Supporting Information

Bicyclic (alkyl)(amino)carbene (BICAAC) as Dual Catalyst: Activation of Primary Amides and CO_2 towards N-methylation

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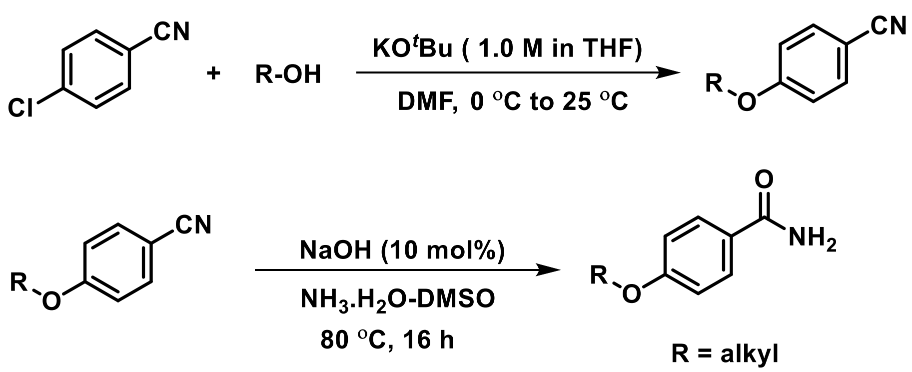
1) Materials and Methods

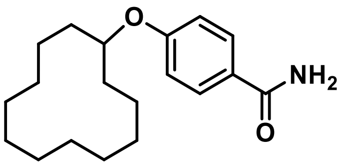
Unless stated otherwise, substrates were obtained from commercial vendors and used as supplied. Pinacolborane was stored under an inert atmosphere in the glovebox and obtained from Sigma Aldrich chemicals. BICAAC[S1] was synthesised and stored in the MBraun glovebox, maintained below 0.1 ppm of O_2 and H_2O levels. Substrates **2ak** and **2al** were prepared from their corresponding acid following the literature procedure.[S2] Solvents were dried over a sodium/benzophenone mixture or CaH_2 and distilled prior to use. Column chromatography was performed on neutral alumina. The reactions were performed with a 25 mL Schlenk tube equipped with a stir bar and a J. Young valve using standard Schlenk techniques or inside an Mbraun glovebox. Carbon dioxide was purchased in a 5.5 purity gas cylinder with 99.995% purity from Praxair. $^{13}CO_2$ cylinder was obtained from Sigma Aldrich. ^{1}H, ^{13}C, ^{11}B and ^{19}F spectra were recorded on a Bruker Avance 500 MHz spectrometer with residual undeuterated solvent as a reference. All ^{13}C ,^{11}B and ^{19}F NMR spectra were obtained with ^{1}H decoupling. Chemical shifts (δ) are given in ppm, and *J* values are given in Hz. High-resolution mass spectrometry (HRMS) was acquired on a Bruker maXis impact spectrometer. GC analysis has been performed using MS and TCD detectors using Clarus 590 (PerkinElmer) instrument.

2) Synthesis and characterisation of primary amide compounds

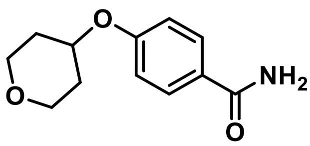
2.1) Synthesis of substrates 2x, 2y, 2ah and 2ai



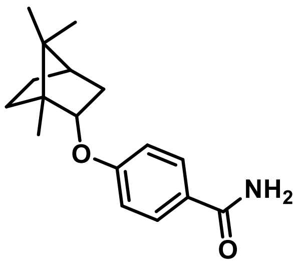
Compounds **2x**, **2y**, **2ah** and **2ai** were prepared by etherification of aryl chlorides containing cyano group, followed by hydration of nitrile to amide as in the reported literature.[S3, S4]



4-(Cyclododecyloxy)benzamide (**2x**): **^{1}H NMR** (500 MHz, $CDCl_3$, 25 °C): δ = 7.75 (d, J = 8.5 Hz, 2H), 6.91 (d, J = 8.5 Hz, 2H), 5.79 (brs, 2H), 4.52-4.47 (m, 1H), 1.83-1.76 (m, 2H), 1.69-1.62 (m, 2H), 1.49-1.44 (m, 4H), 1.41-1.38 (m, 14H); **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$, 25 °C): δ = 169.1, 161.7, 129.4, 125.2, 115.5, 75.8, 28.7, 24.7, 24.4, 23.3, 23.2, 20.8; **HRMS**: m/z calcd. For $C_{19}H_{30}NO_2^+$ $[M + H]^+$ 304.2271, found 304.2281. The compound was purified by column chromatography on neutral alumina with ethyl acetate as eluent.

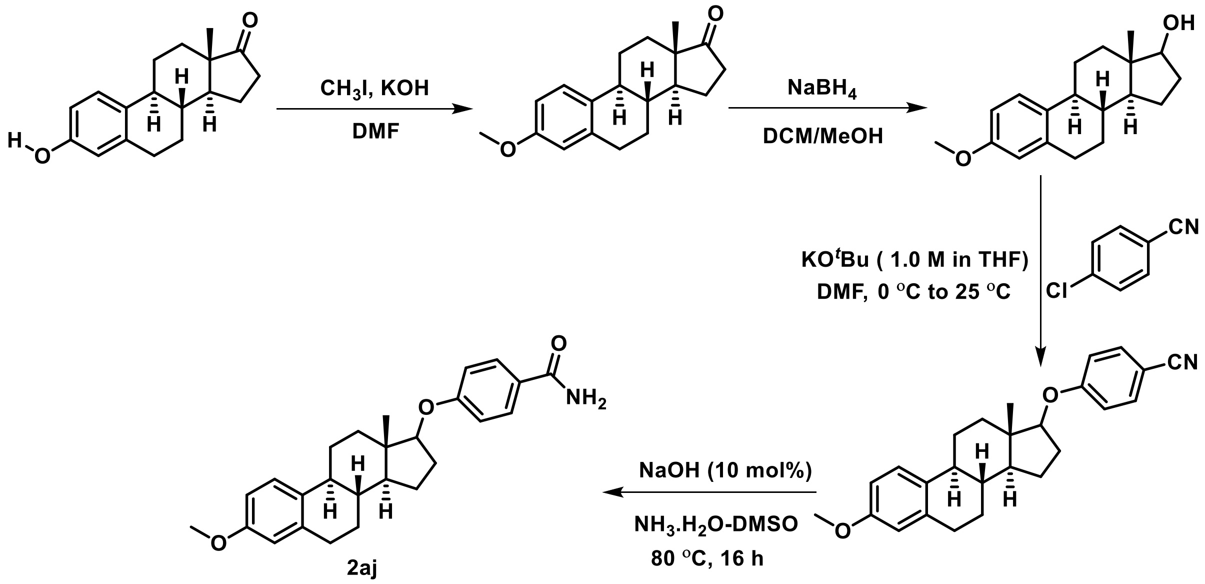


4-((Tetrahydro-2H-pyran-4-yl)oxy)benzamide (**2y**): **^{1}H NMR** (500 MHz, $CDCl_3$, 25 °C): δ = 7.77 (d, J = 9.0 Hz, 2H), 6.94 (d, J = 9.0 Hz, 2H), 5.89 (brs, 2H),), 4.59-4.55 (m, 1H), 4.00-3.96 (m, 2H), 3.62-3.57 (m, 2H), 2.06-2.01 (m, 2H), 1.84-1.77 (m, 2H); **^{13}C{^{1}H} NMR**(125 MHz, $CDCl_3$, 25 °C): δ = 169.1, 160.5, 129.5, 125.9, 115.6, 71.8, 65.1, 31.7; **HRMS**: m/z calcd. For $C_{12}H_{15}NO_3Na^+$ $[M + Na]^+$ 244.0944, found 244.0951. The compound was purified by column chromatography on neutral alumina with ethyl acetate as eluent.



4-(((1S,2S,4R)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl)oxy)benzamide (**2ah**): **^{1}H NMR** (500 MHz, $CDCl_3$, 25 °C): δ = 7.75 (d, J = 9.0 Hz, 2H), 6.85 (d, J = 9.0 Hz, 2H), 5.98 (brs, 2H), 4.38-4.35 (m, 1H), 2.42-2.36 (m, 1H), 2.24-2.18 (m, 1H), 1.80-1.75 (m, 2H), 1.38-1.32 (m, 1H), 1.28-1.22 (m, 1H), 1.10-1.07 (m, 1H), 0.95 (s, 3H), 0.925 (s, 3H), 0.919 (s, 3H); **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$, 25 °C): δ = 169.3, 162.4, 129.4, 125.1, 115.3, 83.3, 49.7, 47.8, 45.3, 36.8, 28.0, 26.9, 19.8, 19.1, 13.8; **HRMS**: m/z calcd. For $C_{17}H_{23}NO_2Na^+$ [M + Na]$^+$ 296.1621, found 296.1620. The compound was purified by column chromatography on neutral alumina with ethyl acetate as eluent.

2.2) Synthesis of substrate 2aj

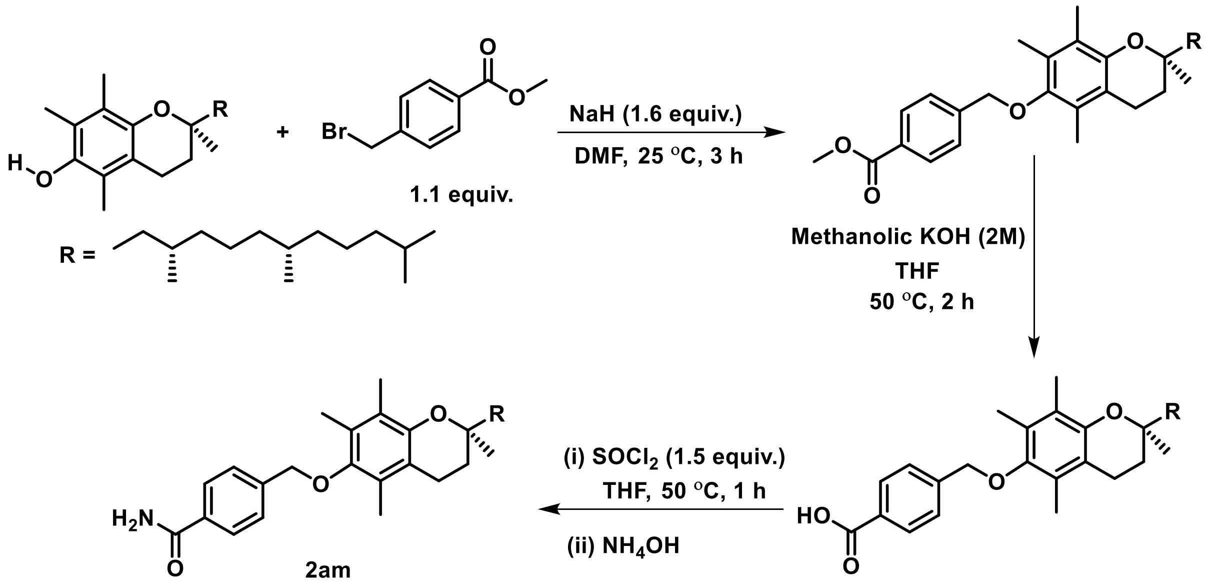


The amide derivative of estrone was prepared by first methylation of its -OH functionality, followed by reduction of ketone moiety. The obtained alcohol was then treated with 4-

chlorobenzonitrile to give the nitrile derivative of estrone which then underwent hydration in presence of 10 mol% of NaOH to give the desired primary amide. [S3, S4, S5, S6]

4-(((8R,9S,13S,14S)-3-methoxy-13-methyl-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]5henanthrene-17-yl)oxy)benzamide (**2aj**): **^{1}H NMR** (500 MHz, $CDCl_3$, 25 °C): δ = 7.75 (d, J = 9.0 Hz, 2H), 7.20 (d, J = 8.5 Hz, 1H), 6.94 (d, J = 8.5 Hz, 2H), 6.72-6.70 (m, 1H), 6.64-6.63 (m, 1H), 5.90 (brs, 2H), 4.29 (t, J = 8.0 Hz, 1H), 3.78 (s, 3H), 2.90-2.86 (m, 2H), 2.61 (s, 1H), 2.34-2.27 (m, 2H), 2.25-2.20 (m, 1H), 2.01-1.97 (m, 1H), 1.93-1.90 (m, 1H), 1.84-1.78 (m, 1H), 1.69-1.61 (m, 1H), 1.55-1.47 (m, 3H), 1.41-1.31 (m, 3H), 0.95 (s, 3H); **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$, 25 °C): δ = 169.1, 162.3, 157.6, 138.0, 132.6, 129.3, 126.5, 125.2, 115.6, 114.0, 111.7, 86.7, 55.3, 50.0, 44.03, 43.99, 41.1, 38.7, 37.7, 29.9, 28.3, 27.4, 26.4, 23.7, 12.2; **HRMS**: m/z calcd. For $C_{26}H_{31}NO_3Na^+$ $[M + Na]^+$ 428.2196, found 428.2184. The compound was purified by column chromatography on neutral alumina with ethyl acetate as eluent.

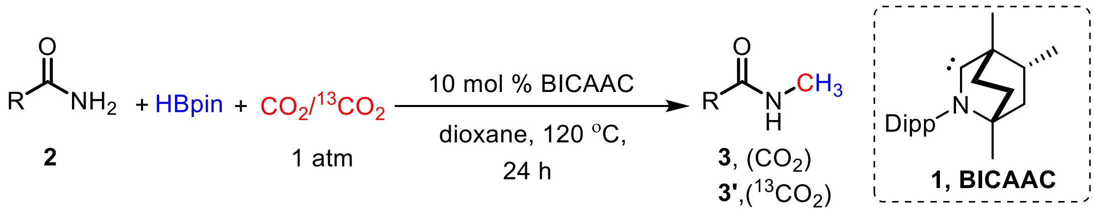
2.3) Synthesis of the substrate 2am



The amide derivative of α-tocopherol was prepared by following the reported literatures. [S2, S7]

4-((((S)-2,5,7,8-tetramethyl-2-((4S,8S)-4,8,12-trimethyltridecyl)chroman-6-yl)oxy)methyl)benzamide (**2am**): **^{1}H NMR** (500 MHz, $CDCl_3$, 25 °C): δ = 7.86 (d, J = 8.0 Hz, 2H), 7.58 (d, J = 8.0 Hz, 2H), 6.10 (d, NH, 2H), 4.76 (s, 2H), 2.59 (t, J = 6.5 Hz, 2H), 2.20 (s, 3H), 2.15 (s, 3H), 2.11 (s, 3H), 1.86-1.75 (m, 3H), 1.64-1.50 (m, 3H), 1.44-1.35 (m, 4H), 1.30-1.21 (m, 10H), 1.16-1.07 (m, 6H), 0.88-0.84 (m, 12H); **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$, 25 °C): δ = 169.4, 148.2, 148.1, 142.5, 132.7, 127.9, 127.7, 127.6, 126.0, 123.2, 117.8, 75.0, 74.0, 40.21, 40.16, 39.5, 37.7, 37.6, 37.5, 37.4, 32.9, 32.8, 31.44, 31.39, 28.1, 24.9, 24.6, 24.0, 22.85, 22.76, 21.2, 20.8, 19.89, 19.83, 19.77, 13.0, 12.1, 11.9; **HRMS**: m/z calcd. For $C_{37}H_{57}NO_3Na^+$ $[M + Na]^+$ 586.4231, found 586.4235. The compound was purified by column chromatography on neutral alumina with ethyl acetate as eluent.

3) Typical procedure for BICAAC-catalysed methylation of amides, synthesis of N-methyl amide derivatives 3a-3al'



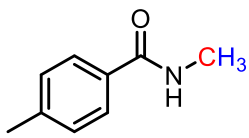
Scheme S1. Freeze-pump-thaw technique during catalysis using Schlenk tube with a J. Young valve.

Inside an argon-filled glovebox, a 25 mL Schlenk tube equipped with a stir bar and a J. Young valve was charged with amide (0.2 mmol), BICAAC (10 mol%), pinacolborane (0.8 mmol) and dioxane (1 mL). The mixture was degassed by a freeze-pump-thaw cycle and exposed to 1 atm of $CO_2/^{13}CO_2$. The reaction flask was sealed tightly and stirred for 24 h at 120 °C. Then the reaction mixture was dried using a high vacuum pump and purified by column chromatography on neutral alumina. The N-methyl amide was then obtained as an analytically pure compound using a hexane-ethyl acetate mixture as the eluent. The corresponding product was identified by ^{1}H and $^{13}C\{^{1}H\}$ NMR spectroscopy in $CDCl_3$ or DMSO-d_6.

4) Analytical and spectral characterisation of N-methyl amide 3a-3al'

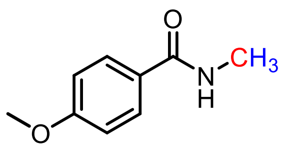
^{1}H and ^{13}C{^{1}H} NMR data for N-methylated products:

4-Methyl-*N*-methylbenzamide (3a)[S8]:



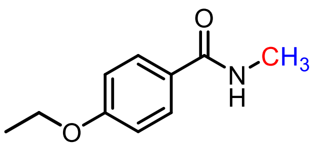
^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 7.65 (d, J = 8.5 Hz, 2H), 7.20 (d, J = 8.0 Hz, 2H), 6.34 (brs, NH, 1H), 2.98 (d, J = 5.0 Hz, 3H), 2.37 (s, 3H); **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$, 25 °C): δ = 168.4, 141.8, 131.8, 129.3, 127.0, 27.0, 21.5. The compound was purified by column chromatography on neutral alumina with hexane and ethyl acetate mixture (80:20 v/v) as eluent. Yield: 77%.

4-Methoxy-*N*-methylbenzamide (3b)[S8]:



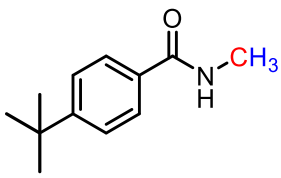
^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 7.73 (d, J = 9.0 Hz, 2H), 6.88 (d, J = 8.5 Hz, 2H), 6.34 (brs, NH, 1H), 3.82 (s, 3H), 2.97 (d, J = 5.0 Hz, 3H); **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$, 25 °C): δ = 168.0, 162.1, 128.7, 127.0, 113.8, 55.5, 26.9. The compound was purified by column chromatography on neutral alumina with a hexane and ethyl acetate mixture (76:24 v/v) as eluent. Yield: 68%.

4-Ethoxy-*N*-methylbenzamide (3c)[S9]:



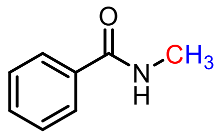
^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 7.71 (d, J = 8.5 Hz, 2H), 6.88 (d, J = 8.5 Hz, 2H), 6.24 (brs, NH, 1H), 4.05 (q, J = 7.0 Hz, 2H), 2.98 (d, J = 5.0 Hz, 3H), 1.41 (t, J = 7.0 Hz, 3H); **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$, 25 °C): δ = 168.0, 161.5, 128.7, 126.8, 114.2, 63.7, 26.9, 14.8; **HRMS:** m/z calcd. For $C_{10}H_{13}O_2Nna^+$ $[M + Na]^+$ 202.0838, found 202.0845. The compound was purified by column chromatography on neutral alumina with a hexane and ethyl acetate mixture (76:24 v/v) as eluent. Yield: 55%.

4-Tert-butyl-*N*-methylbenzamide (3d)[S8]:



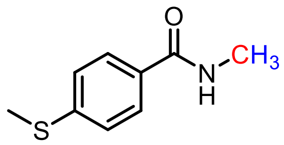
^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 7.70 (d, J = 8.5 Hz, 2H), 7.41 (d, J = 8.5 Hz, 2H), 6.42 (brs, NH, 1H), 2.98 (d, J = 4.5 Hz, 3H), 1.31 (s, 9H); **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$, 25 °C): δ = 168.4, 154.8, 131.8, 126.8, 125.5, 35.0, 31.3, 26.9. The compound was purified by column chromatography on neutral alumina with a hexane and ethyl acetate mixture (84:16 v/v) as eluent. Yield: 69%.

***N*-Methylbenzamide (3e) [S10]:**



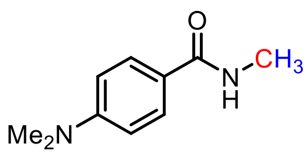
^{1}**H NMR** (500 MHz, $CDCl_3$, 25 °C): δ = 7.76 (d, J = 7.5 Hz, 2H), 7.47 (t, J = 7.5 Hz, 1H), 7.40 (t, J = 7.5 Hz, 2H), 6.39 (brs, NH, 1H), 3.00 (d, J = 5.0 Hz, 3H); ^{13}**C{^{1}H} NMR** (125 MHz, $CDCl_3$, 25 °C): δ = 168.4, 134.7, 131.4, 128.6, 127.0, 26.9. The compound was purified by column chromatography on neutral alumina with a hexane and ethyl acetate mixture (84:16 v/v) as eluent. Yield: 57%.

***N*-Methyl-4-(methylthio)benzamide (3f)[S8]:**



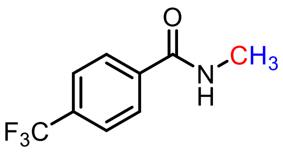
^{1}**H NMR** (500 MHz, $CDCl_3$, 25 °C): δ = 7.67 (d, J = 8.5 Hz, 2H), 7.21 (d, J = 8.0 Hz, 2H), 6.41 (brs, NH, 1H), 2.97 (d, J = 4.5 Hz, 3H), 2.48 (s, 3H); ^{13}**C{^{1}H} NMR** (125 MHz, $CDCl_3$, 25 °C): δ = 167.9, 143.3, 130.8, 127.4, 125.5, 26.9, 15.1. The compound was purified by column chromatography on neutral alumina with a hexane and ethyl acetate mixture (84:16 v/v) as eluent. Yield: 57%.

4-(Dimethylamino)-*N*-methylbenzamide (3g)[S11]:



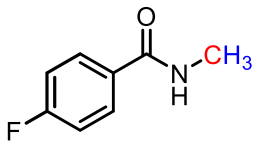
^{1}**H NMR** (500 MHz, $CDCl_3$, 25 °C): δ = 7.67 (d, J = 9.0 Hz, 2H), 6.65 (d, J = 9.0 Hz, 2H), 6.17 (brs, NH, 1H), 2.99 (s, 6H), 2.96 (d, J = 4.5 Hz, 3H)**;** ^{13}**C{^{1}H} NMR** (125 MHz, $CDCl_3$, 25 °C): δ = 168.3, 152.5, 128.4, 121.6, 111.2, 40.2, 26.8. The compound was purified by column chromatography on neutral alumina with a hexane and ethyl acetate mixture (76:24 v/v) as eluent. Yield: 62%.

***N*-Methyl-4-(trifluoromethyl)benzamide (3h)[S12]:**



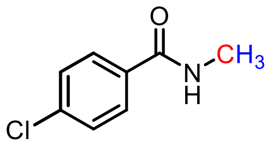
^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.86 (d, J = 8.0 Hz, 2H), 7.66 (d, J = 8.0 Hz, 2H), 6.48 (brs, NH, 1H), 3.01 (d, J = 4.5 Hz, 3H)**;** $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, 25 °C, TMS): δ = 167.2, 138.0, 133.3 (q, J = 32.7 Hz), 127.5, 125.7 (q, J = 3.9 Hz), 123.8 (q, J = 270.5 Hz), 27.1; **$^{19}F\{^1H\}$ NMR** (470 MHz, $CDCl_3$, 25 °C): δ = -62.9. The compound was purified by column chromatography on neutral alumina with hexane and ethyl acetate mixture (82:18 v/v) as eluent. Yield: 58%.

4-Fluoro-*N*-methylbenzamide (3i) [S13, S14, S15]:



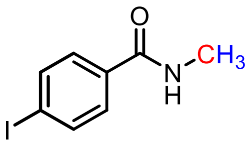
^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 7.78-7.75 (m, 2H), 7.07 (t, J = 9.0 Hz, 2H), 6.39 (brs, NH, 1H), 2.98 (d, J = 4.5 Hz, 3H)**; $^{13}C\{^1H\}$ NMR** (125 MHz, $CDCl_3$, 25 °C): δ = 167.4, 164.7 (d, J = 250 Hz), 130.9 (d, J = 3.3 Hz), 129.3 (d, J = 8.9 Hz), 115.6 (d, J = 21.8 Hz), 27.0; **$^{19}F\{^1H\}$ NMR** (470 MHz, $CDCl_3$, 25 °C): δ = -108.5. The compound was purified by column chromatography on neutral alumina with hexane and ethyl acetate mixture (82:18 v/v) as eluent. Yield: 55%.

4-Chloro-*N*-methylbenzamide (3j)[S15]:



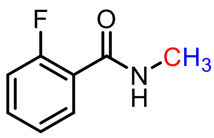
^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.69 (d, J = 8.8 Hz, 2H), 7.38 (d, J = 8.8 Hz, 2H), 6.29 (brs, NH, 1H), 2.99 (d, J = 4.8 Hz, 3H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 167.4, 137.7, 133.1, 128.9, 128.4, 27.0. The compound was purified by column chromatography on neutral alumina with a hexane and ethyl acetate mixture (84:16 v/v) as eluent. Yield: 67%.

4-Iodo-*N*-methylbenzamide (3k)[S16]:



^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 7.75 (d, J = 7.0 Hz, 2H), 7.47 (d, J = 8.5 Hz, 2H), 6.37 (brs, NH, 1H), 2.98 (d, J = 5.0 Hz, 3H); **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$, 25 °C): δ = 167.7, 137.8, 134.1, 128.6, 98.3, 27.0. The compound was purified by column chromatography on neutral alumina with a hexane and ethyl acetate mixture (86:14 v/v) as eluent. Yield: 62%.

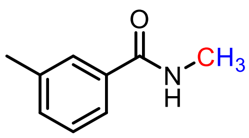
2-Fluoro-*N*-methylbenzamide (3l)[S17]:



^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 8.11(td, J = 8.0, 2.0 Hz, 1H), 7.49-7.44 (m, 1H), 7.28-7.25 (m, 1H), 7.14-7.10 (m, 1H), 6.77 (brs, NH, 1H), 3.04 (dd, J = 4.5, 1.0 Hz, 3H); **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$, 25 °C): δ = 164.1 (d, J = 3.2 Hz), 160.7 (d, J = 245.7 Hz), 133.2 (d, J = 9.2 Hz), 132.1 (d, J = 1.9 Hz), 124.9 (d, J = 2.9 Hz), 121.1 (d, J = 11.8 Hz), 116.0 (d, J =

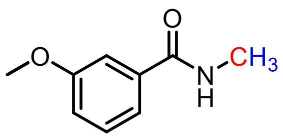
24.9 Hz), 26.9; **^{19}F{^{1}H} NMR** (470 MHz, $CDCl_3$, 25 °C): δ = -114.0. The compound was purified by column chromatography on neutral alumina with hexane and ethyl acetate mixture (90:10 v/v) as eluent. Yield: 37%.

3-Methyl-*N*-methylbenzamide (3m)[S8]:



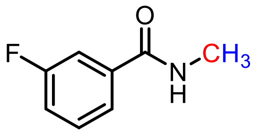
^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 7.56 (s, 1H), 7.51-7.49 (m, 1H), 7.25 (d, J = 4.5 Hz, 2H), 6.46 (brs, NH, 1H), 2.95 (d, J = 4.5 Hz, 3H), 2.33 (s, 3H); **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$, 25 °C): δ = 168.6, 138.4, 134.7, 132.1, 128.4, 127.7, 123.9, 26.9, 21.4. The compound was purified by column chromatography on neutral alumina with hexane and ethyl acetate mixture (80:20 v/v) as eluent. Yield: 69%.

3-Methoxy-*N*-methylbenzamide (3n)[S8]:



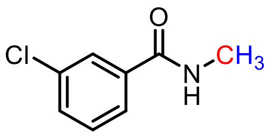
^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 7.33-7.27 (m, 2H), 7.24-7.23 (m, 1H, overlapped with $CDCl_3$), 7.00-6.99 (m,1H), 6.23 (brs, NH, 1H), 3.81 (s, 3H), 2.98 (d, J = 4.5 Hz, 3H); **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$, 25 °C): δ = 168.3, 160.0, 136.3, 129.7, 118.7, 117.7, 112.4, 55.6, 27.0. The compound was purified by column chromatography on neutral alumina with a hexane and ethyl acetate mixture (76:24 v/v) as eluent. Yield: 48%.

3-Fluoro-*N*-methylbenzamide (3o)[S8, S15]:



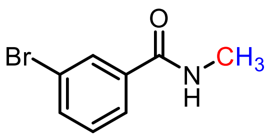
^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 7.51-7.47 (m, 2H), 7.40-7.36 (m, 1H), 7.19-7.16 (m, 1H), 6.31 (brs, NH, 1H), 3.01 (d, J = 5.0 Hz, 3H); **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$, 25 °C): δ = 167.2, 163.9, 161.9, 137.0 (d, J = 6.8 Hz), 130.3 (d, J = 7.6 Hz), 122.4 (d, J = 2.8 Hz), 118.5 (d, J = 21.5 Hz), 114.4 (d, J = 22.9 Hz), 27.0; **^{19}F{^{1}H} NMR** (470 MHz, $CDCl_3$, 25 °C): δ = -111.9. The compound was purified by column chromatography on neutral alumina with a hexane and ethyl acetate mixture (84:16 v/v) as eluent. Yield: 46%.

3-Chloro-*N*-methylbenzamide (3p)[S8]:



^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 7.74 (s, 1H), 7.63-7.61 (m, 1H), 7.43 (d, J = 8.0 Hz, 1H), 7.32 (t, J = 7.5 Hz, 1H), 6.54 (brs, NH, 1H), 2.98 (d, J = 5.0 Hz, 3H); **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$, 25 °C): δ = 167.2, 136.5, 134.8, 131.5, 130.0, 127.4, 125.1, 27.0. The compound was purified by column chromatography on neutral alumina with a hexane and ethyl acetate mixture (84:16 v/v) as eluent. Yield: 68%.

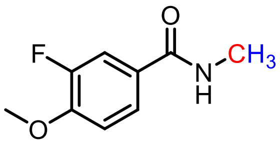
3-Bromo-*N*-methylbenzamide (3q)[S18]:



^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 7.94 (m, 1H), 7.71 (d, J = 8.0 Hz, 1H), 7.62 (d, J = 8.0 Hz, 1H), 7.30 (t, J = 7.5 Hz, 1H), 6.58 (brs, NH, 1H), 3.02 (d, J = 5.0 Hz, 3H); **^{13}C{^{1}H}**

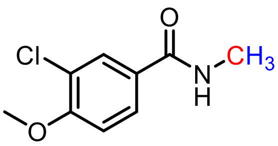
NMR (125 MHz, $CDCl_3$, 25 °C): δ = 167.0, 136.7, 134.4, 130.3, 130.2, 125.6, 122.8, 27.0. The compound was purified by column chromatography on neutral alumina with a hexane and ethyl acetate mixture (76:24 v/v) as eluent. Yield: 60%.

3-Fluoro-4-methoxy-*N*-methylbenzamide (3r):



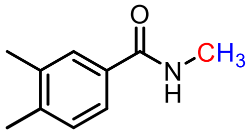
^{1}H NMR (500 MHz, DMSO-d$_6$, 25 °C): δ = 8.37 (brs, NH, 1H), 7.69-7.66 (m, 2H), 7.22 (t, J = 9.0 Hz, 1H), 3.88 (s, 3H), 2.77 (d, J = 4.5 Hz, 3H); **^{13}C{^{1}H} NMR** (125 MHz, DMSO-d$_6$, 25 °C): δ = 165.1, 150.9 (d, J = 242.7 Hz), 149.4 (d, J = 10.4 Hz), 127.1 (d, J = 5.6 Hz), 124.04 (d, J = 2.9 Hz), 114.6 (d, J = 19.2 Hz), 113.2, 56.1, 26.2; **^{19}F{^{1}H} NMR** (470 MHz, DMSO-d$_6$, 25 °C): δ = -135.3; **HRMS:** m/z calcd. For $C_9H_{10}O_2NFNa^+$ $[M + Na]^+$ 206.0588, found 206.0593. The compound was purified by column chromatography on neutral alumina with a hexane and ethyl acetate mixture (74:26 v/v) as eluent. Yield: 75%.

3-Chloro-4-methoxy-*N*-methylbenzamide (3s)[S8]:



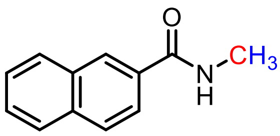
^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 7.79 (s, 1H), 7.66 (d, J = 9.0 Hz, 1H), 6.87 (d, J = 8.5 Hz, 1H), 6.71 (brs, NH, 1H), 3.89 (s, 3H), 2.95 (d, J = 5.0 Hz, 3H); **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$, 25 °C): δ = 166.9, 157.4, 129.2, 127.8, 127.1, 122.5, 111.5, 56.3, 26.9. The compound was purified by column chromatography on neutral alumina with hexane and ethyl acetate mixture (80:20 v/v) as eluent. Yield: 74%.

N,3,4-Trimethylbenzamide (3t)[S13, S19]:



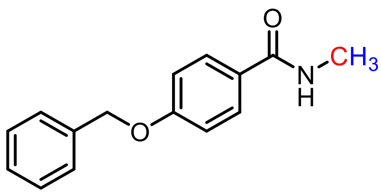
^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 7.55 (brs, 1H), 7.47 (dd, J = 7.5, 1.5 Hz, 1H), 7.14 (d, J = 8.0 Hz, 1H), 6.36 (brs, NH, 1H), 2.97 (d, J = 4.5 Hz, 3H), 2.27 (s, 6H); **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$, 25 °C): δ = 168.5, 140.4, 136.9, 132.3, 129.8, 128.3, 124.3, 26.8, 19.85, 19.82. The compound was purified by column chromatography on neutral alumina with a hexane and ethyl acetate mixture (80:20 v/v) as eluent. Yield: 66%.

N-Methyl-2-naphthamide (3u)[S15]:



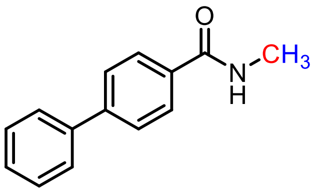
^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 8.27 (s, 1H), 7.84-7.82 (m, 4H), 7.51 (dt, J = 23.0, 7.0 Hz, 2H), 6.70 (brs, NH, 1H), 3.04 (d, J = 4.5 Hz, 3H); **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$, 25 °C): δ = 168.5, 134.8, 132.7, 132.0, 129.0, 128.5, 127.8, 127.7, 127.4, 126.8, 123.7, 27.1. The compound was purified by column chromatography on neutral alumina with hexane and ethyl acetate mixture (82:18 v/v) as eluent. Yield: 58%.

4-(Benzyloxy)-N-methylbenzamide (3v):



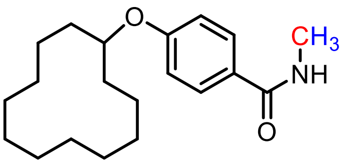
^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 7.73 (d, J = 8.5 Hz, 2H), 7.42-7.37 (m, 4H), 7.34-7.31 (m, 1H), 6.97 (d, J = 8.5 Hz, 2H), 6.33 (brs, NH, 1H), 5.08 (s, 2H), 2.97 (d, J = 5.0 Hz, 3H); **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$, 25 °C): δ = 167.9, 161.3, 136.5, 128.8, 128.7, 128.2, 127.6, 127.3, 114.7, 70.2, 26.9; **HRMS:** m/z calcd. For $C_{15}H_{15}O_2Nna^+$ $[M + Na]^+$ 264.0995, found 264.0995. The compound was purified by column chromatography on neutral alumina with a hexane and ethyl acetate mixture (78:22 v/v) as eluent. Yield: 68%.

***N*-Methyl-(1,1'-biphenyl)-4-carboxamide (3w)[S10]:**



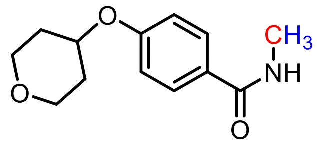
^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 7.85 (d, J = 8.0 Hz, 2H), 7.59 (q, J = 8.5 Hz, 4H), 7.44 (t, J = 7.5 Hz, 2H), 7.37 (t, J = 7.0 Hz, 1H), 6.67 (brs, NH, 1H), 3.02 (d, J = 4.0 Hz, 3H); **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$, 25 °C): δ = 168.2, 144.1, 140.1, 133.3, 128.9, 128.0, 127.5, 127.22, 127.21, 26.9. The compound was purified by column chromatography on neutral alumina with a hexane and ethyl acetate mixture (80:20 v/v) as eluent. Yield: 69%.

4-(Cyclododecyloxy)-*N*-methylbenzamide (3x):



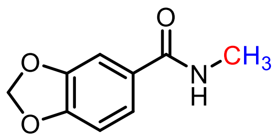
^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 7.70 (d, J = 8.5 Hz, 2H), 6.88 (d, J = 8.5 Hz, 2H), 6.16 (brs, NH, 1H), 4.49-4.45 (m, 1H), 2.98 (d, J = 5.0 Hz, 3H), 1.82-1.75 (m, 2H), 1.67-1.61 (m, 2H), 1.48-1.43 (m, 4H), 1.42-1.37 (m, 14H); **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$, 25 °C): δ = 168.0, 161.1, 128.7, 126.6, 115.5, 75.7, 28.7, 26.9, 24.6, 24.4, 23.25, 23.20, 20.8; **HRMS:** m/z calcd. For $C_{20}H_{31}O_2Nna^+$ $[M + Na]^+$ 340.2247, found 340.2251. The compound was purified by column chromatography on neutral alumina with a hexane and ethyl acetate mixture (84:16 v/v) as eluent. Yield: 70%.

_N_-Methyl-4-[(tetrahydro-2_H_-pyran-4-yl)oxy]benzamide (3y):



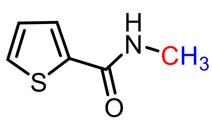
^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 7.71 (d, J = 8.5 Hz, 2H), 6.89 (d, J = 8.5 Hz, 2H), 6.36 (brs, NH, 1H), 4.55-4.50 (m, 1H), 3.98-3.94 (m, 2H), 3.59-3.55 (m, 2H), 2.96 (d, J = 4.5 Hz, 3H), 2.02-1.99 (m, 2H), 1.80-1.74 (m, 2H); **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$, 25 °C): δ = 167.8, 159.8, 128.8, 127.2, 115.5, 71.6, 65.1, 31.7, 26.9; HRMS: m/z calcd. For $C_{13}H_{17}O_3Nna^+$ $[M + Na]^+$ 258.1101, found 258.1110. The compound was purified by column chromatography on neutral alumina with hexane and ethyl acetate mixture (82:18 v/v) as eluent. Yield: 72%.

_N_-Methylbenzo[d][1,3]dioxole-5-carboxamide (3z)[S8]:



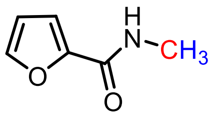
^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 7.26-7.24 (m, 2H), 6.78 (d, J = 7.5 Hz, 1H), 6.18 (brs, NH, 1H), 5.98 (s, 2H), 2.95 (d, J = 5.0 Hz, 3H); **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$, 25 °C): δ = 167.7, 150.2, 148.1, 129.0, 121.5, 108.0, 107.7, 101.7, 27.0. The compound was purified by column chromatography on neutral alumina with a hexane and ethyl acetate mixture (76:24 v/v) as eluent. Yield: 70%.

_N_-Methylthiophene-2-carboxamide (3aa)[S8]:



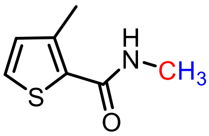
^{1}**H NMR** (500 MHz, $CDCl_3$, 25 °C): δ = 7.53-7.52 (m, 1H), 7.42 (d, J = 4.5 Hz, 1H), 7.04 (t, J = 4.5 Hz, 1H), 6.47 (brs, NH, 1H), 2.97 (d, J = 5.0 Hz, 3H); ^{13}**C{^{1}H} NMR** (125 MHz, $CDCl_3$, 25 °C): δ = 162.9, 139.2, 129.8, 128.1, 127.7, 26.8. The compound was purified by column chromatography on neutral alumina with a hexane and ethyl acetate mixture (84:16 v/v) as eluent. Yield: 67%.

***N*-Methylfuran-2-carboxamide (3ab) [S20, S21]:**



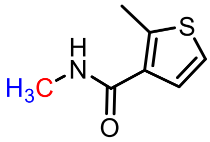
^{1}**H NMR** (500 MHz, $CDCl_3$, 25 °C): δ = 7.40 (dd, J = 1.0 Hz, 1H), 7.08 (m, 1H), 7.47-7.46 (m, 1H), 2.96 (d, J = 5.0 Hz, 3H); ^{13}**C{^{1}H} NMR** (125 MHz, $CDCl_3$, 25 °C): δ = 159.2, 148.3, 143.9, 114.0, 112.2, 26.0. The compound was purified by column chromatography on neutral alumina with a hexane and ethyl acetate mixture (82:18 v/v) as eluent. Yield: 45%.

***N*,3-Dimethylthiophene-2-carboxamide (3ac) [S22]:**



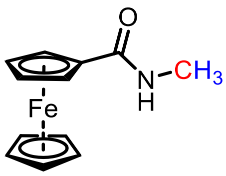
^{1}**H NMR** (500 MHz, $CDCl_3$, 25 °C): δ = 7.22 (d, J = 5.0 Hz, 1H), 6.86 (d, J = 5.0 Hz, 1H), 5.92 (brs, NH, 1H), 2.95 (d, J = 5.0 Hz, 3H), 2.49 (s, 3H); ^{13}**C{^{1}H} NMR** (125 MHz, $CDCl_3$, 25 °C): δ = 164.0, 141.0, 132.0, 131.0, 126.3, 26.8, 15.7. The compound was purified by column chromatography on neutral alumina with a hexane and ethyl acetate mixture (88:12 v/v) as eluent. Yield: 63%.

***N*,2-Dimethylthiophene-3-carboxamide** (**3ad**):



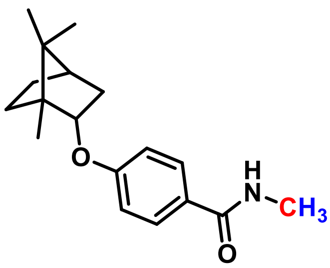
^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 7.08 (d, J = 5.5 Hz, 1H), 7.00 (d, J = 5.0 Hz, 1H), 5.99 (brs, NH, 1H), 2.93 (d, J = 4.0 Hz, 3H), 2.68 (s, 3H); **$^{13}C\{^1H\}$ NMR** (125 MHz, $CDCl_3$, 25 °C): δ = 165.5, 144.4, 132.1, 126.4, 121.9, 26.5, 14.9; **HRMS:** m/z calcd. For $C8H_9ONS^+$ $[M + H]^+$ 156.0478, found 156.0482. The compound was purified by column chromatography on neutral alumina with a hexane and ethyl acetate mixture (82:18 v/v) as eluent. Yield: 58%.

***N*-Methylferrocenecarboxamide (3ag) [S23]:**



^{1}H NMR (500 MHz, DMSO-d_6, 25 °C): δ = 7.70 (brs, NH, 1H), 4.74 (s, 2H), 4.32 (s, 2H), 4.15 (s, 5H), 2.70 (d, J = 4.5 Hz, 3H); **$^{13}C\{^1H\}$ NMR** (125 MHz, DMSO-d_6, 25 °C): δ = 169.3, 76.9, 69.7, 69.2, 68.0, 25.9.The compound was purified by column chromatography on neutral alumina with a hexane and ethyl acetate mixture (78:22 v/v) as eluent. Yield: 57%.

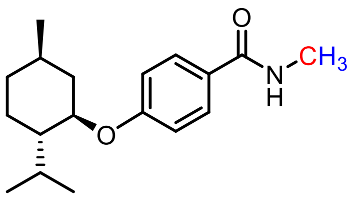
***N*-Methyl-4-(((1S,2S,4R)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl)oxy)benzamide (3ah):**



^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 7.69 (d, J = 8.5 Hz, 2H), 6.84 (d, J = 8.5 Hz, 2H), 6.11 (brs, NH, 1H), 4.36-4.35 (m, 1H), 2.99 (d, J = 4.5 Hz, 3H), 2.40-2.36 (m, 1H), 2.23-2.18

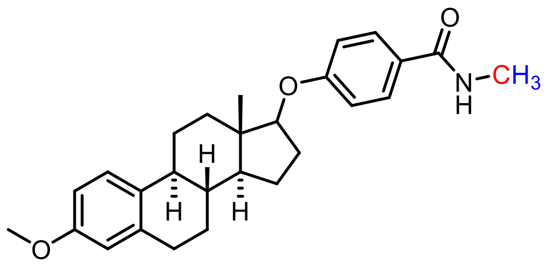
(m, 1H), 1.75 (s, 2H), 1.71 (s, 1H), 1.37-1.32 (m, 1H), 1.27-1.22 (m, 1H), 1.10-1.06 (m, 1H), 0.95 (s, 3H), 0.96 (s, 6H); **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$, 25 °C): δ = 168.1, 161.8, 128.7, 126.3, 115.2, 83.1, 49.6, 47.7, 45.2, 36.8, 28.0, 26.9, 26.8, 19.8, 19.0, 13.8; **HRMS:** m/z calcd. For $C_{18}H_{25}O_2Nna^+$ $[M + Na]^+$ 310.1777, found 310.1789. The compound was purified by column chromatography on neutral alumina with a hexane and ethyl acetate mixture (82:18 v/v) as eluent. Yield: 71%.

4-(((1R,2S,5R)-2-Isopropyl-5-methylcyclohexyl)oxy)-*N*-methylbenzamide (3ai):



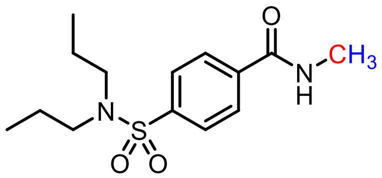
^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 7.71 (d, J = 8.5 Hz, 2H), 6.85 (d, J = 8.5 Hz, 2H), 6.40 (brs, NH, 1H), 4.09-4.04 (m, 1H), 2.96 (d, J = 4.5 Hz, 3H), 2.15-2.10 (m, 2H), 1.72-1.70 (m, 2H), 1.53-1.46 (m, 2H), 1.12-0.99 (m, 2H), 0.97-0.93 (m, 1H), 0.91-0.89 (m, 6H), 0.73 (d, J = 7.0 Hz, 3H); **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$, 25 °C): δ = 168.0, 161.1, 128.8, 126.5, 115.2, 77.7, 48.1, 40.2, 34.5, 31.5, 26.8, 26.2, 23.8, 22.2, 20.8, 16.7; **HRMS:** m/z calcd. For $C_{18}H_{27}O_2Nna^+$ $[M + Na]^+$ 312.1934, found 312.1900. The compound was purified by column chromatography on neutral alumina with a hexane and ethyl acetate mixture (82:18 v/v) as eluent. Yield: 67%.

4-(((8R,9S,13S,14S)-3-Methoxy-13-methyl-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]21henanthrene-17-yl)oxy)-*N*-methylbenzamide (3aj):



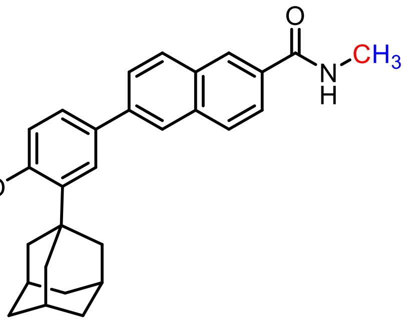
^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 7.72 (d, J = 8.5 Hz, 2H), 7.20 (d, J = 9.0 Hz, 1H), 6.92 (d, J = 8.5 Hz, 2H), 6.73-6.70 (m, 1H), 6.64 (s, 1H), 6.31 (brs, NH, 1H), 4.28 (t, J = 8.0 Hz, 1H), 3.78 (s, 3H), 2.99 (d, J = 3.5 Hz, 3H), 2.90-2.84 (m, 2H), 2.34-2.28 (m, 2H), 2.24-2.19 (m, 1H), 2.00-1.97 (m, 1H), 1.93-1.90 (m, 1H), 1.83-1.77 (m, 1H), 1.68-1.61 (m, 1H), 1.54-1.45 (m, 3H), 1.41-1.28 (m, 3H), 0.96 (s, 3H); **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$, 25 °C): δ = 168.0, 161.7, 157.6, 138.0, 132.5, 128.6, 126.6, 126.4, 115.5, 113.9, 111.6, 86.6, 55.3, 50.0, 44.0, 43.9, 38.6, 37.6, 29.9, 28.3, 27.4, 26.9, 26.4, 23.6, 12.2; **HRMS:** m/z calcd. For $C_{27}H_{34}O_3N$ $[M + H]^+$ 420.2533, found 420.2554. The compound was purified by column chromatography on neutral alumina with a hexane and ethyl acetate mixture (76:24 v/v) as eluent. Yield: 59%.

4-(*N*,*N*-dipropylsulfamoyl)-*N*-methylbenzamide (3ak)[S24]:



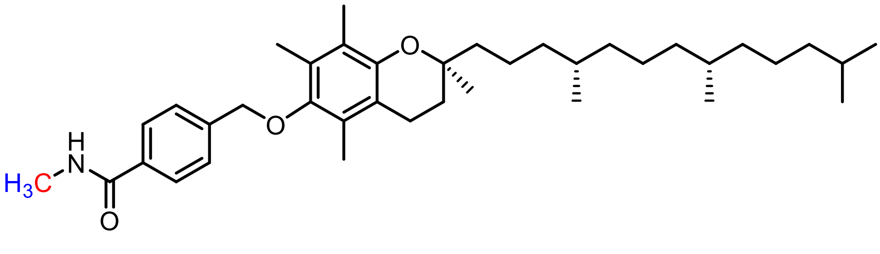
^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 7.84 (d, J = 8.5 Hz, 2H), 7.76 (d, J = 8.0 Hz, 2H), 6.73 (brs, NH, 1H), 3.05 (t, J = 7.5 Hz, 4H), 2.98 (d, J = 4.5 Hz, 3H), 1.50 (sext, J = 7.5 Hz, 4H), 0.83 (t, J = 7.0 Hz, 6H; **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$, 25 °C): δ = 167.1, 142.6, 138.4, 127.8, 127.2, 50.0, 27.0, 22.0, 11.2. The compound was purified by column chromatography on neutral alumina with a hexane and ethyl acetate mixture (70:30 v/v) as eluent. Yield: 63%.

6-(3-(Adamantan-1-yl)-4-methoxyphenyl)-*N*-methyl-2-naphthamide (3al):



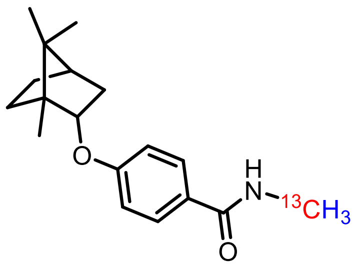
^{1}H NMR (500 MHz, DMSO-d_6, 25 °C): δ = 8.59-8.58 (m, 1H), 8.42 (s, 1H), 8.18 (s, 1H), 8.06-8.03 (m, 2H), 7.92 (d, J = 8.5 Hz, 1H), 7.86 (d, J = 8.5 Hz, 1H), 7.63 (d, J = 8.0 Hz, 1H), 7.57 (s, 1H), 7.11 (d, J = 8.5 Hz, 1H), 3.86 (s, 3H), 2.85 (d, J = 4.0 Hz, 3H), 2.13 (s, 6H), 2.06 (s, 3H), 1.76 (s, 6H); **^{13}C{^{1}H} NMR** (125 MHz, DMSO-d_6, 25 °C): δ = 166.7, 158.5, 139.4, 138.0, 134.6, 131.7, 131.5, 130.9, 129.4, 128.0, 127.0, 125.8, 125.6, 125.0, 124.4, 124.0, 112.7, 55.3, 40.1, 36.6, 36.5, 28.4, 26.3; **HRMS:** m/z calcd. For $C_{29}H_{31}O_2N$ $[M + Na]^+$ 448.2247, found 448.2265. The compound was purified by column chromatography on neutral alumina with a hexane and ethyl acetate mixture (80:20 v/v) as eluent. Yield: 63%.

***N*-Methyl-4-((((S)-2,5,7,8-tetramethyl-2-((4S,8S)-4,8,12-trimethyltridecyl)chroman-6-yl)oxy)methyl)benzamide (3am):**



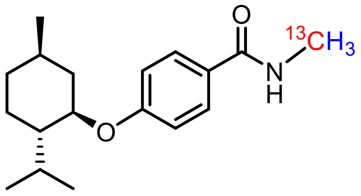
^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 7.81 (d, J = 8.0 Hz, 2H), 7.54 (d, J = 7.5 Hz, 2H), 6.41 (brs, NH, 1H), 4.74 (s, 2H), 3.02 (d, J = 5.0 Hz, 3H), 2.59 (t, J = 6.5 Hz, 2H), 2.20 (s, 3H), 2.15 (s, 3H), 2.11 (s, 3H), 1.86-1.75 (m, 2H), 1.61-1.49 (m, 4H), 1.45-1.35 (m, 4H), 1.29-1.25 (m, 10H), 1.15-1.08 (m, 6H), 0.88-0.85 (m, 12H); **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$, 25 °C): δ = 168.2, 148.2, 148.1, 141.6, 134.0, 127.9, 127.6, 127.2, 126.0, 123.1, 117.8, 75.0, 74.1, 40.2, 39.5, 37.7, 37.6, 37.5, 37.4, 32.9, 32.8, 31.4, 31.3, 28.1, 27.0, 24.9, 24.5, 24.0, 22.8, 22.7, 21.1, 20.8, 19.9, 19.8, 19.7, 13.0, 12.1, 11.9; **HRMS:** m/z calcd. For $C_{38}H_{59}O_3NK^+$ $[M + K]^+$ 616.4127, found 616.4170. The compound was purified by column chromatography on neutral alumina with a hexane and ethyl acetate mixture (80:20 v/v) as eluent. Yield: 79%.

***N*-(Methyl-^{13}C)-4-(((1S,2S,4R)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl)oxy)benzamide (3ah'):**



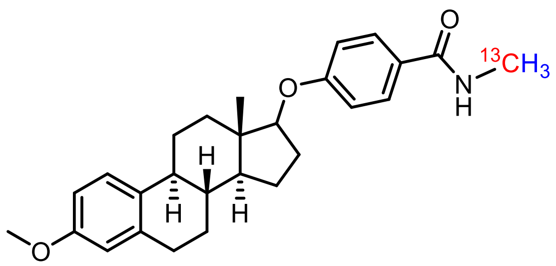
^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 7.70 (d, J = 8.5 Hz, 2H), 6.81 (d, J = 8.0 Hz, 2H), 6.44 (brs, NH, 1H), 4.35-4.33 (m, 1H), 2.95 (dd, J_1 = 138 Hz, J_2 = 4.5 Hz, 3H), 2.39-2.33 (m, 1H), 2.22-2.17 (m, 1H), 1.77-1.73 (m, 2H), 1.38-1.31 (m, 1H), 1.26-1.22 (m, 1H), 1.08-1.05 (m, 1H), 0.93 (s, 3H), 0.91 (s, 6H); **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$, 25 °C): δ = 168.1, 161.8, 128.7, 126.4, 115.2, 83.2, 49.6, 47.7, 45.2, 36.8, 28.0, 26.8, 19.8, 19.0, 13.8; **HRMS:** m/z calcd. For $^{13}CC_{17}H_{25}O_2Nna^+$ $[M + Na]^+$ 311.1856, found 311.1834. The compound was purified by column chromatography on neutral alumina with a hexane and ethyl acetate mixture (82:18 v/v) as eluent. Yield: 71%.

4-(((1R,2S,5R)-2-Isopropyl-5-methylcyclohexyl)oxy)-*N*-(methyl-^{13}C)benzamide (3ai'):



^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 7.70 (d, J = 8.5 Hz, 2H), 6.87 (d, J = 9.0 Hz, 2H), 6.35 (brs, NH, 1H), 4.10-4.05 (m, 1H), 2.95 (dd, J_1 = 138.5 Hz, J_2 = 4.5 Hz, 3H), 2.16-2.10 (m, 2H), 1.73-1.69 (m, 2H), 1.53-1.45 (m, 2H), 1.12-1.00 (m, 2H), 0.97-0.93 (m, 1H), 0.92-0.89 (m, 6H), 0.74 (d, J = 7.0 Hz, 3H); **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$, 25 °C): δ = 168.0, 161.1, 128.8, 126.6, 115.2, 77.7, 48.1, 40.2, 34.5, 31.5, 26.8, 26.3, 23.9, 22.2, 20.8, 16.7; **HRMS:** m/z calcd. For $^{13}CC_{17}H_{28}O_2N^+$ [M + H]$^+$ 291.2193, found 291.2170. The compound was purified by column chromatography on neutral alumina with a hexane and ethyl acetate mixture (82:18 v/v) as eluent. Yield: 69%.

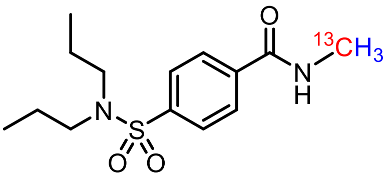
4-(((8R,9S,13S,14S)-3-Methoxy-13-methyl-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]24henanthrene-17-yl)oxy)-*N*-(methyl-^{13}C)benzamide (3aj'):



^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 7.72 (d, J = 8.5 Hz, 2H), 7.20 (d, J = 8.5 Hz, 1H), 6.92 (d, J = 8.5 Hz, 2H), 6.72 (d, J = 8.0 Hz, 1H), 6.65 (s, 1H), 6.41 (brs, NH, 1H), 4.28 (t, J = 7.5 Hz, 1H), 3.78 (s, 3H), 2.97 (dd, J_1 = 138.5 Hz, J_2 = 4.5 Hz, 3H), 2.90-2.86 (m, 2H), 2.34-2.28 (m, 2H), 2.24-2.20 (m, 1H), 2.00-1.97 (m, 1H), 1.93-1.90 (m, 1H), 1.83-1.78 (m, 1H), 1.67-1.61 (m, 1H), 1.52-1.48 (m, 3H), 1.39-1.27 (m, 3H), 0.95 (s, 3H); **^{13}C{^{1}H} NMR** (125

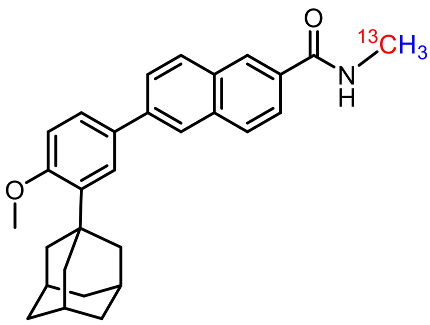
MHz, $CDCl_3$, 25 °C): δ = 168.0, 161.7, 157.6, 138.0, 132.5, 128.6, 126.6, 126.4, 115.4, 113.9, 111.6, 86.6, 55.3, 50.0, 43.95, 43.89, 38.6, 37.6, 29.8, 28.2, 27.4, 26.8, 26.4, 23.6, 12.1; **HRMS:** m/z calcd. For $^{13}CC_{26}H_{33}O_3Nna^+$ $[M + Na]^+$ 443.2431, found 443.2418. The compound was purified by column chromatography on neutral alumina with a hexane and ethyl acetate mixture (76:24 v/v) as eluent. Yield: 63%.

4-(*N*,*N*-Dipropylsulfamoyl)-*N*-(methyl-^{13}C)benzamide (3ak'):



^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 7.84 (d, J = 8.5 Hz, 2H), 7.75 (d, J = 8.5 Hz, 2H), 6.81 (brs, NH, 1H), 3.04 (t, J = 7.5 Hz, 4H), 2.96 (dd, J_1 = 138.5 Hz, J_2 = 4.5 Hz, 3H), 1.50 (sext, J = 7.5 Hz, 4H), 0.83 (t, J = 7.0 Hz, 6H); **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$, 25 °C): δ = 167.1, 142.6, 138.4, 127.8, 127.2, 50.0, 27.0, 22.0, 11.2; **HRMS:** m/z calcd. For $^{13}CC_{13}H_{23}N_2O_3S^+$ $[M + H]^+$ 300.1502, found 300.1524. The compound was purified by column chromatography on neutral alumina with a hexane and ethyl acetate mixture (74:26 v/v) as eluent. Yield: 67%.

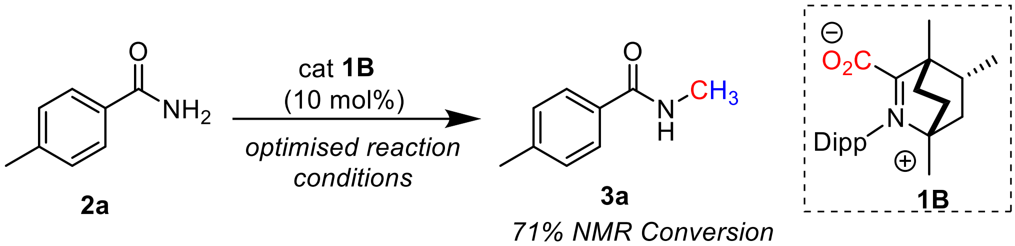
6-(3-(Adamantan-1-yl)-4-methoxyphenyl)-*N*-(methyl-^{13}C)-2-naphthamide (3al'):



^{1}H NMR (500 MHz, DMSO-d$_6$, 25 °C): δ = 8.58 (s, 1H), 8.42 (s, 1H), 8.18 (s, 1H), 8.06-8.04 (m, 2H), 7.92 (d, J = 8.5 Hz, 1H), 7.86 (d, J = 8.5 Hz, 1H), 7.65-7.63 (m, 1H), 7.57 (s, 1H), 7.11 (d, J = 8.5 Hz, 1H), 3.86 (s, 3H), 2.84 (dd, J_1 = 137.5 Hz, J_2 = 4.5 Hz, 3H), 2.14 (s, 6H), 2.07 (s, 3H), 1.76 (s, 6H); **^{13}C{^{1}H} NMR** (125 MHz, DMSO-d$_6$, 25 °C): δ = 166.6, 158.5, 139.4, 138.0, 134.5, 131.7, 131.5, 130.9, 129.3, 128.0, 127.0, 125.8, 125.6, 125.0, 124.3, 124.0, 112.7, 55.3, 40.1, 36.6, 36.5, 28.4, 26.3; **HRMS:** m/z calcd. For $^{13}CC_{28}H_{31}O_2Nna^+$ $[M + Na]^+$ 449.2325, found 449.2363. The compound was purified by column chromatography on neutral alumina with a hexane and ethyl acetate mixture (80:20 v/v) as eluent. Yield: 56%.

5) Control reactions

i) BICAAC-CO_2 adduct (1B) catalysed N-methylation of 4-methyl benzamide: proof to establish that 1B is catalytically active species



Scheme S2. Investigating **1B** as a catalyst for N-methylation of **2a**

A 25 mL Schlenk tube equipped with a stir bar and a J. Young valve was charged with 4-methyl benzamide, **2a** (0.2 mmol), BICAAC-CO_2 (10 mol%), pinacolborane (0.8 mmol) and dioxane (1 mL) inside an argon-filled glovebox. The mixture was degassed by a freeze-pump-thaw cycle and exposed to 1 atm of carbon dioxide. The reaction flask was sealed tightly and stirred for 24 h at 120 °C. Then the reaction mixture was dried using high vacuum pump and analysed by ^{1}H NMR spectroscopy. NMR conversion of 71% was obtained.

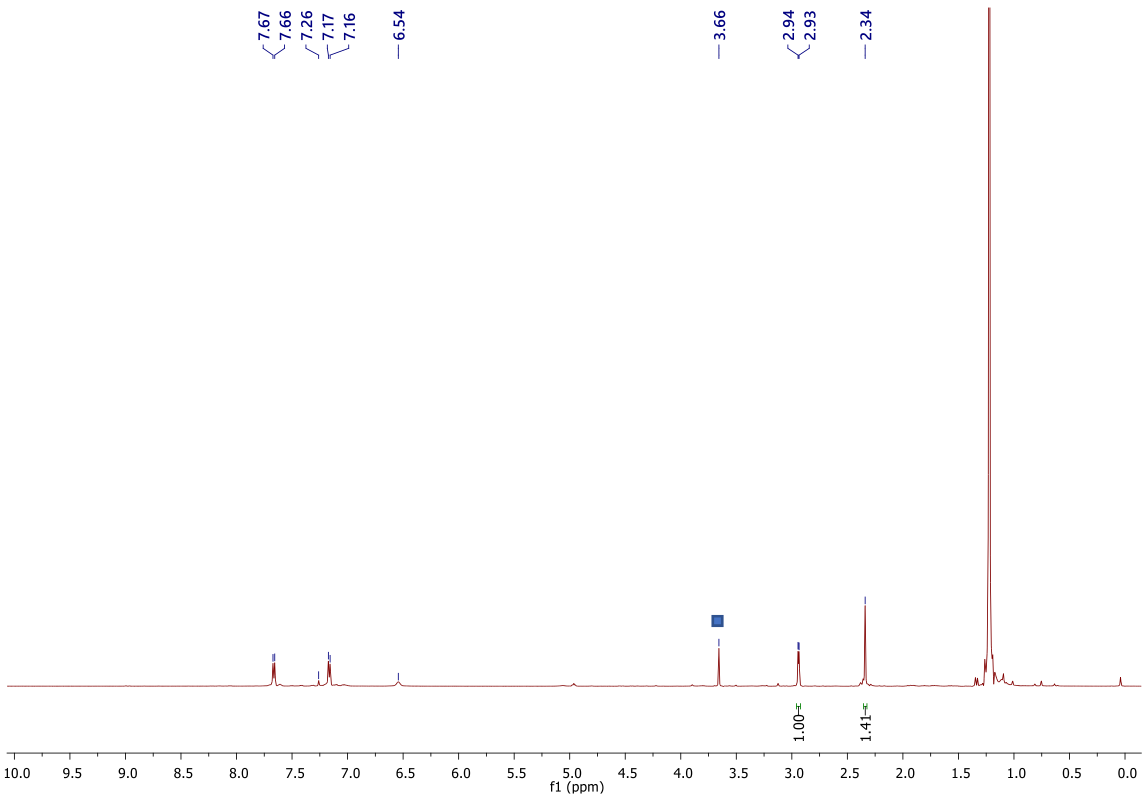
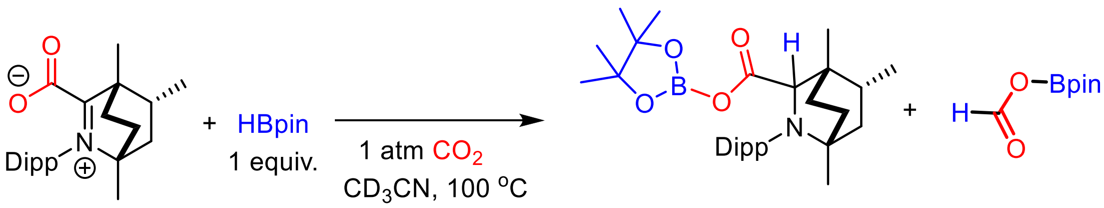


Fig. S1 Reaction mixture ^{1}H NMR spectrum in $CDCl_3$.[S8] ■ denotes residual dioxane.

ii) Characterization of reaction intermediates, 4 and boron formate (5)



Scheme S3. The stoichiometric reaction of **1B** with HBpin in the presence of 1atm CO_2

Inside an argon-filled glovebox, a J. Young NMR tube was charged with BICAAC-CO_2 adduct (35.5 mg), pinacolborane (1 equiv.) and CD_3CN (0.5 mL). The reaction mixture was degassed by a freeze-pump-thaw cycle and exposed to 1 atm of carbon dioxide. This was then heated at 100 °C for 12 h. ^{1}H and $^{11}B\{^{1}H\}$ NMR spectra were recorded for the reaction mixture. From the spectroscopic data, it is clear that a 1:1 diastereomeric mixture of **4,** along with boron formate intermediate (**5**), was identified.

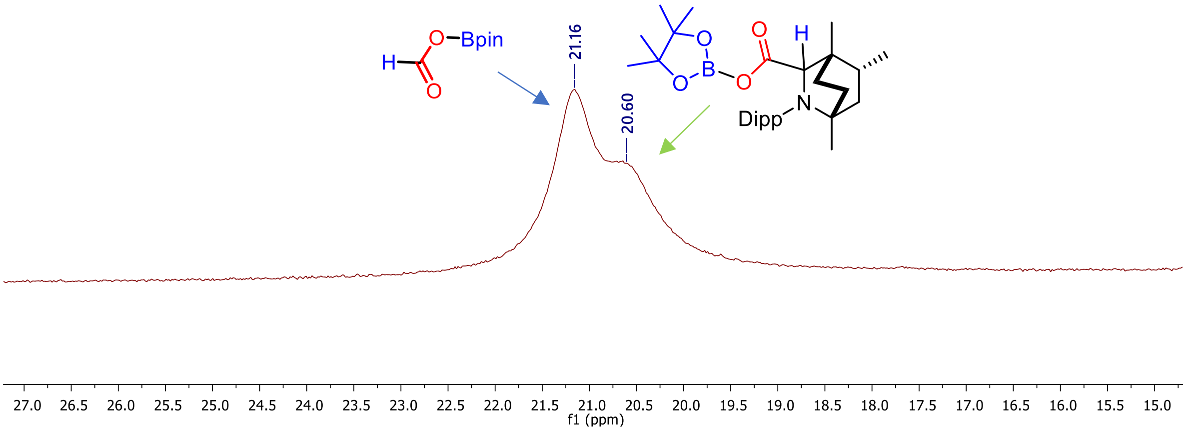


Fig. S2 [11]B{[1]H} NMR reaction mixture spectrum of **1B** with HBpin (in the presence of CO_2) in CD_3CN.[S25]

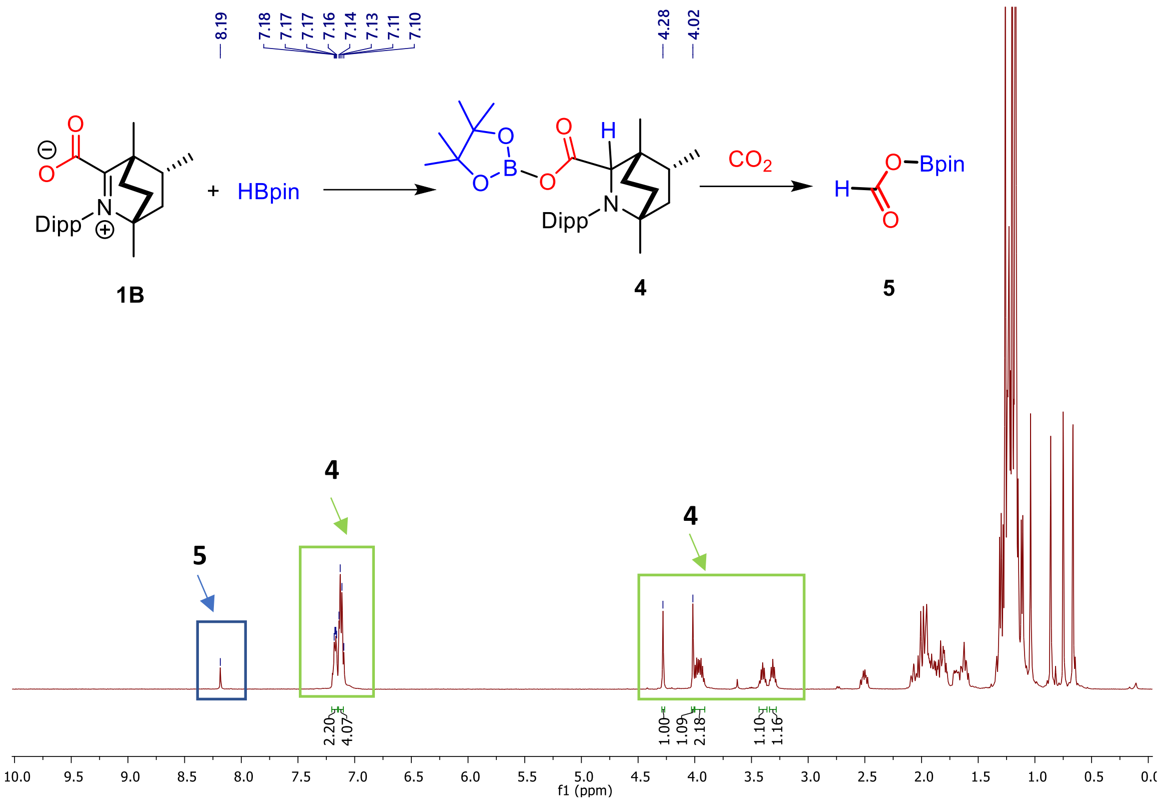
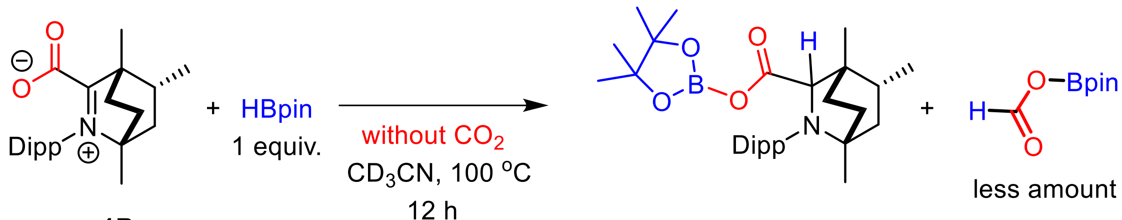


Fig. S3 Reaction mixture [1]H NMR spectrum of **1B** with HBpin in the presence of CO_2 in CD_3CN.The peaks marked in the green and blue boxes correspond to compound **4** and boron formate, **5,** respectively. [S25]

iii) Stoichiometric reaction of 1B with HBPin in the absence of CO_2



Scheme S4. Reaction of BICAAC-CO_2 adduct with 1 equiv. of HBpin in absence of CO_2

Inside an argon-filled glovebox, a J. Young NMR tube was charged with BICAAC-CO_2 adduct (35.5 mg), pinacolborane (1 equiv.) and CD_3CN (0.5 mL). This was then heated at 100 °C for 12 h. ^1H NMR spectrum was recorded for the reaction mixture. From the spectroscopic data, it is clear that boron formate intermediate (**5**) was obtained in less amount in absence of CO_2, indicating that a continuous supply of CO_2 is necessary for generation of boron formate. A stacked $^{11}B\{^1H\}$ NMR spectrum of the two reactions supports the same (Fig. S5)

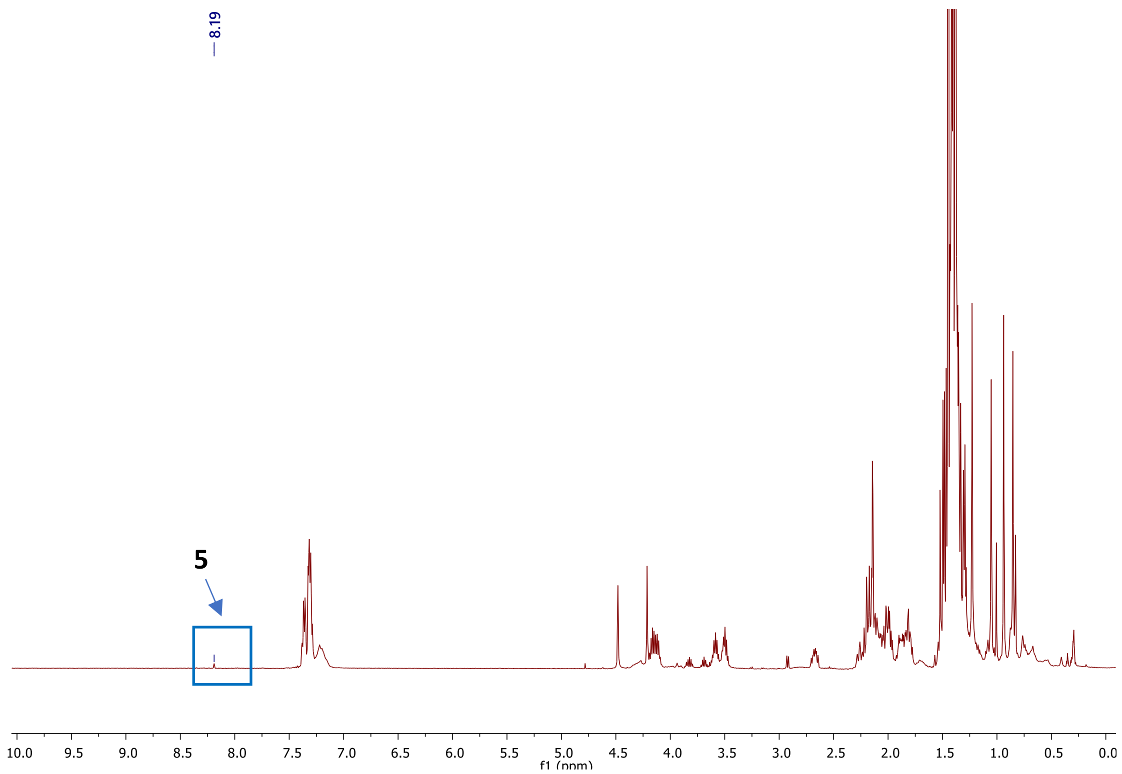


Fig. S4 Reaction mixture ^1H NMR spectrum of **1B** with HBpin (in absence of CO_2) in CD_3CN.

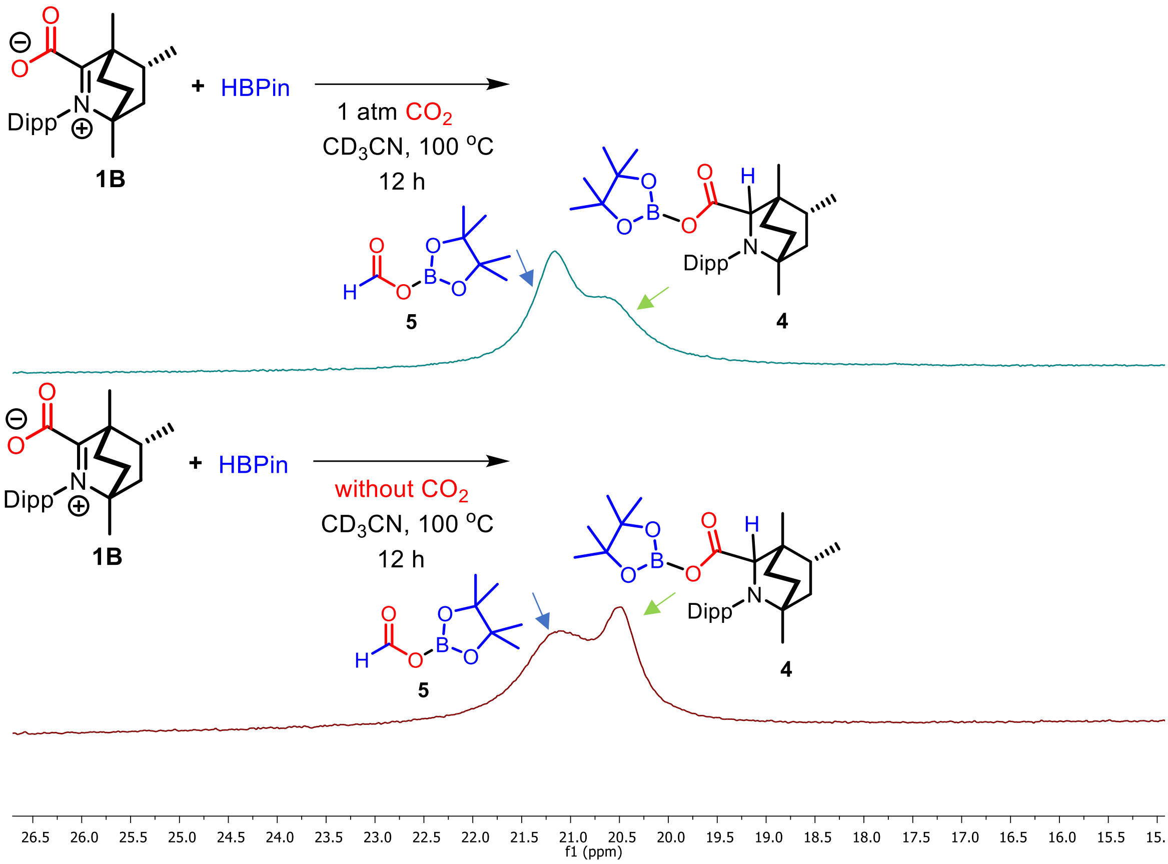
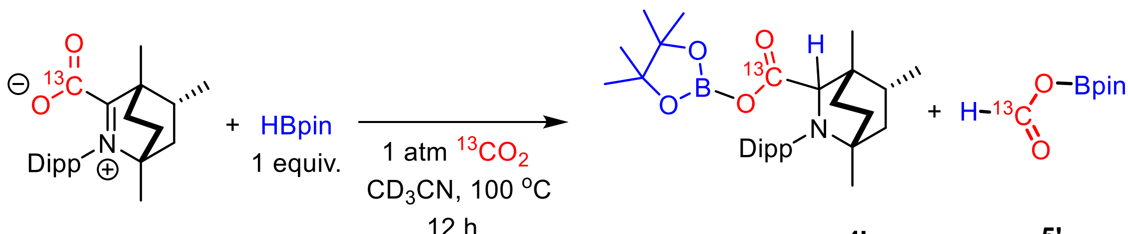


Fig. S5 Stacked $^{11}B\{^1H\}$ NMR plot in the presence and absence of CO_2.

iv) Characterization of ^{13}C labelled reaction intermediates, 4' and boron formate (5')



Scheme S5. The stoichiometric reaction of **1B'** with HBpin in the presence of 1atm $^{13}CO_2$. Inside an argon-filled glovebox, a J. Young NMR tube was charged with BICAAC-$^{13}CO_2$ adduct (35.6 mg), pinacolborane (1 equiv.) and CD_3CN (0.5 mL). The reaction mixture was degassed by a freeze-pump-thaw cycle and exposed to 1 atm of ^{13}C labelled carbon dioxide. This was then heated at 100 °C for 12 h. On completion, ^{1}H, $^{13}C\{^1H\}$ and $^{11}B\{^1H\}$ NMR spectra were recorded for the reaction mixture. From the spectroscopic data, it is clear that a 1:1 diastereomeric mixture of **4'** along with ^{13}C labelled boron formate intermediate (**5'**) was obtained. ^{1}H NMR analysis showed that in the case of **4'**, the -CH peak of the two diastereomers comes as two doublets with coupling constant values of 3.5 and 1.5 Hz, [S26, S27] while the formate peak comes as a doublet with a coupling constant value of 206.5 Hz. [S28] This arises due to the coupling with ^{13}C nucleus.

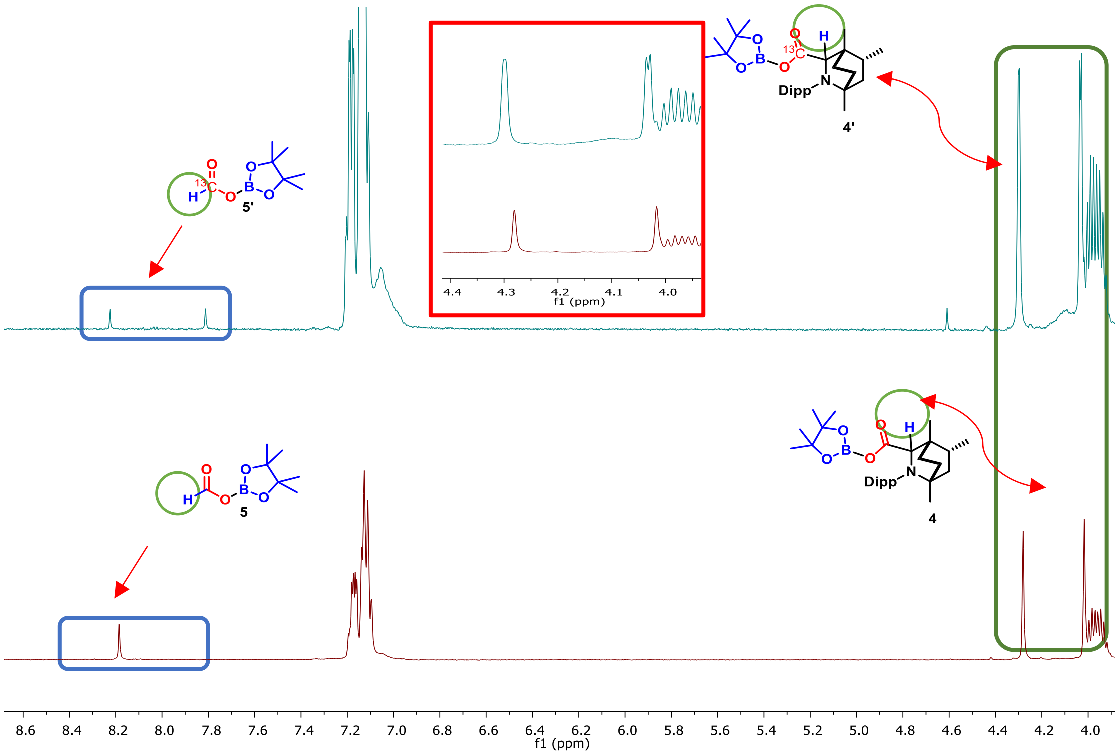


Fig. S6 Stacked plot indicating the effect of $^{13}CO_2$. ^{1}H NMR spectrum of **1B** with HBpin in presence of $^{13}CO_2$ and CO_2 in CD_3CN is given at the top and bottom, respectively. The peaks marked in the green and blue box corresponds to compound **4'** and **5',** respectively.

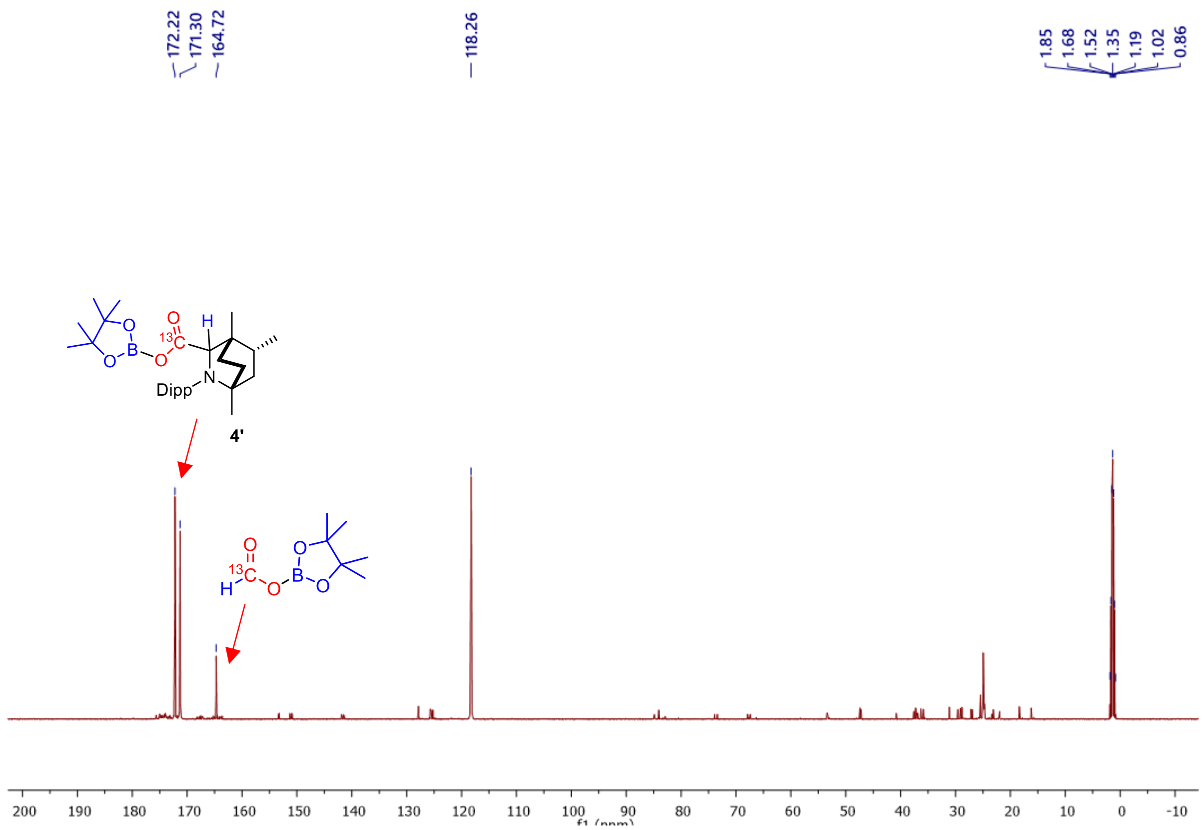


Fig. S7 Reaction mixture $^{13}C\{^{1}H\}$ NMR spectrum of **1B'** with HBpin in presence of $^{13}CO_2$ in CD_3CN.

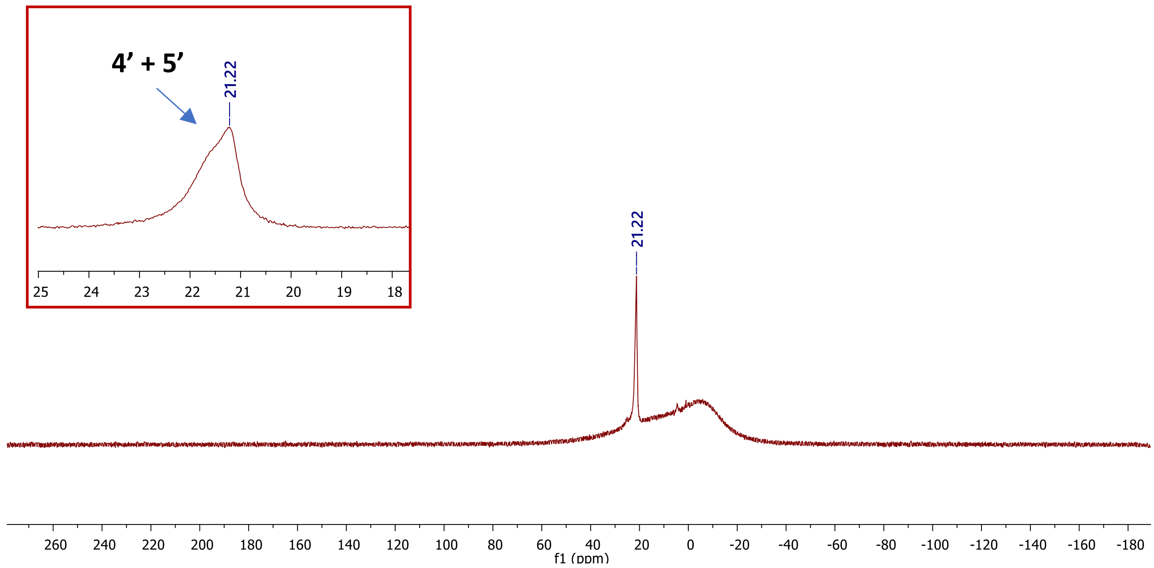


Fig. S8 Reaction mixture $^{11}B\{^{1}H\}$ NMR spectrum of **1B'** with HBpin in presence of $^{13}CO_2$ in CD_3CN.

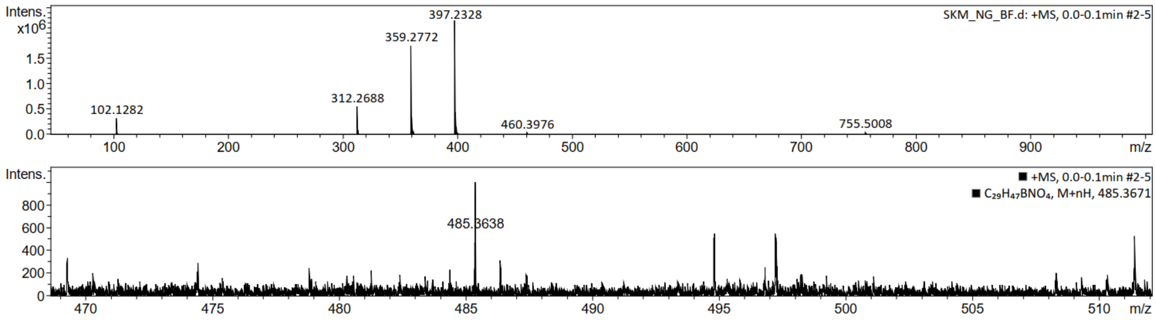
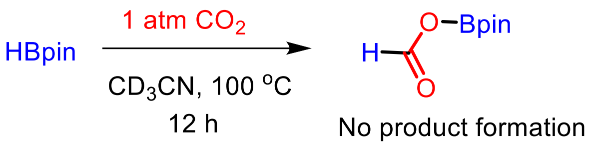


Fig. S9 HRMS spectrum of **4'**.

v) Reaction of HBPin with CO_2 in the absence of catalyst BICAAC



Scheme S6. The reaction between HBpin and CO_2 in CD_3CN

A J. Young NMR tube was charged with pinacolborane (0.2 mmol) and CD_3CN (0.5 mL) inside an argon-filled glovebox. The reaction mixture was degassed by a freeze-pump-thaw cycle and exposed to 1 atm of carbon dioxide. This was then heated at 100 °C for 12 h. Then ^{1}H NMR spectrum was recorded where the formation of boron formate was not observed, supporting the fact that BICAAC is necessary for this step.

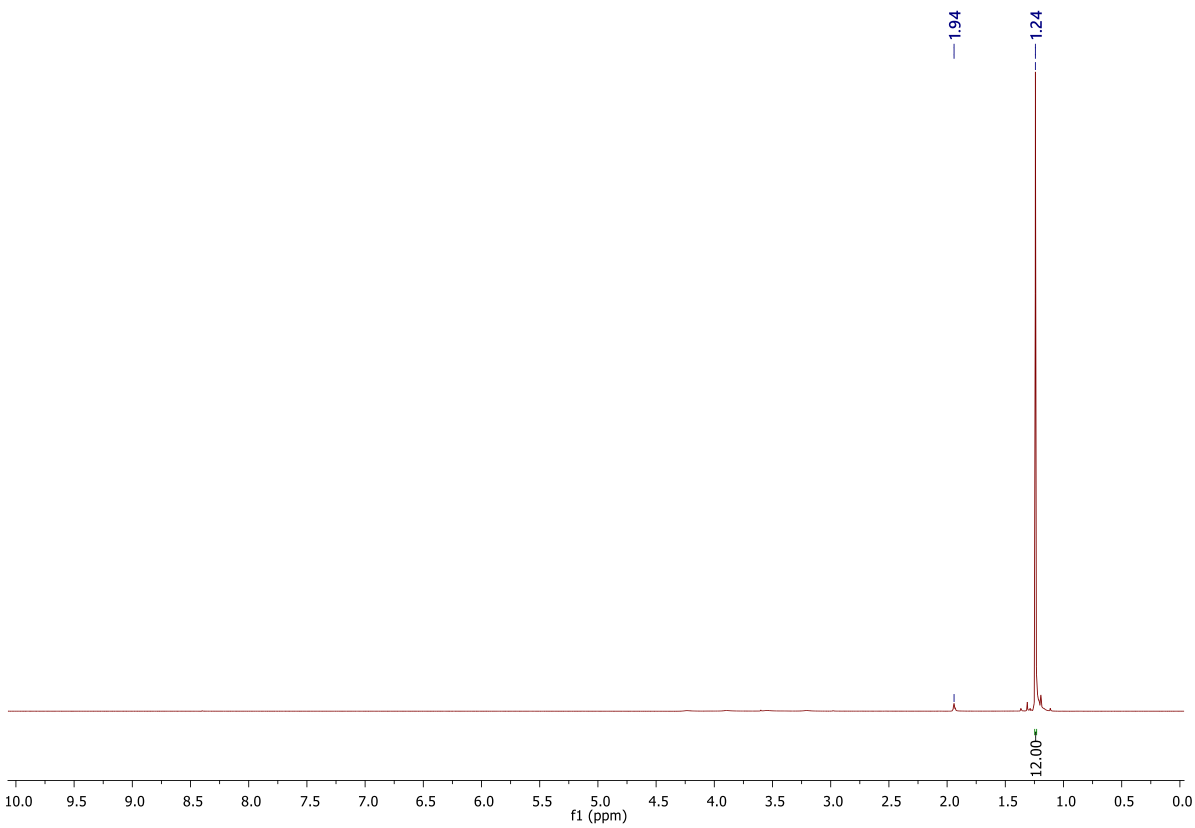
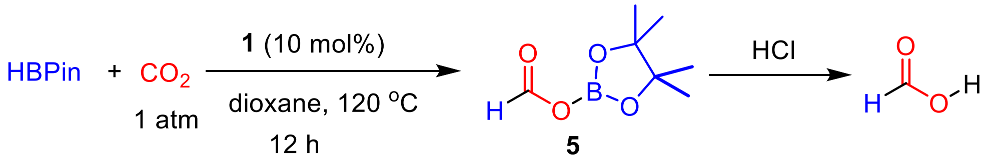


Fig. S10 [1]H NMR spectrum of the reaction mixture (HBpin and CO_2 in CD_3CN).

vi) Proof of boron formate



Scheme S7. The reaction between HBpin and CO_2 in the presence of catalyst **1**

Inside an argon-filled glovebox, a 25 mL Schlenk flask was charged with pinacolborane (0.3 mmol), BICAAC (10 mol%) and dioxane (1 mL). The mixture was degassed by a freeze-pump-thaw cycle and exposed to 1 atm of carbon dioxide. The reaction flask was stirred for 12 h at 120 °C. After the reaction was over, it was treated with HCl and its [1]H NMR spectrum was recorded. Spectroscopic peak at δ 8.31 ppm was obtained and it therefore confirmed the formation of formic acid, thereby establishing boron formate to be the catalytic intermediate.

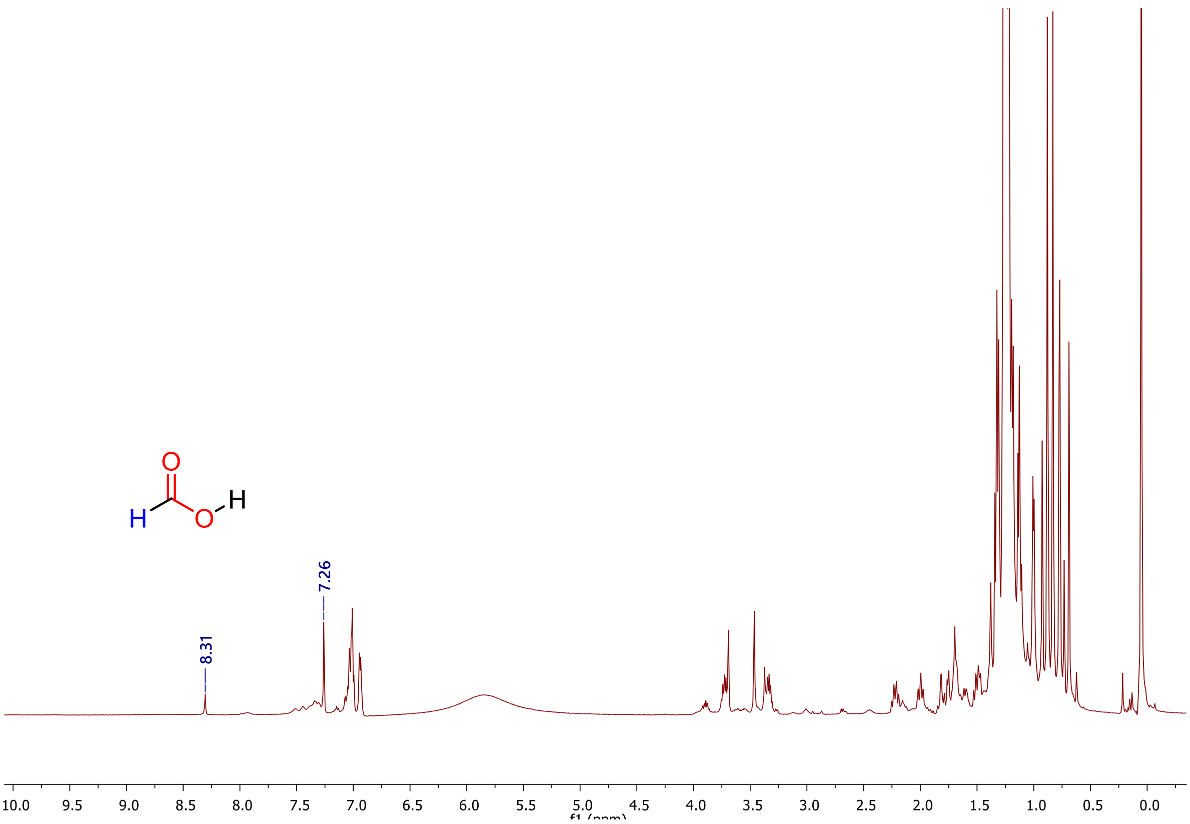
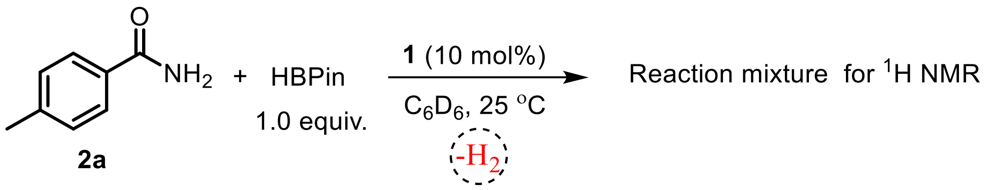


Fig. S11 Reaction mixture ^{1}H NMR spectrum showing the formation of formic acid in $CDCl_3$.[S29]

vii) H_2 evolution experiment



Scheme S8. The reaction between amide and HBpin in the presence of 10 mol% catalyst, **1**

A 2.5 mL screw cap NMR tube was charged with 4-methyl benzamide (0.1 mmol), BICAAC (10 mol%), HBpin (1 equiv.) and C_6D_6 (0.6 mL) under an argon atmosphere. Eventually, gas evolution was observed, which was confirmed to be dihydrogen from ^{1}H NMR (δ = 4.47 ppm) spectroscopy and GC analysis.

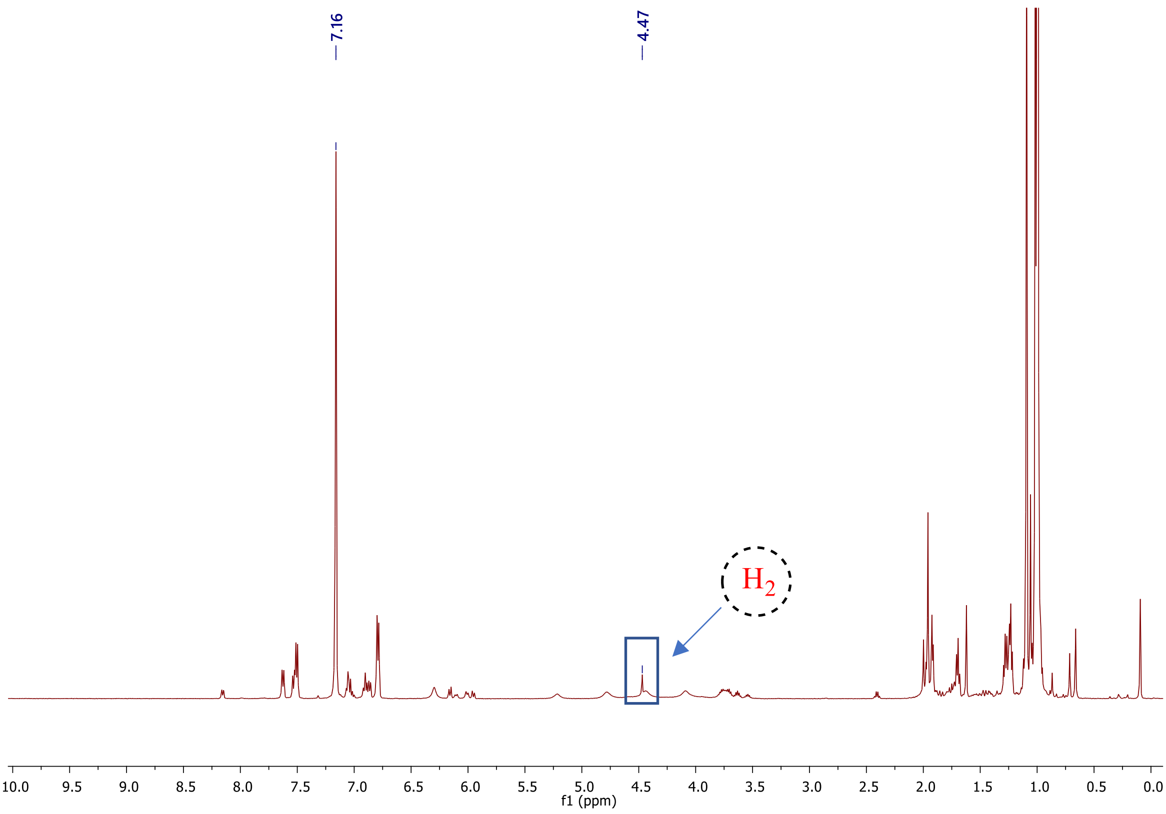


Fig. S12 Reaction mixture ^{1}H NMR spectrum of **2a**, HBpin, and BICAAC at 25 °C in C_6D_6.[S30]

Page 1 of 1

Software Version	: 6.3.4.0700		Date	: 03-01-2023 14:21:52
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Instrument Name	: Clarus590		Channel	: B
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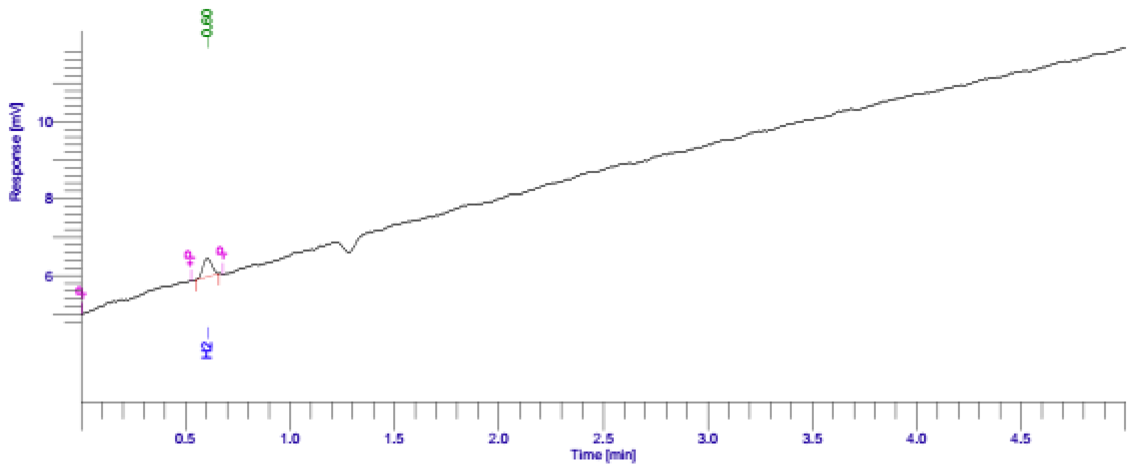


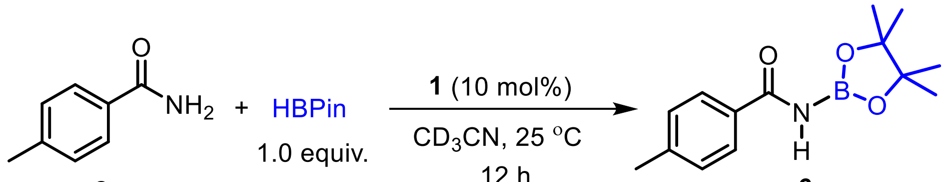
H2 REPORT

Peak #	Time [min]	Area [µV·s]	Height [µV]	Area [%]	Norm. Area [%]	BL	Area/Height [s]
1	0.605	1446.33	478.37	100.00	100.00	BB	3.0235
		1446.33	478.37	100.00	100.00		

Fig. S13 Retention time graph of the reaction mixture (4-methyl benzamide, HBpin, and BICAAC in C_6D_6 at 25 °C) in gas chromatography confirming H_2 evolution.

viii) Characterisation of N-borylated amide, 6a

(a) <u>The reaction of 2a with HBpin in the presence of 1 at 25 °C</u>



Scheme S9. Reaction between 4-methyl benzamide, HBpin in the presence of 10 mol% catalyst, **1** in CD_3CN at 25 °C.

A 2.5 mL screw cap NMR tube was charged with 4-methyl benzamide **2a** (0.15 mmol), BICAAC (10 mol%), HBpin (1 equiv.) and acetonitrile-d_3 (0.6 mL) under an argon atmosphere. After 12 h, it was analysed by ^{1}H and ^{11}B{^{1}H} NMR spectroscopy (see Fig. S14 and S15). It was then transferred to a vial and solvent was removed and washed with hexane to remove unreacted HBpin, and ^{1}H, ^{11}B{^{1}H} and ^{13}C{^{1}H} spectrum was further recorded.

^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 7.72 (d, *J* = 8.0 Hz, 2H), 7.22 (d, *J* = 7.5 Hz, 2H), 6.50 (brs, NH, 1H), 2.38 (s, 3H), 1.33 (s, 12H); **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$, 25 °C): δ = 169.5, 142.8, 131.9, 129.4, 127.7, 83.9, 24.7, 21.6; **^{11}B{^{1}H} NMR** (128 MHz, $CDCl_3$, 25 °C): 24.1ppm.

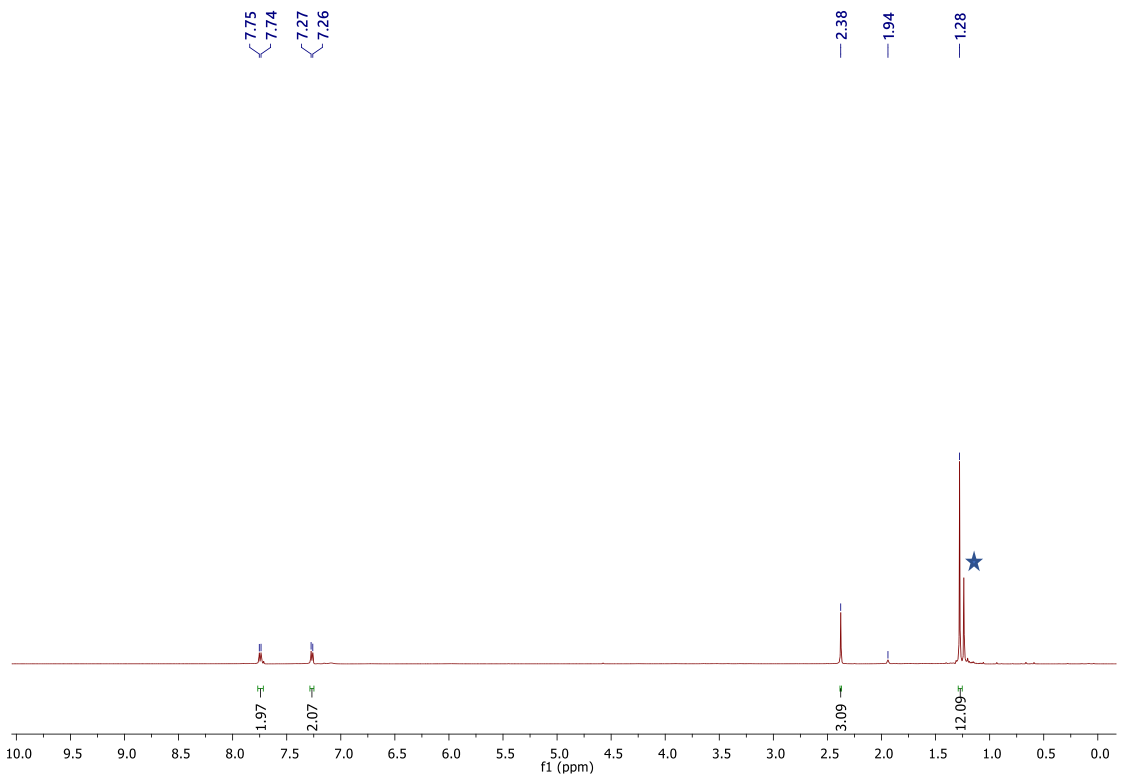


Fig. S14 Reaction mixture ^{1}H NMR spectrum in CD_3CN. ★ denotes peak arising from HBpin.

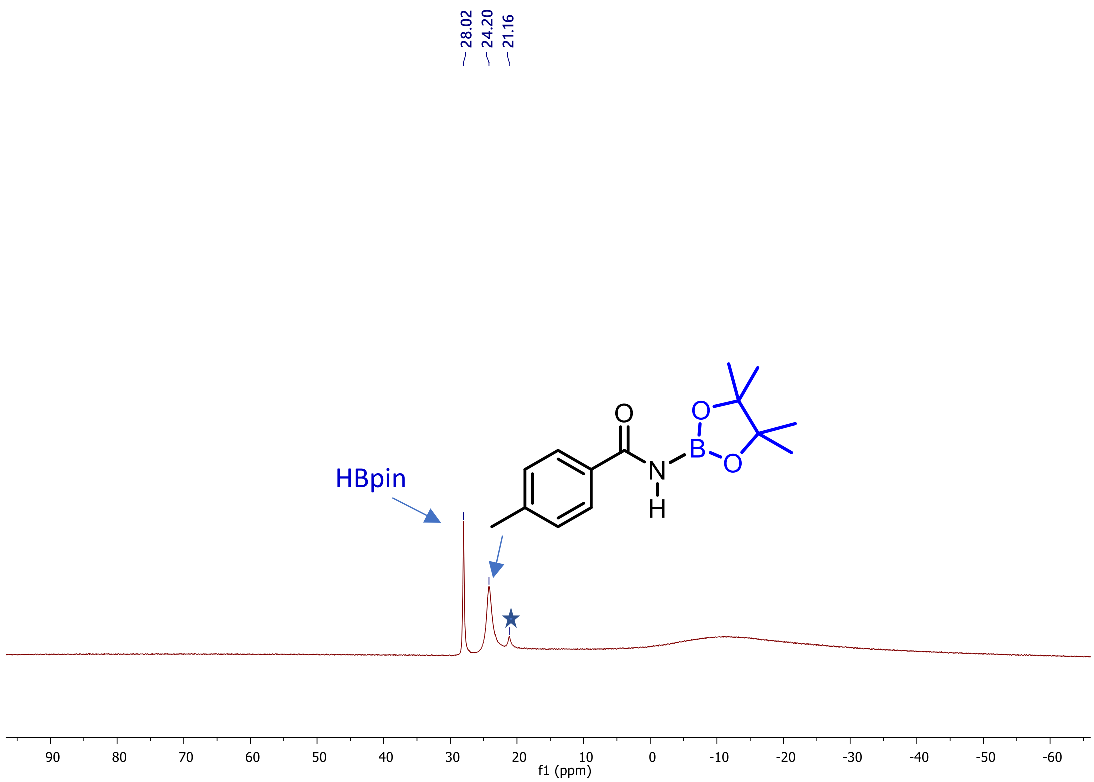


Fig. S15 Reaction mixture [11]B{[1]H} NMR spectrum in CD_3CN. ★ denotes $(Bpin)_2O$

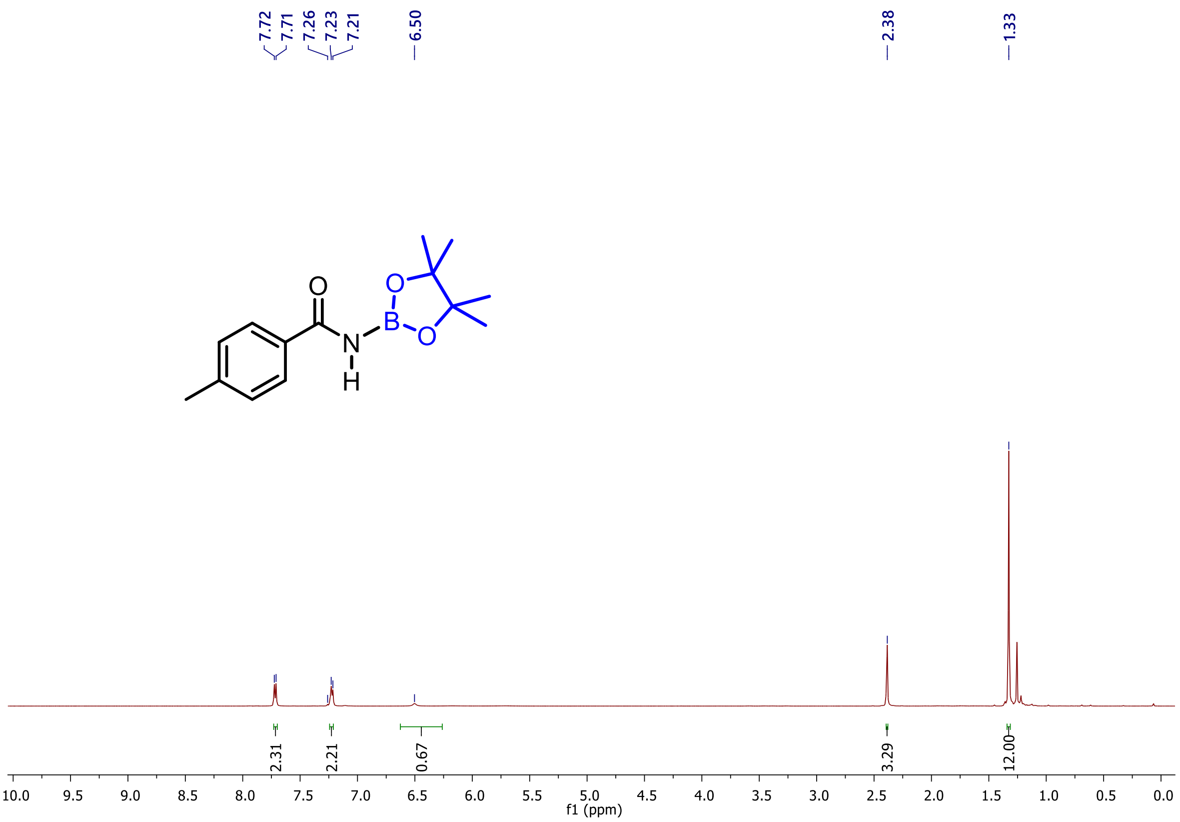


Fig. S16 [1]H NMR spectrum of **6a** in $CDCl_3$.[S31]

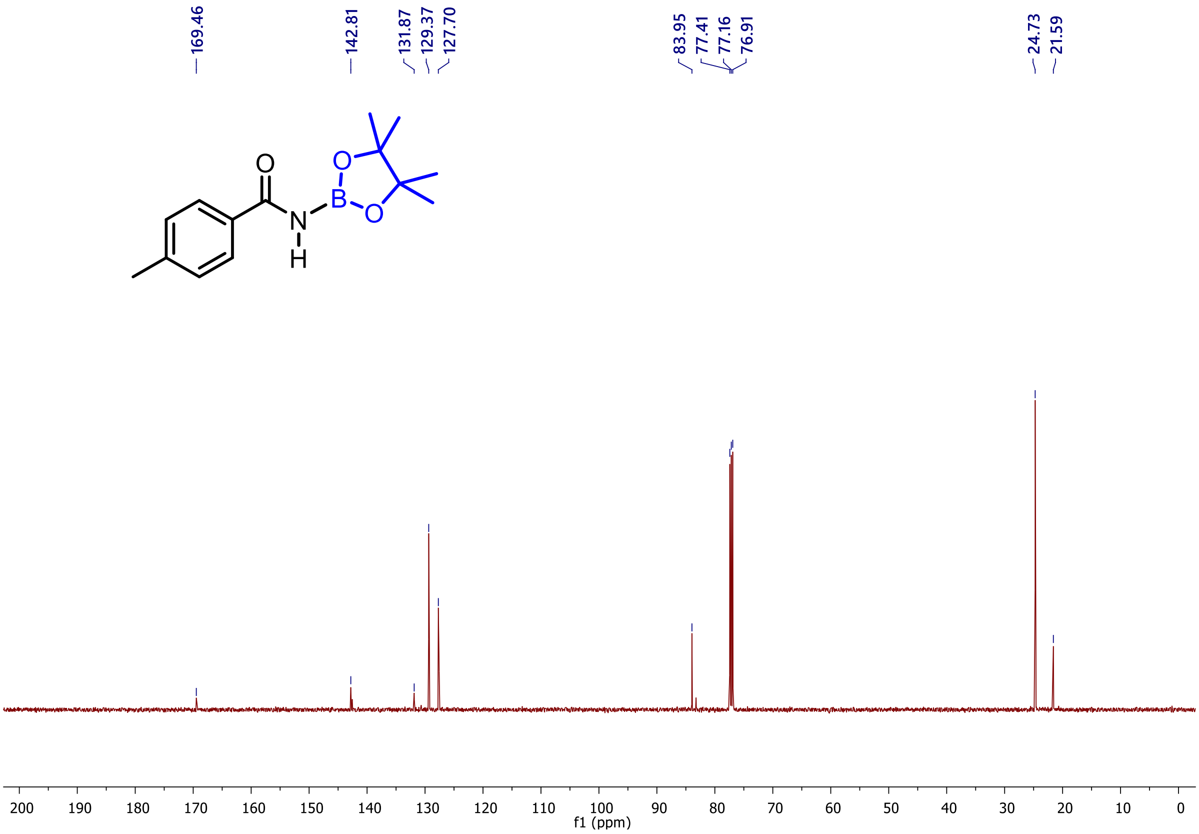


Fig. S17 $^{13}C\{^{1}H\}$ NMR spectrum of **6a** in $CDCl_3$. [S31]

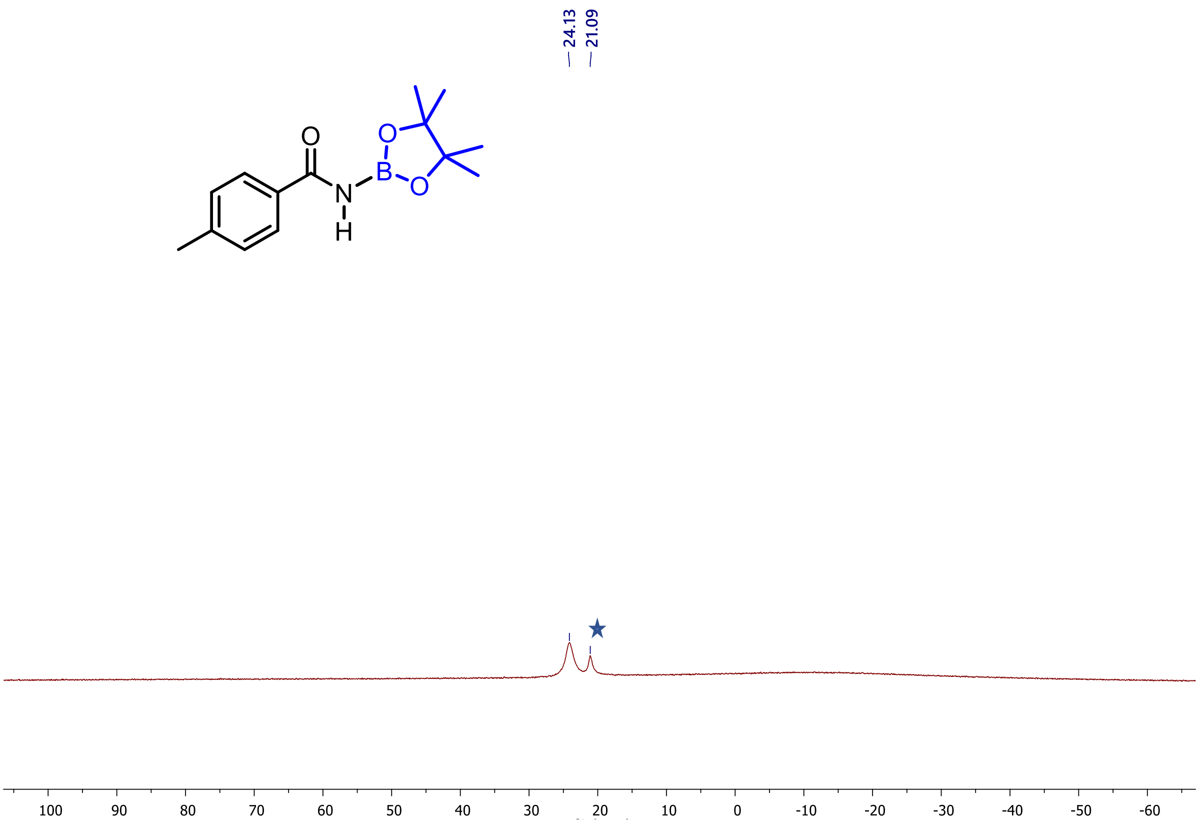
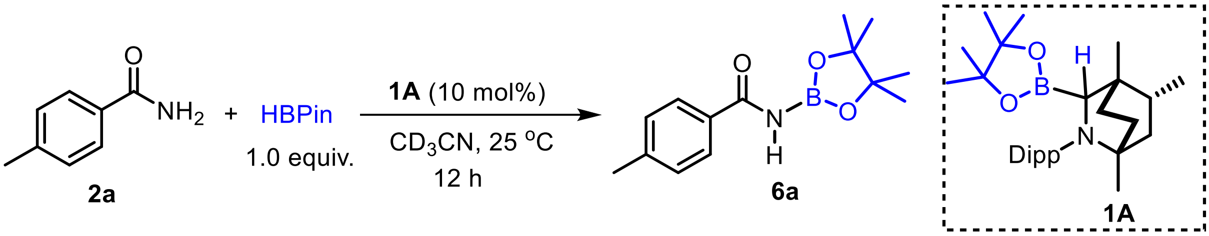


Fig. S18 $^{11}B\{^{1}H\}$ NMR spectrum of **6a** in $CDCl_3$. [S31] ★ denotes $(Bpin)_2O$

(b) BICAAC(H).Bpin (1A) catalysed N-borylation of amide: proof to establish that 1A is a catalytically active species



Scheme S10. The reaction between 4-methyl benzamide, HBpin in the presence of 10 mol% of **1A** in CD_3CN at 25 °C.

A 2.5 mL screw cap NMR tube was charged with 4-methyl benzamide **2a** (0.15 mmol), **1A** (10 mol%), HBpin (1 equiv.) and acetonitrile-d_3 (0.6 mL) under an argon atmosphere. After 12 h, it was analysed by $^{11}B\{^1H\}$ NMR spectroscopy. $^{11}B\{^1H\}$ NMR spectrum revealed that N-borylated amide was obtained, supporting **1A** to be the active catalyst for this step.

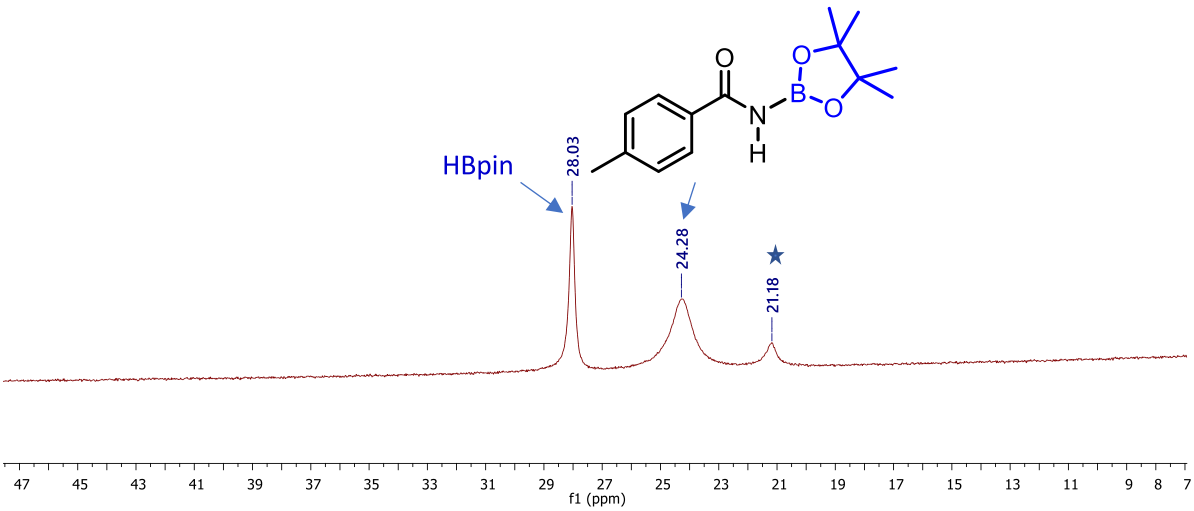
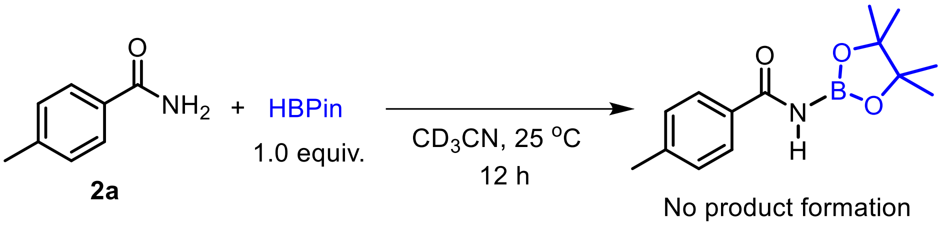


Fig. S19 $^{11}B\{^1H\}$ NMR spectrum of the reaction mixture **2a**, HBpin, and **1A** in CD_3CN at 25 °C. ★ denotes $(Bpin)_2O$.

(c) Reaction of 2a with HBpin in the absence of catalyst at 25 °C



Scheme S11. Reaction between 4-methyl benzamide and HBpin in CD_3CN at 25 °C.

A 2.5 mL screw cap NMR tube was charged with 4-methyl benzamide **2a** (0.15 mmol), HBpin (1 equiv.) and acetonitrile-d_3 (0.6 mL) under an argon atmosphere. After 12 h, it was analysed by $^{11}B\{^1H\}$ NMR spectroscopy, where the formation of N-borylated amide was not observed, supporting the fact that BICAAC is necessary for this step.

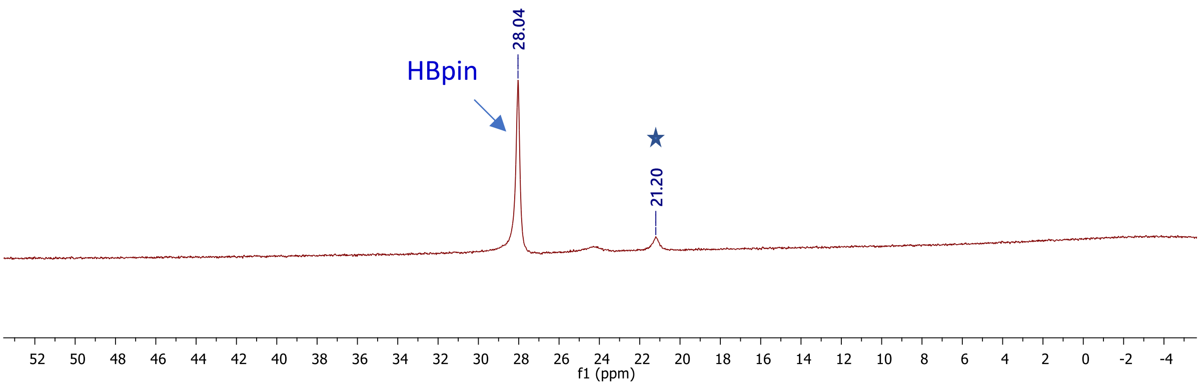
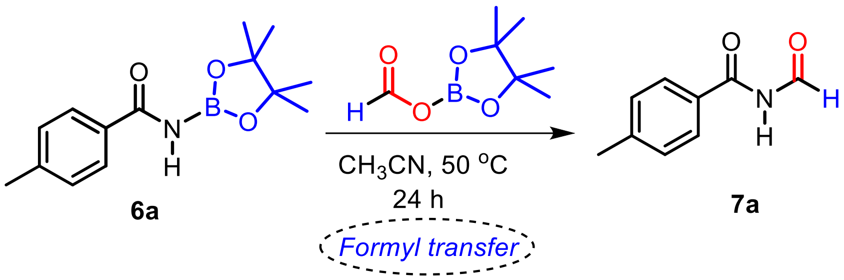


Fig. S20 $^{11}B\{^1H\}$ NMR spectrum of the reaction mixture **2a**, and HBpin in CD_3CN at 25 °C. ★ denotes $(Bpin)_2O$.

viii) Proof of formyl transfer



Scheme S12. Reaction of **6a** and boron formate at 50 °C

Inside an argon-filled glovebox, a 25 mL Schlenk flask was charged with 4-methyl benzamide **2a** (0.2 mmol), pinacol borane (1 equiv.), BICAAC (10 mol%) in acetonitrile (1 mL) at 25 °C and stirred overnight. In another 50 mL Schlenk flask, CO_2 hydroboration was carried out by treating HBpin (0.2 mmol), with 10 mol% of **1** under atmospheric pressure of CO_2 and the reaction was stirred at 100 °C for 12 h. Then, the reaction mixture containing N-borylated amide (**7a**) was transferred to the 50 mL Schlenk flask comprising of CO_2 reduced product reaction mixture, and this reaction was continued for stirring for 24 h at 50 °C. After completion of the reaction, the solvent was removed by vacuum, and the reaction mixture was analysed by ^{1}H NMR spectroscopy. A doublet at δ 9.41 ppm was observed in ^{1}H NMR reaction mixture spectrum in $CDCl_3$, thus, an N-formylated product was detected.

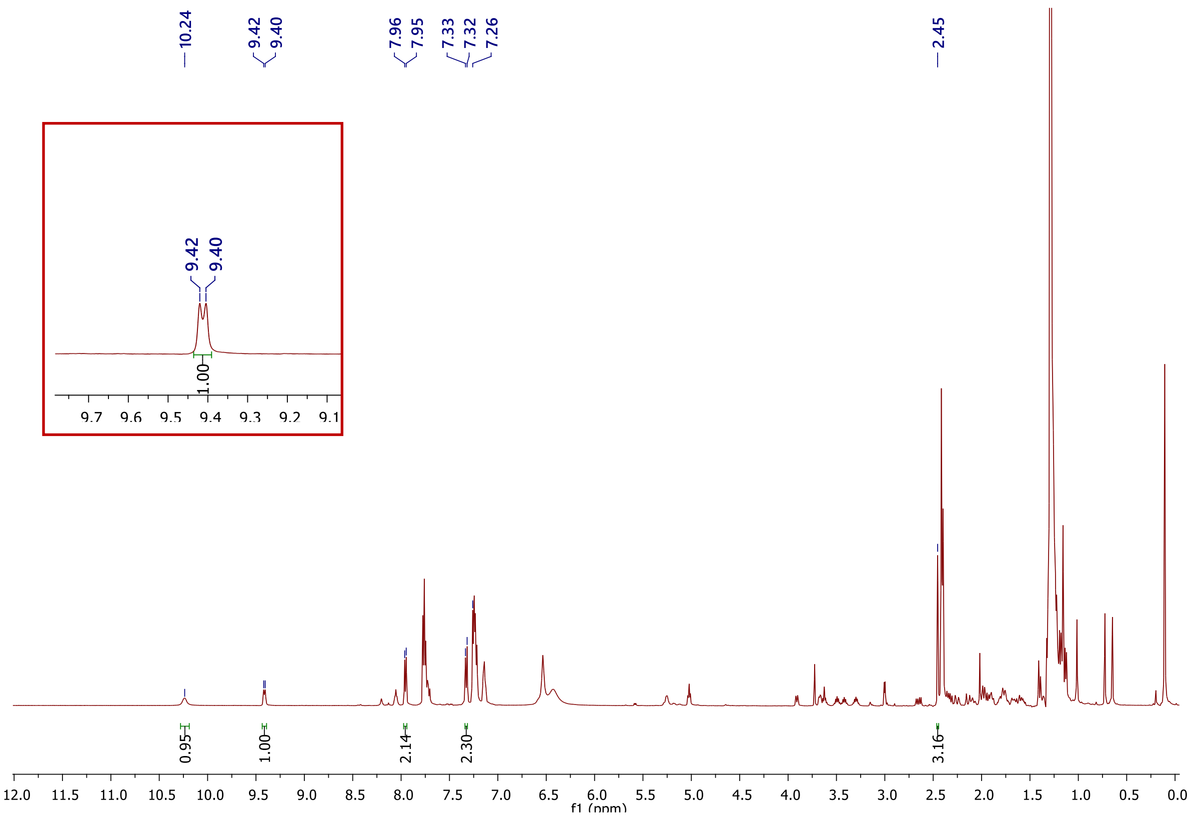
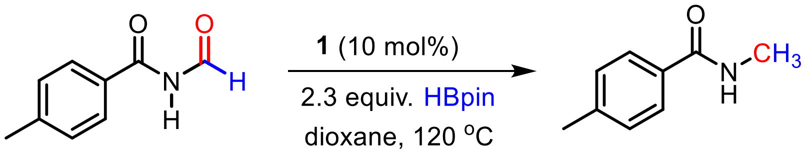


Fig. S21 Reaction mixture ^{1}H NMR spectrum confirming the formation of **7a** in $CDCl_3$.[S32]

ix) Reaction between N-formylated amide (7a) and HBpin: proof to establish that N-methylation proceeds via N-formylation



7a **3a**

Scheme S14. The reaction of **7a** with HBpin in the presence of 10 mol% **1**

Inside an argon-filled glovebox, a 25 mL Schlenk tube equipped with a stir bar and a J. Young valve was charged with *N*-formyl-4-methylbenzamide **7a** (0.2 mmol), BICAAC (10 mol%), pinacolborane (0.46 mmol) and dioxane (1 mL). The mixture was degassed by a freeze-pump-thaw cycle and exposed to 1 atm of carbon dioxide. The reaction flask was sealed tightly and stirred for 24 h at 120 °C. Then the reaction mixture was dried using a high vacuum pump and was analysed by ^{1}H spectroscopy in $CDCl_3$. It was then purified by column chromatography on neutral alumina. The N-methyl amide was obtained as an analytically pure compound using a hexane-ethyl acetate mixture as the eluent. The corresponding product was identified by ^{1}H spectroscopy in $CDCl_3$.

^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 7.66 (d, *J* = 8.0 Hz, 2H), 7.20 (d, *J* = 8.0 Hz, 2H), 6.36 (brs, NH, 1H), 2.98 (d, *J* = 4.5 Hz, 3H), 2.37 (s, 3H) ppm. Yield: 67%.

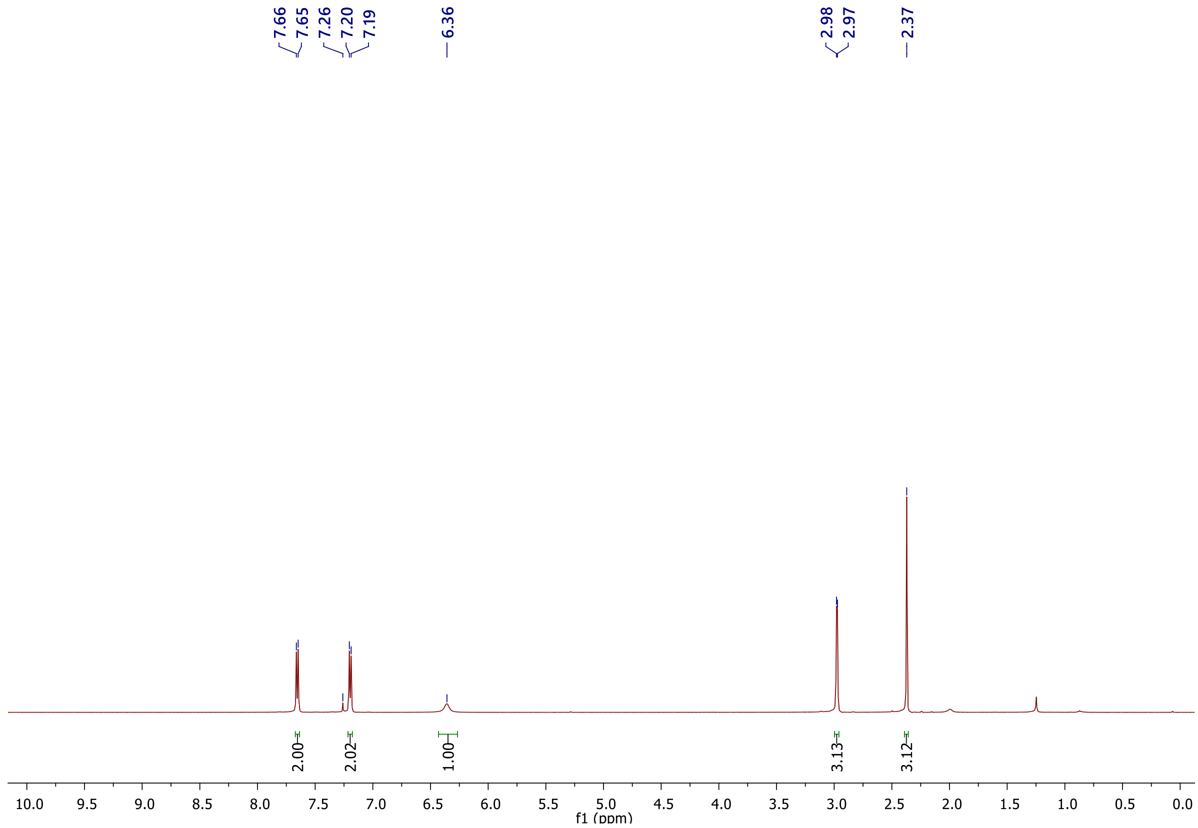
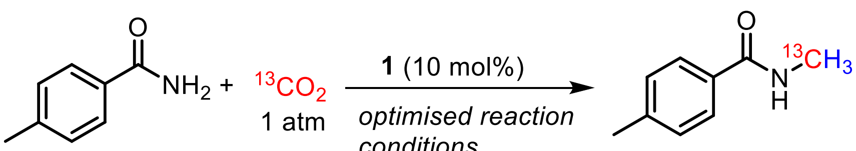


Fig. S22 ^{1}H NMR spectrum of **3a** in $CDCl_3$.[S8]

ix) Catalysis of 4-methyl benzamide (2a) carried out in presence of ^{13}C labelled CO_2: proof of CO_2 as methyl source



Scheme S15. N-methylation of **2a** using $^{13}CO_2$

A 25 mL Schlenk tube equipped with a stir bar and a J. Young valve was charged with 4-methyl benzamide, **2a** (0.2 mmol), BICAAC (10 mol%), pinacolborane (0.8 mmol) and dioxane (1 mL) inside an argon-filled glovebox. The mixture was degassed by a freeze-pump-thaw cycle and exposed to 1 atm of ^{13}C labelled carbon dioxide. The reaction flask was sealed tightly and stirred for 24 h at 120 °C. On completion, the reaction mixture was dried using a high vacuum pump and was then purified by column chromatography on neutral alumina. The N-methyl amide was obtained as an analytically pure compound using a hexane-ethyl acetate mixture as the eluent. The corresponding product was identified by ^{1}H and ^{13}C{^{1}H} NMR spectroscopy in $CDCl_3$. **^{1}H NMR** (500 MHz, $CDCl_3$, 25 °C): δ = 7.65 (d, *J* = 8.0 Hz, 2H), 7.19 (d, *J* = 7.5 Hz, 2H), 6.40 (brs, NH, 1H), 2.96 (dd, J_1 = 138.0 Hz, J_2 = 4.5 Hz, 3H), 2.37 (s, 3H); **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$, 25 °C): δ = 168.4, 141.8, 131.9, 129.3, 127.0, 26.9, 21.5; **HRMS**: m/z calcd. for $^{13}CC_8H_{12}NO^+$ [M + H]$^+$ 151.0992, found 151.0949. Yield: 73%.

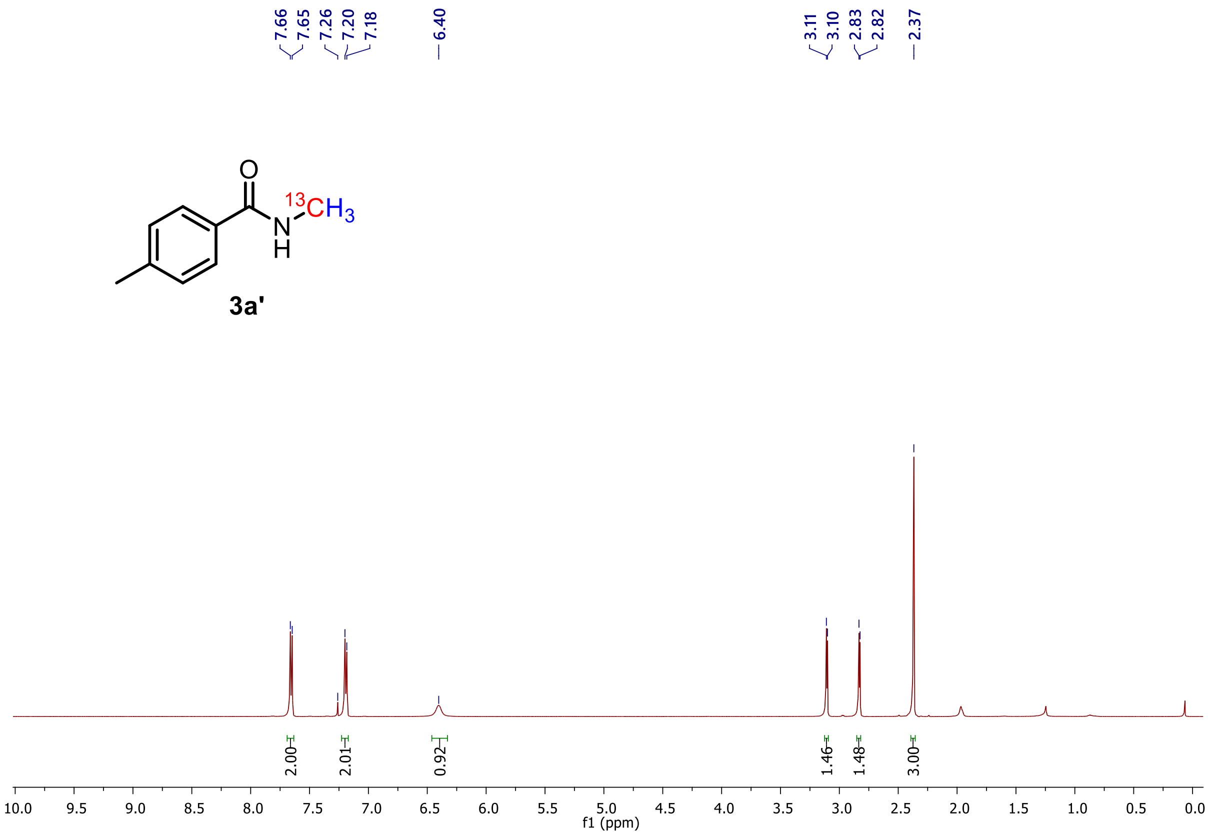


Fig. S23 ^{1}H NMR spectrum of **3a'** in $CDCl_3$.

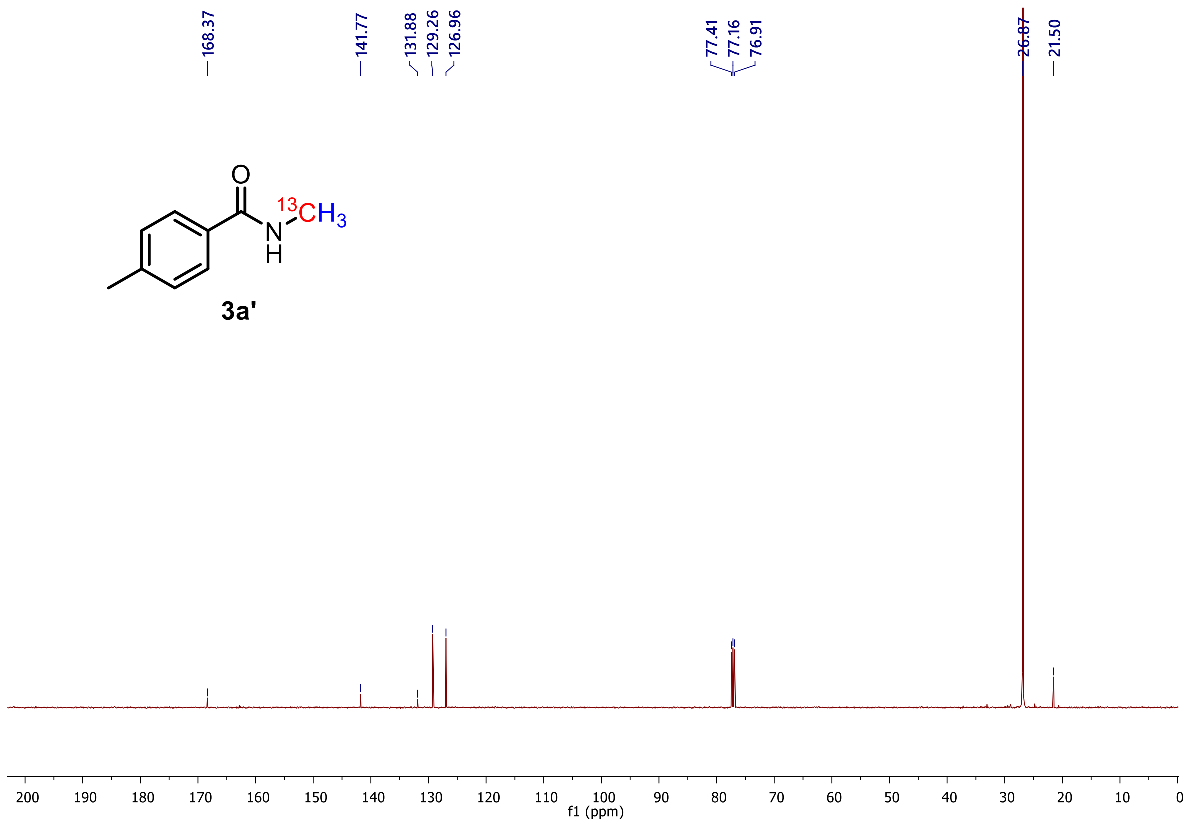
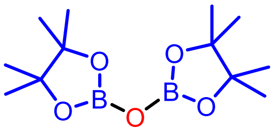


Fig. S24 $^{13}C\{^{1}H\}$ NMR spectrum of **3a'** in $CDCl_3$.

x) Characterization of $(Bpin)_2O$ dimer as a by-product:

Under an argon atmosphere, a 25 mL Schlenk tube equipped with a stir bar and a J. Young valve was charged with amide (0.2 mmol), 1 (10 mol%), pinacolborane (0.8 mmol) and dioxane (1 mL). The mixture was degassed by freeze-pump-thaw and was exposed to carbon dioxide in the frozen state. It was next allowed slowly to warm to room temperature and stirred at 120 °C for 24 h. Next, the solvent was evaporated under reduced pressure and analysed by NMR spectroscopy. The ^{1}H and ^{11}B NMR spectra identified the formation of Bpin-O-Bpin as a by-product.



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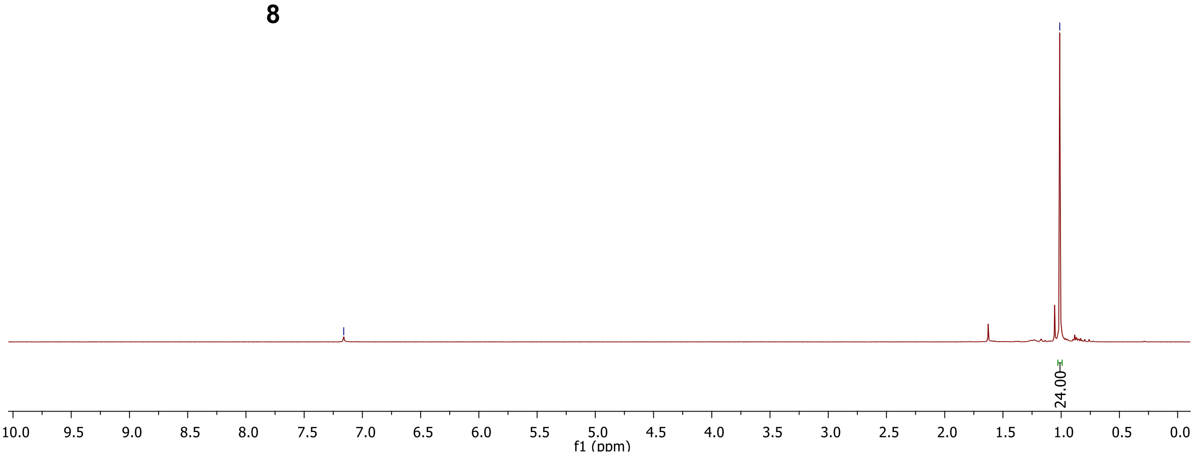
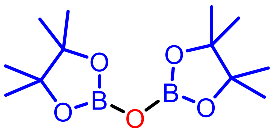


Fig. S25 ^{1}H NMR spectrum of **8** in C_6D_6.[S33]



8

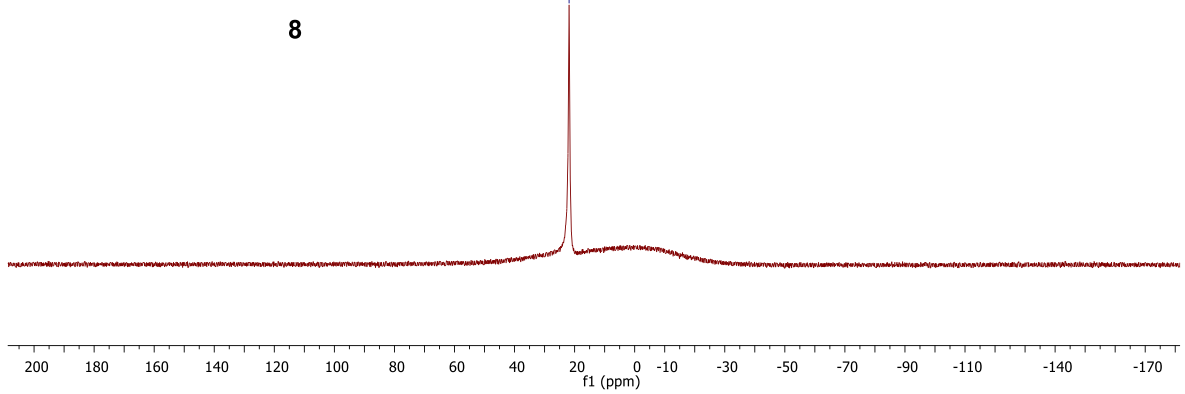


Fig. S26 $^{11}B\{^{1}H\}$ NMR spectrum of **8** in C_6D_6. [S33]

6) ^{1}H and ^{13}C{^{1}H} NMR spectra of N-methyl amide 3a-3al'

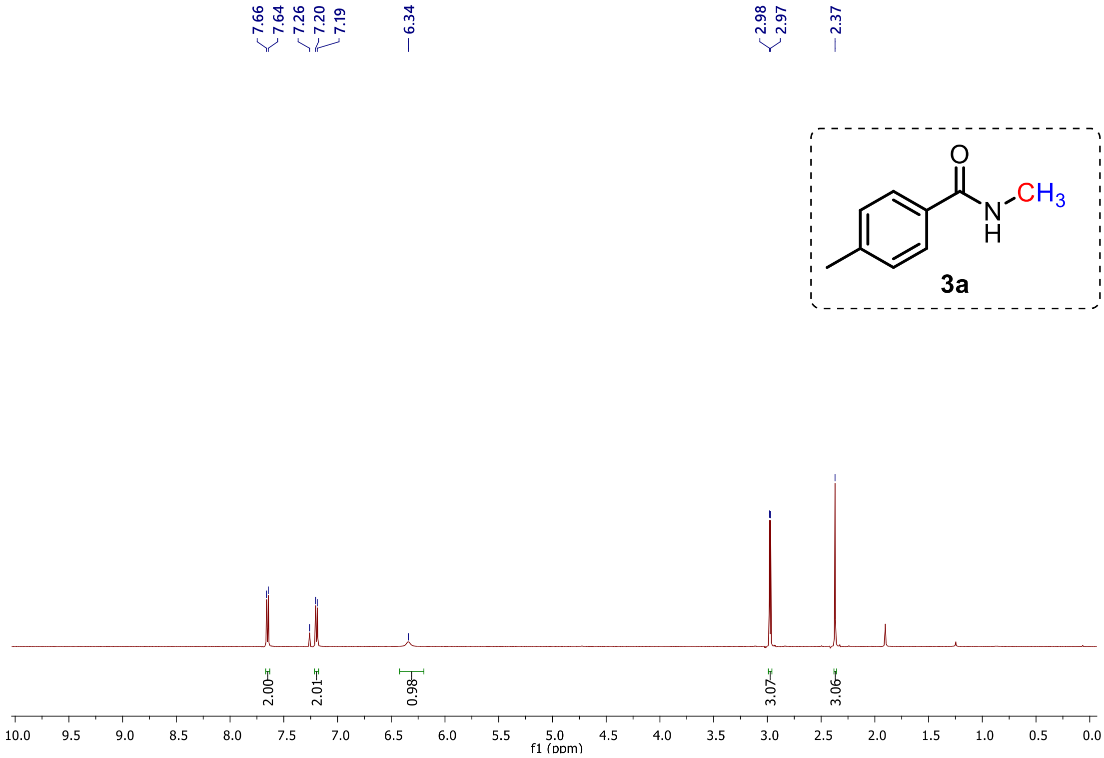


Fig. S27 ^{1}H NMR spectrum of **3a** in $CDCl_3$.

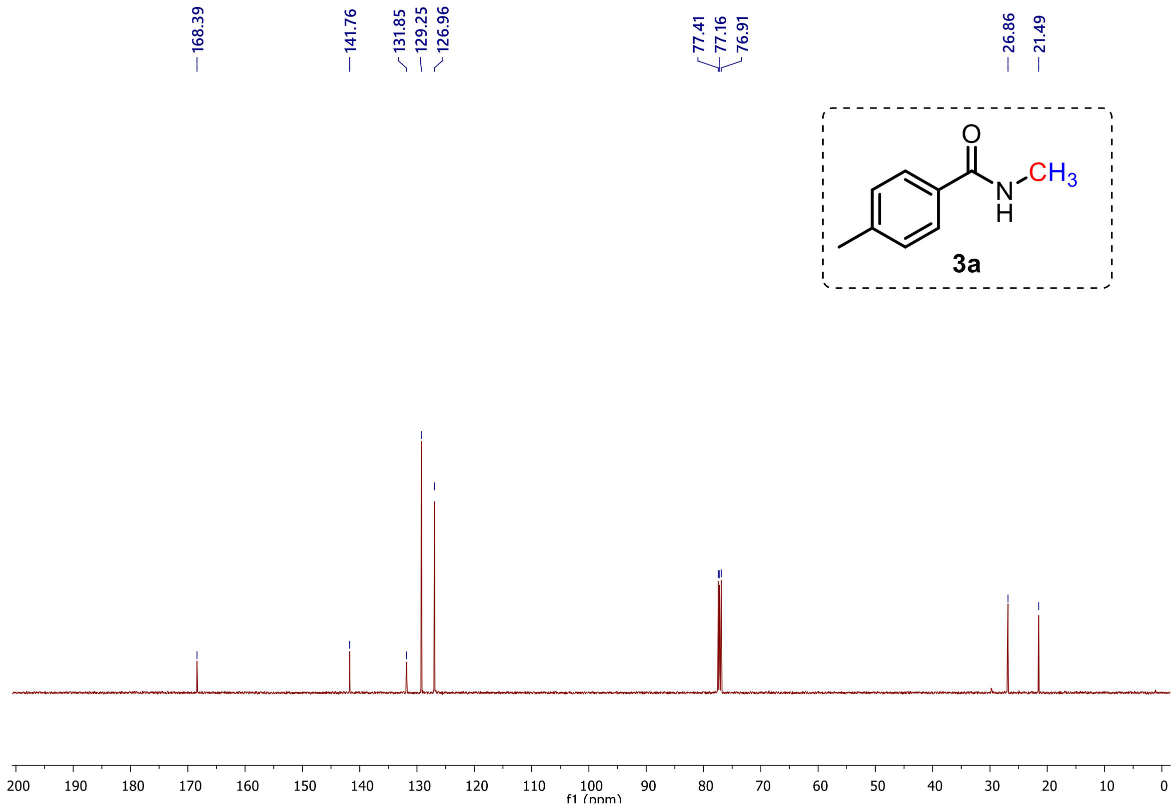


Fig. S28 ^{13}C{^{1}H} NMR spectrum of **3a** in $CDCl_3$.

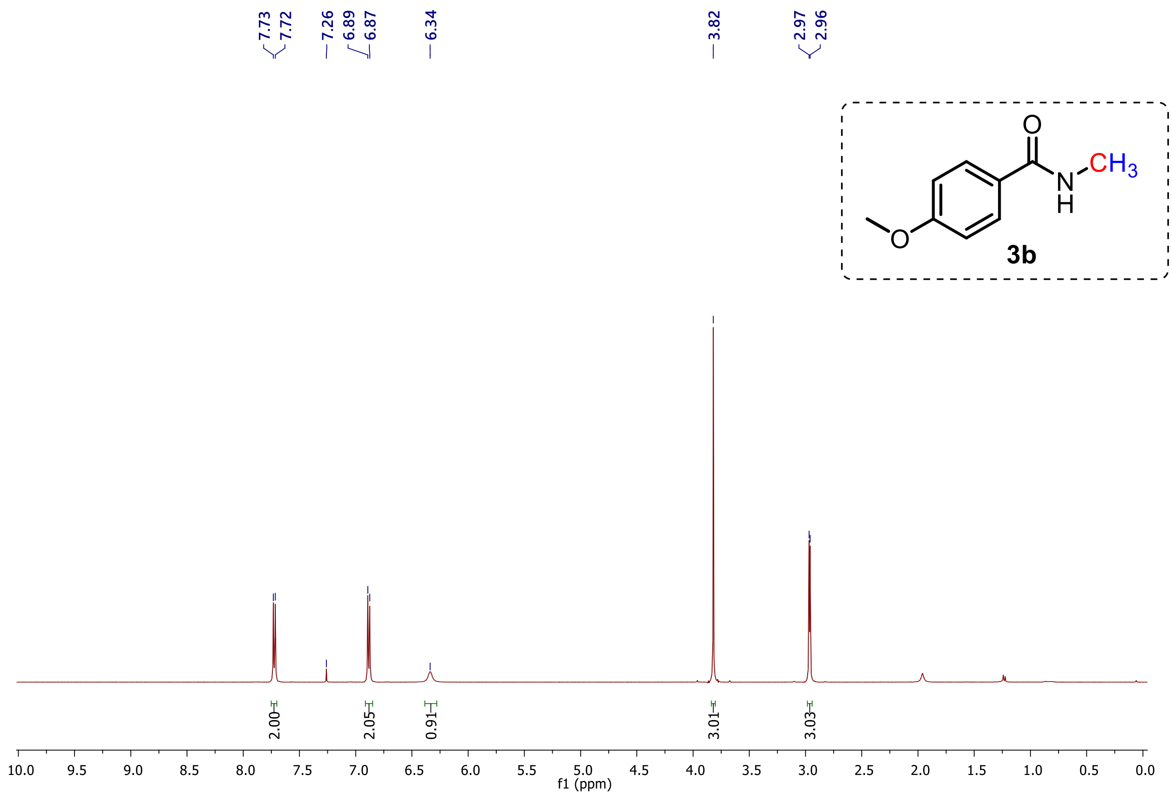


Fig. S29 ^{1}H NMR spectrum of **3b** in $CDCl_3$.

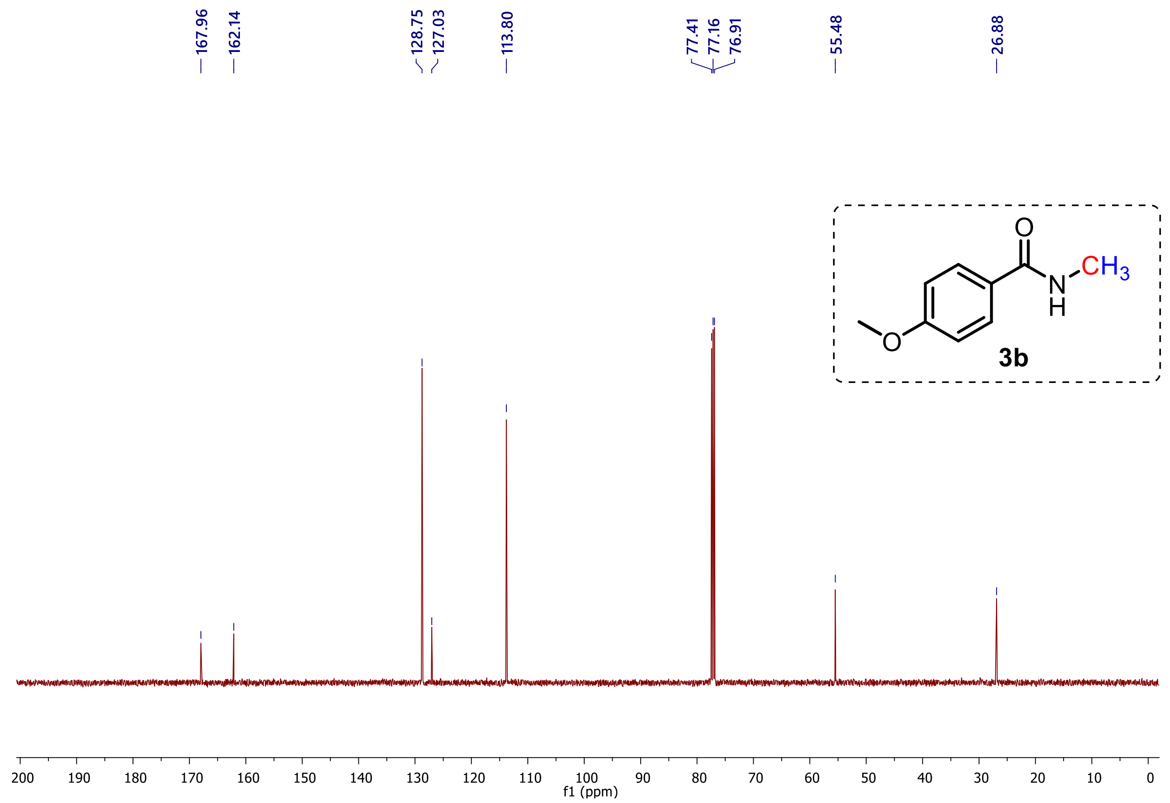


Fig. S30 $^{13}C\{^{1}H\}$ NMR spectrum of **3b** in $CDCl_3$.

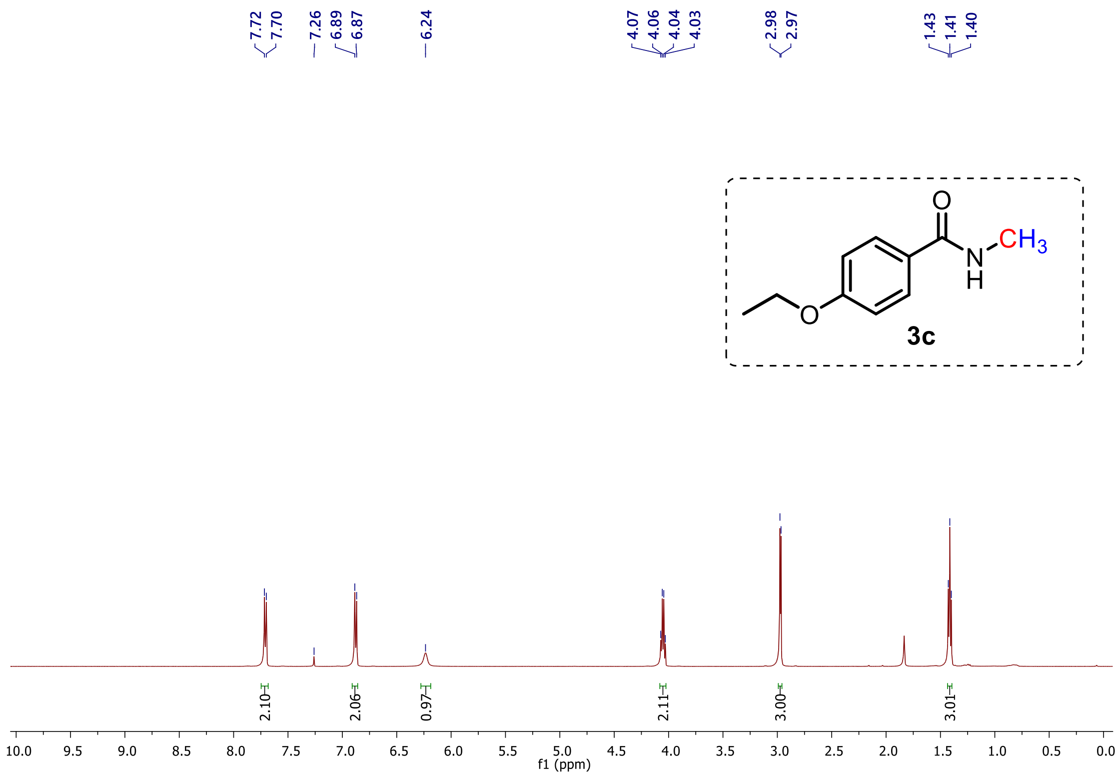


Fig. S31 ^{1}H NMR spectrum of **3c** in $CDCl_3$.

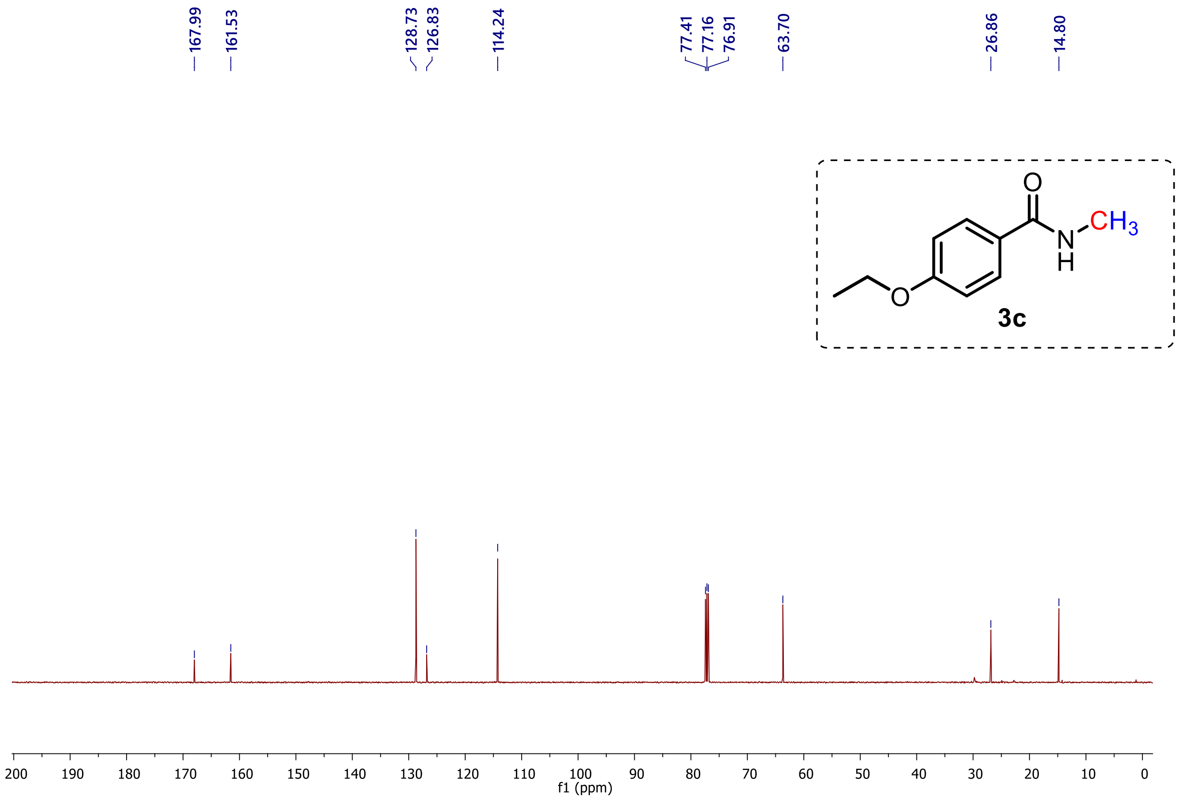


Fig. S32 $^{13}C\{^{1}H\}$ NMR spectrum of **3c** in $CDCl_3$.

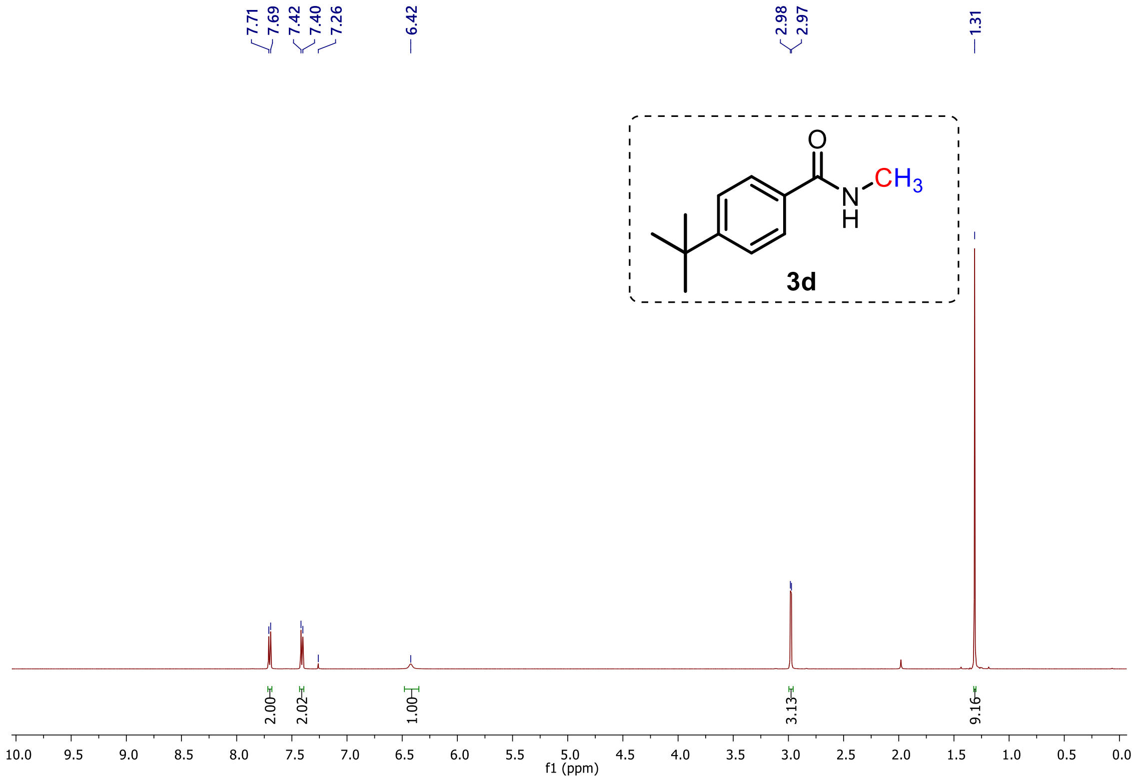


Fig. S33 ^{1}H NMR spectrum of **3d** in $CDCl_3$.

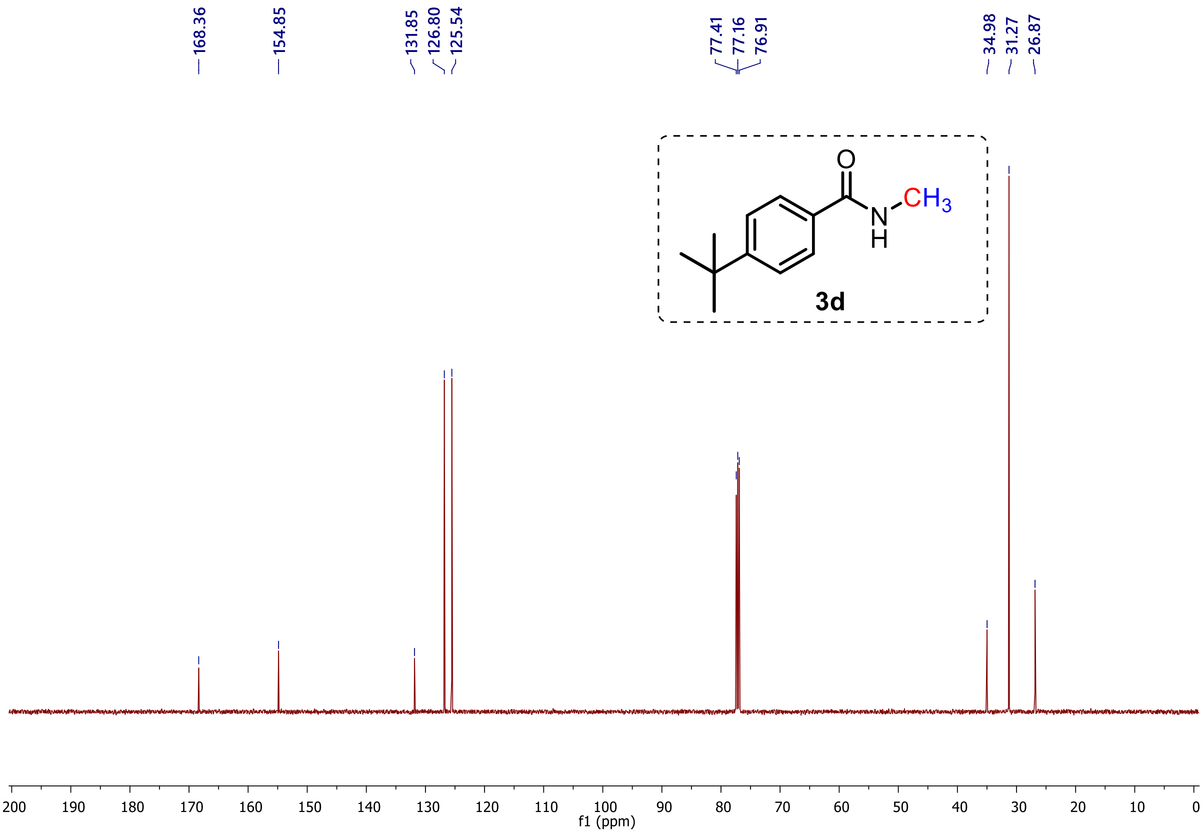


Fig. S34 $^{13}C\{^{1}H\}$ NMR spectrum of **3d** in $CDCl_3$.

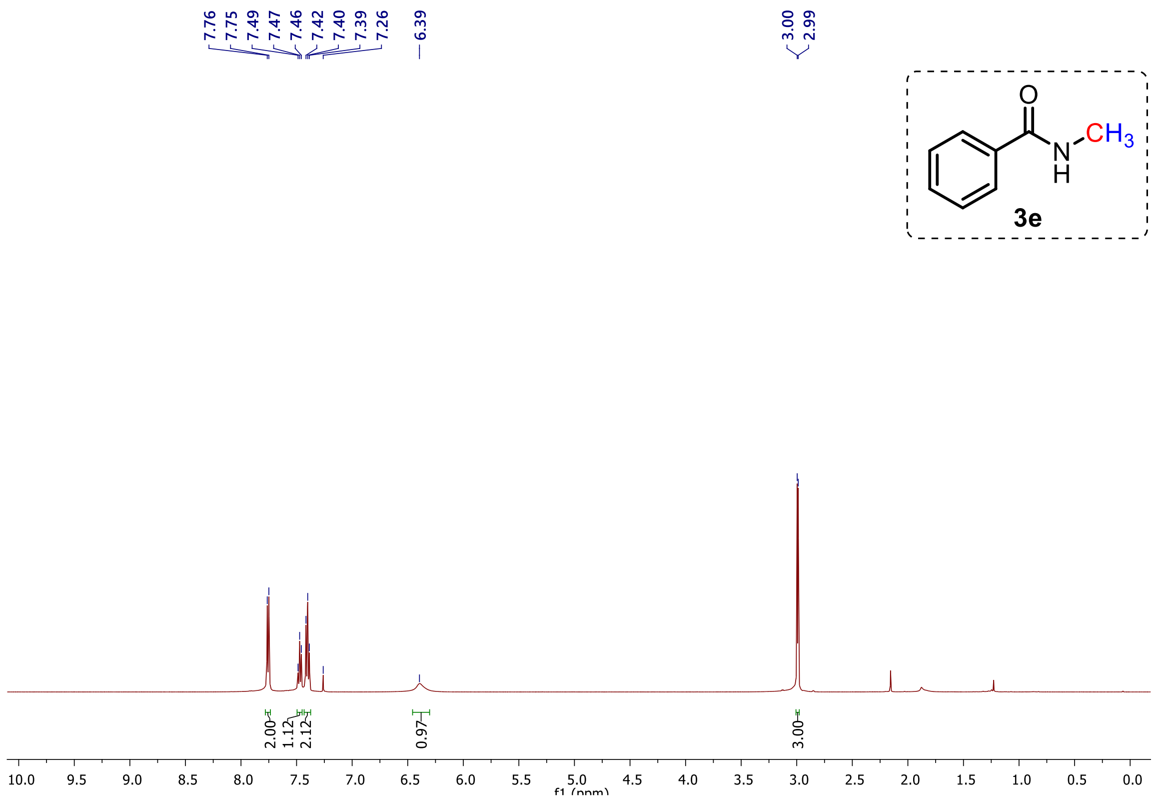


Fig. S35 ^{1}H NMR spectrum of **3e** in $CDCl_3$.

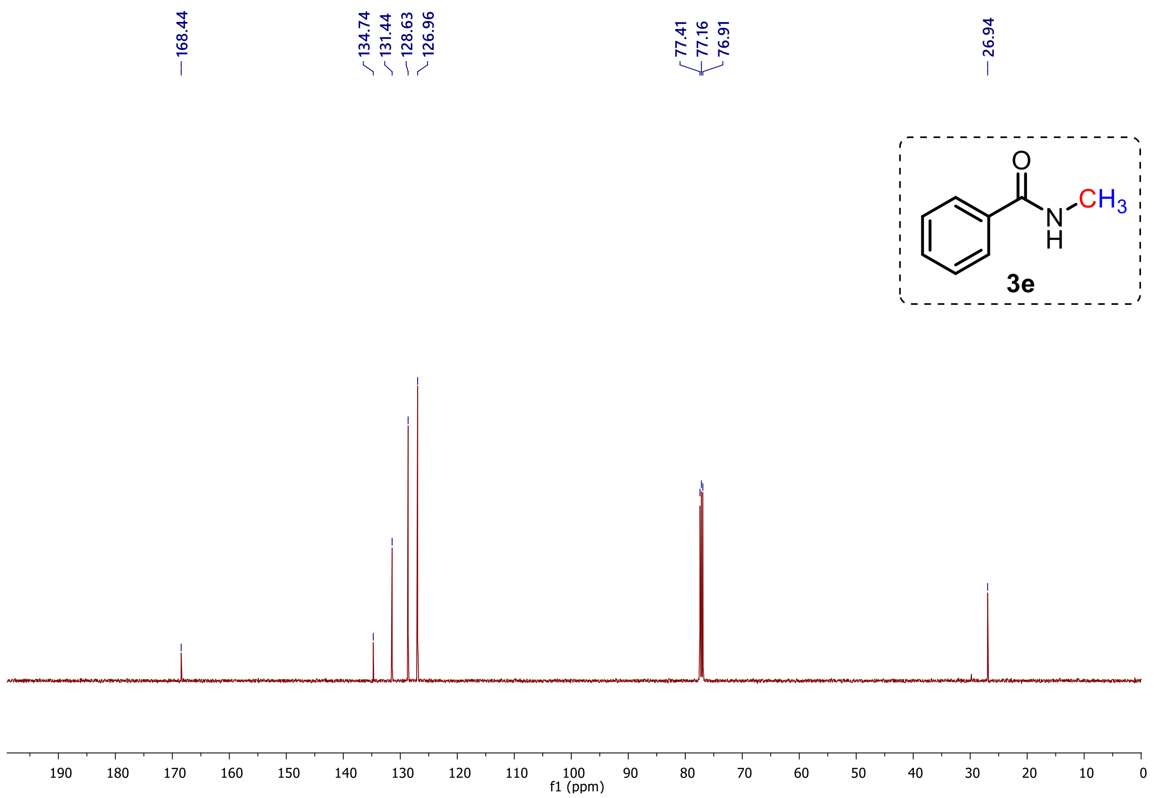


Fig. S36 $^{13}C\{^{1}H\}$ NMR spectrum of **3e** in $CDCl_3$.

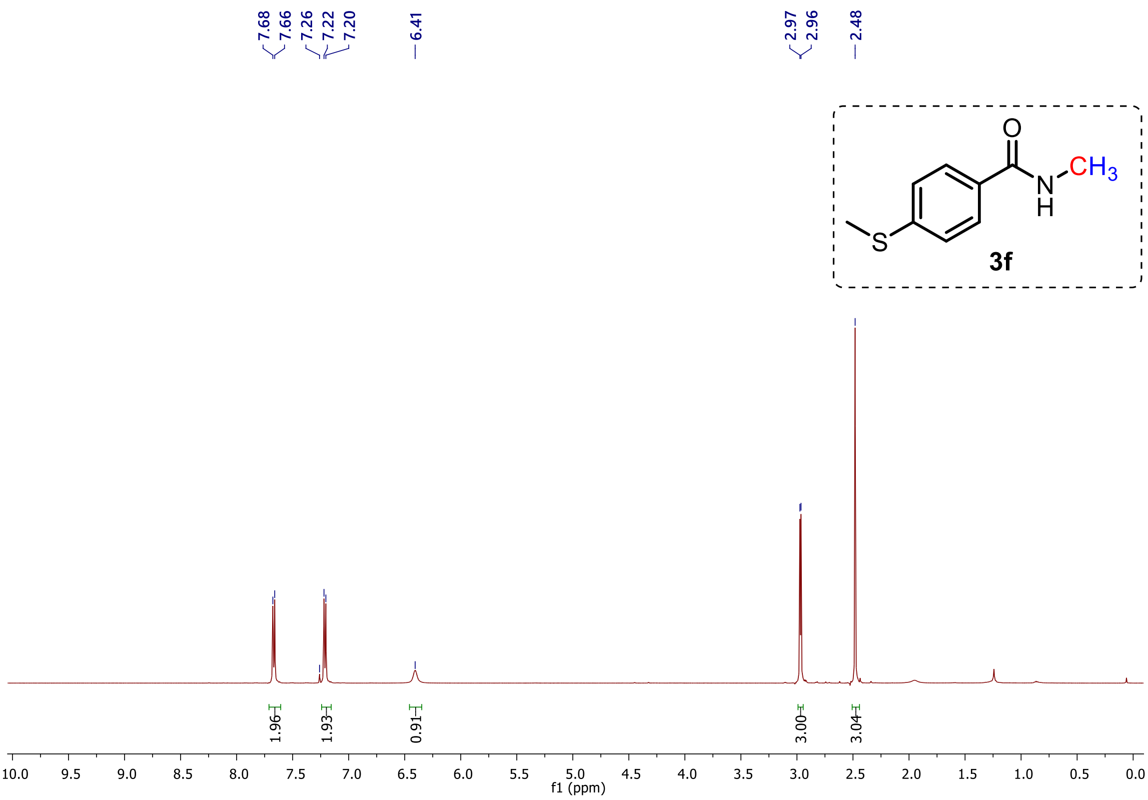


Fig. S37 ^{1}H NMR spectrum of **3f** in $CDCl_3$.

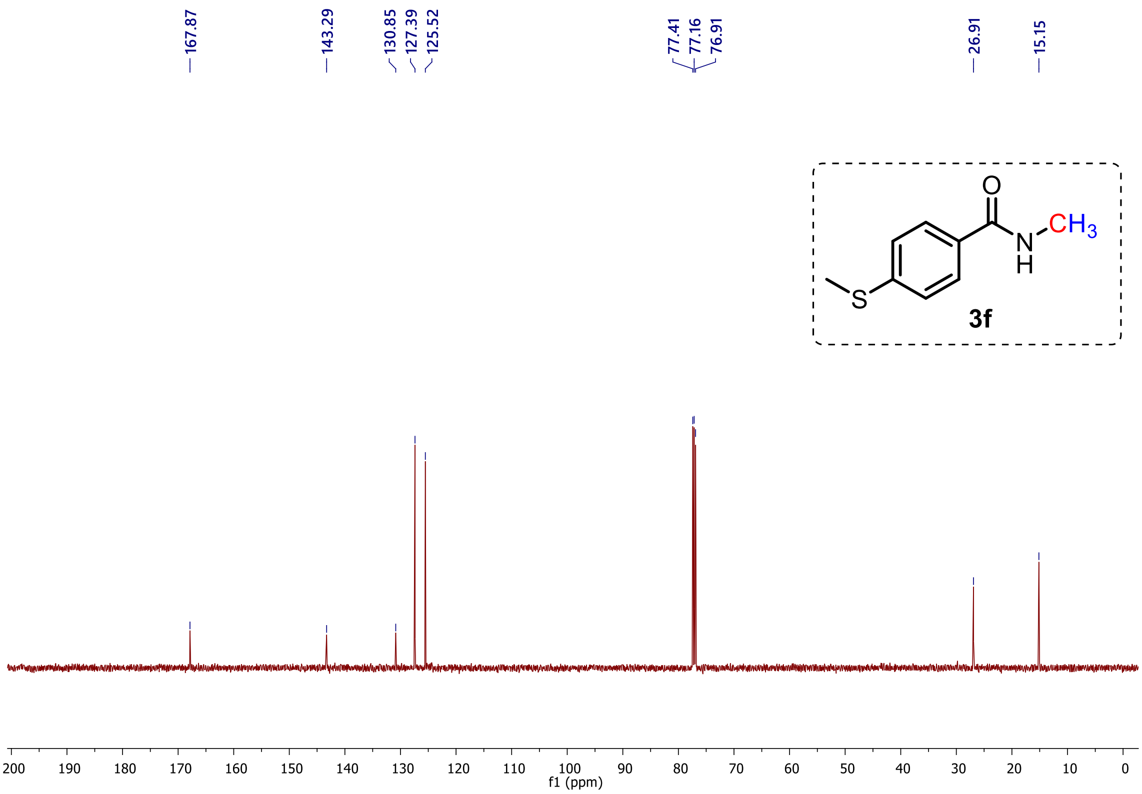


Fig. S38 $^{13}C\{^{1}H\}$ NMR spectrum of **3f** in $CDCl_3$.

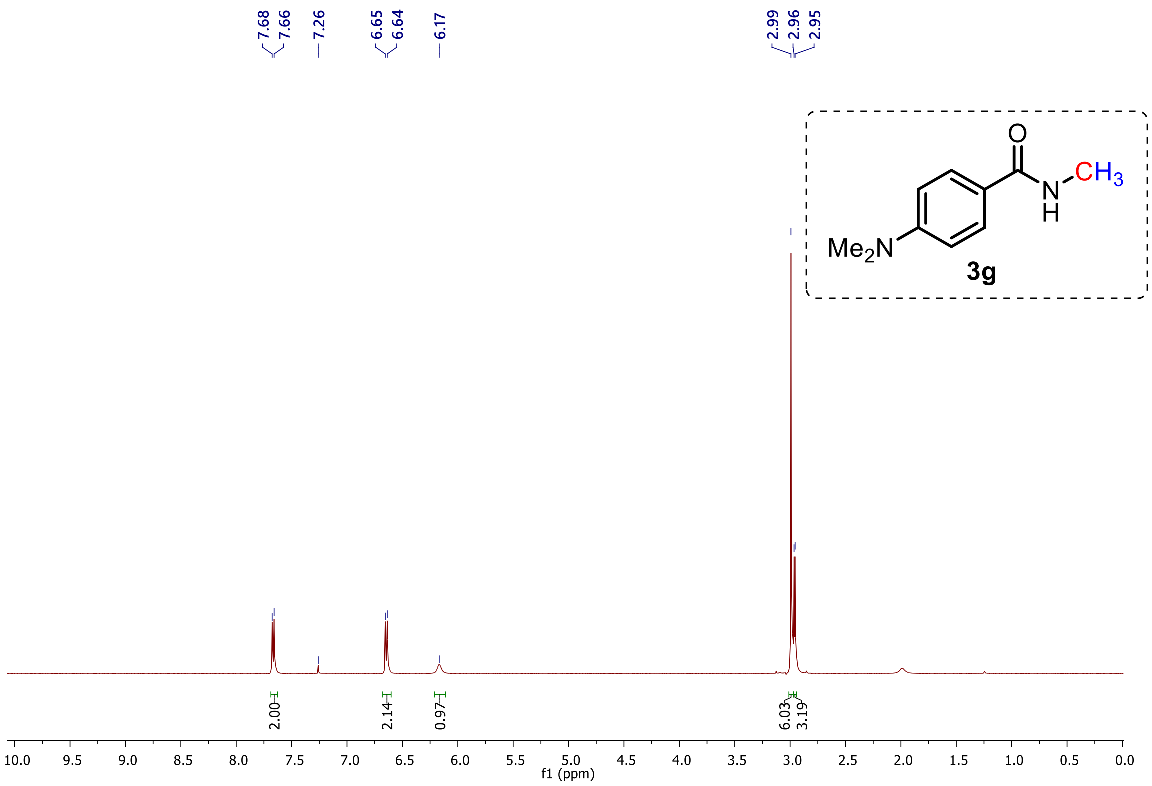


Fig. S39 ^{1}H NMR spectrum of **3g** in $CDCl_3$.

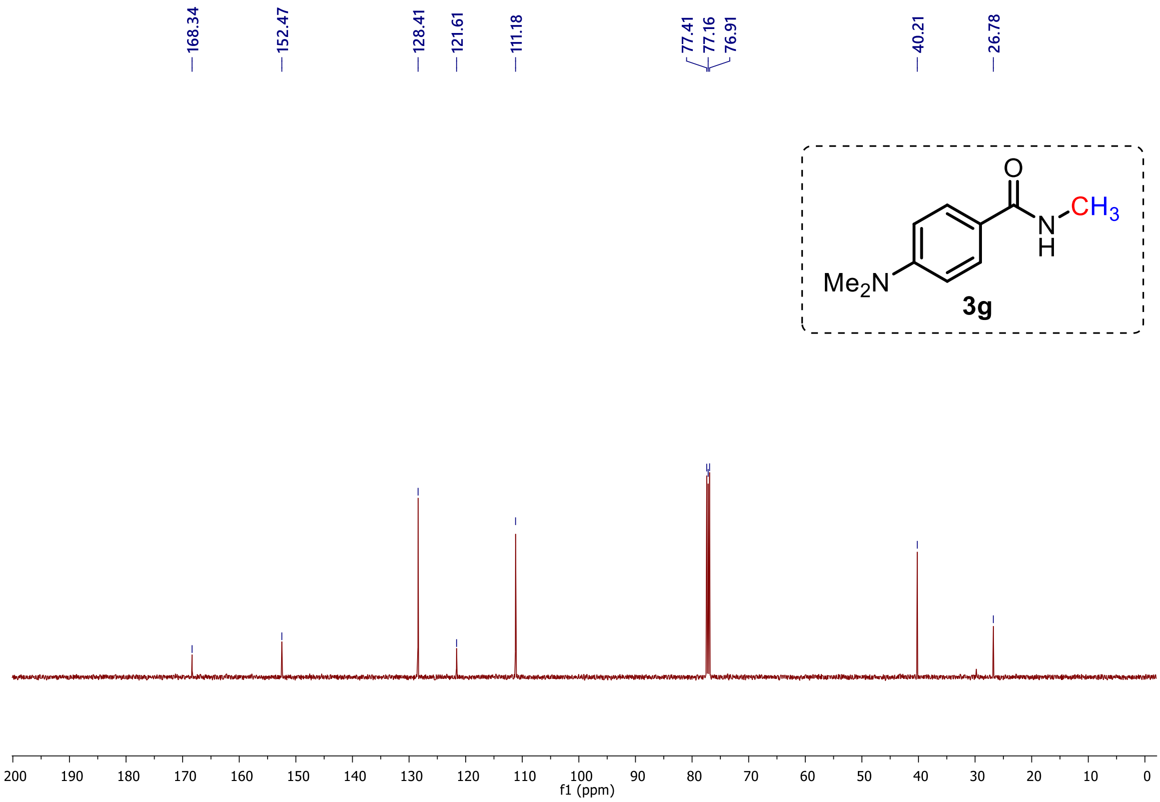


Fig. S40 ^{13}C{^{1}H} NMR spectrum of **3g** in $CDCl_3$.

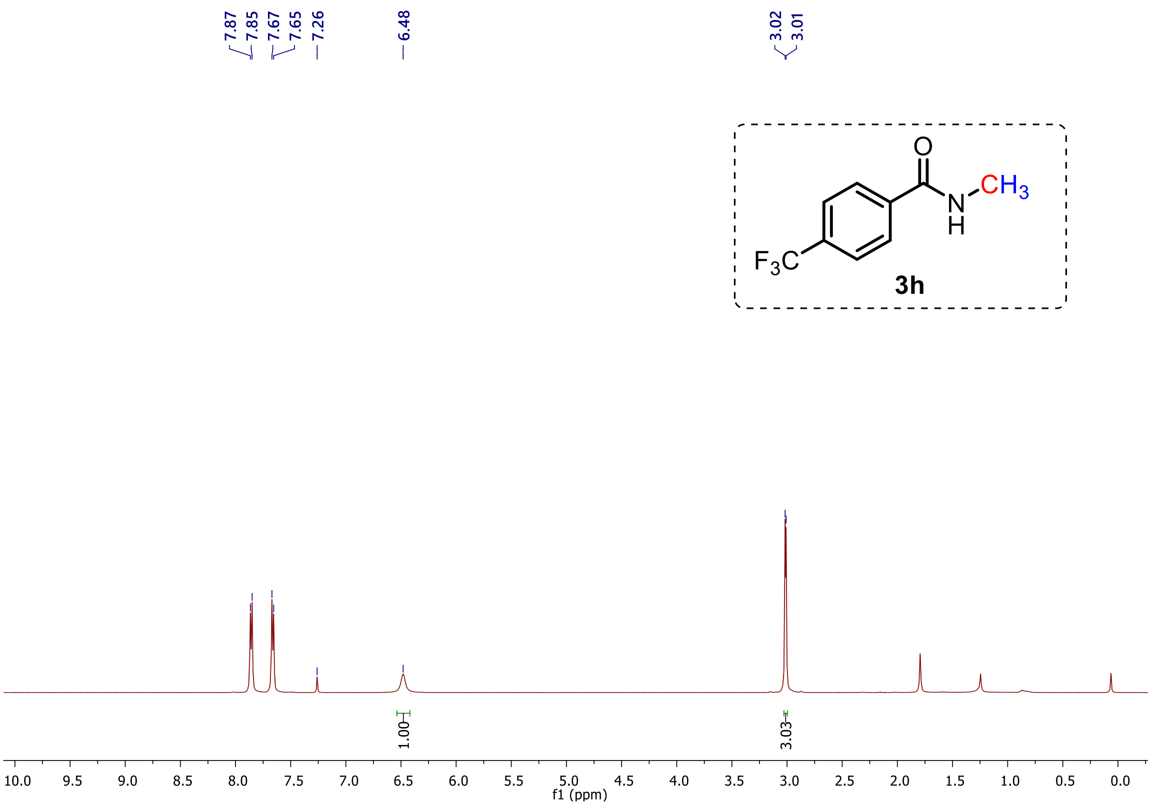


Fig. S41 ^{1}H NMR spectrum of **3h** in $CDCl_3$.

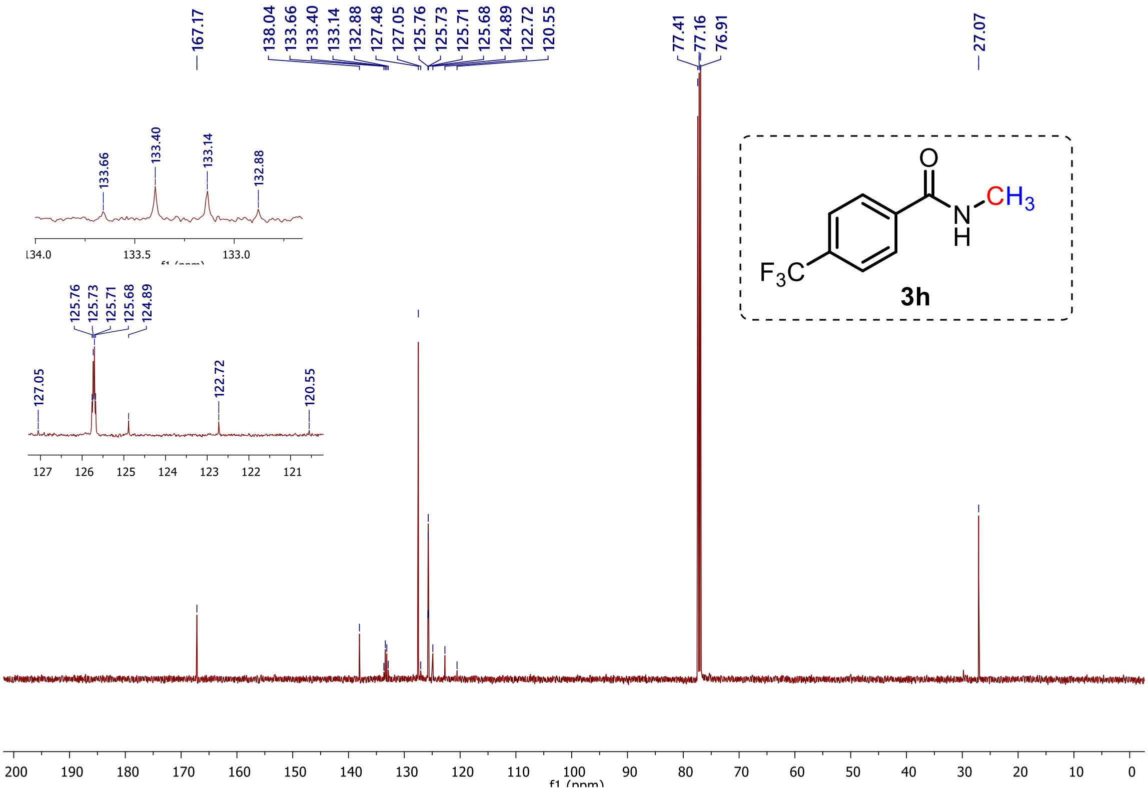


Fig. S42 $^{13}C\{^{1}H\}$ NMR spectrum of **3h** in $CDCl_3$.

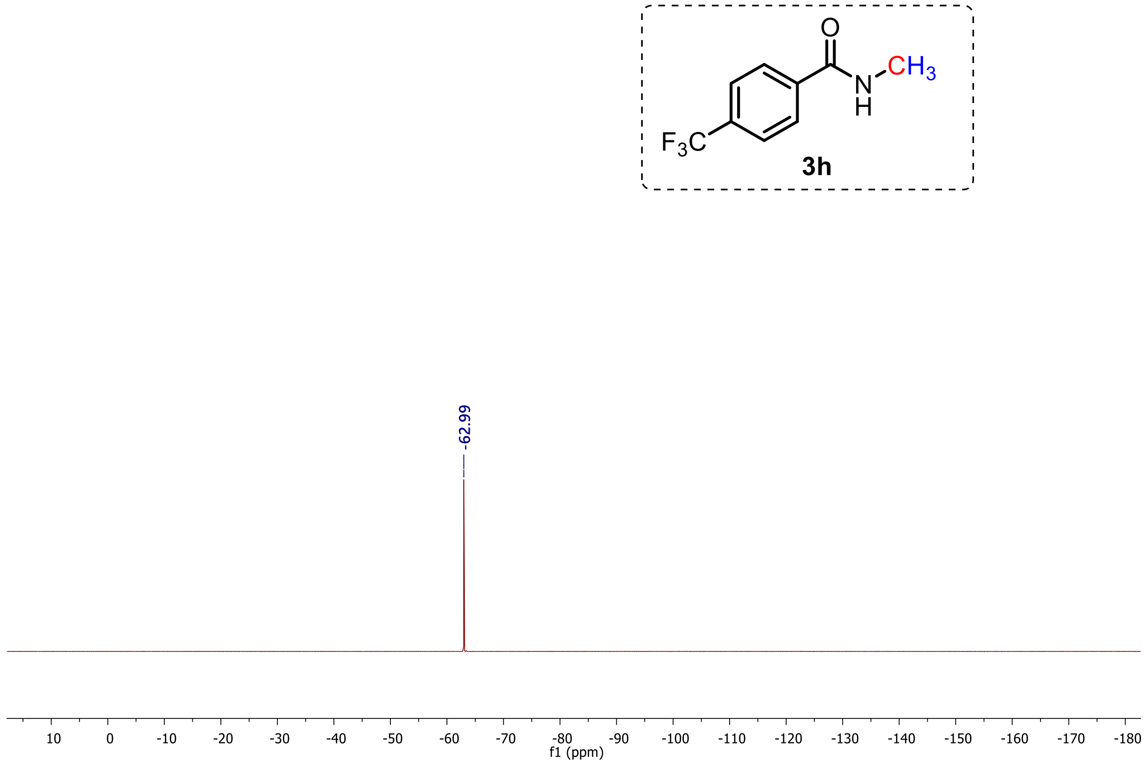


Fig. S43 $^{19}F\{^{1}H\}$ NMR spectrum of **3h** in $CDCl_3$.

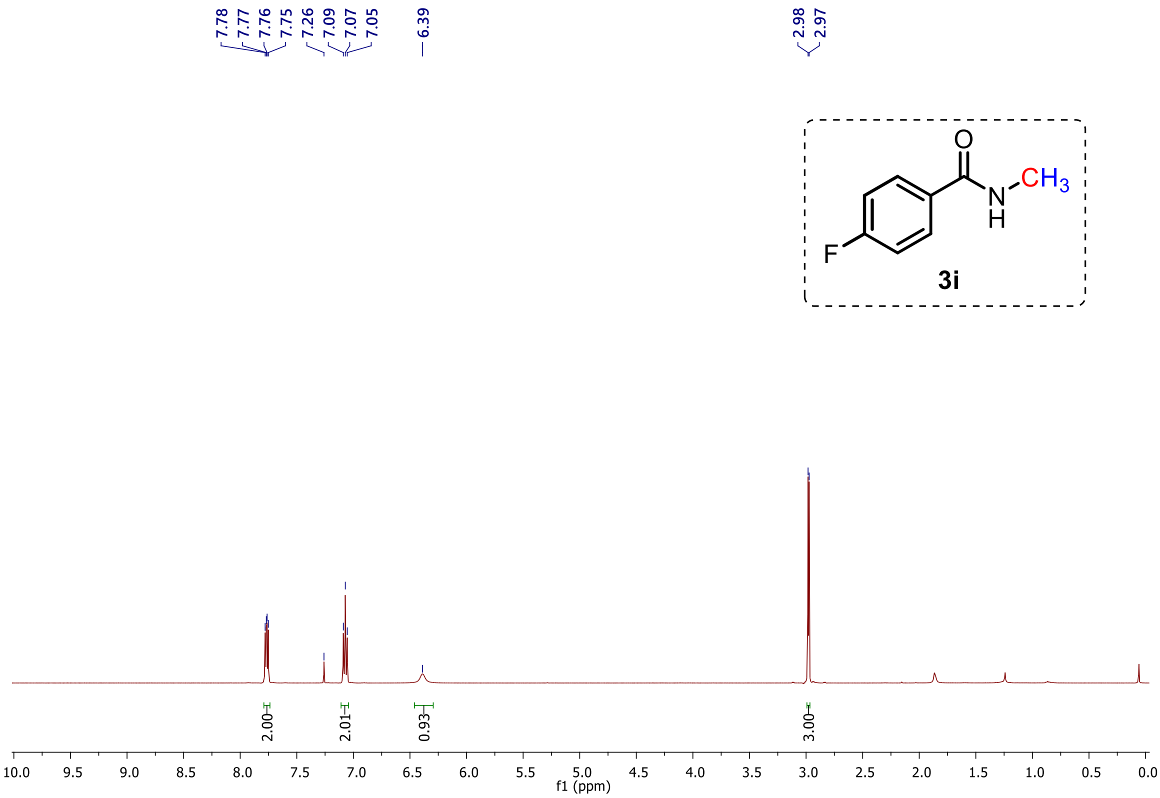


Fig. S44 ^{1}H NMR spectrum of **3i** in $CDCl_3$.

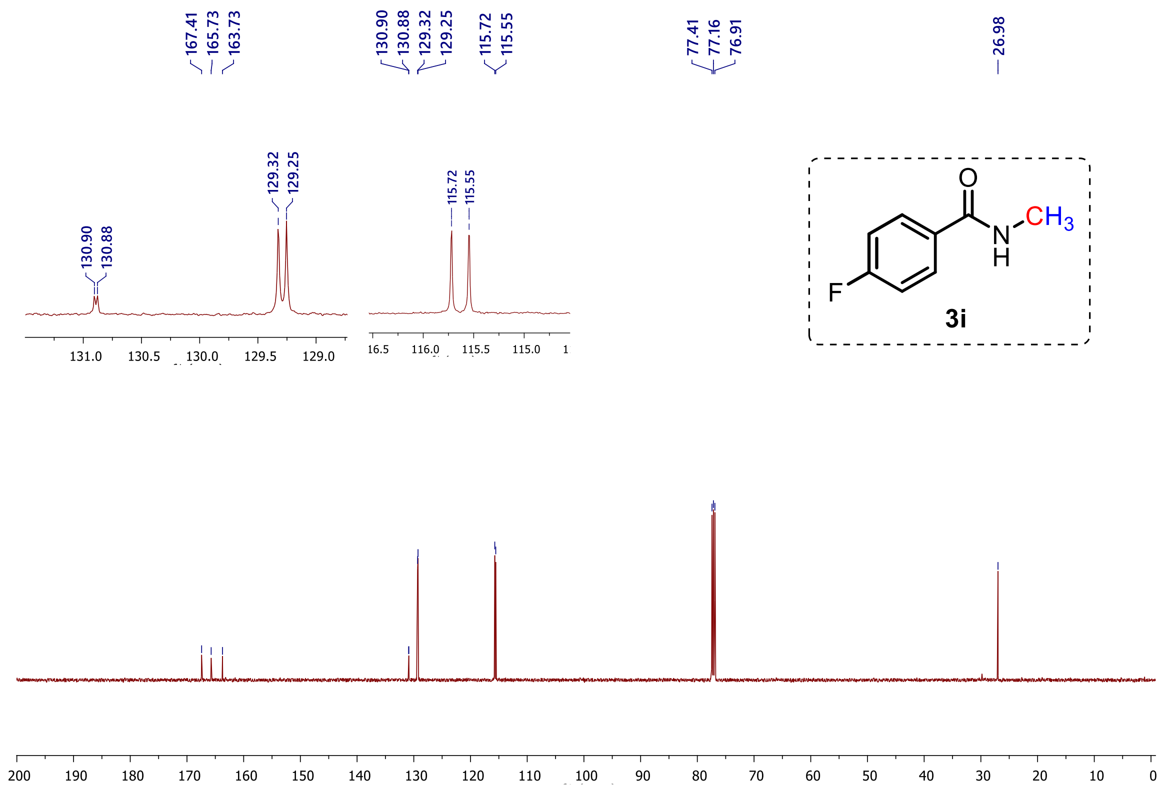


Fig. S45 $^{13}C\{^{1}H\}$ NMR spectrum of **3i** in $CDCl_3$.

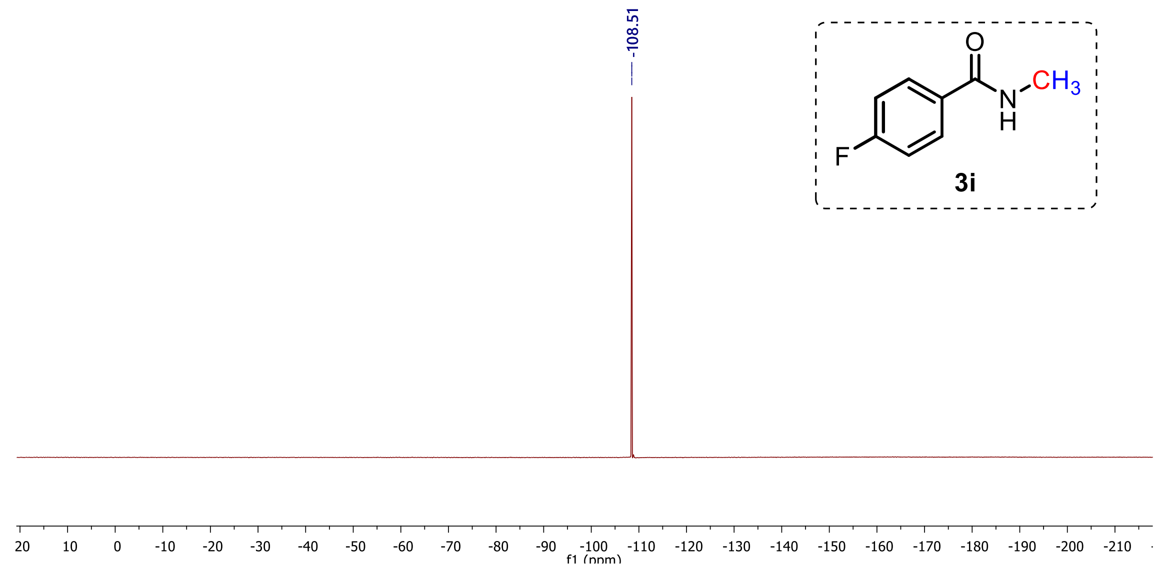


Fig. S46 $^{19}F\{^{1}H\}$ NMR spectrum of **3i** in $CDCl_3$.

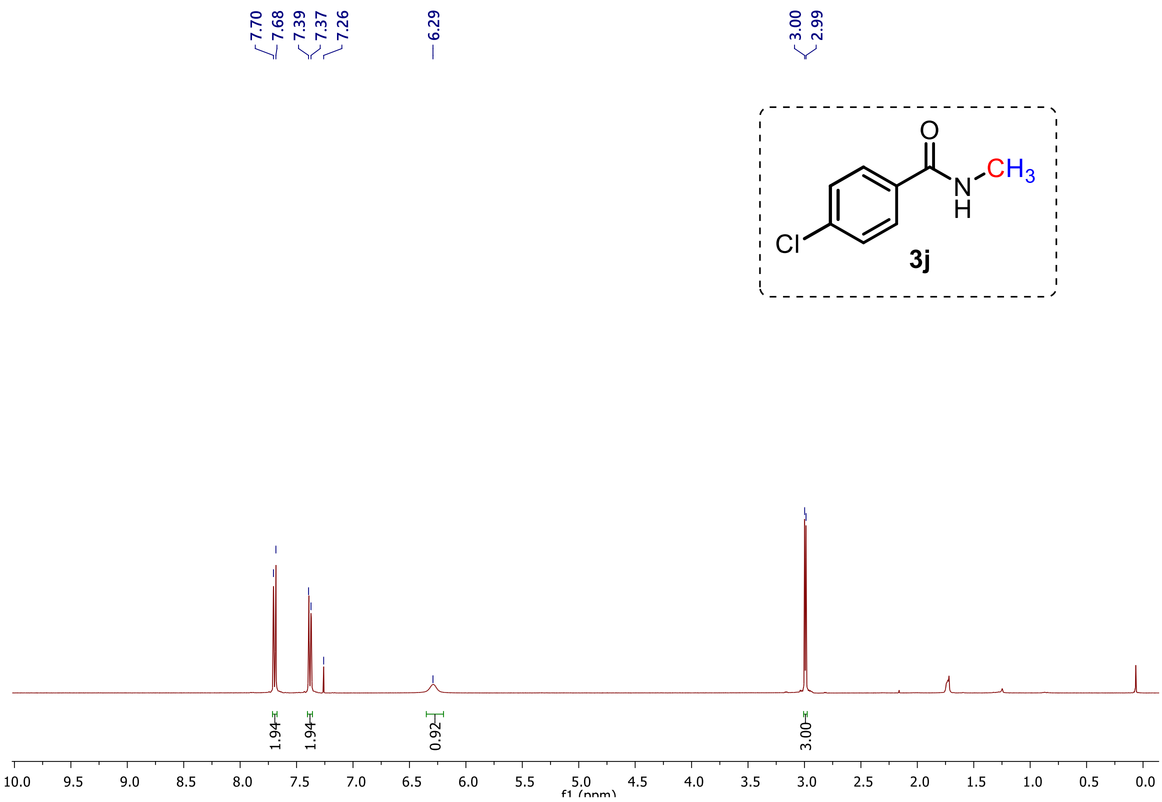


Fig. S47 ^{1}H NMR spectrum of **3j** in $CDCl_3$.

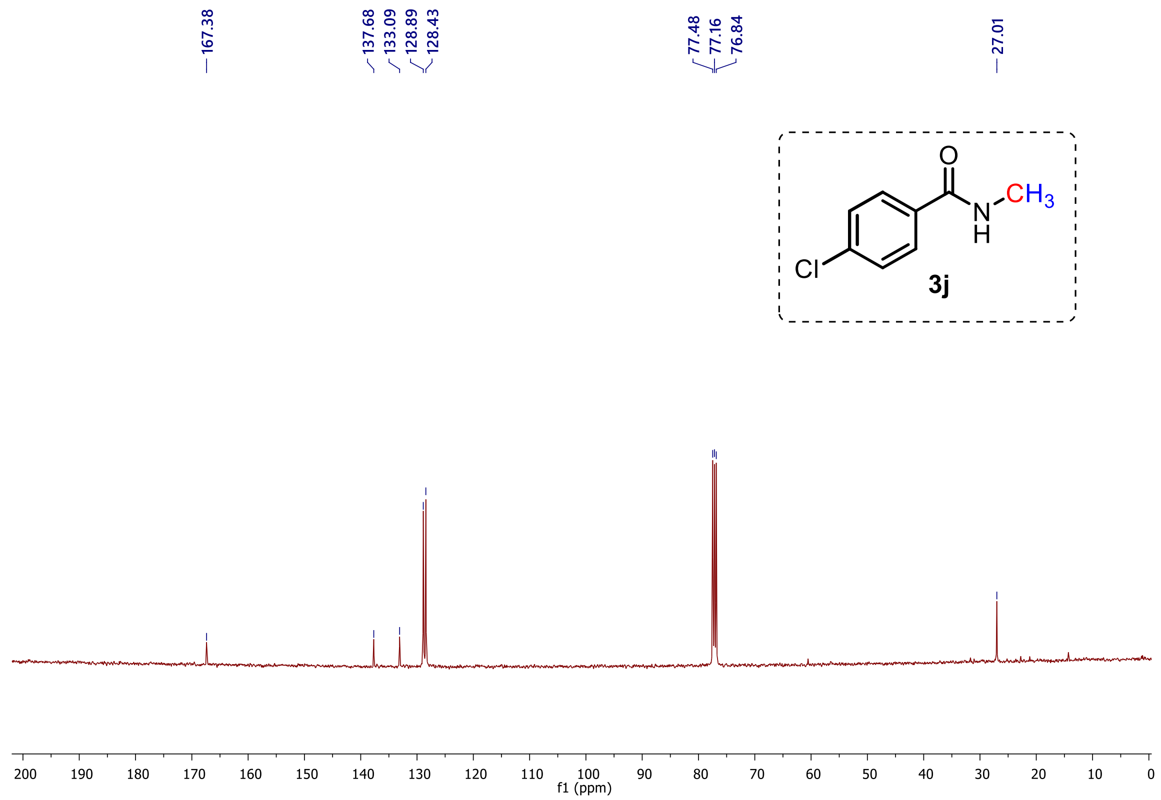


Fig. S48 ^{13}C{^{1}H} NMR spectrum of **3j** in $CDCl_3$.

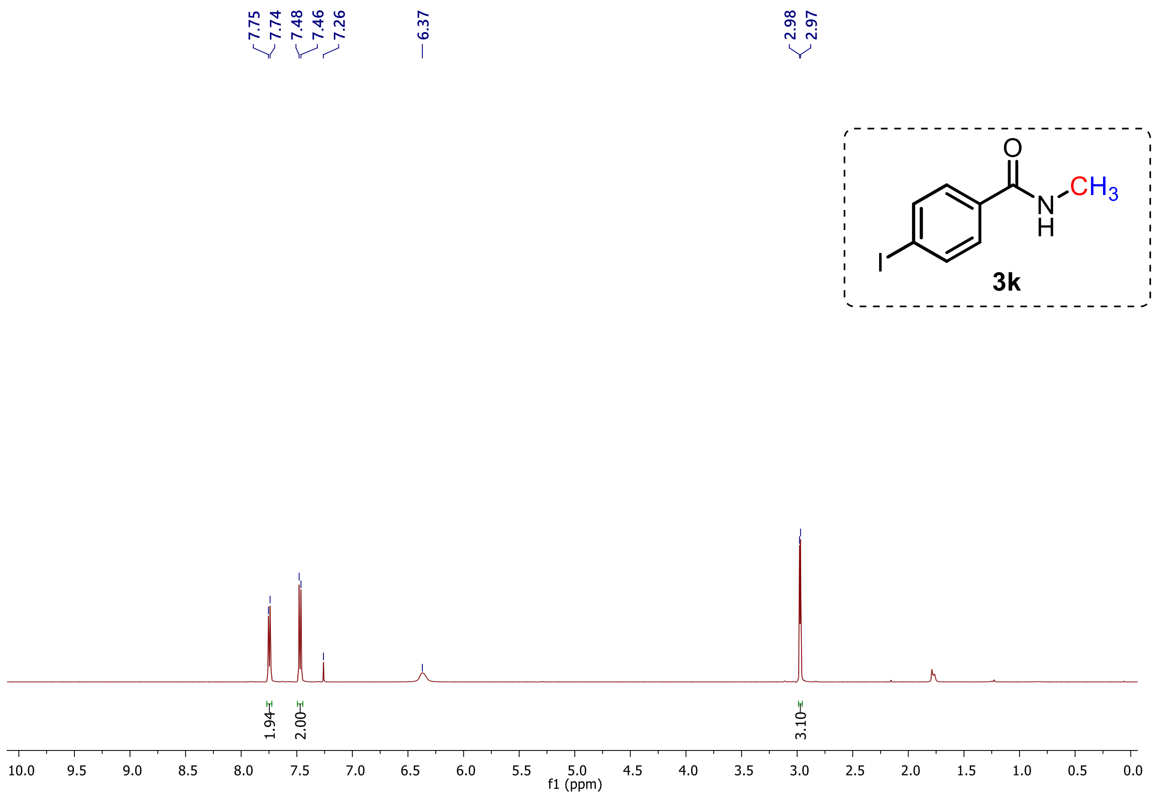


Fig. S49 [1]H NMR spectrum of **3k** in $CDCl_3$.

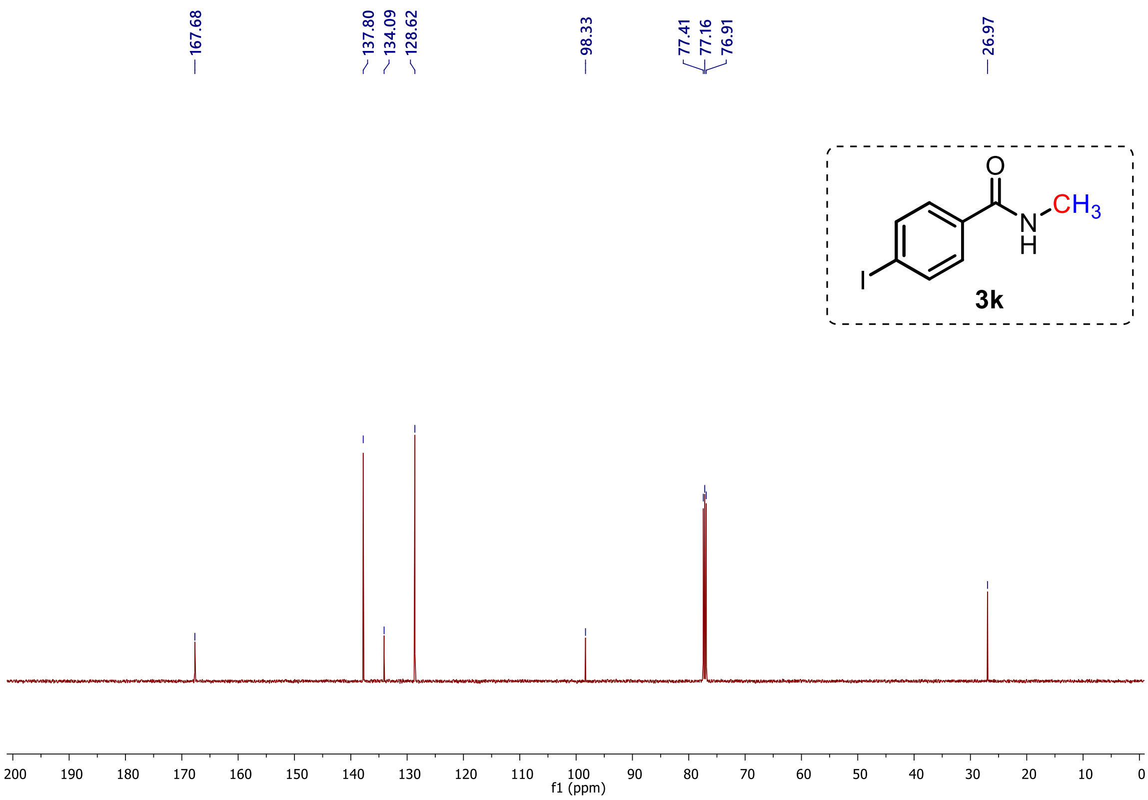


Fig. S50 [13]C{[1]H} NMR spectrum of **3k** in $CDCl_3$.

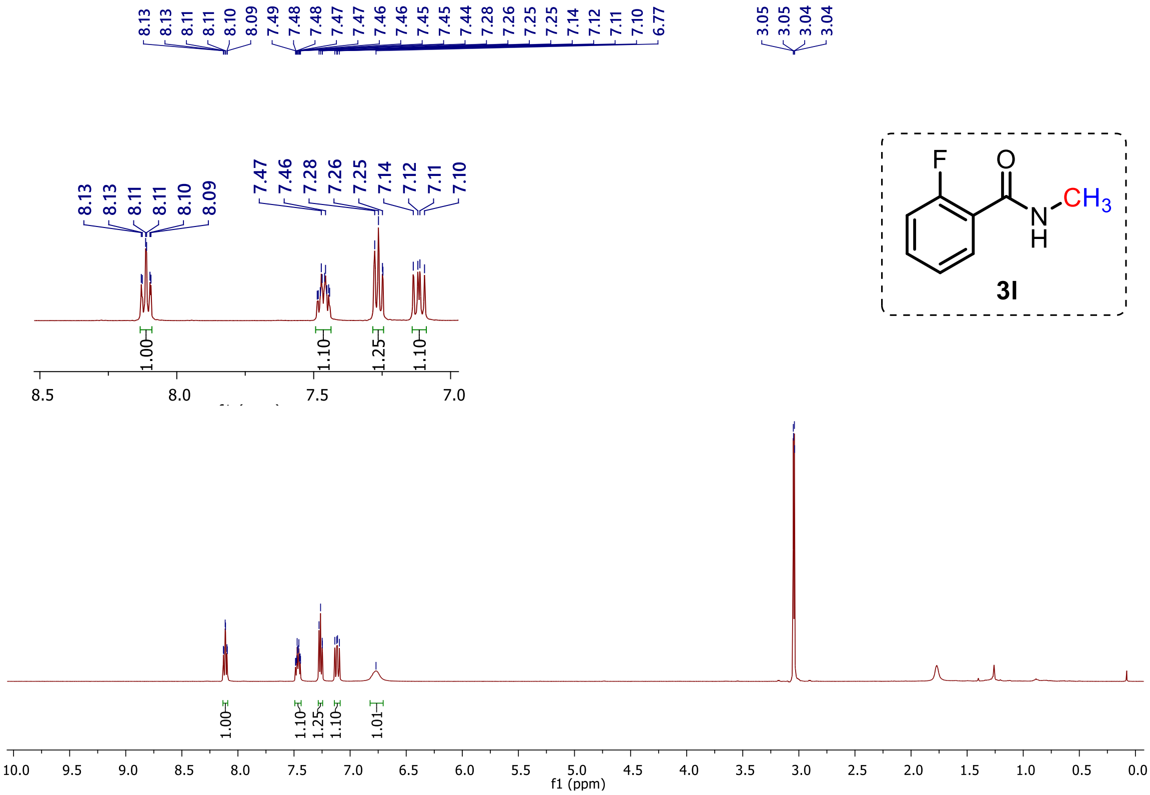


Fig. S51 ^{1}H NMR spectrum of **3l** in $CDCl_3$.

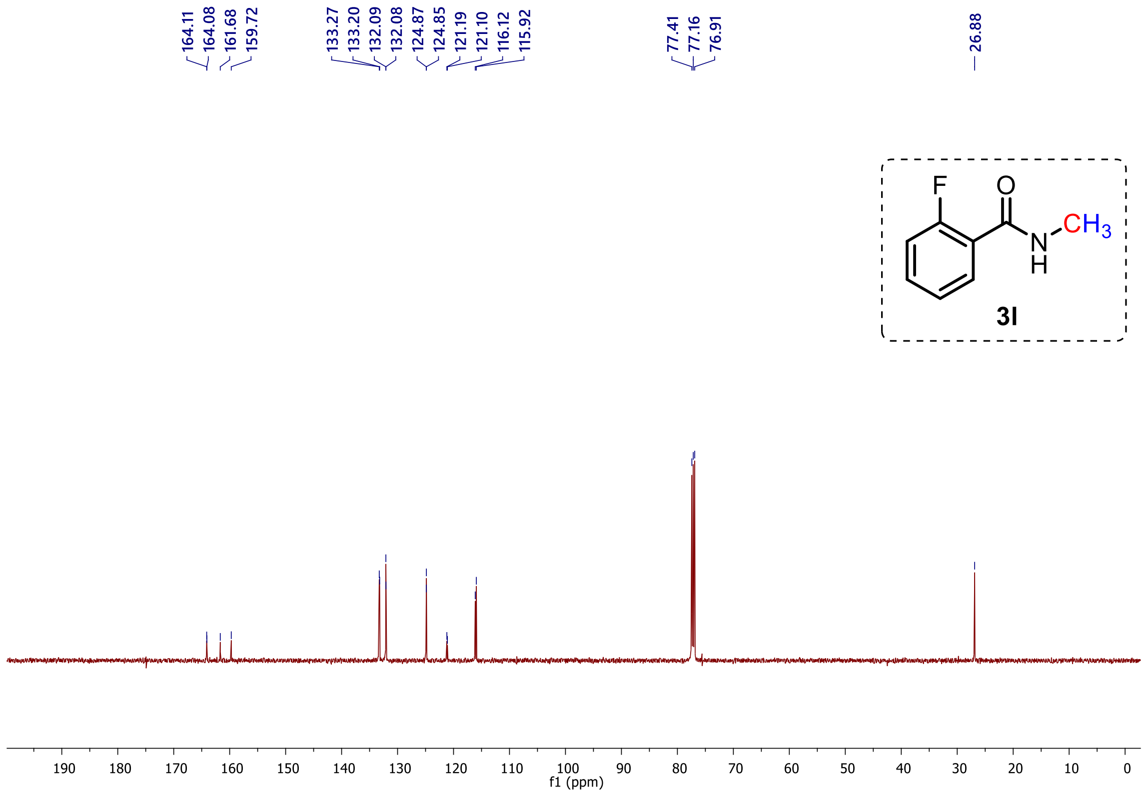


Fig. S52 $^{13}C\{^{1}H\}$ NMR spectrum of **3l** in $CDCl_3$.

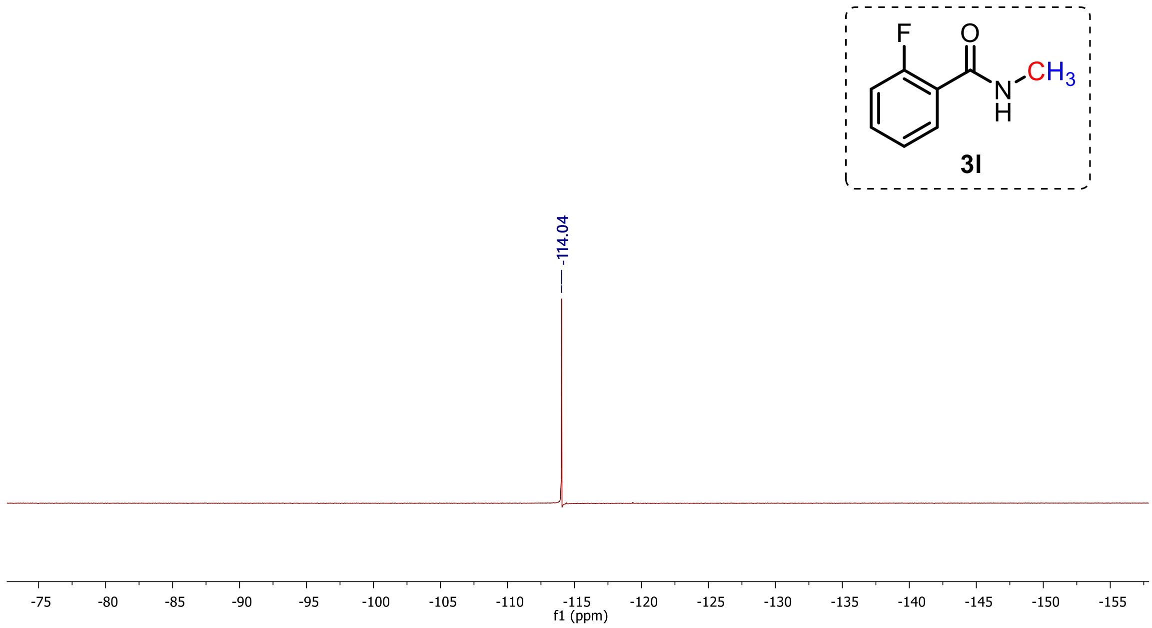


Fig. S53 [19]F{[1]H} NMR spectrum of **3l** in $CDCl_3$.

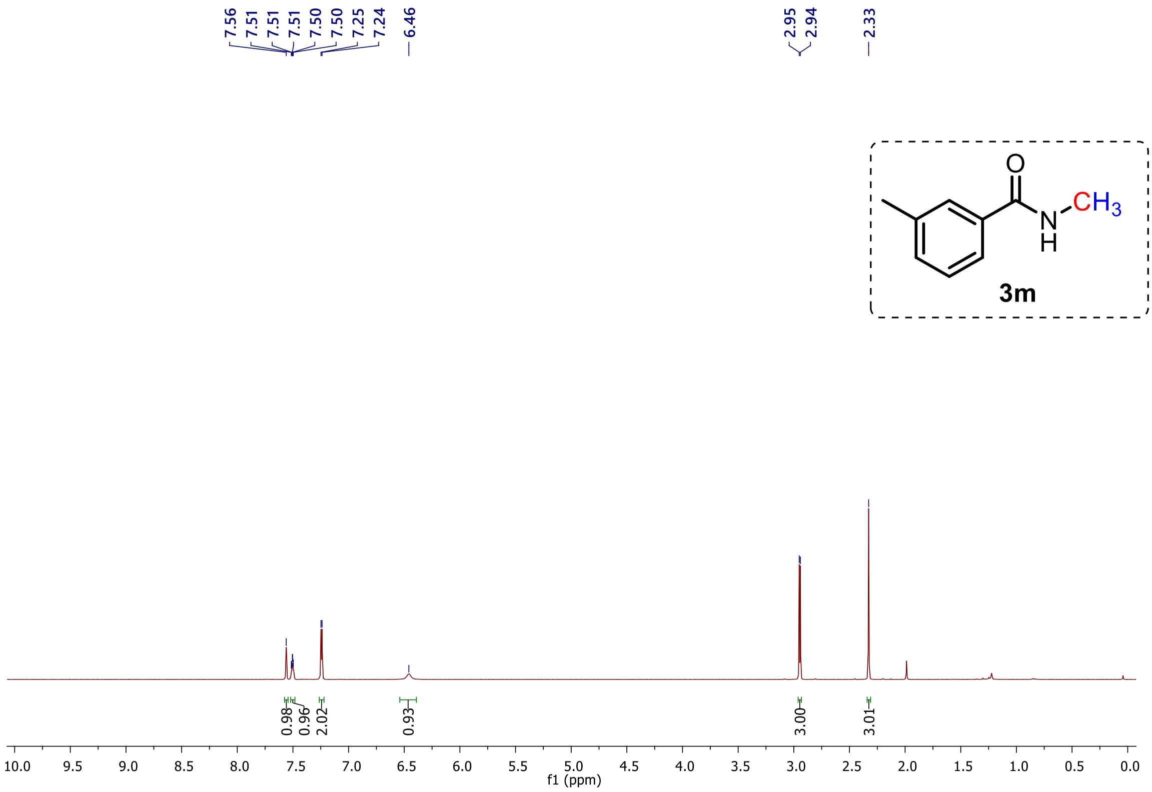


Fig. S54 [1]H NMR spectrum of **3m** in $CDCl_3$.

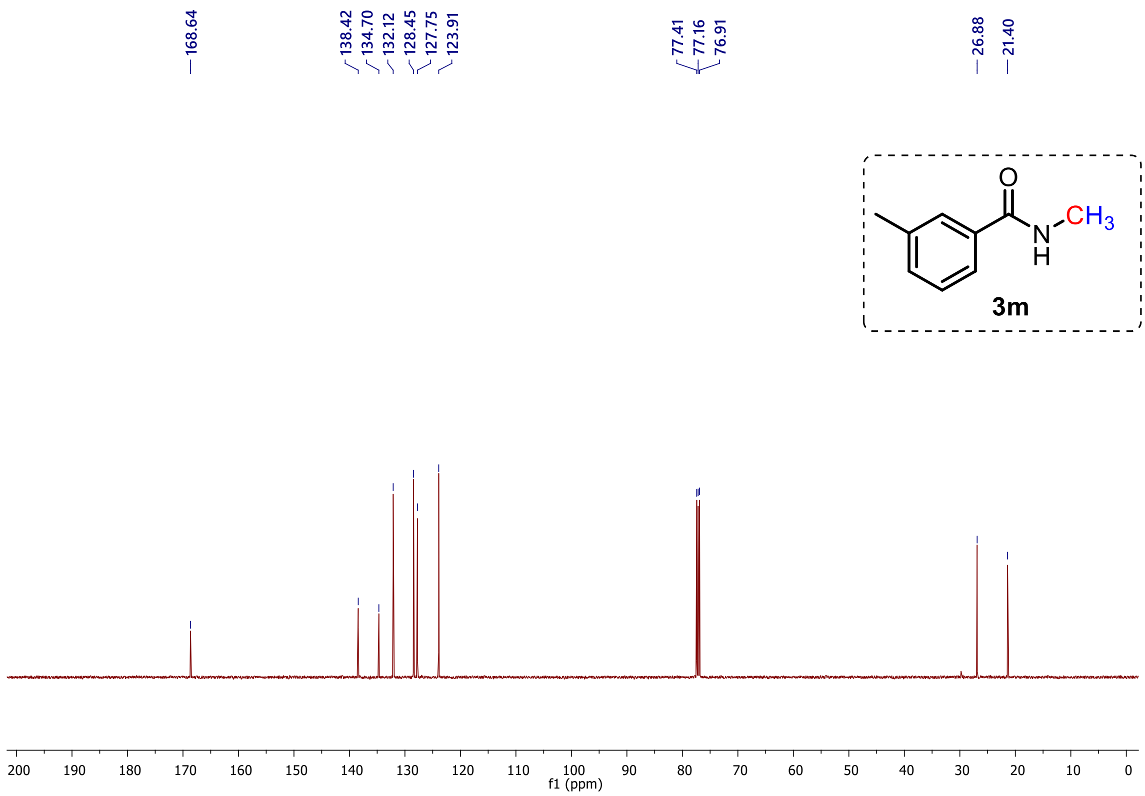


Fig. S55 $^{13}C\{^{1}H\}$ NMR spectrum of **3m** in $CDCl_3$.

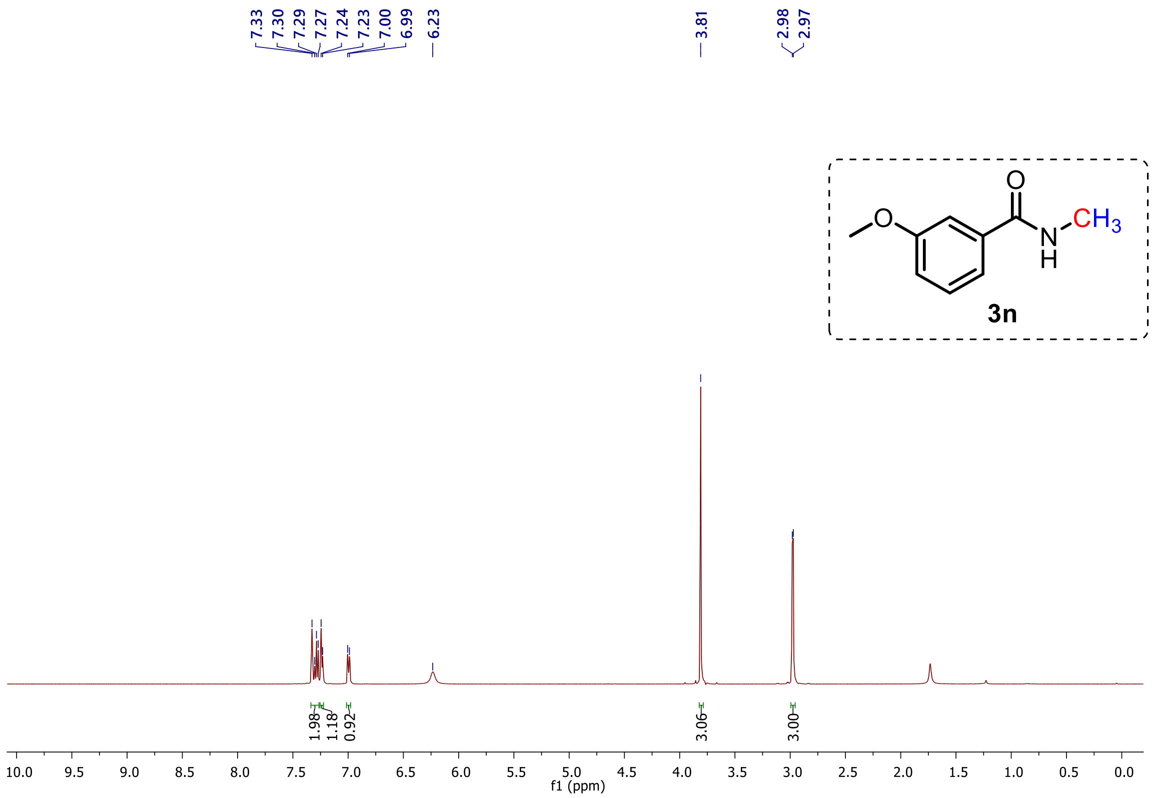


Fig. S56 ^{1}H NMR spectrum of **3n** in $CDCl_3$.

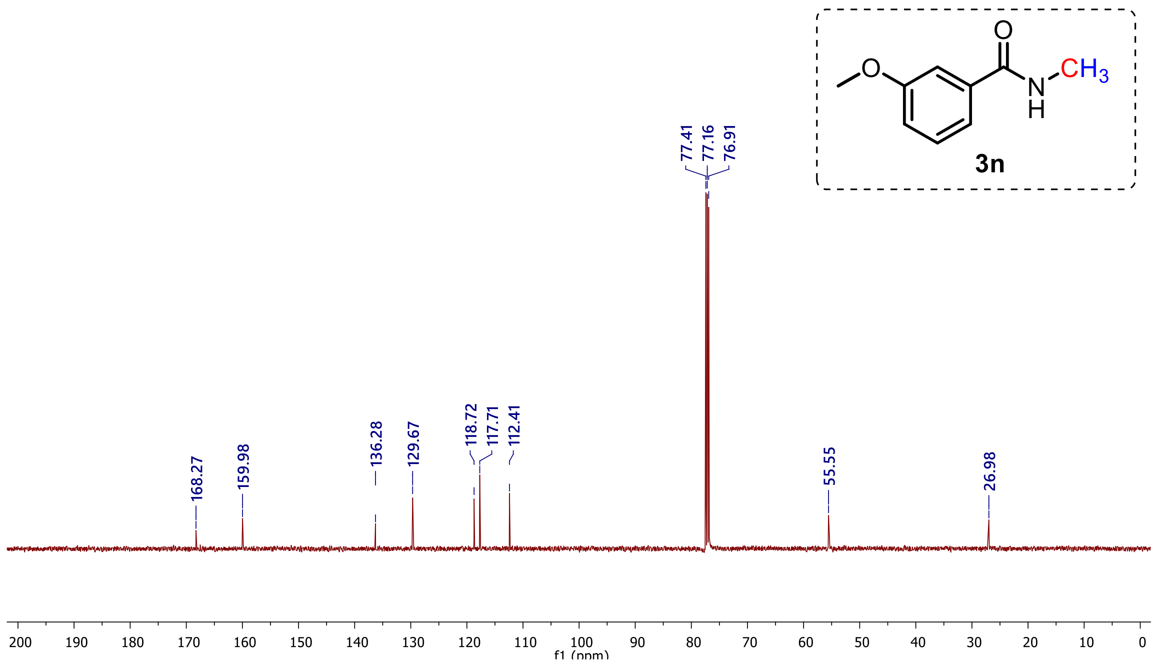


Fig. S57 $^{13}C\{^{1}H\}$ NMR spectrum of **3n** in $CDCl_3$.

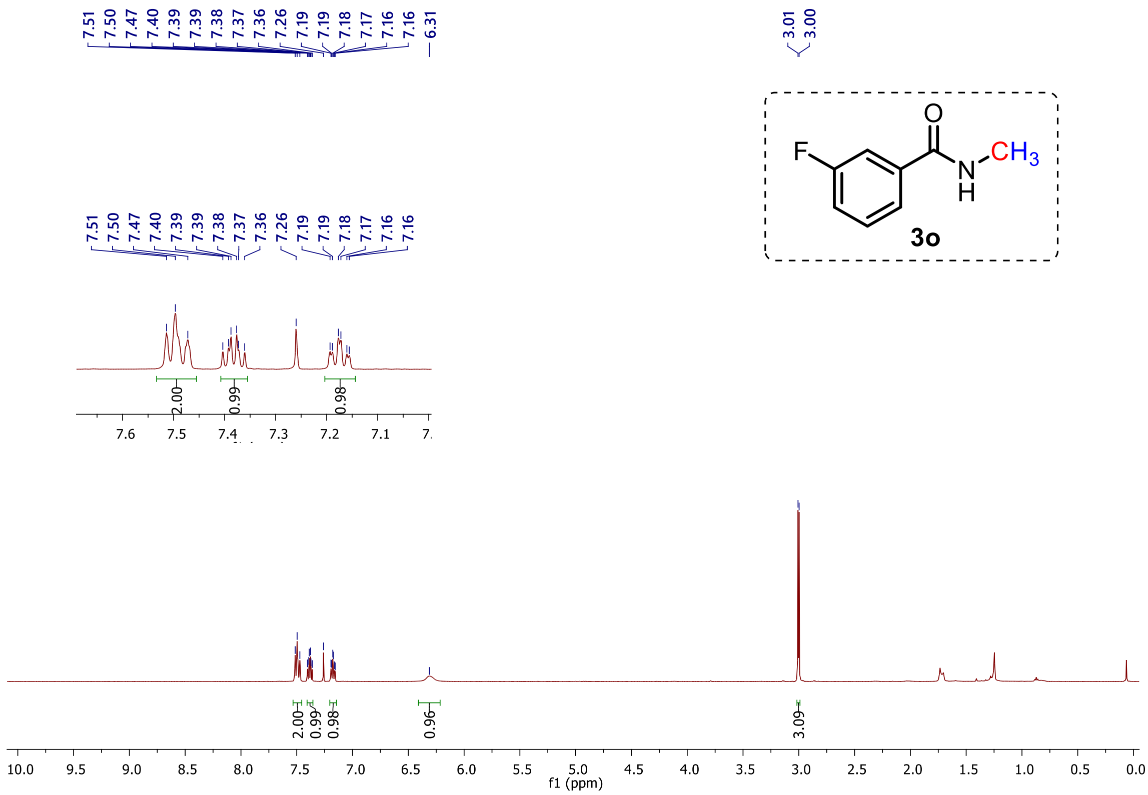


Fig. S58 ^{1}H NMR spectrum of **3o** in $CDCl_3$.

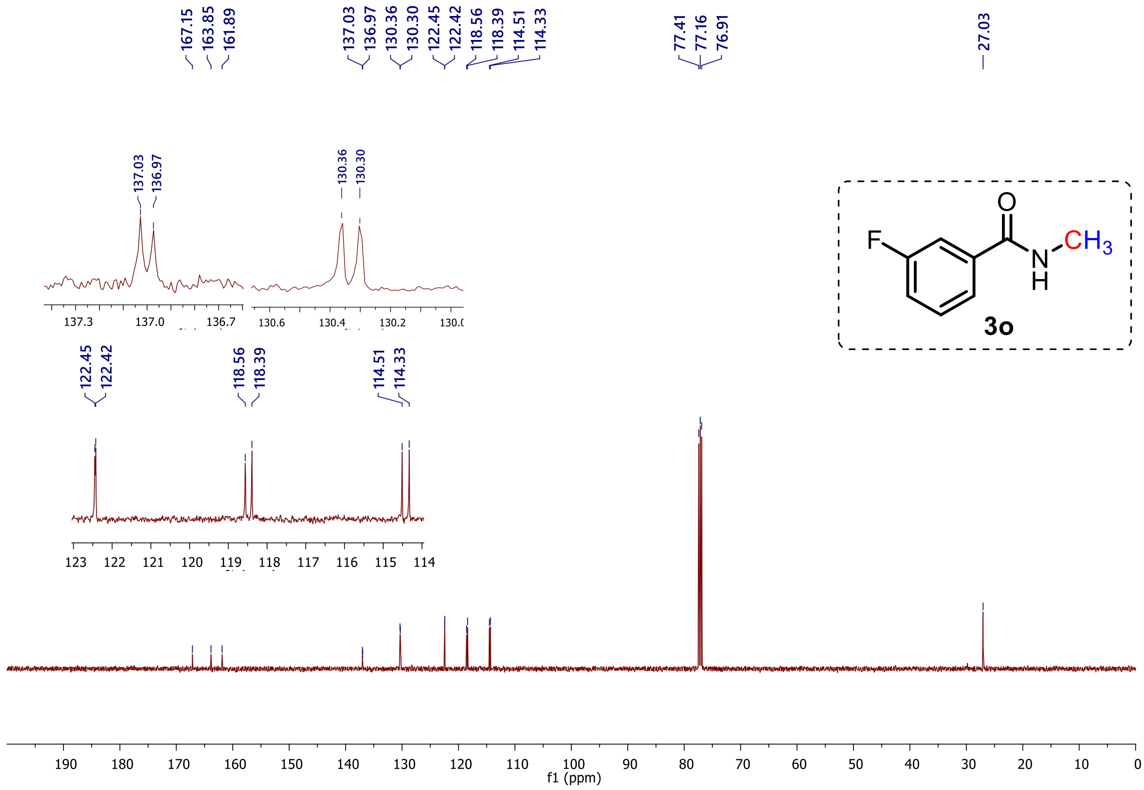


Fig. S59 $^{13}C\{^1H\}$ NMR spectrum of **3o** in $CDCl_3$.

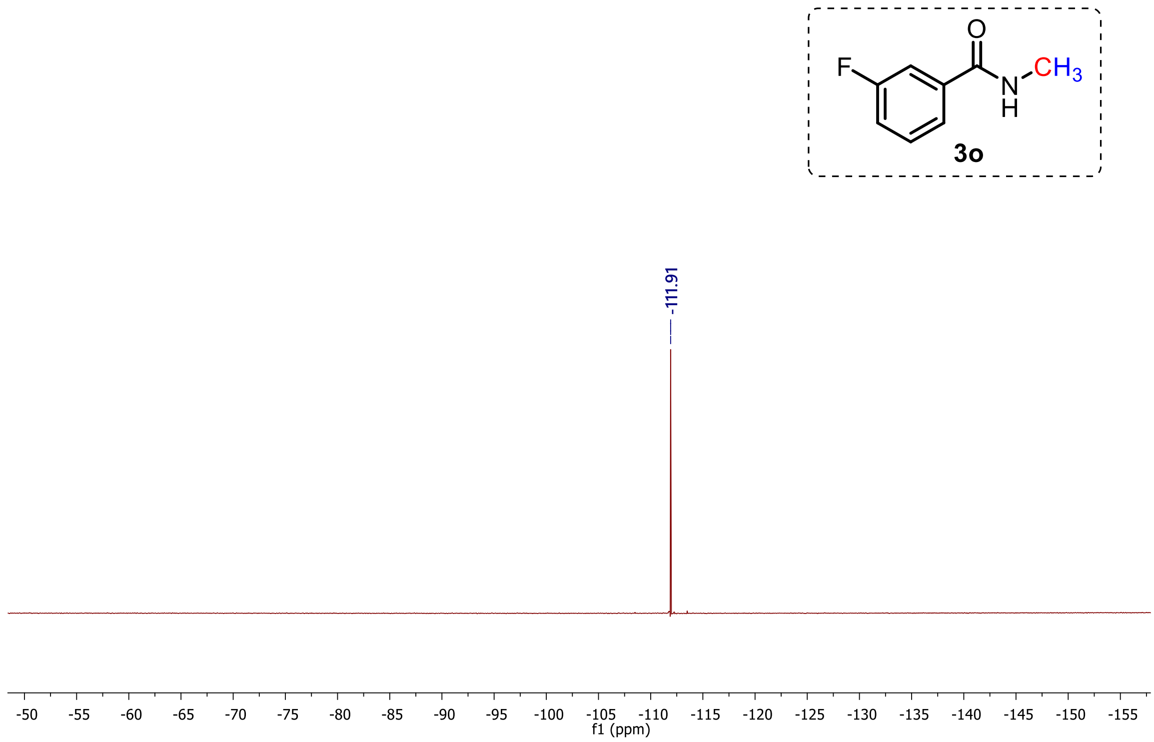


Fig. S60 $^{19}F\{^1H\}$ NMR spectrum of **3o** in $CDCl_3$.

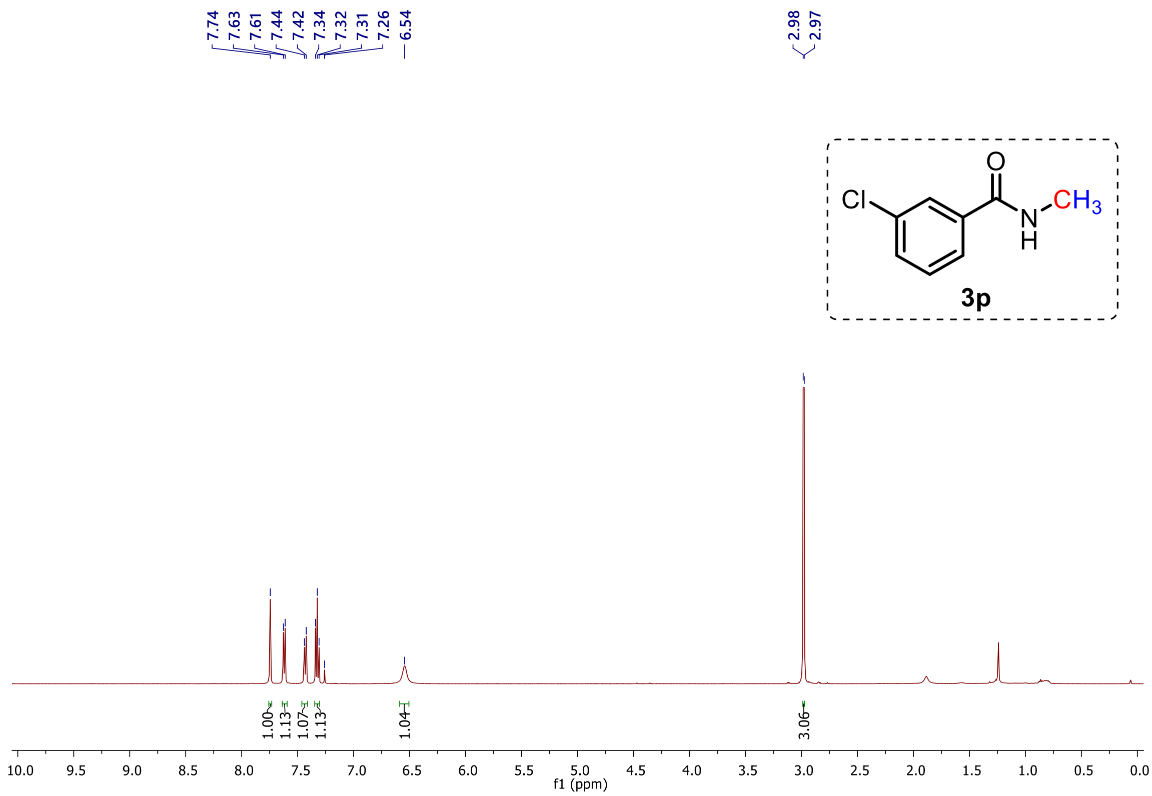


Fig. S61 ^{1}H NMR spectrum of **3p** in $CDCl_3$.

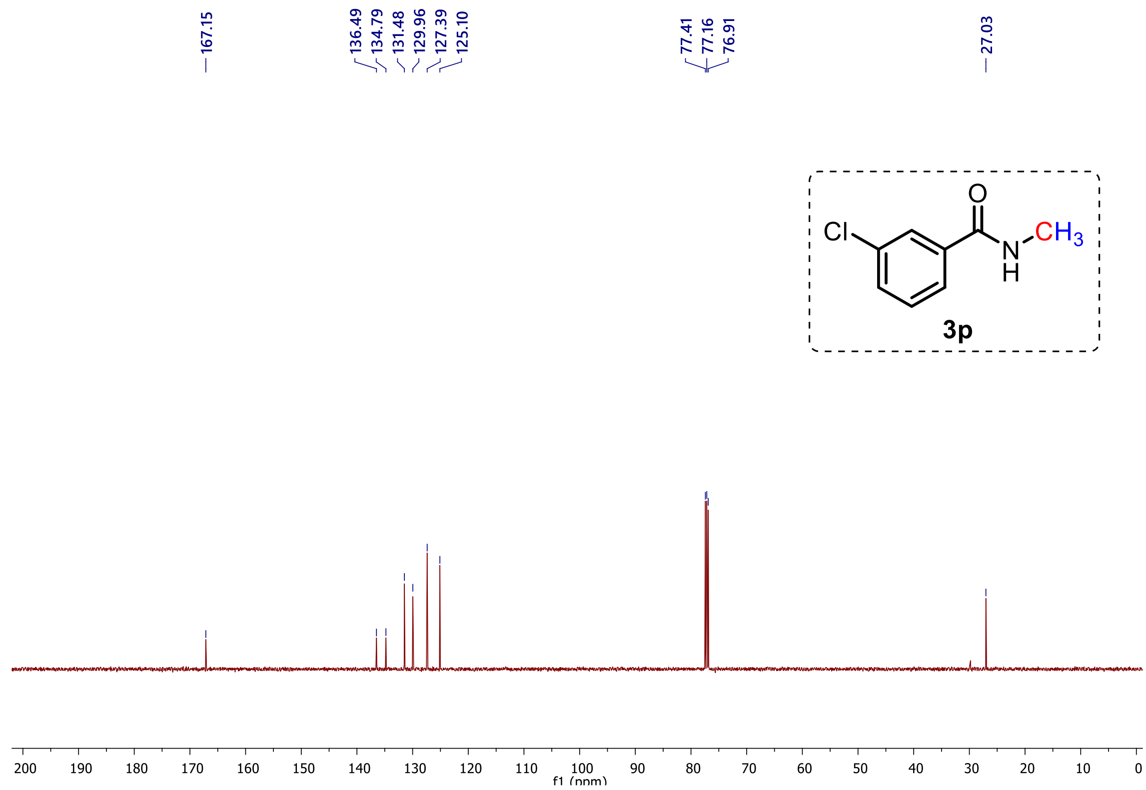


Fig. S61 ^{13}C{^{1}H} NMR spectrum of **3p** in $CDCl_3$.

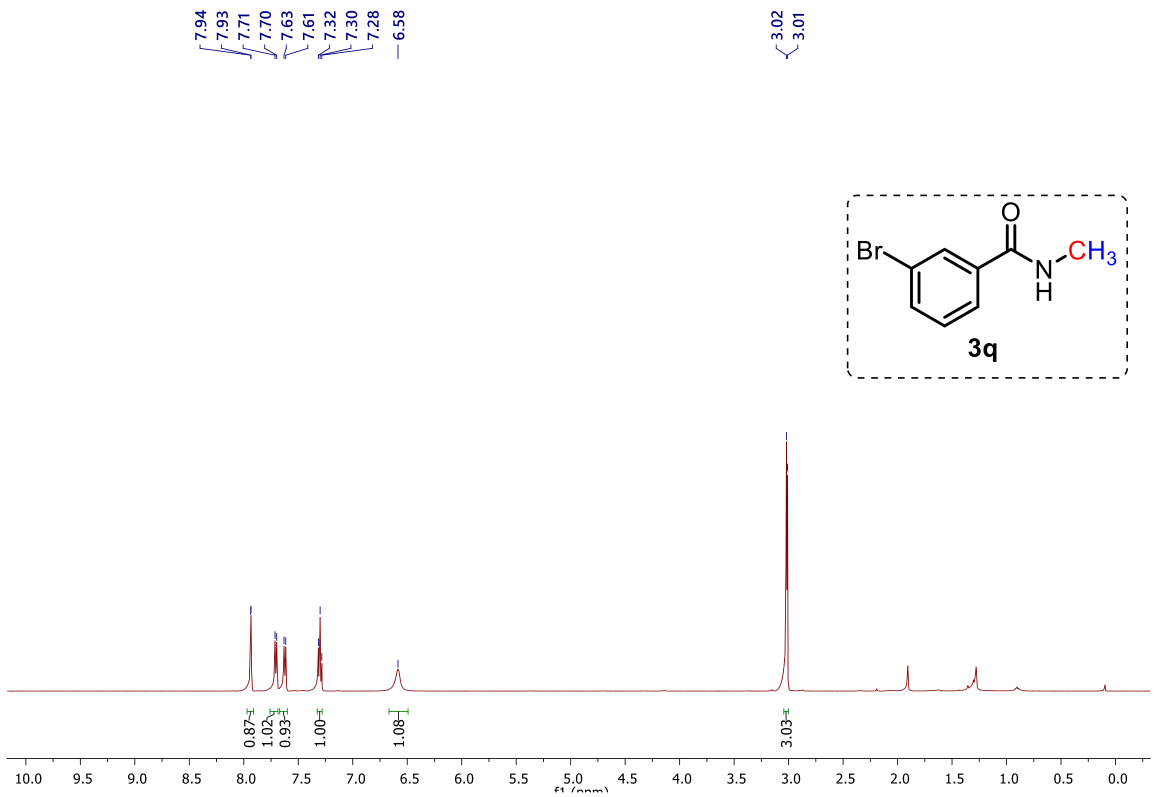


Fig. S62 ^{1}H NMR spectrum of **3q** in $CDCl_3$.

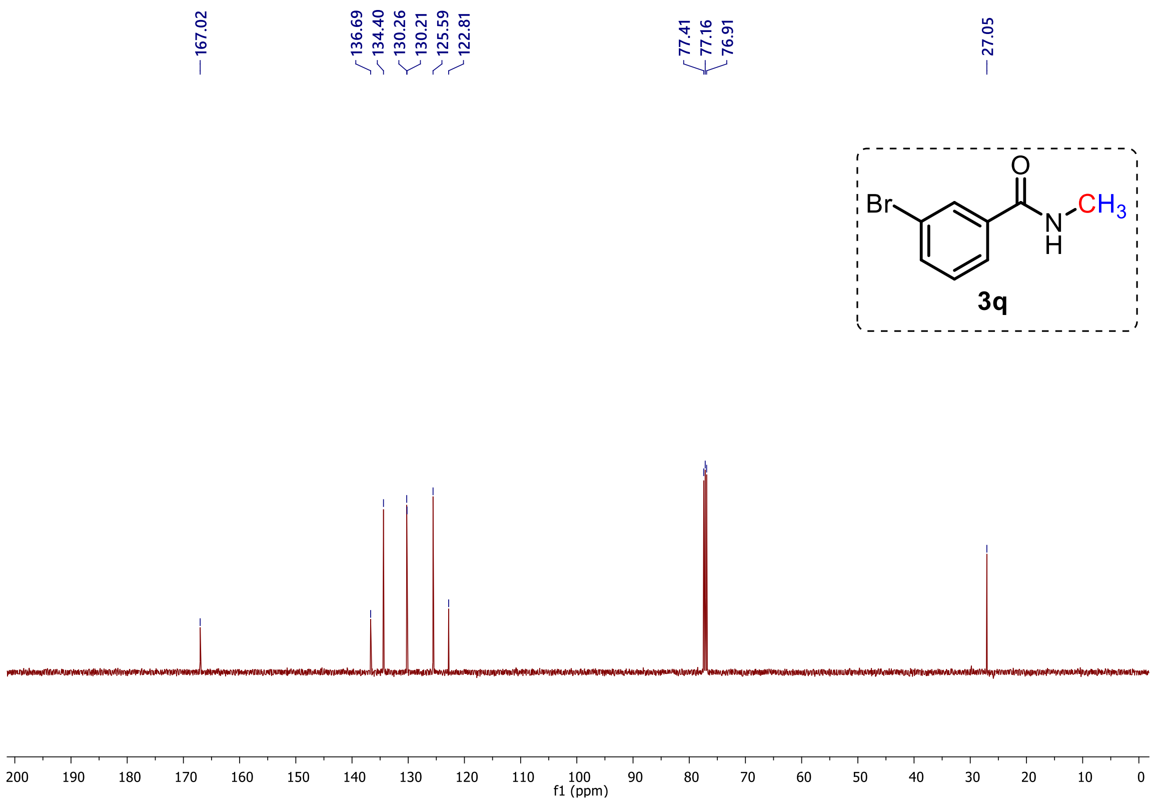


Fig. S63 ^{13}C{^{1}H} NMR spectrum of **3q** in $CDCl_3$.

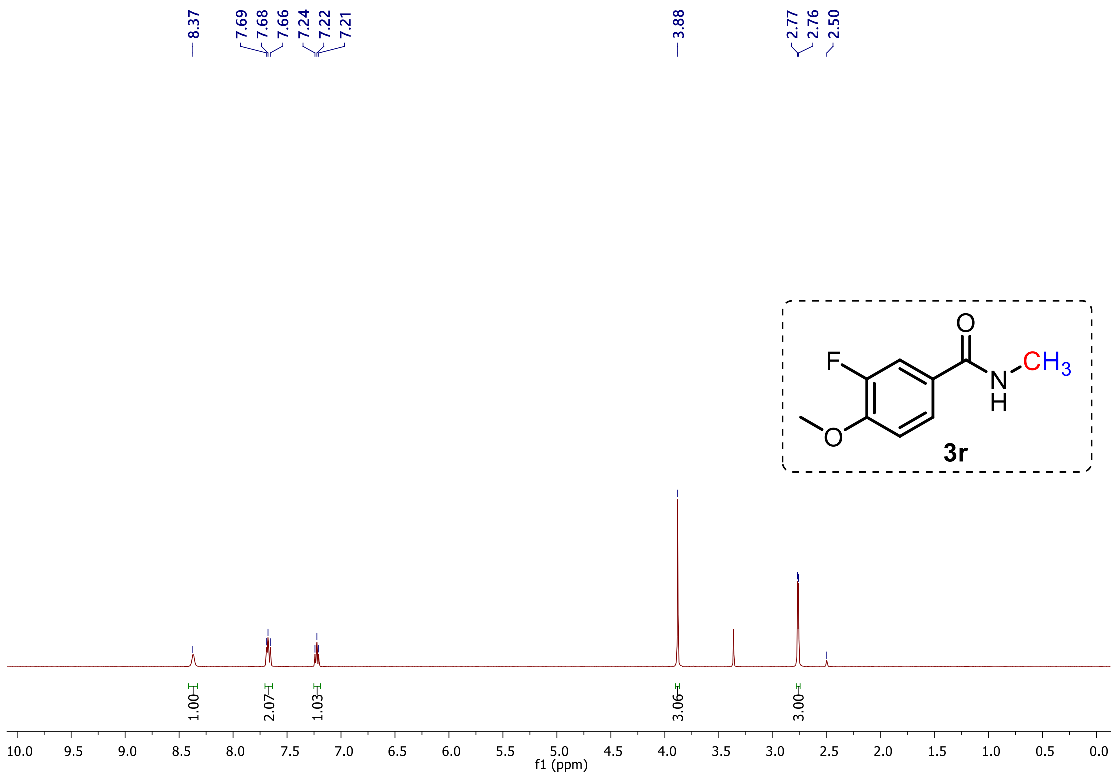


Fig. S64 ^{1}H NMR spectrum of **3r** in DMSO-d$_6$.

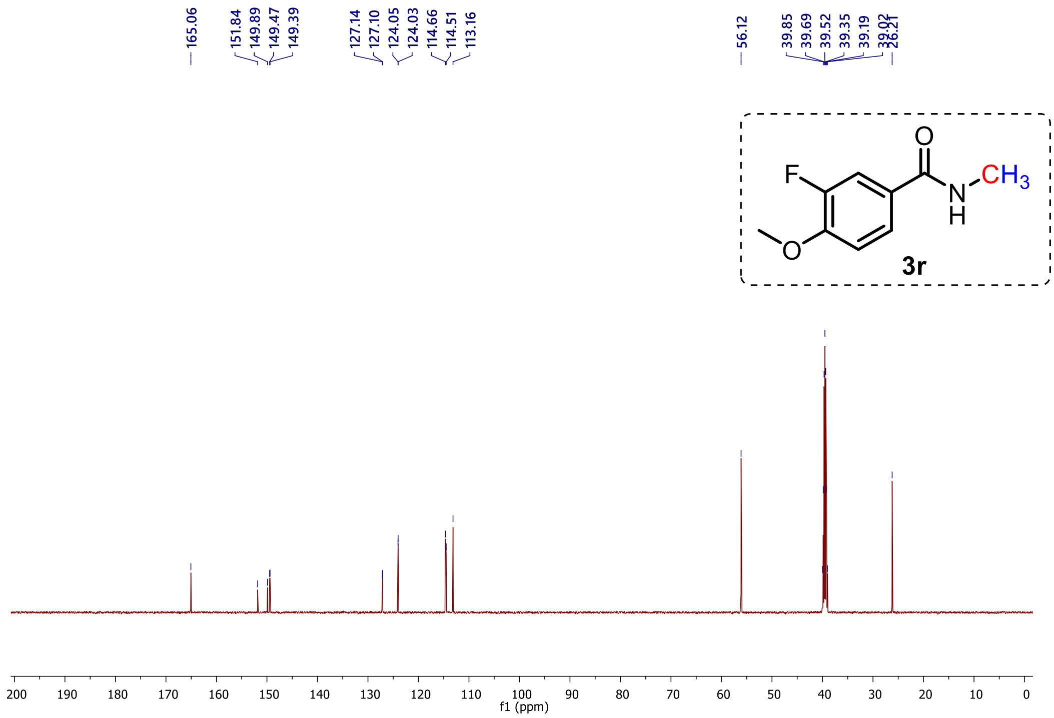


Fig. S65 ^{13}C{^{1}H} NMR spectrum of **3r** in DMSO-d$_6$.

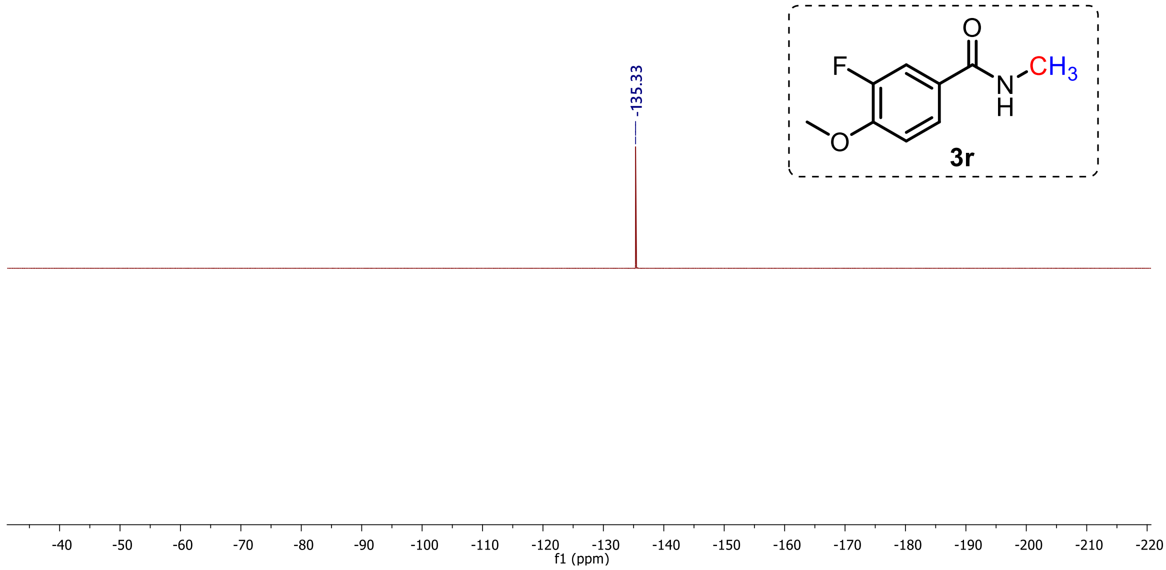


Fig. S66 $^{19}F\{^{1}H\}$ NMR spectrum of **3r** in DMSO-d$_6$.

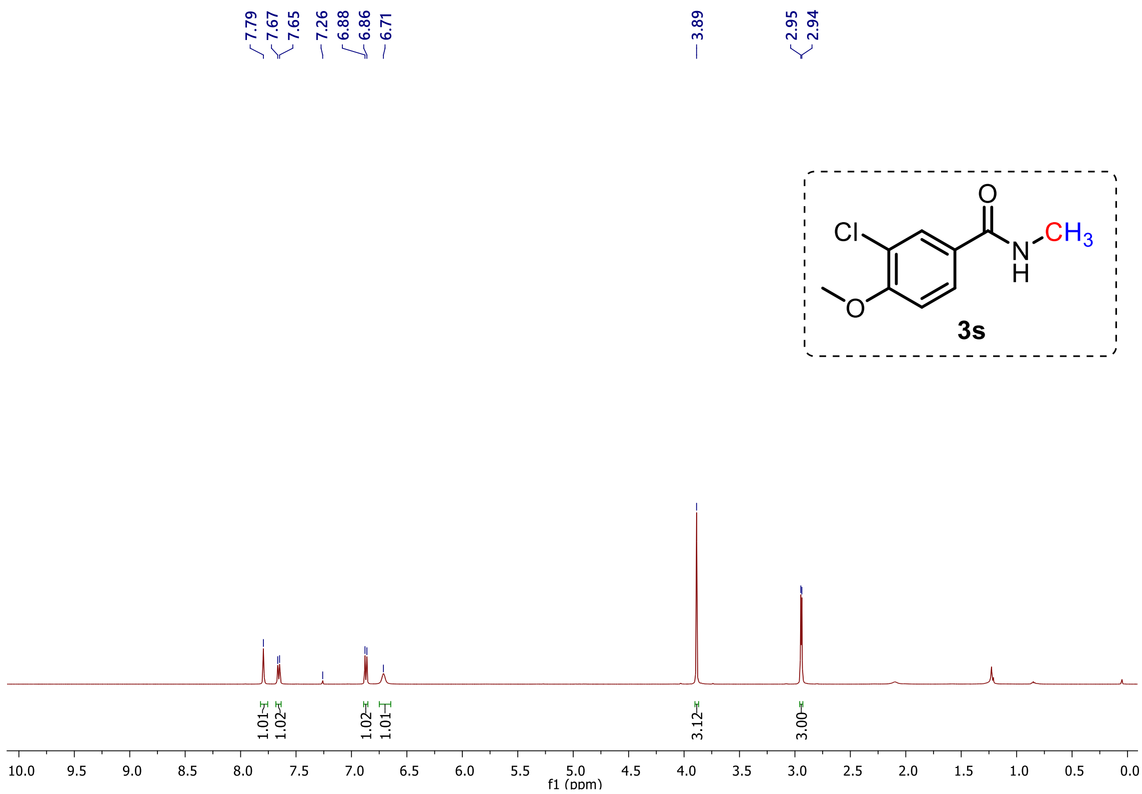


Fig. S67 ^{1}H NMR spectrum of **3s** in $CDCl_3$.

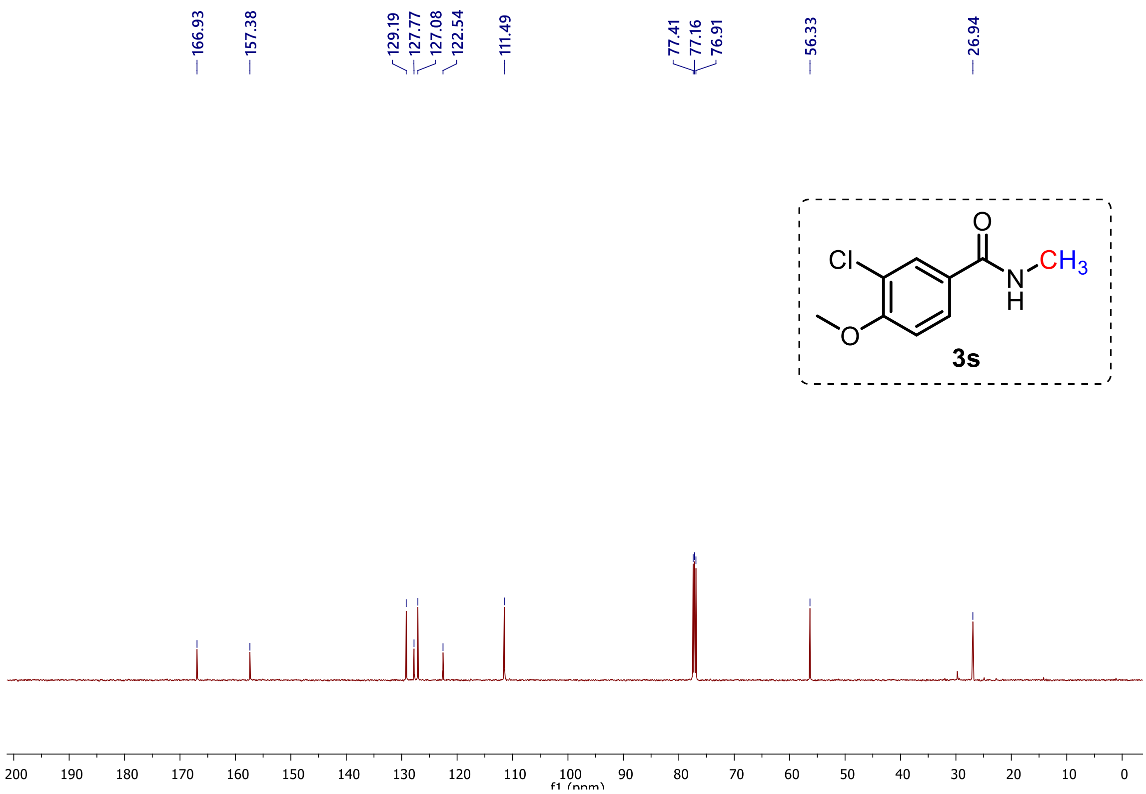


Fig. S68 $^{13}C\{^{1}H\}$ NMR spectrum of **3s** in $CDCl_3$.

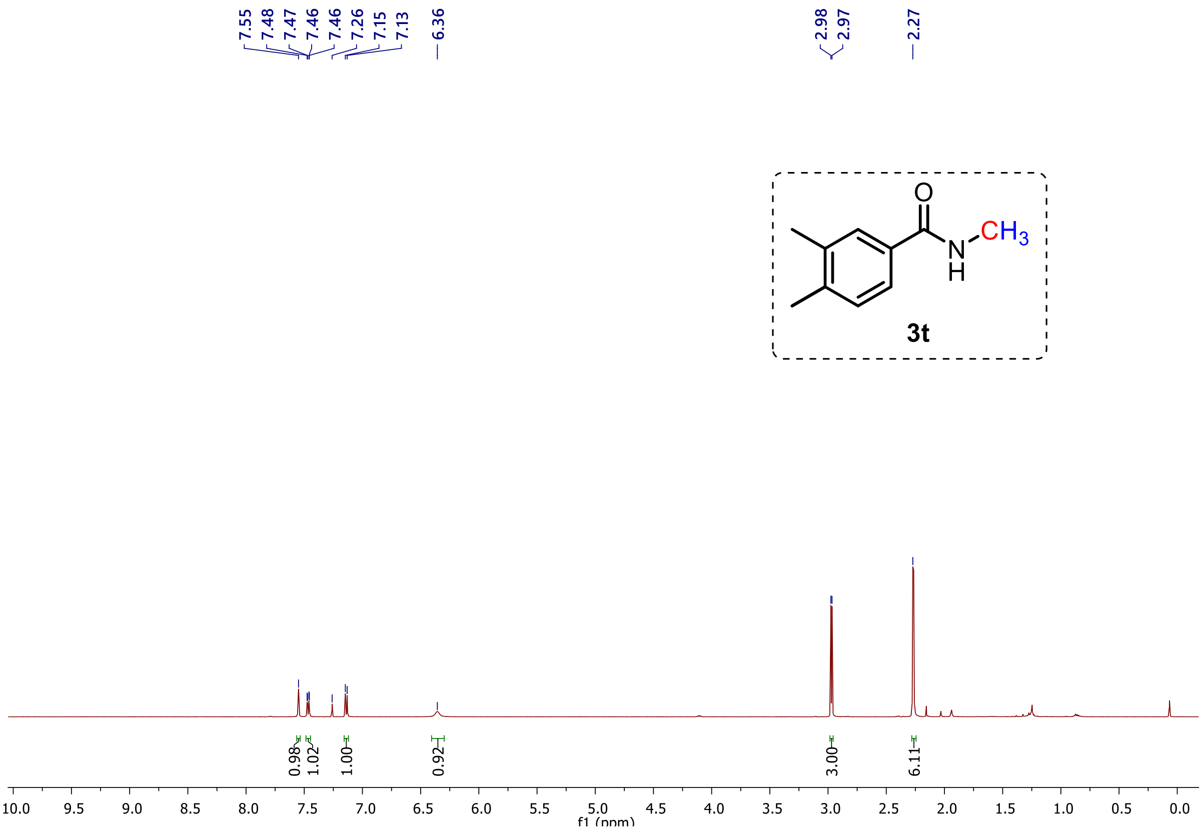


Fig. S69 ^{1}H NMR spectrum of **3t** in $CDCl_3$.

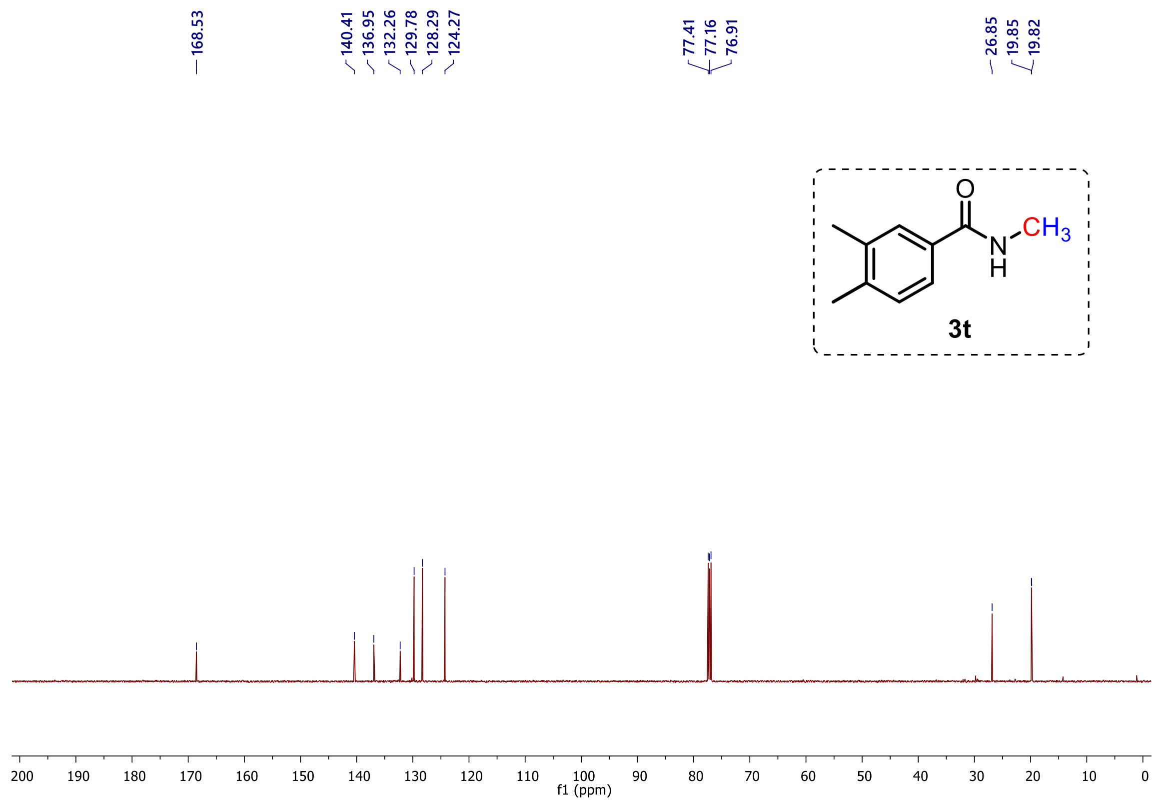


Fig. S70 $^{13}C\{^{1}H\}$ NMR spectrum of **3t** in $CDCl_3$.

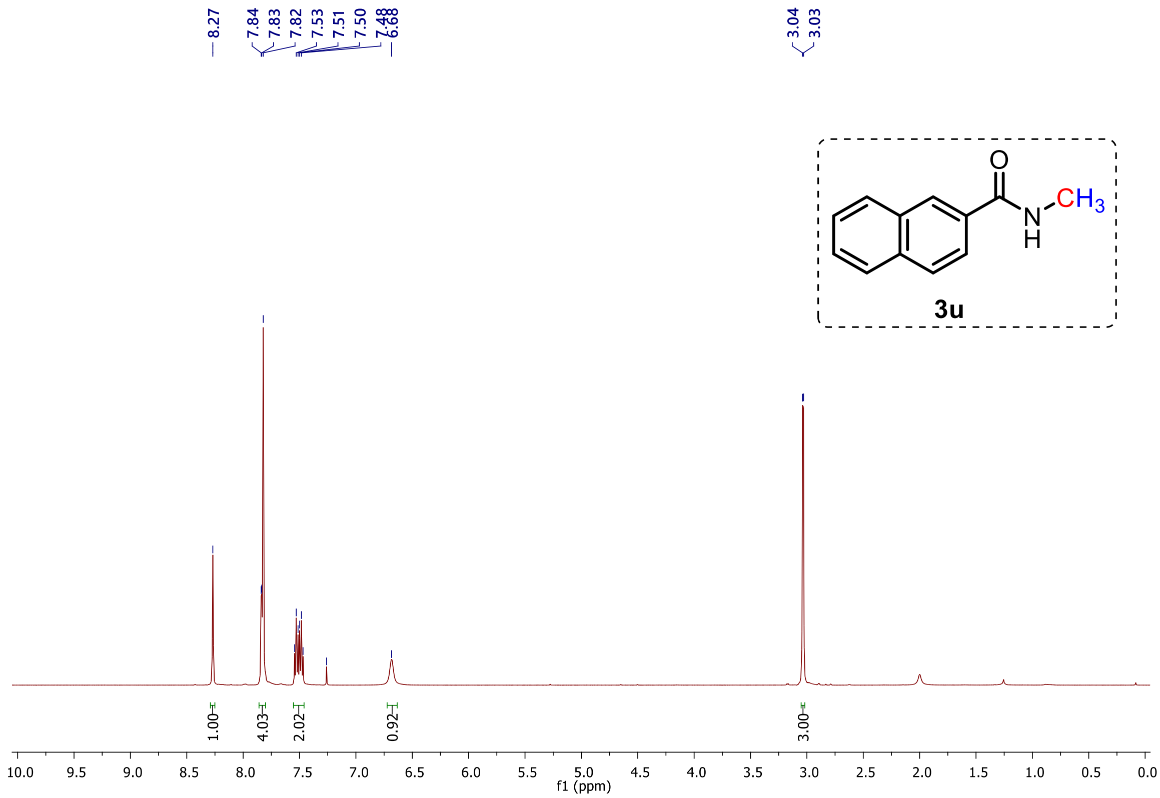


Fig. S71 ^{1}H NMR spectrum of **3u** in $CDCl_3$.

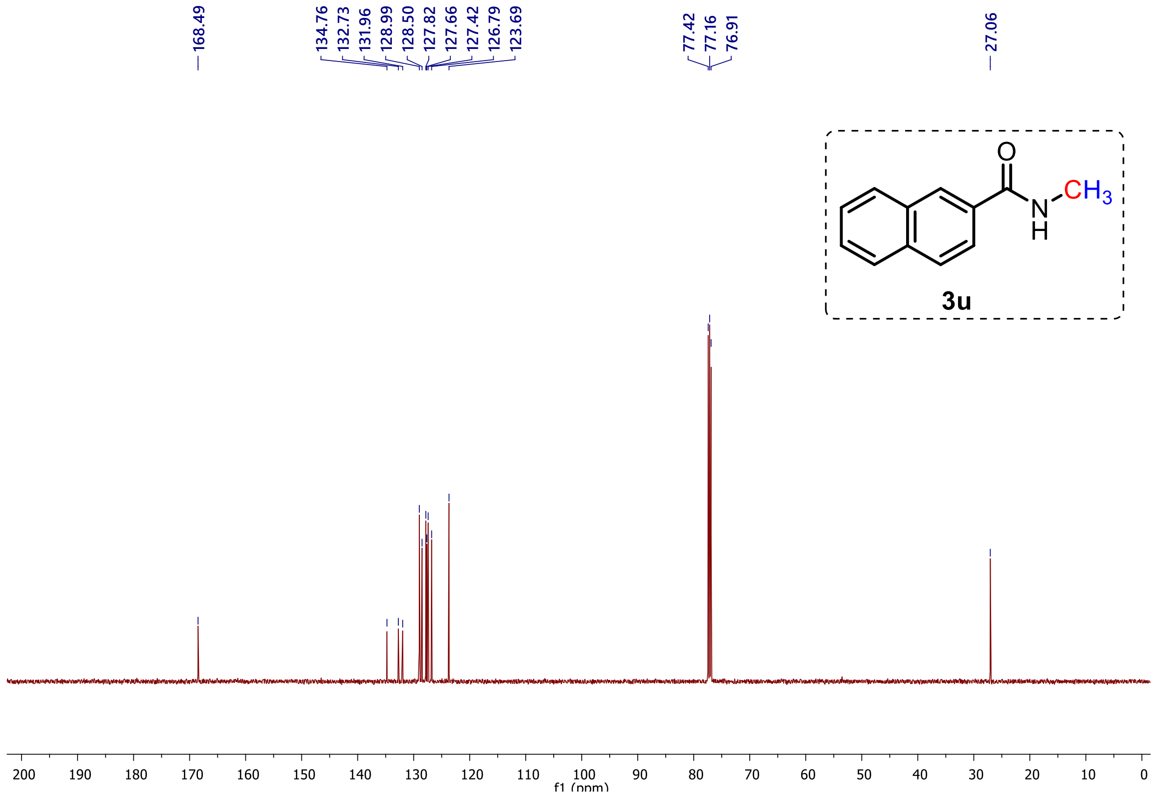


Fig. S72 $^{13}C\{^{1}H\}$ NMR spectrum of **3u** in $CDCl_3$.

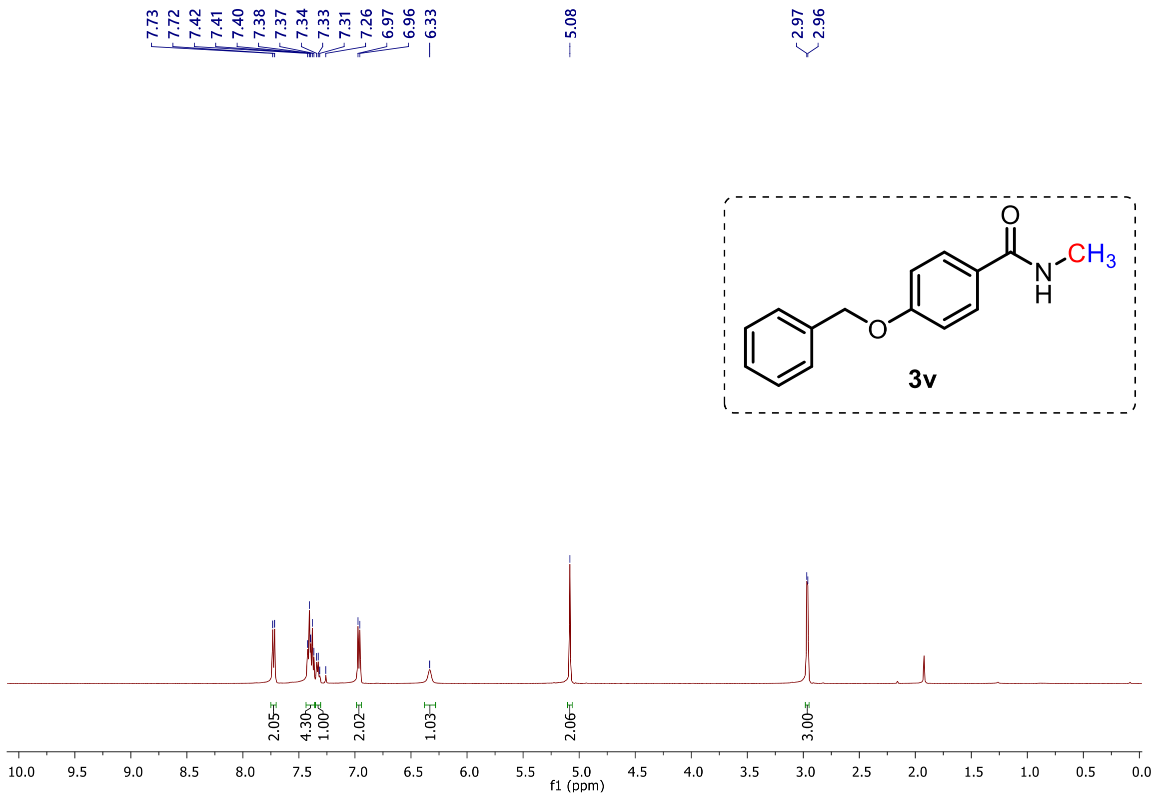


Fig. S73 ^{1}H NMR spectrum of **3v** in $CDCl_3$.

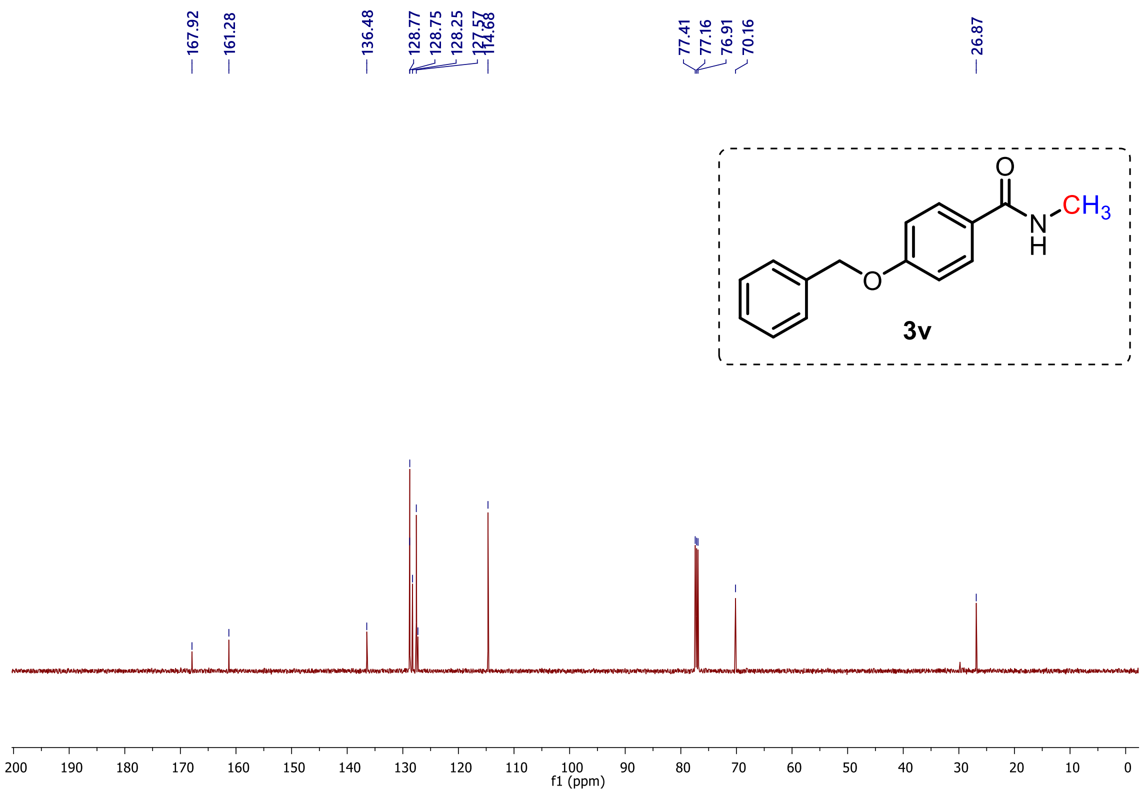


Fig. S74 $^{13}C\{^{1}H\}$ NMR spectrum of **3v** in $CDCl_3$.

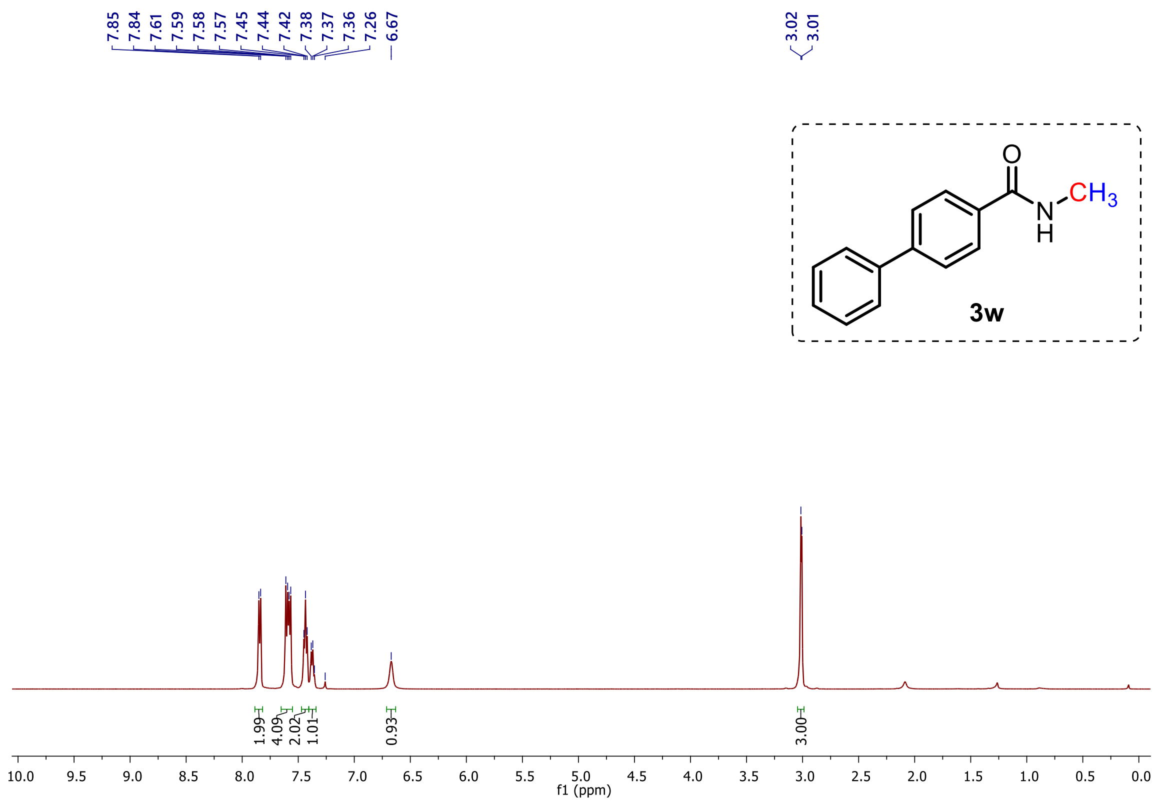


Fig. S75 ^{1}H NMR spectrum of **3w** in $CDCl_3$.

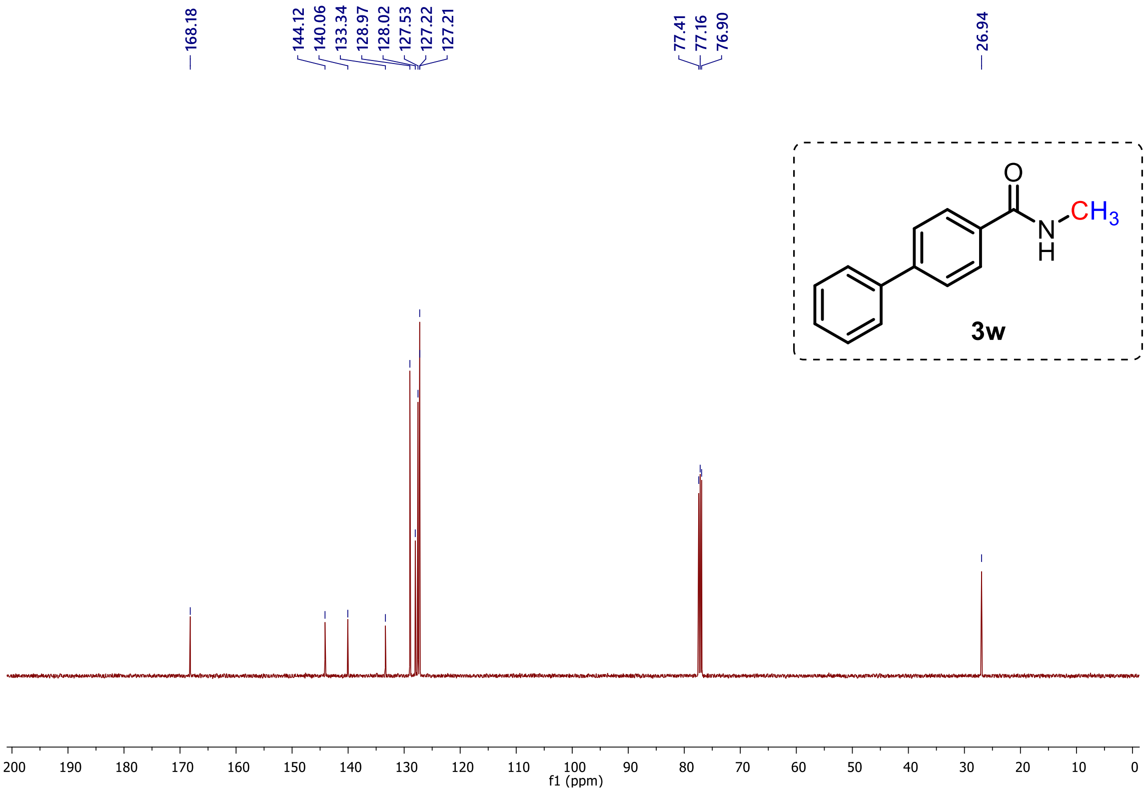


Fig. S76 $^{13}C\{^{1}H\}$ NMR spectrum of **3w** in $CDCl_3$.

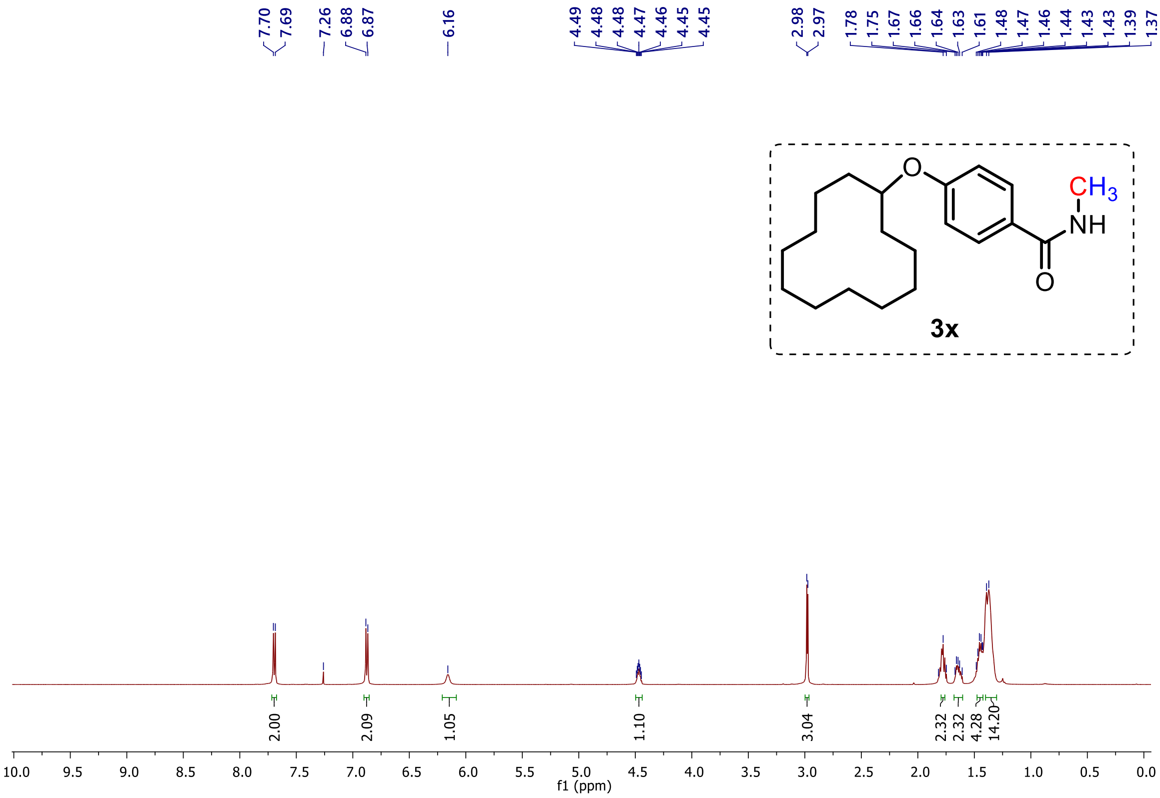


Fig. S77 ^{1}H NMR spectrum of **3x** in $CDCl_3$.

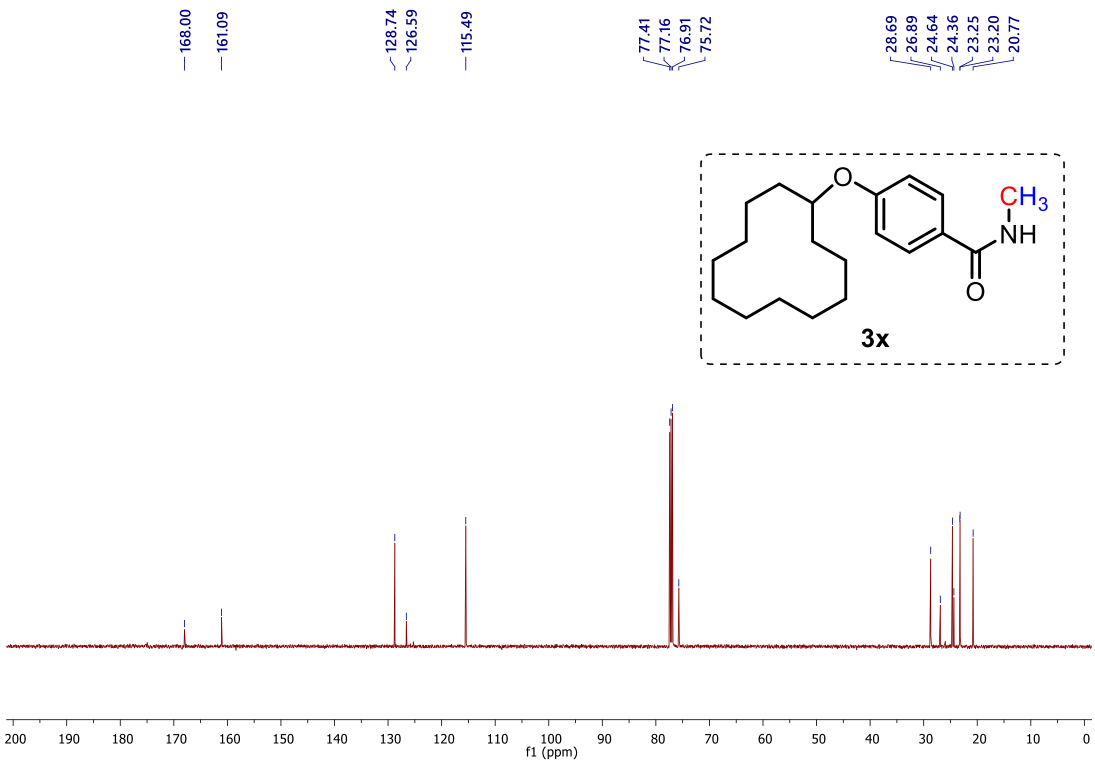


Fig. S78 $^{13}C\{^1H\}$ NMR spectrum of **3x** in $CDCl_3$.

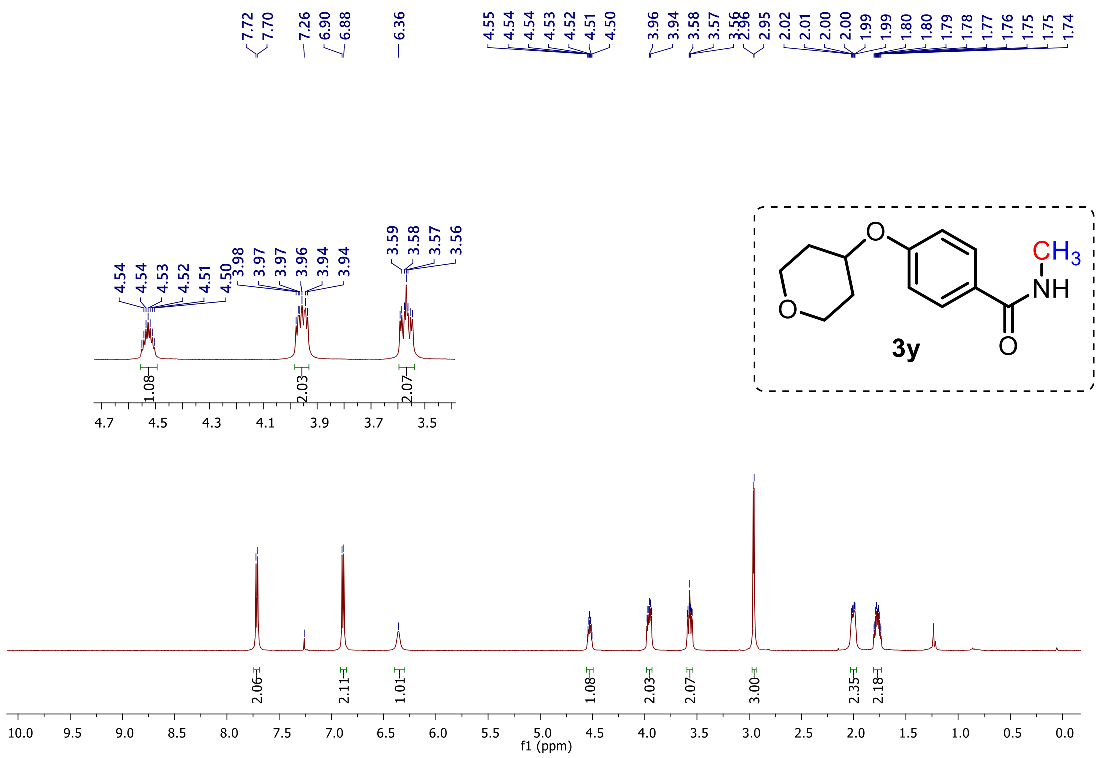


Fig. S79 ^1H NMR spectrum of **3y** in $CDCl_3$.

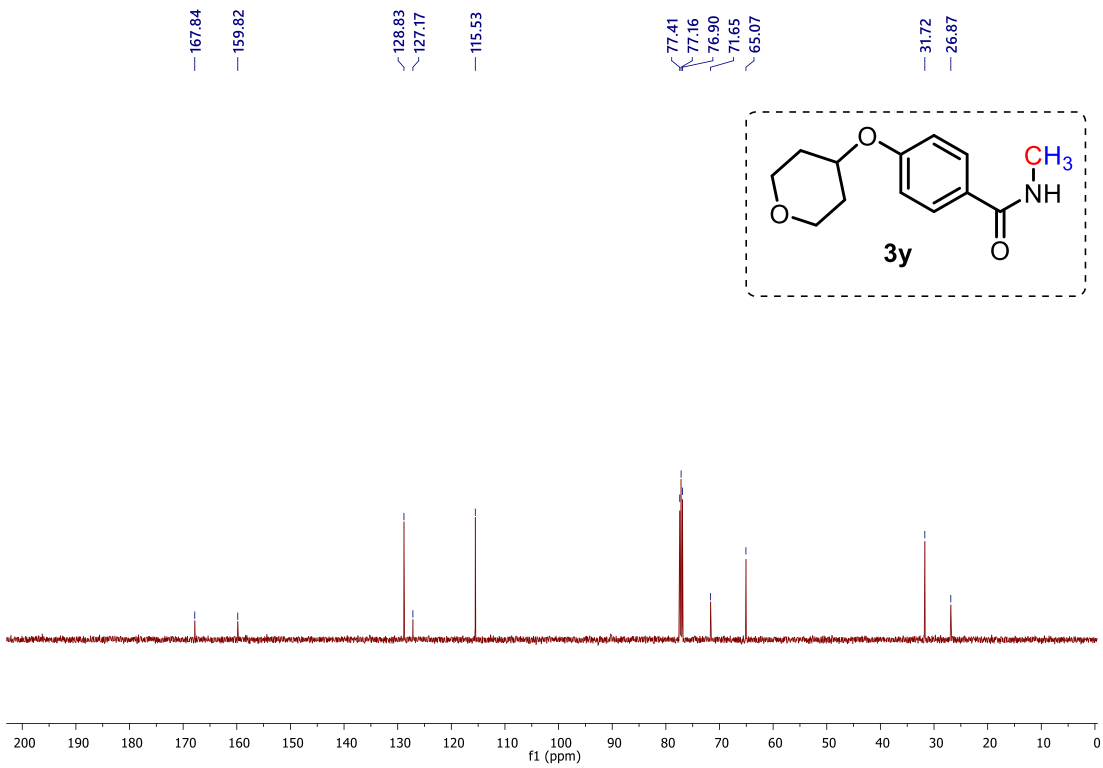


Fig. S80 $^{13}C\{^1H\}$ NMR spectrum of **3y** in $CDCl_3$.

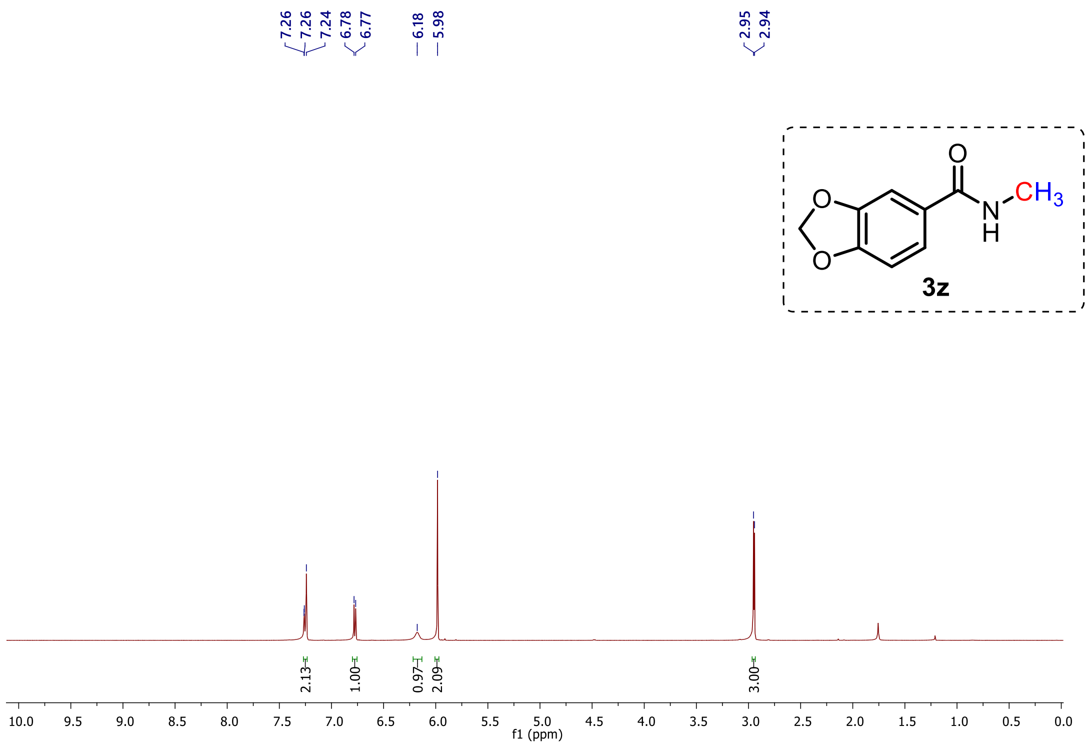


Fig. S81 ^1H NMR spectrum of **3z** in $CDCl_3$.

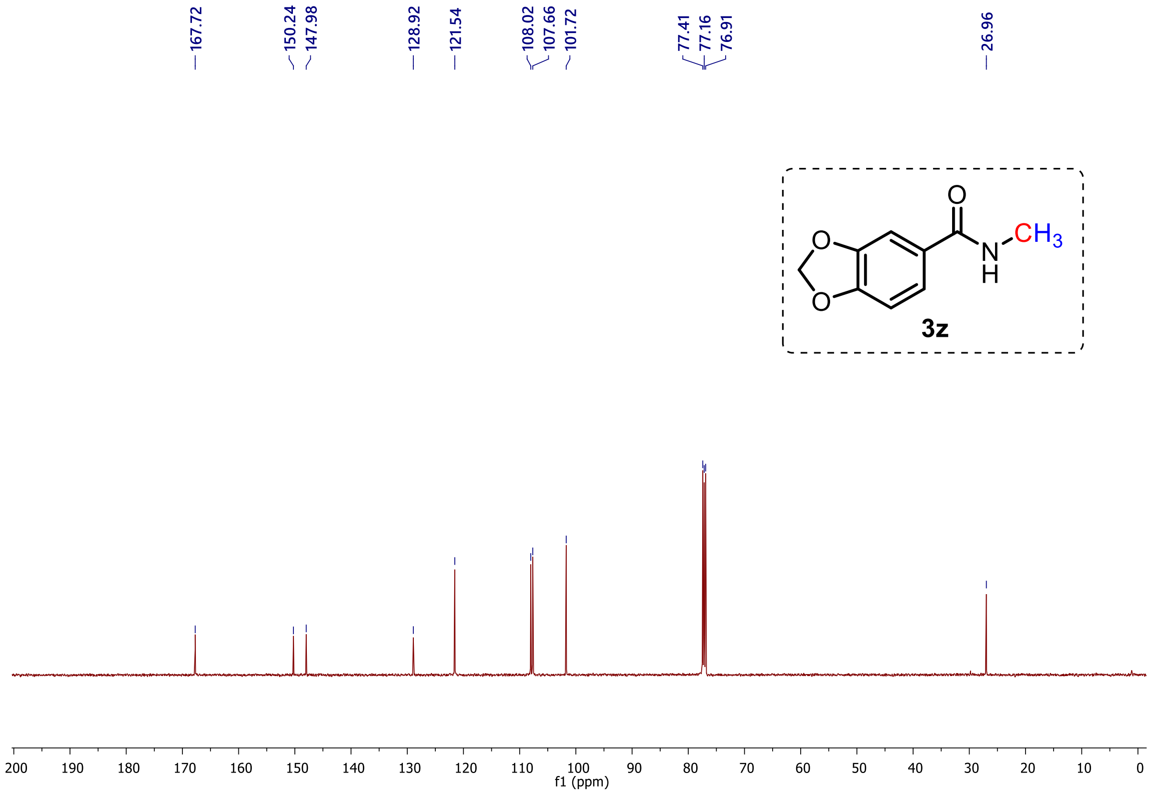


Fig. S82 $^{13}C\{^{1}H\}$ NMR spectrum of **3z** in $CDCl_3$.

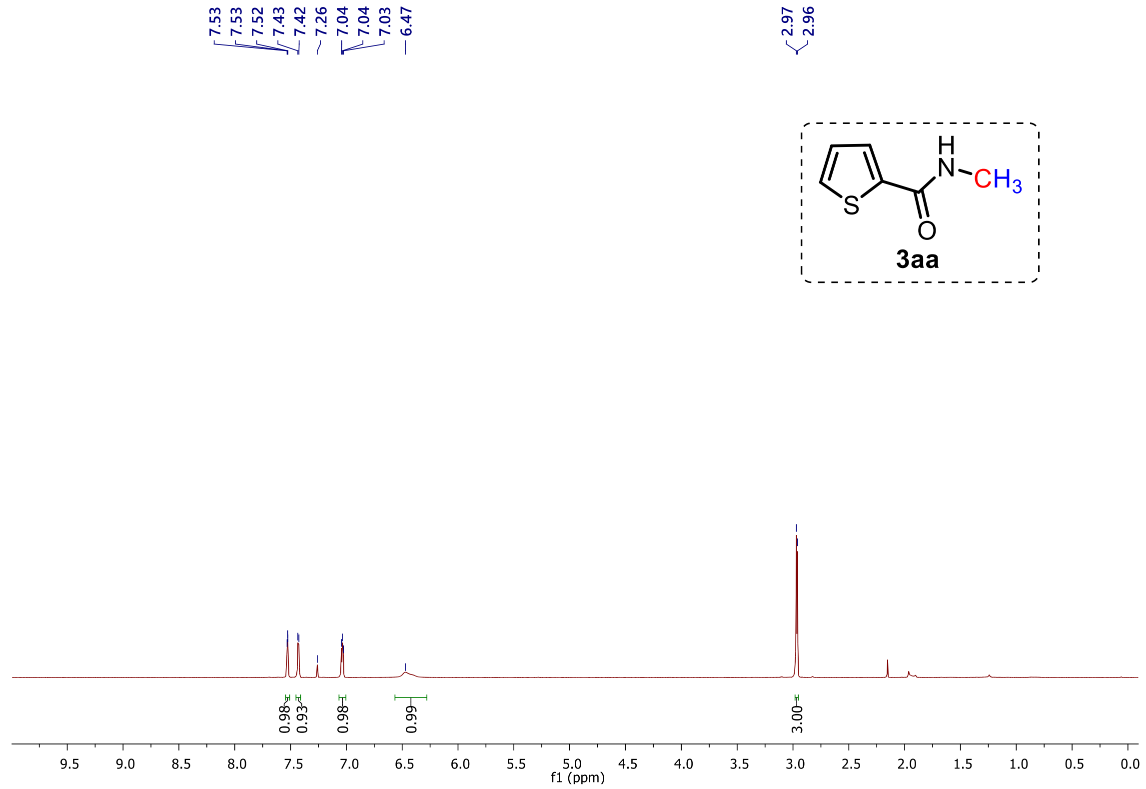


Fig. S83 ^{1}H NMR spectrum of **3aa** in $CDCl_3$.

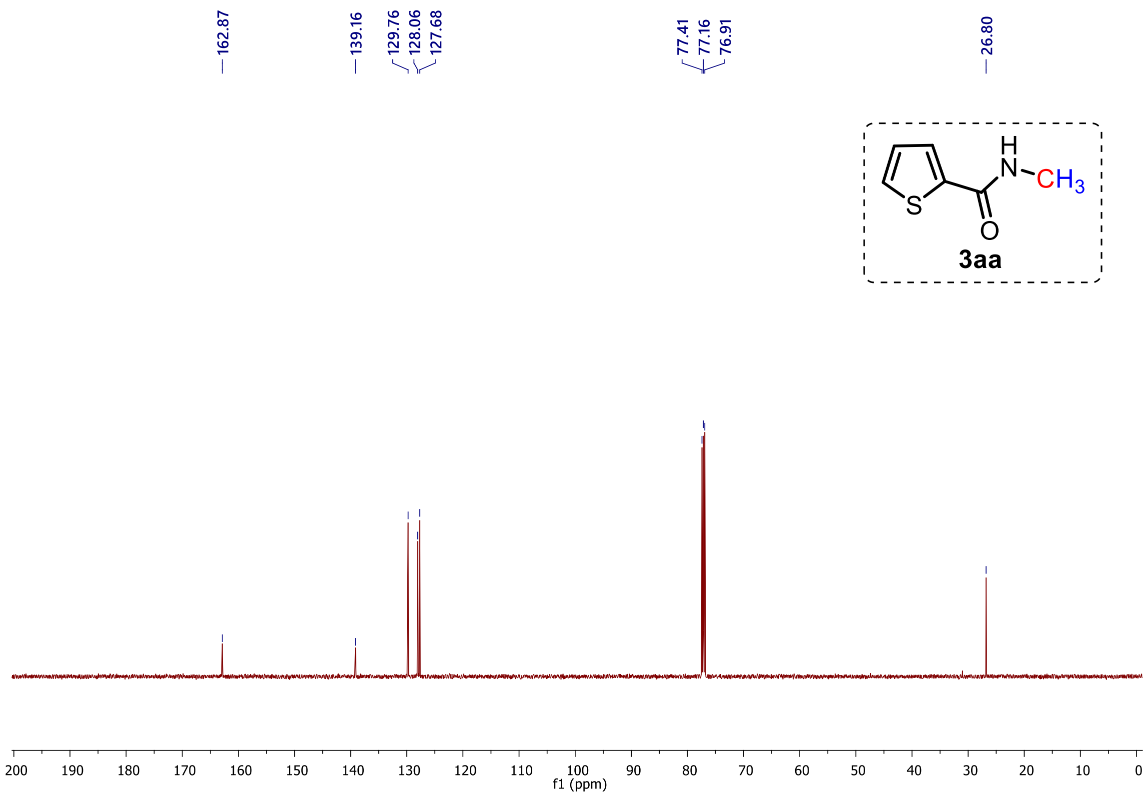


Fig. S84 $^{13}C\{^{1}H\}$ NMR spectrum of **3aa** in $CDCl_3$.

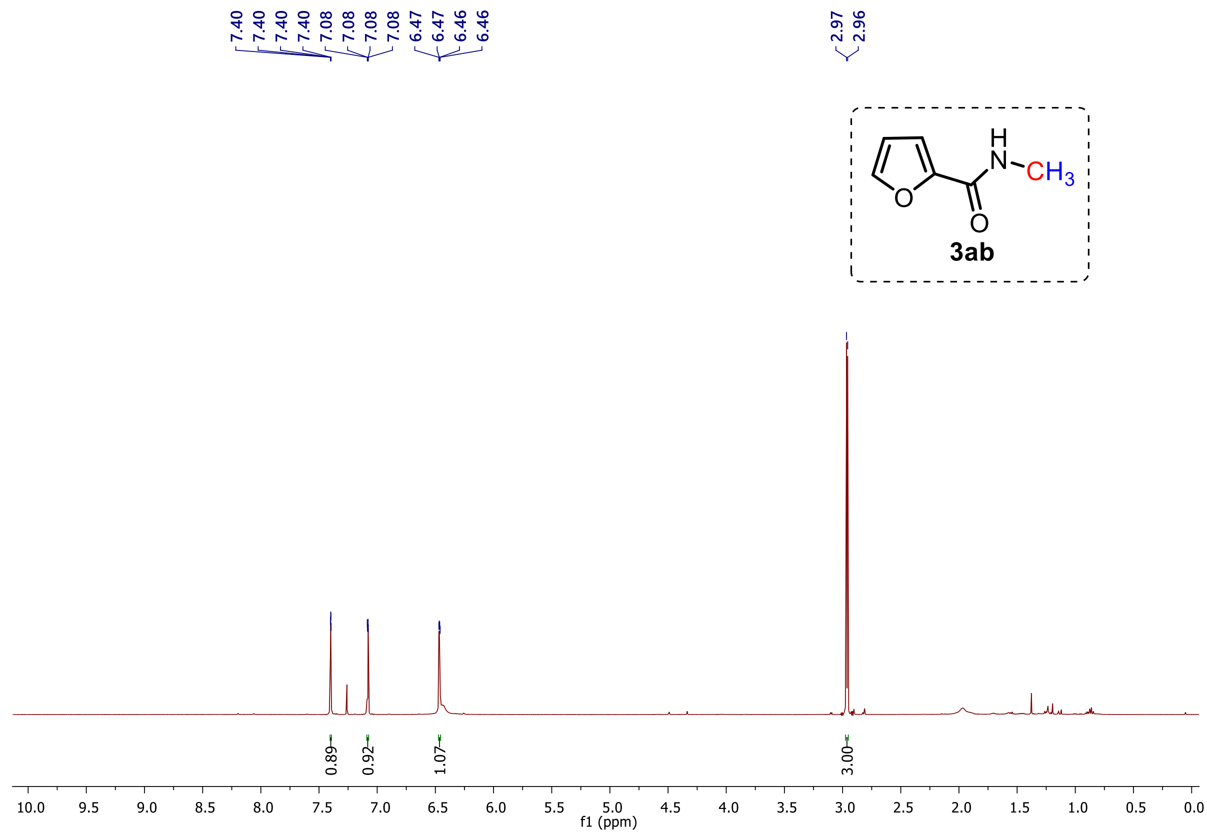


Fig. S85 ^{1}H NMR spectrum of **3ab** in $CDCl_3$.

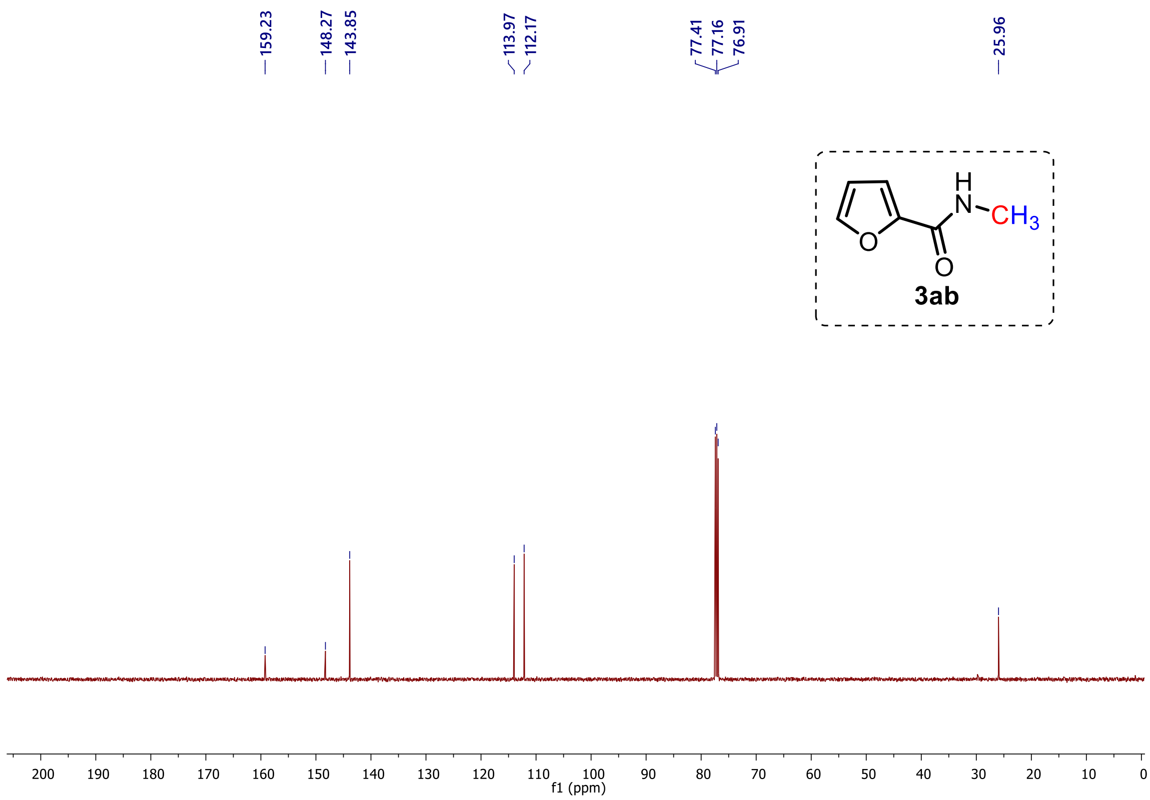


Fig. S86 $^{13}C\{^{1}H\}$ NMR spectrum of **3ab** in $CDCl_3$.

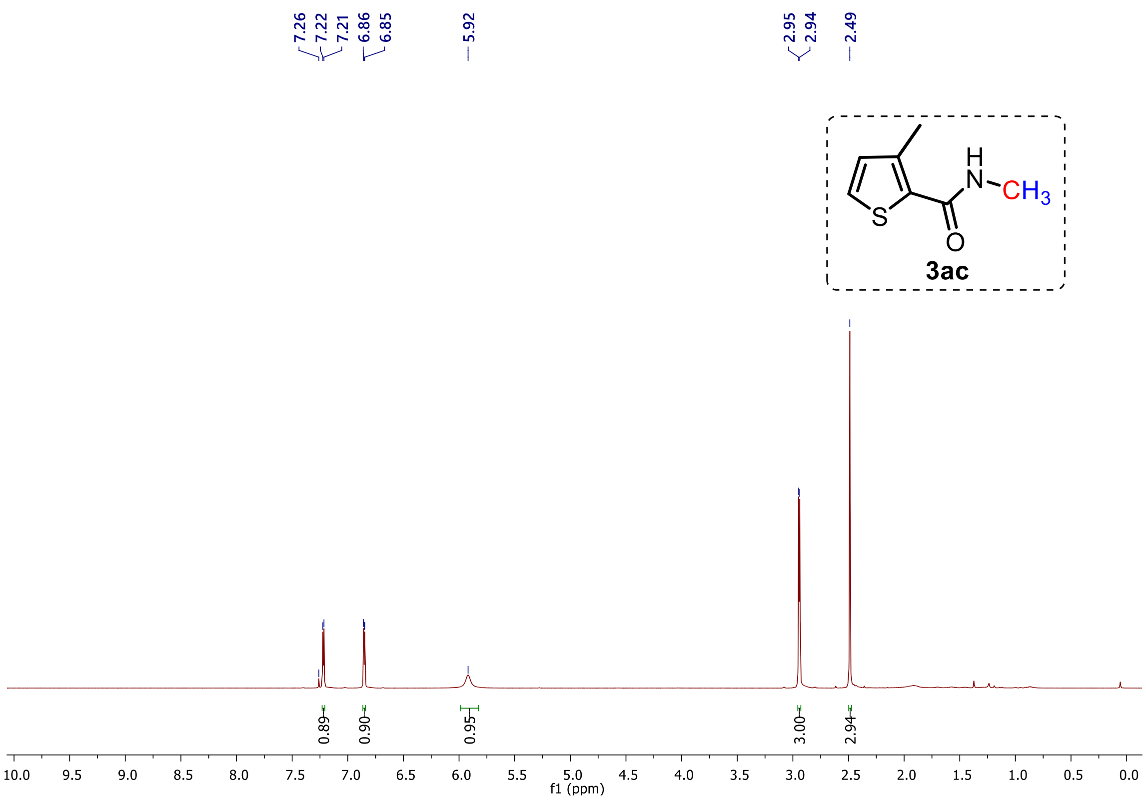


Fig. S87 ^{1}H NMR spectrum of **3ac** in $CDCl_3$.

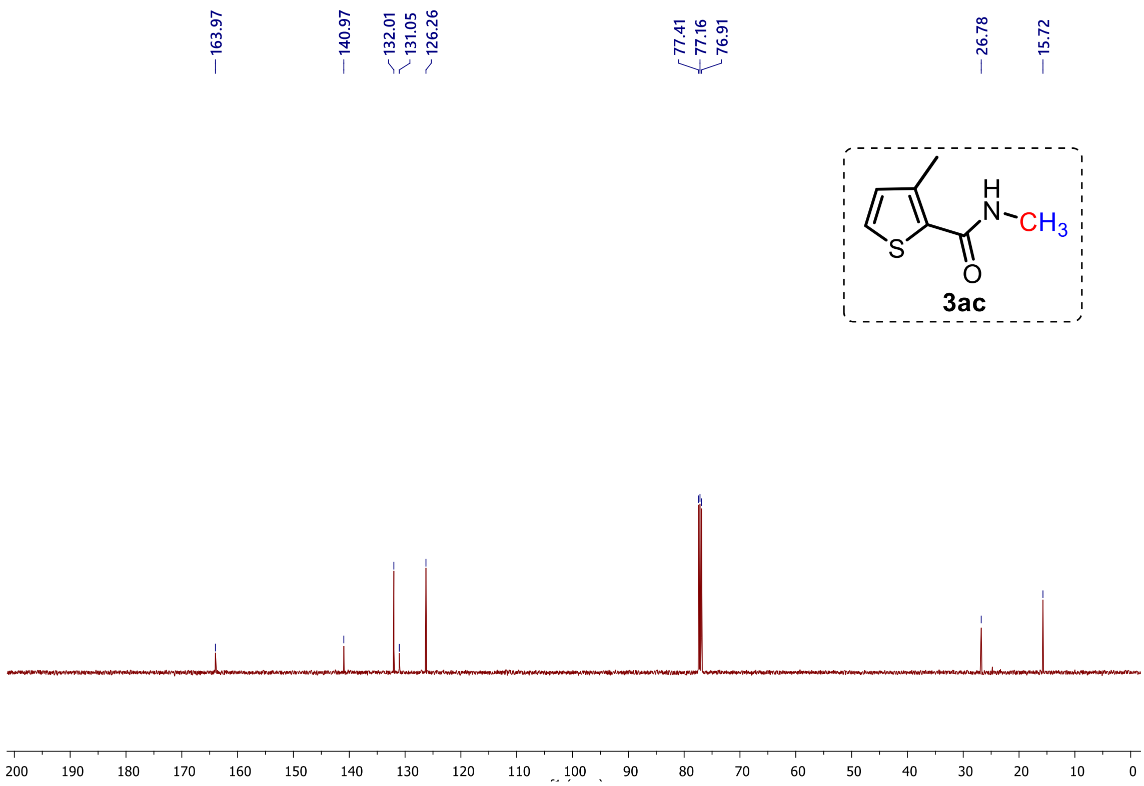


Fig. S88 $^{13}C\{^1H\}$ NMR spectrum of **3ac** in $CDCl_3$.

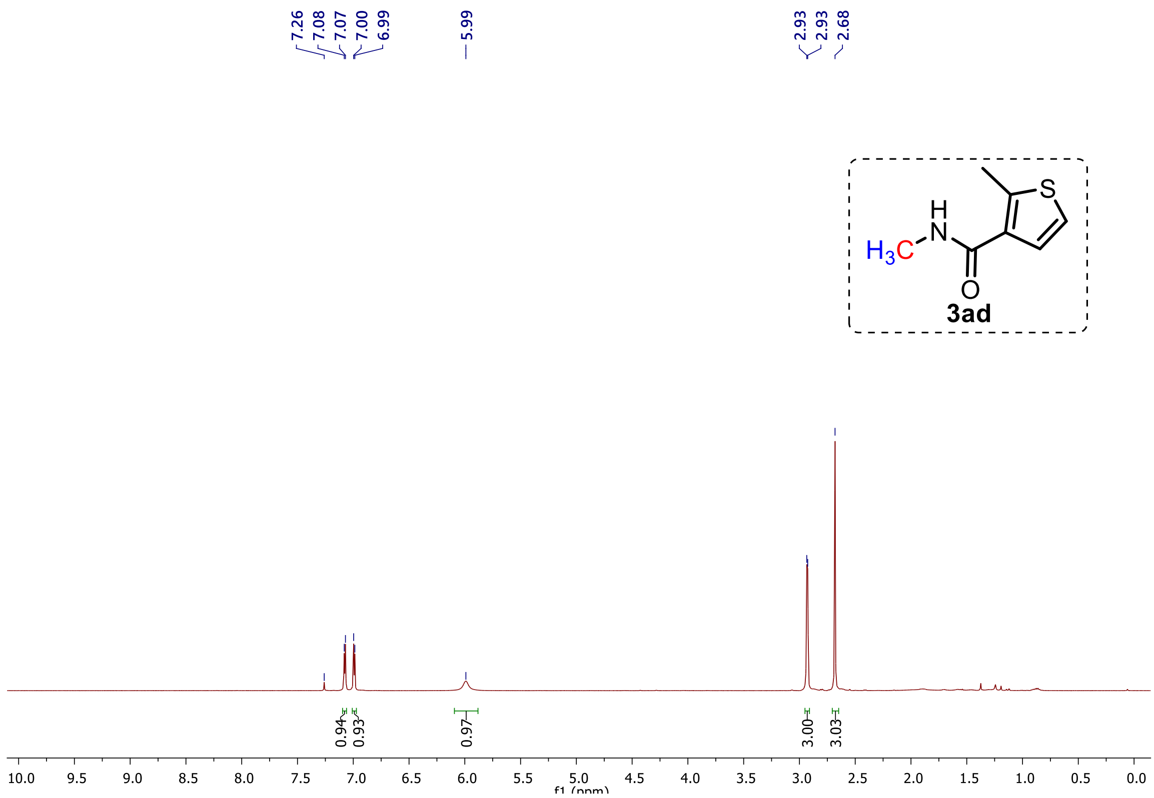


Fig. S89 ^1H NMR spectrum of **3ad** in $CDCl_3$.

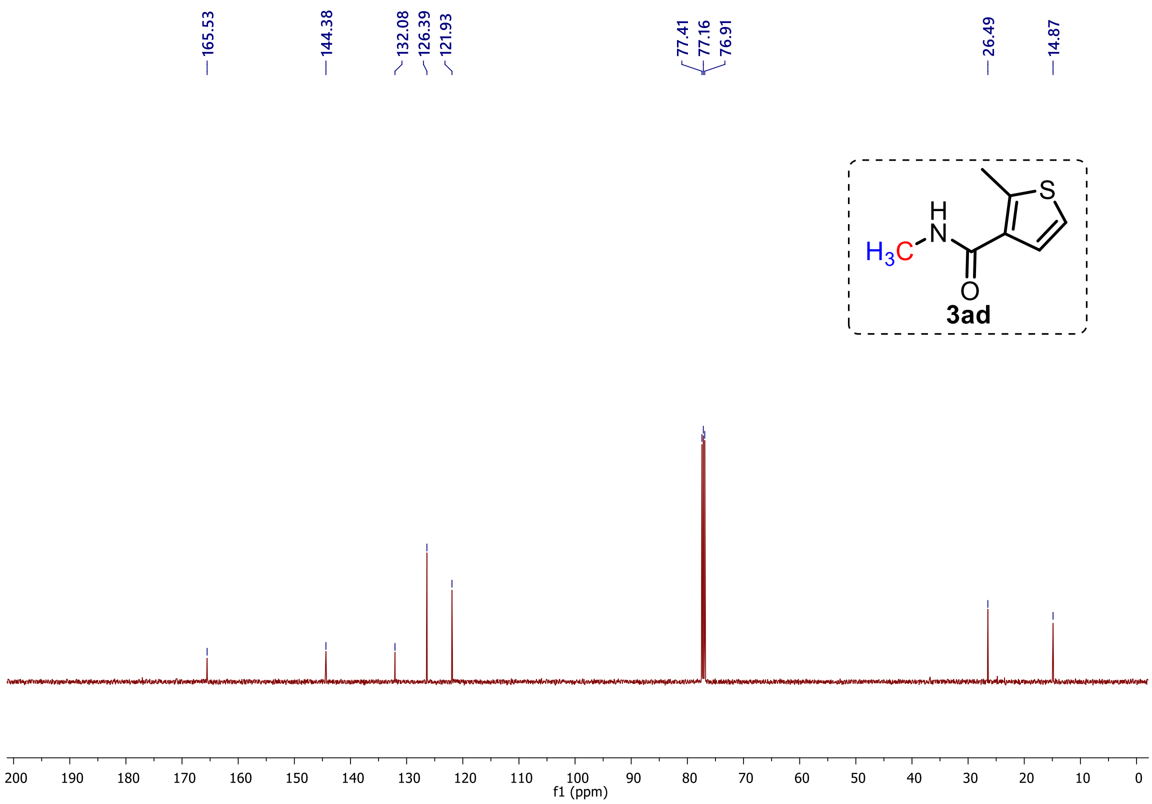


Fig. S90 $^{13}C\{^{1}H\}$ NMR spectrum of **3ad** in $CDCl_3$.

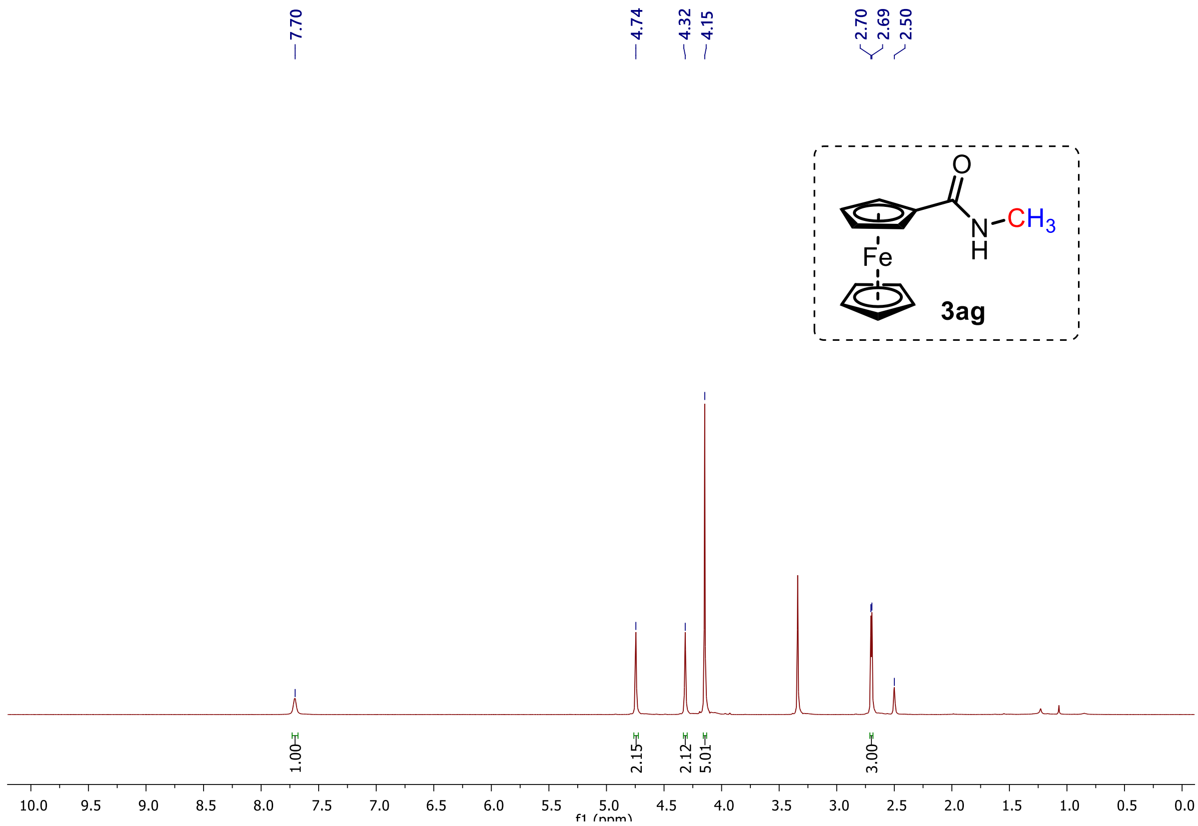


Fig. S91 ^{1}H NMR spectrum of **3ag** in DMSO-d_6.

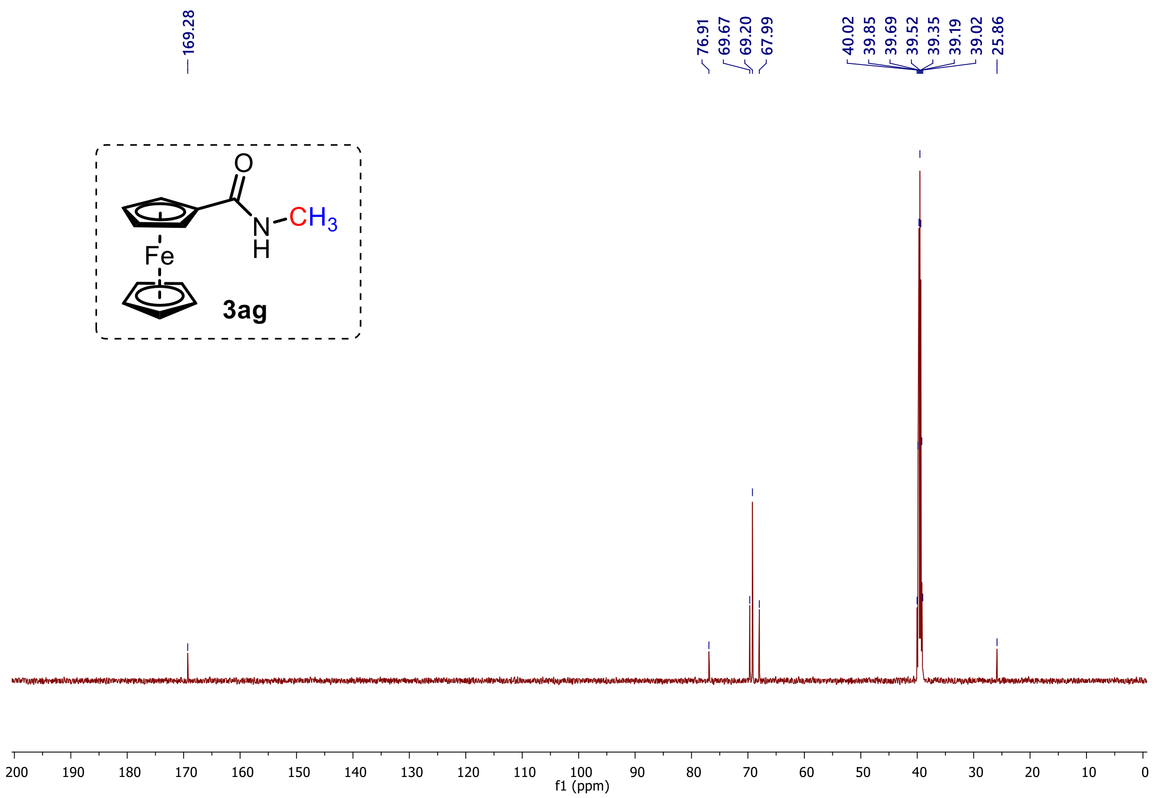


Fig. S92 $^{13}C\{^1H\}$ NMR spectrum of **3ag** in DMSO-d_6.

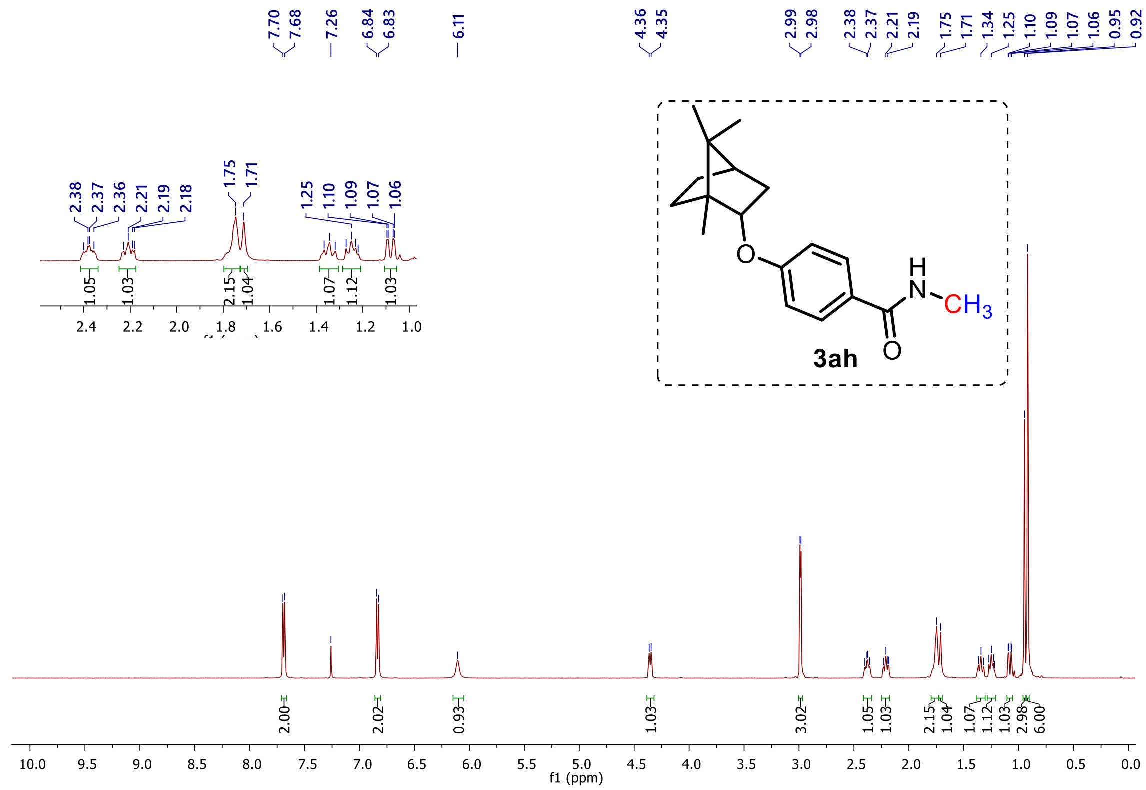


Fig. S93 ^1H NMR spectrum of **3ah** in $CDCl_3$.

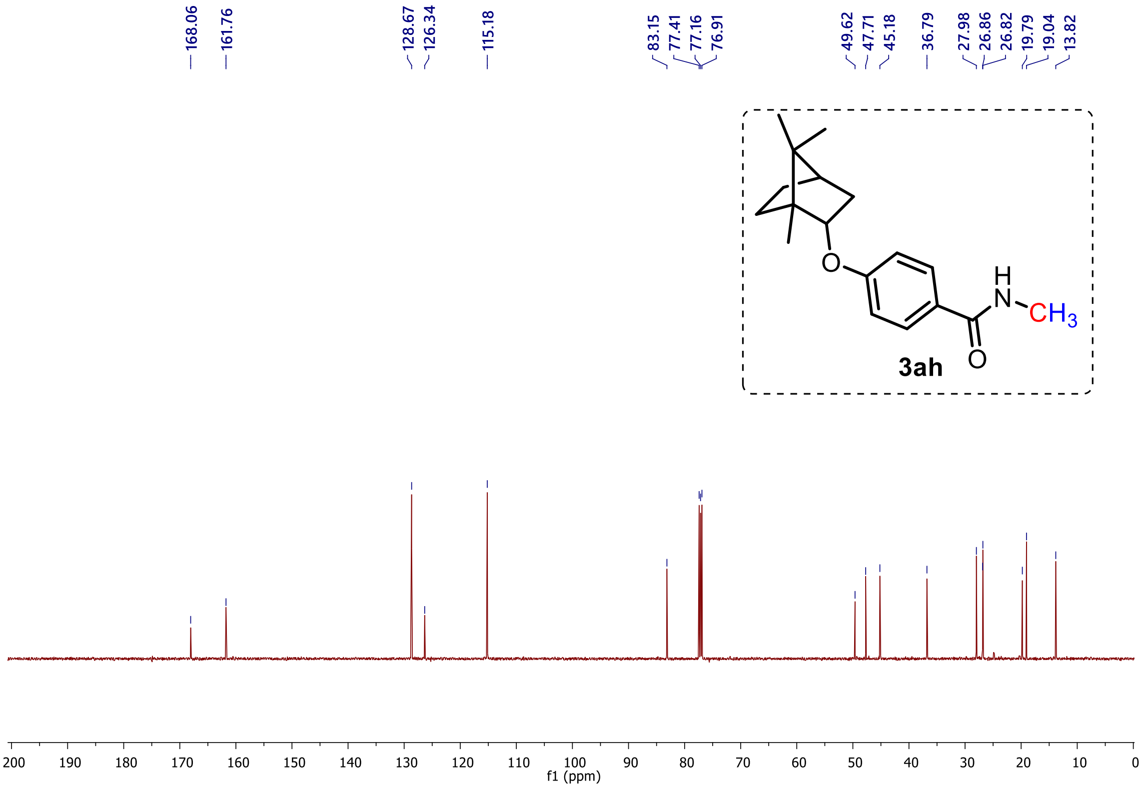


Fig. S94 $^{13}C\{^{1}H\}$ NMR spectrum of **3ah** in $CDCl_3$.

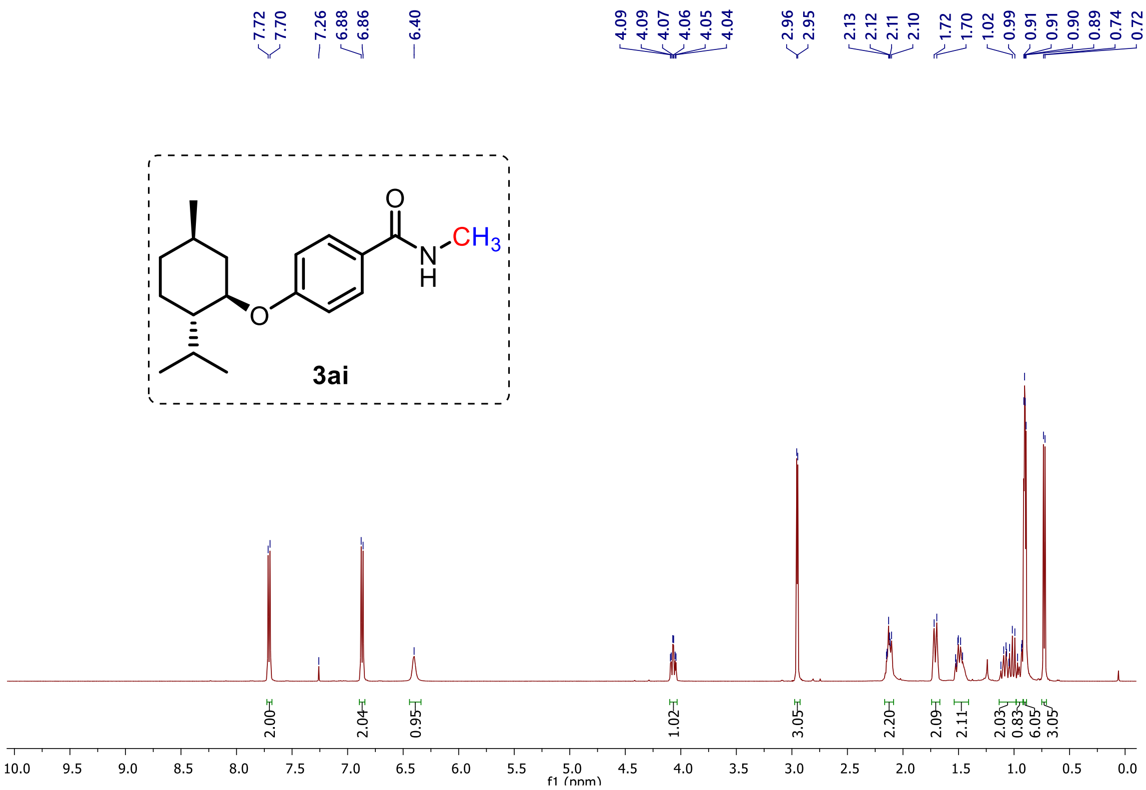


Fig. S95 ^{1}H NMR spectrum of **3ai** in $CDCl_3$.

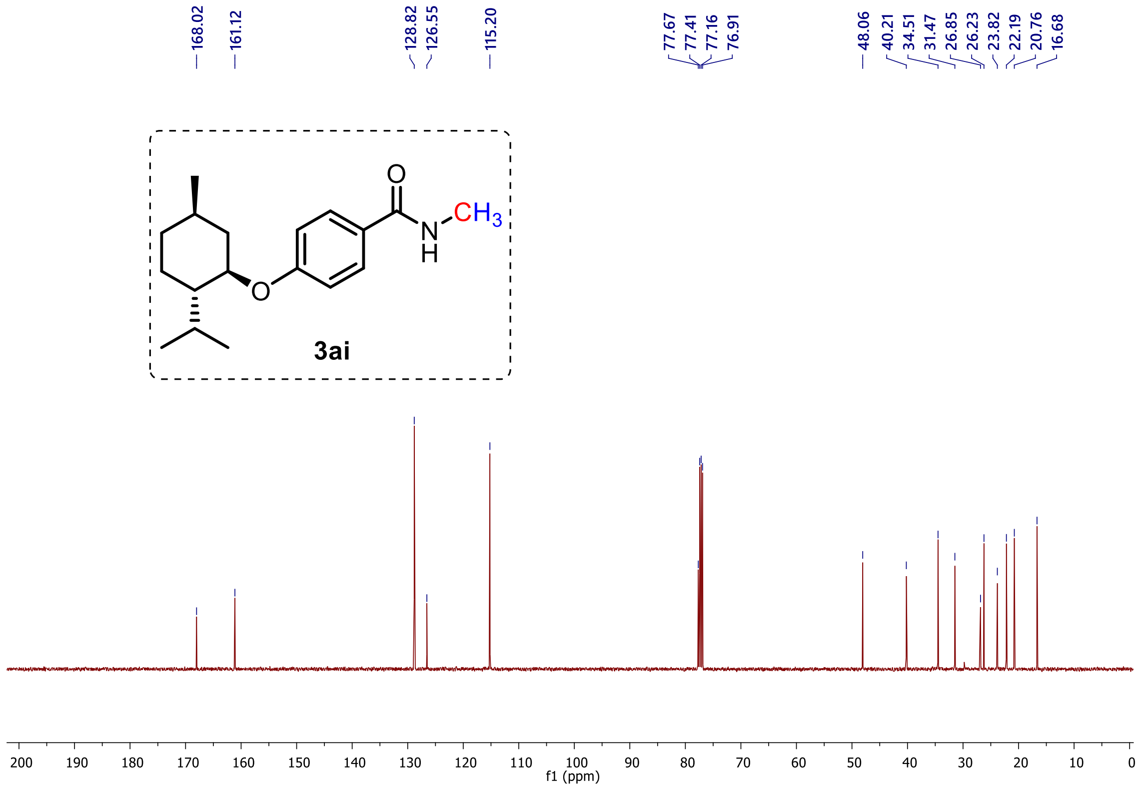


Fig. S96 $^{13}C\{^1H\}$ NMR spectrum of **3ai** in $CDCl_3$.

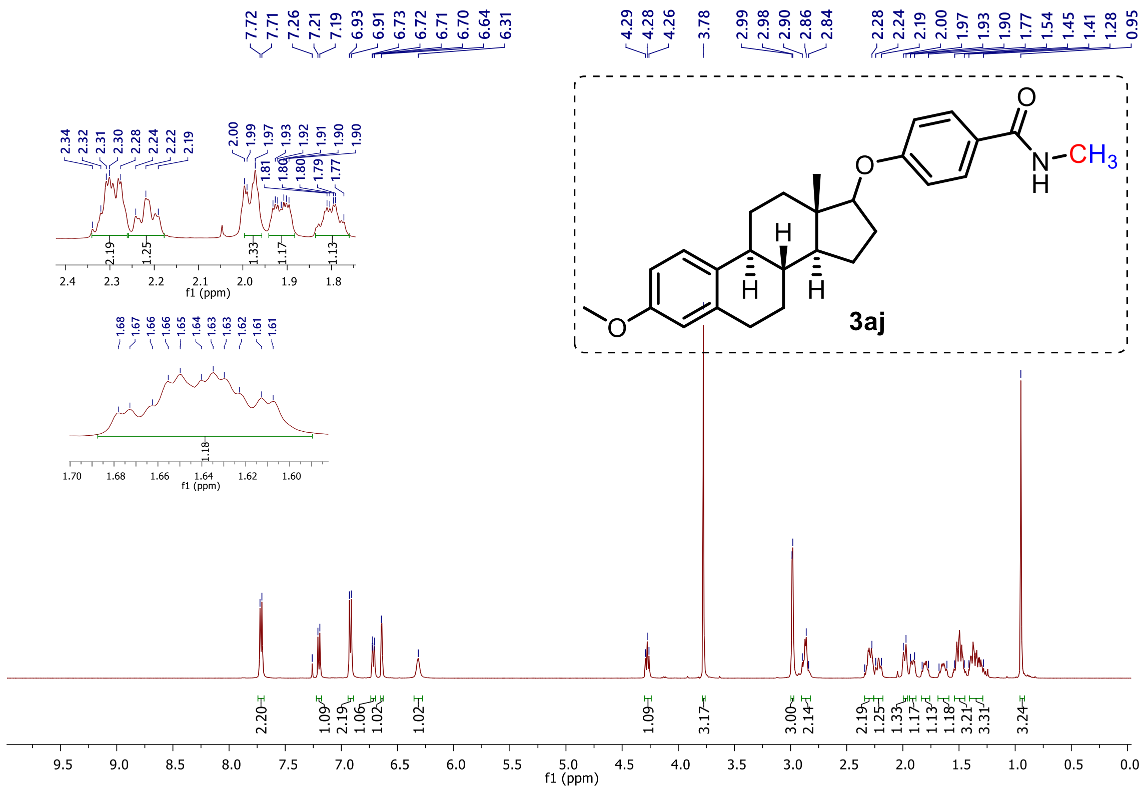


Fig. S97 ^1H NMR spectrum of **3aj** in $CDCl_3$.

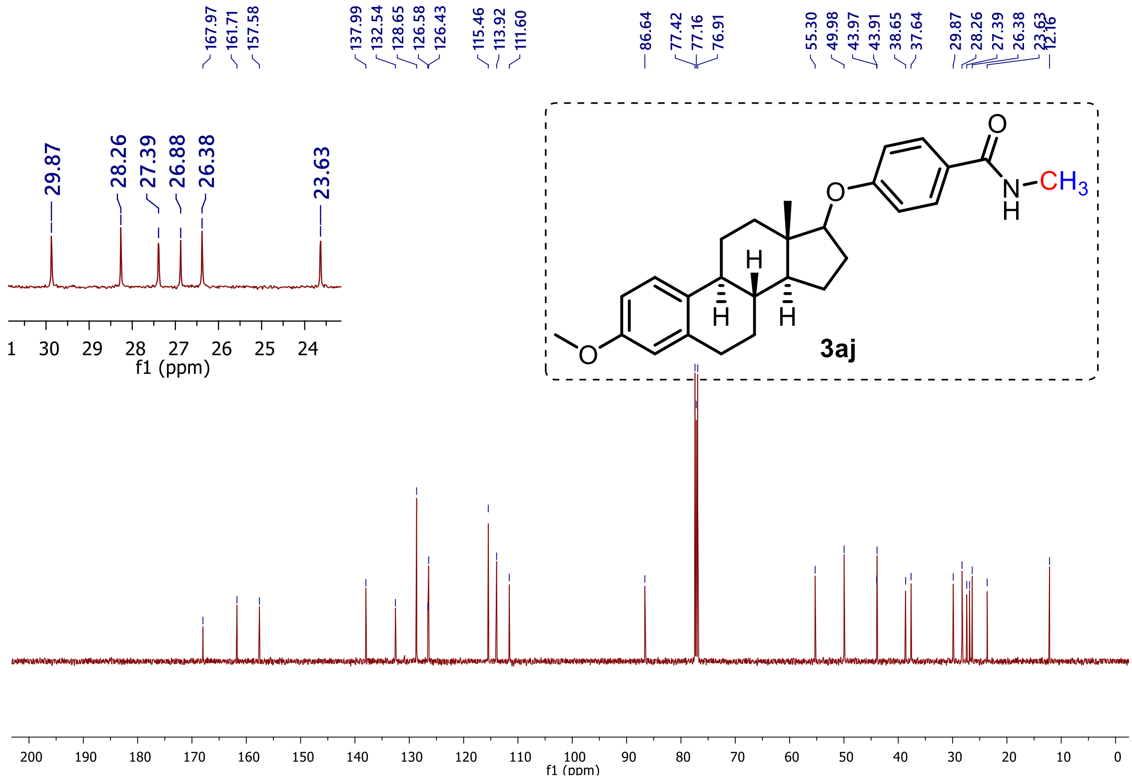


Fig. S98 $^{13}C\{^{1}H\}$ NMR spectrum of **3aj** in $CDCl_3$.

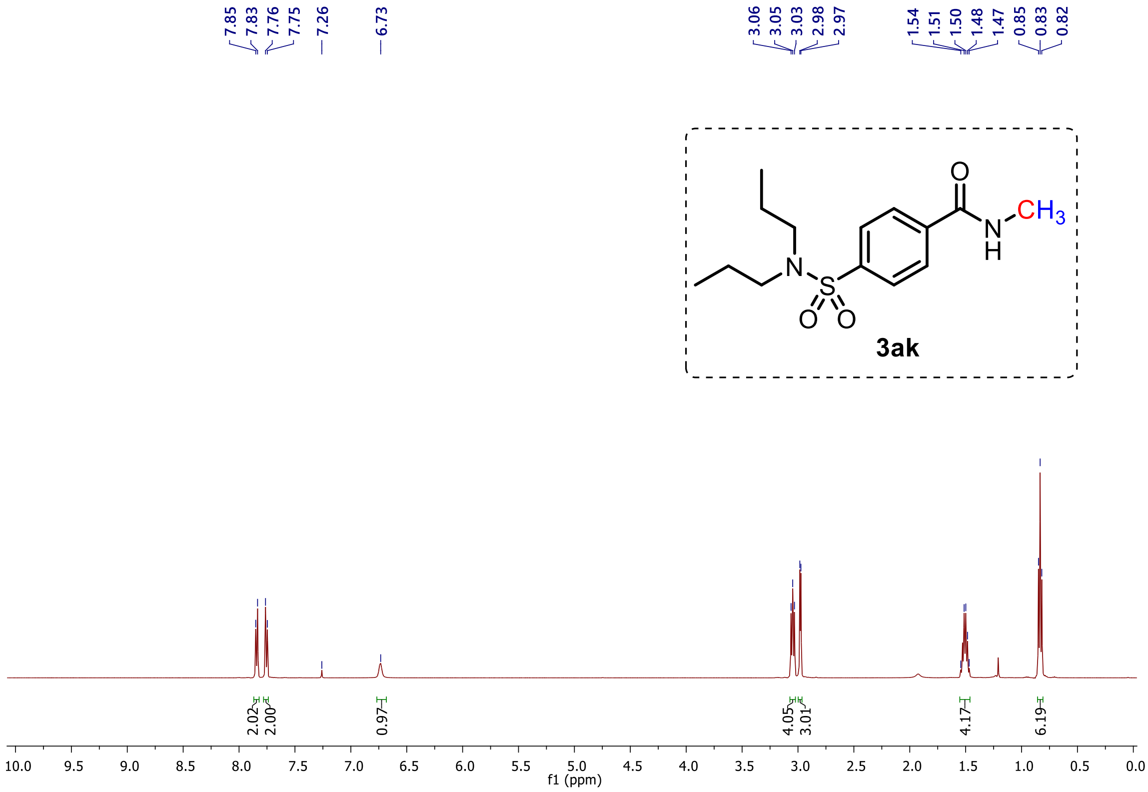


Fig. S99 ^{1}H NMR spectrum of **3ak** in $CDCl_3$.

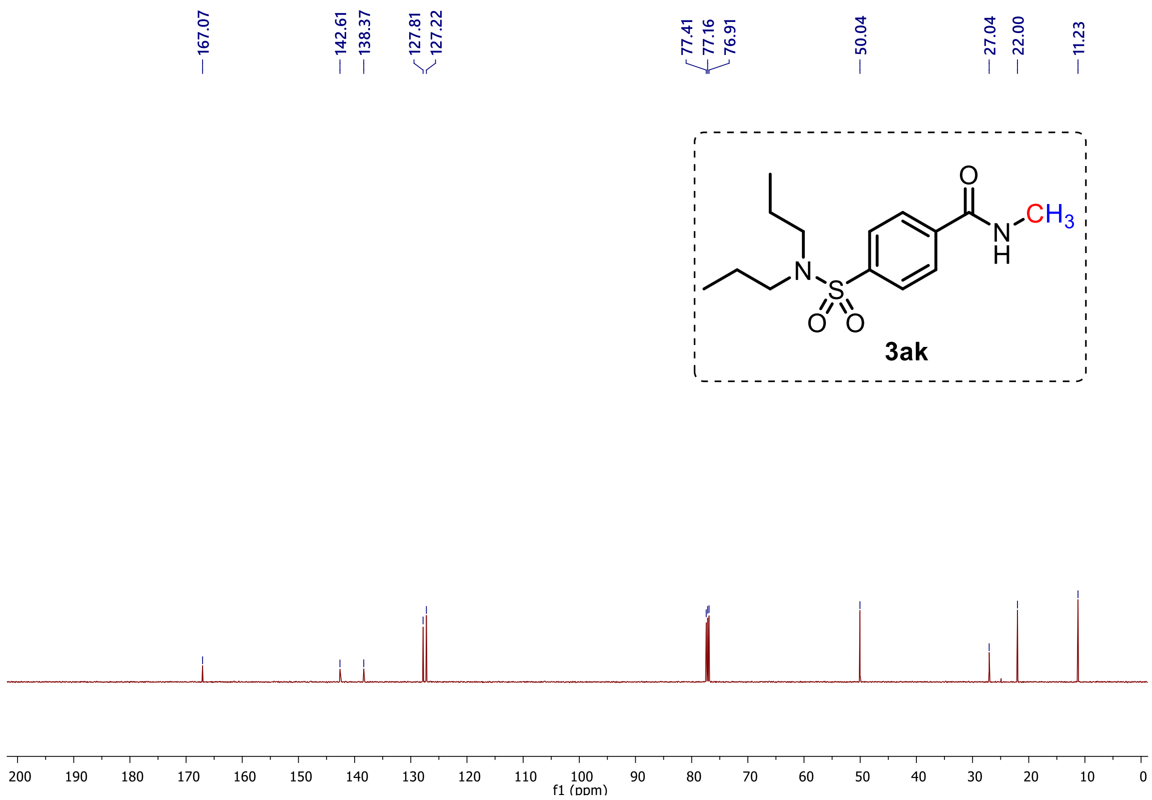


Fig. S100 $^{13}C\{^{1}H\}$ NMR spectrum of **3ak** in $CDCl_3$.

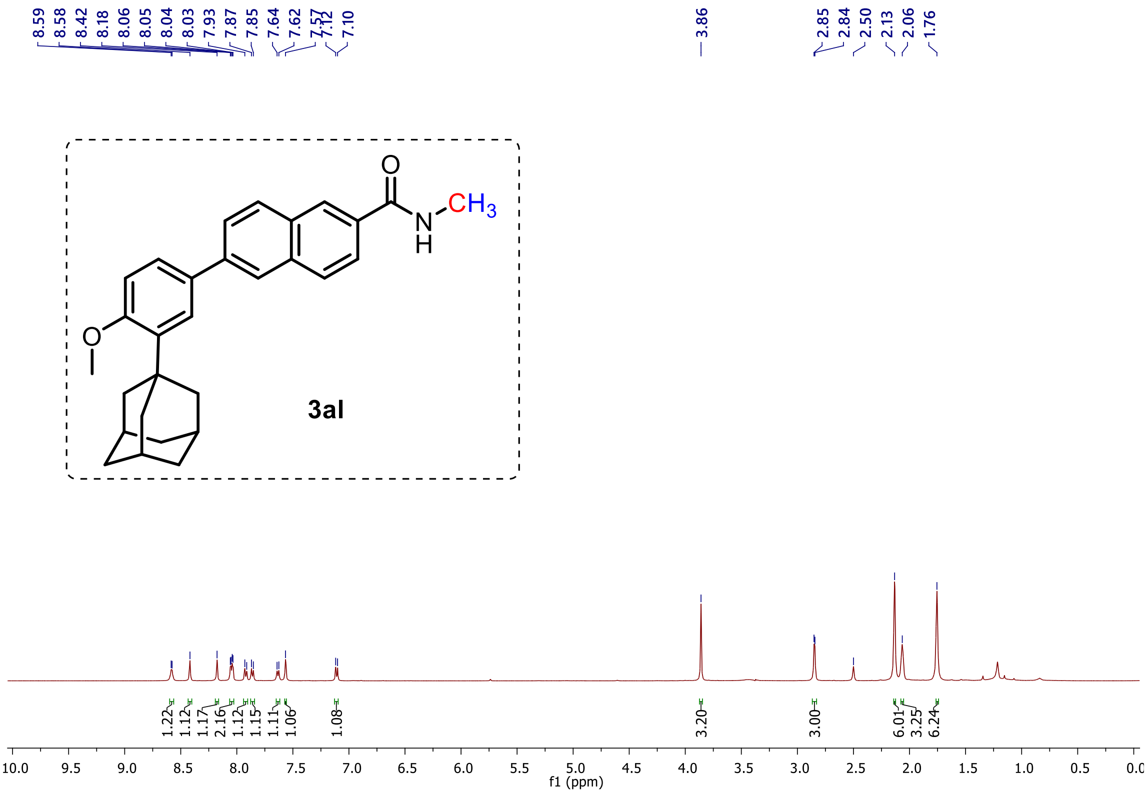


Fig. S101 ^{1}H NMR spectrum of **3al** in in DMSO-d_6.

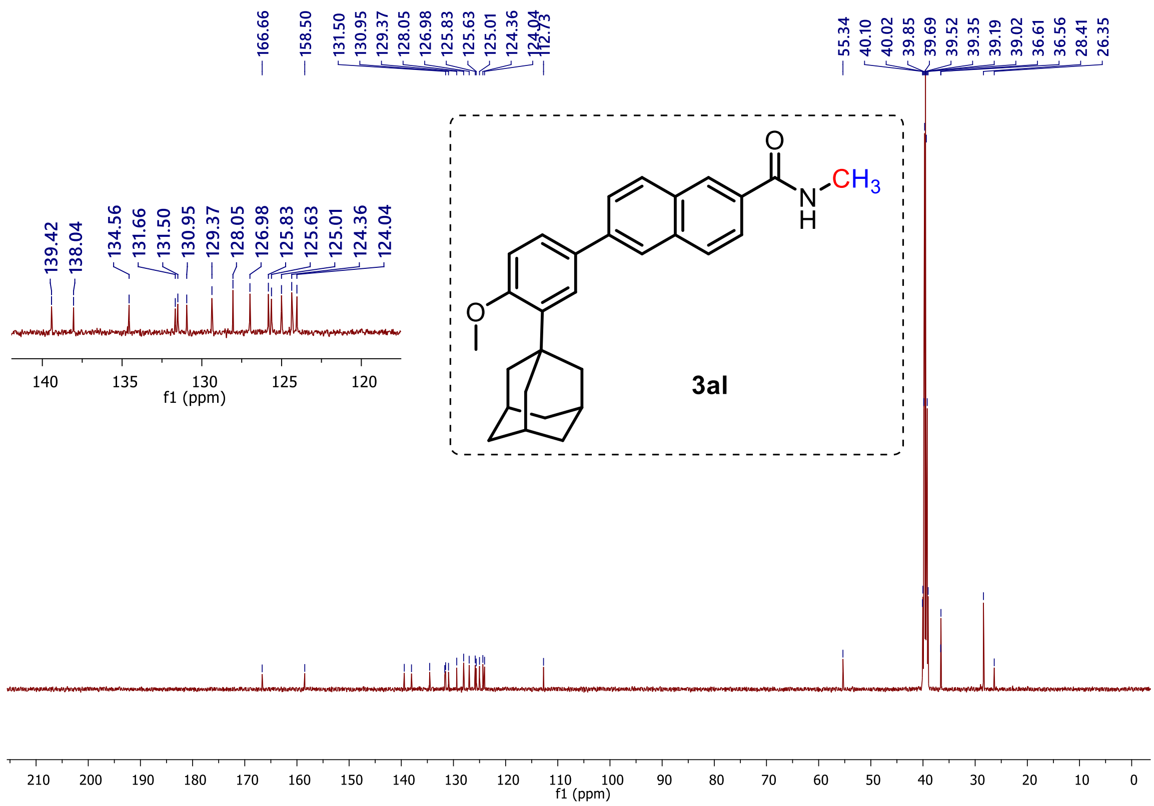


Fig.S102 ^{13}C{^{1}H} NMR spectrum of **3al** in in DMSO-d$_6$.

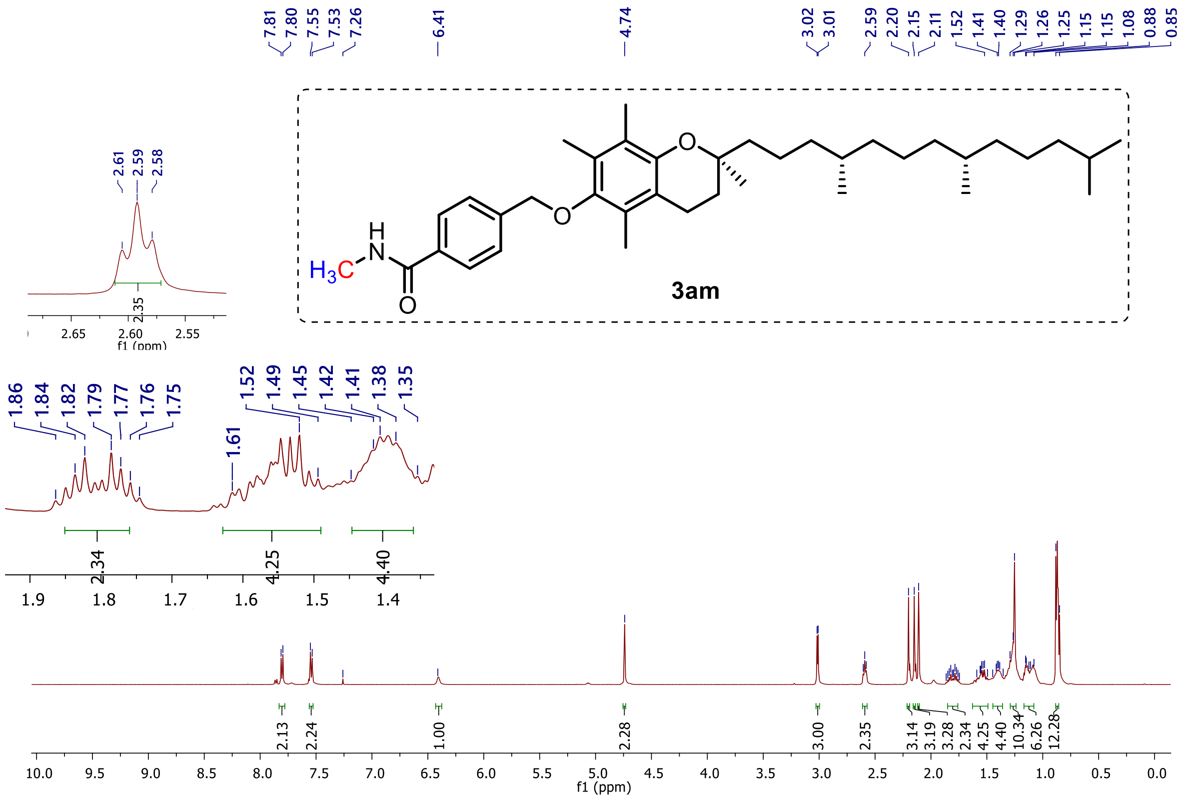


Fig.S103 ^{1}H NMR spectrum of **3am** in $CDCl_3$.

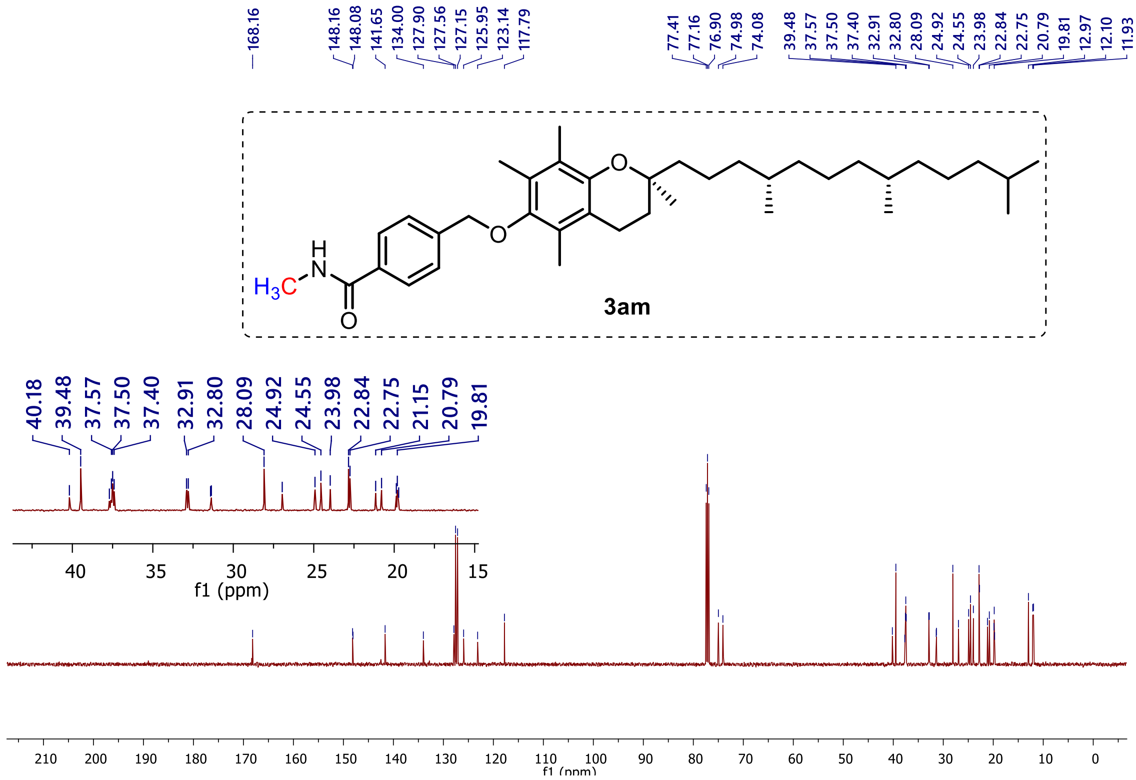


Fig.S104 $^{13}C\{^{1}H\}$ NMR spectrum of **3am** in $CDCl_3$.

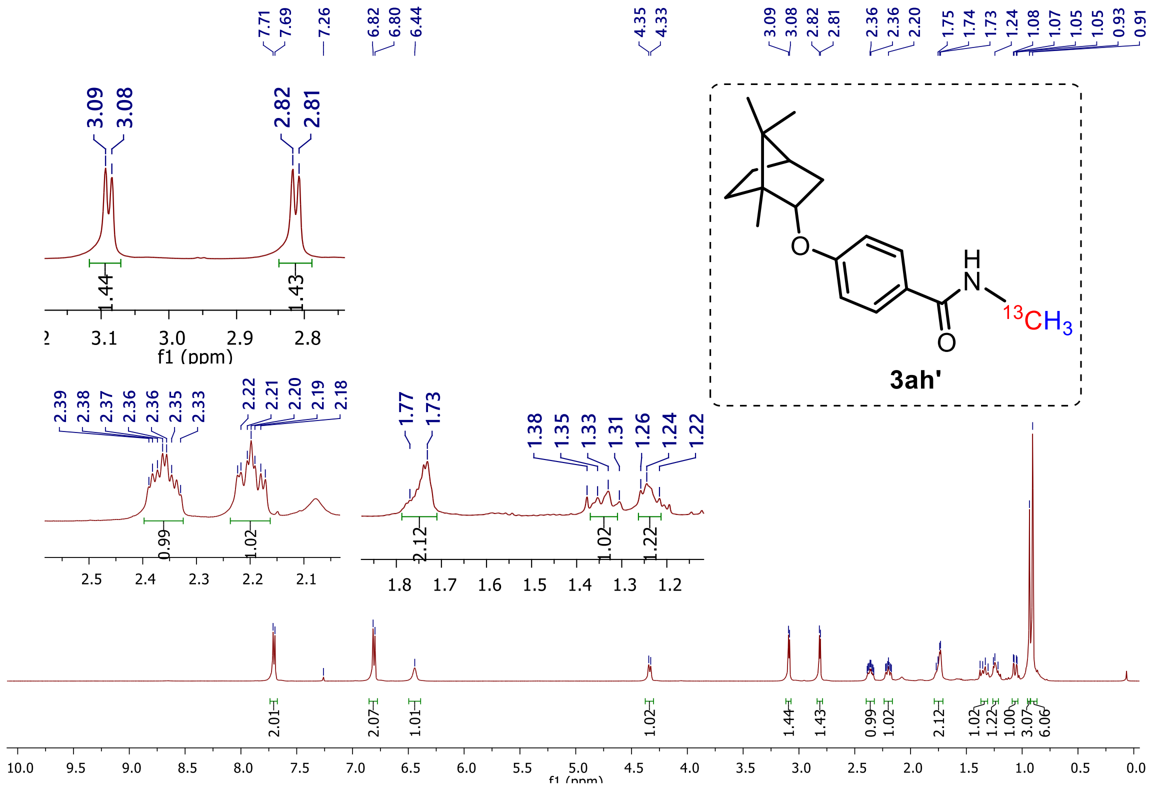


Fig.S105 ^{1}H NMR spectrum of **3ah’** in $CDCl_3$.

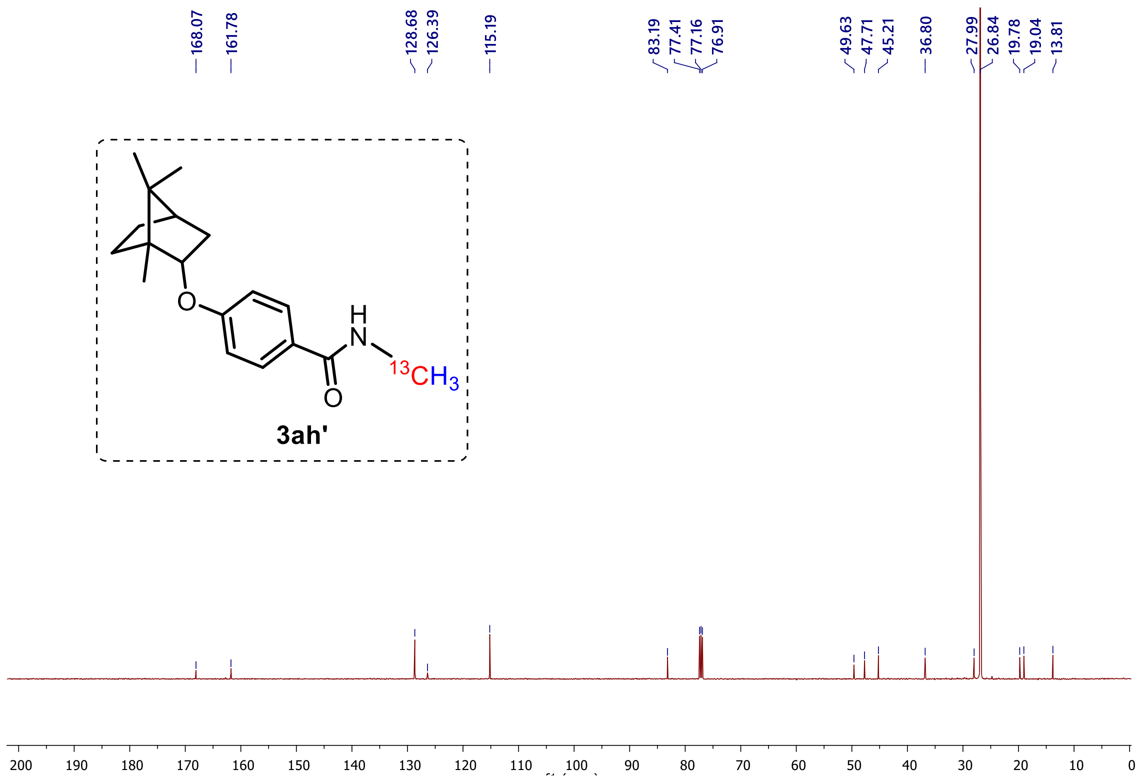


Fig.S106 $^{13}C\{^{1}H\}$ NMR spectrum of **3ah'** in $CDCl_3$.

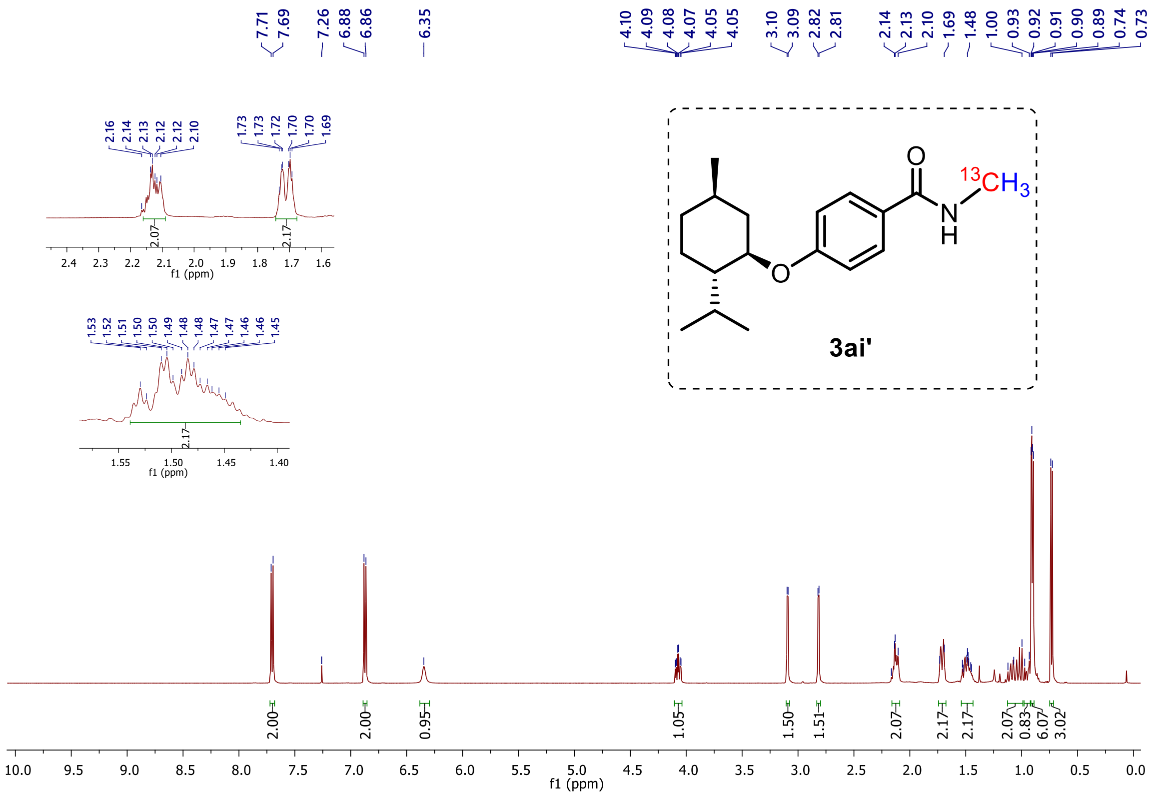


Fig.S107 ^{1}H NMR spectrum of **3ai'** in $CDCl_3$.

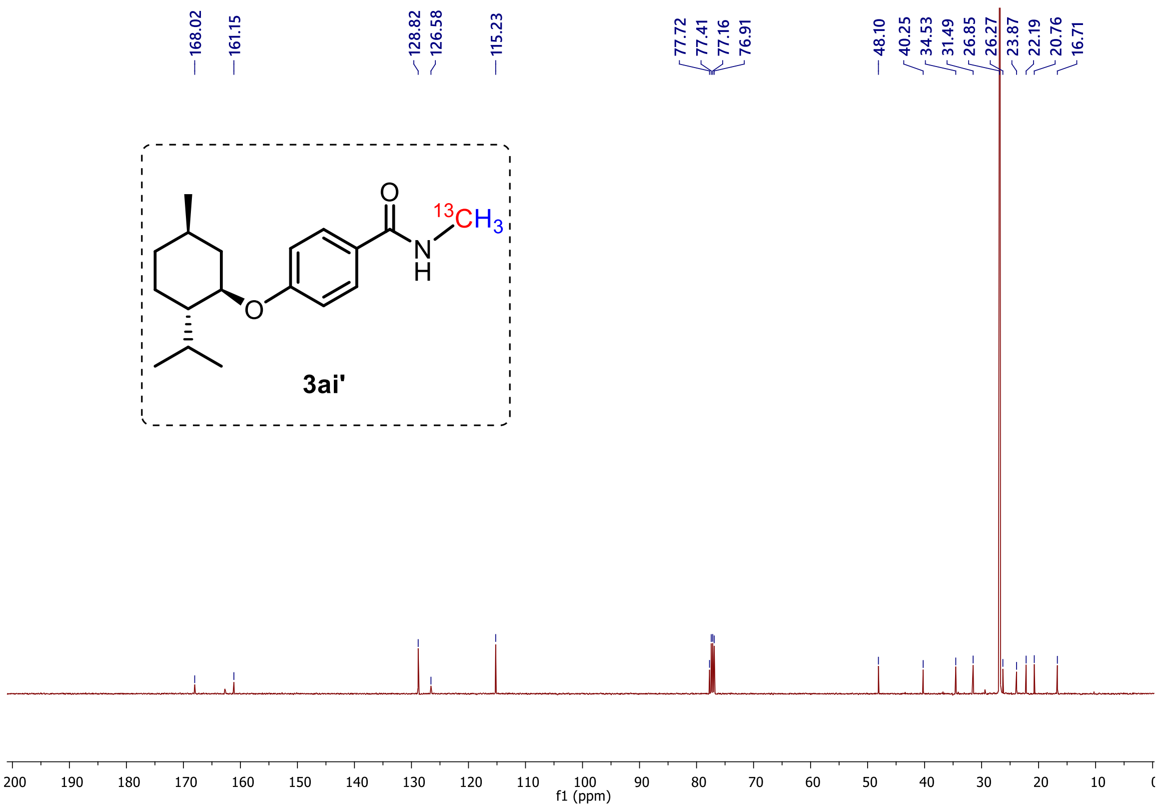


Fig.S108 ^{13}C{^{1}H} NMR spectrum of **3ai’** in $CDCl_3$.

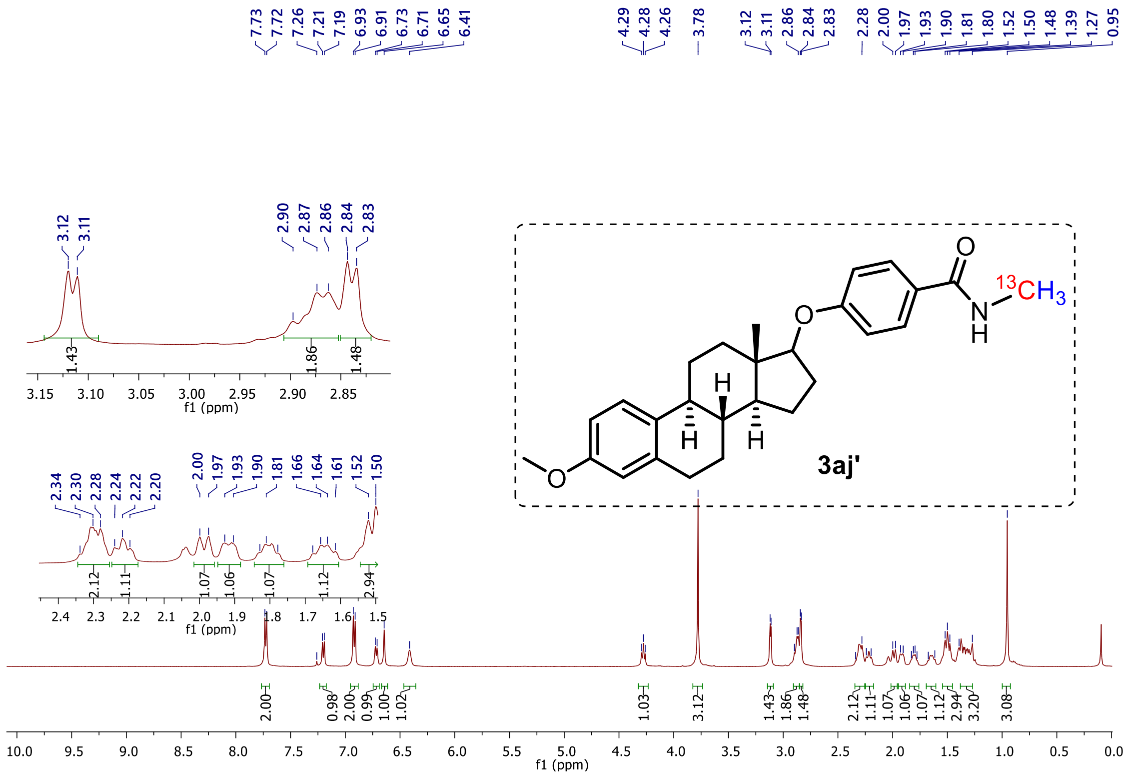


Fig.S109 ^{1}H NMR spectrum of **3aj’** in $CDCl_3$.

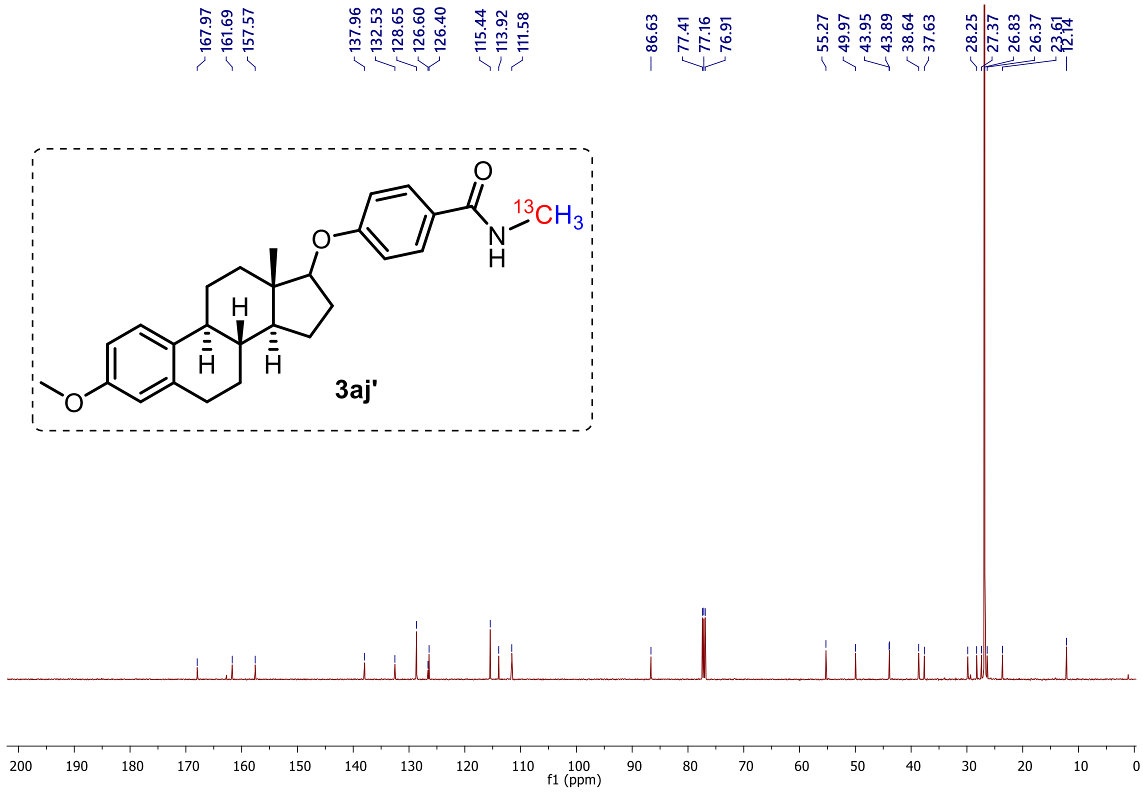


Fig.S110 $^{13}C\{^{1}H\}$ NMR spectrum of **3aj'** in $CDCl_3$.

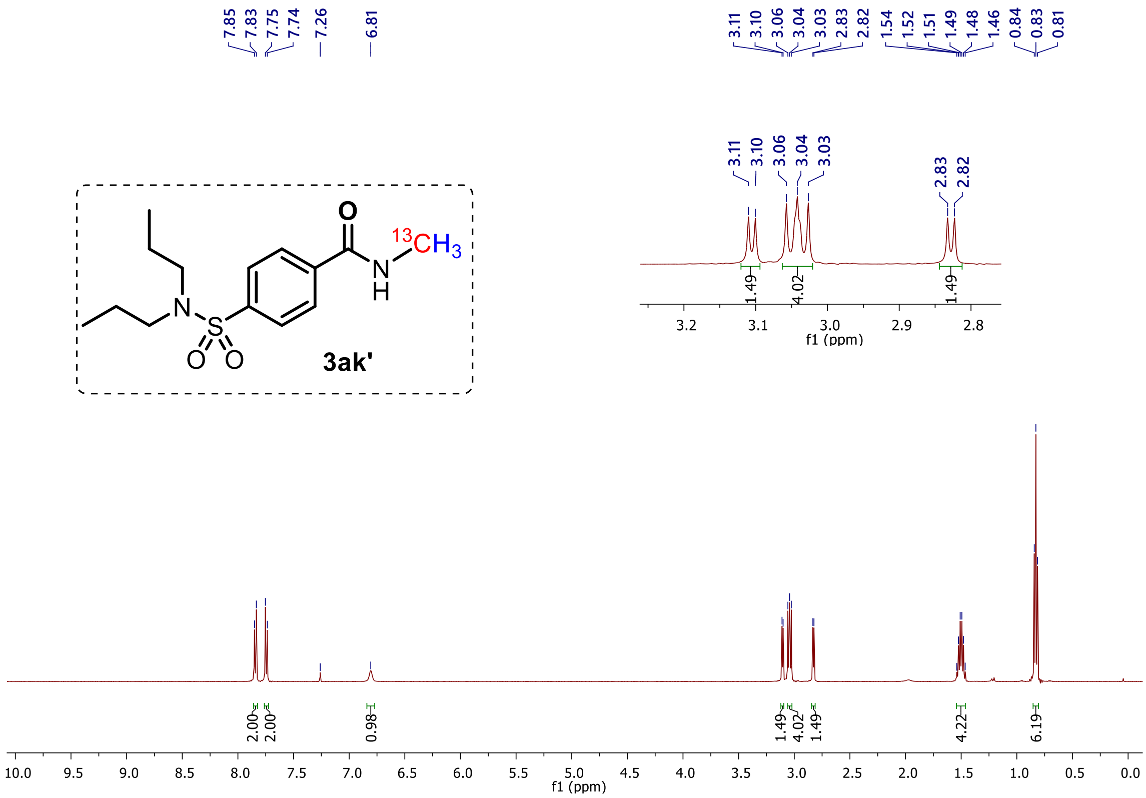


Fig.S111 ^{1}H NMR spectrum of **3ak'** in $CDCl_3$.

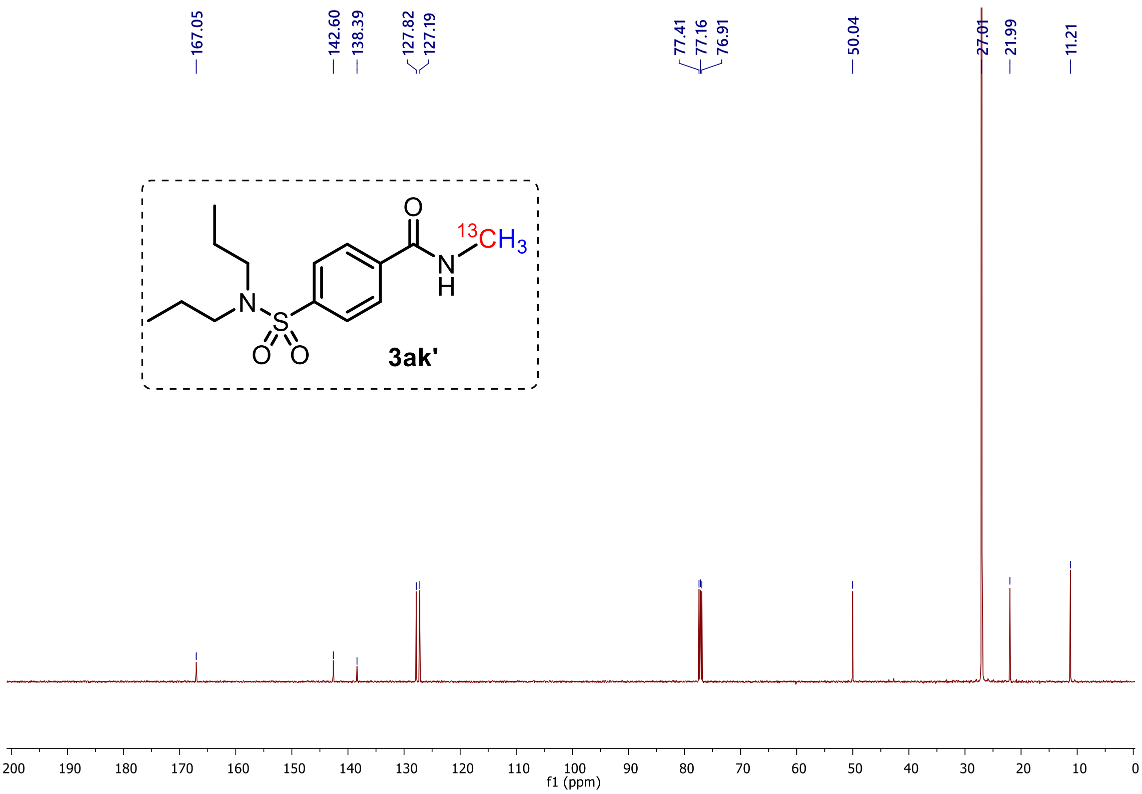


Fig.S112 $^{13}C\{^1H\}$ NMR spectrum of **3ak'** in $CDCl_3$.

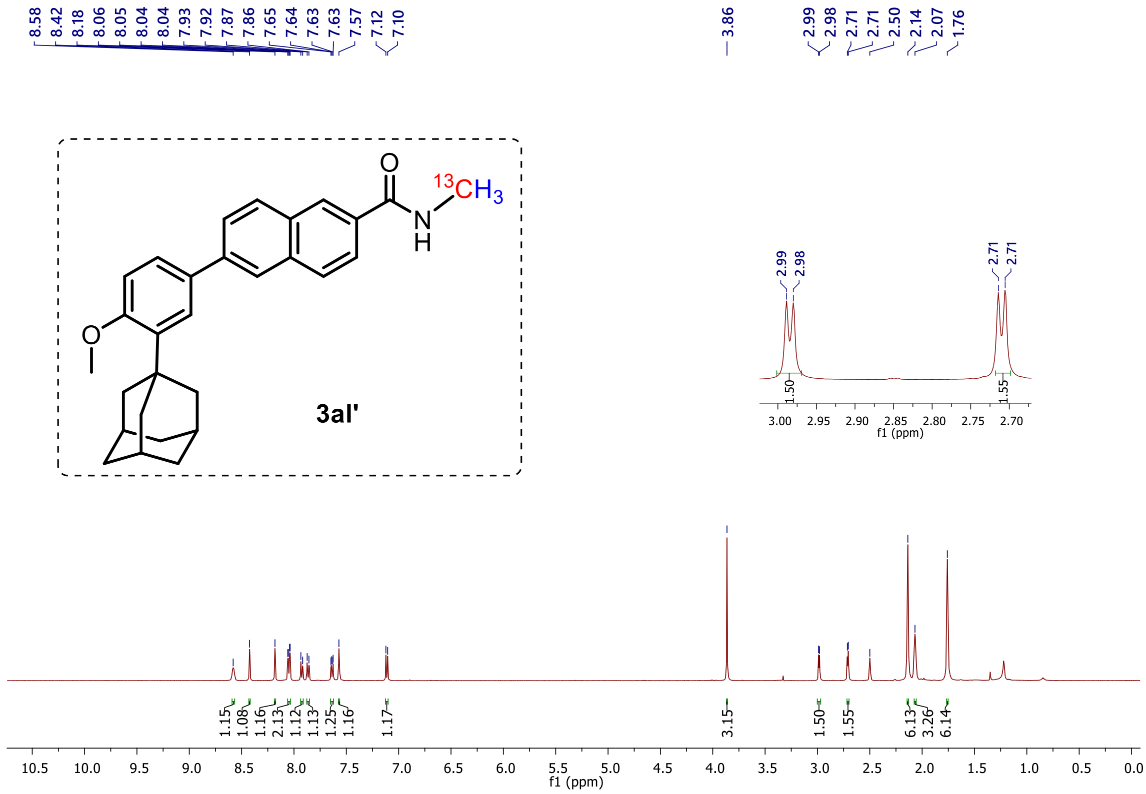


Fig.S113 ^1H NMR spectrum **3al'** in DMSO-d_6.

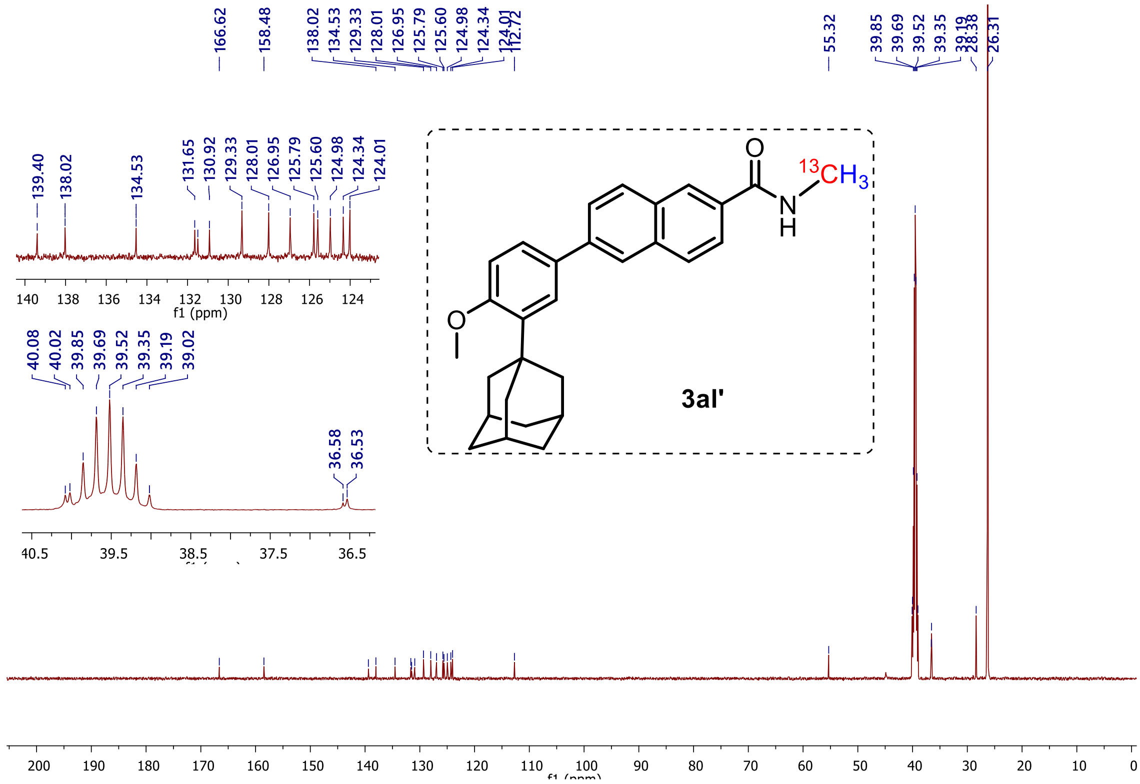


Fig.S114 *$^{13}C\{^{1}H\}$ NMR spectrum **3al'** in DMSO-d_6.*

7) ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of primary amide substrates

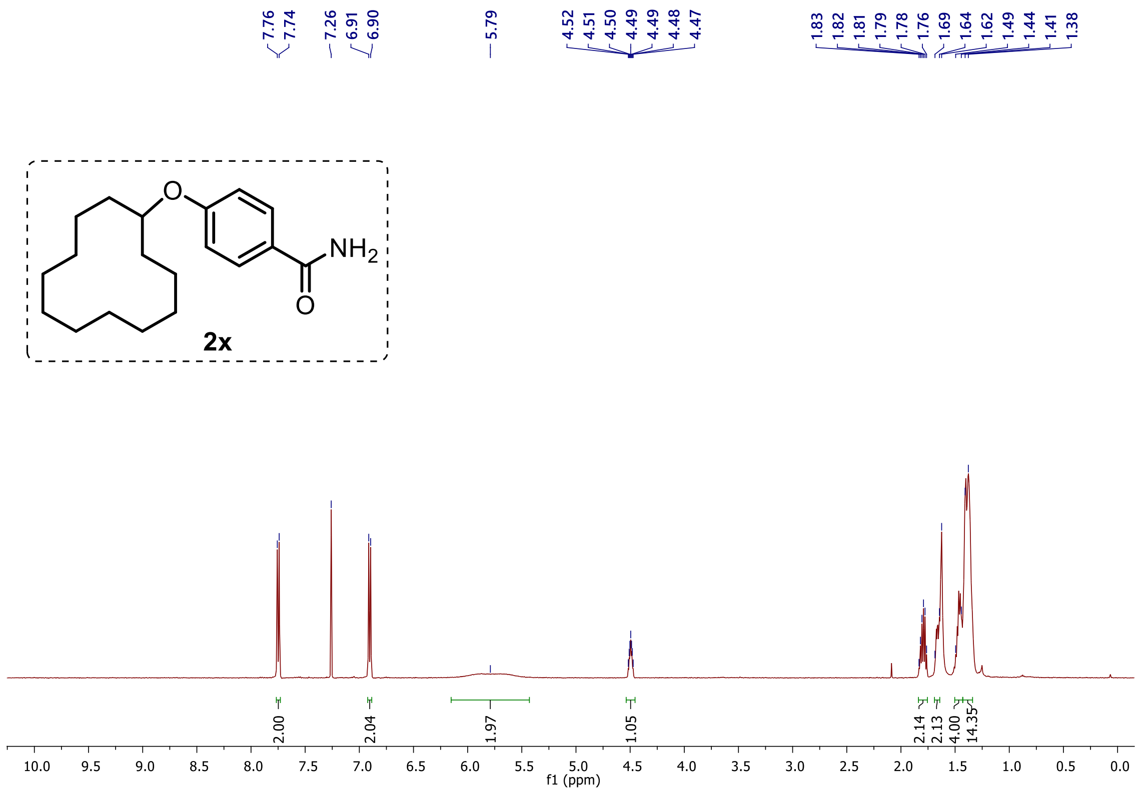


Fig.S115 ^{1}H NMR spectrum of **2x** in $CDCl_3$.

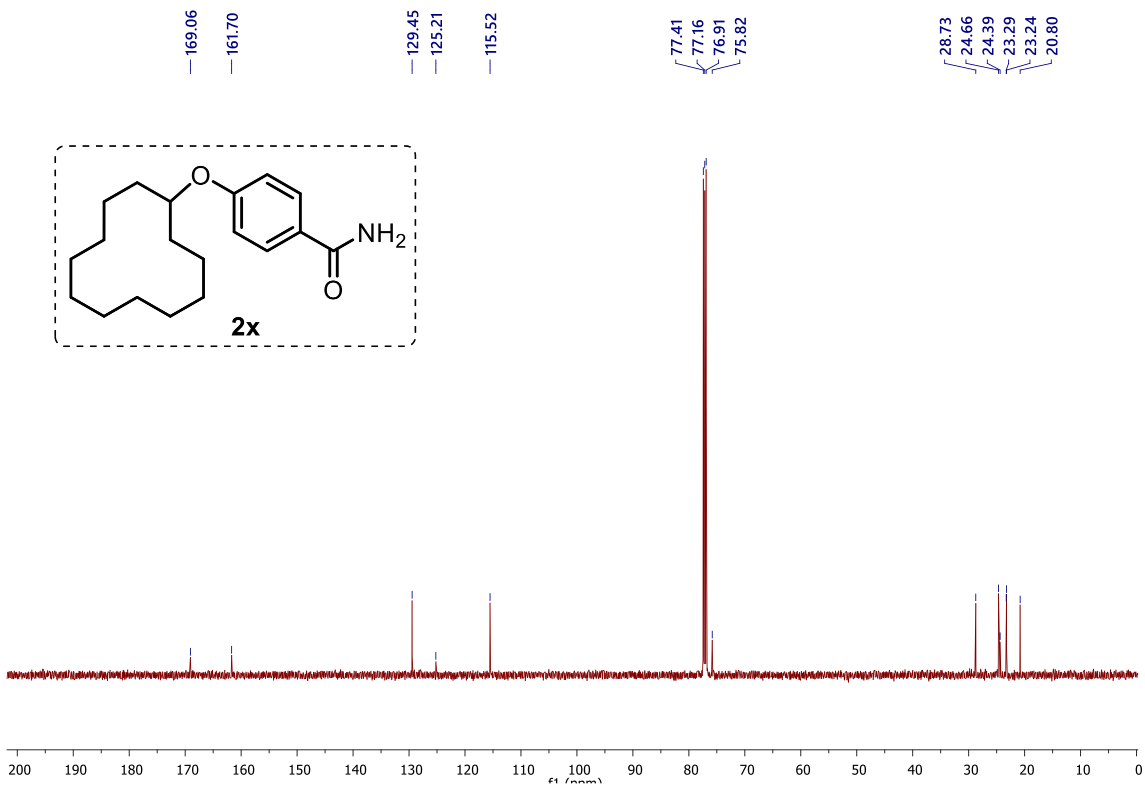


Fig.S116 ^{13}C{^{1}H} NMR spectrum of **2x** in $CDCl_3$.

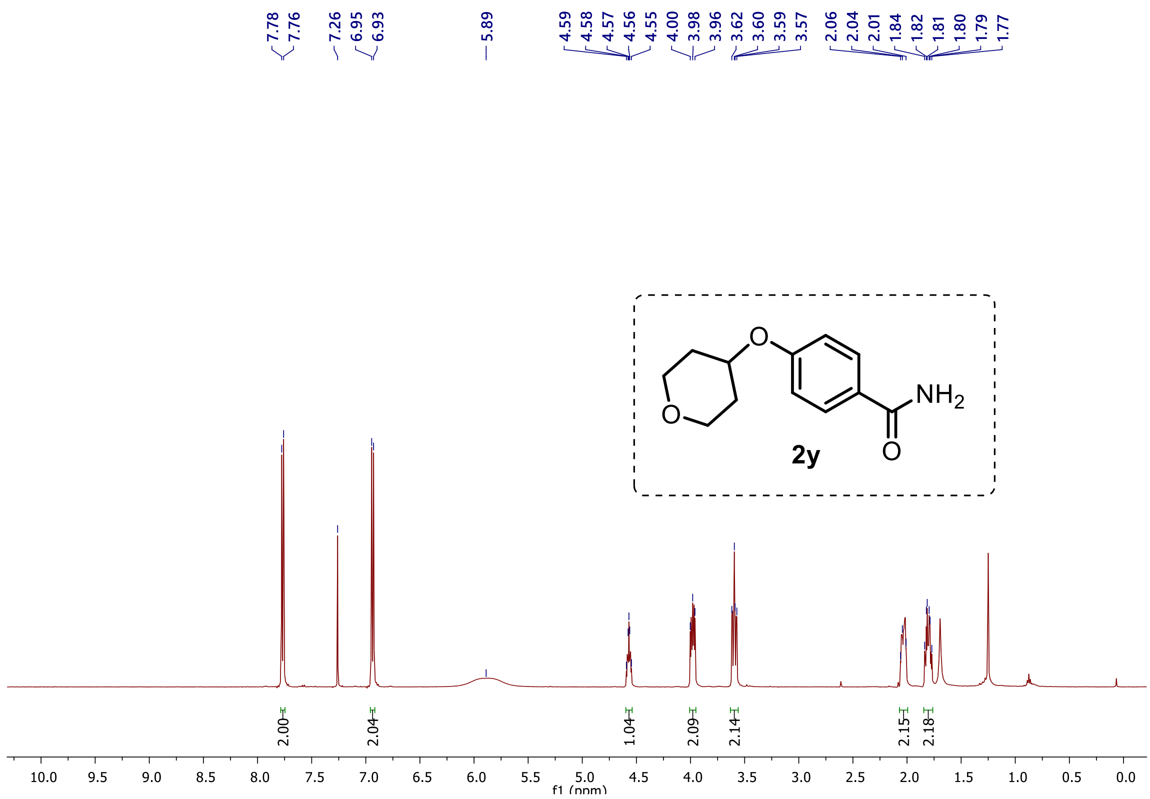


Fig.S117 ^{1}H NMR spectrum of **2y** in $CDCl_3$.

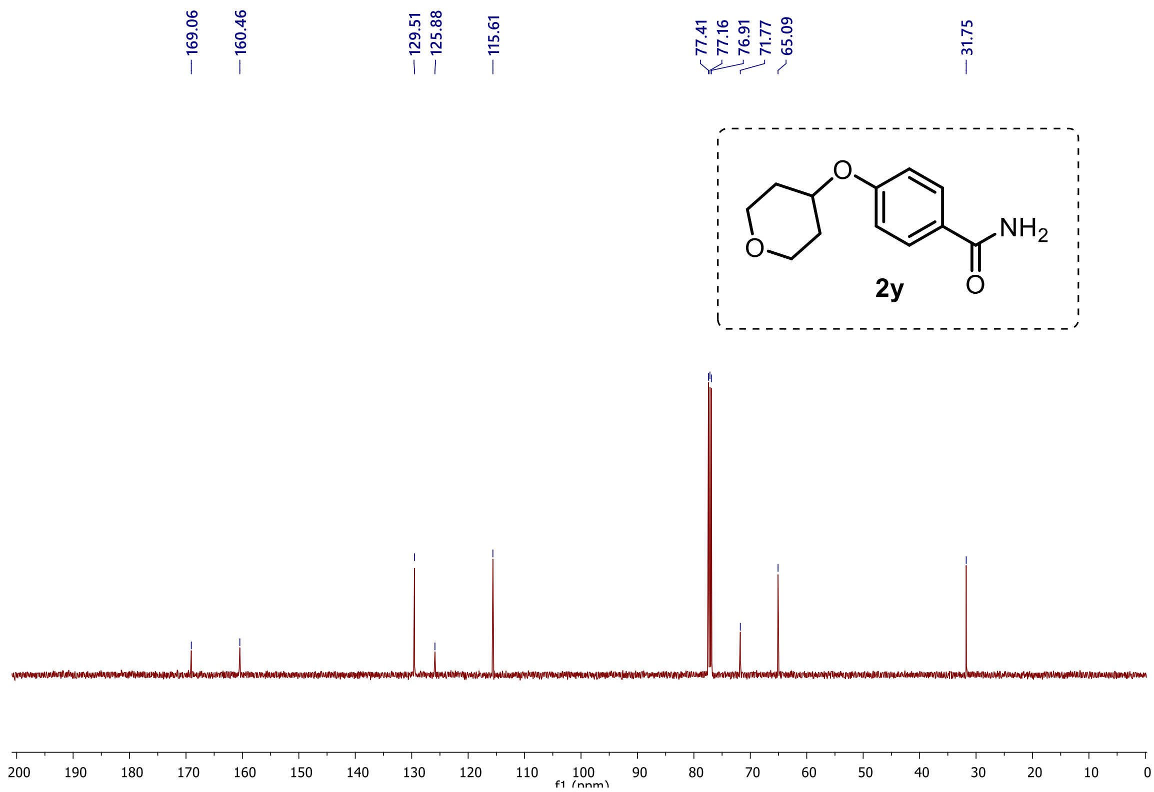


Fig.S118 $^{13}C\{^{1}H\}$ NMR spectrum of **2y** in $CDCl_3$.

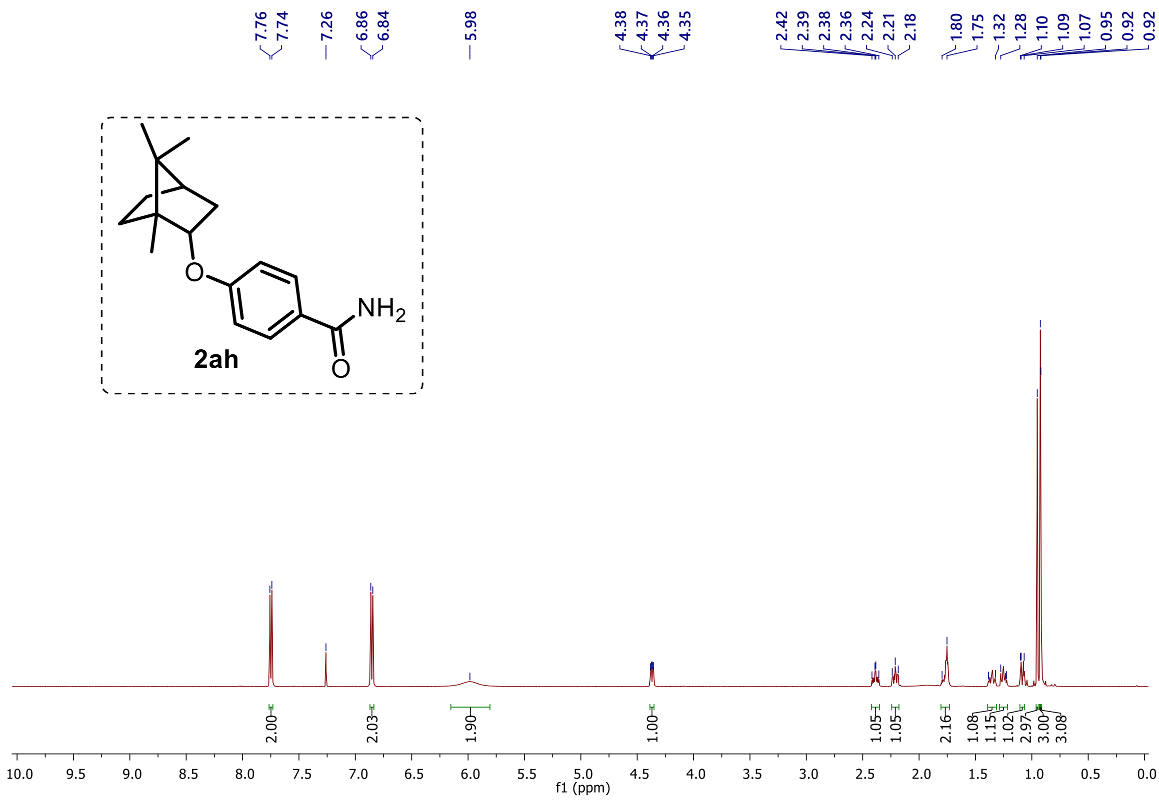


Fig.S119 ^{1}H NMR spectrum **2ah** in $CDCl_3$.

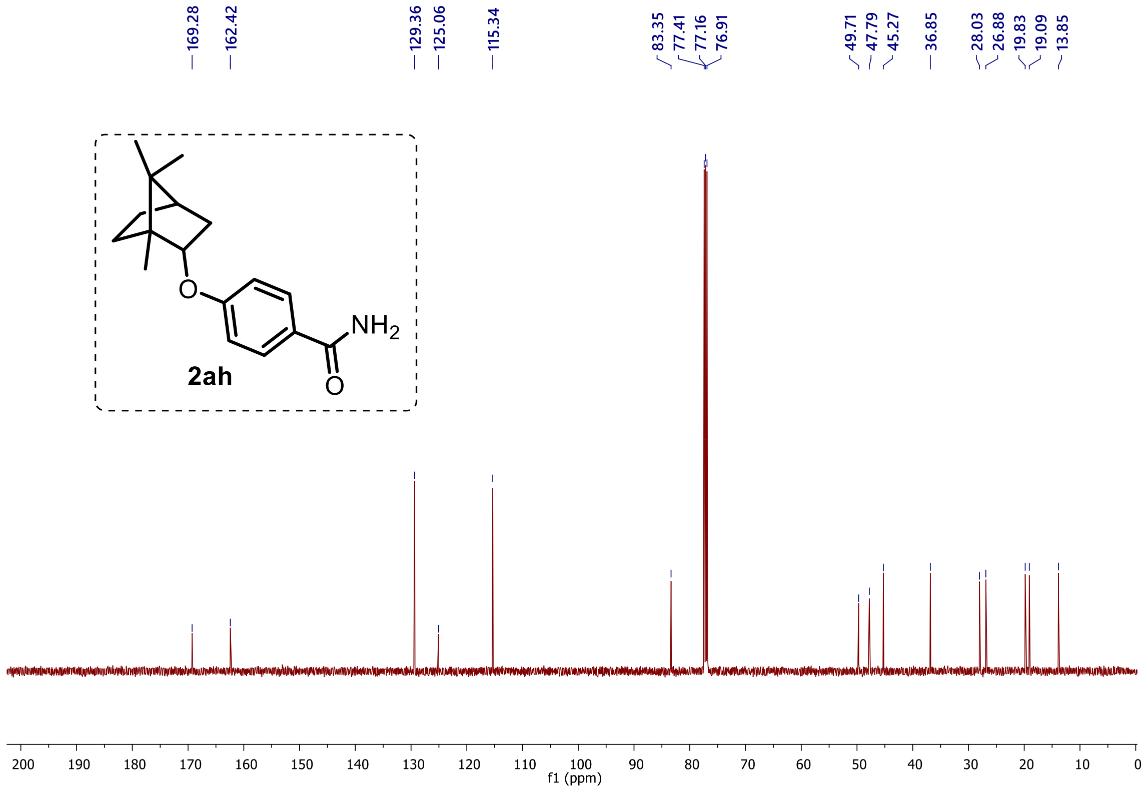


Fig.S120 $^{13}C\{^{1}H\}$ NMR spectrum **2ah** in $CDCl_3$.

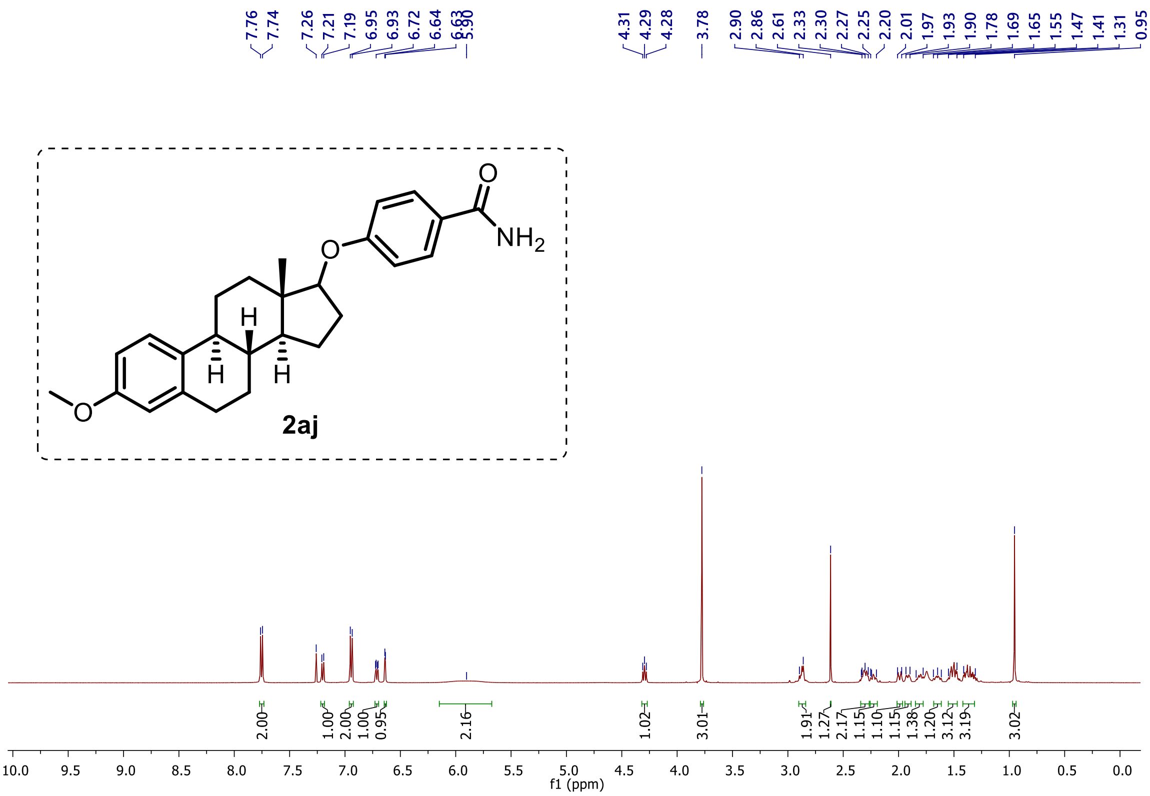


Fig.S121 ^{1}H NMR spectrum of **2aj** in $CDCl_3$.

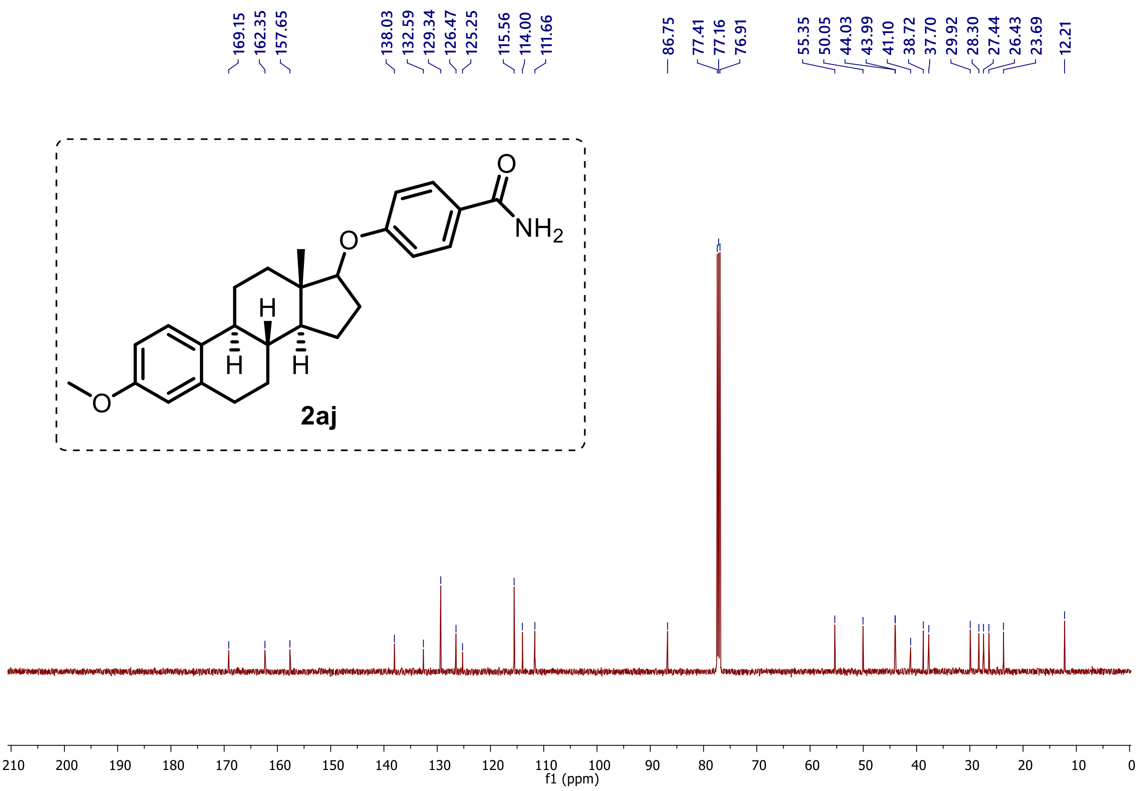


Fig.S122 $^{13}C\{^{1}H\}$ NMR spectrum of **2aj** in $CDCl_3$.

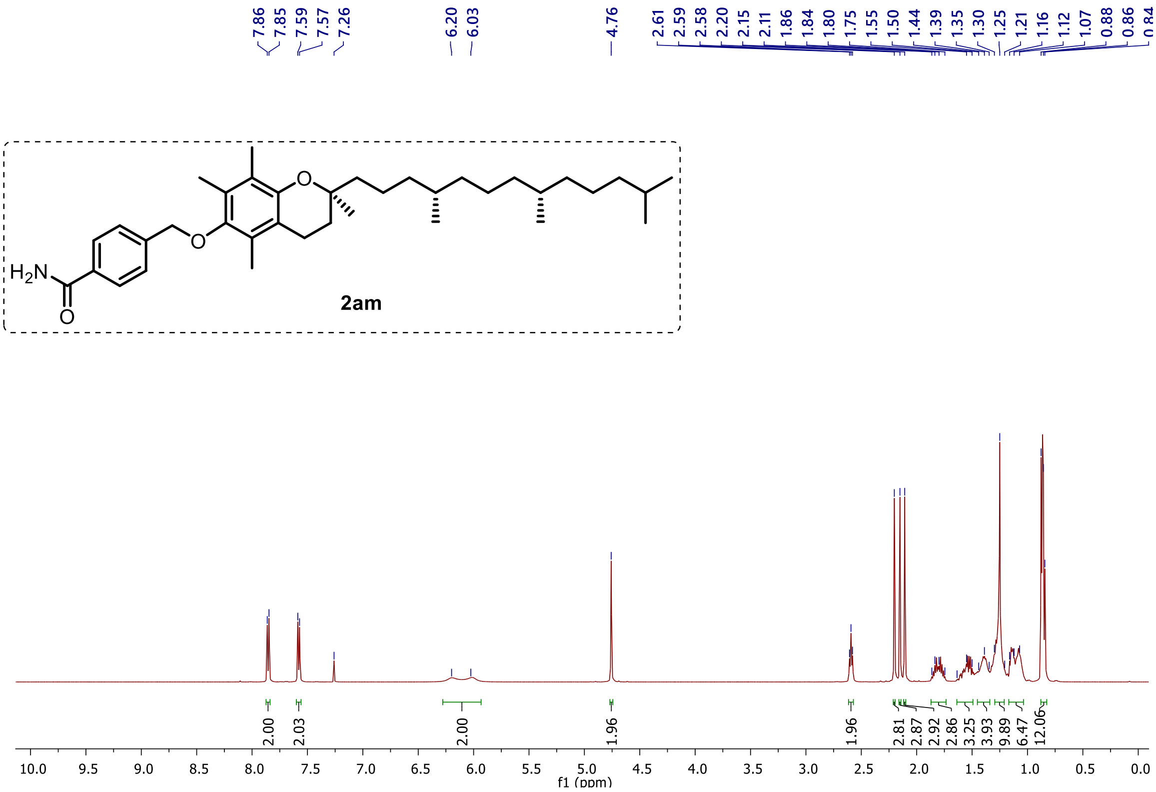


Fig.S123 ^{1}H NMR spectrum of **2am** in $CDCl_3$.

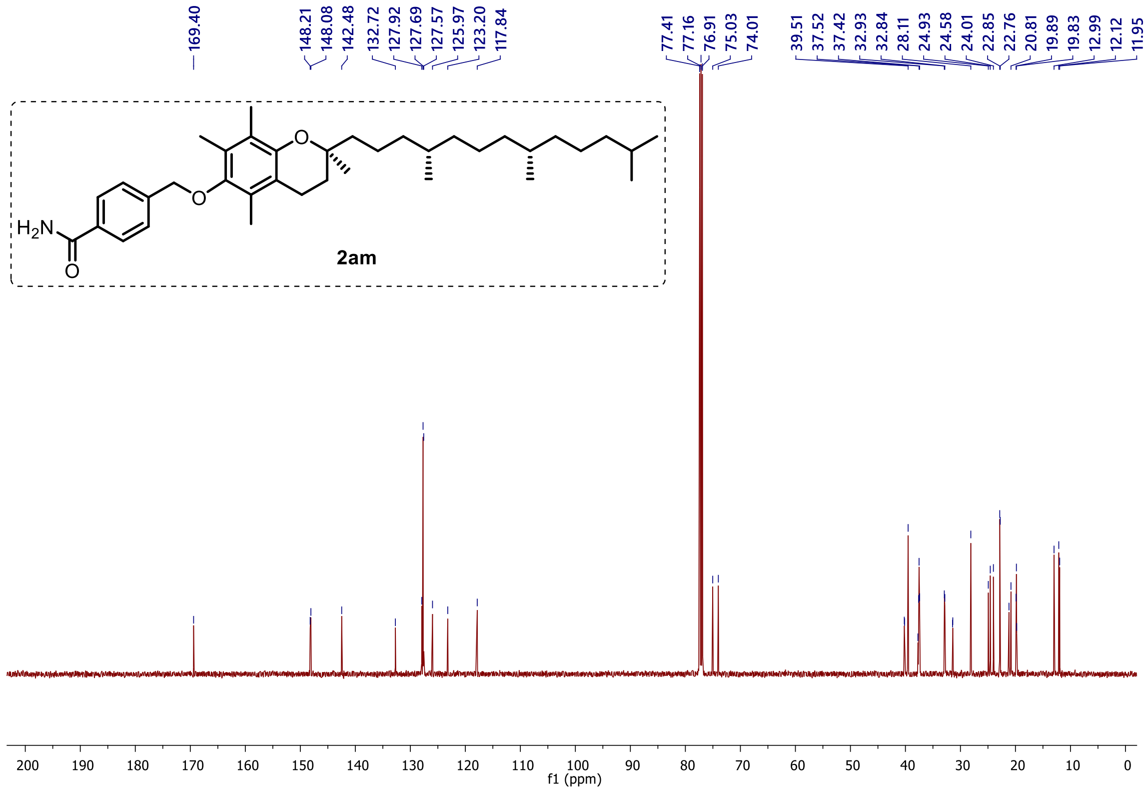
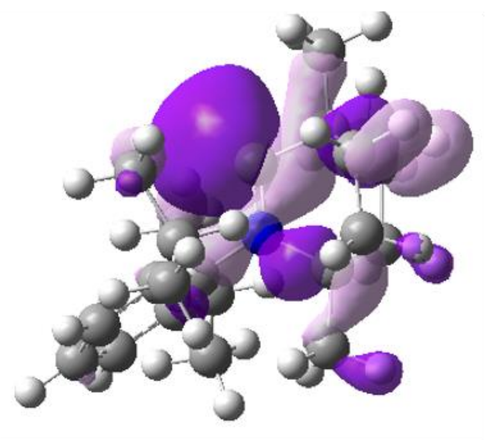


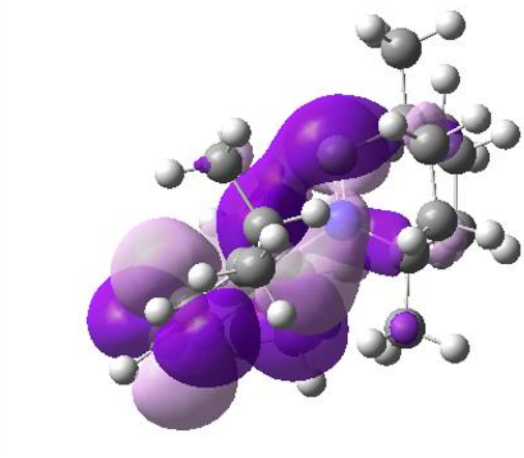
Fig.S124 $^{13}C\{^{1}H\}$ NMR spectrum of **2am** in $CDCl_3$.

8) Computational study

All the geometries of reactants, products, transition states and intermediates are optimised by employing M06-2X[S34-S36] functional adapting with a 6-31G* basis set. The DFT calculations are carried out using the gaussian 16 program package. The frequency calculations are executed using the same level of theory to affirm the true optimisation. The IRC calculations are employed to ensure the transition states. The solvent calculations are carried out using the CPCM solvent model considering 1,4-dioxane as a solvent by employing M06-2X/6-311++G**// M06-2X/6-31G* methodology.



A



B

Fig.S125 Computed HOMO (A) and LUMO (B) of BICAAC, **1**

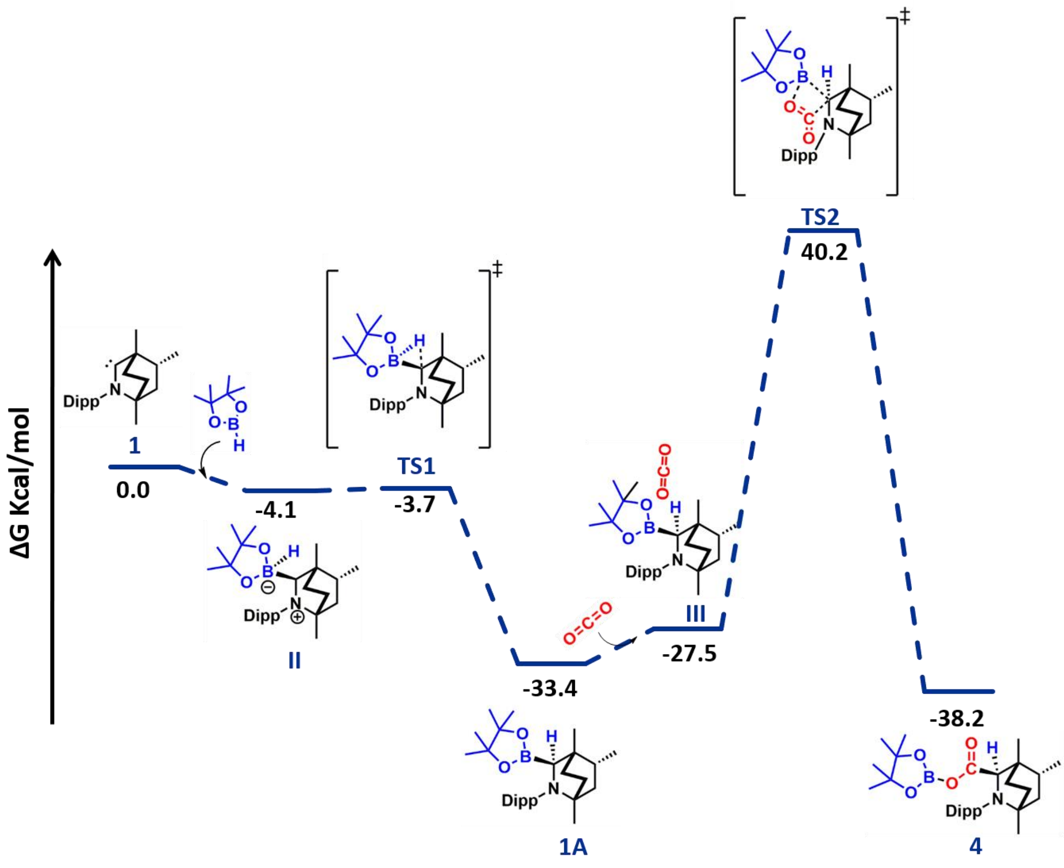


Fig.S126 Computed Gibbs free energy profile for pathway A, i.e., via BICAAC(H).Bpin (**1A**)

Detailed pathway for the dehydrogenation and formation of N-B bond step

The conversion of amide, **2** to N-borylated amide, **6** catalysed by **1A** may occur through a concerted transition state. In the amide molecule, the nitrogen atom in the HOMO-1 orbital contains a p orbital with a Mulliken atomic charge of -0.806. This p orbital can donate electron density to the vacant p orbital of the boron atom in **1A**, which has a Mulliken atomic charge of 0.600 and is the LUMO of **1A** (see Fig. S127). This interaction can cause the hydrogen atom attached to **1A** to become hydridic, while the hydrogen atom attached to the nitrogen atom in the amide molecule becomes protonic, ultimately resulting in the release of H_2.

The formation of N-B bond may be the driving force for this reaction.

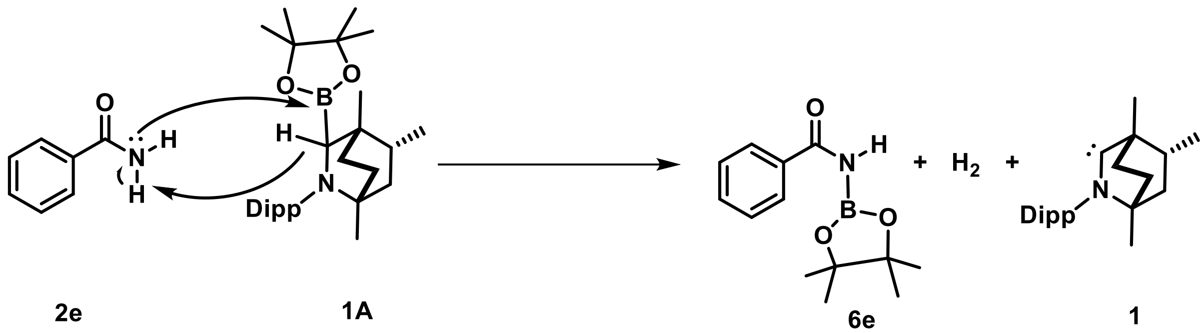
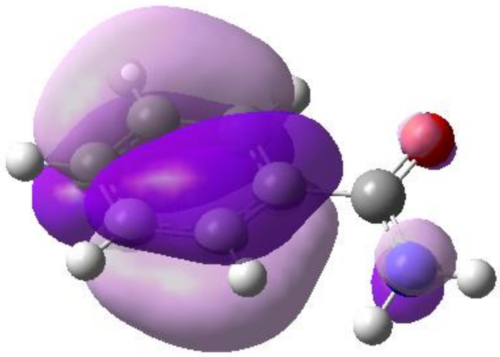
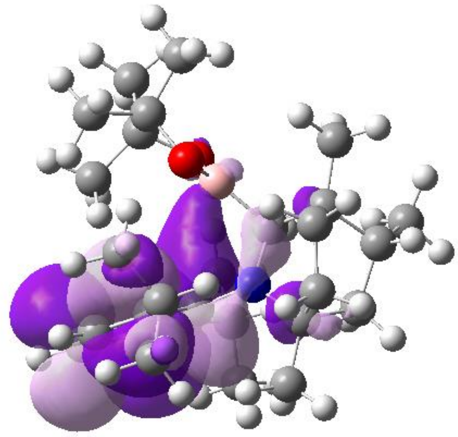


Fig.S127 Probable mechanism for formation of N-borylated amide, **6e**





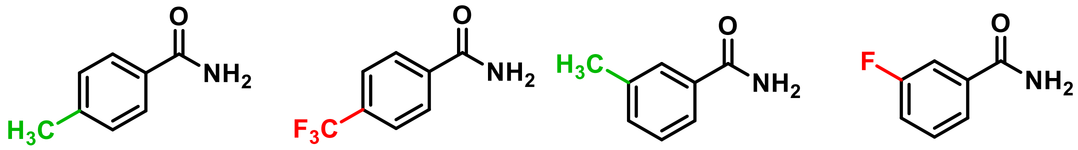
C **D**

Fig.S128 Computed HOMO-1 of benzamide, **2e** (C) and LUMO (D) of **1A**

<u>NBO analysis for reactivity difference between electron-rich and electron-poor amides</u>

We have observed the electron-deficient amides results in significantly inferior reactivity over the electron-rich amides. The reason behind such low-reactivity may be related to the availability of electron density on the N atom of amide molecule. As the first step of amide activation involves the interaction of primary amide with borane to form N-borylated amide, more electron rich the N atom would facilitate its interaction with electron deficient boron moiety.

We have computed the NBO (Natural Bond Orbital) analysis for nitrogen atom charge for two *para* substituted amides, **2a** and **2h**, and for two *meta* substituted amides, **2m** and **2o** using M06-2X/6-311++G**//M06-2X/6-31G* level of theory, which also supports the explanation.



2a, 77% **2h**, 58% **2m**, 69% **2o**, 46%

NBO	-0.832	-0.827	-0.831	-0.829

Fig.S129 The calculated atomic charge on amide nitrogen by M06-2X/6-311++G**//M06-2X/6-31G*

Coordinates:

1

C	-3.10064500	0.32652800	0.20606200
C	-2.41543600	-0.79252800	-0.62808900
C	-0.96331900	-0.24208700	1.43914000
C	-2.20538100	0.66475900	1.42079500
H	-4.05454100	-0.08651500	0.56363000
H	-1.90101300	1.71636300	1.39700000
H	-2.74292700	0.51949700	2.36475700
C	-1.00054700	-0.37955400	-1.01635100
C	-1.49478100	-1.68443200	1.56237100
H	-0.67251700	-2.37898700	1.76152000
H	-2.15222700	-1.71892100	2.43829500
C	-2.25865800	-2.04445000	0.27513300
H	-1.72100000	-2.81190900	-0.29508900
H	-3.25100000	-2.45342900	0.49874700
N	-0.31710500	-0.12455900	0.08269500
C	-3.21802400	-1.14837900	-1.87572000
H	-3.19547000	-0.33119900	-2.60117400
H	-2.77969200	-2.02512300	-2.36301900

H	-4.26296100	-1.37440200	-1.62875300
C	-0.01460200	0.11656500	2.56976300
H	0.86387600	-0.53591300	2.57785400
H	0.33092000	1.15269100	2.49215800
H	-0.53992900	0.00029100	3.52335700
C	1.10074000	0.16938100	-0.02923400
C	1.52618700	1.50672100	-0.06815200
C	2.00959900	-0.89609900	-0.12086100
C	2.89573900	1.76202400	-0.14680800
C	3.37116600	-0.59312200	-0.20251700
C	3.81526300	0.72175500	-0.19972700
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H	4.09284000	-1.40103200	-0.27746700
H	4.87786400	0.93755700	-0.25692400
C	1.54895800	-2.33815000	-0.23859600
C	2.41700200	-3.31958300	0.55236300
C	1.47065700	-2.72495600	-1.72186400
H	0.53520500	-2.40293400	0.15940800
H	2.52190600	-3.01094600	1.59782200
H	1.96490100	-4.31624600	0.53141700
H	3.42052600	-3.41187700	0.12443500
H	0.78235700	-2.05318900	-2.24377600
H	2.45890400	-2.64954600	-2.18964900
H	1.11692600	-3.75627800	-1.83179200
C	0.52370500	2.64262400	-0.15102300
C	0.15119500	2.86605200	-1.62412600
C	1.00215400	3.94119400	0.49998000
H	-0.38365800	2.32784600	0.37081600
H	-0.22520900	1.93766500	-2.06722800
H	-0.61292500	3.64624800	-1.71671400

H	1.03488000	3.18253600	-2.18979300
H	1.34942100	3.77560000	1.52516800
H	1.81952500	4.39981800	-0.06614200
H	0.18294200	4.66625400	0.52678000
C	-3.40328700	1.58185000	-0.61449000
H	-4.11624000	1.38289500	-1.41895700
H	-3.83022500	2.36079500	0.02638500
H	-2.48574900	1.97928900	-1.06460800

II

C	-2.28759500	2.66605100	0.56038200
C	-1.20900400	2.38116500	-0.54030600
C	-2.75075700	0.31472300	-0.21668500
C	-3.03795000	1.35396900	0.88140300
H	-2.98987900	3.37212600	0.09463400
H	-2.71459400	0.95432300	1.84903200
H	-4.11896600	1.52082700	0.94193800
C	-0.46775000	1.10683600	-0.18698600
C	-3.06648000	1.01703200	-1.55718400
H	-3.18419400	0.29810000	-2.37173400
H	-4.04233500	1.49929800	-1.43000800
C	-1.97766800	2.05273800	-1.84776400
H	-1.26354500	1.67929000	-2.59095700
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H	0.33646900	3.79500600	0.07978100
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H	-0.90859300	4.45845000	-1.00596900
C	-3.55789800	-0.96310700	-0.06660900

H	-3.33296500	-1.67221100	-0.86934600
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H	-4.61971100	-0.70521500	-0.12645700
C	3.01941800	-0.16560300	0.31276500
C	3.26301200	1.16868000	-0.48292100
B	1.10717000	1.18926300	0.29263900
O	1.73277300	0.01855000	0.88147200
O	1.95019300	1.58400200	-0.82950100
C	4.02657800	-0.40933800	1.43572100
H	3.79944200	-1.36161800	1.92675000
H	5.04981200	-0.46451500	1.04566600
H	3.97814300	0.38137800	2.18784100
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H	3.95864700	-1.67370900	-0.97200900
H	2.58840300	-2.24199500	0.01599300
H	2.28833800	-1.25351300	-1.41554400
C	3.89811700	2.26088700	0.38587700
H	4.93705300	2.03217200	0.64462100
H	3.87578000	3.20125600	-0.17310500
H	3.32895700	2.40202900	1.30964400
C	4.07232200	0.99542300	-1.76189900
H	4.19432100	1.96617200	-2.25210800
H	5.06815200	0.59159000	-1.54632500
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C	-0.75400700	-1.27954500	0.09796200
C	-0.48586600	-1.73277400	1.39804100
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C	-0.04836600	-3.05181100	1.53584200
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C	0.35764900	-0.81282600	-3.04066400
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H	0.07333300	-0.36308300	-3.99899100
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C	0.57776500	-0.96616500	3.57040300
C	-1.90832900	-1.22599600	3.42098500
H	-0.69909900	0.18037000	2.31787900
H	1.49219400	-0.75775500	3.01428000
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H	-2.82155700	-1.09481600	2.83348100
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H	-1.99225600	-0.60017000	4.31580200
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H	-1.31860500	4.30091600	1.63276200
H	-2.54496900	3.42938400	2.56347500
H	-0.95395600	2.69480800	2.27829100

TS1

C	-1.57188100	3.11291600	0.33517100
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C	-2.65463100	0.88298700	-0.08351100
C	-2.57767400	2.07523700	0.88049400
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C	-2.93372300	1.48236400	-1.48131000
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C	-1.66513700	2.18940200	-1.98113300
H	-1.14173100	1.57922000	-2.72703600
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N	-1.29519700	0.25406300	-0.10173500
C	0.42136100	3.37728900	-1.22940300
H	1.17757500	3.49710700	-0.45184600
H	0.92894600	2.97990800	-2.11118700
H	0.00020500	4.36024700	-1.47279000
C	-3.73084200	-0.11589900	0.30493900
H	-3.75977200	-0.96016200	-0.39116300
H	-3.57601900	-0.51263800	1.31099700
H	-4.70161900	0.38827900	0.27454800
C	3.04474200	-0.75891600	-0.08960500
C	3.50253600	0.72114200	-0.28987100
B	1.24278500	0.68472700	-0.11676400
O	1.67278000	-0.61603800	0.28152000
O	2.31594000	1.33613900	-0.79096700
C	3.77636600	-1.51311400	1.01377500
H	3.35326800	-2.51849000	1.10418500

H	4.84357100	-1.60637400	0.78253900
H	3.67059100	-1.01344000	1.97924500
C	3.10338900	-1.56513200	-1.38764900
H	4.13138500	-1.83459700	-1.65257700
H	2.52080300	-2.48180100	-1.25135000
H	2.66615700	-0.99911000	-2.21445700
C	3.87578100	1.39722000	1.03260700
H	4.82254800	1.01853800	1.43060400
H	3.97530100	2.47277000	0.85819700
H	3.09440000	1.24500000	1.78510400
C	4.62026600	0.91243900	-1.30468100
H	4.87811900	1.97368200	-1.37073500
H	5.51730000	0.35953500	-1.00436800
H	4.31268800	0.57494800	-2.29644800
C	-1.10747800	-1.14413700	0.22188400
C	-0.84133300	-1.51426800	1.54891900
C	-1.17302000	-2.09518600	-0.81021600
C	-0.65668000	-2.86983800	1.82834900
C	-0.96564200	-3.43586300	-0.48679500
C	-0.71330400	-3.82433500	0.82381000
H	-0.44921100	-3.17640900	2.85021000
H	-1.00575200	-4.18833900	-1.26819500
H	-0.55940000	-4.87319500	1.05917500
C	-1.41487200	-1.67898600	-2.25068700
C	-2.20850800	-2.71070200	-3.05614400
C	-0.08925700	-1.35380100	-2.94893900
H	-2.00407200	-0.75959600	-2.23066100
H	-3.12207000	-3.01368900	-2.53443100
H	-2.48876900	-2.28880000	-4.02633800
H	-1.61665900	-3.61020100	-3.25495900

H	0.45383600	-0.56343500	-2.42162900
H	0.55353300	-2.24064300	-2.97518400
H	-0.26817500	-1.02794100	-3.97996600
C	-0.70138700	-0.50649200	2.67855200
C	0.66850700	-0.61729200	3.35973400
C	-1.82143000	-0.65174200	3.71622900
H	-0.75683300	0.49501300	2.24500400
H	1.46251100	-0.55268700	2.61285600
H	0.78877200	0.19050100	4.08976500
H	0.76974900	-1.56763600	3.89620800
H	-2.81401500	-0.50392900	3.27986900
H	-1.80264600	-1.64894600	4.16971600
H	-1.69224400	0.08276300	4.51830600
H	0.75803100	1.38748200	0.94362600
C	-0.77885500	3.76027500	1.46706700
H	-0.16514600	4.59256500	1.11284800
H	-1.46838600	4.15020000	2.22335200
H	-0.11964600	3.03272500	1.95392000

1A

C	-2.49059600	2.71621900	-0.02384600
C	-1.08324700	2.38834900	-0.59057500
C	-2.61130300	0.28921800	-0.76452600
C	-3.24956900	1.37642000	0.12948300
H	-3.00001700	3.33033700	-0.78154100
H	-3.23548600	1.04670200	1.17585100
H	-4.30416400	1.49805900	-0.14589700
C	-0.53732400	1.17523100	0.21238700
C	-2.45256000	0.94850400	-2.15208900
H	-2.28112900	0.19911300	-2.93175800

H	-3.38626700	1.46325100	-2.41333600
C	-1.27834000	1.94710000	-2.05641200
H	-0.34693200	1.48720100	-2.40869600
H	-1.46441600	2.82902100	-2.68181000
N	-1.25302200	-0.01216800	-0.26338300
C	-0.12861800	3.57538600	-0.50765900
H	0.17159200	3.77989500	0.52744000
H	0.77637500	3.37454300	-1.09260500
H	-0.59437800	4.48259600	-0.91035100
C	-3.48313200	-0.95326600	-0.79326800
H	-3.02118200	-1.75133800	-1.37886800
H	-3.65300800	-1.33253500	0.22055000
H	-4.45225000	-0.71347600	-1.24207300
C	3.07962400	0.47735300	0.97783000
C	3.19123800	0.86704000	-0.52738500
B	1.03212200	0.97571100	0.15805600
O	1.77229000	0.98519300	1.31511300
O	1.80930800	0.79171300	-0.95970200
C	4.11419800	1.11974900	1.88611000
H	3.95162700	0.78817600	2.91543200
H	5.12508300	0.82302000	1.58643900
H	4.04398800	2.20909900	1.86250900
C	3.02566400	-1.03480200	1.19169000
H	4.00639800	-1.49707000	1.04152900
H	2.69644300	-1.23369800	2.21580400
H	2.30388300	-1.50170200	0.51095800
C	3.63880900	2.31314800	-0.73117200
H	4.70008800	2.43999000	-0.49707600
H	3.47697400	2.58849900	-1.77719600
H	3.05727000	2.99384900	-0.10120100

C	4.04570100	-0.07355200	-1.36064900
H	4.03831300	0.24755000	-2.40652700
H	5.08127200	-0.05251300	-1.00360600
H	3.68041100	-1.10087500	-1.31321400
C	-0.76187600	-1.30290800	0.09600900
C	-0.74623800	-1.72189900	1.44736100
C	-0.20624900	-2.15051800	-0.89688400
C	-0.13814900	-2.93334700	1.78657200
C	0.36353800	-3.36747600	-0.51472500
C	0.41618000	-3.75666800	0.81735600
H	-0.11596200	-3.24192900	2.82911400
H	0.78370600	-4.01745500	-1.27865200
H	0.87750000	-4.69958600	1.09588200
C	-0.21667100	-1.80070700	-2.37588600
C	-1.06771900	-2.79195100	-3.18257200
C	1.19433100	-1.73884200	-2.97089100
H	-0.64900700	-0.80371200	-2.46600800
H	-2.08422800	-2.88753300	-2.79155200
H	-1.13351200	-2.47131700	-4.22786800
H	-0.61506900	-3.79009200	-3.16971100
H	1.77510700	-0.95467900	-2.48495400
H	1.72034300	-2.69420600	-2.85872900
H	1.13976900	-1.51560700	-4.04227900
C	-1.40813900	-0.92091900	2.55596800
C	-0.38763200	-0.42744800	3.58858100
C	-2.51760500	-1.73245300	3.23728200
H	-1.87960500	-0.04972600	2.09867500
H	0.40026300	0.16468000	3.11430000
H	-0.88073600	0.18638000	4.35045700
H	0.08402000	-1.27504800	4.10029000

H	-3.25307900	-2.09165700	2.51059300
H	-2.10950500	-2.60537400	3.75805600
H	-3.03752800	-1.11607900	3.97836900
H	-0.75116900	1.38362500	1.28015200
C	-2.49728200	3.50576100	1.28354200
H	-2.06127200	4.50196300	1.16390400
H	-3.52527600	3.63177300	1.63977100
H	-1.93967600	2.98291000	2.06976800

III

C	-1.63607700	-3.25320000	-0.64242000
C	-0.30843800	-2.55308200	-0.25296600
C	-2.30849500	-1.34191500	0.89590500
C	-2.78980800	-2.33264700	-0.18836700
H	-1.67707500	-4.19021200	-0.06679600
H	-3.18822300	-1.77118600	-1.04291700
H	-3.62237800	-2.92499200	0.21018300
C	-0.43207600	-1.05544500	-0.66143100
C	-1.54784600	-2.19388800	1.93229100
H	-1.37812900	-1.62803400	2.85425100
H	-2.15018300	-3.07189100	2.19956500
C	-0.20729200	-2.61527600	1.28485600
H	0.58997700	-1.93633900	1.61010000
H	0.07788100	-3.62853100	1.59387700
N	-1.31752400	-0.41357900	0.30929500
C	0.90218900	-3.20732300	-0.91130500
H	0.93385700	-3.00225000	-1.98721900
H	1.83373300	-2.83312500	-0.47101200
H	0.88220200	-4.29441200	-0.76928200
C	-3.50947600	-0.60465100	1.46638100

H	-3.21783900	0.19565500	2.14783000
H	-4.09824500	-0.15352400	0.65936800
H	-4.14936700	-1.30830800	2.00838300
C	-1.41530600	1.00827700	0.35748400
C	-1.96685200	1.73072600	-0.72655800
C	-0.91975800	1.71556700	1.48370200
C	-1.99592100	3.12730100	-0.68269900
C	-1.02596700	3.10837500	1.50705000
C	-1.54348600	3.81783800	0.43165900
H	-2.40477400	3.67775400	-1.52656700
H	-0.67394200	3.65283200	2.37919600
H	-1.59539600	4.90214500	0.46448100
C	-0.26579700	1.02774000	2.67499300
C	-1.17418400	1.03498300	3.91358600
C	1.07503600	1.66822800	3.05375000
H	-0.06294700	-0.00553700	2.38097000
H	-2.12526000	0.52500400	3.74552700
H	-0.67225200	0.53933300	4.75167700
H	-1.39696500	2.06443800	4.21797300
H	1.78069000	1.60076100	2.22442600
H	0.95929800	2.71934400	3.33928800
H	1.51013400	1.14007600	3.90704500
C	-2.54940600	1.04309000	-1.94993600
C	-1.67900100	1.28886600	-3.18929500
C	-3.99749900	1.47485400	-2.21149100
H	-2.56566600	-0.02945700	-1.75075400
H	-0.65071500	0.94758600	-3.03063300
H	-2.08740800	0.76126100	-4.05831500
H	-1.64932100	2.35817500	-3.43054800
H	-4.62398300	1.32202000	-1.32712200

H	-4.05882800	2.53320500	-2.48603500
H	-4.42058200	0.89446400	-3.03815700
C	-1.77048700	-3.61724400	-2.11948900
H	-1.65725100	-2.73447200	-2.76020000
H	-1.02854600	-4.35861500	-2.42978300
H	-2.76358300	-4.03696000	-2.31222400
C	3.10726300	-1.48396900	1.97073900
O	3.59628500	-2.06015000	1.08424900
O	2.64520700	-0.93391500	2.88284300
C	2.73475000	0.53027500	-1.96894300
C	2.64156400	1.16200300	-0.54354700
B	0.94653600	-0.30370900	-0.83934900
O	1.44027400	-0.09149300	-2.10131400
O	1.74757400	0.24059200	0.13989300
C	3.77949300	-0.57823500	-2.06959900
H	3.62618000	-1.11851300	-3.00783100
H	4.79489000	-0.16975000	-2.06527800
H	3.68354600	-1.28786300	-1.24270600
C	2.90977200	1.53179900	-3.09976100
H	3.83689400	2.10075100	-2.97087900
H	2.96519100	0.99838500	-4.05274700
H	2.07024600	2.22835900	-3.14546300
C	3.96239900	1.23610400	0.20368100
H	4.65539300	1.90120700	-0.32290800
H	3.80107800	1.64289600	1.20670000
H	4.43079500	0.25364500	0.29266000
C	1.94745600	2.52396400	-0.55518100
H	1.75090000	2.84496700	0.47035600
H	2.57069200	3.27887900	-1.04412600
H	0.98229900	2.46996300	-1.07320500

H	-0.86225900	-1.05448100	-1.68338100

TS2

C	-0.38418500	3.25813100	0.55324400
C	0.00970300	2.50999700	-0.76122100
C	-2.27753300	1.60956500	0.09322800
C	-1.75673400	2.71517700	1.03843600
H	-0.52935300	4.30176400	0.24518400
H	-1.70669500	2.34739300	2.06761100
H	-2.49717500	3.52440900	1.04658400
C	0.06344400	0.98370100	-0.41567900
C	-2.46518600	2.26510700	-1.28604100
H	-2.81637300	1.50981800	-1.99450000
H	-3.24360100	3.03389000	-1.21376600
C	-1.12651600	2.87627000	-1.74479900
H	-0.88122400	2.58947700	-2.76643600
H	-1.18847300	3.97093200	-1.74641700
N	-1.27835400	0.51758500	-0.07492800
C	1.32771800	3.05527400	-1.30180500
H	2.16607800	2.86390600	-0.63016400
H	1.58005000	2.60267600	-2.26574800
H	1.23027900	4.13828200	-1.44554700
C	-3.60186100	1.06029800	0.59945200
H	-4.03546900	0.36214500	-0.12044400
H	-3.48947300	0.54106800	1.55549900
H	-4.30400100	1.88863700	0.73529200
C	-1.43214500	-0.77190000	0.55330000
C	-0.98061300	-1.02118700	1.87088900
C	-2.03811300	-1.82738900	-0.17051900
C	-1.05880000	-2.30974600	2.39810800

C	-2.09112400	-3.10445400	0.39588500
C	-1.59178700	-3.35814100	1.66300200
H	-0.70195100	-2.48961200	3.40928600
H	-2.54226400	-3.91402300	-0.17219500
H	-1.63843600	-4.35836800	2.08329000
C	-2.68883500	-1.65091800	-1.53406400
C	-4.18133600	-2.01545400	-1.49306100
C	-2.00641000	-2.50452000	-2.61398300
H	-2.60250900	-0.59851700	-1.81121900
H	-4.71780500	-1.48131500	-0.70436300
H	-4.65359200	-1.78014000	-2.45277400
H	-4.31639600	-3.08723200	-1.31203000
H	-0.92088300	-2.38344900	-2.61999500
H	-2.20991900	-3.56822900	-2.44598400
H	-2.39160100	-2.24425700	-3.60529700
C	-0.45682500	0.07515500	2.77707500
C	0.94737400	-0.22240400	3.30303600
C	-1.42266800	0.34691400	3.93675400
H	-0.39252300	0.98309600	2.18464500
H	1.60624300	-0.45289900	2.46490000
H	1.34434500	0.63990000	3.85172400
H	0.95200600	-1.08084200	3.98412100
H	-2.42773500	0.59165100	3.57884600
H	-1.50582900	-0.53065200	4.58720600
H	-1.06206400	1.18477600	4.54450800
C	0.69218800	3.30401900	1.64281900
H	1.10087200	2.32110900	1.89928400
H	1.53229000	3.93483200	1.33779300
H	0.27323800	3.73055300	2.56087000
C	0.06679400	-0.04269400	-2.36372300

O	0.95950200	-0.88220400	-2.28088000
O	-0.82463500	0.39966700	-2.96829000
C	3.65999300	-0.08731700	-0.36955000
C	3.03294700	-1.46859500	0.01076700
B	1.43132100	-0.16020400	-0.88272100
O	2.62541200	0.51423500	-1.16803900
O	1.62826300	-1.14360200	0.09698000
C	4.92940400	-0.17755800	-1.20402300
H	5.29423200	0.82931400	-1.42628200
H	5.71293900	-0.71322900	-0.65680600
H	4.74535000	-0.68973100	-2.15011000
C	3.89371100	0.81605800	0.84044800
H	4.72447600	0.45977500	1.45755000
H	4.13398000	1.82304200	0.48612700
H	2.99685300	0.87837800	1.46573300
C	3.22220900	-2.52561200	-1.08225300
H	4.25369700	-2.89050500	-1.10211300
H	2.55711300	-3.36661000	-0.86725400
H	2.97380100	-2.13913400	-2.07321500
C	3.50016000	-2.04443400	1.33913900
H	2.91336400	-2.93877000	1.56846500
H	4.55557500	-2.33029000	1.27312300
H	3.38677900	-1.34091200	2.16418500
H	0.71547700	0.94097900	0.48159700

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C	0.05211700	-2.80624700	1.32930900
C	0.15011100	-2.37598800	-0.15565600
C	2.23895000	-1.52870100	1.14089500
C	1.17440900	-2.08546100	2.10941800

H	0.25142800	-3.88790000	1.34079800
H	0.76153000	-1.26380600	2.70769300
H	1.65308900	-2.77376300	2.81618800
C	0.28776800	-0.81554700	-0.17607400
C	2.64077400	-2.69413700	0.22046800
H	3.54260200	-2.43742300	-0.34518300
H	2.88041600	-3.57424300	0.83105500
C	1.45351400	-2.97425300	-0.72663200
H	1.63693000	-2.54098400	-1.71477200
H	1.30982900	-4.05228900	-0.86610400
N	1.62779000	-0.49099100	0.27624000
C	-1.04649900	-2.86145100	-0.97053900
H	-1.97324800	-2.36862300	-0.66402600
H	-0.89156700	-2.68310000	-2.04089000
H	-1.17510000	-3.94083000	-0.83023400
C	3.41066200	-0.97698800	1.93686800
H	4.15886500	-0.51148700	1.29288500
H	3.07404700	-0.22282100	2.65649400
H	3.88635800	-1.79425300	2.48806600
C	-4.49277600	1.01815100	-0.86475100
C	-4.10733700	-0.05282700	0.20812500
B	-2.38627400	0.29141300	-1.21710100
O	-3.46238700	0.84025800	-1.85743400
O	-2.66733700	-0.11801100	0.06525800
C	-4.37105900	2.44786200	-0.34211400
H	-4.43989200	3.13696200	-1.18758300
H	-5.16917000	2.68297000	0.36831800
H	-3.40600700	2.60609400	0.15059500
C	-5.84810000	0.80362500	-1.51840400
H	-6.64574300	0.83907200	-0.76873100

H	-6.02889800	1.59608900	-2.24942200
H	-5.89190500	-0.15544800	-2.03774600
C	-4.44205500	0.32318400	1.64107800
H	-5.52345600	0.45097300	1.75817500
H	-4.11670800	-0.47474200	2.31510700
H	-3.94495700	1.24881400	1.93696000
C	-4.64910400	-1.44194300	-0.12036500
H	-4.18020600	-2.17067900	0.54750100
H	-5.73307500	-1.48983000	0.01850300
H	-4.41669900	-1.71990100	-1.15370800
C	2.10571600	0.85641100	0.22557600
C	1.57107100	1.85586400	1.06882100
C	3.13966900	1.18854900	-0.68305300
C	2.07611500	3.15583600	1.00020600
C	3.63569600	2.49452200	-0.69300400
C	3.11305100	3.47646000	0.13633500
H	1.65678100	3.92520600	1.64398100
H	4.43938400	2.74818200	-1.37945600
H	3.50750500	4.48778200	0.10500800
C	3.72867500	0.19444600	-1.67253600
C	5.19255700	-0.14204600	-1.35770200
C	3.62852800	0.72205700	-3.11071800
H	3.12887500	-0.71525200	-1.61385700
H	5.31555700	-0.60728200	-0.37558400
H	5.58797500	-0.83560400	-2.10795400
H	5.81412800	0.76055200	-1.37899500
H	2.60756100	1.02451500	-3.34841300
H	4.29622700	1.57688900	-3.26883200
H	3.92532700	-0.06232900	-3.81501700
C	0.43739300	1.58036700	2.04117100

C	-0.84235700	2.28617200	1.57582200
C	0.78640100	1.97718100	3.47950400
H	0.24626300	0.50679800	2.04269200
H	-1.07428100	2.02149800	0.53895500
H	-1.69453100	2.00173200	2.20336200
H	-0.72503500	3.37471100	1.62501600
H	1.69559600	1.47181000	3.81993500
H	0.94933200	3.05594900	3.57120000
H	-0.03073800	1.70639000	4.15667600
C	-1.31223200	-2.58058100	1.98031500
H	-1.63088100	-1.53533100	1.89020200
H	-2.08646200	-3.20884300	1.52822700
H	-1.26153700	-2.82932700	3.04577300
C	0.04266900	-0.30519800	-1.59376500
O	0.85213200	-0.34719900	-2.47551800
O	-1.19423000	0.19613800	-1.88406700
H	-0.50004500	-0.39241700	0.46147500

IV

C	2.95735900	-0.56160300	-0.78672700
C	2.24189900	-1.16048000	0.46292800
C	0.62798300	-1.14641200	-1.55964200
C	1.92607400	-0.40856100	-1.92860600
H	3.71414200	-1.30035800	-1.08831500
H	1.69917900	0.64960700	-2.10177000
H	2.31321300	-0.81305000	-2.87086100
C	0.95435900	-0.40390900	0.75012100
C	1.03136800	-2.59624900	-1.21684600
H	0.15474500	-3.25003200	-1.18522800
H	1.65815400	-2.95605100	-2.04108500

C	1.80490200	-2.60411200	0.10920300
H	1.17631200	-2.98509900	0.92369100
H	2.68824800	-3.25085500	0.05518800
N	0.15809100	-0.47536000	-0.29483900
C	3.14034100	-1.16731800	1.69506000
H	3.33538000	-0.15004500	2.04368300
H	2.64848600	-1.70817500	2.51042800
H	4.09803300	-1.65937500	1.48454700
C	-0.40836200	-1.10358900	-2.66924400
H	-1.32570400	-1.62575100	-2.37866500
H	-0.67492500	-0.07862800	-2.94158500
H	0.00339300	-1.60099000	-3.55335000
C	-1.14489200	0.16252400	-0.25011100
C	-1.26567500	1.53278000	-0.52307400
C	-2.26198500	-0.62604600	0.07716900
C	-2.55089900	2.08480600	-0.54376800
C	-3.52139700	-0.02966100	0.05390700
C	-3.67069500	1.31336200	-0.27468800
H	-2.66808700	3.14213500	-0.76530900
H	-4.39825300	-0.61973900	0.30034500
H	-4.65956000	1.76093700	-0.29846300
C	-2.08847700	-2.05783400	0.55146000
C	-3.27861300	-2.96347500	0.23129100
C	-1.78872700	-2.05433200	2.05809100
H	-1.21408100	-2.47552500	0.04526200
H	-3.55461400	-2.91106000	-0.82713800
H	-3.02916900	-4.00163200	0.47097600
H	-4.15870700	-2.69851800	0.82637400
H	-0.91003500	-1.43953000	2.27806100
H	-2.63970100	-1.63758800	2.60820900

H	-1.61296800	-3.07466400	2.41708500
C	-0.07250100	2.44413000	-0.75530100
C	-0.13378700	3.68283500	0.15045000
C	0.03435700	2.87983800	-2.22188300
H	0.83101700	1.89058000	-0.48589900
H	-0.39084900	3.41625800	1.17917000
H	0.83281100	4.19566200	0.15424000
H	-0.88786700	4.39452400	-0.20288700
H	0.12105900	2.02595500	-2.90061100
H	-0.85459700	3.44877600	-2.51671600
H	0.91019200	3.52119100	-2.36797600
C	3.67429900	0.75910100	-0.50326000
H	2.99429800	1.48842500	-0.04849800
H	4.51653100	0.62326300	0.18051100
H	4.06372300	1.18599200	-1.43386800
C	0.76864500	1.58262100	2.56270300
O	-0.28515600	1.32785100	2.98656600
O	1.81766900	1.98094800	2.23580100

TS3

C	2.98923600	-0.41864900	-0.75954200
C	2.27562200	-1.10602800	0.44572800
C	0.68636500	-1.02348400	-1.59809100
C	1.96899300	-0.23254600	-1.90662600
H	3.76974000	-1.11970200	-1.08889300
H	1.71585400	0.82675300	-2.02856300
H	2.37920400	-0.57723200	-2.86266100
C	0.96442700	-0.40406600	0.74645000
C	1.12367300	-2.47875200	-1.32764900
H	0.26404700	-3.15508900	-1.34157800

H	1.76810100	-2.77716500	-2.16259300
C	1.88300000	-2.53922000	0.00532000
H	1.25802600	-2.98423200	0.78931900
H	2.78640100	-3.15456700	-0.07420100
N	0.18022400	-0.43469500	-0.30604600
C	3.15771000	-1.15781900	1.68876900
H	3.32411800	-0.15750100	2.09521200
H	2.67021400	-1.75559900	2.46617900
H	4.12860000	-1.61533100	1.46255700
C	-0.33706500	-0.94647200	-2.71747900
H	-1.24394100	-1.50676700	-2.46814100
H	-0.62630500	0.08478900	-2.93742300
H	0.09867800	-1.38455600	-3.62113700
C	-1.13954300	0.16877300	-0.24334700
C	-1.28843800	1.54850600	-0.44375800
C	-2.23860700	-0.66340300	0.03038800
C	-2.58612500	2.07062200	-0.44485900
C	-3.51120200	-0.09525500	0.02991600
C	-3.68898800	1.26004200	-0.22569600
H	-2.72668400	3.13535800	-0.60966500
H	-4.37583600	-0.71757300	0.23690000
H	-4.68773500	1.68568700	-0.23189500
C	-2.03586000	-2.11624600	0.42205300
C	-3.20097000	-3.02792800	0.03347400
C	-1.75327800	-2.19793200	1.92960600
H	-1.14696800	-2.48357000	-0.09806800
H	-3.46705900	-2.91794600	-1.02305500
H	-2.92963200	-4.07264600	0.21329800
H	-4.09308800	-2.81969700	0.63307800
H	-0.89148600	-1.58033900	2.20119700

H	-2.61792200	-1.83057900	2.49324700
H	-1.56220100	-3.23492400	2.22787400
C	-0.11568500	2.49885600	-0.61833800
C	-0.20695000	3.68145500	0.35689400
C	-0.01524800	3.01825300	-2.05796900
H	0.80090000	1.95381700	-0.37740300
H	-0.44016500	3.34951800	1.37178400
H	0.74371900	4.22263100	0.38035800
H	-0.98610700	4.38768100	0.05003600
H	0.09431400	2.20613900	-2.78334800
H	-0.91644300	3.58165300	-2.32475100
H	0.84536800	3.68743800	-2.16363600
C	3.66418400	0.90338400	-0.39265100
H	2.95978700	1.58418900	0.09862300
H	4.50470800	0.75142600	0.28977500
H	4.04828500	1.39465900	-1.29313300
C	0.63517900	1.25283100	2.50945100
O	-0.42404800	0.96729200	2.91736300
O	1.66246800	1.79103300	2.31398200

1B

C	-3.05388800	0.07878200	0.64115800
C	-2.37470700	-0.98051100	-0.28055200
C	-0.79877300	-0.41186800	1.71556600
C	-2.07655600	0.44432700	1.78578200
H	-3.93368400	-0.42118700	1.06712000
H	-1.79638500	1.50266400	1.73322500
H	-2.53776000	0.28465100	2.76622700
C	-1.02525300	-0.44439600	-0.64994600
C	-1.21429000	-1.89522000	1.78471600

H	-0.32038500	-2.52474600	1.83073400
H	-1.75695900	-2.03754600	2.72509800
C	-2.09063400	-2.24770300	0.56805400
H	-1.59865900	-2.98829600	-0.07088800
H	-3.05323800	-2.67128400	0.87390600
N	-0.23126000	-0.18379800	0.34522000
C	-3.20156200	-1.31777400	-1.51625600
H	-3.29058100	-0.44965400	-2.17371700
H	-2.71451900	-2.11413700	-2.08586300
H	-4.20202400	-1.64967400	-1.21947200
C	0.19491300	-0.04965300	2.80432100
H	1.10739000	-0.64684500	2.73087700
H	0.47597000	1.00525200	2.75845900
H	-0.26932400	-0.24324200	3.77574100
C	1.12830500	0.28110400	0.13306900
C	1.36808900	1.66179900	0.06694100
C	2.14633600	-0.67711200	0.00980200
C	2.69892400	2.07497400	-0.02314500
C	3.45785400	-0.20676600	-0.07756500
C	3.73643800	1.15373600	-0.07224400
H	2.91945300	3.13763200	-0.07016900
H	4.27053100	-0.92207300	-0.16621300
H	4.76429700	1.49706300	-0.13697800
C	1.88540400	-2.17233300	-0.07692600
C	2.46274300	-2.91706800	1.13305500
C	2.44730800	-2.74402700	-1.38489200
H	0.80354500	-2.33359100	-0.10975700
H	2.05918500	-2.54839500	2.08228000
H	2.24051300	-3.98677200	1.06125400
H	3.55176200	-2.80504800	1.17255100

H	2.00996200	-2.22333700	-2.23888500
H	3.53867300	-2.65578100	-1.41903100
H	2.19741200	-3.80758400	-1.45865900
C	0.26128000	2.70264600	0.03086900
C	0.33869400	3.52628400	-1.26108000
C	0.29385300	3.61877300	1.25978100
H	-0.69861100	2.18074500	0.00716500
H	0.28731600	2.86875600	-2.13099700
H	-0.50574300	4.22226600	-1.30342900
H	1.26071700	4.11688900	-1.29936700
H	0.18595100	3.06419900	2.19790600
H	1.23820100	4.17183100	1.30877100
H	-0.51833400	4.35089400	1.20454800
C	-3.51517600	1.31208800	-0.13906600
H	-2.71857900	1.68081100	-0.79794000
H	-4.37953200	1.08295300	-0.76790800
H	-3.80530500	2.11209400	0.54935200
C	-0.60242400	-0.21885400	-2.10281700
O	-0.05444100	-1.20294400	-2.60953300
O	-0.94477200	0.90415600	-2.50349700

V

C	-0.47493600	-2.48522400	-1.79556100
C	-0.40030700	-2.37848600	-0.24169800
C	-2.67434000	-1.42180300	-1.08683000
C	-1.80475800	-1.85624600	-2.28034800
H	-0.48076700	-3.56043600	-2.01735800
H	-1.60976300	-0.98138500	-2.91161600
H	-2.38361100	-2.56414500	-2.88294000
C	-0.67796000	-0.94898300	0.11245300

C	-2.92360500	-2.65995800	-0.20143300
H	-3.62208400	-2.40320400	0.60083200
H	-3.41670700	-3.41046100	-0.82808900
C	-1.58674700	-3.17995300	0.35660200
H	-1.54793300	-3.08538600	1.44662300
H	-1.43236000	-4.23693600	0.11490400
N	-1.81981100	-0.47854700	-0.29015800
C	0.93026500	-2.86314400	0.32311000
H	1.75578300	-2.21403100	0.01369900
H	0.89228500	-2.86423500	1.41577600
H	1.12879700	-3.88129900	-0.02975000
C	-3.97435200	-0.77206900	-1.52529900
H	-4.57242700	-0.45201800	-0.66817200
H	-3.79802500	0.09970400	-2.15963000
H	-4.55115600	-1.50568800	-2.09603100
C	4.94959100	0.96435800	0.33780400
C	4.35361500	-0.44927100	0.64832200
B	3.18681500	0.55331900	-1.01602400
O	3.92475200	1.56978500	-0.47507900
O	3.50513400	-0.68085000	-0.50225600
C	6.21073000	0.90262200	-0.52411600
H	6.45242400	1.91263500	-0.86589700
H	7.06396300	0.50836700	0.03652700
H	6.04836800	0.27364600	-1.40503000
C	5.18911100	1.83747900	1.55946000
H	5.90951000	1.36497800	2.23628600
H	5.59668900	2.80175200	1.24257300
H	4.25921000	2.01822200	2.10077800
C	5.37851000	-1.57148300	0.71936200
H	6.09661800	-1.38554900	1.52551500

H	4.86672900	-2.51511200	0.93092000
H	5.92320400	-1.68058000	-0.22076400
C	3.47480500	-0.45448400	1.89563900
H	2.93890300	-1.40601900	1.95744200
H	4.08374400	-0.34613100	2.79932700
H	2.72488100	0.33843300	1.86149700
C	-2.25691200	0.86671100	0.04378000
C	-1.95454600	1.91866100	-0.83469100
C	-2.98005500	1.04826000	1.23259600
C	-2.50340600	3.16849100	-0.54206400
C	-3.50030700	2.32124800	1.47597200
C	-3.28656800	3.36631900	0.58758300
H	-2.29645600	4.00319400	-1.20552800
H	-4.07128800	2.49397000	2.38383200
H	-3.70592000	4.34659500	0.79194500
C	-3.17713900	-0.04492900	2.27119300
C	-4.65713300	-0.41250000	2.43240800
C	-2.57172100	0.37505600	3.61696000
H	-2.62610300	-0.93416900	1.95063200
H	-5.11115400	-0.73611500	1.48961300
H	-4.76896300	-1.22267000	3.16028500
H	-5.23244800	0.44496800	2.79795100
H	-1.50826900	0.59395900	3.50121000
H	-3.08426300	1.25327600	4.02433600
H	-2.67966000	-0.44026000	4.33974300
C	-1.02942600	1.77510400	-2.03224600
C	0.13970200	2.76409700	-1.93389600
C	-1.77552700	1.95986000	-3.35927800
H	-0.59267600	0.77312800	-2.00920700
H	0.67722000	2.62598300	-0.99372000

H	0.83747600	2.59099200	-2.75943600
H	-0.21098000	3.79964400	-2.00635000
H	-2.58034400	1.22975000	-3.49429400
H	-2.22111600	2.95901900	-3.41801900
H	-1.08032500	1.85455900	-4.19842400
C	0.73598600	-1.84168400	-2.47048100
H	0.88187600	-0.81716500	-2.10812000
H	1.65923000	-2.38787000	-2.26143600
H	0.59616200	-1.80856200	-3.55575500
C	0.26839800	-0.10320200	0.96185000
O	0.18687000	-0.40071400	2.16073000
O	0.95794100	0.69714200	0.31090800
H	2.47294900	0.70390400	-1.95279700

TS4

C	0.46207500	-2.69641100	1.70067900
C	0.38388900	-2.45089800	0.16174500
C	2.53718200	-1.35212300	1.14591300
C	1.64294000	-1.88529900	2.27790600
H	0.68317500	-3.76770600	1.80153500
H	1.27468300	-1.03332300	2.86274500
H	2.25540700	-2.49797600	2.94769400
C	0.55549100	-0.98300000	-0.11468200
C	2.91876200	-2.54149700	0.23617200
H	3.67670800	-2.22919700	-0.48770300
H	3.38217300	-3.29683700	0.87993900
C	1.66132600	-3.08966300	-0.45742600
H	1.66403500	-2.87435000	-1.53070000
H	1.57734500	-4.17503200	-0.33962500
N	1.64958100	-0.44617600	0.33854500

C	-0.86976900	-3.03718800	-0.47756900
H	-1.76819200	-2.49332000	-0.17212700
H	-0.79274500	-2.98374700	-1.56656700
H	-0.96558700	-4.08726700	-0.17930100
C	3.76288300	-0.62618200	1.67090300
H	4.37223200	-0.22180300	0.85888800
H	3.49282100	0.19791600	2.33519100
H	4.36794300	-1.34219900	2.23463200
C	-4.53571300	1.01873400	-0.25892300
C	-4.12480500	-0.42186400	-0.71743800
B	-2.53435200	0.44276000	0.66528400
O	-3.33779500	1.52774600	0.34155200
O	-3.10359000	-0.75985500	0.23851800
C	-5.60653000	1.00466800	0.83384800
H	-5.70150100	2.01503800	1.24112800
H	-6.58132500	0.68870300	0.44848900
H	-5.31445000	0.33471200	1.64842100
C	-4.95718000	1.94394700	-1.39153200
H	-5.83049900	1.54233300	-1.91795500
H	-5.22370200	2.92256900	-0.98155700
H	-4.14395600	2.08265200	-2.10606200
C	-5.23381900	-1.46073000	-0.61740400
H	-6.08259800	-1.18406100	-1.25261900
H	-4.85569000	-2.42937700	-0.95918800
H	-5.58390200	-1.57380900	0.41063800
C	-3.51592200	-0.45194500	-2.12027700
H	-3.05563300	-1.43171500	-2.28465700
H	-4.28613000	-0.30057300	-2.88421800
H	-2.73577800	0.30269000	-2.23547900
C	2.05174800	0.91801600	0.02220000

C	1.68169400	1.95712900	0.88950700
C	2.84048100	1.12468900	-1.12122600
C	2.22281200	3.21942700	0.63781500
C	3.34412700	2.41078700	-1.32745000
C	3.06199300	3.44390200	-0.44502400
H	1.96367000	4.04325400	1.29611300
H	3.96147100	2.60142600	-2.20062600
H	3.47257000	4.43381900	-0.61801500
C	3.13958300	0.04670900	-2.15126600
C	4.64057900	-0.25989800	-2.22909500
C	2.60229800	0.45147800	-3.53042000
H	2.60666800	-0.86503200	-1.86856800
H	5.05872500	-0.55081600	-1.25957900
H	4.82415400	-1.07380600	-2.93805300
H	5.19781700	0.61621100	-2.57772800
H	1.52728200	0.63521800	-3.48415600
H	3.10829500	1.34850900	-3.90328400
H	2.78178800	-0.35658400	-4.24696700
C	0.68486300	1.79374400	2.02401800
C	-0.46965900	2.79209000	1.86222900
C	1.34094600	1.95694800	3.40058000
H	0.24853600	0.79189600	1.95963500
H	-0.92587100	2.70360600	0.87367100
H	-1.24256300	2.59148400	2.60986400
H	-0.12126000	3.82086100	2.00634500
H	2.11737500	1.20794000	3.58795900
H	1.80257500	2.94592500	3.49637800
H	0.58601100	1.86233600	4.18754200
C	-0.83874200	-2.40147500	2.44123200
H	-1.15607000	-1.36574300	2.28593300

H	-1.65286600	-3.04844700	2.10616400
H	-0.69832100	-2.55886900	3.51585600
C	-0.31592200	-0.19405100	-1.09515400
O	-0.10964400	-0.59583700	-2.24275000
O	-1.03922600	0.71972300	-0.64174700
H	-1.84375300	0.44745600	1.63996700

VI

C	0.11040600	-2.50067600	1.85929800
C	0.30021400	-2.45464700	0.31259200
C	2.22473200	-1.15698000	1.49294500
C	1.15277400	-1.57138900	2.51390600
H	0.34937200	-3.53902200	2.12812900
H	0.67266500	-0.67199400	2.91487500
H	1.65255200	-2.06761100	3.35264800
C	0.52135800	-1.03627400	-0.15792600
C	2.77952900	-2.44354700	0.83982100
H	3.65462400	-2.20457200	0.22918100
H	3.12303000	-3.08951600	1.65489700
C	1.67714900	-3.12228000	0.01289900
H	1.87165300	-3.04409900	-1.06136500
H	1.58516900	-4.18544400	0.25738000
N	1.50662900	-0.39593000	0.40683100
C	-0.81179900	-3.17501100	-0.44407900
H	-1.76793100	-2.65008400	-0.36342200
H	-0.55036900	-3.26893500	-1.50268300
H	-0.92142000	-4.18323600	-0.03000100
C	3.33023900	-0.33315800	2.12615500
H	4.05969100	0.00654800	1.38810300
H	2.93612300	0.54268000	2.64254400

H	3.84528400	-0.96222900	2.85796600
C	-4.12103400	1.14350000	-0.35105200
C	-4.27231800	-0.38809000	-0.61245700
B	-2.04060400	0.14306900	-0.37737200
O	-2.74598300	1.36650600	-0.63092300
O	-3.02367700	-0.88759500	-0.14085800
C	-4.37922800	1.50363200	1.11541600
H	-4.05705000	2.53606600	1.28268000
H	-5.43852000	1.42237600	1.38137100
H	-3.79844800	0.84965900	1.77511700
C	-4.96329600	2.02730000	-1.26151100
H	-6.03053200	1.80470400	-1.14731300
H	-4.80311000	3.07857800	-1.00313900
H	-4.68122500	1.88863700	-2.30712600
C	-5.39538200	-1.06022500	0.16526600
H	-6.36478300	-0.61021400	-0.07744900
H	-5.43881200	-2.12273500	-0.09429500
H	-5.22753900	-0.97952300	1.24178400
C	-4.39797800	-0.70630700	-2.10511300
H	-4.26556300	-1.78369000	-2.24434200
H	-5.37921100	-0.42280800	-2.50063700
H	-3.62013200	-0.19033700	-2.67508200
C	1.94822000	0.93233200	-0.00950100
C	1.45546700	2.05958800	0.67612300
C	2.90858100	1.03155800	-1.03515200
C	1.94862700	3.30878700	0.29184300
C	3.36301800	2.30913700	-1.36822900
C	2.89255800	3.43881100	-0.71531300
H	1.57787800	4.19520800	0.79767900
H	4.10179800	2.41391700	-2.15707500

H	3.26068100	4.42145100	-0.99324300
C	3.50273600	-0.15473100	-1.78137600
C	4.98221700	-0.35109900	-1.42025100
C	3.36084100	0.00832400	-3.30050700
H	2.94613700	-1.05345300	-1.50852200
H	5.13875900	-0.51419100	-0.34939300
H	5.38704200	-1.21577100	-1.95656900
H	5.57072400	0.52640000	-1.70910200
H	2.32476000	0.20350000	-3.57845500
H	3.99382800	0.82117600	-3.67268800
H	3.67928300	-0.91299900	-3.79821900
C	0.42827500	2.01767000	1.79951700
C	-0.80649000	2.86236400	1.45493800
C	1.01058700	2.51166200	3.13241200
H	0.08952100	0.98622300	1.92240400
H	-1.25500400	2.58052400	0.50078700
H	-1.56713200	2.72274500	2.23080500
H	-0.55108500	3.92805000	1.43113900
H	1.86098000	1.92055100	3.48195700
H	1.34380200	3.55148100	3.04740900
H	0.23674500	2.47476700	3.90570500
C	-1.30659700	-2.20612400	2.34687600
H	-1.64958900	-1.22065800	2.02159900
H	-2.02285000	-2.93934100	1.96861500
H	-1.32670100	-2.24444500	3.44141100
C	-0.03715100	-0.67000500	-1.54001300
O	0.70011200	-1.05242000	-2.43389800
O	-1.19650800	-0.15669400	-1.64965900
H	-1.19755600	0.15472500	0.53052200

TS5

C	0.03164300	-2.46688500	1.87705200
C	0.23766200	-2.43414900	0.33358300
C	2.15652800	-1.14040000	1.52324300
C	1.05832800	-1.51944700	2.53028900
H	0.28002800	-3.49935800	2.16054400
H	0.56973800	-0.60622900	2.88833700
H	1.53189200	-1.99026400	3.39852900
C	0.46462800	-1.01405000	-0.15111000
C	2.70625800	-2.44622200	0.90768200
H	3.60514700	-2.23469400	0.32185900
H	3.00913600	-3.09047900	1.74034600
C	1.61504000	-3.10833300	0.05470900
H	1.83135500	-3.02351700	-1.01495500
H	1.51193100	-4.17298300	0.28803500
N	1.47535000	-0.39090700	0.40774700
C	-0.85716700	-3.17397200	-0.42901200
H	-1.82414800	-2.67023800	-0.36252000
H	-0.58422500	-3.27265400	-1.48467000
H	-0.95121000	-4.18192000	-0.01001600
C	3.26374400	-0.32480300	2.16541600
H	4.01652600	-0.01565700	1.43759100
H	2.87874200	0.57046500	2.65416600
H	3.74940400	-0.94914200	2.92110400
C	-4.03283900	1.16613100	-0.34091800
C	-4.28442300	-0.34573800	-0.63675600
B	-2.01935900	0.04417900	-0.48671500
O	-2.65462400	1.31377000	-0.66287400
O	-3.04766100	-0.93051800	-0.23531600
C	-4.22658900	1.50277700	1.14007700

H	-3.86429100	2.51932100	1.31953300
H	-5.27908400	1.45301300	1.43799300
H	-3.64978400	0.81409000	1.76740700
C	-4.84580200	2.12353700	-1.20226000
H	-5.92055400	1.96447500	-1.05736400
H	-4.61185300	3.15583600	-0.92455600
H	-4.60689800	1.99462300	-2.25966300
C	-5.41007400	-0.97664800	0.17058000
H	-6.36143200	-0.46596500	-0.01687600
H	-5.52466600	-2.02658500	-0.11627100
H	-5.19229200	-0.93807500	1.24048300
C	-4.48749400	-0.61418400	-2.13041900
H	-4.42932700	-1.69316900	-2.30171300
H	-5.46265200	-0.25804000	-2.47914700
H	-3.70081700	-0.13259300	-2.71850700
C	1.95107700	0.92016500	-0.01496100
C	1.45465200	2.06311800	0.64169600
C	2.95390500	0.99604500	-1.00161100
C	1.98955300	3.30021400	0.27458400
C	3.44697700	2.26226700	-1.32330900
C	2.97617400	3.40511100	-0.69393900
H	1.62011400	4.19688500	0.76304300
H	4.21867300	2.34736400	-2.08261000
H	3.37748800	4.37811000	-0.95977400
C	3.55253200	-0.20567800	-1.71844200
C	5.01777100	-0.42306800	-1.31389300
C	3.45928100	-0.05204300	-3.24247300
H	2.97269500	-1.09181200	-1.45379700
H	5.14146100	-0.58397800	-0.23854200
H	5.42372000	-1.29675500	-1.83458700

H	5.62864700	0.44326200	-1.58992000
H	2.43638900	0.16154600	-3.55346200
H	4.11875200	0.74600800	-3.60076200
H	3.77444700	-0.98291500	-3.72431600
C	0.37988700	2.04499000	1.72106000
C	-0.80855100	2.93423800	1.33235800
C	0.91835400	2.50722900	3.08333900
H	0.00044300	1.02440700	1.81826300
H	-1.24139000	2.64857500	0.37211200
H	-1.59219300	2.83848300	2.09136000
H	-0.51084400	3.98833600	1.29757700
H	1.72006800	1.87441300	3.47201800
H	1.30463300	3.53013500	3.01882900
H	0.10664600	2.50532600	3.81776000
C	-1.39178000	-2.18665500	2.35425000
H	-1.74186900	-1.20360000	2.02981300
H	-2.09827000	-2.92622400	1.96974100
H	-1.41958700	-2.22633600	3.44856000
C	-0.01055800	-0.71156800	-1.58326000
O	0.76964200	-1.06996900	-2.44511400
O	-1.19640900	-0.25802400	-1.74337100
H	-1.13124100	-0.03997100	0.41644500

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