Supporting Information

Interrupted *intra* [3+2] to 5-endo-dig Cyclization: [3 + 2] cycloaddition of nitrile ylides of diazo esters: Photo induced solvent free gem-diamination to α-amino-α-substituted α-amino esters

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Content

1. Reagent Information

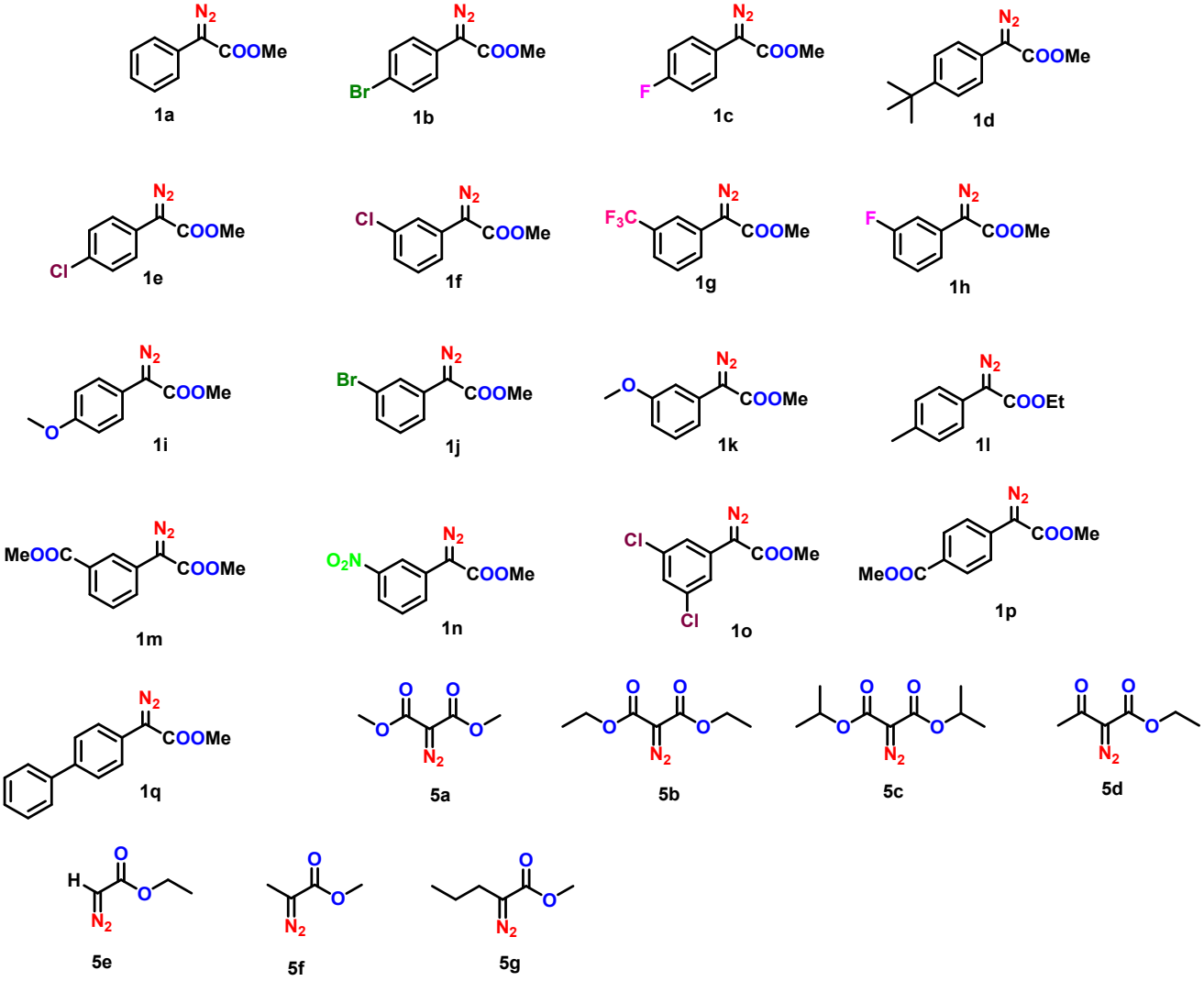
All the reactions were carried out in 20 ml borosilicate glass vials. All the chemicals were purchased from Sigma Aldrich, Alfa Aesar and TCI-India. Solvents were bought from commercial sources and were used without further purification. Silica gel (100 - 200 mesh) was used for column chromatography obtained from Merck. Petroleum ether and ethyl acetate mixture was used as a gradient elution for column chromatography. A gradient elution using petroleum ether and ethyl acetate was performed, based on Merck aluminium thin layer chromatography (TLC) sheets.

2. Analytical Information

Photochemical reactions were carried out in 20 ml borosilicate glass vials. The description of the light set-up used for this transformation include, a (420-450) nm 34 W Kessil Lamp attached with a cooling fan. The reactions were monitored through TLC by visualising in UV detector. All purifications were done in silica gel (100-200 mesh size) column chromatography. All ^{1}H and ^{13}C NMR spectra were recorded taking tetramethyl silane (TMS) as an internal standard at ambient temperature unless otherwise indicated with Bruker 400 MHz instruments at 400 MHz for ^{1}H and 100 MHz for ^{13}C NMR spectroscopy. Splitting patterns are designated as singlet (s), broad singlet (br s), doublet (d), triplet (t), quartet (q), quintet (quin) doublet of doublets (dd) and triplet of doublets (td). Splitting patterns that could not be interpreted or easily visualized are designated as multiplet (m). Ultraperformance liquid chromatography was carried out using an Agilent 6540 accurate mass Q-TOF LC/MS (Agilent Technologies, USA). MS analyses were performed under the following operation parameters: dry gas temperature 350 °C, dry gas (N_2) flow rate 10 L/min, nebulizer pressure 30 psi, Vcap 4000, and fragmentor voltage 100 V. Mass spectra were acquired in the positive-ion mode by scanning from 100 to 1500 at the mass to charge ratio (m/z). The mobile-phase composition used for UHPLC–QTOF MS comprised H_2O (A) and ACN (B), with optimized linear gradient elution. The injection volume was 5 μL. The flow rate was set at 0.3 mL/min. Accurate mass analysis calibration was carried out using the ESI-low concentration tuning mix solution provided by Agilent Technologies, USA. The accuracy error threshold was set at 5 ppm.

3. General synthetic procedure:

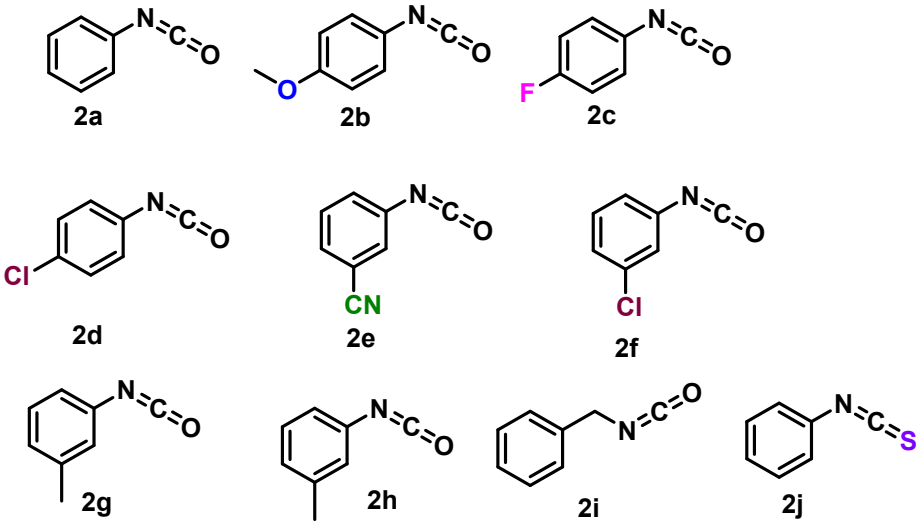
3.1 Synthesis of aryl diazo esters (1a-1q) to (5a-5d):



Scheme S1: Structures of aryl diazoesters used in this study.

All aryl diazo acetates were prepared by reported procedure. Aryl acetates (1 equivalent, 5 mmol) were dissolved in acetonitrile (10ml) in a clean oven dried round bottom flask, added DBU (1,8-Diazabicyclo[5.4.0]undec-7-ene) (1.2equivalent, 6 mmol), stirred for 10 minutes, pABSA (4-Acetamidobenzenesulfonyl azide) (1.2 equivalent, 6 mmol) was added, stirred for 4 hours in dark ant r.t; after completion acetonitrile was removed under vacuum, diluted with ethyl acetate (25ml), washed with water and organic layer was dried with brine and sodium sulphate, purified with flash column chromatography in silica gel (100-200 mesh size) with 5% ethyl acetate in hexane to yield 92-98%. [1]

3.2 Used isocyanates:



Scheme S2: Structures of various aryl isocyanates

The photoreactor used is the Kessil Photo Reaction PR160L-370 Gen 2

Specification:

Power Consumption (AC) 370nm Gen 2 (max 44W), 370nm (max 43W), 390nm (max 52W), 427nm & 440nm (max 45W), 456nm (max 50W), 467nm (max 44W), 525nm (max 44W)

Input Voltage 100-240 VAC
Operating Temperature 0 - 40°C / 32 - 104°F
Beam Angle 56°
Wavelength Options 370nm, 390nm, 427nm, 440nm, 456nm, 467nm, 525nm
Dimensions (H x D) 4.49" x 2.48" / 11.4cm x 6.3cm

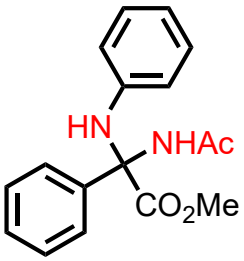
3.3 General synthetic procedure for synthesis of 4a-4aaf

Compounds synthesised using general procedure; **1a** (0.50 mmol, 1.2equiv.) (0.42 mmol, 1equiv.), and **2a** (0.42 mmol, 1equiv.) was dissolved in **3a** acetonitrile (1.26 mmol, 3equiv.) oven dried borosilicate glass vial, stirred and irradiated with 450nM LED for 6hr. The reaction was monitored by TLC and once it indicates complete consumption of the starting material, the solvent was removed under reduced pressure. Without any further work up column chromatography was done in silica gel (100-200 mesh size) with (15-30) % ethyl acetate in hexane to obtain the pure compounds.

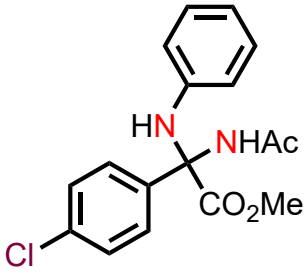
Figure S2. Dedicated Kessil photo reactor used in this work

4. Characterization data:

methyl 2-acetamido-2-phenyl-2-(phenylamino) acetate (4a); 4a was synthesised using general procedure; **1a** (0.50 mmol, 1.2equiv.), **2a** (0.42 mmol, 1equiv.), was dissolved in **3a** acetonitrile (1.26 mmol, 3equiv.) oven dried borosilicate glass vial, stirred and irradiated with 450nM LED for 6hr. The reaction was monitored by TLC. After completion solvent was removed under reduced pressure. Without any further work up column chromatography was done in silica gel (100-200 mess size) with ethyl acetate (15-30%) in hexane to afford the desired product, **4a,** as yellow solid, (76%, 95.23mg); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.76 – 7.73 (m, 2H), 7.43 – 7.37 (m, 3H), 7.14 (s, 1H), 7.09 – 7.05 (m, 2H), 6.68 – 6.74 (m, 1H), 6.49 – 6.47 (m, 2H), 5.79 (s, 1H), 3.71 (s, 3H), 1.90 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 170.9, 169.7, 143.4, 137.7, 129.1, 129.0, 128.9, 126.5, 119.4, 116.5, 74.2, 53.7, 22.9. HRMS (ESI-TOF) m/z calcd for $C_{17}H_{18}N_2O_3$ $[M+H]^+$299.139, found 249.0207.

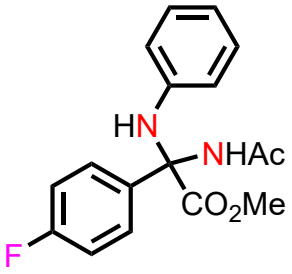


methyl 2-acetamido-2-(4-chlorophenyl)-2-(phenylamino)acetate (4b); 4b was synthesised using general procedure; **1e** (0.50 mmol, 1.2equiv.), **2a** (0.42 mmol, 1equiv.), was dissolved in **3a** acetonitrile (1.26 mmol, 3equiv.) oven dried borosilicate glass vial, sti rred and irradiated with 450nM LED for 6hr. The reaction was monitored by TLC. After completion solvent was removed under reduced pressure. Without any further work up column chromatography was done in silica gel (100-200 mess size) with



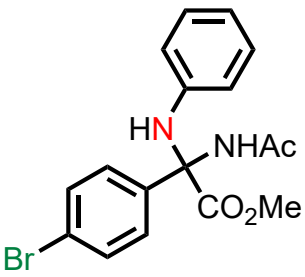
ethyl acetate (15-30%) in hexane to afford the desired product, **4b,** as yellow solid, (71%, 99.23mg); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.71 – 7.67 (m, 2H), 7.39 – 7.36 (m, 2H), 7.12 – 7.07 (m, 3H), 6.80 (t, *J* = 7.4 Hz, 1H), 6.49 (d, *J* = 7.6 Hz, 2H), 5.75 (s, 1H), 3.72 (s, 3H), 1.91 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 170.7, 169.8, 143.3, 136.6, 135.3, 129.3, 129.1, 128.2, 119.9, 116.7, 74.2, 54.0, 23.0. HRMS (ESI-TOF) m/z calcd for $C_{17}H_{17}ClN_2O_3$ $[M+H]^+$333.1000, found 249.0207.

methyl 2-acetamido-2-(4-fluorophenyl)-2-(phenylamino)acetate (4c); 4c was synthesised using general procedure; **1c** (0.50 mmol, 1.2equiv.), **2a** (0.42 mmol, 1equiv.), was dissolved in **3a** acetonitrile (1.26 mmol, 3equiv.) oven dried borosilicate glass vial, stirred and irradiated with 450nM LED for 6hr. The reaction was monitored by TLC. After completion solvent was removed under reduced pressure. Without any further work up column chromatography was done in silica gel (100-200 mess size) with ethyl acetate (15-30%) in hexane to afford the desired product, **4c,**

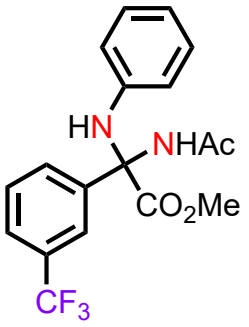


as yellow solid, (86%, 114.26mg); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.75 – 7.71 (m, 2H), 7.12 – 7.06 (m, 4H), 7.03 (s, 1H), 6.80 (t, *J* = 7.4 Hz, 1H), 6.50 (d, *J* = 7.8 Hz, 2H), 5.75 (s, 1H), 3.73 (s, 3H), 1.92 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 170.9, 169.7, 163.2 (d, *J* = 247 Hz), 143.4, 133.8 (d, *J* = 3 Hz), 129.1, 128.7 (d, *J* = 8 Hz), 119.9, 116.7, 116.1 (d, *J* = 22 Hz), 74.1, 53.9, 23.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ -112.85. HRMS (ESI-TOF) m/z calcd for $C_{18}H_{15}FN_2O_3$ $[M+H]^+$317.1296, found 317.1297.

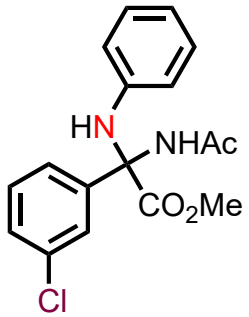
methyl 2-acetamido-2-(4-bromophenyl)-2-(phenylamino)acetate (4d); 4d was synthesised using general procedure; **1b** (0.50 mmol, 1.2equiv.), **2a** (0.42 mmol, 1equiv.), was dissolved in **3a** acetonitrile (1.26 mmol, 3equiv.) oven dried borosilicate glass vial, stirred and irradiated with 450nM LED for 6hr. The reaction was monitored by TLC. After completion solvent was removed under reduced pressure. Without any further work up column chromatography was done in silica gel (100-200 mess size) with ethyl acetate (15-30%) in hexane to afford the desired product, **4d,** as yellow solid, (73%, 115.66mg); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.63 – 7.60 (m, 2H), 7.54 – 7.50 (m, 2H), 7.15 (s, 1H), 7.11 – 7.07 (m, 2H), 6.79 (t, *J* = 7.4 Hz, 1H), 6.50- 6.47 (d, *J* = 7.3 Hz, 2H), 5.75 (s, 1H), 3.72 (s, 3H), 1.90 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 170.6, 169.9, 143.2, 137.1, 132.2, 131.9, 129.1, 128.5, 123.6, 119.9, 116.7, 74.2, 54.0, 23.0. HRMS (ESI-TOF) m/z calcd for $C_{18}H_{15}BrN_2O_3$$[M+H]^+$387.0339, found 387.0338.



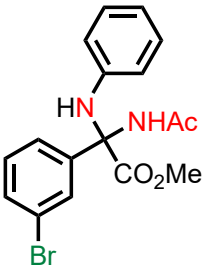
methyl 2-acetamido-2-(phenylamino)-2-(3-(trifluoromethyl)phenyl)acetate (4e); 4e was synthesised using general procedure; **1g** (0.50 mmol, 1.2equiv.), **2a** (0.42 mmol, 1equiv.), was dissolved in **3a** acetonitrile (1.26 mmol, 3equiv.) oven dried borosilicate glass vial, stirred and irradiated with 450nM LED for 6hr. The reaction was monitored by TLC. After completion solvent was removed under reduced pressure. Without any further work up column chromatography was done in silica gel (100-200 mess size) with ethyl acetate (15-30%) in hexane to afford the desired product, **4e,** as yellow solid, (88%, 135.39mg); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.03 (s, 1H), 7.95 (d, *J* = 8.0 Hz, 1H), 7.63 (d, *J* = 7.7 Hz, 1H), 7.53 (t, *J* = 8.0 Hz, 1H), 7.15 – 7.10 (m, 3H), 6.83 (t, *J* = 7.4 Hz, 1H), 6.53 – 6.50 (m, 2H), 5.76 (s, 1H), 3.74 (s, 3H), 1.93 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 170.7, 169.8, 143.2, 139.5, 131.6 (d, *J* = 32 Hz), 130.3, 129.6, 129.2, 126.1 (d, *J* = 3 Hz), 123.6 (d, *J* = 3 Hz), 123.7 123.6, 122.6, 120.5, 117.3 (d, *J* = 3 Hz), 74.5, 54.1, 23.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.47. HRMS (ESI-TOF) m/z calcd for $C_{18}H_{17}F_3N_2O_3$ $[M+H]^+$367.1264, found 367.1254.



methyl 2-acetamido-2-(3-chlorophenyl)-2-(phenylamino)acetate (4f); 4f was synthesised using general procedure; **1f** (0.50 mmol, 1.2equiv.), **2a** (0.42 mmol, 1equiv.), was dissolved in **3a** acetonitrile (1.26 mmol, 3equiv.) oven dried borosilicate glass vial, stirred and irradiated with 450nM LED for 6hr. The reaction was monitored by TLC. After completion solvent was removed under reduced pressure. Without any further work up column chromatography was done in silica gel (100-200 mess size) with ethyl acetate (15-30%) in hexane to afford the desired product, **4f,** as yellow solid, (76%, 106.22mg); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.70 – 7.67 (m, 2H), 7.39 – 7.36 (m, 2H), 7.13 – 7.09 (m, 2H), 6.99 (s, 1H), 6.81 (t, *J* = 7.4 Hz, 1H), 6.50 (d, *J* = 8.0 Hz, 2H), 5.73 (s, 1H), 3.73 (s, 3H), 1.92 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 170.7, 169.8, 143.3, 136.6, 135.3, 129.3, 129.1, 129.0, 128.8, 128.2, 119.9, 116.7, 74.2, 54.0, 23.0. HRMS (ESI-TOF) m/z calcd for $C_{17}H_{17}ClN_2O_3$ $[M+H]^+$333.1000, found 333.1001.

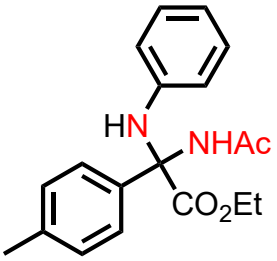


methyl 2-acetamido-2-(3-bromophenyl)-2-(phenylamino)acetate (4g); 4g was synthesised using general procedure; **1j** (0.50 mmol, 1.2equiv.), **2a** (0.42 mmol, 1equiv.), was dissolved in **3a** acetonitrile (1.26 mmol, 3equiv.) oven dried borosilicate glass vial, stirred and irradiated with 450nM LED for 6hr. The reaction was monitored by

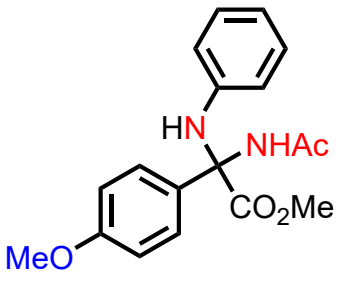


TLC. After completion solvent was removed under reduced pressure. Without any further work up column chromatography was done in silica gel (100-200 mess size) with ethyl acetate (15-30%) in hexane to afford the desired product, **4g,** as yellow solid, (71%, 112.49mg); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.91 (t, *J* = 2.0 Hz, 1H), 7.69 – 7.67 (m, 1H), 7.53- 7.50 (m, 1H), 7.28(d, *J* = 7.9 Hz, 1H), 7.13 – 7.08 (m, 2H), 7.04 (s, 1H), 6.83- 6.79 (m, 1H), 6.52 – 6.49 (m, 2H), 5.74 (s, 1H), 3.74 (s, 3H), 1.92 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 170.6, 169.7, 143.2, 140.5, 132.4, 130.6, 129.7, 129.2, 125.5, 123.3, 120.1, 116.9, 74.1, 54.1, 23.1. HRMS (ESI-TOF) m/z calcd for $C_{17}H_{17}BrN_2O_3$ $[M+H]^+$377.0495, found 377.0496.

ethyl 2-acetamido-2-(phenylamino)-2-(p-tolyl)acetate (4h); 4h was synthesised using general procedure; **1l** (0.50 mmol, 1.2equiv.), **2a** (0.42 mmol, 1equiv.), was dissolved in **3a** acetonitrile (1.26 mmol, 3equiv.) oven dried borosilicate glass vial, stirred and irradiated with 450nM LED for 6hr. The reaction was monitored by TLC. After completion solvent was removed under reduced pressure. Without any further work up column chromatography was done in silica gel (100-200 mess size) with ethyl acetate (15-30%) in hexane to afford the desired product, **4h,** as yellow solid, (70%, 95.96mg); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.62 – 7.60 (m, 2H), 7.20 (d, *J* = 8.1 Hz, 2H), 7.10 – 7.06 (m, 2H), 6.99 (s, 1H), 6.78 – 6.74 (m, 1H), 6.53 – 6.50 (m, 2H), 5.75 (s, 1H), 4.21- 4.13 (m, 2H), 2.36 (s, 3H), 1.91 (s, 3H), 1.16 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 170.6, 169.5, 143.7, 129.8, 128.9, 126.5, 119.4, 116.6, 74.3, 62.9, 23.1, 21.2, 13.9. HRMS (ESI-TOF) m/z calcd for $C_{19}H_{22}N_2O_3$ $[M+H]^+$327.1703, found 327.1702.

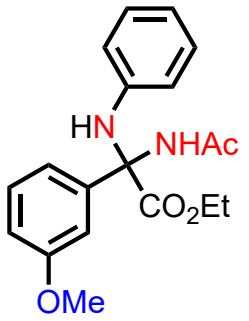


methyl 2-acetamido-2-(4-methoxyphenyl)-2-(phenylamino)acetate (4i); 4i was synthesised using general procedure; **1i** (0.50 mmol, 1.2equiv.), **2a** (0.42 mmol, 1equiv.), was dissolved in **3a** acetonitrile (1.26 mmol, 3equiv.) oven dried borosilicate glass vial, stirred and irradiated with 450nM LED for 6hr. The reaction was monitored by TLC. After completion solvent was removed under reduced pressure. Without any further work up column chromatography was done in silica gel (100-200 mess size) with ethyl acetate (15-30%) in hexane to afford the desired product, **4i,** as yellow solid, (66%, 91.02mg); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.33- 7.30 (m, 3H), 7.11 – 7.07 (m, 2H), 6.99 (s, 1H), 6.93- 6.89 (m, 1H), 6.78 (t, *J* = 7.4 Hz, 1H), 6.50 (d, *J* = 7.5 Hz, 2H), 5.78 (s, 1H), 3.80 (s, 3H), 3.73 (s, 3H), 1.91 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 170.9, 169.2, 160.2, 143.5, 139.6, 130.1, 129.0, 119.6, 118.7, 116.7, 114.5, 112.7, 74.3,

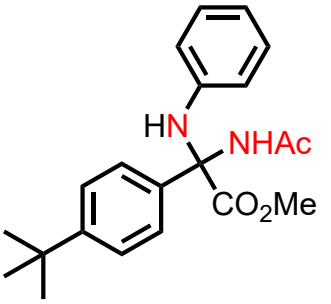


55.5, 53.9, 23.1. HRMS (ESI-TOF) m/z calcd for $C_{18}H_{20}N_2O_4$ $[M+H]^+$329.1496, found 329.1497.

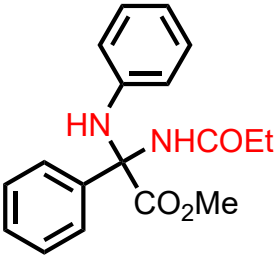
methyl 2-acetamido-2-(3-methoxyphenyl)-2-(phenylamino)acetate (4j); 4j was synthesised using general procedure; **1k** (0.50 mmol, 1.2equiv.), **2a** (0.42 mmol, 1equiv.), was dissolved in **3a** acetonitrile (1.26 mmol, 3equiv.) oven dried borosilicate glass vial, stirred and irradiated with 450nM LED for 6hr. The reaction was monitored by TLC. After completion solvent was removed under reduced pressure. Without any further work up column chromatography was done in silica gel (100-200 mess size) with ethyl acetate (15-30%) in hexane to afford the desired product, **4j,** as yellow solid, (73%, 104.97mg); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.33- 7.31 (m, 3H), 7.10 – 7.06 (m, 2H), 7.02 (s, 1H), 6.93 – 6.89 (m, 1H), 6.79 – 6.75 (m, 1H), 6.51 – 6.49 (m, 2H), 5.78 (s, 1H), 3.80 (s, 3H), 3.72 (s, 3H), 1.91 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 170.6, 169.4, 159.9, 143.2, 139.3, 129.8, 128.7, 119.3, 118.4, 116.4, 114.1, 112.4, 74.0, 55.2, 53.6, 22.8. HRMS (ESI-TOF) m/z calcd for $C_{17}H_{17}ClN_2O_3$ $[M+H]^+$333.1000, found 249.0207. HRMS (ESI-TOF) m/z calcd for $C_{18}H_{20}N_2O_4$ $[M+H]^+$329.1496, found 329.1442.



methyl 2-acetamido-2-(4-(tert-butyl)phenyl)-2-(phenylamino)acetate (4k); 4k was synthesised using general procedure; **1d** (0.50 mmol, 1.2equiv.), **2a** (0.42 mmol, 1equiv.), was dissolved in **3a** acetonitrile (1.26 mmol, 3equiv.) oven dried borosilicate glass vial, stirred and irradiated with 450nM LED for 6hr. The reaction was monitored by TLC. After completion solvent was removed under reduced pressure. Without any further work up column chromatography was done in silica gel (100-200 mess size) with ethyl acetate (15-30%) in hexane to afford the desired product, **4k,** as yellow solid, (74%, 110.16mg); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.67 – 7.63 (m, 2H), 7.42 – 7.38 (m, 2H), 7.18 (s, 1H), 7.08 – 7.04 (m, 2H), 6.75 (t, *J* = 7.2 Hz, 1H), 6.48 (d, *J* = 7.5 Hz, 2H), 5.76 (s, 1H), 3.71 (s, 3H), 1.88 (s, 3H), 1.32 (s, 9H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ171.2, 169.7, 152.1, 143.6, 134.6, 128.9, 126.4, 126.1, 119.3, 119.5, 74.2, 53.8, 34.7, 31.7, 23.0. HRMS (ESI-TOF) m/z calcd for $C_{21}H_{26}N_2O_3$ $[M+H]^+$355.2016, found 355.2015.

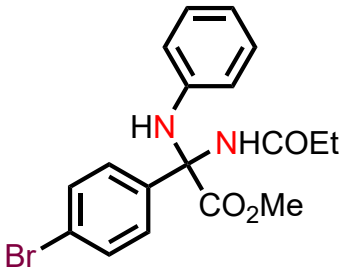


methyl 2-phenyl-2-(phenylamino)-2-propionamidoacetate (4l); 4l was synthesised using general procedure; **1a** (0.50 mmol, 1.2equiv.), **2a** (0.42 mmol,

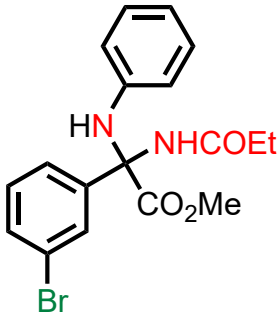


1equiv.), was dissolved in **3a** acetonitrile (1.26 mmol, 3equiv.) oven dried borosilicate glass vial, stirred and irradiated with 450nM LED for 6hr. The reaction was monitored by TLC. After completion solvent was removed under reduced pressure. Without any further work up column chromatography was done in silica gel (100-200 mess size) with ethyl acetate (15-30%) in hexane to afford the desired product, **4l,** as yellow solid, (75%, 98.39mg); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.77 – 7.75 (m, 2H), 7.41- 7.34 (m, 2H), 7.09 - 7.05 (m, 2H), 7.02 (s, 1H), 6.76 (t, *J* = 7.2 Hz, 1H), 6.51- 6.49 (m, 2H), 5.81 (s, 1H), 3.72 (s, 3H), 2.20 – 2.07 (m, 2H), 0.94 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 173.6, 171.1, 143.4, 138.1, 129.2, 129.1, 128.9, 126.6, 119.6, 116.8, 74.3, 60.5, 53.9, 9.6. HRMS (ESI-TOF) m/z calcd for $C_{18}H_{20}N_2O_4$ $[M+Na]^+$335.1366, found 335.1365.

methyl 2-(4-bromophenyl)-2-(phenylamino)-2-propionamidoacetate (4m); 4m was synthesised using general procedure; **1b** (0.50 mmol, 1.2equiv.), **2a** (0.42 mmol, 1equiv.), was dissolved in **3a** acetonitrile (1.26 mmol, 3equiv.) oven dried borosilicate glass vial, stirred and irradiated with 450nM LED for 6hr. The reaction was monitored by TLC. After completion solvent was removed under reduced pressure. Without any further work up column chromatography was done in silica gel (100-200 mess size) with ethyl acetate (15-30%) in hexane to afford the desired product, **4m,** as yellow solid, (75%, 123.24mg); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.65 – 7.62 (m, 2H), 7.55 – 7.52 (m, 2H), 7.12 – 7.08 (m, 2H), 6.96 (s, 1H), 6.80 (t, *J* = 7.2 Hz, 1H), 6.50 (d, *J* = 7.5 Hz, 2H), 5.74 (s, 1H), 3.73 (s, 3H), 2.19 – 2.07 (m, 2H), 0.94 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 173.6, 170.7, 143.3, 137.3, 132.2, 129.0, 128.5, 123.6, 120.0, 116.9, 74.1, 54.0, 29.4, 9.6. HRMS (ESI-TOF) m/z calcd for $C_{18}H_{19}BrN_2O_3$ $[M+H]^+$391.0652, found 391.0653.

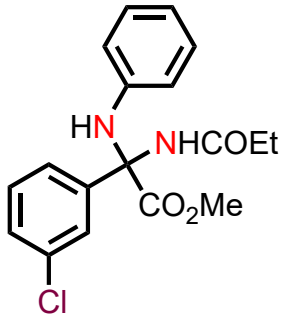


methyl 2-(3-bromophenyl)-2-(phenylamino)-2-propionamidoacetate (4n) ;4n was synthesised using general procedure; **1j** (0.50 mmol, 1.2equiv.), **2a** (0.42 mmol, 1equiv.), was dissolved in **3a** acetonitrile (1.26 mmol, 3equiv.) oven dried borosilicate glass vial, stirred and irradiated with 450nM LED for 6hr. The reaction was monitored by TLC. After completion solvent was removed under reduced pressure. Without any further work up column chromatography was done in silica gel (100-200 mess size) with ethyl acetate (15-30%) in hexane to afford the desired product, **4n,** as yellow solid, (72%, 118.31mg); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.94 (t, *J* = 1.9 Hz, 1H), 7.72-7.70 (m, 1H),

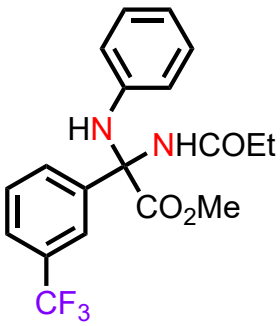


7.54 – 7.52 (m, 1H), 7.31-7.27 (m, 1H), 7.13- 7.08 (m, 3H), 6.84- 6.79 (m, 1H), 6.53 – 6.41 (m, 2H), 5.78 (s, 1H), 3.75 (s, 3H), 2.21- 2.08 (m, 2H), 0.95 (t, J = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 173.6, 170.6, 143.2, 140.6, 132.3, 130.6, 129.8, 129.0, 125.5, 123.2, 120.1, 117.0, 74.0, 54.0, 29.4, 9.6. HRMS (ESI-TOF) m/z calcd for $C_{18}H_{19}BrN_2O_3$ $[M+H]^+$391.0652, found 391.0654.

methyl 2-(3-chlorophenyl)-2-(phenylamino)-2-propionamidoacetate (4o); 4o was synthesised using general procedure; **1f** (0.50 mmol, 1.2equiv.), **2a** (0.42 mmol, 1equiv.), was dissolved in **3a** acetonitrile (1.26 mmol, 3equiv.) oven dried borosilicate glass vial, stirred and irradiated with 450nM LED for 6hr. The reaction was monitored by TLC. After completion solvent was removed under reduced pressure. Without any further work up column chromatography was done in silica gel (100-200 mess size) with ethyl acetate (15-30%) in hexane to afford the desired product, **4o,** as yellow solid, (66%, 96.13mg); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.65 – 7.62 (m, 2H), 7.55 – 7.53 (m, 2H), 7.12 – 7.08 (m, 2H), 6.94 (s, 1H), 6.82- 6.78 (m, 1H), 6.52- 6.49 (m, 2H), 5.73 (s, 1H), 3.73 (s, 3H), 2.19- 2.07 (m, 2H), 0.94 (t, J = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 1703.6, 170.7, 143.3, 137.4, 132.3, 129.1, 128.5, 123.6, 120.1, 117.0, 74.1, 54.0, 29.5, 9.6. HRMS (ESI-TOF) m/z calcd for $C_{18}H_{19}ClN_2O_3$ $[M+H]^+$347.1157, found 347.1167.

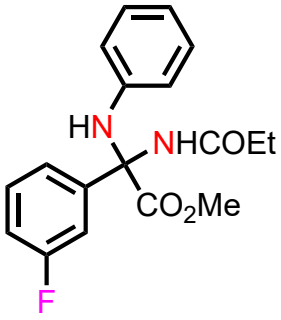


methyl 2-(phenylamino)-2-propionamido-2-(3-(trifluoromethyl)phenyl)acetate (4p); 4p was synthesised using general procedure; **1g** (0.50 mmol, 1.2equiv.), **2a** (0.42 mmol, 1equiv.), was dissolved in **3a** acetonitrile (1.26 mmol, 3equiv.) oven dried borosilicate glass vial, stirred and irradiated with 450nM LED for 6hr. The reaction was monitored by TLC. After completion solvent was removed under reduced pressure. Without any further work up column chromatography was done in silica gel (100-200 mess size) with ethyl acetate (15-30%) in hexane to afford the desired product, **4p,** as yellow solid, (93%, 148.57mg); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.03 (s, 1H), 7.96 (d, J = 7.6 Hz, 1H), 7.65 (d, J = 7.6 Hz, 1H), 7.54 (t, J = 7.8 Hz, 1H), 7.14 – 7.10 (m, 2H), 7.04 (s, 1H), 6.83 (t, J = 7.4 Hz, 1H), 6.54 – 6.51 (m, 2H), 5.75 (s, 1H), 3.75 (s, 3H), 2.21- 2.09 (m, 2H), 0.95 (t, J = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 173.6, 170.7, 143.3, 139.7, 131.6 (d, J = 32 Hz), 130.3, 129.6, 129.2, 126.1 (d, J = 3 Hz), 123.6 (d, J = 3 Hz), 120.5, 117.3 (d, J = 3 Hz), 54.1, 9.6. ^{19}F NMR (376 MHz,

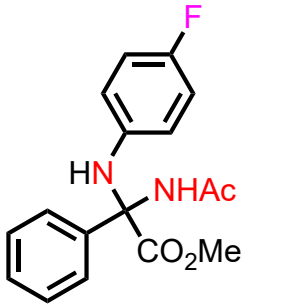


$CDCl_3$) δ -62.47. HRMS (ESI-TOF) m/z calcd for $C_{19}H_{19}F3N_2O_3$ $[M+H]^+$381.1421, found 381.1400.

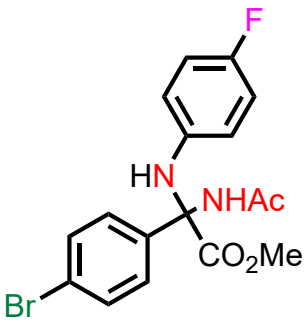
methyl 2-(3-fluorophenyl)-2-(phenylamino)-2-propionamidoacetate (4q); 4q was synthesised using general procedure; **1h** (0.50 mmol, 1.2equiv.), **2a** (0.42 mmol, 1equiv.), was dissolved in **3a** acetonitrile (1.26 mmol, 3equiv.) oven dried borosilicate glass vial, stirred and irradiated with 450nM LED for 6hr. The reaction was monitored by TLC. After completion solvent was removed under reduced pressure. Without any further work up column chromatography was done in silica gel (100-200 mess size) with ethyl acetate (15-30%) in hexane to afford the desired product, **4q,** as yellow solid, (89%, 123.48mg); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.55- 7.53 (m, 1H), 7.49 (dt, *J* = 10.1, 2.3 Hz, 1H), 7.40-7.34 (m, 1H), 7.11 – 7.05 (m, 4H), 6.79 (t, *J* = 7.2 Hz, 1H), 6.51 (dd, *J* = 8.6, 1.1 Hz, 2H), 5.77 (s, 1H), 3.73 (s, 3H), 2.19- 2.07 (m, *J* = 2H), 0.94 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 173.7, 170.7, 163.2 (d, *J* = 245 Hz), 143.3, 140.9 (d, *J* = 7 Hz), 130.6 (d, *J* = 8 Hz), 129.1, 129.0, 122.3 (d, *J* = 3 Hz), 120.0, 117.0, 116.2 (d, *J* = 21 Hz), 114.2 (d, *J* = 24 Hz), 74.1 (d, *J* = 2 Hz), 54.0, 9.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ -111.50. HRMS (ESI-TOF) m/z calcd for $C_{18}H_{19}FN_2O_3$ $[M+H]^+$331.1452, found 331.1451.



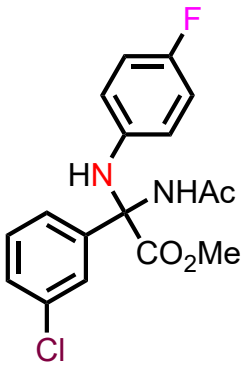
methyl 2-acetamido-2-((4-fluorophenyl)amino)-2-phenylacetate (4r); 4r was synthesised using general procedure; **1a** (0.44 mmol, 1.2equiv.), **2c** (0.36 mmol, 1equiv.), was dissolved in **3a** acetonitrile (1.26 mmol, 3equiv.) oven dried borosilicate glass vial, stirred and irradiated with 450nM LED for 6hr. The reaction was monitored by TLC. After completion solvent was removed under reduced pressure. Without any further work up c olumn chromatography was done in silica gel (100-200 mess size) with ethyl acetate (15-30%) in hexane to afford the desired product, **4r,** as yellow solid, (70%, 79.17mg); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.72 – 7.69 (m, 2H), 7.42 – 7.38 (m, 3H), 7.20 (s, 1H), 7.01 – 6.96 (m, 2H), 6.39 – 6.36 (m, 2H), 5.82 (s, 1H), 3.69 (s, 3H), 1.90 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 170.6, 169.9, 157.4 (d, *J* = 237 Hz), 139.5 (d, *J* = 2 Hz), 137.1, 132.3, 131.8, 128.5, 123.7, 118.5 (d, *J* = 7 Hz), 115.8, 115.7 (d, *J* = 22 Hz), 74.8, 54.0, 23.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ -124.02. HRMS (ESI-TOF) m/z calcd for $C_{17}H_{17}FN_2O_3$ $[M+H]^+$317.1296, found 317.1297.



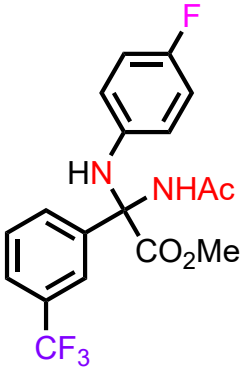
methyl 2-acetamido-2-(4-bromophenyl)-2-((4-fluorophenyl)amino)acetate (4s); 4s was synthesised using general procedure; **1b** (0.44 mmol, 1.2equiv.), **2c** (0.36 mmol, 1equiv.)**,** was dissolved in **3a** acetonitrile (1.26 mmol, 3equiv.) oven dried borosilicate glass vial, stirred and irradiated with 450nM LED for 6hr. The reaction was monitored by TLC. After completion solvent was removed under reduced pressure. Without any further work up column chromatography was done in silica gel (100-200 mess size) with ethyl acetate (15-30%) in hexane to afford the desired product, **4s,** as yellow solid, (74%, 105.02mg); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.63 – 7.59 (m, 2H), 7.55 – 7.51 (m, 2H), 7.08 (s, 1H), 6.83 – 6.78 (m, 2H), 6.48 – 6.45 (m, 2H), 5.63 (s, 1H), 3.72 (s, 3H), 1.90 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 170.6, 169.9, 157.45(d, *J* = 237 Hz), 139.5 (d, *J* = 2 Hz), 137.1, 132.3, 128.5, 123.7, 118.5(d, *J* = 7 Hz), 115.7 (d, *J* = 22 Hz), 74.8, 54.0, 23.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ -124.02. HRMS (ESI-TOF) m/z calcd for $C_{17}H_{16}BrFN_2O_3$ $[M+H]^+$395.0401, found 395.0402.



methyl 2-acetamido-2-(3-chlorophenyl)-2-((4-fluorophenyl)amino)acetate (4t); 4t was synthesised using general procedure; **1f** (0.44 mmol, 1.2equiv.), **2c** (0.36 mmol, 1equiv.)**,** was dissolved in **3a** acetonitrile (1.26 mmol, 3equiv.) oven dried borosilicate glass vial, stirred and irradiated with 450nM LED for 6hr. The reaction was monitored by TLC. After completion solvent was removed under reduced pressure. Without any further work up column chromatography was done in silica gel (100-200 mess size) with ethyl acetate (15-30%) in hexane to afford the desired product, **4t,** as yellow solid, (76%, 95.97mg); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.75 (t, *J* = 2.0 Hz, 1H), 7.64- 7.61 (m, 1H), 7.37-7.33 (m, 2H), 7.12 (s, 2H), 7.11 (s, 1H), 6.84 – 6.78 (m, 2H), 6.48 (dd, *J* = 8.9, 4.5 Hz, 2H), 5.64 (s, 1H), 3.73 (s, 3H), 1.91 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 170.6, 169.9, 157.45 (d, *J* = 237 Hz), 140.2, 139.5 (d, *J* = 2 Hz), 135.2, 130.3, 129.5, 126.9, 124.9, 118.5(d, *J* = 7 Hz), 115.7 (d, *J* = 22 Hz), 74.7, 54.1, 23.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ -124.02. HRMS (ESI-TOF) m/z calcd for $C_{17}H_{16}FClN_2O_3$ $[M+H]^+$351.0906, found 351.0905.

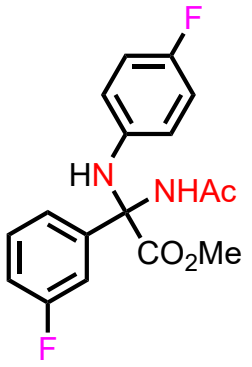


methyl 2-acetamido-2-((4-fluorophenyl)amino)-2-(3-(trifluoromethyl)phenyl)acetate (4u); 4u was synthesised using general procedure; **1g** (0.44 mmol, 1.2equiv.), **2c** (0.36 mmol, 1equiv.)**,** was dissolved in **3a** acetonitrile (1.26 mmol, 3equiv.) oven dried

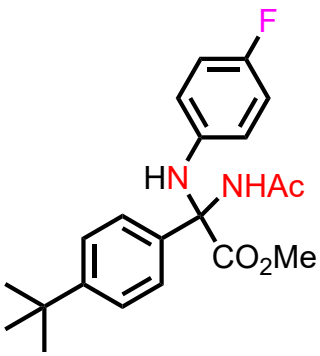


borosilicate glass vial, stirred and irradiated with 450nM LED for 6hr. The reaction was monitored by TLC. After completion solvent was removed under reduced pressure . Without any further work up column chromatography was done in silica gel (100-200 mess size) with ethyl acetate (15-30%) in hexane to afford the desired product, **4u,** as yellow solid, (86%, 118.98mg); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.02 (s, 1H), 7.93 (d, *J* = 7.6 Hz, 1H), 7.65 (d, *J* = 7.6 Hz, 1H), 7.54 (t, *J* = 7.8 Hz, 1H), 7.15 (s, 1H), 6.87 – 6.80 (m, 2H), 6.52 – 6.48 (m, 2H), 5.65 (s, 1H), 3.74 (s, 3H), 1.93 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.6, 169.9, 157.7(d, *J* = 237 Hz), 139.4(d, *J* = 2 Hz), 131.6(d, *J* = 32 Hz), 130.2, 129.6, 126.2(d, *J* = 3 Hz), 125.3, 123.7(d, *J* = 4 Hz), 122.6, 118.9(d, *J* = 8 Hz), 115.9, 115.7, 75.1, 54.2, 23.1 .^{19}F NMR (376 MHz, $CDCl_3$) δ -62.47, -123.52. HRMS (ESI-TOF) m/z calcd for $C_{18}H_{16}F_4N_2O_3$ $[M+H]^+$385.1170, found 385.1160.

methyl 2-acetamido-2-(3-fluorophenyl)-2-((4-fluorophenyl)amino)acetate (4v); 4v was synthesised using general procedure; **1h** (0.44 mmol, 1.2equiv.), **2c** (0.36 mmol, 1equiv.)**,** was dissolved in **3a** acetonitrile (1.26 mmol, 3equiv.) oven dried borosilicate glass vial, stirred and irradiated with 450nM LED for 6hr. The reaction was monitored by TLC. After completion solvent was removed under reduced pressure. Without any further work up column chromatography was done in silica gel (100-200 mess size) with ethyl acetate (15-30%) in hexane to afford the desired product, **4v,** as yellow solid, (84%, 101.09mg); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.53 – 7.45 (m, 2H), 7.39 - 7.34 (m, 1H), 7.24 (s, 1H), 7.07 (td, *J* = 8.7, 2.3 Hz, 1H), 6.781-6.76 (m, 2H), 6.45 (dd, *J* = 8.8, 4.4 Hz, 2H), 5.65 (s, 1H), 3.71 (s, 3H), 1.89 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 170.5, 169.9, 165.7 (d, *J* = 246 Hz), 157.3(d, *J* = 237 Hz), 140.6(d, *J* = 7 Hz), 139.4(d, *J* = 2 Hz), 130.6(d, *J* = 8 Hz), 122.2(d, *J* = 3 Hz), 118.4(d, *J* = 7 Hz), 116.4, 116.2, 115.7, 115.5, 114.3, 114.0, 74.6(d, *J* = 2 Hz), 54.0, 22.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ -124.02. HRMS (ESI-TOF) m/z calcd for $C_{17}H_{16}F_2N_2O_3$ $[M+H]^+$335.1202, found 335.1201.

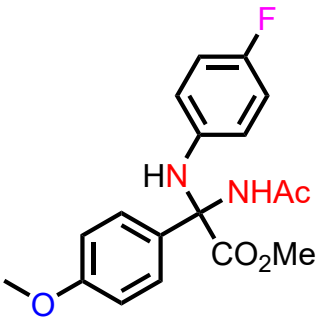


methyl 2-acetamido-2-(4-(tert-butyl)phenyl)-2-((4-fluorophenyl)amino)acetate (4w); 4w was synthesised using general procedure; **1d** (0.44 mmol, 1.2equiv.), **2c** (0.36 mmol, 1equiv.)**,** was dissolved in **3a** acetonitrile (1.26 mmol, 3equiv.) oven dried borosilicate glass vial, stirred and irradiated with 450nM LED for 6hr. The reaction was monitored by TLC. After completion solvent was removed under reduced pressure. Without any further work up column chromatography was done in silica gel (100-200 mess size)

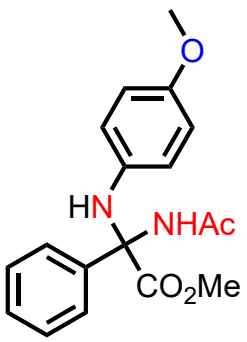


with ethyl acetate (15-30%) in hexane to afford the desired product, **4w,** as yellow solid, (75%, 100.55mg); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.64 – 7.61 (m, 2H), 7.42 – 7.39 (m, 2H), 7.03 (s, 1H), 6.81- 6.75 (m, 2H), 6.46 (dd, *J* = 8.9, 4.5 Hz, 2H), 5.65 (s, 1H), 3.72 (s, 3H), 1.90 (s, 3H), 1.32 (s, 9H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 171.2, 169.7, 157.45 (d, *J* = 237 Hz), 155.9, 152.3, 139.9, 134.7, 126.3, 126.1, 118.5(d, *J* = 7 Hz), 115.7 (d, *J* = 22 Hz), 74.8, 53.8, 34.7, 31.3, 23.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ -125.00. HRMS (ESI-TOF) m/z calcd for $C_{21}H_{25}FN_2O_3$ $[M+H]^+$373.1922, found 373.1932.

methyl 2-acetamido-2-((4-fluorophenyl)amino)-2-(3-methoxyphenyl)acetate (4x); 4x was synthesised using general procedure; **1i** (0.44 mmol, 1.2equiv.), **2c** (0.36 mmol, 1equiv.)**,**, was dissolved in **3a** acetonitrile (1.26 mmol, 3equiv.) oven dried borosilicate glass vial, stirred and irradiated with 450nM LED for 6hr. The reaction was monitored by TLC. After completion solvent was removed under reduced pressure. Without any further work up column chromatography was done in silica gel (100-200 mess size) with ethyl acetate (15-30%) in hexane to afford the desired product, **4x,** as yellow solid, (70%, 87.28mg); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.35 – 7.29 (m, 3H), 6.97 (s, 1H), 6.92 (dt, *J* = 5.9, 1.6 Hz, 1H), 6.82- 6.90 (m, 2H), 6.47 (dd, *J* = 9.0, 4.6 Hz, 2H), 5.67 (s, 1H), 3.81 (s, 3H), 3.73 (s, 3H), 1.91 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 170.9, 169.7, 160.3, 139.7, 139.6, 130.2, 118.6, 118.5(d, *J* = 7 Hz), 115.7 (d, *J* = 22 Hz), 114.5, 112.7, 74.8, 55.5, 53.9, 23.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ -124.70. HRMS (ESI-TOF) m/z calcd for $C_{18}H_{19}FN_2O_4$ $[M+H]^+$347.1402, found 347.1401.

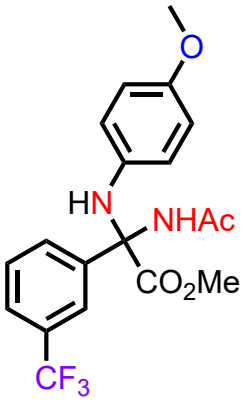


methyl 2-acetamido-2-((4-methoxyphenyl)amino)-2-phenylacetate (4y); 4y was synthesised using general procedure; **1a** (0.40 mmol, 1.2equiv.), **2b** (0.33 mmol, 1equiv.), was dissolved in **3a** acetonitrile (1.26 mmol, 3equiv.) oven dried borosilicate glass vial, stirred and irradiated with 450nM LED for 6hr. The reaction was monitored by TLC. After completion solvent was removed under reduced pressure. Without any further work up column chromatography was done in silica gel (100-200 mess size) with ethyl acetate (15-30%) in hexane to afford the desired product, **4y,** as brownish solid, (74%, 80.18mg); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.77 – 7.75 (m, 2H), 7.43- 7.37 (m, 3H), 7.09 (s, 1H), 6.69 – 6.65 (m, 2H), 6.52 – 6.47 (m, 2H), 5.50 (s, 1H), 3.71

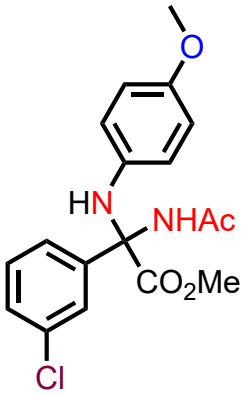


(d, J = 3.3 Hz, 6H), 1.89 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 171.2, 169.8, 153.9, 138.4, 137.2, 129.1, 129.0, 126.6, 119.1, 114.5, 75.4, 55.6, 53.8, 23.1. HRMS (ESI-TOF) m/z calcd for $C_{18}H_{20}N_2O_4$ $[M+H]^+$329.1496, found 329.1429.

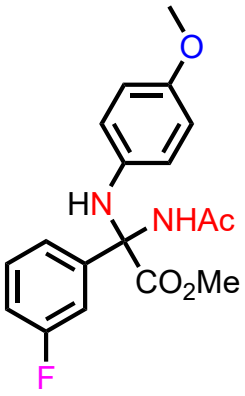
methyl 2-acetamido-2-((4-methoxyphenyl)amino)-2-(3-(trifluoromethyl)phenyl)acetate (4z); 4z was synthesised using general procedure; **1g** (0.40 mmol, 1.2equiv.), **2b** (0.33 mmol, 1equiv.), was dissolved in **3a** acetonitrile (1.26 mmol, 3equiv.) oven dried borosilicate glass vial, stirred and irradiated with 450nM LED for 6hr. The reaction was monitored by TLC. After completion solvent was removed under reduced pressure. Without any further work up column chromatography was done in silica gel (100-200 mess size) with ethyl acetate (15-30%) in hexane to afford the desired product, **4z,** as brownish solid, (96%, 125.56mg); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.04 (s, 1H), 7.95 (d, J = 8.0 Hz, 1H), 7.63 (d, J = 7.7 Hz, 1H), 7.53 (t, J = 7.8 Hz, 1H), 7.13 (s, 1H), 6.74 – 6.70 (m, 2H), 6.57 – 6.53 (m, 2H), 5.46 (m, 1H), 3.72 (d, J = 4.0 Hz, 6H), 1.94 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 170.8, 169.9, 154.6, 140.0, 138.4 (d, J = 320 Hz), 131.4 (d, J = 32 Hz), 130.2, 129.8 (d, J = 75 Hz), 126.0 (d, J = 4 Hz) 123.8 (d, J = 4 Hz), 120.0, 114.7, 75.8, 55.6, 54.0, 23.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.43. HRMS (ESI-TOF) m/z calcd for $C_{19}H_{19}F_3N_2O_4$ $[M+H]^+$397.1370, found 397.1360.



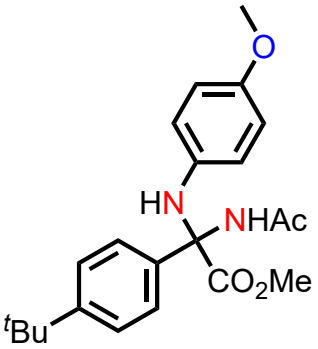
methyl 2-acetamido-2-(3-chlorophenyl)-2-((4-methoxyphenyl)amino)acetate (4aa); 4aawas synthesised using general procedure; **1f** (0.40 mmol, 1.2equiv.), **2b** (0.33 mmol, 1equiv.), was dissolved in **3a** acetonitrile (1.26 mmol, 3equiv.) oven dried borosilicate glass vial, stirred and irradiated with 450nM LED for 6hr. The reaction was monitored by TLC. After completion solvent was removed under reduced pressure. Without any further work up column chromatography was done in silica gel (100-200 mess size) with ethyl acetate (15-30%) in hexane to afford the desired product, **4aa,** as brownish solid, (80%, 95.78mg); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.77 – 7.74 (m, 2H), 7.41 – 7.38 (m, 2H), 7.01 (s, 1H), 6.69 – 6.67 (m, 2H), 6.54 – 6.50 (m, 2H), 5.50 (s, 1H), 3.72 (d, J = 2.9 Hz, 6H), 1.92 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 171.3, 169.7, 154.0, 138.4, 137.2, 129.1, 129.0, 126.6, 119.2, 114.5, 75.5, 55.6, 53.8, 23.2. HRMS (ESI-TOF) m/z calcd for $C_{18}H_{19}ClN_2O_4$ $[M+H]^+$363.1106, found 363.1105.



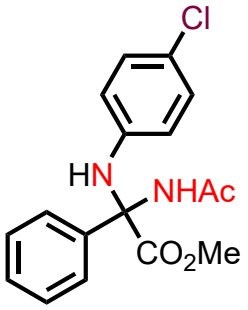
methyl 2-acetamido-2-(3-fluorophenyl)-2-((4-methoxyphenyl)amino)acetate (4ab); 4ab was synthesised using general procedure; **1h** (0.40 mmol, 1.2equiv.), **2b** (0.33 mmol, 1equiv.), was dissolved in **3a** acetonitrile (1.26 mmol, 3equiv.) oven dried borosilicate glass vial, stirred and irradiated with 450nM LED for 6hr. The reaction was monitored by TLC. After completion solvent was removed under reduced pressure. Without any further work up column chromatography was done in silica gel (100-200 mess size) with ethyl acetate (15-30%) in hexane to afford the desired product, **4ab,** as brownish solid, (94%, 107.44mg); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.77 (d, *J* = 2.0 Hz, 1H), 7.65- 7.62 (m, 1H), 7.35- 7.30 (m, 2H), 7.17 (s, 1H), 6.70 – 6.66 (m, 2H), 6.52 – 6.48 (m, 2H), 5.45 (s, 1H), 3.72 (d, *J* = 5.6 Hz, 6H), 1.89 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 170.7, 169.9, 154.2, 140.7, 136.8, 138.4 (d, *J* = 320 Hz), 131.4 (d, *J* = 32 Hz), 130.2, 135.0, 130.1, 129.8 (d, *J* = 75 Hz), 126.0 (d, *J* = 4 Hz), 125.0, 123.8 (d, *J* = 4 Hz), 119.5, 114.5, 75.3, 55.5, 53.9, 23.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ -124.70. HRMS (ESI-TOF) m/z calcd for $C_{18}H_{19}FN_2O_4$ $[M+H]^+$347.1402, found 347.1403.



methyl 2-acetamido-2-(4-(tert-butyl)phenyl)-2-((4-methoxyphenyl)amino)acetate (4ac); 4ac was synthesised using general procedure; **1d** (0.40 mmol, 1.2equiv.), **2b** (0.33 mmol, 1equiv.), was dissolved in **3a** acetonitrile (1.26 mmol, 3equiv.) oven dried borosilicate glass vial, stirred and irradiated with 450nM LED for 6hr. The reaction was monitored by TLC. After completion solvent was removed under reduced pressure. Without any further work up column chromatography was done in silica gel (100-200 mess size) with ethyl acetate (15-30%) in hexane to afford the desired product, **4ac,** as brownish solid, (74%, 85.09mg); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.66 – 7.64 (m, 2H), 7.41 – 7.39 (m, 2H), 7.07 (s, 1H), 6.68 – 6.66 (m, 2H), 6.52 – 6.49 (m, 2H), 5.48 (s, 1H), 3.71 (d, *J* = 6.7 Hz, 6H), 1.88 (s, 3H), 1.32 (s, 9H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 171.4, 169.7, 153.8, 152.0, 137.4, 135.2, 126.3, 125.9, 118.9, 114.5, 75.3, 55.6, 53.7, 34.7, 31.3, 23.1. HRMS (ESI-TOF) m/z calcd for $C_{22}H_{28}N_2O_4$ $[M+H]^+$385.2122, found 385.2121.

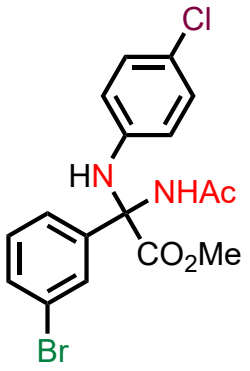


methyl 2-acetamido-2-((4-chlorophenyl)amino)-2-phenylacetate (4ad); 4ad was synthesised using general procedure; **1a** (0.39 mmol, 1.2equiv.), **2d** (0.32 mmol, 1equiv.), was dissolved in **3a** acetonitrile

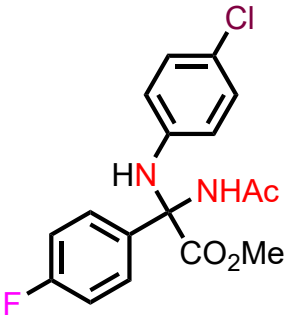


(1.26 mmol, 3equiv.) oven dried borosilicate glass vial, stirred and irradiated with 450nM LED for 6hr. The reaction was monitored by TLC. After completion solvent was removed under reduced pressure. Without any further work up column chromatography was done in silica gel (100-200 mess size) with ethyl acetate (15-30%) in hexane to afford the desired product, **4ad,** as white solid, (79%, 84.12mg); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.72 – 7.69 (m, 2H), 7.42 – 7.37 (m, 3H), 7.20 (s, 1H), 7.01 – 6.96 (m, 2H), 6.39 – 6.35 (m, 2H), 5.82 (s, 1H), 3.69 (s, 3H), 1.90 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 170.7, 169.9, 142.0, 137.3, 129.3, 129.2, 128.9, 126.6, 124.2, 117.6, 74.1, 53.9, 22.9. HRMS (ESI-TOF) m/z calcd for $C_{17}H_{17}ClN_2O_3$ $[M+H]^+$333.1000, found 333.1001.

methyl 2-acetamido-2-(3-bromophenyl)-2-((4-chlorophenyl)amino)acetate (4ae); 4ae was synthesised using general procedure; **1j** (0.39 mmol, 1.2equiv.), **2d** (0.32 mmol, 1equiv.), was dissolved in **3a** acetonitrile (1.26 mmol, 3equiv.) oven dried borosilicate glass vial, stirred and irradiated with 450nM LED for 6hr. The reaction was monitored by TLC. After completion solvent was removed under reduced pressure. Without any further work up column chromatography was done in silica gel (100-200 mess size) with ethyl acetate (15-30%) in hexane to afford the desired product, **4ae,** as white solid, (74%, 97.48mg); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.88 (t, *J* = 1.9 Hz, 1H), 7.66 – 7.63 (m, 1H), 7.54 – 7.51 (m, 1H), 7.29 (d, *J* = 8.0 Hz, 1H), 7.05 (dd, *J* = 8.0, 6.0 Hz, 3H), 6.45 – 6.41 (m, 2H), 5.77 (s, 1H), 3.73 (s, 3H), 1.93 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 170.4, 169.8, 141.8, 140.0, 132.6, 130.7, 129.7, 129.1, 125.4, 125.0, 123.4, 117.9, 74.0, 54.2, 23.0. HRMS (ESI-TOF) m/z calcd for $C_{17}H_{16}BrClN_2O_3$ $[M+Na]^+$432.9925, found 432.9924.

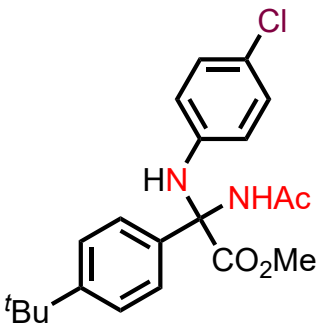


methyl 2-acetamido-2-((4-chlorophenyl)amino)-2-(4-fluorophenyl)acetate (4af); 4af was synthesised using general procedure; **1c** (0.39 mmol, 1.2equiv.), **2d** (0.32 mmol, 1equiv.), **1a** (0.50 mmol, 1.2equiv.), **2a** (0.42 mmol, 1equiv.), was dissolved in **3a** acetonitrile (1.26 mmol, 3equiv.) oven dried borosilicate glass vial, stirred and irradiated with 450nM LED for 6hr. The reaction was monitored by TLC. After completion solvent was removed under reduced pressure. Without any further work up column chromatography was done in silica gel (100-200 mess size) with ethyl acetate (15-30%) in hexane to afford the desired product, **4af,** as white solid, (90%, 101.02mg); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.71 – 7.67 (m, 2H), 7.14 (s, 1H), 7.10-

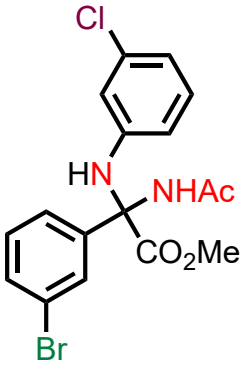


7.06 (m, 2H), 7.05 – 7.01 (m, 2H), 6.43 – 6.39 (m, 2H), 5.79 (s, 1H), 3.71 (s, 3H), 1.91 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 170.6, 169.9, 164.5, 163.3(d, *J* = 248 Hz), 141.9, 133.2(d, *J* = 3 Hz), 129.0, 128.7(d, *J* = 9 Hz), 124.6, 117.7, 116.3(d, *J* = 22 Hz), 73.9, 54.0, 22.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ -124.02. HRMS (ESI-TOF) m/z calcd for $C_{17}H_{16}FClN_2O_3$ $[M+Na]^+$373.0726, found 373.0725.

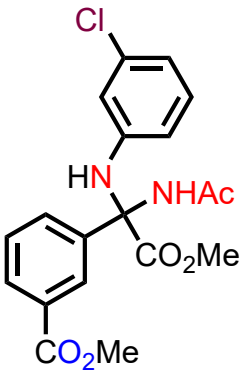
methyl 2-acetamido-2-(4-(tert-butyl)phenyl)-2-((4-chlorophenyl)amino)acetate (4ag); 4agwas synthesised using general procedure; **1d** (0.39 mmol, 1.2equiv.), **2d** (0.32 mmol, 1equiv.), was dissolved in **3a** acetonitrile (1.26 mmol, 3equiv.) oven dried borosilicate glass vial, stirred and irradiated with 450nM LED for 6hr. The reaction was monitored by TLC. After completion solvent was removed under reduced pressure. Without any further work up column chromatography was done in silica gel (100-200 mess size) with ethyl acetate (15-30%) in hexane to afford the desired product, **4ag,** as white solid, (89%, 110.75mg); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.65 – 7.60 (m, 2H), 7.43 – 7.39 (m, 2H), 6.98 (s, 1H), 6.83 – 6.78 (m, 2H), 6.49 – 6.46 (m, 2H), 5.65 (s, 1H), 3.73 (s, 3H), 1.91 (s, 3H), 1.32 (s, 9H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 171.2, 169.7, 152.1, 143.6, 134.6, 128.9, 126.3, 126.0, 119.3, 116.5, 74.2, 53.8, 34.7, 31.3, 23.0. HRMS (ESI-TOF) m/z calcd for $C_{21}H_{25}ClN_2O_3$ $[M+H]^+$389.1626, found 389.1625.



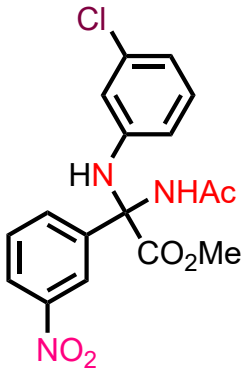
methyl 2-acetamido-2-(3-bromophenyl)-2-((3-chlorophenyl)amino)acetate (4ah); 4ah was synthesised using general procedure; **1j** (0.39 mmol, 1.2equiv.), **2f** (0.32 mmol, 1equiv.), was dissolved in **3a** acetonitrile (1.26 mmol, 3equiv.) oven dried borosilicate glass vial, stirred and irradiated with 450nM LED for 6hr. The reaction was monitored by TLC. After completion solvent was removed under reduced pressure. Without any further work up column chromatography was done in silica gel (100-200 mess size) with ethyl acetate (15-30%) in hexane to afford the desired product, **4ah,** as white solid, (74%, 97.48mg); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.87 (t, *J* = 2.0 Hz, 1H), 7.65-7.62 (m, 1H), 7.53- 7.51 (m, 1H), 7.29 (d, *J* = 8.0 Hz, 1H), 7.11 (s, 1H), 7.01 (t, *J* = 8.1 Hz, 1H), 6.76 (dd, *J* = 8.2, 1.9 Hz, 1H), 6.47 (t, *J* = 2.2 Hz, 1H), 6.37 (dd, *J* = 8.3, 2.3 Hz, 1H), 5.86 (s, 1H), 3.73 (s, 3H), 1.95 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 170.2, 169.9, 144.4, 139.7, 134.7, 132.6, 130.7, 130.1, 129.7, 125.4, 123.4, 119.9, 116.3, 114.7, 73.7, 54.2, 23.0. HRMS (ESI-TOF) m/z calcd for $C_{17}H_{16}BrClN_2O_3$ $[M+H]^+$411.0106, found 411.0105.



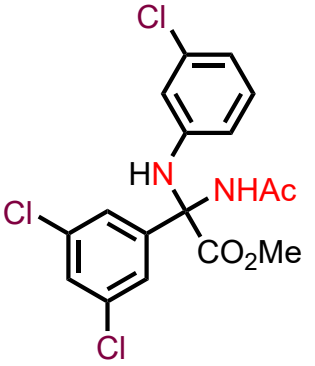
methyl 3-(1-acetamido-1-((3-chlorophenyl)amino)-2-methoxy-2-oxoethyl)benzoate (4ai); 4ai was synthesised using general procedure; **1m** (0.39 mmol, 1.2equiv.), **2f** (0.32 mmol, 1equiv.), was dissolved in **3a** acetonitrile (1.26 mmol, 3equiv.) oven dried borosilicate glass vial, stirred and irradiated with 450nM LED for 6hr. The reaction was monitored by TLC. After completion solvent was removed under reduced pressure. Without any further work up column chromatography was done in silica gel (100-200 mess size) with ethyl acetate (15-30%) in hexane to afford the desired product, **4ai,** as white solid, (87%, 108.00mg); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.04 – 8.02 (m, 2H), 7.81 – 7.77 (m, 2H), 7.43 (s, 1H), 6.97 (t, *J* = 8.1 Hz, 1H), 6.73 – 6.70 (m, 1H), 6.43 (t, *J* = 2.1 Hz, 1H), 6.35 (dd, *J* = 8.2, 2.3 Hz, 1H), 5.95 (s, 1H), 3.90 (s, 3H), 3.69 (s, 3H), 1.94 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 170.1, 170.2, 166.5, 144.4, 142.0, 134.6, 131.1, 130.4, 130.1 130.0, 126.8, 119.6, 116.1, 114.6, 73.9, 54.1, 52.4, 22.9. HRMS (ESI-TOF) m/z calcd for $C_{19}H_{19}ClN_2O_5$ $[M+H]^+$391.1055, found 391.1054.



methyl 2-acetamido-2-((3-chlorophenyl)amino)-2-(3-nitrophenyl)acetate (4aj); 4aj was synthesised using general procedure; **1n** (0.39 mmol, 1.2equiv.), **2f** (0.32 mmol, 1equiv.), was dissolved in **3a** acetonitrile (1.26 mmol, 3equiv.) oven dried borosilicate glass vial, stirred and irradiated with 450nM LED for 6hr. The reaction was monitored by TLC. After completion solvent was removed under reduced pressure. Without any further work up column chromatography was done in silica gel (100-200 mess size) with ethyl acetate (15-30%) in hexane to afford the desired product, **4aj,** as white solid, (89%, 107.59mg); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.89 (t, *J* = 1.9 Hz, 1H), 7.67 – 7.64 (m, 1H), 7.54- 7.52 (m, 1H), 7.38 (s, 1H), 7.29 (d, *J* = 7.8 Hz, 1H), 7.00 (t, *J* = 8.0 Hz, 1H), 6.76 (dd, *J* = 7.9, 1.9 Hz, 1H), 6.47 (t, *J* = 2.1 Hz, 1H), 6.36 (dd, *J* = 8.3, 2.3 Hz, 1H), 5.91 (s, 1H), 3.73 (s, 3H), 1.94 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 170.2, 170.1, 144.3, 139.6, 135.2, 134.6, 132.5, 130.7, 130.1, 129.7, 125.4, 125.1, 123.3, 119.7, 116.2, 114.6, 73.6, 54.1, 22.9. HRMS (ESI-TOF) m/z calcd for $C_{17}H_{16}ClN_3O_5$ $[M+H]^+$378.0851, found 378.0852.

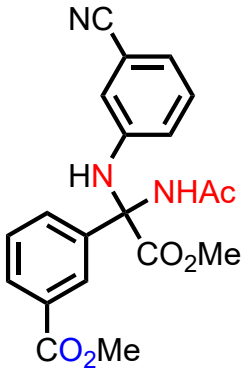


methyl 2-acetamido-2-((3-chlorophenyl)amino)-2-(3,5-dichlorophenyl)acetate (4ak); 4ak was synthesised using general

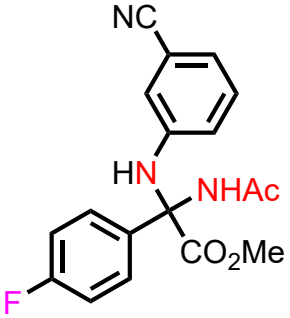


procedure; **1o** (0.39 mmol, 1.2equiv.), **2f** (0.32 mmol, 1equiv.), was dissolved in **3a** acetonitrile (1.26 mmol, 3equiv.) oven dried borosilicate glass vial, stirred and irradiated with 450nM LED for 6hr. The reaction was monitored by TLC. After completion solvent was removed under reduced pressure. Without any further work up column chromatography was done in silica gel (100-200 mess size) with ethyl acetate (15-30%) in hexane to afford the desired product, **4ak,** as white solid, (74%, 95.11mg); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.81 (d, *J* = 2.4 Hz, 1H), 7.54 (dd, *J* = 8.5, 2.3 Hz, 1H), 7.45 (d, *J* = 8.5 Hz, 1H), 7.39 (s, 1H), 7.00 (t, *J* = 8.1 Hz, 1H), 6.76 (dd, *J* = 7.8, 1.9 Hz, 1H), 6.46 (t, *J* = 2.1 Hz, 1H), 6.36 (dd, *J* = 8.1, 2.3 Hz, 1H), 5.88 (s, 1H), 3.72 (s, 3H), 1.92 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 170.2, 170.0, 144.2, 137.6, 134.7, 133.8, 133.5, 131.1, 130.2, 128.8, 126.1, 120.0, 116.2, 114.6, 73.4, 54.3, 22.9. HRMS (ESI-TOF) m/z calcd for $C_{17}H_{15}Cl_3N_2O_3$ $[M+H]^+$401.0221, found 401.0222.

methyl 3-(1-acetamido-1-((3-cyanophenyl)amino)-2-methoxy-2-oxoethyl)benzoate (4al); **4al** was synthesised using general procedure; **1m** (0.42 mmol, 1.2equiv.), **2e** (0.34 mmol, 1equiv.), was dissolved in **3a** acetonitrile (1.26 mmol, 3equiv.) oven dried borosilicate glass vial, stirred and irradiated with 450nM LED for 6hr. The reaction was monitored by TLC. After completion solvent was removed under reduced pressure. Without any further work up column chromatography was done in silica gel (100-200 mess size) with ethyl acetate (15-30%) in hexane to afford the desired product, **4al,** as yellow solid, (80%, 103.73mg); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.06 – 8.04 (m, 2H), 7.77 – 7.75 (m, 2H), 7.49 (s, 1H), 7.19 (t, *J* = 7.9 Hz, 1H), 7.03 – 7.01 (m, 1H), 6.83 (dd, *J* = 8.2, 2.5 Hz, 1H), 6.54 (t, *J* = 1.8 Hz, 1H), 6.15 (s, 1H), 3.92 (s, 3H), 3.71 (s, 3H), 1.97 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 170.3, 169.9, 166.4, 143.6, 141.1, 131.4, 130.5, 130.0, 126.8, 123.0, 121.3, 119.2, 117.6, 112.4, 73.6, 54.2, 52.5, 22.8. HRMS (ESI-TOF) m/z calcd for $C_{20}H_{19}N_3O_5$ $[M+H]^+$382.1397, found 382.1398.

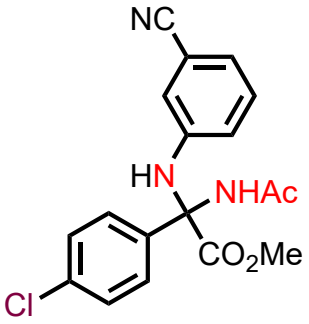


methyl 2-acetamido-2-((3-cyanophenyl)amino)-2-(4-fluorophenyl)acetate (4am); 4am was synthesised using general procedure; **1c** (0.42 mmol, 1.2equiv.), **2e** (0.34 mmol, 1equiv.), was dissolved in **3a** acetonitrile (1.26 mmol, 3equiv.) oven dried borosilicate glass vial, stirred and irradiated with 450nM LED for 6hr. The reaction was monitored by TLC. After completion solvent was removed under reduced pressure. Without any further work up column chromatography was done in silica gel (100-200 mess size) with ethyl acetate (15-30%) in

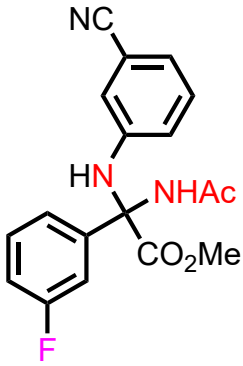


hexane to afford the desired product, **4am,** as yellow solid, (72%, 83.56mg); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.64 – 7.60 (m, 2H), 7.39 – 7.36 (m, 2H), 7.24 – 7.18 (m, 2H), 7.04 (dt, *J* = 7.5, 1.2 Hz, 1H), 6.83 – 6.80 (m, 1H), 6.58 – 6.57 (m, 1H), 6.07 (s, 1H), 3.72 (s, 3H), 1.96 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 170.9, 169.7, 163.2 (d, *J* = 247 Hz), 143.4, 133.8 (d, *J* = 3 Hz), 129.1, 128.7 (d, *J* = 8 Hz), 119.9, 116.7, 116.1 (d, *J* = 22 Hz), 74.1, 53.9, 23.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.47. HRMS (ESI-TOF) m/z calcd for $C_{18}H_{16}FN_3O_3$ $[M+H]^+$342.1248, found 342.1248.

methyl 2-acetamido-2-(3-chlorophenyl)-2-((3-cyanophenyl)amino)acetate (4an); 4an was synthesised using general procedure; **1e** (0.42 mmol, 1.2equiv.), **2e** (0.34 mmol, 1equiv.), was dissolved in **3a** acetonitrile (1.26 mmol, 3equiv.) oven dried borosilicate glass vial, stirred and irradiated with 450nM LED for 6hr. The reaction was monitored by TLC. After completion solvent was removed under reduced pressure. Without any further work up column chromatography was done in silica gel (100-200 mess size) with ethyl acetate (15-30%) in hexane to afford the desired product, **4an,** as yellow solid, (77%, 93.67mg); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.63 – 7.60 (m, 2H), 7.48 (s, 1H), 7.37 – 7.34 (m, 2H), 7.20 (t, *J* = 8.0 Hz, 1H), 7.03-7.01 (m, 1H), 6.83 (dd, *J* = 8.3, 2.4 Hz, 1H), 6.55 (t, *J* = 1.9 Hz, 1H), 6.11 (s, 1H), 3.71 (s, 3H), 1.95 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 170.3, 170.1, 143.6, 135.8, 134.8, 131.6, 130.0, 129.5, 128.2, 122.9, 121.3, 119.2, 117.6, 112.3, 73.2, 54.1, 22.8. HRMS (ESI-TOF) m/z calcd for $C_{18}H_{16}ClN_3O_3$ $[M+H]^+$358.0953, found 358.0954.

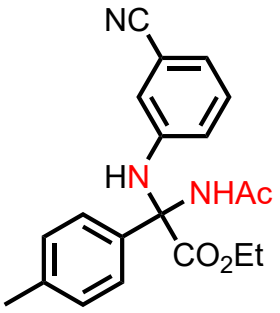


methyl 2-acetamido-2-((3-cyanophenyl)amino)-2-(3-fluorophenyl)acetate (4ao); 4ao was synthesised using general procedure; **1h** (0.42 mmol, 1.2equiv.), **2e** (0.34 mmol, 1equiv.), was dissolved in **3a** acetonitrile (1.26 mmol, 3equiv.) oven dried borosilicate glass vial, stirred and irradiated with 450nM LED for 6hr. The reaction was monitored by TLC. After completion solvent was removed under reduced pressure. Without any further work up column chromatography was done in silica gel (100-200 mess size) with ethyl acetate (15-30%) in hexane to afford the desired product, **4ao,** as yellow solid, (67%, 77.75mg); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.31 – 8.24 (m, 3H), 7.91 – 7.89 (m, 2H), 7.11 (d, *J* = 7.5 Hz, 1H), 6.84 (dd, *J* = 8.3, 2.5 Hz, 1H), 6.61 – 6.60 (m, 1H), 6.08 (s, 1H), 3.75 (s, 3H), 1.99 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 169.8, 169.4, 140.9 (d, *J* = 7 Hz), 130.6 (d, *J* = 8 Hz), 129.1, 129.0,

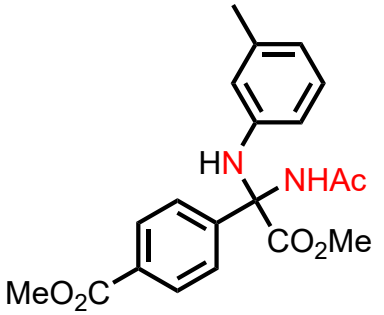


122.3 (d, J = 3 Hz), 120.0, 117.0, 116.2 (d, J = 21 Hz), 114.2 (d, J = 24 Hz), 74.1 (d, J = 2 Hz), 54.0, 22.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.47. HRMS (ESI-TOF) m/z calcd for $C_{18}H_{16}FN_3O_3$ $[M+H]^+$342.1248, found 342.1249.

ethyl 2-acetamido-2-((3-cyanophenyl)amino)-2-(p-tolyl)acetate (4ap); 4ap was synthesised using general procedure; **1d** (0.42 mmol, 1.2equiv.), **2e** (0.34 mmol, 1equiv.), was dissolved in **3a** acetonitrile (1.26 mmol, 3equiv.) oven dried borosilicate glass vial, stirred and irradiated with 450nM LED for 6hr. The reaction was monitored by TLC. After completion solvent was removed under reduced pressure. Without any further work up column chromatography was done in silica gel (100-200 mess size) with ethyl acetate (15-30%) in hexane to afford the desired product, **4ap,** as yellow solid, (77%, 88.32mg); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.62 – 7.60 (m, 2H), 7.20 (d, J = 8.0 Hz, 2H), 7.10- 7.06(m, 1H), 6.99 (s, 1H), 6.78 – 6.74 (m, 1H), 6.52 – 6.50 (m, 2H), 5.75 (s, 1H), 4.20- 4.14 (m, 2H), 2.36 (s, 3H), 1.91 (s, 3H), 1.16 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 170.6, 169.5, 143.7, 139.0, 135.1, 129.8, 128.9, 126.5, 119.4, 116.6, 74.3, 62.9, 23.1, 21.2, 13.9 HRMS (ESI-TOF) m/z calcd for $C_{19}H_{21}ClN_2O_3$ $[M+H]^+$361.1313, found 361.1314.

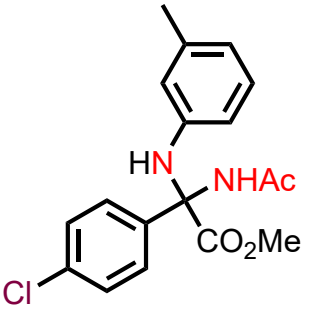


.**methyl 3-(1-acetamido-2-methoxy-2-oxo-1-(m-tolylamino)ethyl)benzoate (4aq); 4aq** was synthesised using general procedure; **1p** (0.45 mmol, 1.2equiv.), **2g** (0.37 mmol, 1equiv.), was dissolved in **3a** acetonitrile (1.26 mmol, 3equiv.) oven dried borosilicate glass vial, stirred and irradiated with 450nM LED for 6hr. The reaction was monitored by TLC. After completion solvent was removed under reduced pressure. Without any further work up column chromatography was done in silica gel (100-200 mess size) with ethyl acetate (15-30%) in hexane to afford the desired product, **4aq,** as white solid, (70%, 95.93mg); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.06 (d, J = 8.4 Hz, 2H), 7.82 (d, J = 8.4 Hz, 2H), 7.12 (s, 1H), 6.96 (t, J = 7.8 Hz, 1H), 6.63 (d, J = 7.6 Hz, 1H), 6.41 (s, 1H), 6.23 – 6.20 (m, 1H), 5.73 (s, 1H), 3.92 (s, 3H), 3.71 (s, 3H), 2.21 (s, 3H), 1.95 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 170.6, 169.8, 166.6, 143.2, 143.0, 139.1, 130.9, 130.3, 128.9,

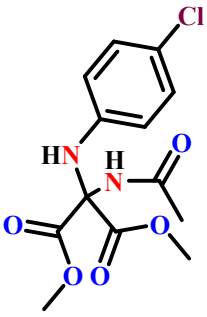


126.8, 121.0, 118.0, 113.3, 74.5, 54.1, 52.4, 23.2, 21.6. HRMS (ESI-TOF) m/z calcd for $C_{20}H_{22}N_2O_5$ $[M+H]^+$371.1601, found 371.1602.

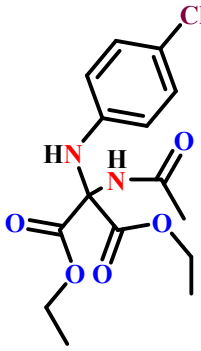
methyl 2-acetamido-2-(4-chlorophenyl)-2-(m-tolylamino)acetate (4ar); 4ar was synthesised using general procedure; **1e** (0.45 mmol, 1.2equiv.), **2g** (0.37 mmol, 1equiv.), was dissolved in **3a** acetonitrile (1.26 mmol, 3equiv.) oven dried borosilicate glass vial, stirred and irradiated with 450nM LED for 6hr. The reaction was monitored by TLC. After completion solvent was removed under reduced pressure. Without any further work up column chromatography was done in silica gel (100-200 mess size) with ethyl acetate (15-30%) in hexane to afford the desired product, **4ar,** as white solid, (80%, 90.61mg); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.68-7.66 (m, 2H), 7.37 – 7.35 (m, 2H), 7.09 (s, 1H), 6.96 (t, *J* = 7.8 Hz, 1H), 6.62 (d, *J* = 7.6 Hz, 1H), 6.40 (s, 1H), 6.23- 6.20 (m, 1H), 5.68 (s, 1H), 3.71 (s, 3H), 2.21 (s, 3H), 1.93 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 170.8, 169.8, 143.2, 139.1, 136.7, 135.3, 129.2, 129.0, 128.8, 128.2, 120.9, 117.9, 113.2, 74.1, 54.0, 23.1, 21.6. HRMS (ESI-TOF) m/z calcd for $C_{18}H_{19}ClN_2O_3$ $[M+H]^+$347.1157, found 347.1156.



dimethyl 2-acetamido-2-((4-chlorophenyl)amino)malonate (4as); 4as was synthesised using general procedure; **5a** (0.39 mmol, 1.2equiv.), **2d** (0.32 mmol, 1equiv.), was dissolved in **3a** acetonitrile (1.26 mmol, 3equiv.) oven dried borosilicate glass vial, stirred and irradiated with 450nM LED for 6hr. The reaction was monitored by TLC. After completion solvent was removed under reduced pressure. Without any further work up column chromatography was done in silica gel (100-200 mess size) with ethyl acetate (15-30%) in hexane to afford the desired product, **4as,** as yellow semi-solid, (81%, 81.57mg); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.33 (s, 1H), 7.13 – 7.09 (m, 2H), 6.58 – 6.55 (m, 2H), 5.81 (s, 1H), 3.82 (s, 6H), 1.98 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 169.6, 167.5, 141.4, 129.3, 125.0, 116.9, 72.1, 54.6, 22.9. HRMS (ESI-TOF) m/z calcd for $C_{13}H_{15}ClN_2O_5$ $[M+H]^+$315.0742, found 315.0752.

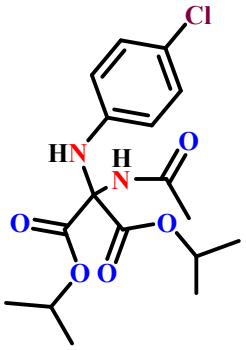


diethyl 2-acetamido-2-((4-chlorophenyl)amino)malonate (4at); 4at was synthesised using general procedure; **5b** (0.39 mmol, 1.2equiv.), **2d** (0.32 mmol, 1equiv.), was dissolved in **3a** acetonitrile (1.26 mmol, 3equiv.) oven dried borosilicate glass vial, stirred and irradiated with 450nM LED for 6hr. The

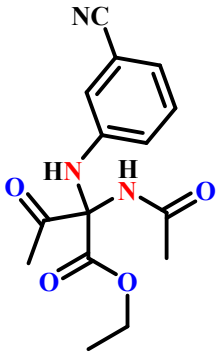


reaction was monitored by TLC. After completion solvent was removed under reduced pressure. Without any further work up column chromatography was done in silica gel (100-200 mess size) with ethyl acetate (15-30%) in hexane to afford the desired product, **4at,** as yellow semi-solid, (68%, 74.58mg); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.35 (s, 1H), 7.12 – 7.08 (m, 2H), 6.61 – 6.56 (m, 2H), 5.83 (s, 1H), 4.28 (q, *J* = 7.2 Hz, 4H), 1.98 (s, 3H), 1.21 (t, *J* = 7.2 Hz, 6H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 169.5, 167.0, 141.6, 129.1, 124.8, 116.8, 72.2, 63.9, 22.9, 14.0. HRMS (ESI-TOF) m/z calcd for $C_{15}H_{19}ClN_2O_5$ $[M+H]^+$343.1055, found 343.1009.

diisopropyl 2-acetamido-2-((4-chlorophenyl)amino)malonate (4au); 4au was synthesised using general procedure; **5c** (0.39 mmol, 1.2equiv.), **2d** (0.32 mmol, 1equiv.), was dissolved in **3a** acetonitrile (1.26 mmol, 3equiv.) oven dried borosilicate glass vial, stirred and irradiated with 450nM LED for 6hr. The reaction was monitored by TLC. After completion solvent was removed under reduced pressure. Without any further work up column chromatography was done in silica gel (100-200 mess size) with ethyl acetate (15-30%) in hexane to afford the desired product, **4au,** as yellow semi-solid, (86%, 102.05mg); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.33 (s, 1H), 7.11 – 7.07 (m, 2H), 6.62 – 6.58 (m, 2H), 5.82 (s, 1H), 5.10 (p, *J* = 6.3 Hz, 2H), 1.99 (s, 3H), 1.23 (d, *J* = 6.3 Hz, 6H), 1.14 (d, *J* = 6.2 Hz, 6H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 169.3, 166.5, 141.9, 129.1, 124.6, 116.7, 72.3, 71.9, 23.0, 21.5, 21.4. HRMS (ESI-TOF) m/z calcd for $C_{17}H_{23}ClN_2O_5$ $[M+H]^+$371.1368, found 371.1347.

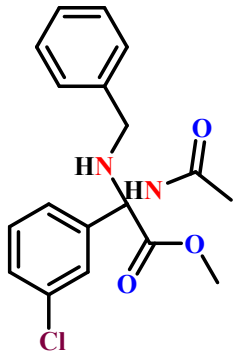


ethyl 2-acetamido-2-((3-cyanophenyl)amino)-3-oxobutanoate (4av); 4av was synthesised using general procedure; **5d** (0.42 mmol, 1.2equiv.), **2e** (0.35 mmol, 1equiv.), was dissolved in **3a** acetonitrile (1.26 mmol, 3equiv.) oven dried borosilicate glass vial, stirred and irradiated with 450nM LED for 6hr. The reaction was monitored by TLC. After completion solvent was removed under reduced pressure. Without any further work up column chromatography was done in silica gel (100-200 mess size) with ethyl acetate (15-30%) in hexane to afford the desired product, **4av,** as yellowish semi-solid, (67%, 64.55mg); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.48 (s, 1H), 7.22 (d, *J* = 7.6 Hz, 1H), 7.07 (d, *J* = 7.6 Hz, 1H), 6.79 (dd, *J* = 8.2, 2.4 Hz, 1H), 6.72 (d, *J* = 2.0 Hz, 1H), 6.17 (s, 1H), 4.32-4.25 (m, 2H), 2.22 (s, 3H), 2.00 (s, 3H), 1.21 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (100

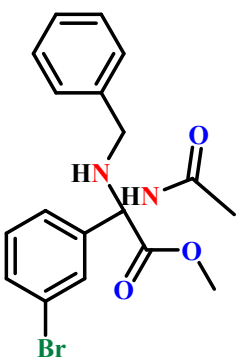


MHz, Chloroform-*d*) δ 169.7, 166.7, 143.3, 130.3, 123.3, 119.0, 113.2, 72.1, 64.2, 23.2, 22.9, 14.0. HRMS (ESI-TOF) m/z calcd for $C_{15}H_{17}N_3O_4$ $[M+H]^+$304.1292, found 304.1272.

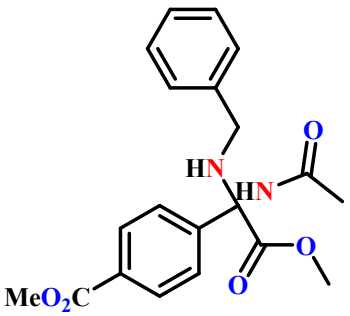
methyl 2-acetamido-2-(benzylamino)-2-(3-chlorophenyl)acetate (4aw); 4aw was synthesised using general procedure; **1f** (0.45 mmol, 1.2equiv.), **2i** (0.37 mmol, 1equiv.), was dissolved in **3a** acetonitrile (1.26 mmol, 3equiv.) oven dried borosilicate glass vial, stirred and irradiated with 450nM LED for 6hr. The reaction was monitored by TLC. After completion solvent was removed under reduced pressure. Without any further work up column chromatography was done in silica gel (100-200 mess size) with ethyl acetate (15-30%) in hexane to afford the desired product, **4aw,** as white solid, (60%, 76.99mg); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.73 (s, 1H), 7.59- 7.57 (m, 1H), 7.39 (d, *J* = 4.4 Hz, 2H), 7.33 (t, *J* = 7.6 Hz, 3H), 7.28 – 7.27 (m, 4H), 3.71 (d, *J* = 12.8 Hz, 1H), 3.63 (s, 3H), 3.49 (d, *J* = 12.8 Hz, 1H), 2.09 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 171.4, 169.6, 141.3, 139.2, 134.7, 129.8, 128.8, 128.5, 128.5, 127.5, 127.4, 127.3, 127.0, 124.7, 53.8, 47.6, 23.6. HRMS (ESI-TOF) m/z calcd for $C_{18}H_{19}ClN_2O_3$ $[M+H]^+$347.1157, found 347.1116.



methyl 2-acetamido-2-(benzylamino)-2-(3-bromophenyl)acetate (4ax); 4ax was synthesised using general procedure; **1j** (0.45 mmol, 1.2equiv.), **2i** (0.37 mmol, 1equiv.), was dissolved in **3a** acetonitrile (1.26 mmol, 3equiv.) oven dried borosilicate glass vial, stirred and irradiated with 450nM LED for 6hr. The reaction was monitored by TLC. After completion solvent was removed under reduced pressure. Without any further work up column chromatography was done in silica gel (100-200 mess size) with ethyl acetate (15-30%) in hexane to afford the desired product, **4ax,** as white solid, (56%, 81.07mg); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.73 (s, 1H), 7.60- 7.57 (m, 1H), 7.39 (d, *J* = 7.2 Hz, 2H), 7.34 (t, *J* = 7.5 Hz, 3H), 7.29 (d, *J* = 4.4 Hz, 4H), 3.73 (d, *J* = 12.8 Hz, 1H), 3.64 (s, 3H), 3.49 (d, *J* = 12.4 Hz, 1H), 2.11 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 171.4, 169.6, 141.3, 139.2, 134.7, 129.8, 128.8, 128.5, 128.5, 127.3, 127.0, 124.7, 53.8, 47.6, 23.6. HRMS (ESI-TOF) m/z calcd for $C_{18}H_{19}BrN_2O_3$ $[M+H]^+$391.0652, found 391.0653.

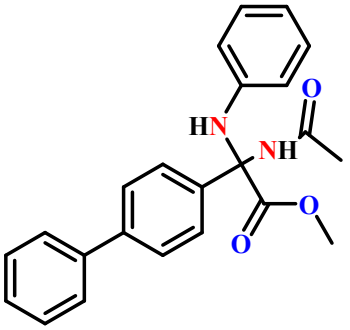


methyl 2-acetamido-2-(benzylamino)-2-(3-bromophenyl)acetate (4ay); 4ay was synthesised using

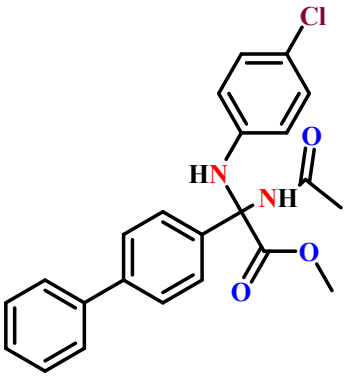


general procedure; **1p** (0.45 mmol, 1.2equiv.), **2i** (0.37 mmol, 1equiv.), was dissolved in **3a** acetonitrile (1.26 mmol, 3equiv.) oven dried borosilicate glass vial, stirred and irradiated with 450nM LED for 6hr. The reaction was monitored by TLC. After completion solvent was removed under reduced pressure. Without any further work up column chromatography was done in silica gel (100-200 mess size) with ethyl acetate (15-30%) in hexane to afford the desired product, **4ay,** as white solid, (55%, 75.37mg); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.06 (d, *J* = 8.4 Hz, 2H), 7.84 (d, *J* = 8.4 Hz, 2H), 7.44 (d, *J* = 6.4 Hz, 2H), 7.39 (t, *J* = 7.4 Hz, 2H), 7.33 – 7.27 (m, 3H), 3.95 (s, 3H), 3.77 (d, *J* = 12.8 Hz, 1H), 3.67 (s, 3H), 3.57 (d, *J* = 12.8 Hz, 1H), 2.14 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 171.3, 169.7, 166.7, 158.4, 144.0, 139.3,139.2, 130.3, 130.1, 130.0, 129.9, 129.2, 128.8, 128.6, 128.5, 128.4, 127.4, 127.3, 127.3, 126.6, 53.8, 52.2, 47.5, 44.5, 23.5. HRMS (ESI-TOF) m/z calcd for $C_{20}H_{22}N_2O_5$ $[M+H]^+$371.1601, found 371.1602.

methyl 2-([1,1'-biphenyl]-4-yl)-2-acetamido-2-(phenylamino)acetate (4az); 4az was synthesised using general procedure; **1q** (0.50 mmol, 1.2equiv.), **2a** (0.42 mmol, 1equiv.), was dissolved in **3a** acetonitrile (1.26 mmol, 3equiv.) oven dried borosilicate glass vial, stirred and irradiated with 450nM LED for 6hr. The reaction was monitored by TLC. After completion solvent was removed under reduced pressure. Without any further work up column chromatography was done in silica gel (100-200 mess size) with ethyl acetate (15-30%) in hexane to afford the desired product, **4az,** as yellow solid, (69%, 108.51mg); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.81 (d, *J* = 8.0 Hz, 2H), 7.63 – 7.57 (m, 4H), 7.43 (t, *J* = 7.6 Hz, 2H), 7.37 (dd, *J* = 13.0, 5.8 Hz, 2H), 7.07 (t, *J* = 7.7 Hz, 2H), 6.76 (t, *J* = 7.3 Hz, 1H), 6.52 (d, *J* = 8.0 Hz, 2H), 5.86 (s, 1H), 3.72 (s, 3H), 1.91 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 171.0, 171.1, 170.0, 143.4, 141.9, 140.1, 136.6, 131.0, 129.0, 128.9, 127.9, 127.7, 127.2, 127.1, 119.9, 119.4, 116.5, 74.2, 60.5, 53.8, 22.9, 21.1, 14.2. HRMS (ESI-TOF) m/z calcd for $C_{23}H_{22}N_2O_3$ $[M+H]^+$375.1703, found 375.1702.

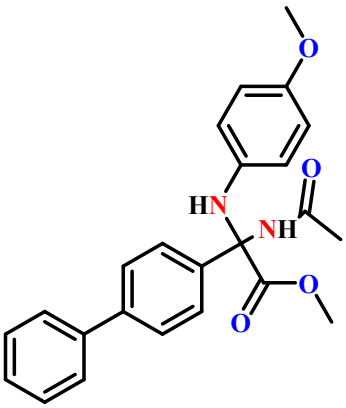


methyl 2-([1,1'-biphenyl]-4-yl)-2-acetamido-2-((4-chlorophenyl)amino)acetate (4aaa); 4aaa was synthesised using general procedure; **1q** (0.39 mmol, 1.2equiv.), **2d** (0.32 mmol, 1equiv.), was dissolved in **3a** acetonitrile (1.26 mmol, 3equiv.) oven dried borosilicate glass vial, stirred and irradiated with 450nM LED for 6hr. The reaction was monitored by TLC. After completion solvent was removed under reduced pressure.

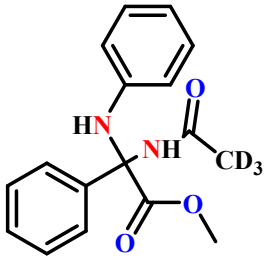


Without any further work up column chromatography was done in silica gel (100-200 mess size) with ethyl acetate (15-30%) in hexane to afford the desired product, **4aaa,** as white solid, (72%, 94.20mg); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.78- 7.75 (m, 2H), 7.63 – 7.58 (m, 4H), 7.45 (t, *J* = 7.5 Hz, 2H), 7.37 (t, *J* = 7.4 Hz, 1H), 7.19 (s, 1H), 7.04 – 6.97 (m, 1H), 6.75 – 6.72 (m, 1H), 6.51 – 6.39 (m, 2H), 5.94 (s, 1H), 3.74 (s, 3H), 1.97 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 170.6, 169.9, 144.7, 142.2, 142.1, 140.1, 136.2, 136.0, 134.6, 130.0, 129.0, 127.9, 127.6, 127.2, 127.0, 124.4, 119.4, 117.7, 116.1, 114.6, 73.9, 54.1, 54.0, 23.0. HRMS (ESI-TOF) m/z calcd for $C_{23}H_{21}BrN_2O_3$ $[M+H]^+$409.1313, found 409.1303.

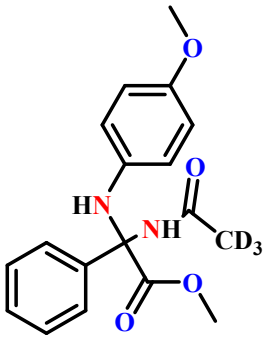
methyl 2-([1,1'-biphenyl]-4-yl)-2-acetamido-2-((4-methoxyphenyl)amino)acetate (4aab); 4aab was synthesised using general procedure; **1q** (0.40 mmol, 1.2equiv.), **2b** (0.34 mmol, 1equiv.), was dissolved in **3a** acetonitrile (1.26 mmol, 3equiv.) oven dried borosilicate glass vial, stirred and irradiated with 450nM LED for 6hr. The reaction was monitored by TLC. After completion solvent was removed under reduced pressure. Without any further work up column chromatography was done in silica gel (100-200 mess size) with ethyl acetate (15-30%) in hexane to afford the desired product, **4aab,** as brown solid, (78%, 107.26mg); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.97 (d, *J* = 8.4 Hz, 2H), 7.79 – 7.74 (m, 4H), 7.60 (t, *J* = 7.6 Hz, 2H), 7.52 (t, *J* = 7.3 Hz, 1H), 7.42 (s, 1H), 6.87– 6.84 (m, 2H), 6.72 – 6.69 (m, 2H), 5.70 (s, 1H), 3.90 (d, *J* = 12.0 Hz, 6H), 2.10 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 171.3, 169.9, 154.0, 141.9, 140.3, 137.3, 137.2, 128.9, 127.7, 127.7, 127.2, 127.1, 119.3, 114.5, 75.5, 55.6, 53.9, 23.2. HRMS (ESI-TOF) m/z calcd for $C_{24}H_{24}N_2O_4$ $[M+H]^+$405.1809, found 405.1808.



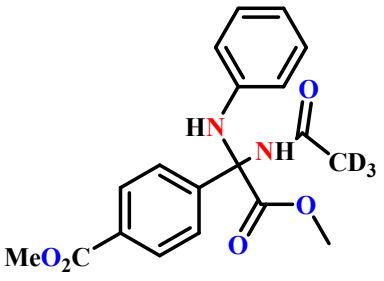
methyl 2-(acetamido-2,2,2-d3)-2-phenyl-2-(phenylamino)acetate (4aac); 4aac was synthesised using general procedure; **1a** (0.50 mmol, 1.2equiv.), **2a** (0.42 mmol, 1equiv.), was dissolved in **3a** acetonitrile (1.26 mmol, 3equiv.) oven dried borosilicate glass vial, stirred and irradiated with 450nM LED for 6hr. The reaction was monitored by TLC. After completion solvent was removed under reduced pressure. Without any further work up column chromatography was done in silica gel (100-200 mess size) with ethyl acetate (15-30%) in hexane to afford the desired product, **4aac,** as dark brown oily liquid, (72%, 91.13mg); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.75 – 7.73 (m, 2H), 7.43 – 7.37 (m, 3H), 7.13 (s, 1H), 7.07 (t, *J* = 7.7 Hz, 2H), 6.77 (t, *J* = 7.3 Hz, 1H), 6.49 (d, *J* = 8.5 Hz,



2H), 5.80 (s, 1H), 3.71 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 171.0, 169.9, 143.5, 137.8, 129.2, 129.1, 129.0, 126.6, 119.5, 116.6, 74.3, 53.9. HRMS (ESI-TOF) m/z calcd for $C_{17}H_{15}D_3N_2O_3$ $[M+H]^+$302.1578, found 302.1578.

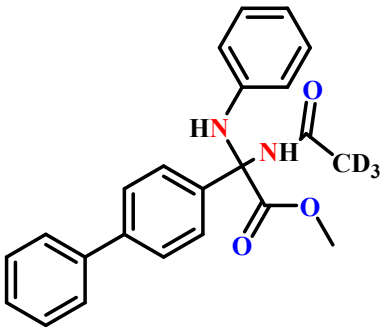


methyl 2-(acetamido-2,2,2-d3)-2-((4-methoxyphenyl)amino)-2-phenylacetate (4aad); 4aad was synthesised using general procedure; **1a** (0.40 mmol, 1.2equiv.), **2b** (0.34 mmol, 1equiv.), was dissolved in **3a** acetonitrile (1.26 mmol, 3equiv.) oven dried borosilicate glass vial, stirred and irradiated with 450nM LED for 6hr. The reaction was monitored by TLC. After completion solvent was removed under reduced pressure. Without any further work up column chromatography was done in silica gel (100-200 mess size) with ethyl acetate (15-30%) in hexane to afford the desired product, **4aad,** dark brown oily liquid, (69%, 77.69mg); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.76 – 7.74 (m, 2H), 7.43 – 7.36 (m, 4H), 7.04 (s, 1H), 6.68 (d, *J* = 8.8 Hz, 2H), 6.51 (d, *J* = 8.6 Hz, 2H), 3.72 (d, *J* = 2.7 Hz, 6H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 171.2, 170.0, 154.0, 138.5, 137.3, 135.1, 130.2, 129.1, 129.0, 126.6, 119.2, 114.5, 75.5, 55.6, 53.8. HRMS (ESI-TOF) m/z calcd for $C_{18}H_{17}D_3N_2O_4$ $[M+H]^+$332.1684, found 332.1674.

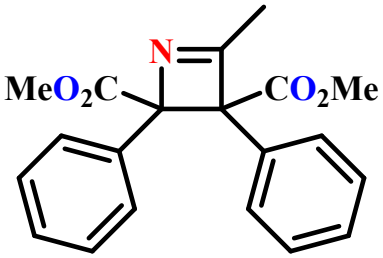


methyl 4-(1-(acetamido-2,2,2-d3)-2-methoxy-2-oxo-1-(phenylamino)ethyl)benzoate (4aae); 4aae was synthesised using general procedure; **1p** (0.50 mmol, 1.2equiv.), **2a** (0.42 mmol, 1equiv.), was dissolved in **3a** acetonitrile (1.26 mmol, 3equiv.) oven dried borosilicate glass vial, stirred and irradiated with 450nM LED for 6hr. The reaction was monitored by TLC. After completion solvent was removed under reduced pressure. Without any further work up column chromatography was done in silica gel (100-200 mess size) with ethyl acetate (15-30%) in hexane to afford the desired product, **4aae,** as dark brown oily liquid, (75%, 113.21mg); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.06 (d, *J* = 8.4 Hz, 2H), 7.83 (d, *J* = 8.0 Hz, 2H), 7.10 (t, *J* = 7.8 Hz, 3H), 6.81 (t, *J* = 7.4 Hz, 1H), 6.50 (d, *J* = 8.0 Hz, 2H), 5.79 (s, 1H), 3.92 (s, 3H), 3.72 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 170.6, 166.6, 143.3, 142.8, 131.0, 130.3, 130.0, 129.2, 126.8, 120.1, 116.8, 74.6, 54.1, 52.4. HRMS (ESI-TOF) m/z calcd for $C_{19}H_{17}D_3N_2O_5$ $[M+H]^+$360.1633, found 360.1634.

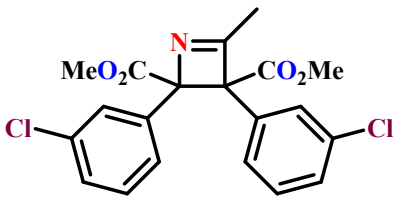
methyl 2-([1,1'-biphenyl]-4-yl)-2-(acetamido-2,2,2-d3)-2-(phenylamino)acetate (4aaf); **4aaf** was synthesised using general procedure; **1q** (0.50 mmol, 1.2equiv.), **2a** (0.42 mmol, 1equiv.), was dissolved in **3a** acetonitrile (1.26 mmol, 3equiv.) oven dried borosilicate glass vial, stirred and irradiated with 450nM LED for 6hr. The reaction was monitored by TLC. After completion solvent was removed under reduced pressure. Without any further work up column chromatography was done in silica gel (100-200 mess size) with ethyl acetate (15-30%) in hexane to afford the desired product, **4aaf,** as dark brown oily liquid, (70%, 110.97mg); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.80 (d, *J* = 8.4 Hz, 2H), 7.63 – 7.58 (m, 4H), 7.45 (t, *J* = 7.6 Hz, 3H), 7.13 – 7.09 (m, 3H), 6.79 (t, *J* = 7.3 Hz, 1H), 6.54 (d, *J* = 8.0 Hz, 2H), 5.82 (s, 1H), 3.75 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 171.1, 167.5, 146.8, 146.5, 143.6, 142.1, 140.3, 136.9, 129.1, 128.9, 127.8, 127.2, 127.1, 119.7, 116.7, 74.4, 53.9. HRMS (ESI-TOF) m/z calcd for $C_{23}H_{19}D_3N_2O_3$ $[M+H]^+$378.1891, found 378.1892.



dimethyl 4-methyl-2,3-diphenyl-2,3-dihydroazete-2,3-dicarboxylate (8a); **8a** was synthesised using general procedure; **1a** (0.44 mmol, 1.2equiv.), **2j** (0.37 mmol, 1equiv.), was dissolved in **3a** acetonitrile (1.26 mmol, 3equiv.) oven dried borosilicate glass vial, stirred and irradiated with 450nM LED for 6hr. The reaction was monitored by TLC. After completion solvent was removed under reduced pressure. Without any further work up column chromatography was done in silica gel (100-200 mess size) with ethyl acetate (15-30%) in hexane to afford the desired product, **8a,** as brown oily liquid, (66%, 82.32mg); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.54 – 7.51 (m, 2H), 7.34 – 7.29 (m, 8H), 3.48 (s, 3H), 3.42 (s, 3H), 2.48 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 169.3, 169.2, 167.6,141.1, 136.8, 128.7, 128.4, 128.3, 128.2, 127.1, 126.3, 95.7, 81.9, 52.9, 52.7, 20.7. HRMS (ESI-TOF) m/z calcd for $C_{20}H_{19}NO_4$ $[M+H]^+$338.1387, found 338.1327.

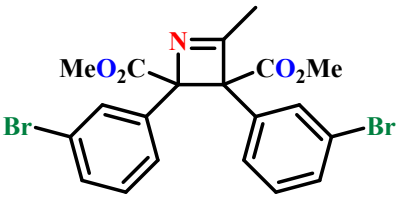


dimethyl 2,3-bis(3-chlorophenyl)-4-methyl-2,3-dihydroazete-2,3-dicarboxylate (8b); **8b** was synthesised using general procedure; **1f** (0.44 mmol, 1.2equiv.), **2j** (0.37 mmol, 1equiv.), was dissolved in **3a** acetonitrile (1.26 mmol, 3equiv.) oven dried borosilicate glass vial, stirred and irradiated with 450nM LED for 6hr. The reaction was monitored by TLC. After completion solvent was removed under reduced pressure. Without any

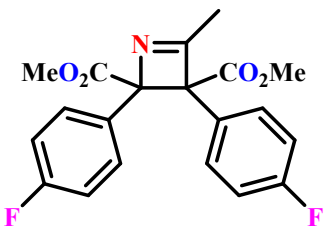


further work up column chromatography was done in silica gel (100-200 mess size) with ethyl acetate (15-30%) in hexane to afford the desired product, **8b,** as brown oily liquid, (69%, 103.71mg); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.30 (s, 1H), 7.21 (d, *J* = 8.0 Hz, 1H), 7.16 -7.13 (m, 2H), 7.04 (q, *J* = 7.9 Hz, 2H), 6.92- 6.91 (m, 1H), 6.83 (d, *J* = 8.0 Hz, 1H), 3.88 (d, *J* = 4.4 Hz, 6H), 2.59 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 172.2, 171.5, 167.8, 135.7, 135.2, 134.1,133.5, 129.7, 129.0, 128.6, 128.5, 128.4, 127.9, 127.4, 125.2, 93.0, 53.7, 53.6, 20.9. HRMS (ESI-TOF) m/z calcd for $C_{20}H_{17}Cl_2NO_4$ $[M+H]^+$406.0607, found 406.0608.

dimethyl 2,3-bis(3-bromophenyl)-4-methyl-2,3-dihydroazete-2,3-dicarboxylate (8c); 8c was synthesised using general procedure; **1j** (0.44 mmol, 1.2equiv.), **2j** (0.37 mmol, 1equiv.), was dissolved in **3a** acetonitrile (1.26 mmol, 3equiv.) oven dried borosilicate glass vial, stirred and irradiated with 450nM LED for 6hr. The reaction was monitored by TLC. After completion solvent was removed under reduced pressure. Without any further work up column chromatography was done in silica gel (100-200 mess size) with ethyl acetate (15-30%) in hexane to afford the desired product, **8c,** as brown oily liquid, (71%, 130.08mg); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.37 (s, 1H), 7.31- 7.27 (m, 3H), 7.05 (s, 1H), 6.99 (q, *J* = 8.0 Hz, 2H), 6.88 (d, *J* = 8.4 Hz, 1H), 3.88 (d, *J* = 4.8 Hz, 6H), 2.59 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 172.1, 171.4, 168.1, 135.9, 135.4, 132.5, 131.6, 131.5, 130.3, 129.2, 128.8, 128.3, 125.7, 121.5, 53.7, 53.6, 20.8. $C_{20}H_{17}Br_2NO_4$ $[M+H]^+$493.9597, found 493.9598.

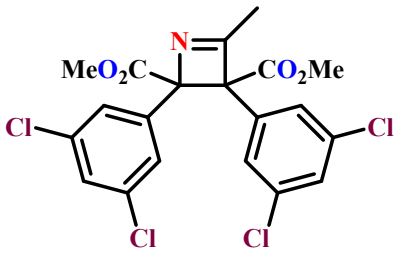


dimethyl 2,3-bis(4-fluorophenyl)-4-methyl-2,3-dihydroazete-2,3-dicarboxylate (8d); 8d was synthesised using general procedure; **1c** (0.44 mmol, 1.2equiv.), **2j** (0.37 mmol, 1equiv.), was dissolved in **3a** acetonitrile (1.26 mmol, 3equiv.) oven dried borosilicate glass vial, stirred and irradiated with 450nM LED for 6hr. The reaction was monitored by TLC. After completion solvent was removed under reduced pressure. Without any further work up column chromatography was done in silica gel (100-200 mess size) with ethyl acetate (15-30%) in hexane to afford the desired product, **8d,** as brown oily liquid, (75%, 103.61mg); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.30- 7.26 (m, 2H), 6.93- 6.89 (m, 2H), 6.80 (t, *J* = 8.5 Hz, 4H), 3.89 (d, *J* =

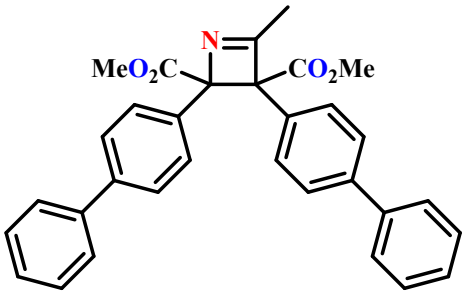


4.6 Hz, 6H), 2.60 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 172.7, 172.0, 167.3, 163.7(d, *J* = 29Hz), 161.3(d, *J* = 30 Hz, 1H), 131.5(d, *J* = 8 Hz), 129.0(d, *J* = 90Hz), 114.9, 114.6, 114.3, 114.1, 53.5(d, *J* = 6Hz), 20.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.47. $C_{20}H_{17}F_2NO_4$ $[M+H]^+$374.1198, found 374.1197.

dimethyl 2,3-bis(3,5-dichlorophenyl)-4-methyl-2,3-dihydroazete-2,3-dicarboxylate (8e); **8e** was synthesised using general procedure; **1o** (0.44 mmol, 1.2equiv.), **2j** (0.37 mmol, 1equiv.), was dissolved in **3a** acetonitrile (1.26 mmol, 3equiv.) oven dried borosilicate glass vial, stirred and irradiated with 450nM LED for 6hr. The reaction was monitored by TLC. After completion solvent was removed under reduced pressure. Without any further work up column chromatography was done in silica gel (100-200 mess size) with ethyl acetate (15-30%) in hexane to afford the desired product, **8e,** as brown oily liquid, (70%, 123.06mg); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.31 (d, *J* = 2.4 Hz, 1H), 7.18- 7.15 (m, 2H), 7.11 (dd, *J* = 8.6, 2.3 Hz, 1H), 6.96 (d, *J* = 2.0 Hz, 1H), 6.76 (dd, *J* = 8.6, 2.3 Hz, 1H), 3.83 (d, *J* = 3.1 Hz, 6H), 2.53 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 171.8, 171.3, 168.2, 133.9, 133.4, 133.1, 132.8, 132.4, 131.8, 131.5, 129.7, 129.3, 128.9, 126.4, 92.6, 60.5, 53.8, 53.7, 20.9. $C_{20}H_{15}Cl_4NO_4$ $[M+H]^+$475.9984, found 475.9974.

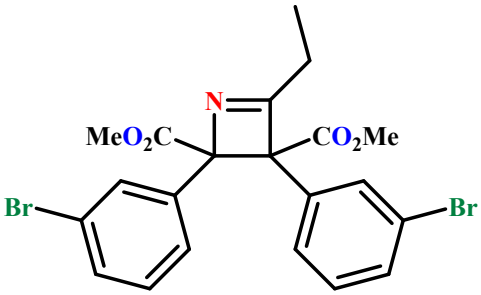


dimethyl 2,3-di([1,1'-biphenyl]-4-yl)-4-methyl-2,3-dihydroazete-2,3-dicarboxylate (8f); **8f** was synthesised using general procedure; **1q** (0.44 mmol, 1.2equiv.), **2j** (0.37 mmol, 1equiv.), was dissolved in **3a** acetonitrile (1.26 mmol, 3equiv.) oven dried borosilicate glass vial, stirred and irradiated with 450nM LED for 6hr. The reaction was monitored by TLC. After completion solvent was removed under reduced pressure. Without any further work up column chromatography was done in silica gel (100-200 mess size) with ethyl acetate (15-30%) in hexane to afford the desired product, **8f,** as brown oily liquid, (79%, 143.10mg); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.49 – 7.45 (m, 5H), 7.42 – 7.32 (m, 8H), 7.29 -7.27 (m, 3H), 6.98 (d, *J* = 8.0 Hz, 2H), 3.89 (d, *J* = 3.6 Hz, 6H), 2.61 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ

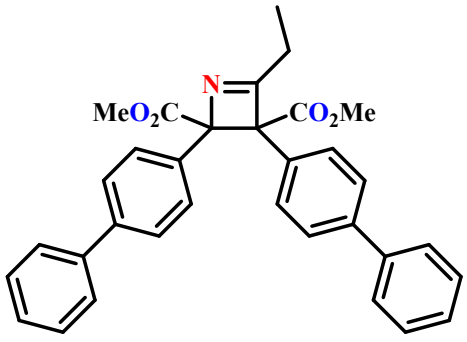


173.0, 172.1, 167.1, 140.9, 140.3, 132.7, 132.0, 130.2, 128.8, 128.8, 127.5, 127.1, 126.3, 125.8, 92.9, 78.5, 53.5, 53.4, 20.9. $C_{32}H_{27}NO_4$ $[M+H]^+$490.2013, found 490.2012.

dimethyl 2,3-bis(3-bromophenyl)-4-ethyl-2,3-dihydroazete-2,3-dicarboxylate (8g); 8g was synthesised using general procedure; **1j** (0.44 mmol, 1.2equiv.), **2j** (0.37 mmol, 1equiv.), was dissolved in **3a** acetonitrile (1.26 mmol, 3equiv.) oven dried borosilicate glass vial, stirred and irradiated with 450nM LED for 6hr. The reaction was monitored by TLC. After completion solvent was removed under reduced pressure. Without any further work up column chromatography was done in silica gel (100-200 mess size) with ethyl acetate (15-30%) in hexane to afford the desired product, **8g,** as brown oily liquid, (69%, 129.99mg); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.38-7.37 (m, 1H), 7.30-7.28 (m, 3H), 7.07-7.06 (m, 1H), 7.01-6.94 (m, 2H), 6.87 (d, *J* = 8.0 Hz, 1H), 3.86 (d, *J* = 3.8 Hz, 6H), 2.91-2.84 (m, 2H), 1.45 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 172.1, 171.4, 136.0, 135.6, 132.6, 131.5, 131.4, 130.4, 128.8, 128.3, 125.7, 122.2, 121.5, 53.6, 32.0, 28.5, 22.8, 12.2. $C_{21}H_{19}Br_2NO_4$ $[M+H]^+$507.9754, found 507.9755.



dimethyl 2,3-di([1,1'-biphenyl]-4-yl)-4-ethyl-2,3-dihydroazete-2,3-dicarboxylate (8h); 8h was synthesised using general procedure; **1q** (0.44 mmol, 1.2equiv.), **2j** (0.37 mmol, 1equiv.), was dissolved in **3a** acetonitrile (1.26 mmol, 3equiv.) oven dried borosilicate glass vial, stirred and irradiated with 450nM LED for 6hr. The reaction was monitored by TLC. After completion solvent was removed under reduced pressure. Without any further work up column chromatography was done in silica gel (100-200 mess size) with ethyl acetate (15-30%) in hexane to afford the desired product, **8h,** as brown oily liquid, (73%, 136.20mg); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.46- 7.42 (m, 5H), 7.39- 7.34 (m, 8H), 7.32 – 7.29 (m, 2H), 7.24 (d, *J* = 3.2 Hz, 1H), 6.97 (d, *J* = 8.0 Hz, 2H), 3.85 (s, 6H), 2.90 (q, *J* = 7.7 Hz, 2H), 1.45 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 172.9, 172.7, 140.9, 140.4, 130.2, 128.8, 127.5, 127.3, 127.1, 126.4, 125.8, 53.4, 12.2. $C_{33}H_{29}NO_4$ $[M+H]^+$504.2169, found 504.2168.



Crystallographic data of 4a

CCDC no	2324472	Radiation (λ)/A°	0.71073
Lattice	monoclinic	ρ/ (g cm-3)	1.283
Formula	C17 H18 N2 O3	μ (Mo Kα) mm-1	0.089
Formula Weight	298.33	θmax/deg	26.930
Space Group	P 1 21/c 1	Collected reflections	25609
a/ A°	17.4417(6)	Unique reflections	3337
b/ A°	7.7336(2)	No of parameters	207
c/ A°	11.8813(4)	R1 [I> 2σI]	0.1015

DFT calculations

All density functional theory (DFT) calculations were performed using the Gaussian09 package. All structures were optimised using the hybrid meta exchange-correlation functional M06-2X (doi.org/10.1007/s00214-007-0310-x) in correlation with the 6-31**G basis set. Frequency calculations were performed on all stationary points (reactants, intermediates, transition states, and products) to confirm their nature. Transition states were characterised as those having a single imaginary frequency, while minima had none. IRC calculations were also performed to further confirm each of these transition states by following the reaction path along the intrinsic reaction coordinate towards both the reactant and product. 3D representations of the transition states (Figure 7, refer the manuscript) were created using CYLview (version 1.0) (CYLview, 1.0b; Legault, C. Y., Université de Sherbrooke, 2009 (http://www.cylview.org)).

Calculation of Gibbs free energy = [(Sum of electronic and thermal energies + Zero point correction)-(Temperature * S * 1.6)/10**6] kcal/mol

A+2a

Sum of electronic and thermal Free Energies= -1030.016557, Zero-point correction= 0.305188, Total S = 164.142, Gibbs free energy = -1029.789671

C	-0.11480	1.87356	-1.13205
C	-1.28319	2.51625	-1.52465
C	0.01751	0.47918	-1.24242
H	-1.35692	3.59484	-1.42154
C	-2.35049	1.78730	-2.03954
C	-1.06282	-0.24769	-1.77142
H	-3.26499	2.28798	-2.34054
H	-0.98655	-1.32373	-1.85421
C	-2.22644	0.40497	-2.15767
H	-3.05108	-0.18201	-2.55153

H	0.69753	2.46309	-0.71431
C	1.24700	-0.18662	-0.79253
N	2.30612	0.57499	-0.50645
C	1.44579	-1.61509	-0.65616
O	0.61578	-2.48643	-0.84417
O	2.71171	-1.91385	-0.24954
C	3.23923	1.24908	-0.32345
C	2.96204	-3.30570	-0.10003
H	2.81493	-3.82924	-1.04743
H	3.99844	-3.38916	0.22518
H	2.29178	-3.74321	0.64377
C	4.17115	2.07398	0.44106
H	3.59969	2.71245	1.12028
H	4.79435	1.40280	1.03804
H	4.81269	2.67068	-0.20804
C	-3.37857	-1.75165	0.63361
C	-3.78018	-0.43016	0.81229
C	-2.07307	-2.12829	0.94093
H	-4.79359	-0.13075	0.56494
H	-1.73602	-3.14573	0.77516
C	-2.88473	0.51895	1.29126
C	-1.17271	-1.19232	1.43321
H	-3.16941	1.55804	1.41171
H	-0.15032	-1.47033	1.66609
C	-1.58122	0.13149	1.59297
H	-4.07881	-2.48475	0.24696
N	-0.68260	1.09970	2.05274
C	0.43233	1.52113	1.98232
O	1.49409	2.03726	2.00560

TS1

Sum of electronic and thermal Free Energies= -1029.988646, Zero-point correction= 0.304824, Total S = 156.509, Gibbs free energy = -1029.758483

C	-0.49561	-1.32540	1.95898

C	-1.78070	-1.66305	2.35852
C	-0.18982	-0.01316	1.56385
H	-1.99697	-2.68237	2.66171
C	-2.78603	-0.69913	2.36801
C	-1.20300	0.95782	1.59354
H	-3.79366	-0.96469	2.67107
H	-0.98816	1.96873	1.27720
C	-2.48884	0.60557	1.98719
H	-3.26770	1.36119	1.98041
H	0.28073	-2.08416	1.96070
C	1.13986	0.27264	1.00768
N	1.94473	-0.70962	0.74762
C	1.63617	1.62594	0.62553
O	0.98003	2.64093	0.64570
O	2.91261	1.58017	0.22165
C	2.29236	-1.59917	-0.00763
C	3.42910	2.82461	-0.24992
H	3.34469	3.59009	0.52375
H	4.47203	2.63620	-0.49679
H	2.87712	3.15075	-1.13403
C	3.28212	-2.69535	0.06911
H	2.95179	-3.49652	-0.59474
H	4.23646	-2.31427	-0.30648
H	3.42198	-3.06277	1.08807
C	-3.49939	0.83467	-1.57700
C	-3.20113	-0.51759	-1.42071
C	-2.46103	1.74870	-1.73962
H	-4.00042	-1.23960	-1.28387
H	-2.67956	2.80569	-1.85717
C	-1.88314	-0.95645	-1.42907
C	-1.13783	1.32217	-1.73968
H	-1.64892	-2.00899	-1.29724

H	-0.31976	2.02836	-1.83583
C	-0.83960	-0.03672	-1.59386
H	-4.53049	1.17227	-1.56875
N	0.50545	-0.41797	-1.53230
C	0.96107	-1.57982	-1.57893
O	1.08765	-2.67165	-2.05124

B

Sum of electronic and thermal Free Energies= -1030.07904, Zero-point correction= 0.310408, Total S = 150.823, Gibbs free energy = -1029.840581

N	-0.08825	-2.31939	-0.11961
C	0.80629	-2.38748	-1.02481
C	-0.25135	-0.90802	0.25717
N	0.58381	-0.16186	-0.68849
C	1.35382	-1.03430	-1.41504
C	0.35518	-0.83883	1.68237
O	-0.27417	-0.82542	2.70528
O	1.69122	-0.86037	1.62407
C	2.34280	-0.87262	2.89639
H	2.07253	0.01890	3.46544
H	2.04915	-1.75868	3.46218
H	3.40960	-0.88558	2.68227
C	-1.70352	-0.46815	0.20789
C	-2.18191	0.56037	1.02084
C	-2.54069	-1.02480	-0.75899
C	-3.48455	1.02418	0.86499
C	-3.84247	-0.55929	-0.91315
C	-4.31691	0.46786	-0.10142
H	-1.54114	1.00105	1.77523
H	-2.17035	-1.82872	-1.38673
H	-3.84768	1.82286	1.50345
H	-4.48720	-1.00159	-1.66571
H	-5.33284	0.83087	-0.21970
C	0.83911	1.23574	-0.60801

C	2.09975	1.67858	-0.20706
C	-0.15755	2.14932	-0.95120
C	2.35697	3.04339	-0.13824
C	0.10468	3.51273	-0.86274
C	1.35901	3.96111	-0.45685
H	2.86202	0.94549	0.03346
H	-1.12206	1.78536	-1.28877
H	3.33873	3.39058	0.16660
H	-0.67046	4.22524	-1.12517
H	1.56141	5.02560	-0.39750
O	2.25213	-0.79372	-2.18877
C	1.31152	-3.63382	-1.65768
H	0.82354	-4.50746	-1.22721
H	1.13715	-3.59775	-2.73668
H	2.39412	-3.69738	-1.51586

TS2

Sum of electronic and thermal Free Energies= -1106.389522, Zero-point correction= 0.332457, Total S = 154.856, Gibbs free energy = -1106.130938

N	-0.38445	-2.19899	0.50066
C	0.36297	-2.51273	-0.48262
C	-0.34791	-0.74016	0.65678
N	0.58708	-0.27484	-0.38131
C	0.98156	-1.31255	-1.14207
C	0.24818	-0.52890	2.06400
O	-0.39860	-0.44429	3.07372
O	1.58303	-0.54807	2.02871
C	2.21144	-0.47663	3.31110
H	1.91505	0.43940	3.82550
H	1.92264	-1.33567	3.91947
H	3.28179	-0.48216	3.11591
C	-1.72848	-0.13078	0.45227
C	-2.23541	0.88911	1.25374
C	-2.43831	-0.53697	-0.68305

C	-3.44586	1.49639	0.92373
C	-3.64247	0.07482	-1.00933
C	-4.15030	1.09469	-0.20498
H	-1.69619	1.21288	2.13454
H	-2.02815	-1.31435	-1.32341
H	-3.83378	2.28927	1.55491
H	-4.18601	-0.24422	-1.89294
H	-5.09148	1.57171	-0.45925
C	1.01442	1.07328	-0.56243
C	2.35835	1.38464	-0.35763
C	0.10654	2.05677	-0.95673
C	2.79324	2.69163	-0.54345
C	0.55132	3.36501	-1.12529
C	1.89038	3.68394	-0.91943
H	3.03780	0.59182	-0.06641
H	-0.93234	1.79860	-1.13322
H	3.83930	2.93614	-0.39094
H	-0.15185	4.13347	-1.42909
H	2.23264	4.70448	-1.05713
O	2.07075	-1.30265	-1.87329
C	0.60557	-3.88338	-0.99849
H	0.12845	-4.62278	-0.35659
H	0.20304	-3.94331	-2.01367
H	1.68175	-4.06764	-1.05761
H	-0.33852	-0.64499	-3.00667
O	0.04662	-1.50581	-2.79181
H	1.37169	-1.42827	-2.75424

C

Sum of electronic and thermal Free Energies= -1106.438574, Zero-point correction= 0.338442, Total S = 153.569, Gibbs free energy = -1106.173391

N	-0.33347	-2.20139	0.22491
C	0.58528	-2.44594	-0.61716

C	-0.44472	-0.75439	0.39778
N	0.41117	-0.17833	-0.65800
C	1.24328	-1.21128	-1.21973
C	0.13415	-0.44453	1.80251
O	-0.42519	0.15225	2.68448
O	1.37907	-0.92475	1.90506
C	2.03108	-0.63672	3.14111
H	2.10805	0.44445	3.28272
H	1.47005	-1.06334	3.97485
H	3.01852	-1.08840	3.06639
C	-1.88151	-0.27658	0.25886
C	-2.24186	1.02748	0.61264
C	-2.83824	-1.11685	-0.30954
C	-3.53664	1.48098	0.38480
C	-4.13527	-0.66182	-0.53090
C	-4.48720	0.63950	-0.18820
H	-1.51329	1.68388	1.07490
H	-2.56580	-2.13526	-0.56307
H	-3.80529	2.49468	0.66465
H	-4.87124	-1.32948	-0.96774
H	-5.49831	0.99568	-0.35883
C	0.86563	1.17216	-0.61178
C	2.01659	1.53663	0.09753
C	0.14058	2.14857	-1.29983
C	2.43137	2.86586	0.10854
C	0.55330	3.47653	-1.27415
C	1.70110	3.83653	-0.57173
H	2.57549	0.76688	0.61741
H	-0.75235	1.84784	-1.83908
H	3.32665	3.14404	0.65564
H	-0.01784	4.22980	-1.80709
H	2.02568	4.87204	-0.55543

O	2.59401	-1.20847	-0.88460
C	1.04257	-3.80297	-1.02144
H	0.42677	-4.56954	-0.55243
H	1.00378	-3.89539	-2.11024
H	2.08692	-3.92792	-0.72084
O	1.20022	-1.18199	-2.62499
H	3.03998	-0.68700	-1.56651
H	0.33637	-0.82029	-2.85927

TS3

Sum of electronic and thermal Free Energies= -1106.38583, Zero-point correction= 0.334286, Total S = 150.613, Gibbs free energy = -1106.123392

N	-0.82285	-1.97363	0.48569
C	-0.05243	-2.56409	-0.33305
C	-0.62720	-0.52850	0.45356
N	0.28674	-0.25560	-0.71142
C	0.76640	-1.68958	-1.27136
C	0.09957	-0.13729	1.76110
O	-0.17763	0.79352	2.46913
O	1.12059	-0.96967	1.99183
C	1.92314	-0.62450	3.12269
H	2.36943	0.36250	2.97489
H	1.31324	-0.60796	4.02723
H	2.69129	-1.39288	3.18633
C	-1.93781	0.21715	0.26865
C	-1.99770	1.60840	0.40264
C	-3.07965	-0.48412	-0.11703
C	-3.18780	2.28145	0.14917
C	-4.26933	0.19474	-0.36723
C	-4.32669	1.57776	-0.23589
H	-1.12189	2.16146	0.72094
H	-3.03367	-1.56302	-0.20967
H	-3.22642	3.36022	0.26180
H	-5.15228	-0.36270	-0.66274

H	-5.25476	2.10644	-0.42881
C	1.20619	0.85053	-0.68476
C	2.45177	0.75542	-0.05916
C	0.83300	2.02587	-1.33708
C	3.30673	1.85337	-0.07485
C	1.69384	3.11840	-1.34180
C	2.93036	3.03531	-0.70768
H	2.74519	-0.17768	0.40507
H	-0.13575	2.07452	-1.82516
H	4.27694	1.77955	0.40605
H	1.39836	4.03225	-1.84635
H	3.60214	3.88725	-0.71342
O	2.10860	-1.95082	-1.18883
C	0.00259	-4.04043	-0.51928
H	1.01305	-4.39637	-0.29937
H	-0.71896	-4.53738	0.12818
H	-0.20667	-4.26928	-1.56841
O	0.26186	-1.54639	-2.49098
H	2.45611	-1.70510	-2.05958
H	-0.17986	-0.45966	-1.81780

D

Sum of electronic and thermal Free Energies= -1106.431943, Zero-point correction= 0.33798, Total S = 157.996, Gibbs free energy = -1106.169333

N	-1.63132	-0.10375	-0.80557
C	-2.68530	-0.06840	-0.10138
C	-0.30453	-0.17016	-0.19714
N	0.56144	-0.60657	-1.31297
C	-3.99426	0.00686	-0.86587
C	-0.25202	-1.27635	0.88650
O	0.11357	-1.14509	2.02644
O	-0.70388	-2.43287	0.38978
C	-0.70042	-3.52004	1.31561
H	0.31925	-3.73232	1.64672

H	-1.30753	-3.27897	2.19132
H	-1.11588	-4.36917	0.77690
C	0.10889	1.20821	0.33622
C	1.22330	1.35087	1.17194
C	-0.53253	2.35980	-0.13078
C	1.65941	2.61616	1.55156
C	-0.09181	3.62380	0.25161
C	1.00283	3.75659	1.09877
H	1.74893	0.47424	1.52963
H	-1.37730	2.27266	-0.80548
H	2.52054	2.70607	2.20590
H	-0.60772	4.50469	-0.11722
H	1.34543	4.74119	1.40067
C	1.96058	-0.64546	-1.08074
C	2.50932	-1.71232	-0.36213
C	2.80723	0.35387	-1.56775
C	3.87618	-1.75826	-0.11095
C	4.17799	0.28729	-1.34152
C	4.71663	-0.76136	-0.60128
H	1.85794	-2.51557	-0.03187
H	2.37789	1.19447	-2.10688
H	4.28989	-2.58907	0.45203
H	4.82444	1.06824	-1.72926
H	5.78423	-0.80615	-0.41368
O	-3.84360	0.21658	-2.17604
C	-2.83277	-0.10892	1.39504
H	-2.00858	0.41230	1.88501
H	-3.78678	0.33103	1.68299
H	-2.83491	-1.15021	1.73744
O	-5.06898	-0.10956	-0.32884
H	-4.73711	0.23128	-2.55125
H	0.32724	-0.00808	-2.10008

TS5

Sum of electronic and thermal Free Energies= -1182.741851, Zero-point correction= 0.36004, Total S = 165.194, Gibbs free energy = -1182.460615

N	-1.63132	-0.10375	-0.80557
C	-2.68530	-0.06840	-0.10138
C	-0.30453	-0.17016	-0.19714
N	0.56144	-0.60657	-1.31297
C	-3.99426	0.00686	-0.86587
C	-0.25202	-1.27635	0.88650
O	0.11357	-1.14509	2.02644
O	-0.70388	-2.43287	0.38978
C	-0.70042	-3.52004	1.31561
H	0.31925	-3.73232	1.64672
H	-1.30753	-3.27897	2.19132
H	-1.11588	-4.36917	0.77690
C	0.10889	1.20821	0.33622
C	1.22330	1.35087	1.17194
C	-0.53253	2.35980	-0.13078
C	1.65941	2.61616	1.55156
C	-0.09181	3.62380	0.25161
C	1.00283	3.75659	1.09877
H	1.74893	0.47424	1.52963
H	-1.37730	2.27266	-0.80548
H	2.52054	2.70607	2.20590
H	-0.60772	4.50469	-0.11722
H	1.34543	4.74119	1.40067
C	1.96058	-0.64546	-1.08074
C	2.50932	-1.71232	-0.36213
C	2.80723	0.35387	-1.56775
C	3.87618	-1.75826	-0.11095
C	4.17799	0.28729	-1.34152
C	4.71663	-0.76136	-0.60128

H	1.85794	-2.51557	-0.03187
H	2.37789	1.19447	-2.10688
H	4.28989	-2.58907	0.45203
H	4.82444	1.06824	-1.72926
H	5.78423	-0.80615	-0.41368
O	-3.84360	0.21658	-2.17604
C	-2.83277	-0.10892	1.39504
H	-2.00858	0.41230	1.88501
H	-3.78678	0.33103	1.68299
H	-2.83491	-1.15021	1.73744
O	-5.06898	-0.10956	-0.32884
H	-4.73711	0.23128	-2.55125
H	0.32724	-0.00808	-2.10008

E

Sum of electronic and thermal Free Energies= -1182.825542, Zero-point correction= 0.367455, Total S = 161.961, Gibbs free energy = -1182.535349

N	-1.34630	-0.53045	-0.72012
C	-2.61389	-0.54039	-0.01121
C	-0.08041	-0.09938	-0.10109
N	0.90272	-0.47554	-1.11592
C	-3.64908	-0.89424	-1.09542
C	0.19604	-0.95222	1.16468
O	0.39885	-0.54781	2.28132
O	0.24931	-2.24675	0.83161
C	0.54943	-3.12861	1.91391
H	1.50998	-2.86275	2.35930
H	-0.22885	-3.06442	2.67878
H	0.58382	-4.12696	1.48235
C	-0.03831	1.41579	0.14826
C	-0.51109	2.00192	1.32742
C	0.39978	2.24477	-0.88845
C	-0.53261	3.38671	1.46128
C	0.37444	3.63005	-0.75098

C	-0.08965	4.20640	0.42634
H	-0.87001	1.37987	2.13608
H	0.77424	1.79455	-1.80168
H	-0.90099	3.82478	2.38339
H	0.72423	4.25605	-1.56571
H	-0.10666	5.28585	0.53863
C	2.28385	-0.47963	-0.83522
C	2.86161	0.20929	0.23791
C	3.11761	-1.19619	-1.70609
C	4.24294	0.17343	0.42070
C	4.48980	-1.22544	-1.51035
C	5.06609	-0.53768	-0.44310
H	2.24842	0.77245	0.93136
H	2.67224	-1.72661	-2.54379
H	4.67263	0.71225	1.25947
H	5.11316	-1.79046	-2.19646
H	6.13937	-0.55941	-0.28925
O	-3.64438	0.04165	-2.07164
C	-2.69740	-1.56745	1.10478
H	-2.09236	-1.24516	1.95418
H	-3.73577	-1.63522	1.43004
H	-2.36582	-2.54167	0.74684
O	-4.39566	-1.83334	-1.09281
H	-4.32669	-0.21087	-2.71200
H	0.60328	-1.35327	-1.52698
O	-3.01075	0.69161	0.56049
H	-2.86301	1.39399	-0.08760
H	-1.44000	0.01323	-1.57656

TS6

Sum of electronic and thermal Free Energies= -1182.729937, Zero-point correction= 0.360975, Total S = 163.536, Gibbs free energy = -1182.446975

N	-1.27828	0.21578	-1.31728
C	-2.38781	0.88508	-1.10507

C	-0.09692	-0.01100	-0.46690
N	0.84805	-0.64543	-1.39803
C	-3.82641	-0.89886	-0.15367
C	-0.53552	-1.03222	0.62018
O	-0.24498	-2.19515	0.63128
O	-1.30535	-0.42574	1.52014
C	-1.84413	-1.27063	2.55114
H	-2.57667	-1.95120	2.11883
H	-1.03308	-1.81600	3.03660
H	-2.34025	-0.59558	3.24467
C	0.45790	1.28654	0.10680
C	1.10501	1.29956	1.34116
C	0.49274	2.43157	-0.69463
C	1.76176	2.44760	1.77693
C	1.14276	3.57949	-0.25625
C	1.77928	3.58989	0.98320
H	1.10765	0.40995	1.96359
H	0.00862	2.42592	-1.66867
H	2.26379	2.44436	2.73870
H	1.15418	4.46502	-0.88319
H	2.28876	4.48437	1.32608
C	2.15039	-0.99780	-0.88423
C	2.40666	-2.31947	-0.52022
C	3.17704	-0.05152	-0.82375
C	3.67512	-2.68213	-0.07902
C	4.44703	-0.42241	-0.39223
C	4.69681	-1.73796	-0.01324
H	1.60254	-3.04053	-0.58835
H	2.97675	0.97860	-1.10942
H	3.86857	-3.71249	0.20146
H	5.23869	0.31873	-0.35042
H	5.68629	-2.02885	0.32444

O	-3.02335	-1.92970	-0.67221
C	-2.59240	1.89008	-0.02558
H	-3.65572	1.89926	0.20875
H	-2.00789	1.68038	0.86537
H	-2.31030	2.86750	-0.43651
O	-4.39727	-1.14515	0.89275
H	-3.13532	-2.70527	-0.09217
H	0.98662	0.03169	-2.14695
O	-3.26103	0.84120	-2.11116
H	-3.93579	0.27114	-1.58069
H	-1.37595	-0.49796	-2.03927

4

Sum of electronic and thermal Free Energies= -993.177352, Zero-point correction= 0.32804, Total S = 149.476, Gibbs free energy = -992.920618

N	-1.57166	-0.72308	-1.23314
C	-2.78080	-1.13399	-0.74096
C	-0.48835	-0.24672	-0.37117
C	-0.40950	-1.16141	0.87915
O	-0.31565	-0.78989	2.01814
O	-0.32923	-2.43987	0.49261
C	-0.31376	-3.37714	1.56955
H	-1.24565	-3.29723	2.13378
H	-0.22413	-4.35943	1.10933
H	0.53037	-3.18019	2.23280
C	-0.72685	1.22127	-0.02853
C	-1.64353	1.57135	0.96743
C	-0.12208	2.22121	-0.79083
C	-1.93716	2.91150	1.19815
C	-0.41696	3.56059	-0.55145
C	-1.32417	3.90901	0.44390
H	-2.11829	0.79524	1.55594

H	0.58630	1.94558	-1.56520
H	-2.64571	3.17615	1.97660
H	0.06716	4.33119	-1.14295
H	-1.55185	4.95329	0.63343
O	-2.97028	-1.34259	0.44469
C	-3.86708	-1.31081	-1.77958
H	-4.50931	-2.13418	-1.46900
H	-4.47131	-0.39991	-1.81200
H	-3.46849	-1.50600	-2.77688
N	0.70934	-0.44316	-1.18238
C	2.00824	-0.25487	-0.65429
C	3.07881	-0.73565	-1.42098
C	2.27864	0.40580	0.54837
C	4.38765	-0.56326	-0.99725
C	3.59962	0.57932	0.95784
C	4.65949	0.10107	0.19768
H	2.86999	-1.24066	-2.36058
H	1.47436	0.77497	1.17272
H	5.19987	-0.94682	-1.60685
H	3.79120	1.09235	1.89498
H	5.68252	0.23955	0.53003
H	-1.54018	-0.33641	-2.16795
H	0.63734	-1.34862	-1.63532

7. References:

(1) Zhang, H.; Wang, H. Y.; Luo, Y.; Chen, C.; Cao, Y.; Chen, P.; Guo, Y. L.; Lan, Y.; Liu, G. *ACS Catal.* **2018**, *8*, 2173−2180.