Supporting information for:

Acid-free regioselective aminocarbonylation of alkenes

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1 General experimental details

$PdCl_2$, $Pd(OAc)_2$ $RhCl_3$, $Pd(acac)_2$ were purchased from Aldrich. $Pd_2(dba)_3$, $Co_2(CO)_8$ was purchased from Acros. $Pd(Ph_3P)_4$ was purchased from Stem. $CoCl_2$ was purchased from VWR. $RuCl_3$ $Ru_3(CO)_{12}$, $Re_2(CO)_{10}$ were purchased from abcr. Xantphos, triphos, PPh_3, Dppe, Dppf, Nixantphos, (±)-Binapo, (R)-Phanephos, DMSO-d_6 were purchased from Aldrich. Tri(o-anisyl)phosphine was purchased from Alfa Aesar and 1,2-bis(diphenylphosphino)benzene was purchased from Acros. All other solvents and reagents were purchased from Alfa Aesar. All chemicals were used as received without further purification. Purification of the products was conducted with technical grade solvents and silica gel. GC was performed on an Agilent 7890 equipped with a HP-5 column. NMR spectra were recorded at 293 K on a Bruker DMX 400 instrument with TMS as internal standard in methanol-d_4. High resolution mass spectrometry was recorded on a Micromass Q-TOF Ultima API (ESI).

2 Catalytic procedures

A mixture of $PdCl_2$ (8.8 mg, 0.05 mmol), ligand (0.06 mmol), olefin (11 mmol), aniline (1.0 mmol) and THF (10 ml) was added to a teflon tube that was placed in an autoclave. The autoclave was sealed and purged with carbon monxide to remove the air and then charged with CO (50 atm). The reaction mixture

was stirred at a required temperature for 2 h. After cooling the CO was released and the reaction mixture was purified by flash column chromatography on silica gel to afford the desired product. The yield of the product was determined by weighing the quality of isolated product or by GC analysis.

3 Optimized reaction conditions

A mixture of catalyst precursor, ligand, aniline, styrene and 10 ml THF was added into a teflon tube which was placed in an autoclave. Then the autoclave was purged and charged with CO at the designed pressure. The reaction mixture was stirred at the designed temperature for 2 h, and then CO was carefully released. The yield was determined by GC analysis relative to the oxidant with n-dodecane as internal standard.

Table S1 The effect of reaction temperature

Entry	T (°C)	Yield (%)	B/L
1	70	6	>99:<1
2	100	83	>99:<1
3	125	95	>99:<1
4	140	96	>99:<1

Reaction conditions: styrene (11 mmol), aniline (1 mmol), $PdCl_2$ (5 mol% based on aniline), P(2-OMePh)$_3$ (240 mol % based on the pre-catalyst), CO (50 atm), t: 2 h, THF 10 ml, Yields were determined by GC analysis relative to the aniline with n-decane as an internal standard.

Table S2 The effect of CO pressure

Entry	CO (atm)	Yield (%)	B/L
1	60	92	>99:<1
2	50	95	>99:<1
3	40	89	>99:<1
4	30	86	>99:<1
5	20	78	>99:<1

Reaction conditions: styrene (11 mmol), aniline (1 mmol), $PdCl_2$ (5 mol% based on aniline), P(2-OMePh)$_3$ (240 mol % based on the pre-catalyst), T: 125 ^{o}C, t: 2 h, THF 10 ml, Yields were determined by GC analysis relative to the aniline with n-decane as an internal standard.

Table S3 The effect of the amount of ligand

Entry	Pd:ligand	Yield (%)	B/L
1	1:1	79	>99:<1
2	1:2	95	>99:<1
3	1:3	95	>99:<1

Reaction conditions: styrene (11 mmol), aniline (1 mmol), $PdCl_2$ (5 mol% based on aniline), P(2-OMePh)$_3$ CO (50 atm), T: 125 ^{o}C, t: 2 h, THF 10 ml, Yields were determined by GC analysis relative to the aniline with n-decane as an internal standard.

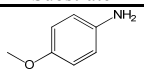
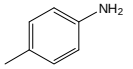
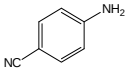
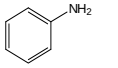
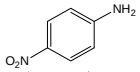
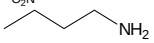
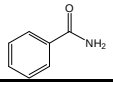
Table S4 The effect of the ration of styrene and aniline

Entry	styrene:aniline (mmol)	Yield (%)	B/L
1	10:1	95	>99:<1
2	1:1	69	>99:<1
3[a]	1:10	10	>99:<1

Reaction conditions: $PdCl_2$ (0.05 mmol), $P(2\text{-}OMePh)_3$ (0.12 mmol), CO (50 atm), T: 125 ^oC, t: 2 h, THF 10 ml, [a]Yield was based on styrene, Yields were determined by GC analysis relative to the aniline with n-decane as an internal standard.

3 The effect of N-H bond dissociation energy

Table S5 Correlation between N-H bond dissociation energy (BDE) and yield.

Entry	Substrate	N-H BDE [16] (Kcal/mol)	Yield (%)
1		87.2	86
2		88.7	80
3		91.8	57
4		92.3	53
5		96.7	4
6		100	0
7		100	0

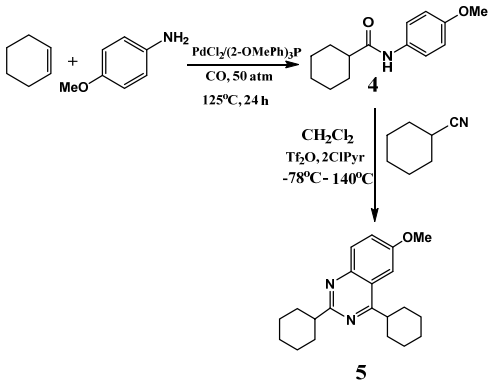
Reaction conditions: styrene (11 mmol), amine (1 mmol), $PdCl_2$ (5 mol% based on the amine). [a] $P(2\text{-}OMePh)_3$ (0.12 mmol), CO (20 atm), THF 10 ml, T: 125 ^oC, t: 2 h. Yields correspond to isolated yields.

4 Procedure for the preparation of 5

A mixture of $PdCl_2$ (8.8 mg, 0.05 mmol), $(2\text{-}OMePh)_3P$ (0.06 mmol), cyclohexene (12 mmol), 4-methoxyaniline (10 mmol) in THF (20 ml) was added to a teflon tube that was placed in an autoclave. The autoclave was sealed and purged with CO to remove the air and then charged with CO to 50 atm. The reaction mixture was stirred at 125^{o}C for 24 h. After cooling the CO was released and the reaction mixture was purified by flash column chromatography on silica gel to afford the desired product **compound 4** (yield= 60%).

Trifluoromethanesulfonic anhydride (90 μL, 0.54 mmol, 1.1 equiv) was added via syringe over 1 min to a stirred mixture of **compound 4** (115 mg, 0.493 mmol, 1 equiv) and 2-chloropyridine (56 μL, 0.59 mmol, 1.2 equiv) in dichloromethane (1.6 mL) at –78 ºC. After 5 min, the reaction mixture was placed in an ice-water bath and warmed to 0 ºC, the nitrile cyclohexanecarbonitrile (59 mg, 0.54 mmol, 1.1 equiv) was

added via syringe, and the resulting solution was allowed to warm to ambient temperature for 5 minutes and the reaction vessel was placed into a autoclave and heated to 140 ºC. After 24h, the autoclave allowed to cool to ambient temperature before aqueous sodium hydroxide solution (1 mL, 1M) was introduced to neutralize the trifluoromethanesulfonate salts. Dichloromethane (5 mL) was added to dilute the mixture and the layers were separated. The organic layer was washed with brine (2 mL), was dried over anhydrous sodium sulfate, and filtered. The volatiles were removed under reduced pressure and the residue was purified by flash column chromatography (eluent: 5% EtOAc in hexanes) on neutralized silica gel to give the quinazoline product as a white solid, and the yield is 52%.



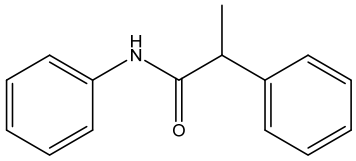
Scheme S1 Transformation of amide to useful compound

The Product NMR: ^{1}H NMR (400 MHz, CDCl3) δ: 7.86 (d, 1H, J = 9.7 Hz), 7.43 (dd, 1H, J = 9.5, 3.0 Hz,), 7.30 (d, 1H, J = 3.0 Hz,), 3.95 (s, 3H), 3.44 (tt, 1H, J = 11.7, 3.5 Hz,), 2.93 (tt, 1H, J = 11.9, 3.7 Hz,), 2.08–1.70 (m, 14 H), 1.58–1.32 (m, 6H).

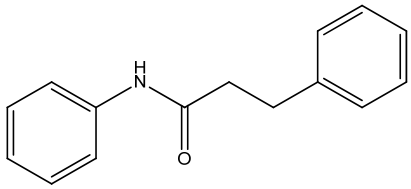
^{13}C NMR (101 MHz, CDCl3) δ: 172.93, 168.37, 157.35, 146.71, 130.53, 125.21, 122.21, 102.23, 55.86, 47.90, 41.53, 32.30, 32.04, 26.73, 26.54, 26.43, 26.32. HRMS (ESI): calcd for C21H29N2O $[M+H]^{+}$: 325.2280, found: 325.2274.

5 Product characterization

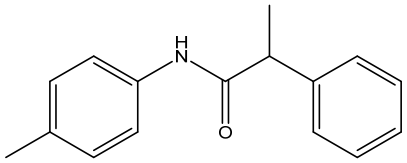
N, 2-diphenylpropanamide ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.04 (s, 1H), 7.63 – 7.54 (m, 2H), 7.47 – 7.15 (m, 7H), 7.02 (tt, J = 7.3, 1.2 Hz, 1H), 3.83 (q, J = 7.0 Hz, 1H), 1.42 (d, J = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 172.64, 142.35, 139.68, 129.12, 128.83, 127.71, 127.14, 123.62, 119.59, 46.40, 19.1; HRMS (ESI): calculated for $C_{15}H_{15}NO$ $[M+H]^{+}$ 226.1233, found 226.1232



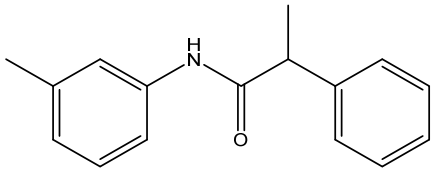
N,3-diphenylpropanamide ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.89 (s, 0H), 7.61 – 7.53 (m, 1H), 7.34 – 7.14 (m, 3H), 7.02 (tt, J = 7.5, 1.2 Hz, 0H), 2.92 (t, J = 8.6, 6.8 Hz, 1H), 2.63 (t, J = 8.5, 7.0 Hz, 1H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 170.80, 141.65, 139.68, 129.11, 128.73, 126.39, 123.46, 119.51, 38.41, 31.28; HRMS (ESI): calculated for $C_{15}H_{15}NO$ $[M+H]^+$ 226.1233, found 226.1232



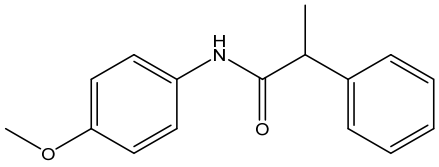
2-phenyl-N-(p-tolyl)propanamide ***(3a$_1$b$_1$)*** ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.96 (s, 1H), 7.53 – 7.43 (m, 2H), 7.41 – 7.37 (m, 2H), 7.33 (dd, J = 8.5, 6.8 Hz, 2H), 7.28 – 7.19 (m, 1H), 7.14 – 7.02 (m, 2H), 3.81 (q, J = 7.0 Hz, 1H), 2.23 (s, 3H), 1.41 (d, J = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 172.38, 142.44, 137.17, 132.49, 129.48, 128.80, 127.70, 127.11, 119.62, 46.35, 20.87, 19.14. HRMS (ESI): calculated for $C_{16}H_{17}NO$ $[M+H]^+$ 240.1388, found 240.1385



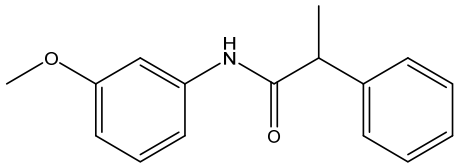
2-phenyl-N-(m-tolyl)propanamide ***(3a$_2$b$_2$)*** ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.97 (s, 1H), 7.49 – 7.12 (m, 8H), 6.84 (d, J = 7.5 Hz, 1H), 3.83 (q, J = 7.0 Hz, 1H), 1.41 (d, J = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 172.54, 142.39, 139.61, 138.29, 128.94, 128.81, 127.70, 127.12, 124.30, 120.16, 116.79, 46.38, 21.61, 19.09. HRMS (ESI): calculated for $C_{16}H_{17}NO$ $[M+H]^+$ 240.1388, found 240.1385



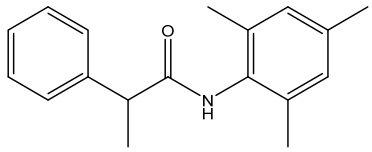
N-(4-methoxyphenyl)-2-phenylpropanamide ***(3a$_3$b$_3$)*** ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.91 (s, 1H), 7.55 – 7.46 (m, 2H), 7.42 – 7.19 (m, 5H), 6.93 – 6.80 (m, 2H), 3.78 (q, J = 7.0 Hz, 1H), 3.70 (s, 3H), 1.41 (d, J = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 172.12, 155.58, 132.83, 128.79, 127.69, 127.09, 121.11, 114.24, 55.60, 46.28, 19.14. HRMS (ESI): calculated for $C_{16}H_{17}NO_2$ $[M+H]^+$ 256.1338, found 256.1339



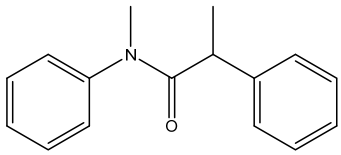
N-(3-methoxyphenyl)-2-phenylpropanamide ***(3a$_4$b$_4$)*** ^{1}H NMR (400 MHz, DMSO-d6) δ 10.42 (s, 1H), 8.11 (s, 1H), 7.80 (dt, J = 6.8, 2.5 Hz, 1H), 7.55 – 7.46 (m, 2H), 7.43 – 7.30 (m, 4H), 7.30 – 7.19 (m, 1H), 3.84 (q, J = 7.0 Hz, 1H), 1.43 (d, J = 7.0 Hz, 3H). 13C NMR (101 MHz, methanol-d_4) δ 170.72, 156.59, 135.54, 131.35, 128.69, 128.17, 126.51, 121.73, 113.53, 54.44, 43.14; HRMS (ESI): calculated for $C_{16}H_{17}NO_2$ $[M+H]^+$ 256.1338, found 256.1339



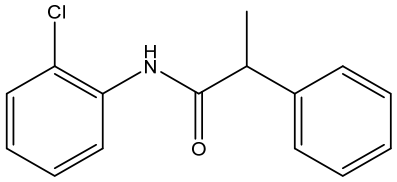
N-mesityl-2-phenylpropanamide ***(3a$_5$b$_5$)*** ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.23 (s, 1H), 7.46 – 7.38 (m, 2H), 7.38 – 7.31 (m, 2H), 7.30 – 7.20 (m, 1H), 6.83 (s, 2H), 3.86 (q, J = 7.0 Hz, 1H), 3.69 (s, 1H), 2.20 (s, 3H), 1.44 (d, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 172.39, 142.57, 135.71, 135.39, 132.81, 128.67, 127.74, 127.04, 45.70, 20.93, 18.87, 18.20; HRMS (ESI): calculated for $C_{18}H_{21}NO$ $[M+H]^+$ 268.1701, found 268.1706



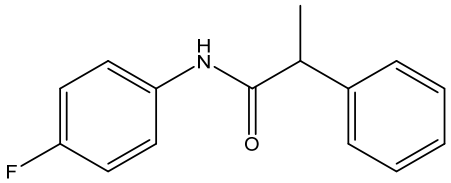
N-methyl-N,2-diphenylpropanamide ***(3a$_6$b$_6$)*** ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.40 (p, J = 6.3 Hz, 3H), 7.28 – 7.08 (m, 5H), 6.96 (d, J = 7.2 Hz, 2H), 3.71 – 3.55 (m, 1H), 3.14 (s, 3H), 1.27 (d, J = 6.9 Hz, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 173.18, 144.04, 142.19, 130.01, 128.69, 128.19, 128.08, 127.66, 126.94, 42.38, 37.62, 20.17. HRMS (ESI): calculated for $C_{16}H_{17}NO$ $[M+H]^+$ 240.1388, found 240.1385



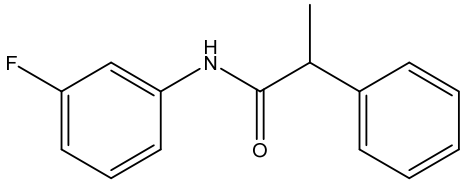
N-(2-chlorophenyl)-2-phenylpropanamide ***(3a$_7$b$_7$)*** ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.55 (s, 1H), 7.66 (dd, J = 8.1, 1.6 Hz, 1H), 7.49 – 7.12 (m, 8H), 4.03 (q, J = 7.0 Hz, 1H), 1.44 (d, J = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 173.00, 142.07, 135.26, 129.88, 128.84, 127.87, 127.81, 127.20, 127.12, 126.78, 126.63, 45.66, 19.01; HRMS (ESI): calculated for $C_{15}H_{14}ClNO$ $[M+H]^+$260.0842, found 260.0831



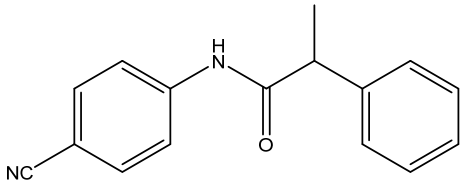
N-(4-fluorophenyl)-2-phenylpropanamide ***(3a$_8$b$_8$)*** ^{1}H NMR (400 MHz, DMSO-d$_6$) δ 10.12 (s, 1H), 7.66 – 7.54 (m, 2H), 7.43 – 7.04 (m, 7H), 3.81 (q, J = 7.0 Hz, 1H), 1.42 (d, J = 6.8, 1.4 Hz, 3H). 13C NMR (101 MHz, DMSO-d$_6$) δ 172.55, 159.56, 157.18, 136.04, 136.09, 127.70, 127.16, 121.38, 121.30, 115.78, 115.56, 46.37, 19.10; HRMS (ESI): calculated for $C_{15}H_{14}FNO$ $[M+H]^+$ 244.1138, found 244.1133



N-(3-fluorophenyl)-2-phenylpropanamide ***(3a$_9$b$_9$)*** ^{1}H NMR (400 MHz, DMSO-d$_6$) δ 10.28 (s, 1H), 7.62 (dt, J = 11.1, 1.9 Hz, 1H), 7.42 – 7.19 (m, 7H), 6.92 – 6.80 (m, 1H), 3.83 (q, J = 7.0 Hz, 1H), 1.42 (d, J = 7.0 Hz, 3H). 13C NMR (101 MHz, DMSO-d$_6$) δ 173.05, 163.75, 161.36, 142.05, 141.44, 141.33, 130.81, 130.72, 128.88, 127.71, 127.24, 115.33, 115.31, 110.19, 109.98, 106.50, 106.23, 46.51, 19.08; HRMS (ESI): calculated for $C_{15}H_{14}FNO$ $[M+H]^+$ 244.1138, found 244.1131

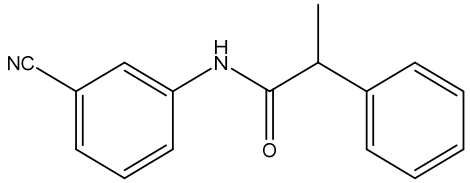


N-(4-cyanophenyl)-2-phenylpropanamid ***(3a$_{10}$b$_{10}$)*** ^{1}H NMR (400 MHz, DMSO-d$_6$) δ 10.49 (s, 1H), 7.82 – 7.70 (m, 4H), 7.44 – 7.30 (m, 4H), 7.29 – 7.20 (m, 1H), 3.86 (q, J = 7.0 Hz, 1H), 1.43 (d, J = 7.0 Hz, 3H). 13C NMR (101 MHz, DMSO-d$_6$) δ 173.49, 143.84, 141.81, 133.70, 128.95, 127.72, 127.33, 119.65, 119.48, 105.40, 104.99, 46.63, 19.08. HRMS (ESI): calculated for $C_{16}H_{14}N_2O$ $[M+H]^+$ 250.1184, found 250.1193

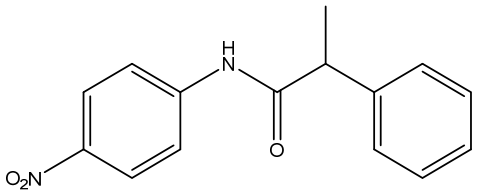


N-(3-cyanophenyl)-2-phenylacetamide ***(3a$_{11}$b$_{11}$)*** ^{1}H NMR (400 MHz, DMSO-*d*$_6$):) δ 10.48 (s, 1H), 7.80 – 7.71 (m, 4H), 7.39 – 7.27 (m, 4H), 7.25 – 7.23 (m, 1H), 3.89-3.84 (q, J = 7.0 Hz, 1H), 1.44-1.42 (d, J =

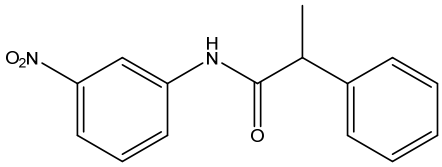
6.9 Hz, 3H).[13]C NMR (101 MHz, methanol-d_4): δ= 173.49, 143.85, 141.81, 133.69, 128.94, 127.73, 127.32, 119.64, 119.48, 105.40, 46.63, 19.08; HRMS (ESI): calculated for $C_{16}H_{14}N_2O$ $[M+H]^+$ 250.1184, found 250.1193



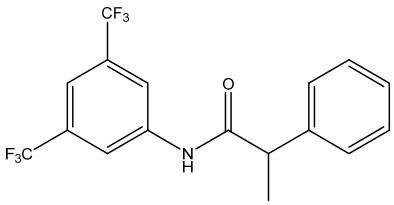
N-(4-nitrophenyl)-2-phenylpropanamide ***(3a$_{12}$b$_{12}$)*** ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.66 (s, 1H), 8.28 – 8.15 (m, 2H), 7.92 – 7.79 (m, 2H), 7.44 – 7.20 (m, 5H), 3.89 (q, J = 7.0 Hz, 1H), 1.44 (d, J = 6.9 Hz, 3H). ^{13}C NMR (101 MHz, DMSO) δ 172.60, 143.57, 143.50, 140.12, 129.44, 128.01, 127.67, 125.00, 118.92, 48.38, 18.45. HRMS (ESI): calculated for $C_{15}H_{12}N_2O$ $[M+H]^+$ 237.103, found 237.1028



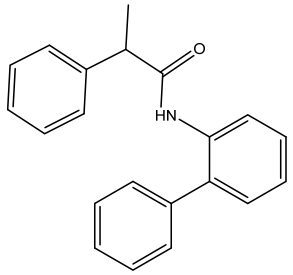
N-(3-nitrophenyl)-2-phenylpropanamide ***(3a$_{13}$b$_{13}$)*** ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.55 (s, 1H), 8.64 (s, 1H), 7.95 – 7.85 (m, 2H), 7.59 (t, J = 8.2 Hz, 1H), 7.44 – 7.20 (m, 5H), 3.86 (q, J = 7.0 Hz, 1H), 1.45 (d, J = 7.0 Hz, 3H). 13C NMR (101 MHz, DMSO-d_6) δ 173.45, 148.38, 141.84, 140.74, 130.63, 129.10, 127.74, 127.34, 125.54, 118.20, 113.70, 46.62, 19.21; HRMS (ESI): calculated for $C_{15}H_{14}N_2O_3$ $[M+H]^+$ 271.1083, found 271.1093



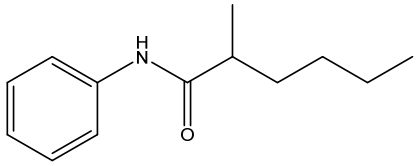
N-(3,5-bis(trifluoromethyl)phenyl)-2-phenylpropanamide ***(3a$_{14}$b$_{14}$)*** ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.72 (s, 1H), 8.29 (s, 2H), 7.75 (s, 1H), 7.44 – 7.20 (m, 5H), 3.85 (q, J = 7.0 Hz, 1H), 1.45 (d, J = 7.0 Hz, 3H). ^{13}C (101 MHz, DMSO-d_6) δ 173.82, 141.55, 141.44, 131.36, 129.00, 127.77, 127.43, 125.01, 122.32, 119.23, 116.51, 46.80, 19.02; HRMS (ESI): calculated for $C_{17}H_{13}F_6NO$ $[M+H]^+$ 362.0980, found 362.0974



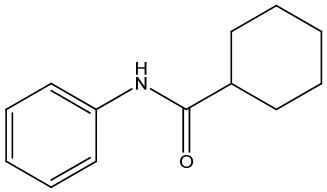
N-([1,1'-biphenyl]-2-yl)-2-phenylpropanamide ***(3a$_{15}$b$_{15}$)*** ^{1}H NMR (400 MHz, DMSO-d$_6$) δ 9.25 (s, 1H), 7.23 (m, 14 H), 3.71 (m, 1H), 1.33 (d, J = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, DMSO-d$_6$) δ 172.89, 141.95, 138.99, 136.70, 135.11, 130.64, 129.14, 128.76, 128.70, 128.08, 127.83, 127.53, 127.23, 127.05, 126.34, 45.68, 40.23, 18.84. HRMS (ESI): calculated for $C_{21}H_{19}NO$ $[M+H]^+$ 301.1467, found 301.1465



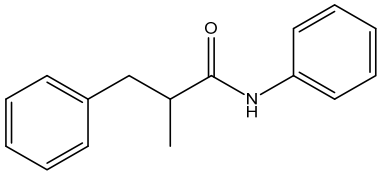
2-methyl-N-phenylhexanamide ***(3a$_{16}$b$_{16}$)*** ^{1}H NMR (400 MHz, DMSO-d$_6$) δ 9.82 (s, 1H), 7.61 (d, J = 7.6 Hz, 2H), 7.34 – 7.20 (d, 2H), 7.02 (t, J = 7.4 Hz, 1H), 1.69 – 1.49 (m, 1H), 1.44 – 1.12 (m, 6H), 1.08 (d, J = 6.8 Hz, 3H), 0.86 (t, J = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, DMSO-d$_6$) δ 175.24, 139.81, 129.07, 123.42, 119.62, 41.03, 33.99, 29.64, 22.64, 18.39, 14.38; HRMS (ESI): calculated for $C_{13}H_{19}NO$ $[M+H]^+$ 206.1545, found 206.1535



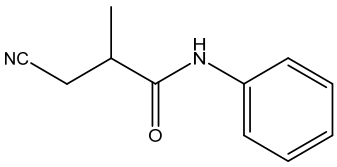
N-Phenylcyclohexanecarboxamide ***(3a$_{17}$b$_{17}$)*** ^{1}H NMR (400 MHz, methanol-d$_4$): δ= 7.59-7.50 (d, 2H), 7.30 (t, J= 8.0Hz 2H), 7.08 (t, J= 7.4Hz, 1H), 2.46-2.30 (m, 1H), 1.93-1.82 (m, 5H), 1.64-1.16 (m, 5H); ^{13}C NMR (101 MHz, methanol-d$_4$): δ= 176.27,138.62, 128.30, 123.61, 119.92, 45.76, 29.30, 25.55, 25.40; HRMS (ESI): calculated for $C_{13}H_{17}NO$ $[M+H]^+$ 204.1390, found 204.1388



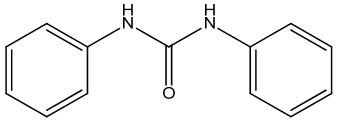
2-methyl-N,3-diphenylpropanamide phenylpropanamide ***(3a$_{18}$b$_{18}$)*** ^{1}H NMR (400 MHz, DMSO-d6) δ 9.82 (s, 1H), 7.62 - 7.51 (m, 2 H), 7.32 - 7.13 (m, 7H), 7.01 (m, 1H), 2.97 (dd, J = 13.2, 7.7 Hz, 1H), 2.78 (h, J = 6.9 Hz, 1H), 2.61 (dd, J =13.2 Hz, 6.8 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-d$_6$) δ 174.46, 140.42, 139.69, 129.30, 129.06, 128.62, 126.46, 123.48, 119.66, 42.90, 42.89, 18.14. HRMS (ESI): calculated for $C_{16}H_{17}NO$ $[M+H]^+$ 240.1388, found 240.1385



3-cyano-2-methyl-N-phenylpropanamide ***(3a$_{19}$b$_{19}$)*** ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.07 (s, 1H), 7.60 (d, J = 7.6 Hz, 2H), 7.32 (t, J = 7.9 Hz, 2H), 7.06 (t, J = 7.4 Hz, 1H), 2.85 (s, 1H), 2.81 – 2.61 (m, 2H), 1.24 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 172.17, 139.37, 129.19, 123.87, 119.90, 119.71, 37.58, 20.84, 17.99. HRMS (ESI): calculated for $C_{11}H_{12}N_2O$ $[M+H]^+$ 189.2338, found 189.2341



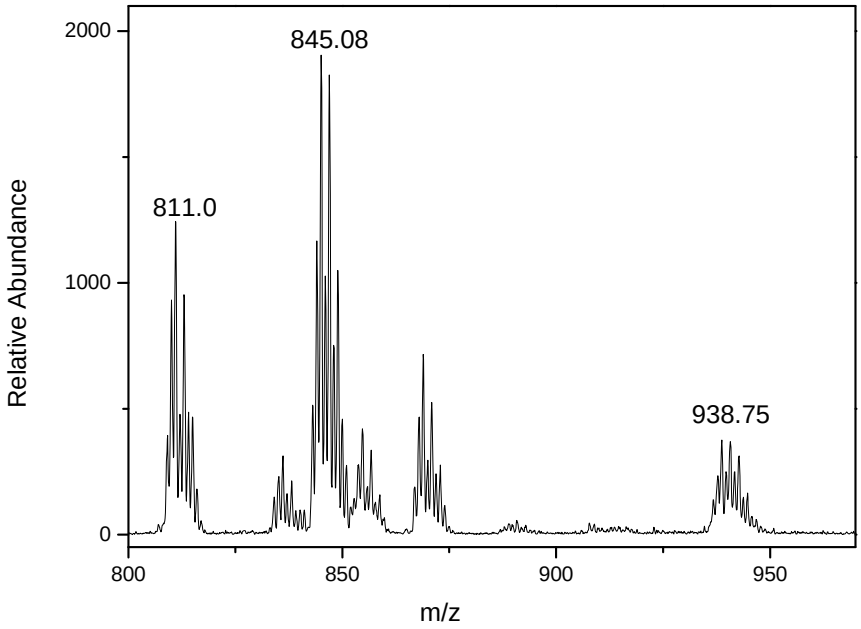
1,3-diphenylurea ^{1}H NMR (400 MHz, DMSO-d_6): δ= 8.67 (s, NH, 2H), 7.46-7.44 (d, J= 8.4Hz, 4H), 7.30-7.26 (t, J= 7.7Hz, 4H), 6.99-6.95 (t, J= 7.0Hz, 2H); ^{13}C NMR (101 MHz, DMSO-d_6): δ= 154.19, 139.08, 128.45, 122.44, 119.01; HRMS (ESI): calculated for $C_{13}H_{12}N_2O$ $[M+H]^+$ 223.0983, found 223.0987



6 Mechanistic studies

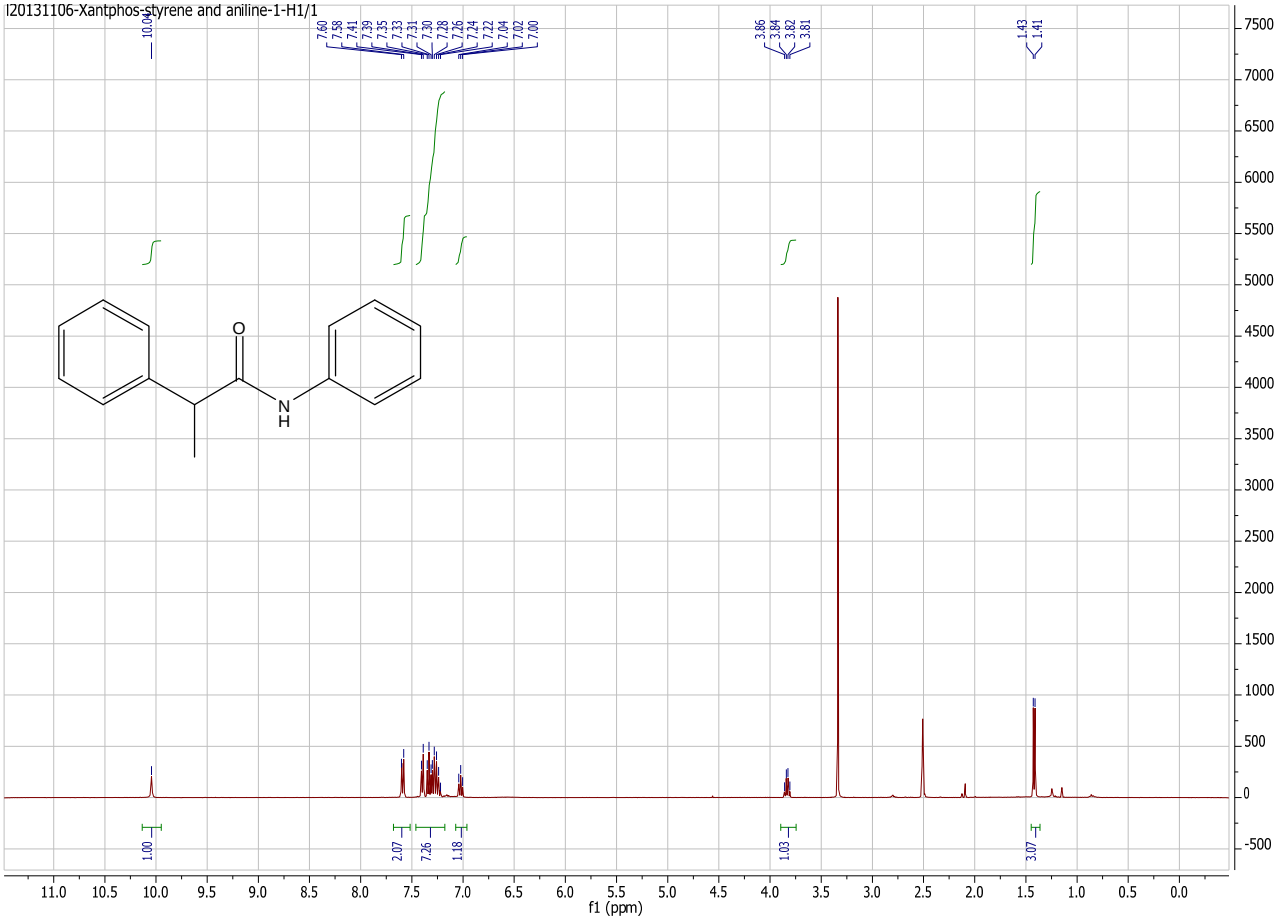
ESI-MS/MS spectra were recorded on BrukerMicroTOF-QII mass equipped with a standard ESI ion source. The basic ESI conditions were: vacuum, 3.7×10-7 mbar; Capillary voltage, 4500 V; Dry Heater temperature, 180oC. Data acquisition and analysis were done with the Bruker Daltonicsmicro TOF control (version3.0) software package.

Following a standard catalytic run for 0.5 h, THF was removed by vacuum and then the reaction mixture was diluted with methanol and analyzed by ESI-MS. The peaks at 811.0, 845.08 and 938.75 were observed that corresponds to the species $[L_2PdH]^+$ (MS: 811.0), $[L_2PdCl]^+$ (MS: 845.08) , $[L_2PdClNH_2Ph]^+$ (MS: 938.75) (L= tris(2-methoxyphenyl)phosphine)

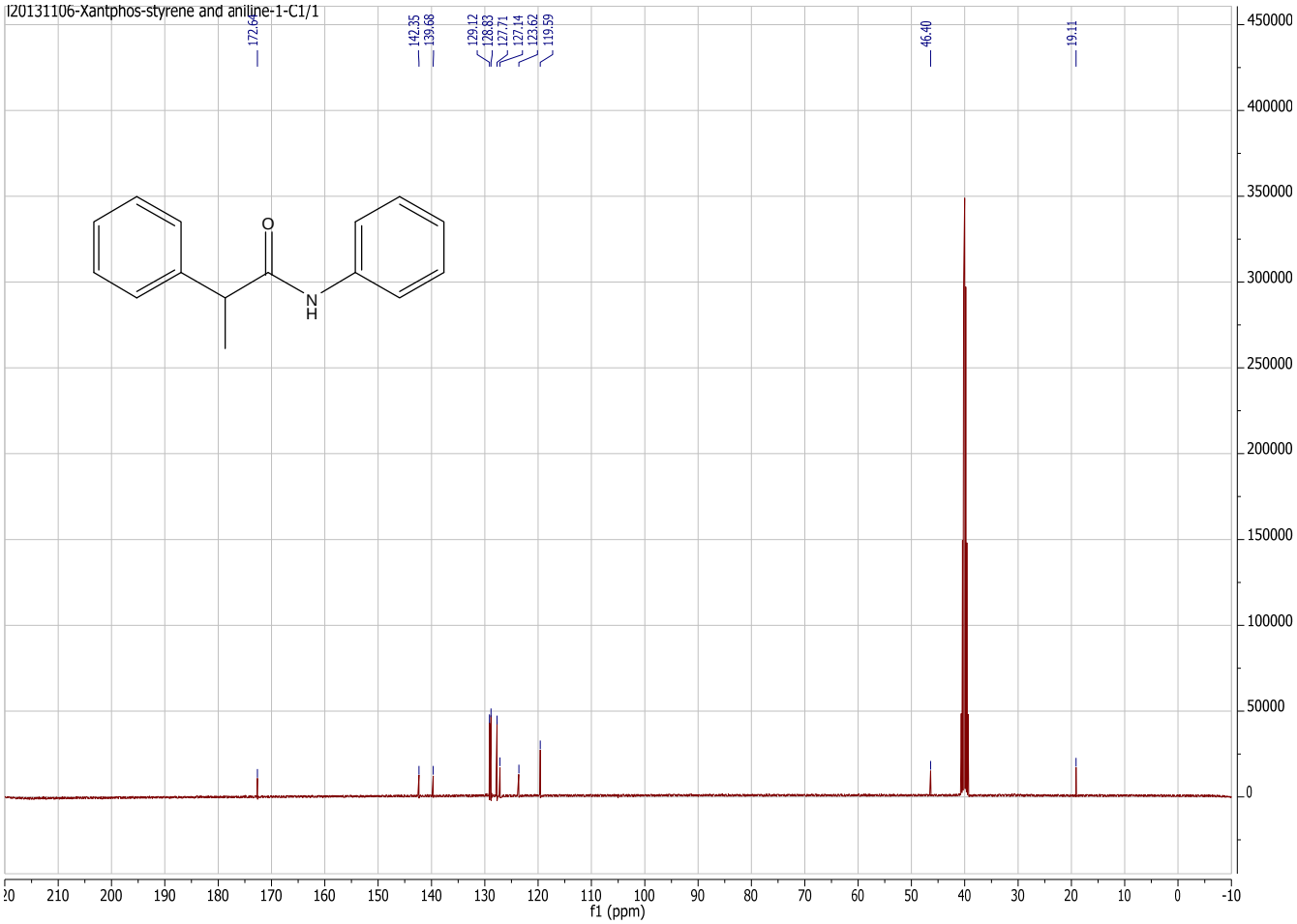

2000
1000
0
Relative Abundance
845.08
811.0
938.75
800
850
900
950
m/z

7 NMR spectra

^{1}H NMR of N,2-diphenylpropanamide

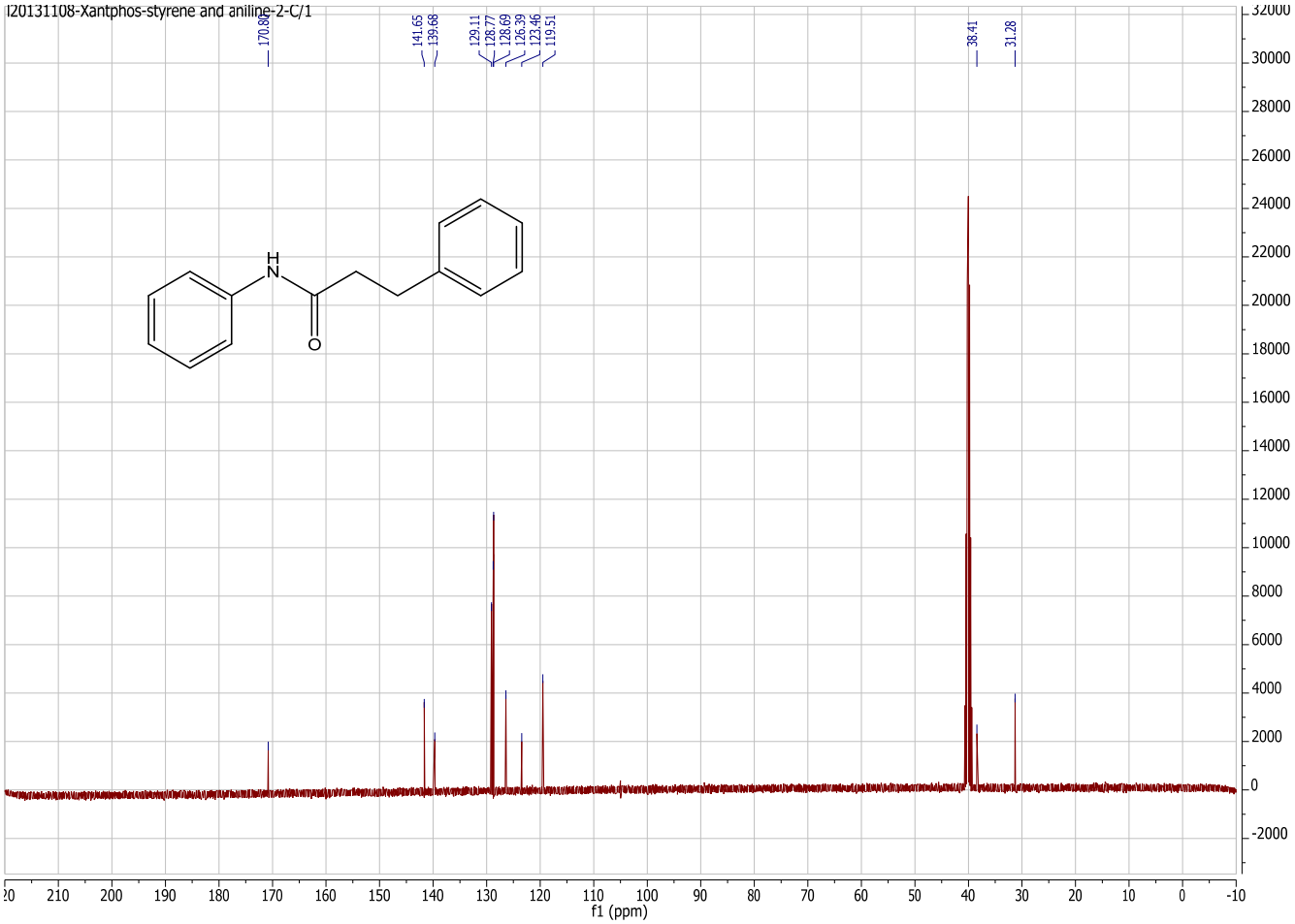


^{13}C NMR of N,2-diphenylpropanamide

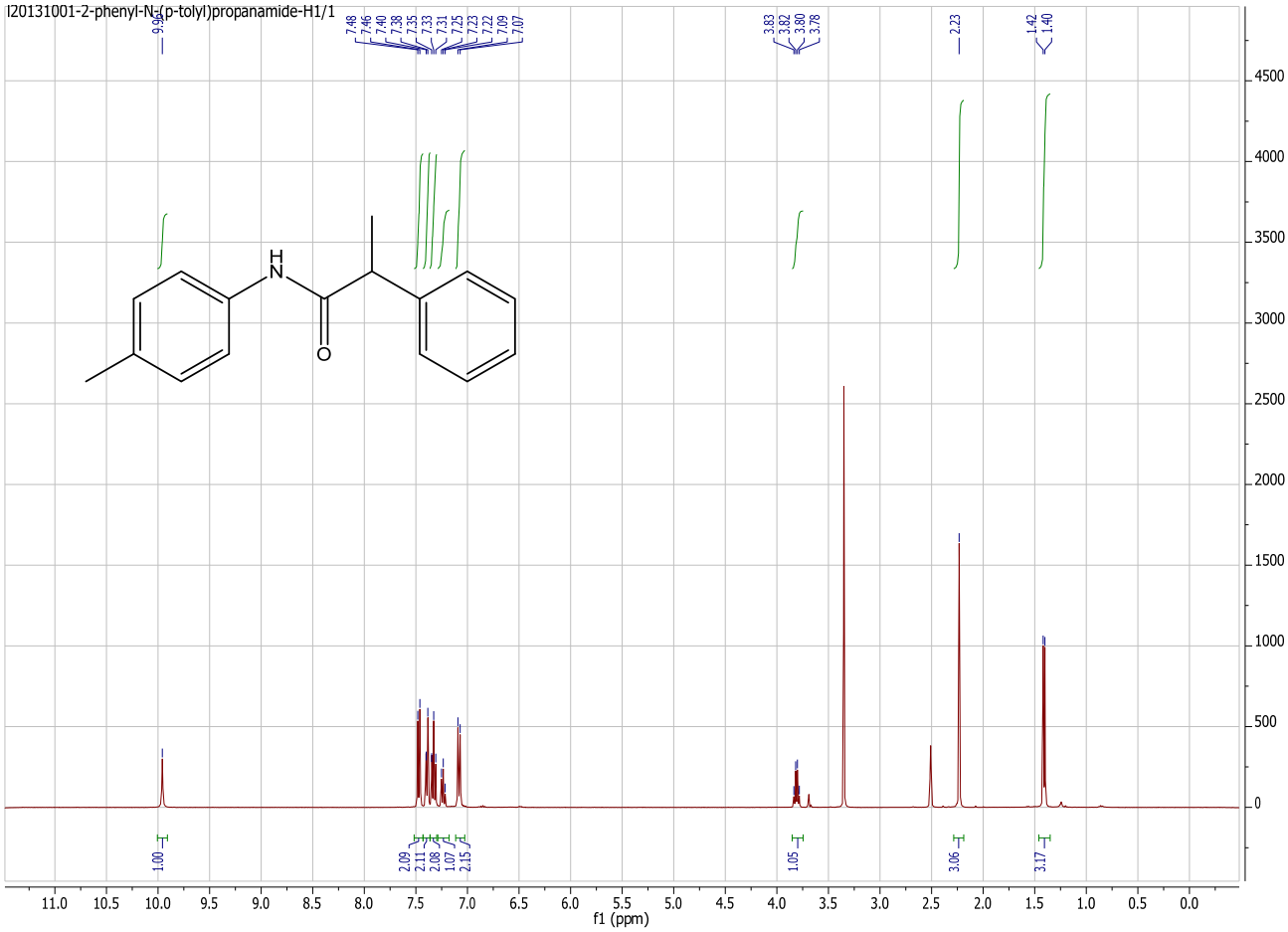


^{1}H NMR of N, 3-diphenylpropanamide

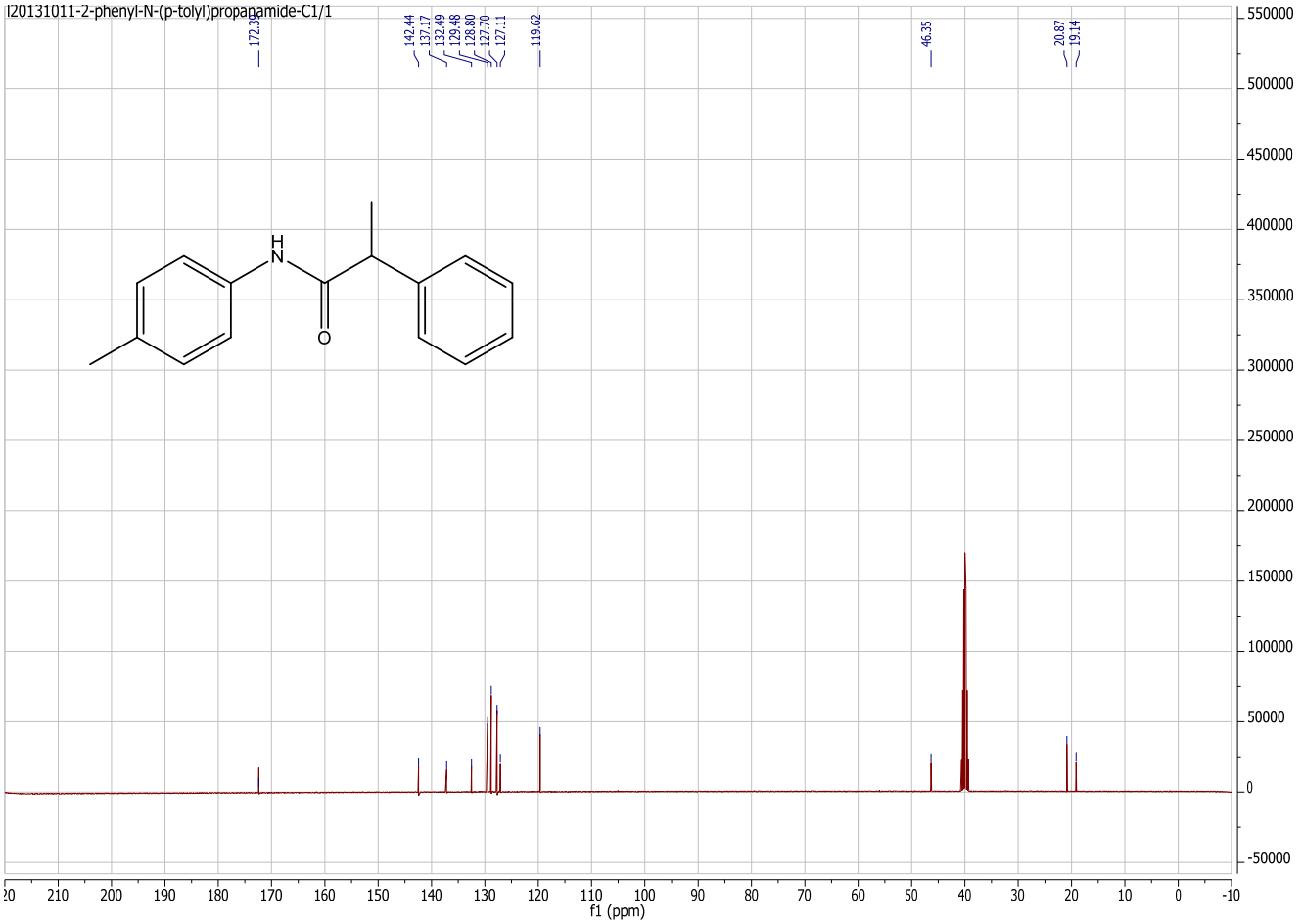
^{13}C NMR of N, 3-diphenylpropanamide



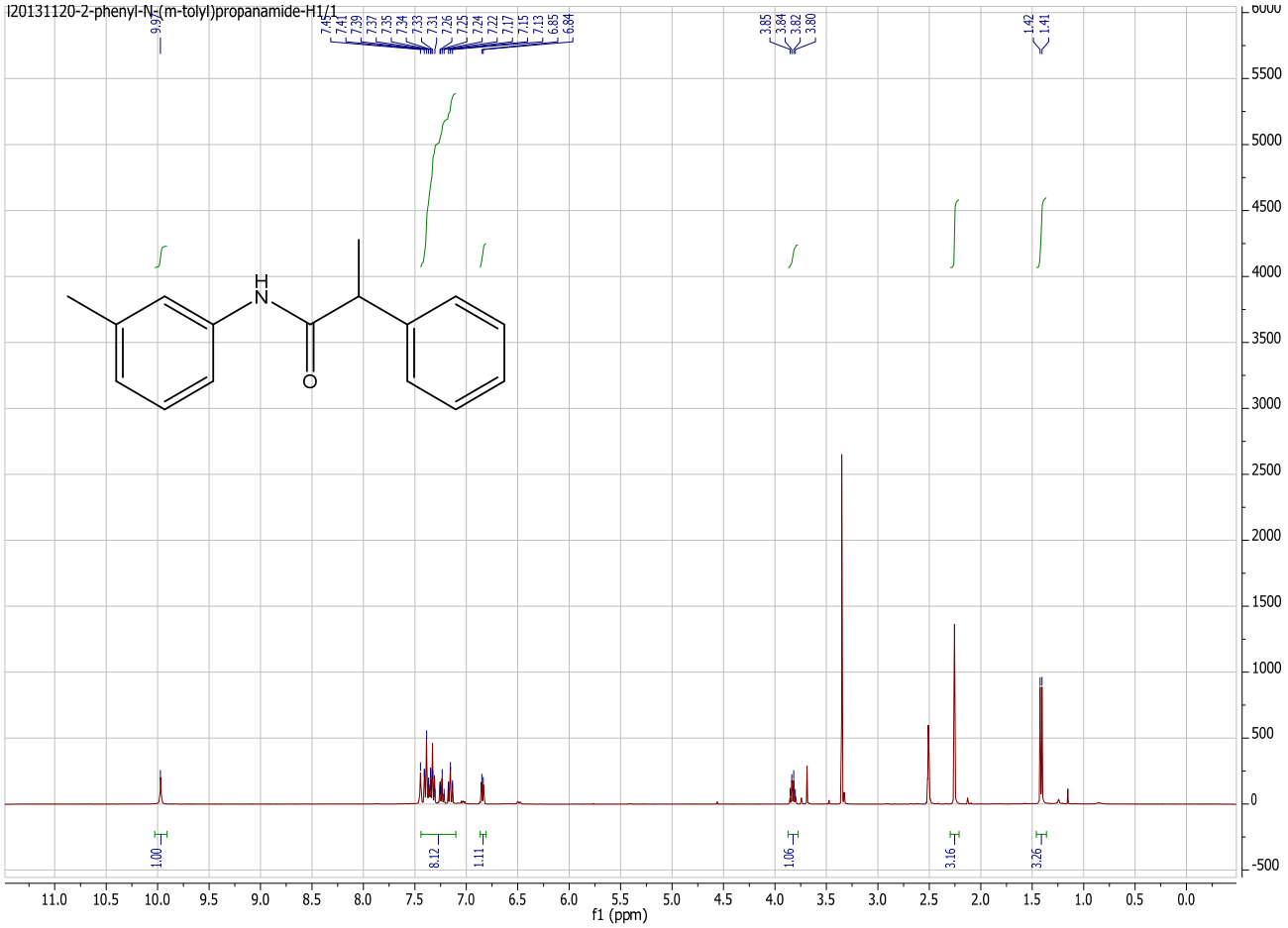
^{1}H NMR of 2-phenyl-N-(p-tolyl)propanamide ($3a_1b_1$)



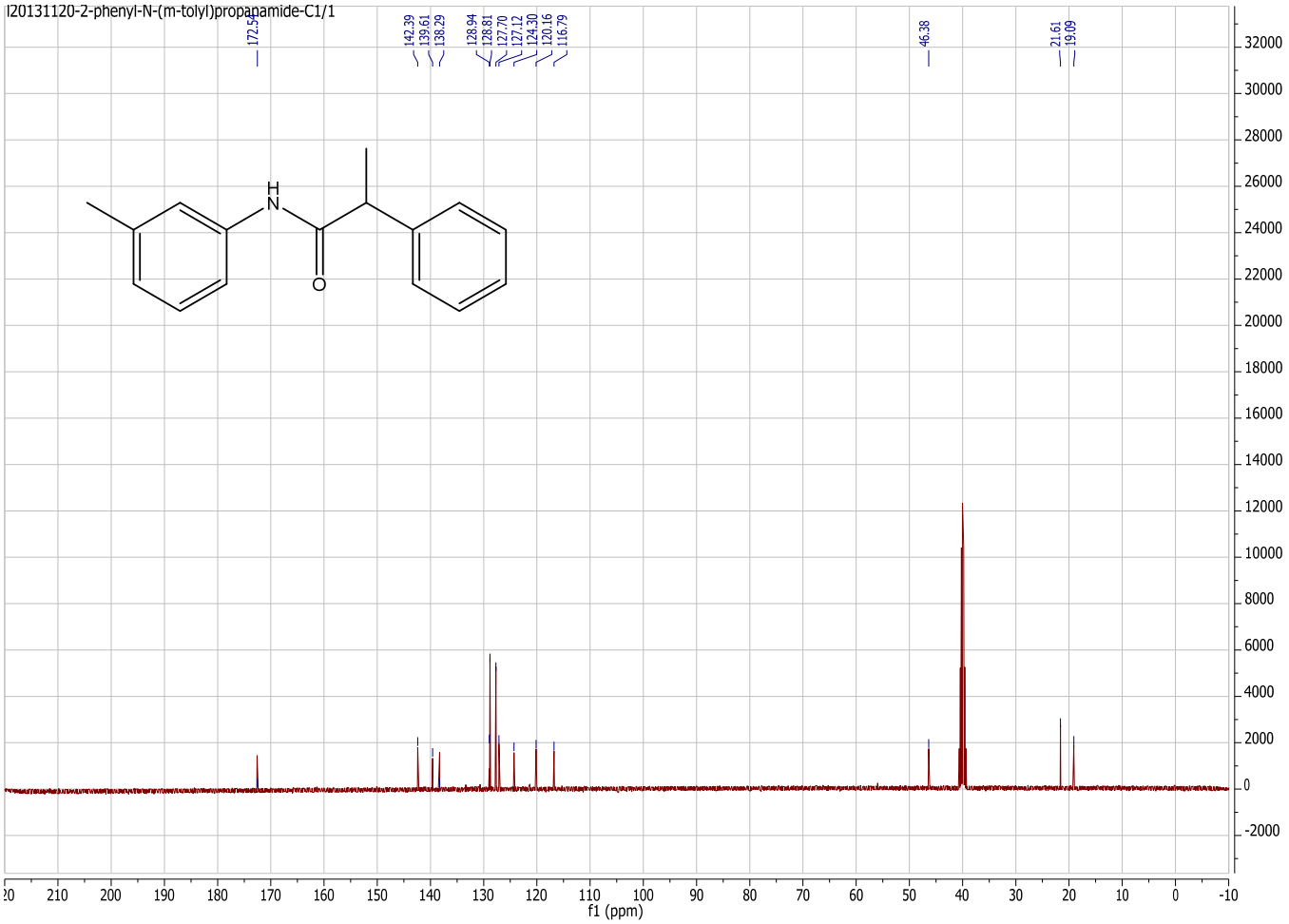
^{13}C NMR of 2-phenyl-N-(p-tolyl)propanamide ($3a_1b_1$)



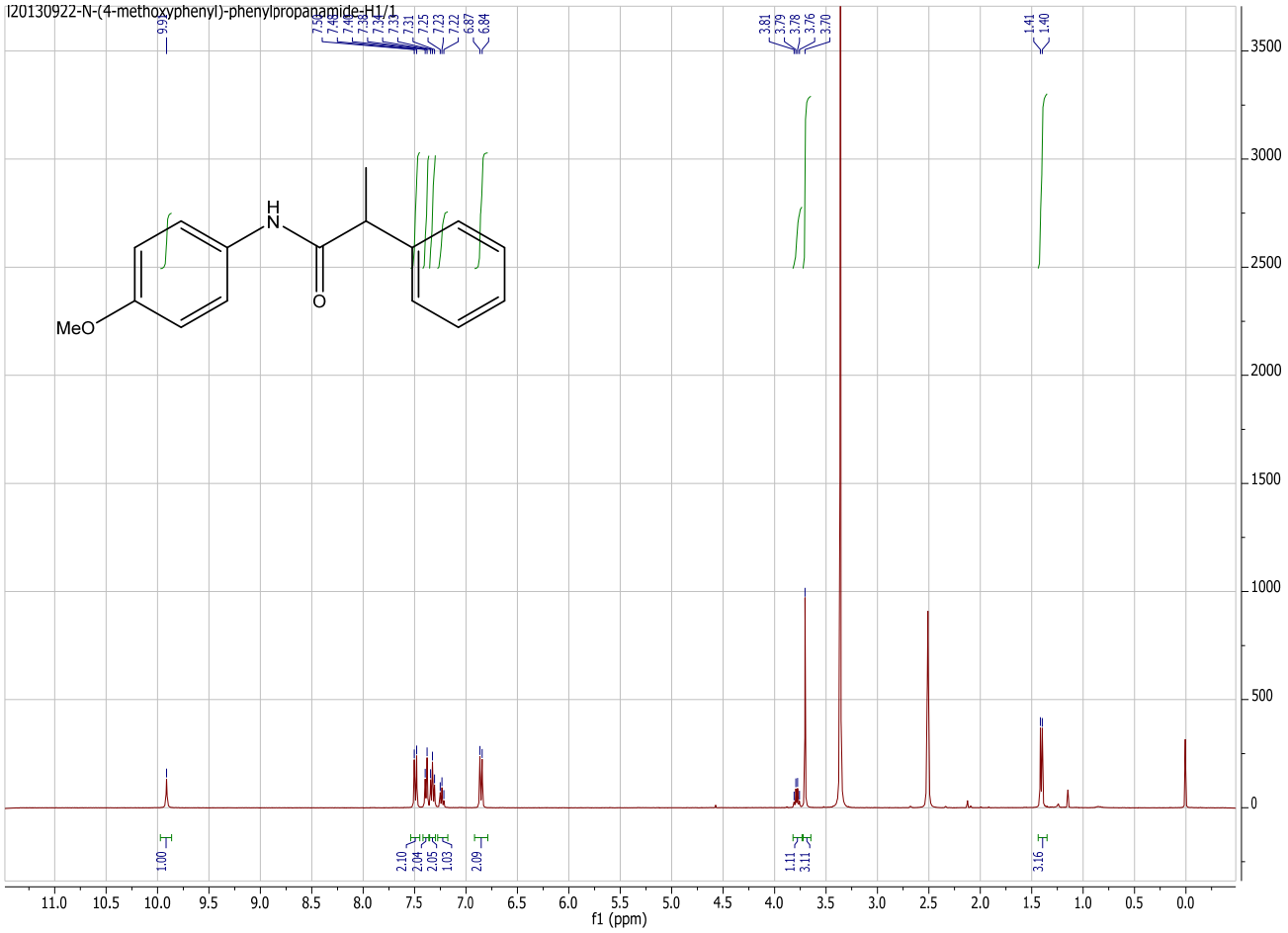
^{1}H NMR of 2-phenyl-N-(m-tolyl)propanamide ($3a_2b_2$)



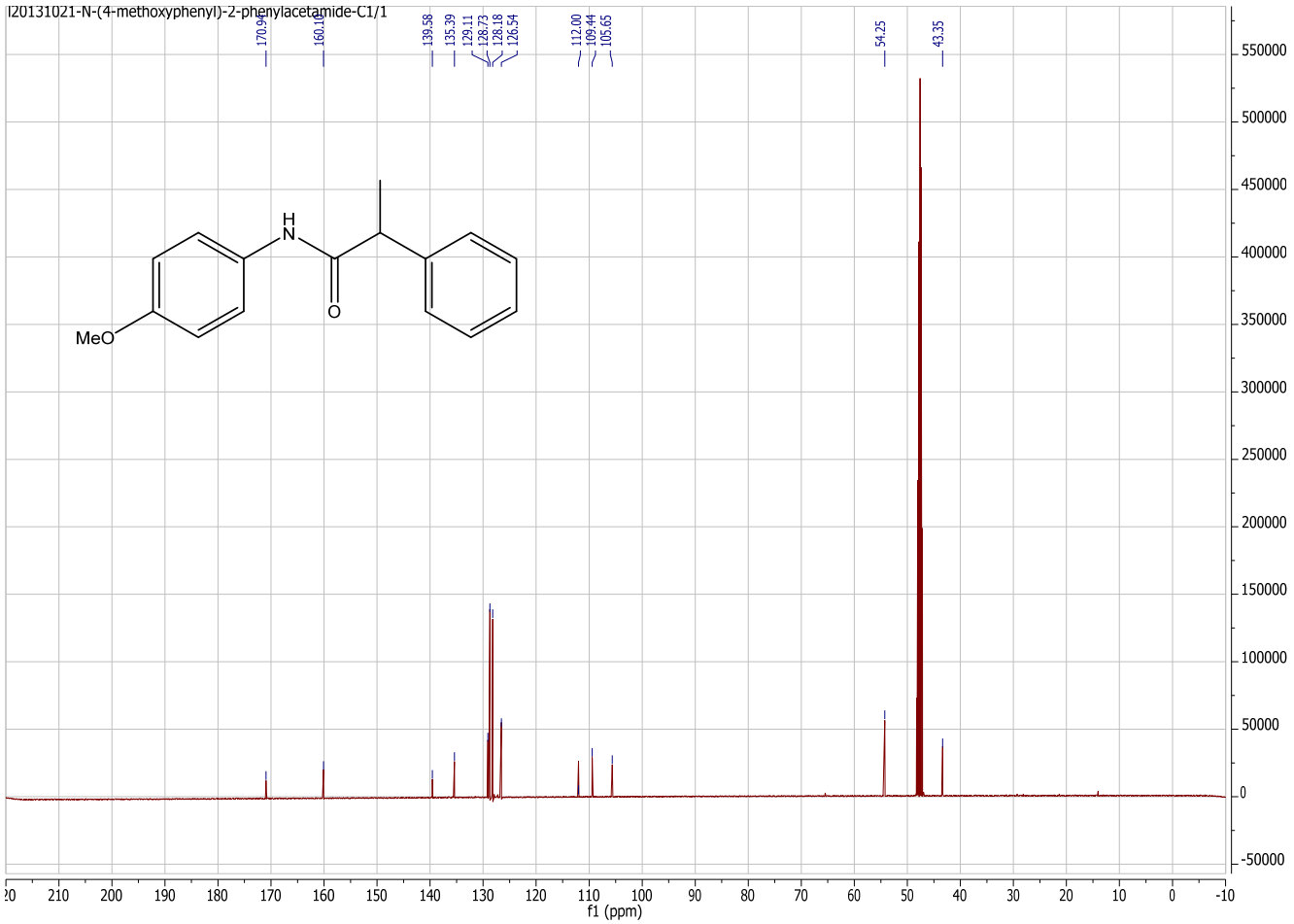
^{13}C NMR of 2-phenyl-N-(m-tolyl)propanamide ($3a_2b_2$)



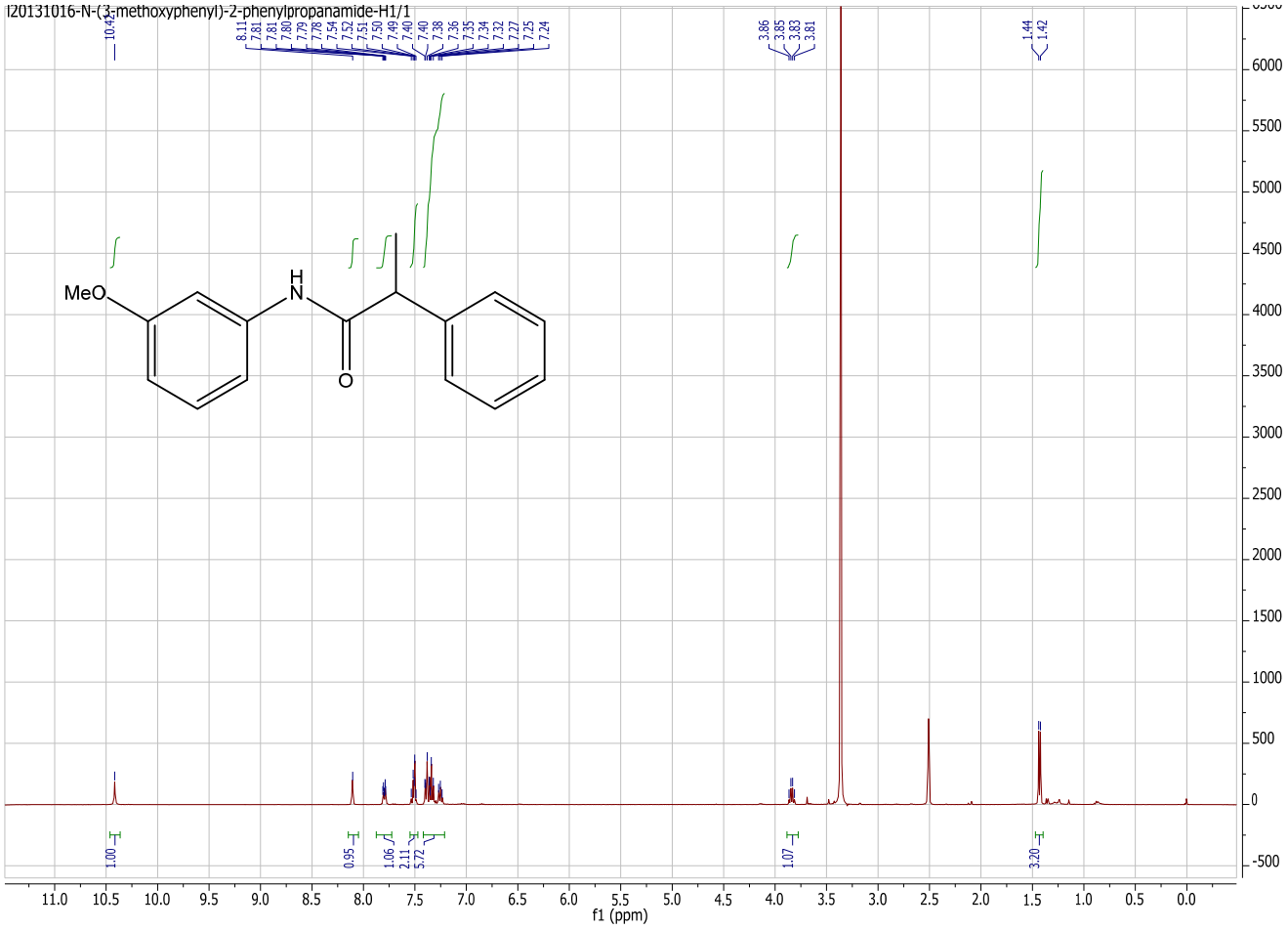
^{1}H NMR of N-(4-methoxyphenyl)-2-phenylpropanamide ($3a_3b_3$)



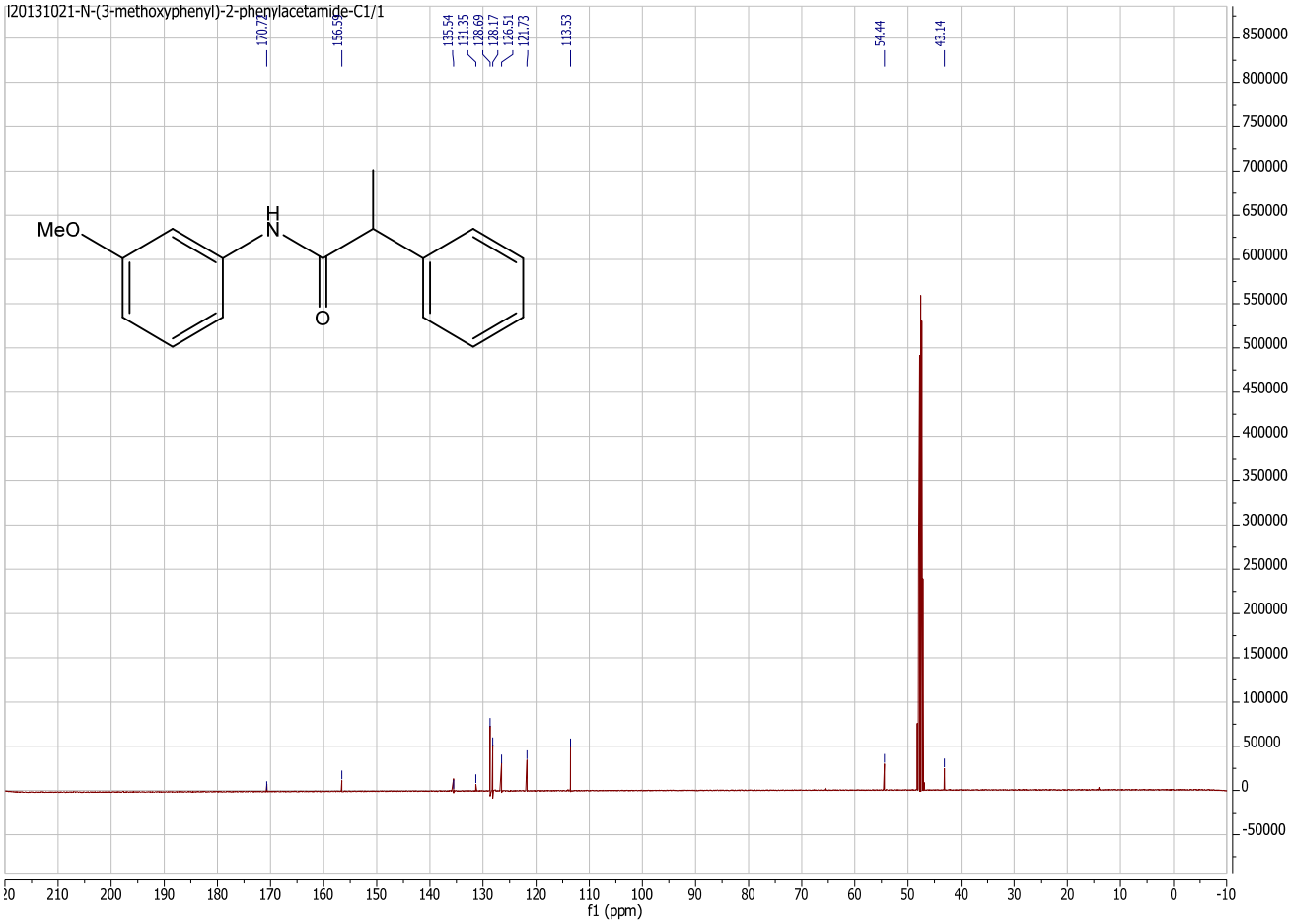
^{13}C NMR of 2-phenyl-N-(m-tolyl)acetamide ($3a_3b_3$)



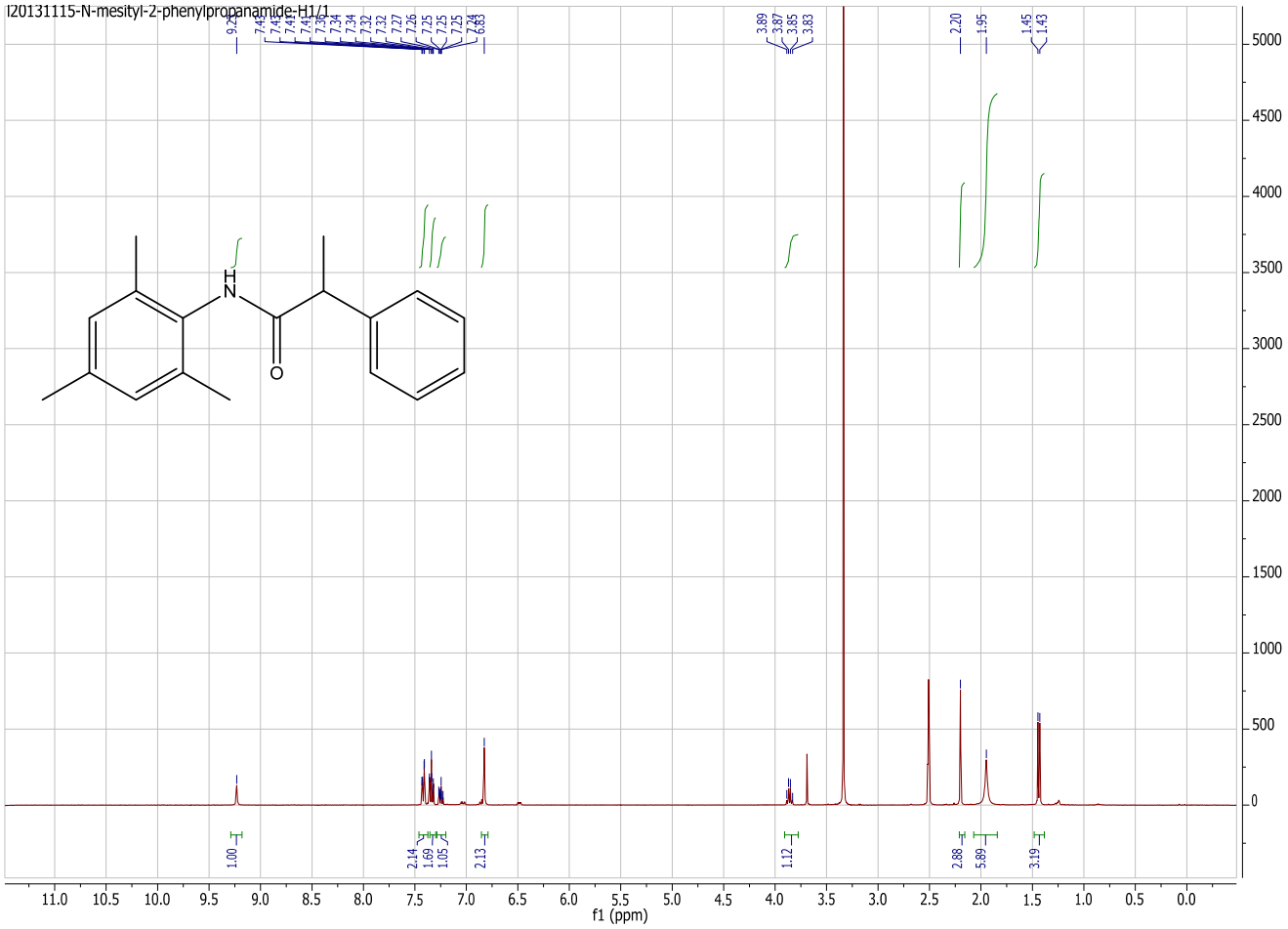
^{1}H NMR of N-(3-methoxyphenyl)-2-phenylpropanamide ($3a_4b_4$)



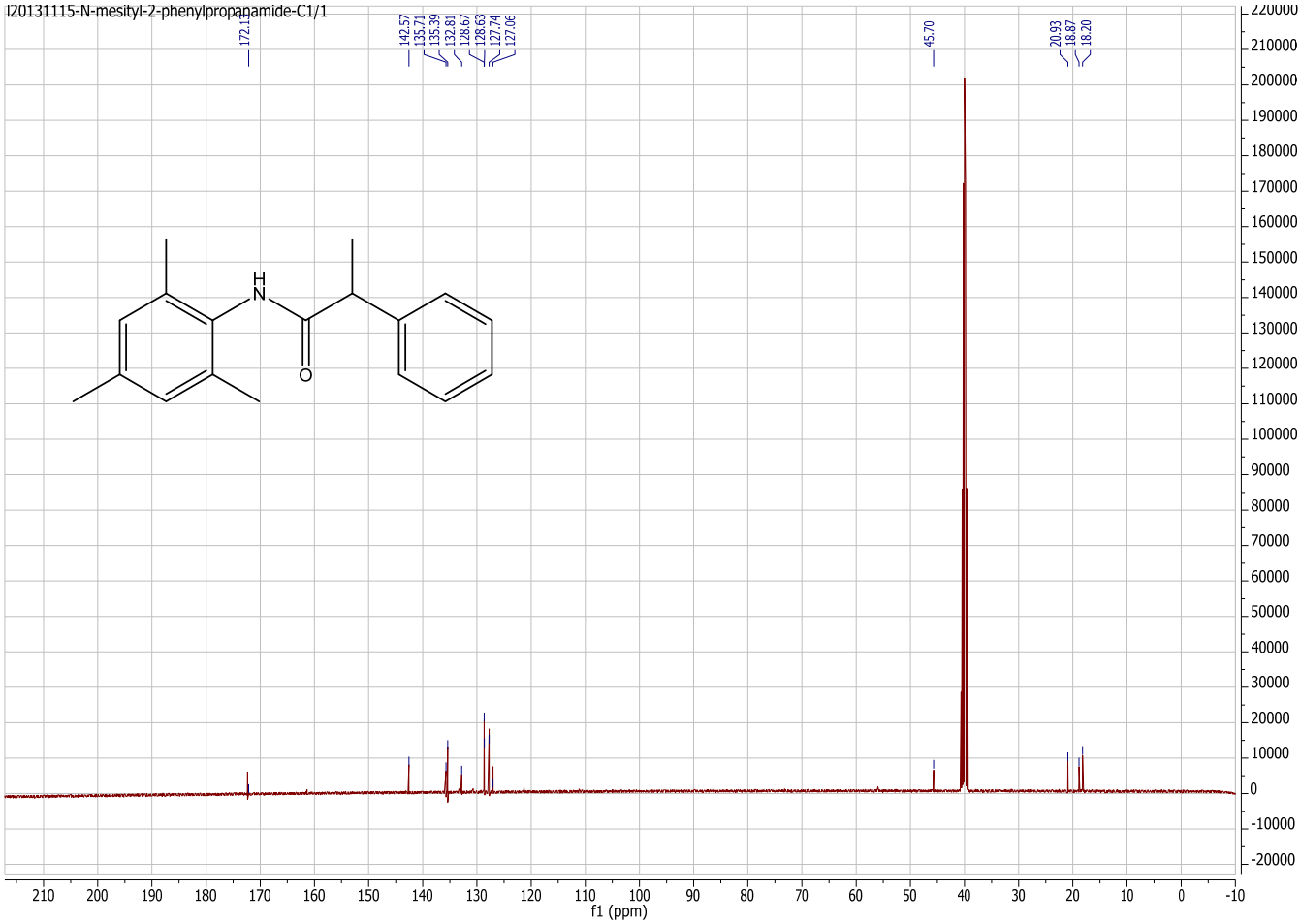
^{13}C NMR of N-(3-methoxyphenyl)-2-phenylpropanamide ($3a_4b_4$)



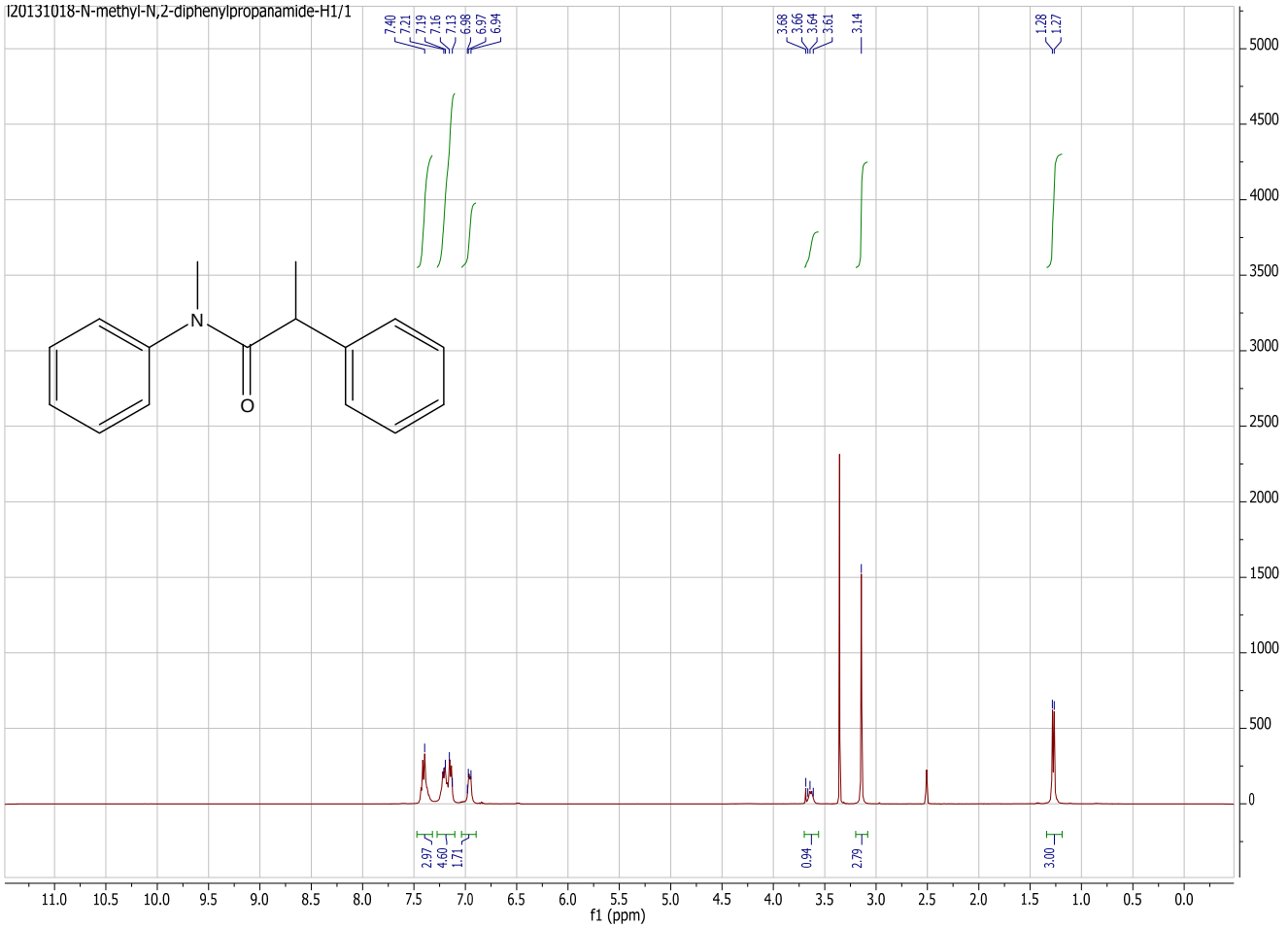
^{1}H NMR of N-mesityl-2-phenylpropanamide ($3a_5b_5$)



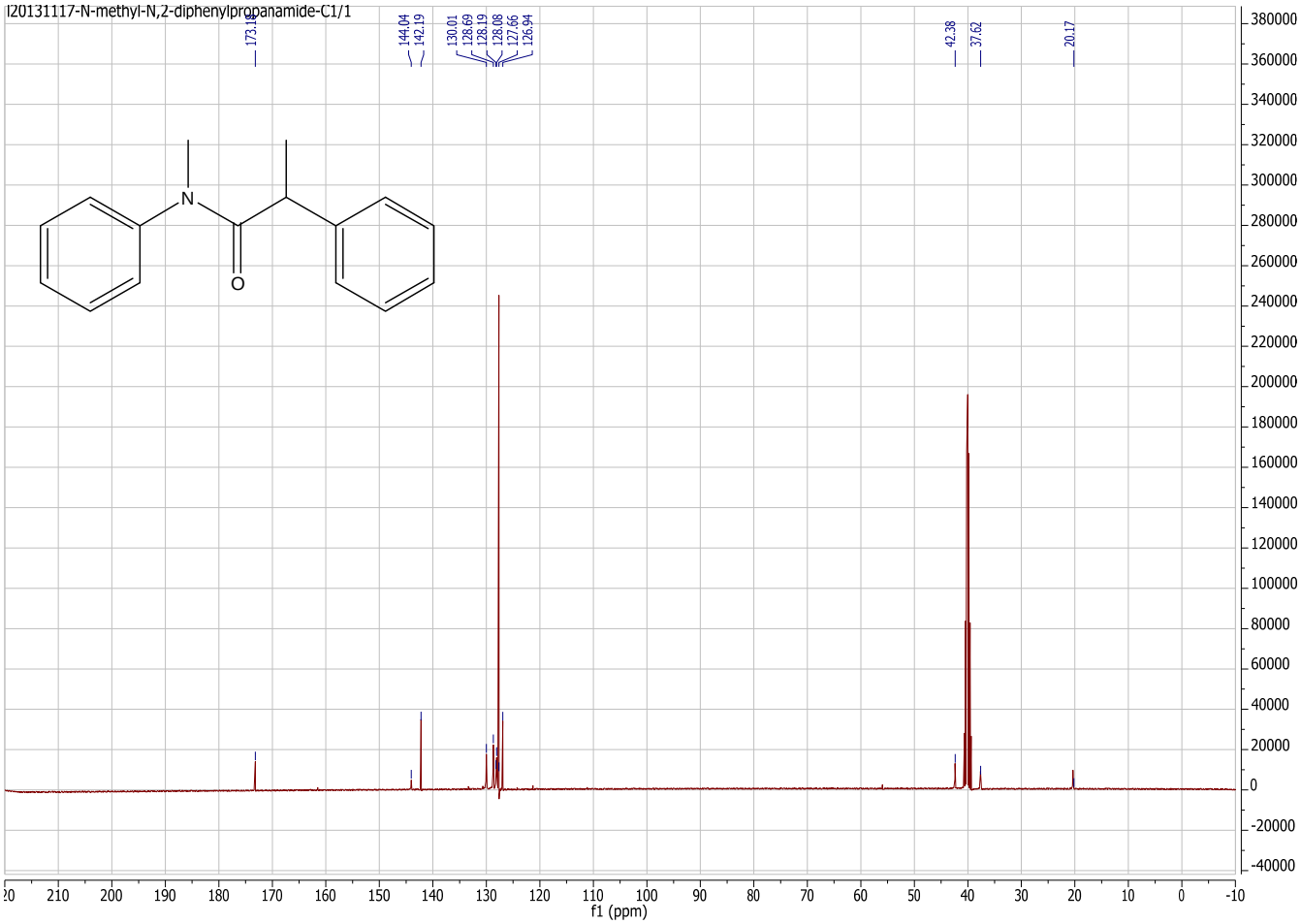
^{13}C NMR of N-mesityl-2-phenylpropanamide ($3a_5b_5$)



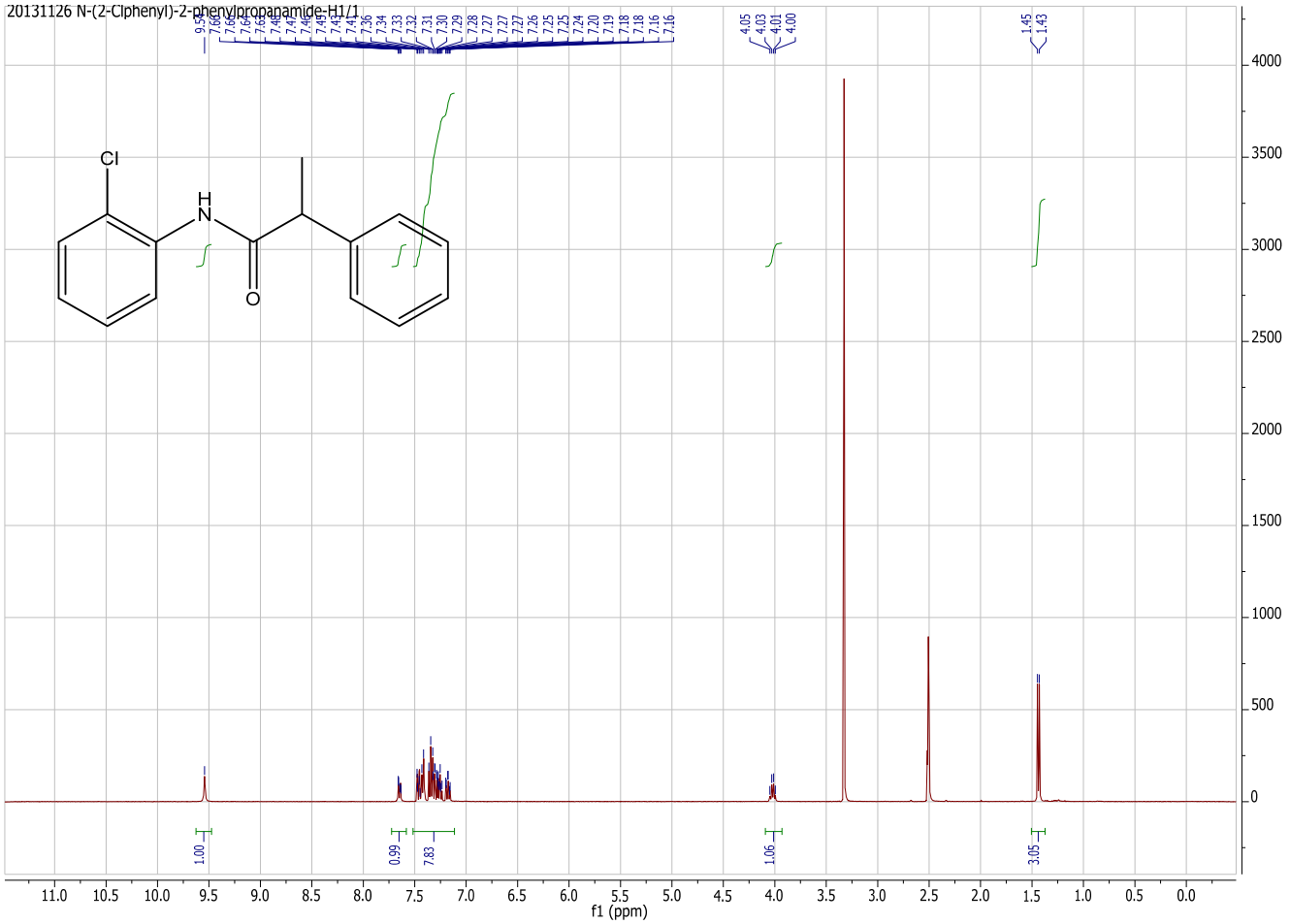
^{1}H NMR of N-methyl-N,2-diphenylpropanamide ($3a_6b_6$)



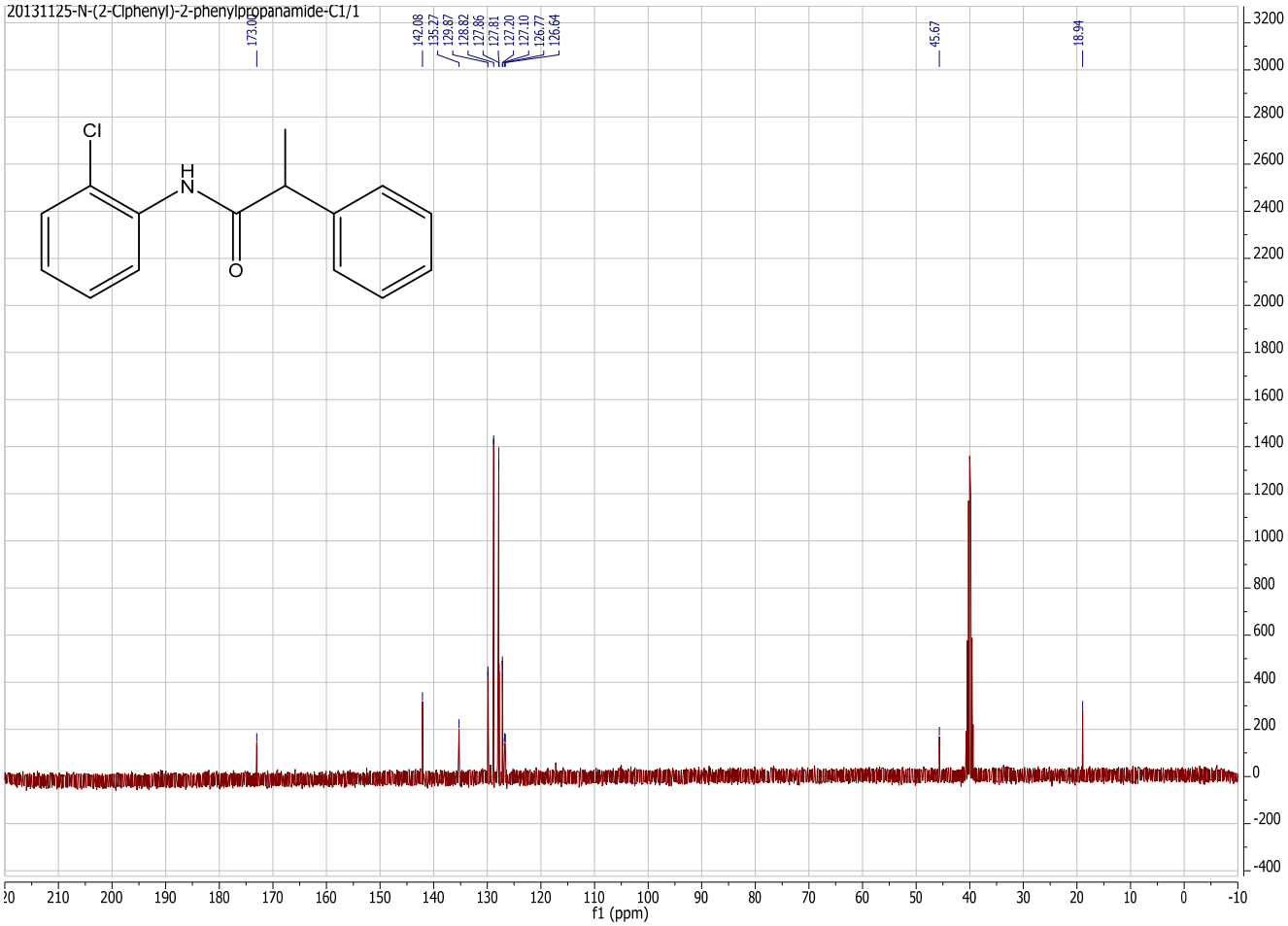
^{13}C NMR of N-methyl-N,2-diphenylpropanamide ($3a_6b_6$)



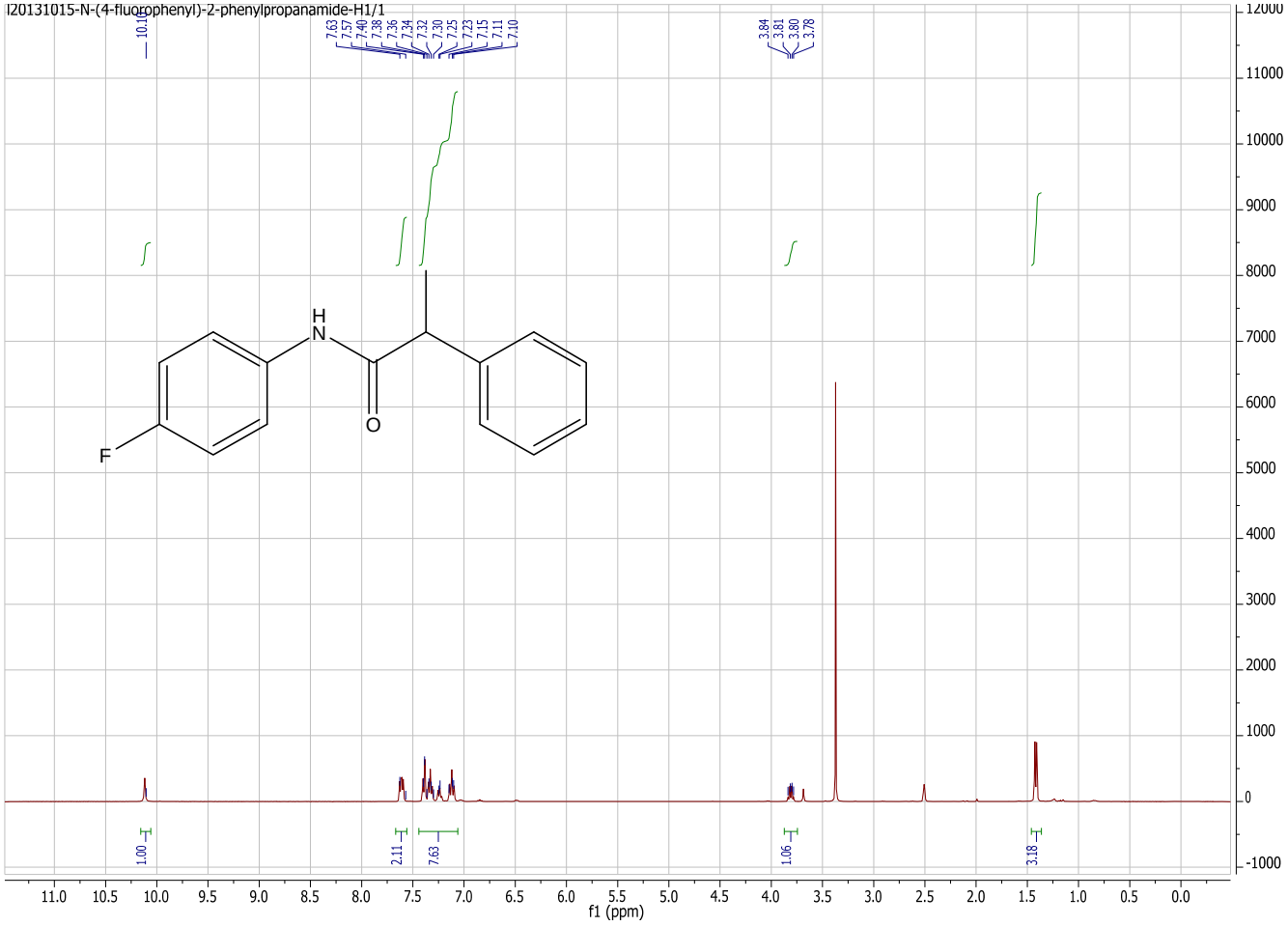
^{1}H NMR of N-(2-chlorophenyl)-2-phenylpropanamide ($3a_7b_7$)



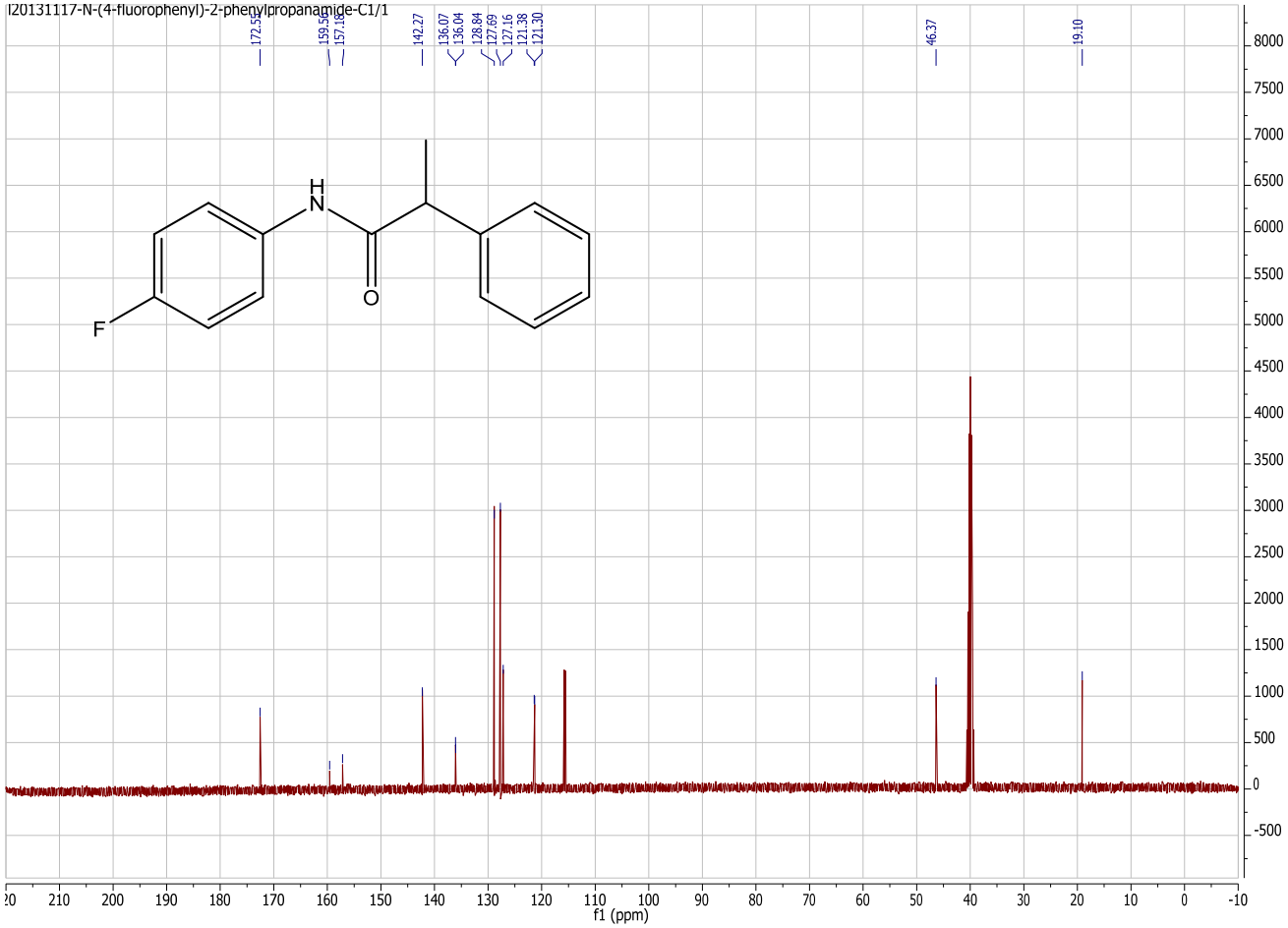
^{13}C NMR of N-(2-chlorophenyl)-2-phenylpropanamide ($3a_7b_7$)



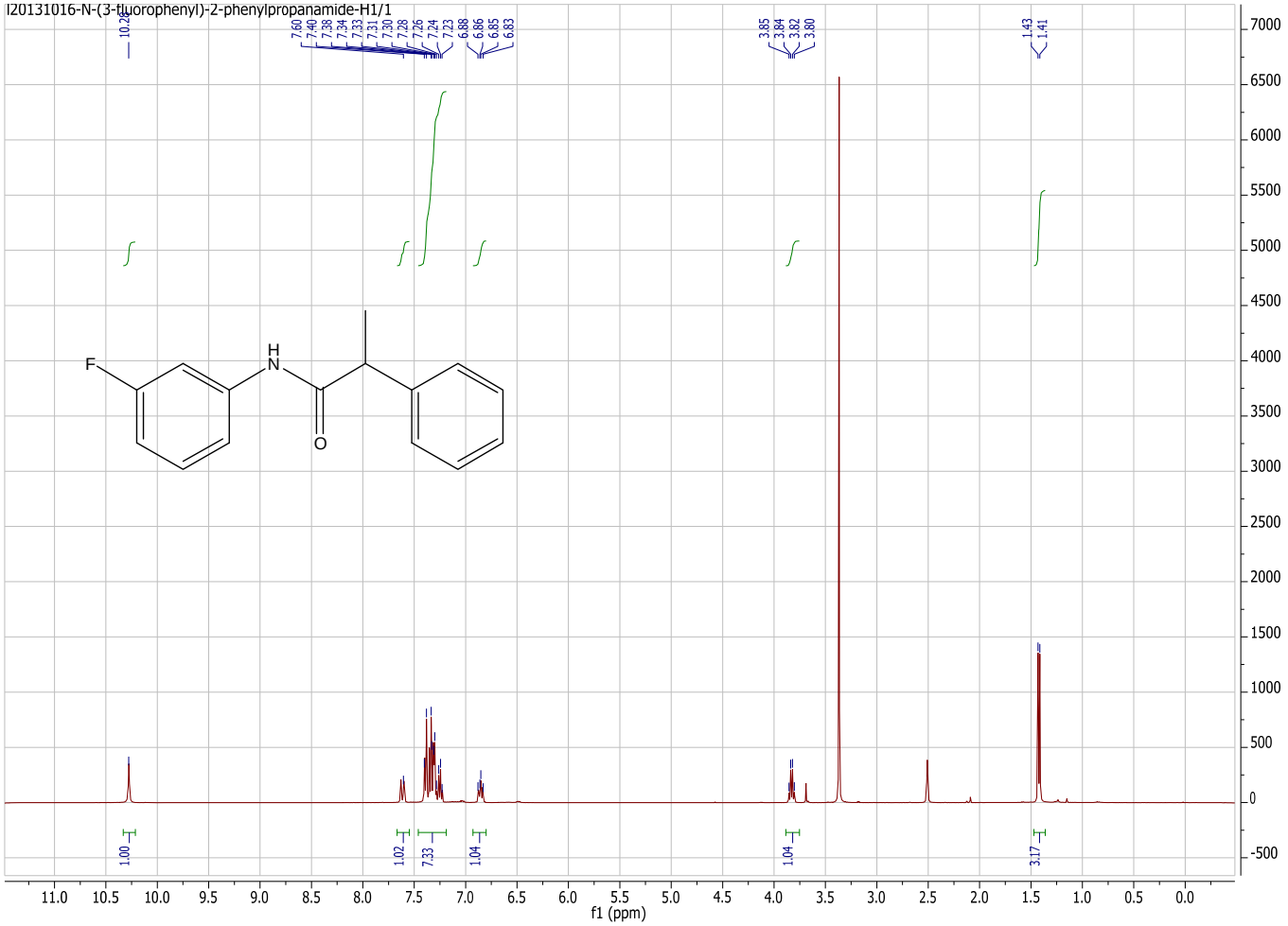
^{1}H NMR of N-(4-fluorophenyl)-2-phenylpropanamide ($3a_8b_8$)



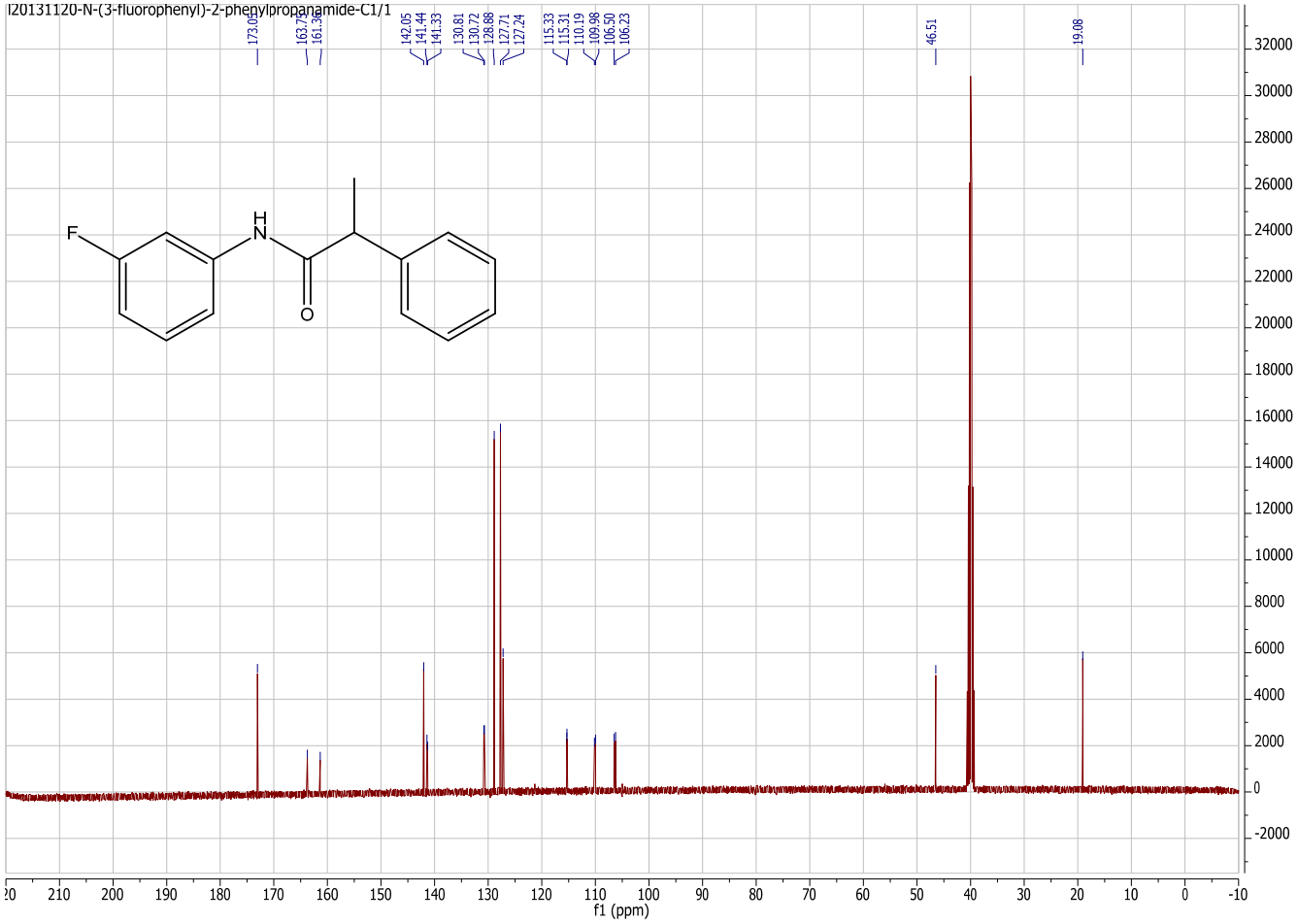
^{13}C NMR of N-(4-fluorophenyl)-2-phenylpropanamide ($3a_8b_8$)



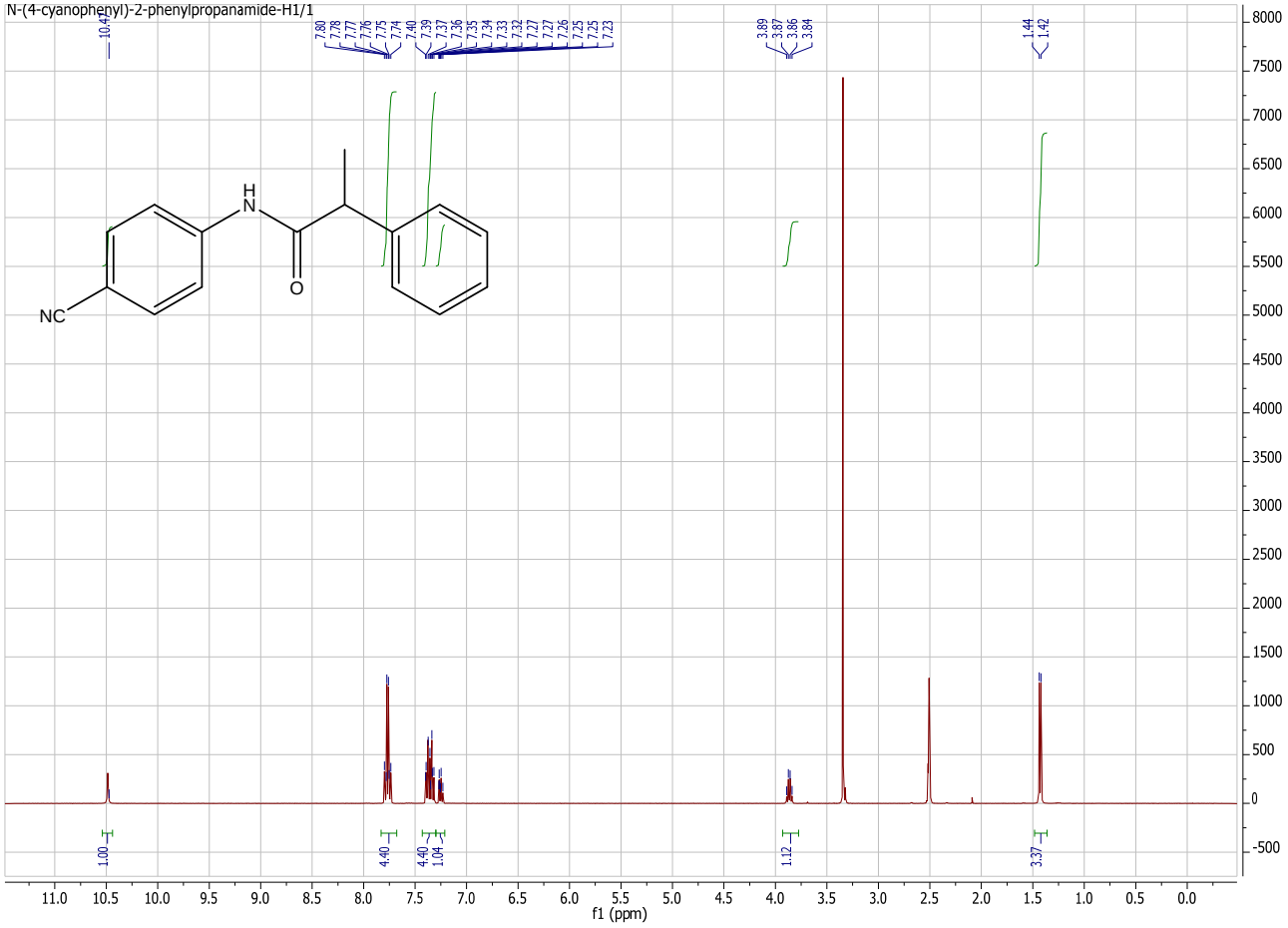
^{1}H NMR of N-(3-fluorophenyl)-2-phenylpropanamide ($3a_9b_9$)



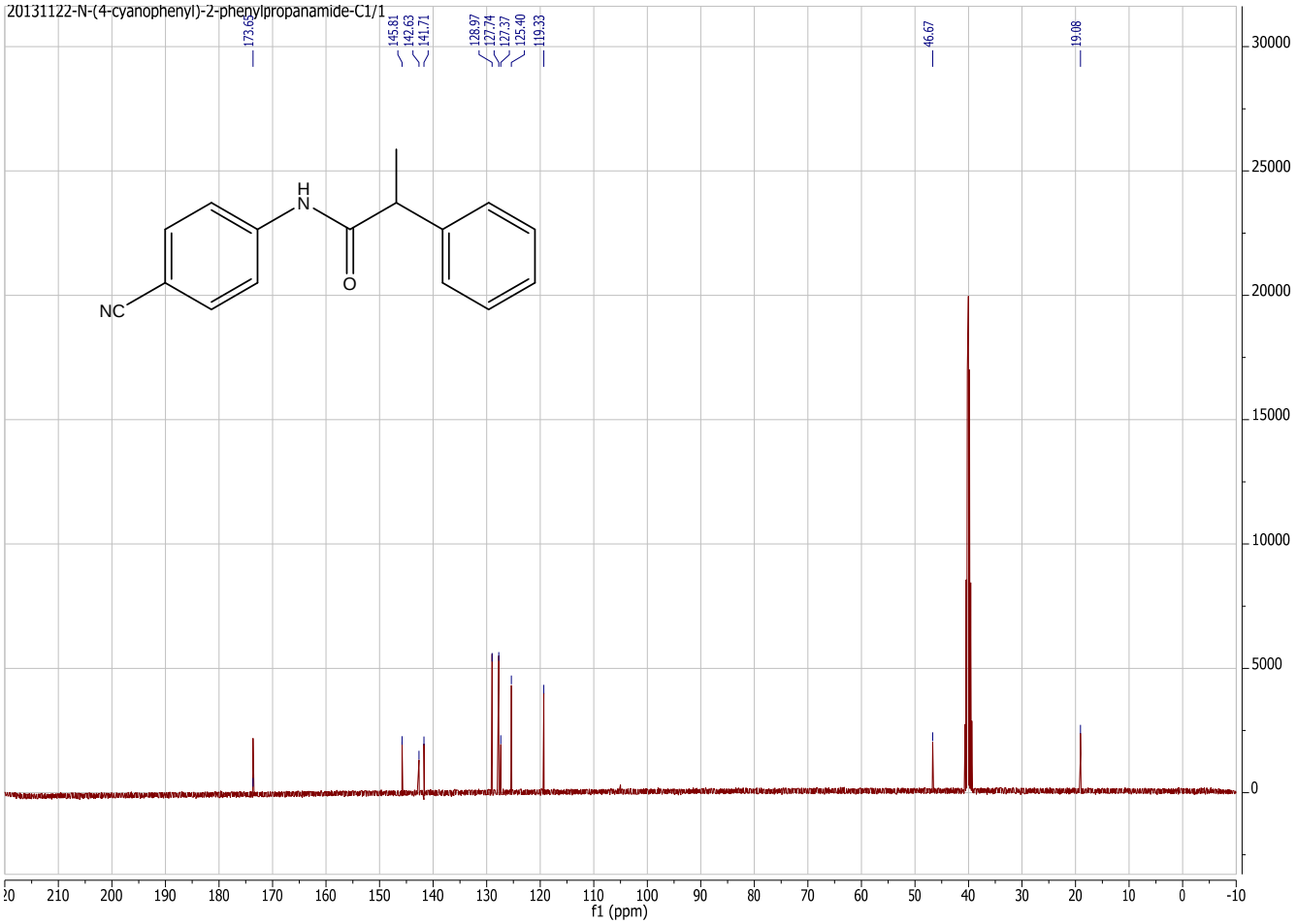
^{13}C NMR of N-(3-fluorophenyl)-2-phenylpropanamide (3a$_9$b$_9$)



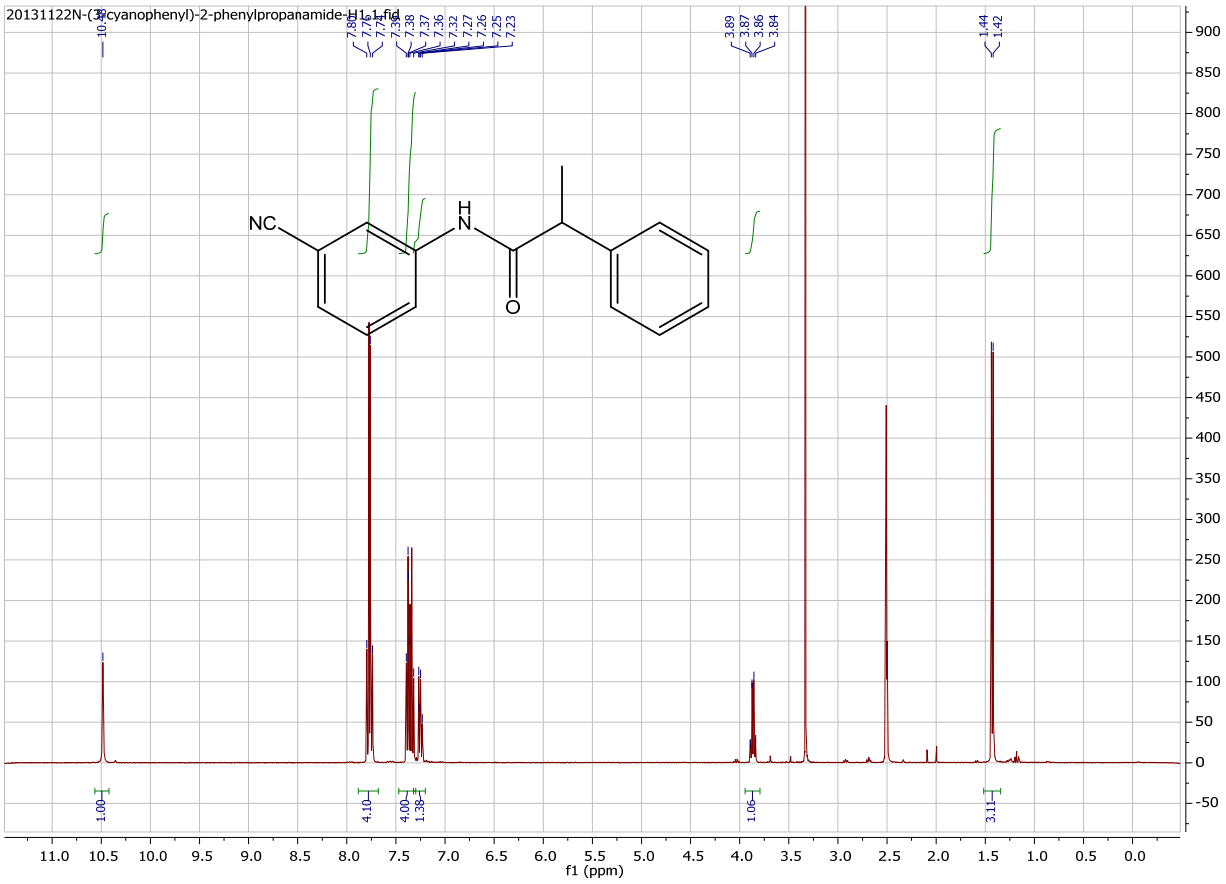
^{1}H NMR of N-(4-cyanophenyl)-2-phenylpropanamide ($3a_{10}b_{10}$)



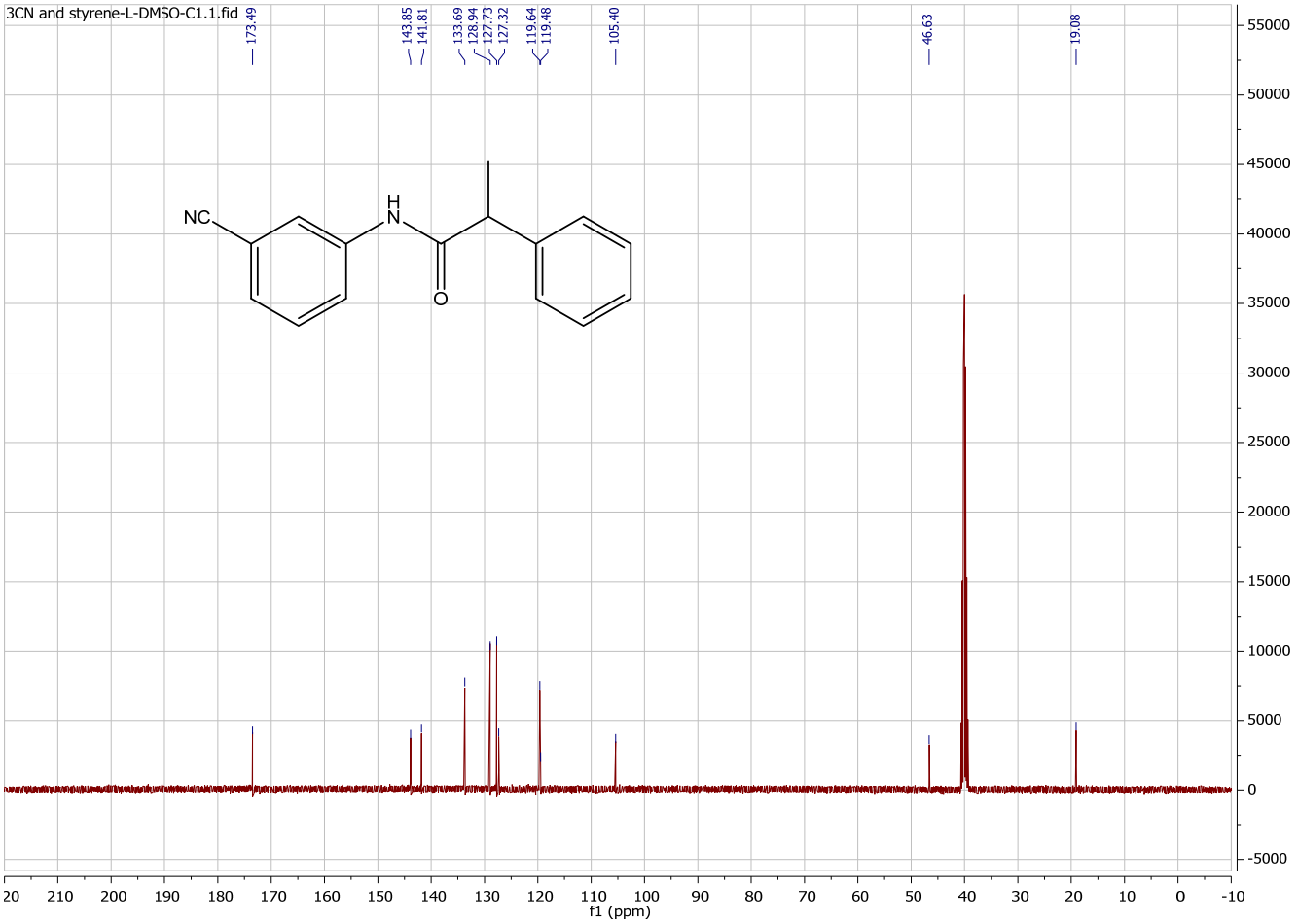
^{13}C NMR of N-(4-cyanophenyl)-2-phenylpropanamide ($3a_{10}b_{10}$)



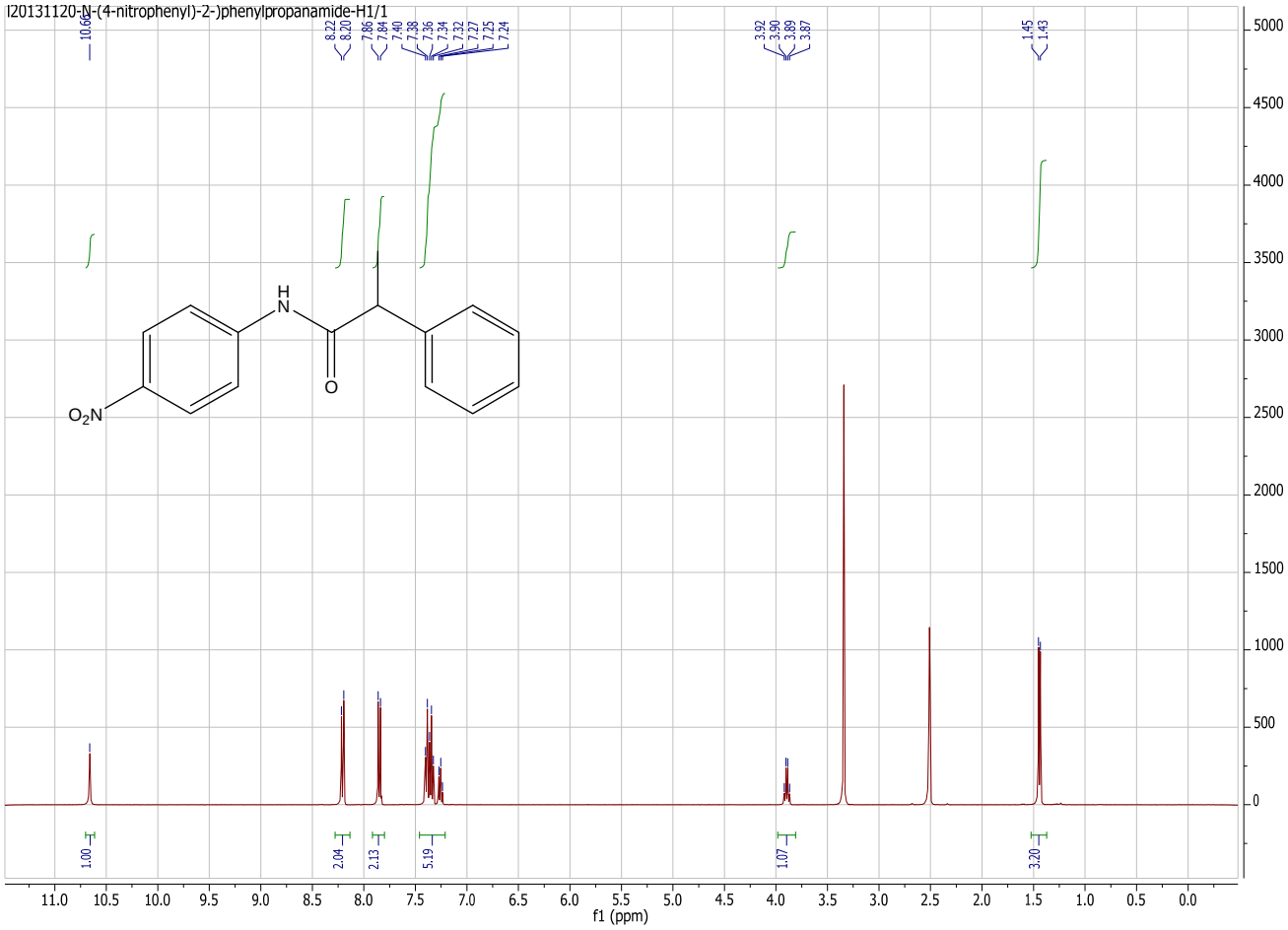
^{1}H NMR of N-(3-cyanophenyl)-2-phenylacetamide ($3a_{11}b_{11}$)



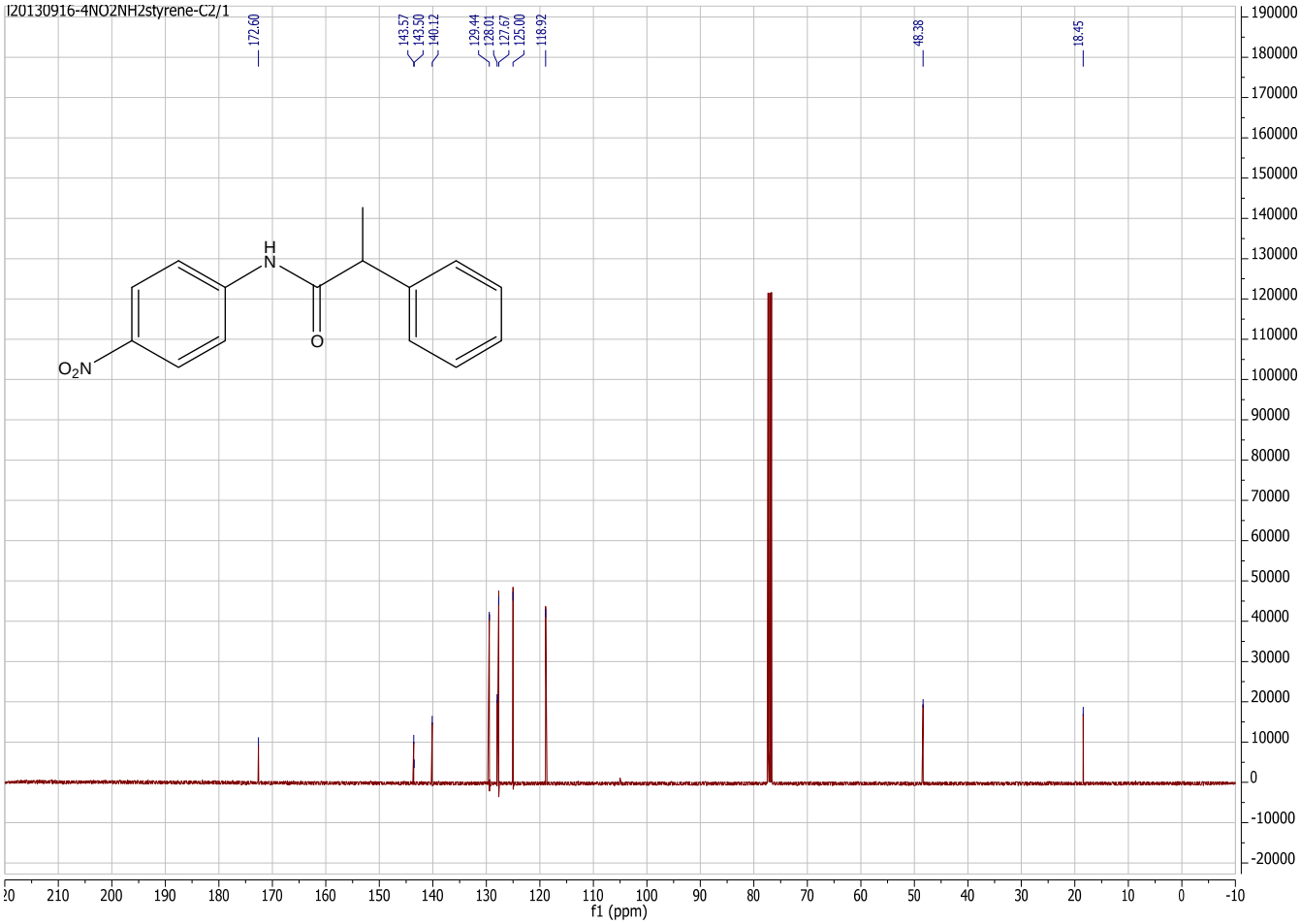
^{13}C NMR of N-(3-cyanophenyl)-2-phenylacetamide ($3a_{11}b_{11}$)



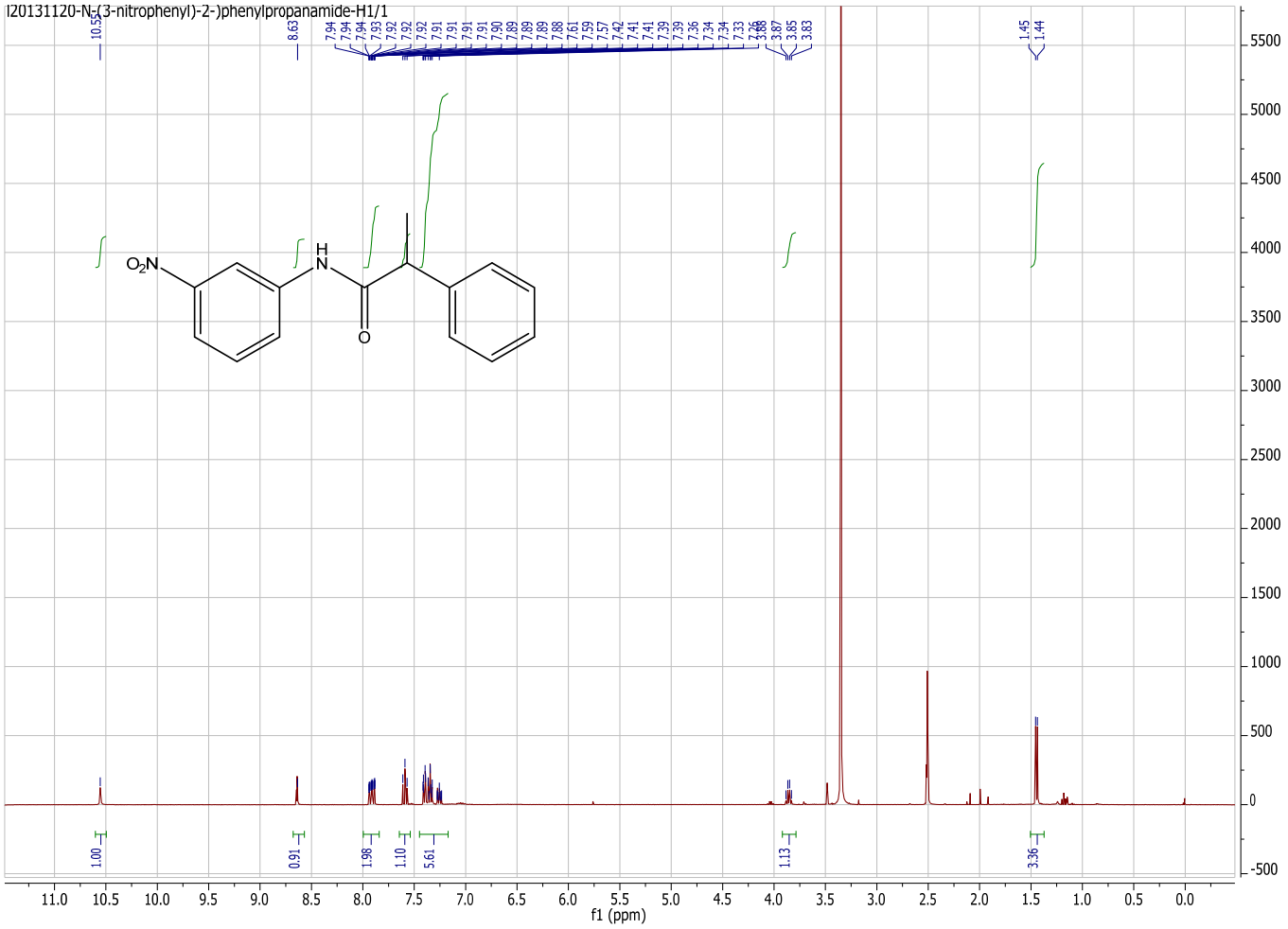
^{1}H NMR of N-(4-nitrophenyl)-2-phenylpropanamide ($3a_{12}b_{12}$)



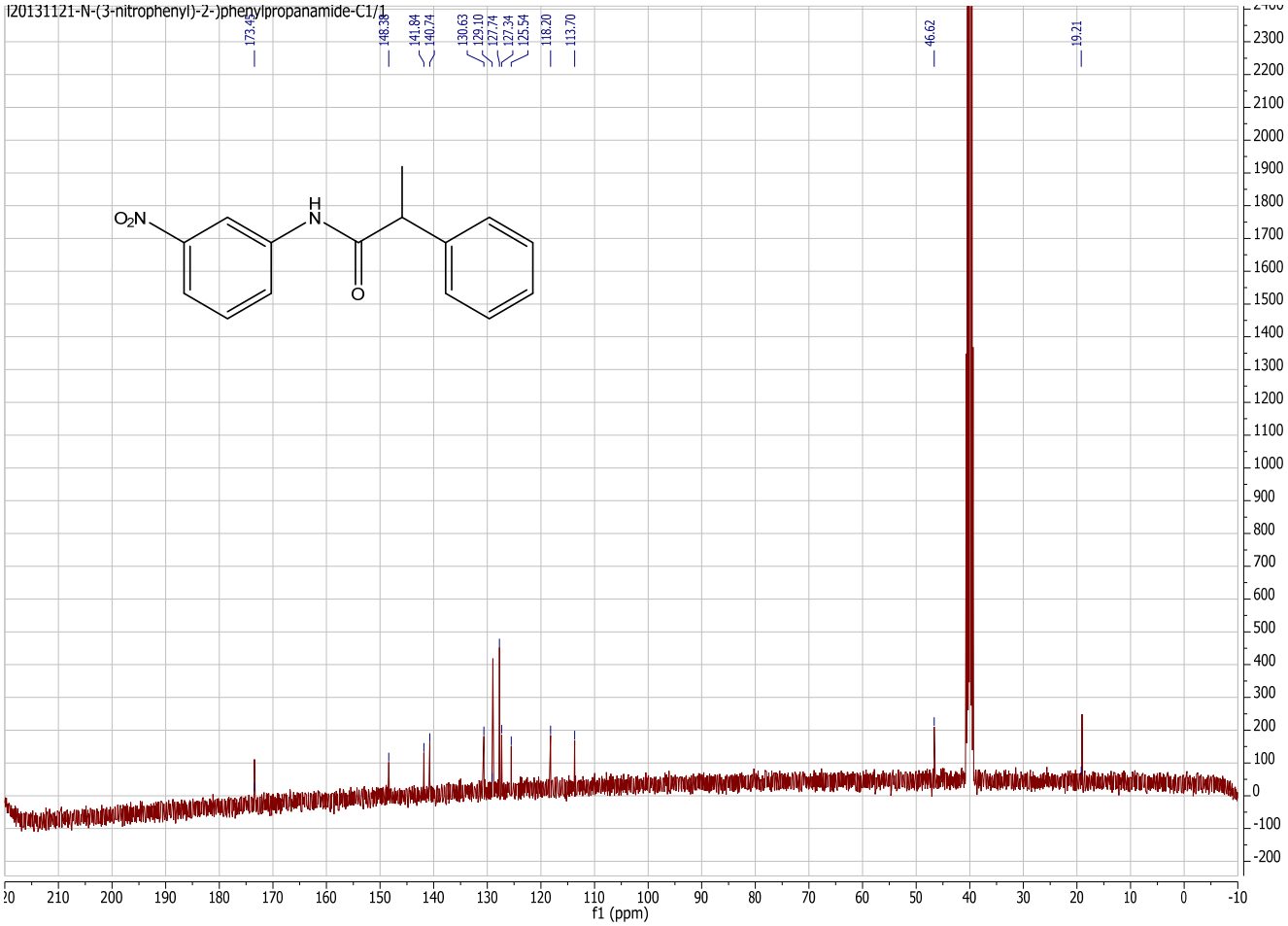
^{13}C NMR of N-(4-nitrophenyl)-2-phenylpropanamide ($3a_{12}b_{12}$)



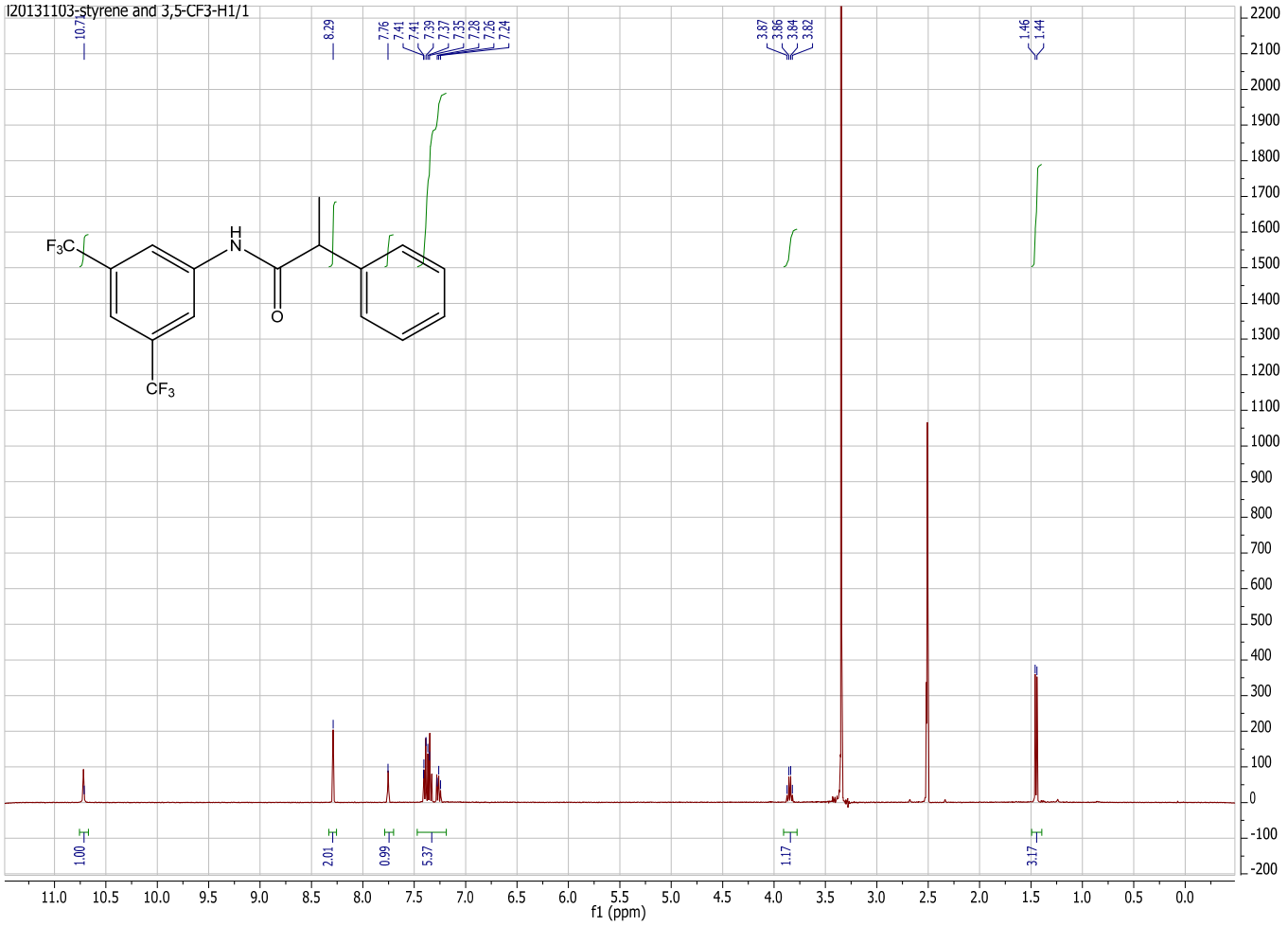
^{1}H NMR of N-(3-nitrophenyl)-2-phenylpropanamide ($3a_{13}b_{13}$)



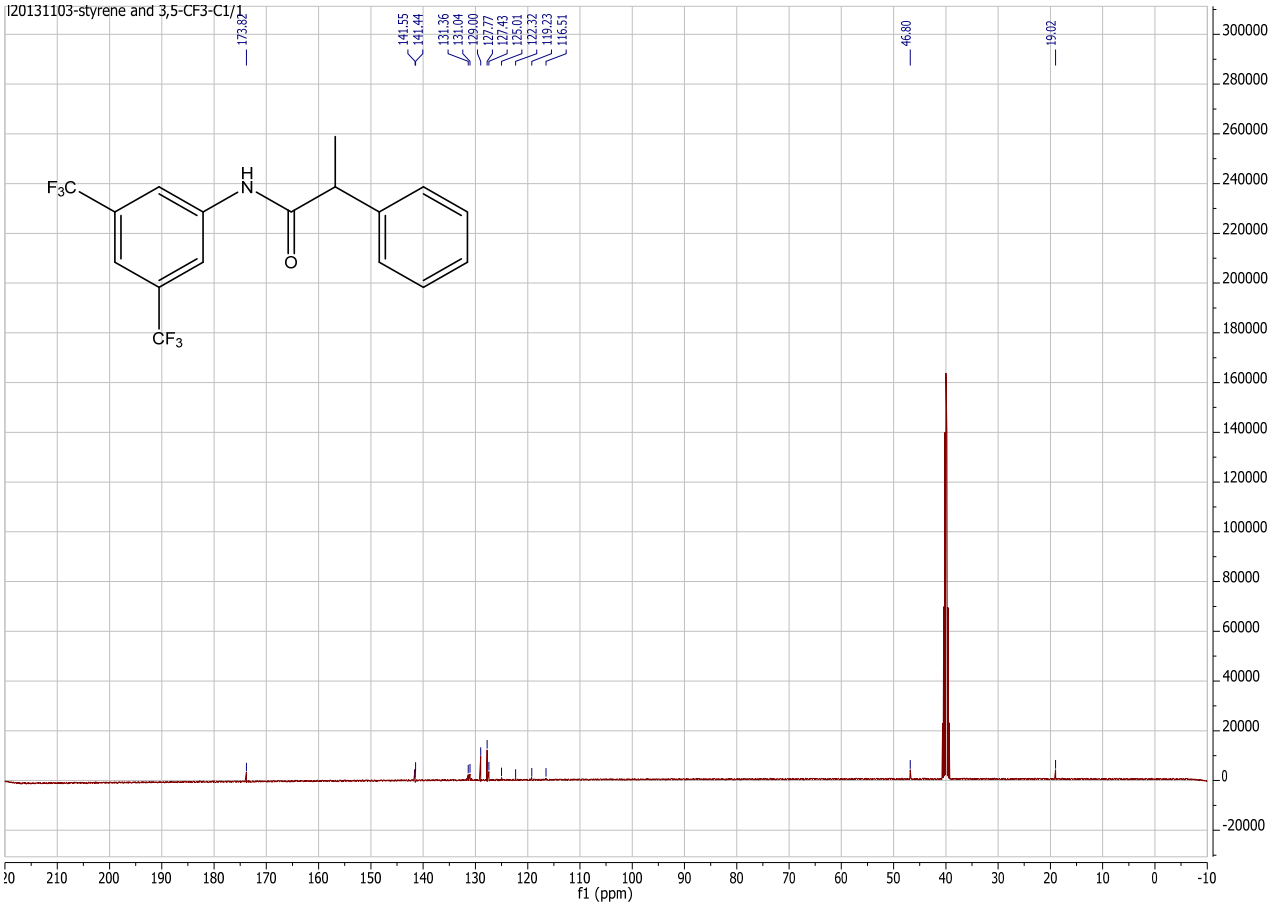
^{13}C NMR of N-(3-nitrophenyl)-2-phenylpropanamide ($3a_{13}b_{13}$)



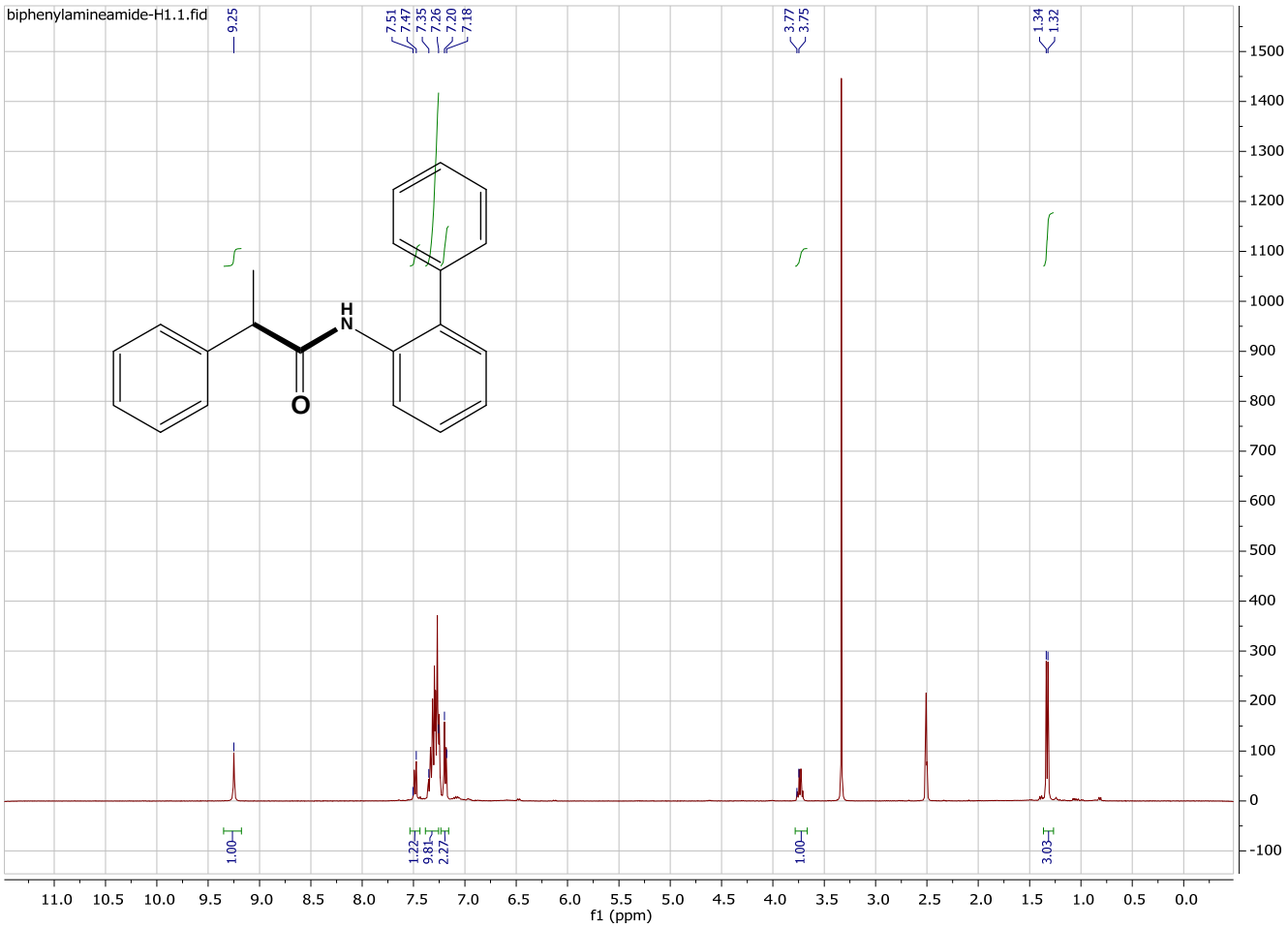
^{1}H NMR of N-(3,5-bis(trifluoromethyl)phenyl)-2-phenylpropanamide ($3a_{14}b_{14}$)



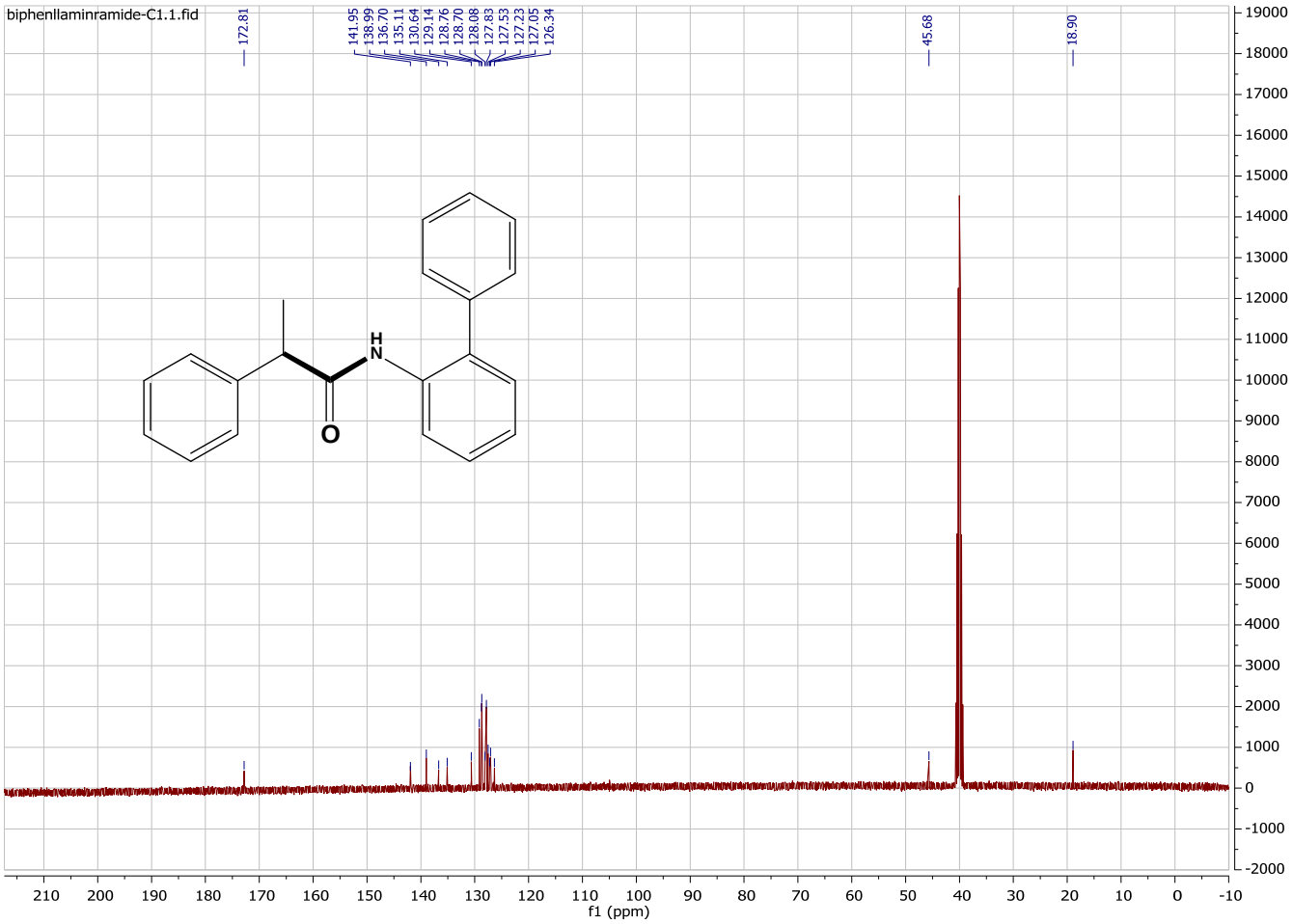
^{13}C NMR of N-(3,5-bis(trifluoromethyl)phenyl)-2-phenylpropanamide ($3a_{14}b_{14}$)



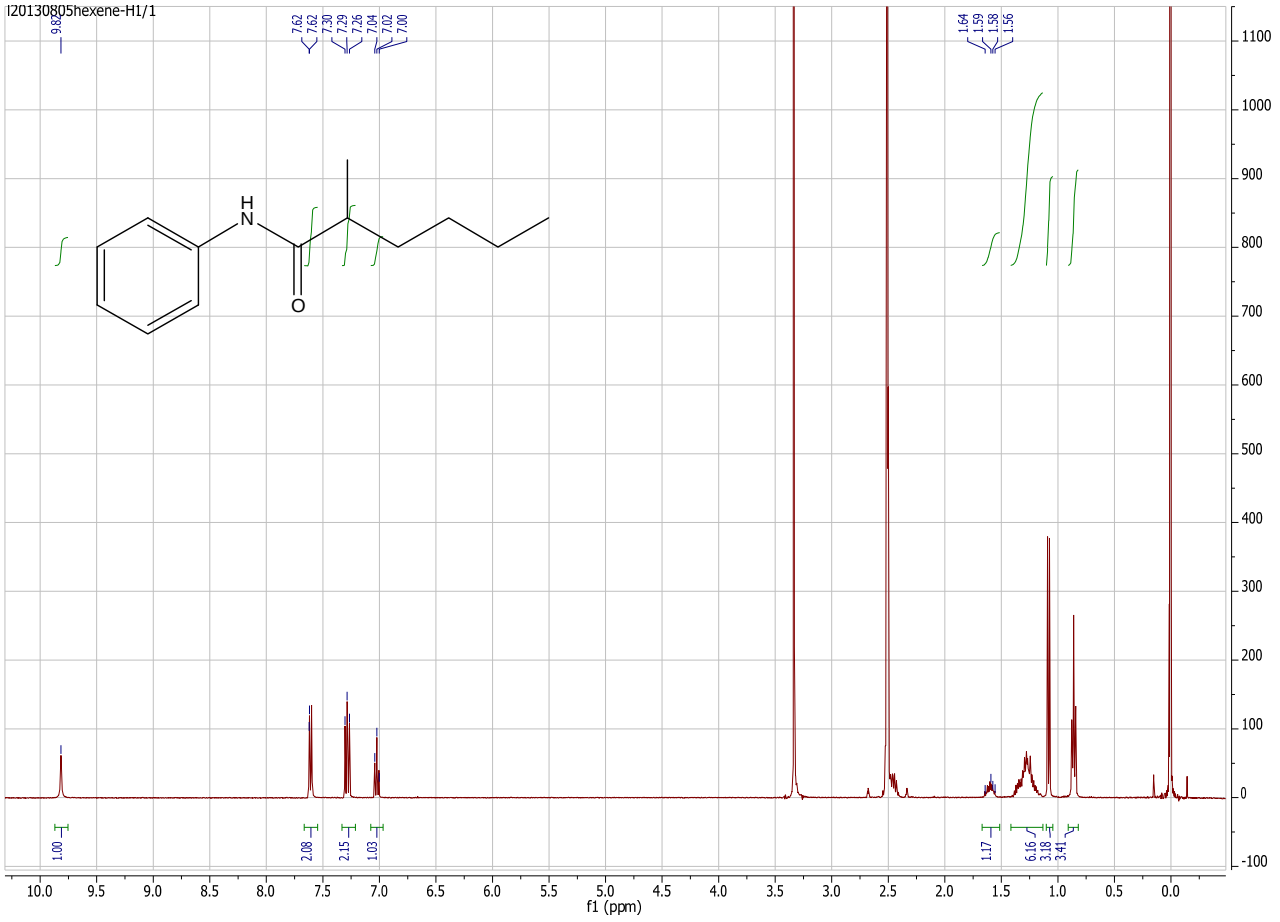
^{1}H NMR of N-([1,1'-biphenyl]-2-yl)-2-phenylpropanamide ($3a_{15}b_{15}$)



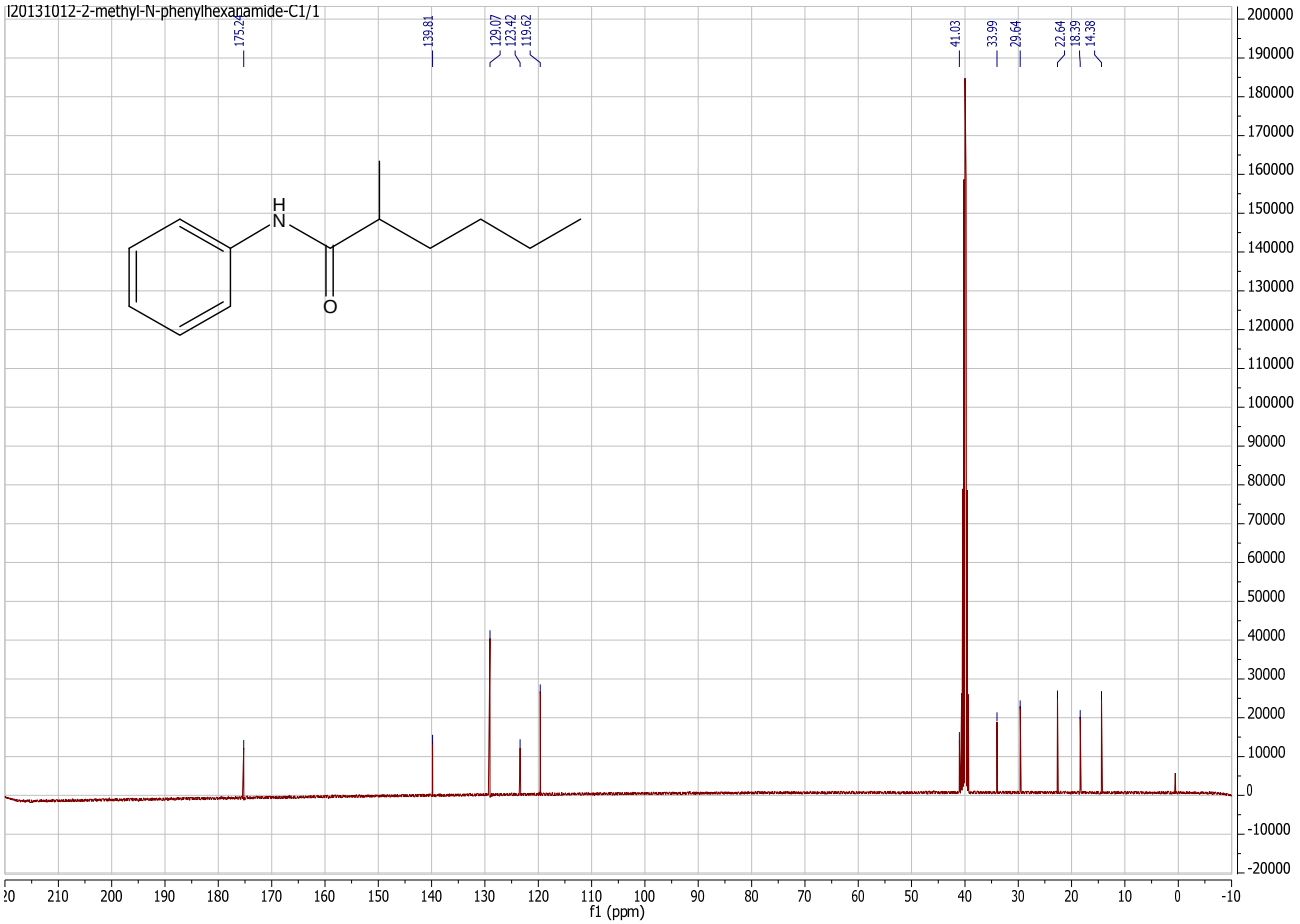
^{13}C NMR of N-([1,1'-biphenyl]-2-yl)-2-phenylpropanamide ($3a_{15}b_{15}$)



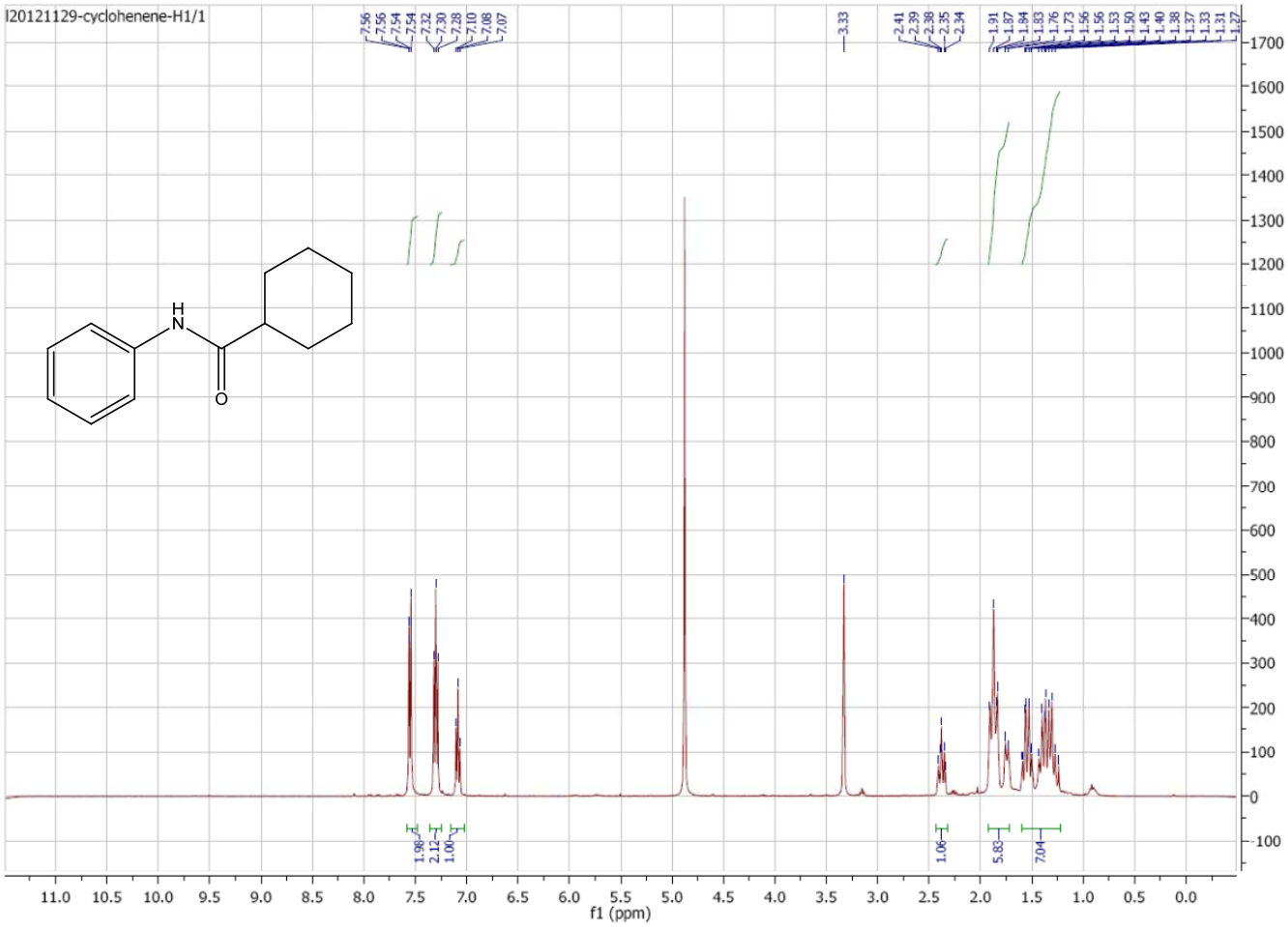
^{1}H NMR of 2-methyl-N-phenylhexanamide ($3a_{16}b_{16}$)



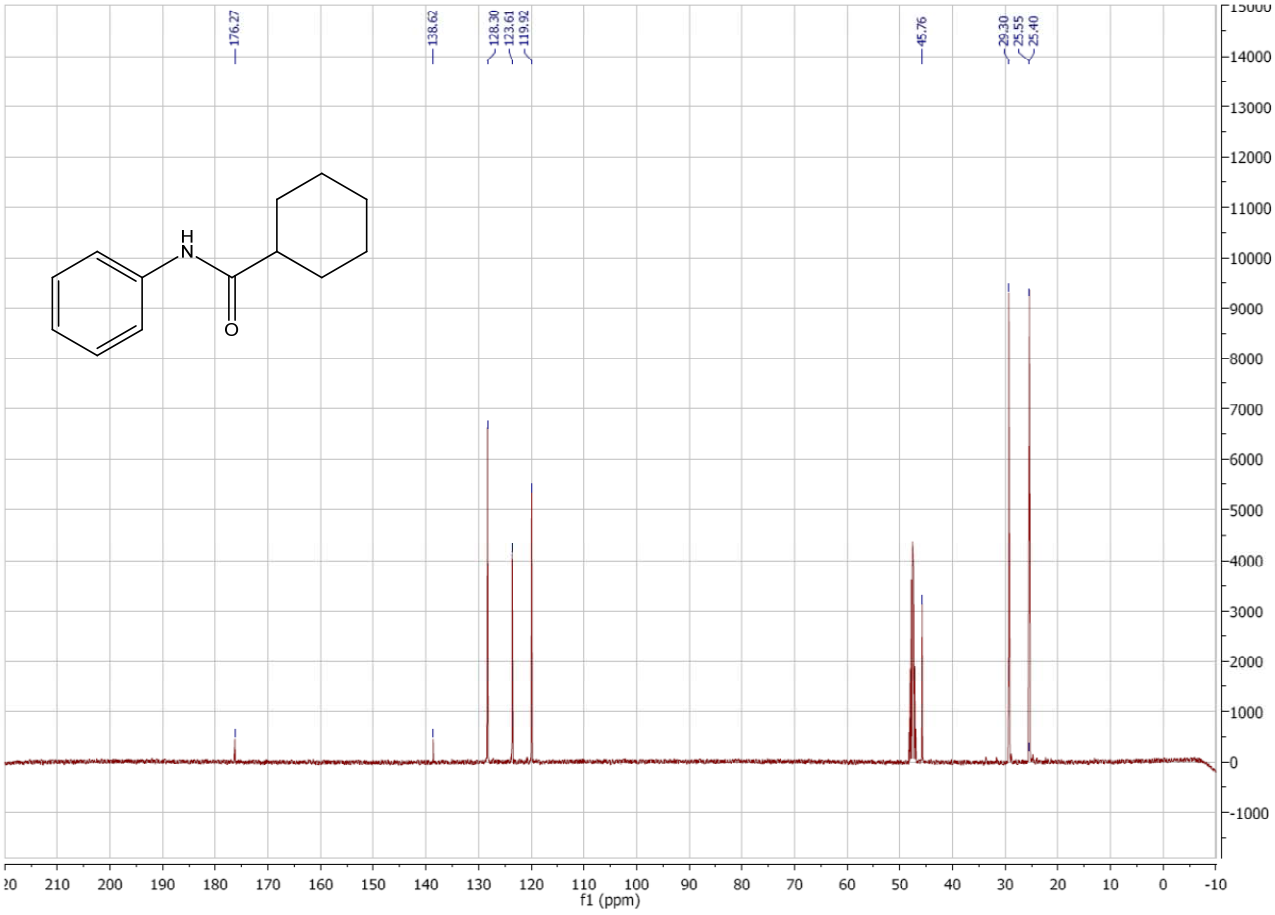
^{13}C NMR of 2-methyl-N-phenylhexanamide ($3a_{16}b_{16}$)



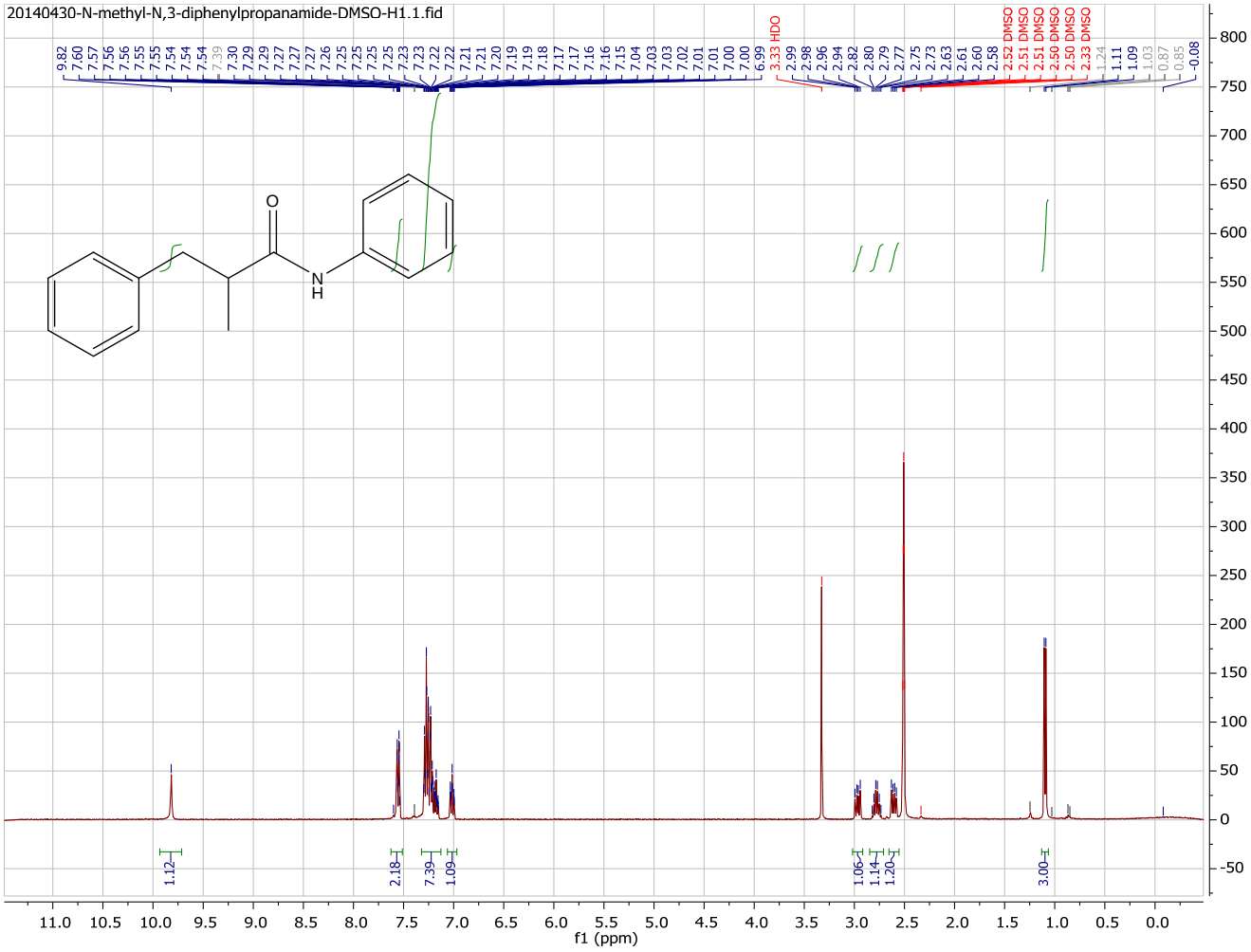
^{1}H NMR of N-phenylcyclohexanecarboxamide ($3a_{17}b_{17}$)



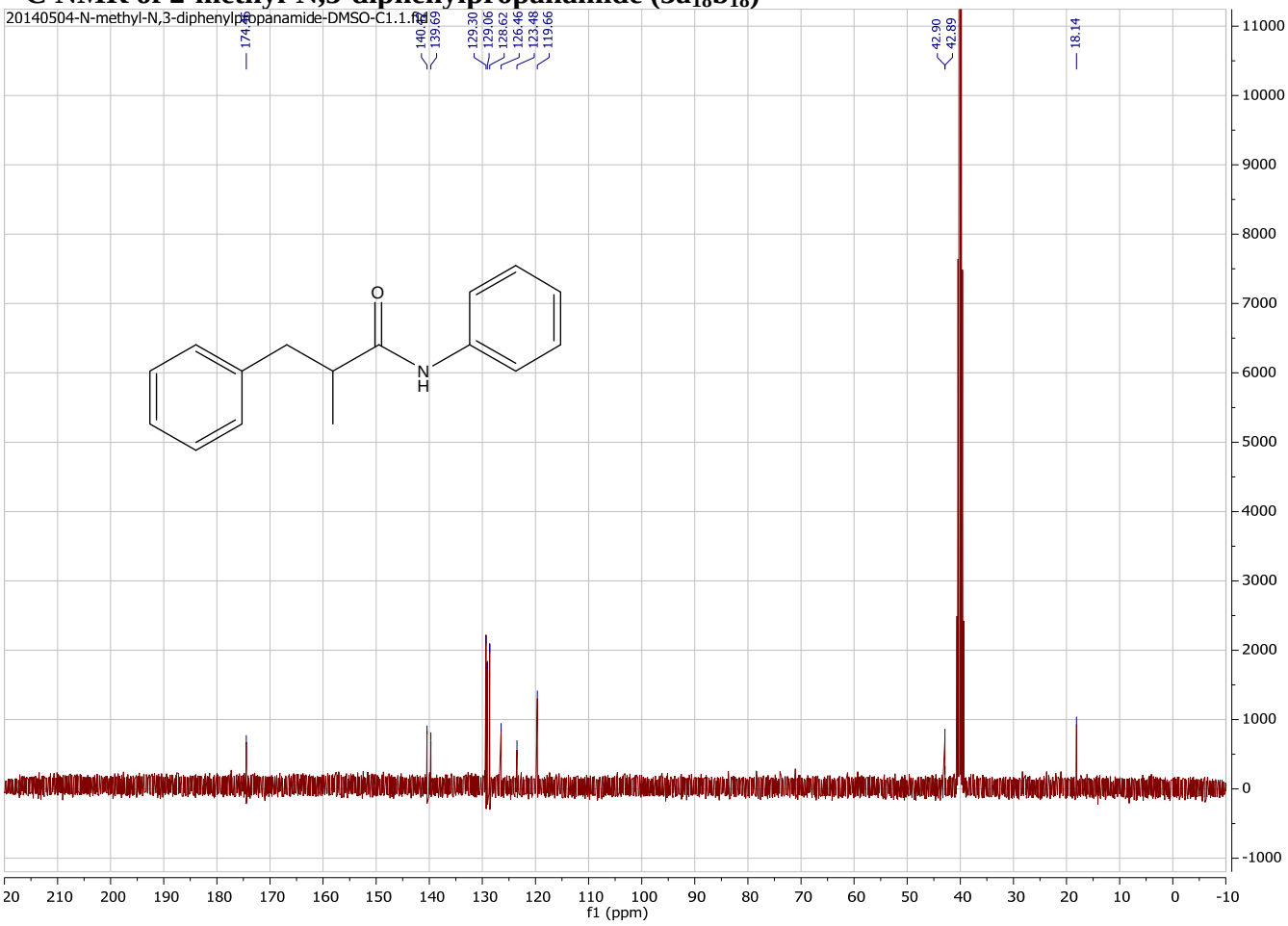
^{13}C NMR of N-phenylcyclohexanecarboxamide ($3a_{17}b_{17}$)



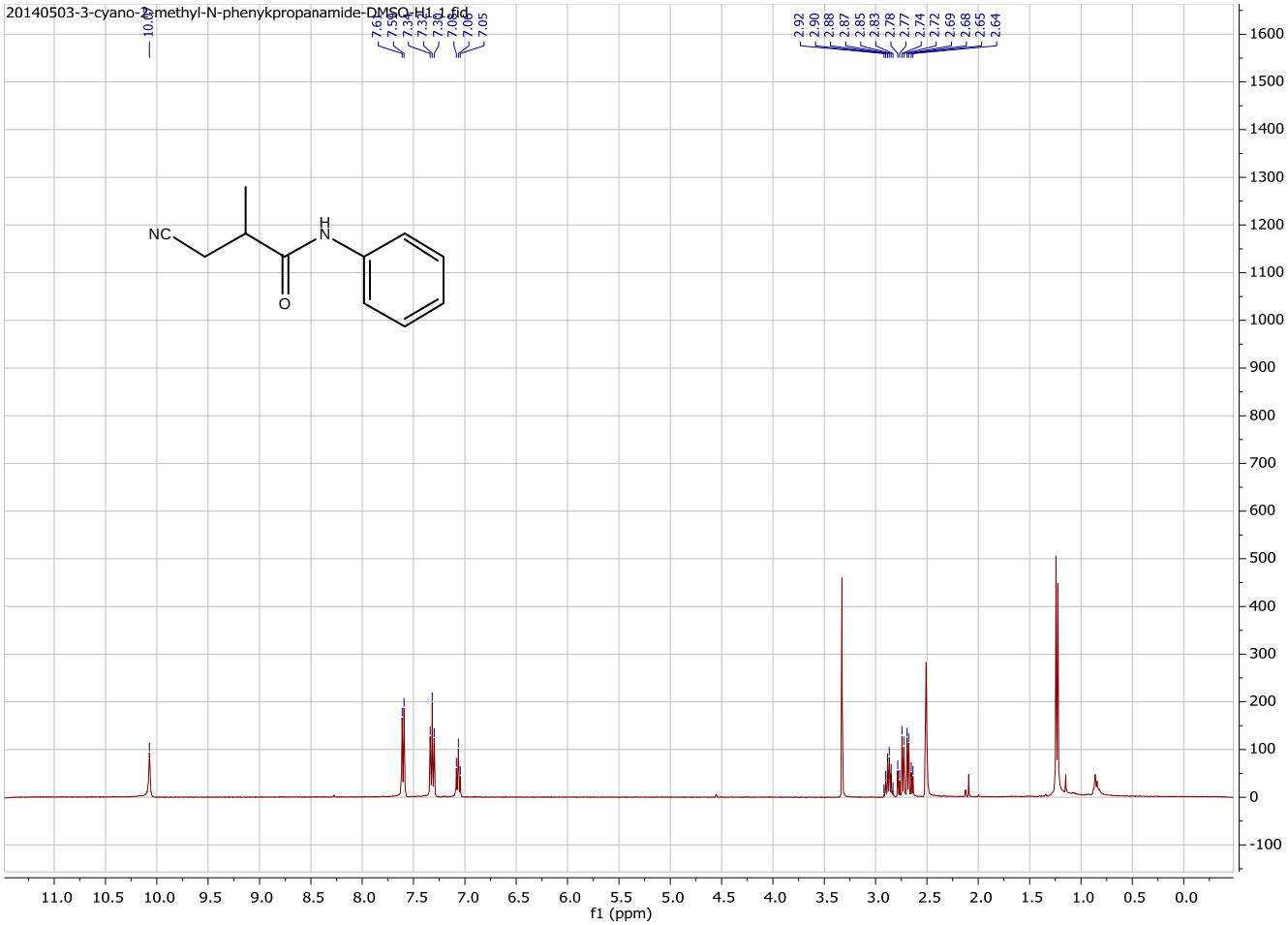
^{1}H NMR of 2-methyl-N,3-diphenylpropanamide ($3a_{18}b_{18}$)



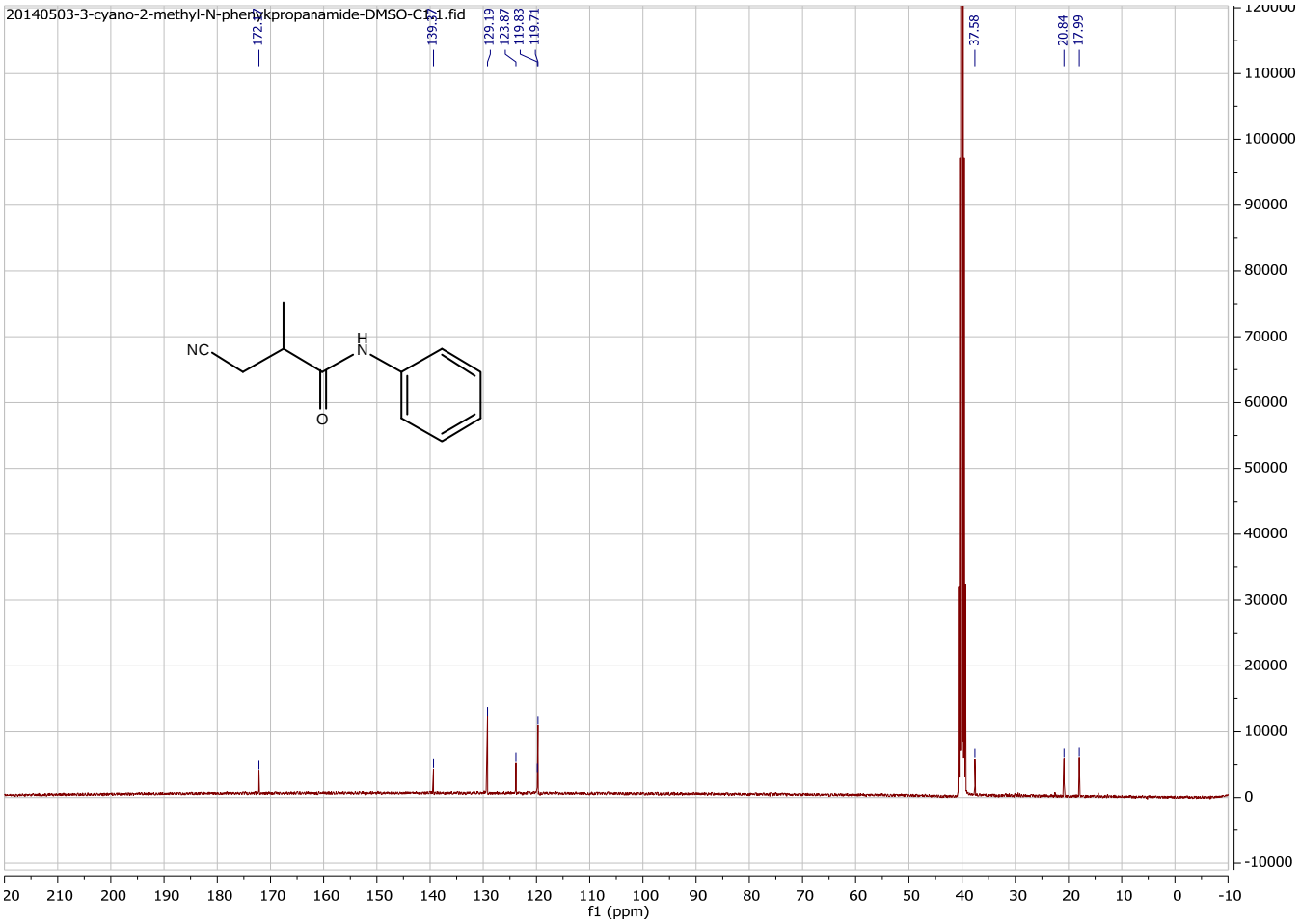
^{13}C NMR of 2-methyl-N,3-diphenylpropanamide ($3a_{18}b_{18}$)



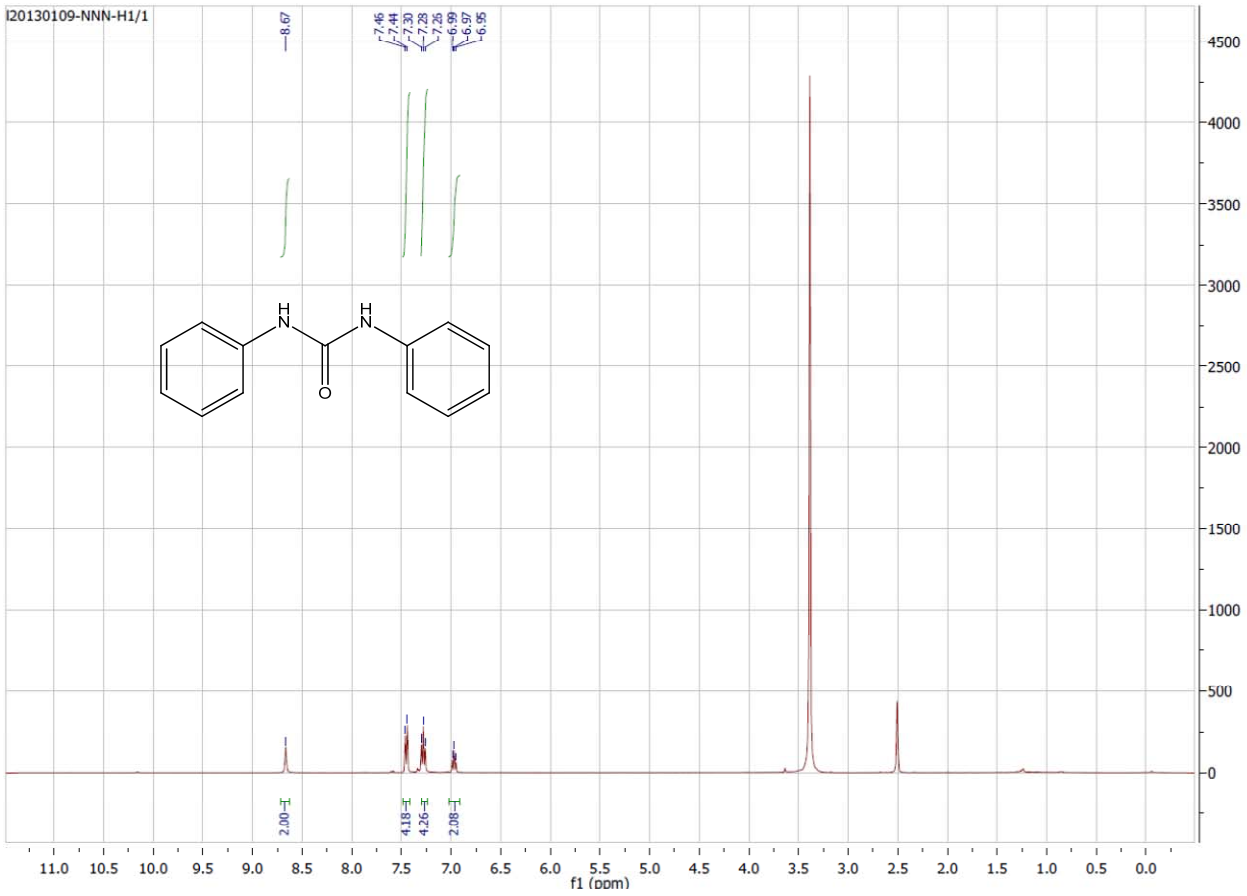
^{1}H NMR of 3-cyano-2-methyl-N-phenylpropanamide ($3a_{19}b_{19}$)



^{13}C NMR of 3-cyano-2-methyl-N-phenylpropanamide ($3a_{19}b_{19}$)



^{1}H NMR of 1, 3-diphenylurea



^{13}C NMR of 1, 3-diphenylurea