Supplementary Material (ESI) for Chemical Communications

Platinum(II)-Catalyzed Intermolecular Hydroamination of Monosubstituted Allenes with Secondary Alkylamines

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Supporting Information

Experimental procedures, analytical and spectroscopic data, and copies of NMR spectra for hydroamination products (35 pages).

Experimental Section

General Methods. Catalytic reactions were performed in thick-walled pressure tubes (Ace Glass) under an atmosphere of dry nitrogen. NMR spectra were obtained on a Varian spectrometer operating at 500 MHz for ^{1}H NMR and 126 MHz for ^{13}C NMR in $CDCl_3$ at 25°C unless noted otherwise. IR spectra were obtained on a Nicolet Avatar 360-FT IR spectrometer. Gas chromatography was performed on a Hewlett-Packard 5890 gas chromatograph equipped with a 15 m or 25 m polydimethylsiloxane capillary column and FID detector. Column chromatography was performed employing 230-400 mesh silica gel (Silicycle). Thin layer chromatography (TLC) was performed on silica gel 60 F_{254} (EMD Chemicals Inc.). Elemental analyses were performed by Complete Analysis Laboratories (Parsippany, NJ).

All solvents were purchased from Aldrich or Acros in anhydrous form and used as received. Phosphine ligands, silver salts, $PtCl_2$, secondary amines, and cyclohexylallene were purchased from major suppliers and were used as received. [P(*t*-Bu)$_2$*o*-biphenyl]AuCl,[1] dimethyl 2-(2,3-butadienyl)malonate,[2] (dppp)$PtCl_2$,[3] (BINAP)$PtCl_2$,[4] (dppf)$PtCl_2$,[5] (BIPHEP)$PtCl_2$,[6] (DPEphos)$PtCl_2$,[7] (xantphos)$PtCl_2$,[8] *n*-octylallene,[9] phenylallene,[10] benzylallene,[11] and napthylallene[10] were prepared employing published procedures.

Bis(phosphine) platinum dichloride complex

(Nixantphos)$PtCl_2$. (Nixantphos)$PtCl_2$ was synthesized in 90% yield as a green solid employing a procedure similar to that used to synthesize (xantphos)$PtCl_2$.[8] ^{1}H NMR (dmso-d_6): δ 9.10 (s, 1 H), 7.32-7.01 (m, 24 H), 6.95 (t, J = 7.2 Hz, 2 H). ^{31}P{^{1}H} NMR (dmso-d_6): δ 4.9 ($J_{Pt\text{-}P}$ = 4600 Hz). Anal. calcd (found) for $C_{36}H_{27}Cl_2NOP_2Pt$: C, 52.89 (52.86); H, 3.33 (3.38).

Allylic Amines

Dimethyl 4-[benzyl(*n*-butyl)amino]-2-butenylmalonate (2a). A suspension of (dppf)$PtCl_2$ (8.2 mg, 0.010 mmol), AgOTf (2.6 mg, 0.010 mmol), ferrocene (3.7 mg, 0.020 mmol; internal standard),

benzyl *n*-butyl amine (36 μL, 33 mg, 0.20 mmol), dimethyl 2,3-butadienylmalonate (**1**; 74 mg, 0.40 mmol) in toluene (0.4 mL) was heated at 80 °C for 24 h. Column chromatography of the crude reaction mixture (SiO_2 pretreated with Et_3N; hexanes–EtOAc = 9:1) gave **2a** (pale yellow oil, 56 mg, 81%) as a 10:1 mixture of *E* and *Z* diastereomers. TLC (hexanes–EtOAc = 7:3): R_f = 0.41. ^{1}H NMR (*E*-isomer): δ 7.32-7.18 (m, 5 H), 5.60 (td, *J* = 6.2, 15.5 Hz, 1 H), 5.50 (td, *J* = 6.5, 15.5 Hz, 1 H), 3.69 (s, 6 H), 3.49 (s, 2 H), 3.41 (t, *J* = 7.5 Hz, 1 H), 2.97 (d, *J* = 6.0 Hz, 2 H), 2.61 (t, *J* = 6.7 Hz, 2 H), 2.35 (t, *J* = 7.5 Hz, 2 H), 1.45-1.39 (m, 2 H), 1.30-1.22 (m, 2 H), 0.85 (t, *J* = 7.2 Hz, 3 H). ^{1}H NMR (*Z*-isomer; partial spectrum): δ 5.53-5.39 (m, 2 H), 3.06 (d, *J* = 6 Hz, 2 H). ^{13}C{^{1}H} NMR (*E*-isomer): δ 169.4, 139.8, 131.1, 128.9, 128.3, 128.2, 126.7, 57.9, 55.5, 53.1, 52.6, 51.8, 31.8, 29.2, 20.6, 14.1. ^{13}C{^{1}H} NMR (*Z*-isomer; partial spectrum): δ 126.9, 58.4, 53.5, 51.6, 50.5, 29.3, 27.1. IR (neat, cm^{-1}): 2954, 2929, 1737, 1436, 1227, 1154, 732, 699. HRMS calcd (found) for $C_{20}H_{29}NO_4$ (MH^+): 348.2177 (348.2166). Anal. calcd (found) for $C_{20}H_{29}NO_4$: C 69.14 (68.99); H 8.41 (8.32).

The *E*-configuration of the major diasteromer of **2a** (and other allylic amines) was established by the large ($^3J_{HH}$ ≈ 15 Hz) coupling constant between the olefinic hydrogen atoms. Assignment of the minor isomer as the *Z*-diastereomer (Z)-**2a**, as opposed to a regioisomer dimethyl 2-[benzyl(butyl)amino]-3-butenyl)malonate (**2a'**) formed by attack of the amine at the more substituted terminal allene carbon, was made from the presence of a two-proton doublet at δ 3.06 (*J* = 6 Hz) assigned to the allylic proton α-to the nitrogen atom of (Z)-**2a**, which would appear as a one-proton multiplet in **2a'**, and by the absence of resonances consistent with a terminal vinyl moiety.

All remaining allylic amines were synthesized employing a procedure similar to that used to synthesize **2a**.

Dimethyl (4-(benzyl(methyl)amino)-2-butenyl)malonate (2b). Pale yellow oil. TLC (hexanes–EtOAc = 2:3): R_f = 0.26. ^{1}H NMR (*E*-isomer): δ 7.32-7.22 (m, 5 H), 5.65 (td, *J* = 6.2, 15 Hz, 1 H), 5.56 (td, *J* = 6.5, 15.5 Hz, 1 H), 3.71 (s, 6 H), 3.45 (t, *J* = 7.5 Hz, 1 H), 3.44 (s, 2 H), 2.96 (d, *J* = 6 Hz, 2 H), 2.65 (t, *J* = 6.75 Hz, 2 H), 2.14 (s, 3 H). ^{1}H NMR (Z-isomer; partial spectrum): δ 5.59-5.45 (m,

2 H), 3.72 (s, 6 H), 3.06 (d, *J* = 6.5 Hz, 2 H), 2.67 (t, *J* = 7 Hz, 2 H), 2.17 (s, 3 H). $^{13}C\{^1H\}$ NMR (E-isomer): δ 169.4, 139.0, 130.9, 129.1, 128.8, 128.3, 127.0, 61.6, 59.3, 52.6, 51.7, 42.0, 31.8. $^{13}C\{^1H\}$ NMR (Z-isomer; partial spectrum): δ 130.7, 127.4, 62.0, 54.0, 52.6, 51.5, 42.3, 27.1. IR (neat, cm^{-1}): 2952, 2785, 1736, 1436, 1229, 1153, 739, 700. HRMS calcd (found) for $C_{17}H_{23}NO_4$ (MH^+): 306.1707 (306.1920). Anal. calcd (found) for $C_{17}H_{23}NO_4$: C, 66.86 (66.77); H, 7.59 (7.48).

Dimethyl 2-(4-morpholinobut-2-enyl)malonate (2c). Peach oil. TLC (hexanes–EtOAc = 1:4): R_f = 0.12. ^1H NMR (*E*-isomer): δ 5.53-5.51 (m, 2 H), 3.67 (s, 6 H), 3.64 (t, *J* = 4.5 Hz, 4 H), 3.39 (t, *J* = 7.5 Hz, 1 H), 2.87 (d, *J* = 5 Hz, 2 H), 2.58 (t, *J* = 6.25 Hz, 2 H), 2.34 (s, 4 H). ^1H NMR (Z-isomer; partial spectrum): δ 5.46-5.43 (m, 2 H), 3.68 (s, 6 H), 3.67 (t, *J* = 7.5 Hz, 1 H), 2.98 (d, *J* = 6.5 Hz, 2 H), 2.64 (t, *J* = 7.5 Hz, 2 H), 2.38 (s, 4 H). $^{13}C\{^1H\}$ NMR (*E*-isomer): δ 169.2, 129.6, 129.5, 66.9, 60.9, 53.5, 52.5, 51.6, 31.6. $^{13}C\{^1H\}$ NMR (*Z*-isomer; partial spectrum): δ 169.3, 129.2, 128.1, 67.9, 55.3, 53.6, 52.6, 51.4, 30.9, 27.0. IR (neat, cm^{-1}): 2954, 2853, 2808, 1734, 1437, 1227, 1154, 1116, 864. HRMS calcd (found) for $C_{13}H_{21}NO_5$ (M^+): 271.1420 (271.1418). Anal. calcd (found) for $C_{13}H_{21}NO_5$: C, 57.55 (57.44), H, 7.80 (7.70).

Dimethyl 2-(4-(piperidin-1-yl)but-2-enyl)malonate (2d). Caramel oil. TLC (CH_2Cl_2–MeOH = 9:1): R_f = 0.25. ^1H NMR (*E*-isomer): δ 5.60 (td, *J* = 7, 15 Hz, 1 H), 5.51 (td, *J* = 7, 15.5 Hz, 1 H), 3.71 (s, 6 H), 3.43 (t, *J* = 7.5 Hz, 1 H), 2.87 (d, *J* = 6.5 Hz, 2 H), 2.61 (t, *J* = 7.25 Hz, 2 H), 2.47-2.19 (m, 4 H), 1.58-1.53 (m, 4 H), 1.43-1.32 (m, 2 H). ^1H NMR (Z-isomer; partial spectrum): δ 5.55-5.41 (m, 2 H), 3.72 (s, 6 H), 3.40 (t, *J* = 8 Hz, 1 H), 2.98 (d, *J* = 7 Hz, 2 H), 2.66 (t, *J* = 7.4 Hz, 2 H). $^{13}C\{^1H\}$ NMR (*E*-isomer): δ 169.4, 130.4, 128.9, 61.4, 54.4, 52.6, 51.7, 31.7, 26.0, 24.4. $^{13}C\{^1H\}$ NMR (Z-isomer; partial spectrum): δ 130.2, 127.3, 54.6, 51.5, 31.6, 24.3, 22.7. IR (neat, cm^{-1}): 2933, 2852, 2796, 1736, 1436, 1229, 1153, 977. HRMS calcd (found) for $C_{14}H_{23}NO_4$ (M^+): 269.1627 (269.1625). Anal. calcd (found) for $C_{14}H_{23}NO_4$: C, 62.43 (62.29); H, 8.61 (8.45).

Dimethyl 2-(4-(pyrrolidin-1-yl)but-2-enyl)malonate (2e). Golden yellow oil. TLC (CH_2Cl_2–MeOH = 9:1): R_f = 0.22. ^1H NMR (*E*-isomer): δ 5.66 (td, *J* = 6.5, 15.5 Hz, 1 H), 5.56 (td, *J* = 7, 15 Hz,

1 H), 3.71 (s, 6 H), 3.43 (t, *J* = 7.5 Hz, 1 H), 3.05 (d, *J* = 6 Hz, 2 H), 2.61 (t, *J* = 7 Hz, 2 H), 2.54-2.45 (m, 4 H), 1.81-1.70 (m, 4 H). ^{1}H NMR (Z-isomer; partial spectrum): δ 5.59-5.33 (m, 2 H), 3.72 (s, 6 H), 3.40 (t, *J* = 7.5 Hz, 1 H), 3.18 (d, *J* = 6.5 Hz, 2 H), 2.67 (t, *J* = 7 Hz, 2 H). ^{13}C{^{1}H} NMR (*E*-isomer): δ 169.3, 130.6, 128.5, 57.9, 53.8, 52.6, 51.6, 31.6, 23.4. ^{13}C{^{1}H} NMR (*Z*-isomer; partial spectrum): δ 54.0, 51.5, 51.0, 27.1, 23.3. IR (neat, cm^{-1}): 2956, 2787, 1734, 1436, 1228, 1198, 1153. HRMS calcd (found) for $C_{13}H_{21}NO_4$ (MH^+): 256.1551 (256.1548).

Dimethyl 2-(4-(dibutylamino)but-2-entyl)malonate (2f). Amber oil. TLC (hexanes–EtOAc = 1.5:1): R_f = 0.20. ^{1}H NMR (*E*-isomer): δ 5.57 (td, *J* = 6.5, 15.5 Hz, 1 H), 5.49 (td, *J* = 6.5, 15 Hz, 1 H), 3.70 (s, 6 H), 3.41 (t, *J* = 7.5 Hz, 1 H), 2.98 (d, *J* = 6.3 Hz, 2 H), 2.60 (t, *J* = 7 Hz, 2 H), 2.33 (dd, *J* = 7.0, 8.5 Hz, 4 H), 1.40-1.34 (m, 4 H), 1.25 (qd, *J* = 7.4, 8 Hz, 4 H), 0.87 (t, *J* = 7.2 Hz, 6 H). ^{1}H NMR (Z-isomer; partial spectrum): δ 5.51-5.36 (m, 2 H), 3.71 (s, 6 H), 3.39 (t, *J* = 7.5 Hz, 1 H), 3.07 (d, *J* = 5 Hz, 2 H), 2.65 (t, *J* = 7.5 Hz, 2 H). ^{13}C{^{1}H} NMR (E-isomer): δ 169.4, 131.0, 128.1, 56.0, 53.4, 52.5, 51.8, 31.8, 29.2, 20.8, 14.1. ^{13}C{^{1}H} NMR (*Z*-isomer; partial spectrum): δ 126.6, 53.8, 52.6, 51.6, 50.9, 29.3, 27.1. IR (neat, cm^{-1}): 2955, 2931, 2863, 2798, 1738, 1436, 1228, 1153, 974. HRMS calcd (found) for $C_{17}H_{31}NO_4$ (M^+): 313.2253 (313.2252). Anal. calcd (found) for $C_{17}H_{31}NO_4$: C, 65.14 (65.01); H, 9.97 (9.92).

Dimethyl 2-(4-(diethylamino)but-2-enyl)malonate (2g). Amber oil. TLC (CH_2Cl_2–MeOH = 9:1): R_f = 0.39. ^{1}H NMR (*E*-isomer): δ 5.56 (td, *J* = 6.5, 15 Hz, 1 H), 5.49 (td, *J* = 6.5, 15 Hz, 1 H), 3.68 (s, 6 H), 3.40 (t, *J* = 7.5 Hz, 1 H), 2.99 (d, *J* = 6 Hz, 2 H), 2.58 (t, *J* = 7 Hz, 2 H), 2.44 (q, *J* = 7 Hz, 4 H), 0.96 (t, *J* = 7 Hz, 6 H). ^{1}H NMR (*Z*-isomer; partial spectrum): δ 5.52-5.38 (m, 2 H), 3.69 (s, 6 H), 3.37 (t, *J* = 7.5 Hz, 1 H), 3.08 (d, *J* = 6.5 Hz, 2 H). ^{13}C{^{1}H} NMR (*E*-isomer): δ 169.3, 130.6, 128.4, 54.9, 52.3, 51.7, 46.4, 31.7, 11.6. ^{13}C{^{1}H} NMR (*Z*-isomer; partial spectrum): δ 126.9, 52.6, 51.5, 49.7, 46.8, 27.1, 11.8. IR (neat, cm^{-1}): 2968, 2799, 1736, 1436, 1227, 1199, 1154, 1030, 975. HRMS calcd (found) for $C_{13}H_{23}NO_4$ (M^+): 257.1627 (257.1626). Anal. calcd (found) for $C_{13}H_{23}NO_4$: C, 60.68 (60.44); H, 9.01 (8.98).

Dimethyl 2-(4-(dibenzylamino)but-2-enyl)malonate (2h). Pale yellow oil. TLC (hexanes–EtOAC = 7:3): R_f = 0.59. ^{1}H NMR (*E*-isomer): δ 7.36 (d, *J* = 7 Hz, 4 H), 7.32 (t, *J* = 7.5 Hz, 4 H), 7.23 (t, *J* = 7.25 Hz, 2 H), 5.66 (td, *J* = 6.5, 16 Hz, 1 H), 5.57 (td, *J* = 6.5, 15.5 Hz, 1 H), 3.69 (s, 6 H), 3.54 (s, 4 H), 3.45 (t, *J* = 7.5 Hz, 1 H), 3.01 (d, *J* = 6 Hz, 2 H), 2.65 (t, *J* = 7.2 Hz, 2 H). ^{1}H NMR (*Z*-isomer; partial spectrum): δ 5.60-5.45 (m, 1 H), 3.70 (s, 6 H), 3.56 (s, 4 H), 3.38 (t, *J* = 7.5 Hz, 1 H), 3.09 (d, *J* = 6.5 Hz, 2 H), 2.63 (t, *J* = 8 Hz, 2 H). ^{13}C{^{1}H} NMR (*E*-isomer): δ 169.4, 139.7, 131.0, 128.8, 128.7, 128.2, 126.9, 67.7, 55.1, 52.6, 51.8, 31.8. ^{13}C{^{1}H} NMR (*Z*-isomer; partial spectrum): δ 130.9, 128.9, 58.2, 51.6, 50.2, 27.1. IR (neat, cm^{-1}): 3027, 2952, 2796, 1736, 1436, 1230, 1153, 743, 699. HRMS calcd (found) for $C_{23}H_{27}NO_4$ (M^+): 381.1940 (381.1940). Anal. calcd (found) for $C_{23}H_{27}NO_4$: C, 72.42 (72.58); H, 7.13 (7.05).

***N*-benzyl-*N*-butylundec-2-en-1-amine (2i).** Pale yellow oil. TLC (hexanes–EtOAc = 9:1): R_f = 0.46. ^{1}H NMR (*E*-isomer): δ 7.34-7.29 (m, 4 H), 7.23 (t, *J* = 6.75 Hz, 1 H), 5.56 (td, *J* = 6.5, 15 Hz, 1 H), 5.49 (td, *J* = 6, 15.75 Hz, 1 H), 3.55 (s, 2 H), 3.01 (d, *J* = 6 Hz, 2 H), 2.42 (t, *J* = 7.5 Hz, 2 H), 2.03 (td, *J* = 6.5, 7 Hz, 2 H), 1.50-1.44 (m, 2 H), 1.38-1.21 (m, 14 H), 0.88 (t, *J* = 7.25 Hz, 6 H). ^{1}H NMR (*Z*-isomer; partial spectrum): δ 5.59-5.56 (m, 2 H), 3.07 (d, *J* = 6 Hz, 2 H). ^{13}C{^{1}H} NMR (*E*-isomer): δ 140.1, 134.0, 129.0, 128.1, 127.3, 126.7, 58.0, 56.0, 53.1, 32.5, 32.0, 29.6, 29.5, 29.4, 29.3, 29.2, 22.8, 20.7, 14.2, 14.1. ^{13}C{^{1}H} NMR (*Z*-isomer): δ 132.7, 128.6, 127.1, 58.3, 53.4, 50.4, 31.7, 29.7, 27.6, 20.6. IR (neat, cm^{-1}): 2955, 2924, 1854, 1454, 971, 732, 697. HRMS calcd (found) for $C_{22}H_{37}N$ (M^+): 315.2926 (315.2929). Anal. calcd (found) for $C_{22}H_{37}N$: C, 83.74 (83.69); H, 11.82 (11.74).

***N*-benzyl-*N*-(3-cyclohexylallyl)butan-1-amine (2j).** Pale yellow oil. TLC (hexanes-EtOAc = 9:1): R_f = 0.39. ^{1}H NMR (E-isomer): δ 7.34-7.28 (m, 4 H), 7.24-7.21 (m, 1 H), 5.52 (dd, *J* = 6.2, 15.7 Hz, 1 H), 5.44 (dtd, *J* = 1, 6.5, 15.5 Hz, 1 H), 3.55 (s, 2 H), 3.01 (d, *J* = 6.5 Hz, 2 H), 2.41 (t, *J* = 7.5 Hz, 2 H), 1.99-1.93 (m, 1 H), 1.74-1.66 (m, 4 H), 1.67-1.62 (m, 1 H), 1.49-1.43 (m, 2 H), 1.33-1.23 (m, 4 H), 1.20-1.14 (m, 1 H), 1.12-1.03 (m, 2 H) 0.88 (t, *J* = 7.25 Hz, 3 H). ^{1}H NMR (*Z*-isomer; partial spectrum): δ 5.47-5.36 (m, 2 H), 3.08 (d, *J* = 6 Hz, 2 H). ^{13}C{^{1}H} NMR (*E*-isomer): δ 140.1, 139.9, 129.0, 128.1,

126.7, 124.6, 58.0, 56.1, 53.1, 40.6, 33.1, 29.2, 26.3, 26.1, 20.7, 14.1. $^{13}C\{^1H\}$ NMR (*Z*-isomer; partial spectrum): δ 31.7, 22.7. IR (neat, cm^{-1}): 2923, 2851, 2792, 1449, 971, 732, 697. HRMS calcd (found) for $C_{20}H_{31}N$ (M^+): 285.2457 (285.2458). Anal. calcd (found) for $C_{20}H_{31}N$: C, 84.15 (84.06); H, 10.95 (10.76).

***N*-benzyl-*N*-butyl-4-phenylbut-2-en-1-amine (2k).** Yellow oil. TLC (hexanes–EtOAc = 9:1): R_f = 0.32. ^1H NMR (*E*-isomer): δ 7.40-7.19 (m, 10H), 5.75 (td, *J* = 7, 15 Hz, 1 H), 5.57 (td, *J* = 6.5, 15.5 Hz, 1 H), 3.58 (s, 2 H), 3.39 (d, *J* = 6.5 Hz, 2 H), 3.07 (d, *J* = 6.25 Hz, 2 H), 2.45 (t, *J* = 7.25 Hz, 2 H), 1.51-1.45 (m, 2 H), 1.35-1.27 (m, 2 H), 0.89 (t, *J* = 7.25 Hz, 3 H). ^1H NMR (*Z*-isomer; partial spectrum): δ 5.78-5.59 (m, 2 H), 3.60 (s, 2 H), 3.20 (d, *J* = 6 Hz, 2 H), 2.50 (t, *J* = 7.25 Hz, 2 H). $^{13}C\{^1H\}$ NMR (*E*-isomer): δ 140.7, 140.0, 132.1, 129.2, 129.0, 128.6, 128.5, 128.2, 126.7, 126.0, 58.2, 55.8, 53.2, 39.0, 29.3, 20.3, 14.1. $^{13}C\{^1H\}$ NMR (*Z*-isomer): δ 126.8, 126.3, 56.3, 53.4, 29.4, 20.6. IR (neat, cm^{-1}): 3027, 2955, 2929, 2794, 1453, 972, 732, 696. HRMS calcd (found) for $C_{21}H_{27}N$ (MH^+): 294.2223 (294.2221). Anal. calcd (found) for $C_{21}H_{27}N$: C, 85.95 (85.76); H, 9.27 (8.97).

***N*-benzyl-*N*-(3-phenylallyl)butan-1-amine (2l).** Pale yellow oil. TLC (hexanes–EtOAc = 9:1): R_f = 0.45. ^1H NMR (*E*-isomer): δ 7.37 (t, *J* = 7 Hz, 4 H), 7.34-7.30 (m, 4 H), 7.26-7.21 (m, 2 H), 6.53 (d, *J* = 16 Hz, 1 H), 6.30 (td, *J* = 6.5, 16 Hz, 1 H), 3.63 (s, 2 H), 3.24 (d, *J* = 6.75 Hz, 2 H), 2.50 (t, *J* = 7.5 Hz, 2 H), 1.55-1.49 (m, 2 H), 1.37-1.30 (m, 2 H), 0.90 (t, *J* = 7.25 Hz, 3 H). $^{13}C\{^1H\}$ NMR (*E*-isomer): δ 139.9, 137.4, 132.2, 129.0, 128.6, 128.2, 128.1, 127.3, 126.8, 126.3, 58.3, 56.3, 53.4, 29.4, 20.7, 14.2. IR (neat, cm^{-1}): 3026, 2955, 2929, 2869, 2794, 966, 732, 693. HRMS calcd (found) for $C_{20}H_{25}N$ (MH^+): 280.2067 (280.2066).

***N*-benzyl-*N*-(3-(naphthalene-1-yl)allyl)butan-1-amine (2m).** Yellow oil. TLC (hexanes–EtOAc = 9:1): R_f = 0.36. ^1H NMR (*E*-isomer): δ 8.11 (d, *J* = 7.75 Hz, 1 H), 7.86 (d, *J* = 7.5 Hz, 1 H), 7.77 (d, *J* = 8.5 Hz, 1 H), 7.58 (d, *J* = 7 Hz, 1 H), 7.53-7.48 (m, 2 H), 7.45 (t, *J* = 7.5 Hz, 1 H), 7.41 (d, *J* = 7.75 Hz, 2 H), 7.35 (t, *J* = 7.5 Hz, 2 H), 7.30-7.25 (m, 2 H), 6.33 (td, *J* = 6.5, 15.5 Hz, 1 H), 3.70 (s, 2 H), 3.37 (d, *J* = 6.5 Hz, 2 H), 2.58 (t, *J* = 7.25 Hz, 2 H), 1.60-1.54 (m, 2 H), 1.41-1.33 (m, 2 H), 0.92 (t, *J* = 7.5 Hz, 3

H). $^{13}C\{^{1}H\}$ NMR (*E*-isomer): δ 139.9, 135.2, 133.7, 131.3, 131.2, 129.4, 129.0, 128.6, 128.3, 127.7, 126.9, 126.0, 125.8, 123.9. IR (neat, cm^{-1}): 3059, 2954, 2929, 2864, 2796, 969, 775, 732, 698. HRMS calcd (found) for $C_{24}H_{27}N$ (M^+): 329.2143 (329.2148). Anal. calcd (found) for $C_{24}H_{27}N$: C, 87.49 (87.42); H, 8.26 (8.07).

Control Experiments

Treatment of a mixture of dimethyl (2,3-butadienyl) malonate (**1**; 74 mg, 0.40 mmol) and benzyl *n*-butyl amine (36 μL, 0.20 mmol) with either $PtCl_2$(dppf) (8.2 mg, 0.010 mmol) or dppf (5.5 mg, 0.010 mmol) and triflic acid (0.9 μL, 0.01 mmol) in toluene at 80 °C for 24 h resulted in no detectable formation of **2a** or other hydroamination products. These control experiments ruled out acid- and ligand-catalyzed pathways. Treatment of a mixture of **1** (74 mg, 0.40 mmol) and benzyl *n*-butyl amine (36 μL, 0.20 mmol) with AgOTf (2.6 mg, 0.010 mmol) in toluene at 80 °C for 24 h formed traces (<10%) of **2a**. Although it is apparent that this reaction is slightly silver-catalyzed, the low yield established that both $PtCl_2$(dppf) and AgOTf are required for efficient hydroamination.

Figure S1. ^{1}H NMR of dimethyl (4-(benzyl(butyl)amino)-2-butenyl)malonate (**2a**) in $CDCl_3$.

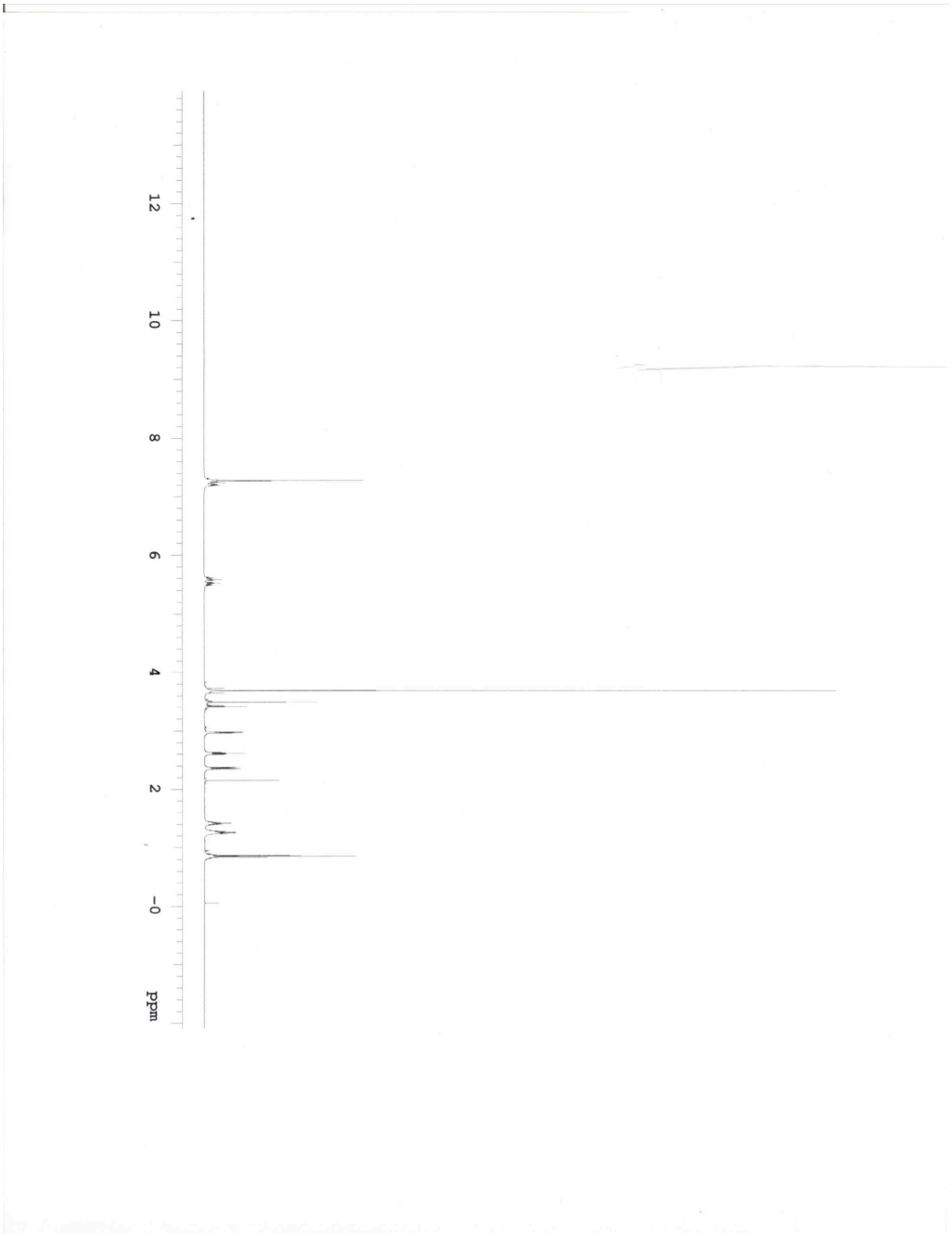


Figure S2. ^{13}C NMR of dimethyl (4-(benzyl(butyl)amino)-2-butenyl)malonate (**2a**) in $CDCl_3$.

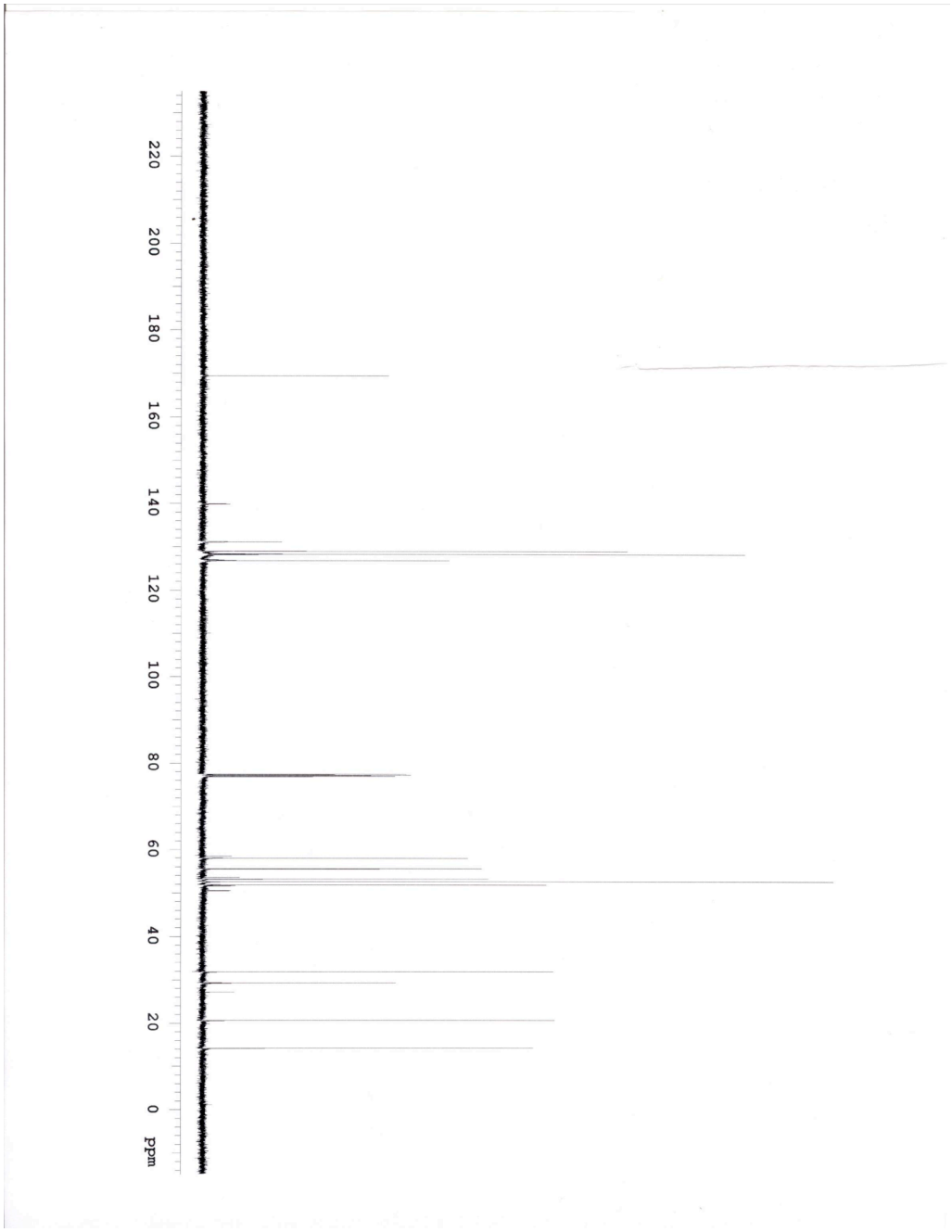


Figure S3. ^{1}H NMR of dimethyl 2-(4-(benzyl(methyl)amino)but-2-enyl)malonate (**2b**) in $CDCl_3$.

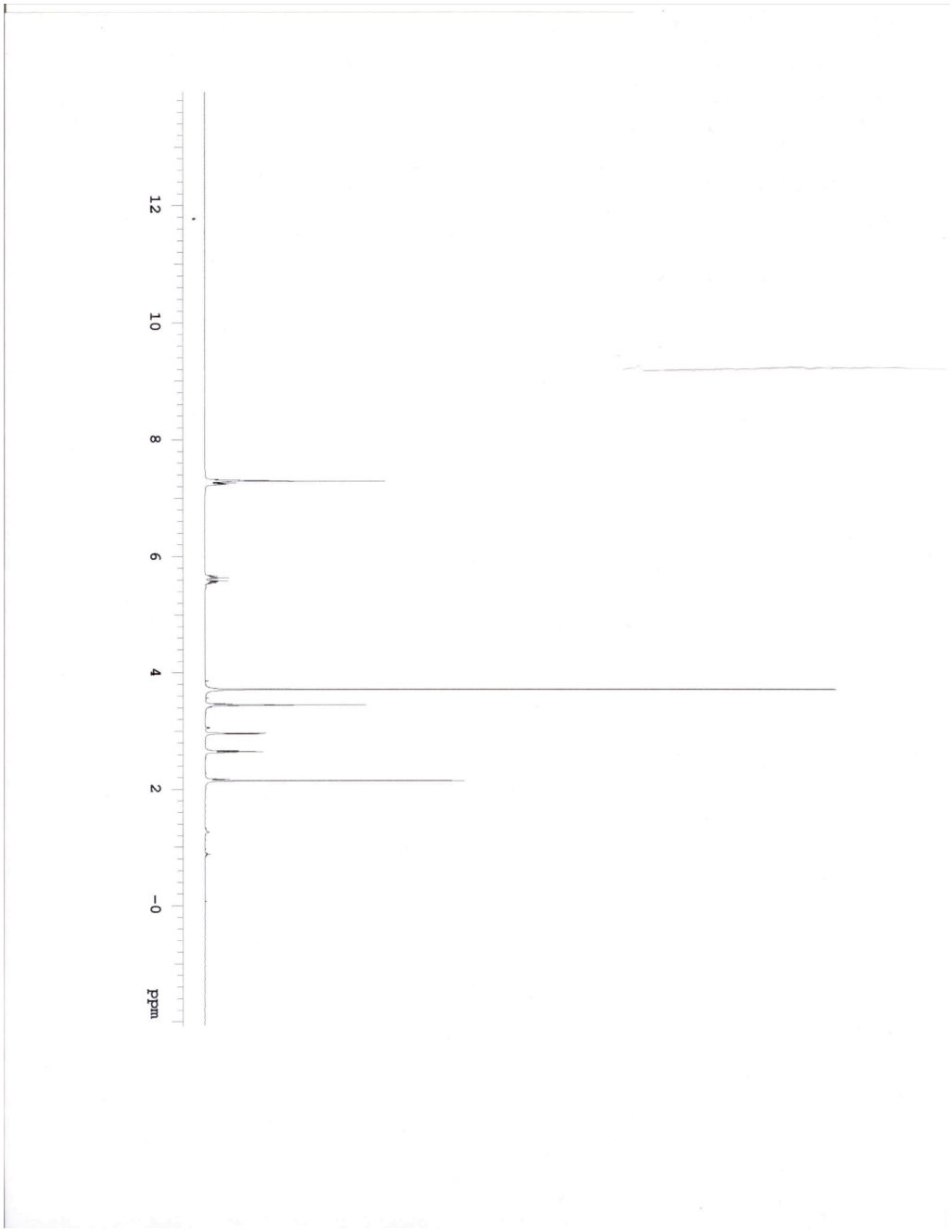


Figure S4. ^{13}C NMR of dimethyl 2-(4-(benzyl(methyl)amino)but-2-enyl)malonate (**2b**) in $CDCl_3$.

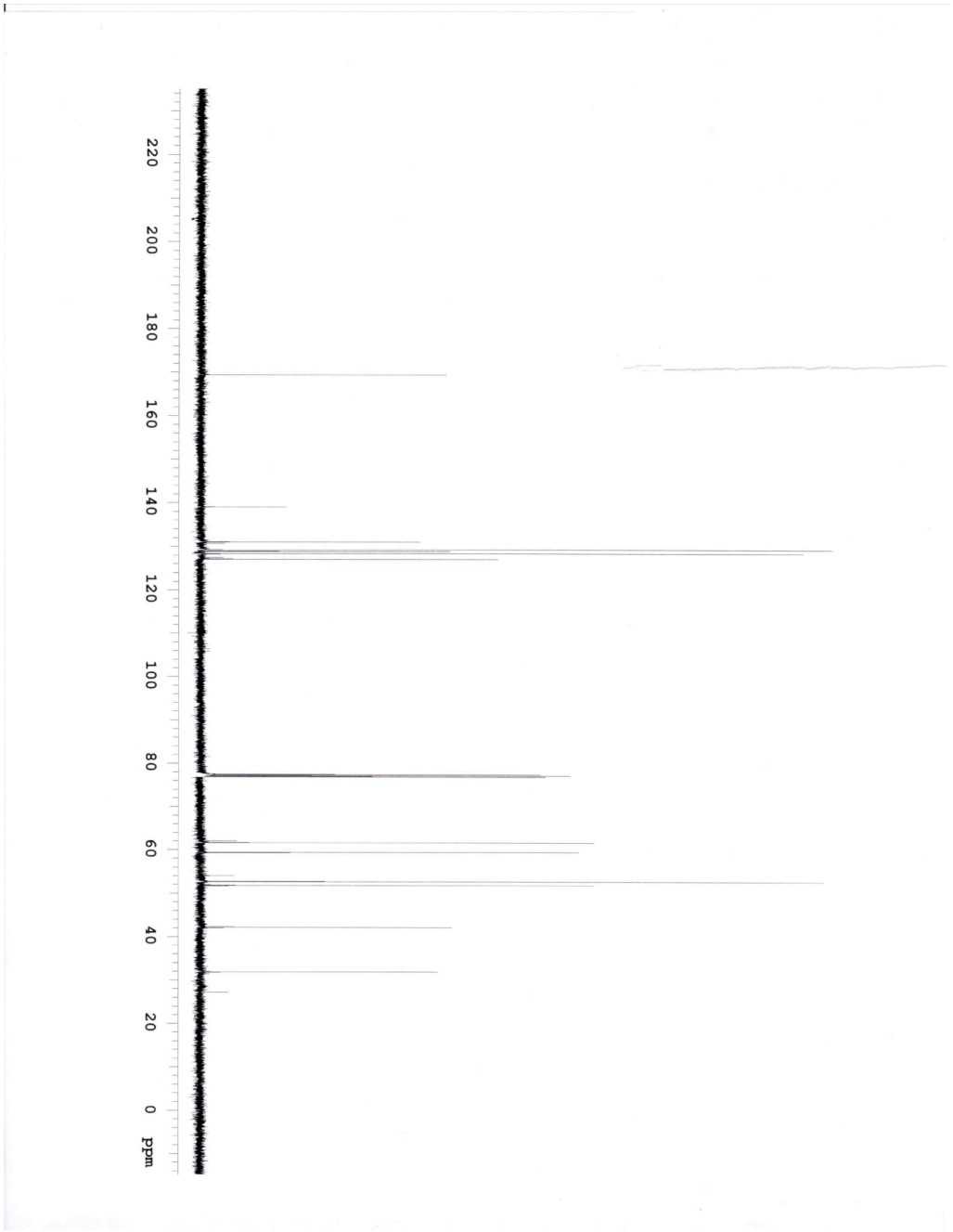


Figure S5. ^{1}H NMR of dimethyl 2-(4-morpholinobut-2-enyl)malonate (**2c**) in $CDCl_3$.

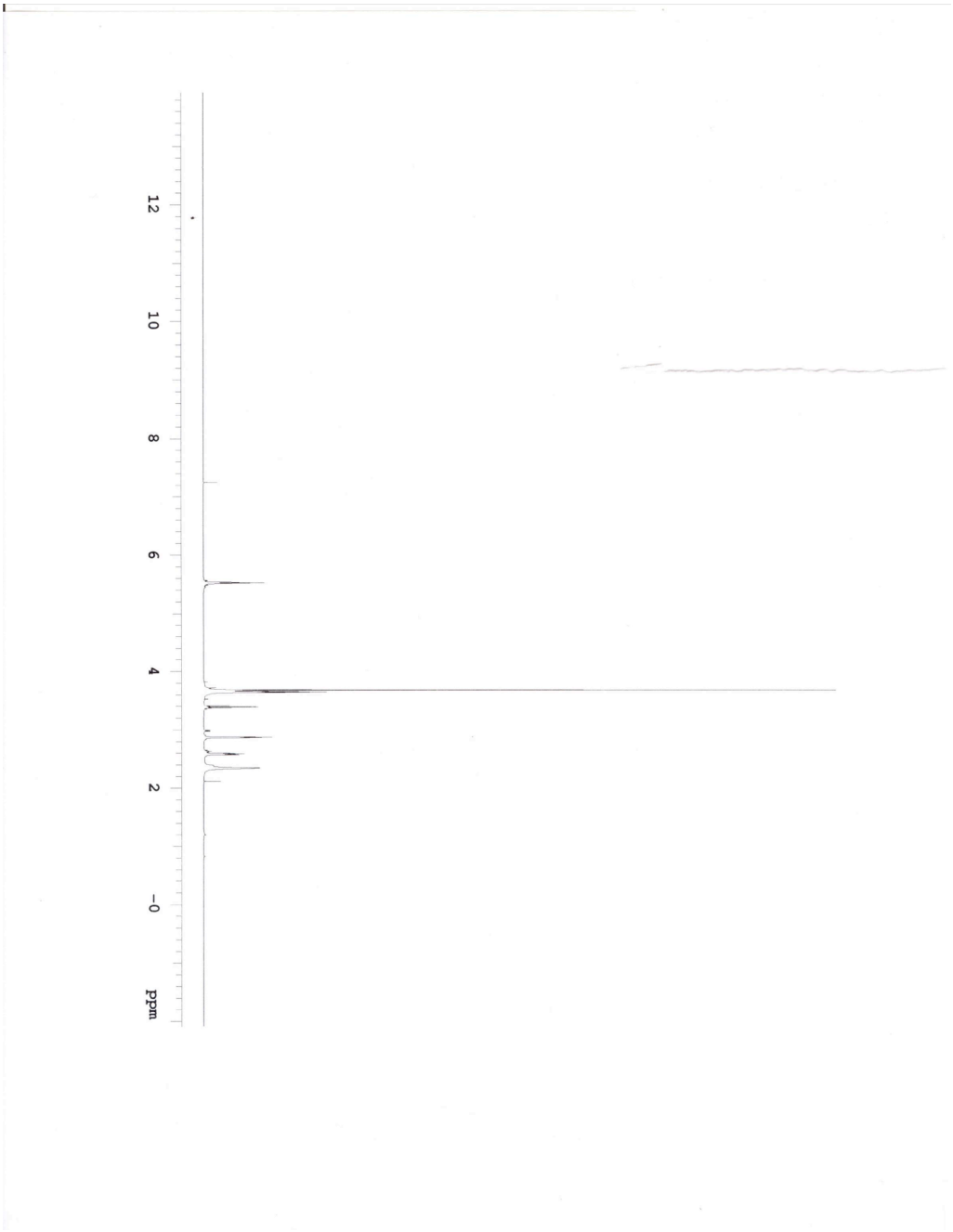


Figure S6. ^{13}C NMR (101 MHz) of dimethyl 2-(4-morpholinobut-2-enyl)malonate (**2c**) in $CDCl_3$.

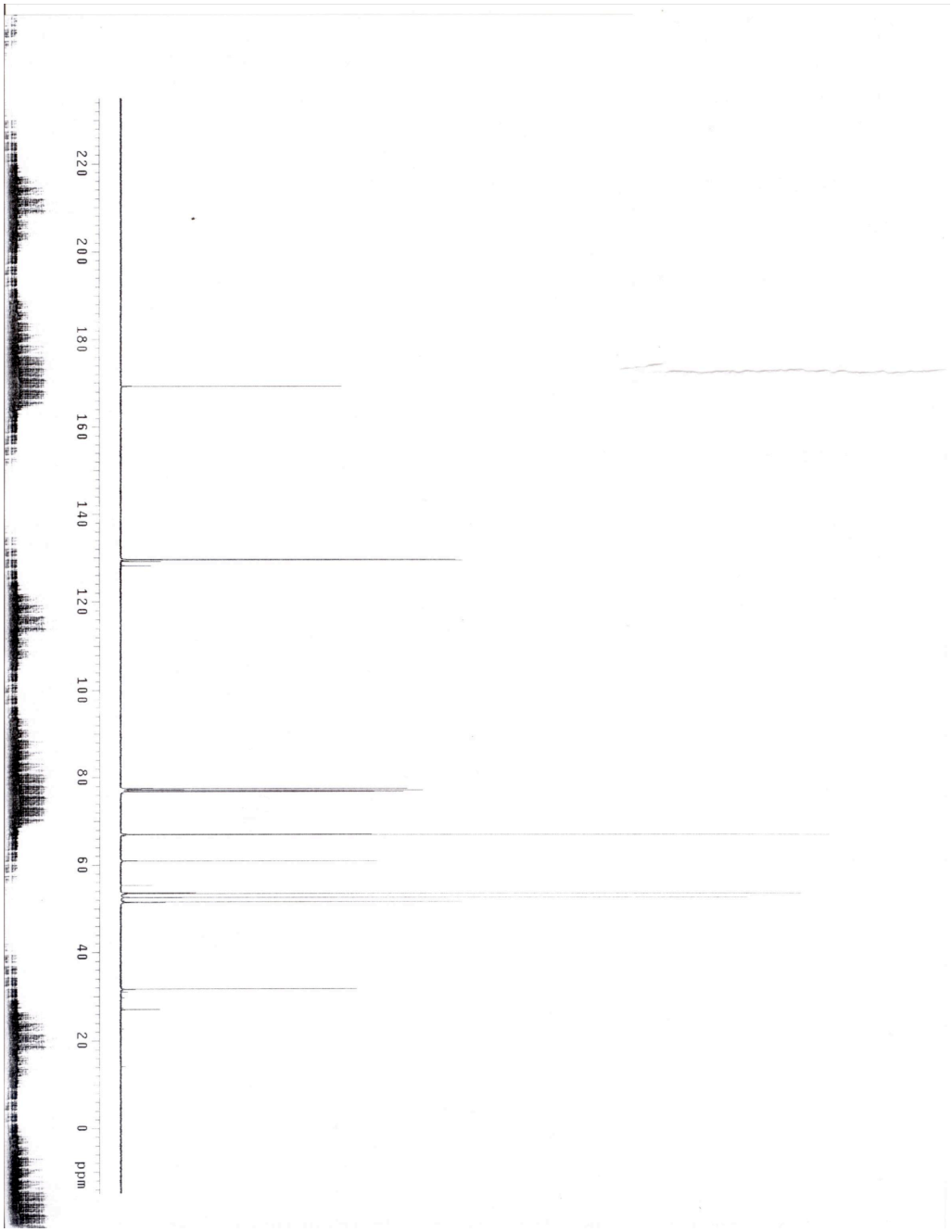


Figure S7. ^{1}H NMR of dimethyl 2-(4-(piperidin-1-yl)but-2-enyl)malonate (**2d**) in $CDCl_3$.

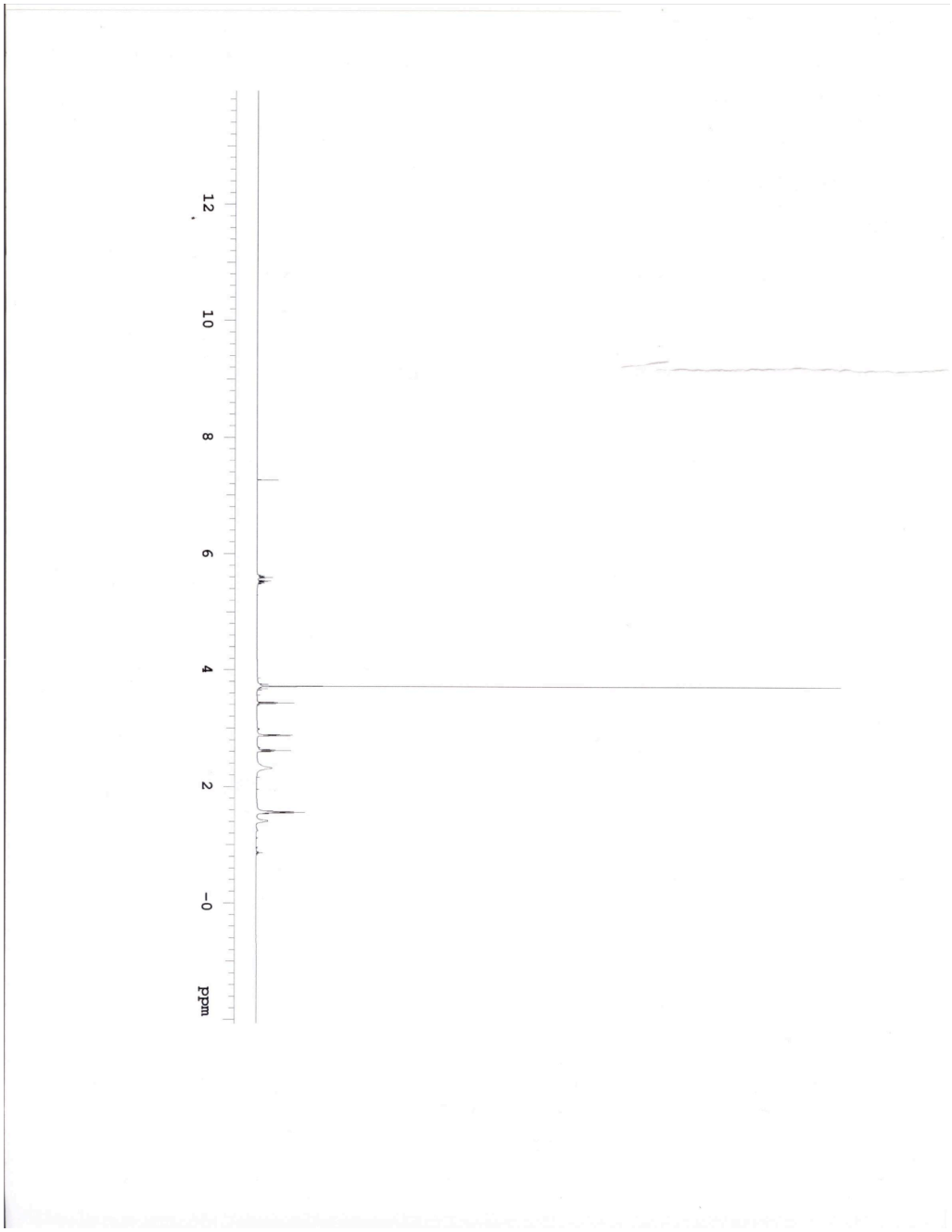


Figure S8. ^{13}C NMR of dimethyl 2-(4-(piperidin-1-yl)but-2-enyl)malonate (**2d**) in $CDCl_3$.

Figure S9. ^{1}H NMR of dimethyl 2-(4-(pyrrolidin-1-yl)but-2-enyl)malonate (**2e**) in $CDCl_3$.

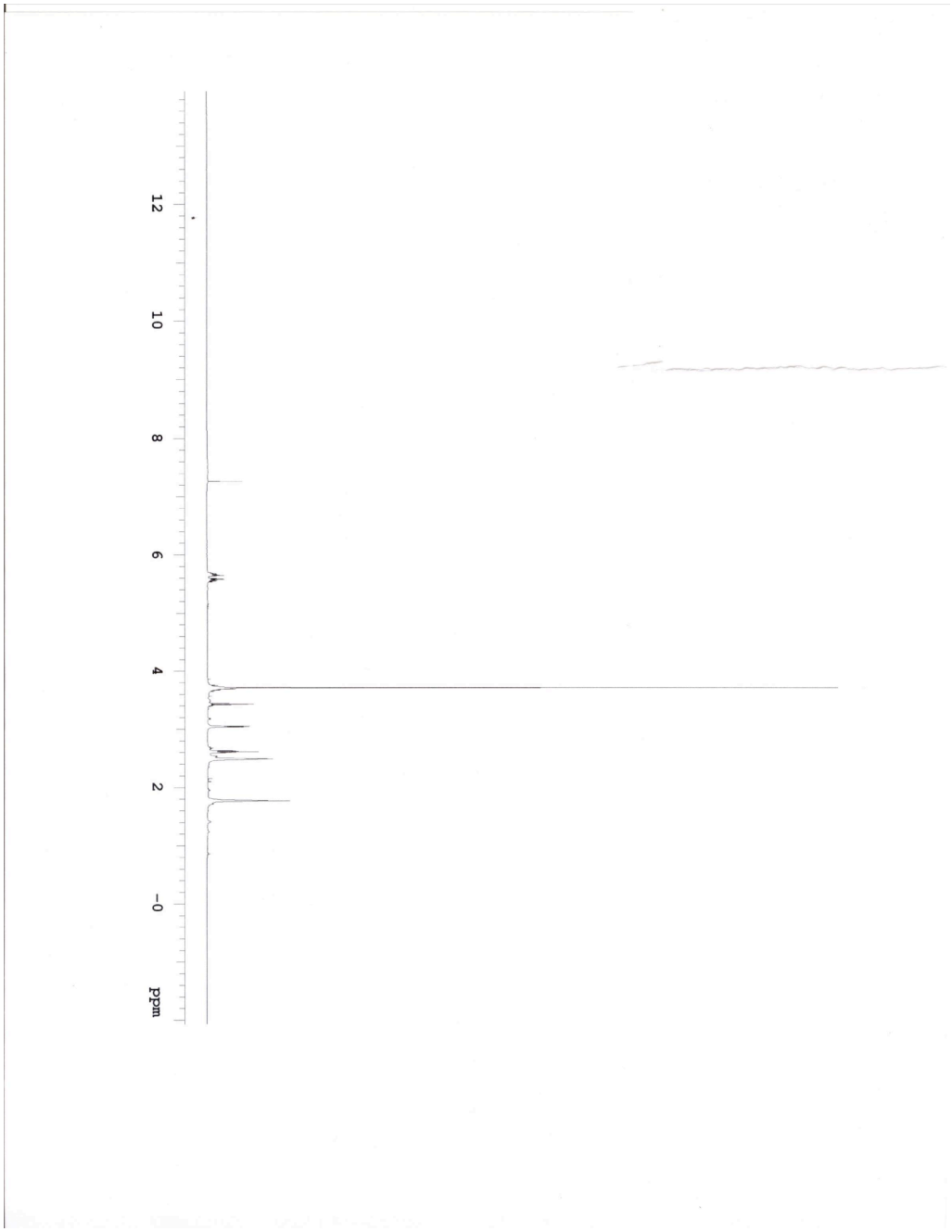


Figure S10. ^{13}C NMR of dimethyl 2-(4-(pyrrolidin-1-yl)but-2-enyl)malonate (**2e**) in $CDCl_3$.

Figure S11. ^{1}H NMR of dimethyl 2-(4-(dibutylamino)but-2-entyl)malonate (**2f**) in $CDCl_3$.

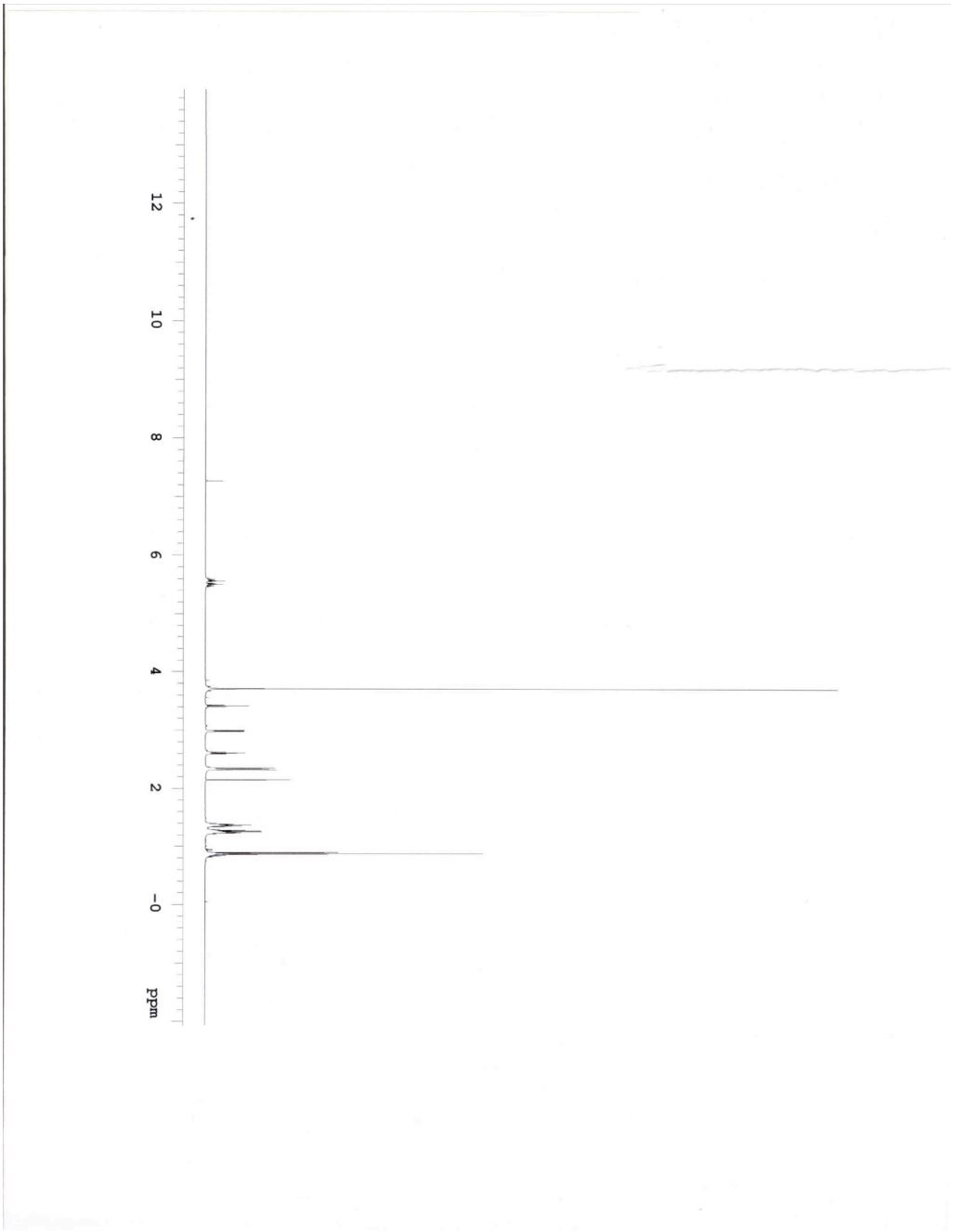


Figure S12. ^{13}C NMR of dimethyl 2-(4-(dibutylamino)but-2-entyl)malonate (**2f**) in $CDCl_3$.

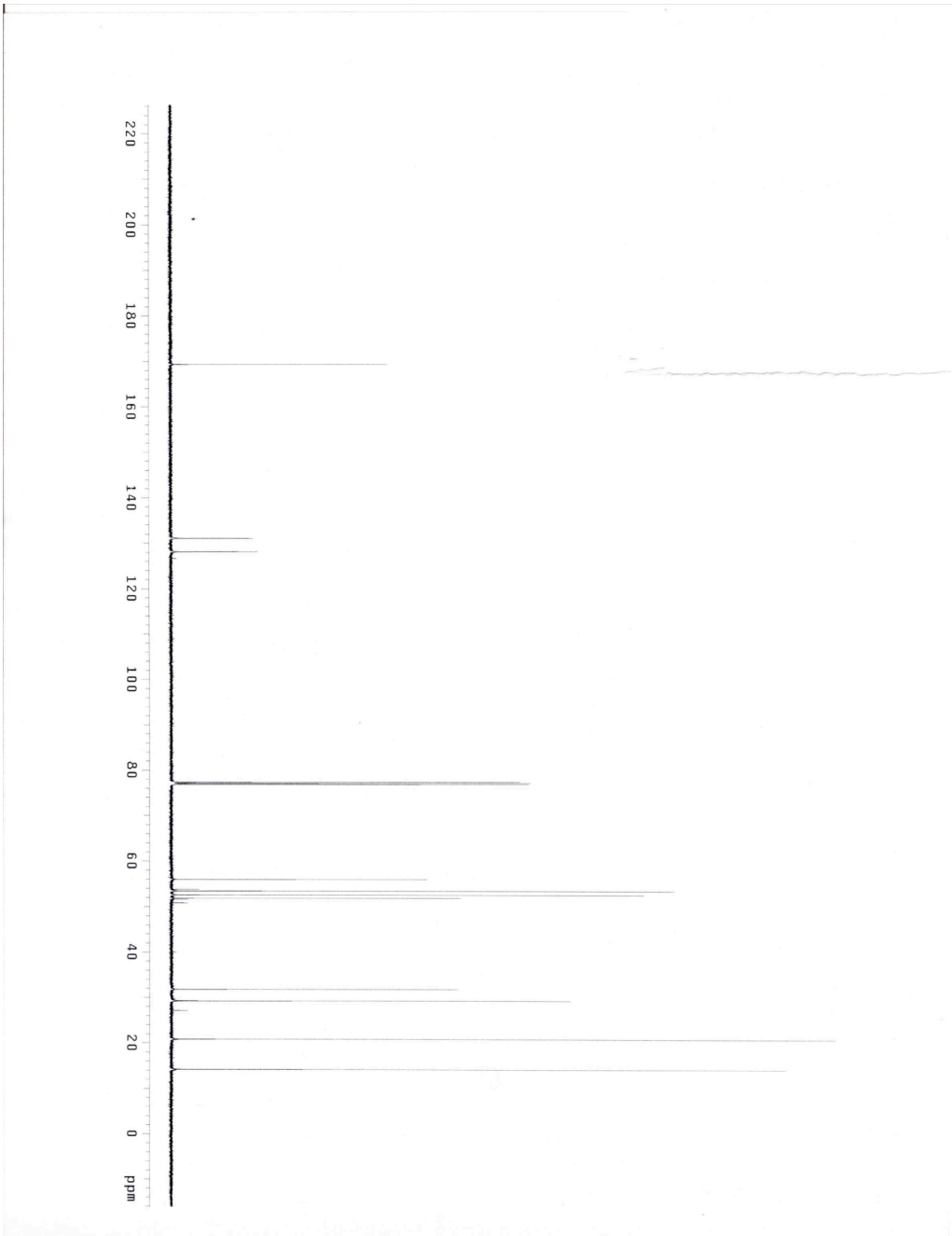


Figure S13. ^{1}H NMR of dimethyl 2-(4-(diethylamino)but-2-enyl)malonate (**2g**) in $CDCl_3$.

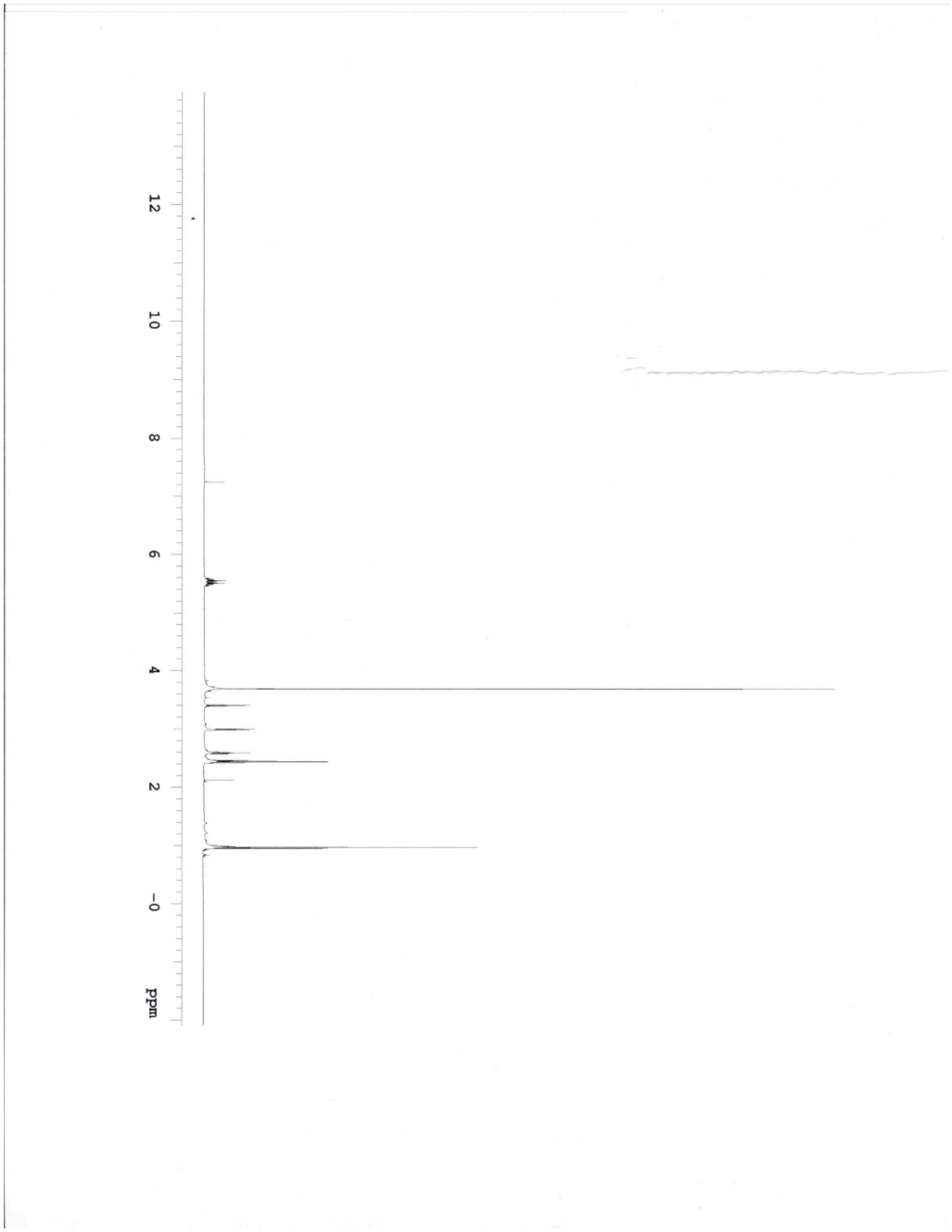


Figure S14. ^{13}C NMR of dimethyl 2-(4-(diethylamino)but-2-enyl)malonate in (**2g**) $CDCl_3$.

Figure S15. ^{1}H NMR of dimethyl 2-(4-(dibenzylamino)but-2-enyl)malonate (**2h**) in $CDCl_3$.

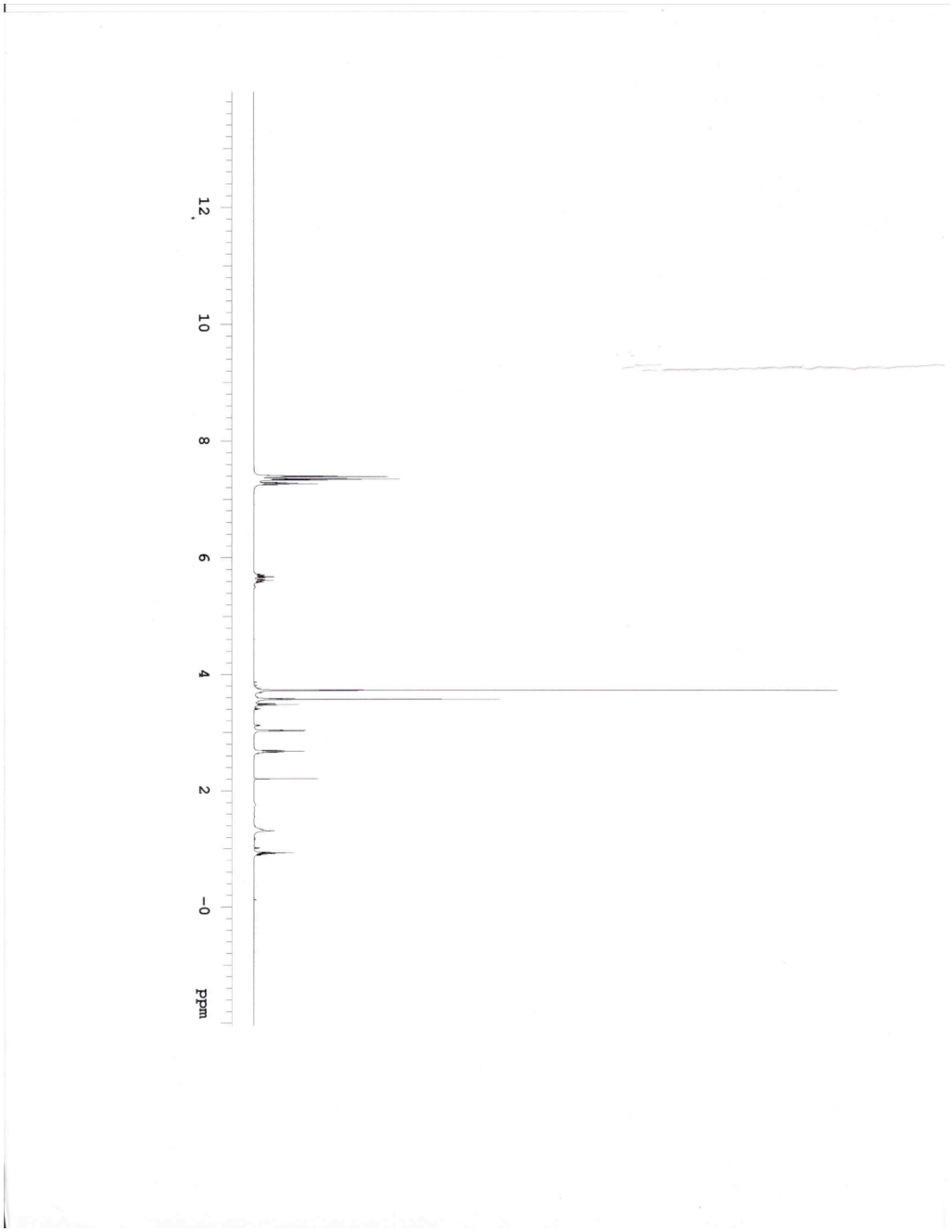


Figure S16. ^{13}C NMR (101 MHz) of dimethyl 2-(4-(dibenzylamino)but-2-enyl)malonate (**2h**) in $CDCl_3$.

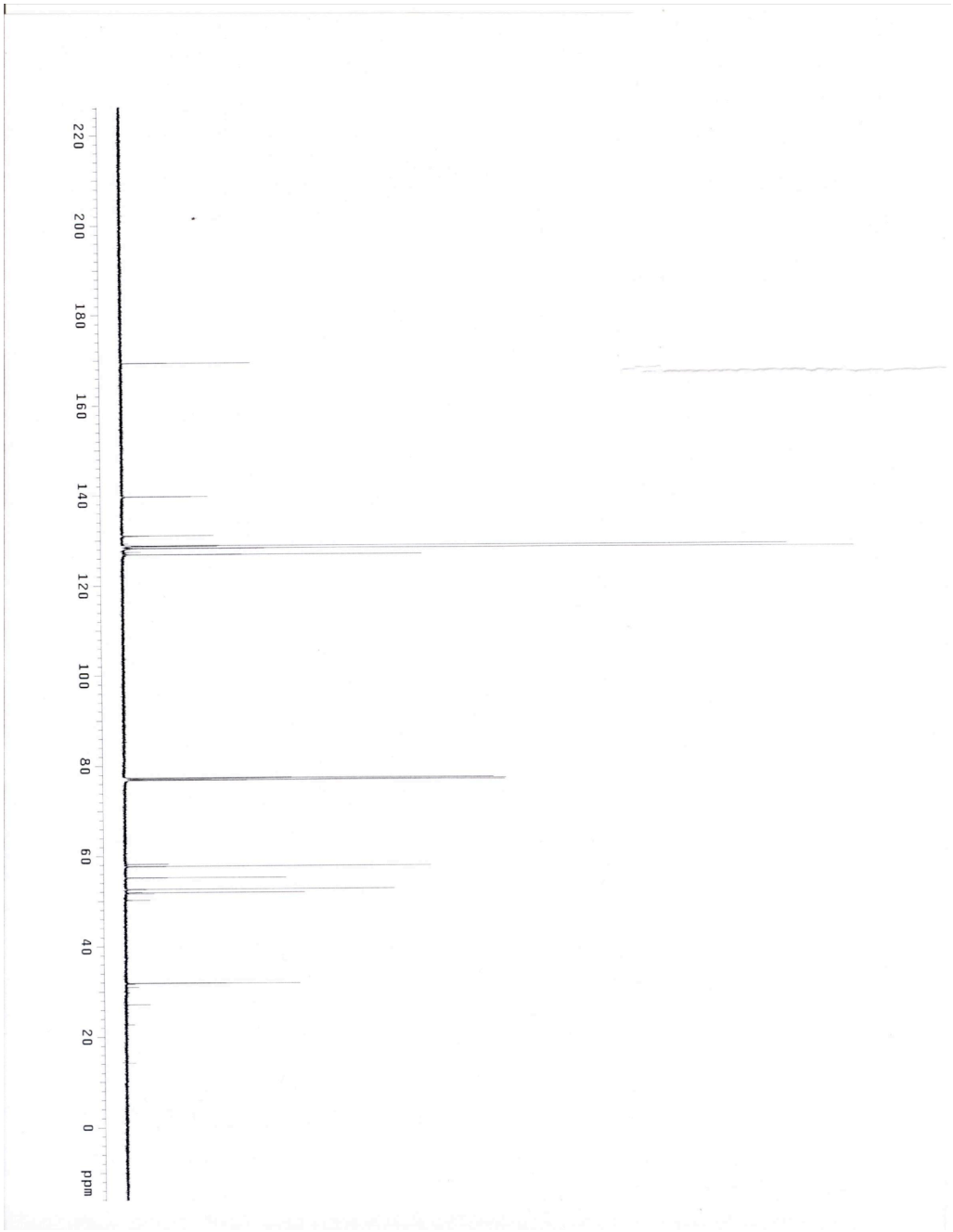


Figure S17. ^{1}H NMR of N-benzyl-N-butylundec-2-en-1-amine (**2i**) in $CDCl_3$.

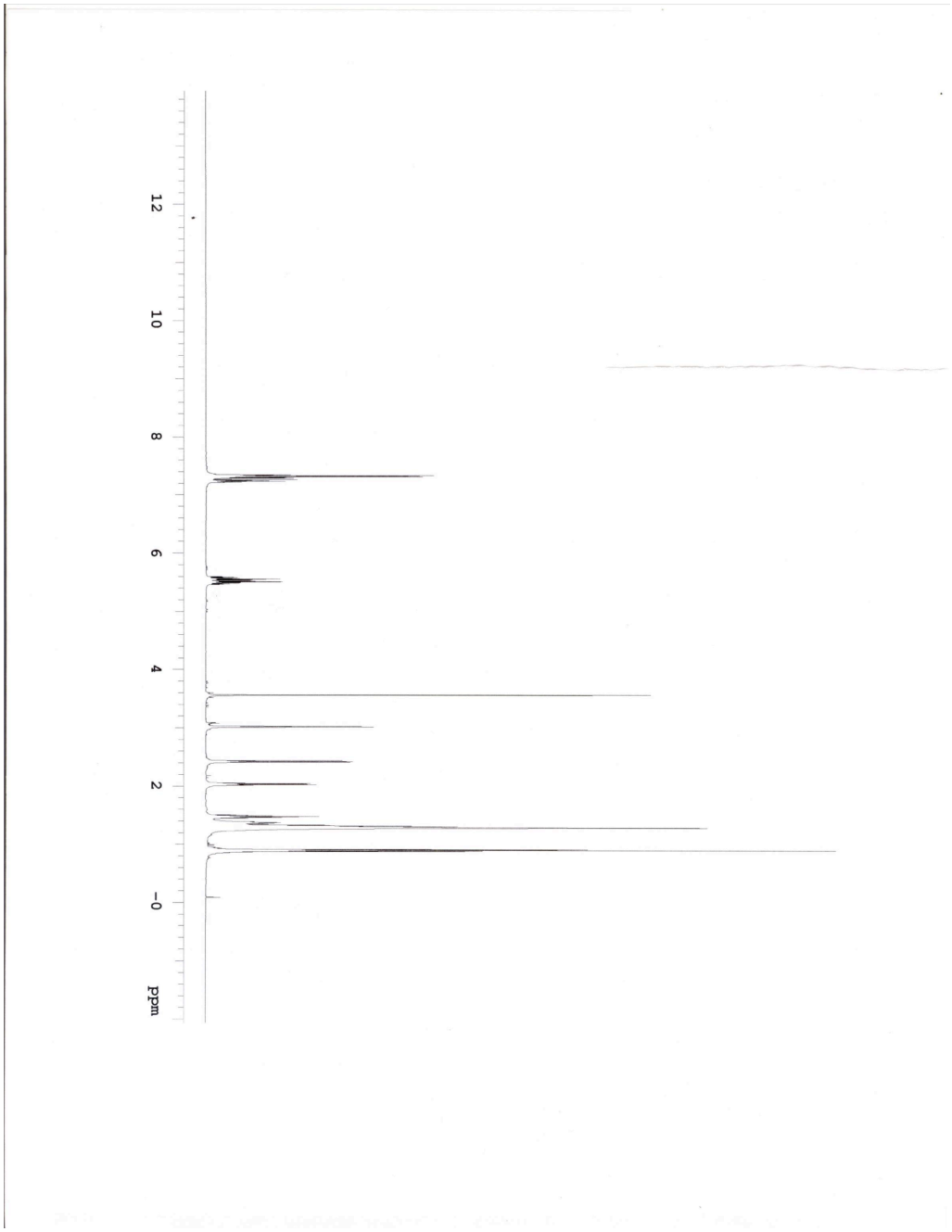


Figure S18. ^{13}C NMR of N-benzyl-N-butylundec-2-en-1-amine (**2i**) in $CDCl_3$.

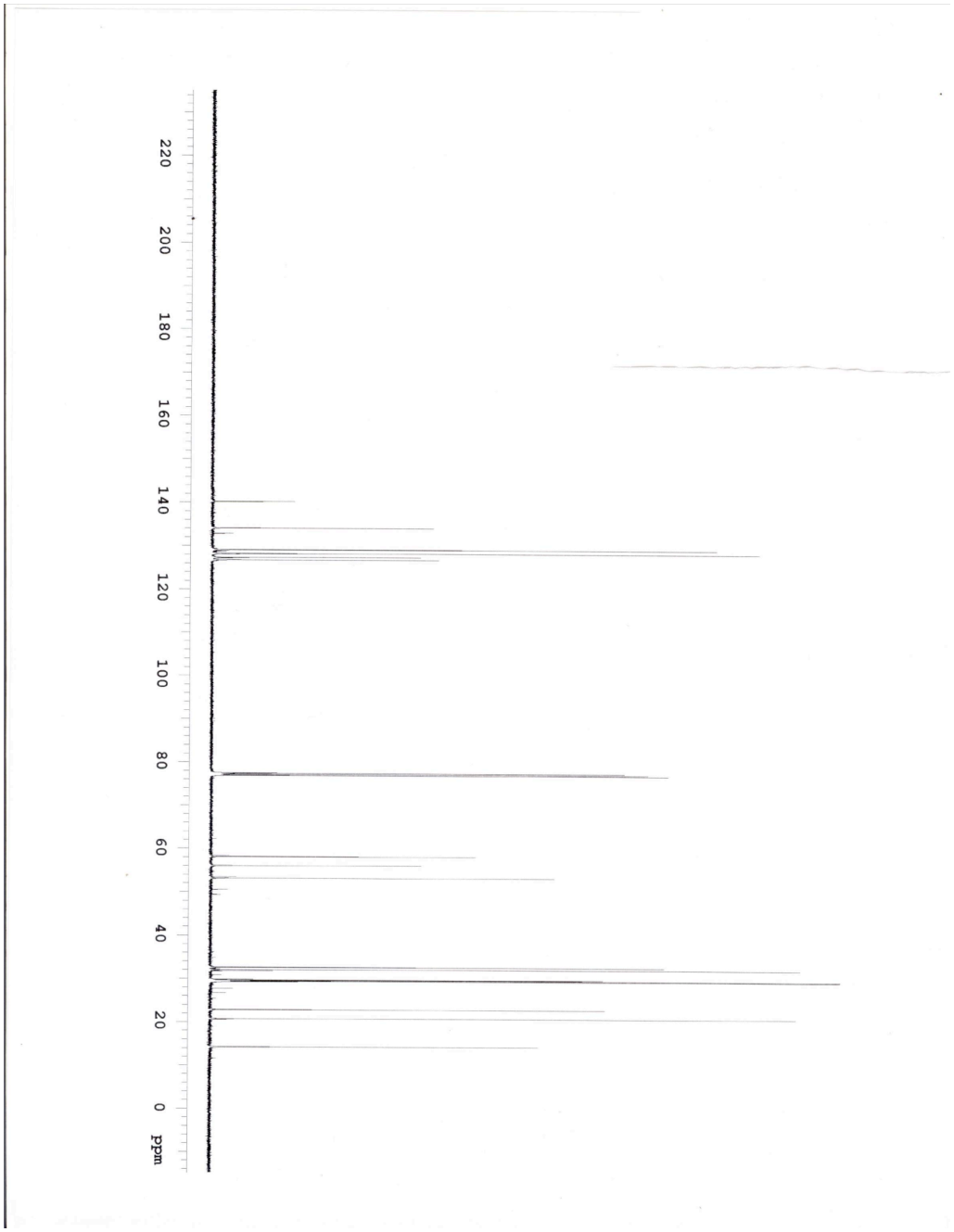


Figure S19. ^{1}H NMR of N-benzyl-N-(3-cyclohexylallyl)butan-1-amine (**2j**) in $CDCl_3$.

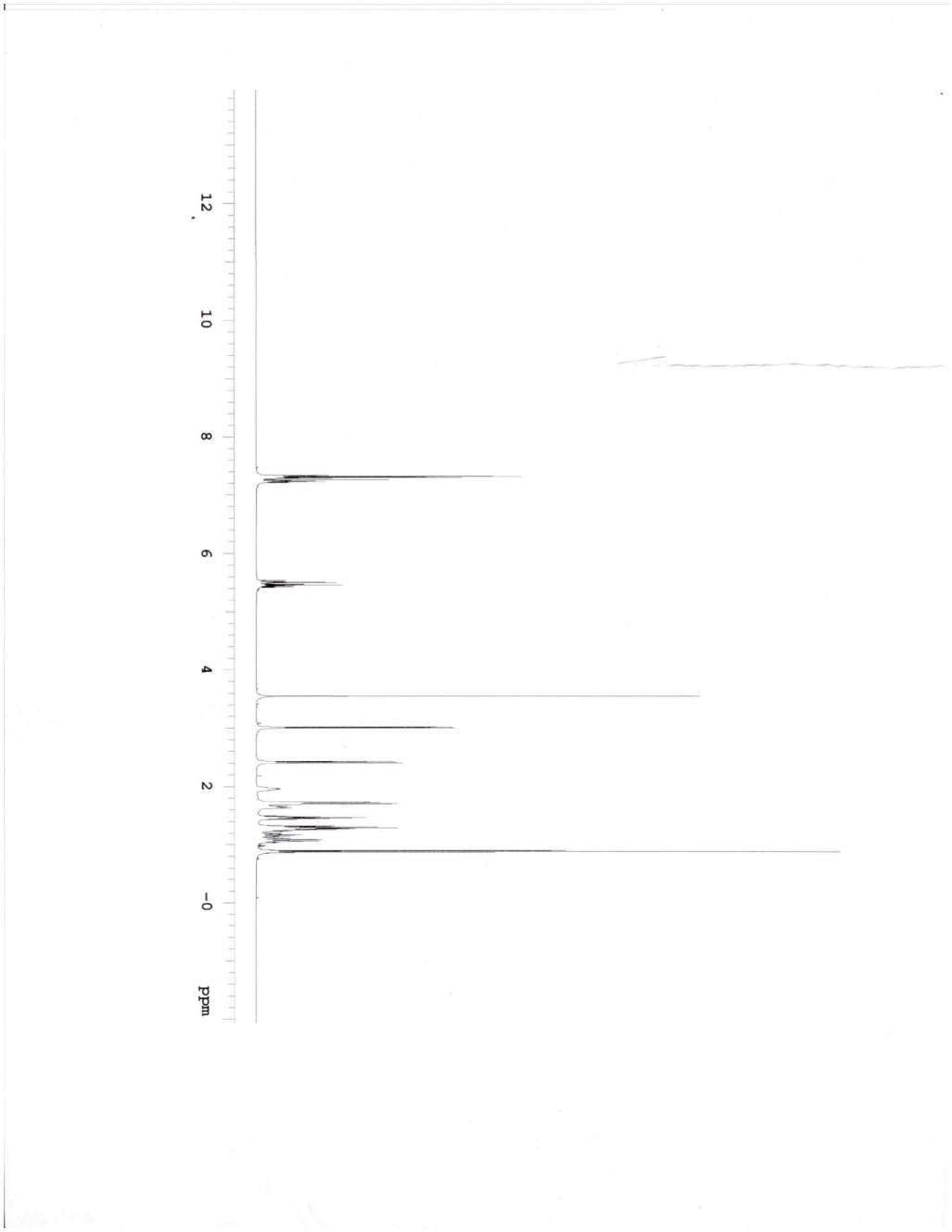


Figure S20. ^{13}C NMR of N-benzyl-N-(3-cyclohexylallyl)butan-1-amine (**2j**) in $CDCl_3$.

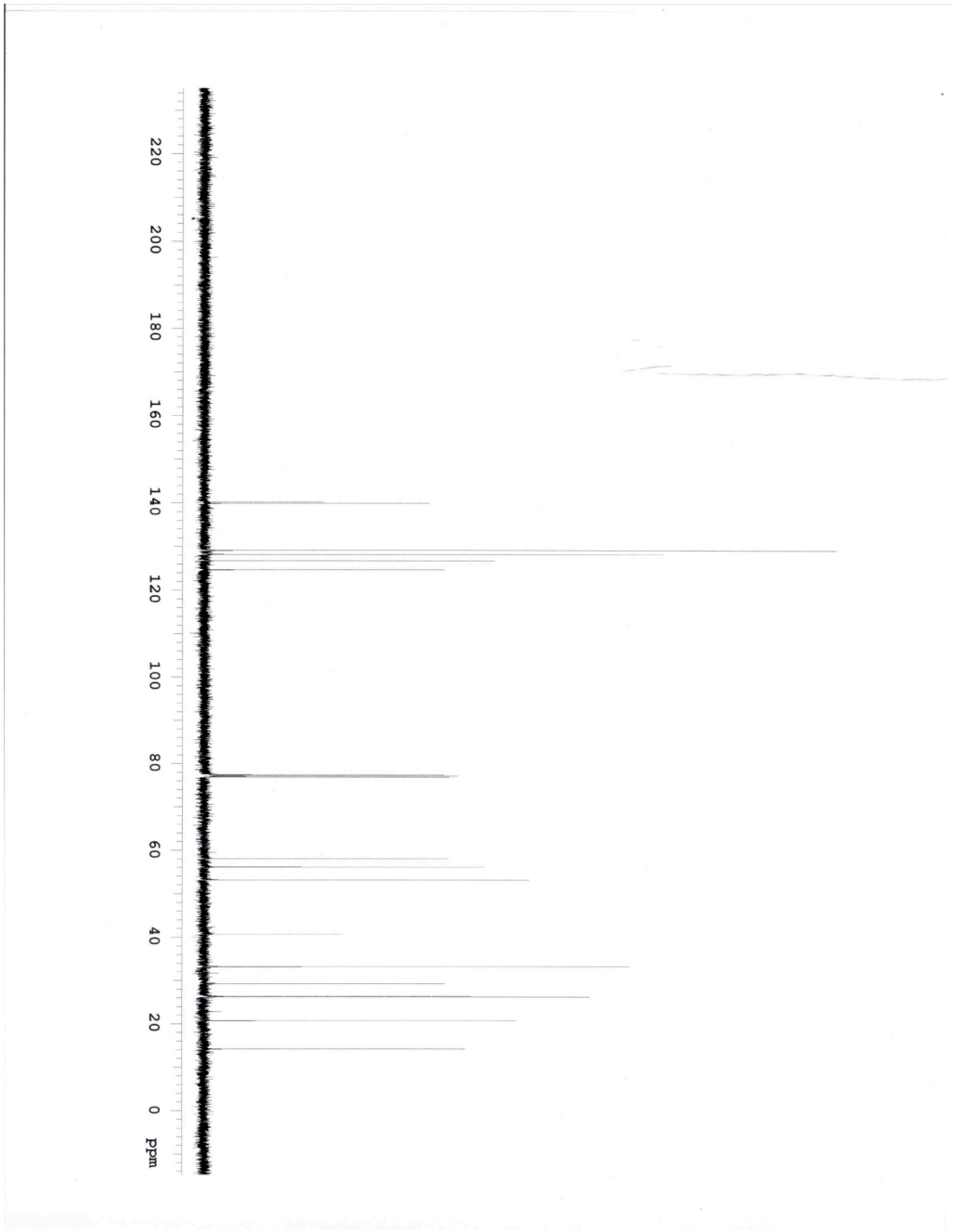


Figure S21. ^{1}H NMR of N-benzyl-N-butyl-4-phenylbut-2-en-1-amine (**2k**) in $CDCl_3$.

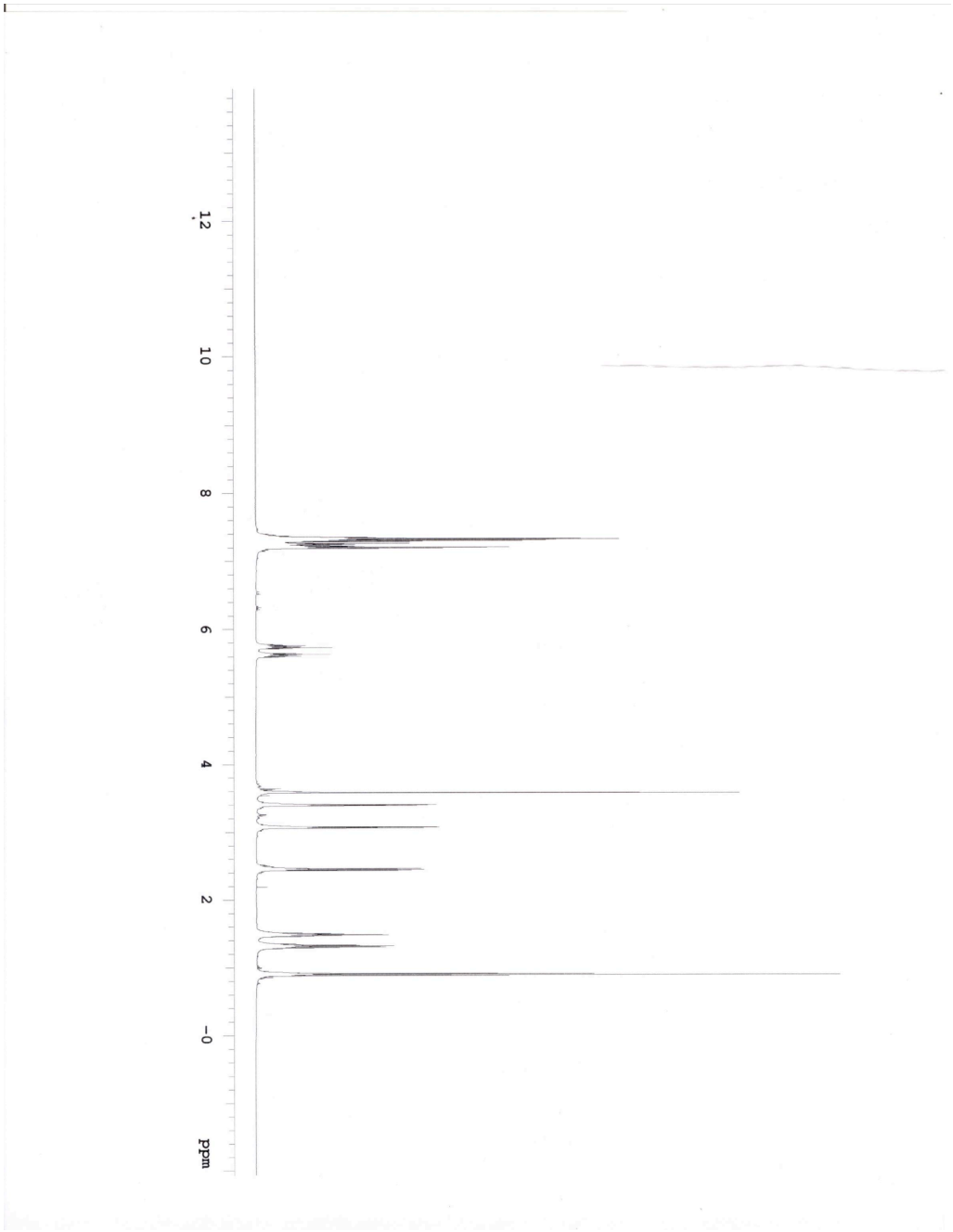


Figure S22. ^{13}C NMR of N-benzyl-N-butyl-4-phenylbut-2-en-1-amine (**2k**) in $CDCl_3$.

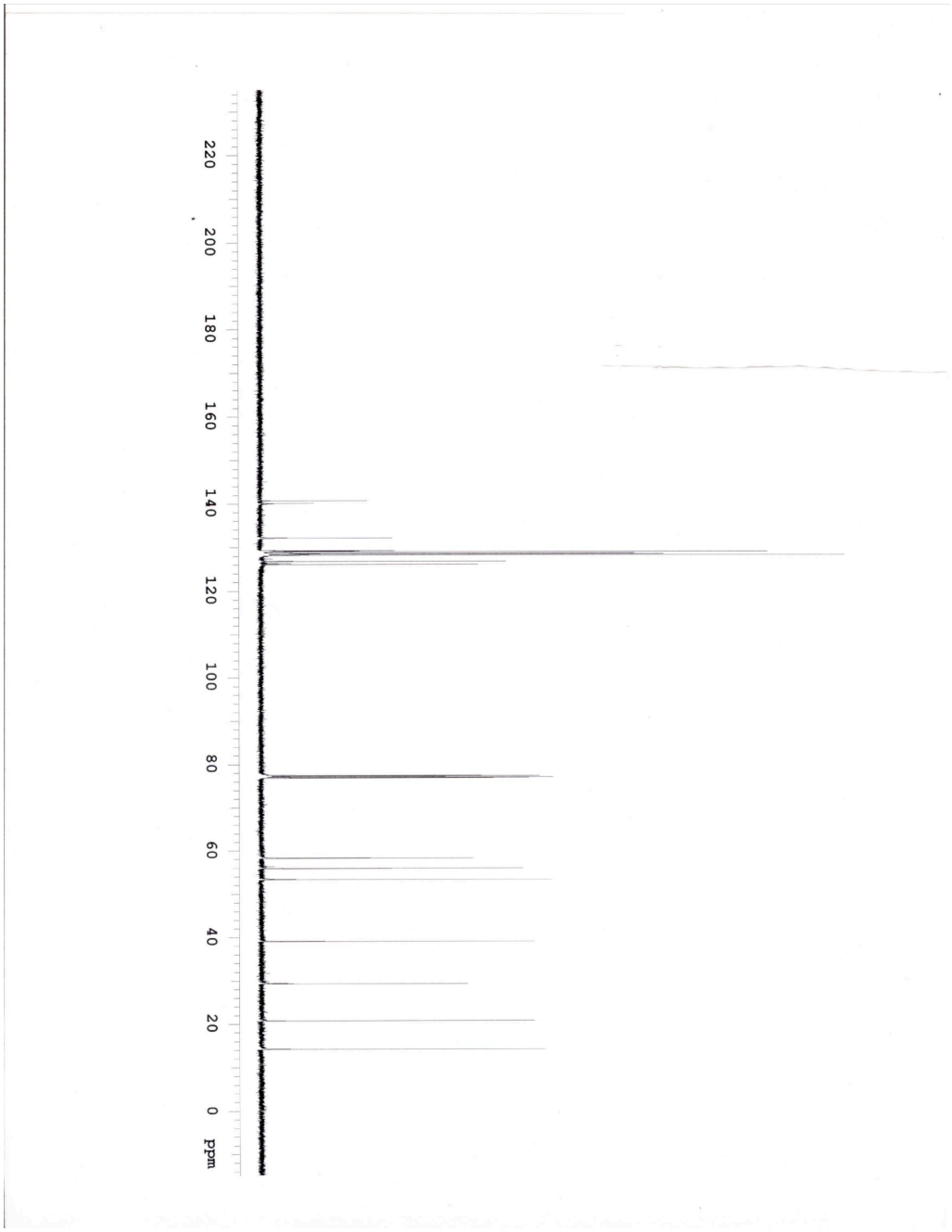


Figure S23. ^{1}H NMR of N-benzyl-N-(3-phenylallyl)butan-1-amine (**2l**) in $CDCl_3$.

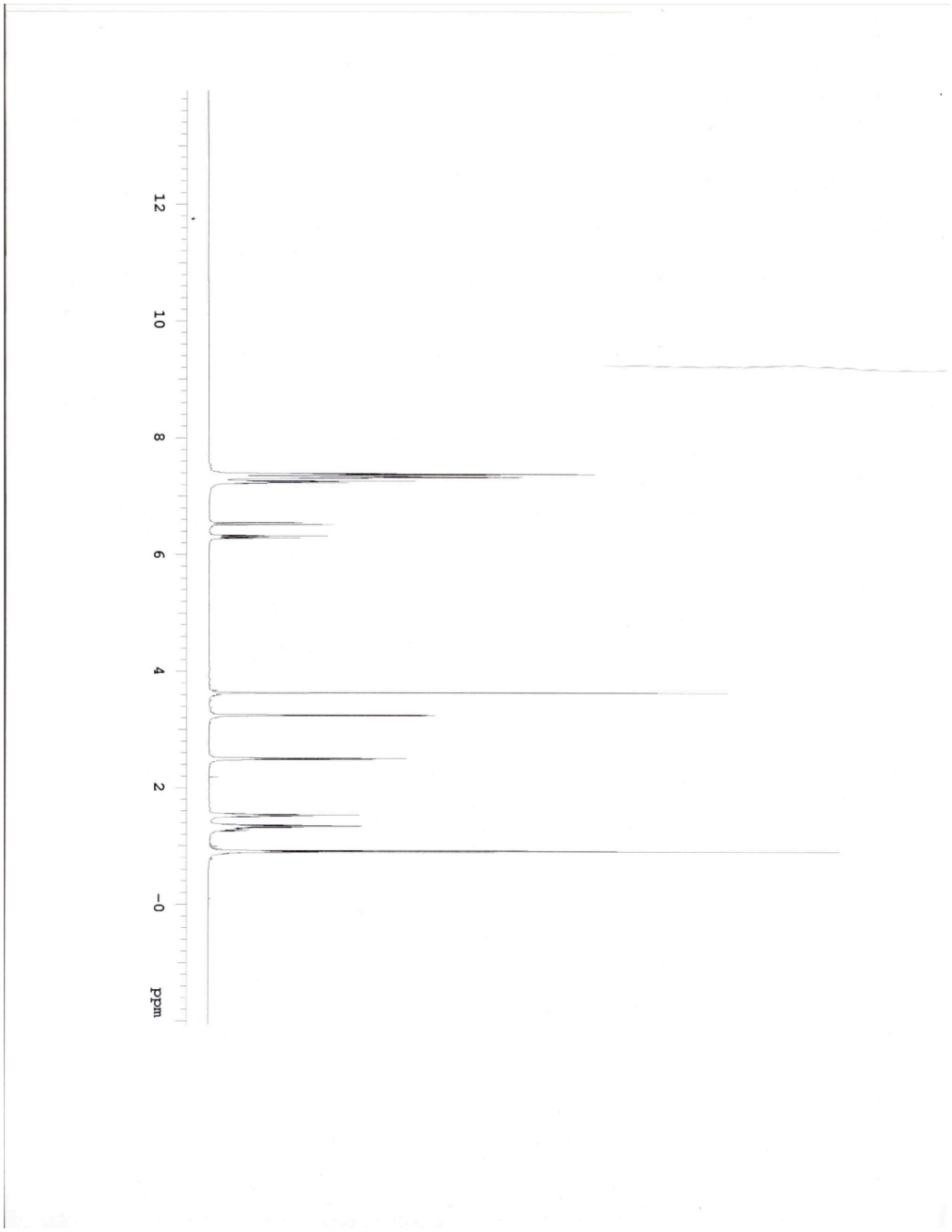


Figure S24. ^{13}C NMR of N-benzyl-N-(3-phenylallyl)butan-1-amine (**2l**) in $CDCl_3$.

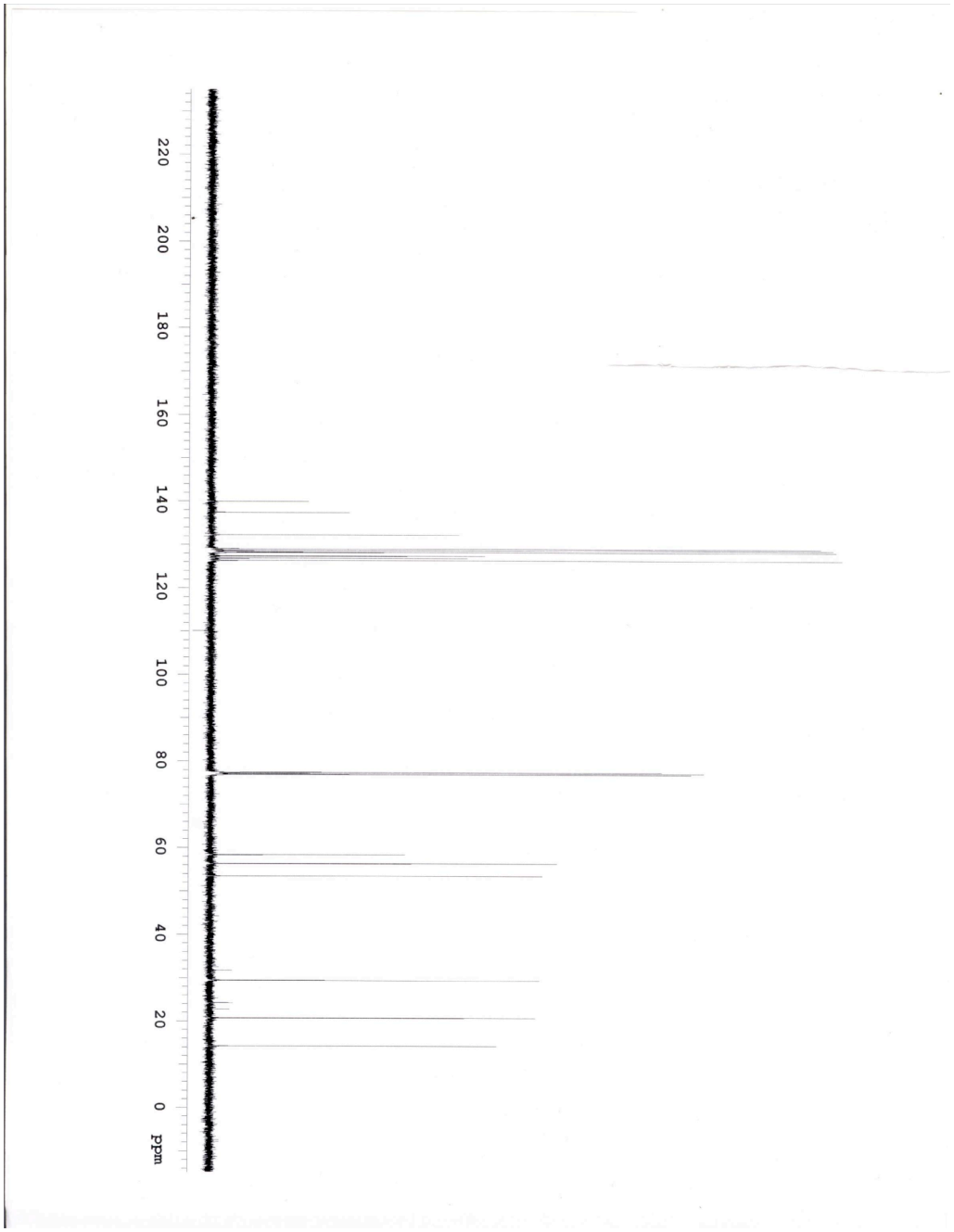


Figure S25. ^{1}H NMR of N-benzyl-N-(3-(naphthalene-1-yl)allyl)butan-1-amine (**2m**) in $CDCl_3$.

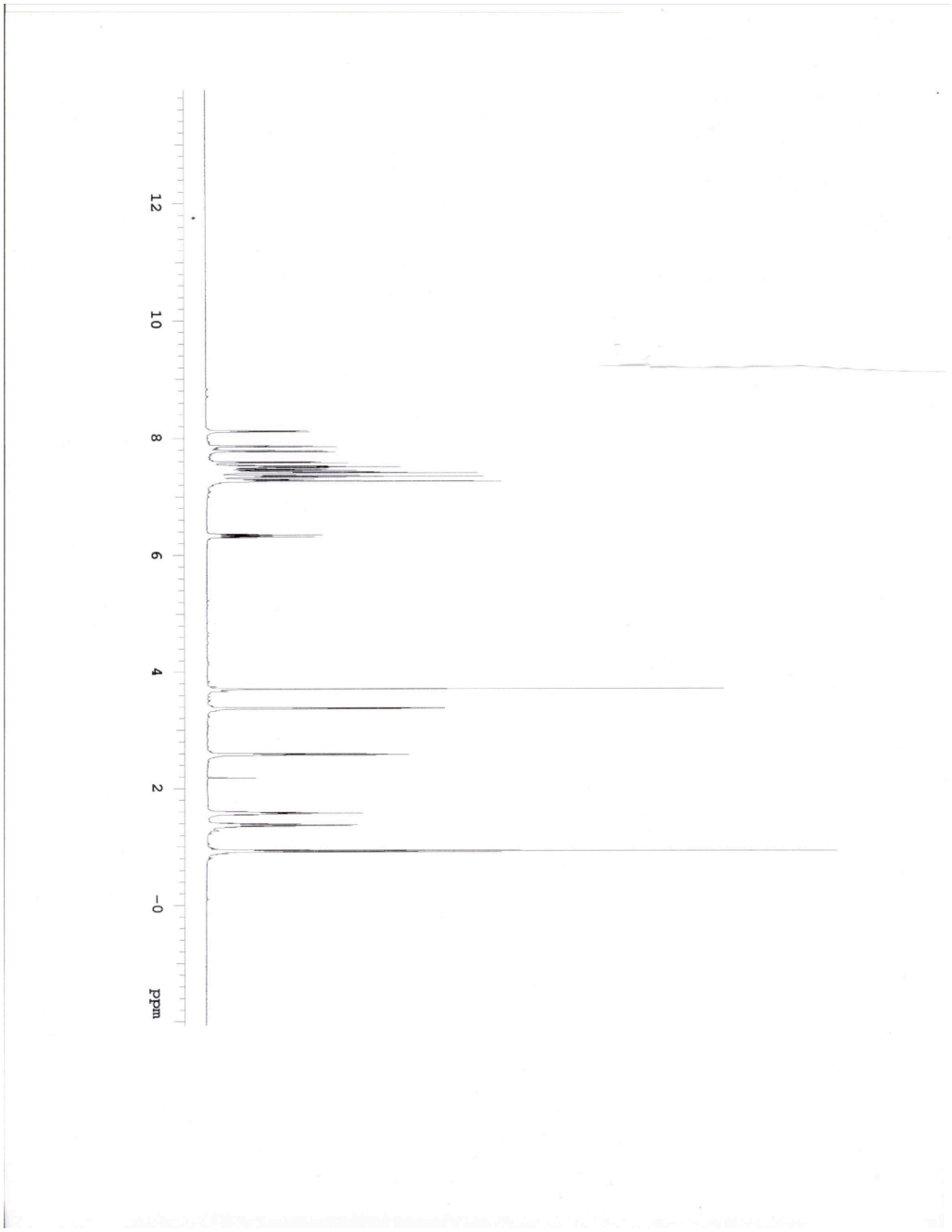
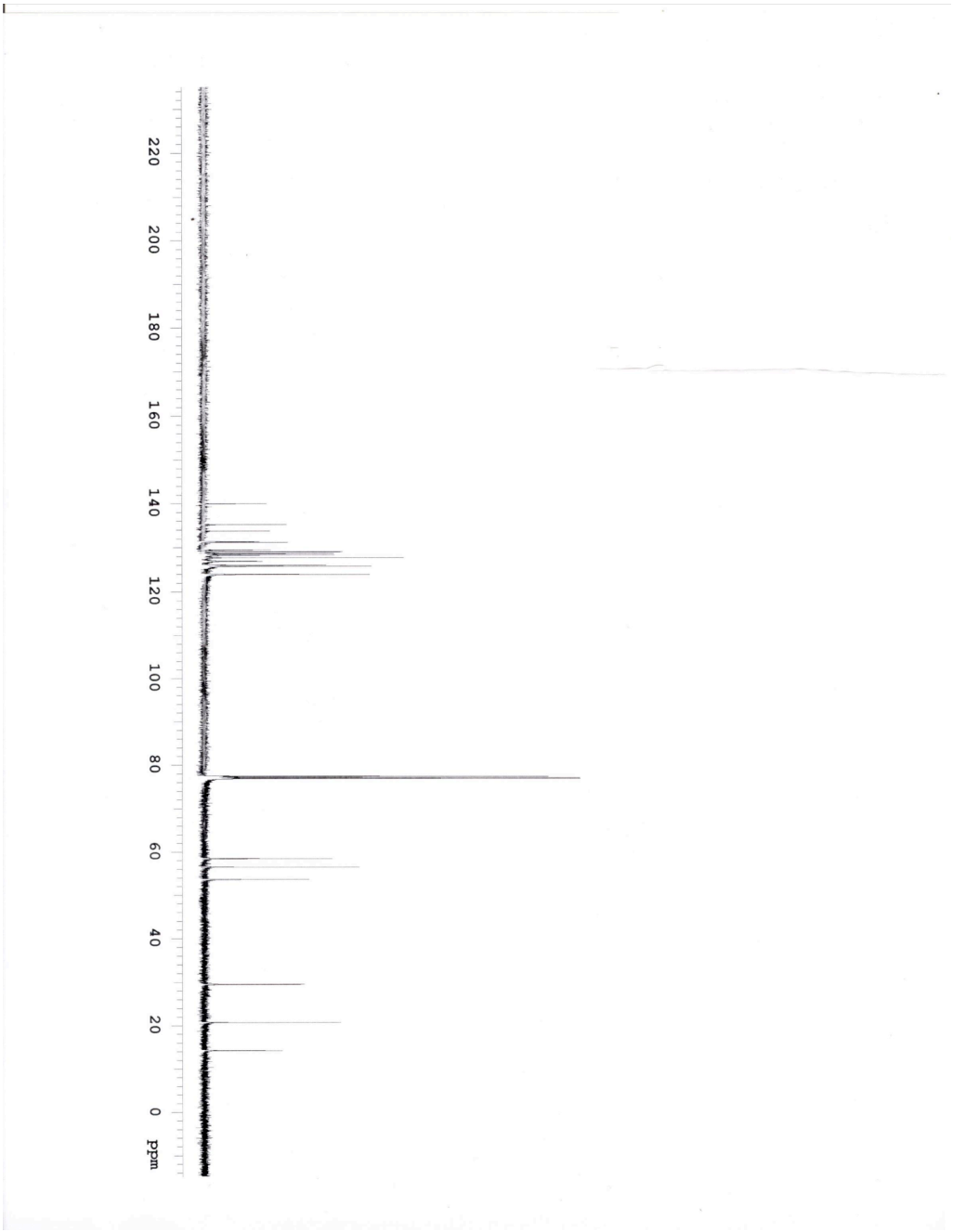


Figure S26. ^{13}C NMR of N-benzyl-N-(3-(naphthalene-1-yl)allyl)butan-1-amine (**2m**) in $CDCl_3$.



References

1. Nieto-Oberhuber, C.; López, S.; Echavarren, A. M. *J. Am. Chem. Soc.* **2005,** *127*, 6178-6179.
2. Kinder, R. E.; Zhang, Z.; Widenhoefer, R. A. *Org. Lett.* **2008,** *10*, 3157-3159.
3. Appleton, T. G.; Bennett, M. A.; Tomkins, I. B. *J. Chem. Soc., Dalton Trans.* **1976,** *5*, 439-446.
4. Colladon, M.; Scarso, A.; Strukul, G. *Synlett* **2006,** *20*, 3515-3520.
5. Stang, P. J.; Olenyuk, B.; Fan, J.; Arif, A. M. *Organometallics* **1996,** *15*, 904-908.
6. Tudor, M. D.; Becker, J. J.; White, P. S.; Gagné, M. R. *Organometallics* **2000,** *19*, 4376-4384.
7. Kranenburg, M.; Kamer, P. C. J.; van Leeuwen, P. W. N. M. *Eur. J. Inorg. Chem.* **1998,** 155-157.
8. Petöcz, G.; Berente, Z.; Kégl, T.; Kollár, L. *J. Organomet. Chem.* **2004,** *689*, 1188-1193.
9. Kuang, J.; Ma, S. *J. Org. Chem.* **2009,** *74*, 1763-1765.
10. Nakamura, H.; Ishikura, M.; Sugiishi, T.; Kamakura, T.; Biellmann, J. *Org. Biomol. Chem.* **2008,** *6*, 1471-1477.
11. Hirao, T.; Misu, D.; Yao, K.; Agawa, T. *Tetrahedron Lett.* **1986,** *27*, 929-932.