flash column chromatography (Hexane/EtOAc = 9/1) to afford (*E*)-**2s** (46.2 mg, 85%) as colorless solid (m.p. = 54 – 56 °C) (*E*/*Z* > 95/5).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.68 (d, *J* = 8.0 Hz, 2H), 7.55 (d, *J* = 8.0 Hz, 2H), 7.50 – 7.36 (m, 0.3H), 6.37 (d, *J* = 13.9 Hz, 0.7H), 5.09 (dd, *J* = 14.0, 7.2 Hz, 1H), 3.14 (d, *J* = 89.7 Hz, 3H), 1.86 – 1.54 (m, 3H) ppm.

^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.7, 139.4, 132.0 (q, *J* = 32.9 Hz), 130.3, 128.7 – 127.5 (m), 125.6 (q, *J* = 3.8 Hz), 123.8 (d, *J* = 272.4 Hz), 107.3, 30.6, 15.4 ppm.

IR (ATR): 3081, 2925, 1643, 1579, 1515, 1481, 1456, 1436, 1408, 1395, 1374, 1324, 1299, 1281, 1169, 1129, 1110, 1073, 1018, 940, 853, 768, 754, 740, 681, 616, 457 cm^{-1}.

***N*,*N*-di(1-propenyl)benzamide (2t).**[29]



An oven-dried 5 mL vial with a stirring bar was charged sequentially with $CoBr_2$ (9.8 mg, 0.045 mmol, 0.2 eq), dppe (35.6 mg, 0.089 mmol, 0.4 eq), acetonitrile (0.5 mL), ZnI_2 (142.6 mg, 0.447 mmol, 2 eq) and activated zinc powder (8.8 mg, 0.134 mmol, 0.6 eq). The resulting mixture was bubbled with argon for 2 minutes, capped and stirred at room temperature for 10 min. A solution of compound **1t** (45.0 mg, 0.223 mmol, 1 eq) in acetonitrile (1.7 mL) was then added. The mixture was purged with argon for an additional 2 min, sealed, and stirred at 80 °C in an oil bath for 16 h. Upon cooling to room temperature, the reaction mixture was diluted with CH_2Cl_2 (15 mL), filtered through a short pad of silica gel and the pad was washed with EtOAc (30 mL). The organic solution was concentrated under reduced pressure, and the residue was purified by dry-flash column chromatography (Hexane/EtOAc = 9/1) to afford **2t** (36.0 mg, 80%) as inseparable mixture of (*E*,*E*)-**2t** and (*E*,*Z*)-**2t** (colorless oil). The (*E*,*E*)/(*E*,*Z*) ratio ((*E*,*E*)/(*E*,*Z*) = 1/1.3) was determined by integration of well-resolved signals in the ^{1}H NMR spectrum.

(*E*,*E*)-**2t**:

Resolved signals:

^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.47 (d, *J* = 14.0 Hz, 2H), 5.25 (dq, *J* = 13.7, 6.8 Hz, 2H), 1.64 (dd, *J* = 6.8, 1.7 Hz, 6H) ppm.

(*E*,*Z*)-**2t**:

Resolved signals:

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.03 (s, 1H), 5.98 (dq, *J* = 7.9, 1.8 Hz, 1H), 5.42 (s, 1H), 5.14 (dq, *J* = 13.6, 6.7 Hz, 1H), 1.72 (dd, *J* = 6.7, 1.6 Hz, 3H), 1.33 (s, 3H) ppm.

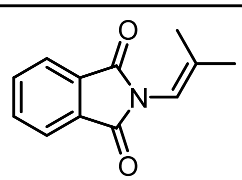
Unresolved signals:

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.54 – 7.30 (m, 5H (*E*,*E*)-**2t** and 5H (*E*,*Z*)-**2t**) ppm.

^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.9, 168.8, 136.1, 135.9, 130.3, 130.1, 128.9, 128.4, 128.0, 128.0, 127.8, 126.1, 110.0, 15.3, 15.2, 12.4, 1.1 ppm.

IR (ATR): 3463, 3073, 3035, 2959, 2924, 2856, 1738, 1649, 1602, 1580, 1493, 1447, 1402, 1388, 1368, 1327, 1307, 1292, 1277, 1254, 1165, 1100, 1076, 1029, 945, 901, 794, 744, 719, 698, 636 cm^{-1}.

***N*-(2-methyl-1-propenyl)phthalimide (2z).**[30]


2z

Following the general procedure A, reaction was performed using **1z** (45.0 mg, 0.223 mmol), $CoBr_2$ (4.9 mg, 0.022 mmol), dppe (17.8 mg, 0.045 mmol), Zn (4.4 mg, 0.067 mmol) and ZnI_2 (71.3 mg, 0.223 mmol) in the 2.2 mL of CH_3CN at 80 °C for 16 h, followed by dry-flash column chromatography (Hexane/EtOAc = 9/1) to afford 43.7 mg of inseparable mixture of **2z** and recovery of the substrate **1z**. The molar ratio of **2z** and recovery of the substrate **1z** (**2z**/**1z** = 1/5) was determined by integration of well-resolved signals in the ^{1}H NMR spectrum. Overall yield of isomerization: 16%, recovery of **1z**: 81%.

Resolved signals:

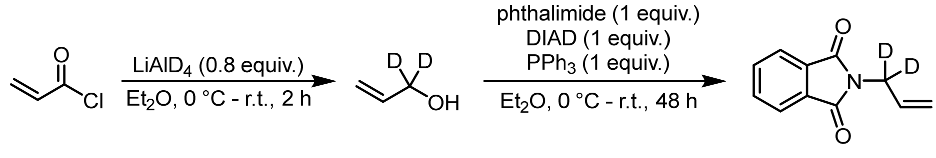
^{1}H NMR (400 MHz, Chloroform-*d*) δ 5.87 (hept, *J* = 1.5 Hz, 1H), 1.89 (d, *J* = 1.5 Hz, 3H), 1.64 (d, *J* = 1.3 Hz, 3H) ppm.

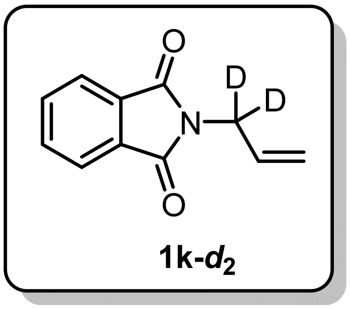
^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.5, 139.1, 134.2, 132.2, 123.5, 112.3, 22.8, 19.0 ppm.

Unresolved signals:

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.87 – 7.81 (m, 2H **1z** and 2H **2z**), 7.74 – 7.67 (m, 2H **1z** and 2H **2z**) ppm.

***N*-(1,1-d_2-allyl)phthalimide (1k-d_2).**





The synthesis of 1,1-d_2-allyl alcohol was carried out following a reported procedure.[31] Lithium aluminum deuteride (148.4 mg, 3.533 mmol, 0.80 eq) was suspended in anhydrous diethyl ether (8 mL) and the resulting suspension was cooled to 0 °C under an argon atmosphere. A solution of acryloyl chloride (357.2 µL, 4.420 mmol, 1.0 eq) in anhydrous diethyl ether (3 mL) was added dropwise over 30 min, ensuring that the temperature of the reaction mixture did not exceed 5 °C. After the addition was complete, the reaction mixture was allowed to warm to room temperature and stirred for an additional 2 h. The reaction mixture was then cooled to 0 °C, and water (1 mL), 15% aqueous sodium hydroxide (1 mL), and water (1 mL) were added dropwise in sequence. The resulting precipitate was removed by filtration and washed thoroughly with diethyl ether. The filtrate was dried over anhydrous sodium sulfate, filtered, and used in the next step without further purification.

Phthalimide (650.3 mg, 4.420 mmol, 1.0 eq), triphenylphosphine (1.16 g, 4.420 mmol, 1.0 eq), and diisopropyl azodicarboxylate (DIAD, 867.7 µL, 4.420 mmol, 1.0 eq) were added sequentially to a diethyl ether solution of 1,1-d_2-allyl alcohol at 0 °C under an argon atmosphere. The reaction mixture was then allowed to warm to room temperature and reaction progress was monitored by TLC. After 48 h, reaction was diluted with Hexane and filtered. The filtrate was concentrated under reduced pressure, and the residue was purified by dry-flash column chromatography

(Hexane/EtOAc = 95/5) to afford **1k-*d*₂** (108.1 mg, 13%, not optimized) as colorless solid (m.p. = 59 – 61 °C).

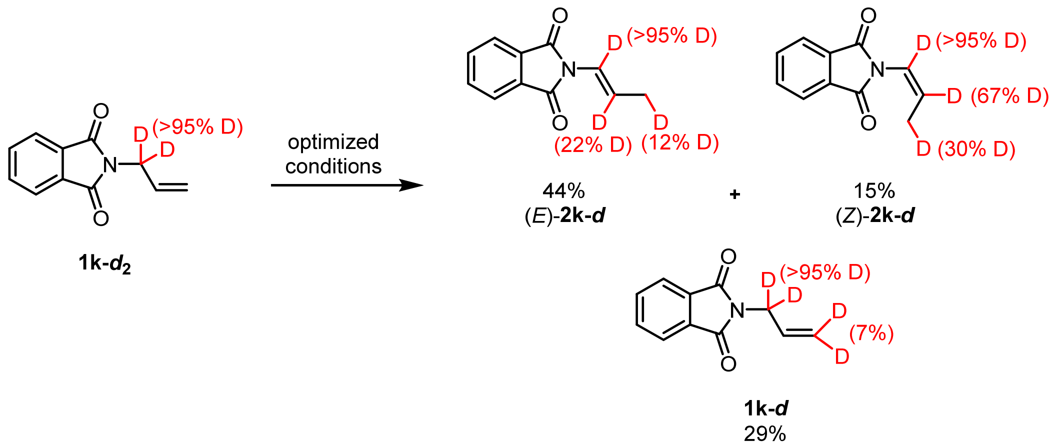
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.88 – 7.82 (m, 2H), 7.74 – 7.69 (m, 2H), 5.88 (dd, *J* = 17.1, 10.2 Hz, 1H), 5.25 (dd, *J* = 17.1, 1.1 Hz, 1H), 5.19 (dd, *J* = 10.2, 1.2 Hz, 1H) ppm.

The signal of deuterated carbon in ^{13}C NMR is missing. This is a known phenomenon.[32]

^{13}C NMR (126 MHz, Chloroform-*d*) δ 168.0, 134.1, 132.2, 131.5, 123.4, 118.0 ppm.

IR (ATR): 3455, 3223, 3086, 3034, 3013, 2928, 2853, 2307, 2143, 2095, 1987, 1927, 1839, 1818, 1769, 1714, 1698, 1613, 1514, 1467, 1449, 1394, 1287, 1215, 1192, 1166, 1112, 1090, 1073, 1058, 1006, 970, 932, 917, 824, 794, 724, 704, 686, 642, 531, 512, 423 cm^{-1}.

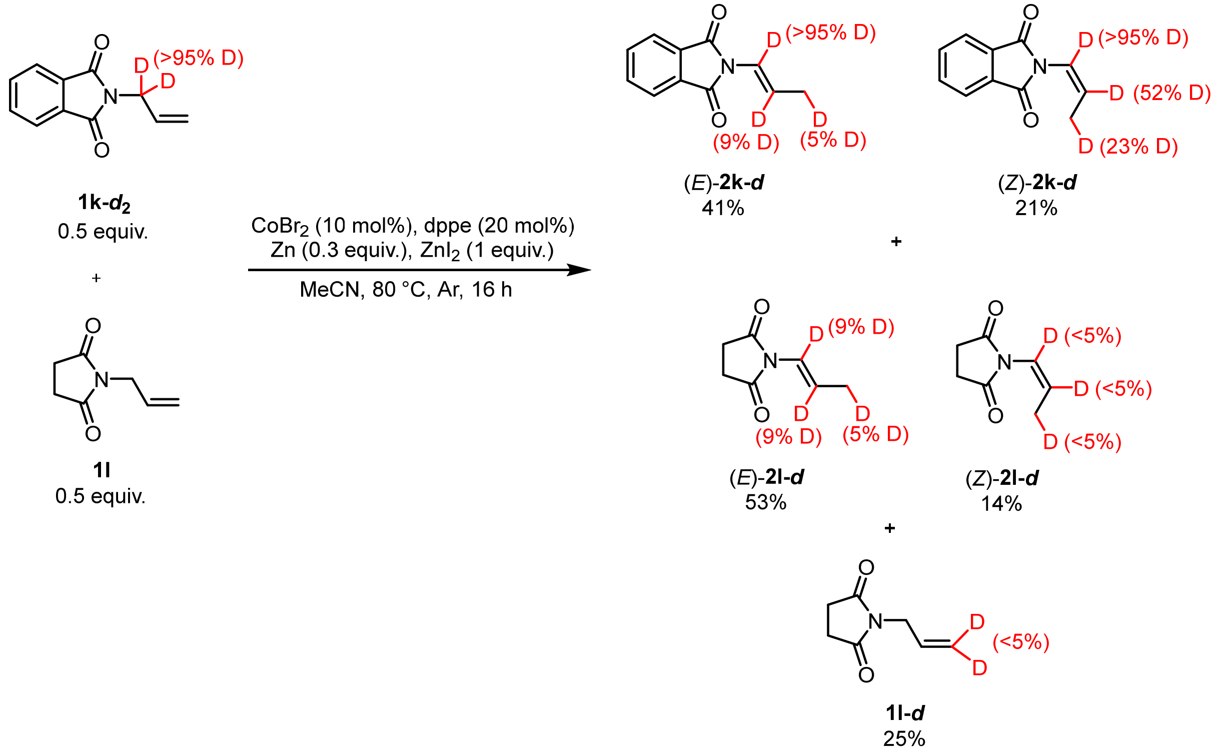
Isomerization of deuterated substrate 1k-d_2



Following the general procedure A, reaction was performed with **1k-*d*₂** (42.3 mg, 0.223 mmol), $CoBr_2$ (4.9 mg, 0.022 mmol), dppe (17.8 mg, 0.045 mmol), Zn (4.4 mg, 0.067 mmol) and ZnI_2 (71.3 mg, 0.223 mmol) in the 2.2 mL of CH_3CN at 80 °C for 16 h, followed by dry-flash column chromatography (Hexane/EtOAc = 98/2 – Hexane/EtOAc = 95/5) to afford (*E*)- **2k-*d*** (18.6 mg, 44%) as yellow solid and 18.6 mg of inseparable mixture of (*Z*)-**2k-*d*** and additionally deuterated recovery of the substrate **1k-*d***. The molar ratio of (*Z*)-**2k-*d*** and recovered starting material **1k-*d*** was determined by integration of well-resolved signals in the ^{1}H NMR spectrum. The extent of deuteration was determined by quantitative ^{2}H NMR spectroscopy.

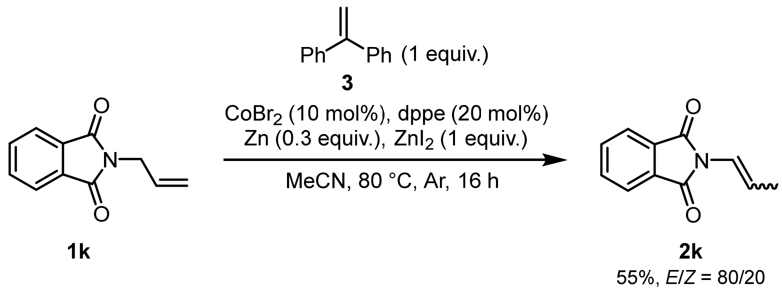
Both (*E*)-**2k-*d*** and (*Z*)-**2k-*d*** exhibit different multiplets compared to their non-deuterated analogues ((*E*)-**2k** and (*Z*)-**2k**). The methyl group of the 1-propenyl moiety shows a characteristic multiplet, indicative of partial deuteration at this position. In the ^{13}C NMR spectrum of (*E*)-**2k-*d***, a triplet corresponding to the deuterated C2 position of the 1-propenyl group is clearly visible.

Crossover experiment



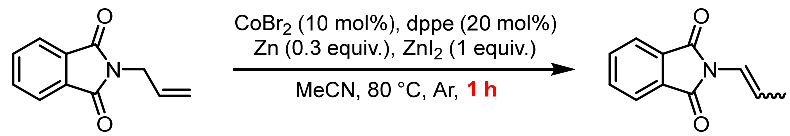
An oven-dried 5 mL vial with a stirring bar was charged sequentially with $CoBr_2$ (9.8 mg, 0.044 mmol, 0.1 eq), dppe (35.6 mg, 0.09 mmol, 0.2 eq), acetonitrile (1 mL), ZnI_2 (142.6 mg, 0.446 mmol, 1 eq) and activated zinc powder (8.8 mg, 0.134 mmol, 0.3 eq). The resulting mixture was bubbled with argon for 2 minutes, capped and stirred at room temperature for 10 min. A solution of compound **1k-*d*₂** (42.3 mg, 0.223 mmol, 0.5 eq) and **1l** (31.1 mg, 0.223 mmol, 0.5 eq) in acetonitrile (3.4 mL) was then added. The mixture was purged with argon for an additional 2 min, sealed, and stirred at 80 °C in an oil bath for 16 h. Upon cooling to room temperature, the reaction mixture was diluted with CH_2Cl_2 (15 mL), filtered through a short pad of silica gel and the pad was washed with EtOAc (30 mL). The organic solution was concentrated under reduced pressure, and the residue was purified by dry-flash column chromatography (Hexane/EtOAc = 98/2 – Hexane/EtOAc = 7/3) to afford (*E*)-**2k-*d*** (17.3 mg, 41%) as yellow solid, 20.3 mg of inseparable mixture of (*Z*)-**2k-*d*** and starting material, (*E*)-**2l-*d*** (16.6 mg, 53%) as colorless solid and 12.2 mg of inseparable mixture of (*Z*)-**2l-*d*** and deuterated substrate **1l-*d***. The molar ratios were determined by integration of well-resolved signals in the ^{1}H NMR spectrum. The extent of deuteration was determined by quantitative ^{2}H NMR spectroscopy.

Radical trapping experiment

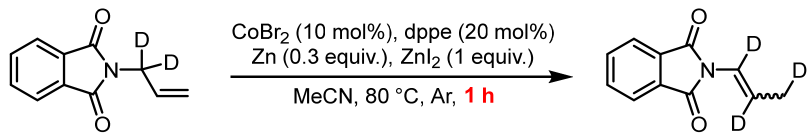


An oven-dried 5 mL vial with a stirring bar was charged sequentially with $CoBr_2$ (4.9 mg, 0.022 mmol, 0.1 eq), dppe (17.8 mg, 0.045 mmol, 0.2 eq), acetonitrile (0.5 mL), ZnI_2 (71.3 mg, 0.223 mmol, 1 eq) and activated zinc powder (4.4 mg, 0.067 mmol, 0.3 eq). The resulting mixture was bubbled with argon for 2 minutes, capped and stirred at room temperature for 10 min. A solution of compound **1k** (41.8 mg, 0.223 mmol, 1 eq) and 1,1-diphenylethylene (**3**, 40.3 mg, 0.223 mmol, 1 eq) in acetonitrile (1.7 mL) was then added. The mixture was purged with argon for an additional 2 min, sealed, and stirred at 80 °C in an oil bath for 16 h. Upon cooling to room temperature, the reaction mixture was diluted with CH_2Cl_2 (15 mL), filtered through a short pad of silica gel and the pad was washed with EtOAc (30 mL). The organic solution was concentrated under reduced pressure, and the residue was purified by gravity column chromatography (Hexane-Hexane/EtOAc = 95/5) to afford recovery of **3** (33.9 mg, 84%), (*E*)-**2k** (18.4 mg, 44%) as yellow solid and 13.8 mg of inseparable mixture of (*Z*)-**2k** and recovery of the substrate **1k**. The molar ratio of (*Z*)-**2k** and recovered starting material **1k** ((*Z*)-**2k**/**1k** = 1/2) was determined by integration of well-resolved signals in the ^{1}H NMR spectrum. Overall yield of isomerization: 55%, *E*/*Z* ratio = 80/20, recovery of **1k**: 22%.

Conversion after 1 hour



1k → **2k** 67%, *E*/*Z* = 77/23



1k-*d*$_2$ → **2k-*d*** 26%, *E*/*Z* = 48/52

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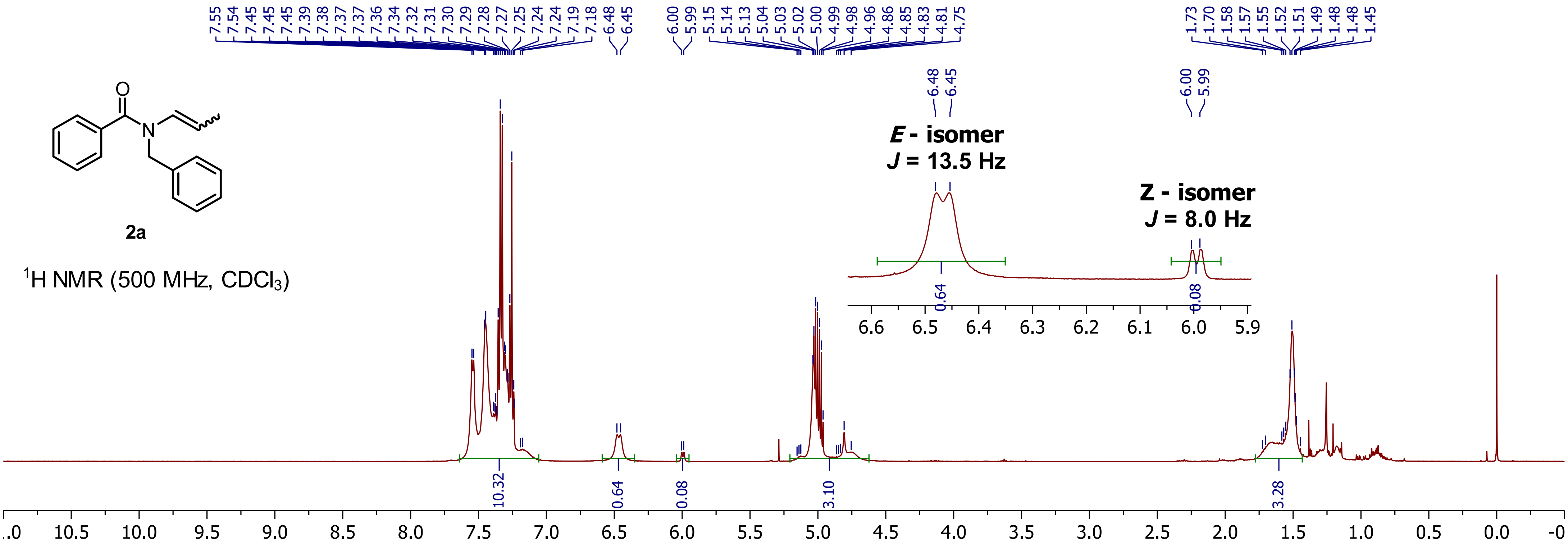
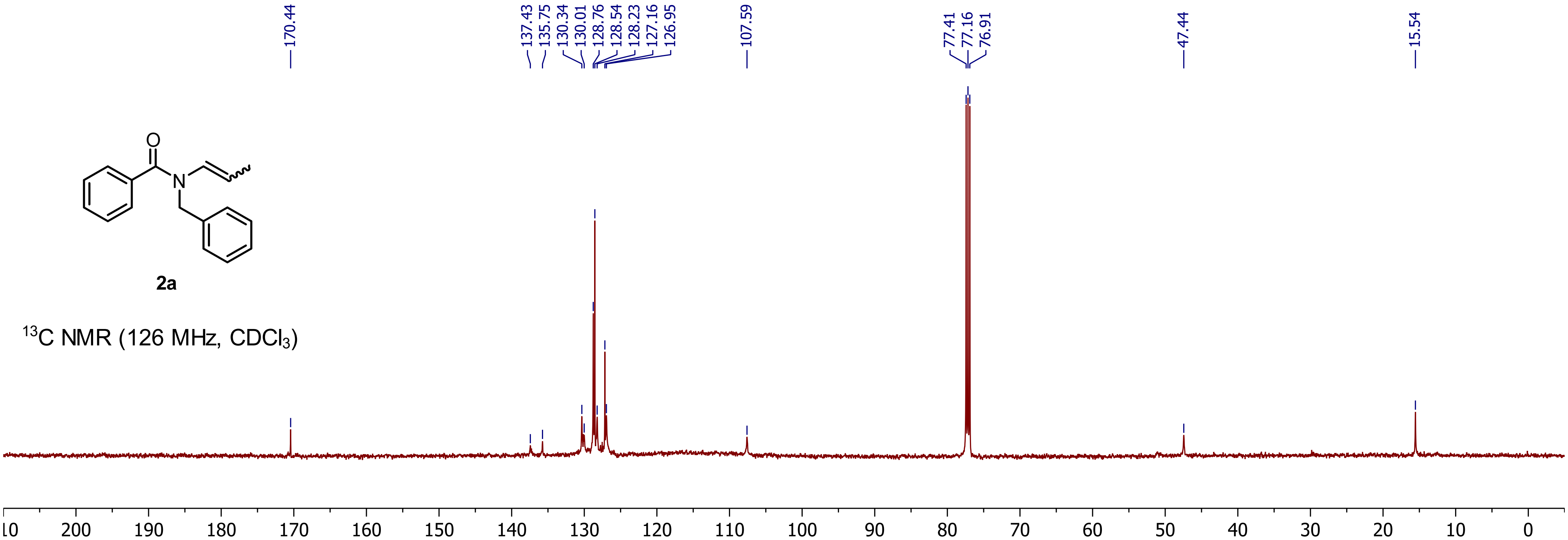
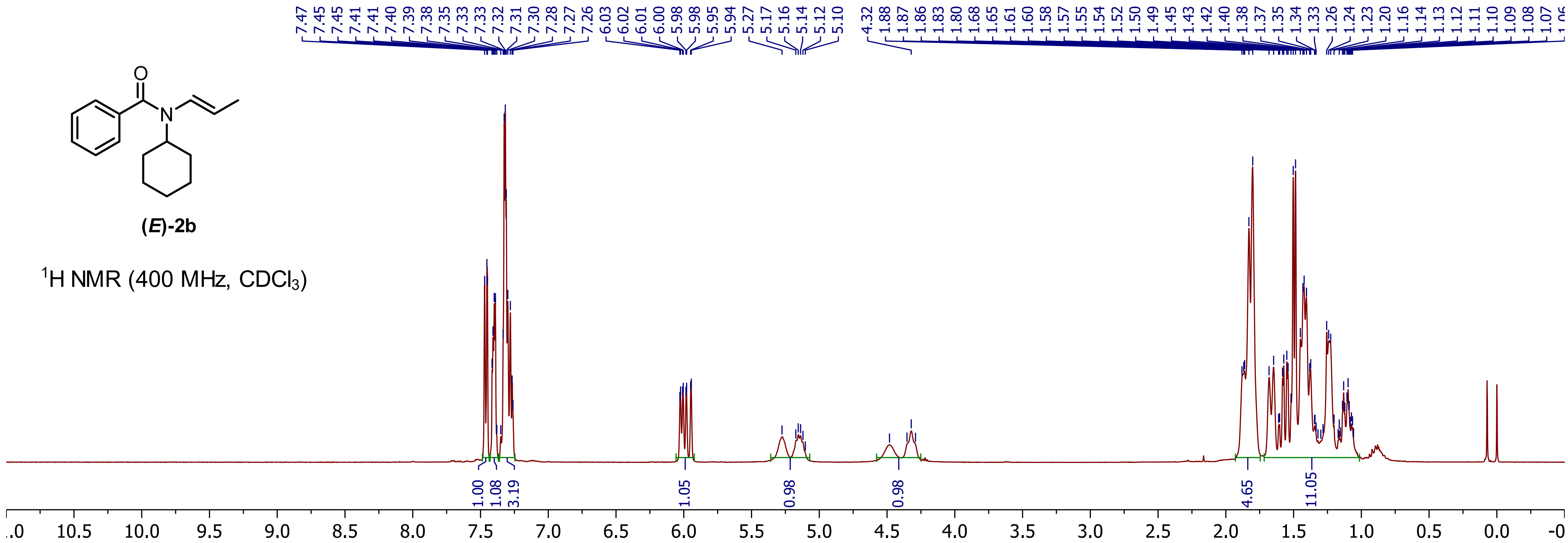
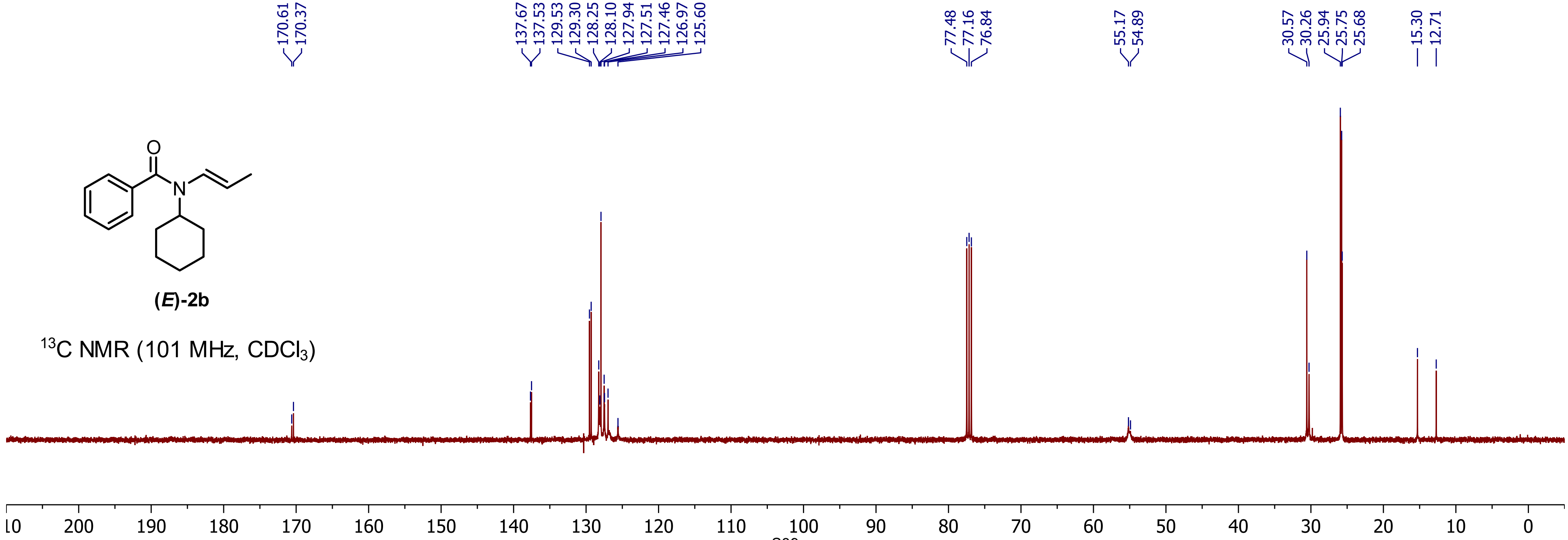
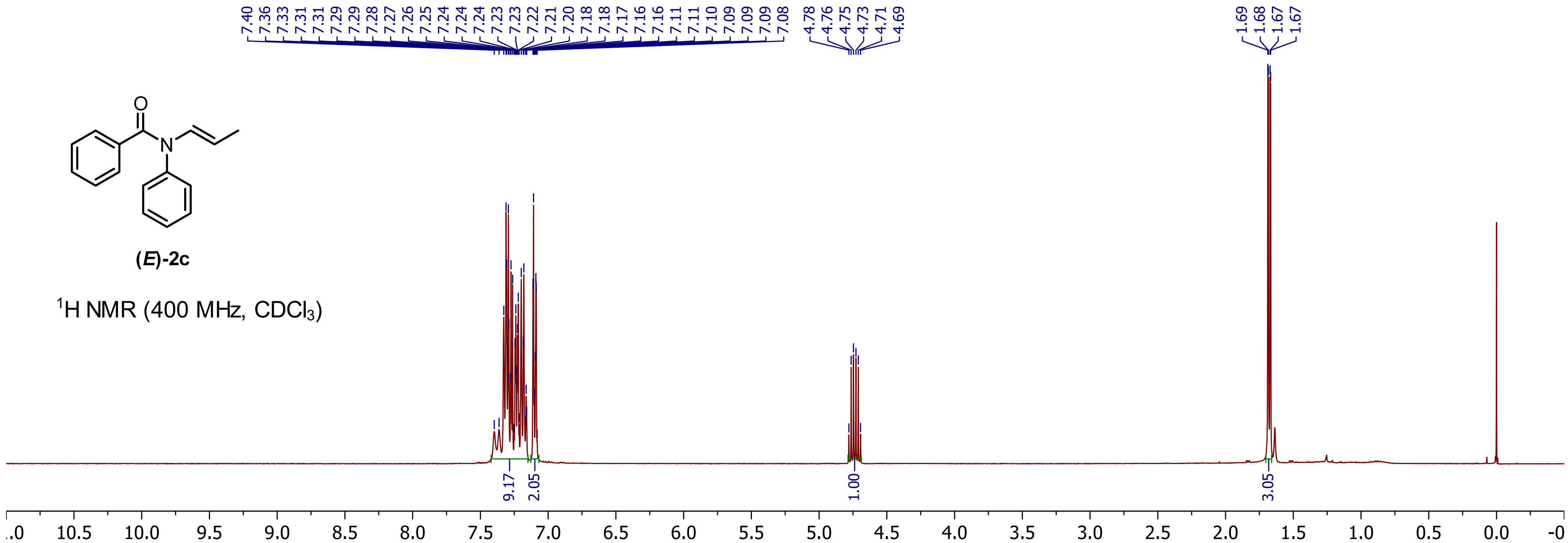
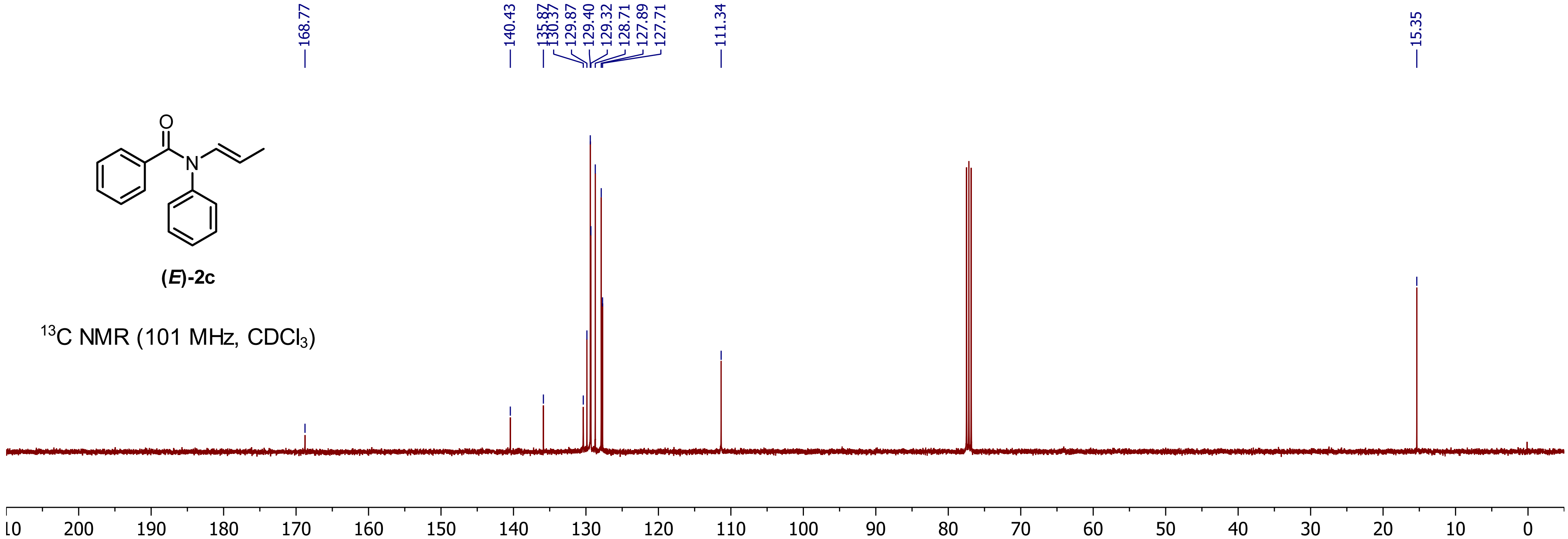

2a
^{1}H NMR (500 MHz, CDCl$_3$)
E - isomer
J = 13.5 Hz
Z - isomer
J = 8.0 Hz

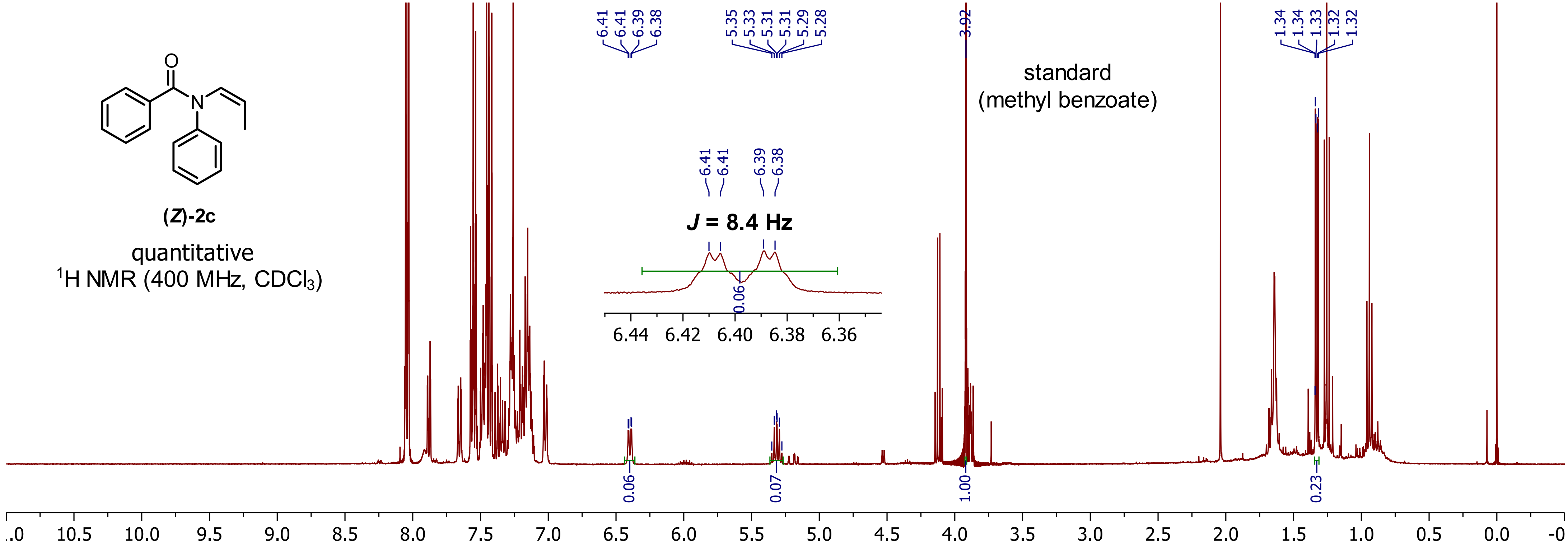

2a
^{13}C NMR (126 MHz, CDCl$_3$)


(*E*)-2b
^{1}H NMR (400 MHz, $CDCl_3$)

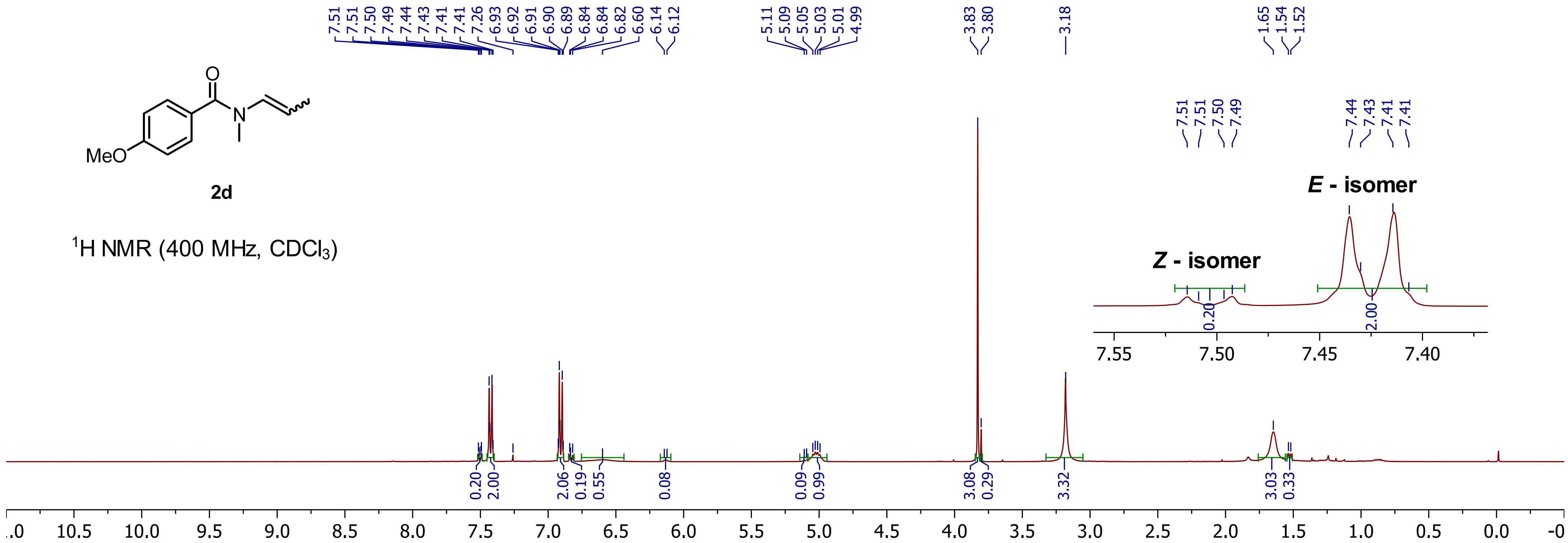

(*E*)-2b
^{13}C NMR (101 MHz, $CDCl_3$)

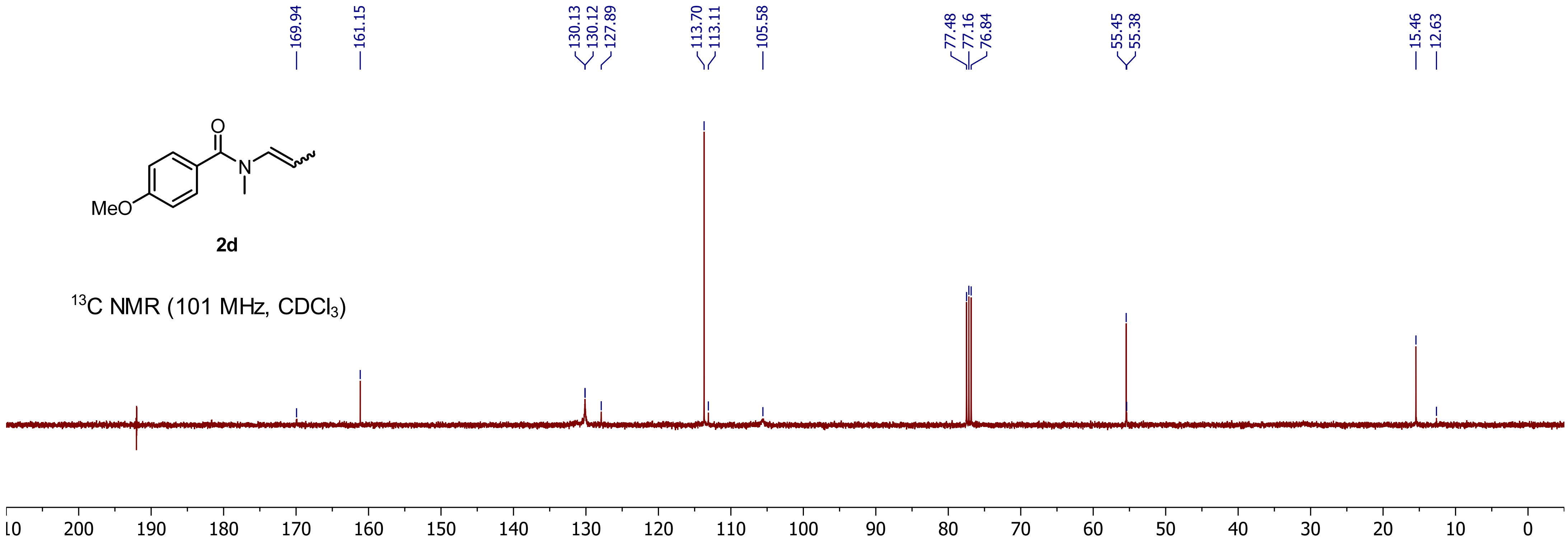

(E)-2c
1H NMR (400 MHz, CDCl3)
7.40 7.36 7.33 7.31 7.31 7.29 7.29 7.28 7.27 7.26 7.25 7.24 7.24 7.24 7.23 7.23 7.22 7.21 7.20 7.18 7.18 7.17 7.16 7.16 7.11 7.11 7.10 7.09 7.09 7.09 7.08
4.78 4.76 4.75 4.73 4.71 4.69
1.69 1.68 1.67 1.67
9.17 2.05 1.00 3.05

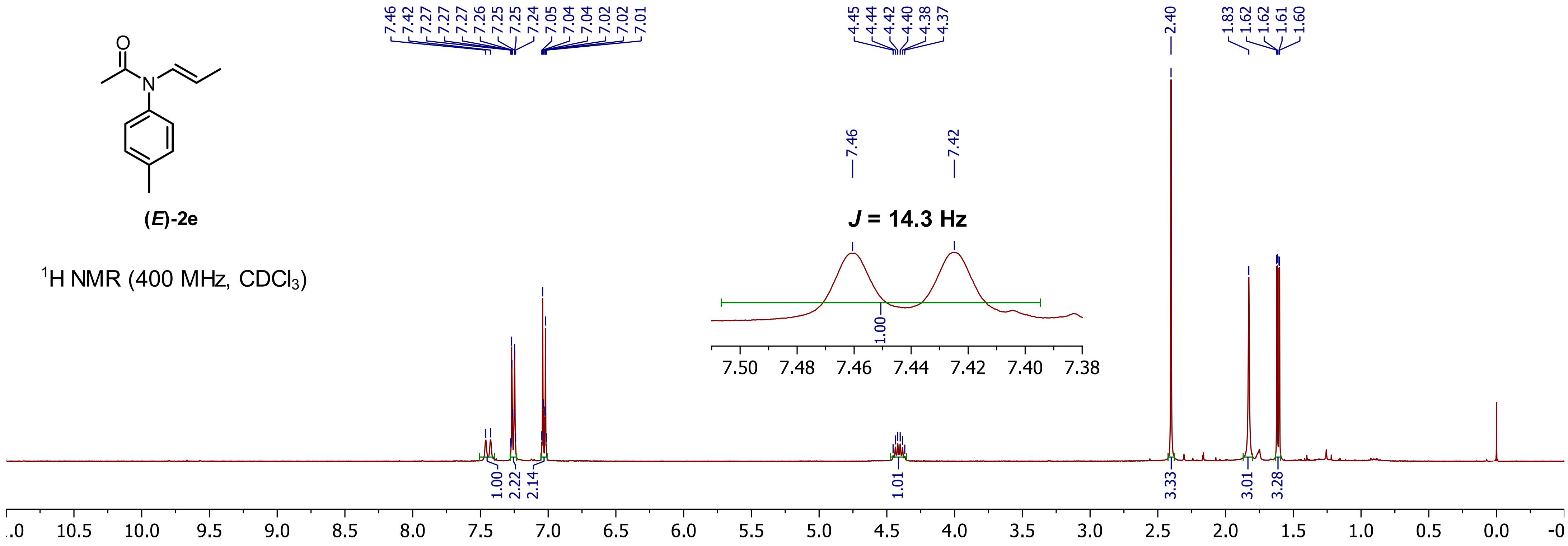

(E)-2c
13C NMR (101 MHz, CDCl3)
168.77
140.43 135.87 130.37 129.87 129.40 129.32 128.71 127.89 127.71
111.34
15.35

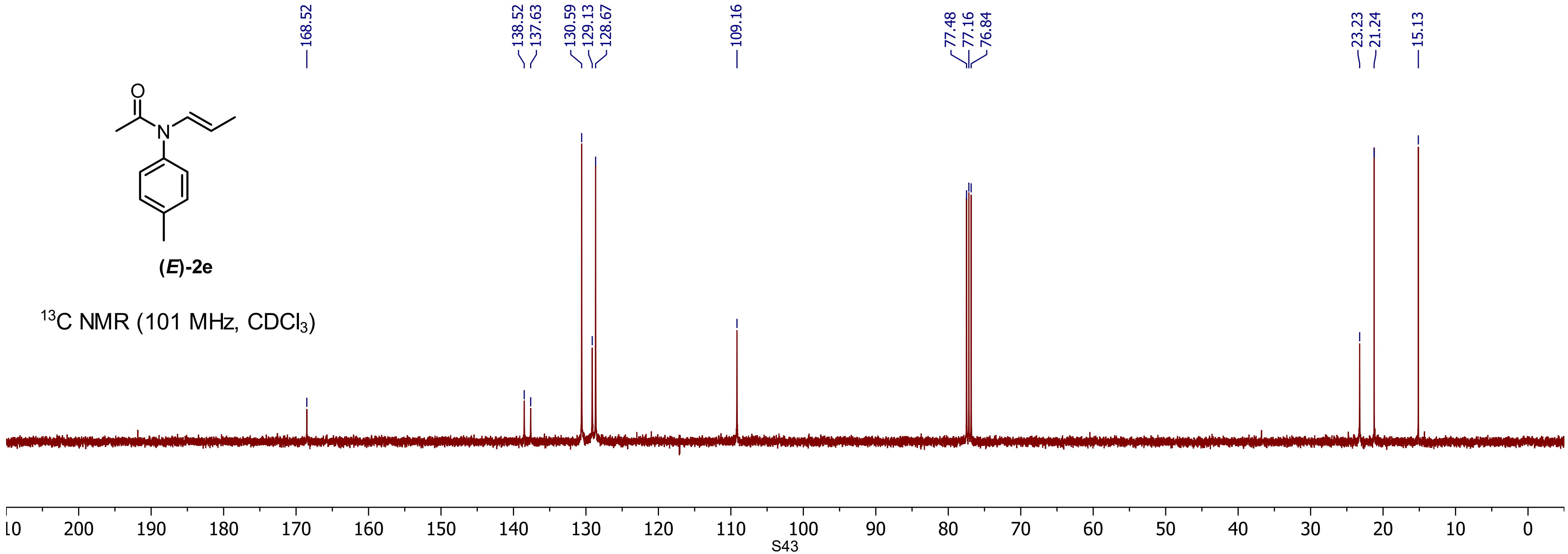


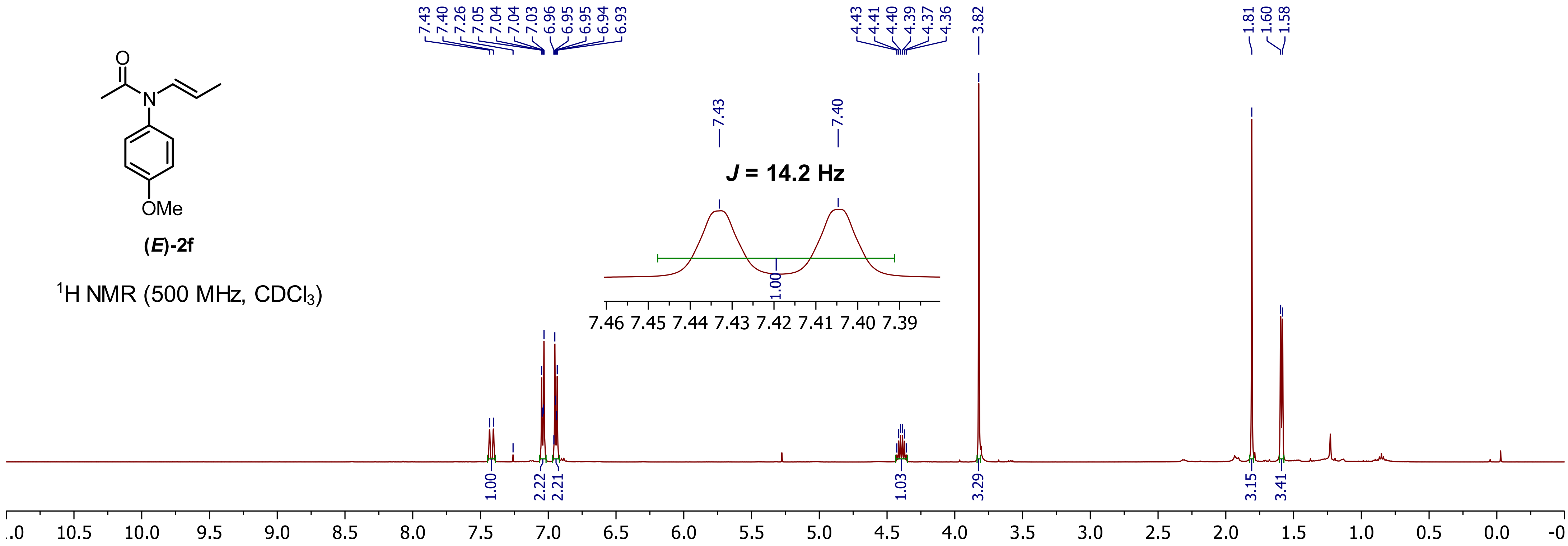
(Z)-2c
quantitative
¹H NMR (400 MHz, CDCl₃)
standard
(methyl benzoate)
J = 8.4 Hz
6.41
6.41
6.39
6.38
5.35
5.33
5.31
5.31
5.29
5.28
3.92
1.34
1.34
1.33
1.32
1.32
0.06
0.07
1.00
0.23
6.44 6.42 6.40 6.38 6.36
.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0

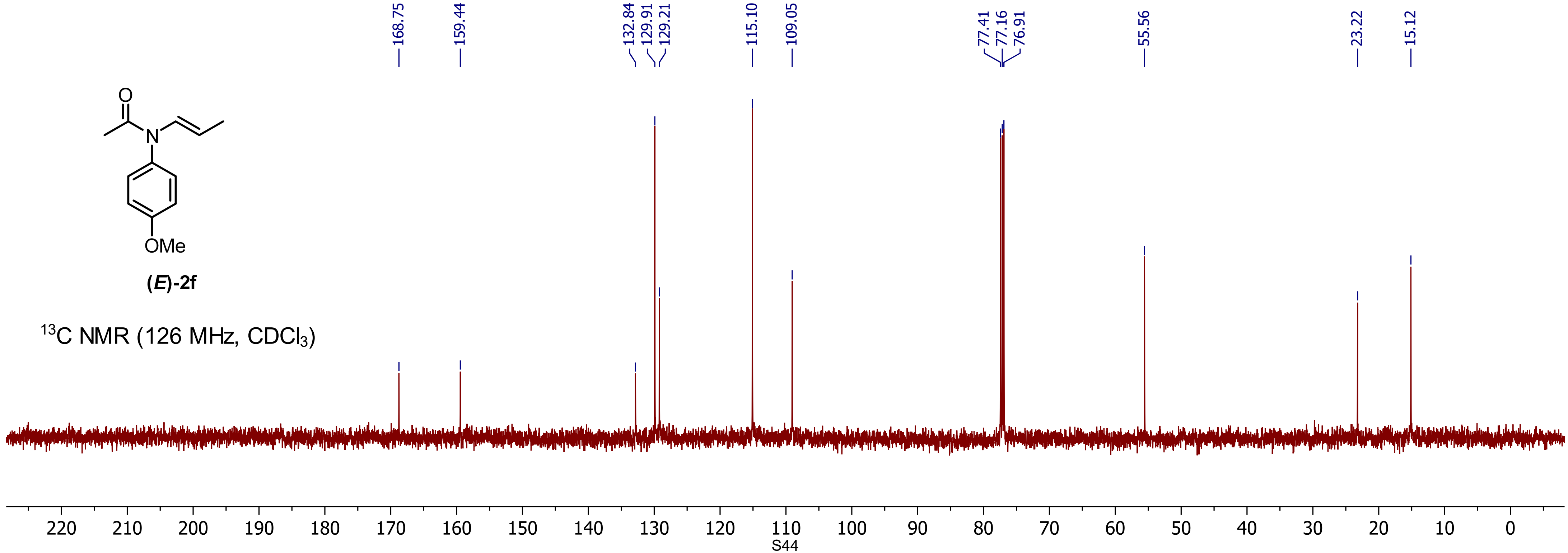

2d
^{1}H NMR (400 MHz, CDCl$_3$)
7.51 7.51 7.50 7.49 7.44 7.43 7.41 7.41 7.26 6.93 6.92 6.91 6.90 6.89 6.84 6.84 6.82 6.60 6.14 6.12
5.11 5.09 5.05 5.03 5.01 4.99
3.83 3.80
3.18
1.65 1.54 1.52
0.20 2.00 2.06 0.19 0.55 0.08 0.09 0.99 3.08 0.29 3.32 3.03 0.33
Z - isomer
E - isomer

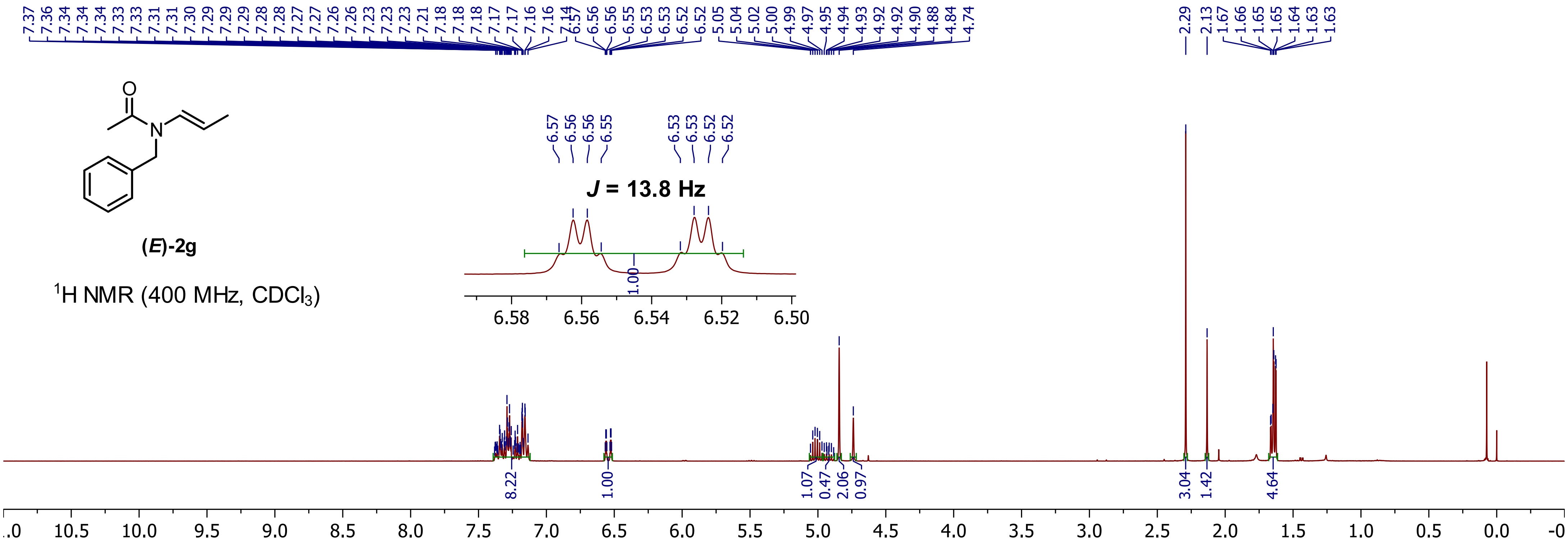

2d
^{13}C NMR (101 MHz, CDCl$_3$)
169.94 161.15 130.13 130.12 127.89 113.70 113.11 105.58 77.48 77.16 76.84 55.45 55.38 15.46 12.63


(E)-2e
¹H NMR (400 MHz, CDCl3)
J = 14.3 Hz
7.46
7.42
7.27
7.27
7.27
7.26
7.25
7.25
7.24
7.05
7.04
7.04
7.02
7.02
7.01
4.45
4.44
4.42
4.40
4.38
4.37
2.40
1.83
1.62
1.62
1.61
1.60
1.00
2.22
2.14
1.01
3.33
3.01
3.28

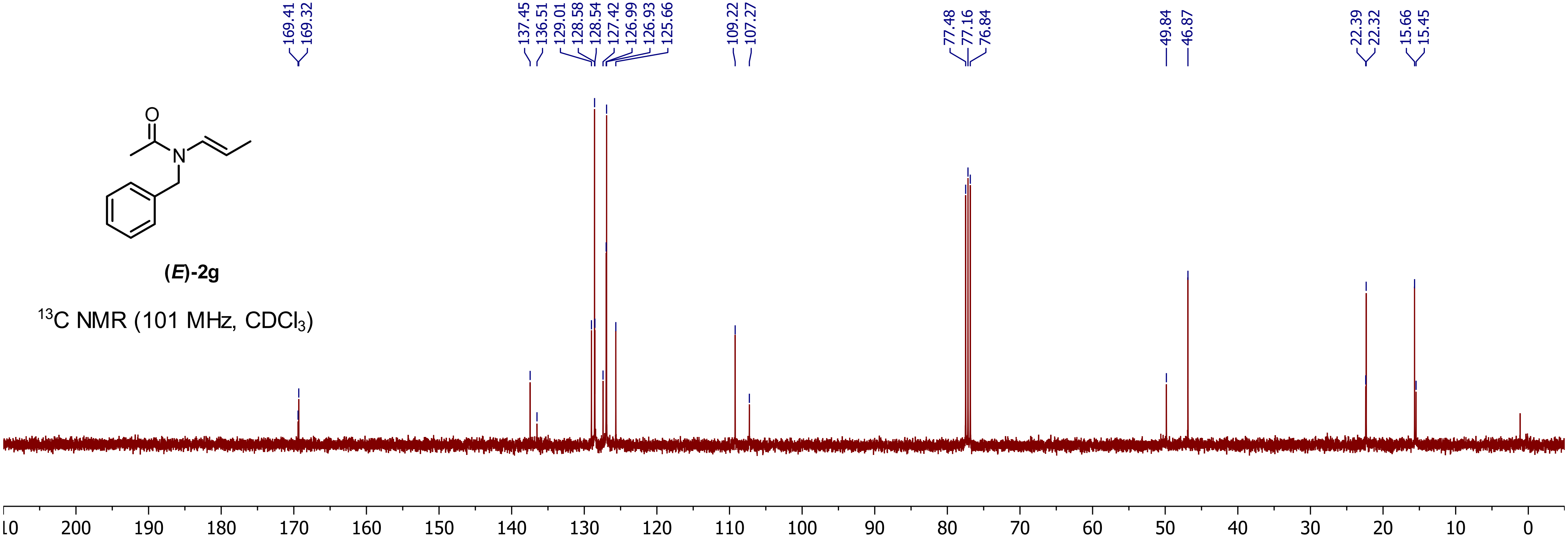

(E)-2e
¹³C NMR (101 MHz, CDCl3)
168.52
138.52
137.63
130.59
129.13
128.67
109.16
77.48
77.16
76.84
23.23
21.24
15.13


(E)-2f
1H NMR (500 MHz, CDCl3)
7.43 7.40 7.26 7.05 7.04 7.04 7.03 6.96 6.95 6.95 6.94 6.93
4.43 4.41 4.40 4.39 4.37 4.36
3.82
1.81 1.60 1.58
J = 14.2 Hz
7.46 7.45 7.44 7.43 7.42 7.41 7.40 7.39
1.00 2.22 2.21 1.03 3.29 3.15 3.41
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

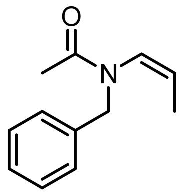

(E)-2f
13C NMR (126 MHz, CDCl3)
168.75 159.44 132.84 129.91 129.21 115.10 109.05 77.41 77.16 76.91 55.56 23.22 15.12
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0



(*E*)-2g
^{1}H NMR (400 MHz, $CDCl_3$)
J = 13.8 Hz

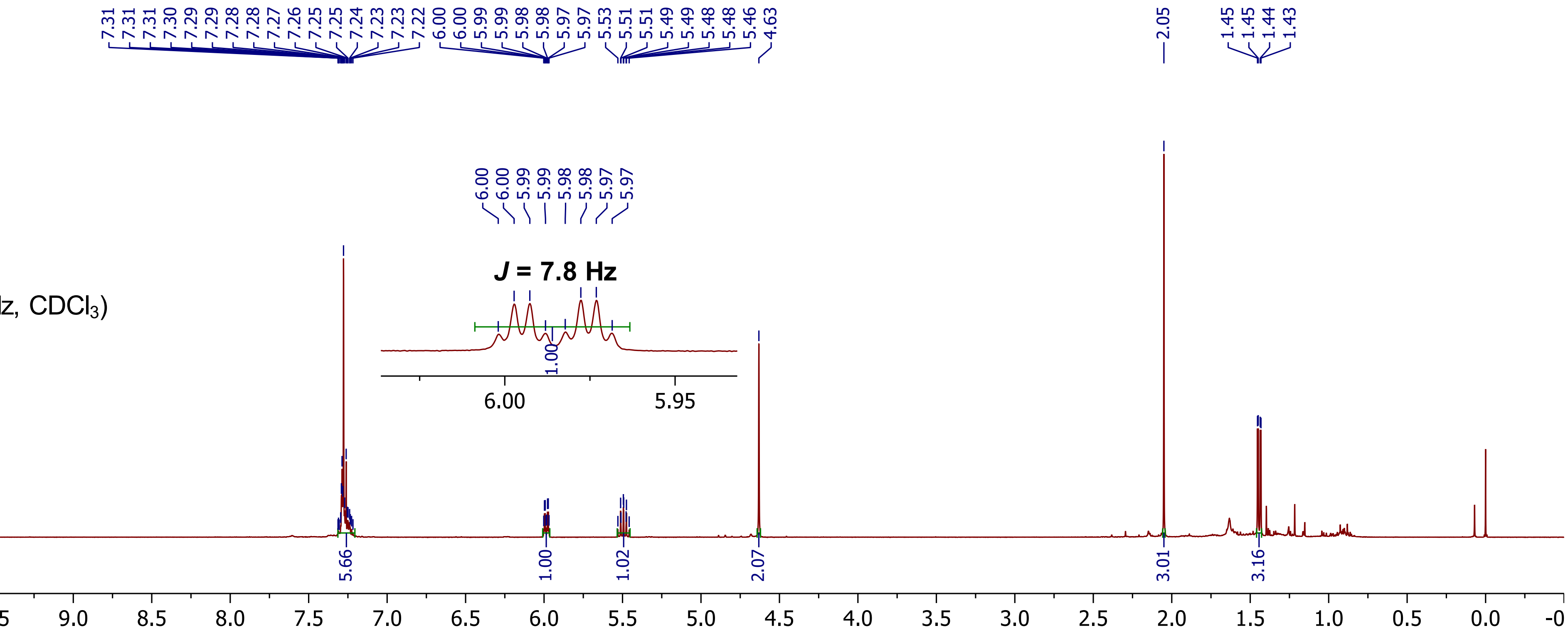


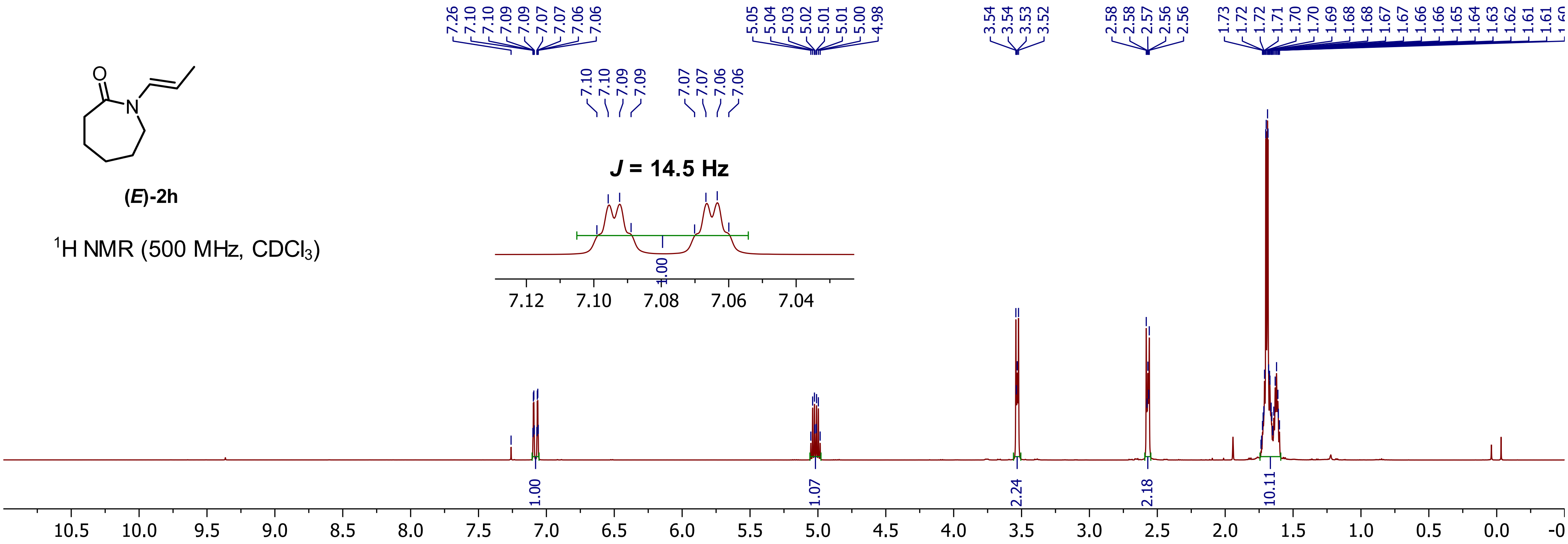
(*E*)-2g
^{13}C NMR (101 MHz, $CDCl_3$)

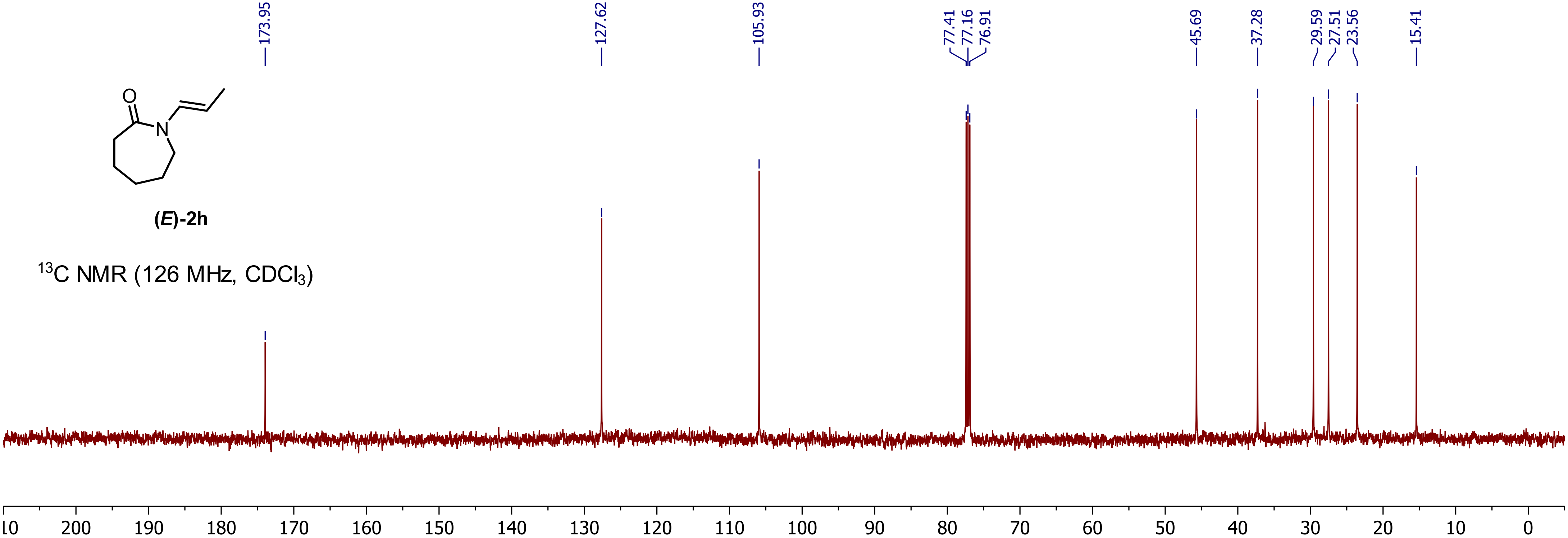


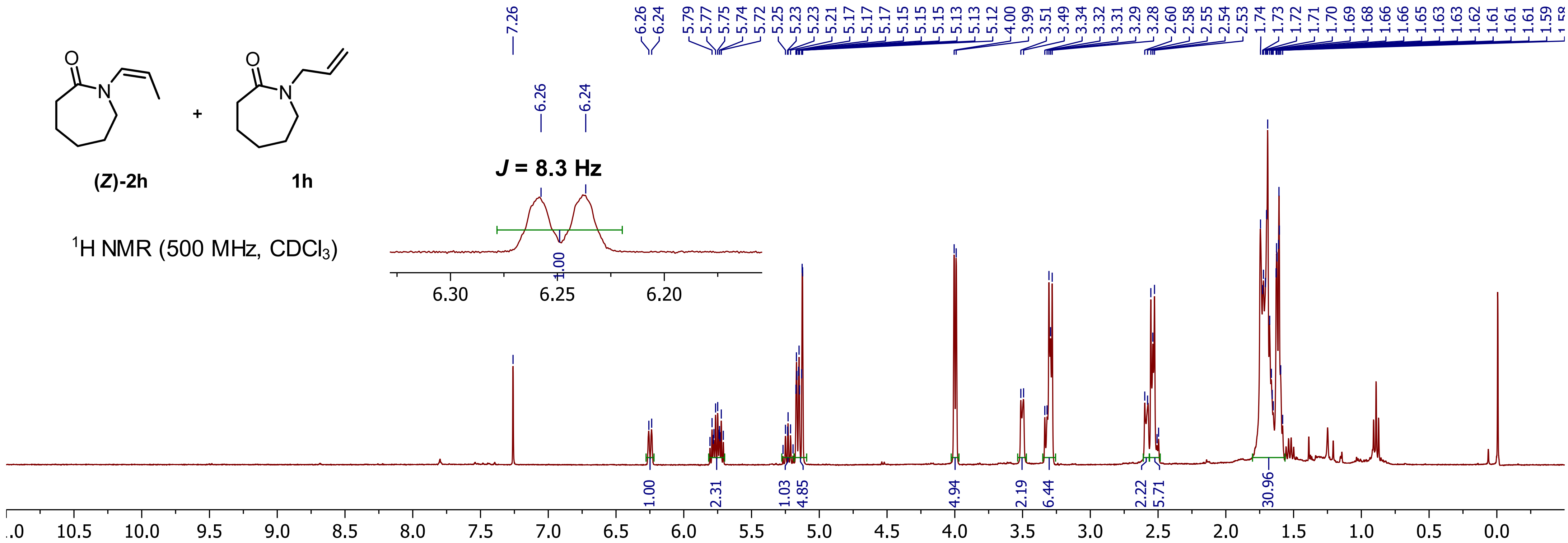
(*Z*)-2g

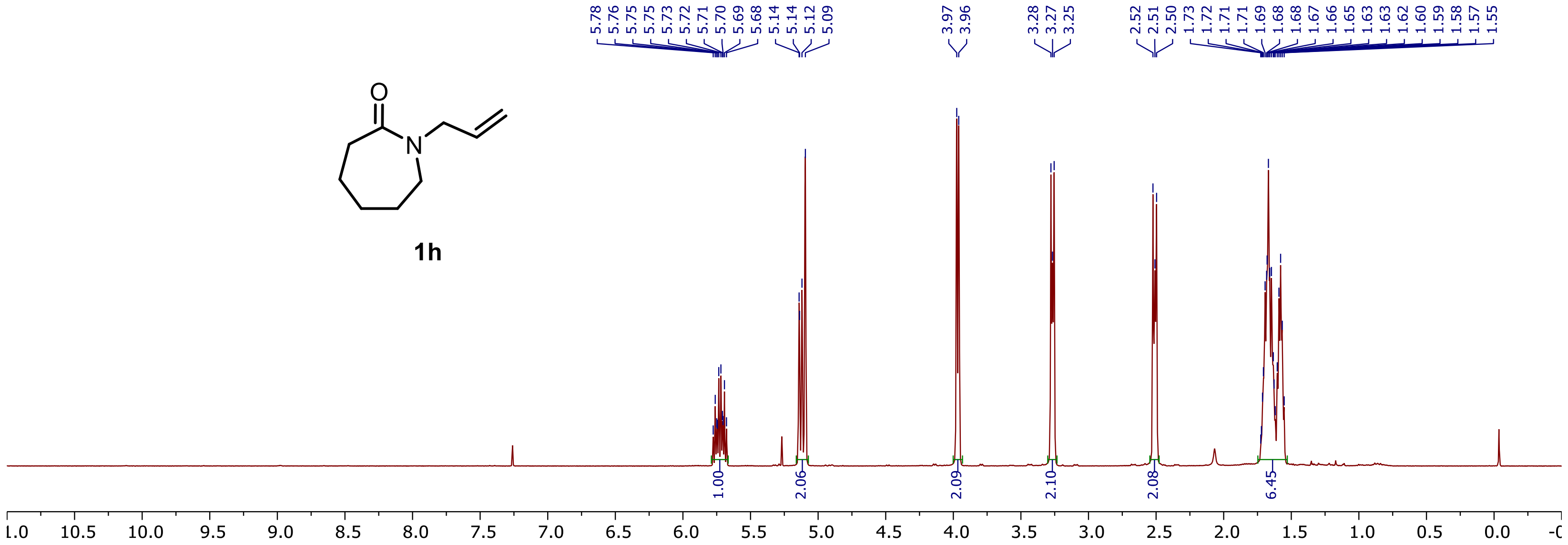
[1]H NMR (500 MHz, $CDCl_3$)

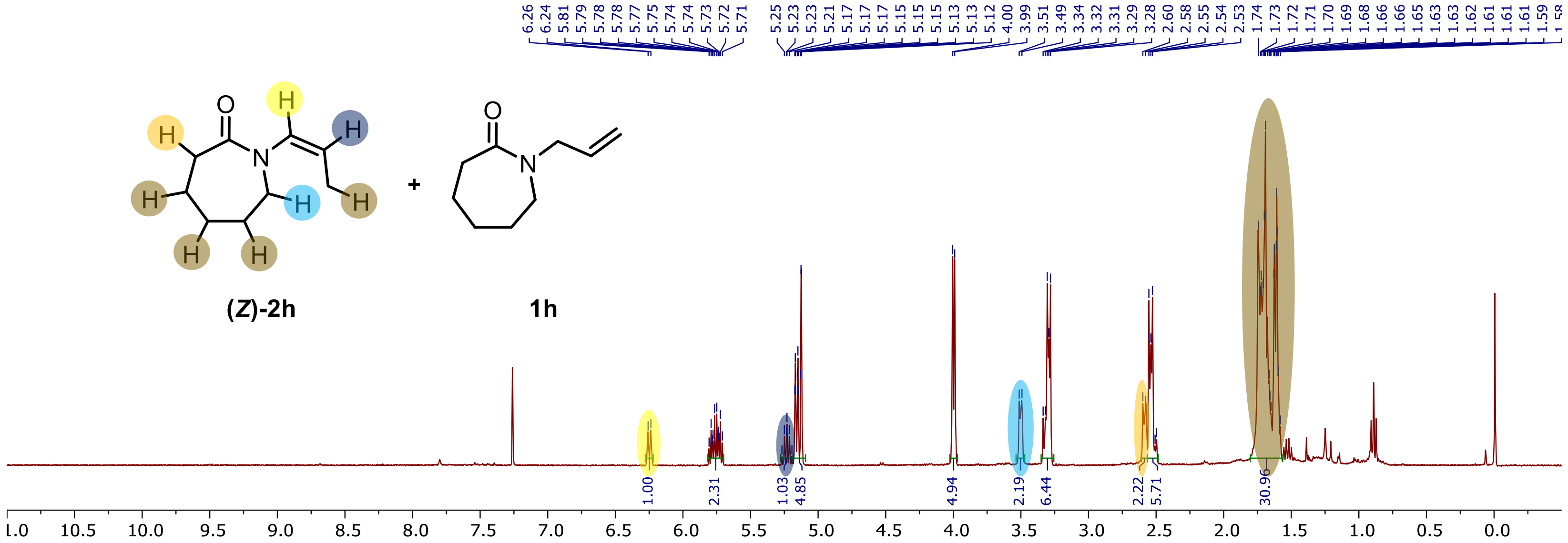


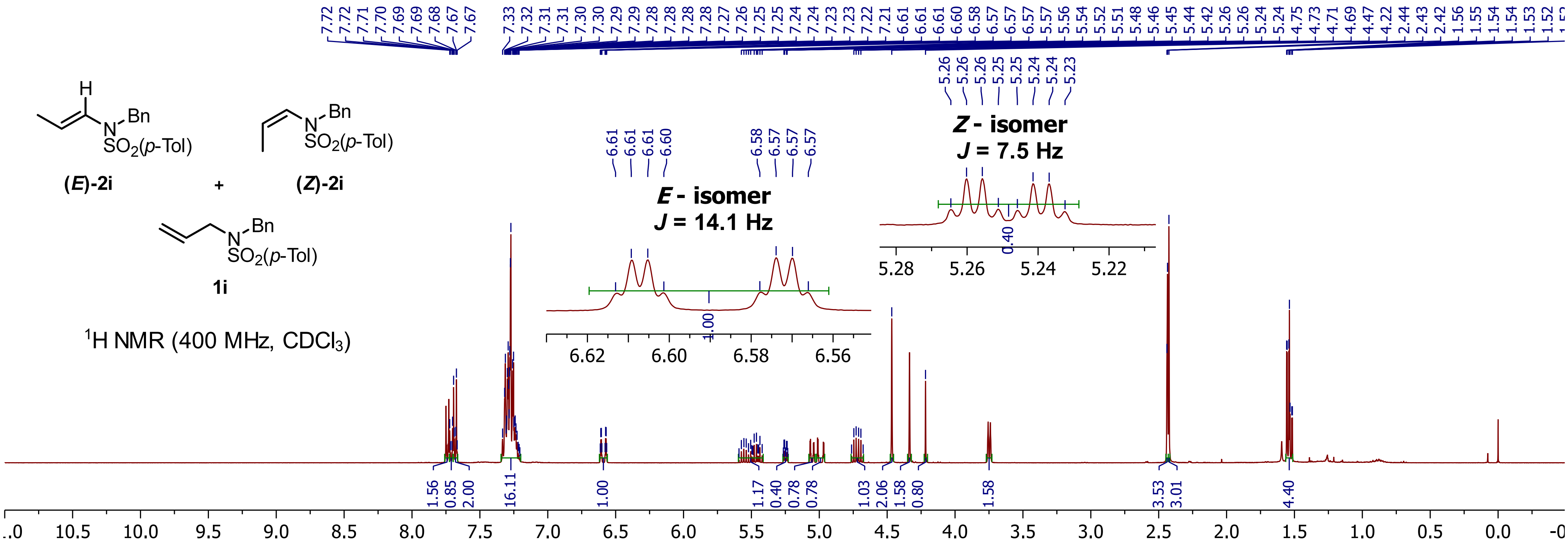

(E)-2h
^{1}H NMR (500 MHz, $CDCl_3$)
J = 14.5 Hz

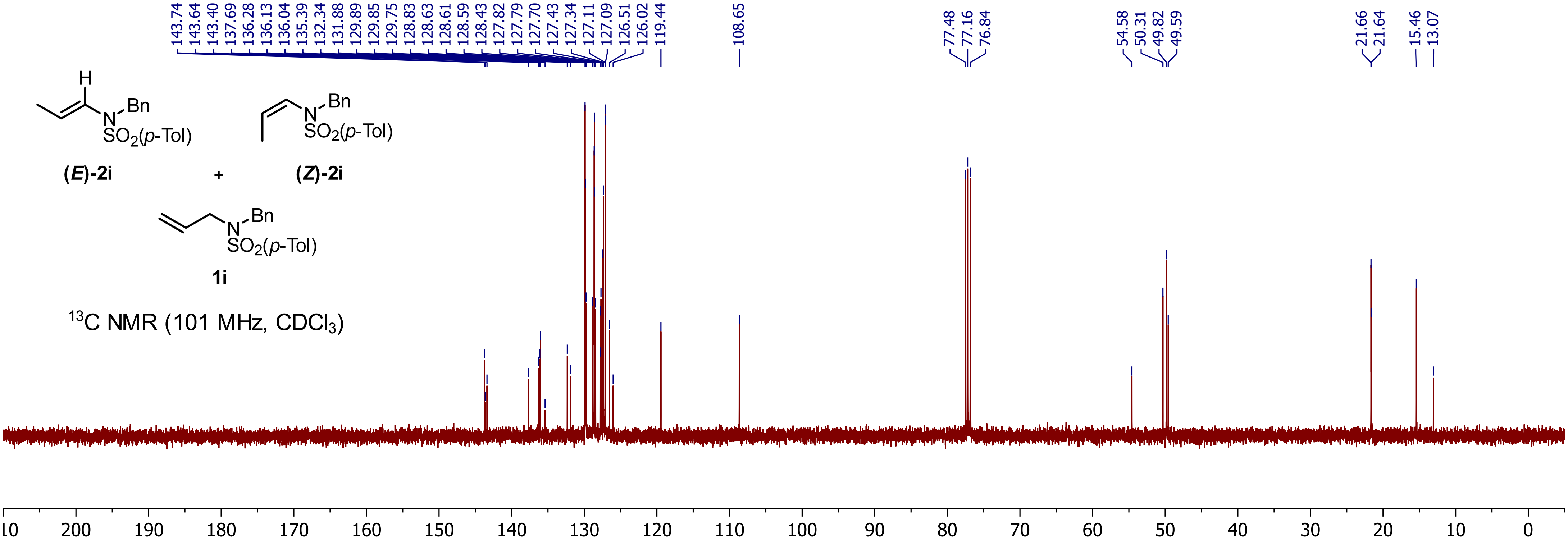

(E)-2h
^{13}C NMR (126 MHz, $CDCl_3$)

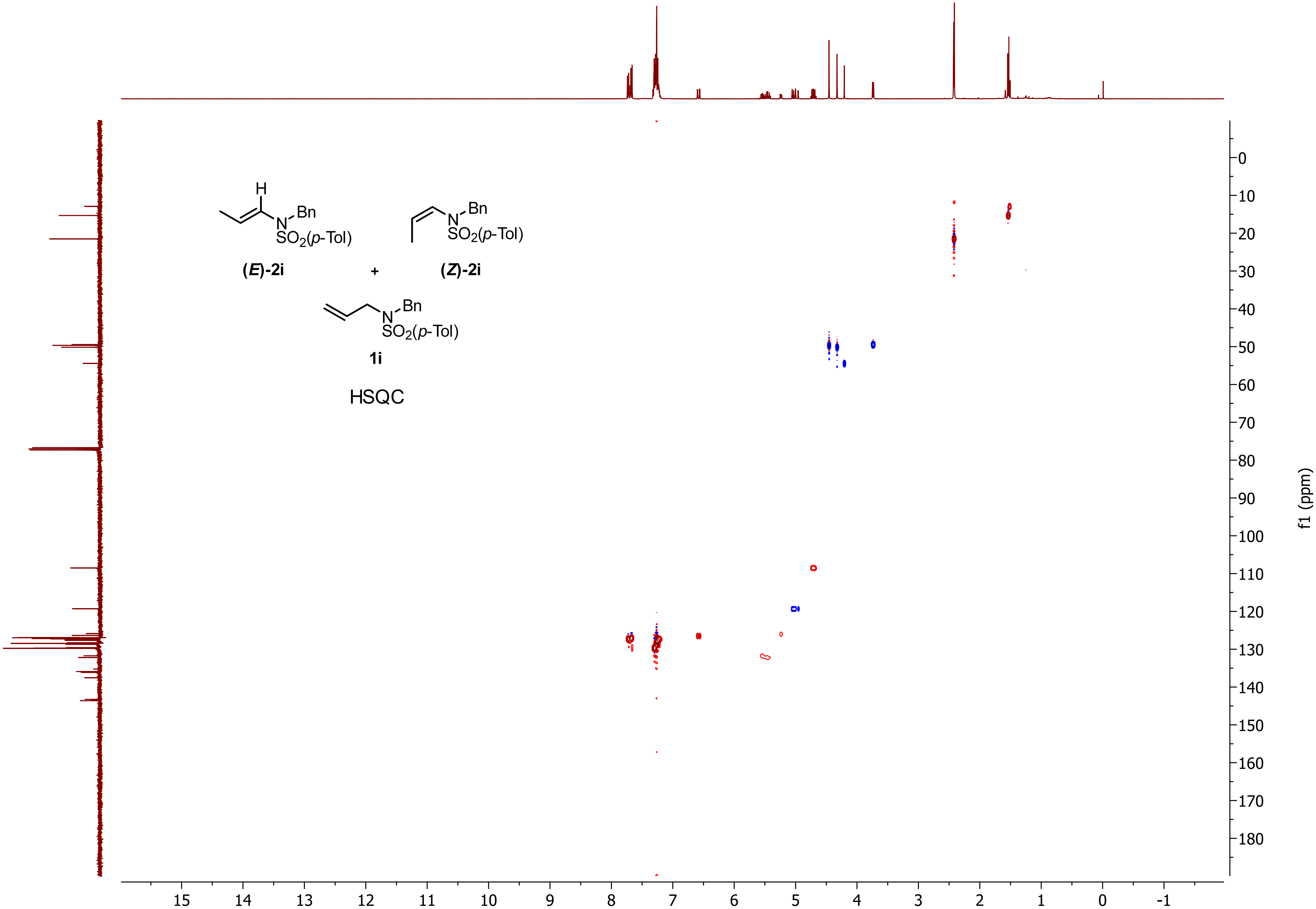

(Z)-2h
+
1h
1H NMR (500 MHz, CDCl3)
J = 8.3 Hz

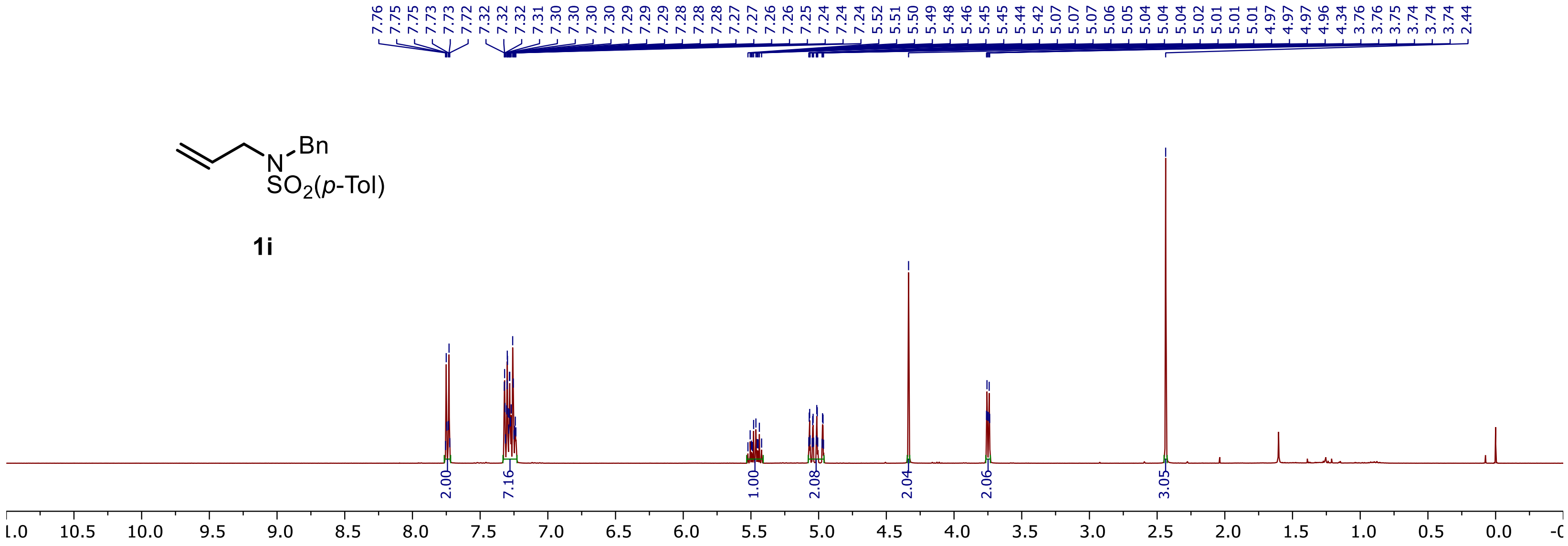

5.78 5.76 5.75 5.75 5.73 5.72 5.71 5.70 5.69 5.68 5.14 5.14 5.12 5.09 3.97 3.96 3.28 3.27 3.25 2.52 2.51 2.50 1.73 1.72 1.71 1.71 1.69 1.68 1.67 1.66 1.65 1.63 1.62 1.60 1.59 1.58 1.57 1.55
O
N
1h
1.00 2.06 2.09 2.10 2.08 6.45
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

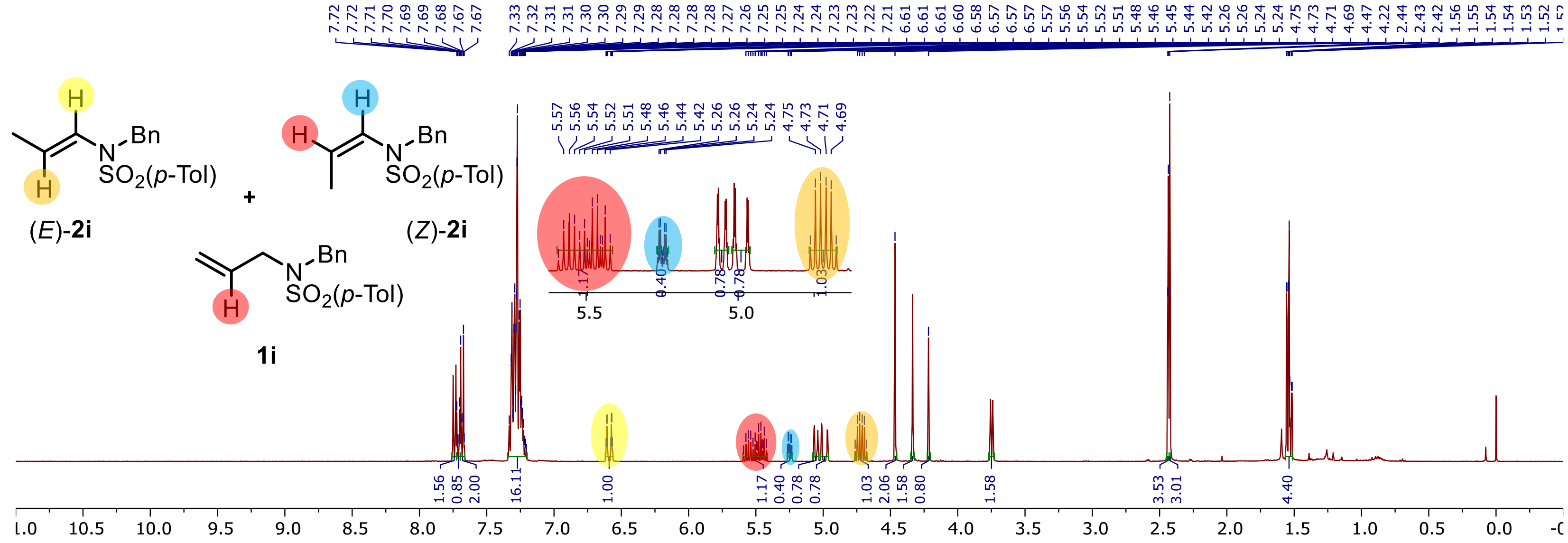

6.26 6.24 5.81 5.79 5.78 5.78 5.77 5.75 5.74 5.74 5.73 5.72 5.71 5.25 5.23 5.23 5.21 5.17 5.17 5.17 5.15 5.15 5.15 5.13 5.13 5.12 4.00 3.99 3.51 3.49 3.34 3.32 3.31 3.29 3.28 2.60 2.58 2.55 2.54 2.53 1.74 1.73 1.72 1.71 1.70 1.69 1.68 1.66 1.66 1.65 1.63 1.63 1.62 1.61 1.61 1.61 1.59 1.58
(Z)-2h
+
1h
1.00 2.31 1.03 4.85 4.94 2.19 6.44 2.22 5.71 30.96
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

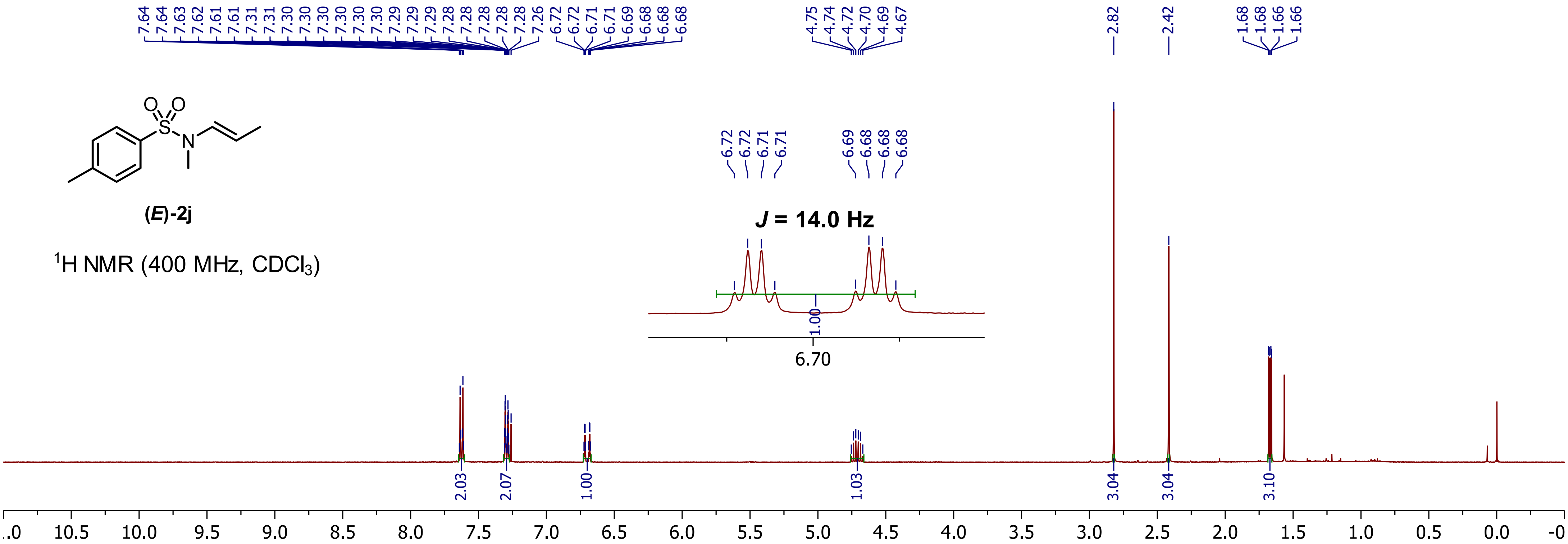

(E)-2i
+
(Z)-2i
1i
1H NMR (400 MHz, CDCl3)
E - isomer
J = 14.1 Hz
Z - isomer
J = 7.5 Hz

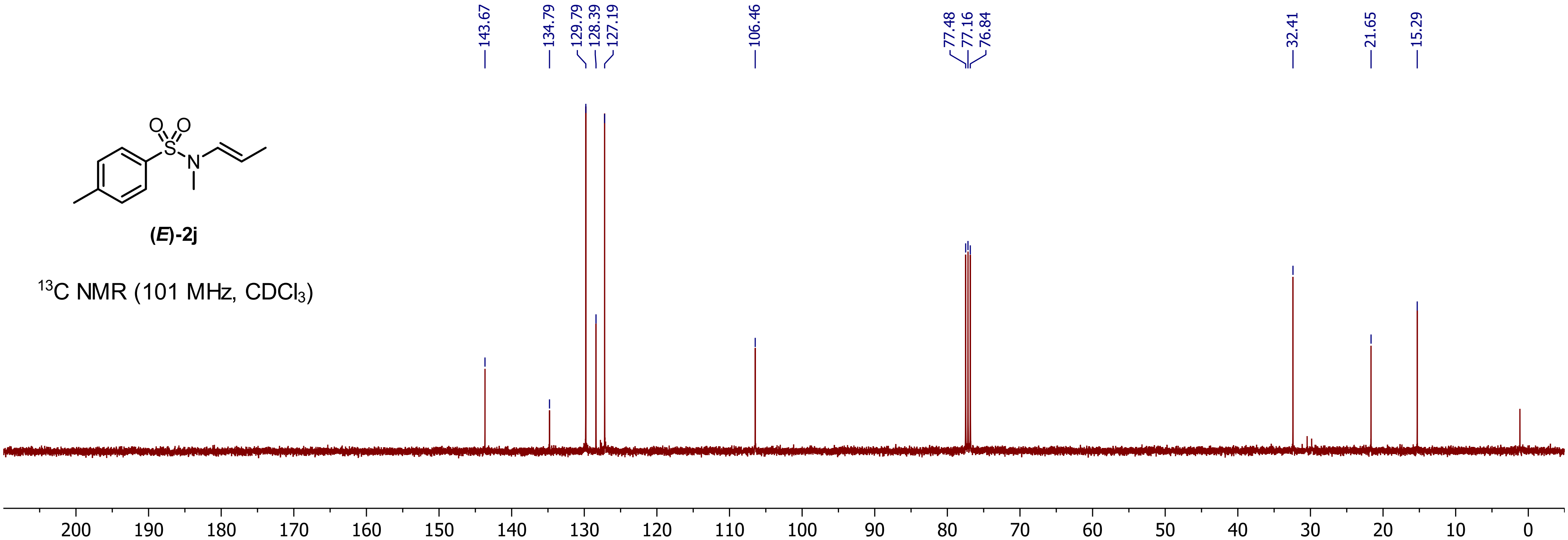

(E)-2i
+
(Z)-2i
1i
13C NMR (101 MHz, CDCl3)

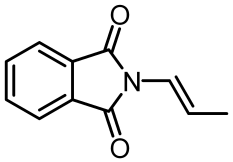

(E)-2i
+
(Z)-2i
1i
HSQC
f1 (ppm)





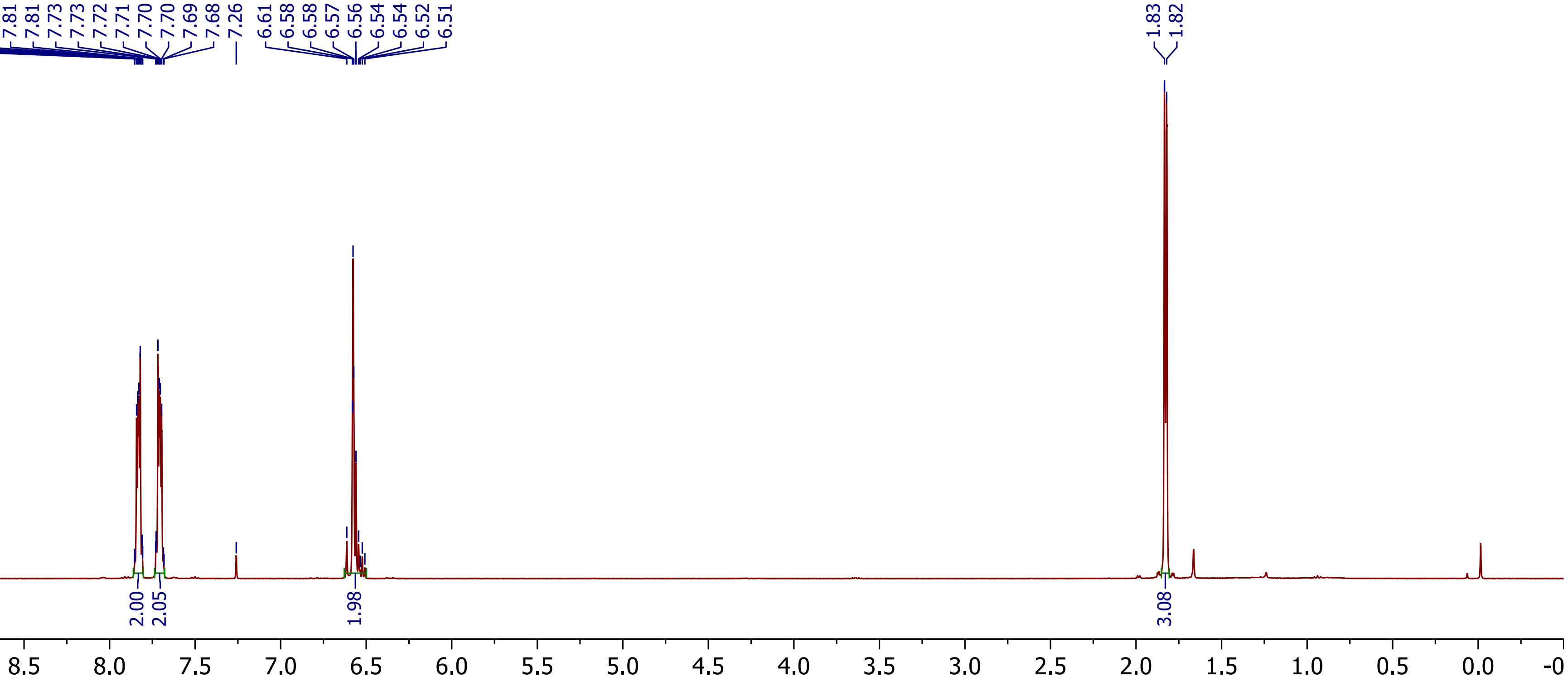

(E)-2j
^{1}H NMR (400 MHz, CDCl$_3$)
J = 14.0 Hz

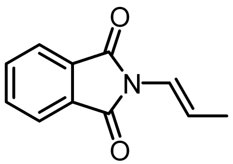

(E)-2j
^{13}C NMR (101 MHz, CDCl$_3$)



(*E*)-2k

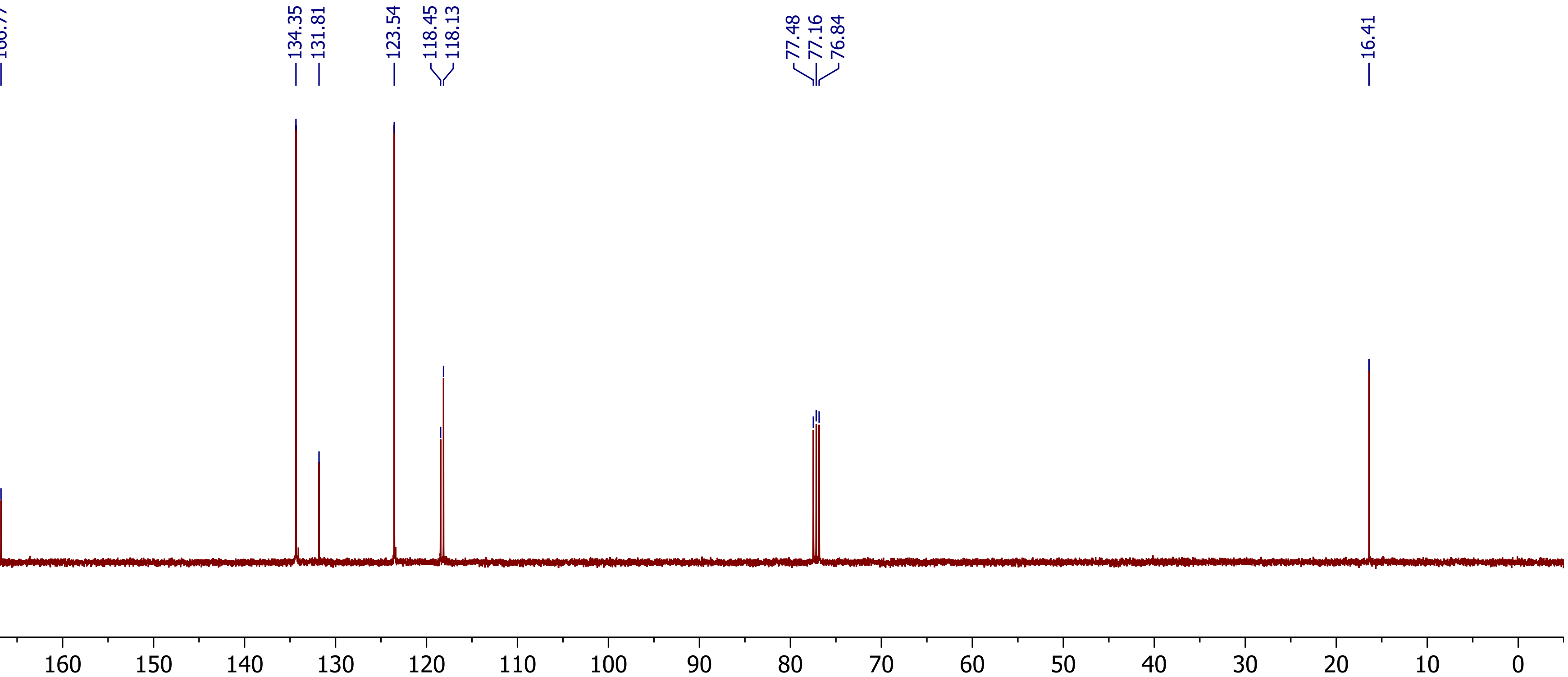
^{1}H NMR (400 MHz, $CDCl_3$)

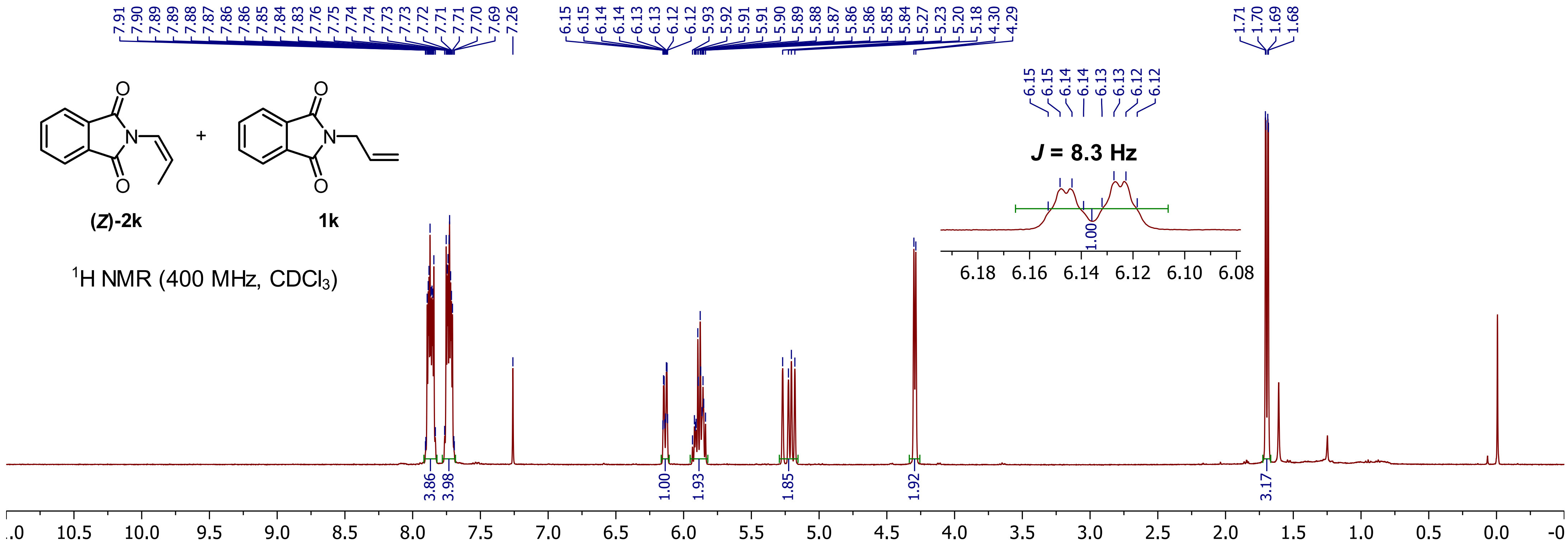


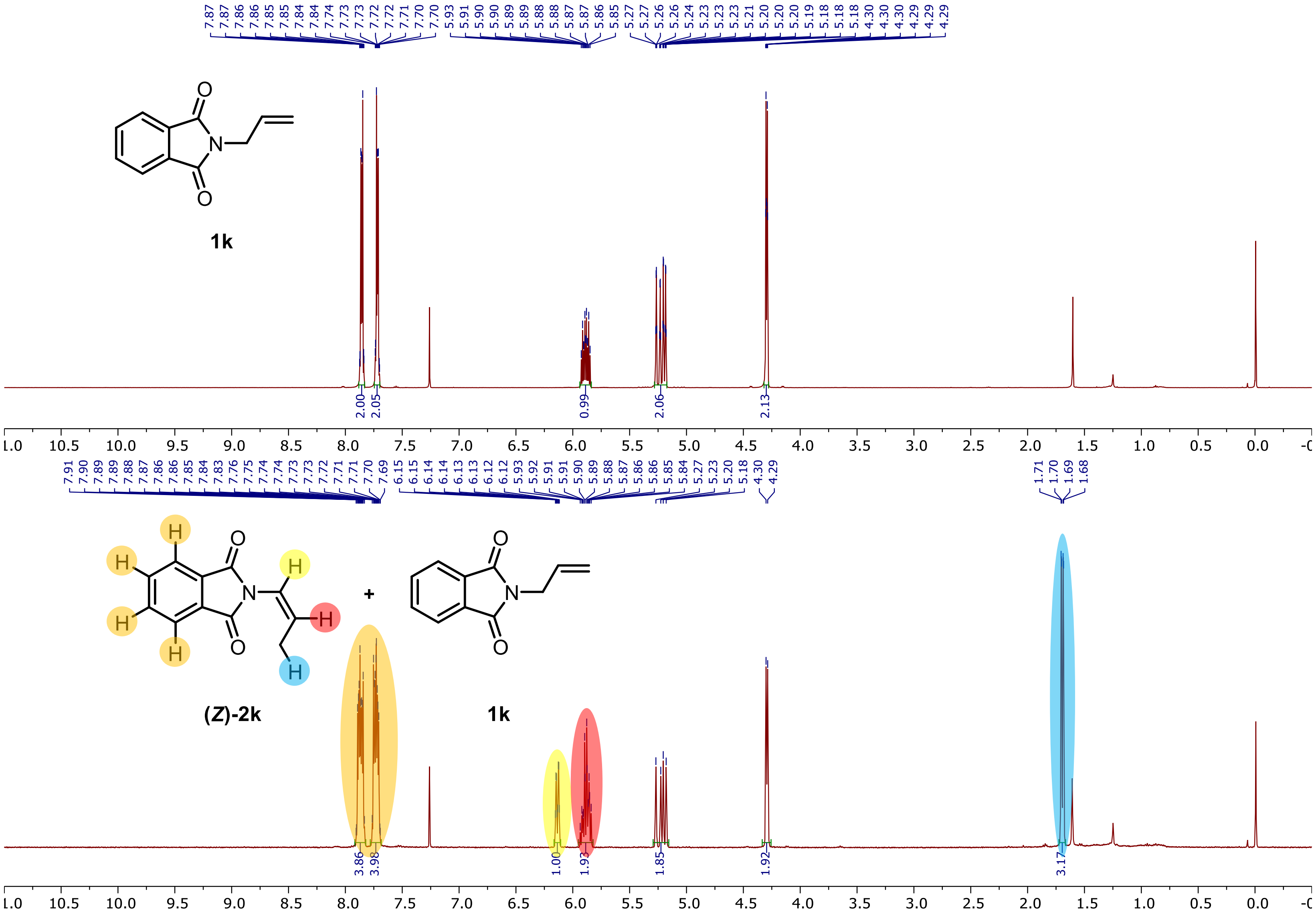


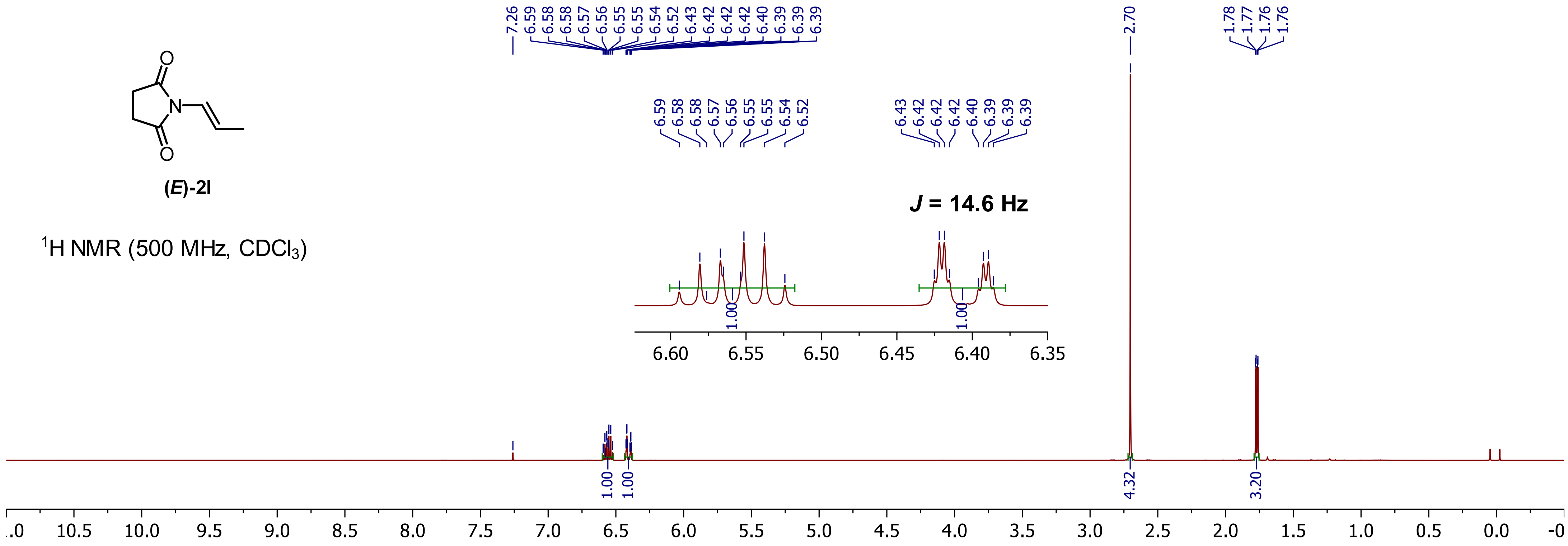
(*E*)-2k

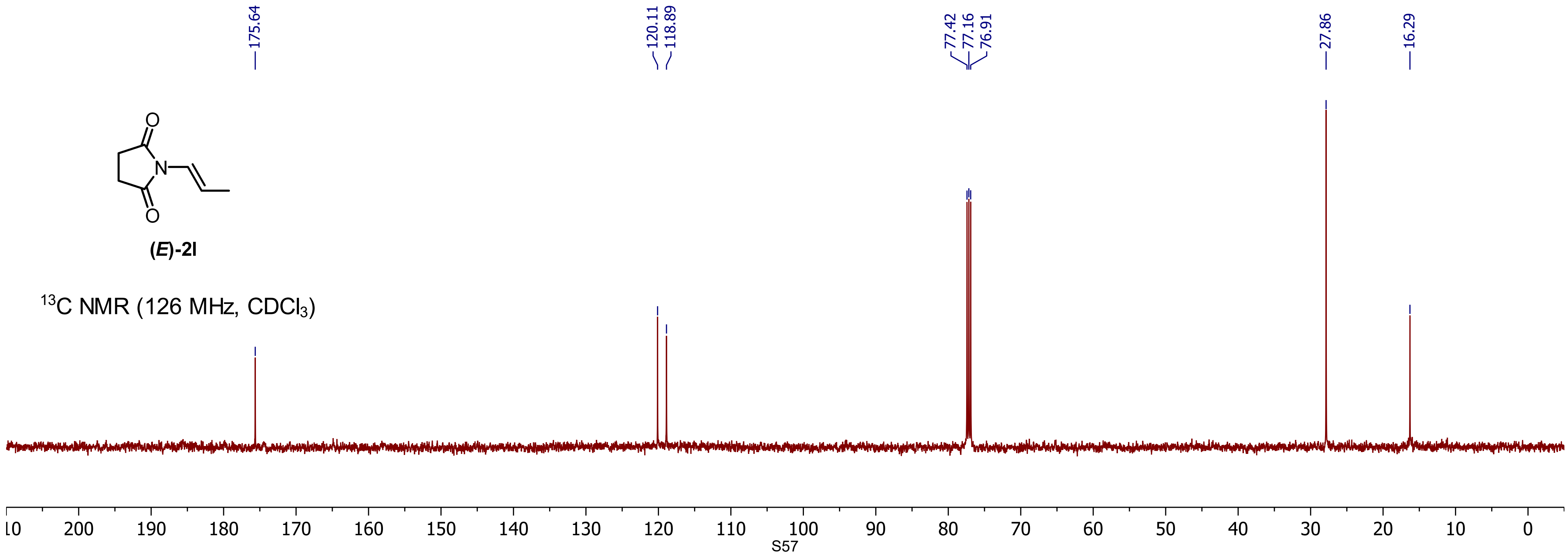
^{13}C NMR (101 MHz, $CDCl_3$)

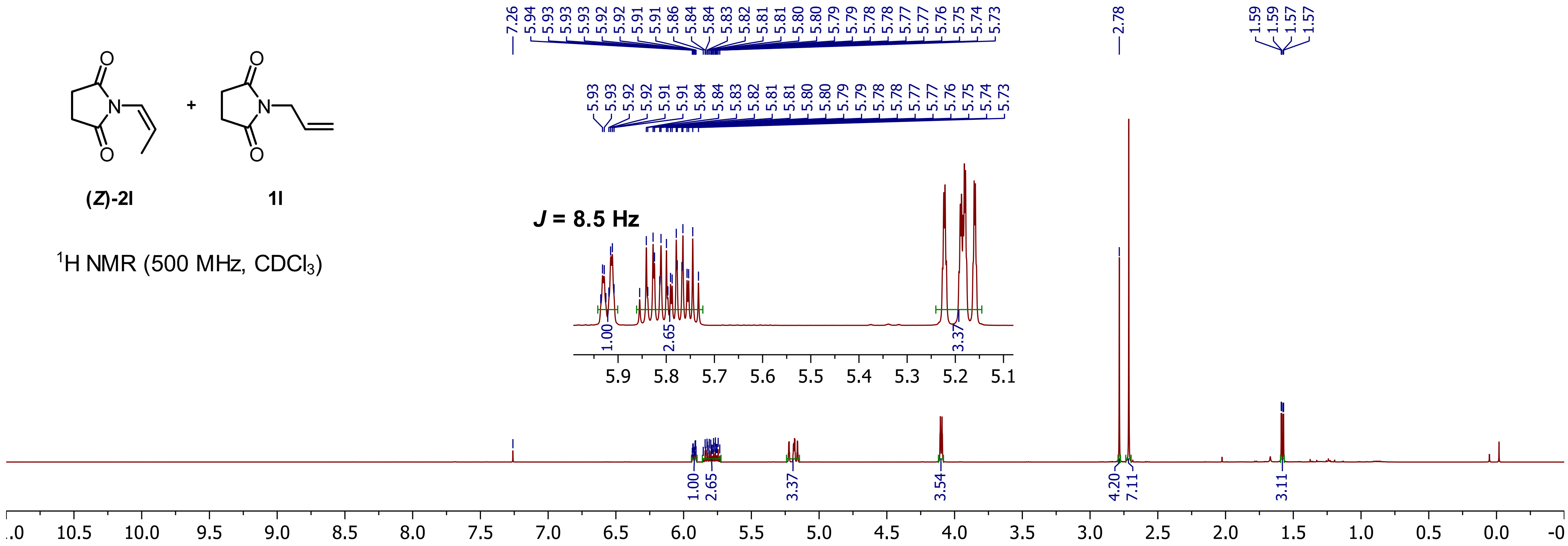


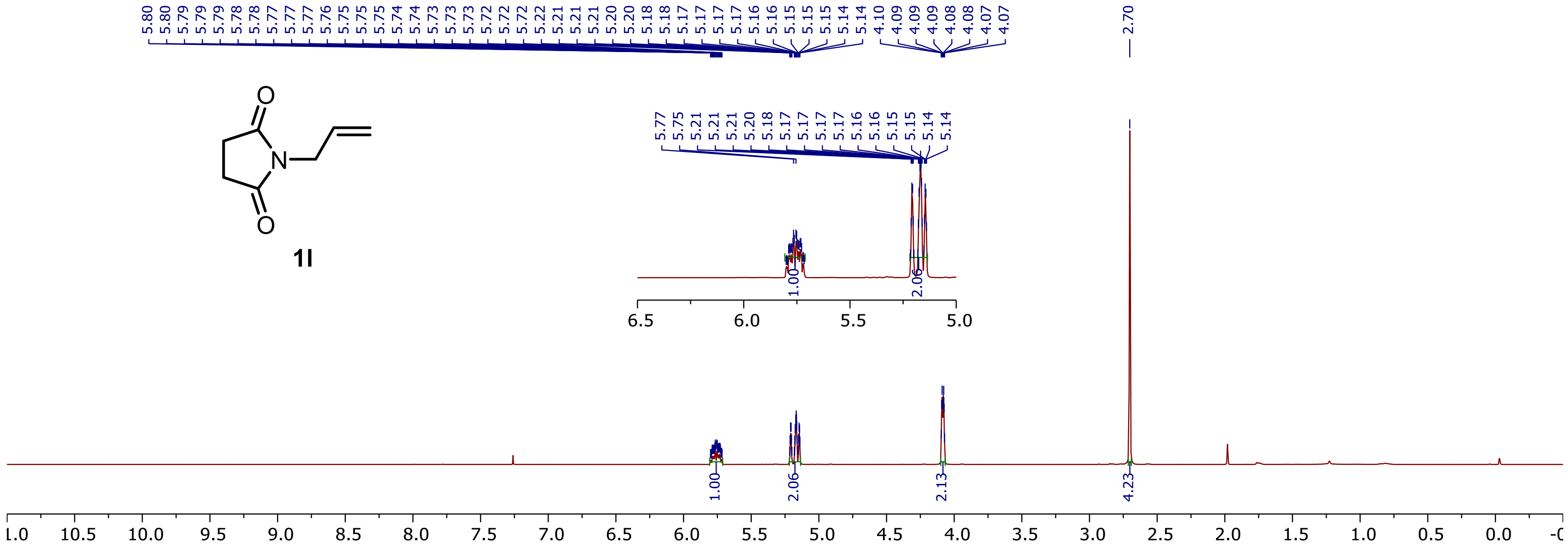

(Z)-2k
1k
¹H NMR (400 MHz, CDCl₃)
J = 8.3 Hz

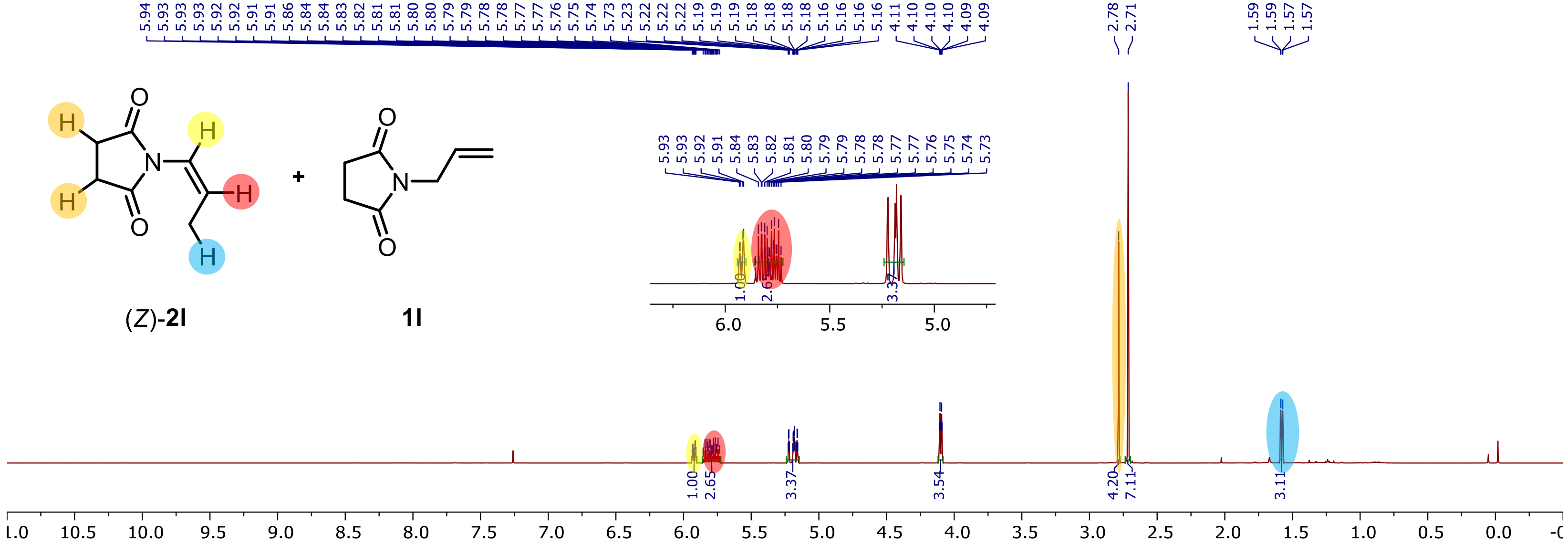

1k
(Z)-2k
+
1k

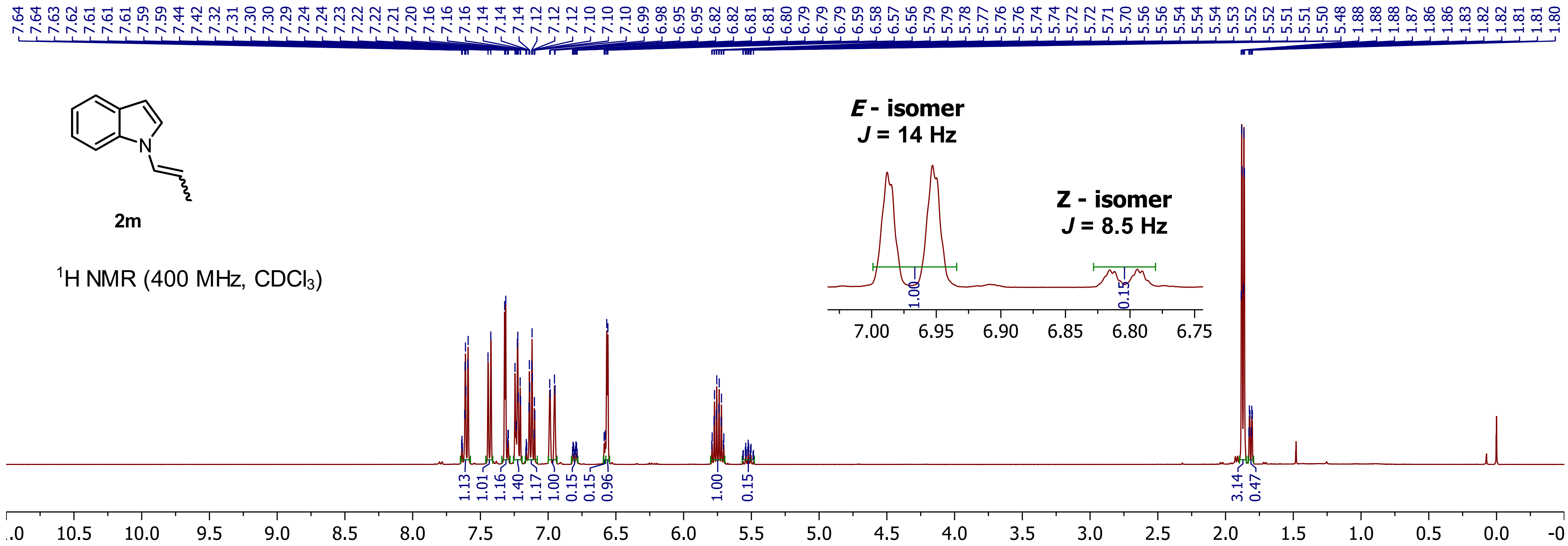

(*E*)-2l
^{1}H NMR (500 MHz, $CDCl_3$)
J = 14.6 Hz

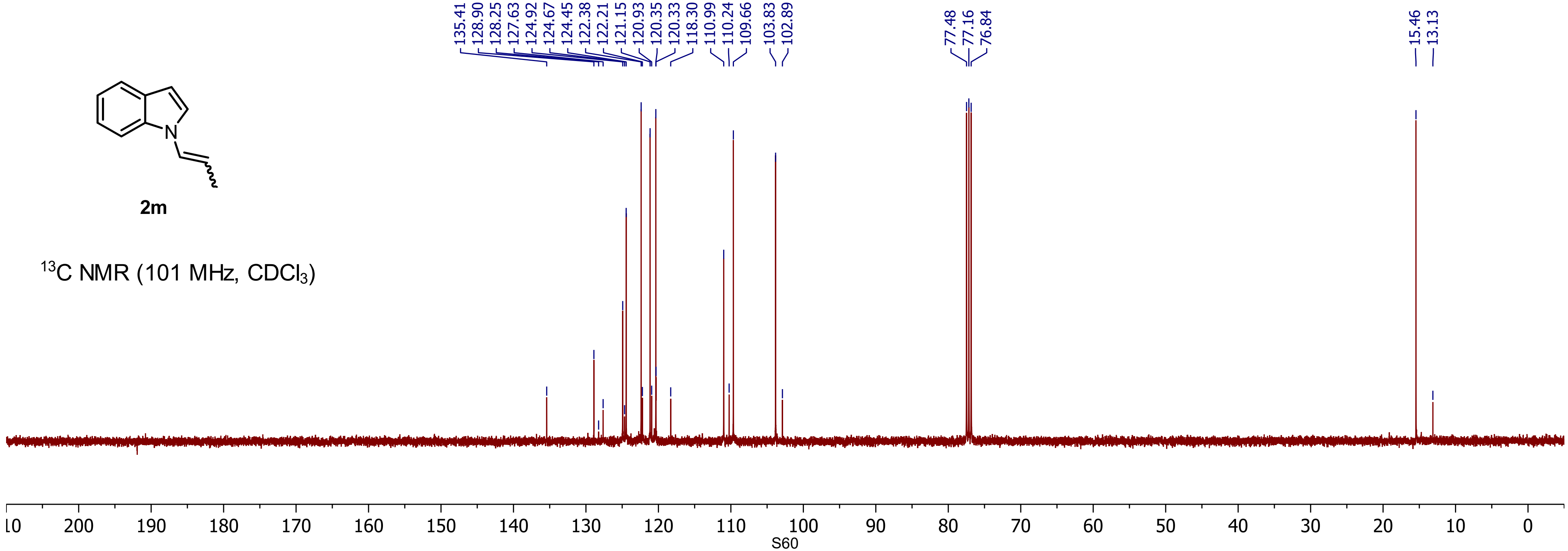

(*E*)-2l
^{13}C NMR (126 MHz, $CDCl_3$)

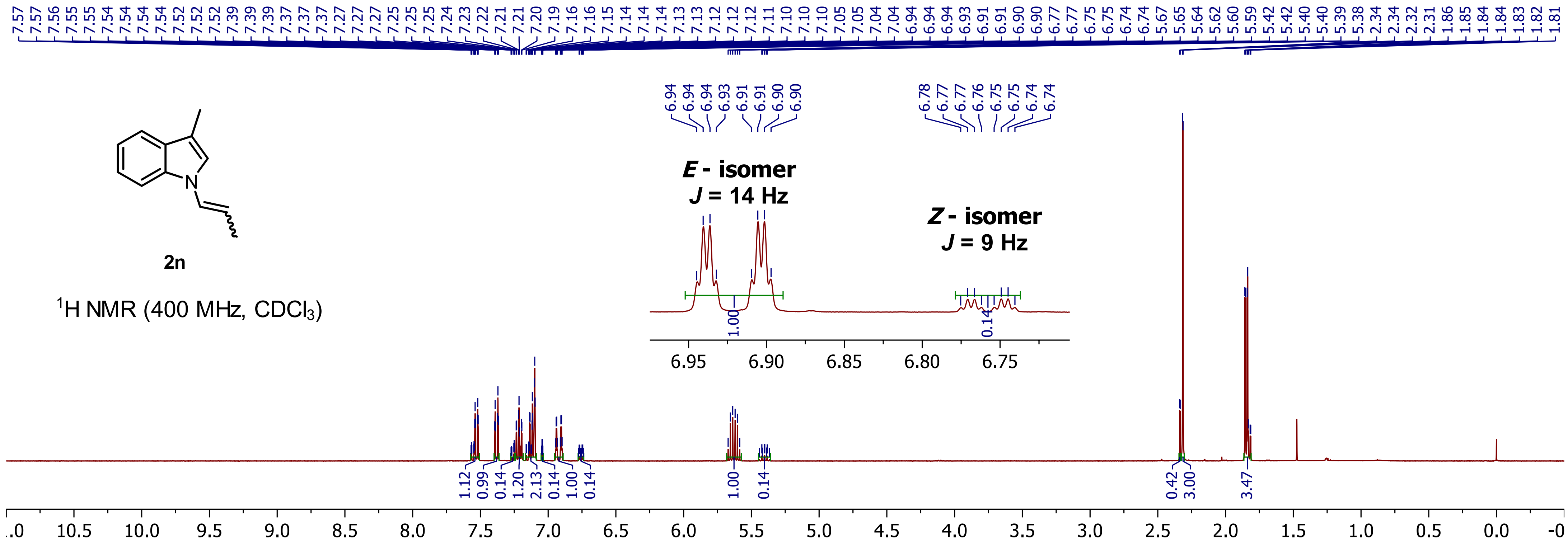

(Z)-2l
1l
¹H NMR (500 MHz, CDCl₃)
J = 8.5 Hz

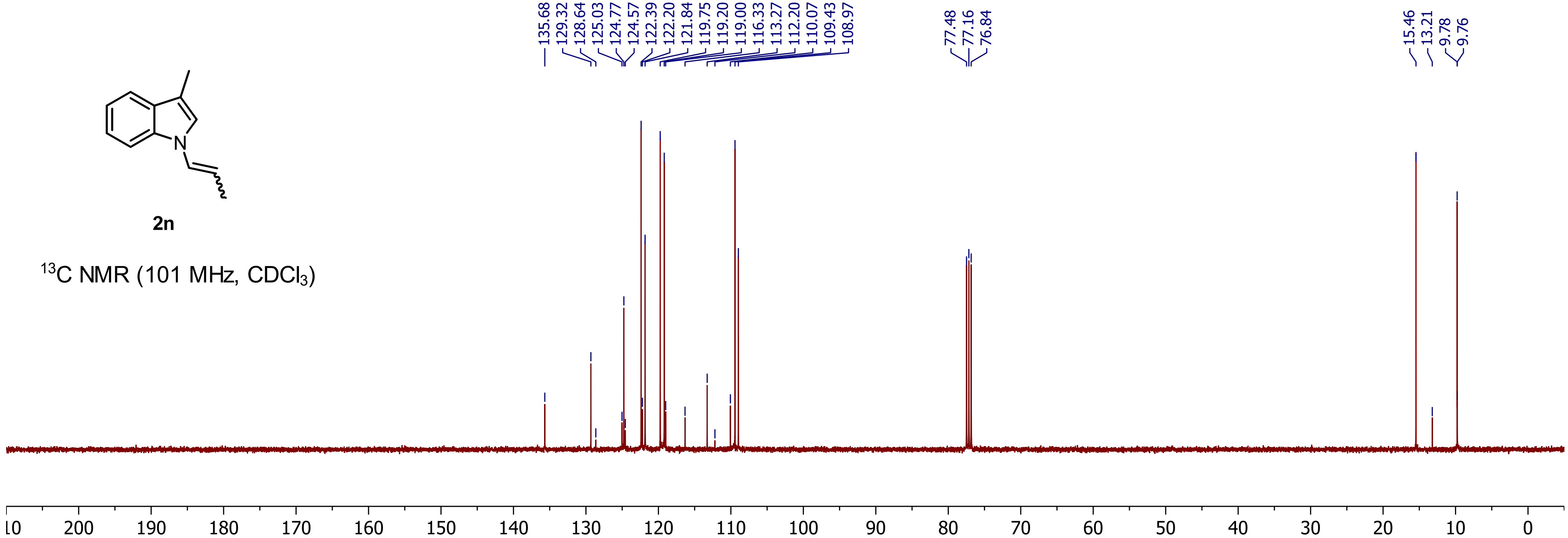

1l

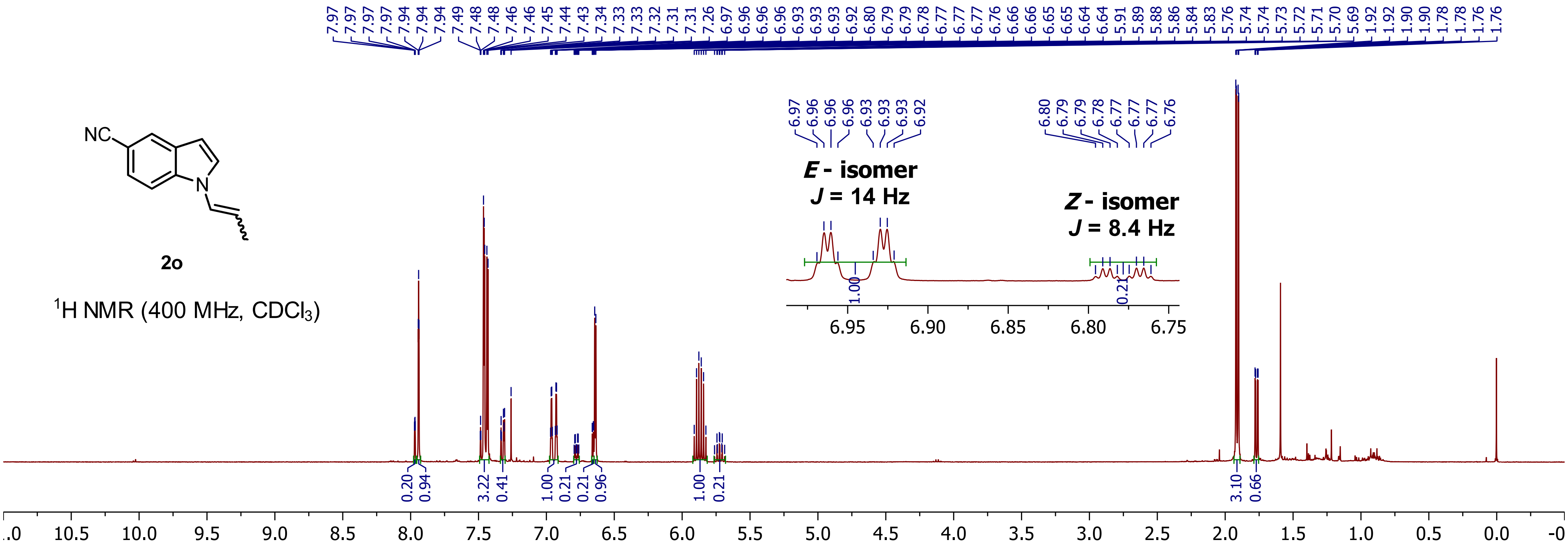

(Z)-2l
+
1l

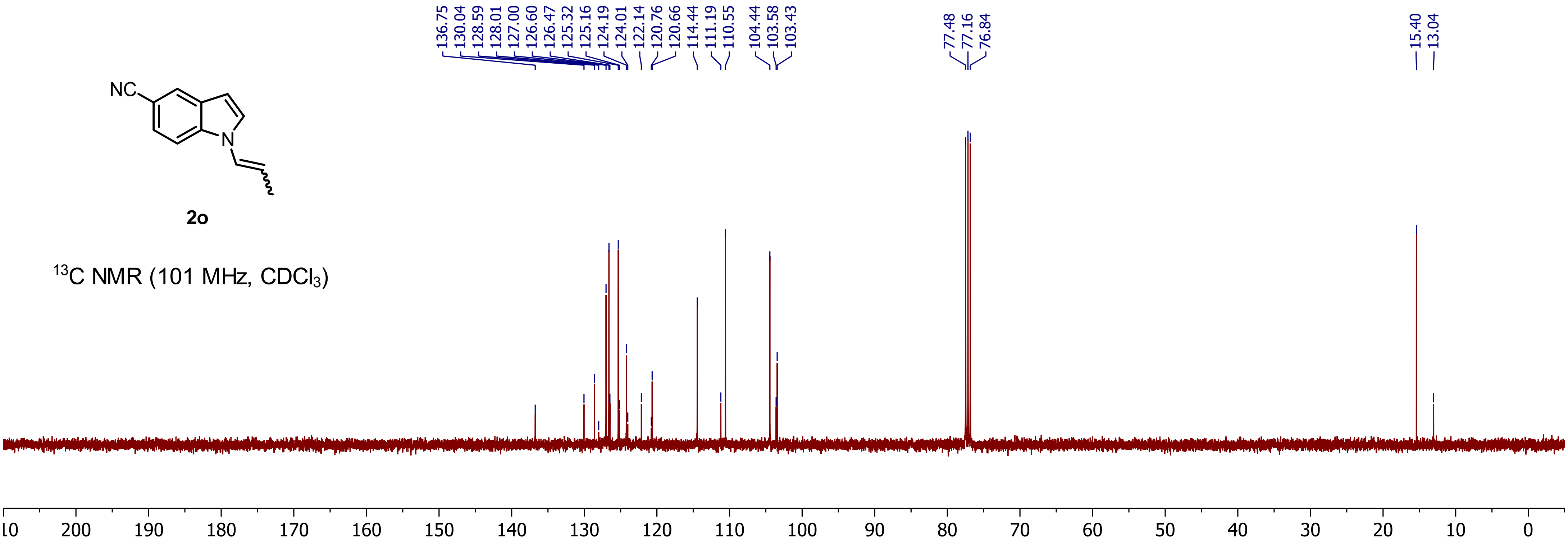

7.64 7.64 7.63 7.62 7.61 7.61 7.61 7.59 7.59 7.44 7.42 7.32 7.31 7.30 7.30 7.29 7.24 7.24 7.23 7.22 7.22 7.21 7.20 7.16 7.16 7.16 7.14 7.14 7.14 7.12 7.12 7.12 7.10 7.10 7.10 6.99 6.98 6.95 6.95 6.82 6.82 6.81 6.81 6.80 6.79 6.79 6.79 6.59 6.58 6.57 6.56 5.79 5.79 5.78 5.77 5.76 5.76 5.74 5.74 5.72 5.72 5.71 5.70 5.56 5.56 5.54 5.54 5.54 5.53 5.52 5.52 5.51 5.51 5.50 5.48 1.88 1.88 1.88 1.87 1.86 1.86 1.83 1.82 1.82 1.81 1.81 1.80
N
2m
^{1}H NMR (400 MHz, CDCl$_3$)
E - isomer
J = 14 Hz
Z - isomer
J = 8.5 Hz
1.00
0.15
7.00 6.95 6.90 6.85 6.80 6.75
1.13 1.01 1.16 1.40 1.17 1.00 0.15 0.15 0.96
1.00 0.15
3.14 0.47
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0

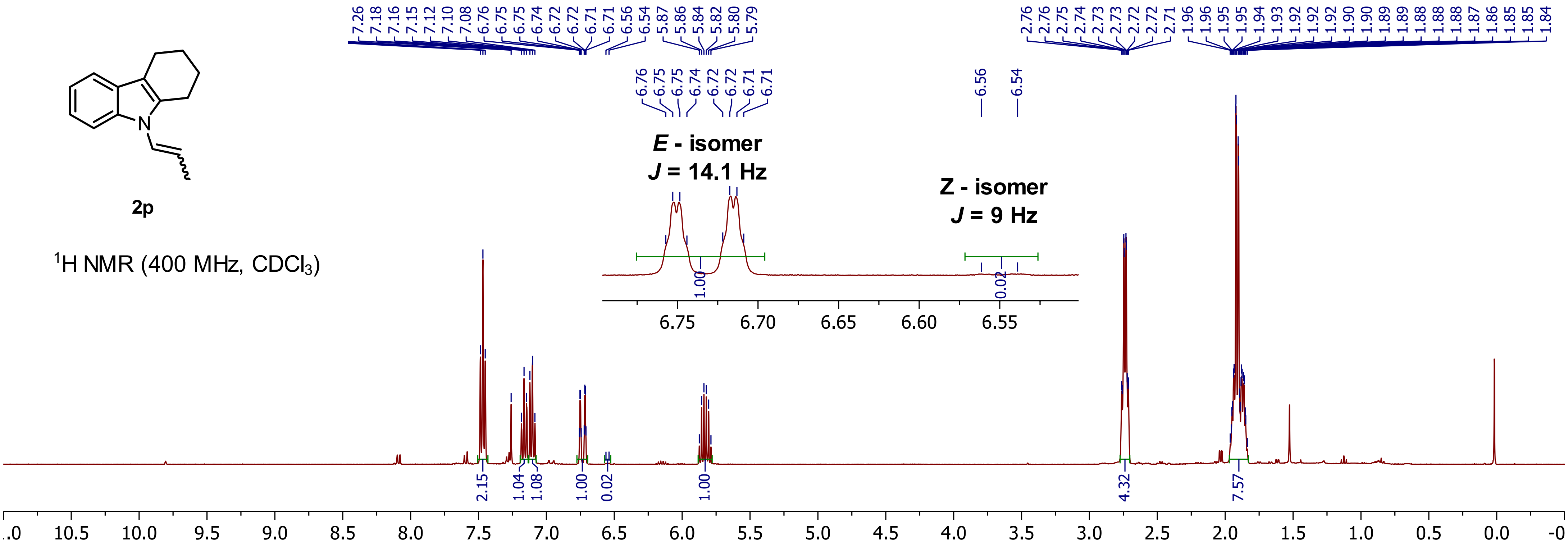

135.41 128.90 128.25 127.63 124.92 124.67 124.45 122.38 122.21 121.15 120.93 120.35 120.33 118.30 110.99 110.24 109.66 103.83 102.89
77.48 77.16 76.84
15.46 13.13
N
2m
^{13}C NMR (101 MHz, CDCl$_3$)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

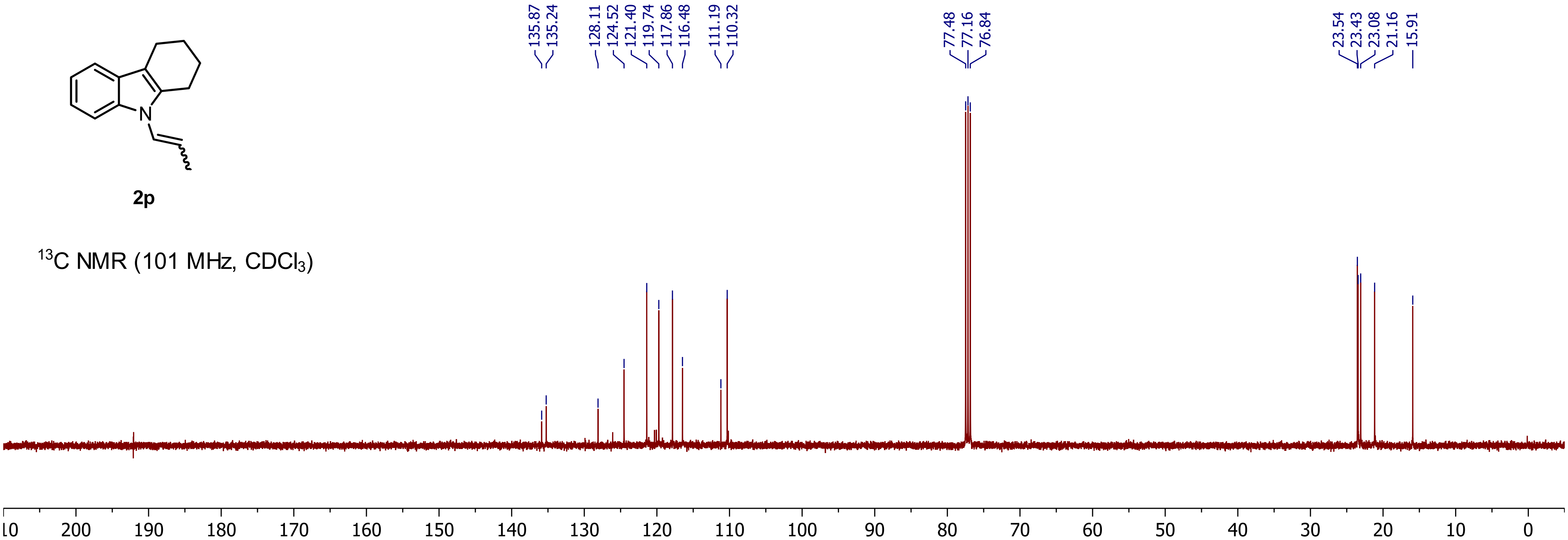

2n
^{1}H NMR (400 MHz, $CDCl_3$)
E - isomer
J = 14 Hz
Z - isomer
J = 9 Hz

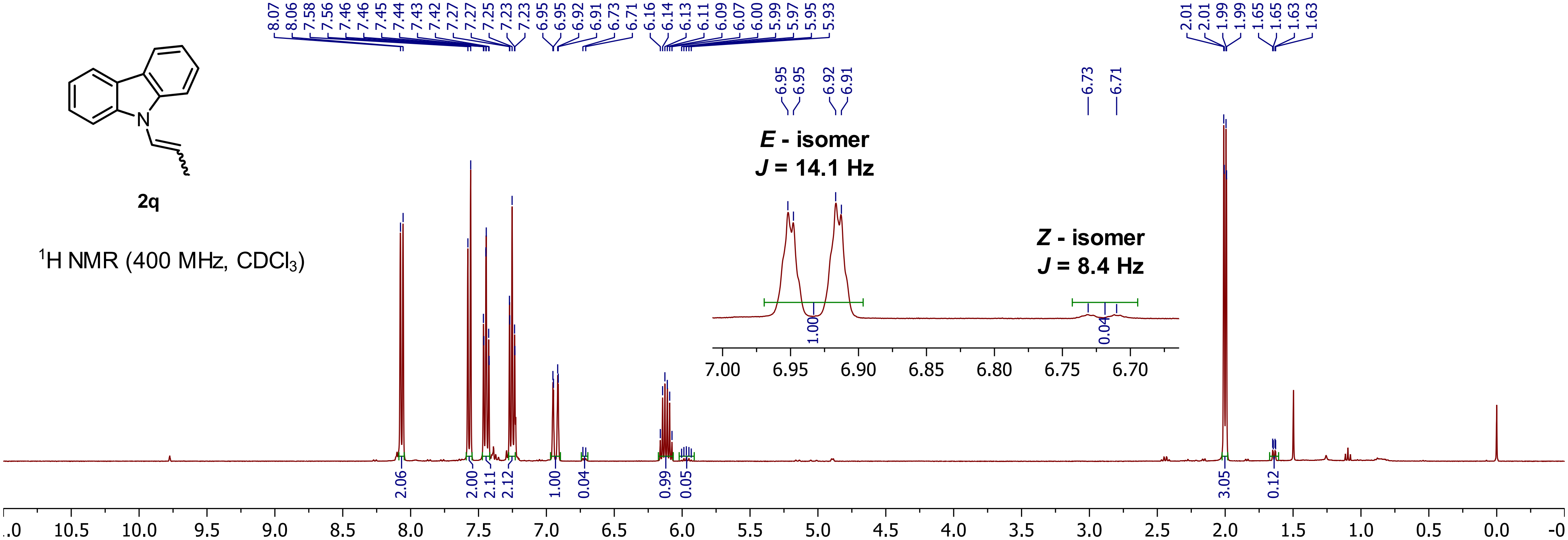

2n
^{13}C NMR (101 MHz, $CDCl_3$)

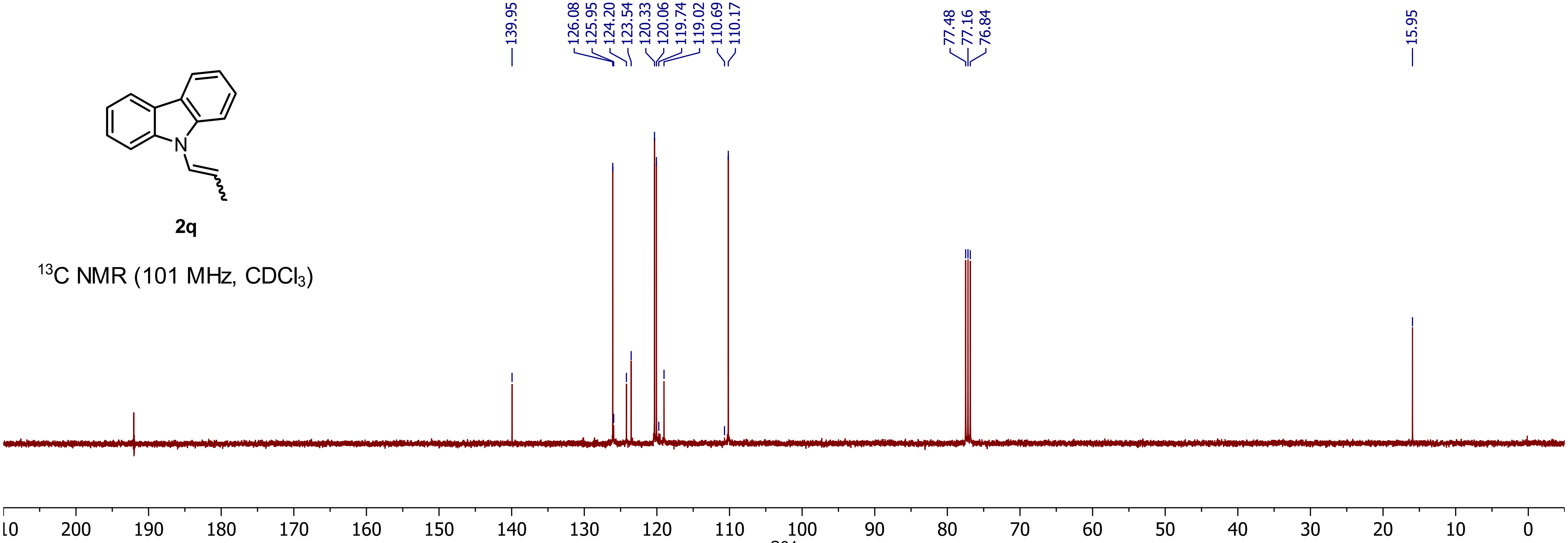

7.97 7.97 7.97 7.97 7.94 7.94 7.94 7.49 7.48 7.48 7.46 7.46 7.45 7.44 7.43 7.34 7.33 7.33 7.32 7.31 7.31 7.26 6.97 6.96 6.96 6.96 6.93 6.93 6.93 6.92 6.80 6.79 6.79 6.78 6.77 6.77 6.77 6.76 6.66 6.66 6.65 6.65 6.64 6.64 5.91 5.89 5.88 5.86 5.84 5.83 5.76 5.74 5.74 5.73 5.72 5.71 5.70 5.69 1.92 1.92 1.90 1.90 1.78 1.78 1.76 1.76
NC
N
2o
^{1}H NMR (400 MHz, CDCl$_3$)
E - isomer
J = 14 Hz
Z - isomer
J = 8.4 Hz
0.20 0.94 3.22 0.41 1.00 0.21 0.21 0.96 1.00 0.21 3.10 0.66

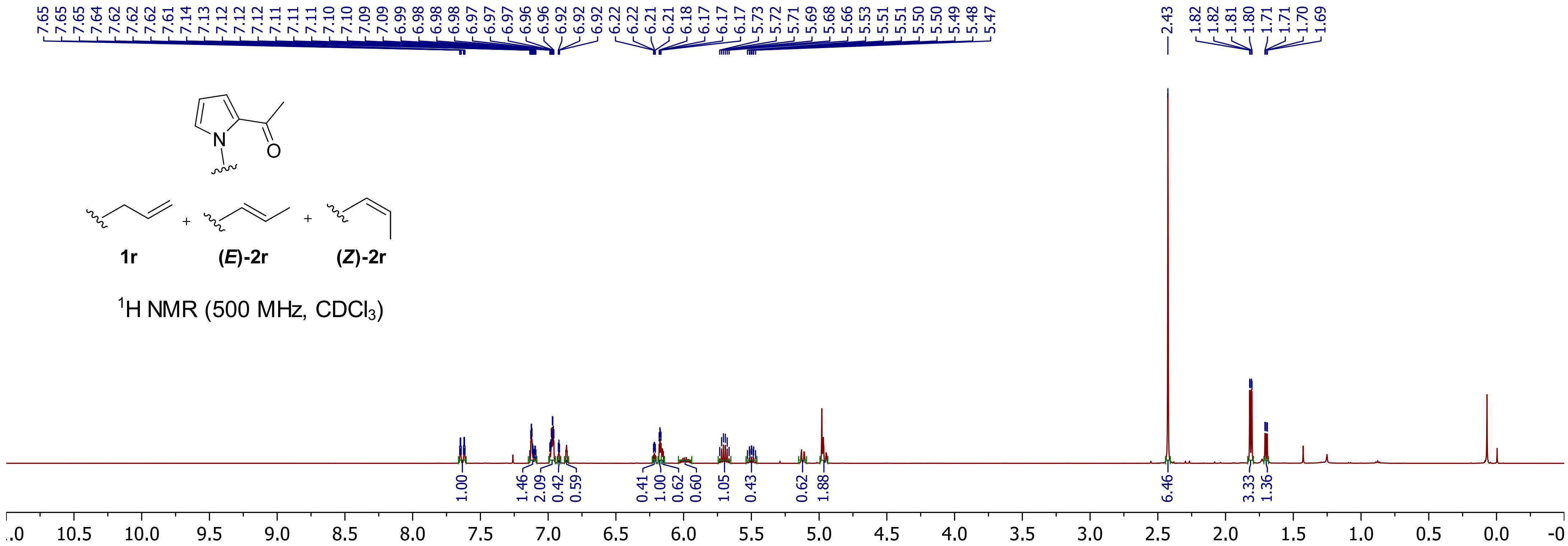

136.75 130.04 128.59 128.01 127.00 126.60 126.47 125.32 125.16 124.19 124.01 122.14 120.76 120.66 114.44 111.19 110.55 104.44 103.58 103.43 77.48 77.16 76.84 15.40 13.04
NC
N
2o
^{13}C NMR (101 MHz, CDCl$_3$)

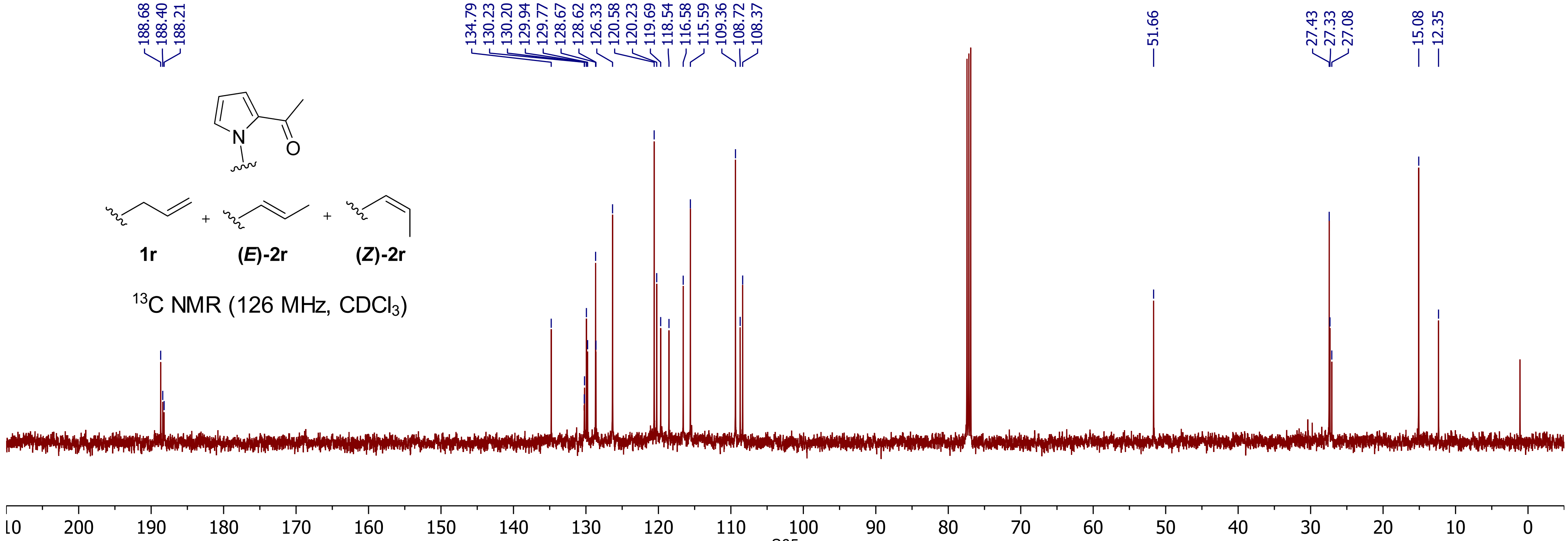

N
2p
1H NMR (400 MHz, CDCl3)
E - isomer
J = 14.1 Hz
Z - isomer
J = 9 Hz
6.75
6.70
6.65
6.60
6.55
2.15
1.04
1.08
1.00
0.02
1.00
4.32
7.57

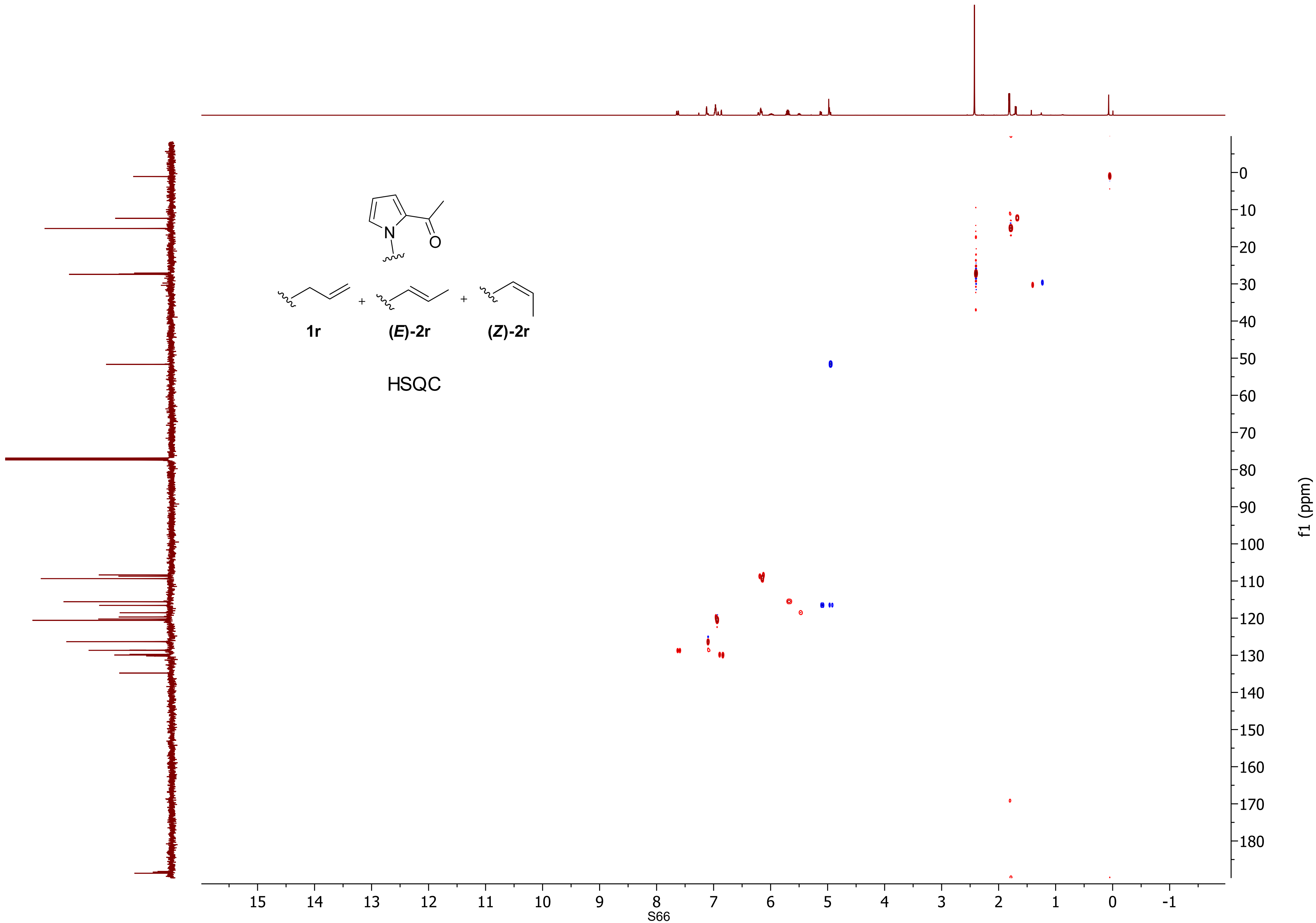

N
2p
13C NMR (101 MHz, CDCl3)
135.87
135.24
128.11
124.52
121.40
119.74
117.86
116.48
111.19
110.32
77.48
77.16
76.84
23.54
23.43
23.08
21.16
15.91

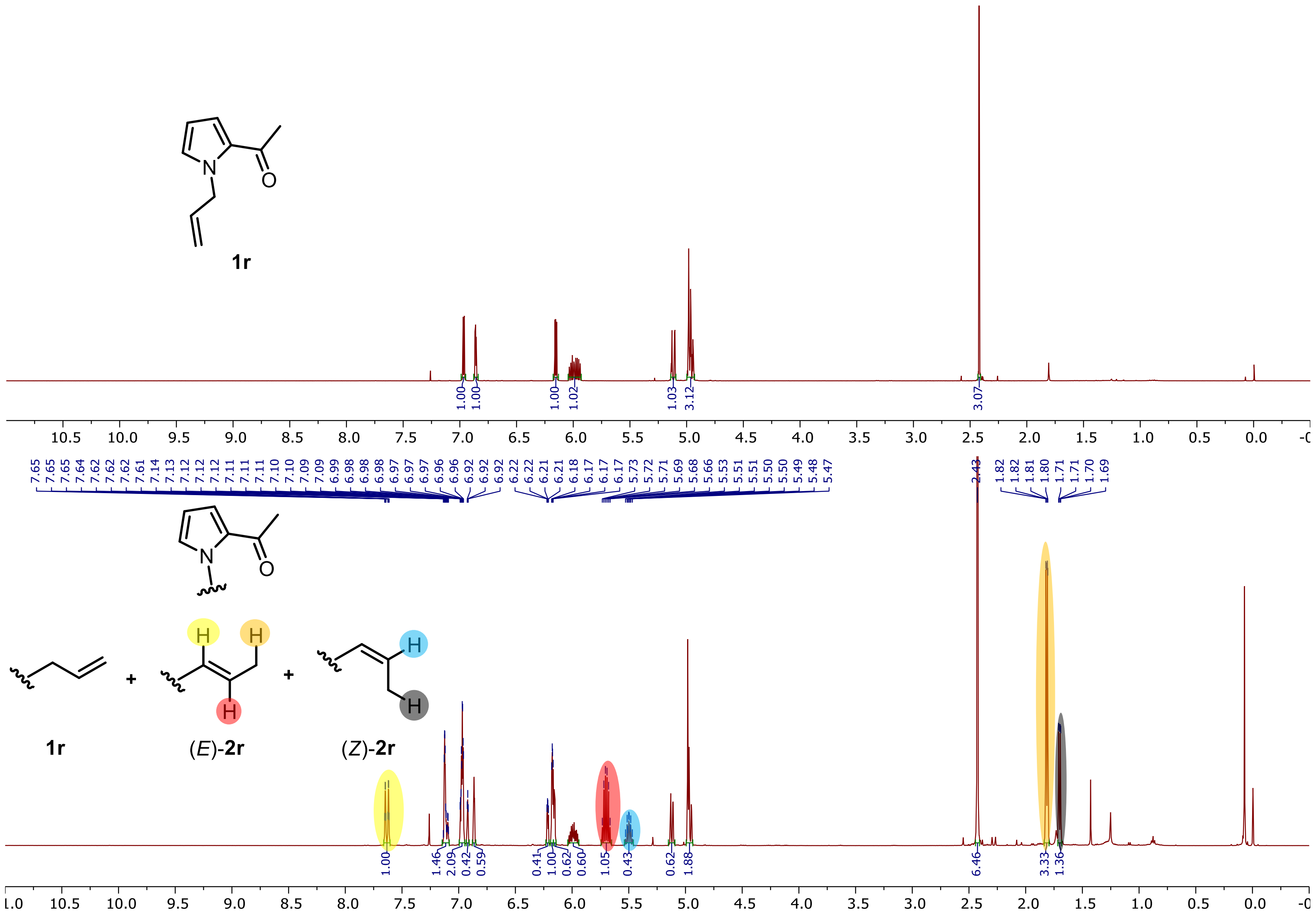

2q
^{1}H NMR (400 MHz, $CDCl_3$)
8.07 8.06 7.58 7.56 7.46 7.46 7.45 7.44 7.43 7.42 7.27 7.27 7.25 7.23 7.23 6.95 6.95 6.92 6.91 6.73 6.71 6.16 6.14 6.13 6.11 6.09 6.07 6.00 5.99 5.97 5.95 5.93
2.01 2.01 1.99 1.99 1.65 1.65 1.63 1.63
E - isomer
J = 14.1 Hz
Z - isomer
J = 8.4 Hz
2.06 2.00 2.11 2.12 1.00 0.04 0.99 0.05 3.05 0.12
1.00 0.04


2q
^{13}C NMR (101 MHz, $CDCl_3$)
139.95
126.08 125.95 124.20 123.54 120.33 120.06 119.74 119.02 110.69 110.17
77.48 77.16 76.84
15.95

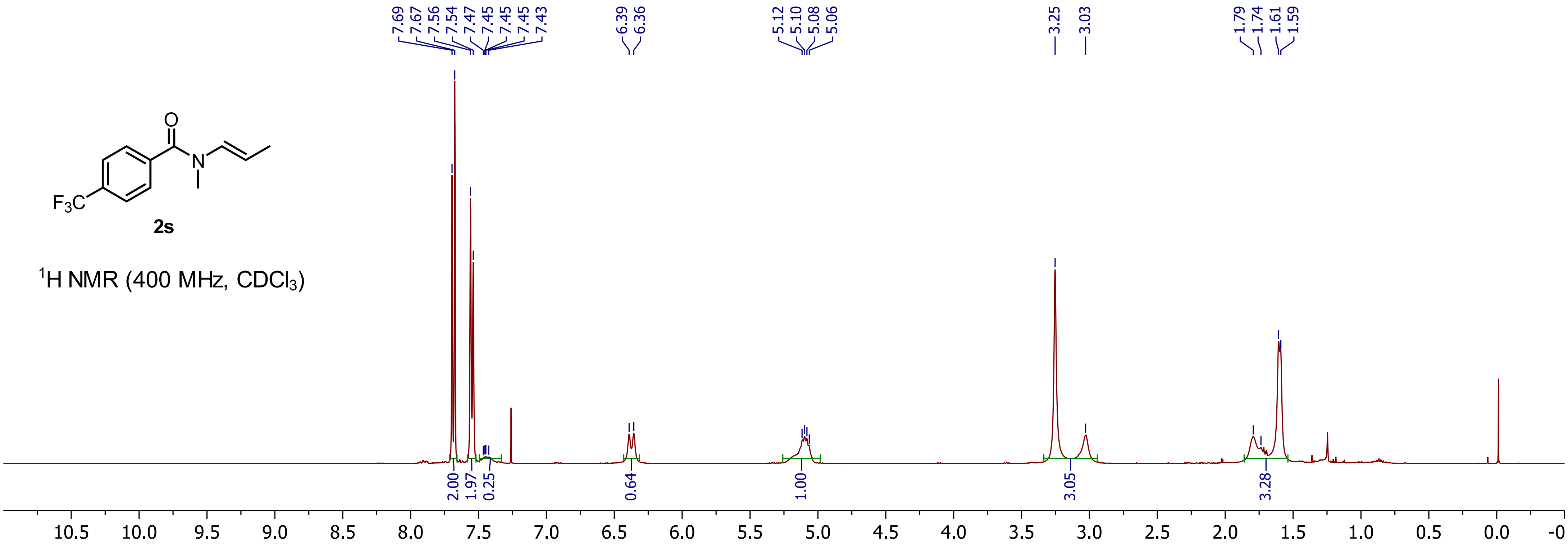

1r
(E)-2r
(Z)-2r
1H NMR (500 MHz, CDCl3)


1r
(E)-2r
(Z)-2r
13C NMR (126 MHz, CDCl3)

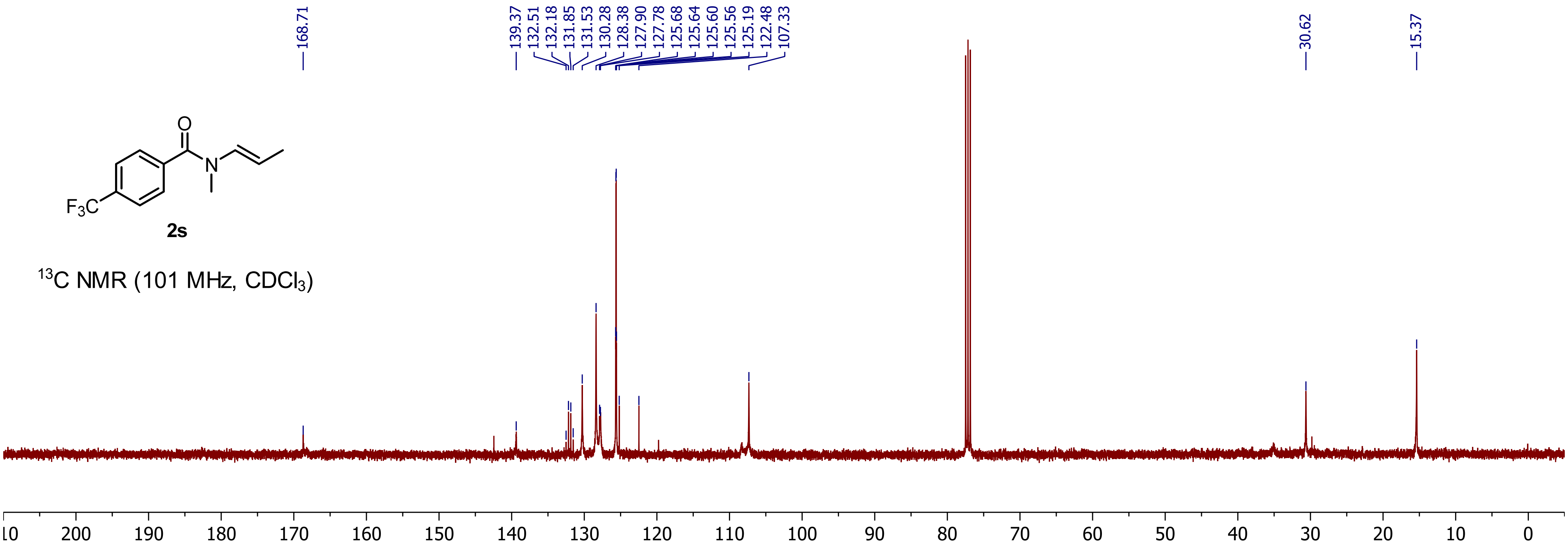

N
O
1r
(E)-2r
(Z)-2r
HSQC
f1 (ppm)



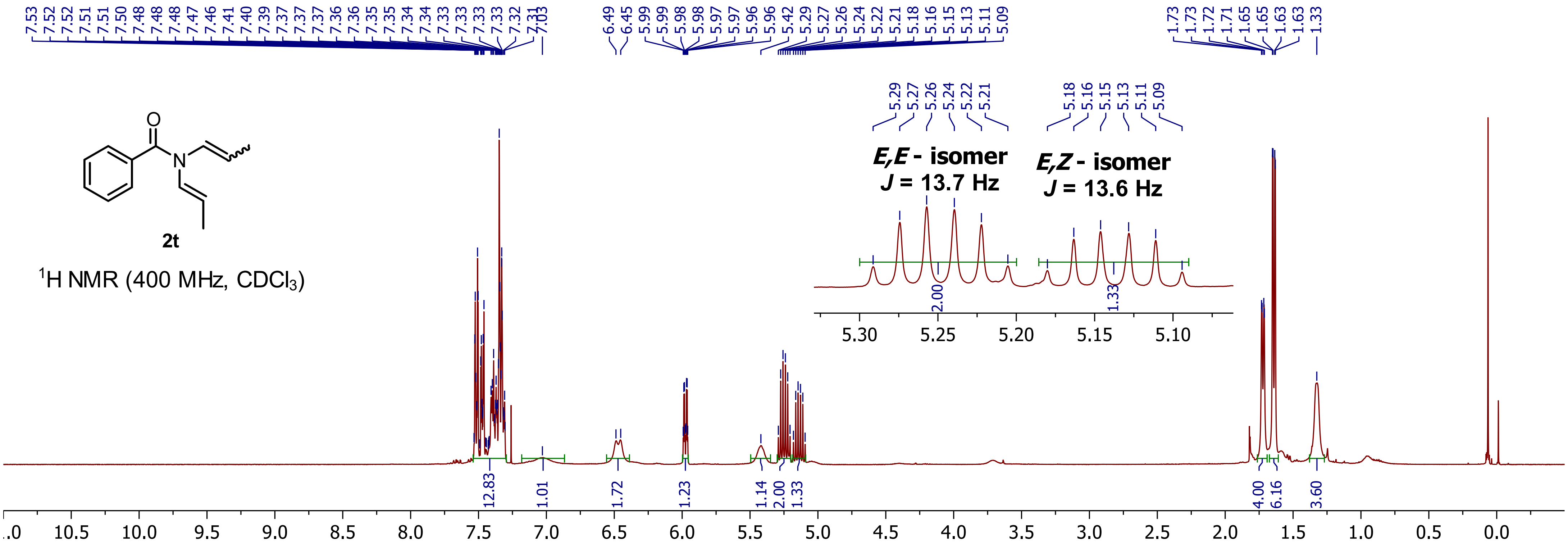
1r
1r
(E)-2r
(Z)-2r

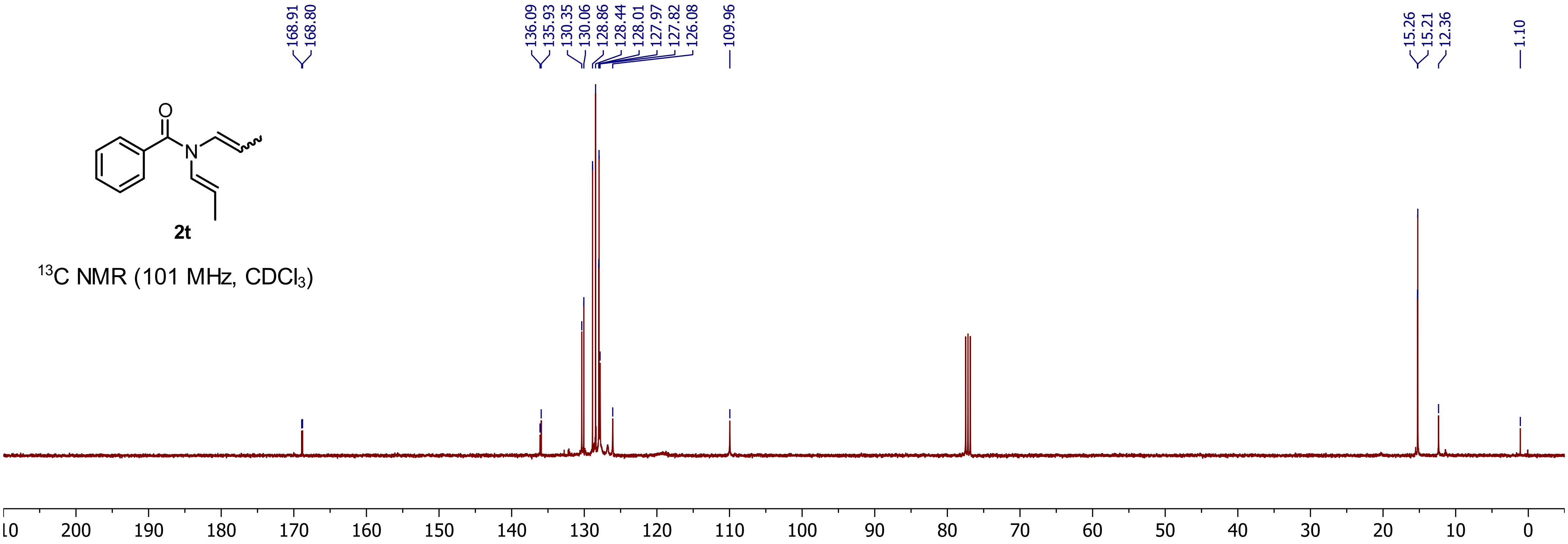


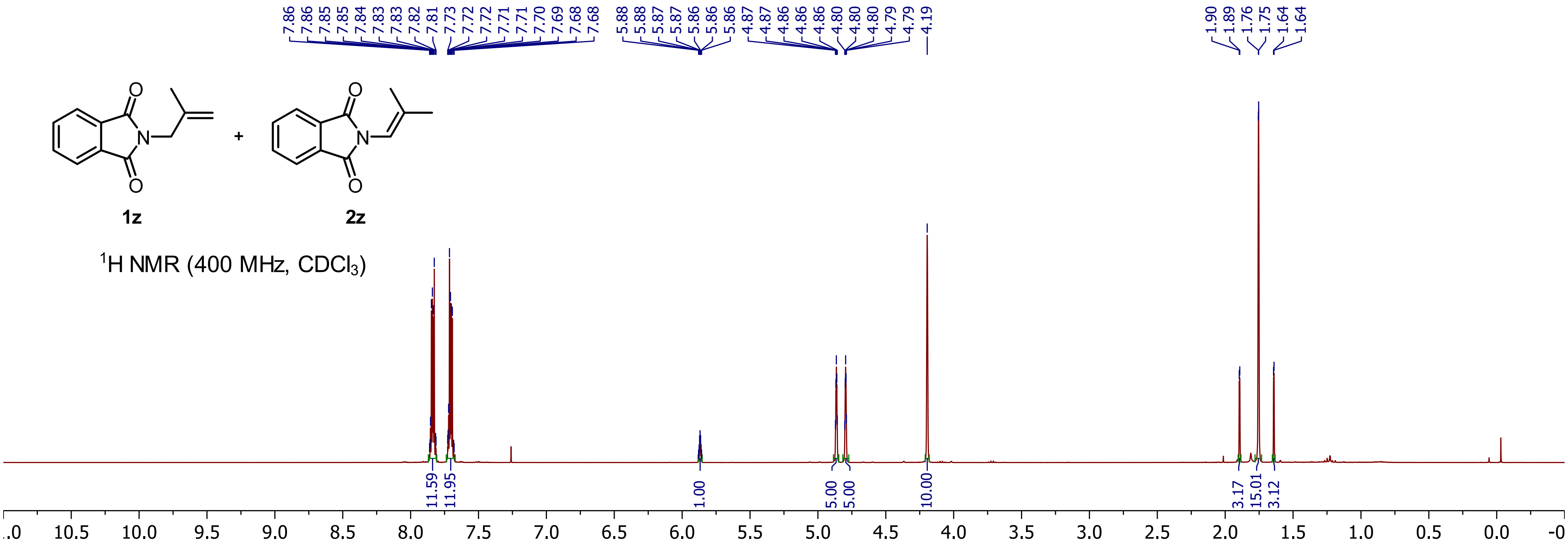
2s
1H NMR (400 MHz, CDCl3)
7.69 7.67 7.56 7.54 7.47 7.45 7.45 7.45 7.43
6.39 6.36
5.12 5.10 5.08 5.06
3.25 3.03
1.79 1.74 1.61 1.59
2.00 1.97 0.25 0.64 1.00 3.05 3.28
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

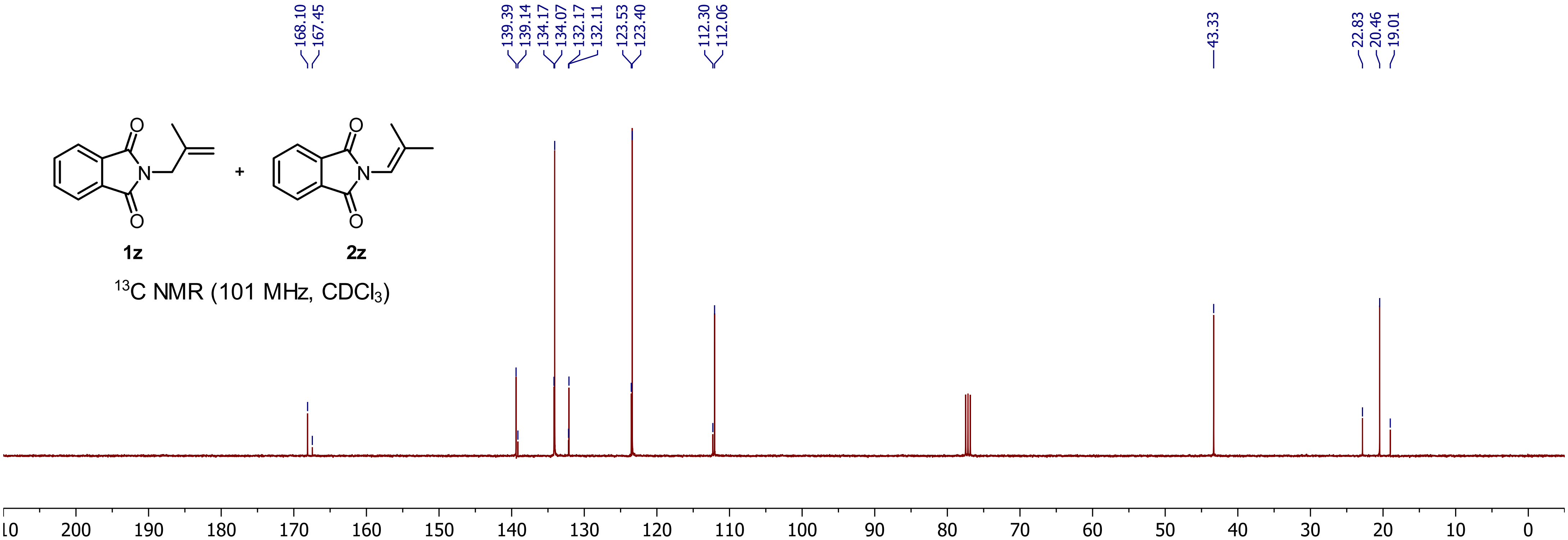


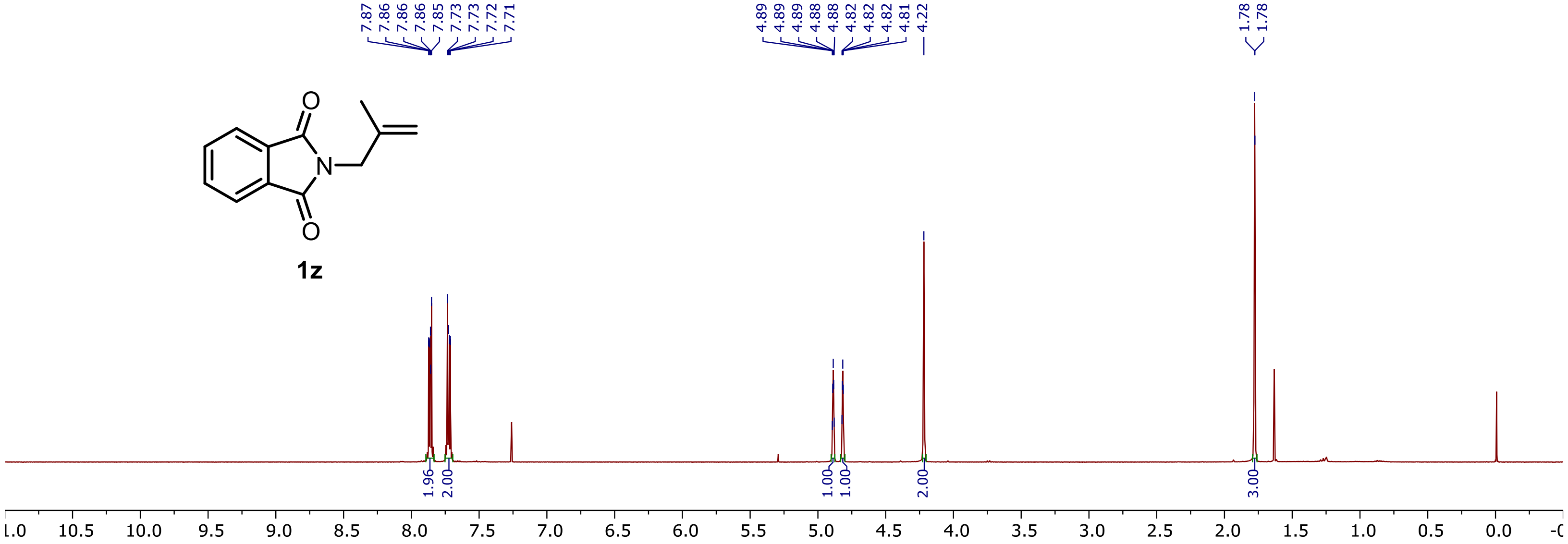
2s
13C NMR (101 MHz, CDCl3)
168.71
139.37 132.51 132.18 131.85 131.53 130.28 128.38 127.90 127.78 125.68 125.64 125.60 125.56 125.19 122.48 107.33
30.62
15.37
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

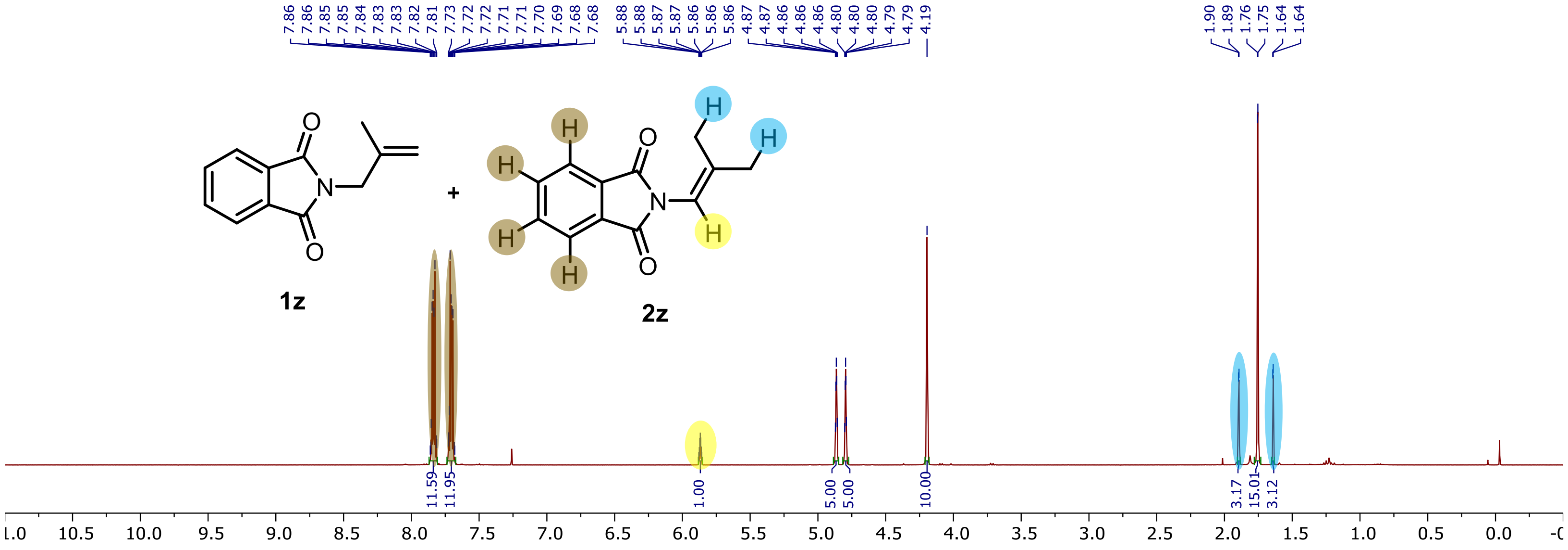

E,E - isomer
J = 13.7 Hz
E,Z - isomer
J = 13.6 Hz
2t
^{1}H NMR (400 MHz, CDCl$_3$)

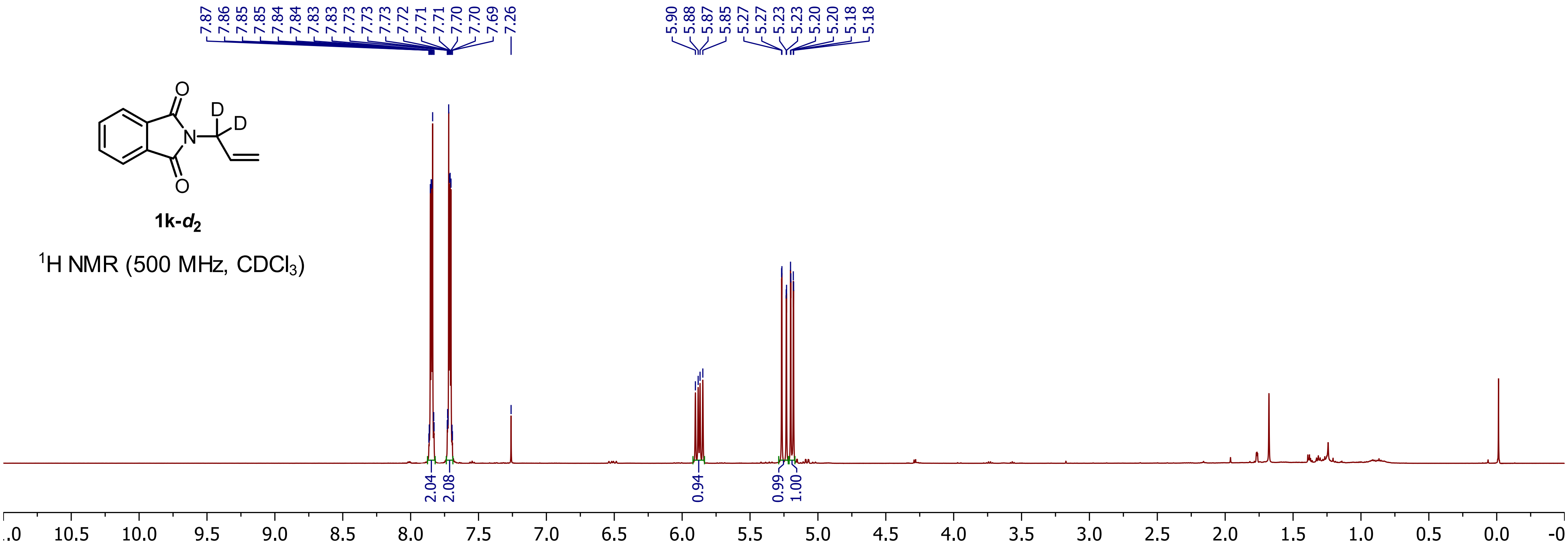

2t
^{13}C NMR (101 MHz, CDCl$_3$)

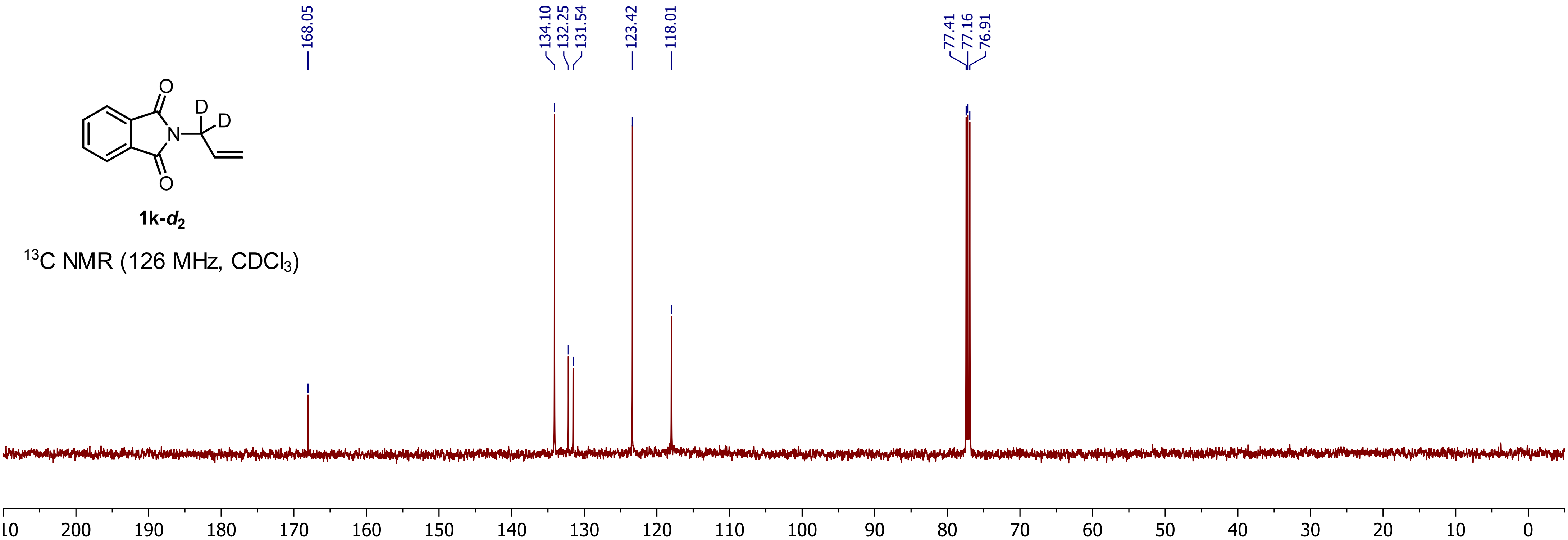

7.86 7.86 7.85 7.85 7.84 7.83 7.83 7.82 7.81 7.73 7.72 7.72 7.71 7.71 7.70 7.69 7.68 7.68 5.88 5.88 5.87 5.87 5.86 5.86 5.86 4.87 4.87 4.86 4.86 4.86 4.80 4.80 4.80 4.79 4.79 4.19 1.90 1.89 1.76 1.75 1.64 1.64
O
N
O
+
O
N
O
1z
2z
^{1}H NMR (400 MHz, $CDCl_3$)
11.59 11.95 1.00 5.00 5.00 10.00 3.17 15.01 3.12
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

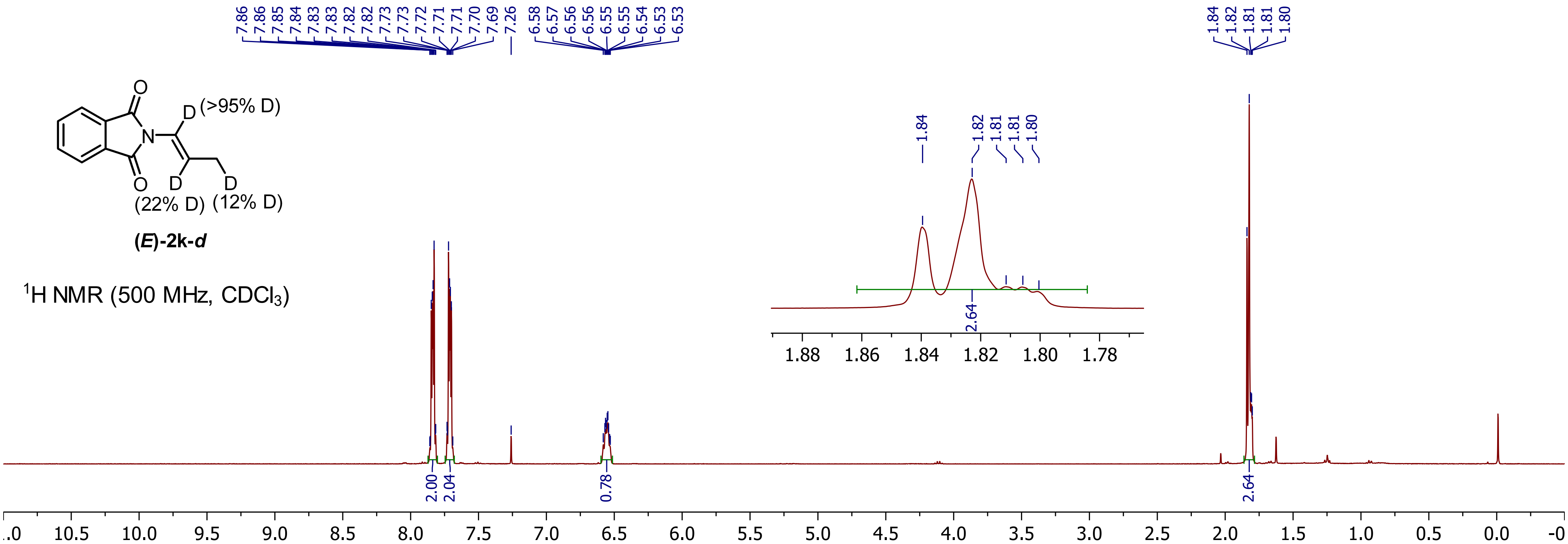

168.10 167.45 139.39 139.14 134.17 134.07 132.17 132.11 123.53 123.40 112.30 112.06 43.33 22.83 20.46 19.01
O
N
O
+
O
N
O
1z
2z
^{13}C NMR (101 MHz, $CDCl_3$)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

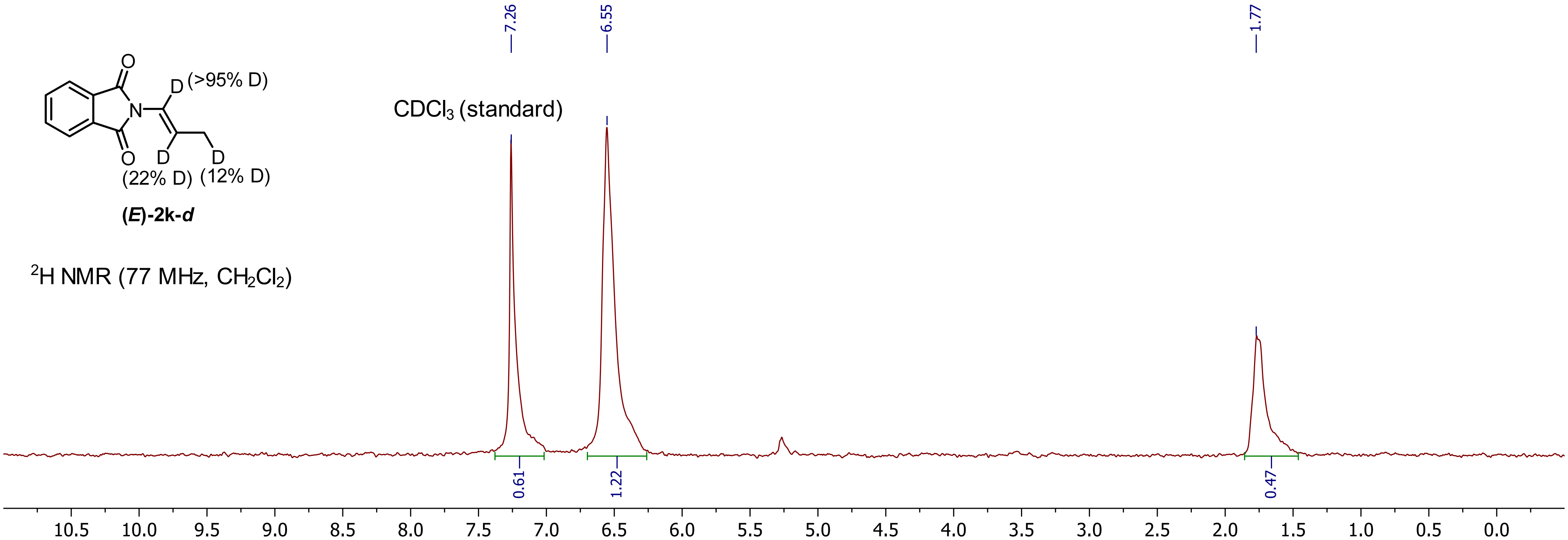

1z


1z
2z


7.87 7.86 7.85 7.85 7.84 7.84 7.83 7.83 7.73 7.73 7.73 7.72 7.71 7.71 7.70 7.70 7.69 7.26
5.90 5.88 5.87 5.85 5.27 5.27 5.23 5.23 5.20 5.20 5.18 5.18
O
D
D
N
O
1k-d_2
^{1}H NMR (500 MHz, $CDCl_3$)
2.04 2.08
0.94
0.99 1.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

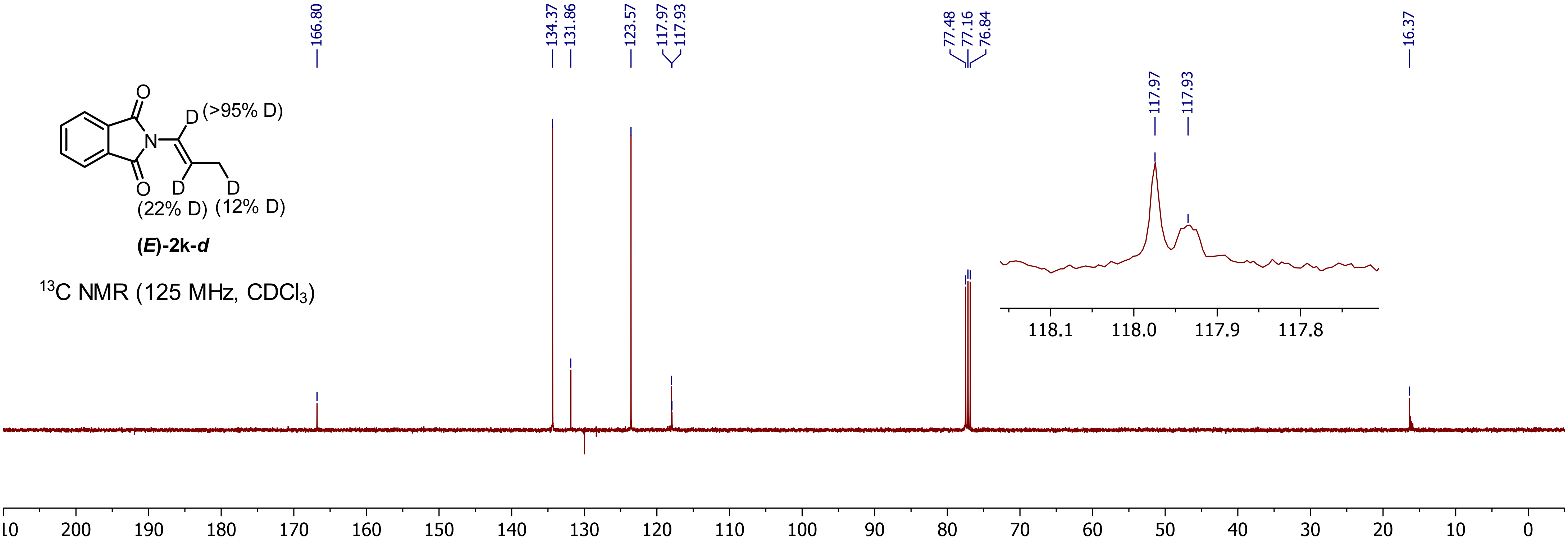

168.05
134.10 132.25 131.54
123.42
118.01
77.41 77.16 76.91
O
D
D
N
O
1k-d_2
^{13}C NMR (126 MHz, $CDCl_3$)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

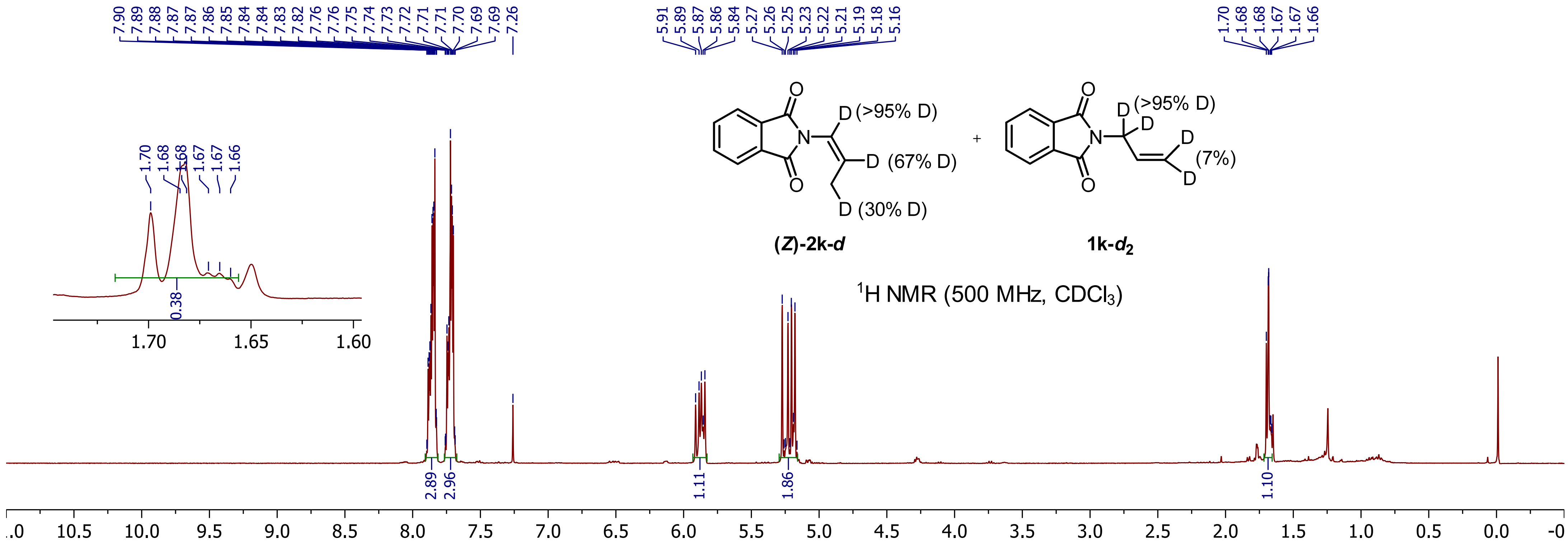

(>95% D)
(22% D) (12% D)
(E)-2k-d
1H NMR (500 MHz, CDCl3)
7.86 7.86 7.85 7.84 7.83 7.83 7.82 7.82 7.73 7.73 7.72 7.71 7.71 7.70 7.69 7.26 6.58 6.57 6.56 6.56 6.55 6.55 6.54 6.53 6.53
1.84 1.82 1.81 1.81 1.80
2.00 2.04 0.78 2.64

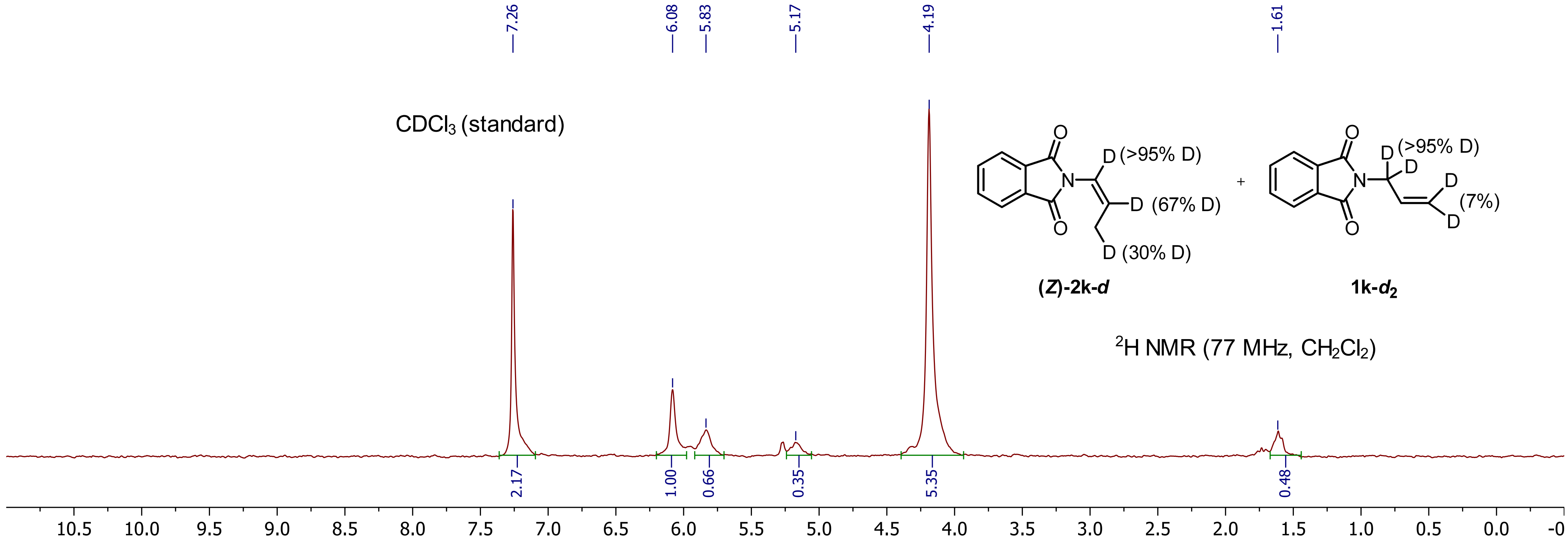

(>95% D)
(22% D) (12% D)
(E)-2k-d
2H NMR (77 MHz, CH2Cl2)
CDCl3 (standard)
7.26 6.55 1.77
0.61 1.22 0.47

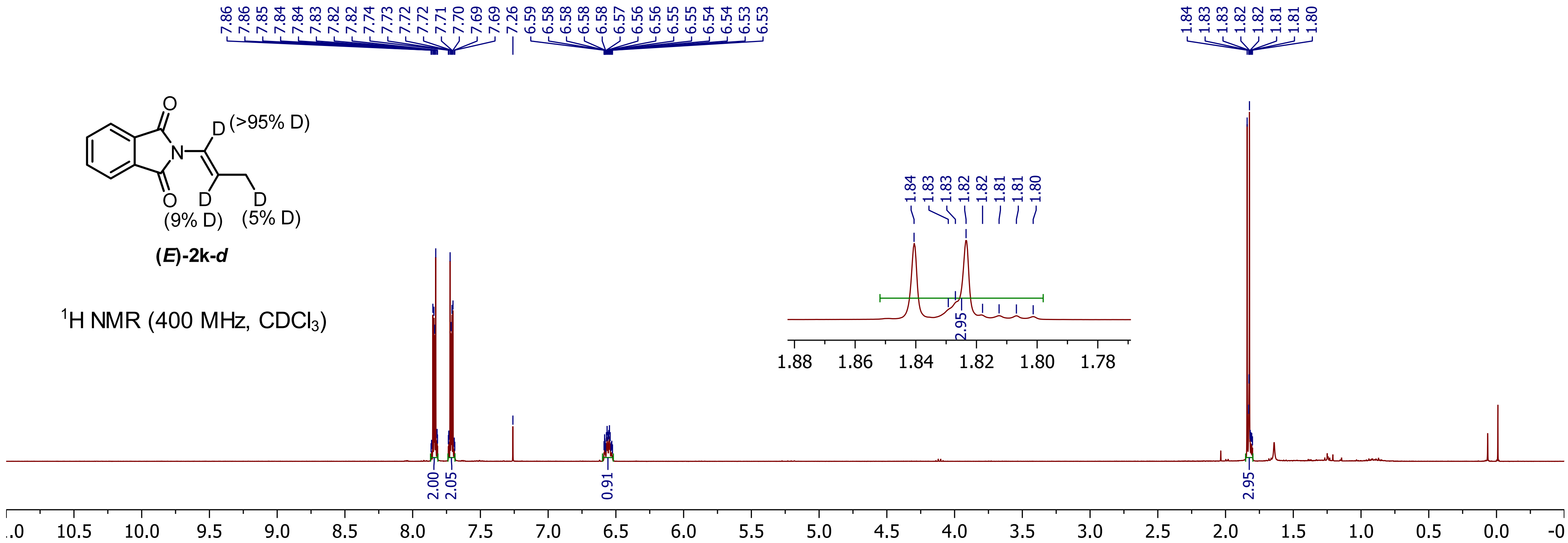
(*E*)-2k-*d*

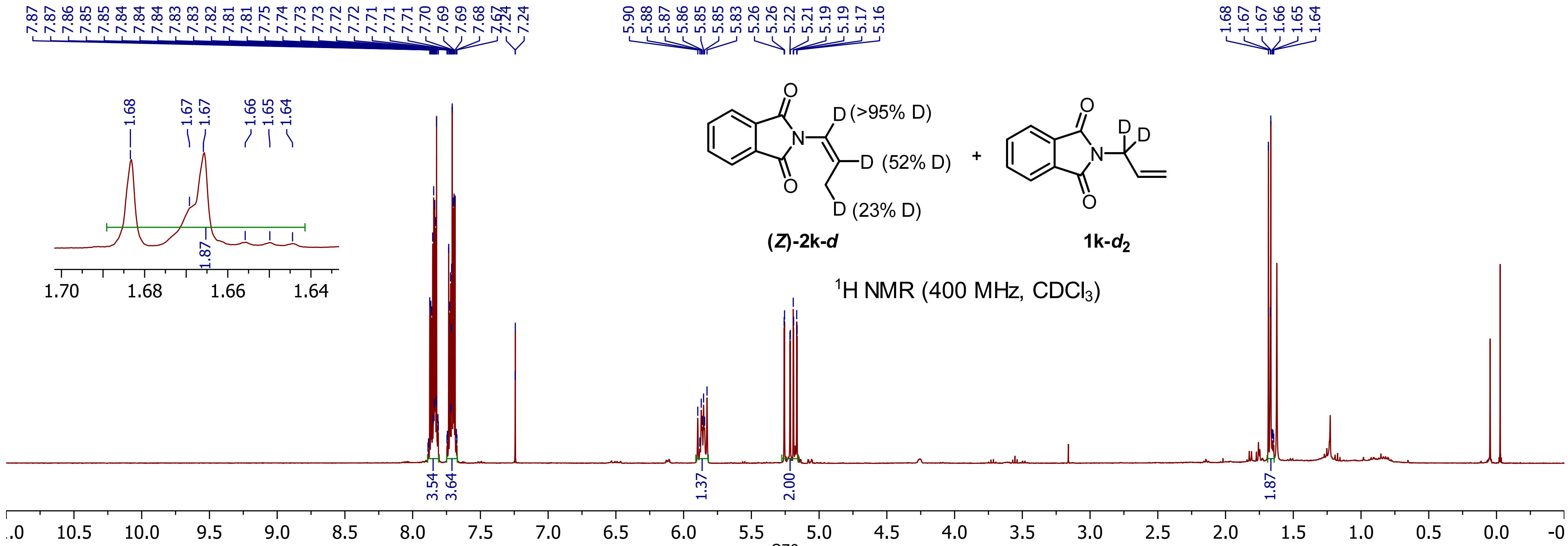
^{13}C NMR (125 MHz, $CDCl_3$)

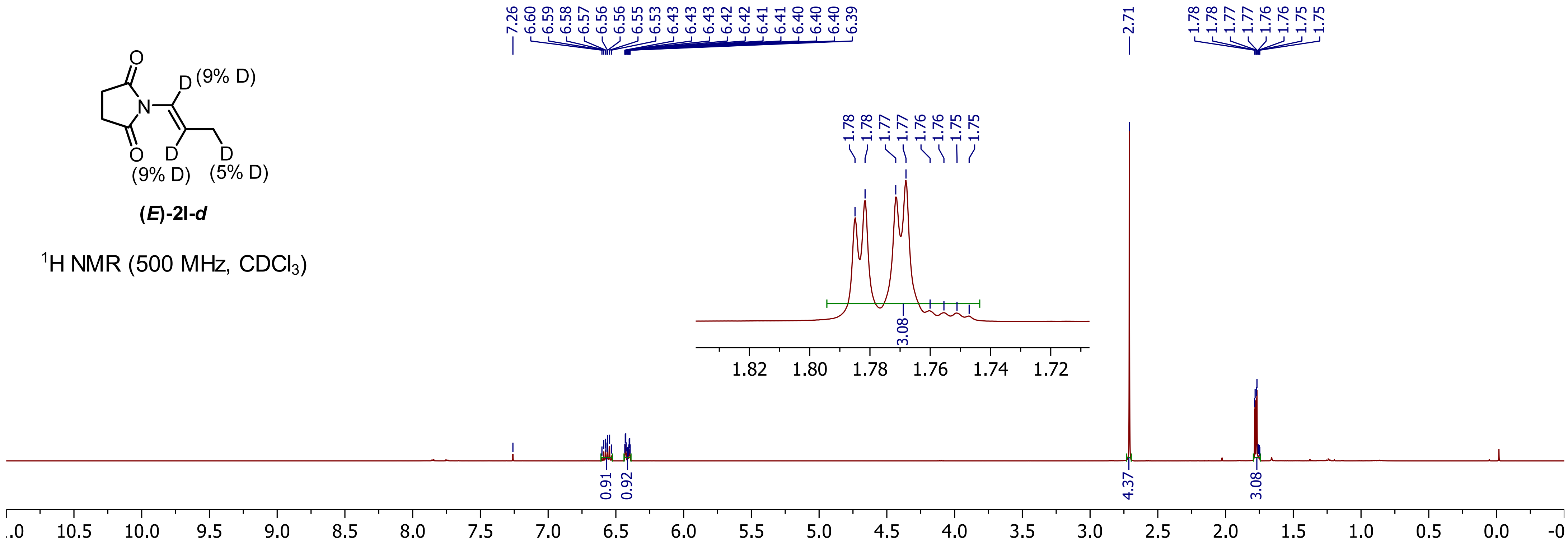


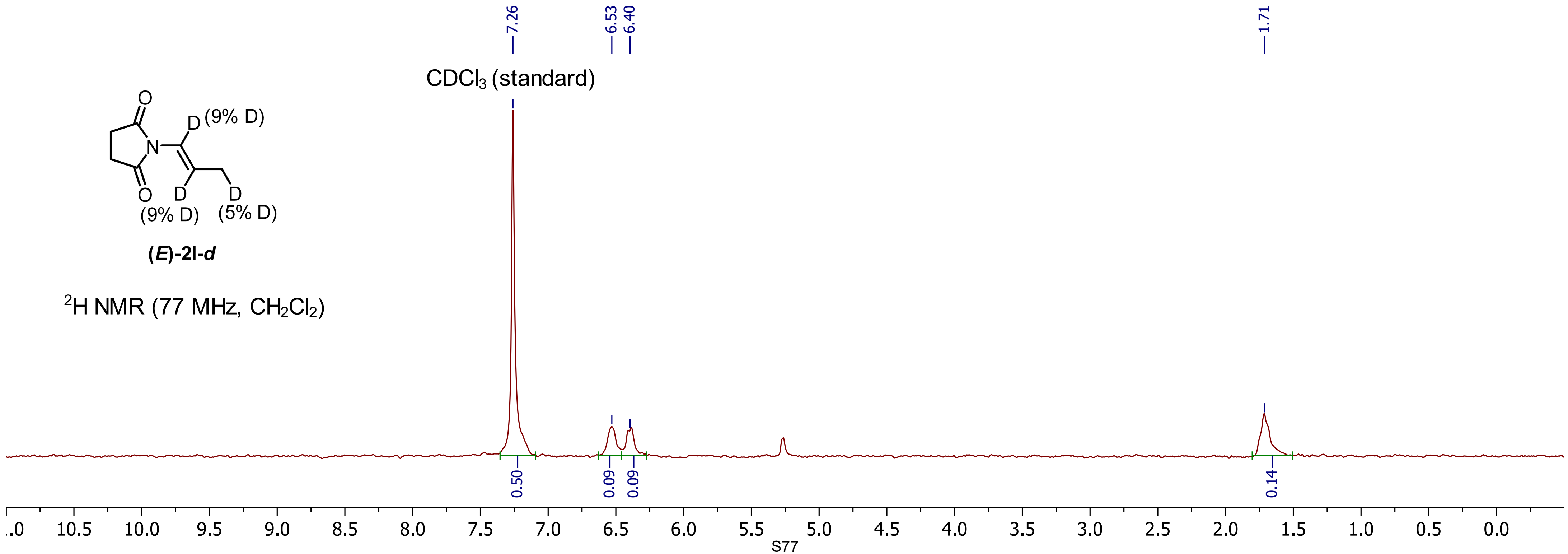

(Z)-2k-d
1k-d_2
D (>95% D)
D (67% D)
D (30% D)
D (7%)
^{1}H NMR (500 MHz, $CDCl_3$)

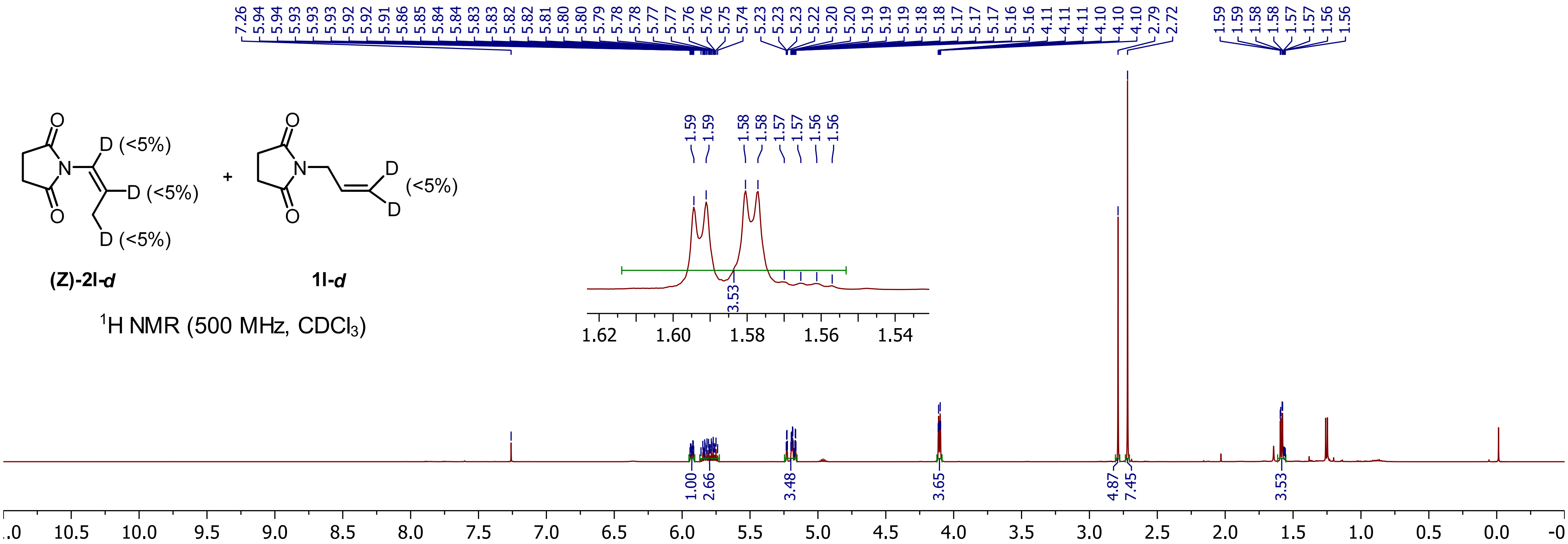

$CDCl_3$ (standard)
(Z)-2k-d
1k-d_2
D (>95% D)
D (67% D)
D (30% D)
D (7%)
^{2}H NMR (77 MHz, CH_2Cl_2)

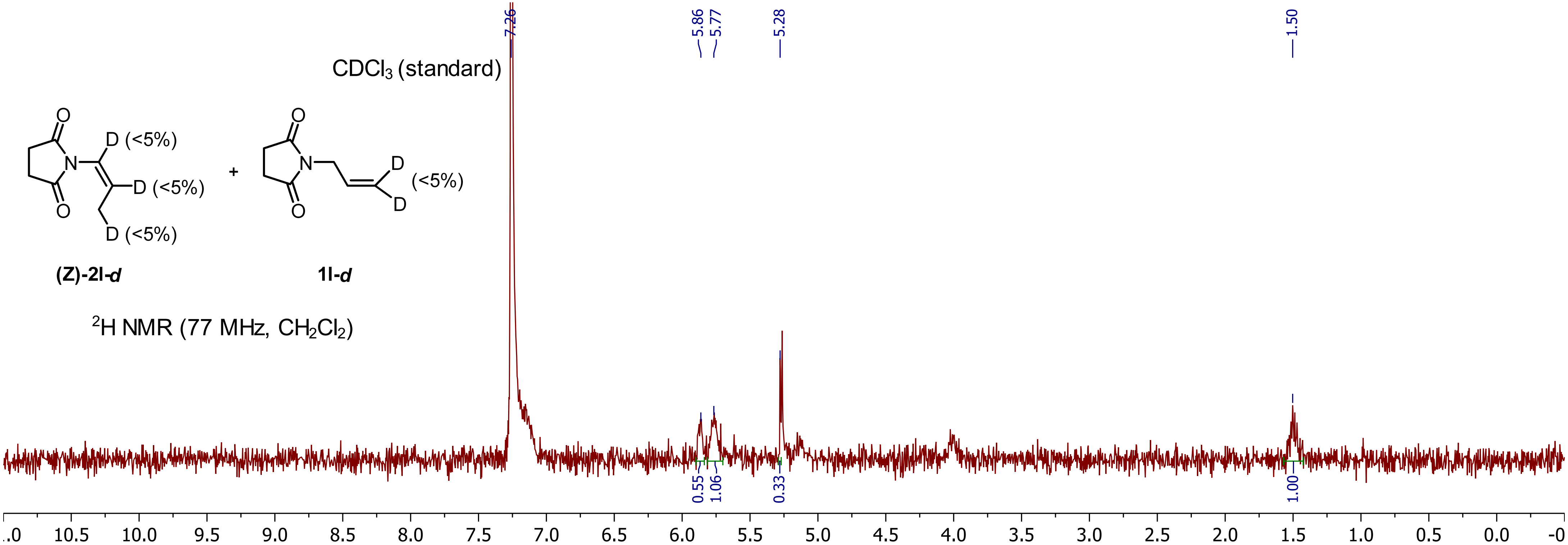

D (>95% D)
(9% D)
(5% D)
(E)-2k-d
^{1}H NMR (400 MHz, CDCl$_3$)
2.00
2.05
0.91
2.95


D (>95% D)
D (52% D)
D (23% D)
(Z)-2k-d
+
1k-d_2
^{1}H NMR (400 MHz, CDCl$_3$)
3.54
3.64
1.37
2.00
1.87


(9% D)
(9% D)
(5% D)
(E)-2l-d
1H NMR (500 MHz, CDCl3)
7.26 6.60 6.59 6.58 6.57 6.56 6.56 6.55 6.53 6.43 6.43 6.43 6.42 6.42 6.41 6.41 6.40 6.40 6.40 6.39
2.71
1.78 1.78 1.77 1.77 1.76 1.76 1.75 1.75
3.08
1.82 1.80 1.78 1.76 1.74 1.72
0.91 0.92 4.37 3.08
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0


7.26
6.53 6.40
1.71
CDCl3 (standard)
(9% D)
(9% D)
(5% D)
(E)-2l-d
2H NMR (77 MHz, CH2Cl2)
0.50 0.09 0.09 0.14
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0


D (<5%)
D (<5%)
D (<5%)
+
(<5%)
(Z)-2l-d
1l-d
1H NMR (500 MHz, CDCl3)


CDCl3 (standard)
D (<5%)
D (<5%)
D (<5%)
+
(<5%)
(Z)-2l-d
1l-d
2H NMR (77 MHz, CH2Cl2)