Supplementary Material

Aza-Michael Additions of Benzylamine to Acrylates Promoted by Microwaves and Conventional Heating Using DBU as Catalyst via Solvent-Free Protocol

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Experimental Part

General. All chemicals used for, were obtained commercially (Aldrich) and used without further purification. Reactions were monitored by TLC on Al plates coated with silica gel with fluorescent indicator (60 F_{254}). Column chromatography (CC) was performed on silica gel (230-400 mesh Merck). Melting points were measured in open capillary tubes using a Melt-temp electrothermal apparatus and are uncorrected. The reactions with microwaves were carried out in Discover CEM equipment. NMR Spectra: Varian Gemini at 200 (^{1}H) and 50 MHz (^{13}C), Varian Inova at 400 (^{1}H) and 100 MHz (^{13}C), Bruker AVANCE III HD 500 MHz (^{1}H) and 125 MHz (^{13}C), spectra were obtained in chloroform-D (99.8%) +0.03% V/V TMS of Cambridge Isotope Laboratories, Inc. The chemical shift (δ in ppm rel. to Me_4Si as internal standard, *J* in Hz. HR-MS: MStation JMS-700 JEOL apparatus, in m/z.

Method for (rac)-methyl 3-(benzylamino)-3-(4-nitrophenyl)propanoate (3), (E)-N-benzyl-3-(4-nitrophenyl)acrylamide (4). Into a glass microwave reaction vessel a 5 mL flask provided with magnetic stirrer were added methyl 3-(4-nitrophenyl)acrylate **1** (0.5 mmol), benzylamine (2 mmol) and DBU (30 μL, 0.1 mmol). The reaction was heating at 75 °C and 75 W in microwave for 10 min. After completion the reaction was purified on column, hexane/ethyl acetate 80:20 was used for separation. **Compound 3.** Yield: 36%. **^{1}H NMR** (600 MHz, $CDCl_3$): δ 2.04 (s, 1H), 2.62 (dd, *J* = 15.9, 5.2 Hz, 1H), 2.72 (dd, *J* = 15.9, 8.6 Hz, 1H), 3.54 (d, *J* = 13.2 Hz, 1H), 3.63 (d, *J* = 12.3 Hz, 1H), 3.64 (s, 3H), 4.23 (dd, *J* = 8.6, 5.2 Hz, 1H), 7.22-7.34 (m, 5H), 7.57 (d, *J* = 8.7 Hz, 2H), 8.22 (d, *J* = 8.7 Hz, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$): δ 42.47, 51.56, 51.99, 58.37, 124.07, 127.33, 128.18, 128.28, 128.62, 139.66, 147.58, 150.38, 171.64. **Compound 4.** ^{1}H NMR (600 MHz, CDCl3) δ: 4.59 (d, *J* = 5.6 Hz, 2H), 6.09 (s, 1H), 6.55 (d, *J* = 15.6 Hz, 1H), 7.28-7.39 (m, 5H), 7.63 (d, *J* = 8.7 Hz, 2H), 7.72 (d, *J* = 15.6 Hz, 1H), 8.22 (d, *J* = 8.7 Hz, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ: 44.20, 124.31, 124.68, 127.95, 128.11, 128.53, 129.00, 137.88, 139.02, 141.15, 148.32, 164.76. Data were consistent with that reported [30].

Method for (rac)-tert-butyl 3-(benzylamino)-3-(4-nitrophenyl)propanoate (5). Into a glass microwave reaction vessel of 5 mL flask provided with magnetic stirrer were added *tert*-butyl 3-(4-nitrophenyl)acrylate **2** (0.5 mmol) benzylamine (2 mmol) and DBU (30 μL, 0.1 mmol). The reaction

was heating at 75°C and 75 W in microwave for 10 min. After completion the reaction was purified on column, hexane/ethyl acetate 80:20 was used for separation. Yield: 44%. **^{1}H NMR** (200 MHz, $CDCl_3$) δ (ppm) 1.38 (s, 9H, *tert*-Bu), 1.99 (br, 1H, NH), 2.48-2.71 (m, 2H, CH_2), 3.46-3.66 (t, 2H, CH_2), 4.10-4.23 (m, 1H, CH), 7.12-8.28 (m, 9H, Ar-H). **^{13}C NMR** (50 MHz, $CDCl_3$) δ (ppm) 28.0, 43.7, 51.54, 58.6, 81.2, 123.7, 127.1, 128.0, 128.1, 128.4, 139.6, 150.5, 170.2. FAB-MS: 357 ([M + H]$^+$). HR-FAB-MS: 357.18 ([M + H]$^+$, $C_7H_{14}NO$+; calc. 356.42).

Method for (rac)-methyl 3-(benzylamino)-3-(4-methoxyphenyl)propanoate (8) and N-benzyl-3-(4-methoxyphenyl)acrylamide (9). Into a glass microwave reaction vessel containing a magnetic stirrer, were addicted methyl 3-(4-methoxyphenyl)acrylate **6** (0.192 g, 1 mmol), benzylamine (440 μL, 4 mmol) and DBU (30 μL, 0.2 mmol). The mixture was placed in a *Discover CEM* equipment at 130 °C, 100 W (20 W) and 1 psi, during 2 h. After completion the reaction was concentrated to dryness and purified on column, hexane/ethyl acetate 95:5 to 80:20 was used for separation. **Compound 8.** Yield: 38 %. (yellow oil) **^{1}H NMR** (200 MHz, $CDCl_3$), δ (ppm), 1.92 (s, 1H, NH), 2.66 (m, 2H, CH_2CO), 3.63 (s, 3H, CH_3O), 3.42-3.73 (m, 2H, CH_2Ph), 3.81 (s, 3H, CH_3O), 4.07 (m, 1H, CH), 6.79-7.43(m, 9H, Ar-H); **^{13}C NMR** (50MHz, $CDCl_3$), δ (ppm) 43.10, 51.37, 51.71, 55.39, 58.30, 114.13, 127.01, 128.27, 128.32, 128.47, 134.64, 140.47, 159.11, 172.45. **Compound 9.** Yield: 10%. **^{1}H NMR** (200 MHz, $CDCl_3$), δ (ppm), 3.81 (s, 3H, CH_3O), 4.52 (d, *J* = 6, 2 Hz, 2H, CH_2Ph), 6.16 (br, 1H, NH), 6.27 (d, *J* = 6 Hz, 1H, CH), 6.74-7.54 (m, 9H, Ar-H), 7.58 (d, *J* = 8 Hz, 1H, CHPh). **^{13}C NMR** (50 MHz, $CDCl_3$), δ (ppm), 43.90, 55.44, 114.35, 118.24, 127.60, 127.99, 128.81, 129.47, 138.49, 141.05, 161.01, 166.35. Data were consistent with that reported [31,32].

Method for (rac)-tert-butyl 3-(benzylamino)-3-(4-methoxyphenyl)propanoate (10). Into a glass microwave reaction vessel containing a magnetic stirrer, were addicted *tert*-butyl 3-(4-methoxyphenyl)acrylate **7** (0.234 g, 1 mmol), benzylamine (440 μL, 4 mmol) and DBU (30 μL, 0.2 mmol). The mixture was placed in a *Discover CEM* equipment at 130 °C, 100 W (20 W) and 1 psi, during 2 h. After completion the reaction was concentrated to dryness and purified on column, hexane/ethyl acetate 95:5 to 80:20 was used for separation. Yield: 39 %. (yellow oil). **^{1}H NMR** (200 MHz $CDCl_3$), δ (ppm), 1.37 (s, 9H, *tert*-Bu), 2.04 (br, 1H, NH), 2.42-2.79 (m, 2H, CH_2CO), 3.44-3.68 (m, 2H, CH_2Ph), 3.82 (s, 3H, CH_3O), 4.05 (m, 1H, CH), 6.67-7.46 (m, 9H, Ar-H); **^{13}C NMR** (50MHz $CDCl_3$), , δ (ppm) 28.0, 44.3, 51.3, 55.2, 58.5, 80.5, 113.8, 126.8, 128.3, 134.7, 140.4, 158.8, 171.1. Elemental analysis for $C_{21}H_{27}NO_3$: Observed: %C= 74.0614, %H= 7.7957, %N= 4.0996, Calculate: %C= 73.8730, %H= 7.9700, %N=4.1015.

Method for (rac)-methyl 3-(benzylamino)-3-phenylpropanoate (13). Into a flask containing a magnetic stirrer, were added methyl 3-phenylacrylate **11** (0.100 g, 0.62 mmol), benzylamine (270 μL, 2.48 mmol) and DBU (18.5 μL, 0.124 mmol). The mixture was placed in an oil bath at 75 °C for 4 h. After completion the reaction was concentrated to dryness and purified on column, hexane/ethyl acetate 95:5 to 80:20 was used for separation. Yield: 59 % (amber oil). **^{1}H NMR** (500 MHz, $CDCl_3$), δ (ppm): 2.25 (br, 1H, NH), 2.64 (dd, *J* = 15.6, 5.2 Hz, 1H, CH_2CO_2), 2.75 (dd, *J* = 15.6, 8.8 Hz, 1H, CH_2CO_2), 3.54 (d, *J* = 13.2 Hz, 1H, CH_2Ph), 3.63 (s, 3H, CH_3O), 3.66 (d, *J* = 13.2 Hz, 1H, CH_2Ph), 4.12 (dd, *J* = 8.8, 5.2 Hz, 1H, CH), 7.22-7.37 (m, 10H, H-Ar); **^{13}C NMR** (125 MHz, $CDCl_3$), δ (ppm): 42.78, 51.25, 51.66, 58.80, 126.98, 127.19, 127.60, 128.21, 128.37, 128.67, 140.00, 142.26, 172.22. Data were consistent with that reported [33].

Method for (E)-N-benzyl-3-phenylpropenamide (14). Into a glass microwave reaction vessel containing a magnetic stirrer, were added methyl 3-phenylacrylate **11** (0.162 g, 1 mmol), benzylamine (436 μL, 4 mmol) and DBU (30 μL, 0.2 mmol). The mixture was placed in a *Discover CEM* equipment at 130 °C, 150 W and 1 psi, for 1.5 h. After completion the reaction was concentrated to dryness and purified on column, hexane/ethyl acetate 95:5 to 80:20 was used for separation. Yield: 32 % (white solid). **^{1}H-NMR** (500 MHz, $CDCl_3$), δ (ppm): 4.57 (d, *J* = 5.8 Hz, 2H, CH_2Ph), 6.00 (br, 1H, NH), 6.42 (d, *J* = 15.6 Hz, 1H, CH=CH), 7.26-7.50 (m, 10 H, H-Ar), 7.67 (d, *J* =

15.6 Hz, 1H, CH=CH). **^{13}C NMR** (125 MHz, $CDCl_3$), δ (ppm): 44.02, 120.54, 127.74, 127.95, 128.08, 128.91, 128.96, 129.87, 134.92, 138.33, 141.59, 165.89. Data were consistent with that reported [34].

Method for (rac)-tert-butyl 3-(benzylamino)-3-phenylpropanoate (15). Into a glass microwave reaction vessel containing a magnetic stirrer, were added *tert*-butyl 3-phenylacrylate **12** (0.162 g, 1 mmol), benzylamine (436 μL, 4 mmol) and DBU (30 μL, 0.2 mmol). The mixture was placed in a *Discover CEM* equipment at 130 °C, 150 W and 1 psi, for 6 h. After completion the reaction was concentrated to dryness and purified on column, hexane/ethyl acetate 95:5 to 80:20 was used for separation. Yield: 74.34 % (Yellow oil), **^{1}H-NMR** (200 MHz, $CDCl_3$), δ (ppm), 1.36 (s, 9H, *tert*-Bu), 2.10 (br, 1H, NH), 2.57 (m, 2H, CH_2), 3.56 (m, 2H,CH_2), 4.08 (m, 1H, CH), 7.11-7.43 (m, 10H, Ar-H); **^{13}C NMR** (50 MHz, $CDCl_3$), δ (ppm), 28.0, 44.3, 51.4, 59.2, 80.6, 126.8, 127.2, 127.3, 128.1, 128.3, 128.4, 140.4, 142.7, 171.04. Data were consistent with that reported [35].

Method for (rac)-methyl 3-(benzylamino)butanoate (17). Into a glass microwave reaction vessel containing a magnetic stirrer, were addicted methyl crotonate **16** (106 μL, 1 mmol), benzylamine (110 μL, 4 mmol). The mixture was placed in a *Discover CEM* equipment at 75°C, 50 W (15 W) for 4 h. After completion the reaction was purified by FC (hexane/ethyl acetate 8:2 to 60:40). Yield: 73 %. (yellow oil). **^{1}H NMR** (200 MHz, $CDCl_3$), δ (ppm), 1.16 (d, J = 5.9 Hz, 3H, CH_3), 1.87 (br, 1H, NH), 2.63-2.11 (m, 2H), 3.16 (m, 1H), 3.67 (s, 3H, CH_3O), 3.79 (d, 5.9 Hz), 7.21-7.33 (m, 5H, Ar-H), **^{13}C NMR (**150 MHz $CDCl_3$), δ (ppm), 20.54, 41.50, 49.74, 51.27, 51.60, 127.02, 128.19, 128.50, 140.43, 172.88. Spectroscopy data were compared with those reported [33].

Method for (rac)-methyl 3-(benzylamino)-2-methylpropanoate (19). A mixture of methyl methacrylate **18** (1 mmol, 0.1 g), benzylamine (1 mmol, 109.22 μL) and DBU (0.02 mmol, 3.98 μL) was placed into a microwave reaction vial provided with a magnetic stirrer. The capped vial was placed in a microwave synthesis equipment at 75 °C and 50 W for 4 h. The crude product was purified by FC (hexane/ethyl acetate 98:2 to 90:10) to produce (±)-**19**. Yield: 87 % (Colorless oil). **^{1}H NMR** (200 MHz $CDCl_3$), δ (ppm), 1.18 (d, J = 4 Hz, 3H, CH_3); 1.61 (br, 1H, NH), 2.54-2.76 (m, 1H, CH-NH), 2.78-2.98 (m, 2H, CH), 3.68 (s, 3H, CH_3O), 3.79 (s, 2H, CH_2Ph), 7.09-7.49 (m, 5H, Ar-H). **^{13}C NMR** (50 MHz $CDCl_3$), δ (ppm), 15.5, 40.1, 51.8, 52.1, 53.8, 127.0, 128.1, 128.4, 140.0, 176.2. Spectroscopy data were compared with those reported [33].

Method for (rac)-ethyl 3-(benzylamino)-2-phenylpropanoate (21). Into a 10 mL flask provided with magnetic stirrer were added ethyl 2-phenylacrylate **20** (0.43 mmol, 75 mg), benzylamine (0.43 mmol, 0.046 g, 47 μl) and DBU (0.2 mmol, 1.31 mg, 1.3 μL). The reaction was kept a room temperature for 30 min. After was purified on column, hexane/ethyl acetate 8:2 was used for separation. Yield: 56% (colorless oil). ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm), 1.6 (d, J = 2 Hz, 3H, CH_3), 1.63 (br, 1H, NH), 2.92 (dd, J = 5, J = 5, 1 H, CH) , 3.28 (dd, J = 5 Hz, J = 5 Hz, 2H, CH_2), 3.80 (s, 1H, CH_2Ph),), 3.82 (dd, J^3 = 4 Hz, J^3 = 4 Hz, 1 H, CH), 4.08-4.19 (m, 2 H, CH_2CH_3), 7.21-7.33 (10H, Ar-H). **^{13}C NMR** (75 MHz $CDCl_3$), δ (ppm), 14.3, 52.3, 53.8, 61,0, 127.1, 127.6, 128.2, 128.2, 128.6, 128.9, 137.6, 140.3, 173.3. Spectroscopy data were compared with those reported [29].

Method for methyl 3-(benzylamino)propanoate (23) and dimethyl 3,3'-(benzylazanediyl)dipropionate(24). Into a 10 mL flask provided with magnetic stirrer were added methyl acrylate **22** (1 mmol, 90.62 μl) and benzylamine (1.1 mmol, 120 μL). The mixture was cooled to 0 °C during 2.5 h. After completion the reaction, the crude product was purified by FC (hexane/ethyl acetate 8:2). **Compound 23** Yield: 56 % (Colorless oil). **^{1}H NMR** (200 MHz, $CDCl_3$), δ (ppm), 1.83 (s, 1H, NH), 2.53 (t, J = 6.0 Hz, 2H, CH_2), 2.89 (t, J = 3.37 Hz, 2H, CH_2), 3.67 (t, J = 6.0 Hz, 2H, CH_2), 3.80 (s, 2H, CH_2), 7.30 (m, 5H, Ar-H). **^{13}C NMR** (50 MHz, $CDCl_3$) δ (ppm), 34. 5, 44.4, 51.5, 53.7, 126.9, 128.0, 128.3, 140.1, 173.1. **Compound 24** Yield: 5 %. **^{1}H NMR** (200 MHz, $CDCl_3$), δ (ppm), 2.47 (t, J = 6 Hz, 4H, CH_2), 2.80 (t, J = 6 Hz, 4H, CH_2-N), 3.58 (s, 2H, CH_2Ph), 3.64 (s, 6H, OCH_3) 7.27 (m, 5H, Ar-H). **^{13}C NMR** (50 MHz, $CDCl_3$) δ (ppm), 32.6, 49.2, 51.4, 58.3, 127.0, 128.1, 128.6, 138.9, 172.8. Spectroscopy data were compared with those reported [23].

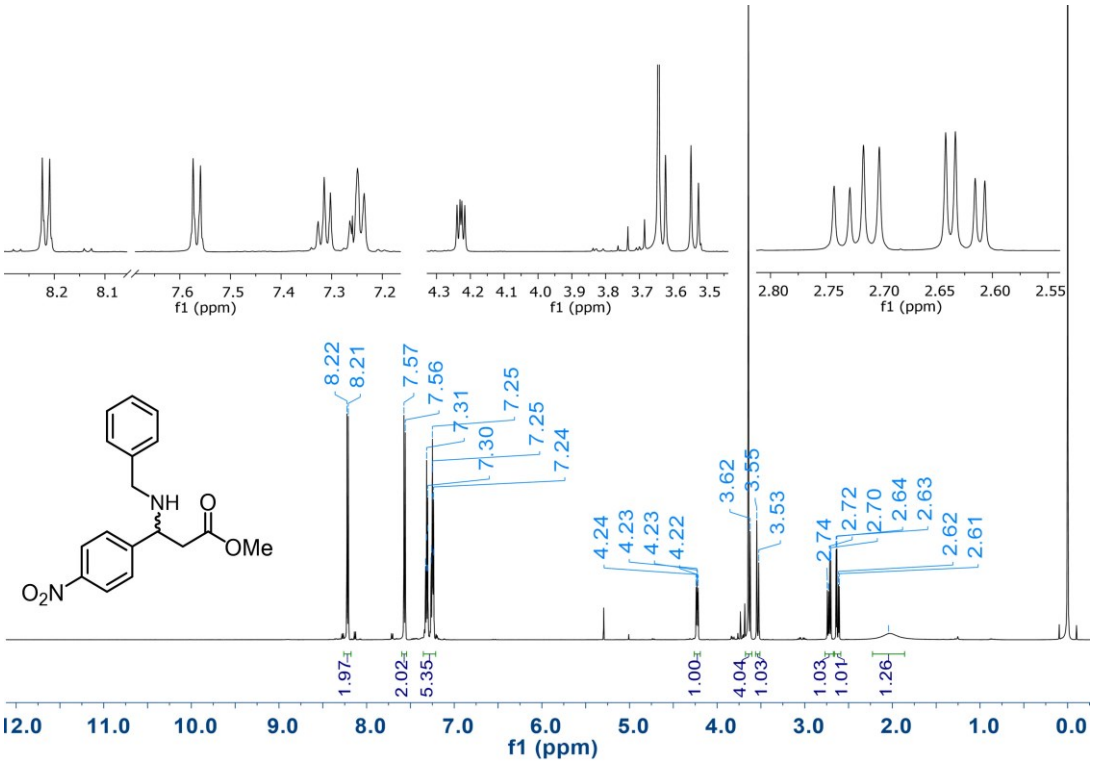

Figure S1. ^{1}H RMN (600 MHz, $CDCl_3$) for (*rac*)-methyl 3-(benzylamino)-3-(4-nitrophenyl)propanoate **3**.

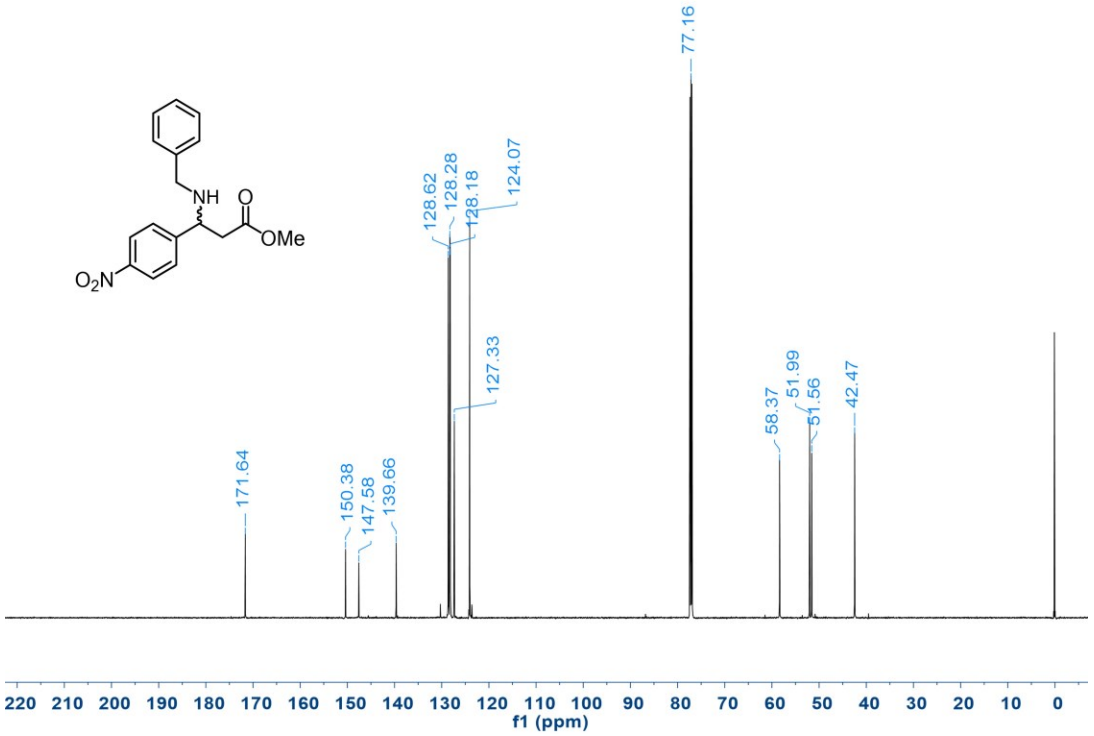

Figure S2. ^{13}C RMN (150 MHz, $CDCl_3$) for (*rac*)-methyl 3-(benzylamino)-3-(4-nitrophenyl)propanoate **3.**

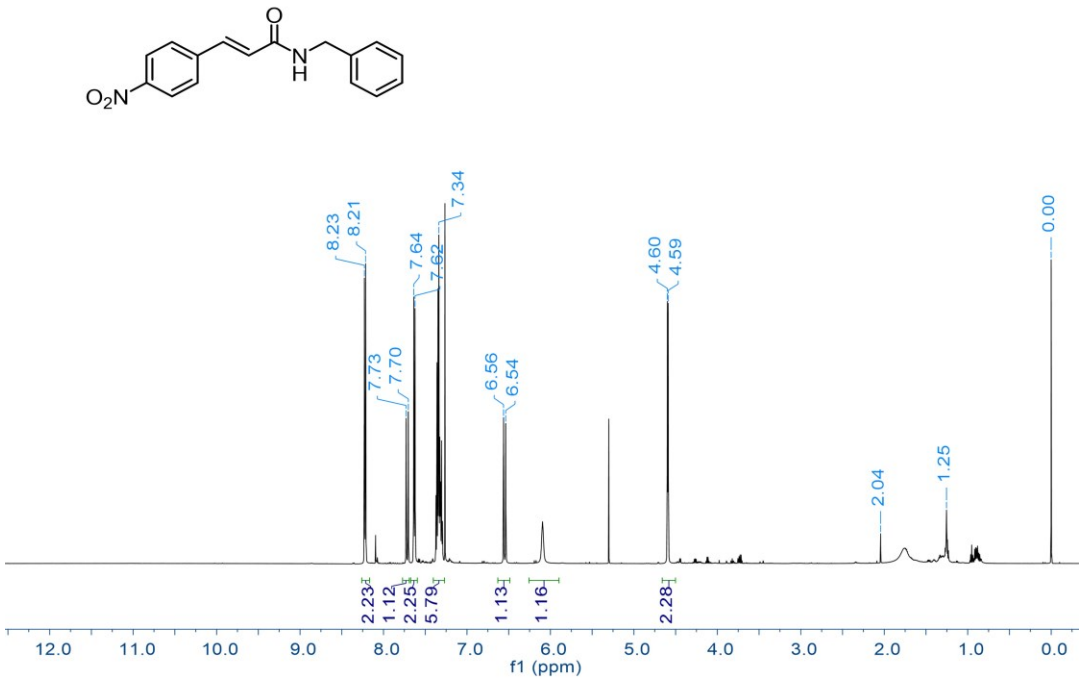

Figure S3. [1]H NMR (600 MHz, $CDCl_3$) for (*E*)-*N*-benzyl-3-(4-nitrophenyl)acrylamide **4.**

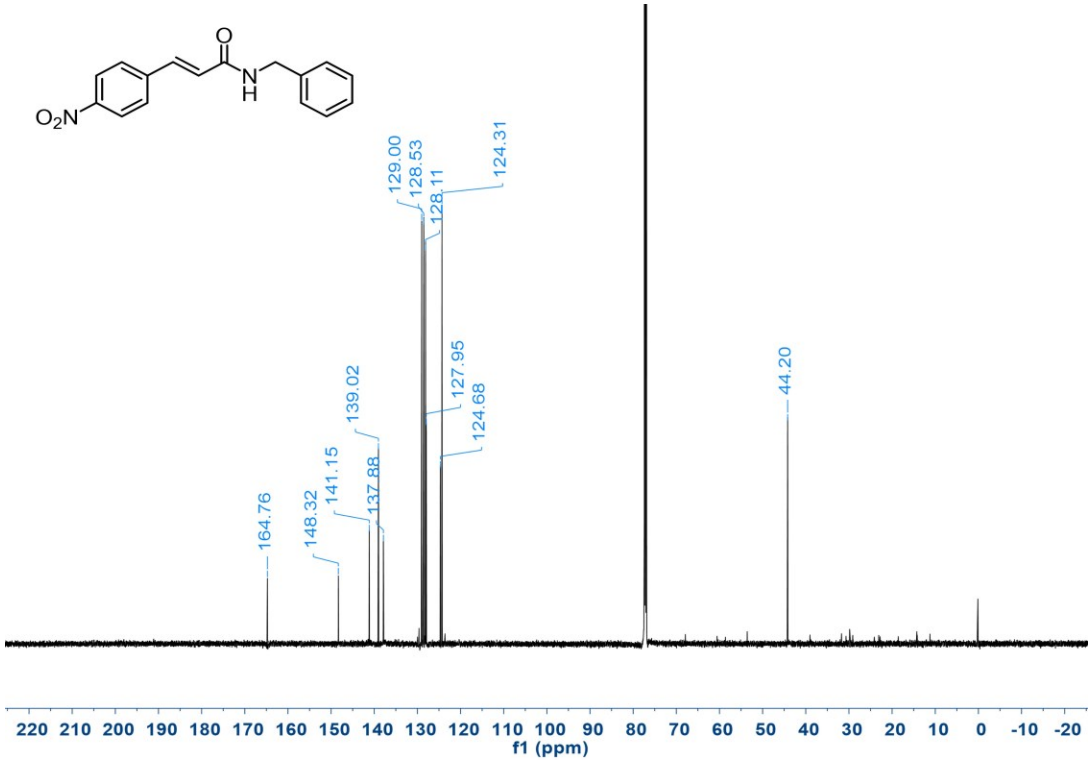

Figure S4. [13]C NMR (150 MHz, $CDCl_3$) for (*E*)-*N*-benzyl-3-(4-nitrophenyl)acrylamide **4.**

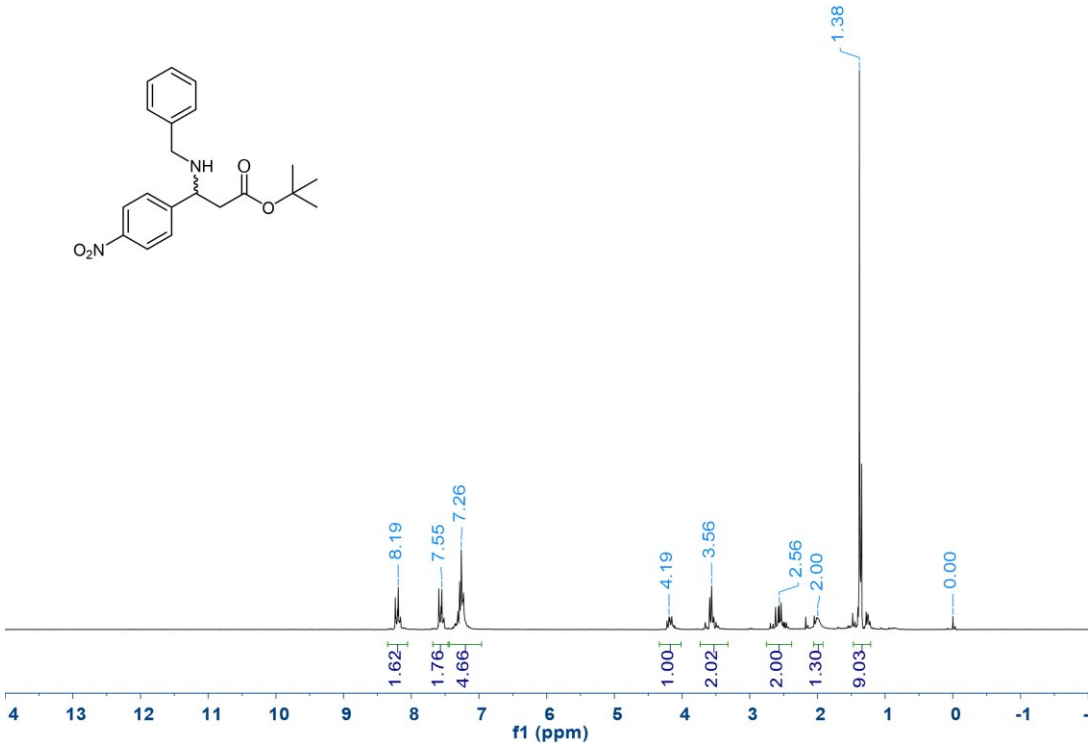

Figure S5. [1]H NMR (200 MHz, CDCl[3]) for (*rac*)-*tert*-butyl 3-(benzylamino)-3-(4-nitrophenyl)propanoate **5.**

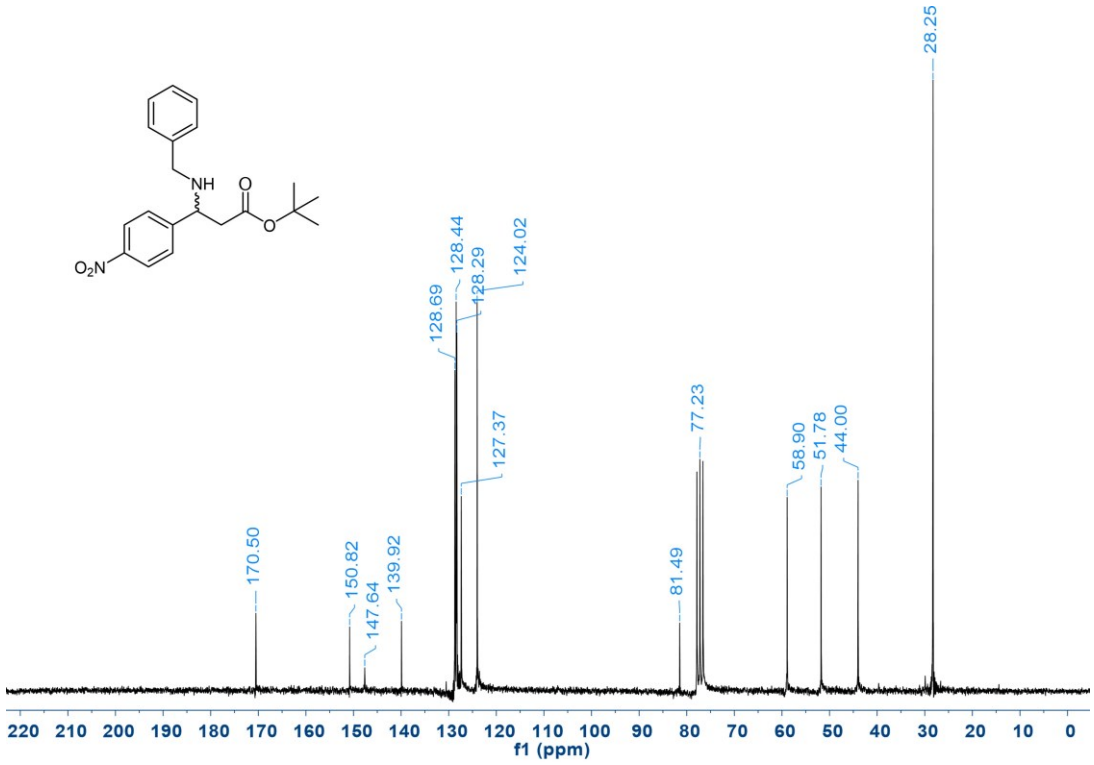

Figure S6. [13]C NMR (50 MHz, CDCl[3]) for (*rac*)-*tert*-butyl 3-(benzylamino)-3-(4-nitrophenyl)propanoate **5.**

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[ Elemental Composition ]
Data  : JEG012                          Date : 02-Mar-2020 11:59
Sample: JEG09-45                      Operator name M.en ITA Victoria Labastida G
Note : Dr.Jaime Escalante/Daniel      Centro de Investigaciones Quimicas UAEM
Inlet : Direct                         Ion Mode : FAB+
RT : 3.64 min                          Scan#: (54,56)+5
Elements : C 40/0, H 49/0, O 6/0, N 2/0
Mass Tolerance      : 1000ppm, 3mmu if m/z < 3, 5mmu if m/z > 5
Unsaturation (U.S.) : -0.5 - 10.0

Observed m/z Int%   Err[ppm / mmu]    U.S.  Composition
  357.1800   100.0     -4.1 /  -1.5    9.5  C 20 H 25 O 4 N 2
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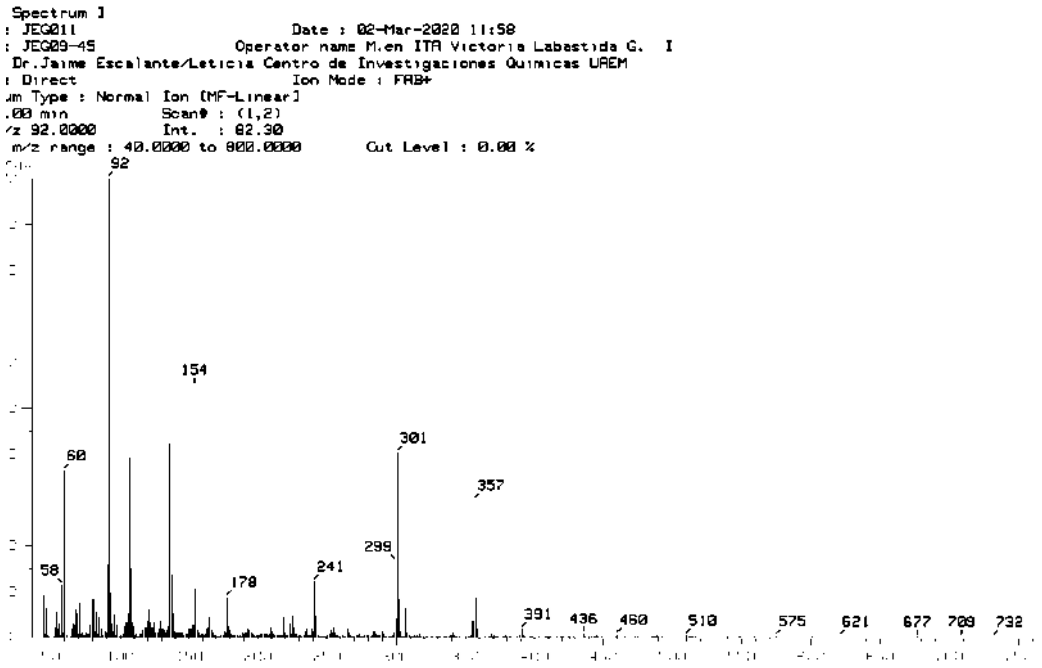

Figure S7. High Resolution Mass Spectrometry (HR-MS) for (*rac*)-*tert*-butyl 3-(benzylamino)-3-(4-nitrophenyl)propanoate **5.**

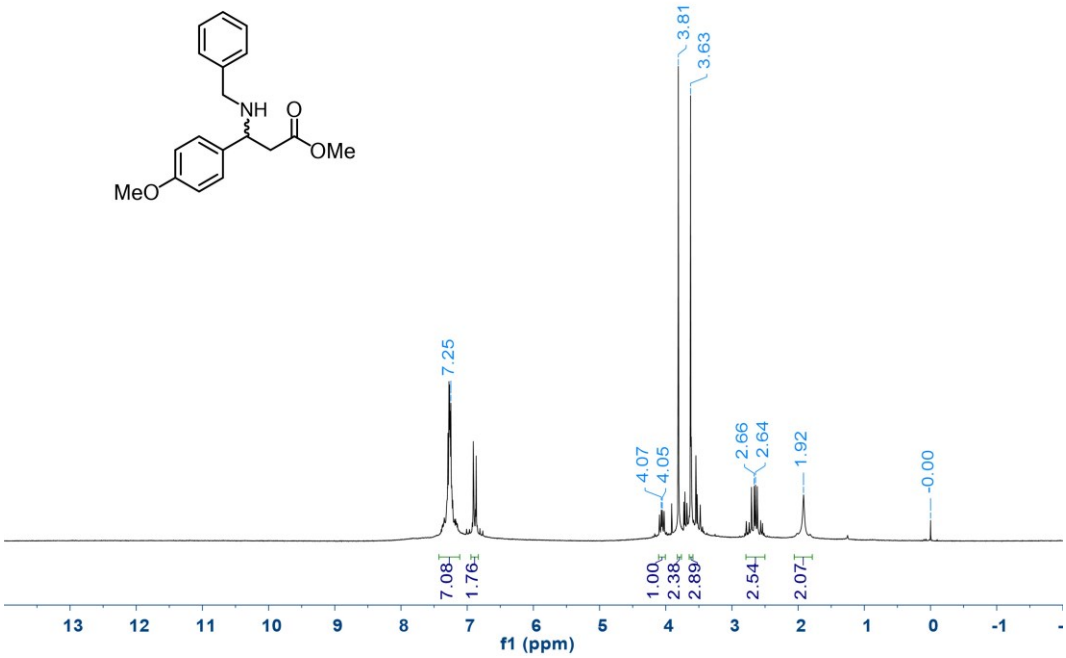

Figure S8. ^{1}H NMR (200 MHz, $CDCl_3$) for (*rac*)-methyl 3-(benzylamino)-3-(4-methoxyphenyl)propanoate **8.**

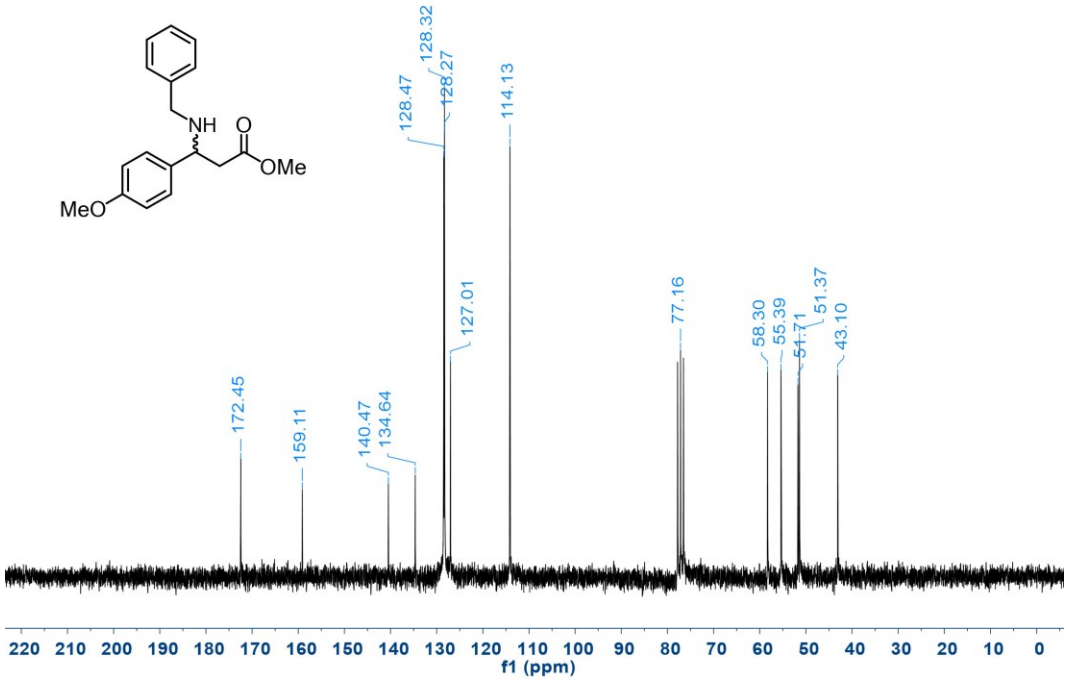

Figure S9 ^{13}C NMR (50 MHz, $CDCl_3$) for methyl (*rac*)-methyl 3-(benzylamino)-3-(4-methoxyphenyl)propanoate **8.**

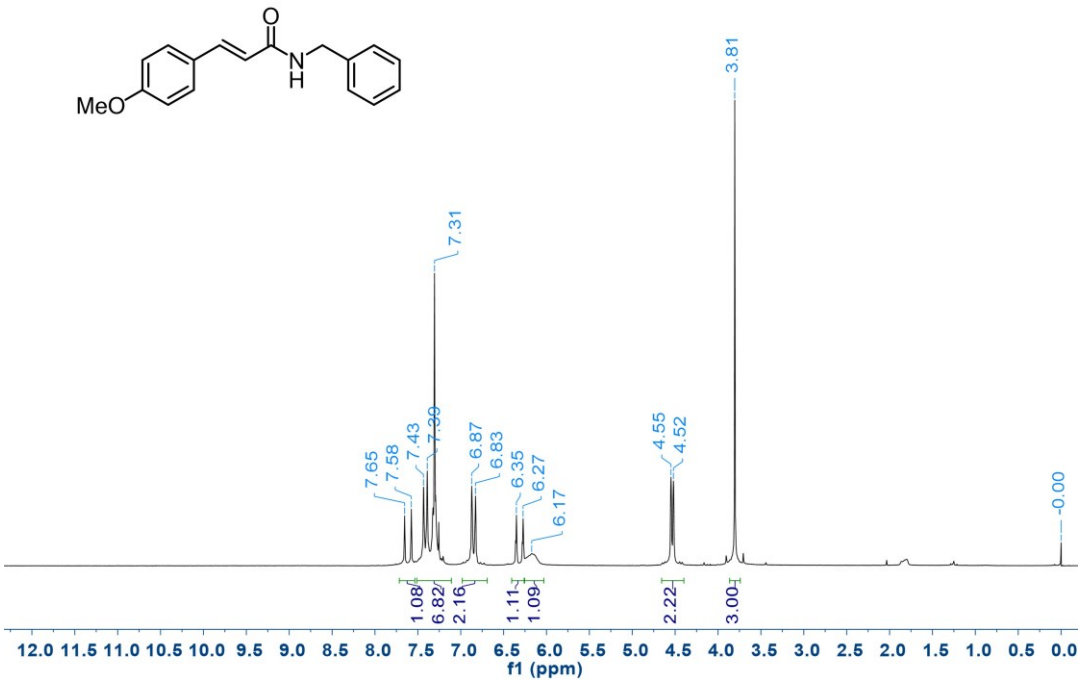

Figure S10. ^{1}H NMR (200 MHz, $CDCl_3$) for *N*-benzyl-3-(4-methoxyphenyl)acrylamide **9.**

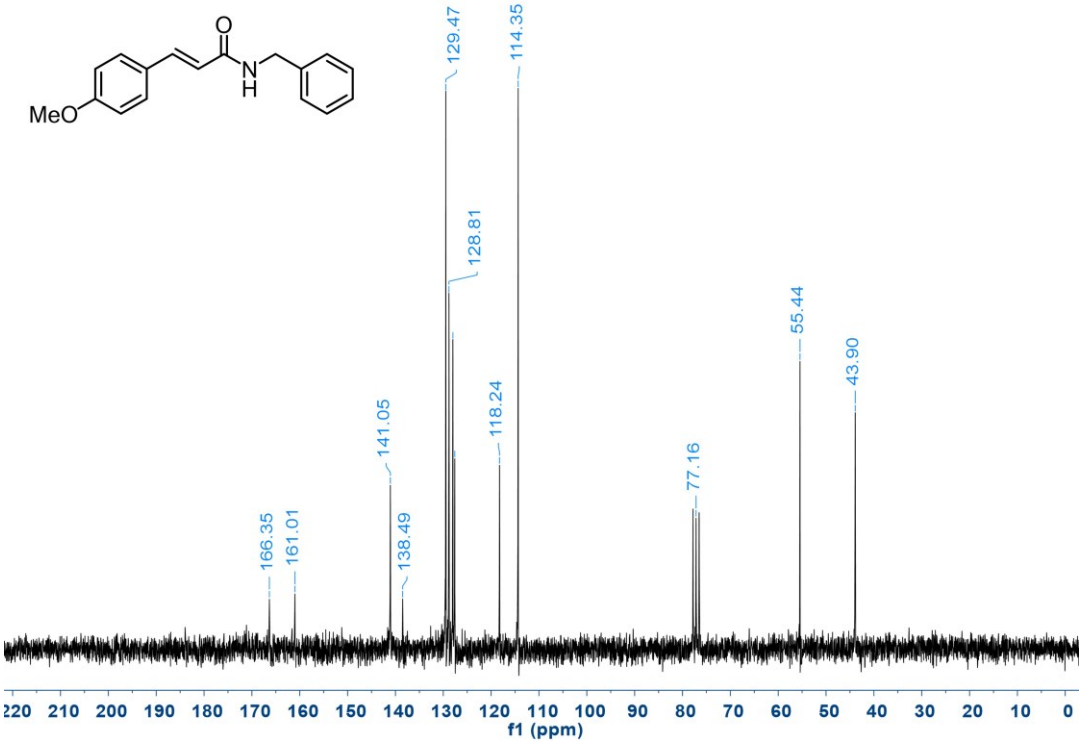

Figure S11. ^{13}C NMR (50 MHz, $CDCl_3$) for *N*-benzyl-3-(4-methoxyphenyl)acrylamide **9.**

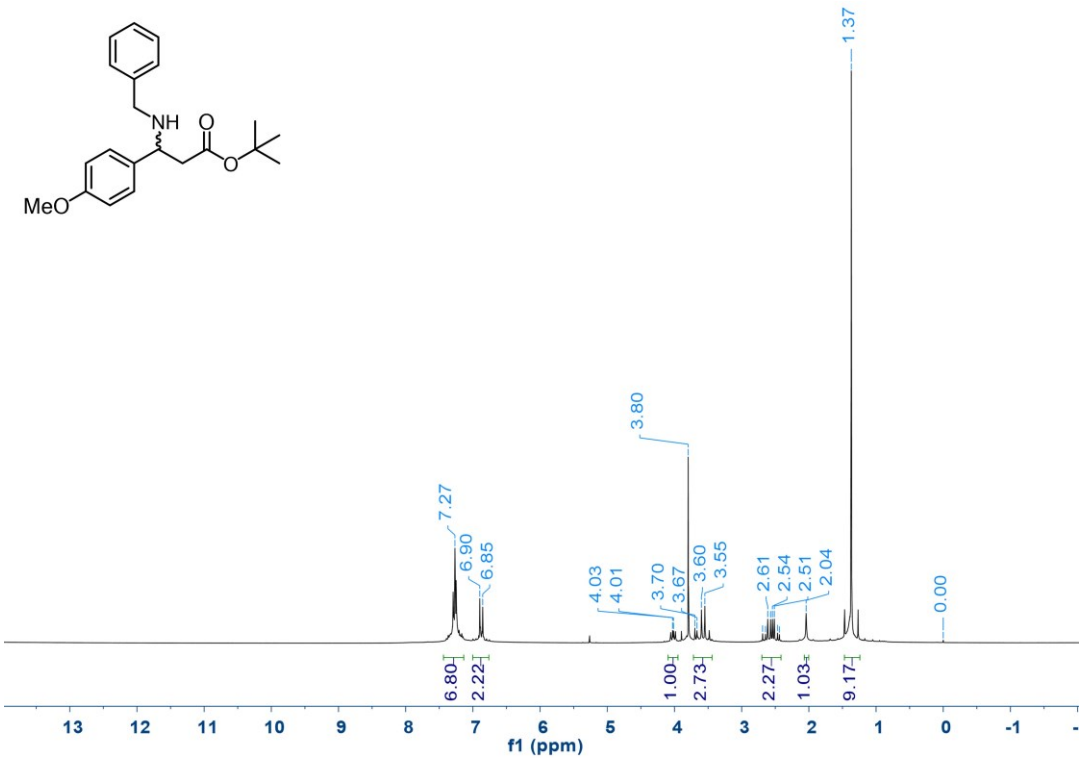

Figure S12. [1]H NMR (200 MHz, $CDCl_3$) for (*rac*)-*tert*-butyl 3-(benzylamino)-3-(4-methoxyphenyl)propanoate **10.**

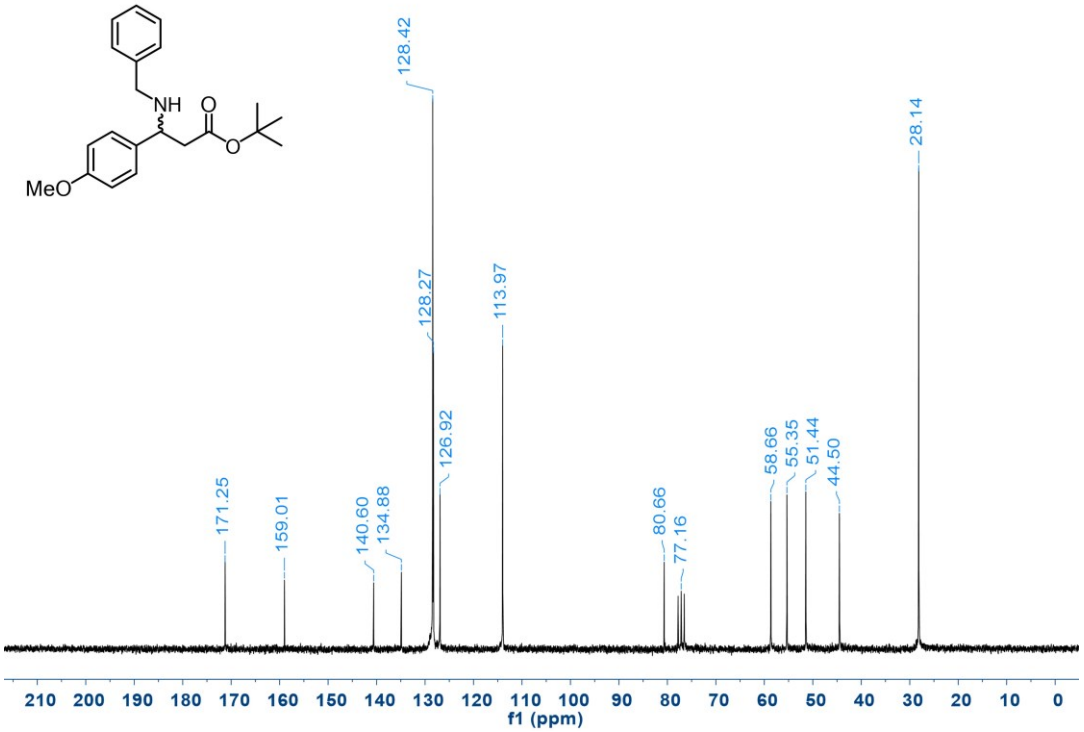

Figure S13. [13]C NMR (50 MHz, $CDCl_3$) for (*rac*)-*tert*-butyl 3-(benzylamino)-3-(4-methoxyphenyl)propanoate **10.**

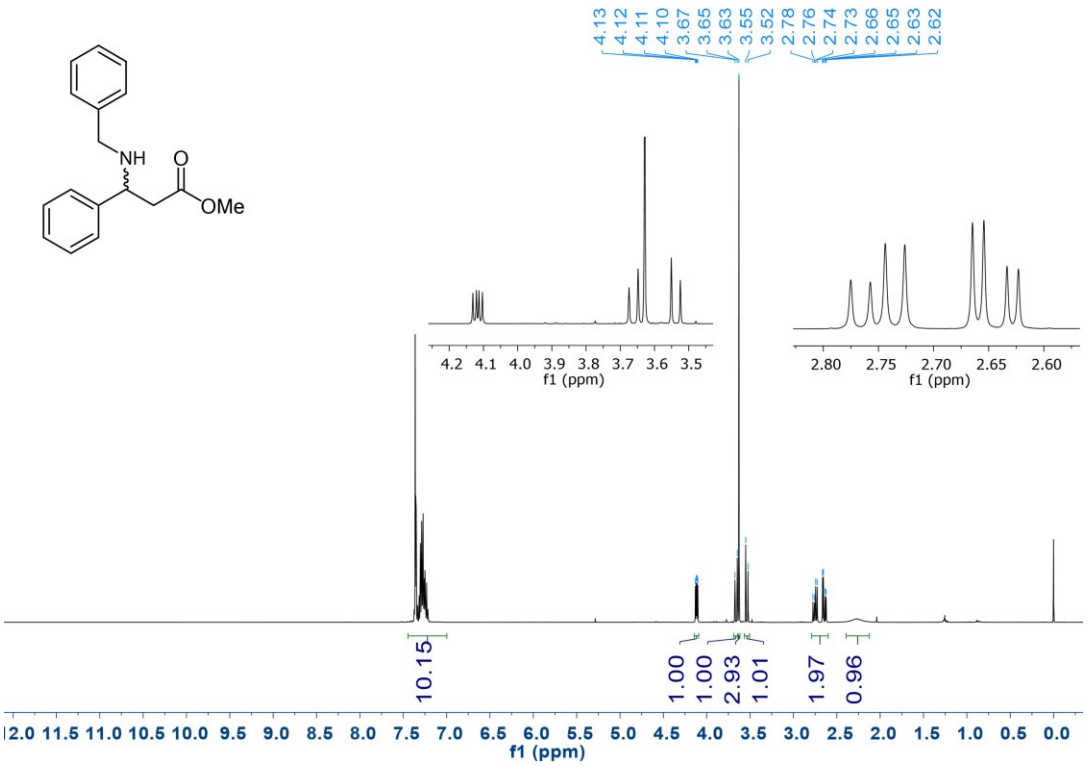

Figure S14. ^{1}H NMR (500 MHz, $CDCl_3$) for (*rac*)-methyl 3-(benzylamino)-3-phenylpropanoate **13.**

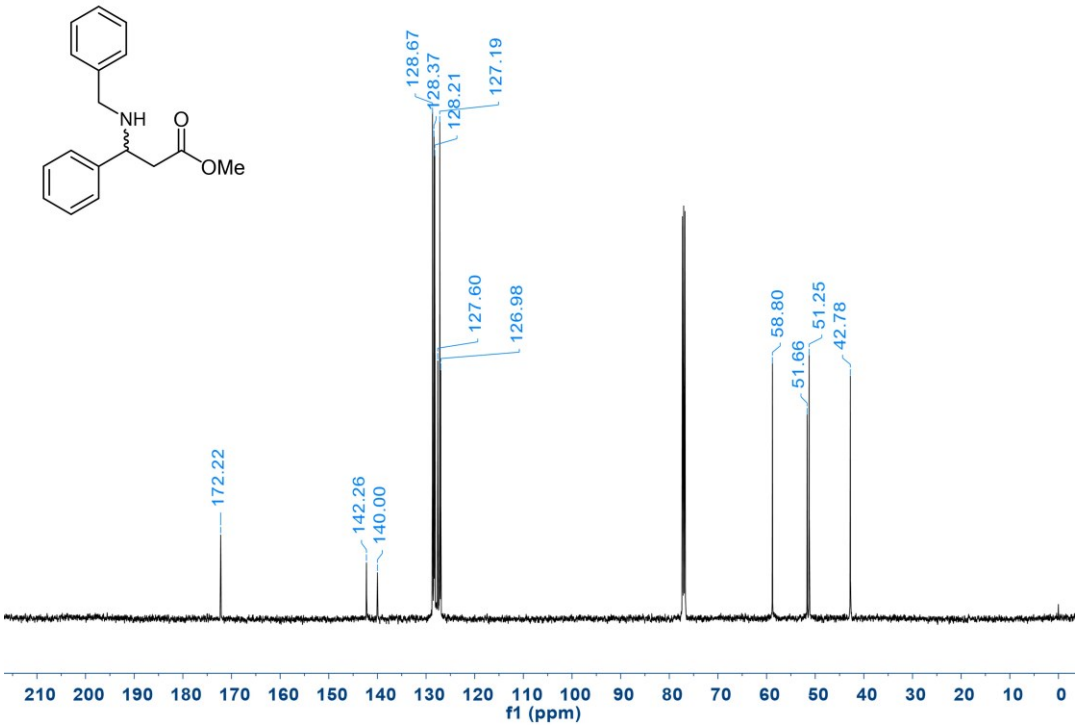

Figure S15. ^{13}C NMR (125 MHz, $CDCl_3$) for (*rac*)-methyl 3-(benzylamino)-3-phenylpropanoate **13.**

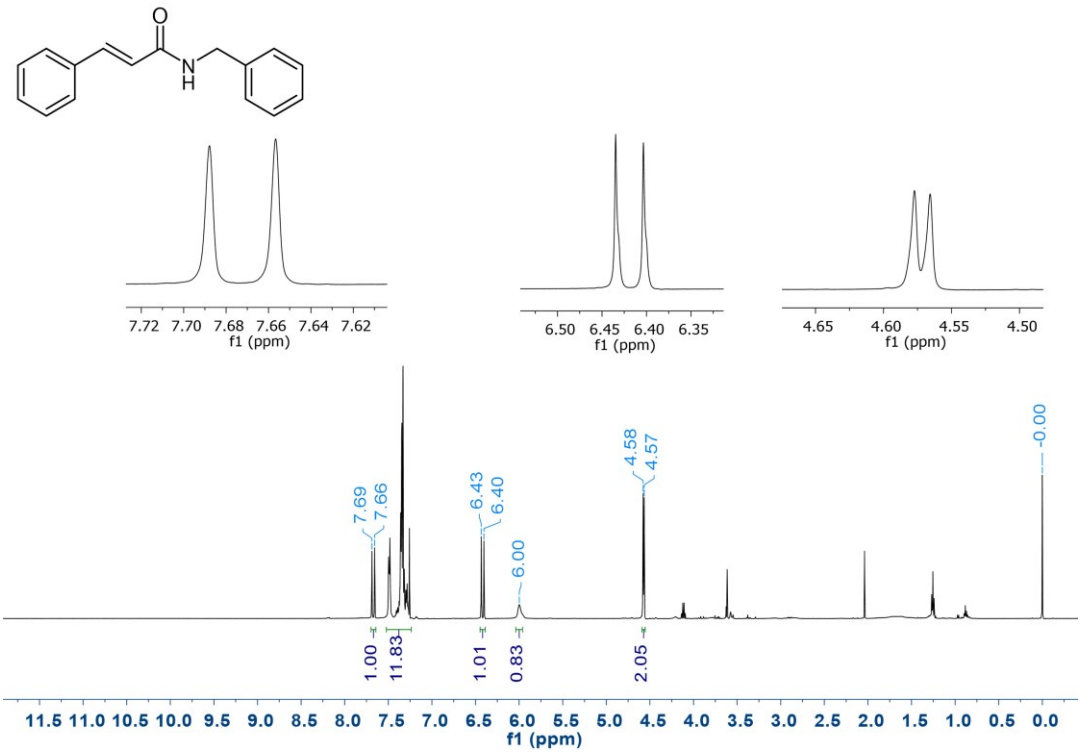

Figure S16. ^{1}H NMR (500 MHz, $CDCl_3$) for (*E*)-*N*-benzyl-3-phenylpropenamide **14.**

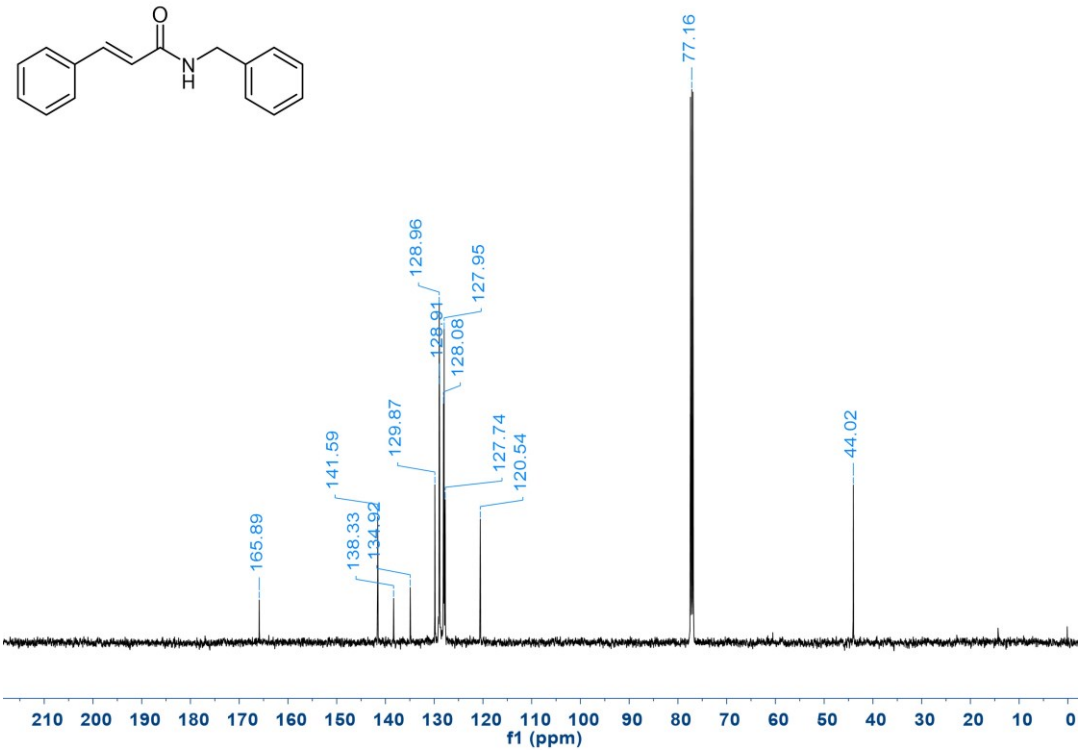

Figure S17. ^{1}H NMR (125 MHz, $CDCl_3$) for (*E*)-*N*-benzyl-3-phenylpropenamide **14.**

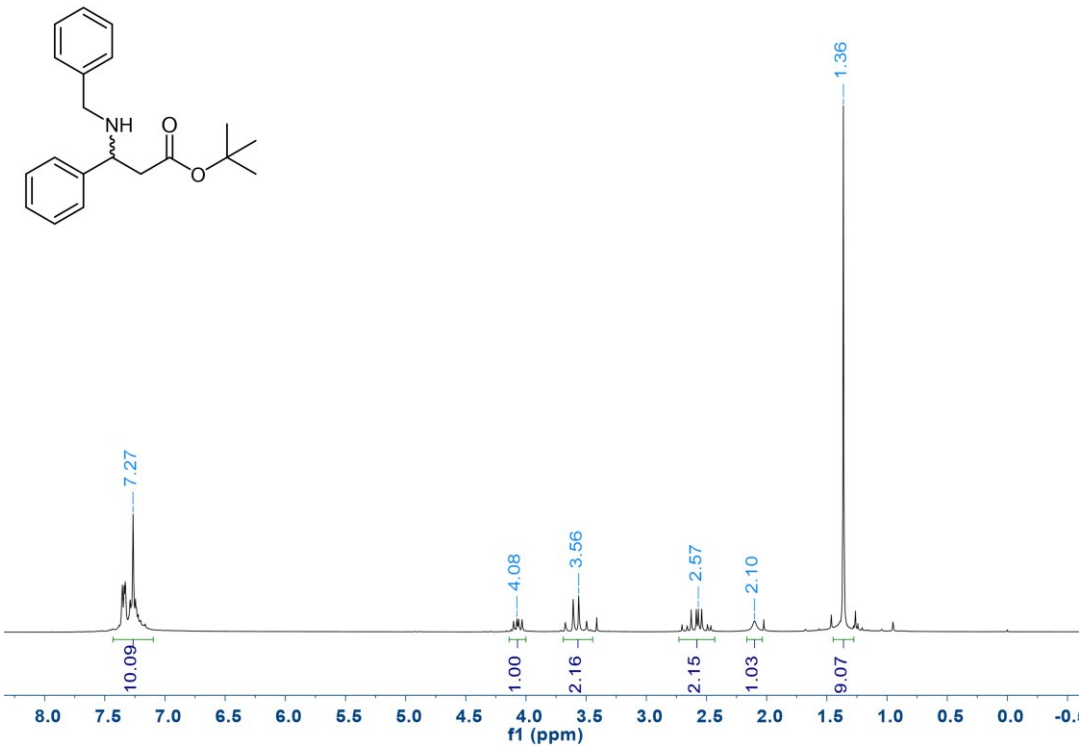

Figure S18. [1]H NMR (200 MHz, $CDCl_3$) for (*rac*)-*tert*-butyl 3-(benzylamino)-3-phenylpropanoate **15.**

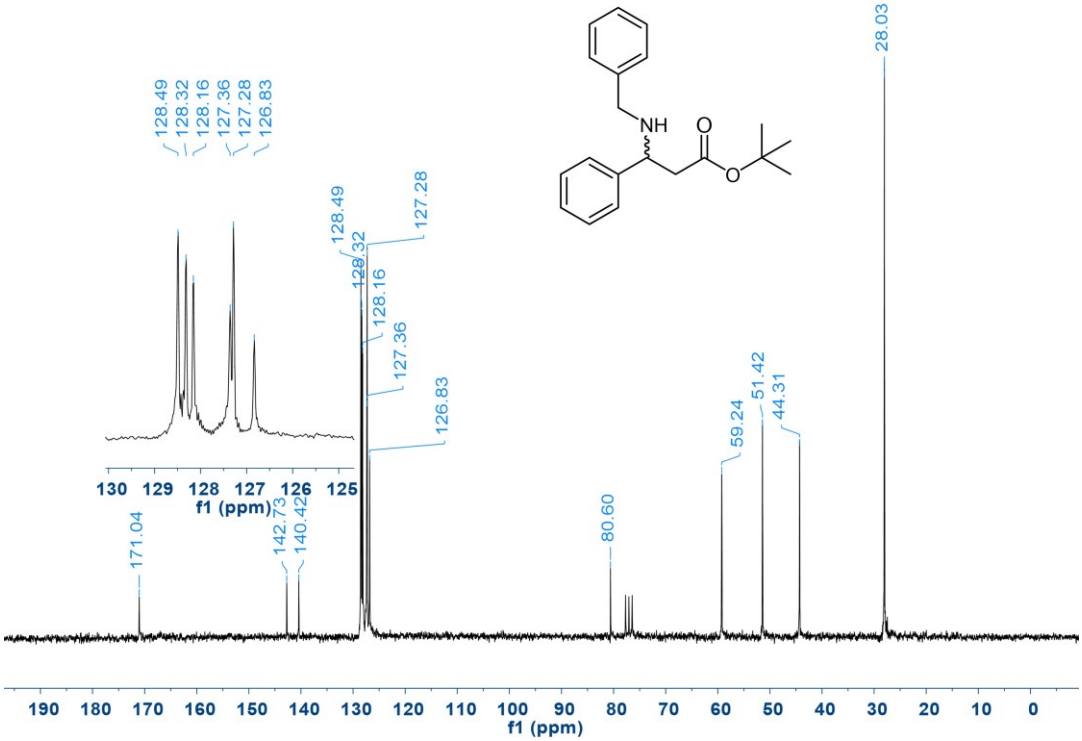

Figure S19. [13]C NMR (50 MHz, $CDCl^3$) for (*rac*)-*tert*-butyl 3-(benzylamino)-3-phenylpropanoate **15.**

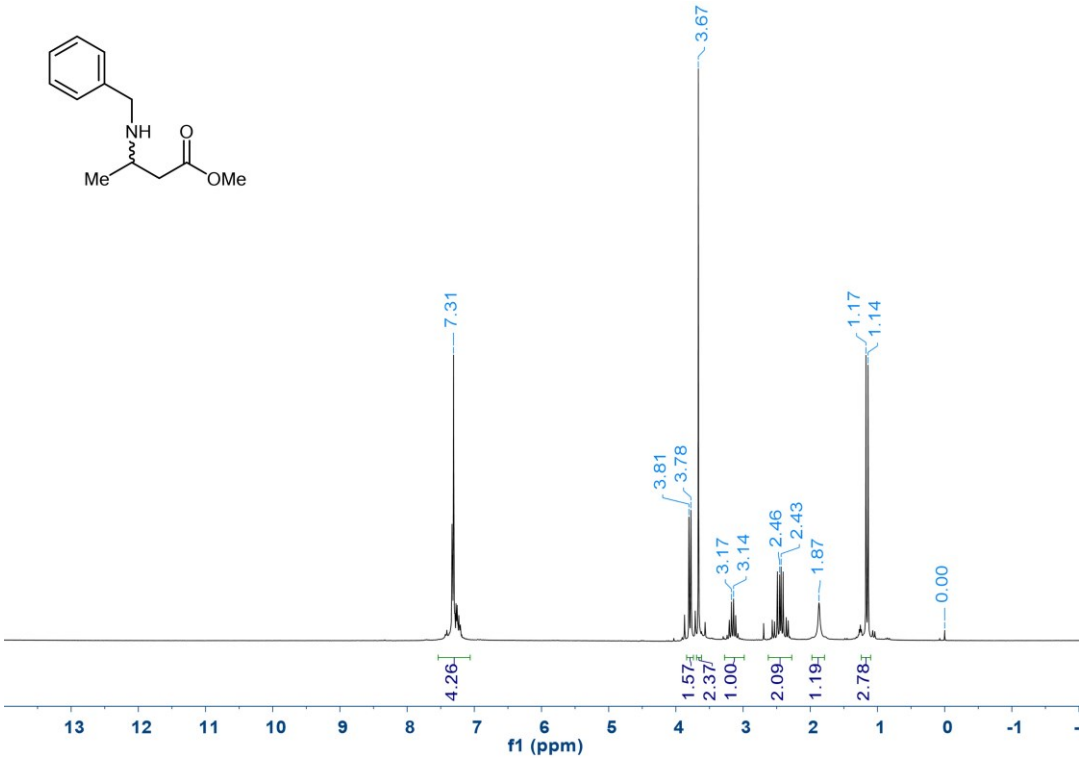

Figure S20. (200 MHz, $CDCl_3$) for (*rac*)-methyl 3-(benzylamino)butanoate **17.**

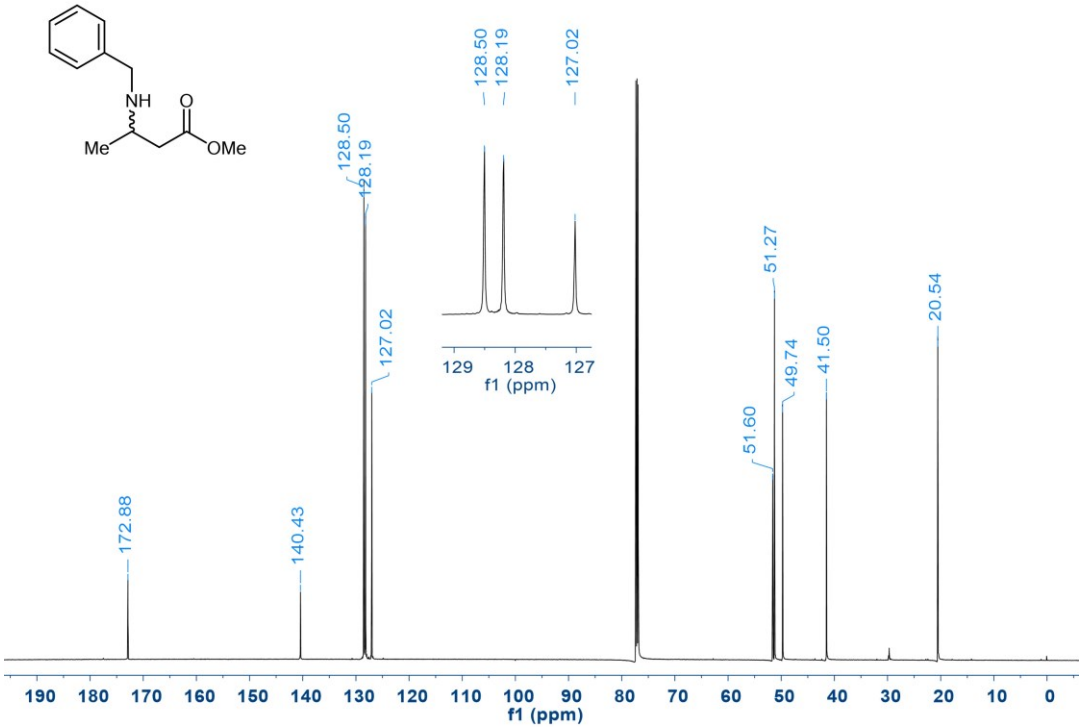

Figure S21. ^{13}C NMR (150 MHz, $CDCl_3$) for (*rac*)-methyl 3-(benzylamino)butanoate **17.**

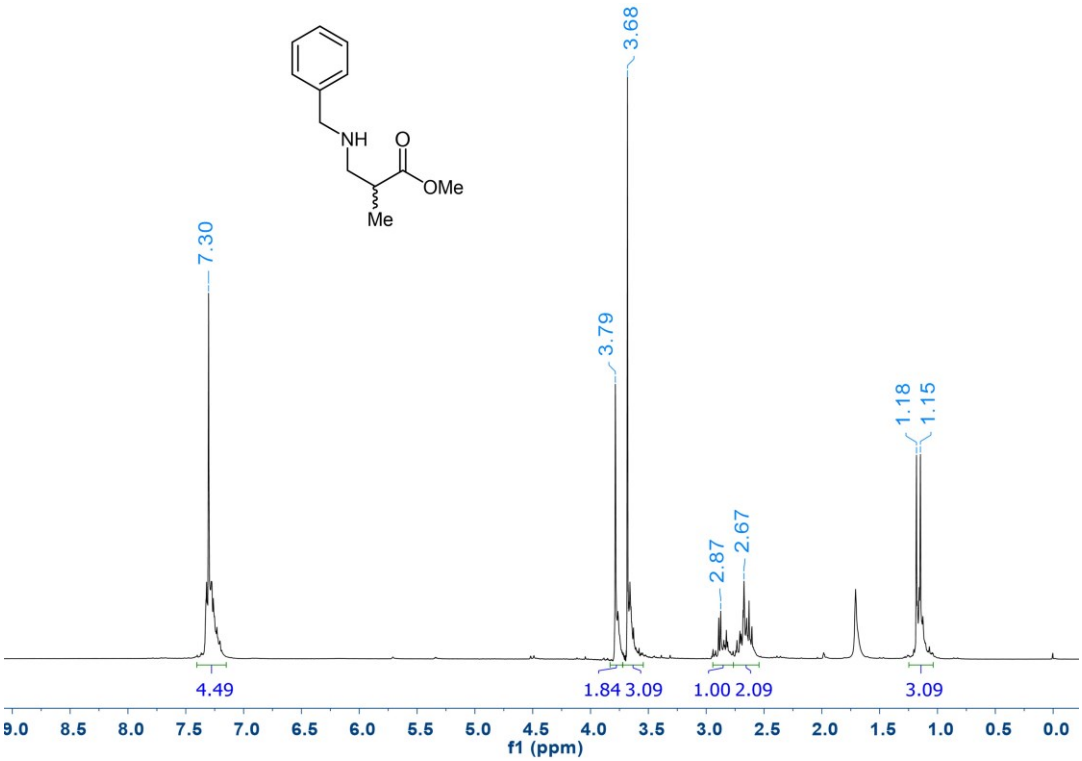

Figure S22. ^{1}H NMR (200 MHz, $CDCl_3$) for (*rac*)-methyl 3-(benzylamino)-2-methylpropanoate **19.**

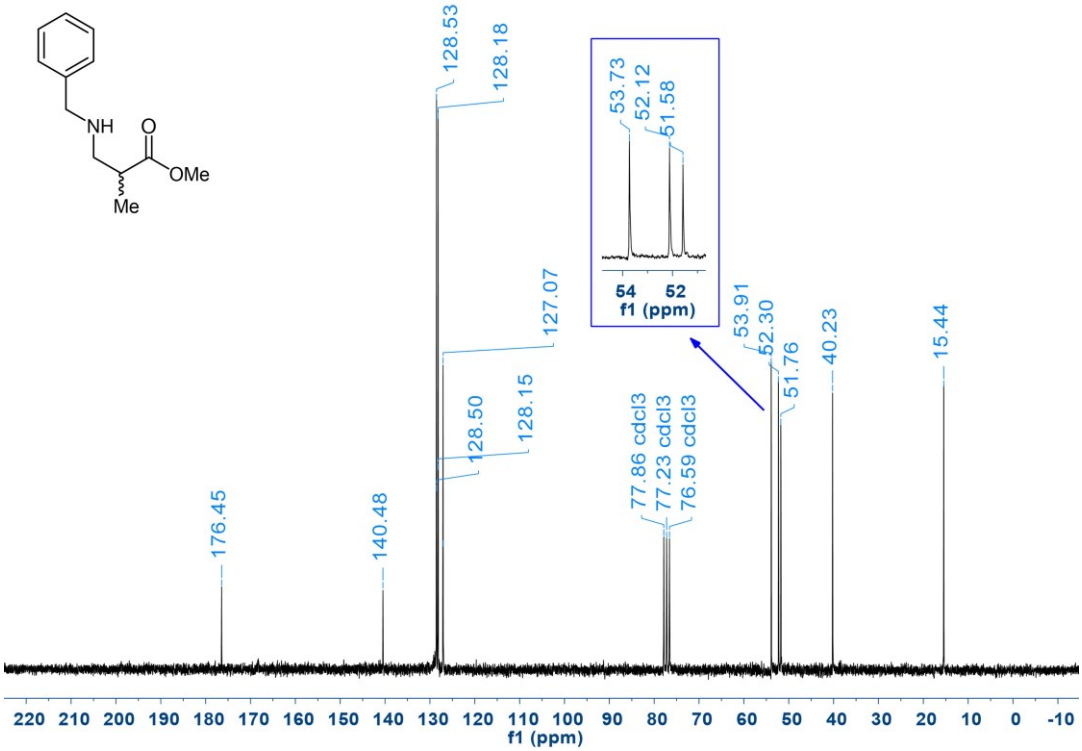

Figure S23. ^{1}H NMR (200 MHz, $CDCl_3$) for (*rac*)-methyl 3-(benzylamino)-2-methylpropanoate 19.

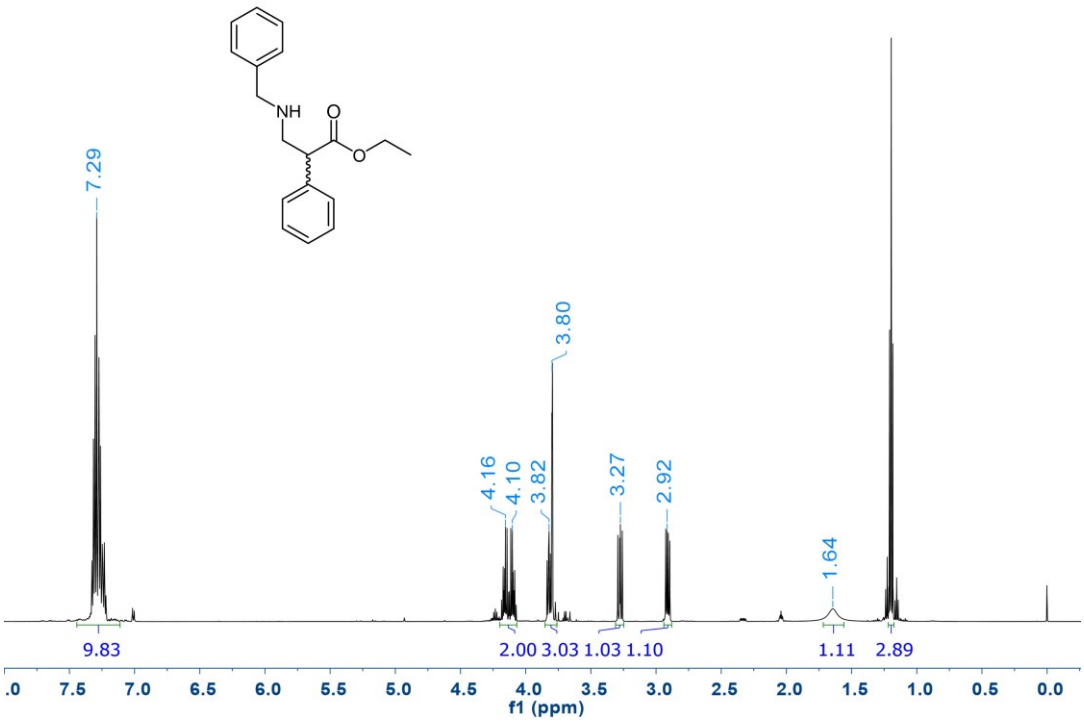

Figure S24. ^{1}H NMR (500 MHz, $CDCl_3$) for (*rac*)-ethyl 3-(benzylamino)-2-phenylpropanoate **21.**

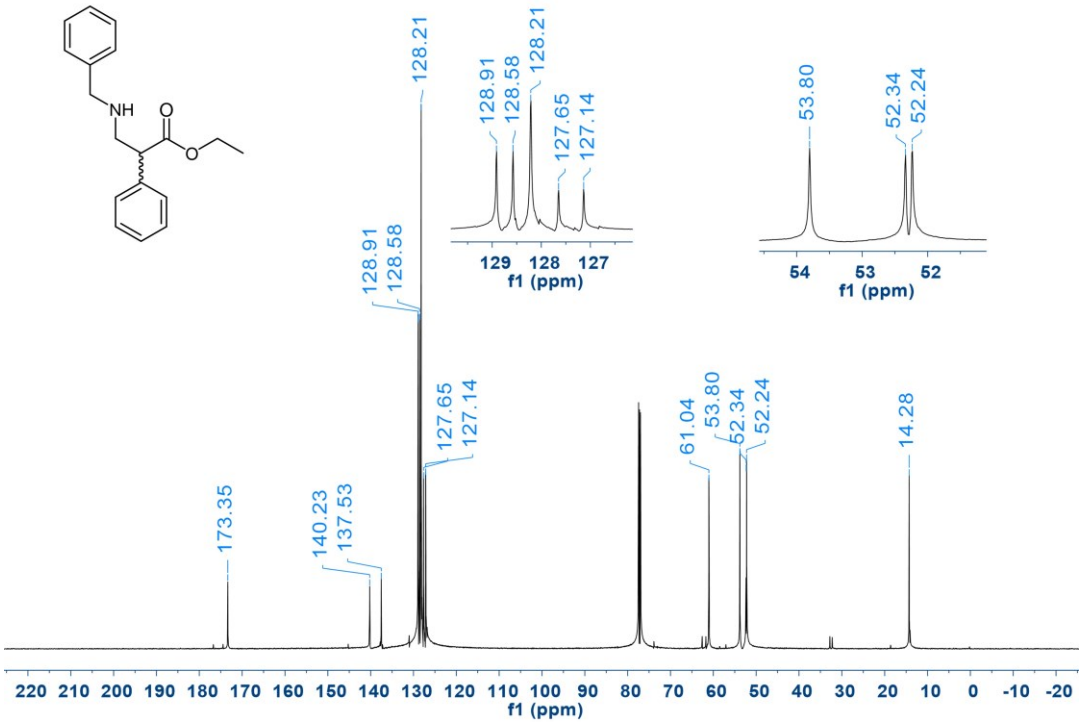

Figure S25. ^{13}C NMR (125 MHz, $CDCl_3$) for (*rac*)-ethyl 3-(benzylamino)-2-phenylpropanoate **21.**

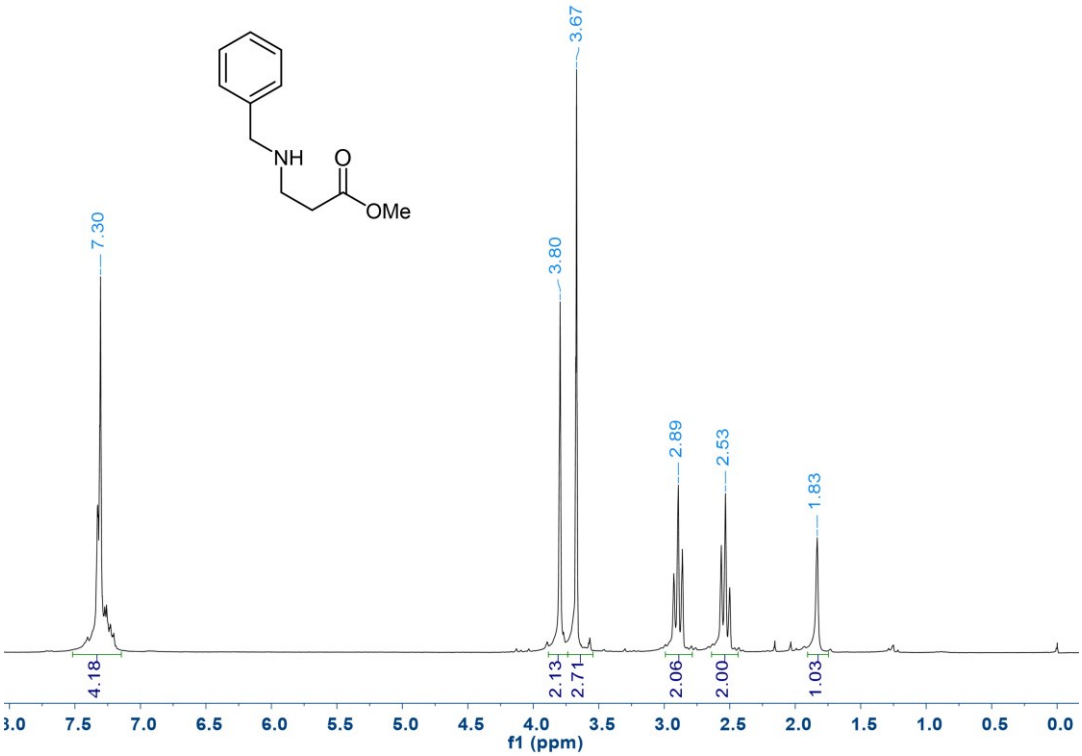

Figure S26. ^{1}H NMR (200 MHz, $CDCl_3$) for methyl 3-(benzylamino)propanoate **23.**

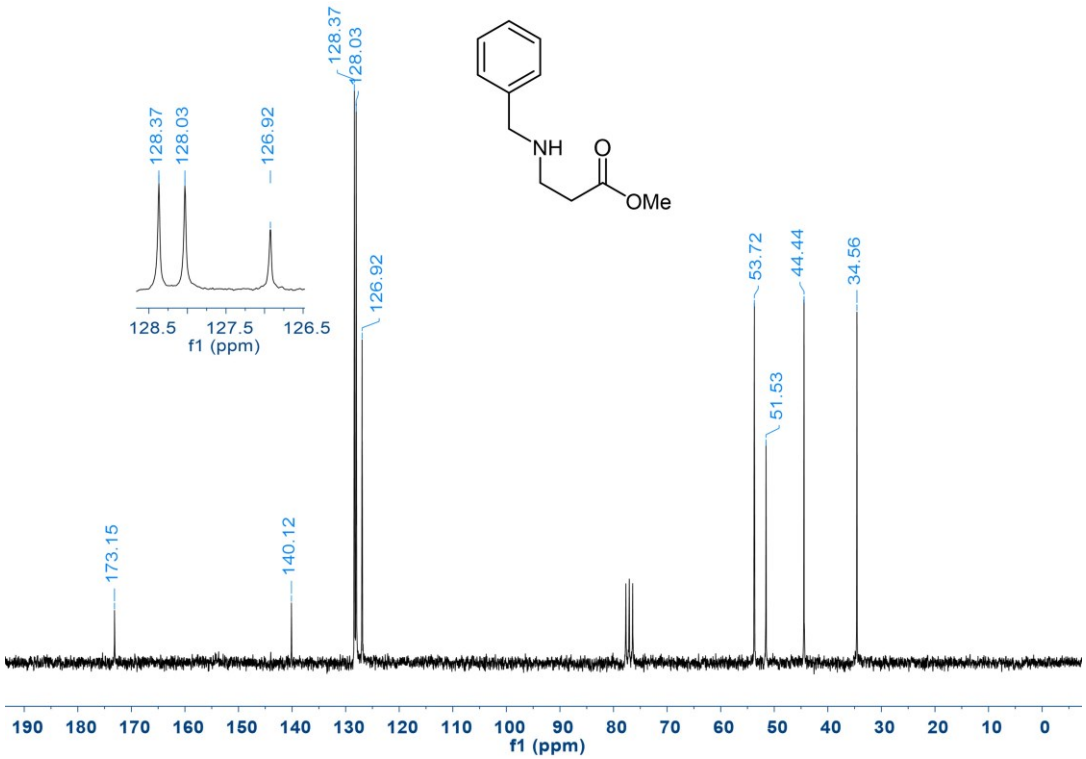

Figure S27. ^{13}C NMR (50 MHz, $CDCl_3$) for methyl 3-(benzylamino)propanoate **23.**

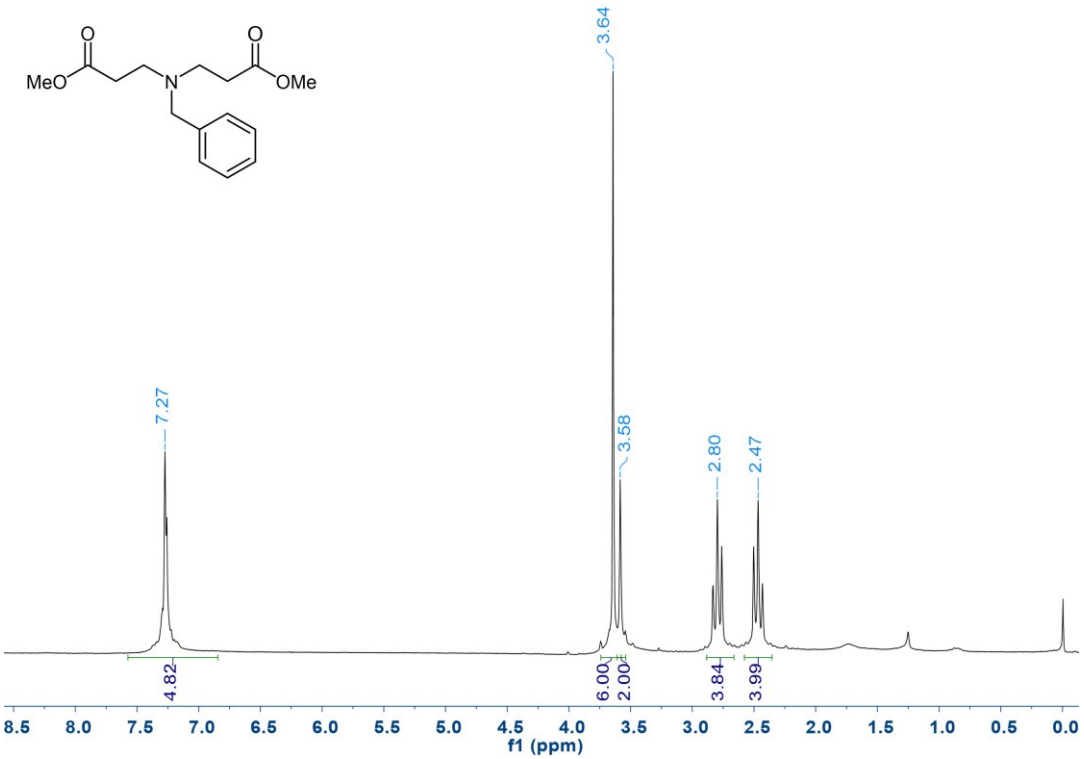

Figure S28. [1]H NMR (200 MHz, $CDCl_3$) for dimethyl 3,3′-(benzylazanediyl)dipropionate**24**.

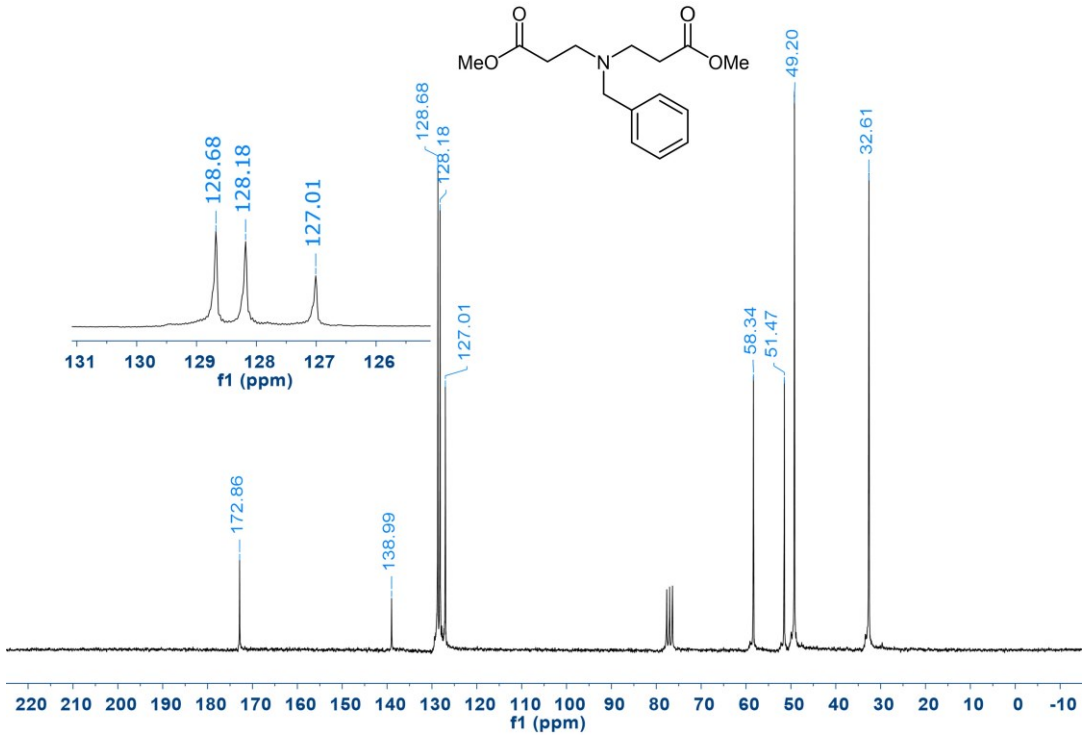

Figure S29. [13]C NMR (50 MHz, $CDCl_3$) for dimethyl 3,3′-(benzylazanediyl)dipropionate**24.**