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Supporting Information for:

Enantioselective direct α-alkylation of cyclic ketones by means of photo-organocatalysis

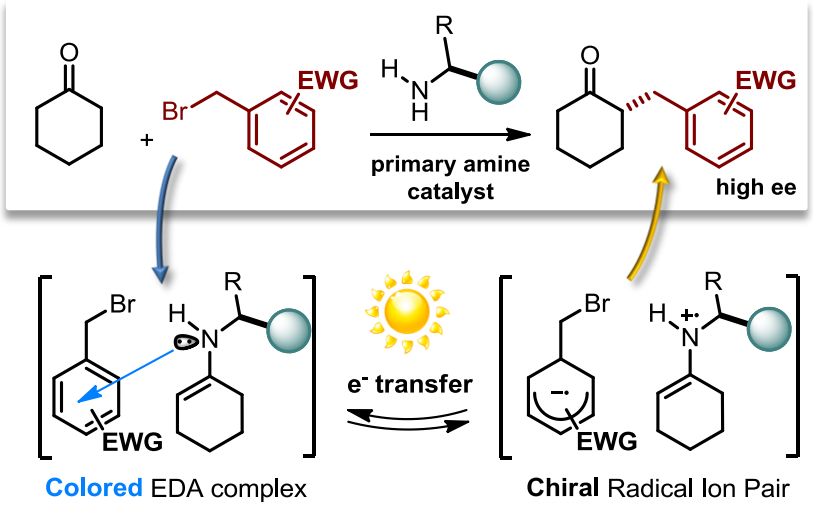
Elena Arceo,[1,‡] Ana Bahamonde,[1,‡] Giulia Bergonzini,[1] and Paolo Melchiorre*[1,2]

[1]ICIQ - *Institute of Chemical Research of Catalonia, Avenida Països Catalans 16 - 43007 Tarragona, Spain*
[2]*ICREA - Institució Catalana de Recerca i Estudis Avançats, Passeig Lluís Companys 23 - 08010 Barcelona, Spain*

[‡]EA & AB contributed equally to this work.

*To whom correspondence should be addressed. E-mail: pmelchiorre@iciq.es

Supporting Information



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A. General Information

The ^{1}H and ^{13}C NMR spectra were recorded at 400 MHz or 500 MHz for ^{1}H and at 100 MHz or 125 MHz for ^{13}C, respectively. The chemical shifts (δ) for ^{1}H and ^{13}C are given in ppm relative to residual signals of the solvents ($CHCl_3$ @ 7.26 ppm ^{1}H NMR, 77.0 ppm ^{13}C NMR). Coupling constants are given in Hz. When necessary, ^{1}H and ^{13}C signals were assigned by means of g-COSY 2D-NMR sequence. The following abbreviations are used to indicate the multiplicity: s, singlet; d, doublet; t, triplet; q, quartet; qn, quintet; m, multiplet; bs, broad signal.
Mass spectra (high and low resolution) were obtained from the ICIQ High Resolution Mass Spectrometry Unit on a Bruker Maxis Impact (QTOF) or Waters Micromass LCT-Premier (TOF) in Electrospray Ionization (ESI) by direct infusion.
Optical rotations were measured on a Polarimeter Jasco P-1030 and are reported as follows: $[\alpha]_D$ rt (*c* in g per 100 mL, solvent).

The authors are indebted to the team of the Research Support Area at ICIQ.

General Procedures. All reactions were set up under an argon atmosphere in oven-dried glassware using standard Schlenk techniques, unless otherwise stated. Synthesis grade solvents were used as purchased and the reaction mixtures were deoxygenated by three cycles of freeze-pump-thaw. Chromatographic purification of products was accomplished using force-flow chromatography (FC) on silica gel (35-70 mesh). For thin layer chromatography (TLC) analysis throughout this work, Merck precoated TLC plates (silica gel 60 GF_{254}, 0.25 mm) were employed, using UV light as the visualizing agent and an acidic mixture of para-anisaldehyde or basic aqueous potassium permangante ($KMnO_4$) stain solutions, and heat as developing agents. Organic solutions were concentrated under reduced pressure on a Büchi rotatory evaporator.

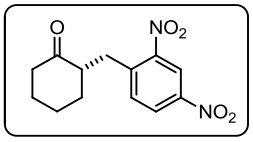
Determination of Enantiomeric Purity. HPLC analysis on chiral stationary phase was performed on an Agilent 1200-series instrumentation. Daicel Chiralpak IC and IB columns with hexane:^{i}PrOH as the eluent were used. HPLC traces were compared to racemic samples prepared using a) a catalytic amount of benzylamine (20 mol%) and irradiation with a 23 W compact fluorescent bulb for the α-benzylation of ketones (products **3a** to **3k**) or b) one equivalent of a preformed enamine (1-pyrrolidino-1-cyclohexene, Aldrich) and irradiation with a 15 W-black light CFL for the phenacylation of cyclic ketones (products **4a** to **4h**).

Materials. Reagents were purchased at the highest commercial quality and used without further purification, unless otherwise stated. Chiral primary amine catalysts **A** and **E** were synthesized by a Mitsunobu reaction from the commercially available cinchona alkaloids, according to (*1*). The bifunctional catalyst **C** was synthetized following a one-step procedure from commercially available *(1R,2R)*-1,2-diphenylethylenediamine, according to the literature procedure in (*2*). All the cyclic ketones used (**1**) are commercially available, as well as most of the alkyl halides used within the study. 2-Cyano-4-nitrobenzyl bromide **2k** was prepared by brominating the commercially available 2-methyl-5-nitrobenzonitrile, according to (*3*).

B. General Procedure for the Light-driven Asymmetric Alkylation of Ketones

General procedure for the photochemical α-asymmetric benzylation of ketones:
A 10 mL Schlenk tube was charged with the aminocatalyst **A** (20 mol%), toluene (0.2 M referring to the alkyl bromide **2**), trifluoroacetic acid, TFA, (40 mol%), the ketone **1** (4 eq), sodium acetate (2 eq) and the alkylating agent **2** (1 eq). The reaction mixture was degassed via freeze pump thaw (x 3 cycles), and the vessel refilled with nitrogen. After the reaction mixture was thoroughly degassed, the vial was sealed and positioned approximately in the middle of a dewar flask containing an EtOH bath at 0˚C, 10 cm away from 3 light sources. Three household full spectrum 23 W compact fluorescent light (CFL) bulbs were used for irradiating the reaction mixture. After stirring for the indicated time, the crude mixture was purified by flash column chromatography to afford the title compound **3** in the stated yield and optical purity.

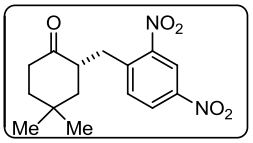
(*S*)-2-(2,4-dinitrobenzyl)cyclohexanone (3a)



Prepared according to the general procedure using the amino catalyst **A** (0.02 mmol, 6.5 mg, 0.2 eq), toluene (0.2 M, 500 μL), trifluoroacetic acid (0.04 mmol, 3 μL, 40 mol%), sodium acetate (0.2 mmol, 16.4 mg, 2 eq), cyclohexanone **1a** (0.4 mmol, 42 μL, 4 eq) and 2,4-dinitrobenzyl bromide **2a** (0.1 mmol, 26 mg, 1 eq). Time of irradiation: 45 h. Purification by flash column chromatography (gradient eluent from pure pentane to 10:1 pentane:AcOEt mixture) afforded the title compound (16.5 mg, 60 % yield, 90 % ee) as a yellow oil.
A larger scale reaction was performed according to the general procedure using the amino catalyst **A** (0.2 mmol, 65 mg, 20 mol%), toluene (0.2 M, 5 mL), trifluoroacetic acid (0.4 mmol, 30 μL, 40 mol%), sodium acetate (2 mmol, 164 mg, 2 eq), cyclohexanone **1a** (4 mmol, 420 μL, 4 eq) and 2,4-dinitrobenzyl bromide **2a** (1 mmol, 260 mg, 1 eq). Time of irradiation: 45 h. Purification by flash column chromatography (gradient eluent from pure hexane to 10:1 hexane:AcOEt mixture) afforded the title compound (206.1 mg, 74 % yield, 91 % ee) as a yellow oil.

The enantiomeric excess was determined by HPLC analysis on a Daicel Chiralpak IC column, 70:30 hexane:iPrOH, flow rate 1.00 mL/min, λ = 254 nm: τ_{major} = 22.1 min, τ_{minor} = 27.5 min.
$[\alpha]^{28}_D$ = -42.6 ± 0.7 (c = 1.0, $CHCl_3$, 90 % ee).
HRMS: calculated for $C_{13}H_{14}N_2O_5$ (M+2Na): 301.0795, found: 301.0802.
^{1}H (CDCl$_3$, 400 MHz): δ 8.79 (d, = 2.4Hz, 1H), 8.36 (dd, = 2.4Hz, *J* = 8.6Hz, 1H), 7.79 (d, *J* = 8.6Hz, 1H), 3.53 (dd, *J* = 7.6Hz, *J* = 13.5Hz, 1H), 2.88 (dd, *J* = 5.1Hz, *J* = 13.5Hz, 1H), 2.70-2.69 (m, 1H), 2.48-2.41 (m, 1H), 2.37-2.27 (m, 1H), 2.24-2.01 (m, 2H), 1.97-1.89 (m, 1H), 1.75-1.65 (m, 2H), 1.60-1.51 (m, 1H). **^{13}C (CDCl$_3$, 100 MHz)**: δ 211.2, 149.3, 146.4, 143.0, 135.0, 126.6, 129.2, 51.7, 42.3, 34.9, 33.1, 28.1, 25.4.

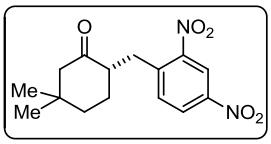
(*S*)-2-(2,4-dinitrobenzyl)-4,4-dimethylcyclohexanone (3b)



Prepared according to the general procedure using the amino catalyst **A** (0.02 mmol, 6.5 mg, 0.2 eq), toluene (0.2 M, 500 μL), trifluoroacetic acid (0.04 mmol, 3 μL, 40 mol%), sodium acetate (0.2 mmol, 16.4 mg, 2 eq), 4,4-dimethylcyclohexanone **1b** (0.4 mmol, 50.5 mg, 4 eq) and 2,4-dinitrobenzyl bromide **2a** (0.1 mmol, 26 mg, 1 eq). Time of irradiation: 60 h. Purification by flash column chromatography (eluent 2:1 DCM:hexane mixture) afforded the title compound (15.0 mg, 65 % yield, 82 % ee) as an orange solid.
The enantiomeric excess was determined by HPLC analysis on a Daicel Chiralpak IC column, 70:30 hexane:iPrOH, flow rate 1.00 mL/min, λ = 254 nm: τ_{major} = 16.9 min, τ_{minor} = 19.9 min.
$[\alpha]^{28}_D$ = -32 ± 2 (c = 1.0, $CHCl_3$, 82 % ee).

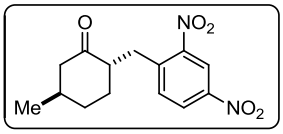
HRMS: calculated for $C_{15}H_{20}N_2O_5$ (M+2Na): 329.1108, found: 329.1110.
^{1}H ($CDCl_3$, 400 MHz): δ 8.79 (d, *J* = 2.8Hz, 1H), 8.36 (dd, *J* = 2.4Hz, *J* = 8.5Hz, 1H), 7.81 (d, *J* = 8.5Hz, 1H), 3.51 (dd, *J* = 7.8Hz, *J* = 13.1Hz), 2.94-2.85 (m, 1H), 2.77 (dd, *J* = 4.8Hz, *J* = 13.1Hz, 1H), 2.53-2.46 (m, 1H), 2.32-2.25 (m, 1H), 1.83-1.74 (m, 2H), 1.73-1.63 (m, 1H), 1.54 (t, *J* = 13.0 Hz 1H), 1.22 (s, 3H), 1.01 (s, 3H). **^{13}C ($CDCl_3$, 100 MHz)**: δ 211.7, 143.0, 135.0, 126.6, 120.2, 47.5, 47.4, 40.2, 38.4, 33.0, 31.2, 31.1, 29.7, 24.2.

(*S*)-2-(2,4-dinitrobenzyl)-5,5-dimethylcyclohexanone (3c)



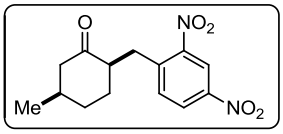
Prepared according to the general procedure using the amino catalyst **A** (0.02 mmol, 6.5 mg, 0.2 eq), toluene (0.2 M, 500 μL), trifluoroacetic acid (0.04 mmol, 3 μL, 40 mol%), sodium acetate (0.2 mmol, 16.4 mg, 2 eq), 3,3-dimethylcyclohexanone **1c** (0.4 mmol, 55.5 μL, 4 eq) and 2,4-dinitrobenzyl bromide **2a** (0.1 mmol, 26 mg, 1 eq). Time of irradiation: 60 h. Purification by flash column chromatography (eluent 2:1 DCM:hexane mixture) afforded the title compound (17.6 mg, 57 % yield, 94 % ee) as a yellow oil.
The enantiomeric excess was determined by HPLC analysis on a Daicel Chiralpak IC column, 70:30 hexane:iPrOH, flow rate 1.00 mL/min, λ = 254 nm: τ_{major} = 15.6 min, τ_{minor} = 20.1 min.
$[\alpha]^{28}_D$ = -28 ± 1 (c = 1.0, $CHCl_3$, 94 % ee).
HRMS: calculated for $C_{15}H_{20}N_2O_5$ (M+2Na): 329.1108, found: 329.1110.
^{1}H ($CDCl_3$, 400 MHz): δ 8.79 (d, *J* = 2.3Hz, 1H), 8.36 (dd, *J* = 2.3Hz, *J* = 8.5Hz, 1H), 7.80 (d, *J* = 8.5Hz, 1H), 3.55-3.47 (m, 1H), 2.88 (dd, *J* = 5.1Hz, *J* = 13.6Hz, 1H), 2.72-2.61 (m, 1H), 2.25 (d, *J* = 12.7Hz, 1H), 2.13(dd, *J* = 2.2Hz, *J* = 12.7Hz, 1H), 2.10-2.03 (m, 1H), 1.73-1.59 (m, 3H), 1.09 (s, 3H), 0.90 (s, 3H). Residual peaks of benzene and water at δ 7.38 and 1.29. **^{13}C ($CDCl_3$, 100 MHz)**: δ 210.7, 149.3, 146.4, 143.0, 135.0, 126.6, 102.3, 55.1, 50.7, 38.3, 37.4, 32.9, 31.8, 30.5, 29.7, 25.0.

(*2S*,5*R*)-2-(2,4-dinitrobenzyl)-5-methylcyclohexanone (3d)



Prepared according to the general procedure using the amino catalyst **A** (0.02 mmol, 6.5 mg, 0.2 eq), toluene (0.2 M, 500 μL), trifluoroacetic acid (0.04 mmol, 3 μL, 40 mol%), sodium acetate (0.2 mmol, 16.4 mg, 2 eq), (R)-3-methylcyclohexanone **1d** (0.4 mmol, 49 μg, 4 eq) and 2,4-dinitrobenzyl bromide **2a** (0.1 mmol, 26 mg, 1 eq). Time of irradiation: 65 h. Purification by flash column chromatography (eluent from pure hexane to 10:1 hexane:EtOAc mixture) afforded the title compound (12.8 mg, 43 % yield, 10:1 d.r) as a yellow oil. The diastereomeric ratio was determined by ^{1}H NMR.
$[\alpha]^{28}_D$ = -10 ± 1 (c = 0.5, $CHCl_3$)
HRMS: calculated for $C_{14}H_{16}N_2O_5$ (M-H): 291.0986, found: 291.0992.
^{1}H ($CDCl_3$, 400 MHz): δ 8.79 (d, *J* = 2.4 Hz, 1H), 8.36 (dd, *J* = 8.6, 2.4 Hz, 1H), 7.80 (d, *J* = 8.6 Hz, 1H), 3.51 (dd, *J* = 13.6, 7.6 Hz, 1H), 2.87 (dd, *J* = 13.6, 5.1 Hz, 1H), 2.74 – 2.61 (m, 1H), 2.44 – 2.37 (m, 1H), 2.21 – 2.12 (m, 1H), 2.03 (dd, *J* = 12.74, 12.78 Hz, 1H), 1.97 – 1.85 (m, 2H), 1.52 (td, *J* = 12.5, 11.8, 2.6 Hz, 1H), 1.47 – 1.39 (m, 1H), 1.05 (d, *J* = 6.2 Hz, 3H). **^{13}C ($CDCl_3$, 100 MHz)**: δ 210.58, 149.30, 146.39, 143.03, 135.02, 126.60, 120.25, 50.80, 50.39, 35.88, 33.94, 33.69, 32.89, 22.29.

(*2R*,5*R*)-2-(2,4-dinitrobenzyl)-5-methylcyclohexanone (3e)

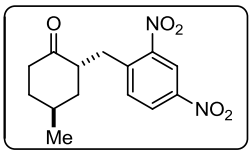


Prepared according to the general procedure using the amino catalyst **E** (0.02 mmol, 6.5 mg, 0.2 eq), toluene (0.2 M, 500 μL), trifluoroacetic acid (0.04 mmol, 3 μL, 40 mol%), sodium acetate (0.2 mmol, 16.4 mg, 2 eq), (R)-3-methylcyclohexanone **1d** (0.4 mmol, 49 μg, 4 eq) and 2,4-dinitrobenzyl bromide **2a** (0.1 mmol, 26 mg, 1 eq). Time of irradiation: 65 h. Purification by flash column chromatography (eluent 3:2 hexane:DCM mixture) afforded the title compound (16.6 mg, 57 % yield, 12:1 d.r) as a yellow oil. The diastereomeric ratio was determined by ^{1}H NMR.
$[\alpha]^{27}_D$ = +38 ± 1 (c = 1.0, $CHCl_3$)

HRMS: calculated for $C_{14}H_{16}N_2O_5$ (M-H): 291.0986, found: 291.0994.
^{1}H ($CDCl_3$, 400 MHz): δ 8.78 (d, *J* = 2.4 Hz, 1H), 8.36 (dd, *J* = 8.5, 2.4 Hz, 1H), 7.77 (d, *J* = 8.6 Hz, 1H), 3.51 (dd, *J* = 13.6, 7.8 Hz, 1H), 2.91 (dd, *J* = 13.6, 5.2 Hz, 1H), 2.80 – 2.68 (m, 1H), 2.53 (dd, *J* = 13.0, 5.4 Hz, 1H), 2.50 – 2.41 (m, 1H), 2.24 – 2.16 (m, 1H), 2.09 – 1.91 (m, 3H), 1.84 – 1.71 (m, 1H), 1.71 – 1.63 (m, 1H), 0.98 (d, *J* = 7.1 Hz, 3H). **^{13}C ($CDCl_3$, 100 MHz)**: δ 211.16, 146.41, 142.83, 134.84, 126.64, 120.27, 51.27, 48.33, 33.13, 32.30, 30.60, 29.74, 18.76.

All proton signals of compounds **3d** and **3e** were unambiguously assigned using traditional 1D and 2D NMR methods. Identification of *alpha* proton signals was performed by selective 1D-NOESY by correlation between the substituted *alpha* proton and the *alpha'* proton in the same face (H^a) [when CO-C**H**(CH_2Ar) is irradiated CO-C**H**^{a}H^b-CH(Me) is correlated].
To determine if proton in C**H**(Me) is in equatorial or axial position, coupling constants of C**H**(Me) and CO-C**H**^{a}H^b were compared between **3d** and **3e**. CO-C**H**^{a}H^b appears as a double doublet with a geminal coupling and large diaxial coupling of 12.74, 12.78 Hz in **3d**, consistent with geminal and axial-axial couplings for a six-membered ring, requiring axial orientations for CO-C**H**^{a}H^b, C**H**(Me), and CO-C**H**(CH_2Ar), and enabling assignment of the relative stereochemistry shown. On the other hand, compound **3e**, CO-C**H**^{a}H^b appears as a double doublet with a geminal coupling and smaller axial-equatorial coupling of 13.0, 5.4 Hz, consistent with geminal and axial-equatorial couplings for a six-membered ring, and enabling assignment of the relative stereochemistry shown in the drawing.

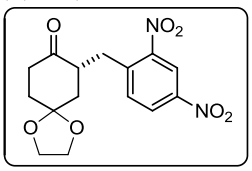
(*2S,4S*)-2-(2,4-dinitrobenzyl)-4-methylcyclohexanone (3f)



Prepared according to the general procedure using the amino catalyst **A** (0.02 mmol, 6.5 mg, 0.2 eq), toluene (0.2 M, 500 μL), trifluoroacetic acid (0.04 mmol, 3 μL, 40 mol%), sodium acetate (0.2 mmol, 16.4 mg, 2 eq), 4-methylcyclohexanone **1f** (0.4 mmol, 40 μg, 4 eq) and 2,4-dinitrobenzyl bromide **2a** (0.1 mmol, 26 mg, 1 eq). Time of irradiation: 65 h. Purification by flash column chromatography (eluent 20:1 hexane:EtOAc mixture) afforded the title compound (28.4 mg, 94 % yield, 18:1 d.r, 94 % ee) as a brown. The enantiomeric excess was determined by HPLC analysis on a Daicel Chiralpak IC column, 85:15 hexane:iPrOH, flow rate 1.00 mL/min, λ = 254 nm: τ_{major} = 31 min, τ_{minor} = 37 min.
$[\alpha]^{28}_D$ = -67 ± 1 (c = 1.0, $CHCl_3$, 94 % ee).
HRMS: calculated for $C_{14}H_{16}N_2O_5$ (M+Na): 315.0951, found: 315.0953.

The relative stereochemistry was determined by selective 1D-NOESY correlation between the substituted *alpha* proton and the methyl group in position 4 [when CO-C**H**(CH_2Ar) is irradiated 4-**Me** is correlated]
^{1}H ($CDCl_3$, 400 MHz): δ 8.79 (d, *J* = 2.4 Hz, 1H), 8.36 (dd, *J* = 8.5, 2.4 Hz, 1H), 7.77 (d, *J* = 8.5 Hz, 1H), 3.53 – 3.46 (m, 1H), 2.99 – 2.87 (m, 2H), 2.53 – 2.44 (m, 1H), 2.35 (dt, *J* = 14.3, 5.0 Hz, 1H), 2.23 – 2.15 (m, 1H), 2.00 – 1.90 (m, 2H), 1.87 – 1.77 (m, 2H), 1.19 (d, *J* = 7.0 Hz, 3H). **^{13}C ($CDCl_3$, 100 MHz)**: δ 211.33, 149.28, 146.40, 143.00, 135.05, 126.61, 120.26, 50.57, 42.82, 41.44, 35.94, 33.06, 32.12, 21.06.

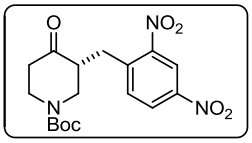
(*S*)-7-(2,4-dinitrobenzyl)-1,4-dioxaspiro[4.5]decan-8-one (3g)



Prepared according to the general procedure using the amino catalyst **A** (0.02 mmol, 6.5 mg, 0.2 eq), toluene (0.2 M, 500 μL), trifluoroacetic acid (0.04 mmol, 3 μL, 40 mol%), sodium acetate (0.2 mmol, 16.4 mg, 2 eq), 1,4-cyclohexanedione monoethylene acetal **1g** (0.4 mmol, 62.47 mg, 4 eq) and 2,4-dinitrobenzyl bromide **2a** (0.1 mmol, 26 mg, 1 eq). Time of irradiation: 68 h. Purification by flash column chromatography (eluent 10:1 hexane: AcOEt mixture) afforded the title compound (23.5 mg, 70 % yield, 95 % ee) as a yellow oil.

The enantiomeric excess was determined by HPLC analysis on a Daicel Chiralpak IC column, 75:25 hexane:iPrOH, flow rate 1.00 mL/min, λ = 254 nm: τ_{minor} = 38 min, τ_{major} = 41 min.
$[\alpha]^{28}_D$ = -58 ± 2 (c = 1.0, $CHCl_3$, 95 % ee).
HRMS: calculated for $C_{15}H_{16}N_2O_7$ (M-H): 335.0885, found: 335.0885.
^{1}H (CDCl$_3$, 400 MHz) δ 8.81 (d, *J* = 2.4 Hz, 1H), 8.37 (dd, *J* = 8.5, 2.4 Hz, 1H), 7.77 (d, *J* = 8.5 Hz, 1H), 4.20 – 3.92 (m, 4H), 3.56 (dd, *J* = 13.7, 7.6 Hz, 1H), 3.19 – 3.08 (m, 1H), 2.84 (dd, *J* = 13.7, 5.2 Hz, 1H), 2.65 (m, 1H), 2.41 (m, 1H), 2.15 (m, 1H), 2.12 – 1.95 (m, 2H), 1.89 (t, *J* = 13.2 Hz, 1H). **^{13}C (CDCl$_3$, 100 MHz)**: δ 209.70, 149.28, 146.50, 142.57, 134.75, 126.73, 120.37, 106.94, 64.89, 64.66, 47.54, 41.25, 38. 11, 34.76, 32.56.

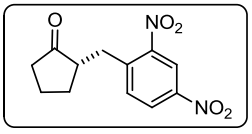
(*S*)-*tert*-butyl 3-(2,4-dinitrobenzyl)-4-oxopiperidine-1-carboxylate (3h)



Prepared according to the general procedure using the amino catalyst **A** (0.02 mmol, 6.5 mg, 0.2 eq), toluene (0.2 M, 500 μL), trifluoroacetic acid (0.04 mmol, 3 μL, 40 mol%), sodium acetate (0.2 mmol, 16.4 mg, 2 eq), 1-boc-4-piperidone **1h** (0.4 mmol, 79.7 mg, 4 eq) and 2,4-dinitrobenzyl bromide **2a** (0.1 mmol, 26 mg, 1 eq). Time of irradiation: 65 h. Purification by flash column chromatography (eluent 2:1 DCM:hexane mixture) afforded the title compound (26.0 mg, 69 % yield, 94 % ee) as a yellow solid.

The enantiomeric excess was determined by HPLC analysis on a Daicel Chiralpak IC column, 90:10 hexane:iPrOH, flow rate 1.00 mL/min, λ = 254 nm: τ_{minor} = 86 min, τ_{major} = 92 min.
$[\alpha]^{27}_D$ = -22 ± 2 (c = 1.0, $CHCl_3$, 94 % ee).
HRMS: calculated for $C_{17}H_{21}N_3O_7$ (M-H): 378.1307, found: 378.1309.
^{1}H (CDCl$_3$, 400 MHz): δ 8.83 (d, *J* = 2.4 Hz, 1H), 8.39 (dd, *J* = 8.5, 2.4 Hz, 1H), 7.81 (bs, 1H), 4.68 – 4.01 (m, 1H), 3.53 (bs, 1H), 3.19 (bs, 1H), 3.06 – 2.72 (m, 3H), 2.67 – 2.34 (m, 2H), 1.50 (s, 10H). **^{13}C (CDCl$_3$, 100 MHz)**: δ 154.24, 149.24, 146.66, 141.72, 134.80, 126.91, 120.50, 80.97, 44.05, 41.35, 30.16, 28.28.

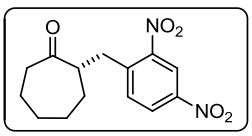
(*S*)-2-(2,4-dinitrobenzyl)cyclopentanone (3i)



Prepared according to the general procedure using the amino catalyst **A** (0.02 mmol, 6.5 mg, 0.2 eq), toluene (0.2 M, 500 μL), trifluoroacetic acid (0.04 mmol, 3 μL, 40 mol%), sodium acetate (0.2 mmol, 16.4 mg, 2 eq), cyclopentanone **1i** (0.4 mmol, 35 μg, 4 eq) and 2,4-dinitrobenzyl bromide **2a** (0.1 mmol, 26 mg, 1 eq). Time of irradiation: 68 h. Purification by flash column chromatography (eluent 2:1 DCM:hexane mixture) afforded the title compound (10.8 mg, 44 % yield, 62 % ee) as an yellow oil.

The enantiomeric excess was determined by HPLC analysis on a Daicel Chiralpak IC column, 70:30 hexane:iPrOH, flow rate 1.00 mL/min, λ = 254 nm: τ_{minor} = 25 min, τ_{major} = 30 min.
$[\alpha]^{28}_D$ = + 31 ± 1 (c = 1.0, $CHCl_3$, 62 % ee).
HRMS: calculated for $C_{12}H_{12}N_2O_5$ (M-H): 263.0673, found: 263.0673.
^{1}H (CDCl$_3$, 400 MHz): δ 8.80 (d, *J* = 2.4 Hz, 1H), 8.39 (dd, *J* = 8.5, 2.4 Hz, 1H), 7.68 (d, *J* = 8.5 Hz, 1H), 3.50 (dd, *J* = 13.8, 6.1 Hz, 1H), 3.02 (dd, *J* = 13.8, 7.6 Hz, 1H), 2.58 – 2.46 (m, 1H), 2.46 – 2.35 (m, 1H), 2.26 – 2.00 (m, 4H), 1.91 – 1.74 (m, 1H), 1.70 – 1.52 (m, 1H). **^{13}C (CDCl$_3$, 100 MHz)**: δ 218.18, 149.31, 146.57, 142.40, 134.14, 126.84, 120.34, 49.88, 37.45, 32.58, 29.61, 20.42.

(*S*)-2-(2,4-dinitrobenzyl)cycloheptanone (3j)

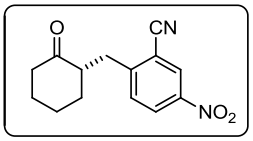


Prepared according to the general procedure using the amino catalyst **A** (0.02 mmol, 6.5 mg, 0.2 eq), toluene (0.2 M, 500 μL), trifluoroacetic acid (0.04 mmol, 3 μL, 40 mol%), sodium acetate (0.2 mmol, 16.4 mg, 2 eq), cycloheptanone **1i** (1 mmol, 118 μg, 10 eq) and 2,4-dinitrobenzyl bromide **2a** (0.1 mmol, 26 mg, 1 eq).

Time of irradiation: 96 h. Purification by flash column chromatography (eluent 10:1 hexane:EtOAc mixture) afforded the title compound (11.1 mg, 38 % yield, 74 % ee) as a yellow oil.

The enantiomeric excess was determined by HPLC analysis on a Daicel Chiralpak IC column, 80:20 hexane:iPrOH, flow rate 1.00 mL/min, λ = 254 nm: τ_{major} = 21 min, τ_{minor} = 29 min.
$[\alpha]^{28}_D$ = -80 ± 1 (c = 2.0, $CHCl_3$, 74 % ee).
HRMS: calculated for $C_{14}H_{16}N_2O_5$ (M-H): 291.0986, found: 291.0985.
^{1}H ($CDCl_3$, 400 MHz): δ 8.79 (d, *J* = 2.4 Hz, 1H), 8.35 (dd, *J* = 8.5, 2.4 Hz, 1H), 7.66 (d, *J* = 8.5 Hz, 1H), 3.54 – 3.41 (m, 1H), 3.10 – 2.96 (m, 2H), 2.50 – 2.43 (m, 2H), 1.99 – 1.79 (m, 5H), 1.73 – 1.43 (m, 3H), 1.39 – 1.23 (m, 3H).**^{13}C ($CDCl_3$, 100 MHz)**: δ 213.49, 149.36, 146.47, 142.60, 134.66, 126.69, 120.34, 52.42, 43.19, 34.98, 32.03, 28.72, 23.58.

(*S*)-5-nitro-2-((2-oxocyclohexyl)methyl)benzonitrile (3k)



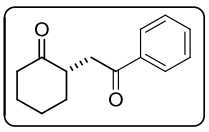
Prepared according to the general procedure using the amino catalyst **A** (0.02 mmol, 6.5 mg, 0.2 eq), toluene (0.2 M, 500 μL), trifluoroacetic acid (0.04 mmol, 3 μL, 40 mol%), sodium acetate (0.2 mmol, 16.4 mg, 2 eq), cyclohexanone **1a** (0.4 mmol, 42 μL, 4 eq) and 2-cyano-4-nitrobenzyl bromide **2b** (0.1 mmol, 24.1 mg, 1 eq). Time of irradiation: 65 h. Purification by flash column chromatography (gradient eluent from pure hexane to 10:1 hexane:AcOEt mixture) afforded the title compound (11.6 mg, 45 % yield, 86 % ee) as a yellow solid.

The enantiomeric excess was determined by HPLC analysis on a Daicel Chiralpak IB column, 70:30 hexane:iPrOH, flow rate 1.00 mL/min, λ = 254 nm: τ_{minor} = 44.6 min, τ_{major} = 32.9 min.
$[\alpha]^{26}_D$ = -19 ± 1 (c = 1.0, $CHCl_3$, 86 % ee).
HRMS: calculated for $C_{14}H_{14}N_2O_3$ (M+Na): 281.0885, found: 281.0897.
^{1}H ($CDCl_3$, 400 MHz): δ 8.49 (d, *J* = 2.4 Hz, 1H), 8.35 (dd, *J* = 8.6, 2.4 Hz, 1H), 7.68 (d, *J* = 8.6 Hz, 1H), 3.47 (dd, *J* = 13.8, 7.2 Hz, 1H), 2.86 (dd, *J* = 13.8, 6.0 Hz, 1H), 2.82 – 2.73 (m, 1H), 2.53 – 2.43 (m, 1H), 2.42 – 2.28 (m, 1H), 2.20 – 2.10 (m, 2H), 1.98 – 1.87 (m, 1H), 1.82 – 1.64 (m, 2H), 1.64 – 1.50 (m, 2H).**^{13}C ($CDCl_3$, 100 MHz):** δ 210.57, 152.01, 146.21, 132.25, 127.74, 127.09, 116.08, 114.21, 51.60, 42.16, 34.67, 34.40, 27.90, 25.22.

General procedure for the photochemical α-asymmetric phenacylation of ketones:

A 10 mL Schlenk tube was charged with the aminocatalyst **A** (20 mol%), toluene (0.2 M referring to the alkyl bromide **2**), trifluoroacetic acid, TFA, (40 mol%), cyclohexanone **1a** (4 eq), sodium acetate (2 eq) and the alkylating agent **2** (1 eq). The reaction mixture was degassed via freeze pump thaw (x 3cycles), and the vessel refilled with nitrogen. After the reaction mixture was thoroughly degassed, the flask was sealed and positioned approximately 10 cm away from the light source. The mixture was irradiated with a 300 W Xe lamp (*Asashi* Spectra Co., Ltd.) for 14 h under magnetic stirring. The temperature of the reaction mixture was maintained at room temperature by a water bath during the reaction. After stirring for the indicated time, the crude mixture was purified by flash column chromatography to afford the title compound **4** in the stated yield and optical purity.

***(S)*-2-(2-oxo-2-phenylethyl)cyclohexanone (4a)**

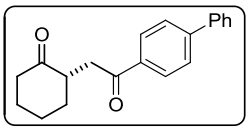


Prepared according to the general procedure using the amino catalyst **A** (0.02 mmol, 6.5 mg, 0.2 eq), toluene (0.2 M, 500 μL), trifluoroacetic acid (0.04 mmol, 3 μL, 40 mol%), sodium acetate (0.2 mmol, 16.4 mg, 2 eq), cyclohexanone **1a** (0.4 mmol, 42 μL, 4 eq) and 2-bromoacetophenone (0.1 mmol, 20 mg, 1 eq). Time of irradiation: 14 h. Purification by flash column chromatography (gradient eluent from pure hexane to 10:1 hexane:AcOEt mixture) afforded the title compound (15.0 mg, 69 % yield, 90 % ee) as a yellow oil.

The enantiomeric excess was determined by HPLC analysis on a Daicel Chiralpak IC column, 85:15 hexane:iPrOH, flow rate 1.00 mL/min, λ = 254 nm: τ_{major} = 20 min, τ_{minor} = 33 min.
$[\alpha]^{28}_{D}$ = -50 ± 2 (c = 1.0, $CHCl_3$, 90 % ee).
Literature value for *(R)*-2-(2-oxo-2-phenylethyl)cyclohexanone $[\alpha]_D$ = +57.8 (c = 1, $CHCl_3$, for 84% ee).
The (*S*)-absolute configuration for compound **4a** was inferred by comparison of the optical rotation with the value reported in the literature. (*4*)

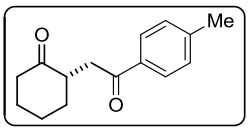
HRMS: calculated for $C_{14}H_{16}O_2$ (M+Na): 239.1043, found: 239.1047.
^{1}H ($CDCl_3$, 400 MHz): δ 8.07 – 7.93 (m, 1H), 7.66 – 7.53 (m, 1H), 7.53 – 7.42 (m, 1H), 3.63 (dd, *J* = 17.7, 6.6 Hz, 1H), 3.28 – 3.12 (m, 1H), 2.71 (dd, *J* = 17.7, 5.7 Hz, 1H), 2.54 – 2.41 (m, 1H), 2.31 – 2.09 (m, 1H), 1.98 – 1.62 (m, 2H), 1.48 (qd, *J* = 12.8, 3.9 Hz, 1H). **^{13}C ($CDCl_3$, 125 MHz)**: δ 211.53, 198.65, 137.09, 133.00, 128.52, 128.08, 46.46, 41.98, 38.35, 34.33, 27.99, 25.38.

***(S)*-2-(2-([1,1'-biphenyl]-4-yl)-2-oxoethyl)cyclohexanone (4b)**



Prepared according to the general procedure using the amino catalyst **A** (0.02 mmol, 6.5 mg, 0.2 eq), toluene (0.2 M, 500 μL), trifluoroacetic acid (0.04 mmol, 3 μL, 40 mol%), sodium acetate (0.2 mmol, 16.4 mg, 2 eq), cyclohexanone **1a** (0.4 mmol, 42 μL, 4 eq) and 2-bromo-4'-phenylacetophenone (0.1 mmol, 27.5 mg, 1 eq). Time of irradiation: 14 h. Purification by flash column chromatography (gradient eluent from pure hexane to 10:1 hexane:AcOEt mixture) afforded the title compound (17.3 mg, 60 % yield, 86 % ee) as a white solid.
The enantiomeric excess was determined by HPLC analysis on a Daicel Chiralpak IC column, 85:15 hexane:iPrOH, flow rate 1.00 mL/min, λ = 254 nm: τ_{minor}= 20 min, τ_{major} = 29 min.
$[\alpha]^{27}_{D}$ = -44 ± 2 (c = 1.0, $CHCl_3$, 86 % ee). HRMS: calculated for $C_{20}H_{20}O_2$ (M+Na): 315.1356, found: 315.1356.
^{1}H ($CDCl_3$, 400 MHz): δ ^{1}H NMR 8.12 – 8.06 (m, 2H), 7.73 – 7.69 (m, 2H), 7.68 – 7.62 (m, 2H), 7.55 – 7.46 (m, 2H), 7.46 – 7.40 (m, 1H), 3.66 (dd, *J* = 17.6, 6.6 Hz, 1H), 3.34 – 3.10 (m, 1H), 2.74 (dd, *J* = 17.6, 5.7 Hz, 1H), 2.56 – 2.42 (m, 2H), 2.31 – 2.12 (m, 2H), 2.00 – 1.90 (m, 1H), 1.90 – 1.75 (m, 1H), 1.75 – 1.64 (m, 1H), 1.50 (qd, *J* = 12.8, 3.9 Hz, 1H). **^{13}C ($CDCl_3$, 100 MHz)**: δ 211.57, 198.26, 145.70, 139.97, 135.80, 128.93, 128.68, 128.17, 127.28, 127.20, 46.56, 42.00, 38.38, 34.37, 28.01, 25.40.

***(S)*-2-(2-oxo-2-(p-tolyl)ethyl)cyclohexanone (4c)**



Prepared according to the general procedure using the amino catalyst **A** (0.02 mmol, 6.5 mg, 0.2 eq), toluene (0.2 M, 500 μL), trifluoroacetic acid (0.04 mmol, 3 μL, 40 mol%), sodium acetate (0.2 mmol, 16.4 mg, 2 eq), cyclohexanone **1a** (0.4 mmol, 42 μL, 4 eq) and 2-bromo-4'-methylacetophenone (0.1 mmol, 21.3 mg, 1 eq). Time of irradiation: 14 h. Purification by flash column chromatography (gradient eluent from pure hexane to 10:1 hexane:AcOEt mixture) afforded the title compound (15.5 mg, 66 % yield, 92 % ee) as a white solid.

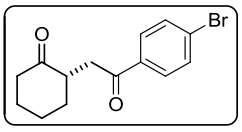
The enantiomeric excess was determined by HPLC analysis on a Daicel Chiralpak IC column, 85:15 hexane:iPrOH, flow rate 1.00 mL/min, λ = 254 nm: τ_{major} = 26 min, τ_{minor} = 38 min.

$[\alpha]^{28}_{D}$ = -68 ± 2 (c = 1.0, $CHCl_3$, 92 % ee).

Characterization data in agreement with the literature (5).

^{1}H ($CDCl_3$, 400 MHz): δ 7.91 (d, *J* = 8.2 Hz, 2H), 7.30 – 7.24 (d, *J* = 8.2 Hz, 2H), 3.60 (dd, *J* = 17.6, 6.4 Hz, 1H), 3.18 (dq, *J* = 12.2, 6.0 Hz, 1H), 2.69 (dd, *J* = 17.6, 6.0 Hz, 1H), 2.50 – 2.44 (m, 2H), 2.43 (s, 3H), 2.28 – 2.11 (m, 2H), 1.95 – 1.87 (m, 1H), 1.87 – 1.64 (m, 2H), 1.46 (qd, *J* = 12.7, 3.9 Hz, 1H). **^{13}C ($CDCl_3$, 100 MHz)**: δ 211.62, 198.28, 143.76, 134.61, 129.20, 128.20, 46.47, 42.00, 38.19, 34.36, 28.00, 25.39, 21.63.

***(S)*-2-(2-(4-bromophenyl)-2-oxoethyl)cyclohexanone (4d)**



Prepared according to the general procedure using the amino catalyst **A** (0.02 mmol, 6.5 mg, 0.2 eq), toluene (0.2 M, 500 μL), trifluoroacetic acid (0.04 mmol, 3 μL, 40 mol%), sodium acetate (0.2 mmol, 16.4 mg, 2 eq), cyclohexanone **1a** (0.4 mmol, 42 μL, 4 eq) and 2,2'-dibromoacetophenone (0.1 mmol, 27.7 mg, 1 eq). Time of irradiation: 14 h. Purification by flash column chromatography (gradient eluent from pure hexane to 10:1 hexane:AcOEt mixture) afforded the title compound (15.4 mg, 52 % yield, 86 % ee) as a yellow solid.

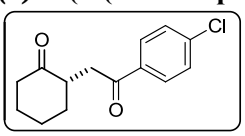
The enantiomeric excess was determined by HPLC analysis on a Daicel Chiralpak IC column, 95:5 hexane:iPrOH, flow rate 1.00 mL/min, λ = 254 nm: τ_{minor}= 36 min, τ_{major} = 41 min.

$[\alpha]^{27}_{D}$ = -40 ± 1 (c = 1.0, $CHCl_3$, 86 % ee).

Characterization data in agreement with the literature (5).

^{1}H ($CDCl_3$, 500 MHz): δ 7.87 (d, *J* = 8.7 Hz, 2H), 7.63 (d, *J* = 8.8 Hz, 2H), 3.58 (dd, *J* = 17.6, 6.9 Hz, 1H), 3.26 – 3.11 (m, 1H), 2.64 (dd, *J* = 17.6, 5.4 Hz, 1H), 2.52 – 2.41 (m, 2H), 2.33 – 2.11 (m, 2H), 1.97 – 1.89 (m, 1H), 1.87 – 1.75 (m, 1H), 1.75 – 1.65 (m, 1H), 1.48 (qd, *J* = 12.8, 3.9 Hz, 1H).^{13}C ($CDCl_3$, 125 MHz): δ 211.38, 197.63, 135.81, 131.83, 129.63, 128.13, 46.52, 41.94, 38.32, 34.30, 27.97, 25.37.

***(S)*-2-(2-(4-chlorophenyl)-2-oxoethyl)cyclohexanone (4e)**



Prepared according to the general procedure using the amino catalyst **A** (0.02 mmol, 6.5 mg, 0.2 eq), toluene (0.2 M, 500 μL), trifluoroacetic acid (0.04 mmol, 3 μL, 40 mol%), sodium acetate (0.2 mmol, 16.4 mg, 2 eq), cyclohexanone **1a** (0.4 mmol, 42 μL, 4 eq) and 2-bromo-4'-chloroacetophenone (0.1 mmol, 23.3 mg, 1 eq). Time of irradiation: 14 h. Purification by flash column chromatography (gradient eluent from pure hexane to 10:1 hexane:AcOEt mixture) afforded the title compound (10 mg, 40 % yield, 87 % ee) as a yellow solid.

The enantiomeric excess was determined by HPLC analysis on a Daicel Chiralpak IB column, 95:5 hexane:iPrOH, flow rate 1.00 mL/min, λ = 254 nm: τ_{major} = 9 min, τ_{minor} = 10 min.

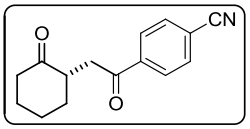
$[\alpha]^{27}_{D}$ = -55 ± 2 (c = 1.0, $CHCl_3$, 87 % ee).

Characterization data in agreement with the literature (6).

^{1}H ($CDCl_3$, 400 MHz): δ 7.95 (d, *J* = 8.6 Hz, 2H), 7.45 (d, *J* = 8.6 Hz, 2H), 3.58 (dd, *J* = 17.6, 6.9 Hz, 1H), 3.30 – 3.08 (m, 1H), 2.64 (dd, *J* = 17.6, 5.4 Hz, 1H), 2.52 – 2.40 (m, 2H), 2.31 – 2.10 (m, 2H), 1.98

– 1.88 (m, 1H), 1.88 – 1.75 (m, 1H), 1.75 – 1.64 (m, 1H), 1.48 (qd, *J* = 12.8, 3.8 Hz, 1H). **^{13}C ($CDCl_3$, 100 MHz)**: δ 211.41, 197.44, 139.42, 135.40, 129.51, 128.83, 46.52, 41.94, 38.34, 34.31, 27.97, 25.37.

***(S)*-4-(2-(2-oxocyclohexyl)acetyl)benzonitrile (4f)**



Prepared according to the general procedure using the amino catalyst **A** (0.02 mmol, 6.5 mg, 0.2 eq), toluene (0.2 M, 500 μL), trifluoroacetic acid (0.04 mmol, 3 μL, 40 mol%), sodium acetate (0.2 mmol, 16.4 mg, 2 eq), cyclohexanone **1a** (0.4 mmol, 42 μL, 4 eq) and 2-bromo-4'-cianoacetophenone (0.1 mmol, 22.4 mg, 1 eq). Time of irradiation: 14 h. Purification by flash column chromatography (gradient eluent from pure hexane to 10:1 hexane:AcOEt mixture) afforded the title compound (10.2 mg, 42 % yield, 88 % ee) as a yellow solid.

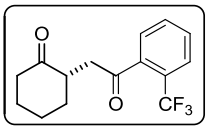
The enantiomeric excess was determined by HPLC analysis on a Daicel Chiralpak IC column, 70:30 hexane:iPrOH, flow rate 1.00 mL/min, λ = 254 nm: τ_{major} = 34 min, τ_{minor} = 38 min.

$[\alpha]^{28}_D$ = -72 ± 2 (c = 1.0, $CHCl_3$, 88 % ee).

HRMS: calculated for $C_{15}H_{15}NO_2$ (M+Na): 264.0995, found: 264.0996.

^{1}H ($CDCl_3$, 400 MHz): δ 8.09 (d, *J* = 8.4 Hz, 2H), 7.79 (d, *J* = 8.4 Hz, 2H), 3.59 (dd, *J* = 17.6, 7.5 Hz, 1H), 3.32 – 3.11 (m, 1H), 2.64 (dd, *J* = 17.6, 5.0 Hz, 1H), 2.55 – 2.38 (m, 2H), 2.32 – 2.13 (m, 2H), 2.06 – 1.87 (m, 1H), 1.88 – 1.76 (m, 1H), 1.76 – 1.64 (m, 1H), 1.51 (qd, *J* = 12.9, 3.8 Hz, 1H). **^{13}C ($CDCl_3$**, 100 MHz): δ 211.20, 197.44, 140.50, 140.13, 132.44, 128.50, 117.99, 116.23, 46.71, 41.85, 38.72, 34.21, 27.90, 25.33.

***(S)*-2-(2-oxo-2-(2-(trifluoromethyl)phenyl)ethyl)cyclohexanone (4g)**



Prepared according to the general procedure using the amino catalyst **A** (0.02 mmol, 6.5 mg, 0.2 eq), toluene (0.2 M, 500 μL), trifluoroacetic acid (0.04 mmol, 3 μL, 40 mol%), sodium acetate (0.2 mmol, 16.4 mg, 2 eq), cyclohexanone **1a** (0.4 mmol, 42 μL, 4 eq) and 2-bromo-2'-trifluoromethylacetophenone (0.1 mmol, 26.7 mg, 1 eq). Time of irradiation: 14 h. Purification by flash column chromatography (gradient eluent from pure hexane to 10:1 hexane:AcOEt mixture) afforded the title compound (13.9 mg, 50 % yield, 76 % ee) as a yellow oil.

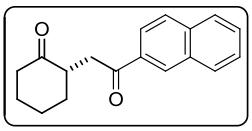
The enantiomeric excess was determined by HPLC analysis on a Daicel Chiralpak IC column, 95:5 hexane:iPrOH, flow rate 1.00 mL/min, λ = 254 nm: τ_{major} = 16 min, τ_{minor} = 20 min.

$[\alpha]^{28}_D$ = -14 ± 1 (c = 0.5, $CHCl_3$, 76 % ee).

HRMS: calculated for $C_{15}H_{15}F_3O_2$ (M+Na): 307.0916, found: 307.0928.

^{1}H ($CDCl_3$, 400 MHz): δ δ 7.78 – 7.69 (m, 2H), 7.68 – 7.62 (m, 1H), 7.61 – 7.53 (m, 1H), 3.42 (dd, *J* = 18.2, 7.5 Hz, 1H), 3.26 – 3.16 (m, 1H), 2.59 (dd, *J* = 18.2, 5.0 Hz, 1H), 2.50 – 2.43 (m, 2H), 2.29 – 2.22 (m, 1H), 2.22 – 2.14 (m, 1H), 1.98 – 1.91 (m, 1H), 1.87 – 1.76 (m, 1H), 1.75 – 1.63 (m, 1H), 1.55 – 1.40 (m, 1H). ^{13}C ($CDCl_3$, 100 MHz): δ 211.29, 202.80, 131.84, 129.87, 127.65, 126.4 (m, 1C, CF_3), 46.50, 43.07, 43.06, 41.87, 33.88, 27.91, 25.32.

***(S)*-2-(2-(naphthalen-2-yl)-2-oxoethyl)cyclohexanone (4h)**



Prepared according to the general procedure using the amino catalyst **A** (0.02 mmol, 6.5 mg, 0.2 eq), toluene (0.2 M, 500 μL), trifluoroacetic acid (0.04 mmol, 3 μL, 40 mol%), sodium acetate (0.2 mmol, 16.4 mg, 2 eq), cyclohexanone **1a** (0.4 mmol, 42 μL, 4 eq) and 2-bromoacetonaphtone (0.1 mmol, 24.9 mg, 1 eq). Time of irradiation: 14 h. Purification by flash column chromatography (gradient eluent from pure hexane to 10:1 hexane:AcOEt mixture) afforded the title compound (19.4 mg,73 % yield, 92 % ee) as a white solid.

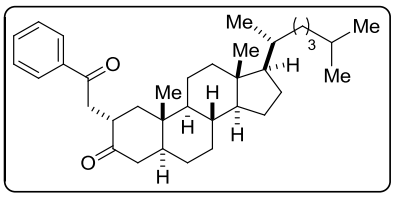
The enantiomeric excess was determined by HPLC analysis on a Daicel Chiralpak IC column, 85:15 hexane:iPrOH, flow rate 1.00 mL/min, λ = 254 nm: τ_{minor} = 26 min, τ_{major} = 29 min.

$[\alpha]^{28}_D$ = -19 ± 1 (c = 0.5, $CHCl_3$, 92 % ee).

HRMS: calculated for $C_{18}H_{18}O_2$ (M+Na): 289.1199, found: 289.1199.

^{1}H (CDCl$_3$, 400 MHz): δ 8.55 (s, 1H), 8.07 (dd, *J* = 8.6, 1.8 Hz, 1H), 8.01 – 7.97 (m, 1H), 7.94 – 7.87 (m, 2H), 7.68 – 7.54 (m, 2H), 3.78 (dd, *J* = 17.5, 6.5 Hz, 1H), 3.26 (dq, *J* = 11.8, 5.8 Hz, 1H), 2.85 (dd, *J* = 17.6, 5.9 Hz, 1H), 2.54 – 2.44 (m, 2H), 2.35 – 2.23 (m, 1H), 2.18 (m, 1H), 2.00 – 1.90 (m, 1H), 1.90 – 1.65 (m, 2H), 1.65 – 1.45 (m, 1H). **^{13}C (CDCl$_3$, 100 MHz)**: δ 211.66, 198.60, 135.60, 134.42, 132.54, 129.77, 129.58, 128.37, 128.36, 127.75, 126.71, 123.89, 46.60, 42.03, 38.40, 34.41, 28.03, 25.41.

***(S)*-2-(2-oxo-2-phenylethyl)cyclohexanone (6)**



Prepared according to the general procedure using 1 equivalent of the ketone, the amino catalyst **A** (0.02 mmol, 6.5 mg, 0.2 eq), toluene (0.2 M, 500 μL), trifluoroacetic acid (0.04 mmol, 3 μL, 40 mol%), sodium acetate (0.2 mmol, 16.4 mg, 2 eq), 5α-cholestan-3-one **5** (0.1 mmol, 38.7 mg, 1 eq) and 2-bromoacetophenone (0.1 mmol, 20 mg, 1 eq). Time of irradiation: 14 h. Purification by flash column chromatography (gradient eluent from pure hexane to 20:1 hexane:AcOEt mixture) afforded the title compound (23 mg, 47 % yield, >20:1 r.r, >20:1 d.r) as a white solid.
HRMS: calculated for $C_{35}H_{52}O_2$ (M+Na): 527.3881, found: 527.3860.

The assignment of the relative stereochemistry shown in the drawing was performed by selective 1D-NOESY by correlation between the substituted *alpha* proton and the methyl group in position 4 [when CO-C**H**(CH_2Ar) is irradiated CO-CH(CH_2Ar)-CH_2-C(**Me**) is correlated].
^{1}H (CDCl$_3$, 400 MHz): δ 8.00 (dd, *J* = 8.4, 1.4 Hz, 2H), 7.68 – 7.53 (m, 1H), 7.53 – 7.43 (m, 2H), 3.61 (dd, *J* = 17.7, 6.3 Hz, 1H), 3.33 – 3.21 (m, 1H), 2.70 (dd, *J* = 17.7, 5.5 Hz, 1H), 2.54 – 2.40 (m, 1H), 2.21 – 2.11 (m, 2H), 2.04 – 1.94 (m, 1H), 1.84 (ddd, *J* = 9.6, 5.7, 3.7 Hz, 1H), 1.78 – 1.67 (m, 1H), 1.64 – 0.96 (m, 28H), 0.96 – 0.82 (m, 10H), 0.82 – 0.71 (m, 1H), 0.70 (s, 3H). **^{13}C (CDCl$_3$, 100 MHz)**: δ 211.33, 198.63, 137.12, 132.96, 128.51, 128.06, 56.28, 56.26, 53.93, 48.12, 46.39, 44.66, 42.62, 42.54, 39.89, 39.51, 38.43, 36.67, 36.15, 35.77, 35.24, 31.77, 29.71, 28.81, 28.23, 28.01, 24.22, 23.82, 22.82, 22.56, 21.59, 18.67, 12.42, 12.09.

C. References

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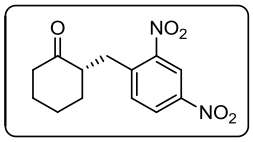
D. NMR spectra



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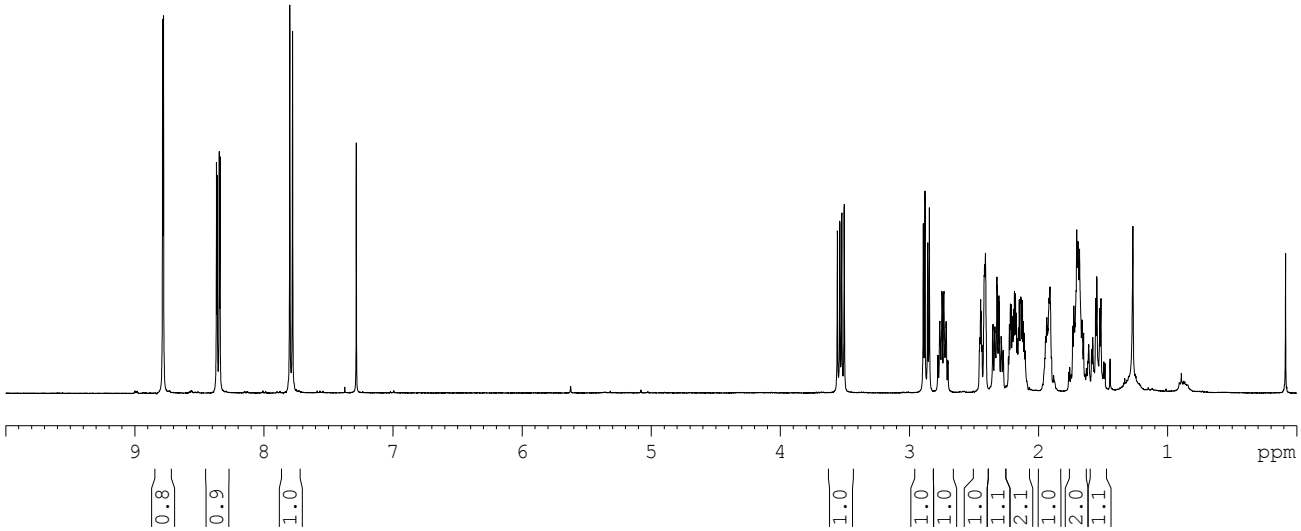

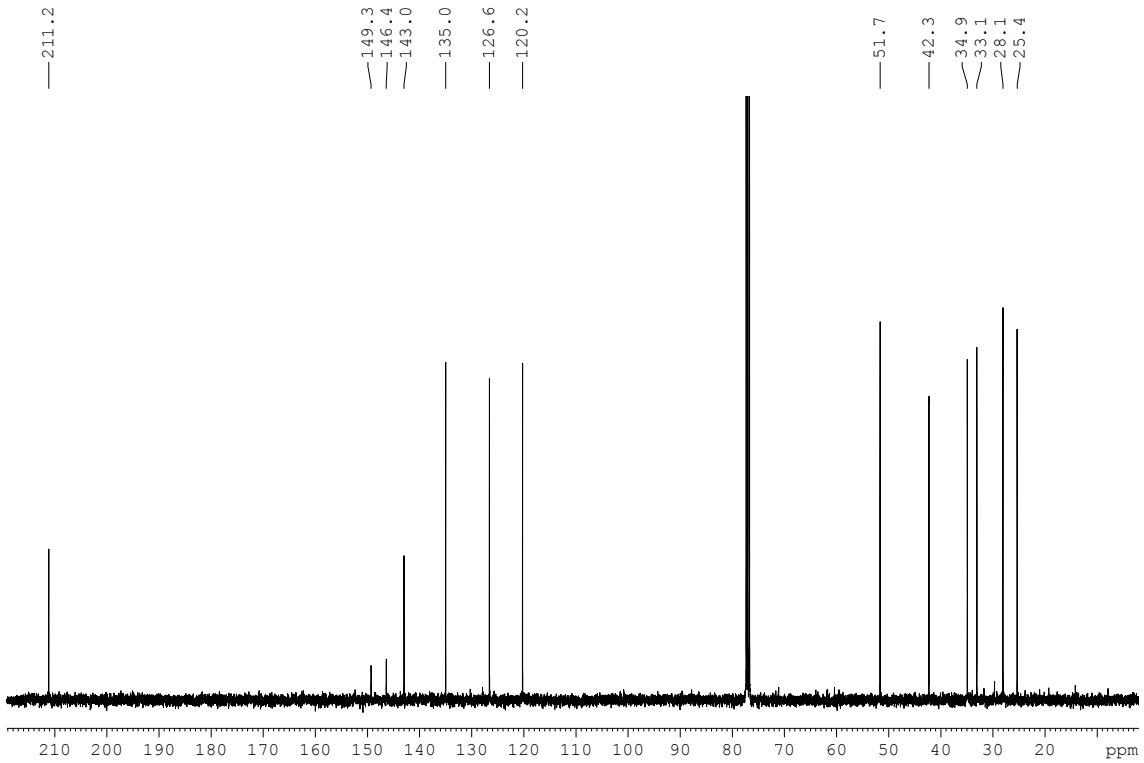

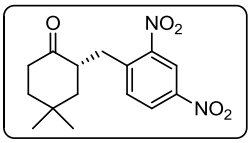
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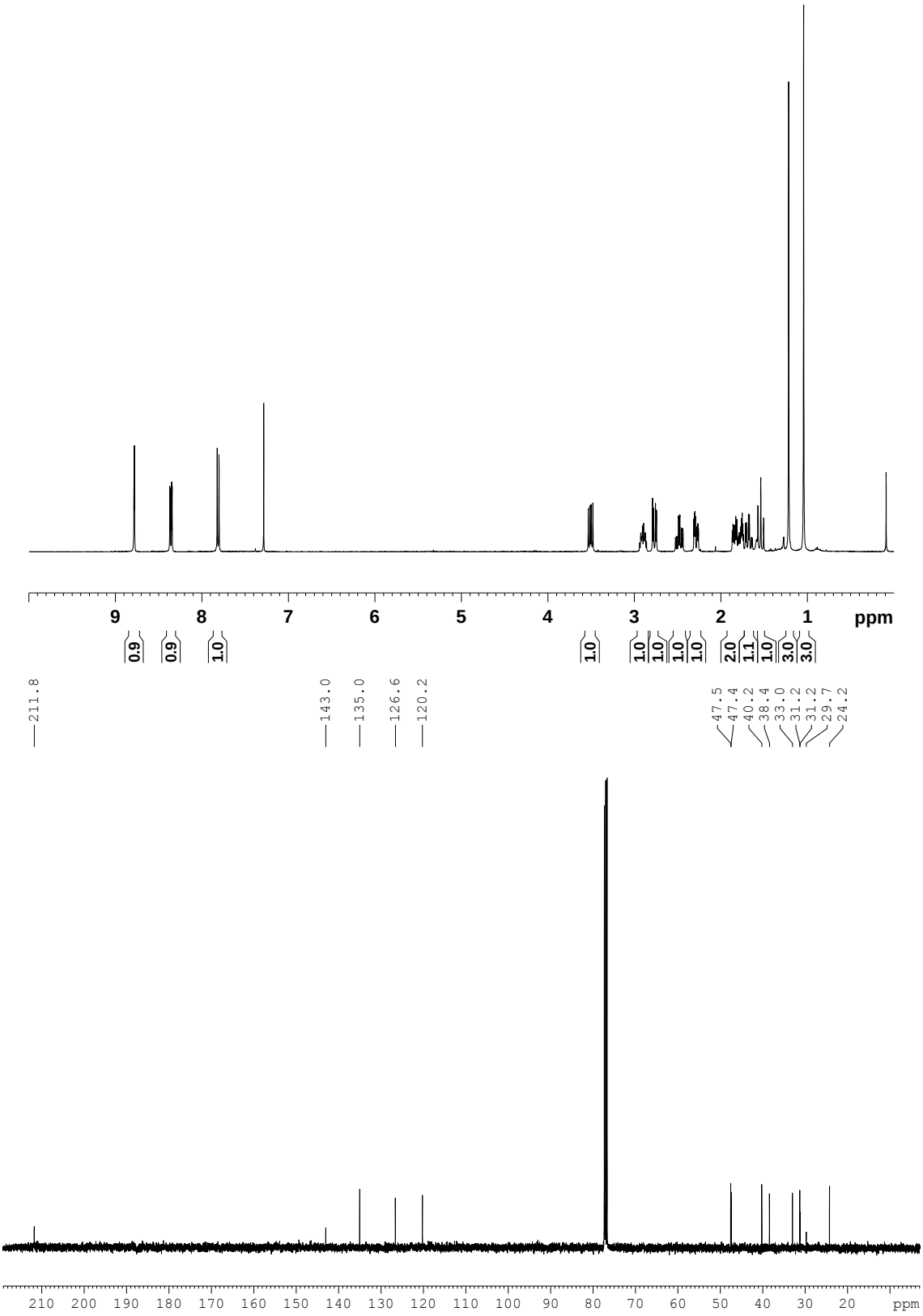
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126.6
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47.5
47.4
40.2
38.4
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29.7
24.2
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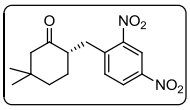
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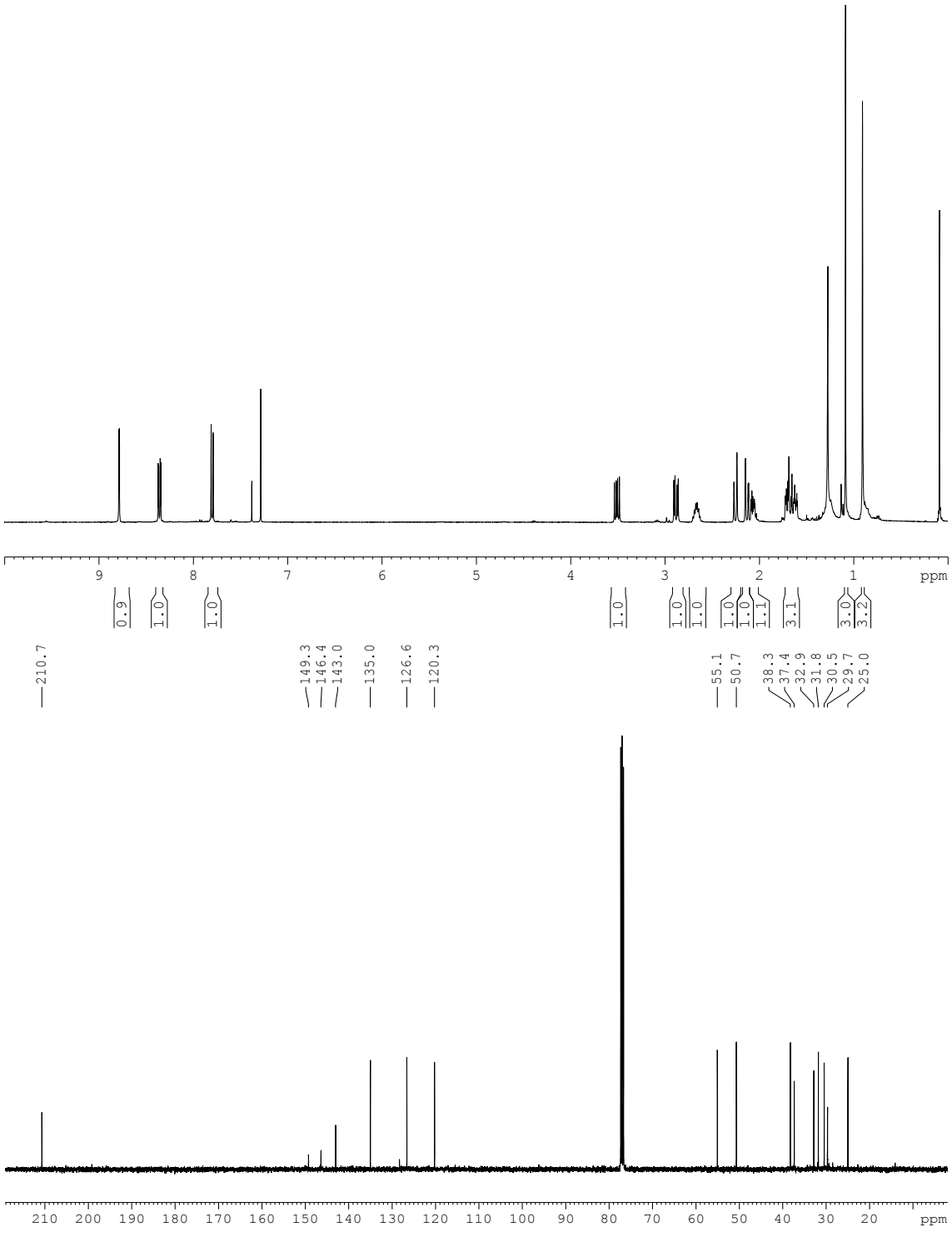
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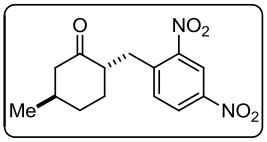
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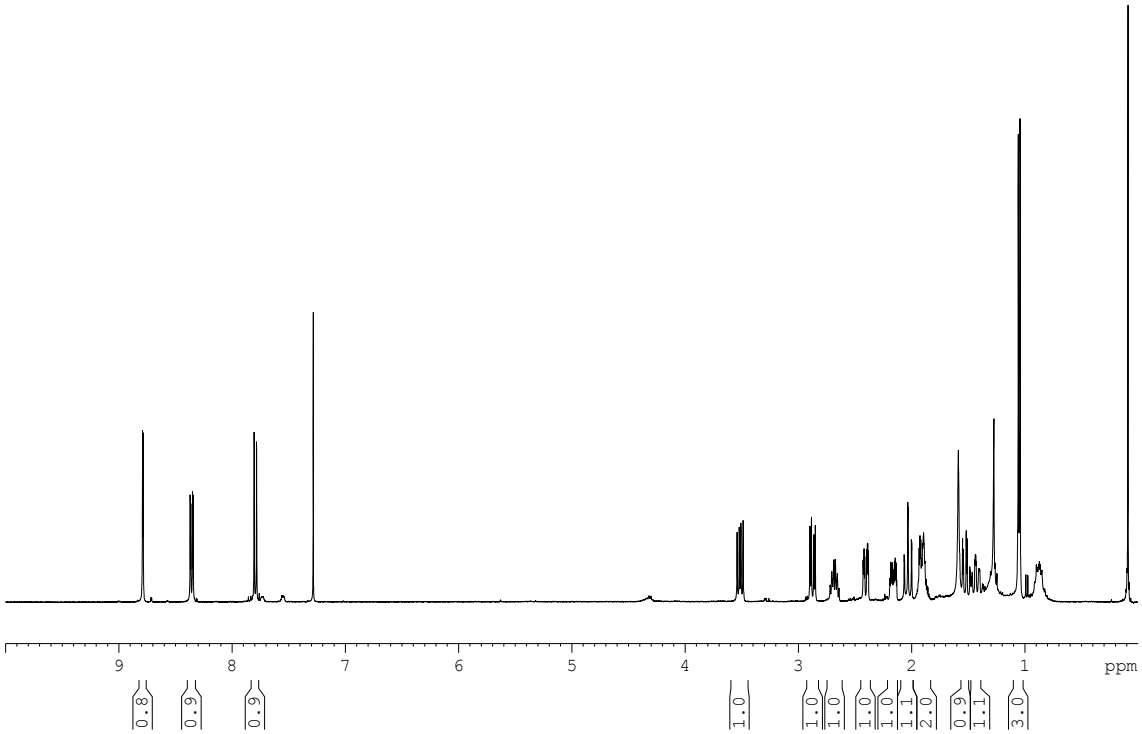
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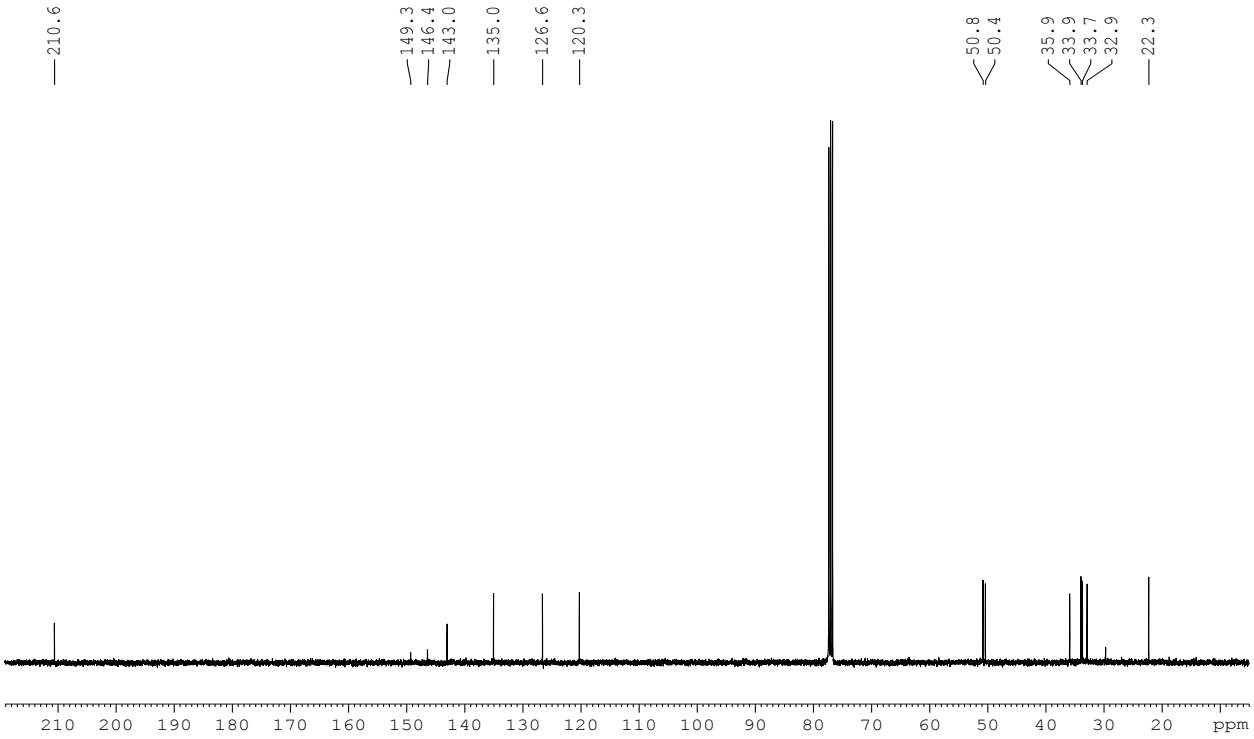
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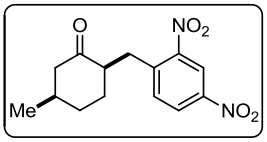
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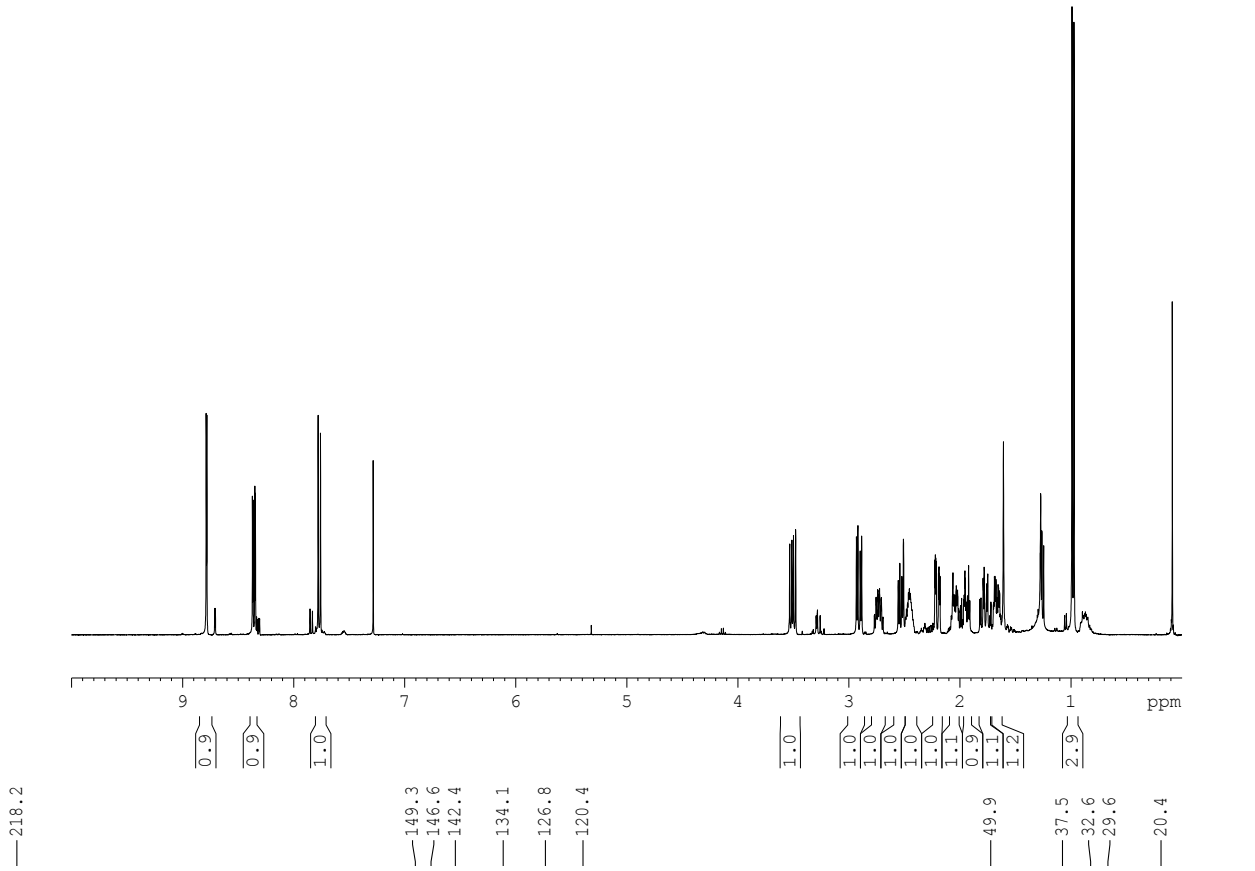
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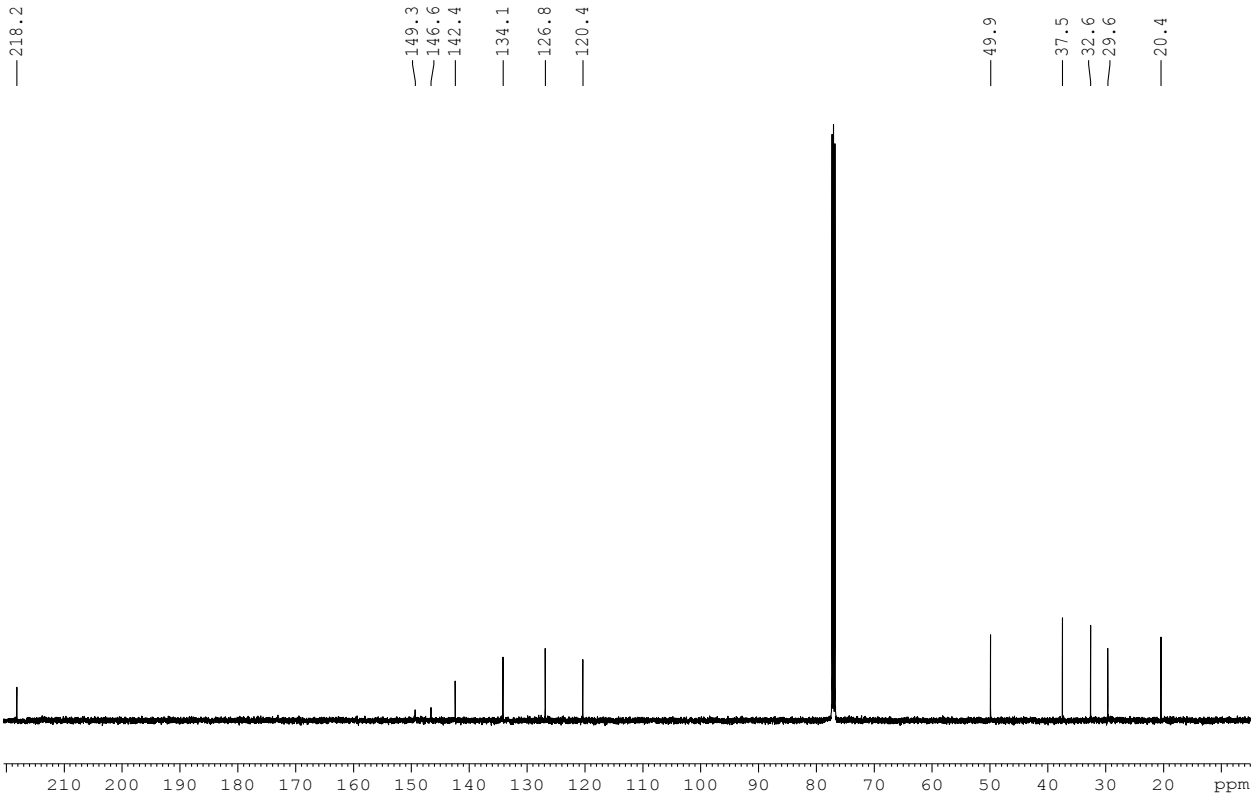
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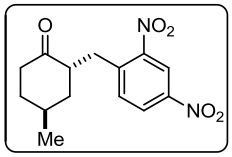
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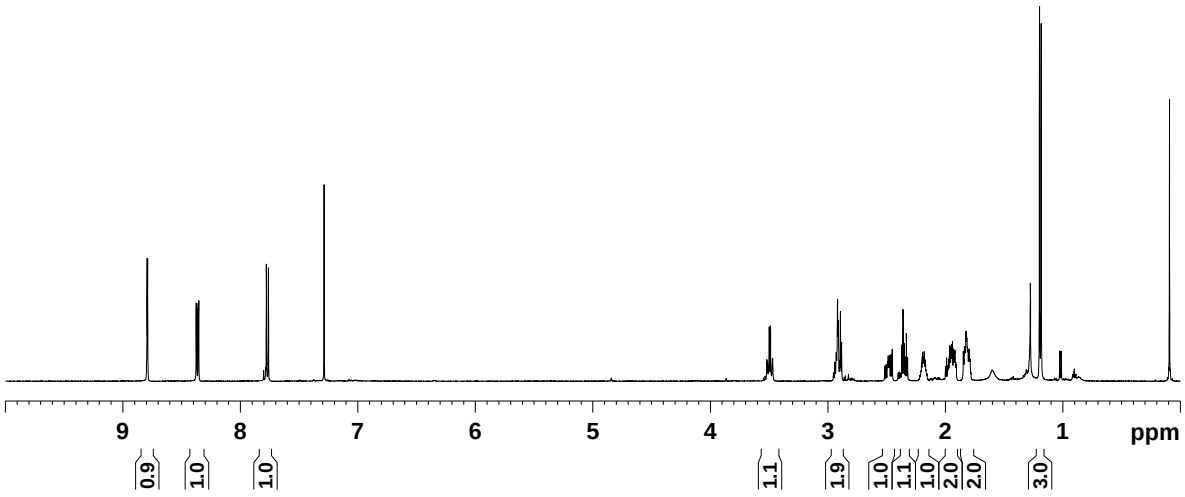
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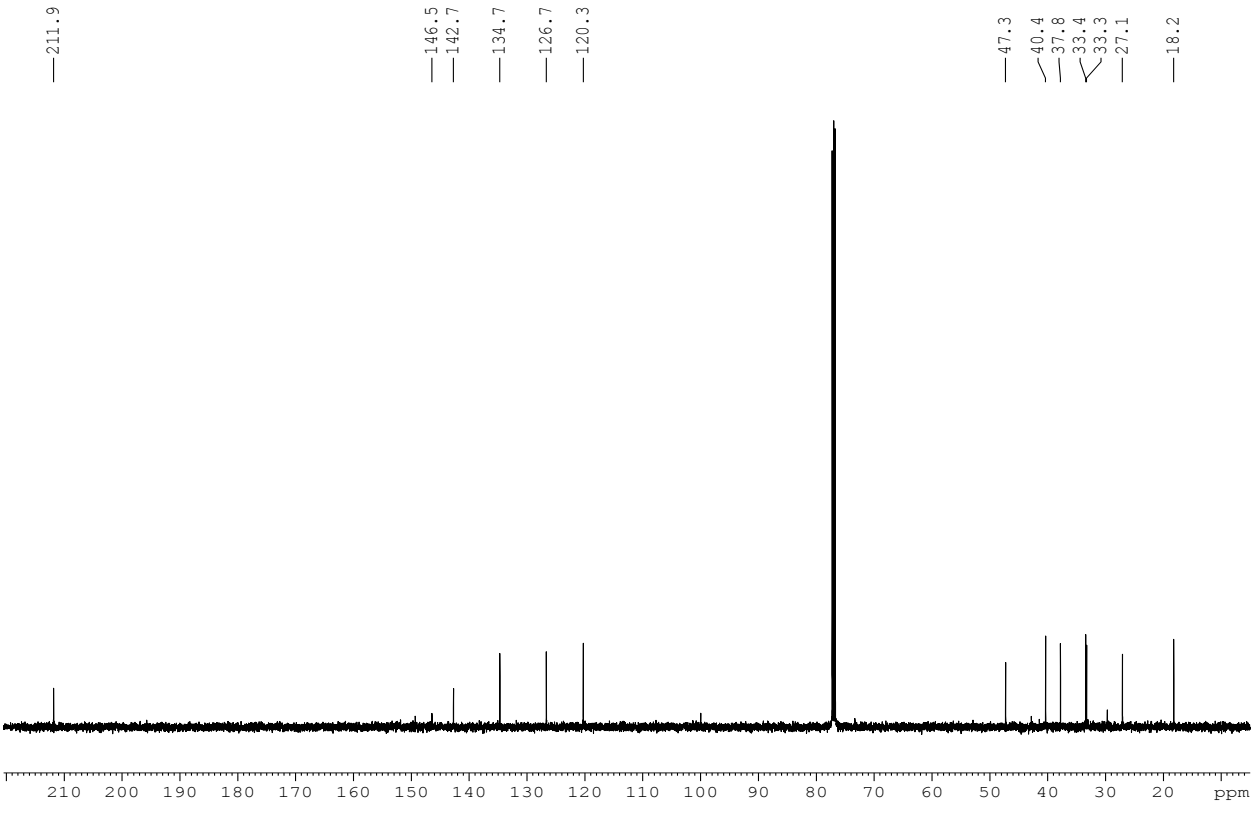
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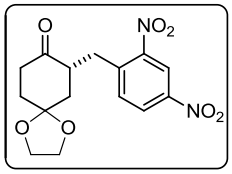
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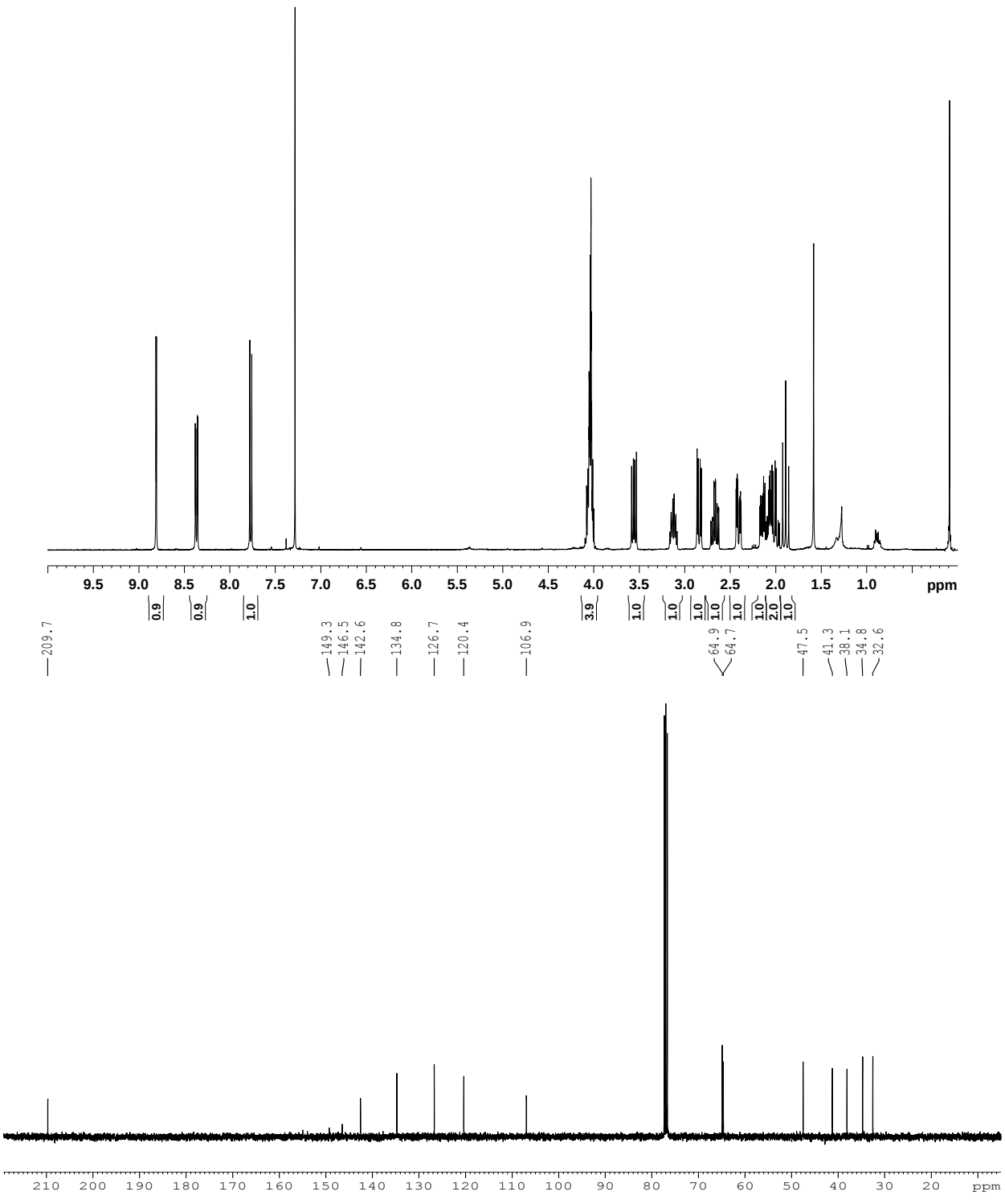
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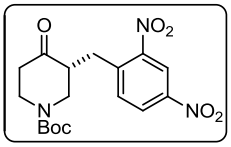
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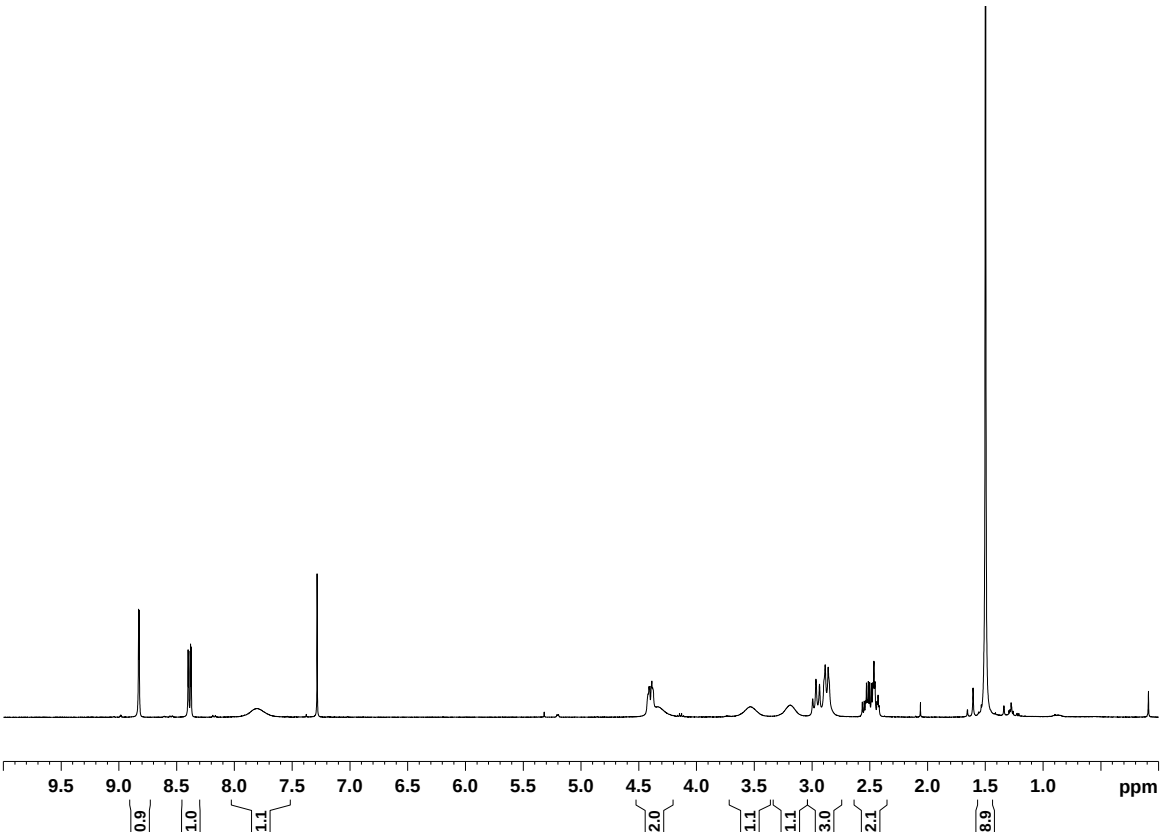
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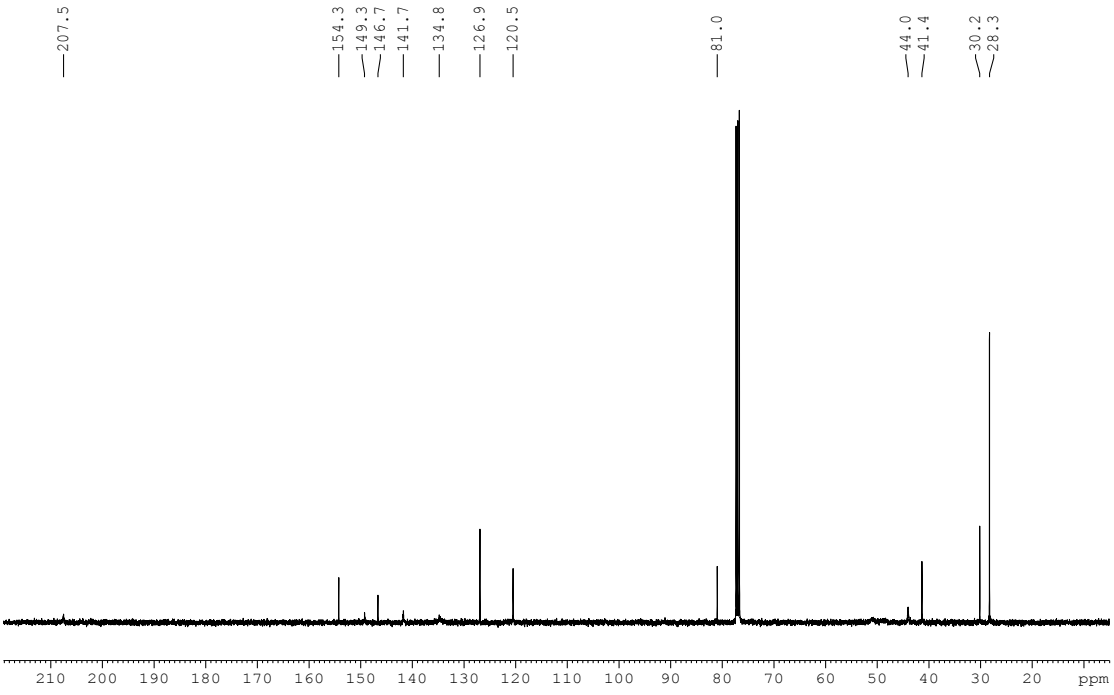
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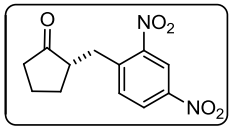
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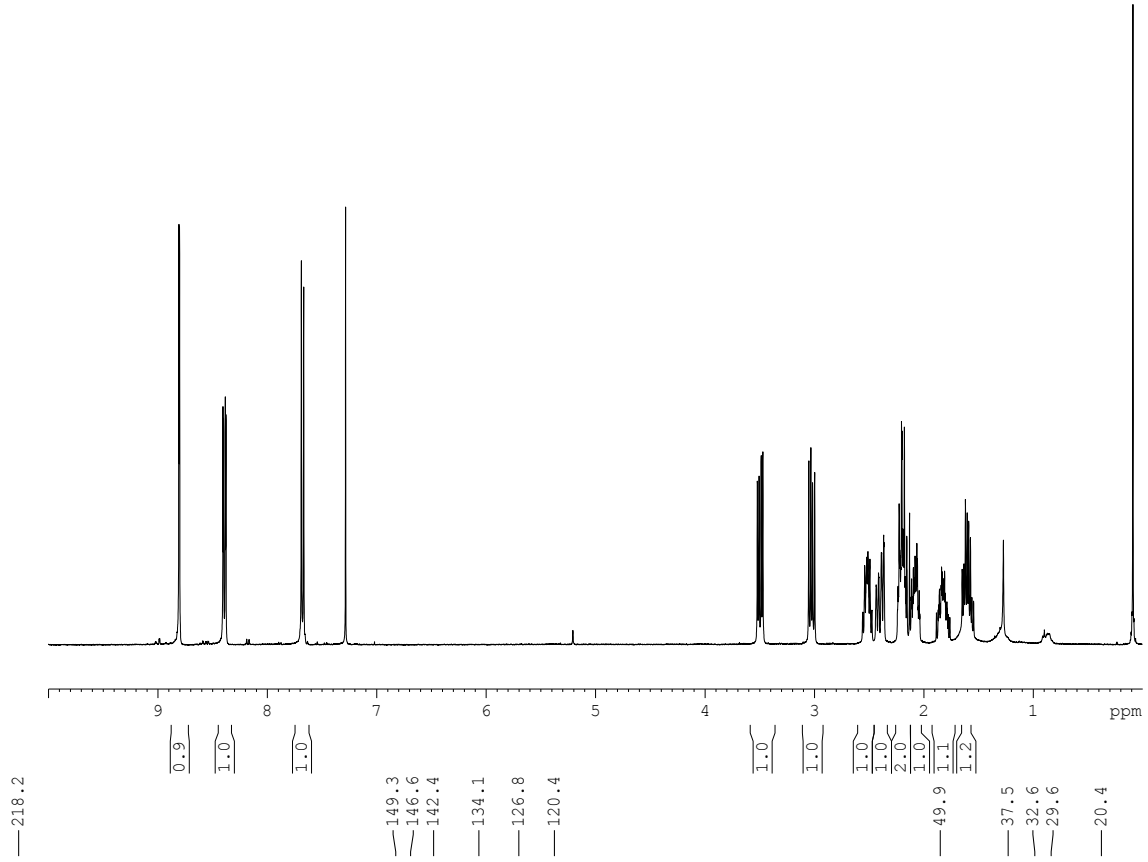
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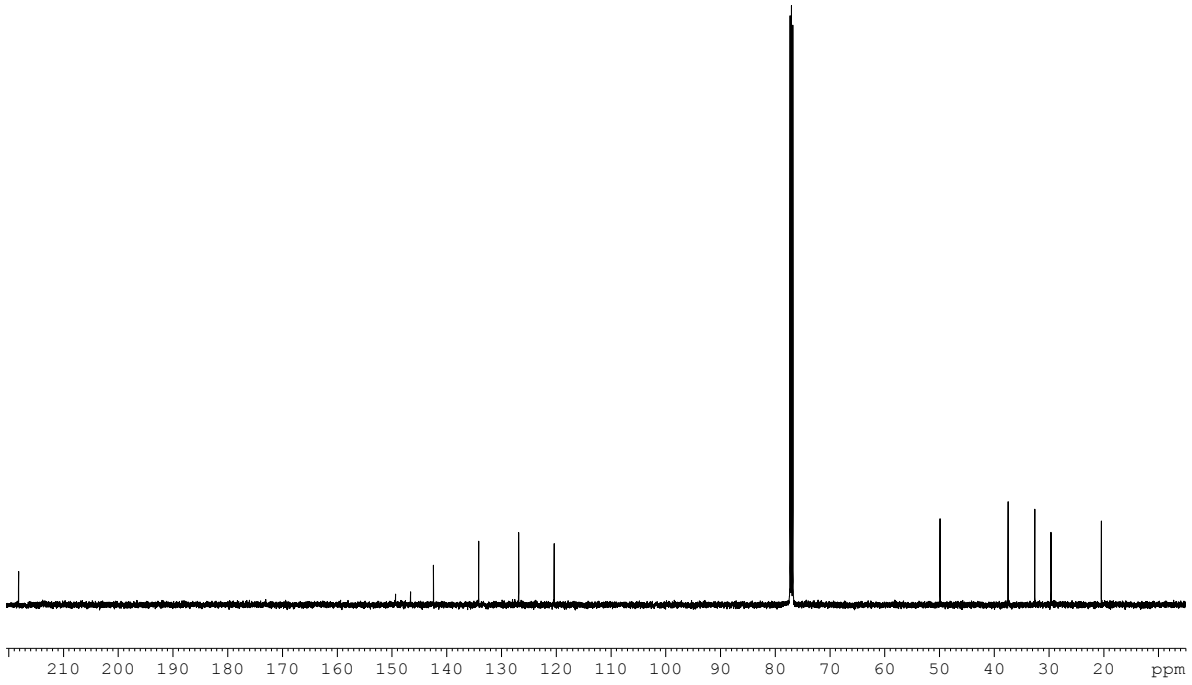
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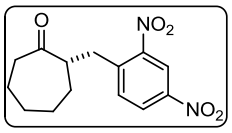
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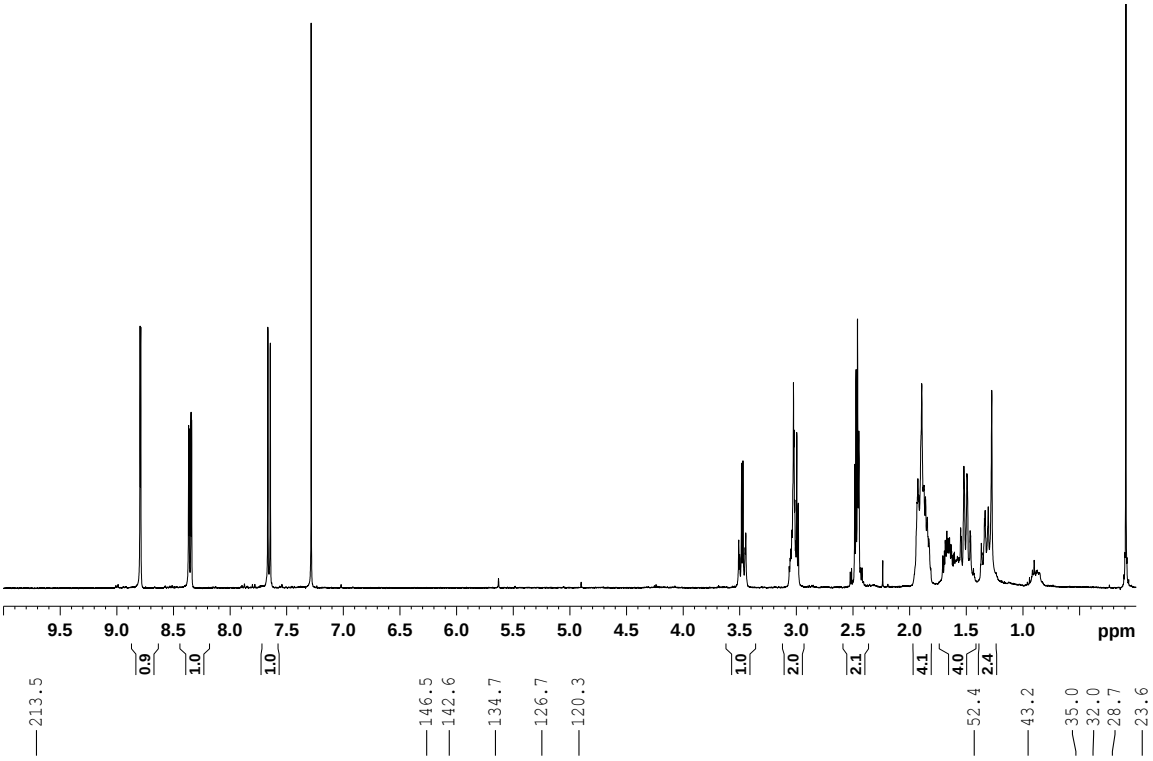
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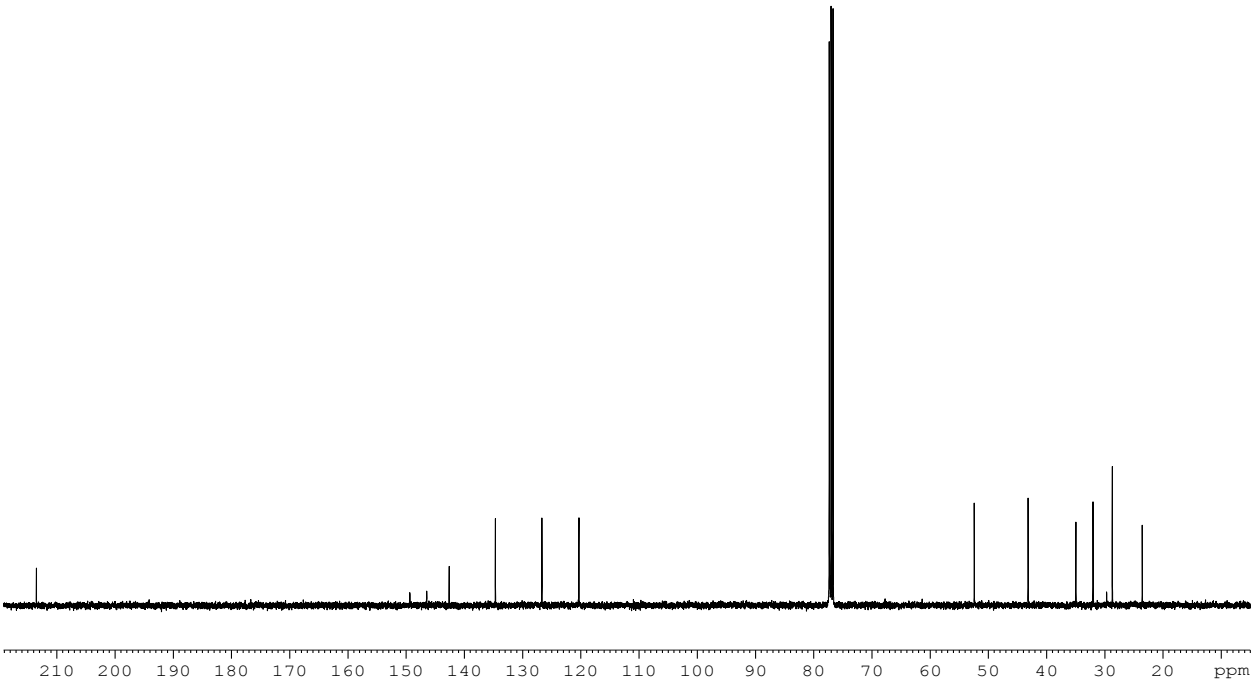
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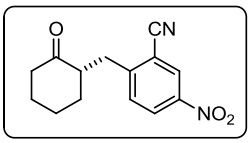
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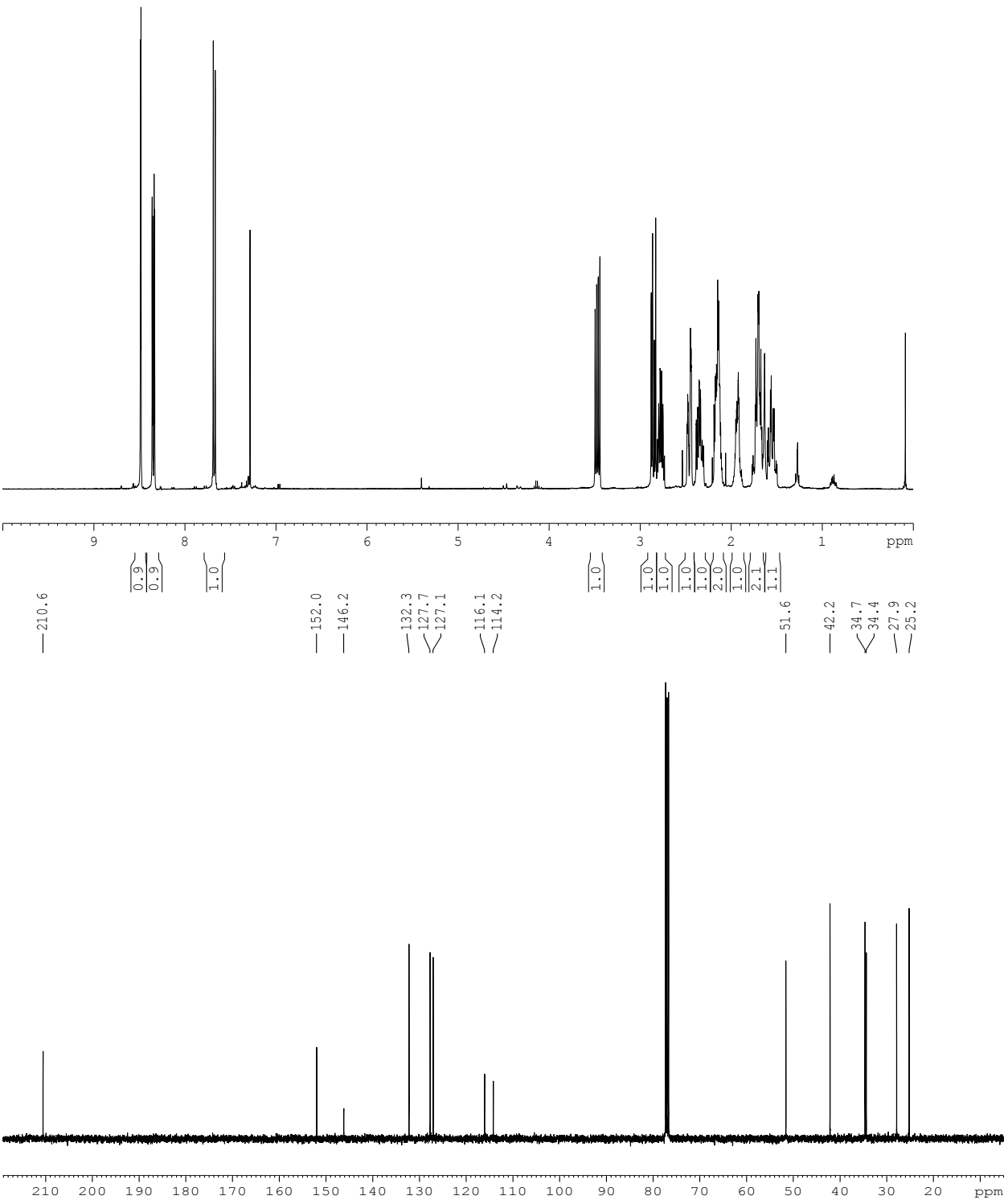
CN
NO2

3k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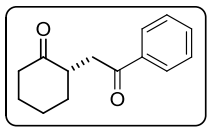

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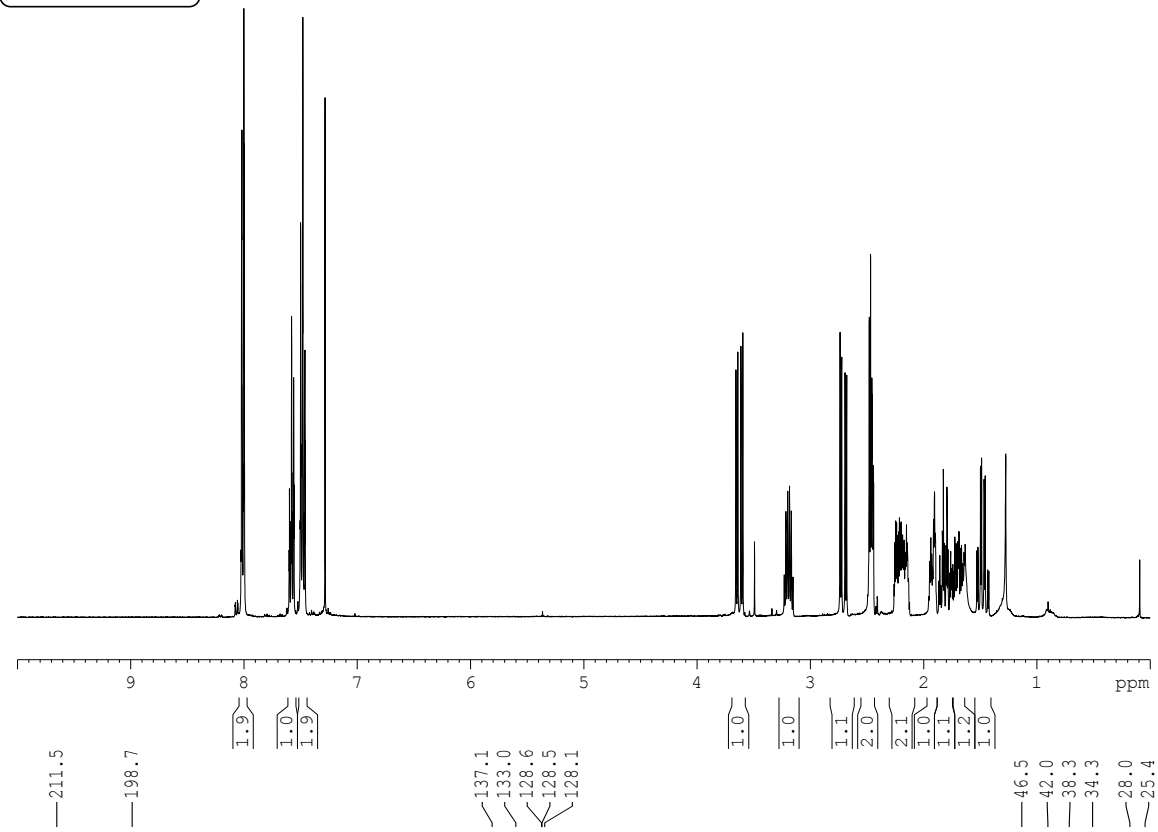
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1.0
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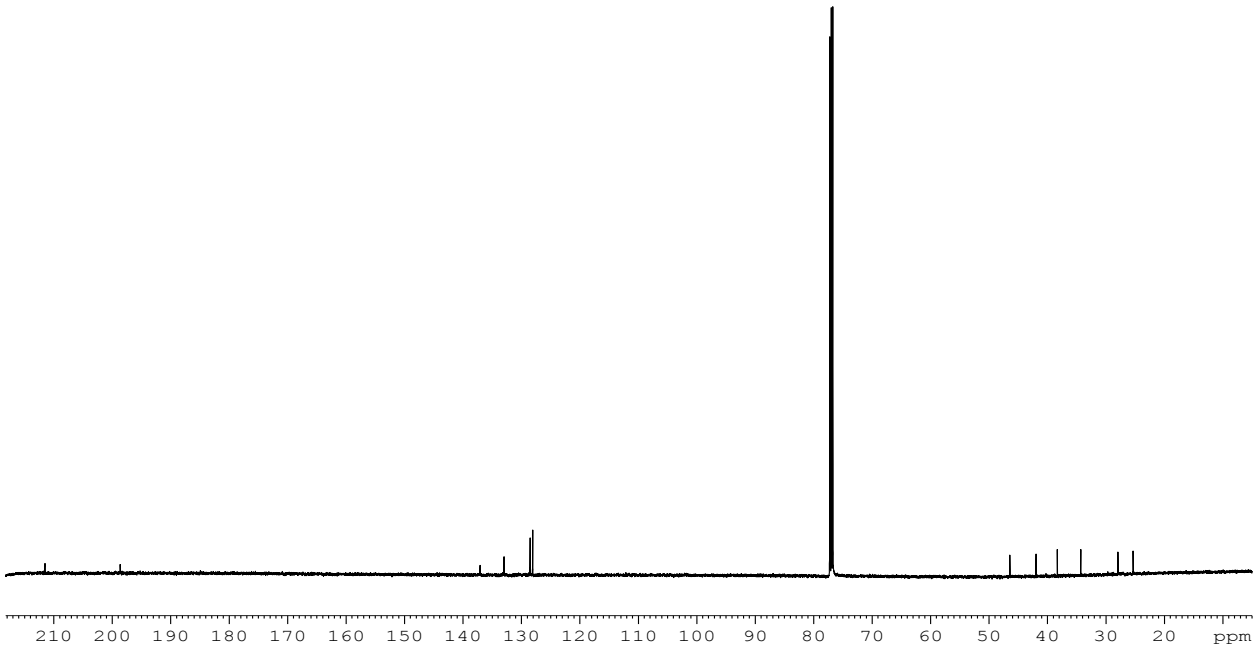
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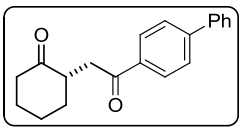
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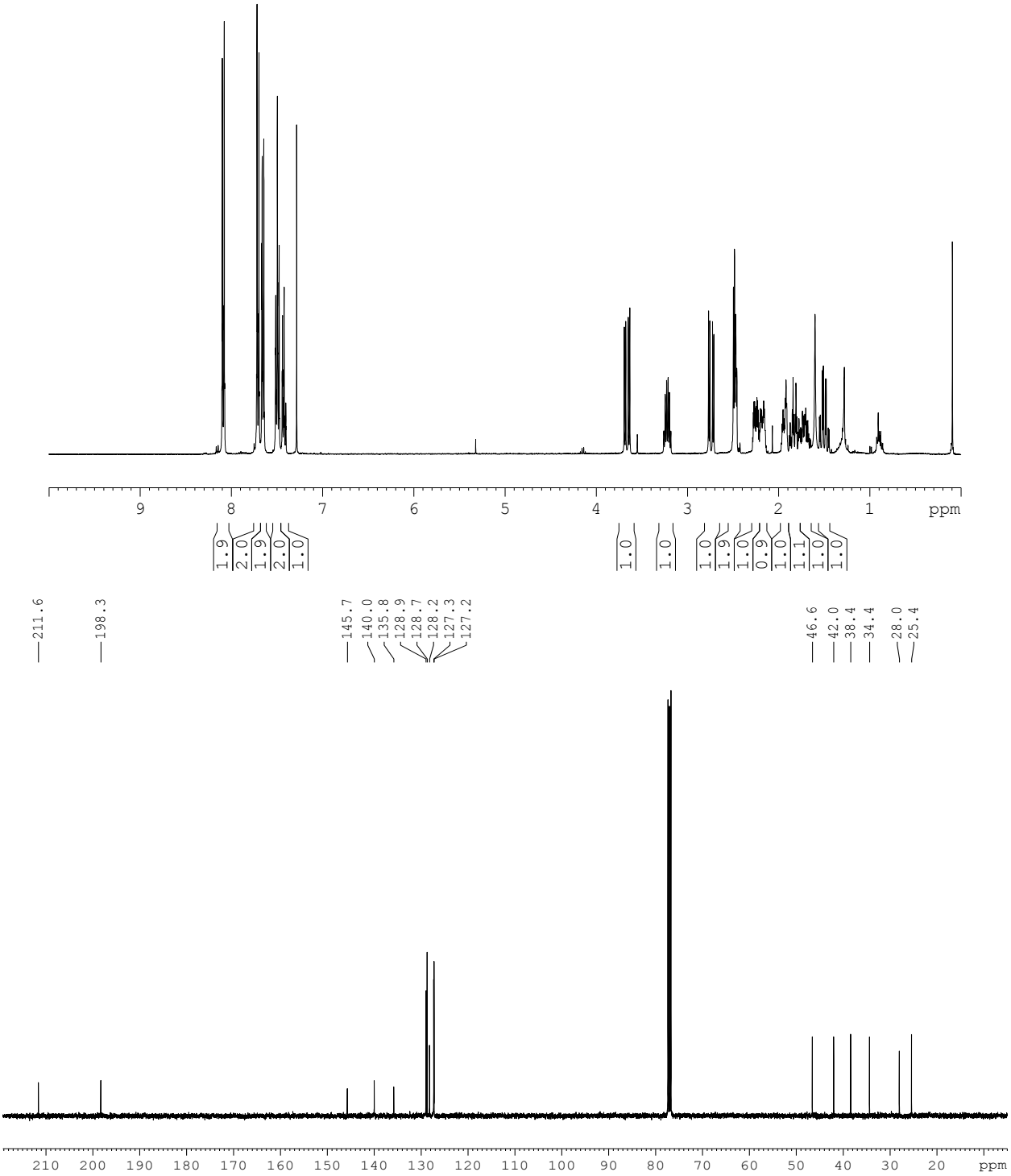
4b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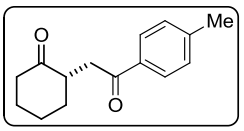
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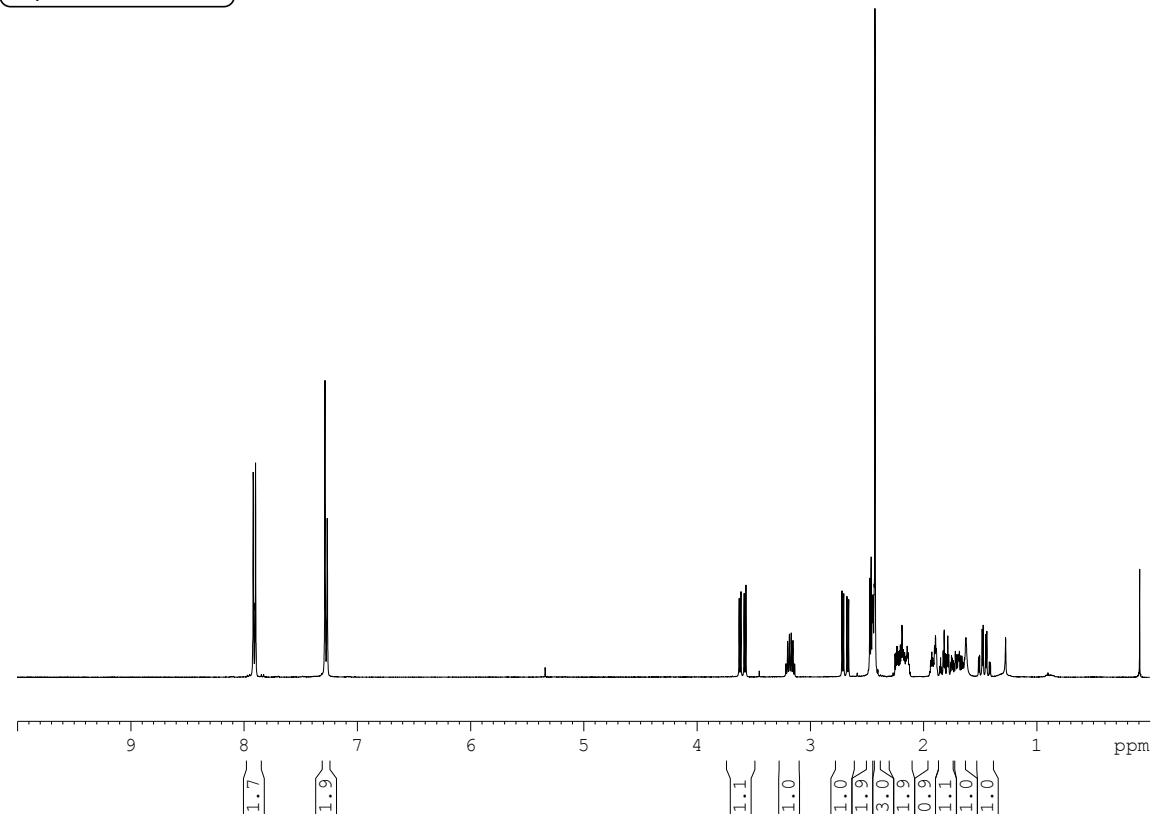
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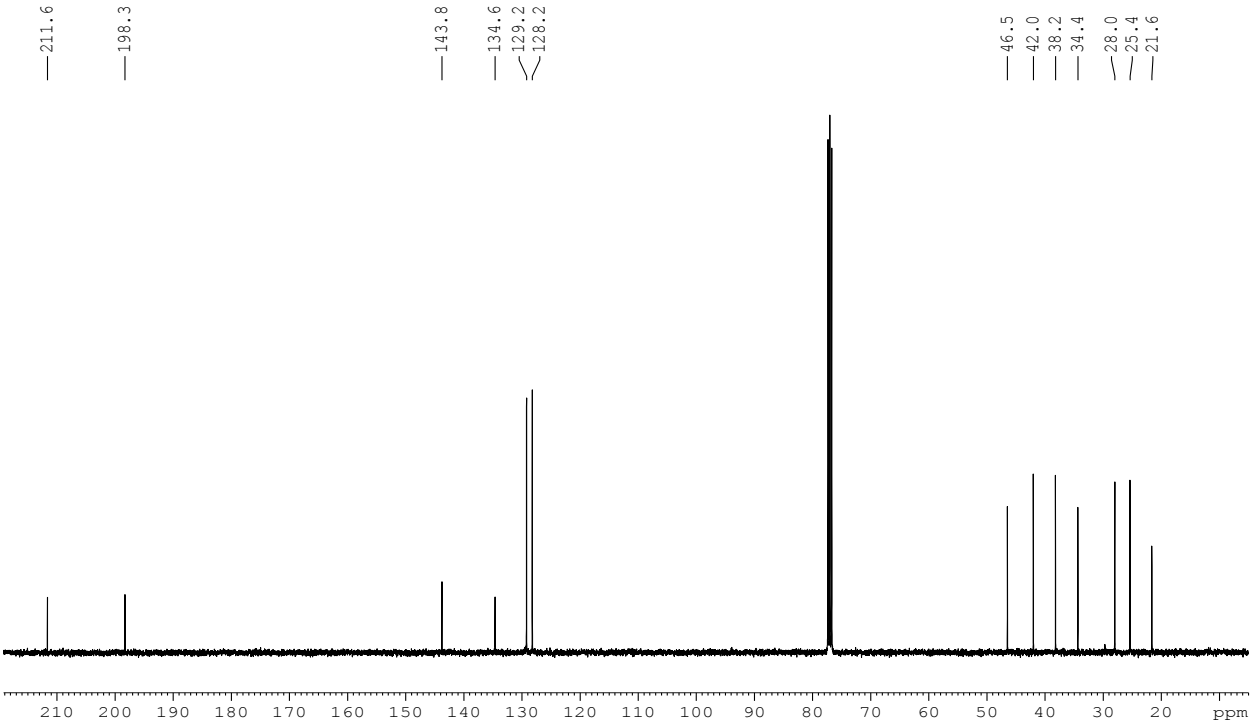
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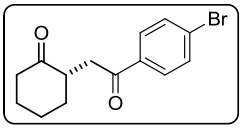
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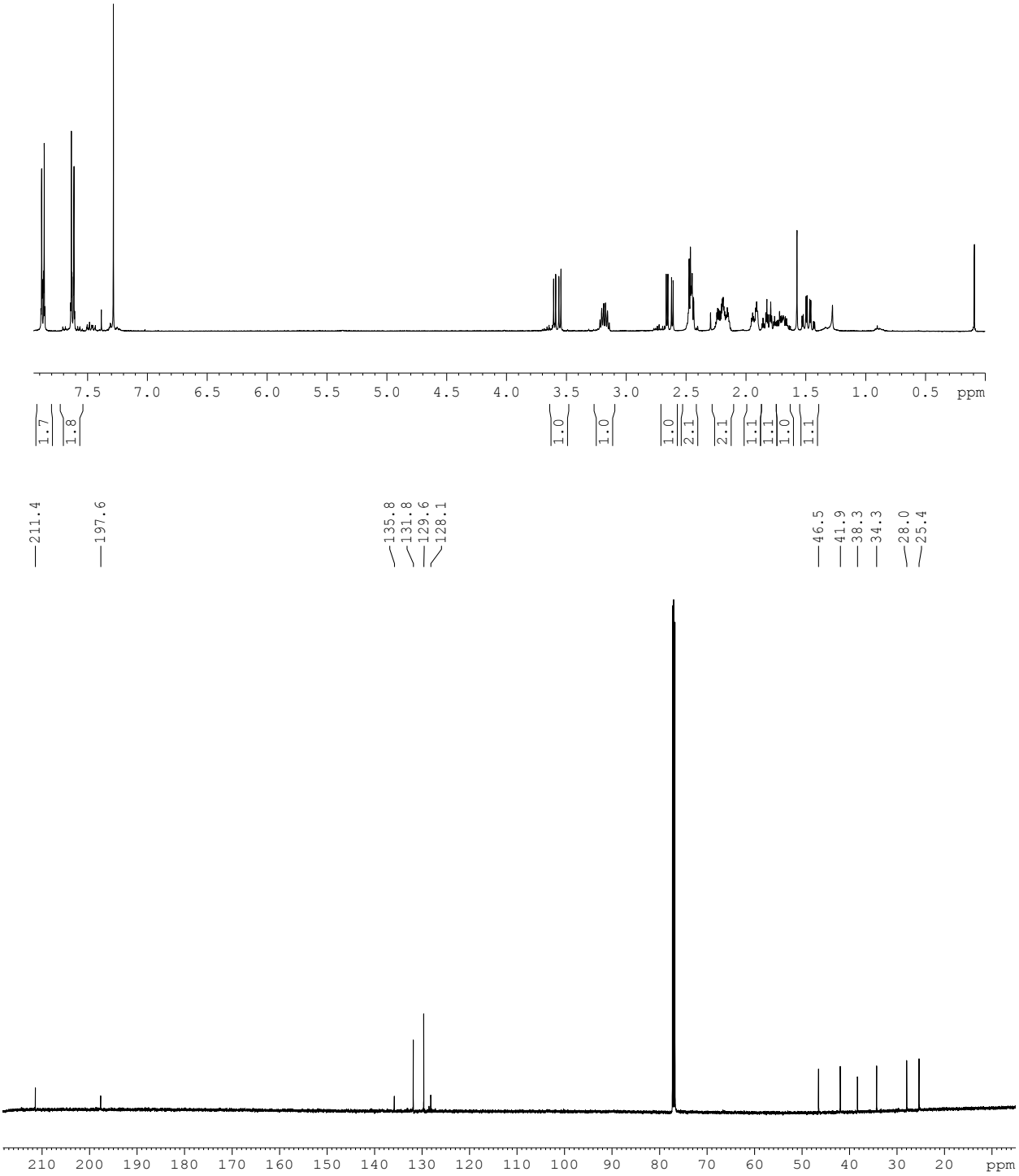
4d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1.8
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1.0
2.1
2.1
1.1
1.1
1.0
1.1
211.4
197.6
135.8
131.8
129.6
128.1
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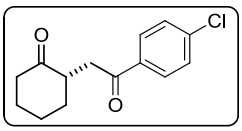
41.9
38.3
34.3
28.0
25.4
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm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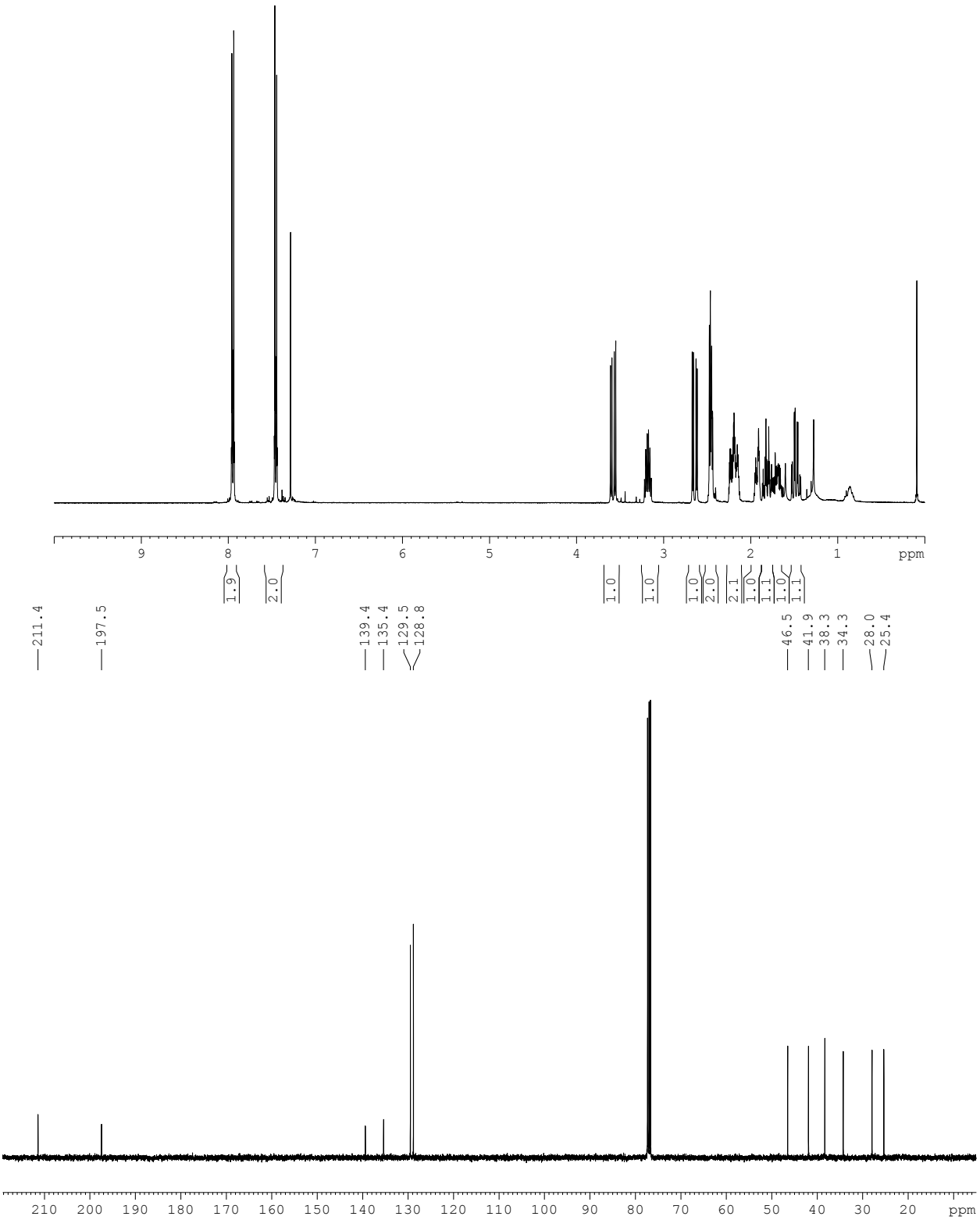
O

4e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28.0
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40
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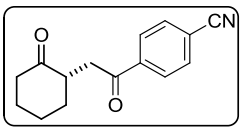
ppm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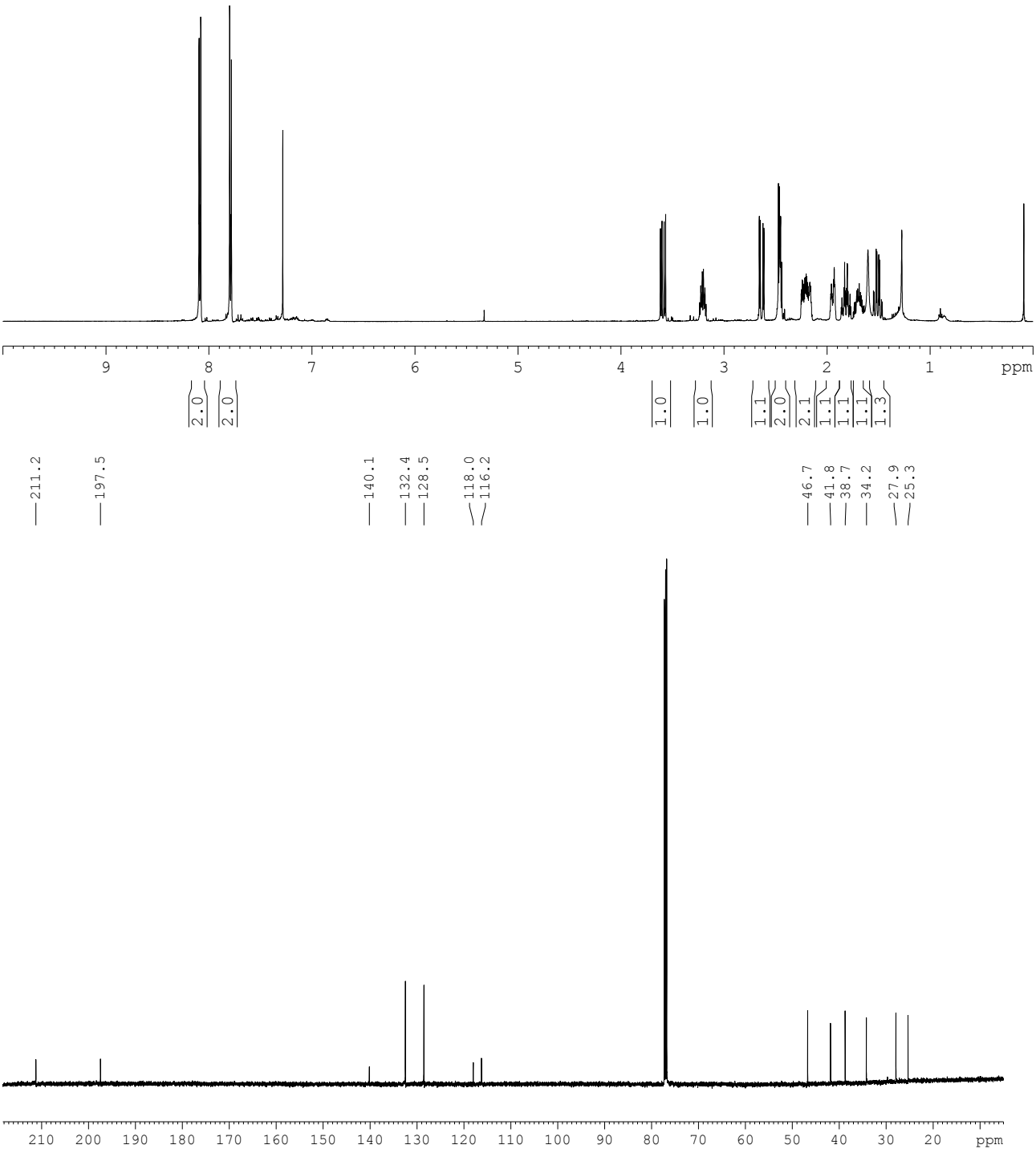
O

4f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34.2
27.9
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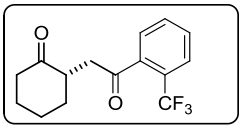
20
ppm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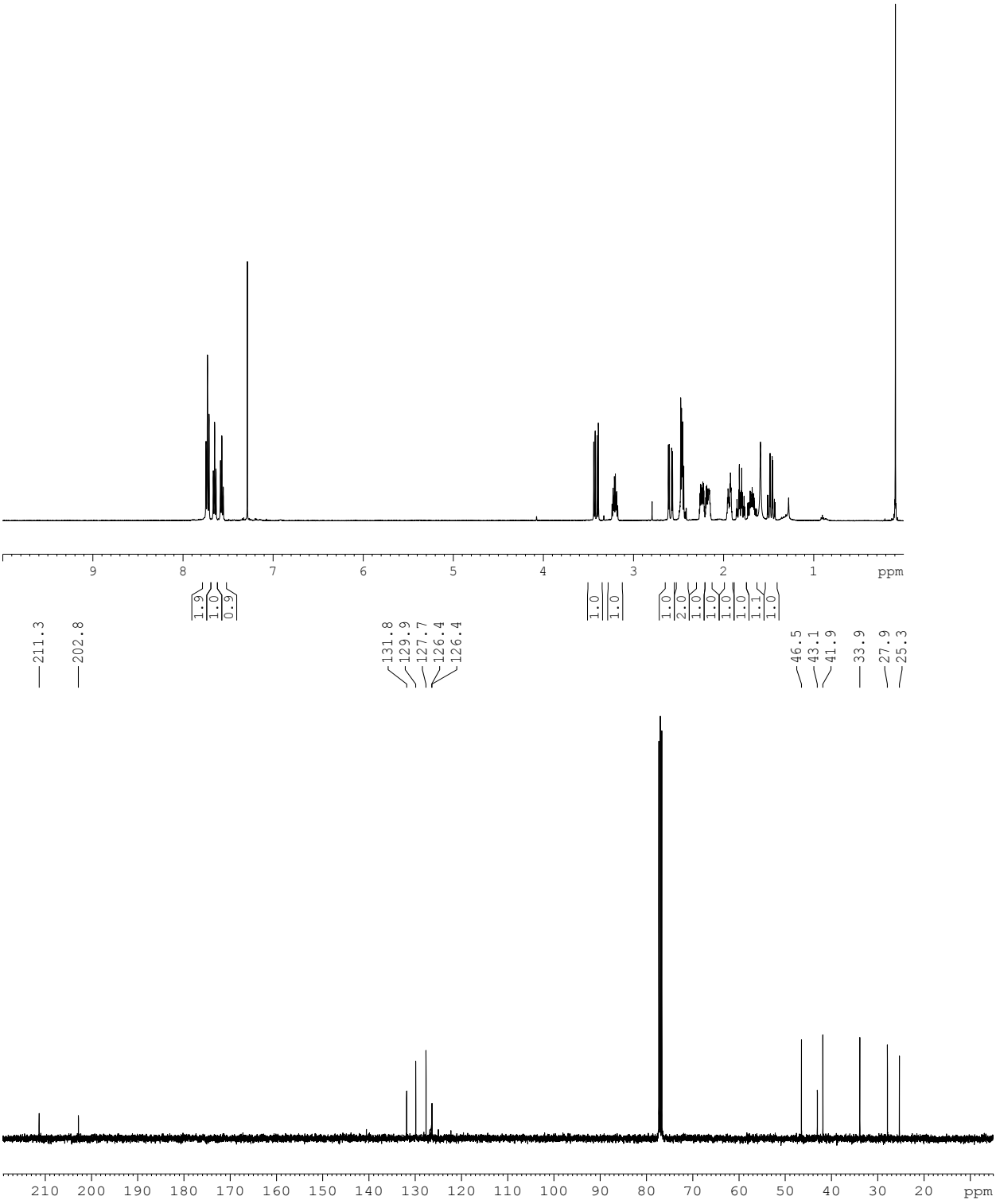
CF3

4g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4
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ppm
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1.1
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202.8
131.8
129.9
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25.3
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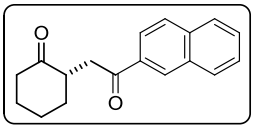

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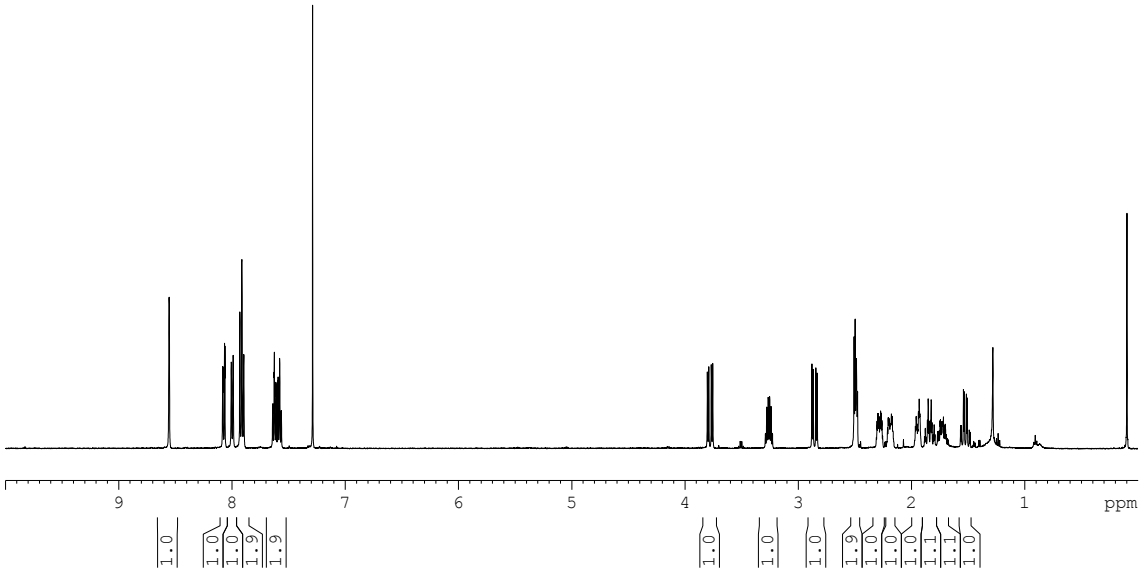
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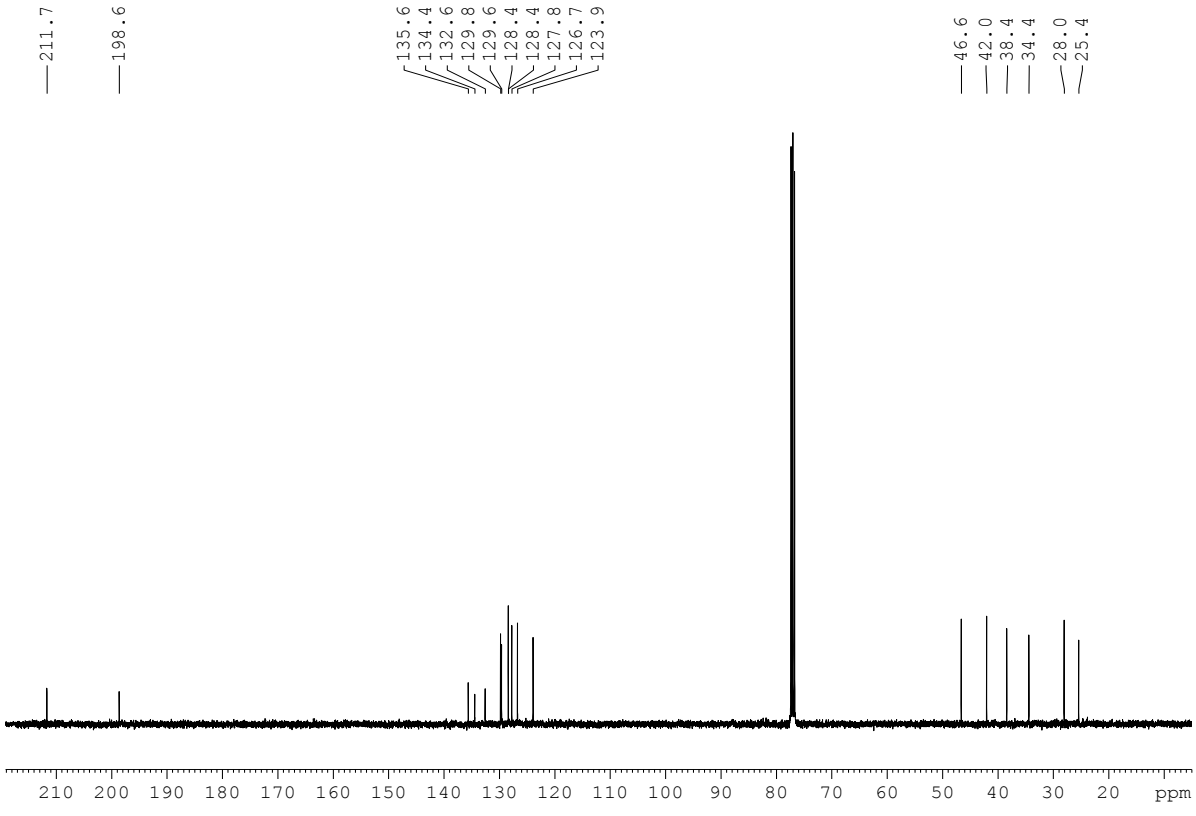
211.7
198.6
135.6
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132.6
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128.4
128.4
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42.0
38.4
34.4
28.0
25.4
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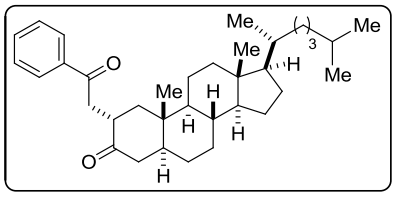
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Me
H
O
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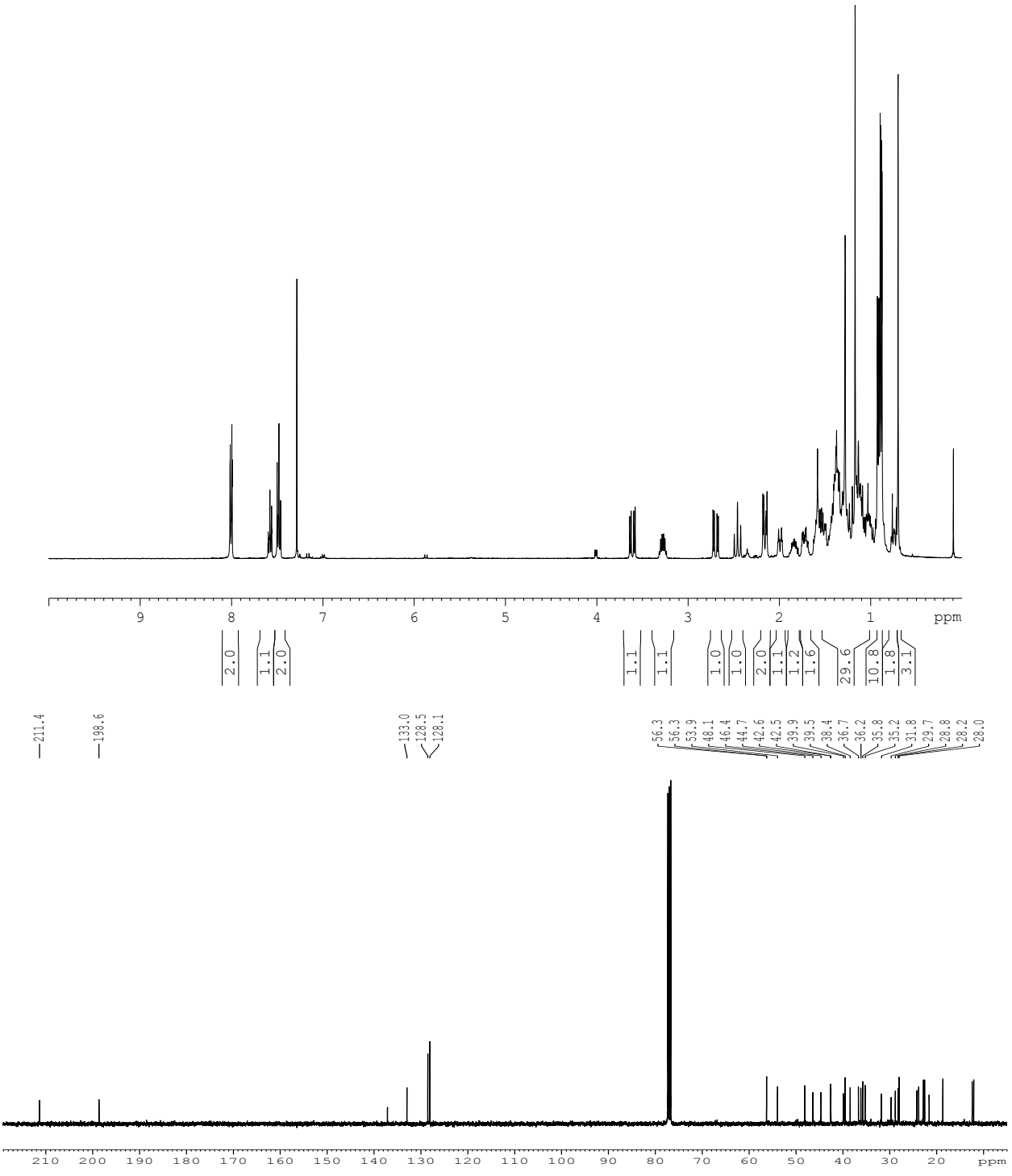
H
H
O
H

6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ppm
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1.1
1.1
1.0
1.0
2.0
1.1
1.2
1.6
29.6
10.8
1.8
3.1
211.4
198.6
133.0
128.5
128.1
56.3
56.3
53.9
48.1
46.4
44.7
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42.5
39.9
39.5
38.4
36.7
36.2
35.8
35.2
31.8
29.7
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28.0
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200
190
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60
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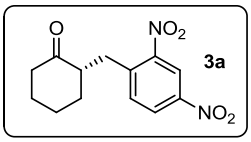
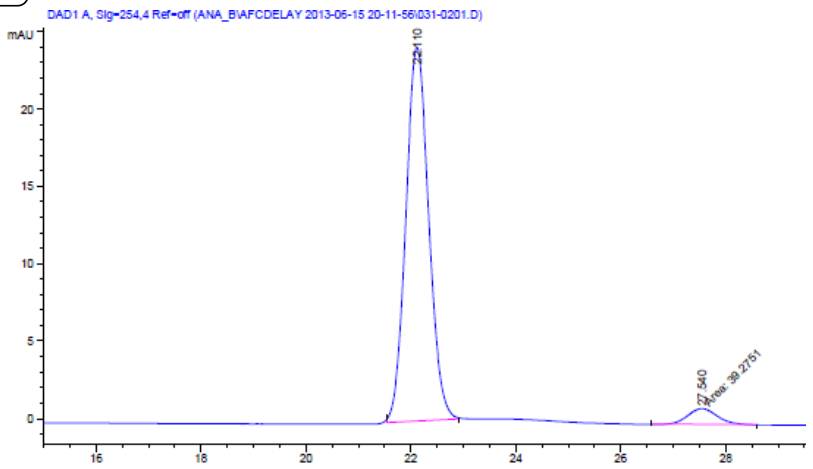
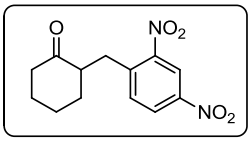
30
20
ppm

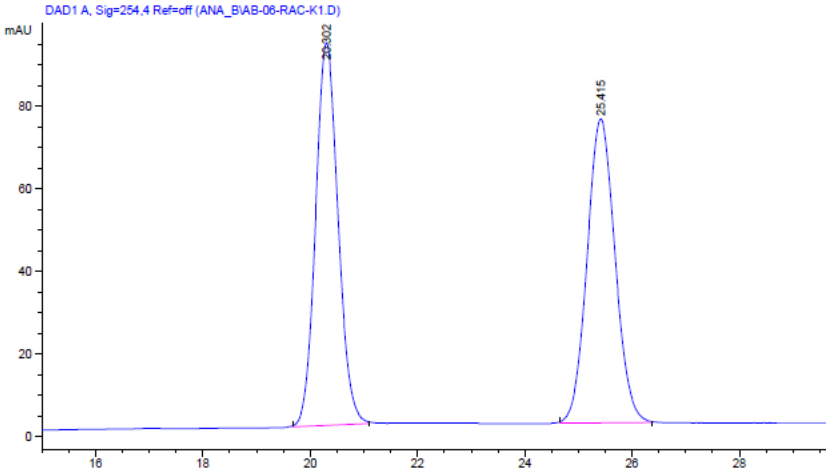
E. HPLC Traces



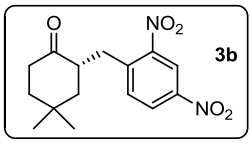


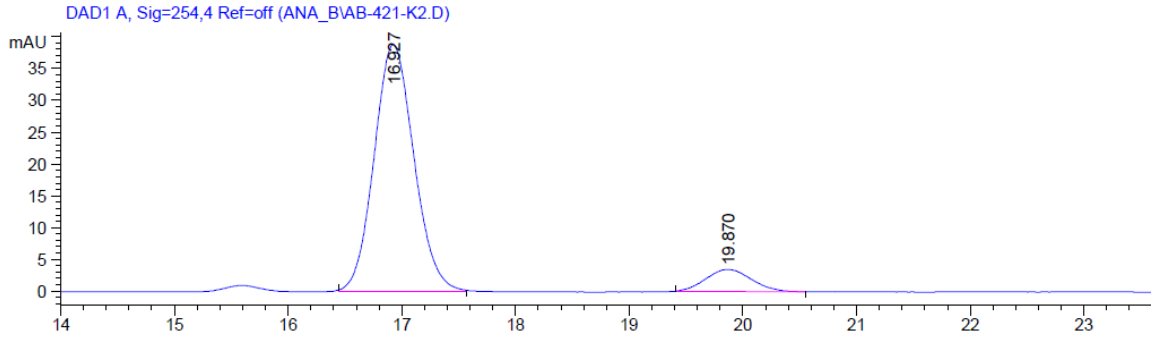
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.110	BB	0.4663	729.57709	24.16118	94.8917
2	27.540	MM	0.6423	39.27505	1.01910	5.1083



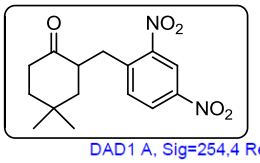


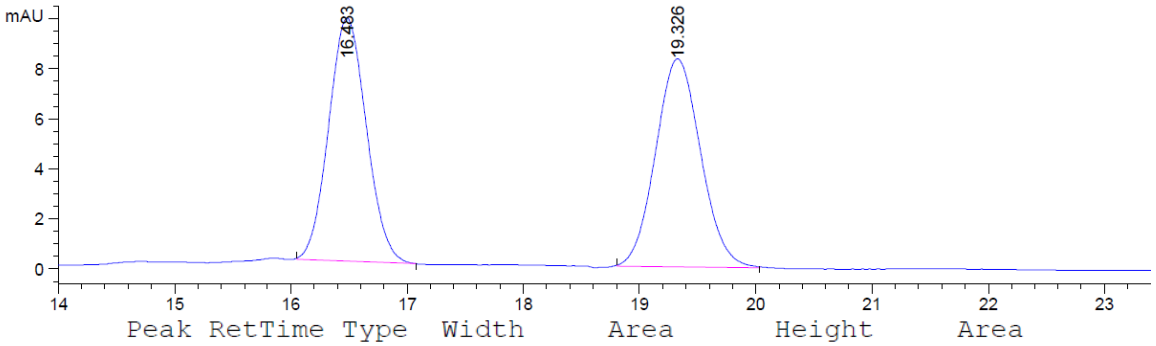
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.302	BB	0.4512	2690.26758	92.52882	50.2350
2	25.415	BB	0.5628	2665.09595	73.53345	49.7650



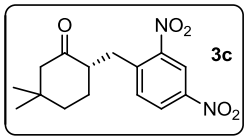


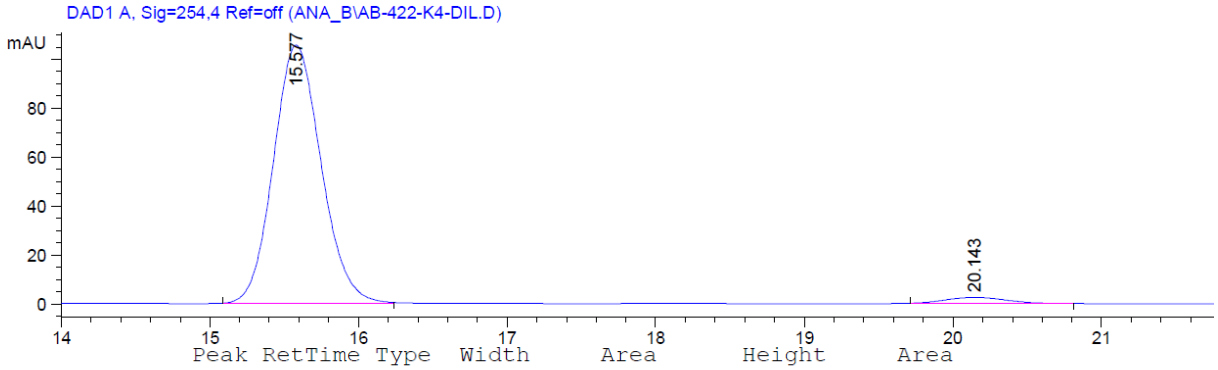
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.927	BB	0.3757	942.32629	38.74703	90.6645
2	19.870	BB	0.4203	97.02951	3.46949	9.3355



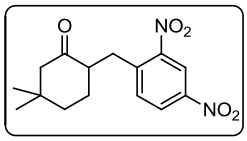


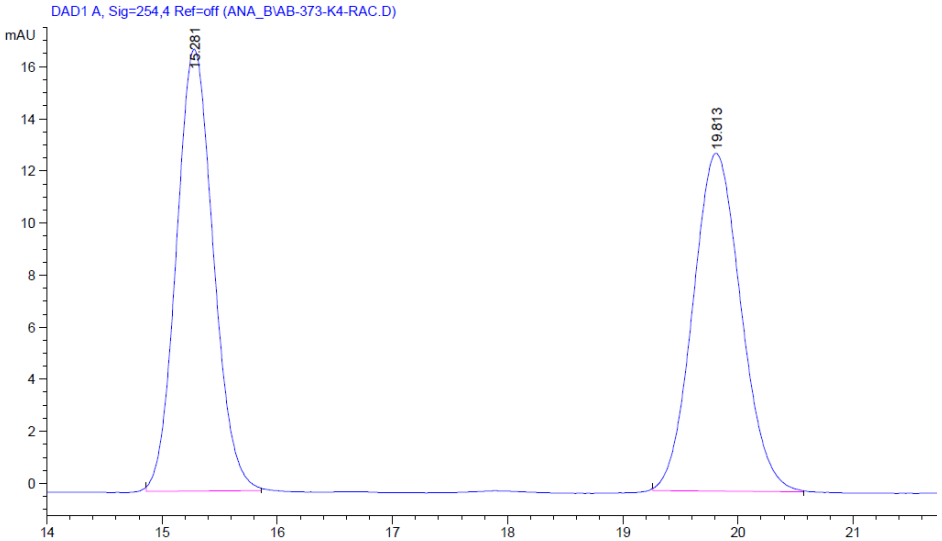
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.483	BB	0.3494	219.39130	9.71717	49.4266
2	19.326	BB	0.4208	224.48204	8.31866	50.5734



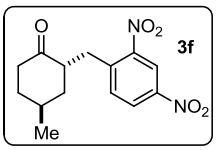


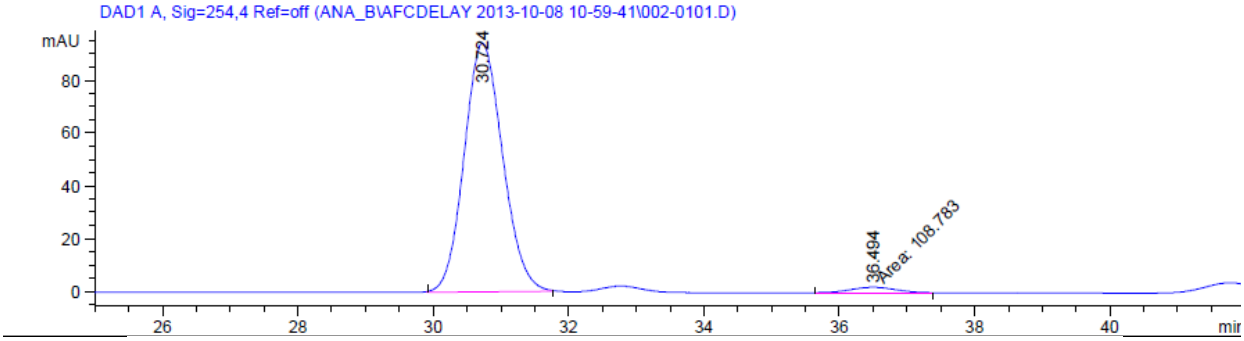
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.577	BB	0.3465	2362.42773	105.81914	97.0772
2	20.143	BB	0.4281	71.12907	2.52949	2.9228



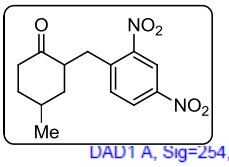


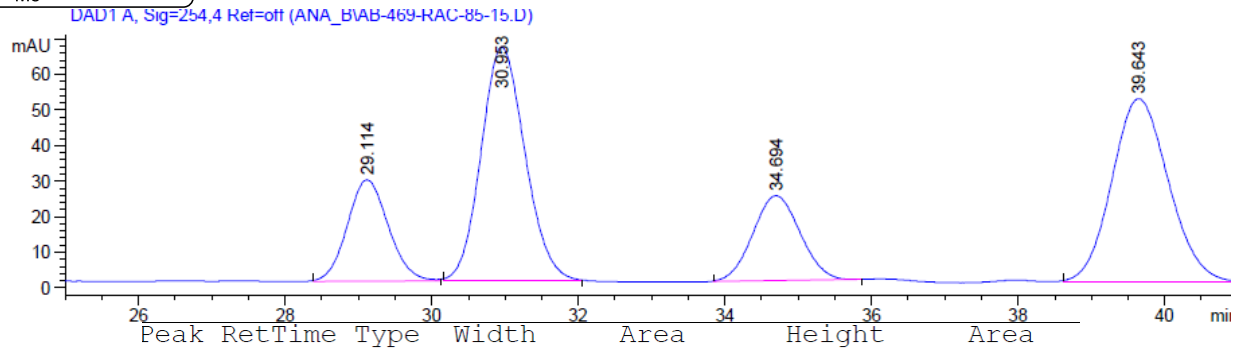
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.281	BB	0.3459	377.86176	16.96019	50.0681
2	19.813	BB	0.4489	376.83380	12.97123	49.9319



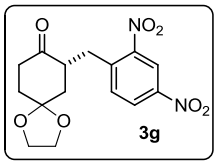


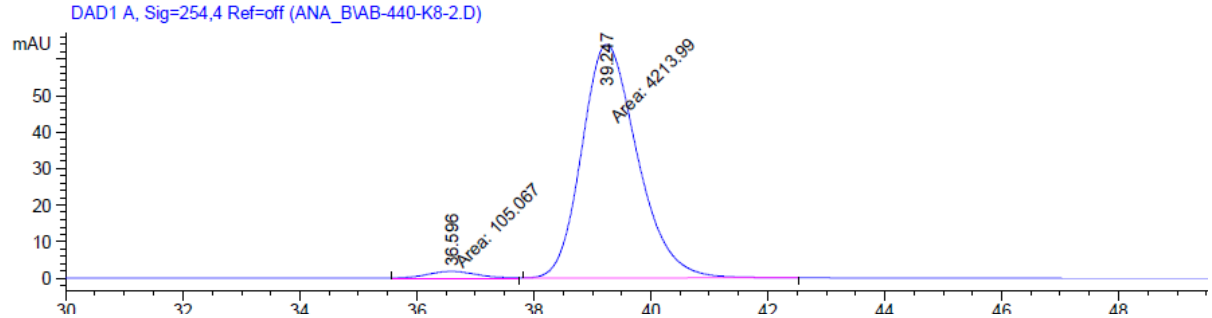
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	30.724	BB	0.6134	3724.71802	94.17875	97.1623
2	36.494	MM	0.8153	108.78313	2.22388	2.8377



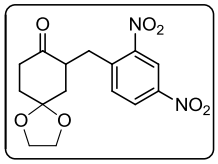


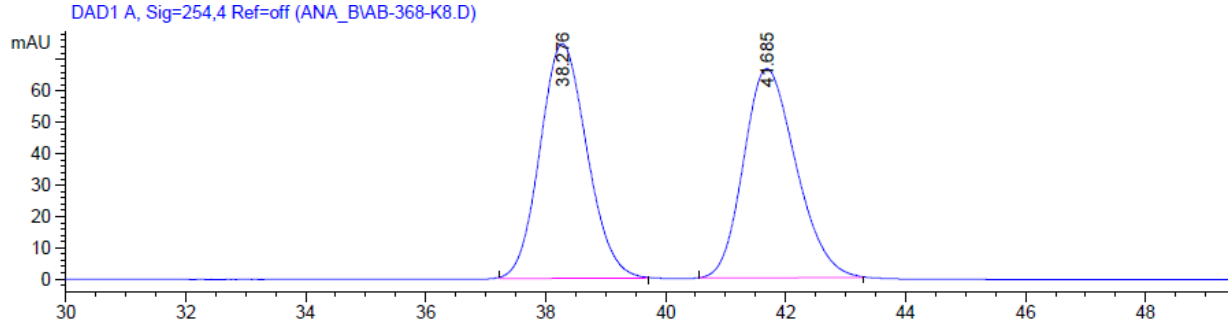
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	29.114	BB	0.6019	1105.77209	28.42373	14.3954
2	30.953	BB	0.6496	2745.58984	65.68738	35.7432
3	34.694	BB	0.6875	1069.65710	23.83961	13.9252
4	39.643	BB	0.8323	2760.40625	51.42143	35.9361
Totals :				7681.42529	169.37214	



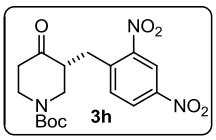


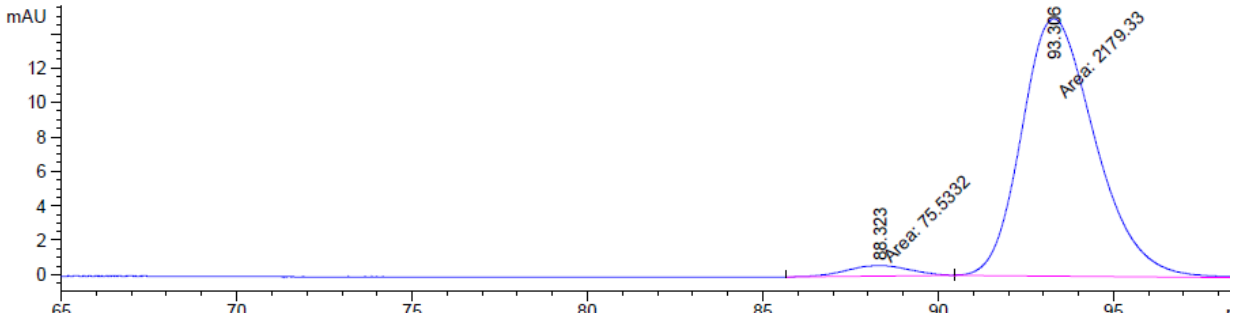
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	36.596	MM	0.9555	105.06693	1.83261	2.4326
2	39.247	MM	1.0983	4213.99023	63.94450	97.5674
Totals :				4319.05716	65.77711	



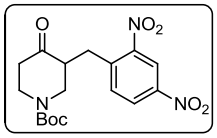


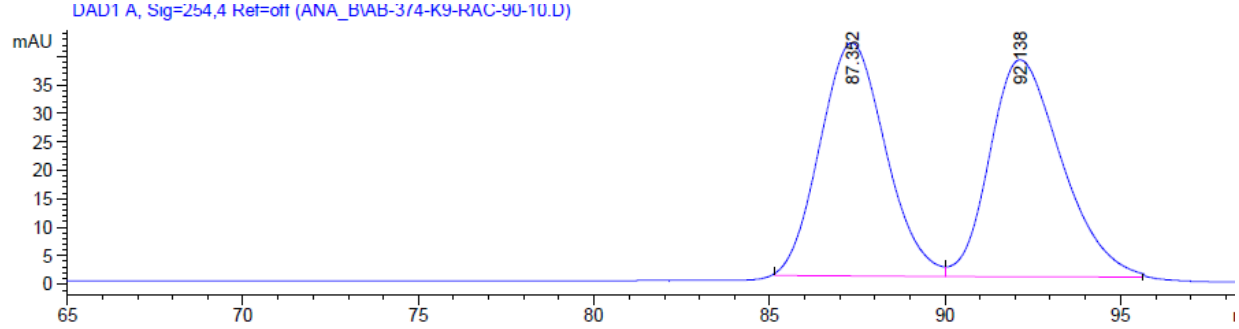
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	38.276	BB	0.8489	4069.20020	74.77117	50.0845
2	41.685	BB	0.9491	4055.46875	66.72111	49.9155
Totals :				8124.66895	141.49228	



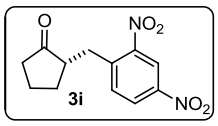


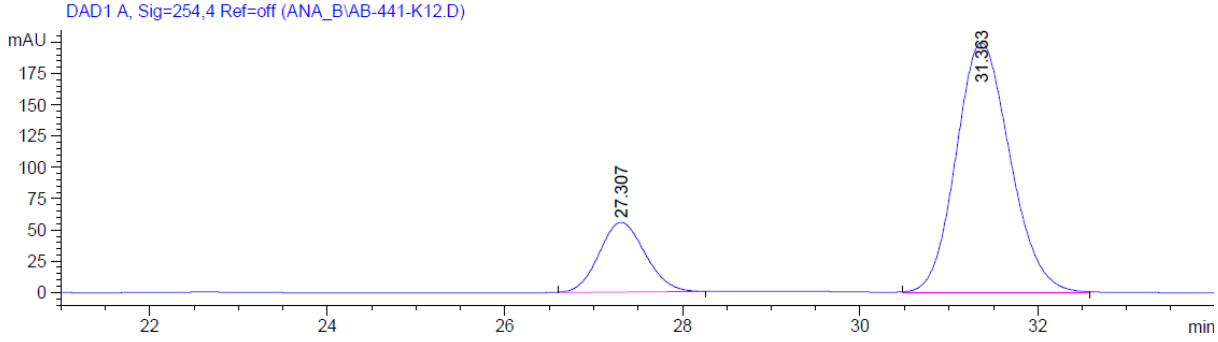
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	88.323	MM	2.0691	75.53325	6.08437e-1	3.3498
2	93.306	MM	2.4300	2179.32568	14.94735	96.6502
Totals :				2254.85893	15.55579	



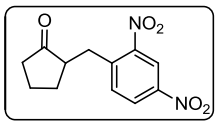


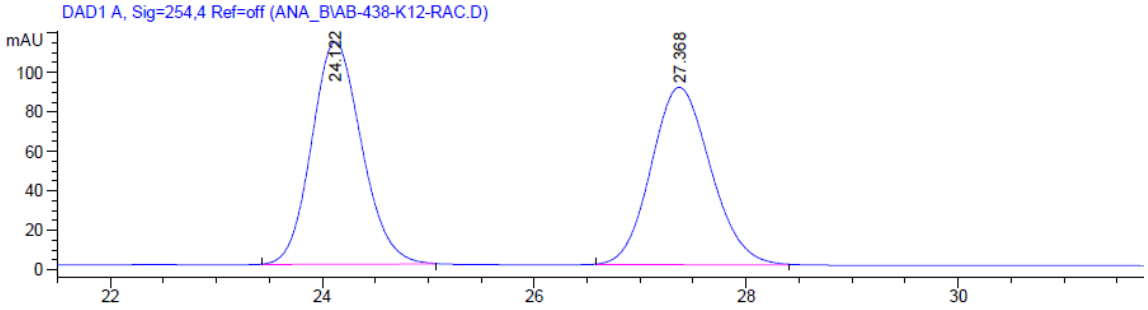
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	87.352	BV	1.9200	5318.54443	40.98330	49.4527
2	92.138	VB	2.0893	5436.27295	38.08477	50.5473
Totals :				1.07548e4	79.06808	



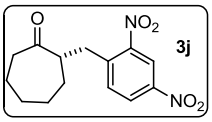


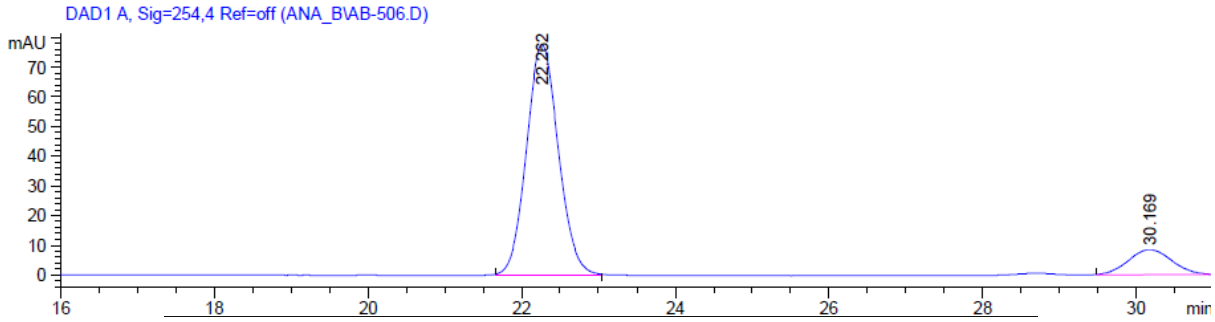
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	27.307	BB	0.5595	2014.98669	55.77878	19.3194
2	31.363	BB	0.6539	8414.87793	199.57164	80.6806
Totals :				1.04299e4	255.35042	



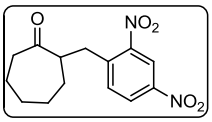


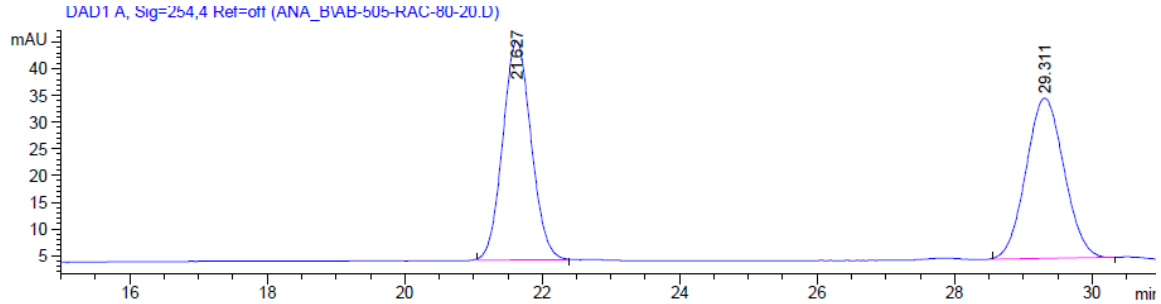
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.122	BB	0.5062	3697.37622	112.84962	51.2746
2	27.368	BB	0.6077	3513.54956	89.94908	48.7254
Totals :				7210.92578	202.79870	



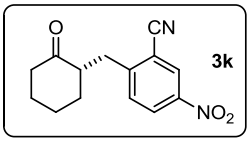


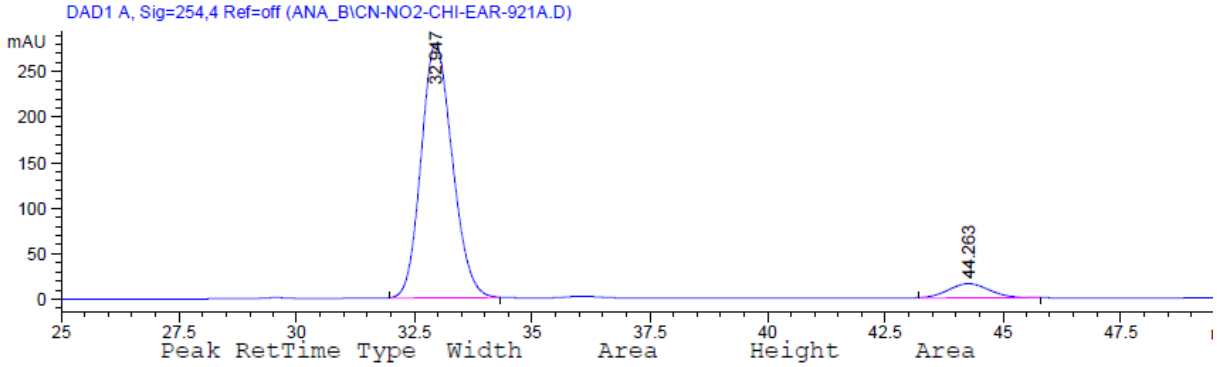
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.262	BB	0.4486	2241.45044	77.69077	87.0666
2	30.169	BB	0.6194	332.96008	8.45651	12.9334
Totals :				2574.41052	86.14729	



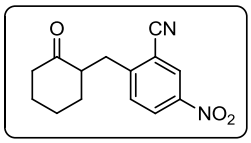


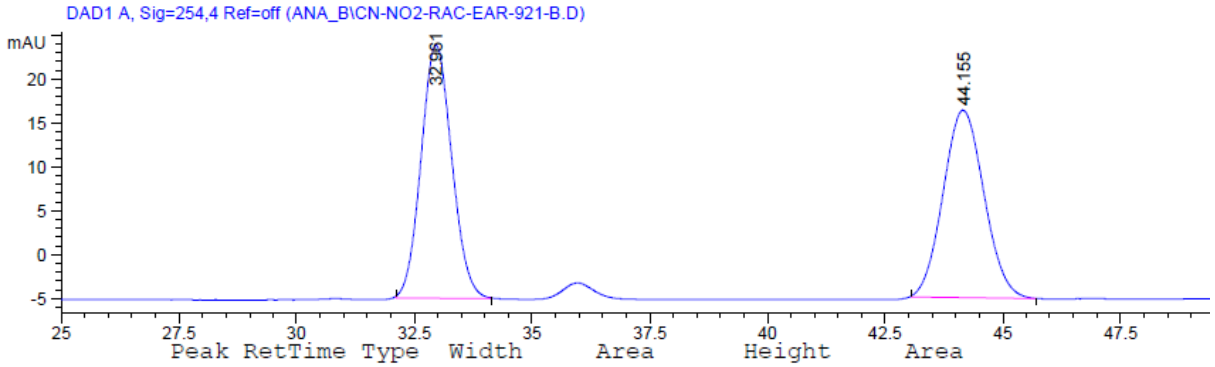
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.627	BB	0.4453	1179.73010	41.04815	50.5202
2	29.311	BB	0.6028	1155.43347	30.03258	49.4798



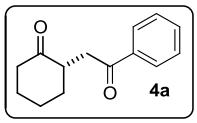


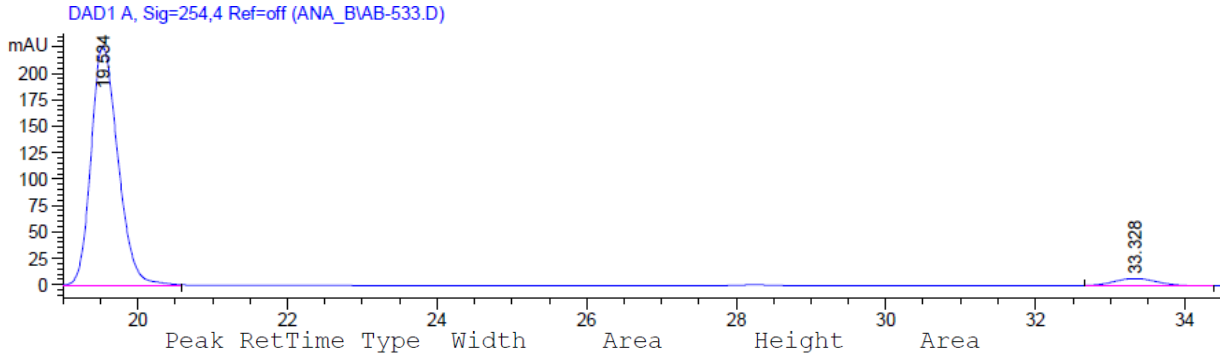
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	32.947	BB	0.7169	1.28933e4	279.14090	93.2121
2	44.263	BB	0.9268	938.91797	15.58528	6.7879



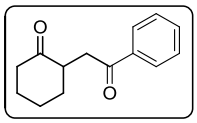


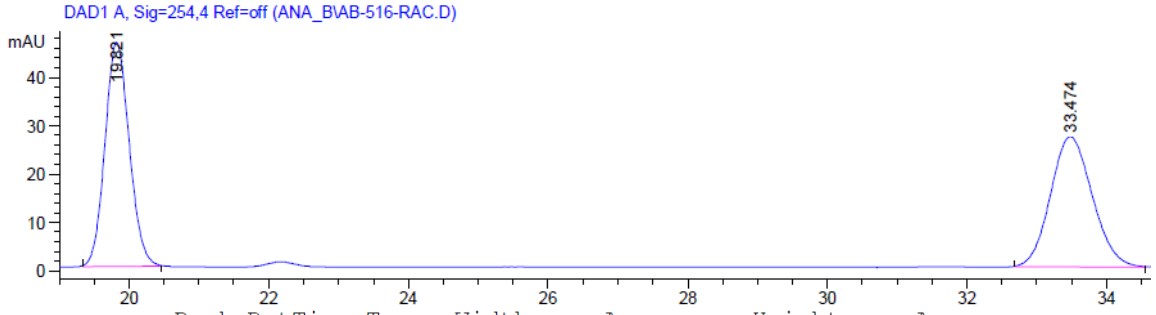
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	32.961	BB	0.7001	1311.93274	28.87609	50.3981
2	44.155	BB	0.9320	1291.20886	21.33744	49.6019



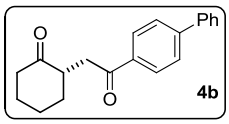


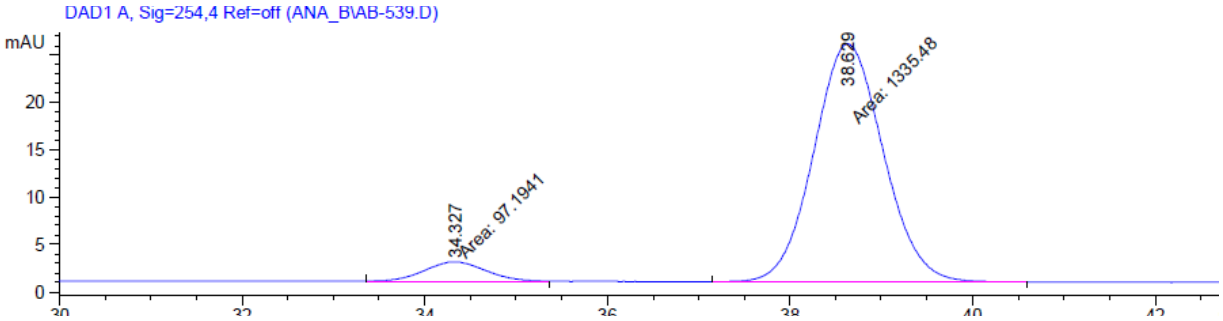
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.534	BB	0.3850	5648.18994	226.42288	95.2547
2	33.328	BB	0.6313	281.37689	6.93632	4.7453
Totals :				5929.56683	233.35920	



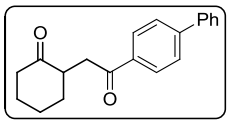


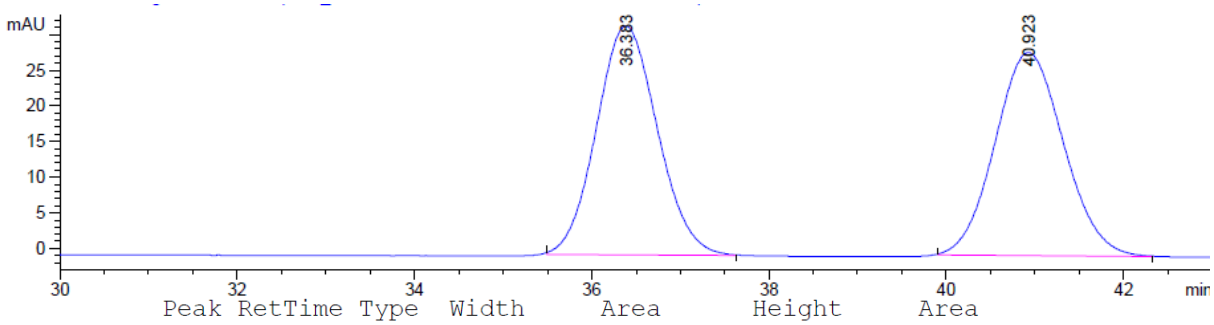
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.821	BB	0.3744	1122.38281	46.37528	50.1193
2	33.474	BB	0.6443	1117.04053	26.90846	49.8807
Totals :				2239.42334	73.28374	



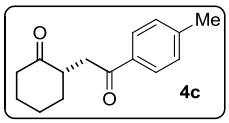


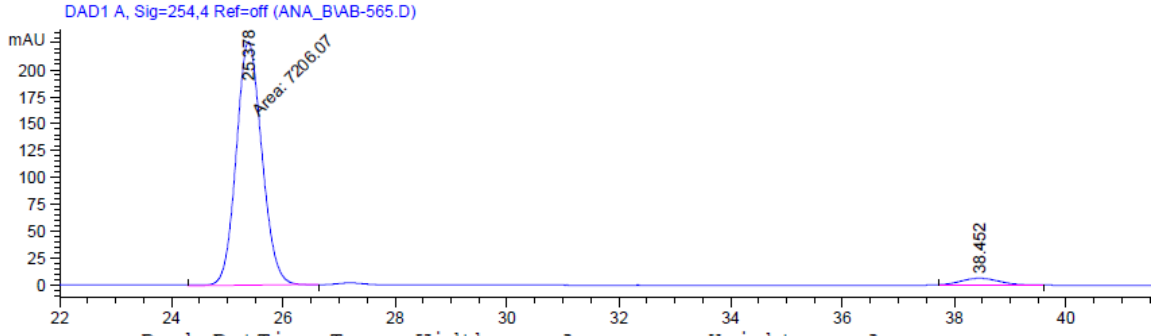
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	34.327	MM	0.7886	97.19407	2.05426	6.7841
2	38.629	MM	0.8852	1335.48450	25.14422	93.2159
Totals :				1432.67857	27.19848	



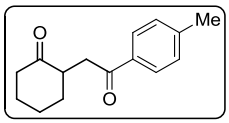


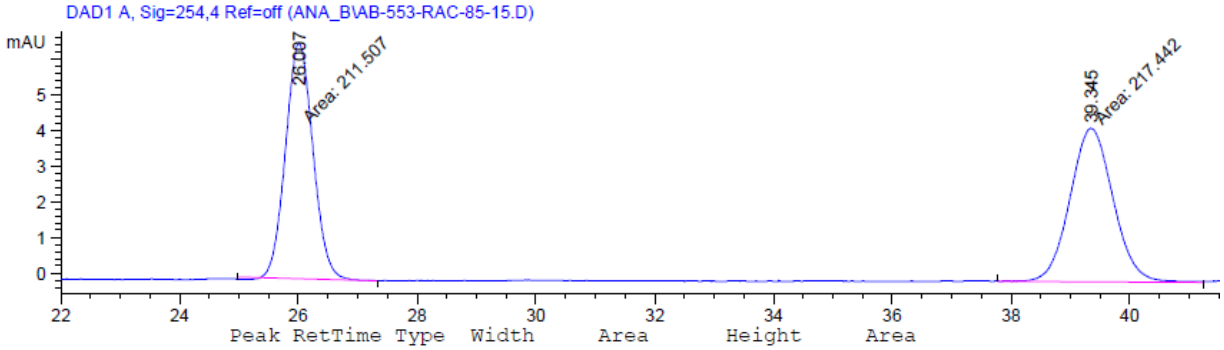
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	36.383	BB	0.7411	1537.60083	32.08611	50.0737
2	40.923	BB	0.8365	1533.07385	28.45915	49.9263
Totals :				3070.67468	60.54526	



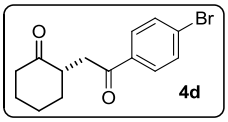


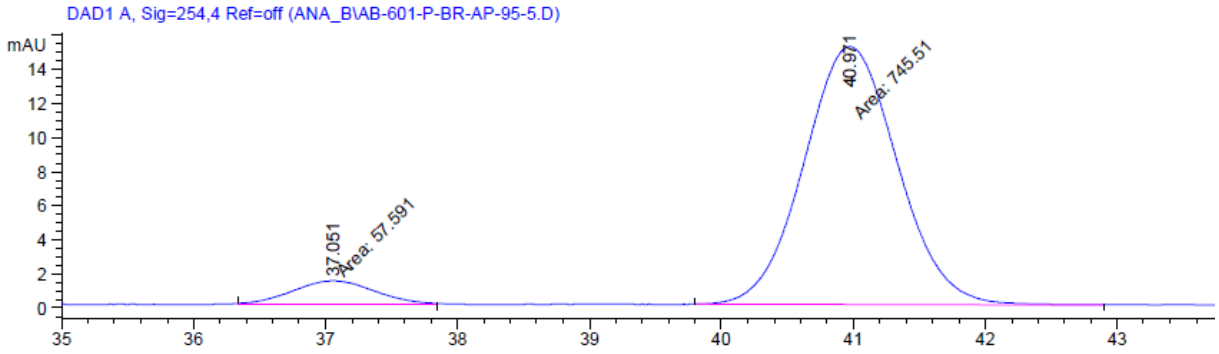
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	25.378	MM	0.5318	7206.06641	225.85201	96.1871
2	38.452	BB	0.6860	285.65414	6.10342	3.8129



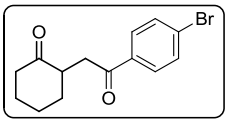


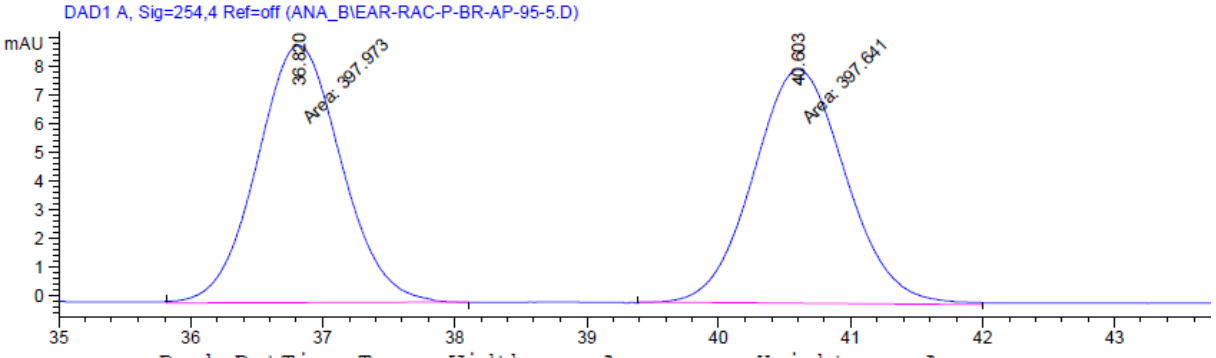
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	26.007	MM	0.5355	211.50705	6.58326	49.3082
2	39.345	MM	0.8438	217.44182	4.29467	50.6918



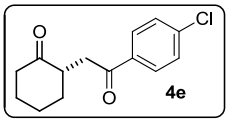


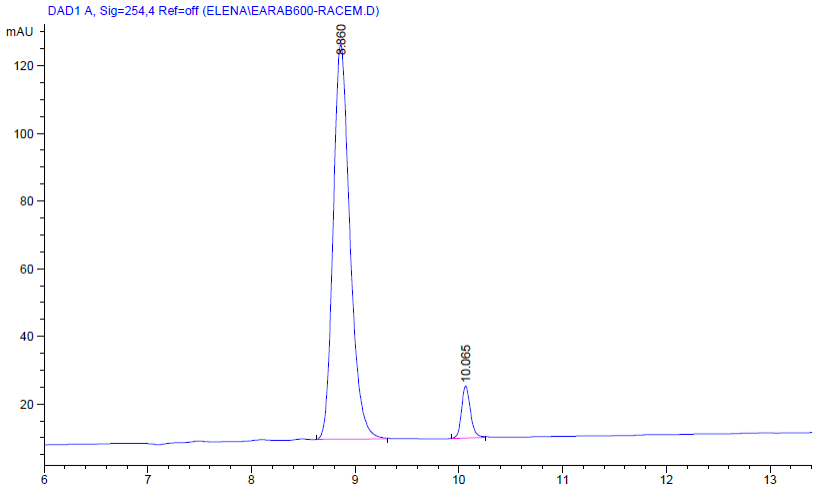
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	37.051	MM	0.7115	57.59101	1.34899	7.1711
2	40.971	MM	0.8218	745.50964	15.12025	92.8289



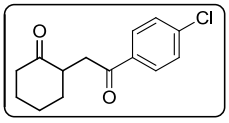


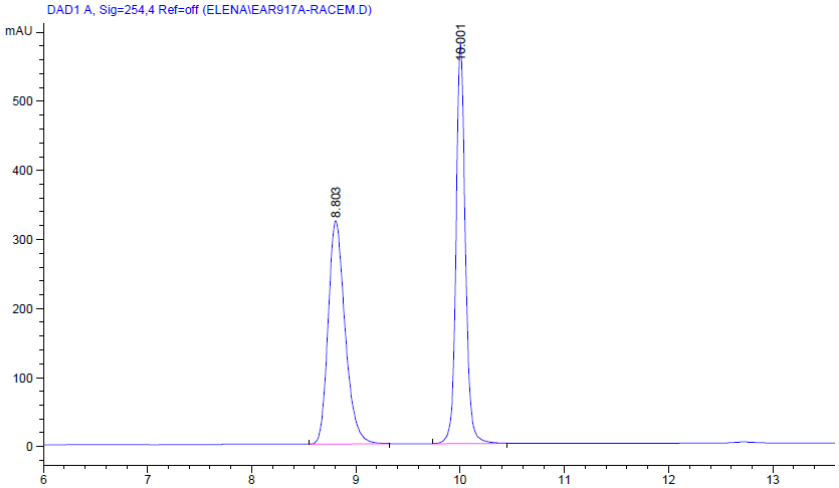
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	36.820	MM	0.7391	397.97253	8.97485	50.0208
2	40.603	MM	0.8140	397.64130	8.14161	49.9792



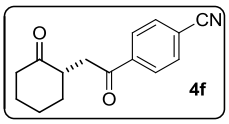


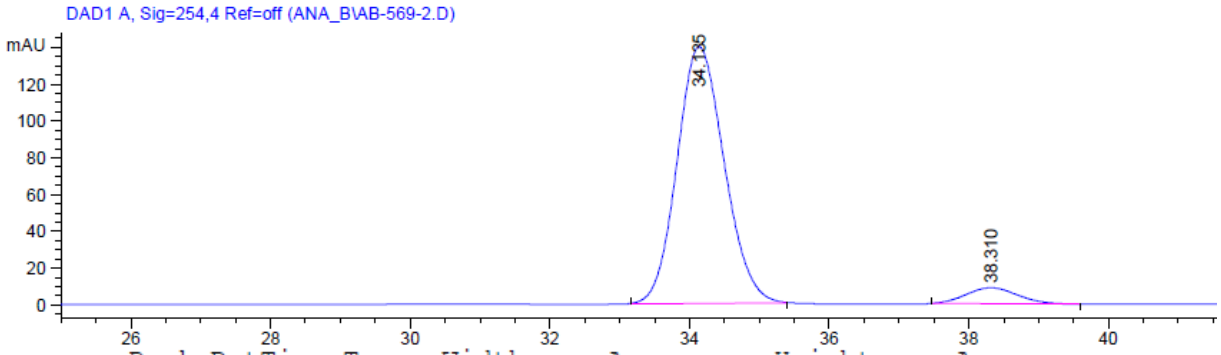
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.860	BB	0.1711	1310.74060	116.65954	93.4329
2	10.065	BB	0.0939	92.12718	15.36624	6.5671
Totals :				1402.86778	132.02578	



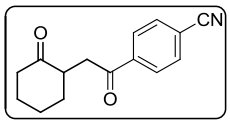


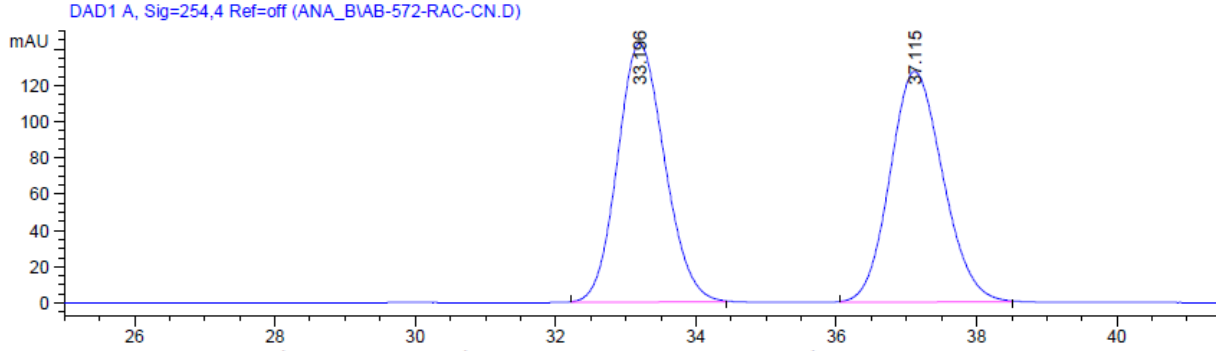
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.803	BB	0.1715	3644.78003	323.32324	50.1711
2	10.001	BB	0.0948	3619.91992	579.87775	49.8289



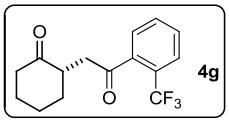


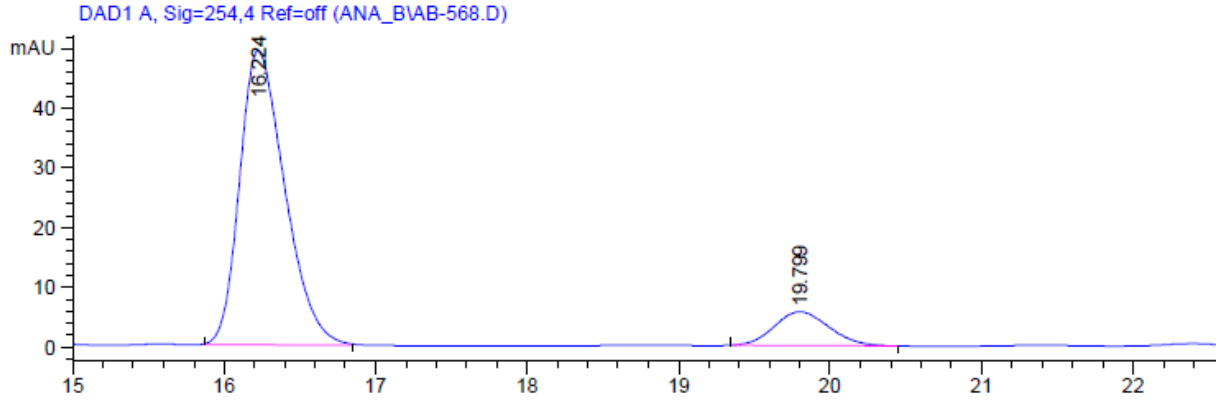
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	34.135	BB	0.7282	6573.98242	139.90878	93.6749
2	38.310	BB	0.7836	443.88428	8.69486	6.3251



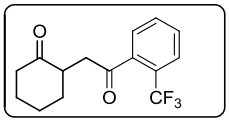


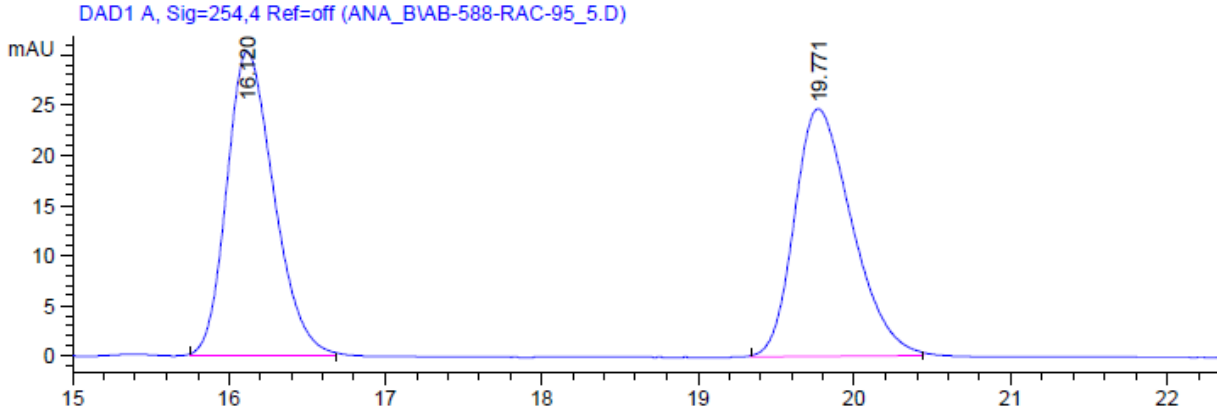
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	33.196	BB	0.7270	6666.82959	142.71358	50.0121
2	37.115	BB	0.8155	6663.59668	127.14260	49.9879



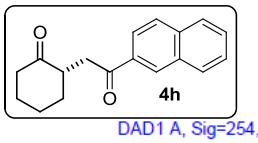


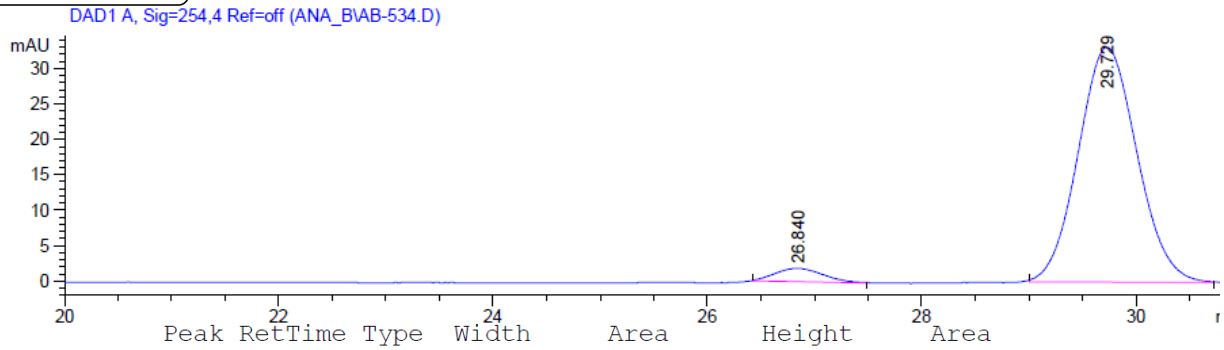
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.224	BB	0.3198	1021.43323	49.28228	87.6478
2	19.799	BB	0.3912	143.95100	5.68824	12.3522



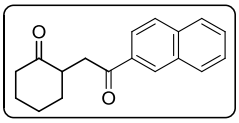


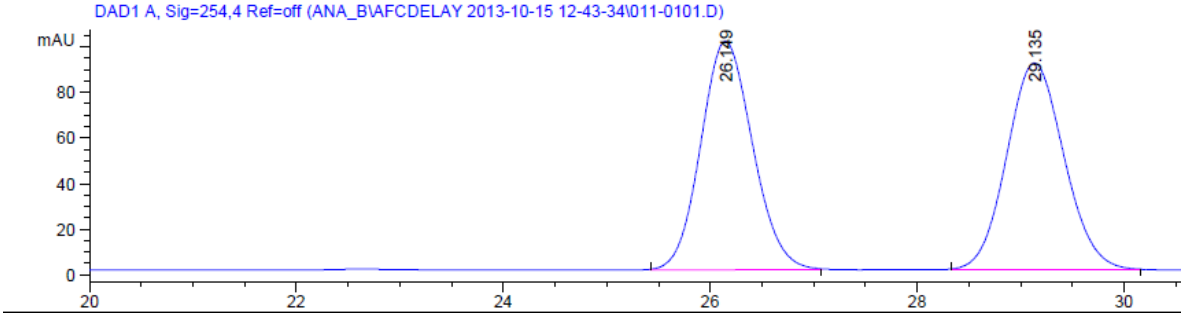
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.120	BB	0.3222	633.67230	30.26892	50.0997
2	19.771	BB	0.3945	631.15082	24.66889	49.9003





Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	26.840	BB	0.4213	57.49100	1.86658	4.3470
2	29.729	BB	0.5879	1265.06506	33.25188	95.6530
Totals :				1322.55607	35.11846	





Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	26.149	BB	0.5402	3483.82983	100.06023	49.9939
2	29.135	BB	0.5993	3484.67871	90.48297	50.0061