Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.


# Transition Metal-Free Aerobic Oxidative Cleavage of C−N Bonds of α-Amino Esters

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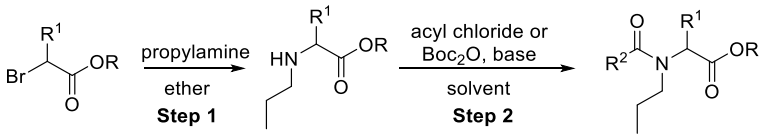
## Contents

# 1. General

All of the chemicals were reagent grade and used as purchased. All of the reactions were performed under an inert atmosphere of dry nitrogen using distilled dry solvents. The reactions were monitored by thin layer chromatography (TLC) analysis using silica gel 60 F-254 TLC plates. The compound spots were visualized using UV light. The melting points were measured using a Buchi B-540 melting point apparatus without correction. Flash column chromatography was carried out on silica gel (230–400 mesh). $^{1}$H NMR (800, 600, 500, or 400 MHz) and $^{13}$C NMR (200, 150, 125, or 100 MHz) spectra were referenced to $Me_4Si$ (0 ppm), residual $CDCl_3$ ($^{1}$H NMR $\delta$ = 7.24 ppm, $^{13}$C NMR $\delta$ = 77.16 ppm), and $CD_3OD$ ($^{1}$H NMR $\delta$ = 3.30 ppm, $^{13}$C NMR $\delta$ = 49.00 ppm). The splitting patterns are indicated as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet) and brs (broad singlet) for the $^{1}$H NMR and $^{13}$C NMR data. The IR spectra were measured on a Fourier-transform infrared spectrometer. Time-resolved IR monitoring was performed with Mettler Toledo ReactIR™ 45m equipped with DS AgX SiComp™ probe. The high-resolution mass spectra (HRMS) were recorded using FAB or ESI/Q-TOF.

# 2. Preparation of the Starting Materials

## General procedure A: synthesis of substrates (7a-g)




**Step 1:** To a stirred solution of propylamine (19.1 mmol, 8.00 equiv) in ether (15 mL) was added α-bromoester (2.39 mmol, 1.00 equiv) dropwise via a syringe. The reaction mixture stirred at room temperature for 12 h. The reaction mixture was then filtered to remove the precipitate. The organic layer was washed with a saturated solution of sodium bicarbonate and brine and dried over $MgSO_4$. Removal of the solvent in vacuo gave the secondary amine as colorless oil, which was used directly without further purification.

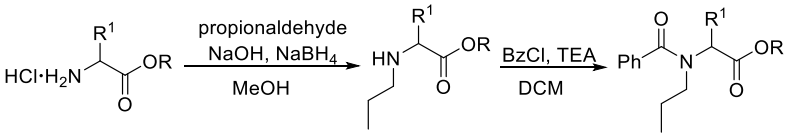
**Step 2: For the synthesis of benzoyl amide or 1-naphthoyl amide (7a-d and 7g):** TEA (2.00 mmol, 2.00 equiv) and benzoyl chloride (1.50 mmol, 1.50 equiv) or 1-naphthoyl chloride (1.50 mmol, 1.50 equiv) were added to the above secondary amine (1.00 mmol, 1.00 equiv) in $CH_2Cl_2$ (10 mL) at 0 °C. After 10 min, the reaction was quenched with $H_2O$ and extracted with $CH_2Cl_2$. The combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and concentrated. The crude product was purified by column chromatography on silica gel using hexane/EtOAc as the eluent.

**Step 2: For the synthesis of Boc amide (7e):** DIPEA (1.07 mmol, 2.00 equiv) and $Boc_2O$ (0.80 mmol, 1.50 equiv) were added to the above secondary amine (0.53 mmol, 1 equiv) in $CH_2Cl_2$ (5 mL) at room temperature. The reaction mixture was stirred for 12 h before the addition of $H_2O$ (10 mL), and extracted with $CH_2Cl_2$. The combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and concentrated. The crude product was purified by column chromatography on silica gel using hexane/EtOAc as the eluent.

**Step 2: For the synthesis of Cbz amide (7f):** $NaHCO_3$ (1.17 mmol, 2.00 equiv) and benzyl chloroformate (0.65 mmol, 1.10 equiv) were added to the above secondary amine (0.59 mmol, 1.00 equiv) in $H_2O$/acetone (1:1, 6 mL) at 0 °C. After 2 h, the reaction was quenched with $H_2O$ and extracted with EtOAc. The combined organic layers were washed with brine, dried over $MgSO_4$,

filtered, and concentrated. The crude product was purified by column chromatography on silica gel using hexane/EtOAc as the eluent.

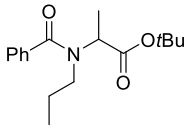
## General procedure B: synthesis of substrates (7h-k)




Propionaldehyde (1.54 mmol, 1.40 equiv) was added to a solution of amino acid ester hydrochloride (1.10 mmol, 1.00 equiv) in MeOH (5 mL) neutralized with NaOH (1.16 mmol, 1.05 equiv). After 10 min at room temperature, the reaction mixture was cooled to 0 °C, and $NaBH_4$ (0.88 mmol, 0.80 equiv) was added. The mixture was stirred at 0 °C for 1 h. The resulting mixture was washed with water and extracted with EtOAc. The combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated to yield the crude secondary amine as a light yellow oil. TEA (2.20 mmol, 2.00 equiv) and benzoyl chloride (1.65 mmol, 1.50 equiv) were added to the above secondary amine in $CH_2Cl_2$ (5 mL) at 0 °C. After 10 min, the reaction was quenched with $H_2O$ and extracted with $CH_2Cl_2$. The combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and concentrated. The crude product was purified by column chromatography on silica gel using hexane/EtOAc as the eluent.

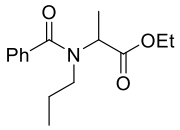
## General procedure C: synthesis of substrates (11a-f)

Substrates **11a-f** are known compounds. Compound **11c** was purchased and used as such; other substrates were obtained following reference[1] and those spectral data are in agreement with the corresponding literature values. To a solution of amino acid ester hydrochloride (1.00 mmol, 1.00 equiv) in $CH_2Cl_2$ (10 mL), TEA (2.00 mmol, 2.00 equiv) and benzoyl chloride (2.00 mmol, 2.00 equiv) were added successively at 0 °C. The reaction mixture was stirred for 30 min at 0 °C. The reaction was quenched with $H_2O$ and extracted with $CH_2Cl_2$. The combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and concentrated. The crude product was purified by column chromatography on silica gel using hexane/EtOAc as the eluent.



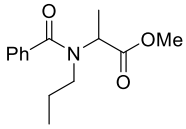
***tert*-Butyl *N*-benzoyl-*N*-propylalaninate (7a)**

Following the general procedure A, the crude product was purified by column chromatography on silica gel (hexane/EtOAc, 5:1) to yield product **7a** (543 mg, 78%) as a colorless oil; Rotamers were observed, and the ratio was 1:1 from $^{1}$H NMR. $^{1}$H NMR ($CDCl_3$, 400 MHz) $\delta$ 7.36–7.33 (m, 5H), 4.26 (s, 1H), 3.58 (s, 0.41H), 3.19–3.08 (m, 1H), 2.89 (s, 0.47H), 2.00–1.33 (m, 14H), 0.91–0.70 (m, 3H); $^{13}$C NMR ($CDCl_3$, 100 MHz) $\delta$ 172.6/171.5, 170.8, 137.0, 129.5, 129.4, 128.7, 128.6, 126.4, 82.2/81.3, 58.4/55.6, 51.2/45.6, 28.1 (3C), 23.1/22.3, 16.0/14.9, 11.8/11.3; IR $\upsilon_{max}$ (neat, $cm^{-1}$) 2975, 2936, 2877, 1732, 1636, 1368, 1155, 1104; HRMS (FAB) calcd for $C_{17}H_{26}NO_3$ 292.1913 ($[M+H]^+$), found 292.1913.



**Ethyl *N*-benzoyl-*N*-propylalaninate (7b).**

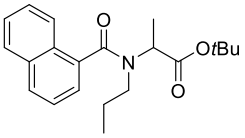
Following the general procedure A, the crude product was purified by column chromatography on silica gel (hexane/EtOAc, 5:1) to yield product **7b** (236 mg, 81%) as a colorless oil; Rotamers were observed, and the ratio was 2:1 from $^{1}$H NMR. $^{1}$H NMR ($CDCl_3$, 400 MHz) $\delta$ 7.34–7.32 (m, 5H), 4.35 (s, 1H), 4.14 (s, 2H), 3.54 (s, 0.40H), 3.19–3.13 (m, 1.23H), 2.95 (s, 0.40H), 1.75–1.37 (m, 5H), 1.24–1.23 (m, 3H), 0.90–0.69 (m, 3H); $^{13}$C NMR ($CDCl_3$, 100 MHz) $\delta$ 172.4, 171.6, 136.8, 129.5, 128.5, 126.5 (3C), 61.6/61.2, 57.6/54.8, 51.2/45.7, 23.0/22.1, 16.0/14.9, 14.3, 11.8/11.2; IR $\upsilon_{max}$ (neat, $cm^{-1}$) 2967, 2935, 2874, 1735, 1632, 1430, 1208, 1100, 700; HRMS (FAB) calcd for $C_{15}H_{22}NO_3$ 264.1600 ($[M+H]^+$), found 264.1604.



**Methyl *N*-benzoyl-*N*-propylalaninate (7c).**

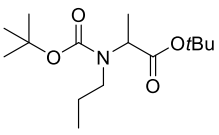
Following the general procedure A, the crude product was purified by column chromatography on silica gel (hexane/EtOAc, 5:1) to yield product **7c** (205 mg, 80%) as a colorless oil; Rotamers were observed, and the ratio was 1.6:1 from $^{1}$H NMR. $^{1}$H NMR ($CDCl_3$, 500 MHz) $\delta$ 7.36–7.34 (m, 5H), 4.40 (s, 1H), 3.72 (s, 3H), 3.54 (s, 0.33H), 3.20–3.14 (m, 1.19H), 2.96 (s, 0.32H), 1.82–1.39 (m, 5H), 0.91–0.71 (m, 3H); $^{13}$C NMR ($CDCl_3$, 125 MHz) $\delta$ 172.0, 171.6, 136.5, 129.4,

128.5, 128.3, 126.3 (2C), 57.4/54.5, 52.2, 50.9/45.5, 22.8/21.9, 16.0/14.8, 11.5/11.0; IR $\upsilon_{max}$ (neat, $cm^{-1}$) 2953, 2874, 2868, 1739, 1631, 1430, 1211, 1103, 701; HRMS (FAB) calcd for $C_{14}H_{20}NO_3$ 250.1443 ($[M+H]^+$), found 250.1446.



***tert*-Butyl *N*-(1-naphthoyl)-*N*-propylalaninate (7d).**

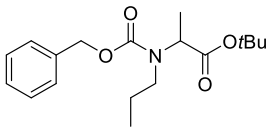
Following the general procedure A, the crude product was purified by column chromatography on silica gel (hexane/EtOAc, 8:1) to yield product **7d** (120 mg, 70%) as a colorless oil; Rotamers were observed, and the ratio was 1:1 from $^1$H NMR. $^1$H NMR ($CDCl_3$, 800 MHz) $\delta$ 8.04–7.78 (m, 3H), 7.51–7.31 (m, 4H), 4.61–4.60 (m, 0.29H), 4.28 (s, 0.25H), 4.16 (q, $J$ = 7.1 Hz, 0.19H), 4.02 (q, $J$ = 7.2 Hz, 0.23H), 3.85–3.79 (m, 0.43H), 3.15 (s, 0.26H), 3.06–2.94 (m, 1.34H), 2.09–1.96 (m, 0.48H), 1.78–1.69 (m, 0.51H), 1.62 (d, $J$ = 7.1 Hz, 1.79H), 1.56–1.55 (m, 5.16H), 1.43 (s, 2.2H), 1.34 (s, 1.61), 1.32 (d, $J$ = 7.1 Hz, 0.63H), 1.25 (d, $J$ = 7.2 Hz, 0.73H), 1.03–0.99 (m, 1.28H), 0.56–0.55 (m, 1.73H); $^{13}$C NMR ($CDCl_3$, 200 MHz) $\delta$ 171.5/171.2, 170.6/170.4, 134.8, 134.6, 134.5, 133.6, 133.4, 133.3, 129.9, 129.8, 129.6, 129.4, 129.1, 128.89, 128.87, 128.4, 128.2, 128.0, 126.9, 126.8, 126.6, 126.5, 126.4, 126.3, 126.0, 125.3, 125.1, 124.94, 124.85, 124.3, 124.0, 123.5, 123.0, 82.02/81.95, 81.4, 58.4/57.9, 55.7/54.8, 51.5/50.3, 46.0/45.5, 28.1, 27.9/27.8, 23.2/22.6, 22.4/22.1, 16.2/16.1, 15.0, 11.8/11.7, 11.1; IR $\upsilon_{max}$ (neat, $cm^{-1}$) 2972, 2933, 2874, 1730, 1633, 1367, 1155, 1110, 779; HRMS (FAB) calcd for $C_{21}H_{28}NO_3$ 342.2069 ($[M+H]^+$), found 342.2072.



***tert*-Butyl *N*-(*tert*-butoxycarbonyl)-*N*-propylalaninate (7e).**

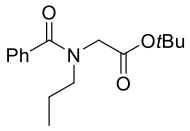
Following the general procedure A, the crude product was purified by column chromatography on silica gel (hexane/EtOAc, 20:1) to yield product **7e** (126 mg, 81%) as a colorless oil; Rotamers were observed, and the ratio was 1:1 from $^1$H NMR. $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 4.19–4.17 (m, 0.45H), 3.91–3.89 (m, 0.45H), 3.26–3.19 (m, 1H), 3.01 (s, 0.51H), 2.87–2.85 (m, 0.50H), 1.55–1.32 (m, 23H), 0.84 (t, $J$ = 7.6 Hz, 3H); $^{13}$C NMR ($CDCl_3$, 100 MHz) $\delta$ 171.8/171.6, 155.5/155.2, 81.02/80.95, 80.1/79.6, 56.6/55.9, 49.1/48.4, 28.6 (4C), 28.2, 28.1, 23.2/22.5, 16.1/15.4,

11.6/11.5; IR $\upsilon_{max}$ (neat, $cm^{-1}$) 2975, 2934, 2876, 1736, 1695, 1367, 1159; HRMS (FAB) calcd for $C_{15}H_{30}NO_4$ 288.2175 ($[M+H]^+$), found 288.2177.



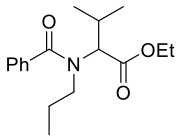
***tert*-Butyl *N*-((benzyloxy)carbonyl)-*N*-propylalaninate (7f).**

Following the general procedure A, the crude product was purified by column chromatography on silica gel (hexane/EtOAc, 20:1) to yield product **7f** (146 mg, 77%) as a colorless oil; Rotamers were observed, and the ratio was 1:1 from $^1$H NMR. $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 7.33–7.27 (m, 5H), 5.21–4.99 (m, 2H), 4.34–4.29 (m, 0.55H), 4.16–4.14 (m, 0.50H), 3.35–3.33 (m, 1H), 3.09–2.98 (m, 1H), 1.64–1.49 (m, 2H), 1.39–1.34 (m, 12H), 0.91–0.82 (m, 3H); $^{13}$C NMR ($CDCl_3$, 100 MHz) $\delta$ 171.4/171.3, 156.2/156.0, 137.1/136.7, 128.6 (2C), 128.0 (2C), 127.9, 81.4/81.3, 67.2/67.1, 56.4/56.2, 49.2/48.2, 28.1 (3C), 23.1/22.4, 16.1/15.5, 11.5; IR $\upsilon_{max}$ (neat, $cm^{-1}$) 2972, 2935, 2875, 1734, 1698, 1248, 1160, 1148, 849; HRMS (FAB) calcd for $C_{18}H_{28}NO_4$ 322.2018 ($[M+H]^+$), found 322.2022.



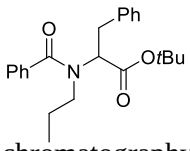
***tert*-Butyl *N*-benzoyl-*N*-propylglycinate (7g).**

Following the general procedure A, the crude product was purified by column chromatography on silica gel (hexane/EtOAc, 5:1) to yield product **7g** (245 mg, 86%) as a colorless oil; Rotamers were observed, and the ratio was 1.6:1 from $^1$H NMR. $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 7.35–7.32 (m, 5H), 4.07 (s, 1.16H), 3.79 (s, 0.76H), 3.44 (t, $J$ = 7.6 Hz, 0.76H), 3.18 (t, $J$ = 7.8 Hz, 1.24H), 1.65–1.48 (m, 2H), 1.45–1.38 (m, 9H), 0.92 (t, $J$ = 7.4 Hz, 1.15H), 0.71 (t, $J$ = 7.4 Hz, 1.86H); $^{13}$C NMR ($CDCl_3$, 100 MHz) $\delta$ 172.3, 168.8/168.3, 136.6/136.3, 129.5, 128.5 (2C), 126.7/126.5 (2C), 82.3/81.8, 52.0/51.9, 48.5/47.5, 28.2/28.0 (3C), 21.8/20.5, 11.5/11.1; IR $\upsilon_{max}$ (neat, $cm^{-1}$) 2973, 2875, 1738, 1636, 1223, 1149, 1101; HRMS (FAB) calcd for $C_{16}H_{24}NO_3$ 278.1756 ($[M+H]^+$), found 278.1763.



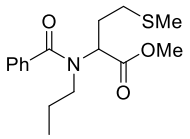
**Ethyl *N*-benzoyl-*N*-propylvalinate (7h).**

Following the general procedure B, the crude product was purified by column chromatography on silica gel (hexane/EtOAc, 5:1) to yield product **7h** (240 mg, 75%) as a colorless oil; Rotamers were observed, and the ratio was 2:1 from $^1$H NMR. $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 7.39–7.35 (m, 5H), 4.20–4.14 (m, 2.43H), 3.86–3.83 (m, 0.70H), 3.61 (s, 0.63H), 3.11–3.10 (m, 1.27H), 2.50 (s, 0.32H), 2.23 (s, 0.71H), 1.95–1.73 (m, 0.67H), 1.46 (s, 1.35H), 1.30–1.26 (m, 3.26H), 1.07–0.60 (m, 9H); $^{13}$C NMR ($CDCl_3$, 100 MHz) $\delta$ 172.9/172.1, 171.1/170.6, 136.7, 129.5, 128.5 (3C), 127.4/126.4, 67.5/63.7, 61.2/61.0, 50.7/44.7, 28.1/22.8, 21.2/19.3, 19.6/19.0, 14.2 (2C), 11.7/11.4; IR $\upsilon_{max}$ (neat, cm$^{-1}$) 2965, 2875, 1736, 1638, 1196, 1094, 1026; HRMS (FAB) calcd for $C_{17}H_{26}NO_3$ 292.1913 ([M+H]$^+$), found 292.1906.




**_tert_-Butyl _N_-benzoyl-_N_-propylphenylalaninate (7i).**

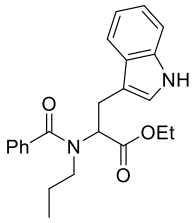
Following the general procedure B, the crude product was purified by column chromatography on silica gel (hexane/EtOAc, 10:1) to yield product **7i** (167 mg, 58%) as a light yellow oil; Rotamers were observed, and the ratio was 2:1 from $^1$H NMR. $^1$H NMR ($CDCl_3$, 800 MHz) $\delta$ 7.34–6.91 (m, 10H), 4.41–3.97 (m, 1H), 3.50–3.40 (m, 1.66H), 3.29 (s, 0.35H), 3.10–3.08 (m, 0.32H), 2.97–2.91 (m, 0.96H), 2.49–2.46 (m, 0.64H), 1.86 (s, 0.43H), 1.71 (s, 0.36H), 1.50–1.46 (m, 8.94H), 1.22–1.18 (m, 1.32H), 0.97 (s, 0.90H), 0.52–0.51 (m, 1.87H); $^{13}$C NMR ($CDCl_3$, 200 MHz) $\delta$ 172.7/171.2, 169.5, 138.8, 136.7/136.2, 129.4/129.3 (2C), 129.2/129.1, 128.5/128.4 (2C), 128.3/128.0 (2C), 126.7/126.6, 126.5/126.2 (2C), 82.4/81.4, 64.1/62.5, 53.1/45.4, 35.4/34.5, 28.0/27.9 (3C), 21.6/21.4, 11.7/11.0; IR $\upsilon_{max}$ (neat, cm$^{-1}$) 2975, 2934, 2876, 1730, 1635, 1250, 1149, 850; HRMS (FAB) calcd for $C_{23}H_{30}NO_3$ 368.2226 ([M+H]$^+$), found 368.2227.




**Methyl _N_-benzoyl-_N_-propylmethioninate (7j).**

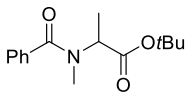
Following the general procedure B, the crude product was purified by column chromatography on silica gel (hexane/EtOAc, 5:1) to yield product **7j** (236 mg, 51%) as a colorless oil; Rotamers were observed, and the ratio was 2:1 from $^1$H NMR. $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 7.35 (s, 5H), 4.51–4.29 (m, 1H), 3.72 (s, 3H), 3.29–3.11 (m, 2H), 2.63–2.23 (m, 4H), 2.09–1.95 (m, 3H),

1.70–1.54 (m, 2H), 0.90–0.68 (m, 3H); $^{13}$C NMR ($CDCl_3$, 100 MHz) $\delta$ 173.0/172.2, 171.5, 136.4, 129.7 (3C), 128.5, 126.6, 60.6/58.1, 52.8, 52.4/45.9, 31.4/30.4, 29.2/28.5, 22.6/21.7, 15.4, 11.8/11.2; IR $\upsilon_{max}$ (neat, cm$^{-1}$) 2961, 2875, 1741, 1638, 1431, 1233, 1105, 702; HRMS (FAB) calcd for $C_{16}H_{24}NO_3S$ 310.1477 ($[M+H]^+$), found 310.1476.




**Ethyl $N^{\alpha}$-benzoyl-$N^{\alpha}$-propyltryptophanate (7k).**

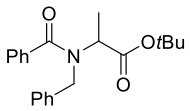
Following the general procedure B, the crude product was purified by column chromatography on silica gel (hexane/EtOAc, 5:1) to yield product **7k** (138 mg, 49%) as a colorless oil; Rotamers were observed, and the ratio was 1:1 from $^1$H NMR. $^1$H NMR ($CDCl_3$, 500 MHz) $\delta$ 8.46–8.37 (m, 1H), 7.68–6.80 (m, 10H), 4.66 (s, 0.38H), 4.39 (s, 0.57H), 4.30–4.16 (m, 2H), 3.70–3.56 (m, 1.60H), 3.36–2.99 (m, 1.78H), 2.62 (s, 0.56H), 1.85–1.71 (m, 1H), 1.31 (t, $J$ = 7.0 Hz, 3H), 1.26–1.20 (m, 1H), 0.97 (s, 1.20H), 0.49–0.47 (m, 1.74H); $^{13}$C NMR ($CDCl_3$, 125 MHz) $\delta$ 173.1/171.7, 170.9, 136.6/135.8, 136.2, 129.3/129.0, 128.3/128.0, 127.5/127.0, 126.4 (2C), 123.4/123.1, 121.9 (2C), 119.4, 118.5/117.8, 112.2/111.3, 109.9, 62.0/61.2, 61.5/60.4, 52.6/45.3, 25.4/24.4, 21.8/21.4, 14.2/14.1, 11.7/10.9; IR $\upsilon_{max}$ (neat, cm$^{-1}$) 3298, 2975, 2875, 1733, 1616, 1434, 1229, 1101, 739; HRMS (FAB) calcd for $C_{23}H_{27}N_2O_3$ 379.2022 ($[M+H]^+$), found 379.2021.




***tert*-Butyl *N*-benzoyl-*N*-methylalaninate (7l).**

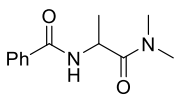
To a suspension of NaH (60% suspension in mineral oil, 72.2 mg, 1.81 mmol) in THF (5 mL) at 0 °C was added dropwise a solution of *tert*-butyl benzoylalaninate[1] (150 mg, 0.60 mmol) in THF (1 mL) at 0 °C. The reaction mixture was stirred at that temperature for 5 min and then $CH_3I$ (0.30 mL, 4.81 mmol) was added. The reaction mixture was allowed to reach room temperature and stirred for 1 h. The reaction mixture was quenched slowly quenched with saturated $NH_4Cl$ solution and extracted with EtOAc. The combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated. The crude product was purified by column chromatography on silica gel (hexane/EtOAc, 5:1) to yield product **7l** (124 mg, 78%) as a colorless oil; Rotamers were observed, and the ratio was 1:1 from $^1$H NMR. $^1$H NMR ($CDCl_3$, 500 MHz) $\delta$ 7.38 (s, 5H), 5.20 (d, $J$ = 6.9 Hz,

0.45H), 4.34 (d, $J$ = 6.7 Hz, 0.43H), 2.91 (d, $J$ = 45.7 Hz, 3H), 1.47–1.32 (m, 12H); $^{13}$C NMR ($CDCl_3$, 125 MHz) $\delta$ 172.3/171.8, 170.8/170.3, 136.3, 129.5, 128.6, 128.4, 126.9, 126.5, 82.1/81.5, 57.8/52.9, 33.7/28.7, 28.03 (3C), 15.1/14.3; IR $\upsilon_{max}$ (neat, $cm^{-1}$) 2978, 2934, 1731, 1638, 1394, 1233, 1155, 1083; HRMS (FAB) calcd for $C_{15}H_{22}NO_3$ 264.1600 ($[M+H]^+$), found 264.1605.



***tert*-Butyl *N*-benzoyl-*N*-benzylalaninate (7m).**

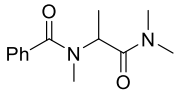
Benzaldehyde (0.17 mL, 1.65 mmol) was added to a solution of L-alanine *t*-butyl ester hydrochloride (200 mg, 1.10 mmol) and TEA (0.15 mL, 1.10 mmol) in MeOH (5 mL) at room temperature and the mixture was stirred for 1 h. $NaBH(OAc)_3$ (350 mg, 1.65 mmol) was added in portions and the mixture was stirred at room temperature for 24 h. The resulting mixture was washed with water and extracted with EtOAc. The combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated to yield crude secondary amine as a yellow oil. TEA (0.31 mL, 2.20 mmol) and benzoyl chloride (0.19 mL, 1.65 mmol) were added to the above secondary amine in $CH_2Cl_2$ (5 mL) at 0 °C. After 10 min, the reaction was quenched with $H_2O$ and extracted with $CH_2Cl_2$. The combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and concentrated. The crude product was purified by column chromatography on silica gel (hexane/EtOAc, 10:1) to yield product **7m** (260 mg, 70%) as a colorless oil; Rotamers were observed, and the ratio was 2:1 from $^{13}$C NMR. $^1$H NMR ($CDCl_3$, 600 MHz) $\delta$ 7.45–7.24 (m, 10H), 5.15 (s, 0.33H), 4.62–4.47 (m, 1.6H), 4.19 (s, 0.36H), 4.04 (s, 0.62H), 1.49–1.27 (m, 12H); $^{13}$C NMR ($CDCl_3$, 150 MHz) $\delta$ 171.8, 170.2, 138.6/137.1, 136.4/136.1, 129.6 (2C), 128.6, 128.4, 127.4, 127.2, 127.0, 126.4 (3C), 82.1/81.1, 58.4/55.9, 53.3/46.4, 27.9 (3C), 16.1/14.3; IR $\upsilon_{max}$ (neat, $cm^{-1}$) 2976, 2934, 1730, 1639, 1240, 1149, 727, 697; HRMS (FAB) calcd for $C_{21}H_{26}NO_3$ 340.1913 ($[M+H]^+$), found 340.1917.



***N*-(1-(Dimethylamino)-1-oxopropan-2-yl)benzamide (7n').**

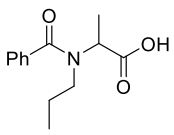
Dimethylamine hydrochloride (253.2 mg, 3.11 mmol) and DIPEA (0.54 mL, 3.11 mmol) was added to a solution of *N*-benzoyl-DL-alanine (300 mg, 1.55 mmol) in $CH_2Cl_2$ (10 mL) at 0 °C. After 10 min, HOBt (419.6 mg, 3.11 mmol) and EDCI·HCl (595.3 mg, 3.11 mmol) were added

to the above complex at 0 °C. The reaction mixture was allowed to reach room temperature and stirred for another 12 h. The resulting mixture was quenched with water and extracted with $CH_2Cl_2$. The combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated. The crude product was purified by column chromatography on silica gel ($CH_2Cl_2$/MeOH, 20:1) to yield product **7n'** (310 mg, 91%) as a white solid; m.p. 132–134 °C; $^1$H NMR ($CDCl_3$, 500 MHz) $\delta$ 7.77 (d, $J$ = 7.7 Hz, 2H), 7.44–7.34 (m, 4H), 5.05–5.00 (m, 1H), 3.06 (s, 3H), 2.94 (s, 3H), 1.37 (d, $J$ = 6.8 Hz, 3H); $^{13}$C NMR ($CDCl_3$, 125 MHz) $\delta$ 172.3, 166.1, 134.0, 131.4, 128.3 (2C), 126.9 (2C), 45.6, 36.8, 35.6, 18.5; IR $\upsilon_{max}$ (neat, cm$^{-1}$) 3296, 2979, 2933, 1626, 1484, 1107, 711; HRMS (FAB) calcd for $C_{12}H_{17}N_2O_2$ 221.1290 ([M+H]$^+$), found 221.1295.



***N*-(1-(Dimethylamino)-1-oxopropan-2-yl)-*N*-methylbenzamide (7n).**

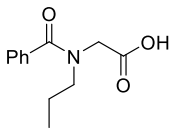
To a suspension of NaH (60% suspension in mineral oil, 109 mg, 2.72 mmol) in THF (5 mL) at 0 °C was added dropwise a solution of **7n'** (200 mg, 0.91 mmol) in THF (2 mL) at 0 °C. The reaction mixture was stirred at that temperature for 5 min and then $CH_3I$ (0.45 mL, 7.26 mmol) was added. The resulting mixture was stirred at 0 °C for 1 h then let to stir at room temperature for 2 h. The reaction mixture was quenched slowly quenched with saturated $NH_4Cl$ solution and extracted with EtOAc. The combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated. The crude product was purified by column chromatography on silica gel ($CH_2Cl_2$/MeOH, 30:1) to yield product **7n** (151 mg, 71%) as a colorless oil; $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 7.36–7.32 (m, 5H), 5.59 (q, $J$ = 6.9 Hz, 1H), 3.08 (s, 3H), 2.94 (s, 3H), 2.83 (s, 3H), 1.35 (d, $J$ = 6.8 Hz, 3H); $^{13}$C NMR ($CDCl_3$, 100 MHz) $\delta$ 171.2, 171.1, 136.1, 129.8, 128.6 (2C), 126.9 (2C), 49.1, 37.0, 36.0, 32.9, 14.4; IR $\upsilon_{max}$ (neat, cm$^{-1}$) 2982, 2934, 1624, 1442, 1391, 1074, 796; HRMS (FAB) calcd for $C_{13}H_{19}N_2O_2$ 235.1447 ([M+H]$^+$), found 235.1444.



***N*-benzoyl-*N*-propylalanine (7o).**

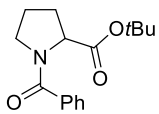
A solution of substrate **7c** (400 mg, 1.60 mmol) and anhydrous LiOH (76.9 mg, 3.20 mmol) in THF (4 mL) and water (80 µL) was refluxed for 12 h. The reaction mixture was acidified

with 1 N HCl until pH 2 and extracted with EtOAc. The combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and concentrated. The crude product was purified by column chromatography on silica gel ($CH_2Cl_2$/MeOH, 30:1) to yield product **7o** (287 mg, 76%) as a white solid; m.p. 116–118 °C; Rotamers were observed, and the ratio was 2:1 from $^1$H NMR. $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 10.58 (s, 1H), 7.37 (s, 5H), 4.37 (q, $J$ = 7.1 Hz, 1H), 3.56–2.89 (m, 2H), 1.80 (s, 0.38H), 1.58–1.50 (m, 3.72H), 1.34 (s, 1H), 0.89–0.70 (m, 3H); $^{13}$C NMR ($CDCl_3$, 100 MHz) $\delta$ 175.8/175.1, 172.9, 136.2/135.8, 129.9, 128.6 (2C), 126.7 (2C), 57.7/55.3, 51.6/46.3, 22.8/22.0, 16.1/14.7, 11.8/11.1; IR $\upsilon_{max}$ (neat, cm$^{-1}$) 3461, 2969, 2938, 2876, 2593, 1738, 1594, 1459, 1429, 1208, 1112, 926; HRMS (FAB) calcd for $C_{13}H_{18}NO_3$ 236.1287 ([M+H]$^+$), found 236.1292.




***N*-benzoyl-*N*-propylglycine (7p).**

To a stirred solution of substrate **7g** (300 mg, 1.08 mmol) in $CH_2Cl_2$ (2 mL) was added TFA (2 mL) at room temperature. After 3 h, the reaction was evaporated at reduced pressure and acidified with 1 N HCl until pH 2. The reaction mixture was extracted with EtOAc, washed with brine, dried over $MgSO_4$, filtered, and concentrated. The crude product was purified using column chromatography on silica gel ($CH_2Cl_2$/MeOH, 30:1) to yield product **7p** (145 mg, 61%) as a white solid; m.p. 90–92 °C; Rotamers were observed, and the ratio was 2:1 from $^1$H NMR. $^1$H NMR ($CDCl_3$, 500 MHz) $\delta$ 10.85 (s, 1H), 7.39–7.32 (m, 5H), 4.21 (s, 1.32H), 3.88 (s, 0.61H), 3.43 (t, $J$ = 7.3 Hz, 0.62H), 3.22 (t, $J$ = 7.5 Hz, 1.31H), 1.61–1.49 (m, 2H), 0.91 (t, $J$ = 7.1 Hz, 1H), 0.72 (t, $J$ = 7.3 Hz, 2H); $^{13}$C NMR ($CDCl_3$, 125 MHz) $\delta$ 173.1/172.73, 172.67/172.2, 135.4/135.1, 129.8/129.7, 128.5/128.4 (2C), 126.6/126.4 (2C), 52.0/50.8, 48.3/46.8, 21.5/20.0, 11.2/10.8; IR $\upsilon_{max}$ (neat, cm$^{-1}$) 3460, 2967, 2936, 2876, 2599, 1736, 1597, 1467, 1216, 1107, 942; HRMS (FAB) calcd for $C_{12}H_{16}NO_3$ 222.1130 ([M+H]$^+$), found 222.1135.

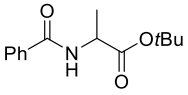



***tert*-butyl benzoylprolinate (7q).**

Substrate **7q** was obtained following a revised reported procedure[2]. To a solution of L-proline *t*-butyl ester hydrochloride (150 mg, 0.72 mmol) in $CH_2Cl_2$ (5 mL), TEA (0.20 mL, 1.44

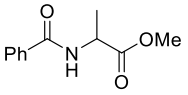
mmol) and benzoyl chloride (0.168 mL, 1.44 mmol) were added successively at 0 °C. The reaction mixture was stirred for 30 min at 0 °C. The reaction was quenched with $H_2O$ and extracted with $CH_2Cl_2$. The combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and concentrated. The crude product was purified using column chromatography on silica gel (hexane/EtOAc, 5:1) to yield product **7q** (160 mg, 81%) as a white solid. The spectral data is in agreement with the corresponding literature values[3].

**_tert_-Butyl benzoylalaninate (11a)[4].**



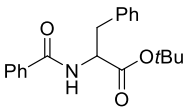
Following the general procedure C, the crude product was purified by column chromatography on silica gel (hexane/EtOAc, 5:1) to yield product **11a** (190 mg, 93%) as a white solid; m.p. 99–101 °C; $^1$H NMR ($CDCl_3$, 500 MHz) $\delta$ 7.78 (d, $J$ = 7.3 Hz, 2H), 7.47 (t, $J$ = 7.4 Hz, 1H), 7.40 (t, $J$ = 7.5 Hz, 2H), 6.80 (d, $J$ = 5.6 Hz, 1H), 4.65 (quint, $J$ = 7.1, 14.2 Hz, 1H), 1.47 (s, 9H), 1.46 (s, 3H); $^{13}$C NMR ($CDCl_3$, 125 MHz) $\delta$ 172.5, 166.6, 134.2, 131.6, 128.5 (2C), 127.0 (2C), 82.2, 49.0, 28.0 (3C), 18.9.

**Methyl benzoylalaninate (11b)[5].**



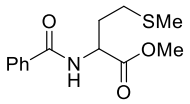
Following the general procedure C, the crude product was purified by column chromatography on silica gel (hexane/EtOAc, 3:1) to yield product **11b** (205 mg, 92%) as a white solid; m.p. 80–82 °C; $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 7.73–7.71 (m, 2H), 7.39–7.35 (m, 1H), 7.29–7.26 (m, 2H), 7.18 (d, $J$ = 6.4 Hz, 1H), 4.68 (quint, $J$ = 7.2, 14.4 Hz, 1H), 3.64 (s, 3H), 1.40 (d, $J$ = 6.8 Hz, 3H); $^{13}$C NMR ($CDCl_3$, 100 MHz) $\delta$ 173.6, 167.0, 133.7, 131.6, 128.4 (2C), 127.1 (2C), 52.4, 48.4, 18.1.

**_tert_-Butyl benzoylphenylalaninate (11d)[6].**



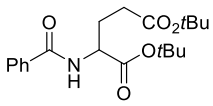
Following the general procedure C, the crude product was purified by column chromatography on silica gel (hexane/EtOAc, 5:1) to yield product **11d** (220 mg, 87%) as a white solid; m.p. 78–80 °C; $^1$H NMR ($CDCl_3$, 500 MHz) $\delta$ 7.72 (d, $J$ = 7.6 Hz, 2H), 7.46 (t, $J$ = 7.4 Hz, 1H),

7.38 (t, *J* = 7.6 Hz, 2H), 7.27–7.17 (m, 5H), 6.73 (d, *J* = 7.2 Hz, 1H), 4.95 (q, *J* = 6.4 Hz, 1H), 3.25–3.18 (m, 2H), 1.42 (s, 9H); $^{13}$C NMR ($CDCl_3$, 125 MHz) $\delta$ 170.7, 166.6, 136.1, 134.0, 131.5, 129.5 (2C), 128.4 (2C), 128.3 (2C), 126.9 (3C), 82.4, 53.8, 37.9, 27.9 (3C).




**Methyl benzoylmethioninate (11e)**[7]**.**

Following the general procedure C, the crude product was purified by column chromatography on silica gel (hexane/EtOAc, 3:1) to yield product **11e** (175 mg, 87%) as a white solid; m.p. 85–87 °C; $^1$H NMR ($CDCl_3$, 500 MHz) $\delta$ 7.79 (d, *J* = 7.5 Hz, 2H), 7.49 (t, *J* = 7.4 Hz, 1H), 7.42 (t, *J* = 7.6 Hz, 2H), 6.97 (d, *J* = 7.2 Hz, 1H), 4.93–4.89 (m, 1H), 3.77 (s, 3H), 2.57–2.52 (m, 2H), 2.30–2.23 (m, 1H), 2.13–2.08 (m, 1H), 2.06 (s, 3H); $^{13}$C NMR ($CDCl_3$, 125 MHz) $\delta$ 172.5, 167.0, 133.7, 131.8, 128.6 (2C), 127.0 (2C), 52.6, 52.0, 31.6, 30.0, 15.5.




**Di-*tert*-butyl benzoylglutamate (11f)**[8]**.**

Following the general procedure C, the crude product was purified by column chromatography on silica gel (hexane/EtOAc, 5:1) to yield product **11f** (206 mg, 84%) as a white solid; m.p. 100–102 °C; $^1$H NMR ($CDCl_3$, 500 MHz) $\delta$ 7.78 (d, *J* = 7.3 Hz, 2H), 7.45 (t, *J* = 7.4 Hz, 1H), 7.38 (t, *J* = 7.5 Hz, 2H), 7.01 (d, *J* = 7.4 Hz, 1H), 4.66–4.62 (m, 1H), 2.42–2.36 (m, 1H), 2.32–2.25 (m, 1H), 2.23–2.16 (m, 1H), 2.05–1.97 (m, 1H), 1.45 (s, 9H), 1.37 (s, 9H); $^{13}$C NMR ($CDCl_3$, 125 MHz) $\delta$ 172.5, 171.2, 166.9, 133.8, 131.6, 128.4 (2C), 127.0 (2C), 82.3, 80.7, 52.8, 31.6, 28.0 (3C), 27.9 (3C), 27.4.

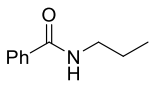
# 3. Experimental Procedures for the Cleavage Reaction

**General Procedure A for substrates 7a-p**

*t*BuOK (1.0 M in THF, 0.2 mmol, 2.00 equiv) was added to a solution of substrate (0.1 mmol, 1.00 equiv) in THF (0.5 mL, 0.2 M) under an $O_2$ atmosphere at 0 °C. The resulting mixture was stirred at 0 °C for about 0.5 h and then warmed to room temperature. After the starting material disappeared by monitoring with TLC, the reaction was quenched with saturated $NH_4Cl$ solution and extracted with EtOAc. The combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated. The crude product was purified by column chromatography on silica gel (hexane/EtOAc) to afford the desired product.

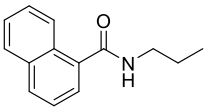
**General Procedure B for substrates 11a-f**

*t*BuOK (1.0 M in THF, 0.3 mmol, 3.00 equiv) was added to a solution of substrate (0.1 mmol, 1.00 equiv) and $P(OEt)_3$ (0.2 mmol, 2.00 equiv) in THF (0.5 mL, 0.2 M) under an $O_2$ atmosphere at 0 °C. The resulting mixture was stirred at 0 °C for about 0.5 h and then warmed to room temperature. After the starting material disappeared by monitoring with TLC, the reaction was quenched with saturated $NH_4Cl$ solution and extracted with EtOAc. The combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated. The crude product was purified by column chromatography on silica gel (hexane/EtOAc) to afford the desired product.



***N*-Propylbenzamide (8a).**

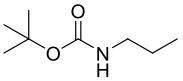
Following the general procedure A, the crude product was purified by column chromatography on silica gel (hexane/EtOAc, 3:1) to yield product **8a** (18.2 mg, 93%) as a white solid; m.p. 82–83 °C; $^1$H NMR ($CDCl_3$, 500 MHz) $\delta$ 7.74 (d, $J$ = 7.8 Hz, 2H), 7.43 (t, $J$ = 7.4 Hz, 1H), 7.36 (t, $J$ = 7.6 Hz, 2H), 6.49 (brs, 1H), 3.36 (q, $J$ = 6.7 Hz, 2H), 1.59 (x, $J$ = 7.3, 14.6 Hz, 2H), 0.93 (t, $J$ = 7.4 Hz, 3H); $^{13}$C NMR ($CDCl_3$, 125 MHz) $\delta$ 167.6, 134.8, 131.2, 128.4 (2C), 126.8 (2C), 41.7, 22.8, 11.4; IR $\upsilon_{max}$ (neat, $cm^{-1}$) 3301, 2956, 2930, 2870, 1632, 1546, 1312, 1150; HRMS (FAB) calcd for $C_{10}H_{14}NO$ 164.1075 ($[M+H]^+$), found 164.1074.



***N*-Propyl-1-naphthamide (8d).**

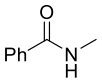
Following the general procedure A, the crude product was purified by column chromatography on silica gel (hexane/EtOAc, 3:1) to yield product **8d** (20.1 mg, 92%) as a white solid; m.p. 89–91 °C; $^{1}$H NMR ($CDCl_3$, 500 MHz) $\delta$ 8.25 (d, $J$ = 7.8 Hz, 1H), 7.85 (dd, $J$ = 7.9, 15.4 Hz, 2H), 7.53–7.47 (m, 3H), 7.39 (t, $J$ = 7.6 Hz, 1H), 6.09 (brs, 1H), 3.45 (q, $J$ = 6.7 Hz, 2H), 1.64 (x, $J$ = 7.3, 14.6 Hz, 2H), 0.98 (t, $J$ = 7.4 Hz, 3H); $^{13}$C NMR ($CDCl_3$, 125 MHz) $\delta$ 169.6, 134.8, 133.6, 130.3, 130.1, 128.2, 127.0, 126.3, 125.4, 124.69, 124.67, 41.7, 22.9, 11.4; IR $\upsilon_{max}$ (neat, cm$^{-1}$) 3274, 2961, 2930, 2872, 1635, 1535, 1305, 779; HRMS (FAB) calcd for $C_{14}H_{16}NO$ 214.1232 ([M+H]$^+$), found 214.1230.

***tert*-Butyl propylcarbamate (8e).**

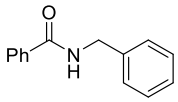


Following the general procedure A, the crude product was purified by column chromatography on silica gel (hexane/EtOAc, 5:1) to yield product **8e** (14.0 mg, 84%) as a colorless oil; $^{1}$H NMR ($CDCl_3$, 400 MHz) $\delta$ 4.66 (brs, 1H), 2.95 (t, $J$ = 7.1 Hz, 2H), 1.42–1.35 (m, 2H), 1.32 (s, 9H), 0.79 (t, $J$ = 7.4 Hz, 3H); $^{13}$C NMR ($CDCl_3$, 100 MHz) $\delta$ 155.9, 78.6, 42.1, 28.2 (3C), 23.1, 11.0; IR $\upsilon_{max}$ (neat, cm$^{-1}$) 3355, 2968, 2934, 2877, 1689, 1517, 1366, 1169. HRMS (ESI) calcd for $C_8H_{18}NO_2$ 160.1332 ([M+H]$^+$), found 160.1332.

***N*-Methylbenzamide (8l).**



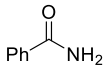
Following the general procedure A, the crude product was purified by column chromatography on silica gel (hexane/EtOAc, 1:1) to yield product **8l** (16.0 mg, 89%) as a white solid; m.p. 79–81 °C; $^{1}$H NMR ($CDCl_3$, 500 MHz) $\delta$ 7.74 (d, $J$ = 7.6 Hz, 2H), 7.40 (t, $J$ = 7.4 Hz, 1H), 7.32 (t, $J$ = 7.7 Hz, 2H), 6.97 (brs, 1H), 2.90 (d, $J$ = 4.8 Hz, 3H); $^{13}$C NMR ($CDCl_3$, 125 MHz) $\delta$ 168.4, 134.4, 131.1, 128.3 (2C), 126.8 (2C), 26.7; IR υmax (neat, cm$^{-1}$) 3323, 2938, 2899, 1634, 1547, 1307, 706; HRMS (FAB) calcd for $C_8H_{10}NO$ 136.0762 ([M+H]$^+$), found 136.0764.



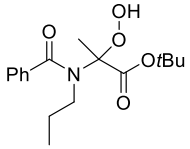
***N*-Benzylbenzamide (8m).**

Following the general procedure A, the crude product was purified by column chromatography on silica gel (hexane/EtOAc, 1:1) to yield product **8m** (15.4 mg, 71%) as a white solid; m.p. 104–105 °C; $^1$H NMR ($CDCl_3$, 500 MHz) $\delta$ 7.79 (d, $J$ = 8.0 Hz, 2H), 7.44 (t, $J$ = 7.4 Hz, 1H), 7.33 (t, $J$ = 7.8 Hz, 2H), 7.30–7.22 (m, 6H), 4.53 (d, $J$ = 5.9 Hz, 2H); $^{13}$C NMR ($CDCl_3$, 125 MHz) δ 167.4, 138.3, 134.2, 131.2, 128.4 (2C), 128.3 (2C), 127.5 (2C), 127.2, 126.9 (2C), 43.7; IR υmax (neat, cm$^{-1}$) 3284, 3061, 1636, 1601, 1547, 1314, 690; HRMS (FAB) calcd for $C_{14}H_{14}NO$ 212.1075 ([M+H]$^+$), found 212.1073.

**Benzamide (12).**



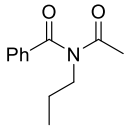
Following the general procedure B, the crude product was purified by column chromatography on silica gel (hexane/EtOAc, 1:1) to yield product **12** (12.7 mg, 87%) as a white solid; m.p. 126–128 °C; $^1$H NMR ($CD_3OD$, 500 MHz) $\delta$ 7.87 (d, $J$ = 7.7 Hz, 2H), 7.51 (t, $J$ = 7.4 Hz, 1H), 7.43 (t, $J$ = 7.7 Hz, 2H); $^{13}$C NMR ($CD_3OD$, 125 MHz) $\delta$ 173.2, 135.7, 133.7, 130.3 (2C), 129.4 (2C); IR $\upsilon_{max}$ (neat, cm$^{-1}$) 3364, 3164, 1653, 1621, 1399, 683; HRMS (FAB) calcd for $C_7H_8NO$ 122.0606 ([M+H]$^+$), found 122.0604.



***tert*-Butyl 2-hydroperoxy-2-(*N*-propylbenzamido)propanoate (9).**

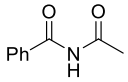
*t*BuOK (1.0 M in THF, 2.75 mL, 2.75 mmol) was added to a solution of substrate **7a** (400 mg, 1.37 mmol) in THF (7 mL, 0.2 M) under an $O_2$ balloon at 0 °C. The resulting mixture was stirred at 0 °C for 5 min and quenched with saturated $NH_4Cl$ solution and extracted with EtOAc. The combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc, 3:1) to yield product **9** (195 mg, 44%) as a colorless oil; The product **9** is unstable, and have a short life span at room temperature or –20 °C. $^1$H NMR ($CDCl_3$, 500 MHz) $\delta$ 10.08 (s, 1H), 7.40–7.35 (m, 5H), 3.37–3.30 (m, 1H), 3.24–3.18 (m, 1H), 1.68 (s, 3H), 1.66–1.51 (m, 2H), 1.49 (s, 9H), 0.65 (t, $J$ = 7.4 Hz, 3H); $^{13}$C NMR ($CDCl_3$, 125 MHz) $\delta$ 173.5, 169.6, 136.5, 129.6, 128.5 (2C), 126.3 (2C), 91.4, 83.0,

47.5, 27.8 (3C), 23.9, 20.9, 11.1; IR $\upsilon_{max}$ (neat, $cm^{-1}$) 3235, 2976, 2875, 1738, 1635, 1395, 1298, 1146, 1118; HRMS (ESI) calcd for $C_{17}H_{25}NO_5$ 346.1625 ($[M+Na]^+$), found 346.1634.



***N*-Acetyl-*N*-propylbenzamide (10).**

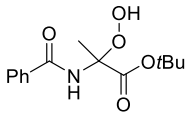
*t*BuOK (1.0 M in THF, 2.75 mL, 2.75 mmol) was added to a solution of substrate **7a** (400 mg, 1.37 mmol) in THF (7 mL, 0.2 M) under an $O_2$ balloon at 0 °C. The resulting mixture was stirred at 0 °C for 5 min and quenched with saturated $NH_4Cl$ solution and extracted with EtOAc. The combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc, 3:1) to yield product **10** (12 mg, 4%) as a colorless oil; $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 7.60–7.58 (m, 2H), 7.55–7.51 (m, 1H), 7.45–7.42 (m, 2H), 3.72–3.68 (m, 2H), 2.12 (s, 3H), 1.63–1.54 (m, 2H), 0.83 (t, $J$ = 7.6 Hz, 3H); $^{13}$C NMR ($CDCl_3$, 100 MHz) $\delta$ 174.8, 173.5, 136.0, 132.6, 129.0 (2C), 128.6 (2C), 48.2, 26.4, 22.5, 11.5; IR $\upsilon_{max}$ (neat, $cm^{-1}$) 2966, 2875, 1687, 1659, 1366, 1234, 701; HRMS (FAB) calcd for $C_{12}H_{16}NO_2$ 206.1181 ($[M+H]^+$), found 206.1181.



***N*-Acetylbenzamide (13).**

*t*BuOK (1.0 M in THF, 0.48 mL, 0.481 mmol) was added to a solution of substrate **11a** (40 mg, 0.160 mmol) in THF (0.8 mL, 0.2 M) under an $O_2$ balloon at 0 °C. The resulting mixture was stirred at 0 °C for 0.5 h and warmed to room temperature. After 24 h, the reaction was quenched with saturated $NH_4Cl$ solution and extracted with EtOAc. The combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc, 3:1) to yield product **13** (6.7 mg, 26%) as a white solid; m.p. 110–112 °C; $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 8.66 (brs, 1H), 7.85–7.82 (m, 2H), 7.62–7.57 (m, 1H), 7.51–7.47 (m, 2H), 2.60 (s, 3H); $^{13}$C NMR ($CDCl_3$, 100 MHz) $\delta$ 173.5, 165.8, 133.5, 132.9, 129.3 (2C), 127.8 (2C), 25.7; IR $\upsilon_{max}$ (neat, $cm^{-1}$) 3298, 2919, 1712, 1693, 1468, 1373, 1290, 1243, 1017; HRMS (FAB) calcd for $C_9H_{10}NO_2$ 164.0712 ($[M+H]^+$), found 164.0709.

**_tert_-Butyl 2-benzamido-2-hydroperoxypropanoate (14).**



*t*BuOK (1.0 M in THF, 0.48 mL, 0.481 mmol) was added to a solution of substrate **11a** (40 mg, 0.160 mmol) in THF (0.8 mL, 0.2 M) under an $O_2$ balloon at 0 °C. The resulting mixture was stirred at 0 °C for 0.5 h and quenched with saturated $NH_4Cl$ solution and extracted with EtOAc. The combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc, 3:1) to yield product **14** (23.4 mg, 52%) as a colorless oil; $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 7.73 (d, $J$ = 7.2 Hz, 2H), 7.69 (s, 1H), 7.46 (t, $J$ = 7.6 Hz, 1H), 7.35 (t, $J$ = 7.8 Hz, 2H), 1.85 (s, 3H), 1.55 (s, 9H); $^{13}$C NMR ($CDCl_3$, 100 MHz) $\delta$ 169.0, 167.3, 134.0, 132.2, 128.8 (2C), 127.3 (2C), 90.4, 84.3, 28.0 (3C), 20.6; IR $\upsilon_{max}$ (neat, cm$^{-1}$) 3298, 2980, 2934, 1733, 1665, 1523, 1326, 1149, 771; HRMS (ESI) calcd for $C_{14}H_{19}NO_5$ 304.1155 ([M+Na]$^+$), found 304.1159.

## 4. ReactIR Monitoring of the Reaction of 7a

To a three-neck 25 mL round-bottom flask were added substrate **7a** (400 mg, 1.37 mmol) and THF (7 mL, 0.2 M). IR probe (DS AgX SiCompTM) was placed on the middle neck of flask and side neck was capped with septum. Oxygen gas was bubbled through the solution for 5 minutes. Then, the reaction was stirred at 0 °C under an $O_2$ balloon. Acquisition was started with the interval of 10 seconds. After steady intensities were maintained, *t*BuOK (1.0 M in THF, 2.75 mL, 2.75 mmol) was added dropwise through side neck in 30 seconds. Figure S1 shows the reaction profile over time. The large absorption beginning at the bottom of the diagram represents the starting material **7a** C=O stretch at 1738 and 1645 $cm^{-1}$. Upon addition of the *t*BuOK, the disappearance of that absorption coincides with the peroxide immediate **9**, rapid growth of three peaks at 1742 (C=O stretch), 1635 (C=O stretch), and 1419 $cm^{-1}$ (O–H bend). As time goes on, the above three peaks disappear, while a new peak at 1667 $cm^{-1}$ was observed, which was assigned to be the C=O stretch of product **8a**. Notably, the peaks at 2339 and 2357 $cm^{-1}$ represent the P-branch and R-branch of the $CO_2$ absorbance respectively. The peak is matched with the major peak of $CO_2$ dissolved in THF ($CO_2$ reference) (Figure S2).

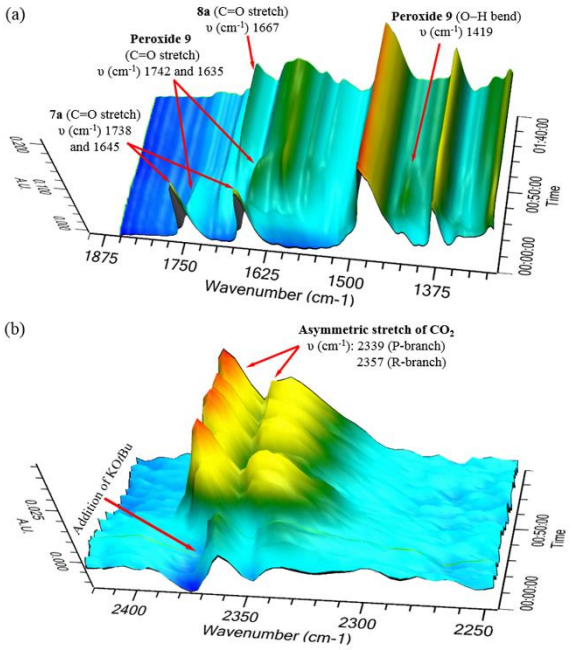



**Figure S1.** Three-dimensional plot of the ReactIR monitoring of the reaction of **7a** in the presence of KO*t*Bu in THF under an $O_2$ atmosphere at 0 °C. KO*t*Bu added at time 2 min.

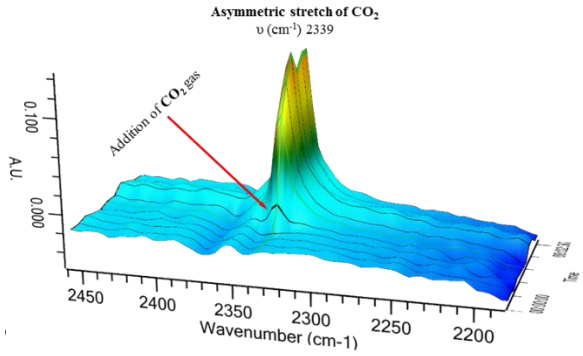



**Figure S2.** ReactIR monitoring of $CO_2$ dissolved in THF ($CO_2$ reference).

# 5. Reference


[1] Q.-K. Kang, S. Selvakumar and K. Maruoka, *Org. Lett.*, 2019, **21**, 2294–2297.

[2] M. J. Costanzo, S. C. Yabut, H. R. Almond, Jr., P. Andrade-Gordon, T. W. Corcoran, L. de Garavilla, J. A. Kauffman, W. M. Abraham, R. Recacha, D. Chattopadhyay and B. E. Maryanoff, *J. Med. Chem.*, 2003, **46**, 3865–3876.

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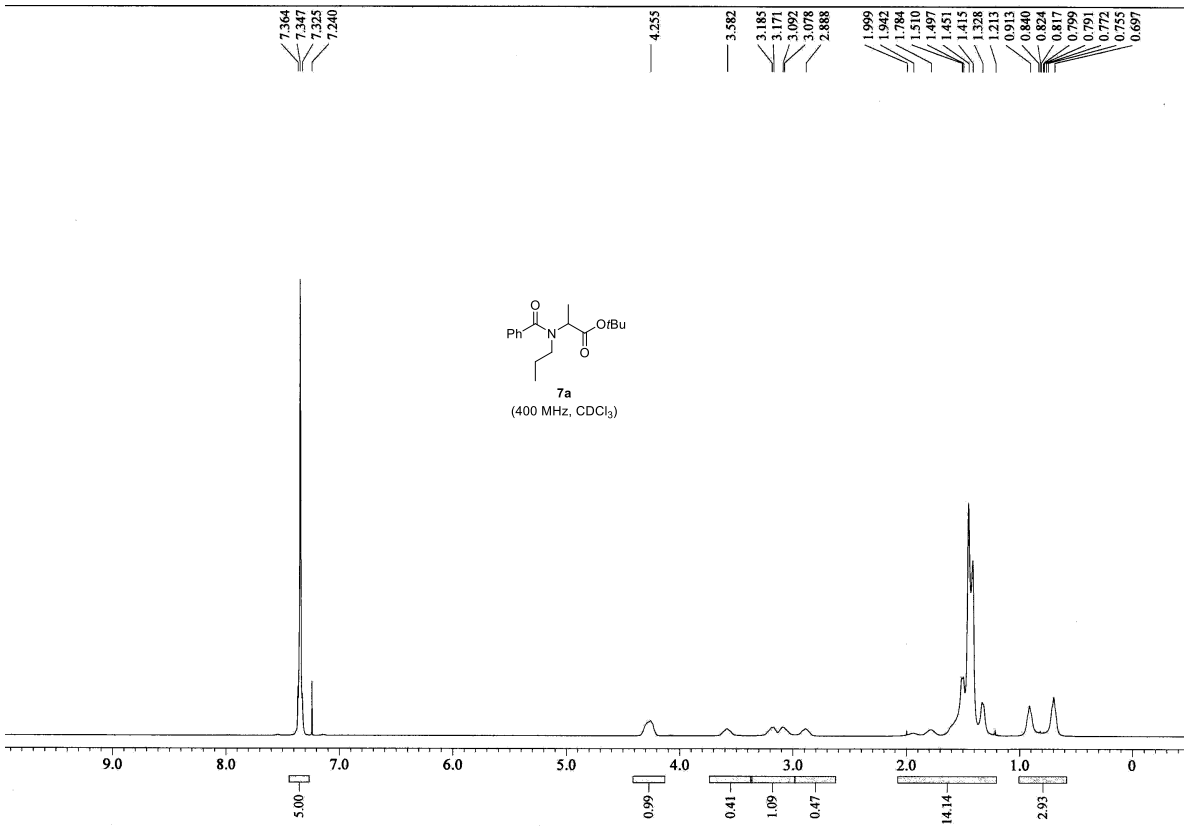
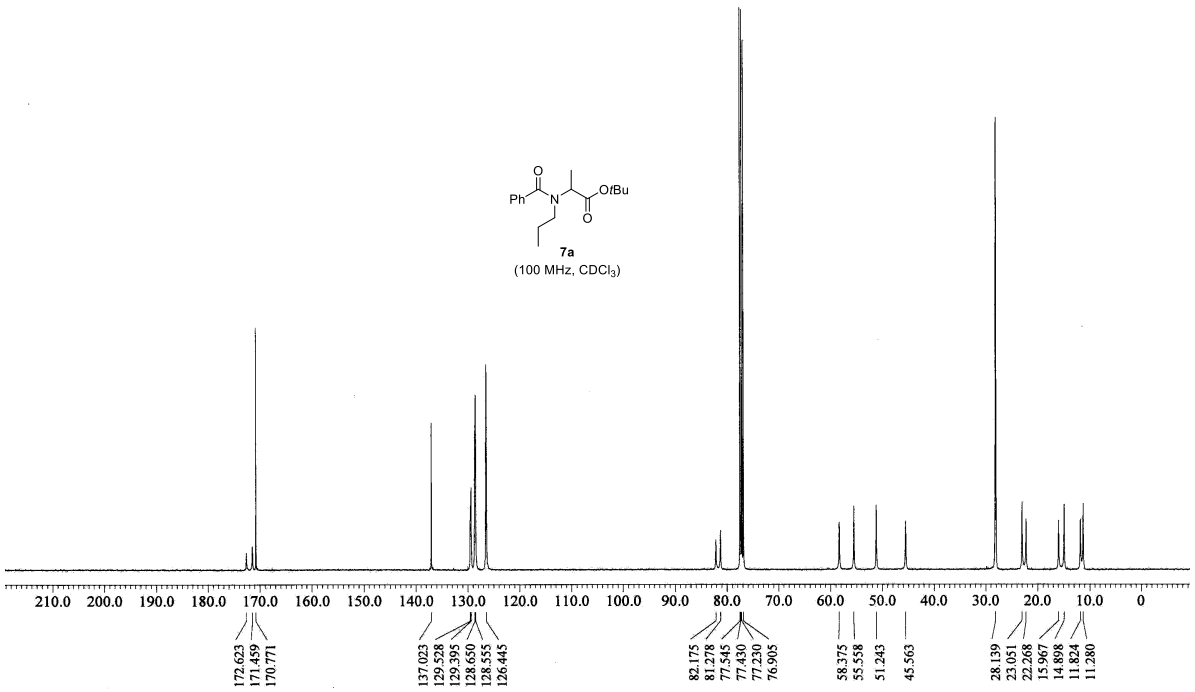
[6] J. D. Goodreid, P. A. Duspara, C. Bosch and R. A. Batey, *J. Org. Chem.*, 2014, **79**, 943−954.

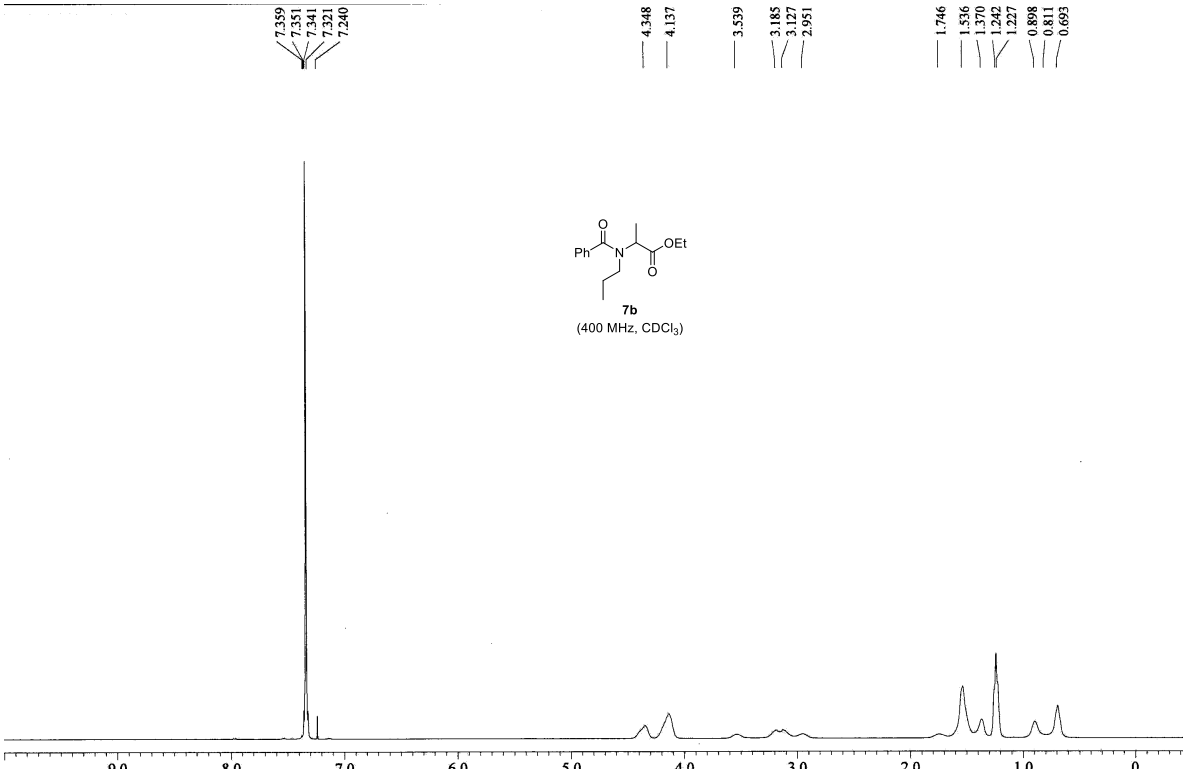
[7] M. Nakagawa, T. Suzuki, T. Kawashima and T. Hino, *Chem. Pharm. Bull.*, 1972, **20**, 2413–2417.

[8] Q.-K. Kang, S. Selvakumar and K. Maruoka, *Org. Lett.*, 2019, **21**, 2294–2297.

# 6. $^{1}$H and $^{13}$C NMR Spectra

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Ph
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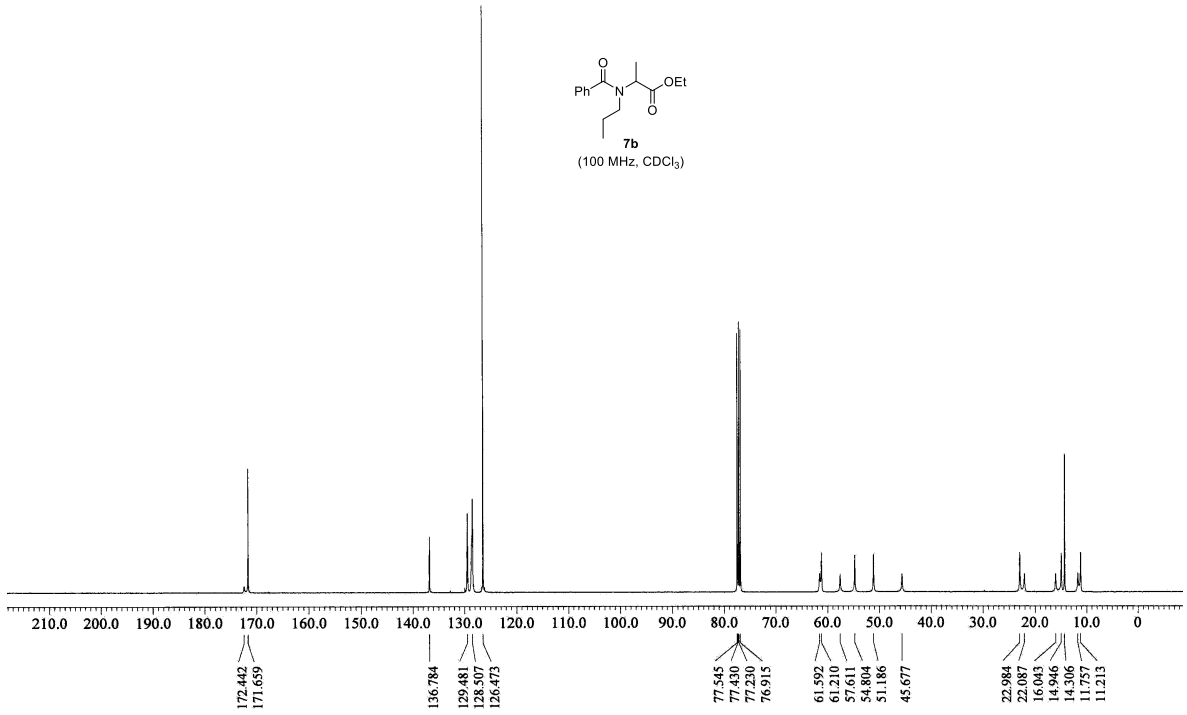
O
7b
(400 MHz, CDCl3)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O
OEt
O
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(100 MHz, CDCl3)
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171.659
136.784
129.481
128.507
126.473
77.545
77.430
77.230
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61.592
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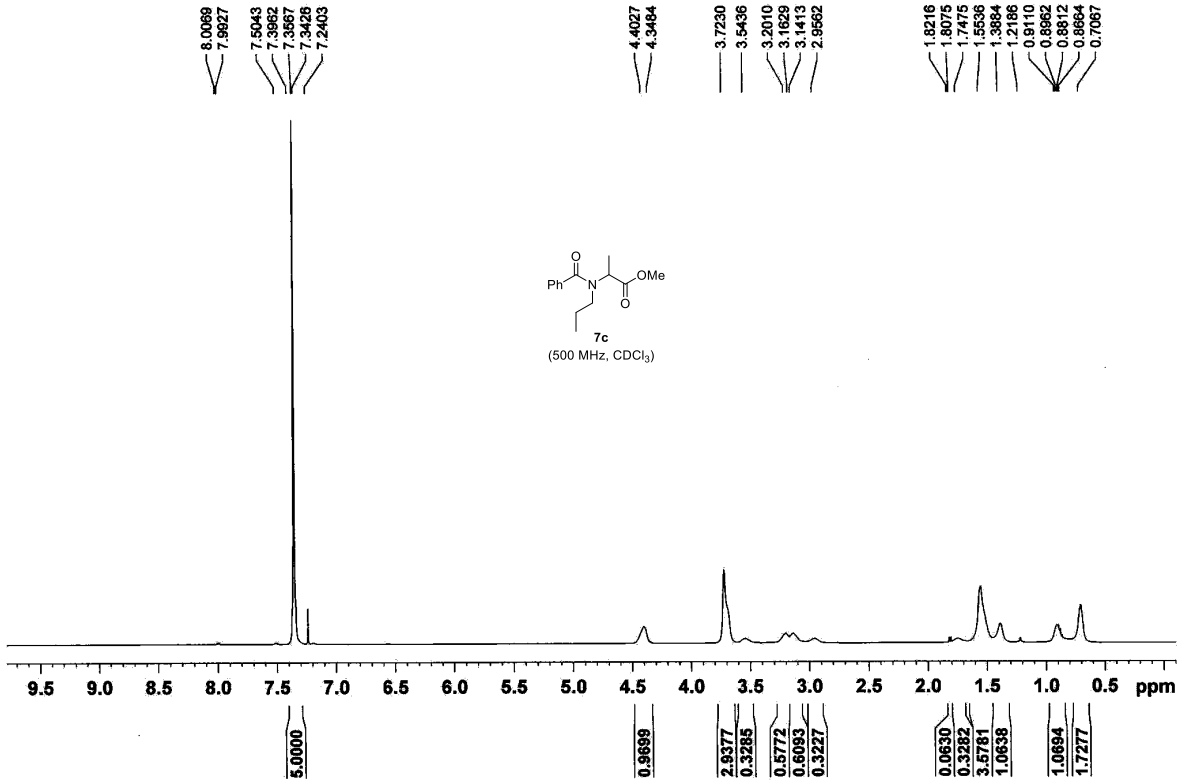
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0.8862
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Ph
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OMe
O
7c
(500 MHz, CDCl3)
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
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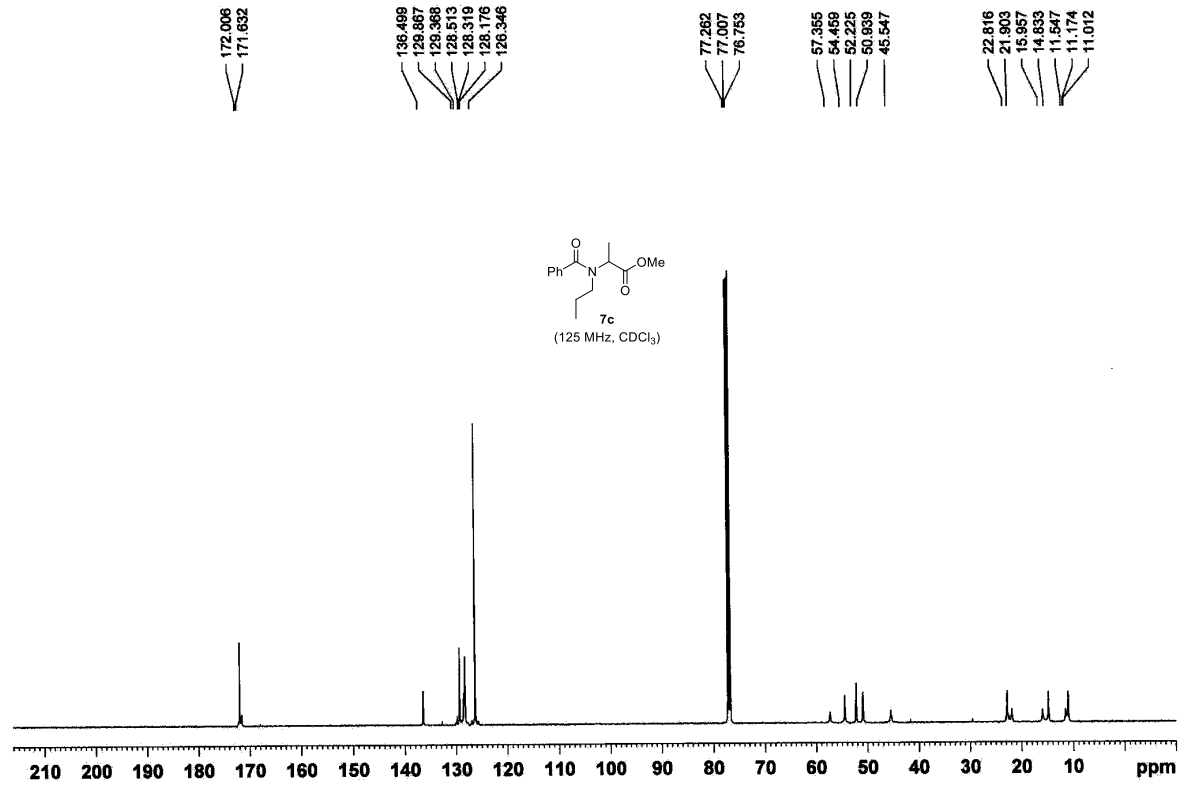
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11.547
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Ph
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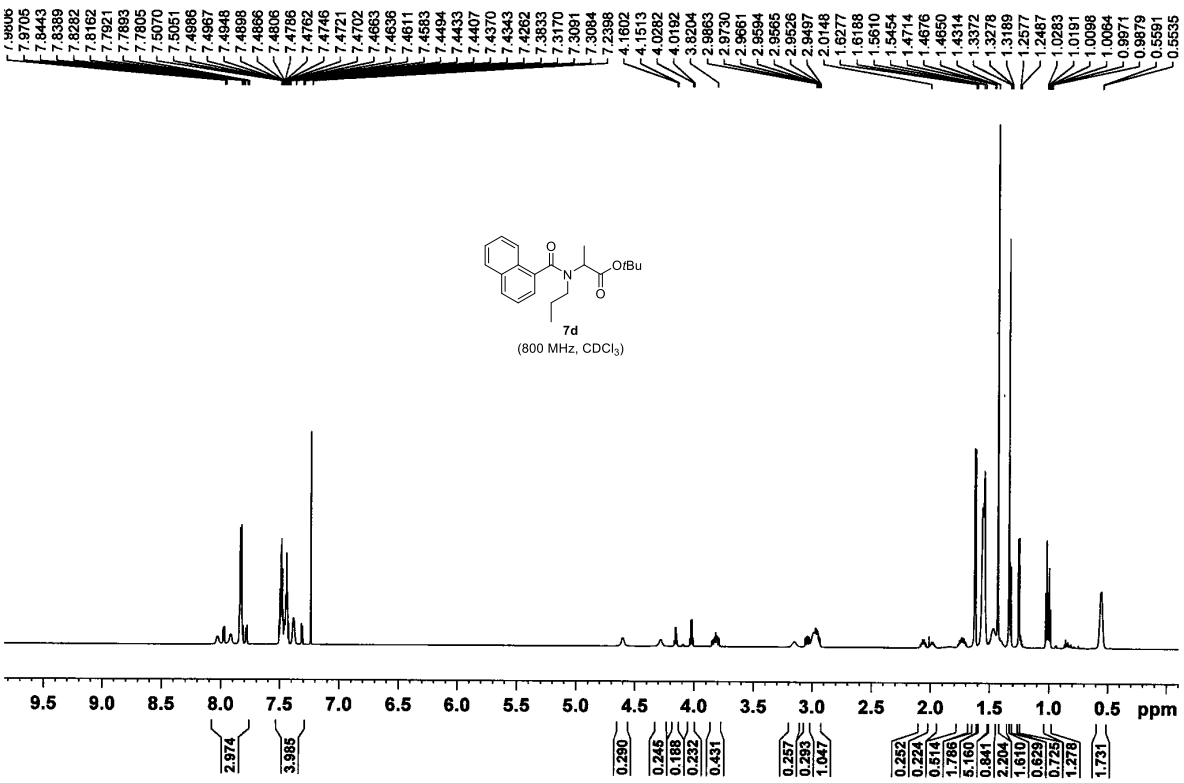
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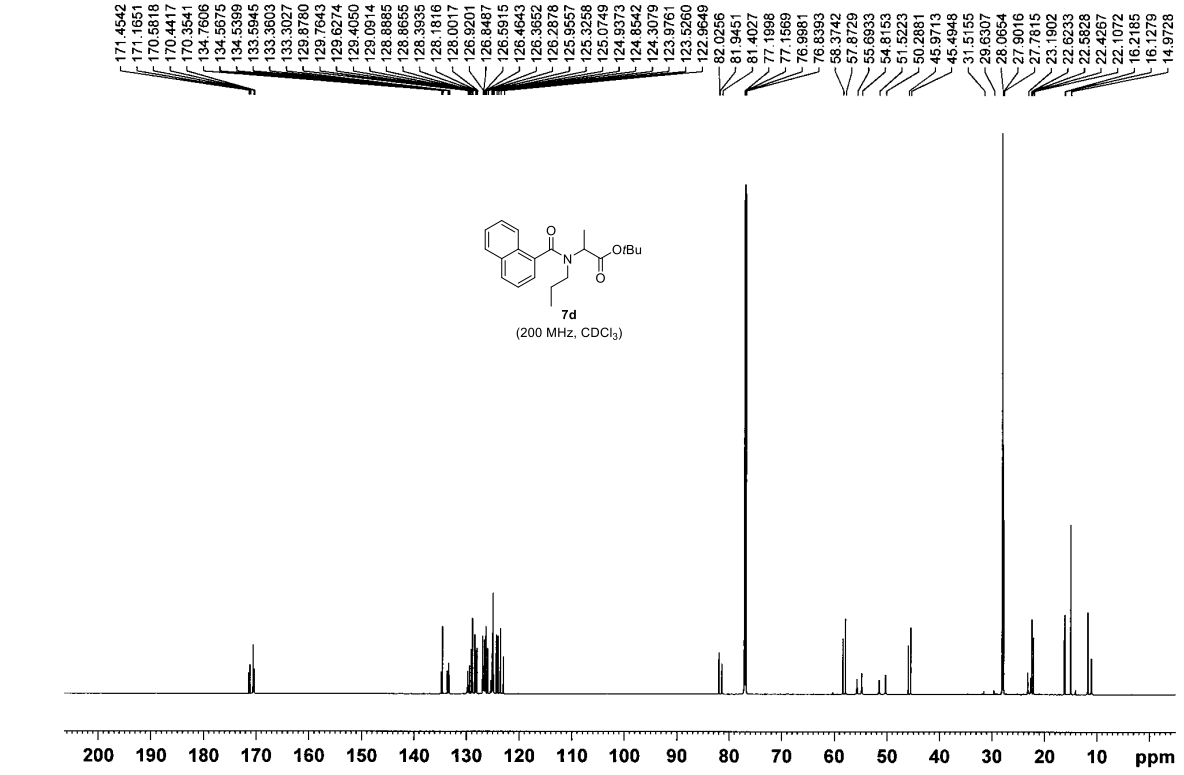
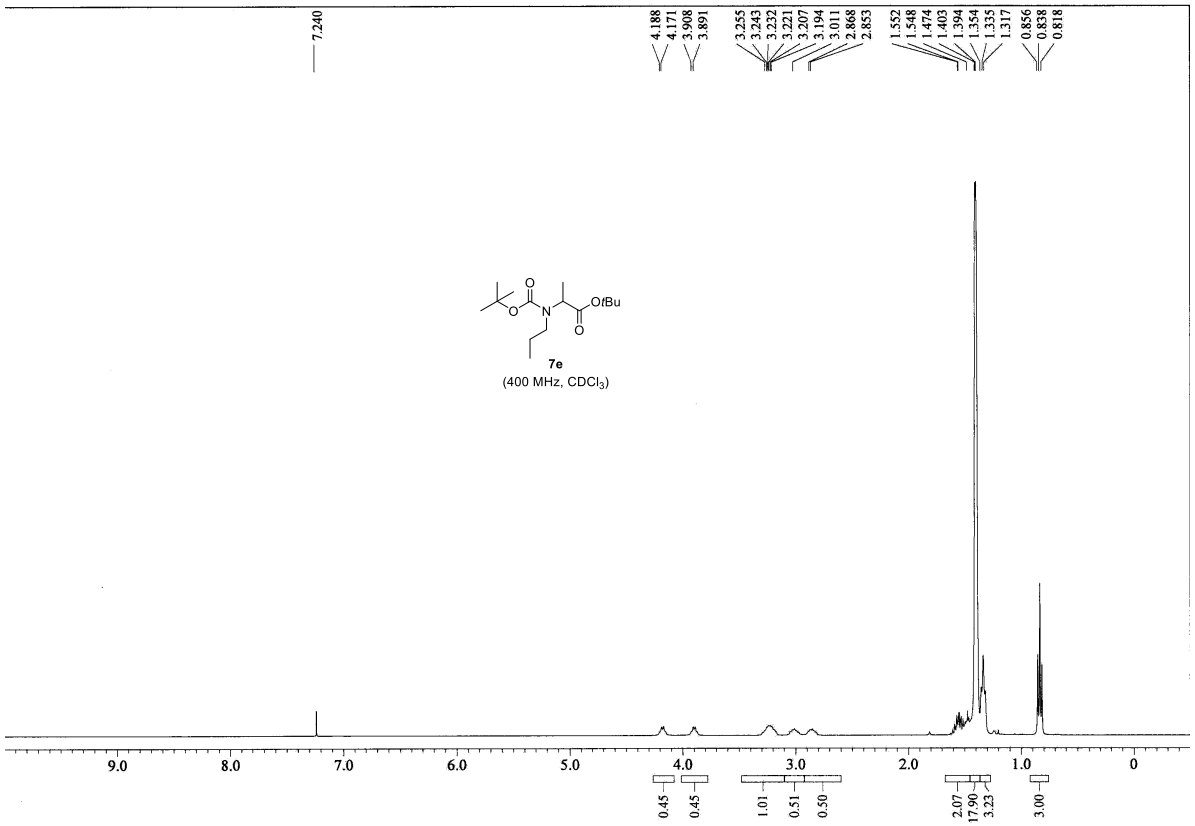
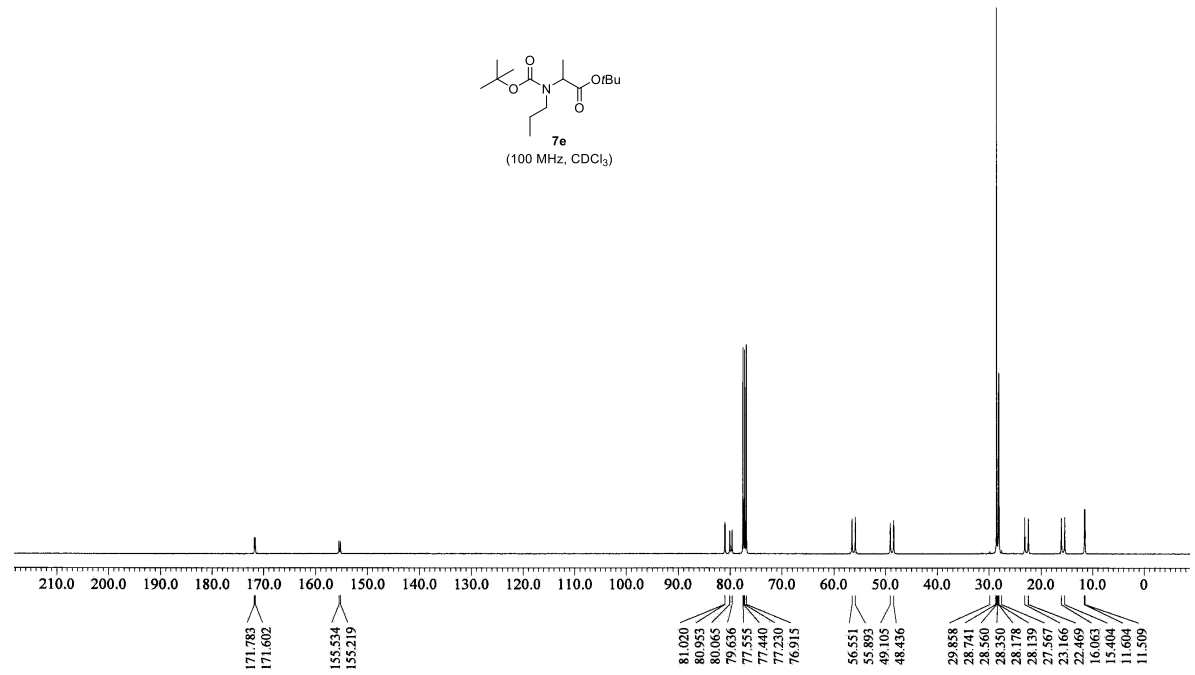
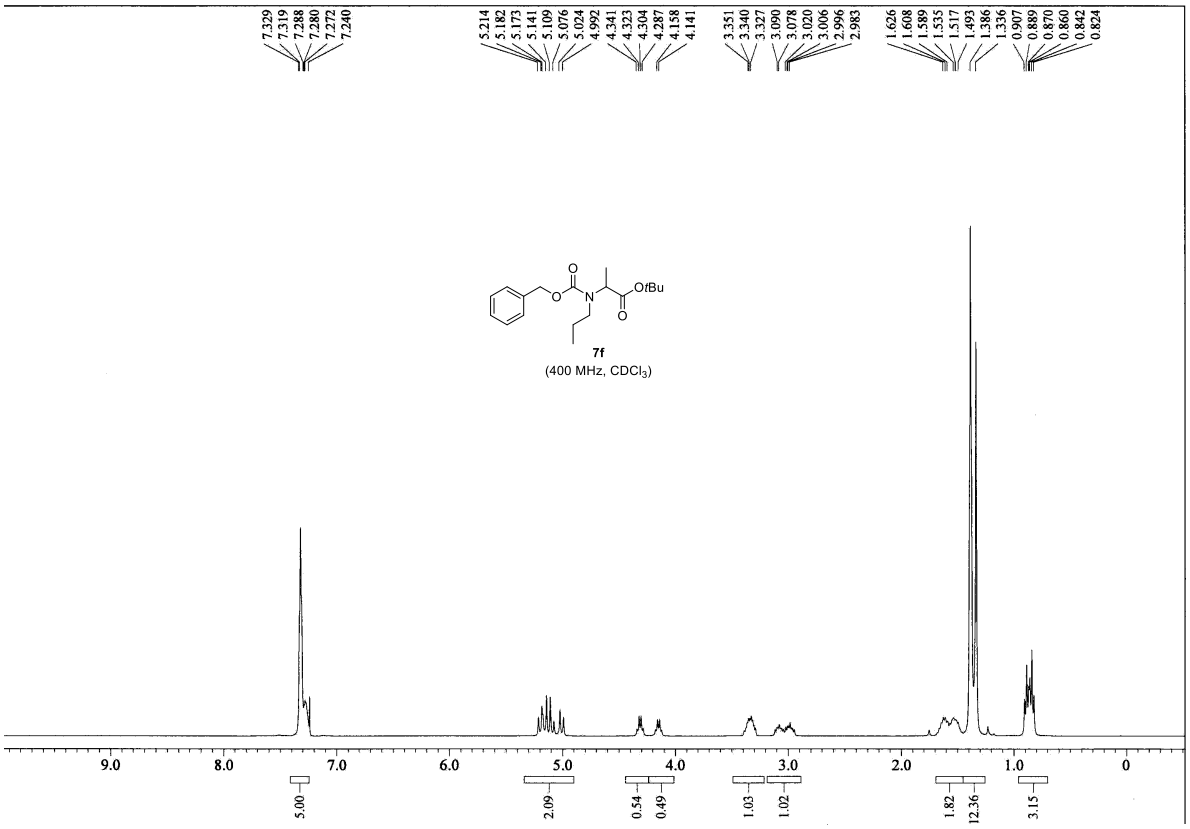
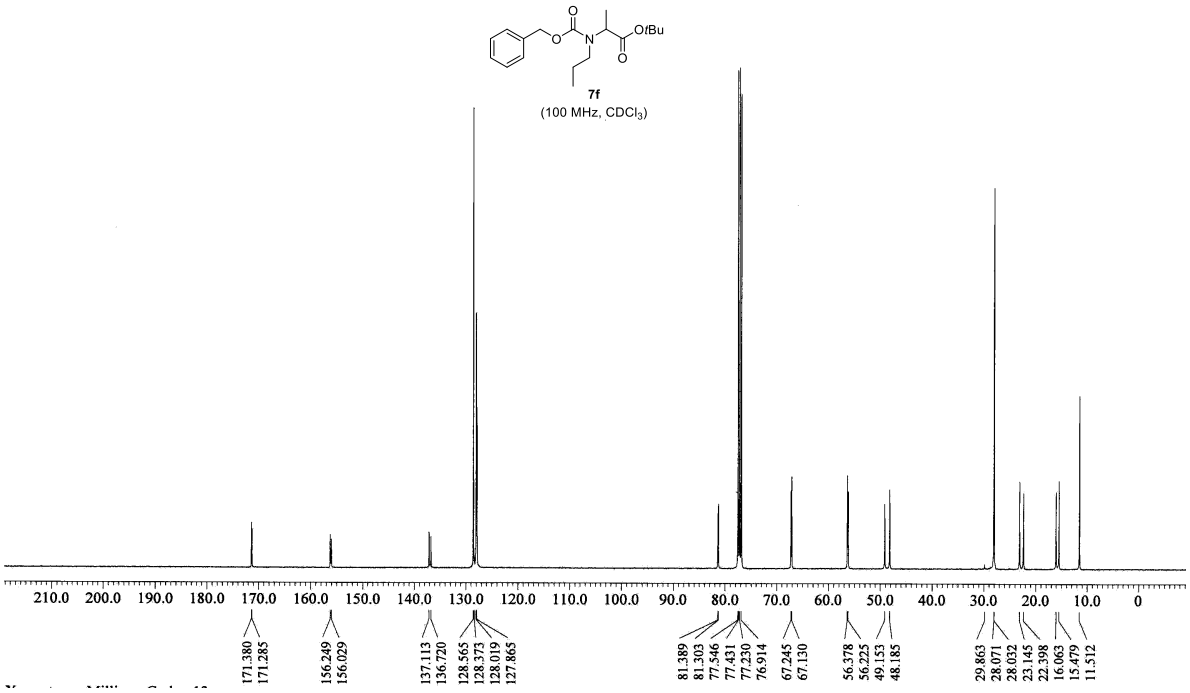
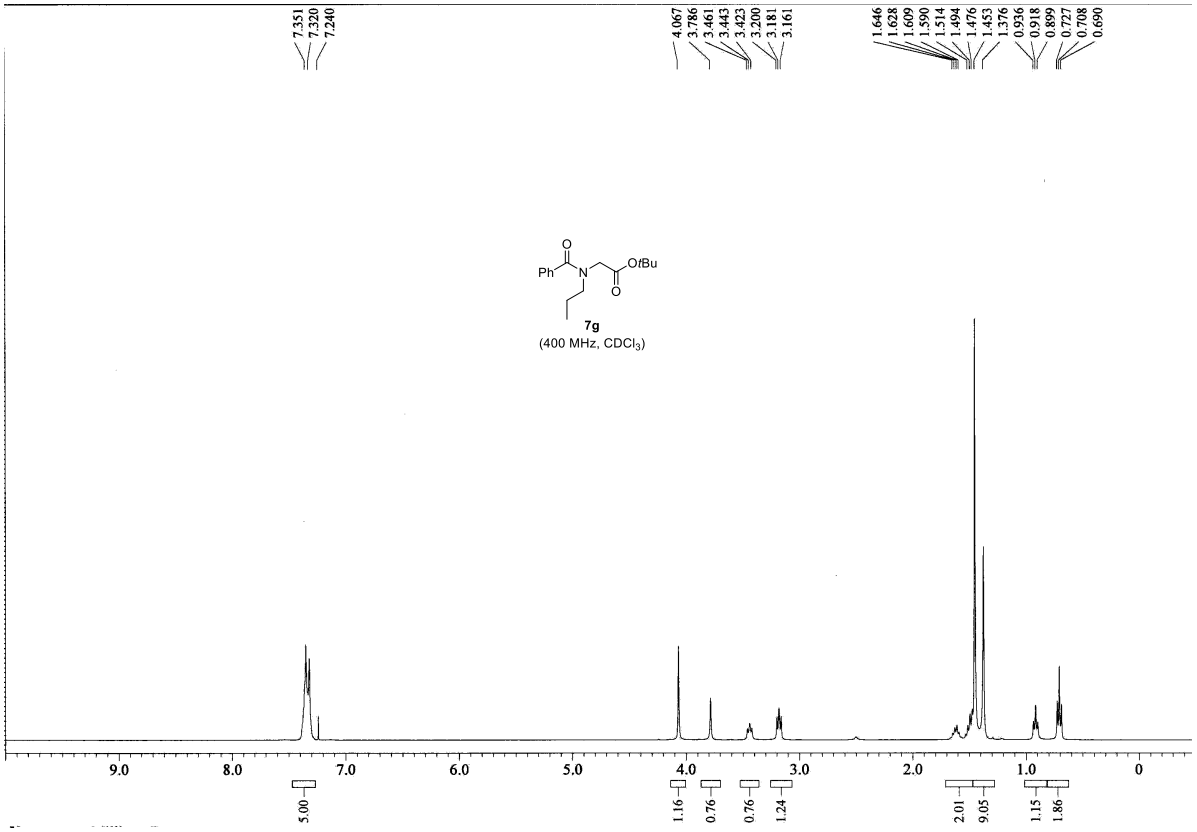

7d
(200 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

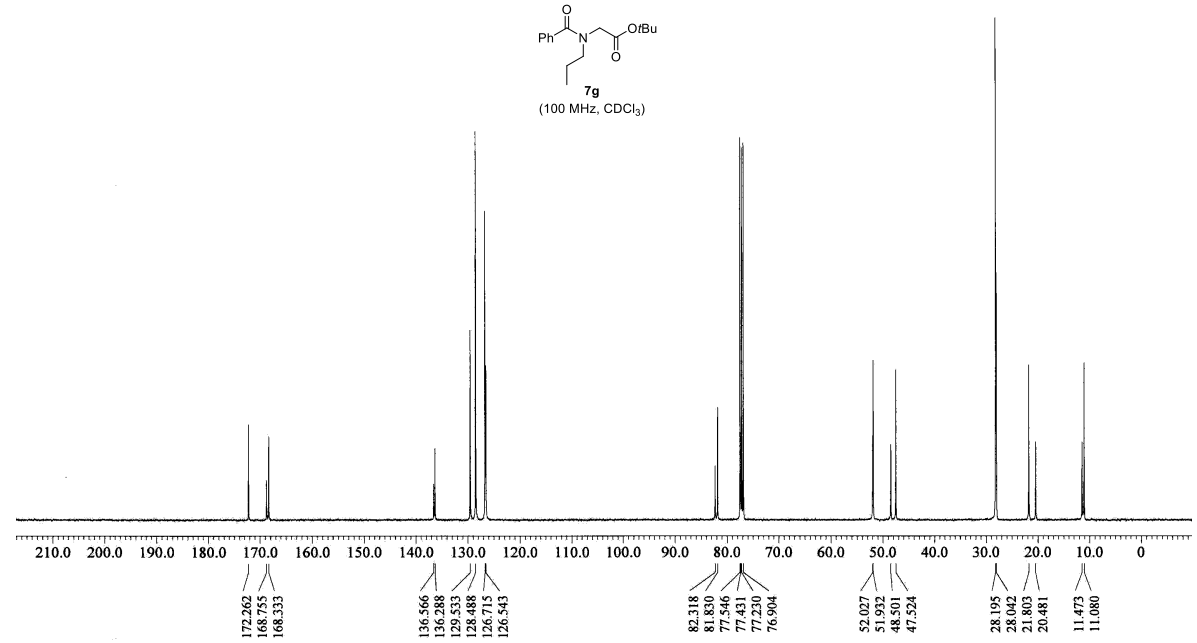

7.240
4.188
4.171
3.908
3.891
3.255
3.243
3.232
3.221
3.207
3.194
3.011
2.868
2.853
1.552
1.548
1.474
1.403
1.394
1.354
1.335
1.317
0.856
0.838
0.818
OtBu
7e
(400 MHz, CDCl3)
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
0.45
0.45
1.01
0.51
0.50
2.07
17.90
3.23
3.00

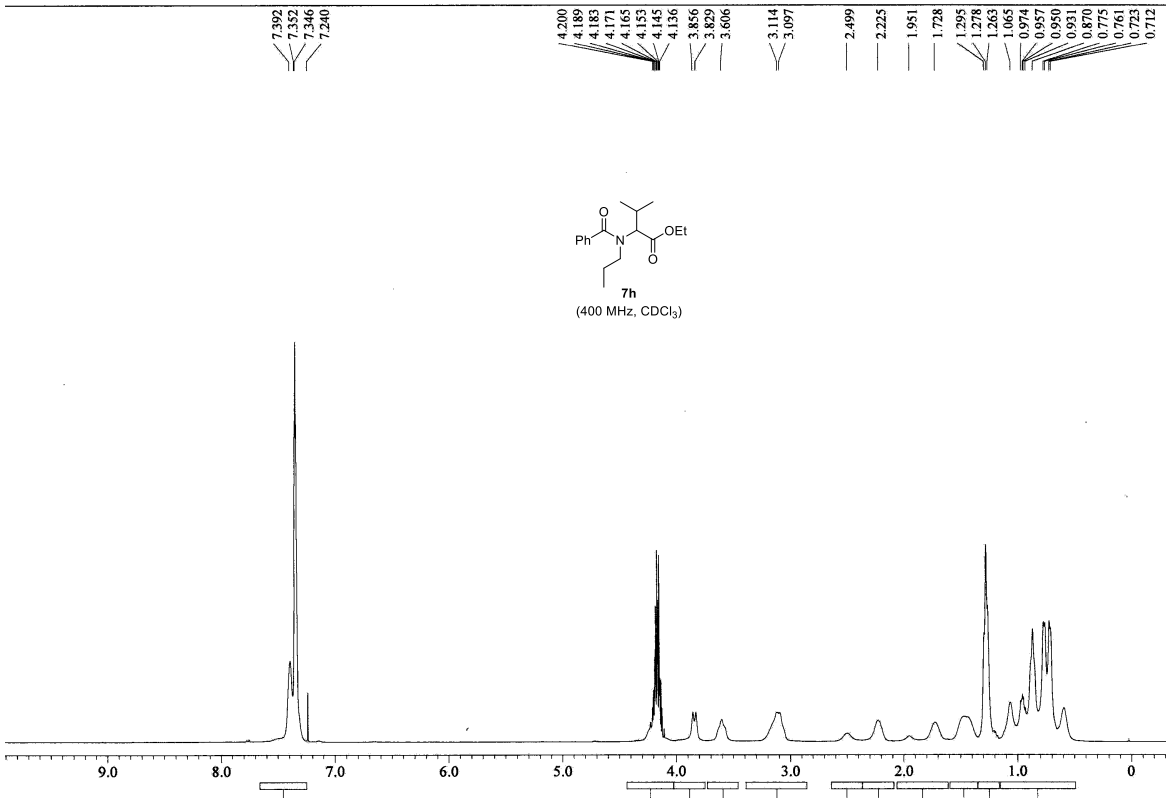

OtBu
7e
(100 MHz, CDCl3)
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
171.783
171.602
155.534
155.219
81.020
80.953
80.065
79.636
77.555
77.440
77.230
76.915
56.551
55.893
49.105
48.436
29.858
28.741
28.560
28.350
28.178
28.139
27.567
23.166
22.469
16.063
15.404
11.604
11.509

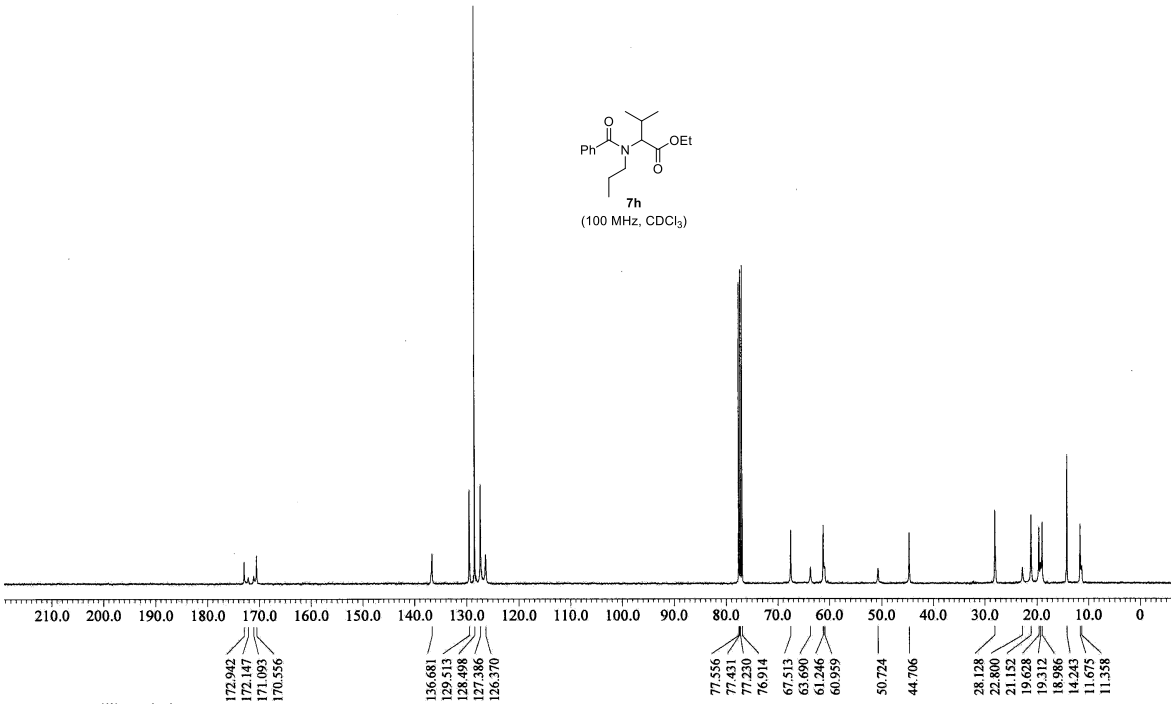

7.329
7.319
7.288
7.280
7.272
7.240
5.214
5.182
5.173
5.141
5.109
5.076
5.024
4.992
4.341
4.323
4.304
4.287
4.158
4.141
3.351
3.340
3.327
3.090
3.078
3.020
3.006
2.996
2.983
1.626
1.608
1.589
1.535
1.517
1.493
1.386
1.336
0.907
0.889
0.870
0.860
0.842
0.824
OtBu
7f
(400 MHz, CDCl3)
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
5.00
2.09
0.54
0.49
1.03
1.02
1.82
12.36
3.15

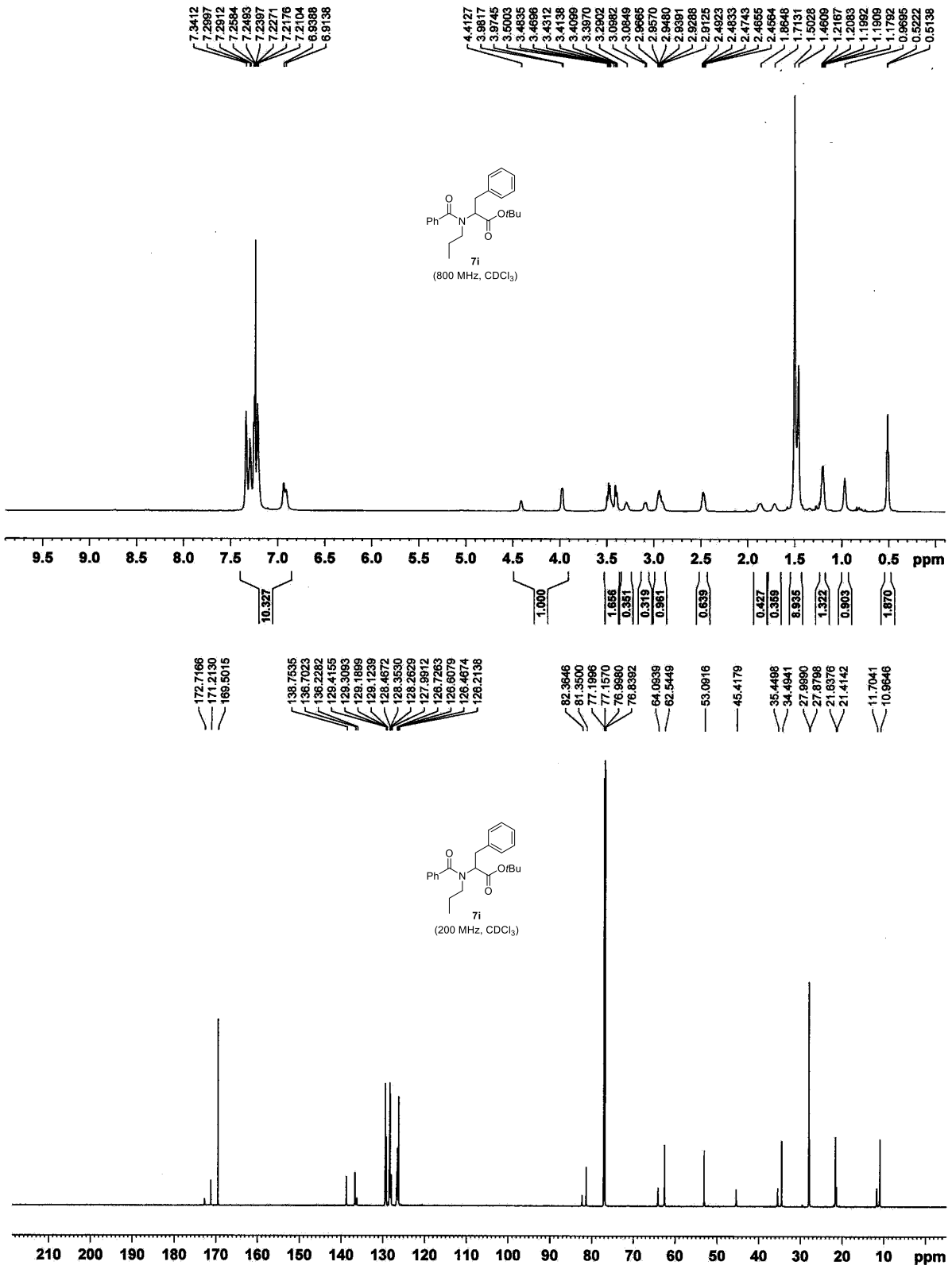

OtBu
7f
(100 MHz, CDCl3)
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
171.380
171.285
156.249
156.029
137.113
136.720
128.565
128.373
128.019
127.865
81.389
81.303
77.546
77.431
77.230
76.914
67.245
67.130
56.378
56.225
49.153
48.185
29.863
28.071
28.032
23.145
22.398
16.063
15.479
11.512

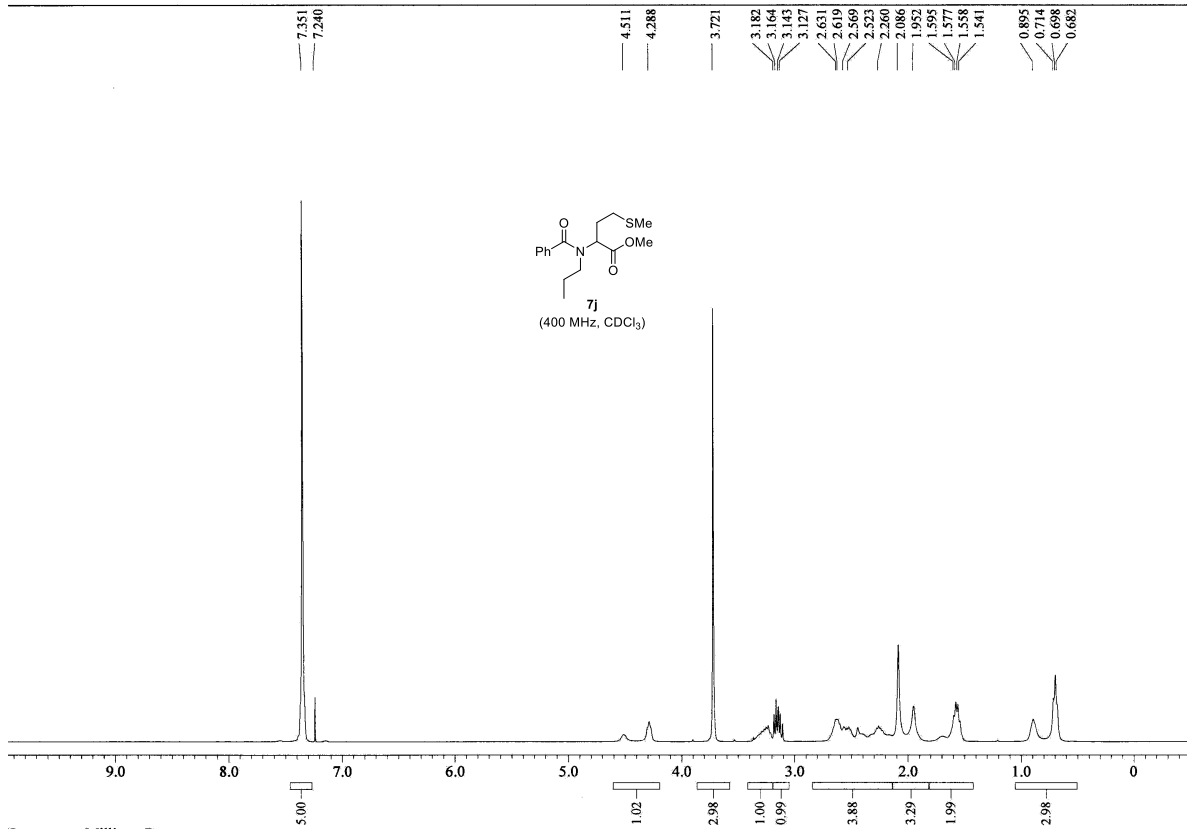

7.351
7.320
7.240
4.067
3.786
3.461
3.443
3.423
3.200
3.181
3.161
1.646
1.628
1.609
1.590
1.514
1.494
1.476
1.453
1.376
0.936
0.918
0.899
0.727
0.708
0.690
Ph
N
OtBu
O
7g
(400 MHz, CDCl3)
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
5.00
1.16
0.76
0.76
1.24
2.01
9.05
1.15
1.86

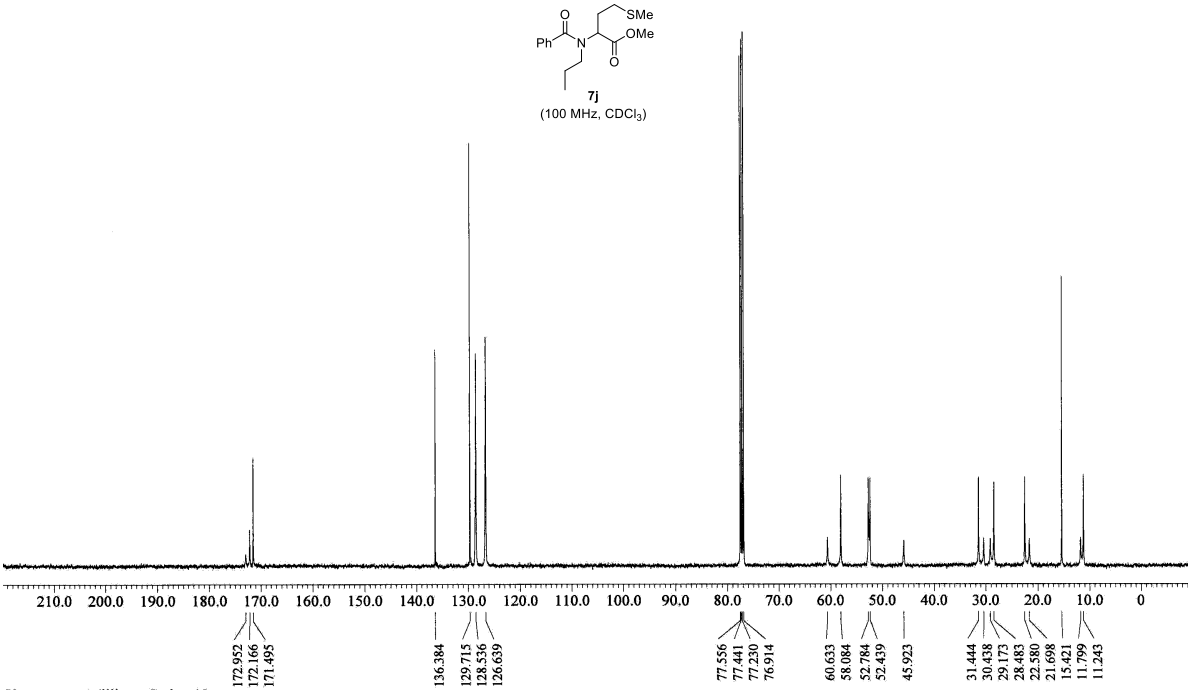

Ph
N
OtBu
O
7g
(100 MHz, CDCl3)
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
172.262
168.755
168.333
136.566
136.288
129.533
128.488
126.715
126.543
82.318
81.830
77.546
77.431
77.230
76.904
52.027
51.932
48.501
47.524
28.195
28.042
21.803
20.481
11.473
11.080

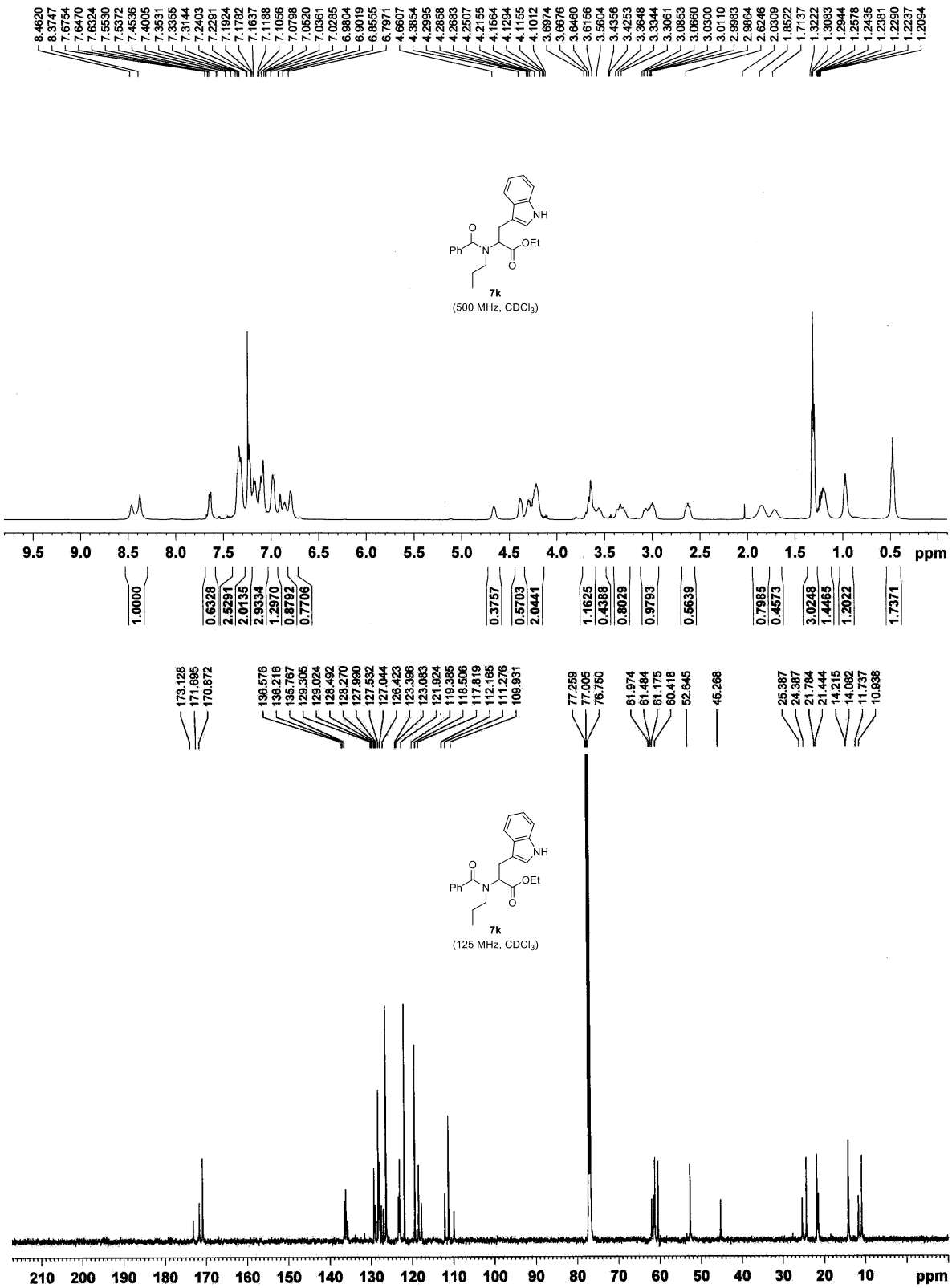

7.392
7.352
7.346
7.240
4.200
4.189
4.183
4.171
4.165
4.153
4.145
4.136
3.856
3.829
3.606
3.114
3.097
2.499
2.225
1.951
1.728
1.295
1.278
1.263
1.065
0.974
0.957
0.950
0.931
0.870
0.775
0.761
0.723
0.712
Ph
N
O
OEt
O
7h
(400 MHz, CDCl3)
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0

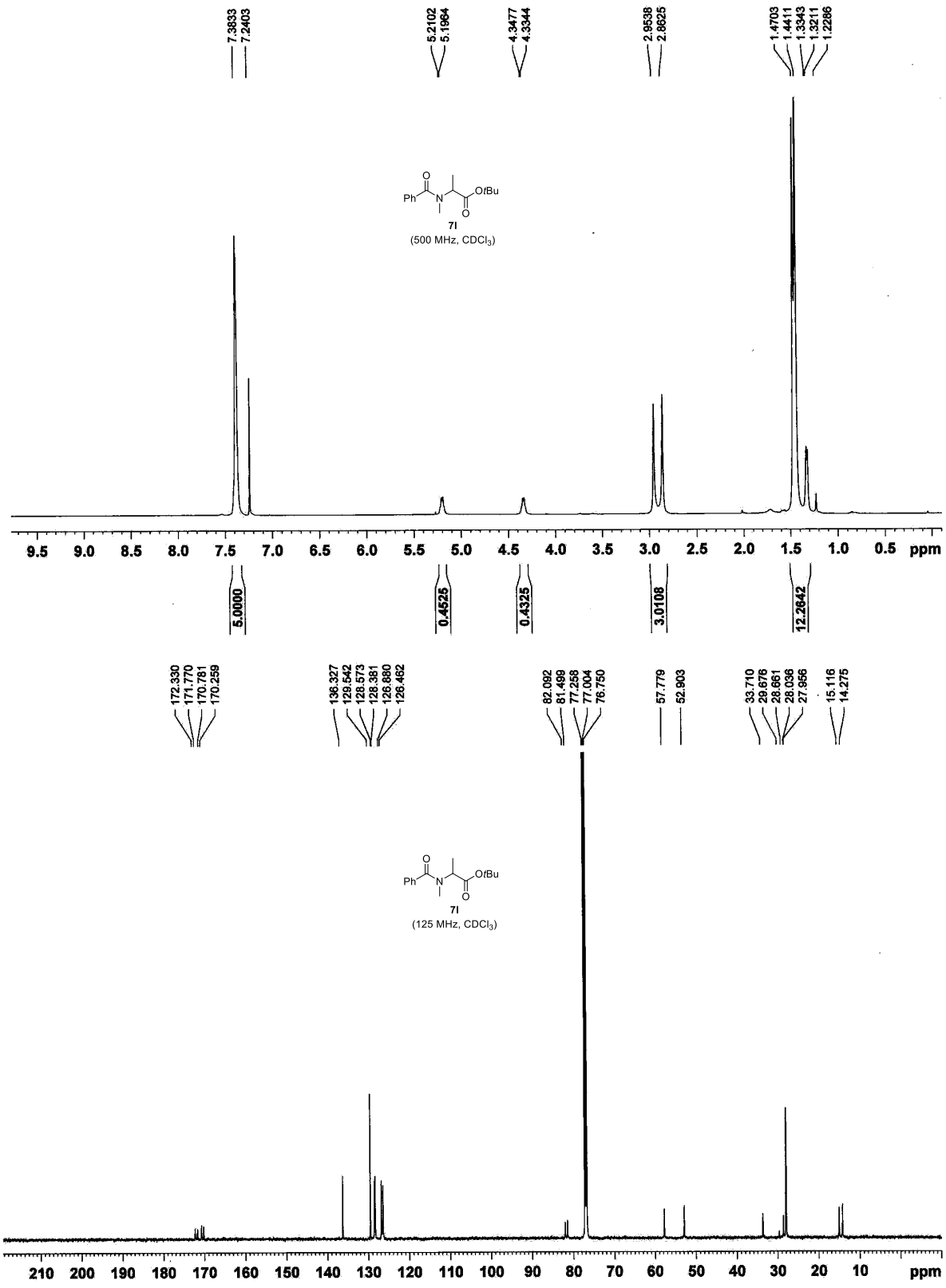

Ph
N
O
OEt
O
7h
(100 MHz, CDCl3)
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
172.942
172.147
171.093
170.556
136.681
129.513
128.498
127.386
126.370
77.556
77.431
77.230
76.914
67.513
63.690
61.246
60.959
50.724
44.706
28.128
22.800
21.152
19.628
19.312
18.986
14.243
11.675
11.358

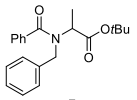

7.3412
7.2997
7.2912
7.2584
7.2493
7.2397
7.2271
7.2176
7.2104
6.9388
6.9138
4.4127
3.9817
3.9745
3.5003
3.4835
3.4686
3.4312
3.4138
3.4099
3.3970
3.2902
3.0982
3.0849
2.9665
2.9570
2.9480
2.9391
2.9288
2.9125
2.4923
2.4833
2.4743
2.4655
2.4564
1.8648
1.7131
1.5028
1.4609
1.2167
1.2083
1.1992
1.1909
1.1792
0.9695
0.5222
0.5138
Ph
N
OtBu
O
7i
(800 MHz, CDCl3)
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 ppm
10.327
1.000
1.656
0.351
0.319
0.961
0.639
0.427
0.359
8.935
1.322
0.903
1.870
172.7166
171.2130
169.5015
138.7535
136.7023
136.2282
129.4155
129.3083
129.1899
129.1239
128.4672
128.3530
128.2629
127.9912
126.7263
126.6079
126.4674
126.2138
82.3646
81.3500
77.1986
77.1570
76.9980
76.8392
64.0939
62.5449
53.0816
45.4179
35.4498
34.4941
27.9990
27.8798
21.6376
21.4142
11.7041
10.9646
Ph
N
OtBu
O
7i
(200 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


7.351
7.240
4.511
4.288
3.721
3.182
3.164
3.143
3.127
2.631
2.619
2.569
2.523
2.260
2.086
1.952
1.595
1.577
1.558
1.541
0.895
0.714
0.698
0.682
SMe
OMe
Ph
N
O
7j
(400 MHz, CDCl3)
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
5.00
1.02
2.98
1.00
0.99
3.88
3.29
1.99
2.98

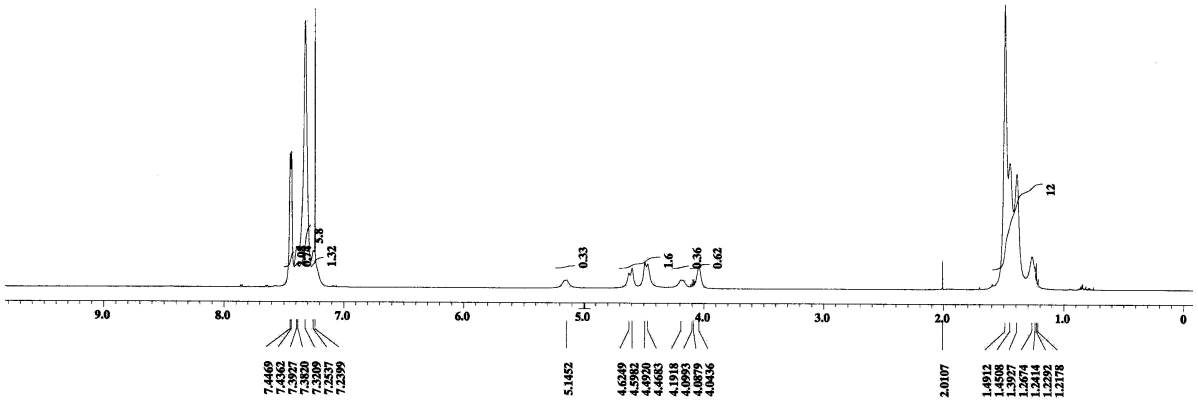

SMe
OMe
Ph
N
O
7j
(100 MHz, CDCl3)
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
172.952
172.166
171.495
136.384
129.715
128.536
126.639
77.556
77.441
77.230
76.914
60.633
58.084
52.784
52.439
45.923
31.444
30.438
29.173
28.483
22.580
21.698
15.421
11.799
11.243

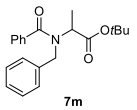

7k
(500 MHz, CDCl3)
7k
(125 MHz, CDCl3)
ppm


7.3833
7.2403
5.2102
5.1964
4.3477
4.3344
2.9538
2.8625
1.4703
1.4411
1.3343
1.3211
1.2286
Ph
N
OtBu
O
7l
(500 MHz, CDCl3)
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 ppm
5.0000
0.4525
0.4325
3.0108
12.2842
172.330
171.770
170.781
170.259
136.327
129.542
128.573
128.381
126.880
126.462
82.092
81.499
77.258
77.004
76.750
57.779
52.903
33.710
29.678
28.661
28.038
27.956
15.116
14.275
Ph
N
OtBu
O
7l
(125 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

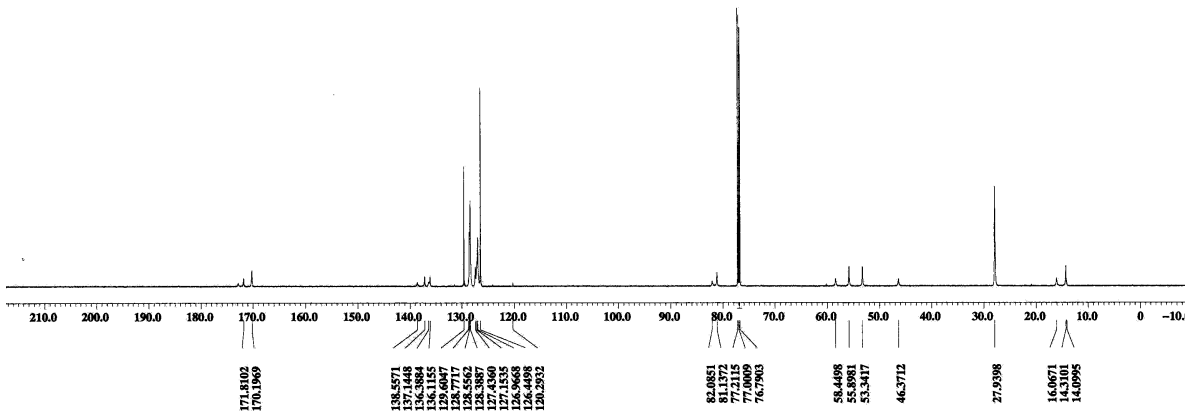


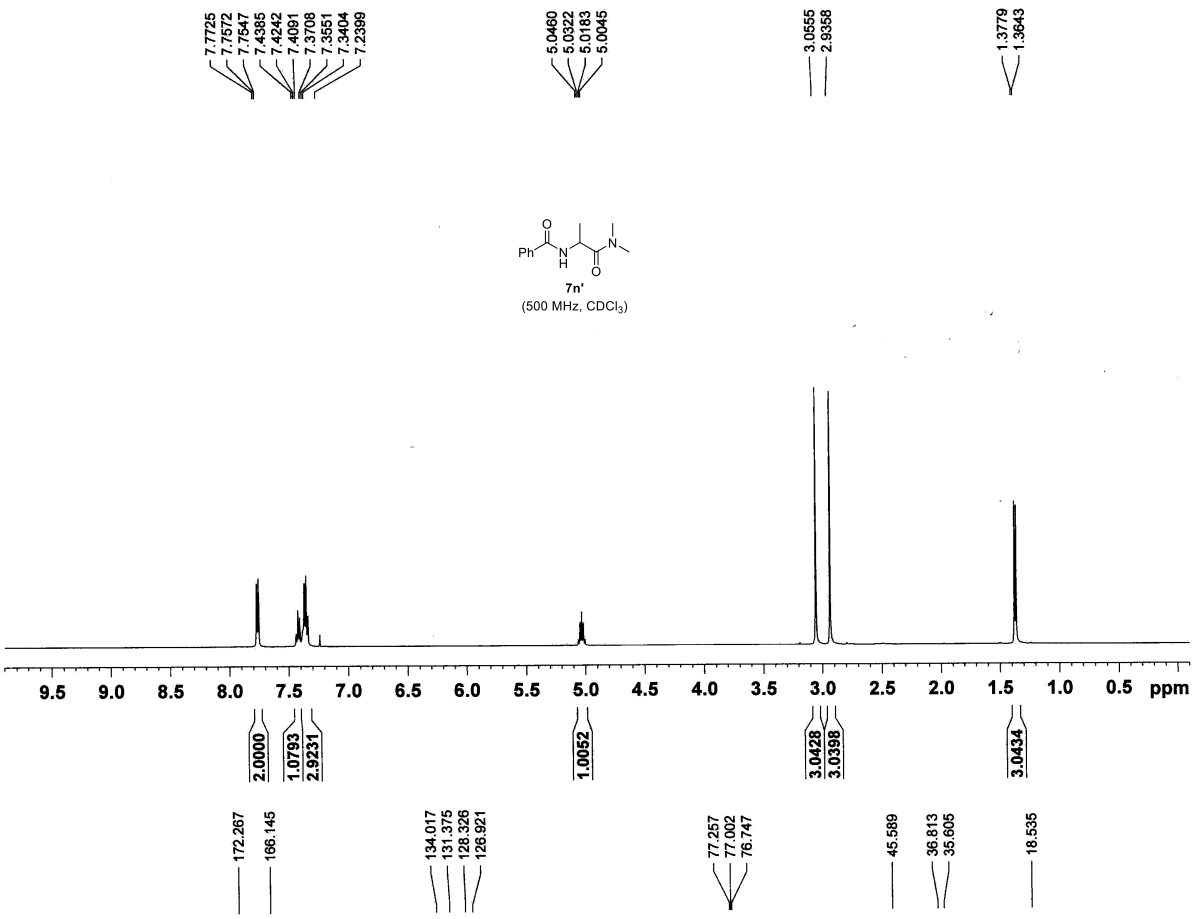
**7m**
(600 MHz, $CDCl_3$)

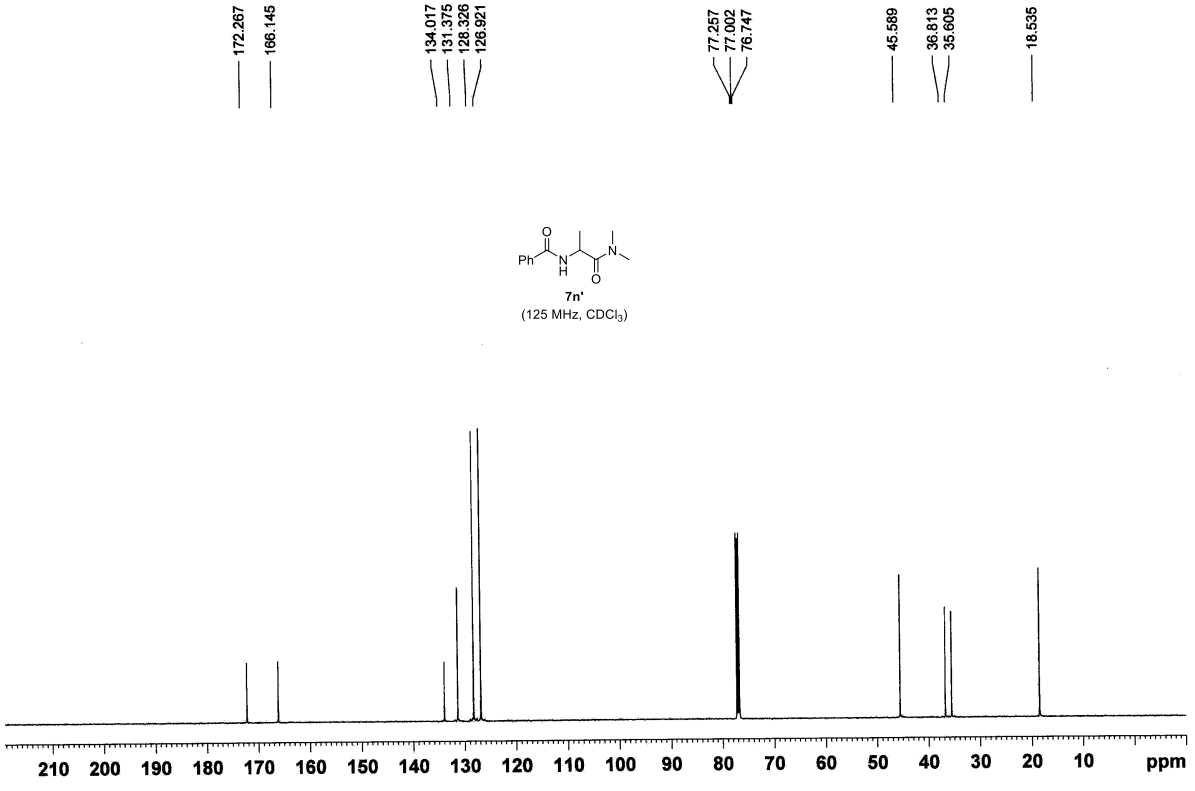


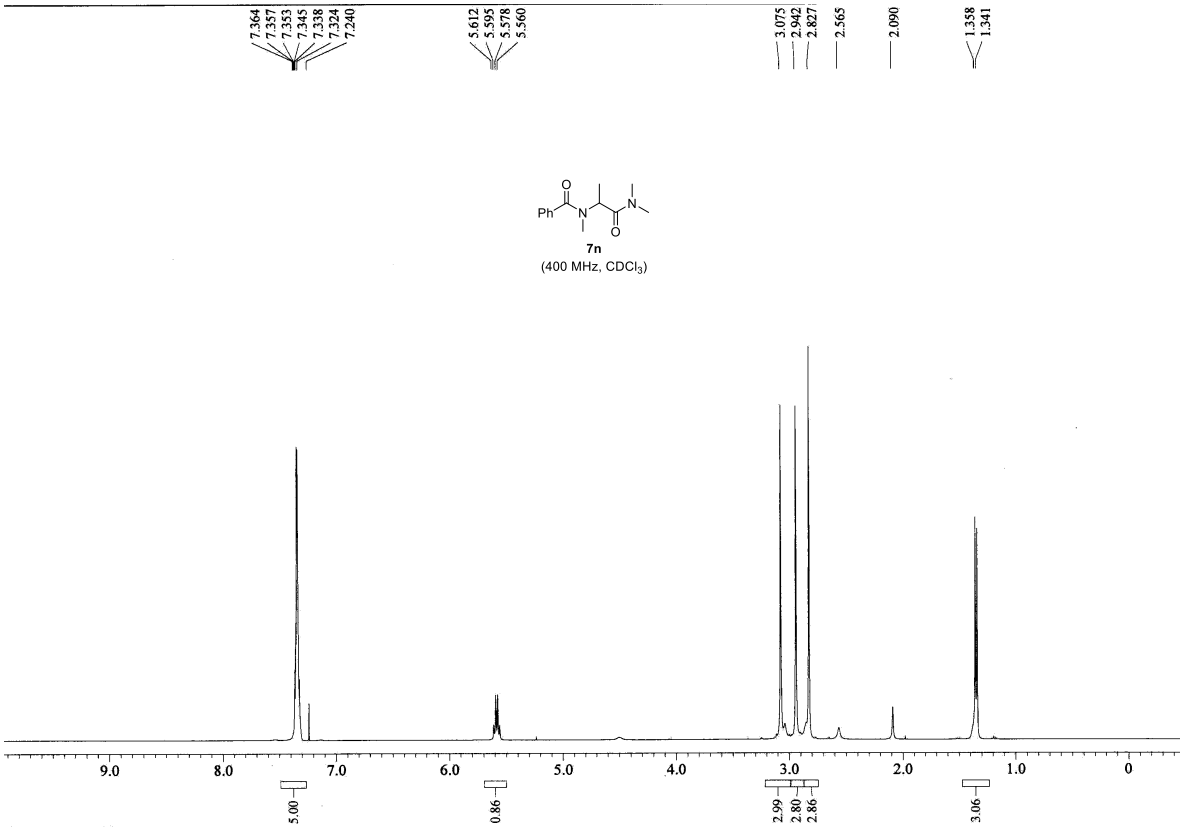



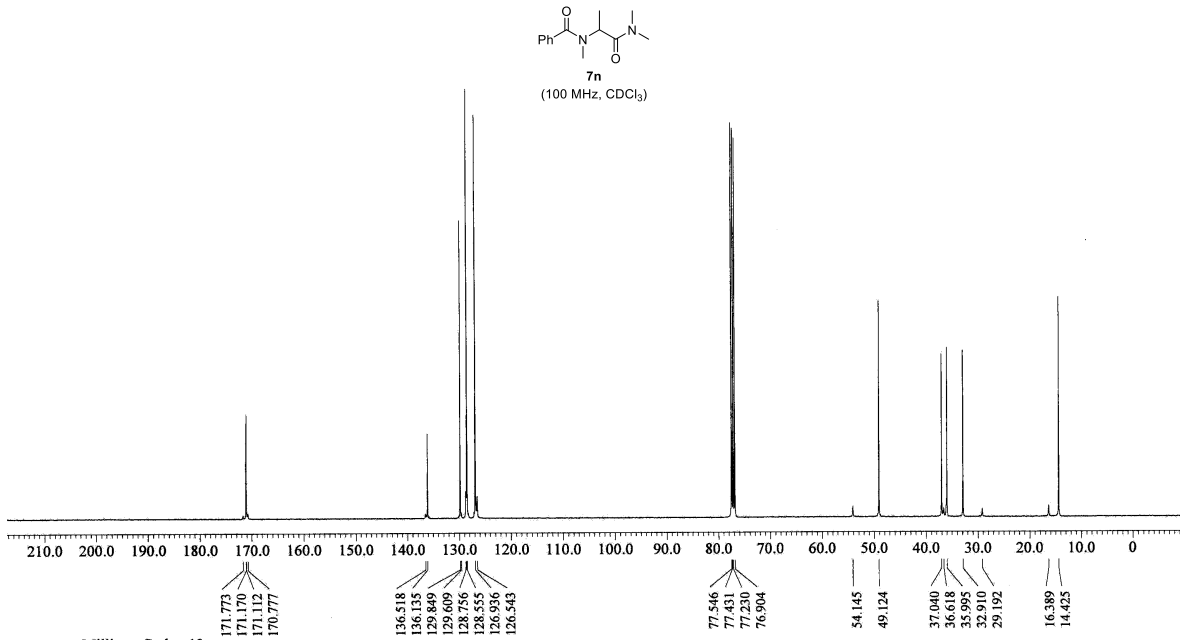
**7m**
(150 MHz, $CDCl_3$)

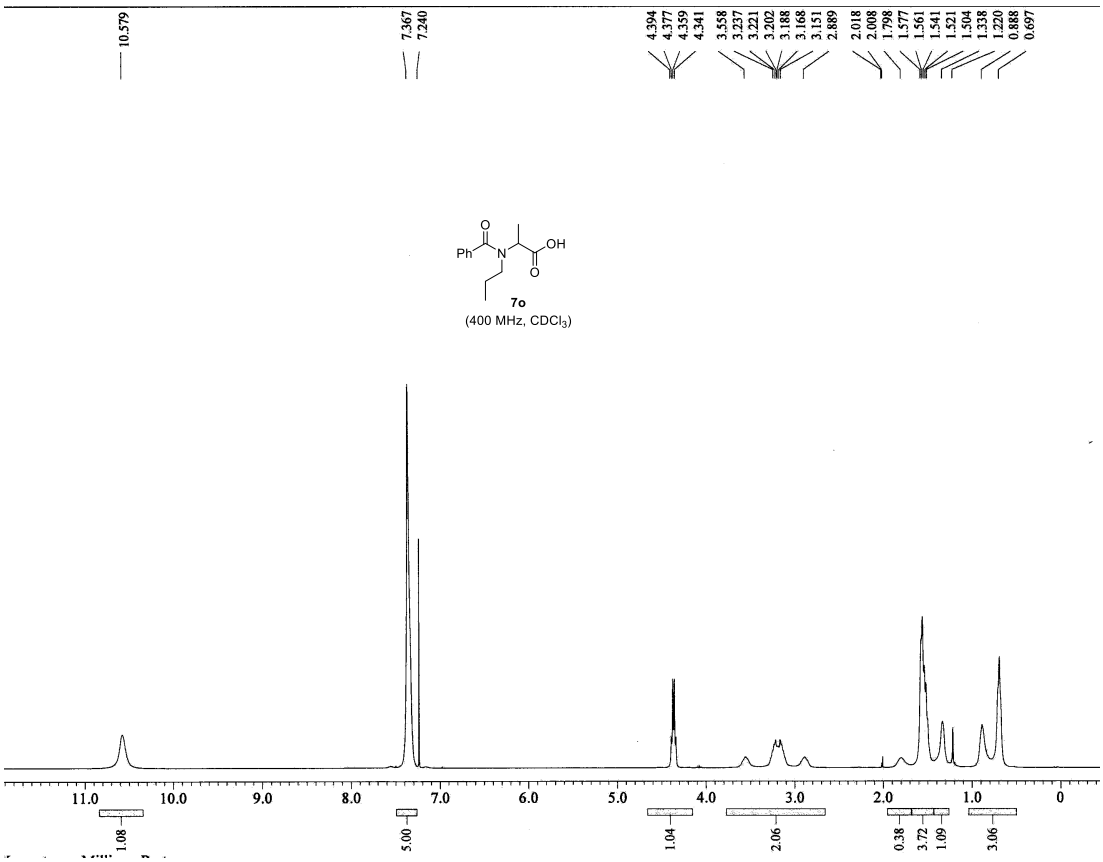


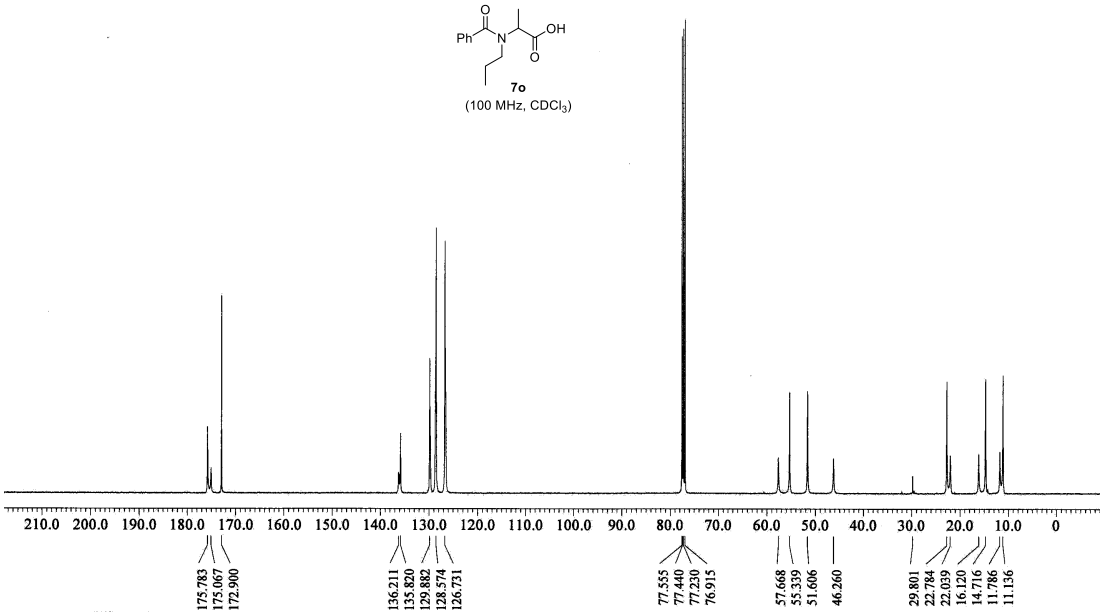

7.7725
7.7572
7.7547
7.4385
7.4242
7.4091
7.3708
7.3551
7.3404
7.2399
5.0460
5.0322
5.0183
5.0045
3.0555
2.9358
1.3779
1.3643
7n'
(500 MHz, CDCl3)
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
2.0000
1.0793
2.9231
1.0052
3.0428
3.0398
3.0434

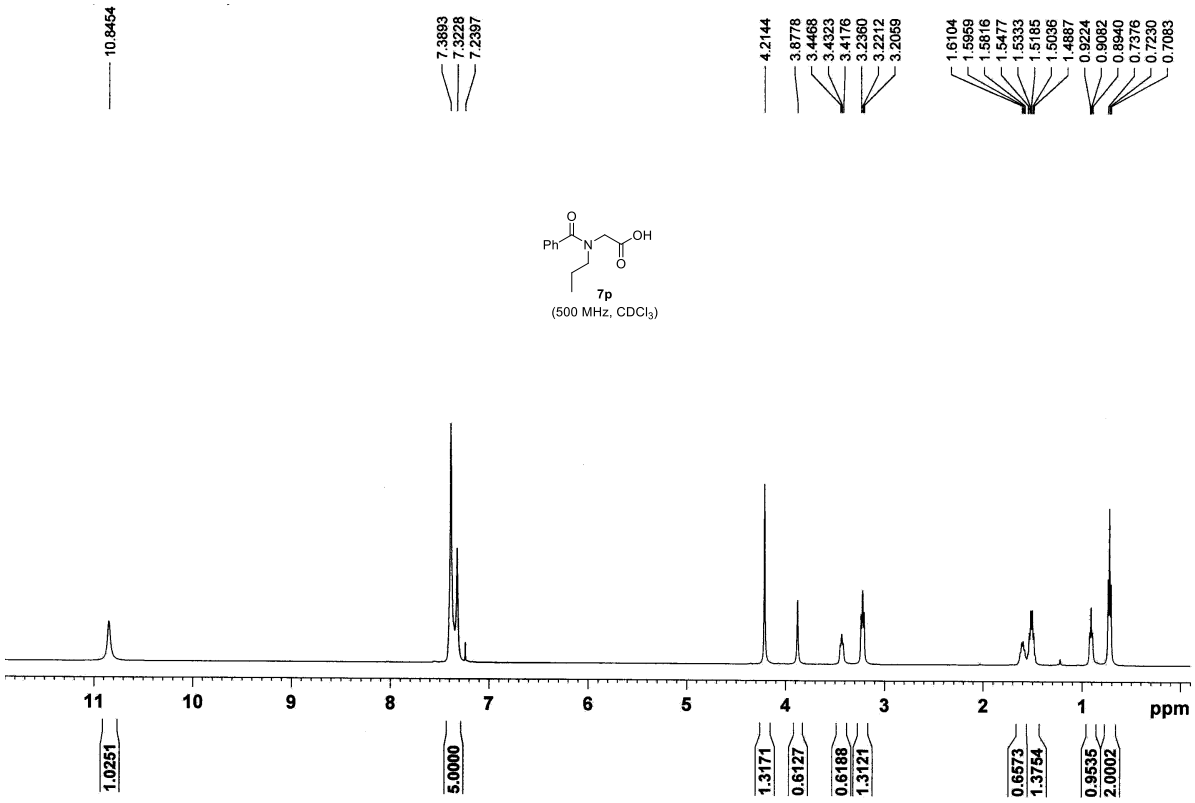

172.267
166.145
134.017
131.375
128.326
126.921
77.257
77.002
76.747
45.589
36.813
35.605
18.535
7n'
(125 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

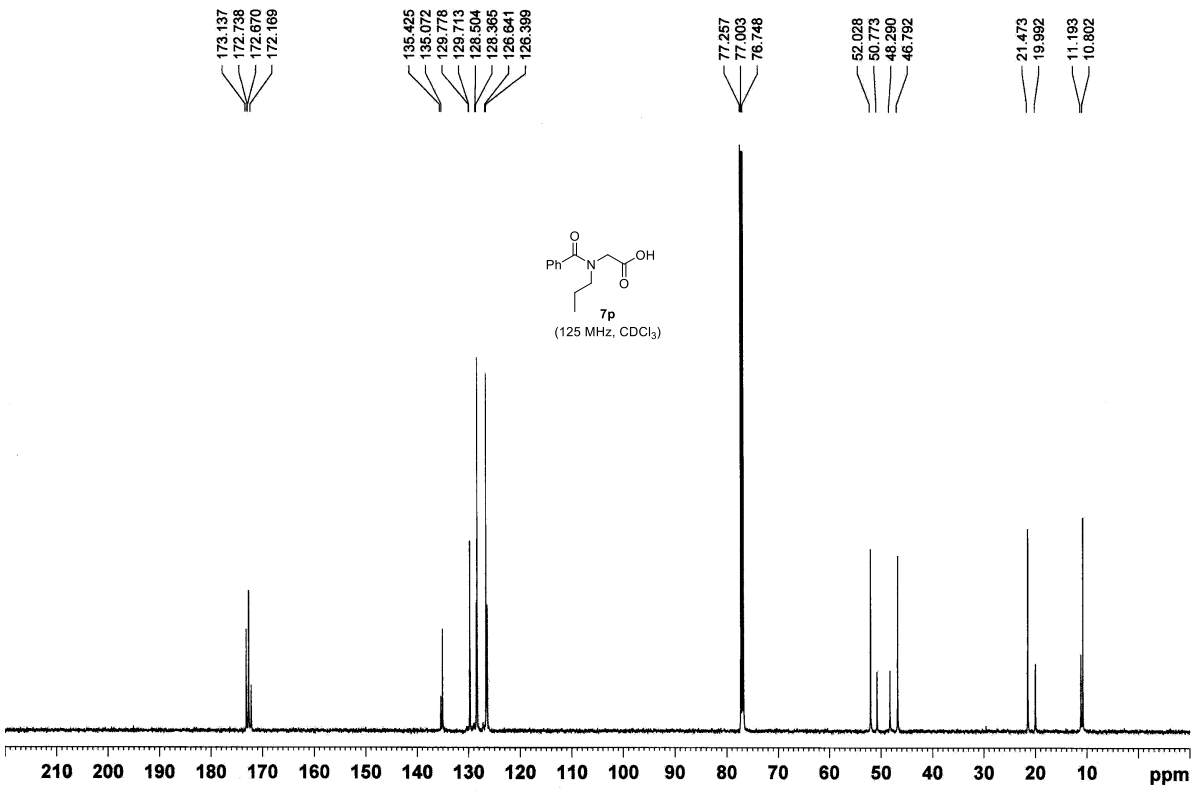

7.364
7.357
7.353
7.345
7.338
7.324
7.240
5.612
5.595
5.578
5.560
3.075
2.942
2.827
2.565
2.090
1.358
1.341
7n
(400 MHz, CDCl3)
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
5.00
0.86
2.99
2.80
2.86
3.06

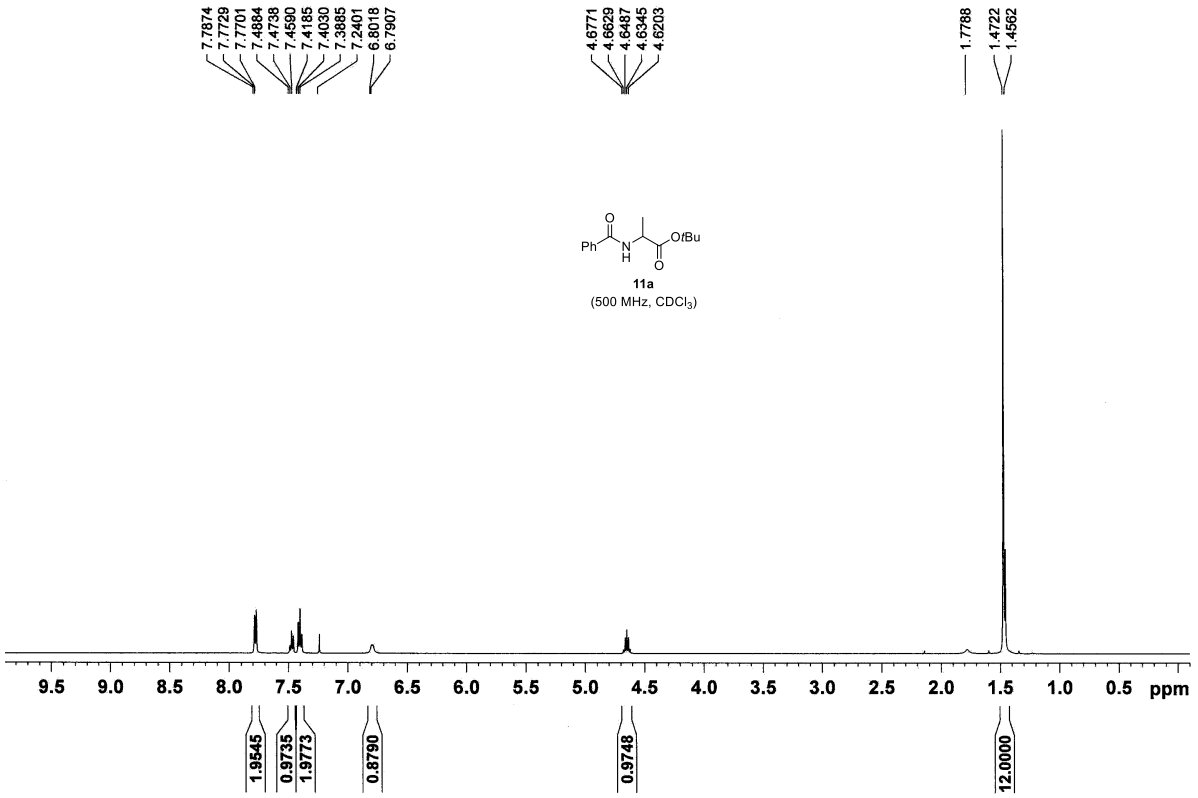

7n
(100 MHz, CDCl3)
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
171.773
171.170
171.112
170.777
136.518
136.135
129.849
129.609
128.756
128.555
126.936
126.543
77.546
77.431
77.230
76.904
54.145
49.124
37.040
36.618
35.995
32.910
29.192
16.389
14.425

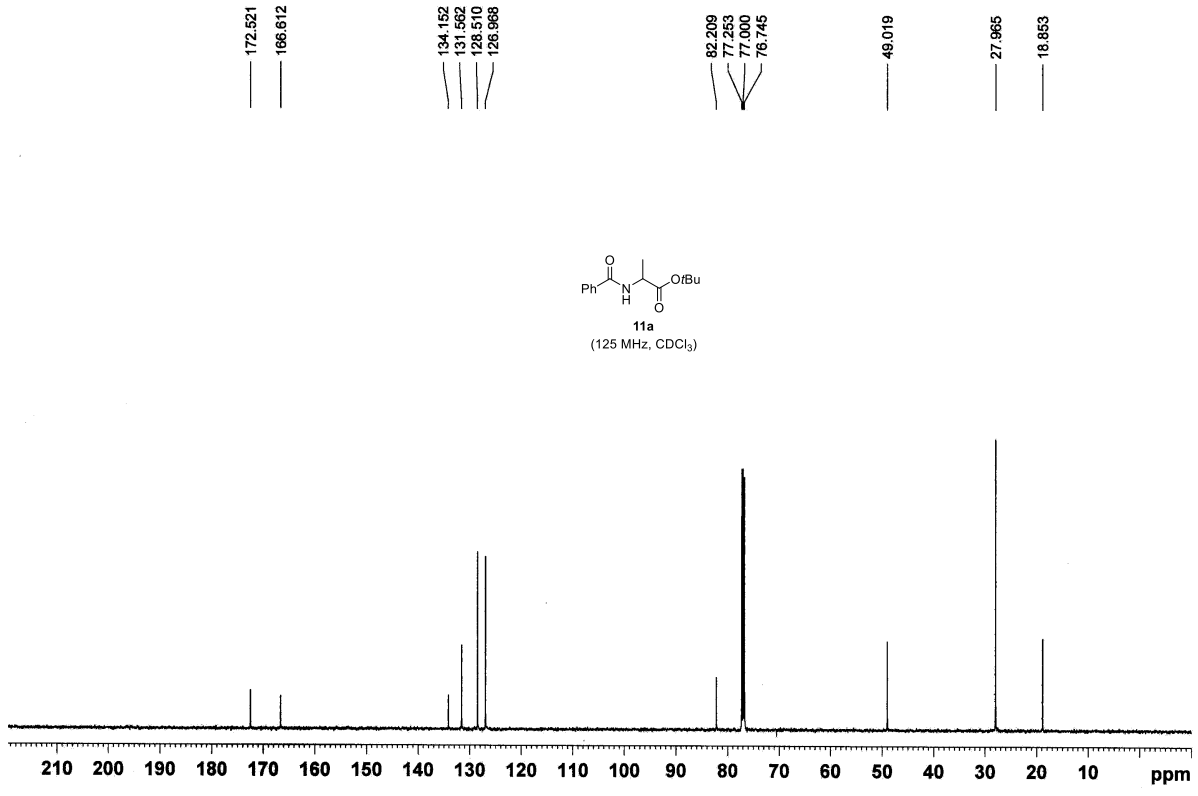

10.579
7.367
7.240
4.394
4.377
4.359
4.341
3.558
3.237
3.221
3.202
3.188
3.168
3.151
2.889
2.018
2.008
1.798
1.577
1.561
1.541
1.521
1.504
1.338
1.220
0.888
0.697
Ph
N
OH
O
O
7o
(400 MHz, CDCl3)
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
1.08
5.00
1.04
2.06
0.38
3.72
1.09
3.06

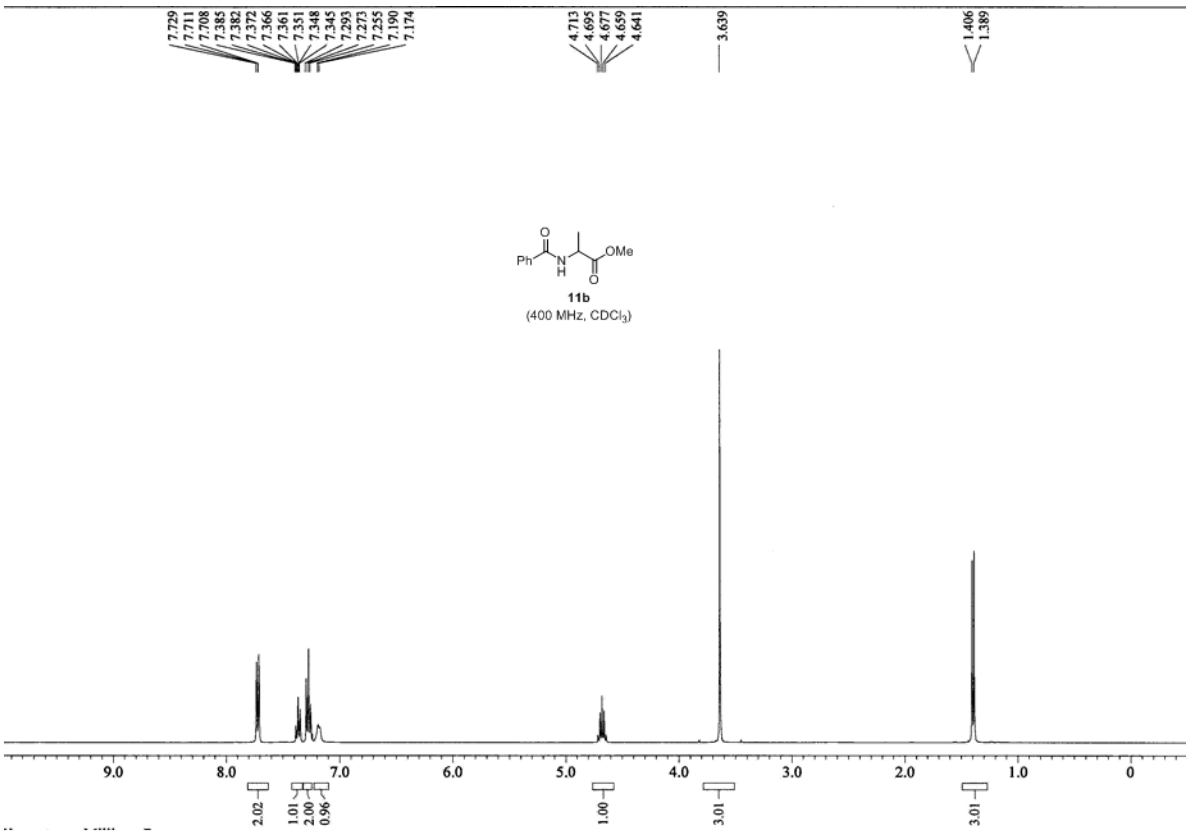

Ph
N
OH
O
O
7o
(100 MHz, CDCl3)
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
175.783
175.067
172.900
136.211
135.820
129.882
128.574
126.731
77.555
77.440
77.230
76.915
57.668
55.339
51.606
46.260
29.801
22.784
22.039
16.120
14.716
11.786
11.136

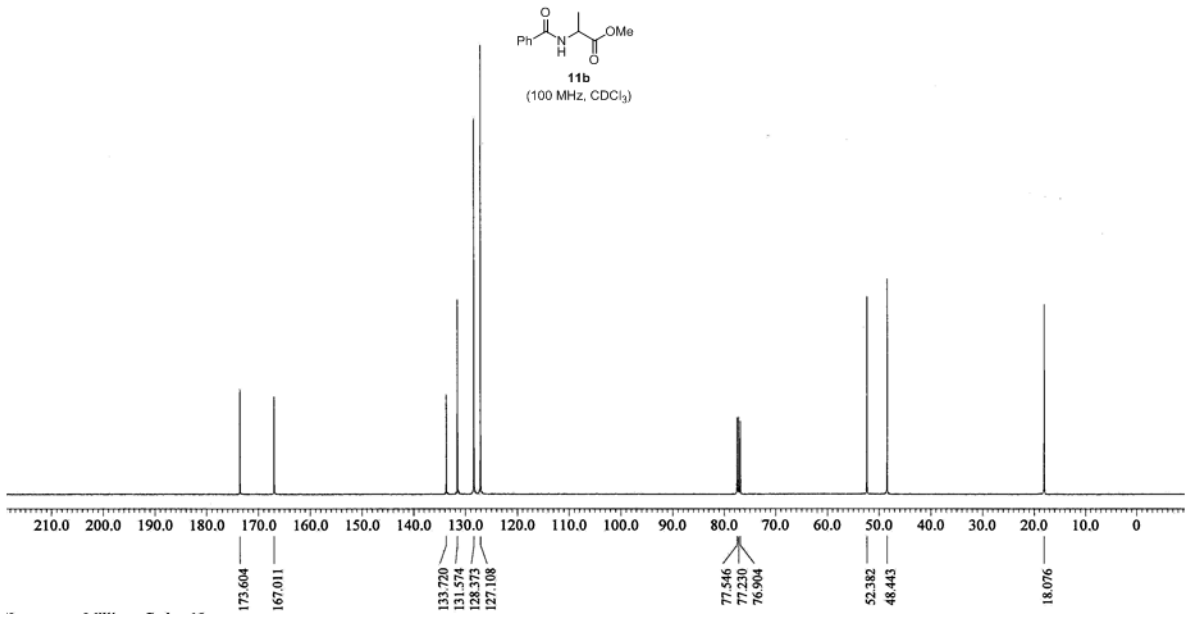

10.8454
7.3893
7.3228
7.2397
4.2144
3.8778
3.4468
3.4323
3.4176
3.2360
3.2212
3.2059
1.6104
1.5959
1.5816
1.5477
1.5333
1.5185
1.5036
1.4887
0.9224
0.9082
0.8940
0.7376
0.7230
0.7083
Ph
N
OH
O
O
7p
(500 MHz, CDCl3)
11
10
9
8
7
6
5
4
3
2
1
ppm
1.0251
5.0000
1.3171
0.6127
0.6188
1.3121
0.6573
1.3754
0.9535
2.0002

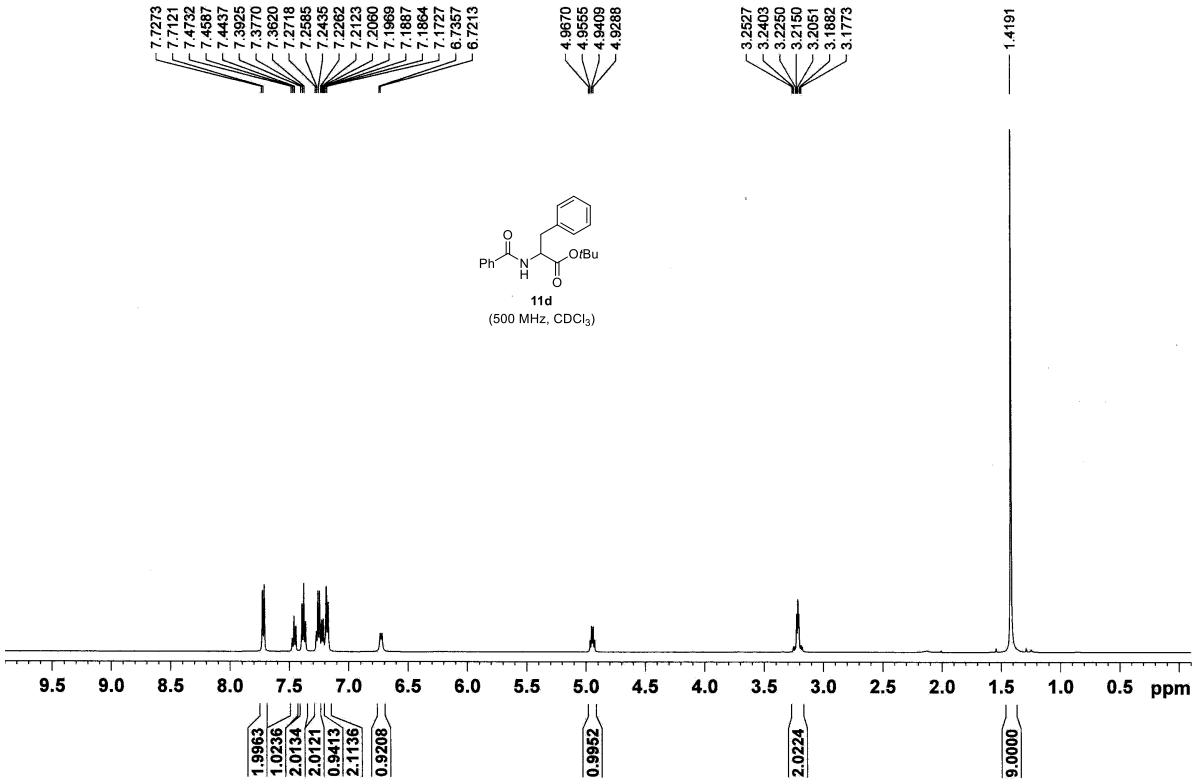

173.137
172.738
172.670
172.169
135.425
135.072
129.778
129.713
128.504
128.365
126.641
126.399
77.257
77.003
76.748
52.028
50.773
48.290
46.792
21.473
19.992
11.193
10.802
Ph
N
OH
O
O
7p
(125 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

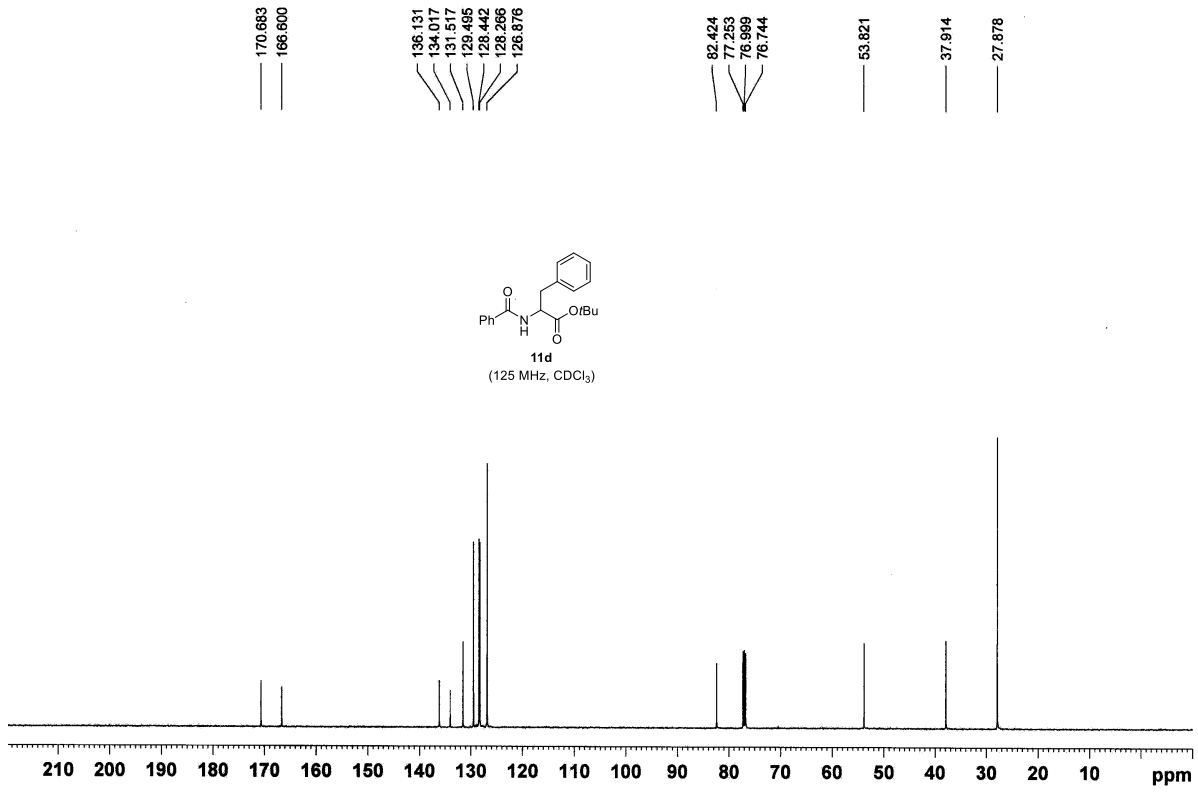

7.7874
7.7729
7.7701
7.4884
7.4738
7.4590
7.4185
7.4030
7.3885
7.2401
6.8018
6.7907
4.6771
4.6629
4.6487
4.6345
4.6203
1.7788
1.4722
1.4562
Ph
N
H
O
OtBu
11a
(500 MHz, CDCl3)
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.9545
0.9735
1.9773
0.8790
0.9748
12.0000

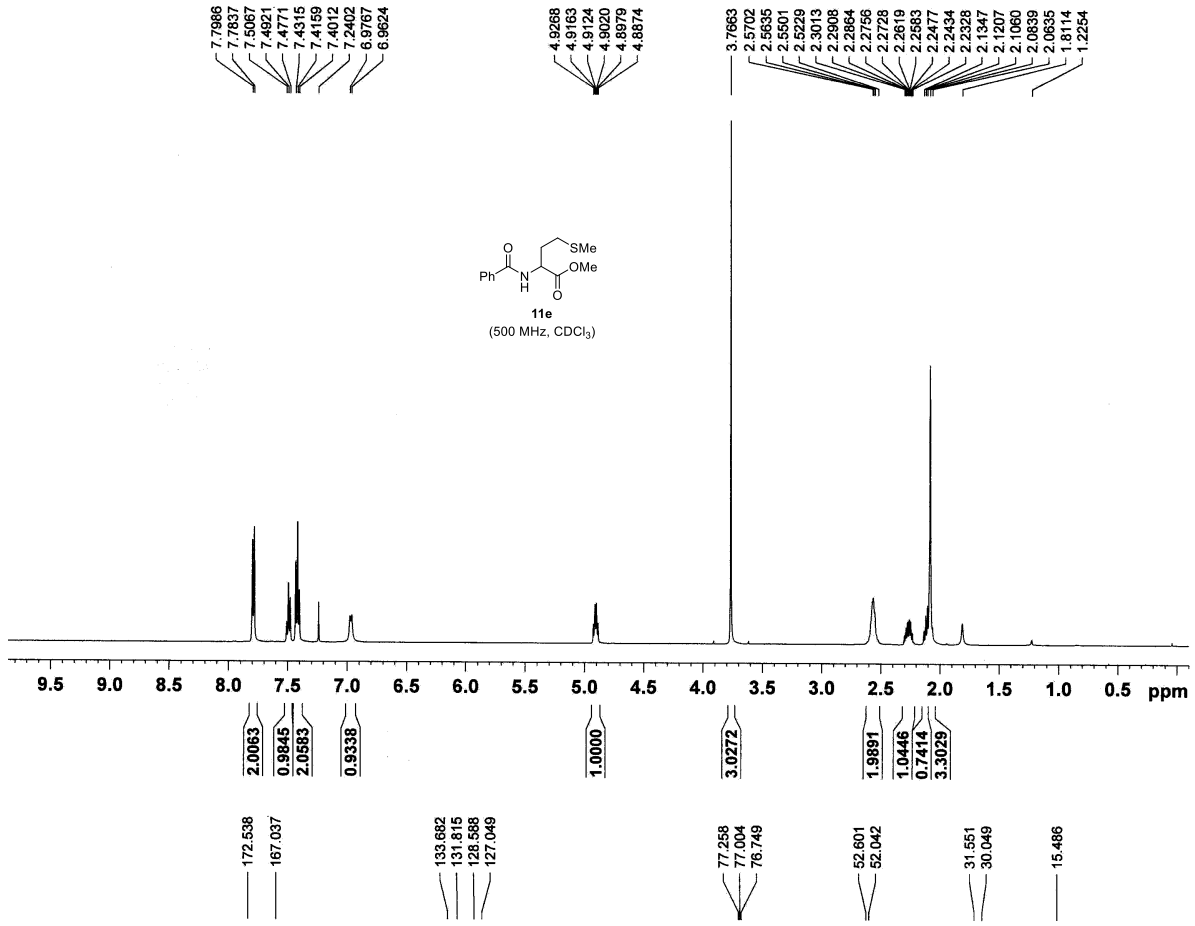

172.521
166.612
134.152
131.562
128.510
126.968
82.209
77.253
77.000
76.745
49.019
27.965
18.853
Ph
N
H
O
OtBu
11a
(125 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

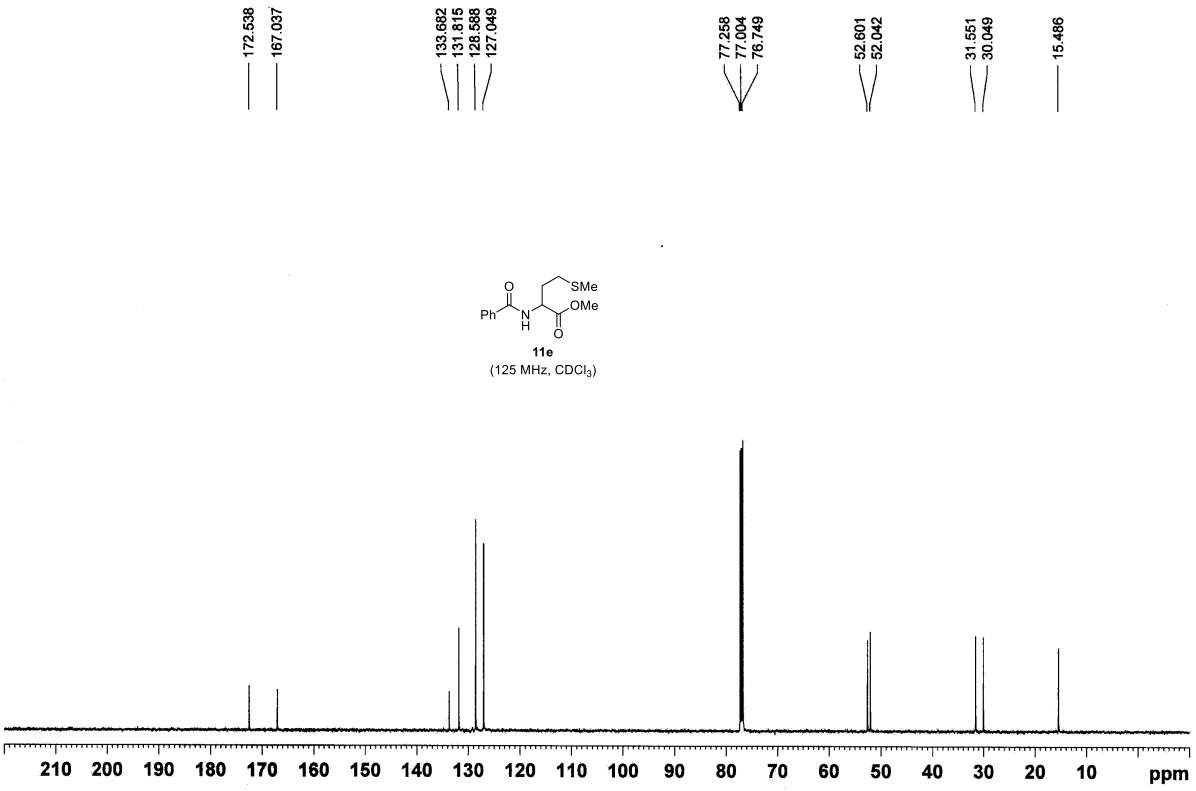

7.729
7.711
7.708
7.385
7.382
7.372
7.366
7.361
7.351
7.348
7.345
7.293
7.273
7.255
7.190
7.174
4.713
4.695
4.677
4.659
4.641
3.639
1.406
1.389
Ph
N
H
O
OMe
11b
(400 MHz, CDCl3)
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
2.02
1.01
2.00
0.96
1.00
3.01
3.01

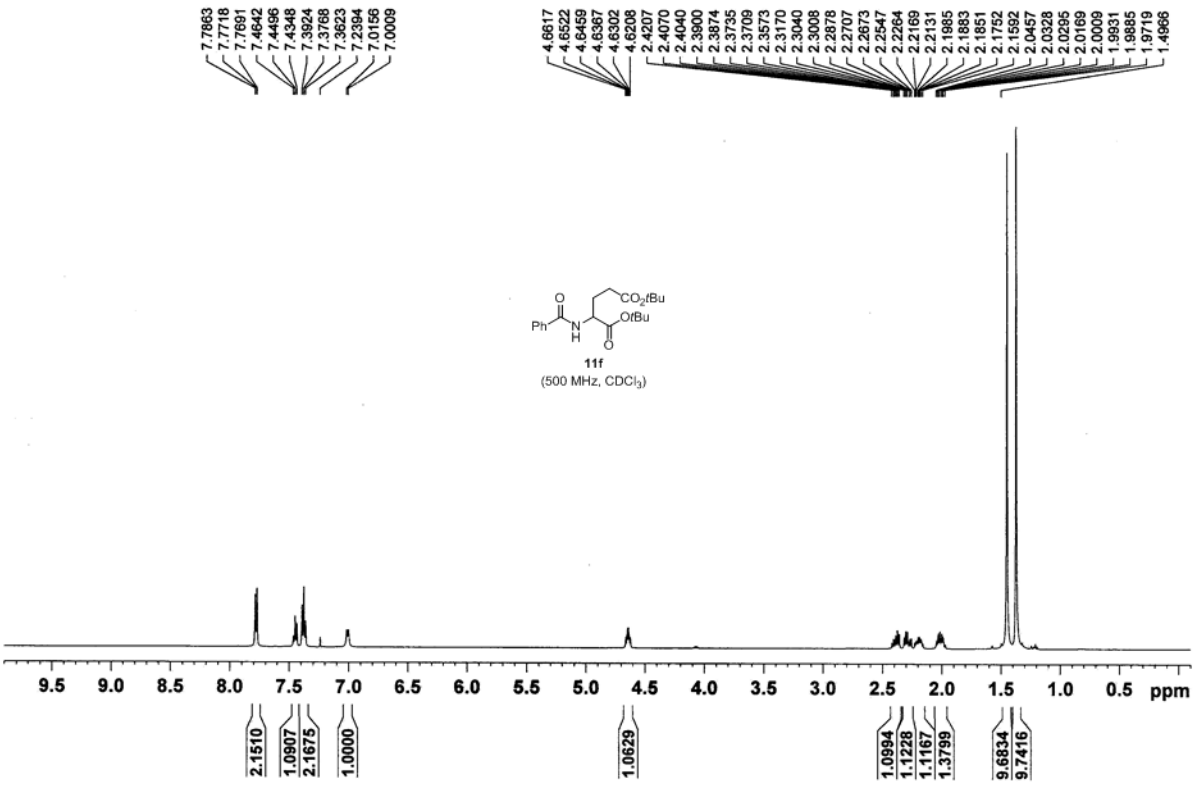

Ph
N
H
O
OMe
11b
(100 MHz, CDCl3)
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
173.604
167.011
133.720
131.574
128.373
127.108
77.546
77.230
76.904
52.382
48.443
18.076

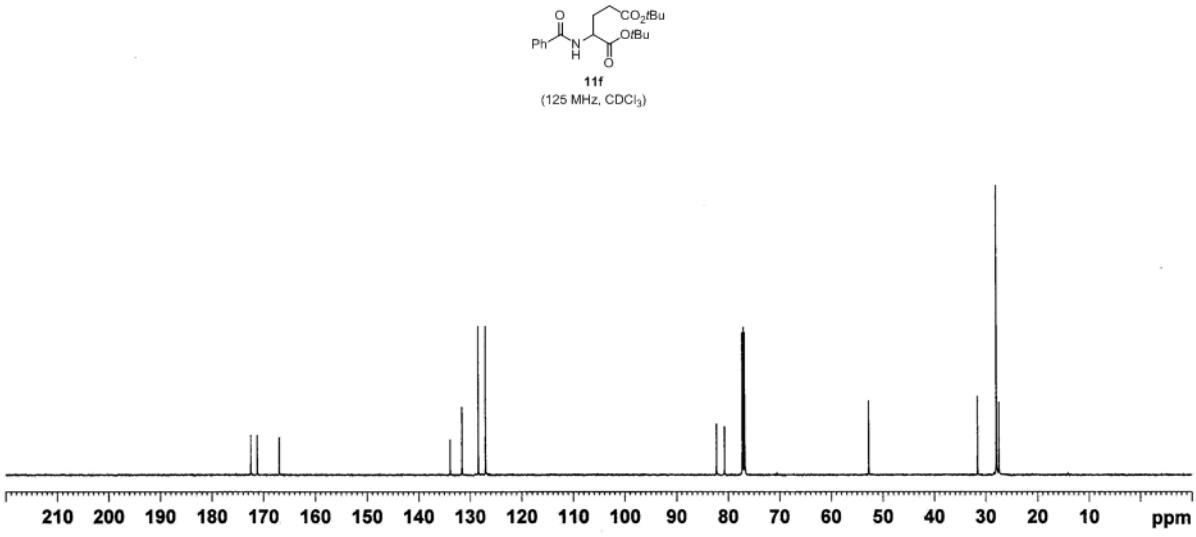

7.7273
7.7121
7.4732
7.4587
7.4437
7.3925
7.3770
7.3620
7.2718
7.2585
7.2435
7.2262
7.2123
7.2060
7.1969
7.1887
7.1864
7.1727
6.7357
6.7213
4.9670
4.9555
4.9409
4.9288
3.2527
3.2403
3.2250
3.2150
3.2051
3.1882
3.1773
1.4191
Ph
N
H
OtBu
11d
(500 MHz, CDCl3)
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.9963
1.0236
2.0134
2.0121
0.9413
2.1136
0.9208
0.9952
2.0224
9.0000

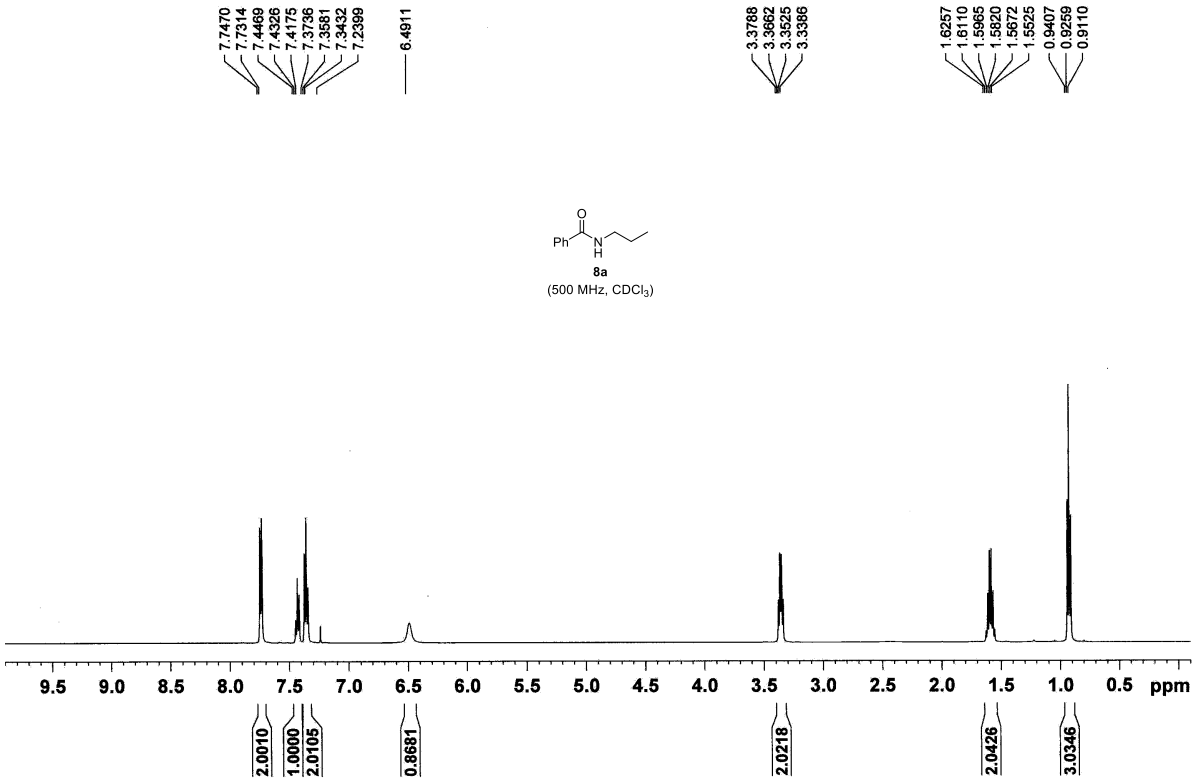

170.683
166.600
136.131
134.017
131.517
129.495
128.442
128.266
126.876
82.424
77.253
76.999
76.744
53.821
37.914
27.878
Ph
N
H
OtBu
11d
(125 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

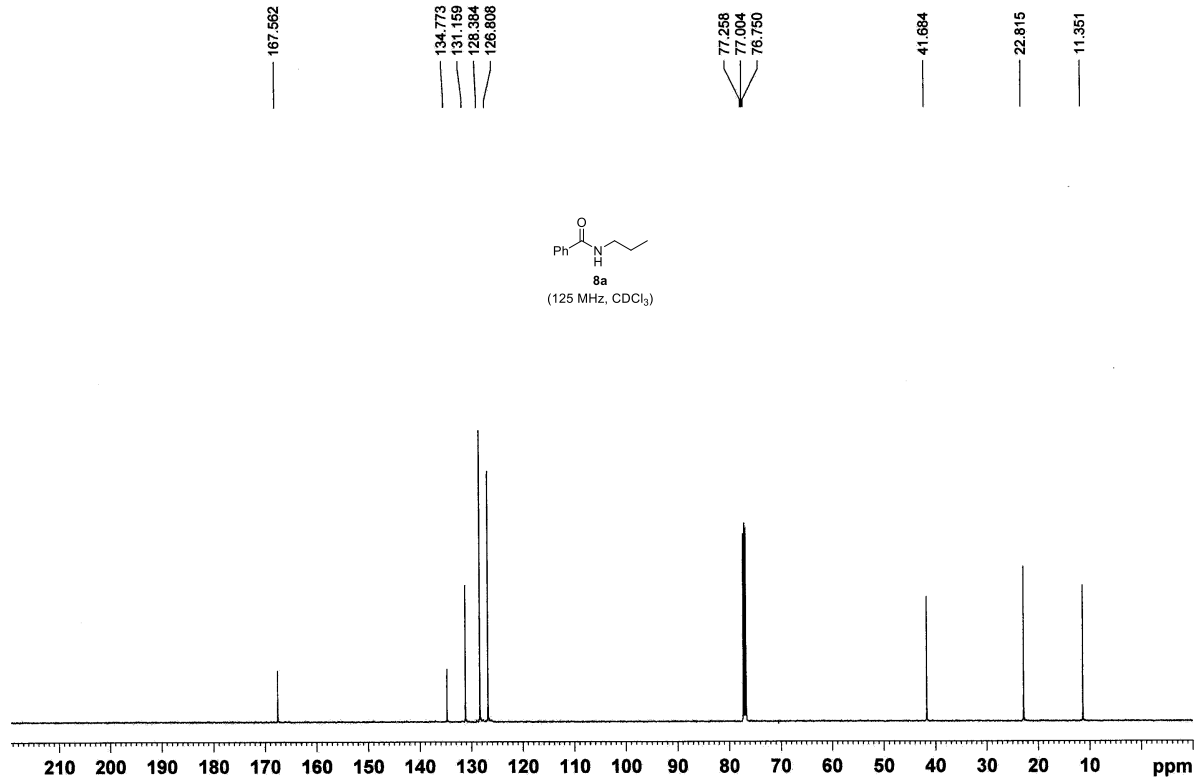

7.7986
7.7837
7.5067
7.4921
7.4771
7.4315
7.4159
7.4012
7.2402
6.9767
6.9624
4.9268
4.9163
4.9124
4.9020
4.8979
4.8874
3.7663
2.5702
2.5635
2.5501
2.5229
2.3013
2.2908
2.2864
2.2756
2.2728
2.2619
2.2583
2.2477
2.2434
2.2328
2.1347
2.1207
2.1060
2.0839
2.0635
1.8114
1.2254
SMe
OMe
Ph
N
H
O
11e
(500 MHz, CDCl3)
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 ppm
2.0063
0.9845
2.0583
0.9338
1.0000
3.0272
1.9891
1.0446
0.7414
3.3029

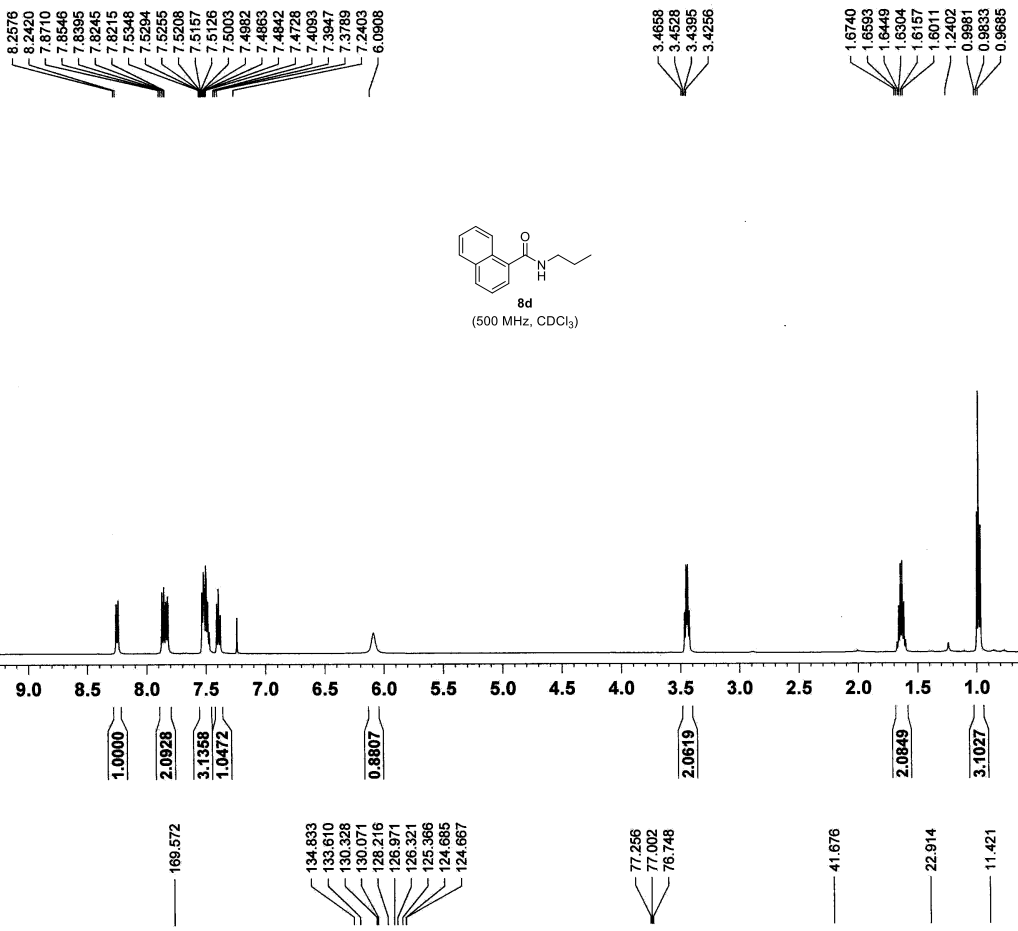

172.538
167.037
133.682
131.815
128.588
127.049
77.258
77.004
76.749
52.601
52.042
31.551
30.049
15.486
SMe
OMe
Ph
N
H
O
11e
(125 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

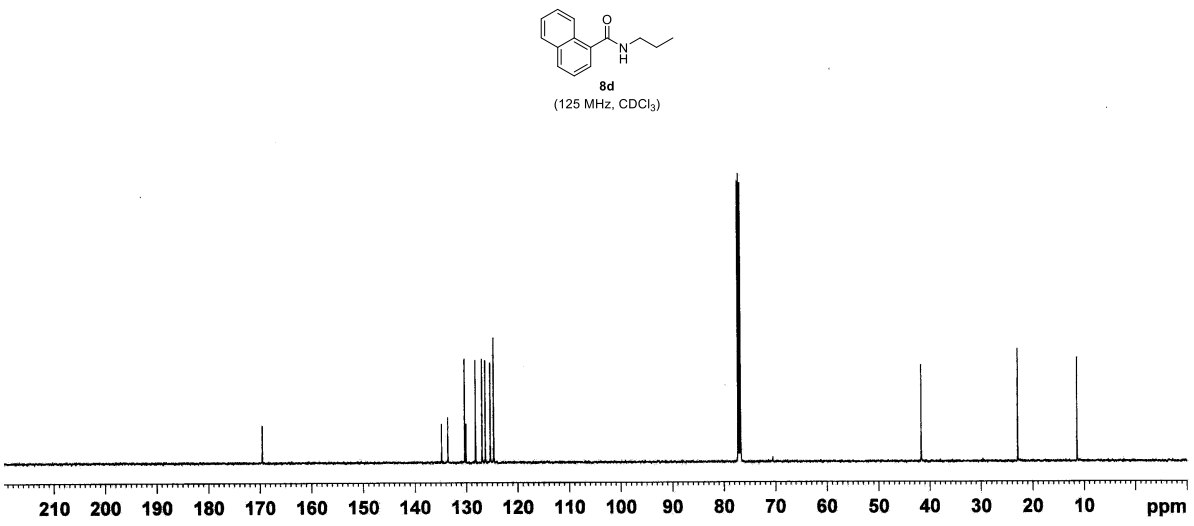

11f
(500 MHz, CDCl3)


11f
(125 MHz, CDCl3)

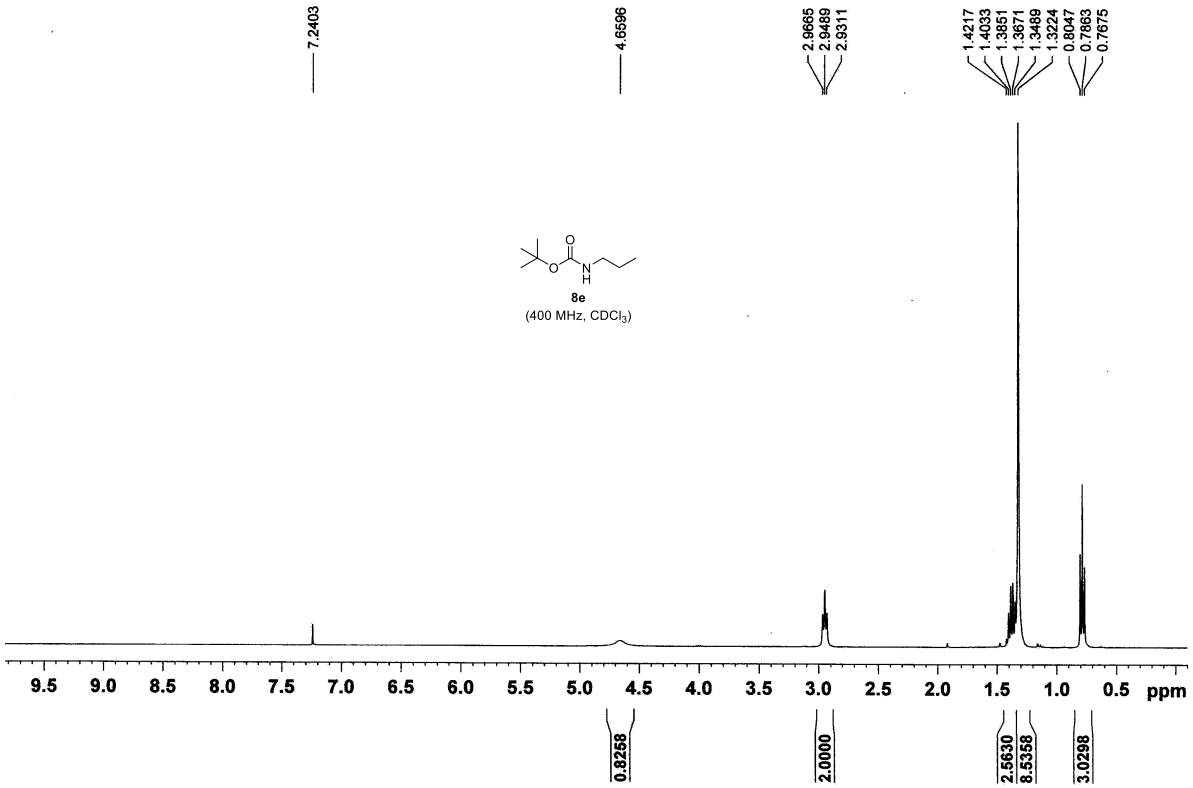

7.7470
7.7314
7.4469
7.4326
7.4175
7.3736
7.3581
7.3432
7.2399
6.4911
3.3788
3.3662
3.3525
3.3386
1.6257
1.6110
1.5965
1.5820
1.5672
1.5525
0.9407
0.9259
0.9110
Ph
N
H
O
8a
(500 MHz, CDCl3)
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
2.0010
1.0000
2.0105
0.8681
2.0218
2.0426
3.0346

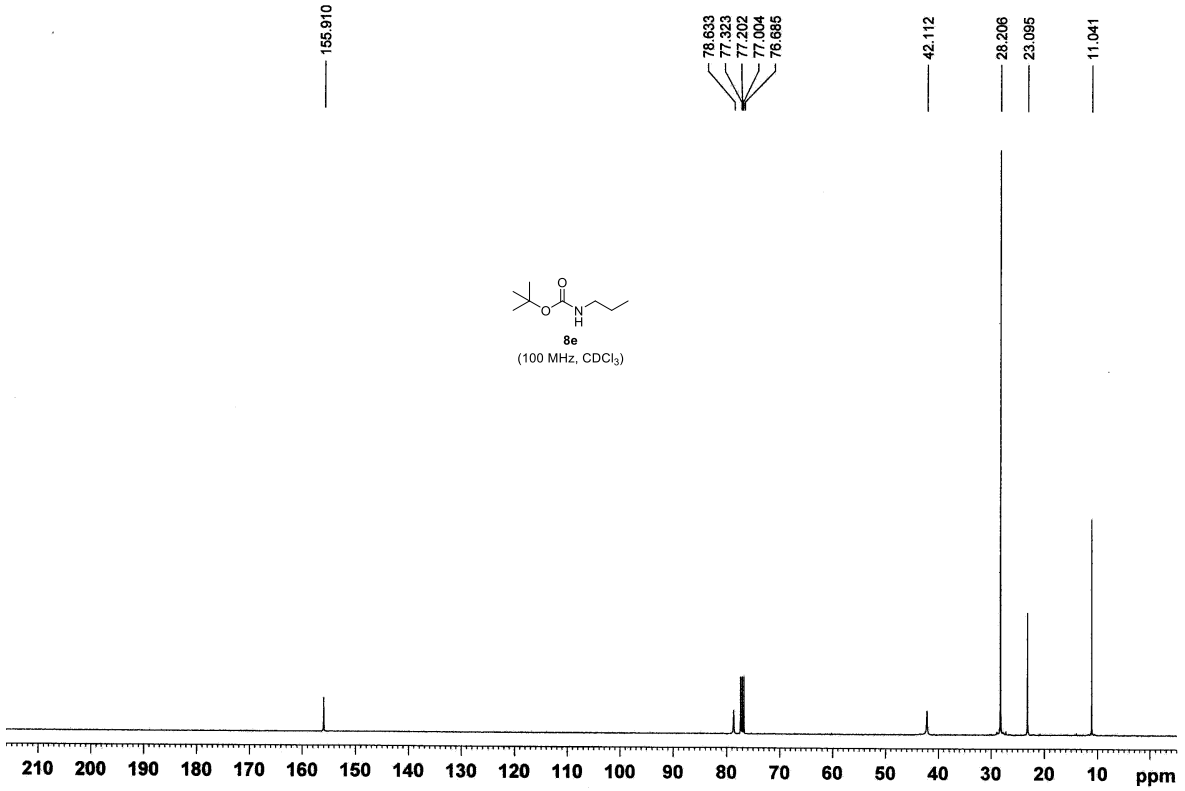

167.562
134.773
131.159
128.384
126.808
77.258
77.004
76.750
41.684
22.815
11.351
Ph
N
H
O
8a
(125 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

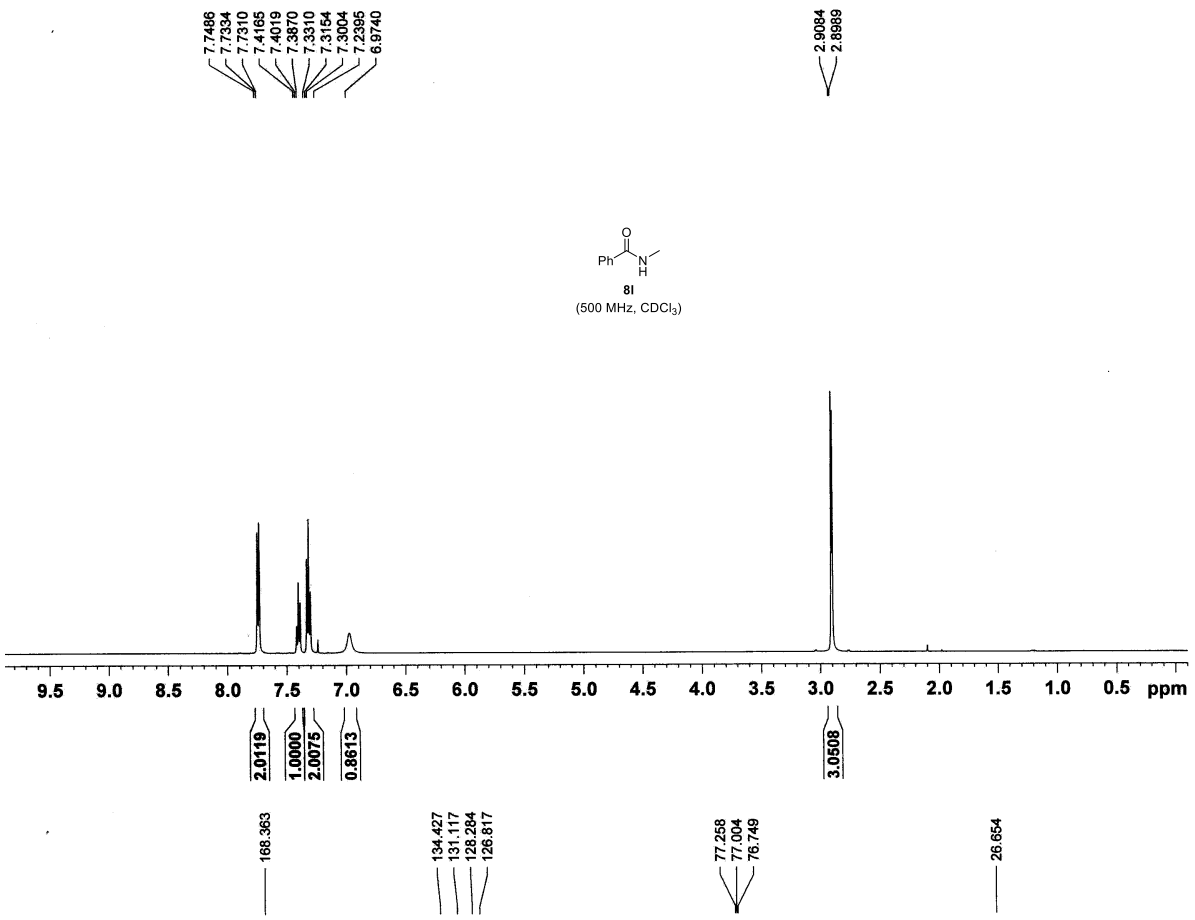

8.2576
8.2420
7.8710
7.8546
7.8395
7.8245
7.8215
7.5348
7.5294
7.5255
7.5208
7.5157
7.5126
7.5003
7.4982
7.4863
7.4842
7.4728
7.4093
7.3947
7.3789
7.2403
6.0908
3.4658
3.4528
3.4395
3.4256
1.6740
1.6593
1.6449
1.6304
1.6157
1.6011
1.2402
0.9981
0.9833
0.9685
8d
(500 MHz, CDCl3)
9.5 9.0 8.5 8.0 7.5 7.0 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 ppm
1.0000
2.0928
3.1358
1.0472
0.8807
2.0619
2.0849
3.1027

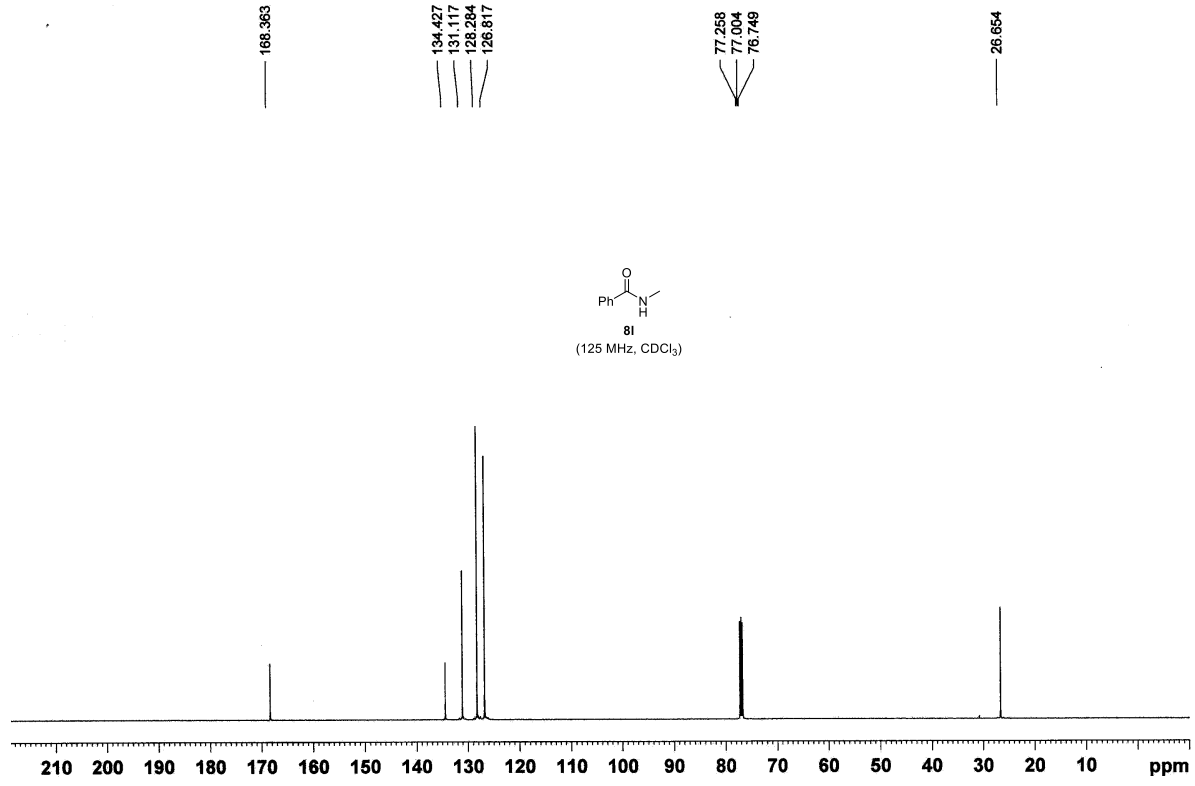

169.572
134.833
133.610
130.328
130.071
128.216
126.971
126.321
125.366
124.685
124.667
77.256
77.002
76.748
41.676
22.914
11.421

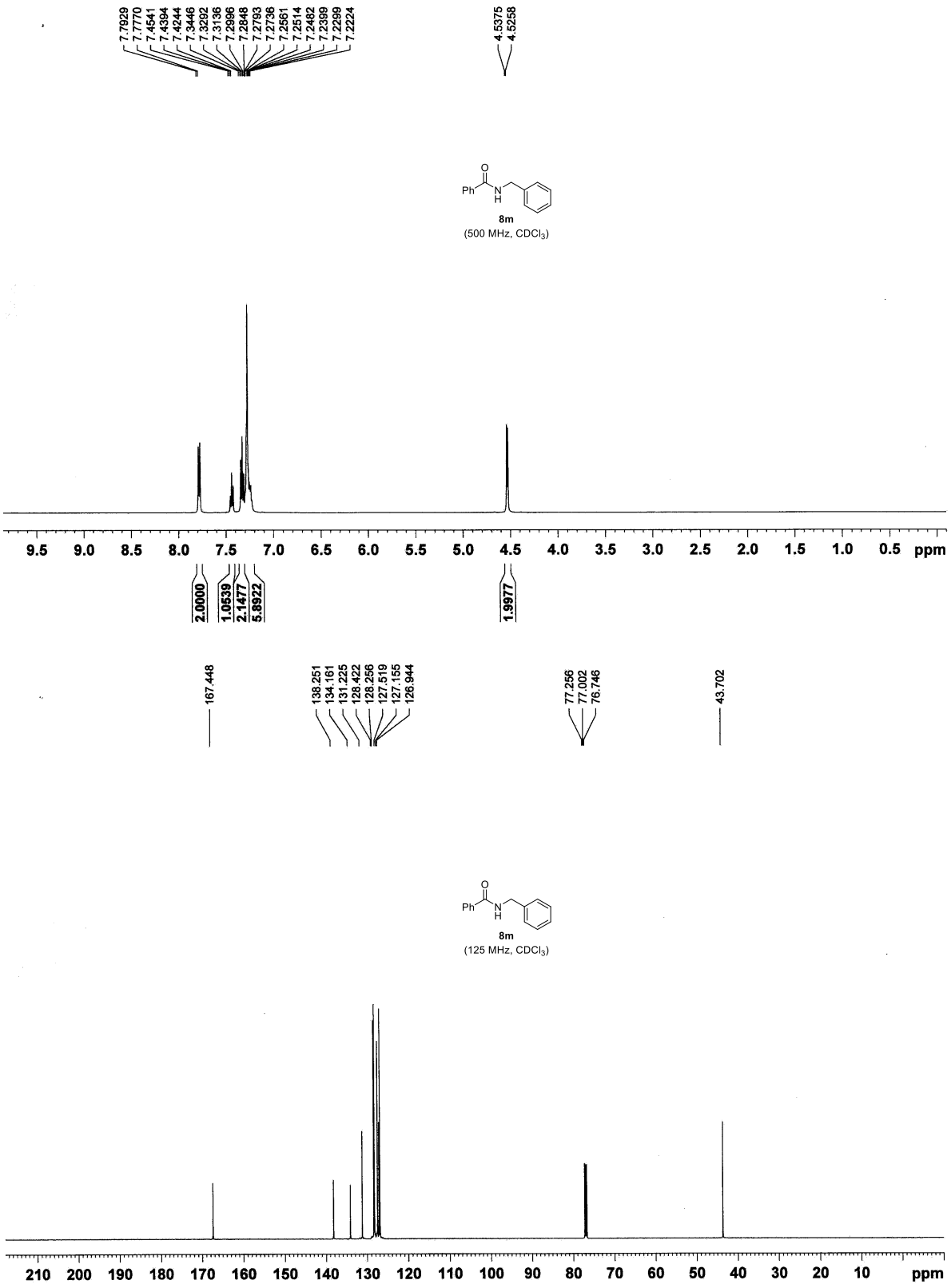

8d
(125 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

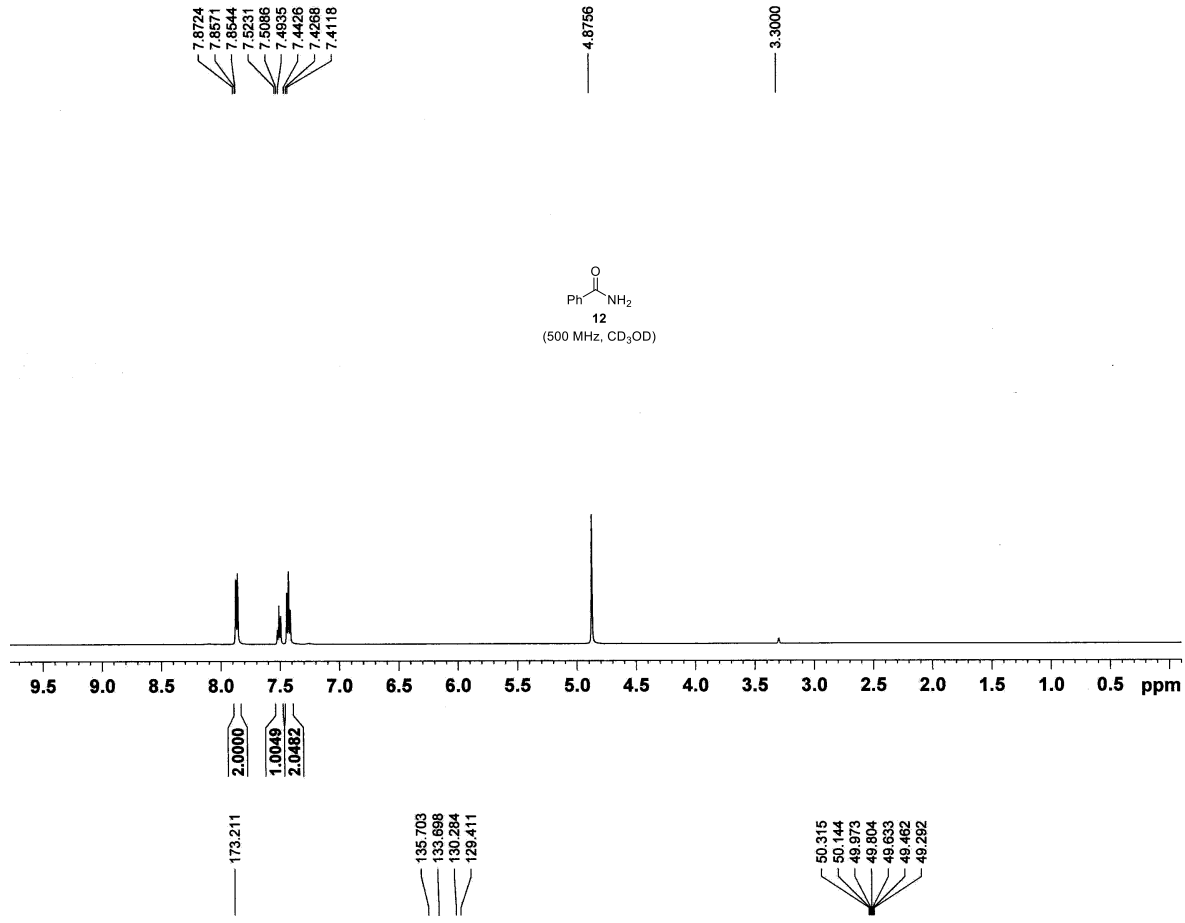

7.2403
4.6596
2.9665
2.9489
2.9311
1.4217
1.4033
1.3851
1.3671
1.3489
1.3224
0.8047
0.7863
0.7675
8e
(400 MHz, CDCl3)
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
0.8258
2.0000
2.5630
8.5358
3.0298

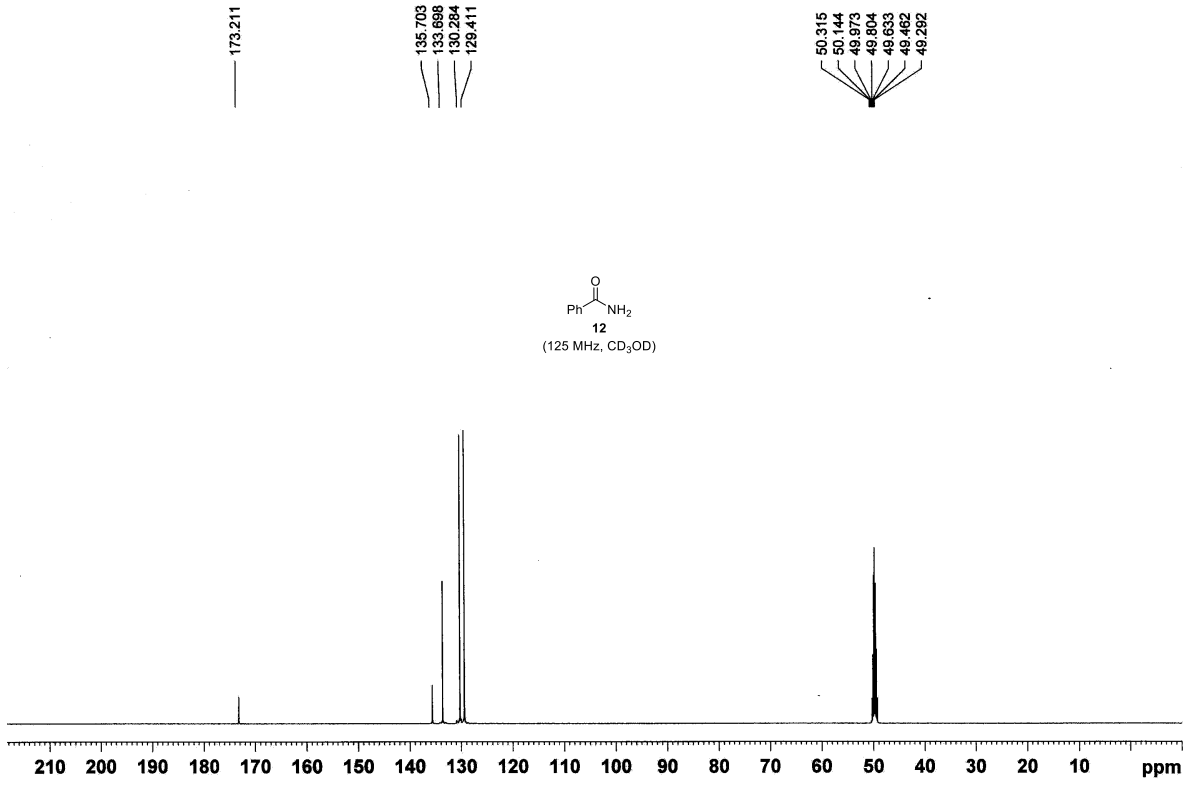

155.910
78.633
77.323
77.202
77.004
76.685
42.112
28.206
23.095
11.041
8e
(100 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

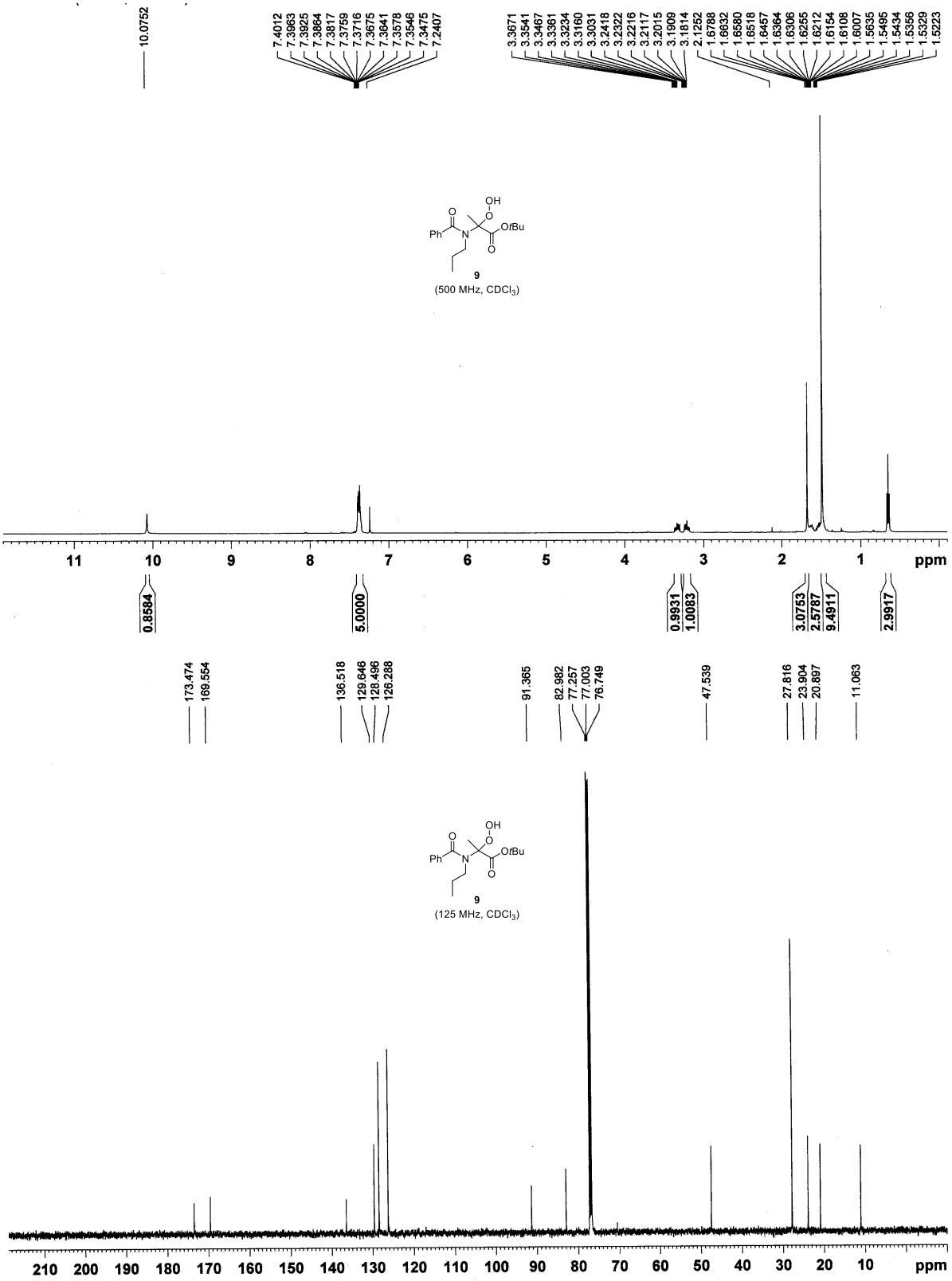

7.7486
7.7334
7.7310
7.4165
7.4019
7.3870
7.3310
7.3154
7.3004
7.2395
6.9740
2.9084
2.8989
Ph
N
H
8l
(500 MHz, CDCl3)
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
2.0119
1.0000
2.0075
0.8613
3.0508

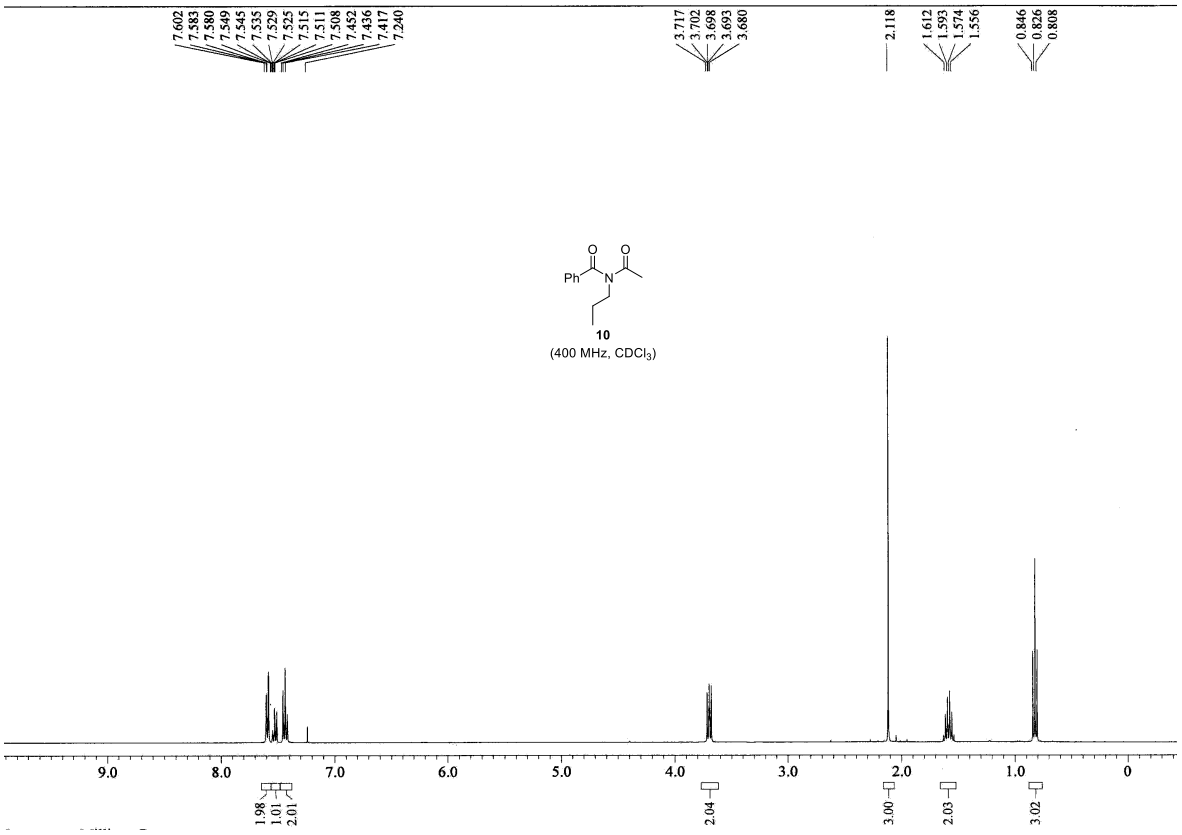

168.363
134.427
131.117
128.284
126.817
77.258
77.004
76.749
26.654
Ph
N
H
8l
(125 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

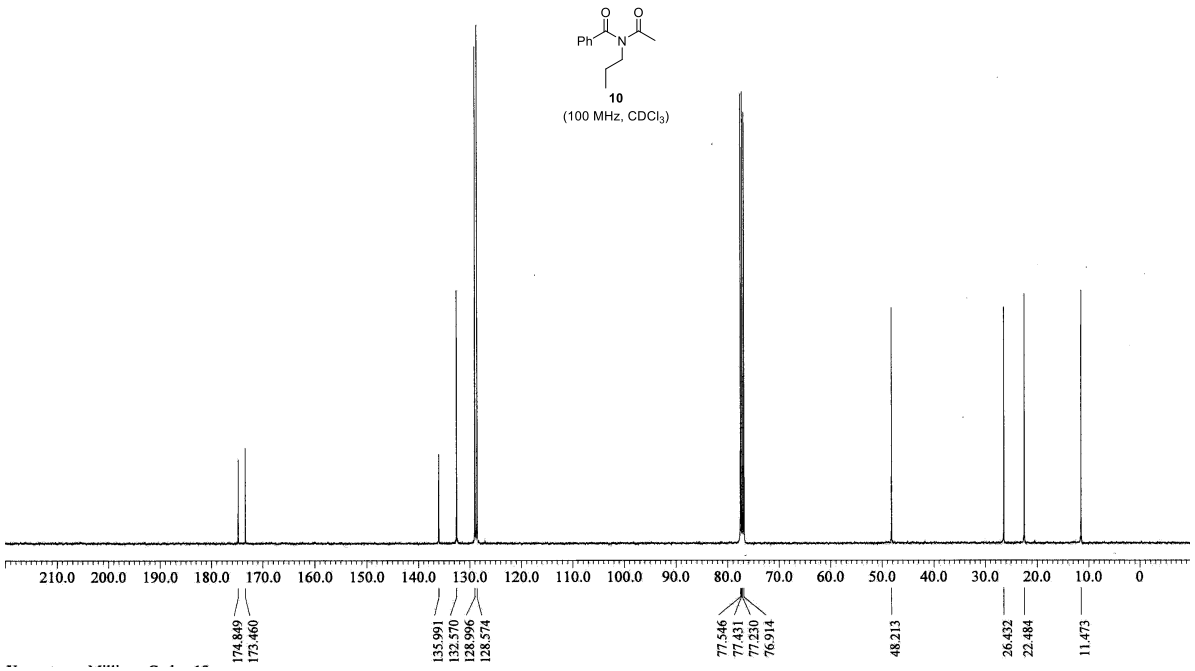

7.7929
7.7770
7.4541
7.4394
7.4244
7.3446
7.3292
7.3136
7.2896
7.2848
7.2793
7.2736
7.2561
7.2514
7.2482
7.2399
7.2299
7.2224
4.5375
4.5258
8m
(500 MHz, CDCl3)
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
2.0000
1.0539
2.1477
5.8922
1.9977
167.448
138.251
134.161
131.225
128.422
128.256
127.519
127.155
126.944
77.256
77.002
76.746
43.702
8m
(125 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

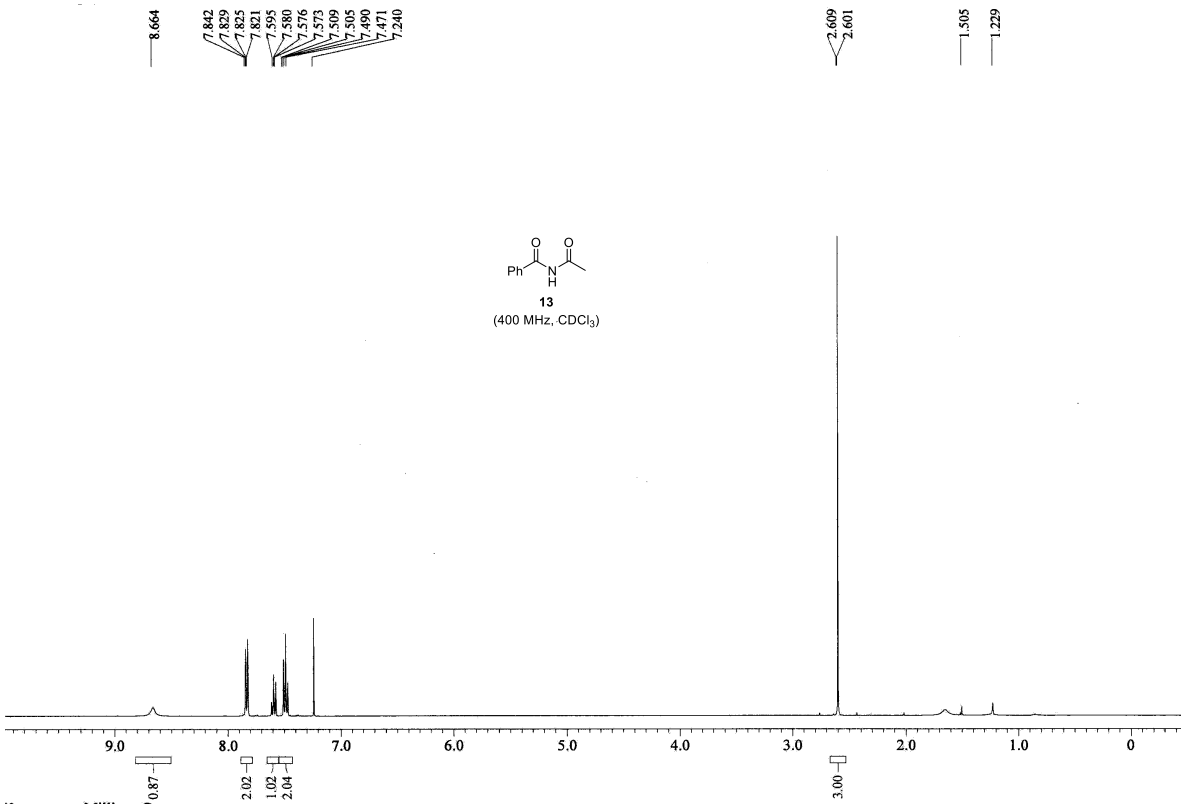

7.8724
7.8571
7.8544
7.5231
7.5086
7.4835
7.4426
7.4268
7.4118
4.8756
3.3000
O
Ph
NH2
12
(500 MHz, CD3OD)
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
2.0000
1.0049
2.0482

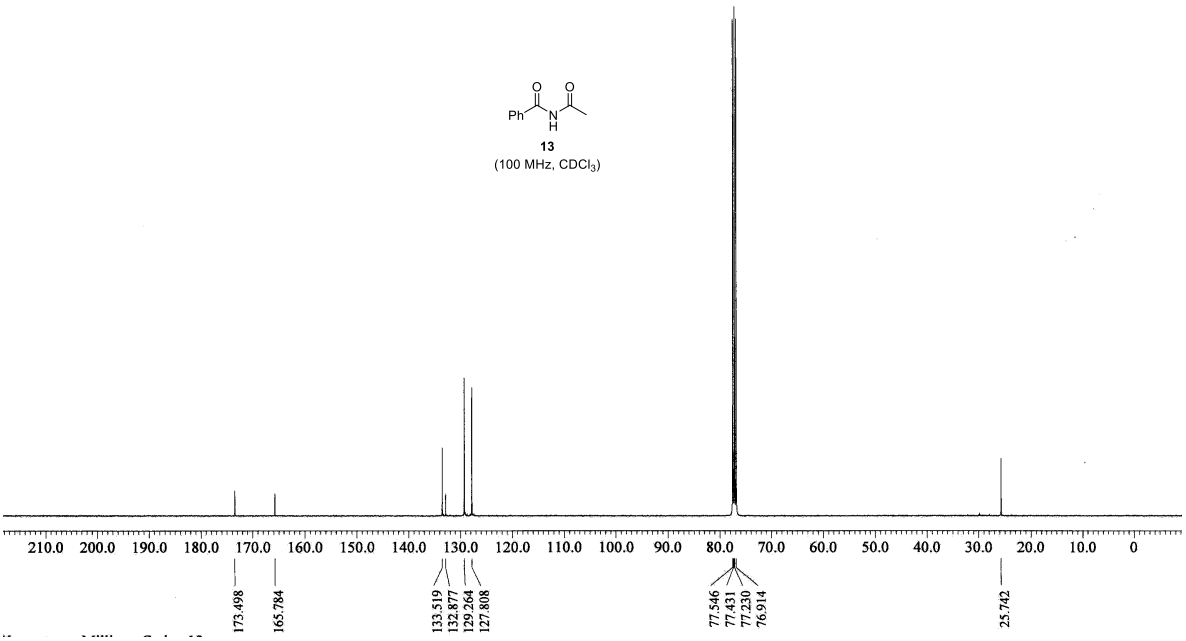

173.211
135.703
133.698
130.284
129.411
50.315
50.144
49.973
49.804
49.633
49.462
49.292
O
Ph
NH2
12
(125 MHz, CD3OD)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

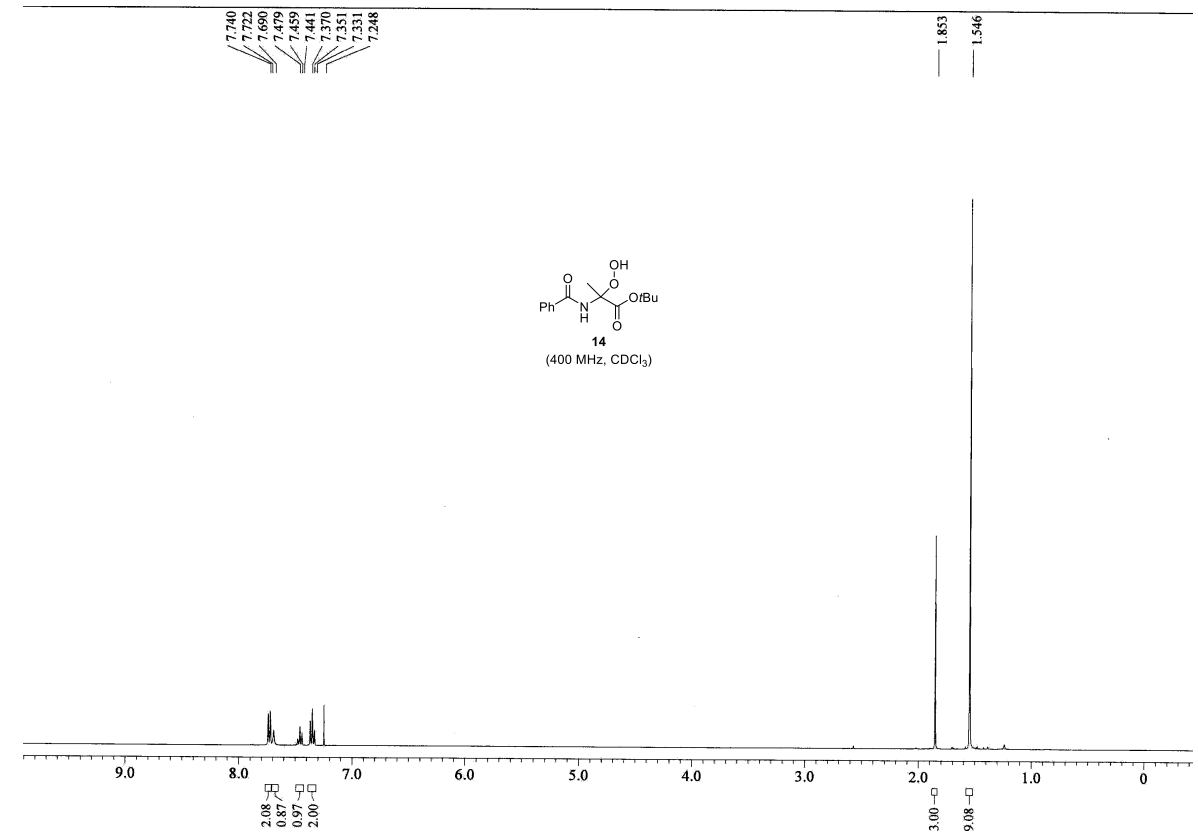

10.0752
7.4012
7.3963
7.3925
7.3864
7.3817
7.3759
7.3716
7.3675
7.3641
7.3578
7.3546
7.3475
7.2407
3.3671
3.3541
3.3467
3.3361
3.3234
3.3160
3.3031
3.2418
3.2322
3.2216
3.2117
3.2015
3.1909
3.1814
2.1252
1.6788
1.6632
1.6580
1.6518
1.6457
1.6364
1.6306
1.6255
1.6212
1.6154
1.6108
1.6007
1.5635
1.5495
1.5434
1.5356
1.5329
1.5223
OH
O
O
Ph
N
OtBu
O
9
(500 MHz, CDCl3)
11
10
9
8
7
6
5
4
3
2
1
ppm
0.8584
5.0000
0.9931
1.0083
3.0753
2.5787
9.4911
2.9917
173.474
169.554
136.518
129.646
128.496
126.288
91.365
82.982
77.257
77.003
76.749
47.539
27.816
23.904
20.897
11.063
OH
O
O
Ph
N
OtBu
O
9
(125 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

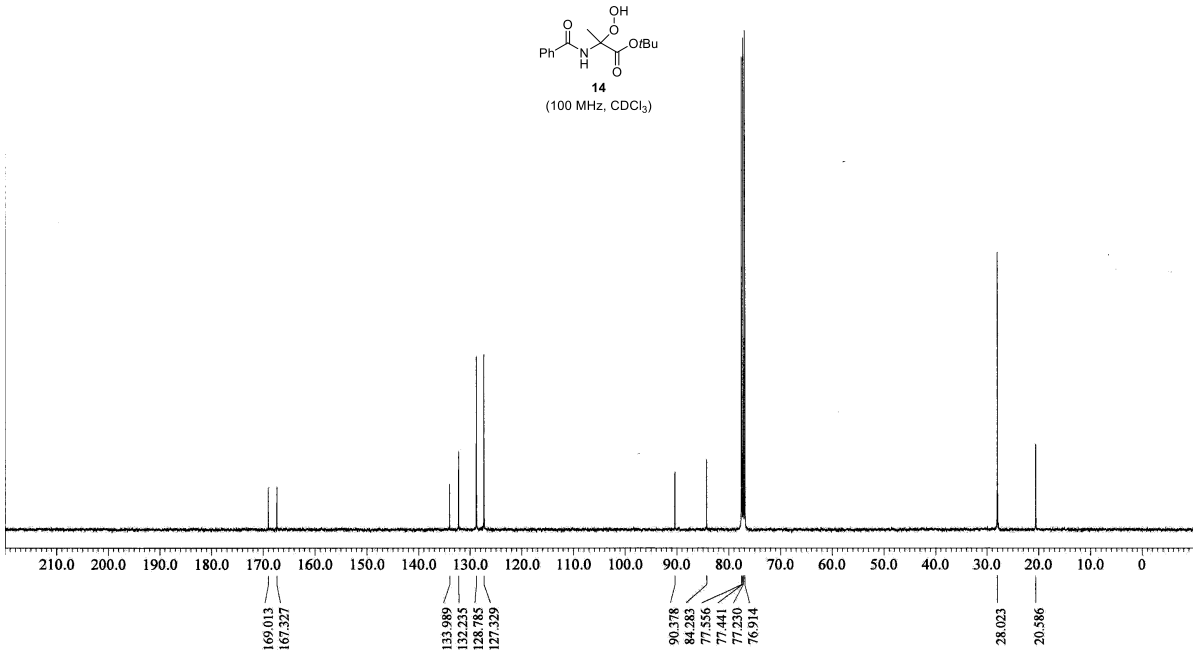

7.602
7.583
7.580
7.549
7.545
7.535
7.529
7.525
7.515
7.511
7.508
7.452
7.436
7.417
7.240
3.717
3.702
3.698
3.693
3.680
2.118
1.612
1.593
1.574
1.556
0.846
0.826
0.808
Ph
O
N
10
(400 MHz, CDCl3)
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
1.98
1.01
2.01
2.04
3.00
2.03
3.02


Ph
O
N
10
(100 MHz, CDCl3)
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
174.849
173.460
135.991
132.570
128.996
128.574
77.546
77.431
77.230
76.914
48.213
26.432
22.484
11.473


8.664
7.842
7.829
7.825
7.821
7.595
7.580
7.576
7.573
7.509
7.505
7.490
7.471
7.240
2.609
2.601
1.505
1.229
Ph
13
(400 MHz, CDCl3)
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
0.87
2.02
1.02
2.04
3.00


Ph
13
(100 MHz, CDCl3)
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
173.498
165.784
133.519
132.877
129.264
127.808
77.546
77.431
77.230
76.914
25.742


7.740
7.722
7.690
7.479
7.459
7.441
7.370
7.351
7.331
7.248
1.853
1.546
OH
O
Ph
N
H
O
O
OtBu
14
(400 MHz, CDCl3)
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
2.08
0.87
0.97
2.00
3.00
9.08


OH
O
Ph
N
H
O
O
OtBu
14
(100 MHz, CDCl3)
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
169.013
167.327
133.989
132.235
128.785
127.329
90.378
84.283
77.556
77.441
77.230
76.914
28.023
20.586