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Supplementary Information for

Metal-Free Photosensitized Radical Relay 1,4-Carboimination Across Two Distinct Olefins

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1. General information

1.1. Reagents, solvents, and experimental conditions

All reagents were purchased from Alfa Aesar, Sigma-Aldrich, Merck, TCI, Fluorochem, Combi-blocks, VWR and used without further purification, except otherwise stated. All the solvents were bought from Acros in AcroSeal® bottles and were directly stored under 3 or 4 Å molecular sieves, replacing the collected volume with argon. All reactions were carried out in an oven-dried glassware under an atmosphere of argon using standard Schlenk technique, unless otherwise noted. Solvents for chromatographic purification (pentane and EtOAc) were purchased as technical grade and purified by atmospheric pressure distillation. Reaction temperatures are referred to the temperature of the heating medium, unless otherwise stated.

Photosensitizer thioxanthone was purchased from Fluorochem and used directly without further purification.

1.2. Analytical techniques

NMR-spectra were recorded on a Bruker Avance II 300, Avance II 400, Agilent DD2 500 or DD2 600 spectrometers. All spectral data was acquired at 295 K, except otherwise stated. Deuterated solvents were purchased from Eurisotop (CDCl₃, deuteration > 99.8%). 1 H and 13 C chemicals shifts (δ) are quoted in parts per million (ppm) against tetramethylsilane (TMS, δ = 0.00 ppm) and were internally referenced to residual CHCl₃ (7.26 ppm for 1 H, 77.16 ppm for 13 C) or DMSO (2.50 ppm for 1 H, 39.52 ppm for 13 C). Coupling constants (J) are reported in Hertz (Hz) to the nearest 0.1 Hz. The following abbreviations (or combinations thereof) were used to explain multiplicities: s = singlet, d = doublet, t = triplet, m = multiplet.

High-resolution mass spectra (HRMS) were obtained by the MS service of the Organisch-Chemisches Institut, Westfälische Wilhelms Universität Münster, using electrospray ionisation (ESI) on a Bruker Daltonics, MicroToF spectrometer and calibrated using formate ion clusters.

Thin layer chromatography was carried out on Merck silica gel 60 F_{254} pre-coated aluminium sheets and were visualized using UV light (254 nm) and stained with basic aqueous potassium permanganate.

1.3. Compound purification

Flash chromatography was carried out using silica gel (Acros Organics, 0.035-0.070 mm, 60 Å) under a light positive pressure of argon, eluting with the specified solvent system as mentioned.

1.4. Photochemical set-up

Photochemical reactions, unless otherwise stated, were performed in a Hepatochem EvoluChemTM PhotoRedOx Box Duo device (Fig. S1) and irradiated with two EvoluChemTM Blue LEDs array (18 W, λ_{max} = 405 nm, HCK1012-01-010). The reaction temperature was measured not to exceed room temperature more than 9 °C, using this setup. A 10 mL Schlenk tube equipped with a PTFE-screw cap and a PTFE-coated rareearth "extra power" oval stirring bar (10 x 5 mm) was used for small scale reactions.



Fig. S1. Experimental set-ups: EvoluChemTM PhotoRedOx Duo (courtesy of EvoluChemTM).

2. Synthesis of starting materials

2.1. Preparation of oximes

Diphenylmethanone oxime (S1)

The title compound was prepared similar to a reported procedure. A round-bottom flask was charged with a magnetic stirring bar, sodium acetate (32.8 g, 400 mmol, 2.0 equiv), and hydroxylamine hydrochloride (20.8 g, 300 mmol, 1.5 equiv). A solution of benzophenone (36.4 g, 200 mmol, 1.0 equiv) in EtOH/H₂O (4/1; 400 mL, 0.50 M) was added and the mixture was stirred at 80 °C for 16 h. The mixture was cooled down to r.t. and EtOH was removed under reduced pressure. H₂O (200 mL) was added and the resulting mixture was extracted with EtOAc (3x 200 mL). The combined organic layers were washed with H₂O (2x 100 mL) and brine (100 mL) and were dried over MgSO₄. Diphenylmethanone oxime (S1; 38.6 g, 196 mmol, 98%) was obtained as a white solid after removal of the solvent under reduced pressure and drying under high vacuum. The isolated product was kept in a fridge under argon due to otherwise observed decomposition. H NMR (400 MHz, CDCl₃) δ = 7.31 – 7.40 (m, 3H), 7.41 – 7.51 (m, 7H), 8.45 (s, 1H) ppm. ¹³C NMR (101 MHz, CDCl₃) δ = 128.0, 128.4, 128.5, 129.2, 129.4, 129.7, 132.8, 136.3, 158.3 ppm. HRMS (ESI): m/z calculated for [C₁₃H₁₁NONa] [M+Na⁺]: 220.0733; found: 220.0732.

(4-Methoxyphenyl)(phenyl)methanone oxime (S2)

The title compound was prepared following an adapted literature procedure.^[1] A round-bottom flask was charged with a magnetic stirring bar, sodium acetate (3.28 g, 40.0 mmol, 2.0 equiv), and hydroxylamine hydrochloride (2.08 g, 29.9 mmol, 1.5 equiv). A solution of (4-methoxyphenyl)(phenyl)methanone (4.24 g, 20.0 mmol, 1.0 equiv) in EtOH/H₂O (4/1; 40 mL, 0.50 M) was added and the mixture was stirred at 80 °C for 16 h. The mixture was cooled down to r.t. and EtOH was removed under reduced pressure. H₂O (20 mL) was added and the resulting mixture was extracted with EtOAc (3x 20 mL). The combined organic layers were washed with H₂O (2x 10 mL) and brine (10 mL) and were dried over MgSO₄. Oxime S2 was obtained after column chromatography (pentane/EtOAc = 9/1) as a white solid in 52:48 E/Z-ratio (3.49 g,

15.4 mmol, 77% yield). ¹H NMR (400 MHz, CDCl₃) δ = 3.79-3.90 (m, 3H), 6.78-6.92 (m, 1H), 6.94-7.05 (m, 1H), 7.30-7.52 (m, 7H), 8.69 (s, 1H) ppm. ¹³C NMR (101 MHz, CDCl₃) δ = 55.4, 55.5, 113.7, 113.9, 124.8, 128.3, 128.4, 128.4, 128.8, 129.1, 129.3, 129.3, 129.5, 131.3, 133.0, 136.8, 157.7, 157.8, 160.2, 160.8 ppm. HRMS (ESI): m/z calculated for [C₁₄H₁₃NO₂Na]⁺ [M+Na]⁺: 250.0839; found: 250.0837.

1-Phenylethan-1-one oxime (S3)

Ph
$$=$$
 [NH₃OH]CI (1.5 equiv.) NaOAc (2.5 equiv.) $=$ Ph $=$ S3

The title compound was prepared similar to a reported procedure. A round-bottom flask was charged with hydroxylammonium chloride (4.17 g, 60.0 mmol, 1.5 equiv), sodium acetate (8.20 g, 100 mmol, 2.5 equiv), acetophenone (4.81 g, 40.0 mmol, 1.0 equiv), distilled water (96 mL), and ethanol (32 mL). After heating to reflux for 7 h, the reaction mixture was cooled to 0 °C. The precipitate was collected by filtration and was then washed with water. The solid was dried and was then purified by column chromatography on silica gel (pentane/ethyl acetate = 3/1 to 1/1). The title compound was obtained as a white solid (4.58 g, 33.9 mmol, 85%). H NMR (400 MHz, CDCl₃) δ = 2.32 (s, 3H), 7.01 (br, 1H), 7.37-7.44 (m, 3H), 7.60-7.67 (m, 2H) ppm. The latest the compound of the latest theorem is a constant of the latest theorem is a reported procedure.

2.2. Preparation of oxime esters

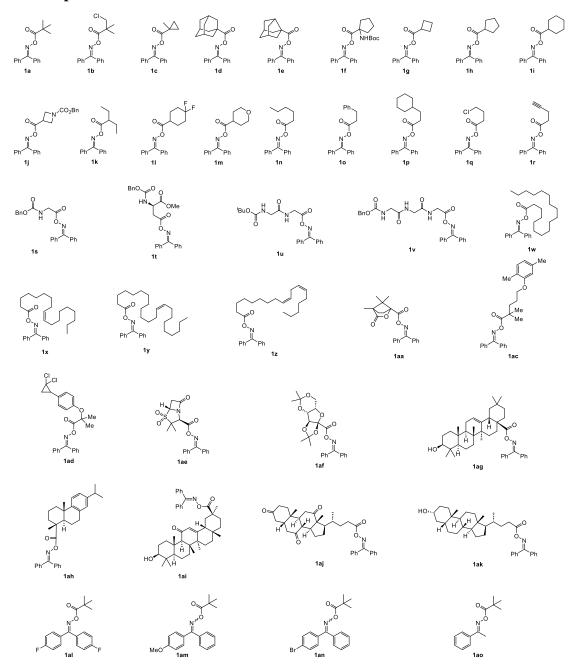


Fig. S2. Synthesized oxime esters.

Preparation of 1a:

To a solution of diphenylmethanone oxime (S1; 1.97 g, 10 mmol, 1.0 equiv.) and pyridine (0.89 mL, 11 mmol, 1.1 equiv.) in dry CH_2Cl_2 (30 mL), pivaloyl chloride (1.23

mL, 10 mmol, 1.0 equiv.) was added dropwise at room temperature under inert atmosphere. The solution was stirred at room temperature overnight. The product was washed with water (100 mL) for three times. The combined organic layers were dried over MgSO₄ and the solvent was removed. The crude residue was purified by flash column chromatography on silica (pentane:EtOAc = 40:1, v/v), to afford **1a** as a white solid (2.56 g, 91% yield). ¹H NMR (400 MHz, CDCl₃) δ = 1.09 (s, 9H), 7.28-7.31 (m, 2H), 7.33-7.37 (m, 2H), 7.41-7.47 (m, 4H), 7.60-7.64 (m, 2H) ppm. ¹³C NMR (101 MHz, CDCl₃) δ = 27.0, 38.5, 128.2, 128.4, 128.6, 129.0, 129.5, 131.0, 132.9, 134.6, 165.7, 175.2 ppm. HRMS (ESI): m/z calculated for [C₁₈H₁₉NNaO₂] [M+Na⁺]: 304.1313, found: 304.1309.

Preparation of other oxime esters from oxime S1:

General procedure (**GP1**): Oxime esters **1** were prepared similar to a reported procedure by Glorius and coworkers.^[3] An oven-dried Schlenk tube was charged with a PTFE-coated stirring bar and diphenylmethanone oxime (**S1**) (1.0 equiv). The tube was evacuated and backfilled with argon three times and then, dry CH₂Cl₂ (0.10 M) was added. Then, EDCI-HCl (2.5 equiv), carboxylic acid (1.0-1.5 equiv), and DMAP (10-20 mol%) were added successively. The reaction mixture was stirred at ambient temperature for 16 h. Distilled water (50 mL) was added and stirring was continued for 10 mins. The organic layer was separated and the aqueous layer was extracted with CH₂Cl₂ (2x30 mL). All organic layers were combined, dried over Na₂SO₄, and concentrated. Purification of the resulting residue by column chromatography on silica gel using the specified solvent system gave the pure oxime esters **1**.

Diphenylmethanone *O*-(3-chloro-2,2-dimethylpropanoyl) oxime (1b)

Following **general procedure GP1**, the title compound was prepared from diphenylmethanone oxime (**S1**) (986 mg, 5.00 mmol, 1.0 equiv), EDCI·HCl (2.40 g, 12.5 mmol, 2.5 equiv), 3-chloropivalic acid (683 mg, 5.00 mmol, 1.0 equiv.), and DMAP (122 mg, 1.00 mmol, 20 mol%) in CH₂Cl₂ (50 mL, 0.10 M). Oxime ester **1b** was obtained after column chromatography (n-pentane/EtOAc = 40/1) as a colorless solid (1.09 g, 3.45 mmol, 69%). ¹H NMR (400 MHz, CDCl₃) δ = 1.18 (s, 6H), 3.43 (s, 2H), 7.29 – 7.39 (m, 4H), 7.40 – 7.52 (m, 4H), 7.59 – 7.66 (m, 2H) ppm. ¹³C NMR (101 MHz, CDCl₃) δ = 23.1, 44.5, 51.6, 128.3, 128.5, 128.5, 129.1, 129.7, 131.2, 132.7, 134.4, 166.2, 171.9 ppm. HRMS (ESI): m/z calculated for [C₁₈H₁₈ClNO₂Na]⁺ [M+Na]⁺: 338.0918; found: 338.0918.

Diphenylmethanone O-(1-methylcyclopropane-1-carbonyl) oxime (1c)

Following **general procedure GP1**, the title compound was prepared from diphenylmethanone oxime (**S1**) (986 mg, 5.00 mmol, 1.0 equiv), EDCI·HCl (2.40 g, 12.5 mmol, 2.5 equiv), 1-methylcyclopropane-1-carboxylic acid (500 mg, 4.99 mmol, 1.0 equiv), and DMAP (122 mg, 1.00 mmol, 20 mol%) in CH₂Cl₂ (50 mL, 0.10 M). Oxime ester **1c** was obtained after column chromatography (*n*-pentane/EtOAc = 30/1) as a colorless solid (879 mg, 3.15 mmol, 63%). ¹H NMR (400 MHz, CDCl₃) δ = 0.58 – 0.66 (m, 2H), 1.09 – 1.16 (m, 5H), 7.28 – 7.38 (m, 4H), 7.39 – 7.51 (m, 4H), 7.58 – 7.65 (m, 2H) ppm. ¹³C NMR (101 MHz, CDCl₃) δ = 17.1, 18.0, 19.0, 128.2, 128.4,

128.6, 129.0, 129.5, 130.9, 132.9, 134.7, 164.9, 173.0 ppm. HRMS (ESI): m/z calculated for $[C_{18}H_{17}NO_2Na]^+[M+Na]^+$: 302.1152; found: 302.1150.

Benzophenone O-((3r,5r,7r)-adamantane-1-carbonyl) oxime (1d)

Following **general procedure GP1**, the title compound was prepared from diphenylmethanone oxime (**S1**) (986 mg, 5.00 mmol, 1.0 equiv), EDCI·HCl (2.40 g, 12.5 mmol, 2.5 equiv), 1-adamantanecarboxylic acid (901 mg, 5.00 mmol, 1.0 equiv), and DMAP (122 mg, 1.00 mmol, 20 mol%) in CH₂Cl₂ (50 mL, 0.10 M). Oxime ester **1d** was obtained after column chromatography (*n*-pentane/EtOAc = 40/1) as a colorless solid (1.48 g, 4.12 mmol, 82%). ¹H NMR (400 MHz, CDCl₃) δ = 1.58 – 1.71 (m, 6H), 1.75 – 1.81 (m, 6H), 1.90 – 1.97 (m, 3H), 7.28 – 7.39 (m, 4H), 7.40 – 7.50 (m, 4H), 7.58 – 7.65 (m, 2H) ppm. ¹³C NMR (101 MHz, CDCl₃) δ = 27.9, 36.5, 38.6, 40.6, 128.1, 128.4, 128.8, 129.1, 129.5, 131.0, 132.9, 134.8, 165.7, 174.4 ppm. HRMS (ESI): m/z calculated for [C₂₄H₂₅NO₂Na]⁺ [M+Na]⁺: 382.1778; found: 382.1777.

Benzophenone O-((2R,3as,5S,6as)-octahydro-2,5-methanopentalene-3a-carbonyl) oxime (1e)

Following **general procedure GP1**, the title compound was prepared from diphenylmethanone oxime (**S1**) (986 mg, 5.00 mmol, 1.0 equiv), EDCI·HCl (2.40 g, 12.5 mmol, 2.5 equiv), 3-noradamantanecarboxylic acid (831 mg, 5.00 mmol, 1.0 equiv), and DMAP (122 mg, 1.00 mmol, 20 mol%) in CH₂Cl₂ (50 mL, 0.10 M). Oxime ester **1e** was obtained after column chromatography (n-pentane/EtOAc = 30/1) as a colorless solid (1.42 g, 4.11 mmol, 82%). ¹H NMR (400 MHz, CDCl₃) δ = 1.46 –

1.56 (m, 4H), 1.56 – 1.65 (m, 2H), 1.68 (dd, J = 10.8, 3.0 Hz, 2H), 1.87 – 1.97 (m, 2H), 2.16 – 2.23 (m, 2H), 2.56 (tt, J = 6.7, 1.5 Hz, 1H), 7.28 – 7.32 (m, 2H), 7.33 – 7.38 (m, 2H), 7.40 – 7.47 (m, 4H), 7.59 – 7.67 (m, 2H) ppm. ¹³C NMR (101 MHz, CDCl₃) δ = 34.7, 37.4, 43.5, 44.2, 46.7, 53.1, 128.1, 128.4, 128.7, 129.0, 129.4, 130.9, 133.0, 134.8, 165.2, 174.3 ppm. HRMS (ESI): m/z calculated for [C₂₃H₂₃NO₂Na]⁺ [M+Na]⁺: 368.1621; found: 368.1619.

tert-Butyl (1-(((diphenylmethylene)amino)oxy)carbonyl)cyclopentyl)carbamate(1f)

Following **general procedure GP1**, the title compound was prepared from diphenylmethanone oxime (**S1**) (256 mg, 1.30 mmol, 1.0 equiv), EDCI·HCl (619 mg, 3.23 mmol, 2.5 equiv), 1-((*tert*-butoxycarbonyl)amino)cyclopentane-1-carboxylic acid (298 mg, 1.30 mmol, 1.0 equiv), and DMAP (31.8 mg, 0.26 mmol, 20 mol%) in CH₂Cl₂ (10 mL, 0.13 M). Oxime ester **1f** was obtained after column chromatography (*n*-pentane/EtOAc = 6/1) as a colorless solid (325 mg, 0.796 mmol, 61%). ¹H NMR (400 MHz, CDCl₃) δ = 1.40 (s, 9H), 1.44 – 1.56 (m, 2H), 1.58 – 1.72 (m, 2H), 1.74 – 1.89 (m, 2H), 2.01 – 2.12 (m, 2H), 4.85 (s, 1H), 7.28 – 7.38 (m, 4H), 7.40 – 7.47 (m, 4H), 7.57 – 7.64 (m, 2H) ppm. ¹³C NMR (101 MHz, CDCl₃) δ = 24.6, 28.4, 37.7, 65.7, 80.0, 128.3, 128.5, 128.7, 129.2, 129.6, 131.0, 132.8, 134.6, 155.0, 165.5, 171.8 ppm. HRMS (ESI): m/z calculated for [C₂₄H₂₈N₂O₄Na]⁺ [M+Na]⁺: 431.1941; found: 431.1937.

Diphenylmethanone *O*-cyclobutanecarbonyl oxime (1g)

Following **general procedure GP1**, the title compound was prepared from diphenylmethanone oxime (**S1**) (986 mg, 5.00 mmol, 1.0 equiv), EDCI·HCl (2.40 g, 12.5 mmol, 2.5 equiv), cyclobutanecarboxylic acid (501 mg, 5.00 mmol, 1.0 equiv), and DMAP (61.1 mg, 0.500 mmol, 10 mol%) in CH₂Cl₂ (50 mL, 0.10 M). Oxime ester **1g** was obtained after column chromatography (100% *n*-pentane to *n*-pentane/EtOAc = 24/1) as a white solid (893 mg, 3.20 mmol, 64%). ¹H NMR (400 MHz, CDCl₃) δ = 1.80 – 1.99 (m, 2H), 2.09 – 2.19 (m, 2H), 2.21 – 2.33 (m, 2H), 3.16 (pd, J = 8.5, 1.1 Hz, 1H), 7.29 – 7.33 (m, 2H), 7.33 – 7.39 (m, 2H), 7.42 – 7.49 (m, 4H), 7.56 – 7.63 (m, 2H) ppm. ¹³C NMR (101 MHz, CDCl₃) δ = 18.7, 25.3, 37.0, 128.2, 128.5, 128.9, 129.1, 129.6, 131.0, 132.8, 134.9, 165.2, 173.0 ppm. HRMS (ESI): m/z calculated for [C₁₈H₁₇NO₂Na]⁺ [M+Na]⁺: 302.1152; found: 302.1150.

Diphenylmethanone *O*-cyclopentanecarbonyl oxime (1h)

Following **general procedure GP1**, the title compound was prepared from diphenylmethanone oxime (**S1**) (986 mg, 5.00 mmol, 1.0 equiv), EDCI-HCl (2.40 g, 12.5 mmol, 2.5 equiv), cyclopentanecarboxylic acid (571 mg, 5.00 mmol, 1.0 equiv), and DMAP (61.1 mg, 0.500 mmol, 10 mol%) in CH₂Cl₂ (50 mL, 0.10 M). Oxime ester **1h** was obtained after column chromatography (100% *n*-pentane to *n*-pentane/EtOAc = 24/1) as a white solid (601 mg, 2.05 mmol, 41%). ¹H NMR (400 MHz, CDCl₃) δ = 1.47 – 1.68 (m, 4H), 1.71 – 1.86 (m, 4H), 2.72 (p, *J* = 7.9 Hz, 1H), 7.29 – 7.39 (m, 4H), 7.40 – 7.51 (m, 4H), 7.56 – 7.64 (m, 2H). ppm. ¹³C NMR (101 MHz, CDCl₃) δ = 25.8, 29.9, 42.7, 128.3, 128.5, 128.8, 129.1, 129.6, 131.0, 132.9, 134.9, 165.2, 174.1 ppm. HRMS (ESI): m/z calculated for [C₁₉H₁₉NO₂Na]⁺ [M+Na]⁺: 316.1308; found: 316.1307.

Diphenylmethanone *O*-cyclohexanecarbonyl oxime (1i)

Following **general procedure GP1**, the title compound was prepared from diphenylmethanone oxime (**S1**) (986 mg, 5.00 mmol, 1.0 equiv), EDCI·HCl (2.40 g, 12.5 mmol, 2.5 equiv), cyclohexanecarboxylic acid (962 mg, 7.5 mmol, 1.5 equiv), and DMAP (122 mg, 1.00 mmol, 20 mol%) in CH₂Cl₂ (50 mL, 0.10 M). Oxime ester **1i** was obtained after column chromatography (n-pentane/EtOAc = 50/1 to 10/1) as a white solid (1.45 g, 4.72 mmol, 94%). ¹H NMR (400 MHz, CDCl₃) δ = 1.14 – 1.28 (m, 3H), 1.35 – 1.47 (m, 2H), 1.55 – 1.62 (m, 1H), 1.62 – 1.74 (m, 2H), 1.74 – 1.85 (m, 2H), 2.31 (tt, J = 11.1, 3.7 Hz, 1H), 7.28 – 7.39 (m, 4H), 7.41 – 7.51 (m, 4H), 7.56 – 7.64 (m, 2H) ppm. ¹³C NMR (101 MHz, CDCl₃) δ = 25.4, 25.8, 28.8, 42.2, 128.3, 128.5, 128.8, 129.1, 129.6, 131.0, 132.9, 134.9, 165.4, 173.3 ppm. HRMS (ESI): m/z calculated for [C₂₀H₂₁NO₂Na]⁺ [M+Na]⁺: 330.1465; found: 330.1464.

Benzyl 3-((((diphenylmethylene)amino)oxy)carbonyl)azetidine-1-carboxylate (1j)

Following **general procedure GP1**, the title compound was prepared from diphenylmethanone oxime (**S1**) (128 mg, 0.649 mmol, 1.0 equiv), EDCI-HCl (309 mg, 1.61 mmol, 2.5 equiv), 1-((benzyloxy)carbonyl)azetidine-3-carboxylic acid (153 mg, 0.650 mmol, 1.0 equiv), and DMAP (15.9 mg, 0.130 mmol, 20 mol%) in CH₂Cl₂ (10 mL, 65 mM). Oxime ester **1j** was obtained after column chromatography (n-pentane/EtOAc = 3/1) as a colorless oil (142 mg, 0.343 mmol, 53%). ¹H NMR (400 MHz, CDCl₃) δ = 3.47 (p, J = 7.6 Hz, 1H), 4.09 – 4.20 (m, 4H), 5.09 (s, 2H), 7.26

-7.31 (m, 2H), 7.31 - 7.41 (m, 7H), 7.42 - 7.50 (m, 4H), 7.54 - 7.62 (m, 2H) ppm. 13 C NMR (101 MHz, CDCl₃) $\delta = 31.8$, 51.7, 66.9, 128.1, 128.3, 128.4, 128.6, 128.7, 129.2, 130.0, 131.4, 132.3, 134.4, 136.6, 156.2, 166.1, 170.2 ppm. HRMS (ESI): m/z calculated for $[C_{25}H_{22}N_2O_4Na]^+[M+Na]^+$: 437.1472; found: 437.1464.

Diphenylmethanone *O*-(2-ethylbutanoyl) oxime (1k)

Following **general procedure GP1**, the title compound was prepared from diphenylmethanone oxime (**S1**) (986 mg, 5.00 mmol, 1.0 equiv), EDCI·HCl (2.40 g, 12.5 mmol, 2.5 equiv), 2-ethylbutanoic acid (581 mg, 5.00 mmol, 1.0 equiv), and DMAP (61.1 mg, 0.500 mmol, 10 mol%) in CH₂Cl₂ (50 mL, 0.10 M). Oxime ester **1k** was obtained after column chromatography (n-pentane/EtOAc = 50/1 to 30/1) as a white solid (573 mg, 1.94 mmol, 39%). ¹H NMR (400 MHz, CDCl₃) δ = 0.84 (t, J = 7.4 Hz, 6H), 1.39 – 1.63 (m, 4H), 2.18 (tt, J = 8.6, 5.5 Hz, 1H), 7.28 – 7.33 (m, 2H), 7.33 – 7.39 (m, 2H), 7.41 – 7.49 (m, 4H), 7.58 – 7.65 (m, 2H) ppm. ¹³C NMR (101 MHz, CDCl₃) δ = 11.8, 25.0, 48.0, 128.2, 128.5, 128.7, 129.1, 129.5, 131.0, 133.0, 134.8, 165.5, 173.3 ppm. HRMS (ESI): m/z calculated for [C₁₉H₂₁NO₂Na]⁺ [M+Na]⁺: 318.1465; found: 318.1462.

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Diphenylmethanone *O*-(4,4-difluorocyclohexane-1-carbonyl) oxime (11)

Following **general procedure GP1**, the title compound was prepared from diphenylmethanone oxime (**S1**) (986 mg, 5.00 mmol, 1.0 equiv), EDCI·HCl (2.40 g, 12.5 mmol, 2.5 equiv), 4,4-difluorocyclohexane-1-carboxylic acid (1.23 g, 7.5 mmol,

1.5 equiv), and DMAP (122 mg, 1.00 mmol, 20 mol%) in CH₂Cl₂ (50 mL, 0.10 M). Oxime ester **1l** was obtained after column chromatography (n-pentane/EtOAc = 30/1 to 5/1) as a white solid (1.51 g, 4.40 mmol, 88%). ¹H NMR (400 MHz, CDCl₃) δ = 1.63 – 1.92 (m, 6H), 1.93 – 2.06 (m, 2H), 2.39 – 2.49 (m, 1H), 7.27 – 7.32 (m, 2H), 7.34 – 7.40 (m, 2H), 7.42 – 7.53 (m, 4H), 7.55 – 7.64 (m, 2H) ppm. ¹³C NMR (101 MHz, CDCl₃) δ = 24.6 – 25.1 (m), 32.4 (t, J = 24.5 Hz), 39.5, 122.6 (t, J = 241.1 Hz), 128.4, 128.6, 128.6, 129.1, 129.8, 131.3, 132.8, 134.5, 166.1, 171.4 ppm. ¹⁹F{¹H} NMR (377 MHz, CDCl₃) δ = -98.9 (d, J = 237.2 Hz), -95.02 (d, J = 236.9 Hz) ppm. HRMS (ESI): m/z calculated for [C₂₀H₁₉NO₂F₂Na]⁺ [M+Na]⁺: 366.1276; found: 366.1272.

Benzophenone *O*-tetrahydro-2*H*-pyran-4-carbonyl oxime (1m)

Following **general procedure GP1**, the title compound was prepared from diphenylmethanone oxime (**S1**) (986 mg, 5.00 mmol, 1.0 equiv), EDCI·HCl (2.40 g, 12.5 mmol, 2.5 equiv), tetrahydro-2*H*-pyran-4-carboxylic acid (0.98 g, 7.5 mmol, 1.5 equiv), and DMAP (122 mg, 1.00 mmol, 20 mol%) in CH₂Cl₂ (50 mL, 0.10 M). Oxime ester **1m** was obtained after column chromatography (*n*-pentane/EtOAc = 20/1 to 10/1) as a white solid (1.20 g, 78%). ¹H NMR (400 MHz, CDCl₃) δ = 1.68-1.73 (m, 4H), 2.51-2.57 (m, 1H), 3.31-3.38 (m, 2H), 3.83-3.89 (m, 2H), 7.26-7.31 (m, 2H), 7.32-7.37 (m, 2H), 7.41-7.48 (m, 4H), 7.57-7.60 (m, 2H) ppm. ¹³C NMR (101 MHz, CDCl₃) δ = 28.3, 39.2, 66.9, 128.3, 128.5, 128.6, 129.0, 129.7, 131.1, 132.7, 134.6, 165.8, 171.5 ppm. HRMS (ESI): m/z calculated for [C₁₉H₁₉NNaO₃]⁺ [M+Na]⁺: 332.1263; found: 332.1263.

1n

Diphenylmethanone *O*-hexanoyl oxime (1n)

Following **general procedure GP1**, the title compound was prepared from diphenylmethanone oxime (**S1**) (986 mg, 5.00 mmol, 1.0 equiv), EDCI·HCl (2.40 g, 12.5 mmol, 2.5 equiv), hexanoic acid (582 mg, 5.01 mmol, 1.0 equiv), and DMAP (61.1 mg, 0.500 mmol, 10 mol%) in CH₂Cl₂ (50 mL, 0.10 M). Oxime ester **1n** was obtained after column chromatography (n-pentane/EtOAc = $50/1 \rightarrow 30/1$) as a white solid (744 mg, 2.52 mmol, 50%). ¹H NMR (400 MHz, CDCl₃) $\delta = 0.80 - 0.93$ (m, 3H), 1.19 – 1.34 (m, 4H), 1.52 – 1.64 (m, 2H), 2.32 (t, J = 7.5 Hz, 2H), 7.29 – 7.40 (m, 4H), 7.42 – 7.49 (m, 4H), 7.56 – 7.64 (m, 2H) ppm. ¹³C NMR (101 MHz, CDCl₃) $\delta = 14.0$, 22.4, 24.5, 31.3, 33.1, 128.3, 128.5, 128.9, 129.2, 129.7, 131.0, 132.9, 134.9, 165.0, 171.4 ppm. HRMS (ESI): m/z calculated for [C₁₉H₂₁NO₂Na]⁺ [M+Na]⁺: 318.1465; found: 318.1460.

Benzophenone *O*-(3-phenylpropanoyl) oxime (10)

Following **general procedure GP1**, the title compound was prepared from diphenylmethanone oxime (**S1**) (986 mg, 5.00 mmol, 1.0 equiv), EDCI·HCl (2.40 g, 12.5 mmol, 2.5 equiv), 3-phenylpropanoic acid (1.13 g, 7.49 mmol, 1.5 equiv), and DMAP (122 mg, 1.00 mmol, 20 mol%) in CH₂Cl₂ (50 mL, 0.10 M). Oxime ester **10** was obtained after column chromatography (n-pentane/EtOAc = 40/1 to 30/1) as a white solid (1.15 g, 70%). ¹H NMR (400 MHz, CDCl₃) δ = 2.65-2.69 (m, 2H), 2.93-2.97 (m, 2H), 7.16-7.31 (m, 7H), 7.35-7.39 (m, 2H), 7.42-7.50 (m, 4H), 7.58-7.62 (m, 2H) ppm. ¹³C NMR (101 MHz, CDCl₃) δ = 30.8, 34.8, 126.4, 128.26, 128.27, 128.42, 128.46, 128.47, 128.6, 128.9, 129.1, 129.68, 129.70, 131.0, 132.6, 134.8, 140.3, 165.0, 170.5 ppm. HRMS (ESI): m/z calculated for [C₂₂H₁₉NNaO₂]⁺ [M+Na]⁺: 352.1313; found: 352.1313.

Diphenylmethanone *O*-(3-cyclohexylpropanoyl) oxime (1p)

Following **general procedure GP1**, the title compound was prepared from diphenylmethanone oxime (**S1**) (986 mg, 5.00 mmol, 1.0 equiv), EDCI·HCl (2.40 g, 12.5 mmol, 2.5 equiv), 3-cyclohexylpropanoic acid (781 mg, 5.00 mmol, 1.0 equiv), and DMAP (122 mg, 1.00 mmol, 20 mol%) in CH₂Cl₂ (50 ml, 0.10 M). Oxime ester **1p** was obtained after column chromatography (n-pentane/EtOAc = 30/1) as a colorless solid (1.54 g, 4.59 mmol, 92%). ¹H NMR (400 MHz, CDCl₃) δ = 0.76 – 0.91 (m, 2H), 1.05 – 1.27 (m, 4H), 1.48 (q, J = 7.3 Hz, 2H), 1.57 – 1.72 (m, 5H), 2.33 (t, J = 7.7 Hz, 2H), 7.29 – 7.39 (m, 4H), 7.40 – 7.51 (m, 4H), 7.56 – 7.63 (m, 2H) ppm. ¹³C NMR (101 MHz, CDCl₃) δ = 26.2, 26.6, 30.6, 32.1, 32.9, 37.0, 128.2, 128.4, 128.8, 129.1, 129.6, 130.9, 132.8, 134.9, 164.9, 171.5 ppm. HRMS (ESI): m/z calculated for [C₂₂H₂₅NO₂Na]⁺ [M+Na]⁺: 358.1778; found: 358.1780.

Diphenylmethanone *O*-(4-chlorobutanoyl) oxime (1q)

Following **general procedure GP1**, the title compound was prepared from diphenylmethanone oxime (**S1**) (986 mg, 5.00 mmol, 1.0 equiv), EDCI-HCl (2.40 g, 12.5 mmol, 2.5 equiv), 4-chlorobutanoic acid (613 mg, 5.00 mmol, 1.0 equiv), and DMAP (61.1 mg, 0.500 mmol, 10 mol%) in CH₂Cl₂ (50 mL, 0.10 M). Oxime ester **1q** was obtained after column chromatography (*n*-pentane/EtOAc = 30/1 to 10/1) as a yellow oil (1.26 g, 4.18 mmol, 84%). ¹H NMR (400 MHz, CDCl₃) δ = 2.01 – 2.13 (m, 2H), 2.54 (t, J = 7.1 Hz, 2H), 3.54 (t, J = 6.3 Hz, 2H), 7.29 – 7.40 (m, 4H), 7.42 – 7.52

(m, 4H), 7.55 - 7.63 (m, 2H) ppm. ¹³C NMR (101 MHz, CDCl₃) $\delta = 27.5$, 30.1, 44.0, 128.4, 128.6, 128.8, 129.2, 129.8, 131.1, 132.7, 134.7, 165.4, 170.4 ppm. HRMS (ESI): m/z calculated for $[C_{17}H_{16}NO_2ClNa]^+$ [M+Na]⁺: 324.0762; found: 324.0760.

Diphenylmethanone *O*-pent-4-ynoyl oxime (1r)

Following **general procedure GP1**, the title compound was prepared from diphenylmethanone oxime (**S1**) (986 mg, 5.00 mmol, 1.0 equiv), EDCI·HC1 (2.40 g, 12.5 mmol, 2.5 equiv), pent-4-ynoic acid (491 mg, 5.01 mmol, 1.0 equiv), and DMAP (122 mg, 1.00 mmol, 20 mol%) in CH₂Cl₂ (50 ml, 0.10 M). Oxime ester **1r** was obtained after column chromatography (n-pentane/EtOAc = 40/1) as a colorless solid (690 mg, 2.49 mmol, 50%). ¹H NMR (400 MHz, CDCl₃) δ = 1.96 (t, J = 2.6 Hz, 1H), 2.42 – 2.53 (m, 2H), 2.55 – 2.64 (m, 2H), 7.30 – 7.39 (m, 4H), 7.41 – 7.52 (m, 4H), 7.55 – 7.63 (m, 2H). ppm. ¹³C NMR (101 MHz, CDCl₃) δ = 14.3, 32.3, 69.4, 82.2, 128.3, 128.5, 128.9, 129.1, 129.8, 131.1, 132.5, 134.7, 165.3, 169.4 ppm. HRMS (ESI): m/z calculated for [C₁₈H₁₅NO₂Na]⁺ [M+Na]⁺: 300.0995; found: 300.0990.

Benzyl (2-(((diphenylmethylene)amino)oxy)-2-oxoethyl)carbamate (1s)

Following **general procedure GP1**, the title compound was prepared from diphenylmethanone oxime (**1**) (986 mg, 5.00 mmol, 1.0 equiv), EDCI-HCl (2.39 g, 12.5 mmol, 2.5 equiv), *N*-benzyloxycarbonyl glycine (1.05 g, 5.00 mmol, 1.0 equiv.) and DMAP (122 mg, 1.00 mmol, 0.2 equiv.) in CH₂Cl₂ (20 ml, 0.10 m). Oxime ester **1s** was obtained after column chromatography (pentane/EtOAc = 7/1 to 5/1, v/v) as a colorless oil (1.28 g, 3.30 mmol, 66%). ¹H NMR (400 MHz, CDCl₃): δ = 4.10-4.12 (m,

2H), 5.11 (s, 2H), 5.37-5.40 (m, 1H), 7.30-7.39 (m, 9H), 7.44-7.47 (m, 4H), 7.56-7.58 (m, 2H) ppm. 13 C NMR (101 MHz, CDCl₃): $\delta = 42.2$, 67.2, 128.2, 128.3, 128.4, 128.5, 128.6, 128.9, 129.2, 130.0, 131.2, 132.1, 134.4, 136.3, 165.6, 168.6 ppm. HRMS (ESI): m/z calculated for [C₂₃H₂₀N₂O₄] [M+Na]⁺: 411.1315; found: 411.1317.

Methyl (R)-2-(((benzyloxy)carbonyl)amino)-4-(((diphenylmethylene)amino)oxy)-4-oxobutanoate (1t)

Following **general procedure GP1**, the title compound was prepared from diphenylmethanone oxime (**S1**) (395 mg, 2.00 mmol, 1.0 equiv), EDCI-HCl (958 mg, 5.00 mmol, 2.5 equiv), Z-D-Asp-OMe (562 mg, 2.00 mmol, 1.0 equiv), and DMAP (48.9 mg, 0.400 mmol, 20 mol%) in CH₂Cl₂ (10 ml, 0.20 M). Oxime ester **1t** was obtained after column chromatography (n-pentane/EtOAc = 3/1) as a colorless solid (803 mg, 1.74 mmol, 87%). ¹H NMR (400 MHz, CDCl₃) δ = 2.93 (dd, J = 17.4, 4.5 Hz, 1H), 3.12 (dd, J = 17.5, 4.6 Hz, 1H), 3.73 (s, 3H), 4.64 (dt, J = 8.8, 4.5 Hz, 1H), 5.11 (s, 2H), 5.72 (d, J = 8.5 Hz, 1H), 7.27 – 7.40 (m, 9H), 7.40 – 7.51 (m, 4H), 7.53 – 7.60 (m, 2H) ppm. ¹³C NMR (101 MHz, CDCl₃) δ = 35.6, 50.3, 53.0, 67.2, 128.2, 128.3, 128.4, 128.5, 128.6, 128.8, 129.1, 129.9, 131.2, 132.3, 134.5, 136.2, 156.0, 165.5, 169.1, 170.9 ppm. HRMS (ESI): m/z calculated for [C₂₆H₂₄N₂O₆Na]⁺ [M+Na]⁺: 483.1527; found: 483.1527.

1u

tert-Butyl (2-((2-(((diphenylmethylene)amino)oxy)-2-oxoethyl)amino)-2-oxoethyl)carbamate (1u)

Following **general procedure GP1**, the title compound was prepared from diphenylmethanone oxime (**S1**) (986 mg, 5.00 mmol, 1.0 equiv), EDCI·HCl (2.40 g, 12.5 mmol, 2.5 equiv), N-Boc-glycylglycine (1.16 g, 4.99 mmol, 1.0 equiv), and DMAP (61.1 mg, 0.500 mmol, 10 mol%) in CH₂Cl₂ (50 mL, 0.10 M). Oxime ester **1u** was obtained after column chromatography (100% n-pentane to n-pentane/EtOAc = 1/2) as a white solid (709 mg, 1.72 mmol, 34%). ¹H NMR (400 MHz, CDCl₃) δ = 1.46 (s, 9H), 3.80 (d, J = 5.9 Hz, 2H), 4.18 (d, J = 5.3 Hz, 2H), 5.10 (s, 1H), 6.64 (t, J = 5.3 Hz, 1H), 7.28 – 7.33 (m, 2H), 7.34 – 7.41 (m, 2H), 7.42 – 7.53 (m, 4H), 7.53 – 7.60 (m, 2H) ppm. ¹³C NMR (101 MHz, CDCl₃) δ = 28.4, 40.6, 44.2, 80.5, 128.4, 128.6, 128.9, 129.2, 130.0, 131.3, 132.1, 134.4, 156.1, 165.7, 168.4, 169.9 ppm. HRMS (ESI): m/z calculated for [C₂₂H₂₅N₃O₅Na]⁺ [M+Na]⁺: 434.1686; found: 434.1687.

$Benzyl~(4,7,10-trioxo-1,1-diphenyl-3-oxa-2,6,9-triazaundec-1-en-11-yl) carbamate\\ (1v)$

Following **general procedure GP1**, the title compound was prepared from diphenylmethanone oxime (**S1**) (296 mg, 1.50 mmol, 1.0 equiv), EDCI-HCl (719 mg, 3.75 mmol, 2.5 equiv), ((benzyloxy)carbonyl)glycylglycylglycine (485 mg, 1.50 mmol, 1.0 equiv.), and DMAP (36.7 mg, 0.300 mmol, 20 mol%) in CH₂Cl₂ (10 mL, 0.15 M). Oxime ester **1v** was obtained after column chromatography *n*-pentane/EtOAc = 1/6 to 1/9) as a colorless solid (563 mg, 1.12 mmol, 75%). ¹H NMR (400 MHz, CDCl₃) δ = 3.84 (d, J = 5.8 Hz, 2H), 3.93 (d, J = 5.7 Hz, 2H), 4.03 (d, J = 5.5 Hz, 2H), 5.06 (s, 2H), 5.97 (t, J = 5.7 Hz, 1H), 7.23 – 7.38 (m, 11H), 7.40 – 7.49 (m, 4H), 7.49 – 7.54 (m, 2H) ppm. ¹³C NMR (101 MHz, CDCl₃) δ = 40.5, 42.8, 44.6, 67.3, 128.1, 128.3, 128.4, 128.6, 128.6, 129.0, 129.1, 130.0, 131.3, 132.0, 134.4, 136.3, 157.1, 165.7, 168.6, 169.7, 170.3 ppm. HRMS (ESI): m/z calculated for [C₂₇H₂₆N₄O₆Na]⁺ [M+Na]⁺: 525.1745; found: 525.1739.

1w

Diphenylmethanone *O*-stearoyl oxime (1w)

Following **general procedure GP1**, the title compound was prepared from diphenylmethanone oxime (**S1**) (1.97 g, 9.99 mmol, 1.0 equiv), EDCI·HCl (4.79 g, 25.0 mmol, 2.5 equiv), stearic acid (2.84 g, 9.98 mmol, 1.0 equiv), and DMAP (244 mg, 2.00 mmol, 20 mol%) in CH₂Cl₂ (100 mL, 0.10 M). Oxime ester **1w** was obtained after column chromatography (n-pentane/EtOAc = 30/1) as a colorless solid (4.10 g, 8.84 mmol, 88%). ¹H NMR (400 MHz, CDCl₃) δ = 0.88 (t, 3H), 1.20 – 1.30 (m, 28H), 1.53 – 1.62 (m, 2H), 2.32 (t, J = 7.5 Hz, 2H), 7.28 – 7.33 (m, 2H), 7.33 – 7.38 (m, 2H), 7.42 – 7.48 (m, 4H), 7.57 – 7.61 (m, 2H) ppm. ¹³C NMR (101 MHz, CDCl₃) δ = 14.2, 22.8, 24.8, 29.2, 29.3, 29.5, 29.5, 29.7, 29.8, 29.8, 29.8, 32.1, 33.2, 128.3, 128.5, 128.9, 129.1, 129.6, 131.0, 132.9, 134.9, 165.0, 171.3 ppm. HRMS (ESI): m/z calculated for $[C_{31}H_{45}NO_2Na]^+[M+Na]^+$: 486.3343; found: 486.3341.

Diphenylmethanone *O***-oleoyl oxime** (1x)

Following **general procedure GP1**, the title compound was prepared from diphenylmethanone oxime (**S1**) (1.97 g, 9.99 mmol, 1.0 equiv), EDCI·HC1 (4.79 g, 25.0 mmol, 2.5 equiv), oleic acid (2.82 g, 9.98 mmol, 1.0 equiv), and DMAP (244 mg, 2.00 mmol, 20 mol%) in CH₂Cl₂ (100 mL, 0.10 M). Oxime ester **1x** was obtained after column chromatography (n-pentane/EtOAc = 30/1) as a colorless solid (3.84 g, 8.32 mmol, 83%). ¹H NMR (400 MHz, CDCl₃) δ = 0.83 – 0.92 (m, 3H), 1.18 – 1.41 (m, 20H), 1.51 – 1.65 (m, 2H), 1.96 – 2.08 (m, 4H), 2.32 (t, J = 7.4 Hz, 2H), 5.29 –

5.43 (m, 2H), 7.29 - 7.38 (m, 4H), 7.40 - 7.49 (m, 4H), 7.57 - 7.63 (m, 2H) ppm. ¹³C NMR (101 MHz, CDCl₃) δ = 14.2, 22.7, 24.7, 27.2, 27.3, 29.0, 29.1, 29.1, 29.4, 29.6, 29.7, 29.8, 31.9, 33.0, 128.2, 128.4, 128.8, 129.0, 129.5, 129.7, 130.0, 130.9, 132.7, 134.8, 164.9, 171.1 ppm. HRMS (ESI): m/z calculated for [C₃₁H₄₃NO₂Na]⁺ [M+Na]⁺: 484.3186; found: 484.3182.

(Z)-Diphenylmethanone *O*-docos-13-enoyl oxime (1y)

Following **general procedure GP1**, the title compound was prepared from diphenylmethanone oxime (**S1**) (1.97 g, 9.99 mmol, 1.0 equiv), EDCI-HCl (4.79 g, 25.0 mmol, 2.5 equiv), erucic acid (3.36 g, 9.92 mmol, 1.0 equiv), and DMAP (244 mg, 2.00 mmol, 20 mol%) in CH₂Cl₂ (100 mL, 0.10 M). Oxime ester **1y** was obtained after column chromatography (n-pentane/EtOAc = 40/1) as a colorless solid (3.43 g, 6.62 mmol, 66%). ¹H NMR (400 MHz, CDCl₃) δ = 0.85 – 0.91 (m, 3H), 1.16 – 1.39 (m, 28H), 1.53 – 1.62 (m, 2H), 1.94 – 2.09 (m, 4H), 2.32 (t, J = 7.5 Hz, 2H), 5.30 – 5.40 (m, 2H), 7.29 – 7.33 (m, 2H), 7.33 – 7.39 (m, 2H), 7.41 – 7.48 (m, 4H), 7.58 – 7.61 (m, 2H) ppm. ¹³C NMR (101 MHz, CDCl₃) δ = 14.2, 22.8, 24.8, 27.3, 29.2, 29.3, 29.4, 29.5, 29.6, 29.7, 29.7, 29.7, 29.9, 29.9, 32.0, 33.2, 128.3, 128.5, 128.9, 129.1, 129.6, 130.0, 130.0, 131.0, 132.8, 134.9, 165.0, 171.3 ppm. HRMS (ESI): m/z calculated for [C₃₅H₅₁NO₂Na]⁺ [M+Na]⁺: 540.3812; found: 540.3811.

Diphenylmethanone *O*-((9Z,12Z)-octadeca-9,12-dienoyl) oxime (1z)

Following **general procedure GP1**, the title compound was prepared from diphenylmethanone oxime (**S1**) (1.97 g, 9.99 mmol, 1.0 equiv), EDCI-HCl (4.79 g, 25.0 mmol, 2.5 equiv), linoleic acid (2.80 g, 9.98 mmol, 1.0 equiv), and DMAP (244 mg, 2.00 mmol, 20 mol%) in CH₂Cl₂ (100 mL, 0.10 M). Oxime ester **1z** was obtained after column chromatography (n-pentane/EtOAc = 40/1) as a colorless solid (3.91 g, 8.51 mmol, 85%). ¹H NMR (400 MHz, CDCl₃) δ = 0.83 – 0.96 (m, 3H), 1.19 – 1.42 (m, 14H), 1.54 – 1.64 (m, 2H), 1.98 – 2.12 (m, 4H), 2.32 (t, J = 7.5 Hz, 2H), 2.73 – 2.84 (m, 2H), 5.29 – 5.43 (m, 4H), 7.29 – 7.39 (m, 4H), 7.40 – 7.49 (m, 4H), 7.57 – 7.63 (m, 2H) ppm. ¹³C NMR (101 MHz, CDCl₃) δ = 14.1, 22.6, 24.8, 25.7, 27.3, 27.3, 29.1, 29.1, 29.2, 29.4, 29.6, 31.6, 33.1, 128.0, 128.1, 128.2, 128.4, 128.8, 129.1, 129.6, 130.1, 130.3, 130.9, 132.8, 134.9, 164.9, 171.2 ppm. HRMS (ESI): m/z calculated for [C₃₁H₄₁NO₂Na]⁺ [M+Na]⁺: 482.2998; found: 482.3025.

(1S,4R)-1-((((Diphenylmethylene)amino)oxy)carbonyl)-4,7,7-trimethyl-2-oxabicyclo[2.2.1]heptan-3-one (1aa)

Following **general procedure GP1**, the title compound was prepared from diphenylmethanone oxime (**S1**) (986 mg, 5.00 mmol, 1.0 equiv), EDCI·HCl (2.40 g, 12.5 mmol, 2.5 equiv), (1*S*)-(-)-camphanic acid (991 mg, 5.00 mmol, 1.0 equiv), and DMAP (122 mg, 1.00 mmol, 20 mol%) in CH₂Cl₂ (50 mL, 0.10 M). Oxime ester **1aa** was obtained after column chromatography (n-pentane/EtOAc = 10/1 to 8/1) as a colorless solid (946 mg, 2.51 mmol, 50%). ¹H NMR (400 MHz, CDCl₃) δ = 0.80 (s, 3H), 0.81 (s, 3H), 1.04 (s, 3H), 1.60 (ddd, J = 13.4, 9.4, 4.3 Hz, 1H), 1.81 (ddd, J = 13.1, 10.7, 4.5 Hz, 1H), 1.94 (ddd, J = 13.6, 9.3, 4.5 Hz, 1H), 2.22 (ddd, J = 13.5, 10.8, 4.3 Hz, 1H), 7.29 – 7.33 (m, 2H), 7.34 – 7.40 (m, 2H), 7.41 – 7.52 (m, 4H), 7.58 – 7.66 (m, 2H) ppm. ¹³C NMR (101 MHz, CDCl₃) δ = 9.7, 16.4, 16.6, 28.9, 30.5, 54.3, 54.7,

90.6, 128.4, 128.6, 128.6, 129.2, 130.0, 131.5, 132.4, 134.0, 164.7, 167.2, 177.9 ppm. HRMS (ESI): *m/z* calculated for [C₂₃H₂₃NO₄Na]⁺[M+Na]⁺: 400.1519; found: 400.1519.

Diphenylmethanone O-(5-(2,5-dimethylphenoxy)-2,2-dimethylpentanoyl) oxime (1ac)

Following **general procedure GP1**, the title compound was prepared from diphenylmethanone oxime (**S1**) (986 mg, 5.00 mmol, 1.0 equiv), EDCI·HCl (2.40 g, 12.5 mmol, 2.5 equiv), gemfibrozil (1.25 g, 4.99 mmol, 1.0 equiv), and DMAP (61.1 mg, 0.500 mmol, 10 mol%) in CH₂Cl₂ (50 mL, 0.10 M). Oxime ester **1ac** was obtained after column chromatography (100% n-pentane to n-pentane/EtOAc = 24/1) as a colorless oil (1.03 g, 2.40 mmol, 48%). ¹H NMR (400 MHz, CDCl₃) δ = 1.12 (s, 6H), 1.52 – 1.72 (m, 4H), 2.15 (s, 3H), 2.31 (s, 3H), 3.78 (t, J = 6.1 Hz, 2H), 6.57 (s, 1H), 6.66 (d, J = 7.5 Hz, 1H), 7.00 (d, J = 7.4 Hz, 1H), 7.27 – 7.32 (m, 2H), 7.34 – 7.39 (m, 2H), 7.41 – 7.50 (m, 4H), 7.59 – 7.66 (m, 2H) ppm. ¹³C NMR (101 MHz, CDCl₃) δ = 15.9, 21.6, 25.2, 25.2, 37.1, 42.1, 68.0, 112.1, 120.8, 123.7, 128.3, 128.5, 128.5, 129.1, 129.5, 130.4, 131.1, 133.0, 134.6, 136.6, 157.1, 165.8, 174.6 ppm. HRMS (ESI): m/z calculated for [C₂₈H₃₁NO₃Na]⁺ [M+Na]⁺: 452.2196; found: 452.2193.

Diphenylmethanone *O*-(2-(4-(2,2-dichlorocyclopropyl)phenoxy)-2-methylpropanoyl) oxime (1ad)

Following **general procedure GP1**, the title compound was prepared from diphenylmethanone oxime (**S1**) (986 mg, 5.00 mmol, 1.0 equiv), EDCI-HCl (2.40 g, 12.5 mmol, 2.5 equiv), Ciprofibrate (1.88 g, 6.50 mmol, 1.3 equiv), and DMAP (122 mg, 1.00 mmol, 20 mol%) in CH₂Cl₂ (50 mL, 0.10 M). Oxime ester **1ad** was obtained after column chromatography (n-pentane /EtOAc = 50/1 to 20/1) as a colorless gum (1.74 g, 3.71 mmol, 74%). ¹H NMR (400 MHz, CDCl₃) δ = 1.50 (s, 6H), 1.78 (dd, J = 8.3, 7.4 Hz, 1H), 1.94 (dd, J = 10.7, 7.4 Hz, 1H), 2.83 (dd, J = 10.7, 8.3 Hz, 1H), 6.74 – 6.83 (m, 2H), 7.05 – 7.16 (m, 4H), 7.29 – 7.50 (m, 6H), 7.56 – 7.63 (m, 2H) ppm. ¹³C NMR (101 MHz, CDCl₃) δ = 25.4, 25.5, 26.0, 35.0, 61.0, 79.0, 119.0, 128.2, 128.4, 128.6, 128.8, 129.3, 129.7, 129.8, 131.3, 132.3, 134.5, 154.9, 166.7, 171.3 ppm. HRMS (ESI): m/z calculated for [C₂₆H₂₃NO₃Cl₂Na]⁺ [M+Na]⁺: 490.0947; found: 490.0946.

1ae

(2S,5R)-2-((((Diphenylmethylene)amino)oxy)carbonyl)-3,3-dimethyl-4-thia-1-azabicyclo[3.2.0]heptan-7-one 4,4-dioxide (1ae)

Following **general procedure GP1**, the title compound was prepared from diphenylmethanone oxime (**S1**) (1.97 g, 9.99 mmol, 1.0 equiv), EDCI·HCl (4.79 g,

25.0 mmol, 2.5 equiv), sulbactam (2.33 g, 9.99 mmol, 1.0 equiv.), and DMAP (244 mg, 2.00 mmol, 20 mol%) in CH₂Cl₂ (100 mL, 0.10 M). Oxime ester **1ae** was obtained after column chromatography (n-pentane/EtOAc = 30/1 to 3/1) as a colorless solid (2.12 g, 5.14 mmol, 51%). ¹H NMR (400 MHz, CDCl₃) δ = 1.17 (s, 3H), 1.33 (s, 3H), 3.33 – 3.47 (m, 2H), 4.33 (s, 1H), 4.45 (dd, J = 4.1, 2.3 Hz, 1H), 7.27 – 7.32 (m, 2H), 7.34 – 7.43 (m, 2H), 7.43 – 7.55 (m, 4H), 7.56 – 7.66 (m, 2H) ppm. ¹³C NMR (101 MHz, CDCl₃) δ = 18.0, 20.5, 38.5, 61.1, 62.6, 62.7, 128.2, 128.7, 128.7, 129.1, 130.0, 131.8, 132.5, 133.5, 164.2, 167.3, 170.5 ppm. HRMS (ESI): m/z calculated for [C₂₁H₂₀N₂O₅SNa]⁺ [M+Na]⁺: 435.0985; found: 435.0984.

BenzophenoneO-((3aS,3bR,7aS,8aR)-2,2,5,5-tetramethyltetrahydro-3aH-[1,3]dioxolo[4',5':4,5]furo[3,2-d][1,3]dioxine-8a-carbonyl) oxime (1af)

Following **general procedure GP1**, the title compound was prepared from diphenylmethanone oxime (**S1**) (986 mg, 5.00 mmol, 1.0 equiv), EDCI·HC1 (2.40 g, 12.5 mmol, 2.5 equiv), (-)-2,3:4,6-di-O-isopropylidene-2-keto-L-gulonic acid monohydrate (1.46 g, 5.00 mmol, 1.0 equiv), and DMAP (122 mg, 1.00 mmol, 20 mol%) in CH₂Cl₂ (50 mL, 0.10 M). Oxime ester **1af** was obtained after column chromatography (n-pentane/EtOAc = 5/1) as a colorless solid (548 mg, 1.21 mmol, 24%). ¹H NMR (400 MHz, CDCl₃) δ = 1.26 (s, 3H), 1.33 (s, 3H), 1.41 (s, 3H), 1.46 (s, 3H), 3.96 – 4.09 (m, 2H), 4.14 (q, J = 2.2 Hz, 1H), 4.28 (d, J = 2.5 Hz, 1H), 4.76 (s, 1H), 7.32 – 7.52 (m, 8H), 7.56 – 7.64 (m, 2H) ppm. ¹³C NMR (101 MHz, CDCl₃) δ = 19.1, 25.6, 27.1, 28.8, 59.9, 72.6, 74.2, 88.0, 97.6, 110.2, 114.5, 128.2, 128.5, 129.5, 129.8, 130.0, 131.1, 132.2, 134.9, 164.2, 166.7 ppm. HRMS (ESI): m/z calculated for $[C_{25}H_{27}NO_7Na]^+[M+Na]^+$: 476.1680; found: 476.1680.

Benzophenone*O*-((4*aS*,6*aS*,6*bR*,8*aR*,10*S*,12*aR*,12*bR*,14*bS*)-10-hydroxy-2,2,6*a*,6*b*,9,9,12*a*-heptamethyl-

1,2,3,4,4*a*,5,6,6*a*,6*b*,7,8,8*a*,9,10,11,12,12*a*,12*b*,13,14*b*-icosahydropicene-4*a*-carbonyl) oxime (1ag)

Following **general procedure GP1**, the title compound was prepared from diphenylmethanone oxime (**S1**) (986 mg, 5.00 mmol, 1.0 equiv), EDCI-HCl (2.40 g, 12.5 mmol, 2.5 equiv), oleanolic acid (2.28 g, 4.99 mmol, 1.0 equiv.), and DMAP (122 mg, 1.00 mmol, 20 mol%) in CH₂Cl₂ (50 mL, 0.10 M). Oxime ester **1ag** was obtained after column chromatography (n-pentane/EtOAc = 10/1 to 6/1) as a colorless solid (389 mg, 0.612 mmol, 12%). ¹H NMR (400 MHz, CDCl₃) δ = 0.67 (s, 3H), 0.76 (s, 3H), 0.79 (s, 3H), 0.85 (s, 3H), 0.86 (s, 3H), 0.89 – 1.03 (m, 6H), 1.05 (s, 3H), 1.10 – 1.22 (m, 3H), 1.28 – 1.77 (m, 16H), 1.87 (td, J = 13.5, 4.1 Hz, 1H), 2.58 (dd, J = 13.7, 4.6 Hz, 1H), 3.19 (dd, J = 10.7, 5.0 Hz, 1H), 4.75 (t, J = 3.6 Hz, 1H), 7.27 – 7.37 (m, 4H), 7.39 – 7.49 (m, 4H), 7.59 – 7.63 (m, 2H) ppm. ¹³C NMR (101 MHz, CDCl₃) δ = 15.4, 15.7, 17.2, 18.4, 23.1, 23.5, 23.5, 26.0, 27.3, 27.6, 28.2, 30.7, 32.6, 32.7, 33.1, 33.9, 37.1, 38.5, 38.9, 39.4, 40.8, 41.6, 45.9, 46.9, 47.7, 55.3, 79.1, 122.6, 128.2, 128.4, 128.6, 129.0, 129.4, 130.9, 133.3, 134.8, 143.4, 164.8, 174.6 ppm. HRMS (ESI): m/z calculated for [C₄₃H₅₇NO₃Na]⁺ [M+Na]⁺: 658.4231; found: 658.4229.

1ah

BenzophenoneO-((1R,4aS,10aR)-7-isopropyl-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene-1-carbonyl) oxime (1ah)

Following **general procedure GP1**, the title compound was prepared from diphenylmethanone oxime (**S1**) (1.97 g, 9.99 mmol, 1.0 equiv), EDCI·HCl (4.80 g, 25.0 mmol, 2.5 equiv), dehydroabietic acid (3.90 g, 13.0 mmol, 1.3 equiv), and DMAP (244 mg, 2.00 mmol, 20 mol%) in CH₂Cl₂ (100 mL, 0.10 M). Oxime ester **1ah** was obtained after column chromatography (n-pentane /EtOAc = 100/1 to 30/1) as a white sticky solid (789 mg, 1.64 mmol, 16%). ¹H NMR (400 MHz, CDCl₃) δ = 1.12 – 1.18 (m, 6H), 1.25 (dd, J = 6.9, 1.1 Hz, 6H), 1.29 – 1.47 (m, 2H), 1.56 – 1.81 (m, 5H), 2.03 (dd, J = 12.5, 2.2 Hz, 1H), 2.21 – 2.29 (m, 1H), 2.62 (ddd, J = 17.6, 11.2, 7.6 Hz, 1H), 2.75 (dd, J = 17.0, 7.1 Hz, 1H), 2.84 (p, J = 6.9 Hz, 1H), 6.84 (d, J = 2.0 Hz, 1H), 6.98 (dd, J = 8.1, 2.0 Hz, 1H), 7.11 (d, J = 8.2 Hz, 1H), 7.24 – 7.40 (m, 7H), 7.40 – 7.49 (m, 1H), 7.60 – 7.67 (m, 2H) ppm. ¹³C NMR (101 MHz, CDCl₃) δ = 16.3, 18.6, 21.7, 24.1, 24.2, 25.1, 29.8, 33.6, 36.8, 37.0, 38.0, 44.6, 47.7, 123.9, 124.1, 127.0, 128.2, 128.5, 128.5, 129.1, 129.4, 131.1, 133.0, 134.6, 134.8, 145.7, 146.9, 165.8, 175.5 ppm. HRMS (ESI): m/z calculated for [C₃₃H₃₇NO₂Na]⁺ [M+Na]⁺: 502.2717; found: 502.2715.

1ai

(2S,4aS,6aS,6bR,8aR,10S,12aS,12bR,14bR)-2-

((((Diphenylmethylene)amino)oxy)carbonyl)-10-hydroxy-2,4a,6a,6b,9,9,12a-heptamethyl-1,3,4,4a,5,6,6a,6b,7,8,8a,9,10,11,12,12a,12b,14b-octadecahydropicen-13(2H)-one (1ai)

Following **general procedure GP1**, the title compound was prepared from diphenylmethanone oxime (**S1**) (493 mg, 2.50 mmol, 1.0 equiv), EDCI·HCl (1.19 g, 6.21 mmol, 2.5 equiv), enoxolone (1.18 g, 2.51 mmol, 1.0 equiv), and DMAP (61.1 mg, 0.500 mmol, 20 mol%) in CH₂Cl₂ (25 mL, 0.10 M). Oxime ester **1ai** was obtained after column chromatography (n-pentane/EtOAc = 4/1 to 2/1) as a colorless solid (1.04 g,

1.60 mmol, 64%). ¹H NMR (400 MHz, CDCl₃) $\delta = 0.63 - 0.71$ (m, 1H), 0.76 (s, 3H), 0.80 (s, 3H), 0.91 – 1.01 (m, 5H), 1.06 (s, 3H), 1.09 (s, 3H), 1.12 (s, 3H), 1.14 – 1.32 (m, 7H), 1.34 – 1.84 (m, 11H), 1.95 (td, J = 13.6, 4.5 Hz, 1H), 2.06 (dd, J = 13.6, 3.6 Hz, 1H), 2.28 (s, 1H), 2.79 (dt, J = 13.4, 3.6 Hz, 1H), 3.22 (dd, J = 10.7, 5.7 Hz, 1H), 5.39 (s, 1H), 7.27 – 7.31 (m, 2H), 7.32 – 7.39 (m, 2H), 7.39 – 7.52 (m, 4H), 7.59 – 7.64 (m, 2H) ppm. ¹³C NMR (101 MHz, CDCl₃) $\delta = 15.7$, 16.5, 17.6, 18.8, 23.6, 26.5, 26.5, 27.4, 28.2, 28.4, 28.4, 31.0, 31.9, 32.9, 37.2, 37.7, 39.2, 39.3, 40.9, 43.2, 44.0, 45.4, 48.0, 55.1, 61.9, 78.9, 128.3, 128.5, 128.5, 128.6, 129.0, 129.7, 131.1, 132.8, 134.5, 165.9, 168.7, 173.5, 200.0 ppm. HRMS (ESI): m/z calculated for [C₄₃H₅₅NO₄Na]⁺ [M+Na]⁺: 672.4023; found: 672.4024

(8R,9S,10S,13R,14S,17R)-17-((R)-5-(((Diphenylmethylene)amino)oxy)-5-oxopentan-2-yl)-10,13-dimethyldecahydro-1H-cyclopenta[a]phenanthrene-3,7,12(2H,4H,8H)-trione (1aj)

Following **general procedure GP1**, the title compound was prepared from diphenylmethanone oxime (**S1**) (986 mg, 5.00 mmol, 1.0 equiv), EDCI·HCl (2.40 g, 12.5 mmol, 2.5 equiv), dehydrocholic acid (2.01 g, 4.99 mmol, 1.0 equiv), and DMAP (61.1 mg, 0.500 mmol, 10 mol%) in CH₂Cl₂ (50 mL, 0.10 M). Oxime ester **1aj** was obtained after column chromatography (100% n-pentane to 100% EtOAc) as a white solid (1.30 g, 2.23 mmol, 45%). ¹H NMR (400 MHz, CDCl₃) δ = 0.80 (d, J = 6.4 Hz, 3H), 1.04 (s, 3H), 1.19 – 1.37 (m, 4H), 1.39 (s, 3H), 1.61 (td, J = 14.1, 5.3 Hz, 1H), 1.76 – 2.48 (m, 16H), 2.78 – 2.96 (m, 3H), 7.28 – 7.40 (m, 4H), 7.41 – 7.49 (m, 4H), 7.55 – 7.62 (m, 2H) ppm. ¹³C NMR (101 MHz, CDCl₃) δ = 12.0, 18.7, 22.0, 25.3, 27.6,

30.3, 30.4, 35.4, 35.4, 36.1, 36.6, 38.8, 42.9, 45.1, 45.7, 45.7, 47.0, 49.1, 51.9, 57.0, 128.3, 128.5, 128.9, 129.2, 129.7, 131.0, 132.8, 134.9, 165.0, 171.5, 208.8, 209.1, 212.1 ppm. HRMS (ESI): *m/z* calculated for [C₃₇H₄₃NO₅Na]⁺ [M+Na]⁺: 604.3033; found: 604.3032.

Benzophenone O-((4R)-4-((3R,8R,9S,10S,13R,14S,17R)-3-hydroxy-10,13-dimethylhexadecahydro-1H-cyclopenta[a]phenanthren-17-yl)pentanoyl) oxime (1ak)

Following **general procedure GP1**, the title compound was prepared from diphenylmethanone oxime (**S1**) (986 mg, 5.00 mmol, 1.0 equiv), EDCI·HCl (2.40 g, 12.5 mmol, 2.5 equiv), lithocholic acid (1.88 g, 4.99 mmol, 1.0 equiv), and DMAP (122 mg, 1.00 mmol, 20 mol%) in CH₂Cl₂ (50 mL, 0.10 M). Oxime ester **1ak** was obtained after column chromatography (n-pentane /EtOAc = 5/1 to 1/1) as a white solid (1.65 g, 2.97 mmol, 59%). ¹H NMR (400 MHz, CDCl₃) δ = 0.61 (s, 3H), 0.85 (d, J = 6.4 Hz, 3H), 0.91 (s, 3H), 0.95 – 1.44 (m, 17H), 1.47 – 1.58 (m, 3H), 1.62 – 1.89 (m, 6H), 1.93 (dt, J = 12.4, 3.0 Hz, 1H), 2.17 – 2.44 (m, 2H), 3.62 (tt, J = 11.1, 4.7 Hz, 1H), 7.29 – 7.39 (m, 4H), 7.41 – 7.50 (m, 4H), 7.55 – 7.63 (m, 2H) ppm. ¹³C NMR (101 MHz, CDCl₃) δ = 12.2, 18.3, 20.9, 23.5, 24.3, 26.5, 27.3, 28.2, 30.1, 30.7, 30.9, 34.7, 35.4, 35.5, 36.0, 36.6, 40.3, 40.6, 42.2, 42.9, 56.0, 56.6, 72.0, 128.3, 128.5, 128.9, 129.2, 129.6, 131.0, 132.8, 134.9, 164.9, 171.8 ppm. HRMS (ESI): m/z calculated for [C₃₇H₄₉NO₃Na]⁺ [M+Na]⁺: 578.3605; found: 578.3602.

Bis(4-fluorophenyl)methanone *O*-pivaloyl oxime (1al)

A round-bottom flask was charged with hydroxylammonium chloride (1.04 g, 15.0 mmol, 1.5 equiv), sodium acetate (1.64 g, 20.0 mmol, 2.0 equiv), and bis(4-fluorophenyl)methanone (2.18 g, 9.99 mmol, 1.0 equiv). Distilled water (4 mL), and ethanol (16 mL) were added and the resulting mixture was stirred at reflux for 18 h. After being cooled down to r.t., the ethanol was removed under reduced pressure. Distilled water (10 mL) was added and the mixture was extracted with CH₂Cl₂ (3x 20 mL). All organic layers were combined, washed with distilled water (2x 5 mL), dried over MgSO₄, and concentrated under reduced pressure. The residue was dried under vacuum and used for the next reaction step without further purification.

The residue was added to a Schlenk tube and the tube was evacuated and backfilled with argon three times. Dry CH₂Cl₂ (30 mL), triethylamine (1.52 g, 15.0 mmol, 1.5 equiv), and then pivaloyl chloride (dropwise; 1.33 g, 11.0 mmol, 1.1 equiv) were added at r.t., and the resulting mixture was stirred at r.t. for 16 h. Distilled water (20 mL) was added, and stirring was continued for 10 more minutes. The layers were separated and the aqueous layer was extracted with CH₂Cl₂ (3x 50 mL). All organic layers were combined, washed with brine (10 mL), dried over MgSO₄, and concentrated under reduced pressure. Column chromatography on silica gel (pentane/ethyl acetate = 50/1 to 15/1) gave the title compound as a white solid (2.39 g, 7.53 mmol, 75%). ¹H NMR (400 MHz, CDCl₃) δ = 1.11 (s, 9H), 7.01-7.11 (m, 2H), 7.12-7.22 (m, 2H), 7.27-7.34 (m, 2H), 7.55-7.65 (m, 2H) ppm. ¹³C{¹H, ¹⁹F} NMR (126 MHz, CDCl₃) δ = 26.9, 38.5, 115.4, 115.6, 128.4, 130.6, 130.8, 131.0, 163.2, 163.5, 164.5, 175.0 ppm. HRMS (ESI): m/z calculated for [C₁₈H₁₇NO₂F₂Na] [M+Na⁺]: 340.1120; found: 340.1113.

(4-Methoxyphenyl)(phenyl)methanone *O*-pivaloyl oxime (1am)

A Schlenk tube was charged with oxime S2 (1.50 g, 6.60 mmol, 1.0 equiv) and was then evacuated and backfilled with argon three times. Dry CH₂Cl₂ (20 mL), pyridine (574 mg, 7.26 mmol, 1.1 equiv), and then pivaloyl chloride (dropwise; 796 mg, 6.60 mmol, 1.0 equiv) were added at r.t., and the resulting mixture was stirred at r.t. for 16 h. Distilled water (20 mL) was added, and stirring was continued for 10 more minutes. The layers were separated and the aqueous layer was extracted with CH₂Cl₂ (3x 50 mL). All organic layers were combined, washed with brine (10 mL), dried over MgSO₄, and concentrated under reduced pressure. The title compound was obtained without further purification as a white solid (1.96 g, 6.29 mmol, 95%) and with an E/Zratio of 53:47. Combined NMR data for both the isomers are reported here. ¹H NMR $(400 \text{ MHz}, \text{CDCl}_3) \delta = 1.00 - 1.22 \text{ (m, 9H)}, 3.77 - 3.92 \text{ (m, 3H)}, 6.82 - 6.91 \text{ (m, 1H)}, 6.92 - 6.91 \text{ (m, 1H)}$ 7.00 (m, 1H), 7.24-7.31 (m, 2H), 7.33-7.39 (m, 1H), 7.41-7.48 (m, 2H), 7.53-7.63 (m, 2H) ppm. ¹³C NMR (101 MHz, CDCl₃) $\delta = 27.1, 27.2, 38.6, 38.7, 55.5, 55.5, 113.5,$ 113.9, 124.9, 127.0, 128.2, 128.4, 128.5, 129.3, 129.4, 130.7, 130.8, 131.0, 133.2, 135.4, 160.6, 162.0, 165.2, 165.5, 175.5, 175.5 ppm. HRMS (ESI): m/z calculated for $[C_{19}H_{21}NO_3Na]$ $[M+Na^+]$: 334.1414; found: 334.1408.

(4-Bromophenyl)(phenyl)methanone *O*-pivaloyl oxime (1an)

A round-bottom flask was charged with hydroxylammonium chloride (1.04 g, 15.0 mmol, 1.5 equiv), sodium acetate (1.64 g, 20.0 mmol, 2.0 equiv), and (4-

bromophenyl)(phenyl)methanone (2.61 g, 10.0 mmol, 1.0 equiv). Distilled water (4 mL), and ethanol (16 mL) were added and the resulting mixture was stirred at reflux for 18 h. After being cooled down to r.t., the ethanol was removed under reduced pressure. Distilled water (10 mL) was added and the mixture was extracted with CH₂Cl₂ (3x 20 mL). All organic layers were combined, washed with distilled water (2x 5 mL), dried over MgSO₄, and concentrated under reduced pressure. The residue was dried under vacuum and used for the next reaction step without further purification.

The residue was added to a Schlenk tube and the tube was evacuated and backfilled with argon three times. Dry CH₂Cl₂ (30 mL), triethylamine (1.52 g, 15.0 mmol, 1.5 equiv), and then pivaloyl chloride (dropwise; 1.33 g, 11.0 mmol, 1.1 equiv) were added at r.t., and the resulting mixture was stirred at r.t. for 16 h. Distilled water (20 mL) was added, and stirring was continued for 10 more minutes. The layers were separated and the aqueous layer was extracted with CH₂Cl₂ (3x 50 mL). All organic layers were combined, washed with brine (10 mL), dried over MgSO₄, and concentrated under reduced pressure. Column chromatography on silica gel (pentane/ethyl acetate = 50/1 to 10/1) gave the title compound as a white solid (1.70 g, 4.72 mmol, 47%). ¹H NMR (400 MHz, CDCl₃) δ = 1.12 (s, 9H), 7.16-7.24 (m, 2H), 7.34-7.40 (m, 2H), 7.43-7.49 (m, 1H), 7.55-7.65 (m, 4H) ppm. ¹³C NMR (101 MHz, CDCl₃) δ = 27.1, 38.6, 124.0, 128.6, 129.0, 130.5, 131.3, 131.6, 131.7, 134.3, 164.5, 175.2 ppm. HRMS (ESI): m/z calculated for [C₁₈H₁₈NO₂BrNa] [M+Na⁺]: 382.0413; found: 382.0410.

(E)-1-Phenylethan-1-one O-pivaloyl oxime (1ao)

The title compound was prepared similar to a reported procedure.^[4] A Schlenk tube was charged with oxime **S3** (676 mg, 5.00 mmol, 1.0 equiv) and was then evacuated and backfilled with argon three times. Then, dry CH₂Cl₂ (10 mL) was added and the mixture was cooled to 0 °C. Dry NEt₃ (759 mg, 7.50 mmol, 1.5 equiv) was added and then, a solution of pivaloyl chloride (603 mg, 5.00 mmol, 1.0 equiv) in dry CH₂Cl₂ (3 mL) was

added dropwise. The mixture was stirred at r.t. for 1 h and was then quenched by the addition of distilled water (10 mL). The phases were separated and the aqueous layer was extracted with CH₂Cl₂ (3x 30 mL). All organic phases were combined, washed with sat. aq. NaHCO₃ (10 mL) and brine (10 mL). After drying over MgSO₄ and removal of the solvent under reduced pressure, the crude was purified by column chromatography on silica gel (pentane/ethyl acetate = 10/1 to 7/1) to afford the title compound as a white solid (1.05 g, 4.79 mmol, 96%). ¹H NMR (400 MHz, CDCl₃) δ = 1.34 (s, 9H), 2.39 (s, 3H), 7.34-7.49 (m, 3H), 7.72-7.80 (m, 2H) ppm. ¹³C NMR (101 MHz, CDCl₃) δ = 14.5, 27.5, 39.0, 127.2, 128.7, 130.7, 135.1, 163.3, 175.2 ppm.

2.3. Preparation of styrene derivatives

General procedure for the synthesis of olefins 2b-2e (GP2)

General procedure (**GP2**):^[5] To a flame-dried 25 mL round-bottom flask, Ph₃PMeBr (1.2 equiv) was added. Under argon atmosphere, 10 mL of tetrahydrofuran and t-BuOK (1.2 equiv) were added at 0 °C. After 1 h, ketone (1.0 equiv) was added at room temperature. When the raw materials are exhausted, the reaction was quenched with ammonium chloride solution, extracted with petroleum ether (20 mL \times 3), dried over anhydrous sodium sulfate, and then purified by flash column chromatography (pentane).

4,4'-(Ethene-1,1-diyl)bis(methylbenzene) (2b)

Following the GP2, **2b** was obtained as a white solid (239 mg, 57% yield). ¹H NMR (400 MHz, CDCl₃): δ = 2.38 (s, 6H), 5.40 (s, 2H), 7.14 – 7.16 (m, 4H), 7.24 – 7.26 (m, 4H) ppm. ¹³C NMR (101 MHz, CDCl₃) δ = 21.2, 113.0, 128.2, 128.8, 137.4, 138.8, 149.8 ppm.

4,4'-(Ethene-1,1-diyl)bis(chlorobenzene) (2c)

Following the GP2, **2c** was obtained as a white solid (502 mg, 73% yield). ¹H NMR (400 MHz, CDCl₃): $\delta = 5.46$ (s, 2H), 7.23 - 7.26 (m, 4H), 7.29 - 7.32 (m, 4H) ppm. ¹³C NMR (101 MHz, CDCl₃) $\delta = 115.2$, 128.6, 129.6, 134.0, 139.5, 148.0 ppm.

4,4'-(Ethene-1,1-diyl)bis(bromobenzene) (2d)

Following the GP2, **2d** was obtained as a white solid (134 mg, 40% yield). ¹H NMR (400 MHz, CDCl₃): $\delta = 5.46$ (s, 2H), 7.17 - 7.20 (m, 4H), 7.45 - 7.48 (m, 4H) ppm. ¹³C NMR (101 MHz, CDCl₃) $\delta = 115.3$, 122.2, 129.9, 131.6, 140.0, 148.1 ppm.

2e

5-Methylene-10,11-dihydro-5*H*-dibenzo[*a*,*d*][7]annulene (2e)

Following the GP2, **2e** was obtained as a white solid (274 mg, 66% yield). ¹H NMR (400 MHz, CDCl₃): δ = 3.26 (s, 4H), 5.54 (s, 2H), 7.22 – 7.24 (m, 2H), 7.27 – 7.34 (m, 4H), 7.46 – 7.49 (m, 2H) ppm. ¹³C NMR (101 MHz, CDCl₃) δ = 33.4, 117.6, 126.3, 127.8, 128.3, 129.0, 138.5, 141.3, 152.0 ppm.

2-Tosylethyl 4-vinylbenzoate (2m)

The title compound was prepared similar to an adapted literature procedure. [6] To a stirred solution of carboxylic acid (444 mg, 3.00 mmol, 1.0 equiv.) and DCC

(dicyclohexylcarbodiimide) (1.24 g, 6.01 mmol, 2.0 equiv.) in CH₂Cl₂ (25 mL) were added DMAP (4-dimethylaminopyridine) (55.0 mg, 0.450 mmol, 15 mol%) and 2-tosylethan-1-ol (600 mg, 3.00 mmol, 1.0 equiv.). The reaction mixture was stirred at room temperature overnight. After filtration, the filtrate was concentrated in vacuo and the residue was purified by column chromatography (pentane/EtOAc = 10/1) to afford ester **2m** as a white solid (510 mg, 1.54 mmol, 51% yield). ¹H NMR (400 MHz, CDCl₃) δ = 2.34 (s, 3H), 3.59 (t, J = 5.9 Hz, 2H), 4.64 (t, J = 5.9 Hz, 2H), 5.45 – 5.33 (m, 1H), 5.86 (dd, J = 17.6, 0.7 Hz, 1H), 6.73 (dd, J = 17.6, 10.9 Hz, 1H), 7.30 – 7.26 (m, 2H), 7.39 – 7.34 (m, 2H), 7.70 – 7.64 (m, 2H), 7.83 – 7.76 (m, 2H) ppm. ¹³C NMR (101 MHz, CDCl₃) δ = 21.7, 55.4, 58.5, 117.0, 126.1, 128.2, 130.1, 130.2, 136.0, 136.7, 142.4, 145.1, 165.7 ppm. HRMS (ESI): m/z calculated for [C₁₈H₁₈O₄SNa]⁺ [M+Na]⁺: 353.0818; found: 353.0813.

3. Reaction development

3.1. Optimization of the reaction conditions

Table S1. Optimization of the reaction conditions^[a,b]

Entry	Photocatalyst	Blue light	1a (mmol)	2a (mmol)	3a (mmol)	Solvent (0.1 M)	Yield of 4 (%) ^[b]
		(nm)					
1	Thioxanthone	405	0.3	0.2	0.4	EtOAc	63, 60 ^[c]
2	-	405	0.3	0.2	0.4	EtOAc	N.R.
3	Thioxanthone	-	0.3	0.2	0.4	EtOAc	N.R.
4	Thioxanthone	450	0.3	0.2	0.4	EtOAc	N.R.
5	Thioxanthone	405	0.3	0.2	0.4	CH_2Cl_2	56
6	Thioxanthone	405	0.3	0.2	0.4	Acetone	54
7	Thioxanthone	405	0.3	0.2	0.4	MeCN	57

8	Thioxanthone	405	0.3	0.2	0.4	DCE	48	_
9	[Ru	450	0.3	0.2	0.4	EtOAc	N.R.	
	$(bpy)_3](PF_6)_2$							
10	[Ir-F]	450	0.3	0.2	0.4	EtOAc	50	
11	Thioxanthone	405	0.3	0.2	0.4	EtOAc	53	
						(0.05		
						M)		
12	Thioxanthone	405	0.3	0.2	0.3	EtOAc	58	
13	Thioxanthone	405	0.2	0.4	0.4	EtOAc	53	
	2+ 2PF ₆	_	'Bu F ₃ C	E F]+ PF ₆ F			
	[Ru (bpy) ₃](PF ₆) ₂		[lr(dF(CF ₃)pp	y) ₂ (dtbbpy)](Pl	F ₆)	Thioxa	anthone	

[a] Reaction conditions: A mixture of **1a**, **2a**, **3a**, photocatalyst (10 mol% for thioxanthone, 1 mol% for others), and solvent (0.1 or 0.05 M) was irradiated by blue LEDs ((18 W, $\lambda_{max} = 405$ nm; 30 w, $\lambda_{max} = 450$ nm) under argon at room temperature for 12 h. [b] NMR yields were given. [c] Isolated yields were given. [Ir-F]: [Ir(dF(CF₃)ppy)₂(dtbbpy)](PF₆).

3.2. Sensitivity assessment

To evaluate the sensitivity of the reaction with respect to small changes in the reaction conditions, a sensitivity assessment according to a procedure from Glorius was conducted.^[7]

Preparation of stock solution 1 (oxime ester 1a): A Schlenk tube was charged with a magnetic stirring bar and oxime ester **1a** (633 mg, 2.25 mmol, 1.5 equiv). The tube was evacuated and backfilled with argon three times and dry EtOAc (6.0 mL) was added.

The mixture was stirred until a clear solution was obtained. The effect of the oxime ester **1a** on the volume of the stock solution was neglected in the following.

Preparation of stock solution 2 (1,1-diphenylethylene (2a) and acrylonitrile (3a)):

A Schlenk tube was charged with a magnetic stirring bar and was evacuated and backfilled with argon three times. 1,1-Diphenylethylene (2a, 271 mg, 1.50 mmol, 1.0 equiv), acrylonitrile (3a, 160 mg, 3.02 mmol, 2.0 equiv), and dry EtOAc (6.0 mL) were added and the solution was stirred for 5 minutes to ensure complete mixing. The effect of alkenes 2a and 3a on the volume of the stock solution was neglected in the following.

Reaction set-up: 11 Schlenk tubes were each charged with a magnetic stirring bar and thioxanthone (each 2.1 mg, 9.9 μmol, 10 mol%). The tubes were evacuated and backfilled with argon three times. To each tube, **stock solution 1** (0.40 mL), **stock solution 2** (0.40 mL), and dry EtOAc (0.20 mL) were added. The tubes were sealed and irradiated at 405 nm for 12 h (r.t.) in the standard photoreactor. Deviations from this procedure are described below. Then, the NMR yields were determined using CH₂Br₂ as internal standard.

Large scale reaction: A Schlenk tube was charged with a magnetic stirring bar, oxime ester **1a** (422 mg, 1.50 mmol, 1.5 equiv), and thioxanthone (21.2 mg, 99.9 μmol, 10 mol%). The Schlenk tube was evacuated and backfilled with argon three times and then, dry EtOAc (10 mL, 0.10 M), 1,1-diphenylethylene (**2a**, 181 mg, 1.00 mmol, 1.0 equiv), and acrylonitrile (**3a**, 106 mg, 2.00 mmol, 2.0 equiv) were added. The tube was sealed and irradiated at 405 nm for 12 h at r.t. (see picture below). After that, the NMR yield was determined using CH₂Br₂ as internal standard.

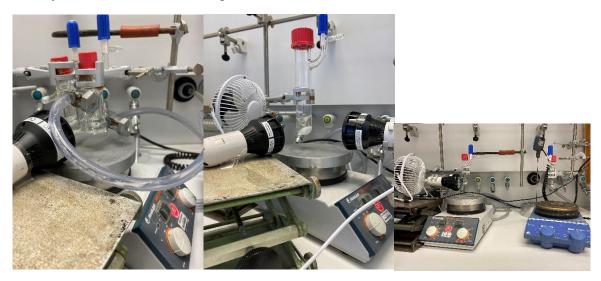


Fig. S3. Special experimental set-ups used for the low-temperature reaction (left), the large scale reaction (middle), and the high- and low-intensity reactions (right).

Table S2. Results of the sensitivity assessment.

Entry	Experiment	Notes	Relative difference in yield (%)	
1	Standard	/	/	
2	Low concentration	+100 µL EtOAc	-6	
3	High concentration	-100 μL EtOAc	0	
4	Low intensity	One lamp 32 cm away from reaction	-7	
	·	(see picture)		
5	High intensity	One lamp 2 cm away from reaction	-20	
		(see picture)		
6	High H ₂ O	+5 μL H ₂ O	-4	
7	Low O_2	Freeze-pump-thaw 3x	+7	
8	High O ₂	Under air	-67	
9	Low temperature	rature Water-cooled Schlenk tube (see		
picture); Yield is deviation from				
		control reaction with water-cooled		
		Schlenk tube filled with water but		
		turned off flow		
10	High temperature	Standard photoreactor with fans	-19	
		turned off		
11	Large scale	Reaction on 1 mmol scale as -17		
		described above and in the picture		

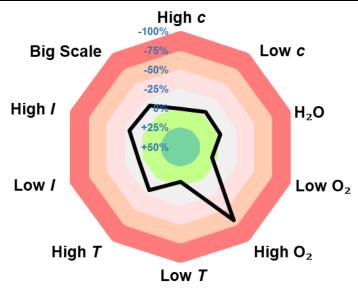


Fig. S4. Sensitivity screening radar diagram.

3.3. Additive-based robustness screening

The reaction's tolerance of functional groups and heterocycles was initially evaluated by conducting an additive-based robustness screening according to a simplified procedure from Glorius.^[8]

Preparation of stock solution 3: A Schlenk tube was charged with a magnetic stirring bar and oxime ester **1a** (844 mg, 3.00 mmol, 1.5 equiv). The tube was evacuated and backfilled with argon three times. Then, dry EtOAc (20 mL, 0.10 M), 1,1-diphenylethylene (**2a**, 360 mg, 2.00 mmol, 1.0 equiv), and acrylonitrile (**3a**, 212 mg, 4.00 mmol, 2.0 equiv) were added. The mixture was stirred until a clear solution was obtained. The effect of oxime ester **1a**, 1,1-diphenylethylene (**2a**), and acrylonitrile (**3a**) on the volume of the stock solution was neglected in the following.

Reaction set-up: 16 Schlenk tubes were each charged with a magnetic stirring bar, thioxanthone (each 2.1 mg, 9.9 μ mol, 10 mol%), and the additive (if solid; 0.10 mmol, 1.0 equiv). The Schlenk tubes were evacuated and backfilled with argon three times and then, the prepared stock solution 3 (1.0 mL) was added to each Schlenk tube, followed by the additive (if liquid; 0.10 mmol, 1.0 equiv). The tubes were sealed and irradiated at 405 nm for 12 h at r.t. The additive recovery was then determined by GC-FID (one-point-calibration). The GC samples were prepared by adding mesitylene – as internal standard – to the rection mixture and then adding 40 μ L of the respective reaction mixture to a short pad of silica – Celite® for the reaction with acetanilide – and eluting with EtOAc (2.0 mL). All GC samples were added back to the respective reaction mixture after measurement and the product yield was determined by ¹H NMR using CH₂Br₂ as internal standard.

Table S3. Results of the additive-based robustness screening. [a,b]

Entry	Additive	Yield Additive	Yield Product	
1	NH ₂	34	8	aniline
2	46	95	44	1-decyne

3	₩ OH	96	57	1-nonanol
4	\	97	45	1-dodecene
5	OnBu	87	51	2-butylfuran
6	Me Me	79	59	3,5-dimethylpyridine
7	N-Bn	90	44	benzylpyrrole
8	S	88	50	benzothiazol
9	0	98	55	6-undecanone
10	√/ ₇ CN	96	60	decanenitrile
11	HN Ph	84	50	acetanilide
12		98	56	bromobenzene
13	⟨Br	92	62	chromanone
14	OMe	90	53	benzaldehyde dimethyl acetal
15	Н	90	48	benzaldehyde
16	none	none	64	control
		Average	Average	
		88	49	

[a] Colorcoding for additive recovery: Green (>66%), yellow (33-66%), and red (<33%). [b] Colorcoding for product yield: Green (>42%), yellow (21-42%), and red (<21%).

Additive recovery 15 N Vield 1 100%

Product yield 15 N vield 100%

Fig. S5. Additive-based robustness screening results depicted as the typical bar charts.

3.4. TEMPO trapping experiment

In an oven-dried 10 ml Schlenk tube equipped with a PTFE-coated rare-earth "extra power" oval stirring bar, oxime ester **1a** (42.2 mg, 0.15 mmol), thioxanthone (2.1 mg, 10 mol%), and 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO; 15.7 mg, 0.1 mmol) were charged under air, then the vessel was evacuated and re-filled with argon for four times. Dry EtOAc (1.0 mL, 0.1 M), styrene **2a** (18.0 mg, 0.1 mmol), and Michael acceptor **3a** (10.6 mg, 0.2 mmol) were added under argon counter flow. The vessel was sealed with the screw cap, then irradiated at 405 nm using the described set-up for 12 hours. After irradiation, the reaction yield was determined by ¹H NMR spectroscopy using CH₂Br₂ as internal standard and the reaction was further analyzed by ESI-HRMS. HRMS (ESI) for **5**: m/z calculated for [C₁₆H₃₀N₂ONa] [M+Na⁺]: 289.2250, found: 289.2247.

3.5. Two component reactions of 1a with 2a or 3a

N-(3,3-Dimethyl-1,1-diphenylbutyl)-1,1-diphenylmethanimine (6)

In an oven-dried 10 ml Schlenk tube equipped with a PTFE-coated rare-earth "extra power" oval stirring bar, oxime ester 1a (84.3 mg, 0.3 mmol) and thioxanthone (4.2 mg, 10 mol%) were charged under air, then the vessel was evacuated and re-filled with argon for four times. Dry EtOAc (2.0 mL, 0.1 M) and styrene 2a (36.0 mg, 0.2 mmol) were added under argon counter flow. The vessel was sealed with the screw cap, then irradiated at 405 nm using the described set-up for 12 hours. After irradiation, the resulting homogenous solution was transferred to a 25 mL round bottom flask with aid of DCM (2 x 3 mL). NEt₃ (approx. 0.5 mL) and SiO₂ were added to this solution and the volatiles were removed under reduced pressure, affording a powder which was loaded on column. Purification by flash column chromatography on SiO₂ (pre-basified with NEt₃) with pentane as eluent afforded the title compound 6 (57 mg, 68%) as a colorless oil. ¹H NMR (400 MHz, CDCl₃): $\delta = 0.76$ (s, 9H), 2.50 (s, 2H), 6.43-6.58 (m, 2H), 6.71-7.22 (m, 11H), 7.30-7.61 (m, 5H), 7.67-7.79 (m, 2H) ppm. ¹³C NMR (101 MHz, CDCl₃): δ = 32.1, 32.3, 52.3, 68.8, 125.6, 126.6, 127.2, 127.6, 127.7, 128.1, 128.5, 129.7, 139.0, 142.2, 151.3, 164.8 ppm. HRMS (ESI): m/z calculated for [C₃₁H₃₁NNa] [M+Na⁺]: 440.2349, found: 440.2347.

Thioxanthone (10 mol%)

Me Me Ph

Blue LEDs (
$$\lambda_{max} = 405 \text{ nm}$$
)

EtOAc (0.1 M), r.t., 12 h

7, 72%

2-((Diphenylmethylene)amino)-4,4-dimethylpentanenitrile (7)

In an oven-dried 10 ml Schlenk tube equipped with a PTFE-coated rare-earth "extra power" oval stirring bar, oxime ester **1a** (84.3 mg, 0.3 mmol) and thioxanthone (4.2 mg, 10 mol%) were charged under air, then the vessel was evacuated and re-filled with argon for four times. Dry EtOAc (2.0 mL, 0.1 M) and Michael acceptor **3a** (10.6 mg, 0.20 mmol) were added under argon counter flow. The vessel was sealed with the screw cap, then irradiated at 405 nm using the described set-up for 12 hours. After irradiation, the resulting homogenous solution was transferred to a 25 mL round bottom flask with aid of DCM (2 x 3 mL). NEt₃ (approx. 0.5 mL) and SiO₂ were added to this solution

and the volatiles were removed under reduced pressure, affording a powder which was loaded on column. Purification by flash column chromatography on SiO₂ (pre-basified with NEt₃) with pentane/EtOAc (400:1 to 200:1, v/v) as eluent afforded the title compound 7 (42 mg, 72%) as a yellow oil. ¹H NMR (400 MHz, CDCl₃): $\delta = 0.85$ (s, 9H), 1.82 (dd, J = 14.1, 6.1 Hz, 1H), 2.07 (dd, J = 14.1, 7.0 Hz, 1H), 4.29 (dd, J = 7.1, 6.1 Hz, 1H), 7.22-7.26 (m, 2H), 7.34-7.39 (m, 2H), 7.41-7.47 (m, 1H), 7.48-7.58 (m, 3H), 7.61-7.70 (m, 2H) ppm. 13 C NMR (101 MHz, CDCl₃): $\delta = 29.7, 30.7, 48.4, 50.5,$ 120.8, 127.5, 128.4, 129.1, 129.1, 129.5, 131.2, 135.5, 138.7, 172.2 ppm. HRMS (ESI): m/z calculated for $[C_{20}H_{22}N_2N_3]$ $[M+N_3^+]$: 313.1675, found: 313.1672.

3.6. Detection of side products

In an oven-dried 10 ml Schlenk tube equipped with a PTFE-coated rare-earth "extra power" oval stirring bar, oxime ester **1a** (84.3 mg, 0.3 mmol) and thioxanthone (4.2 mg, 10 mol%) were charged under air, then the vessel was evacuated and re-filled with argon for four times. Dry EtOAc (2.0 mL, 0.1 M), styrene 2a (36.0 mg, 0.2 mmol), and Michael acceptor 3a (21.2 mg, 0.4 mmol) were added under argon counter flow. The vessel was sealed with the screw cap and then irradiated at 405 nm using the described set-up for 12 hours. After irradiation, the NMR yields for 4 (62%), 6 (< 5%), and 7 (23%) with respect to **1a**) were determined using CH₂Br₂ as internal standard.

3.7. Direct excitation experiment

3.7. Direct excitation experiment

Me Ne Ph + Ph + CN UV LEDs
$$(\lambda_{max} = 365 \text{ nm})$$

EtOAc (0.1 M) , r.t., 36 h

4, 38% NMR yield

In an oven-dried 10 ml Schlenk tube equipped with a PTFE-coated rare-earth "extra power" oval stirring bar, oxime ester 1a (42.2 mg, 0.15 mmol) was charged under air, then the vessel was evacuated and re-filled with argon for four times. Dry EtOAc (1.0 mL, 0.1 M), styrene **2a** (18.0 mg, 0.1 mmol), and Michael acceptor **3a** (10.6 mg, 0.2 mmol) were added under argon counter flow. The vessel was sealed with the screw cap, then irradiated at 365 nm with two 30 W LEDs (EvoluChemTM, HCK1012-01-006) using the described set-up for 36 hours. After irradiation, the reaction yield (38%) was determined by ¹H NMR spectroscopy using CH₂Br₂ as internal standard.

3.8. Quantum yield measurement

Measurement of the photon flux

The photon flux was determined by ferrioxalate actinometry similar to a procedure by Yoon.^[9] A 3 W violet LED ($\lambda_{max} = 395$ nm) was used for the quantum yield measurement instead of the standard 18 W blue LEDs ($\lambda_{max} = 405$ nm).

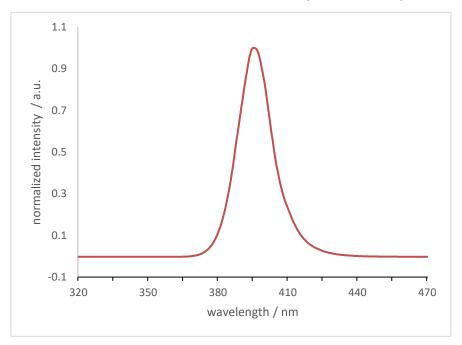


Fig. S6. Emission spectrum of the 3 W violet LED ($\lambda_{max} = 395$ nm) which was used for the quantum yield measurement.

A solution (10 mL, 0.15 M) of potassium ferrioxalate hydrate (737 mg, 1.50 mmol) in aq. H_2SO_4 (50 mM) and a solution (20 mL, 5.0 mM) of 1,10-phenanthroline monohydrate (20 mg, 0.10 mmol) and sodium acetate (4.50 g) in aq. H_2SO_4 (500 mM) were prepared and kept in the dark. All following steps were conducted in the dark as well.

Six Schlenk tubes were charged with the prepared ferrioxalate solution (1.0 mL) and three of these tubes were successively irradiated with a violet LED for 60 s at a distance of 5 cm, while three tubes were left in the dark. Then, to all six Schlenk tubes was added the prepared phenanthroline solution (175 μ L each) and the reaction mixtures were

stirred for 60 mins. For all six solutions, the absorbance at 510 nm was measured and the difference between the average absorbance of the three irradiated samples and the average absorbance of the three control samples was determined ($\Delta A_{510 \text{ nm}} = 2.672$).

The formed amount of Fe(II) was calculated based on the Lambert–Beer law (equation 1) with V = 1.175 mL, l = 1.0 cm, and $\epsilon = 11100$ L·mol⁻¹·cm⁻¹.^[10]

$$n_{Fe(II)} = \frac{V \cdot \Delta A_{510 \text{ nm}}}{l \cdot \varepsilon} \tag{1}$$

The fraction of light which was absorbed by the actinometer at $\lambda = 395$ nm (f) was determined with equation 2 with the absorbance of the ferrioxalate stock solution at $\lambda = 395$ nm being $A_{395 \text{ nm}} > 3$ (f > 0.999).

$$f = 1 - 10^{-A_{395 \text{ nm}}} \tag{2}$$

The photonflux ϕ_q was finally determined using equation 3 with $\phi_F = 1.13$ (at

$$\lambda=392$$
 nm) and $t=60$ s, giving $~\phi_q=4.172\cdot 10^{-9}~mol\cdot s^{-1}.^{[10,11]}$

$$\phi_{\mathbf{q}} = \frac{n_{Fe(II)}}{\phi_{\mathbf{F}} \cdot t \cdot f} \tag{3}$$

Reaction quantum yield

In an oven-dried 10 ml Schlenk tube equipped with a PTFE-coated rare-earth "extra power" oval stirring bar, oxime ester **1a** (42.2 mg, 0.15 mmol) and thioxanthone (2.1 mg, 10 mol%) were charged under air, then the vessel was evacuated and re-filled with argon for four times. Dry EtOAc (1.0 mL, 0.1 M), styrene **2a** (18.0 mg, 0.1 mmol), and Michael acceptor **3a** (10.6 mg, 0.2 mmol) were added under argon counter flow. The Schlenk tube was sealed and irradiated at 395 nm at ambient temperature for 30 minutes using the same setup as for the photon flux determination. Then, the NMR yield was determined (3%) using CH₂Br₂ as internal standard. The same procedure was repeated two more times giving the same yield.

The reaction's quantum yield was determined using equation 4 with the determined photon flux ϕ_q , the irradiation time t = 1800 s, and the fraction of light absorbed

($f_{\rm R} > 0.999$; determined according to equation 2 with $A_{395~\rm nm} > 3$) by the reaction mixture.

$$\phi = \frac{n_{\text{product}}}{\phi_q \cdot t \cdot f_R} \tag{4}$$

The determined quantum yield was $\phi = 0.40$.

3.9. Determination of the initial reaction rate of the formation of 6 and 7

Preparation of stock solution 4: A Schlenk tube was charged with a magnetic stirring bar and **1a** (338 mg, 1.2 mmol). The vessel was then evacuated and re-filled with argon for four times and dry EtOAc (8.0 mL, 0.1 M) followed by **2a** (144 mg, 0.8 mmol) were added under argon counterflow. The solution was vigorously stirred for 10 minutues and kept under argon. The effect of oxime ester **1a** and 1,1-diphenylethylene (**2a**) on the volume of the stock solution was neglected in the following.

Preparation of stock solution 5: A Schlenk tube was charged with a magnetic stirring bar and **1a** (211 mg, 0.75 mmol). The vessel was then evacuated and re-filled with argon for four times and dry EtOAc (5.0 mL, 0.1 M) followed by **3a** (26.5 mg, 0.5 mmol) were added under argon counterflow. The solution was vigorously stirred for 10 minutues and kept under argon. The effect of oxime ester **1a** and acrylonitrile (**3a**) on the volume of the stock solution was neglected in the following.

Reaction set-up: 8 Schlenk tubes were each charged with a stirring bar and thioxanthone (2.1 mg, 10 mol%) under air. The Schlenk tubes were than evacuated and re-filled with argon for four times. To each Schlenk tube was then added either **stock solution 4** (1.0 mL) or **stock solution 5** (1.0 mL) under argon counterflow. The tubes were sealed and irradiated at 405 nm in the standard photosetup for the indicated

reaction time. Care was taken to place each reaction vessel in the same position within the photoreactor to ensure consistent light intensity. Then, the NMR yield was determined using CH_2Br_2 as internal standard.

Results: The obtained NMR yields after the respective reaction time are compiled in Table S4 and visualized in Fig. S7.

Table S4. Yields of **6** and **7** in the respective two-component reaction after the indicated reaction time.

Entry	Alkene/Product	Reaction time (s)	NMR Yield (%)
1	2a/6	0	0
2	2a/6	75	2
3	2a / 6	150	5
4	2a/6	225	8
5	3a/7	0	0
6	3a/7	60	5
7	3a/7	120	10
8	3a/7	180	15

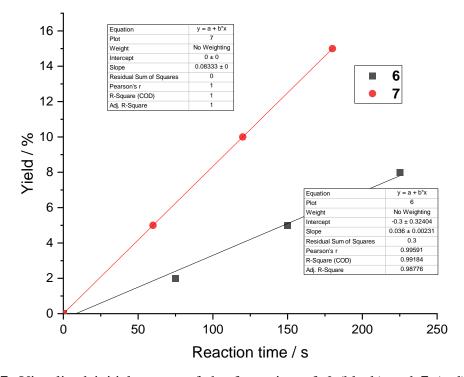


Fig. S7. Visualized initial course of the formation of 6 (black) and 7 (red) in the respective two-component reactions. NMR yields are used.

3.10. Mechanistic analysis for 1,4-carboimination of 1a, 2a, and 3a

Based on previous studies and the carried out mechanistic experiments, $^{[3,12]}$ a mechanistic analysis of the selective 1,4-carboimination of **1a**, **2a**, and **3a** was developed. The reaction starts with an energy transfer-enabled homolysis of **1a** to provide a persistent N-centered iminyl radical **A** and a transient C-centered alkyl radical **B**, which are of ambiphilic and nucleophilic properties, respectively. Then, steered by polar and persistent radical effects (PRE), $^{[13]}$ the nucleophilic C-centered alkyl radical **B** preferentially adds to electron poor olefin **3a** to form an α -cyano-containing C-centered alkyl radical with reduced nucleophilicity (**IM1**). Subsequently, addition of **IM1** to **2a** gives another benzyl stabilized C-centered alkyl radical (**IM2**), which is further trapped by the persistent N-centered iminyl radical **A** to furnish the desired 1,4-carboimination product **4**. Alternatively, radical addition of **IM2** onto **1a** and subsequent fragmentation can form **4** in a radical chain mechanism. $^{[12b,c]}$ The competing 1,2-carboiminations of **2a** or **3a** were observed as minor side reactions.

3.11. General procedure for the 1,4-carboimination

Thioxanthone (10 mol%)

$$R^{1}$$
 R^{2}
 R^{3}
 R^{4}
 R^{5}
 R^{4}
 R^{5}
 R^{2}
 R^{1}
 R^{2}
 R^{1}
 R^{2}
 R^{2}
 R^{1}
 R^{2}
 R^{2

In an oven-dried 10 ml Schlenk tube equipped with a PTFE-coated rare-earth "extra power" oval stirring bar, oxime ester **1** (0.3 mmol, 1.5 equiv., unless otherwise stated), styrene derivatives (0.2 mmol, 1.0 equiv., if solid), Michael acceptors (0.4 mmol, 2.0 equiv., if solid), and thioxanthone photosensitizer (4.2 mg, 10 mol%) were charged under air, then the vessel was evacuated and re-filled with argon for four times. Dry EtOAc (2.0 mL, 0.1 M), appropriate styrene derivatives (0.2 mmol, 1.0 equiv., if liquid),

and Michael acceptors (0.4 mmol, 2.0 equiv., if liquid) were added under argon counter flow. The vessel was sealed with the screw cap, then irradiated at 405 nm using the described set-up for 12 hours, unless otherwise stated. After irradiation, the resulting homogenous solution was transferred to a 25 mL round bottom flask with aid of DCM (2 x 3 mL). NEt₃ (approx. 0.5 mL) and SiO₂ were added to this solution and the volatiles were removed under reduced pressure, affording a powder which was loaded on column. Purification by flash column chromatography on SiO₂, pre-basified with NEt₃ using pentane: EtOAc mixtures afforded the corresponding 1,4-carboimination products.

Note: NEt₃ was used as the product can be partially hydrolyzed by acidic silica, causing a slight decrease in the yield (approx. 5-10%). The amount of Et₃N added to the eluent was approximately 1 ml for 300 ml of solvent. When Et₃N was used for TLC analysis, one Pasteur pipette drop was used for 10 ml of eluent. "Pre-basified" silica refers to silica gel, which have been soaked with 2-3% triethylamine in pentane prior to use.



Fig. S8. Experimental set-up featuring two 18W Blue LEDs (405 nm).

4. Experimental data for the described substances

2-(2-((Diphenylmethylene)amino)-2,2-diphenylethyl)-4,4-dimethylpentanenitrile (4)

Following the general procedure, benzophenone *O*-pivaloyl oxime **1a** (84.3 mg, 0.3 mmol), ethene-1,1-diyldibenzene **2a** (36.0 mg, 0.2 mmol), and acrylonitrile **3a** (21.2 mg, 0.4 mmol) were used. Purification by column chromatography using pre-basified silica with pentane/EtOAc (400:1 to 200:1, v/v) as eluent afforded **4** as colorless oil (56 mg, 60% yield). 1 H NMR (400 MHz, CDCl₃): δ = 0.76 (s, 9H), 1.12-1.16 (m, 1H), 1.63-1.70 (m, 1H), 2.34-2.38 (m, 1H), 2.58-2.64 (m, 1H), 2.97-3.02 (m, 1H), 6.58-6.60 (m, 2H), 7.00-7.19 (m, 9H), 7.23-7.27 (m, 2H), 7.33-7.42 (m, 3H), 7.47-7.53 (m, 2H), 7.71-7.74 (m, 2H) ppm. 13 C NMR (101 MHz, CDCl₃): δ = 22.4, 29.3, 31.0, 46.1, 48.4, 68.7, 124.5, 126.4, 126.5, 126.9, 127.2, 127.4, 128.00, 128.04, 128.12, 128.15, 128.7, 130.2, 130.2, 138.6, 141.6, 148.1, 148.4, 168.8 ppm. HRMS (ESI): m/z calculated for [C₃₄H₃₄N₂Na] [M+Na⁺]: 493.2620, found: 493.2632.

5-Chloro-2-(2-((diphenylmethylene)amino)-2,2-diphenylethyl)-4,4-dimethylpentanenitrile (8)

Following the general procedure, benzophenone O-(3-chloro-2,2-dimethylpropanoyl) oxime **1b** (94.5 mg, 0.3 mmol), ethene-1,1-diyldibenzene **2a** (36.0 mg, 0.2 mmol), and acrylonitrile **3a** (21.2 mg, 0.4 mmol) were used. Purification by column chromatography using pre-basified silica with pentane/EtOAc (400:1 to 200:1, v/v) as eluent afforded **8** as colorless oil (67 mg, 67% yield). 1 H NMR (400 MHz, CDCl₃): δ = 0.80 (s, 3H), 0.92 (s, 3H), 1.32-1.36 (m, 1H), 1.73-1.79 (m, 1H), 2.37-2.41 (m, 1H), 2.59-2.66 (m, 1H), 2.98-3.03 (m, 1H), 3.07-3.10 (m, 1H), 3.19-3.22 (m, 1H), 6.57-6.59 (m, 2H), 7.00-7.20 (m, 9H), 7.24-7.28 (m, 2H), 7.33-7.42 (m, 3H), 7.48-7.50 (m, 2H), 7.70-7.73 (m, 2H) ppm. 13 C NMR (101 MHz, CDCl₃): δ = 22.0, 24.8, 25.2, 35.7, 43.4, 46.0, 55.0, 68.6, 123.8, 126.5, 126.6, 127.0, 127.2, 127.5, 128.04, 128.06, 128.08, 128.2, 128.8, 130.3, 138.6, 141.6, 147.8, 148.2, 169.0 ppm. HRMS (ESI): m/z calculated for $[C_{34}H_{33}ClN_2Na]$ [M+Na⁺]: 527.2230, found: 527.2226.

4-((Diphenylmethylene)amino)-2-((1-methylcyclopropyl)methyl)-4,4-diphenylbutanenitrile (9)

Following the general procedure, benzophenone O-(1-methylcyclopropanecarbonyl) oxime **1c** (83.7 mg, 0.3 mmol), ethene-1,1-diyldibenzene **2a** (36.0 mg, 0.2 mmol), and acrylonitrile **3a** (21.2 mg, 0.4 mmol) were used. Purification by column chromatography using pre-basified silica with pentane/EtOAc (500:1 to 300:1, v/v) as eluent afforded **9** as colorless oil (47 mg, 50% yield). ¹H NMR (400 MHz, CDCl₃): $\delta = 0.06$ -0.21 (m, 2H), 0.27 (dt, J = 9.8, 5.1 Hz, 1H), 0.42 (dt, J = 9.6, 5.0 Hz, 1H), 0.75 (s, 3H), 1.24-1.43 (m, 2H), 2.40 (dd, J = 13.4, 3.5 Hz, 1H), 2.71-2.81 (m, 1H), 2.86 (dd, J = 13.4, 8.0 Hz, 1H), 6.55 (s, 2H), 6.97-7.19 (m, 9H), 7.21-7.26 (m, 2H), 7.31-7.41 (m, 3H), 7.50 (d, J = 18.6 Hz, 2H), 7.67-7.75 (m, 2H) ppm. ¹³C NMR (101 MHz, CDCl₃): $\delta = 12.8$, 13.4, 13.8, 22.0, 24.6, 43.7, 44.0, 68.6, 123.5, 126.47, 126.52, 126.9, 127.2, 127.5, 127.6, 128.02, 128.07, 128.11, 128.2, 128.38, 128.44, 128.7, 129.1, 130.3, 138.6, 141.6, 148.0, 148.4, 168.8 ppm. HRMS (ESI): m/z calculated for [C₃₄H₃₂N₂Na] [M+Na⁺]: 491.2463, found: 491.2453.

2-((3*r*,5*r*,7*r*)-Adamantan-1-ylmethyl)-4-((diphenylmethylene)amino)-4,4-diphenylbutanenitrile (10)

Following the general procedure, benzophenone O-((3r,5r,7r)-adamantane-1-carbonyl) oxime **1d** (107.7 mg, 0.3 mmol), ethene-1,1-diyldibenzene **2a** (36.0 mg, 0.2 mmol), and acrylonitrile **3a** (21.2 mg, 0.4 mmol) were used. Purification by column chromatography using pre-basified silica with pentane/EtOAc (400:1 to 200:1, v/v) as eluent afforded **10** as a white solid (55 mg, 50% yield). ¹H NMR (400 MHz, CDCl₃): δ = 1.01-1.05 (m, 1H), 1.22-1.36 (m, 6H), 1.43-1.71 (m, 7H), 1.84-1.91 (m, 3H), 2.31-

2.36 (m, 1H), 2.64-2.70 (m, 1H), 2.95-3.00 (m, 1H), 6.58-6.60 (m, 2H), 7.00-7.20 (m, 9H), 7.23-7.27 (m, 2H), 7.33-7.42 (m, 3H), 7.45-7.55 (m, 2H), 7.72-7.74 (m, 2H) ppm. 13 C NMR (101 MHz, CDCl₃): δ = 20.4, 28.49, 28.52, 32.8, 36.8, 42.0, 46.1, 49.2, 68.7, 124.7, 126.41, 126.44, 126.9, 127.2, 127.4, 127.97, 128.01, 128.1, 128.2, 128.7, 130.2, 138.6, 141.6, 148.1, 148.4, 168.7 ppm. HRMS (ESI): m/z calculated for [C₄₀H₄₀N₂Na] [M+Na⁺]: 571.3089, found: 571.3082.

4-((Diphenylmethylene)amino)-2-(((2*R*,3*ar*,5*S*,6*as*)-octahydro-2,5-methanopentalen-3*a*-yl)methyl)-4,4-diphenylbutanenitrile (11)

Following the general procedure, benzophenone O-((2R, 3as, 5S, 6as)-octahydro-2,5-methanopentalene-3a-carbonyl) oxime **1e** (103.5 mg, 0.3 mmol), ethene-1,1-diyldibenzene **2a** (36.0 mg, 0.2 mmol), and acrylonitrile **3a** (21.2 mg, 0.4 mmol) were used. Purification by column chromatography using pre-basified silica with pentane/EtOAc (400:1 to 200:1, v/v) as eluent afforded **11** as a white solid (62 mg, 58% yield). 1 H NMR (400 MHz, CDCl₃): δ = 0.84-0.91 (m, 1H), 1.17-1.22 (m, 1H), 1.41-1.62 (m, 9H), 1.78-1.81 (m, 1H), 1.84-1.90 (m, 1H), 2.09-2.12 (m, 2H), 2.37-2.41 (m, 1H), 2.59-2.65 (m, 1H), 2.92-2.97 (m, 1H), 6.57-6.58 (m, 2H), 6.99-7.17 (m, 9H), 7.21-7.28 (m, 2H), 7.32-7.41 (m, 3H), 7.45-7.49 (m, 2H), 7.69-7.71 (m, 2H) ppm. 13 C NMR (101 MHz, CDCl₃): δ = 23.8, 35.0, 37.5, 37.9, 43.6, 43.7, 44.3, 44.7, 45.4, 48.2, 48.3, 48.4, 68.7, 124.3, 126.5, 126.9, 127.3, 127.5, 128.03, 128.06, 128.13, 128.15, 128.7, 128.8, 129.5, 130.2, 138.6, 141.6, 148.2, 148.4, 168.7 ppm. HRMS (ESI): m/z calculated for [C₃₉H₃₈N₂Na] [M+Na⁺]: 557.2933, found: 557.2926.

tert-Butyl

(1-(2-cyano-4-((diphenylmethylene)amino)-4,4-

diphenylbutyl)cyclopentyl)carbamate (12)

Following the general procedure, *tert*-butyl (1-((((diphenylmethylene)amino)oxy)carbonyl)cyclopentyl)carbamate 1f (122.4 mg, 0.3 mmol), ethene-1,1-diyldibenzene 2a (36.0 mg, 0.2 mmol), and acrylonitrile 3a (21.2 mg, 0.4 mmol) were used. Purification by column chromatography using pre-basified silica with pentane/EtOAc (40:1 to 30:1, v/v) as eluent afforded 12 as a white solid (62 mg, 63% yield). Combined NMR data for both the rotamers are reported here. ¹H NMR (400 MHz, CDCl₃): $\delta = 1.22-1.85$ (m, 18H), 2.12-2.18 (m, 1H), 2.32-2.44 (m, 1H), 2.56-2.69 (m, 1H), 2.88-2.93 (m, 1H), 4.24 (s, 1H), 6.57 (m, 2H), 6.99-7.17 (m, 9H), 7.21-7.25 (m, 2H), 7.31-7.39 (m, 3H), 7.42-7.54 (m, 2H), 7.62-7.72 (m, 2H) ppm. ¹³C NMR (101 MHz, CDCl₃): $\delta = 23.0, 23.1, 23.4, 23.5, 28.46, 28.56, 38.2, 38.6, 41.2, 44.5,$ 50.6, 62.4, 62.9, 68.4, 79.2, 120.2, 123.5, 126.45, 126.49, 127.0, 127.3, 127.47, 127.52, 128.00, 128.03, 128.1, 128.2, 128.4, 128.5, 128.8, 129.2, 129.5, 130.2, 131.3, 135.4, 138.6, 141.6, 148.3, 148.6, 154.5, 168.9 ppm. HRMS (ESI): m/z calculated for $[C_{40}H_{43}N_3NaO_2]$ [M+Na⁺]: 620.3253, found: 620.3256.

2-(Cyclobutylmethyl)-4-((diphenylmethylene)amino)-4,4-diphenylbutanenitrile (13)

Following the general procedure, benzophenone *O*-cyclobutanecarbonyl oxime **1g** (83.8 mg, 0.3 mmol), ethene-1,1-diyldibenzene **2a** (36.0 mg, 0.2 mmol), and acrylonitrile **3a** (21.2 mg, 0.4 mmol) were used. Purification by column chromatography using pre-basified silica with pentane/EtOAc (400:1 to 200:1, v/v) as eluent afforded **13** as a white solid (52 mg, 56% yield). ¹H NMR (400 MHz, CDCl₃): δ = 1.24-1.52 (m, 3H), 1.55-2.02 (m, 5H), 2.24-2.40 (m, 2H), 2.49 (m, 1H), 2.86 (dd, J = 13.5, 8.4 Hz, 1H), 6.56 (d, J = 5.4 Hz, 2H), 7.00-7.20 (m, 9H), 7.23-7.27 (m, 3H), 7.32-7.42 (m, 3H), 7.45-7.48 (m, 2H), 7.67-7.76 (m, 2H) ppm. ¹³C NMR (101 MHz, CDCl₃): δ = 18.5, 24.9, 27.9, 28.3, 33.6, 41.1, 43.6, 68.5, 123.0, 126.5, 126.5, 127.0, 127.3,

127.4, 128.0, 128.0, 128.1, 128.2, 128.7, 130.3, 138.6, 141.6, 148.0, 148.4, 168.7 ppm. HRMS (ESI): m/z calculated for [C₃₄H₃₂N₂Na] [M+Na⁺]: 491.2458, found: 491.2459.

2-(Cyclopentylmethyl)-4-((diphenylmethylene)amino)-4,4-diphenylbutanenitrile (14)

Following the general procedure, benzophenone *O*-cyclopentanecarbonyl oxime **1h** (88.0 mg, 0.3 mmol), ethene-1,1-diyldibenzene **2a** (36.0 mg, 0.2 mmol), and acrylonitrile **3a** (21.2 mg, 0.4 mmol) were used. Purification by column chromatography using pre-basified silica with pentane/EtOAc (400:1 to 200:1, v/v) as eluent afforded **14** as a white solid (56 mg, 58% yield). ¹H NMR (400 MHz, CDCl₃): δ = 0.67-0.98 (m, 2H), 1.20 (m, 1H), 1.37-1.54 (m, 5H), 1.56-1.67 (m, 2H), 1.74-1.90 (m, 1H), 2.36 (dd, J = 13.6, 3.6 Hz, 1H), 2.60 (m, 1H), 2.89 (dd, J = 13.6, 8.0 Hz, 1H), 6.56 (d, J = 5.3 Hz, 2H), 6.99-7.19 (m, 9H), 7.22-7.26 (m, 2H), 7.32-7.42 (m, 3H), 7.45-7.49 (m, 2H), 7.67-7.75 (m, 2H) ppm. ¹³C NMR (101 MHz, CDCl₃): δ = 25.0, 25.0, 26.0, 31.8, 32.7, 37.7, 40.6, 44.0, 68.5, 123.3, 126.5, 126.5, 126.9, 127.2, 127.5, 128.0, 128.0, 128.1, 128.1, 128.7, 130.3, 138.6, 141.6, 148.0, 148.4, 168.7 ppm. HRMS (ESI): m/z calculated for [C₃₅H₃₄N₂Na] [M+Na⁺]: 505.2614, found: 505.2616.

2-(Cyclohexylmethyl)-4-((diphenylmethylene)amino)-4,4-diphenylbutanenitrile (15)

Following the general procedure, benzophenone *O*-cyclohexanecarbonyl oxime **1i** (92.2 mg, 0.3 mmol), ethene-1,1-diyldibenzene **2a** (36.0 mg, 0.2 mmol), and acrylonitrile **3a** (21.2 mg, 0.4 mmol) were used. Purification by column chromatography using pre-basified silica with pentane/EtOAc (400:1 to 200:1, v/v) as eluent afforded **15** as a white solid (55 mg, 56% yield). 1 H NMR (400 MHz, CDCl₃): δ

= 0.53-0.76 (m, 2H), 0.96-1.22 (m, 4H), 1.23-1.36 (m, 2H), 1.39-1.66 (m, 5H), 2.32 (dd, J = 13.6, 3.3 Hz, 1H), 2.69 (m, 1H), 2.88 (dd, J = 13.5, 8.2 Hz, 1H), 6.57 (d, J = 7.4 Hz, 2H), 6.99-7.19 (m, 9H), 7.22-7.26 (m, 2H), 7.32-7.41 (m, 3H), 7.45-7.47 (m, 2H) 7.67-7.75 (m, 2H) ppm. 13 C NMR (101 MHz, CDCl₃): δ = 23.9, 26.0, 26.1, 26.4, 32.2, 33.3, 35.0, 41.9, 44.0, 68.6, 123.3, 126.5, 126.9, 127.2, 127.5, 128.0, 128.0, 128.1, 128.1, 128.2, 128.7, 130.3, 138.6, 141.6, 148.0, 148.5, 168.7 ppm. HRMS (ESI): m/z calculated for [C₃₆H₃₆N₂Na] [M+Na⁺]: 519.2771, found: 519.2772.

16

Benzyl 3-(2-cyano-4-((diphenylmethylene)amino)-4,4-diphenylbutyl)azetidine-1-carboxylate (16)

Following the procedure, benzyl 3general ((((diphenylmethylene)amino)oxy)carbonyl)azetidine-1-carboxylate 1j (124.2 mg, 0.3 mmol), ethene-1,1-diyldibenzene 2a (36.0 mg, 0.2 mmol), and acrylonitrile 3a (21.2 mg, 0.4 mmol) were used. Purification by column chromatography using pre-basified silica with pentane/EtOAc (20:1 to 10:1, v/v) as eluent afforded 16 as a white solid (75 mg, 62% yield). ¹H NMR (400 MHz, CDCl₃): $\delta = 1.55-1.83$ (m, 2H), 1.94-2.62 (m, 3H), 2.85-2.95 (m, 1H), 3.26-3.70 (m, 2H), 3.94-4.26 (m, 2H), 5.08-5.09 (m, 2H), 6.53-6.55 (m, 2H), 6.99-7.24 (m, 10H), 7.30-7.54 (m, 11H), 7.62-7.70 (m, 2H) ppm. ¹³C NMR (101 MHz, CDCl₃): $\delta = 25.1$, 27.3, 38.5, 39.1, 43.9, 66.7, 68.5, 122.1, 126.6, 126.8, 127.07, 127.13, 127.5, 127.9, 128.08, 128.10, 128.12, 128.17, 128.3, 128.6, 128.7, 129.1, 129.3, 130.4, 136.8, 138.4, 141.4, 147.5, 147.9, 156.3, 169.1 ppm. HRMS (ESI): m/z calculated for $[C_{41}H_{37}N_3NaO_2]$ $[M+Na^+]$: 626.2783, found: 626.2781.

17

2-(2-((Diphenylmethylene)amino)-2,2-diphenylethyl)-4-ethylhexanenitrile (17)

Following the general procedure, benzophenone O-(2-ethylbutanoyl) oxime **1k** (88.5 mg, 0.3 mmol), ethene-1,1-diyldibenzene **2a** (36.0 mg, 0.2 mmol), and acrylonitrile **3a** (21.2 mg, 0.4 mmol) were used. Purification by column chromatography using prebasified silica with pentane/EtOAc (400:1 to 200:1, v/v) as eluent afforded **17** as a white solid (47 mg, 49% yield). ¹H NMR (400 MHz, CDCl₃): δ = 0.63 (t, J = 7.4 Hz, 3H), 0.72 (t, J = 7.4 Hz, 3H), 0.95-1.24 (m, 5H), 1.24-1.36 (m, 1H), 1.47-1.54 (m, 1H), 2.34 (dd, J = 13.6, 3.3 Hz, 1H), 2.65 (m, 1H), 2.92 (dd, J = 13.6, 8.2 Hz, 1H), 6.58 (d, J = 5.7 Hz, 2H), 6.99-7.19 (m, 9H), 7.23-7.27 (m, 2H), 7.32-7.43 (m, 3H), 7.44-7.53 (m, 2H), 7.69-7.76 (m, 2H) ppm. ¹³C NMR (101 MHz, CDCl₃): δ = 9.7, 10.7, 24.0, 24.7, 25.3, 37.7, 38.1, 44.3, 68.6, 123.2, 126.4, 126.5, 126.9, 127.2, 127.5, 128.00, 128.04, 128.2, 128.7, 130.2, 138.6, 141.6, 148.0, 148.4, 168.8 ppm. HRMS (ESI): m/z calculated for [C₃₅H₃₆N₂Na] [M+Na⁺]: 507.2771, found: 507.2767.

2-((4,4-Difluorocyclohexyl)methyl)-4-((diphenylmethylene)amino)-4,4-diphenylbutanenitrile (18)

Following the general procedure, benzophenone O-(4,4-difluorocyclohexanecarbonyl) oxime **11** (103.0 mg, 0.3 mmol), ethene-1,1-diyldibenzene **2a** (36.0 mg, 0.2 mmol), and acrylonitrile **3a** (21.2 mg, 0.4 mmol) were used. Purification by column chromatography using pre-basified silica with pentane/EtOAc (400:1 to 100:1, v/v) as eluent afforded **18** as a white solid (56 mg, 53% yield). ¹H NMR (400 MHz, CDCl₃): δ = 0.87-1.20 (m, 3H), 1.32-1.43 (m, 2H), 1.47-1.54 (m, 2H), 1.56-1.70 (m, 2H), 1.85-2.04 (m, 2H), 2.33 (dd, J = 13.6, 3.5 Hz, 1H), 2.69 (m, 1H), 2.94 (dd, J = 13.6, 7.8 Hz, 1H), 6.56 (d, J = 7.5 Hz, 2H), 6.99-7.20 (m, 9H), 7.23-7.27 (m, 2H), 7.33-7.42 (m, 3H), 7.45-7.47 (m, 2H), 7.65-7.74 (m, 2H) ppm. 13 C{ 1 H, 19 F} NMR (126 MHz, CDCl₃): δ = 24.5, 27.8, 29.1, 33.1, 33.3, 33.3, 40.1, 44.2, 68.6, 122.8, 123.4, 126.6, 126.6, 127.0, 127.2, 127.5, 128.0, 128.1, 128.1, 128.2, 128.7, 130.4, 138.5, 141.5, 147.7, 148.2, 169.0 ppm. 19 F{ 1 H} NMR (376 MHz, CDCl₃) δ = -102.08 (d, J = 235.2 Hz), -92.04 (d, J =

235.5 Hz) ppm. HRMS (ESI): m/z calculated for $[C_{36}H_{34}F_2N_2Na]$ $[M+Na^+]$: 555.2582, found: 555.2584.

$\begin{tabular}{ll} 4-((Diphenylmethylene)amino)-4,4-diphenyl-2-((tetrahydro-2H-pyran-4-yl)methyl) butanenitrile (19) \end{tabular}$

Following the general procedure, benzophenone *O*-tetrahydro-2*H*-pyran-4-carbonyl oxime **1m** (92.7 mg, 0.3 mmol), ethene-1,1-diyldibenzene **2a** (36.0 mg, 0.2 mmol), and acrylonitrile **3a** (21.2 mg, 0.4 mmol) were used. Purification by column chromatography using pre-basified silica with pentane/EtOAc (100:1 to 30:1, v/v) as eluent afforded **19** as a white solid (68 mg, 68% yield). ¹H NMR (400 MHz, CDCl₃): δ = 0.88-1.02 (m, 1H), 1.04-1.29 (m, 3H), 1.36-1.42 (m, 1H), 1.47-1.58 (m, 2H), 2.31-2.36 (m, 1H), 2.69-2.76 (m, 1H), 2.91-2.96 (m, 1H), 3.19-3.31 (m, 2H), 3.78-3.92 (m, 2H), 6.57 (m, 2H), 6.99-7.21 (m, 9H), 7.23-7.27 (m, 2H), 7.30-7.52 (m, 5H), 7.69-7.72 (m, 2H) ppm. ¹³C NMR (101 MHz, CDCl₃): δ = 23.5, 31.9, 32.5, 32.8, 41.2, 44.0, 67.68, 67.73, 68.5, 123.0, 126.51, 126.56, 127.0, 127.1, 127.5, 128.0, 128.1, 128.2, 128.7, 130.3, 138.5, 141.5, 147.7, 148.2, 168.9 ppm. HRMS (ESI): m/z calculated for [C₃₅H₃₄N₂NaO] [M+Na⁺]: 521.2569, found: 521.2565.

2-(2-((diphenylmethylene)amino)-2,2-diphenylethyl)octanenitrile (20)

Following the general procedure, benzophenone *O*-hexanoyl oxime **1n** (88.5 mg, 0.3 mmol), ethene-1,1-diyldibenzene **2a** (36.0 mg, 0.2 mmol), and acrylonitrile **3a** (21.2 mg, 0.4 mmol) were used. Purification by column chromatography using pre-basified silica with pentane/EtOAc (400:1 to 100:1, v/v) as eluent afforded **20** as a white solid (47 mg, 56% yield). ¹H NMR (400 MHz, CDCl₃): $\delta = 0.84$ (t, J = 7.1 Hz, 3H), 1.04-1.47 (m, 10H), 2.35 (dd, J = 13.6, 3.7 Hz, 1H), 2.58 (m, 1H), 2.86 (dd, J = 13.6, 8.3 Hz,

1H), 6.55 (d, J = 7.2 Hz, 2H), 6.97-7.25 (m, 11H), 7.31-7.49 (m, 5H), 7.66-7.74 (m, 2H) ppm. ¹³C NMR (101 MHz, CDCl₃): $\delta = 14.1$, 22.6, 26.7, 26.7, 28.6, 31.5, 34.1, 43.6, 68.5, 122.9, 126.5, 126.5, 127.0, 127.3, 127.5, 128.04, 128.08, 128.1, 128.2, 128.7, 130.3, 138.6, 141.6, 148.1, 148.5, 168.7 ppm. HRMS (ESI): m/z calculated for [C₃₅H₃₆N₂Na] [M+Na⁺]: 507.2771, found: 507.2768.

2-(2-((Diphenylmethylene)amino)-2,2-diphenylethyl)-5-phenylpentanenitrile (21)

Following the general procedure, benzophenone O-(3-phenylpropanoyl) oxime **10** (98.7 mg, 0.3 mmol), ethene-1,1-diyldibenzene **2a** (36.0 mg, 0.2 mmol), and acrylonitrile **3a** (21.2 mg, 0.4 mmol) were used. Purification by column chromatography using pre-basified silica with pentane/EtOAc (400:1 to 200:1, v/v) as eluent afforded **21** as colorless oil (47 mg, 60% yield). ¹H NMR (400 MHz, CDCl₃): δ = 1.34 (ddt, J = 13.5, 10.9, 5.8 Hz, 1H), 1.46 (dtd, J = 14.4, 9.3, 5.1 Hz, 1H), 1.57-1.76 (m, 2H), 2.31 (dd, J = 13.6, 3.6 Hz, 1H), 2.35-2.55 (m, 2H), 2.56-2.67 (m, 1H), 2.85 (dd, J = 13.5, 8.4 Hz, 1H), 6.50 (s, 2H), 6.94-7.25 (m, 16H), 7.32-7.46 (m, 5H), 7.67-7.73 (m, 2H) ppm. ¹³C NMR (101 MHz, CDCl₃): δ = 26.5, 28.2, 33.2, 34.9, 43.5, 68.3, 122.6, 126.0, 126.5, 127.0, 127.2, 127.4, 127.9, 128.02, 128.07, 128.2, 128.5, 128.7, 130.3, 138.5, 141.4, 141.5, 148.0, 148.5, 168.7 ppm. HRMS (ESI): m/z calculated for [C₃₈H₃₄N₂Na] [M+Na⁺]: 541.2620, found: 541.2615.

5-Cyclohexyl-2-(2-((diphenylmethylene)amino)-2,2-diphenylethyl)pentanenitrile (22)

Following the general procedure, benzophenone *O*-(3-cyclohexylpropanoyl) oxime **1p** (100.5 mg, 0.3 mmol), ethene-1,1-diyldibenzene **2a** (36.0 mg, 0.2 mmol), and acrylonitrile **3a** (21.2 mg, 0.4 mmol) were used. Purification by column

chromatography using pre-basified silica with pentane/EtOAc (400:1 to 300:1, v/v) as eluent afforded **22** as pale yellow oil (54 mg, 52% yield). 1 H NMR (400 MHz, CDCl₃): $\delta = 0.74\text{-}1.13$ (m, 6H), 1.15-1.46 (m, 6H), 1.56-1.68 (m, 5H), 2.33-2.38 (m, 1H), 2.55-2.62 (m, 1H), 2.84-2.90 (m, 1H), 6.54-6.56 (m, 2H), 7.00-7.19 (m, 9H), 7.21-7.27 (m, 2H), 7.32-7.40 (m, 3H), 7.41-7.53 (m, 2H), 7.69-7.72 (m, 2H) ppm. 13 C NMR (101 MHz, CDCl₃): $\delta = 24.0$, 28.5, 26.7, 26.8, 33.3, 33.4, 34.3, 36.6, 37.3, 43.6, 68.4, 122.9, 126.48, 126.49, 127.0, 127.3, 127.5, 128.00, 128.03, 128.08, 128.2, 128.7, 129.4, 130.3, 138.6, 141.6, 148.1, 148.5, 168.7 ppm. HRMS (ESI): m/z calculated for [C₃₈H₄₀N₂Na] [M+Na⁺]: 547.3089, found: 547.3084.

6-Chloro-2-(2-((diphenylmethylene)amino)-2,2-diphenylethyl)hexanenitrile (23)

Following the general procedure, benzophenone O-(4-chlorobutanoyl) oxime **1q** (90.3 mg, 0.3 mmol), ethene-1,1-diyldibenzene **2a** (36.0 mg, 0.2 mmol), and acrylonitrile **3a** (21.2 mg, 0.4 mmol) were used. Purification by column chromatography using prebasified silica with pentane/EtOAc (400:1 to 200:1, v/v) as eluent afforded **23** as a white solid (54 mg, 55% yield). 1 H NMR (400 MHz, CDCl₃): δ = 1.25-1.71 (m, 6H), 2.37 (dd, J = 13.6, 3.9 Hz, 1H), 2.62 (m, 1H), 2.90 (dd, J = 13.6, 7.9 Hz, 1H), 3.39 (m, 2H), 6.55 (d, J = 7.4 Hz, 2H), 6.99-7.20 (m, 9H), 7.22-7.26 (m, 2H), 7.33-7.41 (m, 3H), 7.42-7.46 (m, 2H), 7.67-7.74 (m, 2H) ppm. 13 C NMR (101 MHz, CDCl₃): δ = 24.2, 26.6, 31.8, 33.2, 43.6, 44.4, 68.4, 122.6, 126.6, 126.6, 127.0, 127.2, 127.5, 127.99, 128.02, 128.07, 128.12, 128.2, 128.7, 130.4, 138.5, 141.5, 147.9, 148.3, 168.8 ppm. HRMS (ESI): m/z calculated for [C₃₃H₃₁N₂ClNa] [M+Na⁺]: 513.2068, found: 513.2071.

2-(2-((Diphenylmethylene)amino)-2,2-diphenylethyl)hept-6-ynenitrile (24)

Following the general procedure, benzophenone *O*-pent-4-ynoyl oxime **1r** (83.1 mg, 0.3 mmol), ethene-1,1-diyldibenzene **2a** (36.0 mg, 0.2 mmol), and acrylonitrile **3a** (21.2 mg, 0.4 mmol) were used. Purification by column chromatography using pre-basified silica with pentane/EtOAc (400:1 to 200:1, v/v) as eluent afforded **24** as colorless oil (58 mg, 62% yield). ¹H NMR (400 MHz, CDCl₃): δ = 1.46-1.67 (m, 4H), 1.87 (t, *J* = 2.4 Hz, 1H), 2.04-2.08 (m, 2H), 2.35-2.40 (m, 1H), 2.60-2.67 (m, 1H), 2.82-2.91 (m, 1H), 6.48-6.56 (m, 2H), 6.99-7.19 (m, 9H), 7.20-7.28 (m, 2H), 7.30-7.44 (m, 5H), 7.68-7.72 (m, 2H) ppm. ¹³C NMR (101 MHz, CDCl₃): δ = 17.9, 25.5, 26.4, 33.0, 43.7, 68.4, 69.2, 83.3, 122.4, 126.6, 127.0, 127.2, 127.40, 127.41, 127.49, 127.67, 127.70, 128.0, 128.1, 128.22, 128.28, 128.29, 128.8, 130.3, 138.5, 141.5, 147.9, 148.4, 168.8 ppm. HRMS (ESI): m/z calculated for [C₃₄H₃₀N₂Na] [M+Na⁺]: 489.2307, found: 489.2300.

25

2-Hydroxyethyl 2-((5-((diphenylmethylene)amino)-10,11-dihydro-5H-dibenzo[a,d][7]annulen-5-yl)methyl)-4,4-dimethylpentanoate (25)

Following the general procedure, benzophenone *O*-pivaloyl oxime **1a** (84.3 mg, 0.3 mmol), 5-methylene-10,11-dihydro-5*H*-dibenzo[a,d][7]annulene **2e** (41.2 mg, 0.2 mmol), and 2-hydroxyethyl acrylate **3b** (46.4 mg, 0.4 mmol) were used. Purification by column chromatography using pre-basified silica with pentane/EtOAc (10:1 to 8:1, v/v) as eluent afforded **25** as colorless oil (75 mg, 67% yield). ¹H NMR (400 MHz, CDCl₃): $\delta = 0.69$ (s, 9H), 1.24-1.32 (m, 1H), 1.49-1.54 (m, 1H), 1.85-1.87 (m, 1H), 2.28-2.39 (m, 3H), 2.68-2.85 (m, 3H), 3.24-3.30 (m, 1H), 3.66 (m, 2H), 3.96-4.16 (m, 2H), 6.02-6.05 (m, 2H), 6.69-6.76 (m, 3H), 6.84-6.86 (m, 1H), 6.91-6.99 (m, 2H), 7.06-7.18 (m, 3H), 7.31-7.41 (m, 3H), 7.54-7.61 (m, 4H) ppm. ¹³C NMR (101 MHz, CDCl₃): $\delta = 29.3$, 31.3, 36.1, 36.2, 37.8, 48.7, 54.9, 61.5, 65.8, 72.8, 125.6, 125.97, 126.04, 126.55, 126.66, 126.70, 127.2, 128.0, 128.8, 129.1, 129.3, 130.0, 132.2, 132.3, 139.2, 141.7,

141.8, 141.9, 145.3, 146.8, 169.6, 178.5 ppm. HRMS (ESI): m/z calculated for $[C_{38}H_{41}NNaO_3]$ [M+Na⁺]: 582.2984, found: 582.2984.

2-Hydroxyethyl 2-(2-((diphenylmethylene)amino)-2,2-di-*p*-tolylethyl)-4,4-dimethylpentanoate (26)

Following the general procedure, benzophenone O-pivaloyl oxime **1a** (84.3 mg, 0.3 mmol), 4,4'-(ethene-1,1-diyl)bis(methylbenzene) **2b** (41.6 mg, 0.2 mmol), and 2-hydroxyethyl acrylate **3b** (46.4 mg, 0.4 mmol) were used. Purification by column chromatography using pre-basified silica with pentane/EtOAc (10:1 to 8:1, v/v) as eluent afforded **26** as colorless oil (78 mg, 70% yield). 1 H NMR (400 MHz, CDCl₃): δ = 0.69 (s, 9H), 1.22 (dd, J = 14.0 Hz, 3.6 Hz, 1H), 1.66-1.77 (m, 2H), 2.21 (s, 3H), 2.27-2.31 (m, 1H), 2.33 (s, 3H), 2.55-2.60 (m, 1H), 2.98-3.04 (m, 1H), 3.42-3.47 (m, 1H), 3.49-3.59 (m, 2H), 3.67-3.72 (m, 1H), 6.67-6.76 (m, 4H), 6.84-6.86 (m, 2H), 6.96-7.00 (m, 2H), 7.05-7.11 (m, 3H), 7.30-7.39 (m, 5H), 7.64-7.67 (m, 2H) ppm. 13 C NMR (101 MHz, CDCl₃): δ = 21.0, 21.1, 29.4, 31.1, 37.6, 47.1, 49.8, 61.1, 66.0, 68.8, 126.4, 127.0, 127.2, 127.9, 128.0, 128.2, 128.5, 128.6, 129.9, 135.1, 135.3, 139.0, 142.4, 145.6, 146.7, 167.4, 178.3 ppm. HRMS (ESI): m/z calculated for [C₃₈H₄₃NNaO₃] [M+Na⁺]: 584.3141, found: 584.3141.

2-Hydroxyethyl 2-(2,2-bis(4-chlorophenyl)-2-((diphenylmethylene)amino)ethyl)-4,4-dimethylpentanoate (27)

Following the general procedure, benzophenone *O*-pivaloyl oxime **1a** (84.3 mg, 0.3 mmol), 4,4'-(ethene-1,1-diyl)bis(chlorobenzene) **2c** (49.6 mg, 0.2 mmol), and 2-hydroxyethyl acrylate **3b** (46.4 mg, 0.4 mmol) were used. Purification by column chromatography using pre-basified silica with pentane/EtOAc (10:1 to 8:1, v/v) as eluent afforded **27** as colorless oil (72 mg, 60% yield). ¹H NMR (400 MHz, CDCl₃): δ = 0.68 (s, 9H), 1.19 (dd, J = 14.4 Hz, 3.6 Hz, 1H), 1.60-1.70 (m, 2H), 2.20-2.24 (m, 1H), 2.45-2.51 (m, 1H), 3.00-3.06 (m, 1H), 3.34-3.39 (m, 1H), 3.49-3.58 (m, 2H), 3.65-3.70 (m, 1H), 6.52-6.90 (m, 6H), 7.05 (m, 2H), 7.12-7.16 (m, 1H), 7.24-7.26 (m, 2H), 7.30-7.51 (m, 5H), 7.59-7.62 (m, 2H) ppm. ¹³C NMR (101 MHz, CDCl₃): δ = 29.3, 31.1, 37.5, 47.1, 49.9, 61.1, 66.2, 68.6, 127.0, 127.2, 127.4, 127.7, 128.1, 128.7, 129.5, 130.3, 132.0, 132.2, 138.7, 141.8, 146.5, 147.8, 168.5, 178.0 ppm. HRMS (ESI): m/z calculated for [C₃₆H₃₇Cl₂NNaO₃] [M+Na⁺]: 624.2048, found: 624.2043.

2-Hydroxyethyl 2-(2,2-bis(4-bromophenyl)-2-((diphenylmethylene)amino)ethyl)-4,4-dimethylpentanoate (28)

Following the general procedure, benzophenone *O*-pivaloyl oxime **1a** (84.3 mg, 0.3 mmol), 4,4'-(ethene-1,1-diyl)bis(bromobenzene) **2d** (67.0 mg, 0.2 mmol), and 2-hydroxyethyl acrylate **3b** (46.4 mg, 0.4 mmol) were used. Purification by column chromatography using pre-basified silica with pentane/EtOAc (10:1 to 8:1, v/v) as eluent afforded **28** as colorless oil (92 mg, 67% yield). ¹H NMR (400 MHz, CDCl₃): δ = 0.69 (s, 9H), 1.20 (dd, J = 14.0 Hz, 3.2 Hz, 1H), 1.66-1.71 (m, 2H), 2.20-2.24 (m, 1H), 2.46-2.52 (m, 1H), 3.00-3.05 (m, 1H), 3.34-3.40 (m, 1H), 3.48-3.59 (m, 2H), 3.65-3.71 (m, 1H), 6.74-6.76 (m, 4H), 7.04-7.07 (m, 4H), 7.13-7.18 (m, 1H), 7.30-7.47 (m,

7H), 7.60-7.63 (m, 2H) ppm. 13 C NMR (101 MHz, CDCl₃): δ = 29.3, 31.1, 37.4, 47.0, 49.9, 61.0, 66.2, 68.6, 120.2, 120.3, 127.0, 127.1, 127.4, 128.0, 128.6, 129.9, 130.3, 130.6, 131.0, 138.6, 141.7, 146.9, 148.2, 168.5, 177.9 ppm. HRMS (ESI): m/z calculated for [C₃₆H₃₇Br₂NNaO₃] [M+Na⁺]: 712.1038, found: 712.1038.

29, 54:46 d.r.

2-Hydroxyethyl 2-(2-((diphenylmethylene)amino)-2-phenylethyl)-4,4-dimethylpentanoate (29)

Following the general procedure, benzophenone *O*-pivaloyl oxime **1a** (84.3 mg, 0.3 mmol), styrene **2f** (20.8 mg, 0.2 mmol), and 2-hydroxyethyl acrylate **3b** (46.4 mg, 0.4 mmol) were used. Purification by column chromatography using pre-basified silica with pentane/EtOAc (10:1 to 8:1, v/v) as eluent afforded **29** as colorless oil in 54:46 diastereomeric ratio (51 mg, 56% yield). Combined NMR data for both the isomers are reported here. ¹H NMR (400 MHz, CDCl₃): δ = 0.78-0.84 (m, 9H), 1.18-1.26 (m, 1H), 1.66-1.73 (m, 1H), 1.87-2.13 (m, 2H), 2.18-2.53 (m, 2H), 3.60-3.64 (m, 2H), 3.88-4.06 (m, 2H), 4.32-4.37 (m, 1H), 7.02-7.09 (m, 2H), 7.21-7.44 (m, 11H), 7.63-7.68 (m, 2H) ppm. ¹³C NMR (101 MHz, CDCl₃): δ = 29.50, 29.52, 30.97, 31.10, 39.2, 39.6, 44.7, 45.0, 47.0, 61.1, 61.4, 64.9, 65.3, 66.1, 126.9, 127.1, 127.2, 127.4, 128.0, 128.07, 128.12, 128.14, 128.3, 128.47, 128.50, 128.52, 128.56, 128.73, 128.74, 130.12, 130.16, 136.9, 137.1, 139.9, 140.1, 144.3, 145.0, 167.6, 167.9, 177.59, 177.65 ppm. HRMS (ESI): m/z calculated for [C₃₀H₃₅NNaO₃] [M+Na⁺]: 480.2515, found: 480.2518.

30, 50:50 d.r.

2-Hydroxyethyl 2-(2-(2-bromophenyl)-2-((diphenylmethylene)amino)ethyl)-4,4-dimethylpentanoate (30 and 30')

Following the general procedure, benzophenone O-pivaloyl oxime 1a (84.3 mg, 0.3 mmol), 1-bromo-2-vinylbenzene **2g** (36.4 mg, 0.2 mmol), and 2-hydroxyethyl acrylate 3b (46.4 mg, 0.4 mmol) were used. Purification by column chromatography using prebasified silica with pentane/EtOAc (10:1 to 8:1, v/v) as eluent afforded two separable diastereomers (30 and 30') as colorless oil in 50:50 diastereomeric ratio (30: 26 mg, 30': 26 mg, 48% combined yield). Diastereomer **30**: ¹H NMR (400 MHz, CDCl₃): $\delta = 0.87$ (s, 9H), 1.28-1.32 (m, 1H), 1.72-1.77 (m, 1H), 1.97 (t, J = 6.0 Hz, 1H), 2.03-2.09 (m, 1H), 2.15-2.21 (m, 1H), 2.59-2.66 (m, 1H), 3.62-3.66 (m, 2H), 3.93-4.06 (m, 2H), 4.70-4.73 (m, 1H), 6.93-6.95 (m, 2H), 7.03-7.08 (m, 1H), 7.25-7.45 (m, 8H), 7.58-7.71 (m, 3H) ppm. ¹³C NMR (101 MHz, CDCl₃): $\delta = 29.6$, 31.2, 39.4, 43.9, 47.2, 61.6, 63.2, 66.5, 122.3, 127.8, 127.9, 128.19, 128.21, 128.4, 128.6, 128.8, 129.6, 130.3, 132.7, 136.9, 140.0, 144.6, 169.5, 177.4 ppm. Diastereomer **30'**: ¹H NMR (400 MHz, CDCl₃): $\delta = 0.82$ (s, 9H), 1.29-1.30 (m, 1H), 1.64-1.71 (m, 1H), 1.87-1.93 (m, 1H), 2.04-2.07 (m, 1H), 2.31-2.39 (m, 1H), 2.47-2.53 (m, 1H), 3.66 (m, 2H), 3.93-3.99 (m, 1H), 4.06-4.12 (m, 1H), 4.81-4.84 (m, 1H), 6.96-6.98 (m, 2H), 7.04-7.08 (m, 1H), 7.25-7.45 (m, 8H), 7.66-7.71 (m, 3H) ppm. 13 C NMR (101 MHz, CDCl₃): $\delta = 29.6$, 31.0, 40.0, 43.1, 46.2, 61.3, 63.5, 66.3, 122.4, 127.8, 127.9, 128.2, 128.3, 128.58, 128.64, 128.9, 129.6, 130.4, 132.6, 136.9, 139.8, 144.4, 169.5, 177.6 ppm. HRMS (ESI): m/z calculated for $[C_{30}H_{34}BrNNaO_3]$ [M+Na⁺]: 558.1620, found: 558.1621.

31, 56:44 d.r.

2-Hydroxyethyl 2-(2-(3-chlorophenyl)-2-((diphenylmethylene)amino)ethyl)-4,4-dimethylpentanoate (31)

Following the general procedure, benzophenone *O*-pivaloyl oxime **1a** (84.3 mg, 0.3 mmol), 1-chloro-3-vinylbenzene **2h** (27.7 mg, 0.2 mmol), and 2-hydroxyethyl acrylate **3b** (46.4 mg, 0.4 mmol) were used. Purification by column chromatography using pre-basified silica with pentane/EtOAc (10:1 to 6:1, v/v) as eluent afforded **31** as a colorless sticky solid in 56:44 diastereomeric ratio (30 mg, 30% yield). Combined NMR data for both the isomers are reported here. ¹H NMR (400 MHz, CDCl₃): δ = 0.74-0.89 (m, 9H), 1.15-1.27 (m, 1H), 1.63-1.75 (m, 1H), 1.80 (s, 1H), 1.89-2.53 (m, 3H), 3.55-3.73 (m, 2H), 3.86-4.10 (m, 2H), 4.27-4.38 (m, 1H), 6.98-7.24 (m, 5H), 7.26-7.48 (m, 7H), 7.60-7.74 (m, 2H) ppm. ¹³C NMR (101 MHz, CDCl₃): δ = 29.5, 29.5, 31.0, 31.1, 39.1, 39.5, 44.7, 45.0, 47.0, 47.0, 61.1, 61.4, 64.4, 64.8, 66.1, 66.1, 125.3, 125.6, 127.1, 127.3, 127.3, 127.6, 127.9, 128.0, 128.2, 128.2, 128.4, 128.6, 128.6, 128.7, 128.8, 129.8, 130.3, 130.4, 134.3, 134.3, 136.7, 136.9, 139.6, 139.8, 146.4, 147.1, 168.1, 168.6, 177.4, 177.5 ppm. HRMS (ESI): m/z calculated for [C₃₀H₃₄NO₃ClNa] [M+Na⁺]: 514.2119, found: 514.2120.

32, 56:44 d.r.

2-Hydroxyethyl 2-(2-((diphenylmethylene)amino)-2-(4-fluorophenyl)ethyl)-4,4-dimethylpentanoate (32)

Following the general procedure, benzophenone *O*-pivaloyl oxime **1a** (84.3 mg, 0.3 mmol), 1-fluoro-4-vinylbenzene **2i** (24.4 mg, 0.2 mmol), and 2-hydroxyethyl acrylate **3b** (46.4 mg, 0.4 mmol) were used. Purification by column chromatography using pre-basified silica with pentane/EtOAc (10:1 to 6:1, v/v) as eluent afforded **32** as a colorless sticky solid in 56:44 diastereomeric ratio (36 mg, 38% yield). Combined NMR data for both the isomers are reported here. ¹H NMR (400 MHz, CDCl₃): δ = 0.75-0.88 (m, 9H), 1.15-1.26 (m, 1H), 1.69 (dt, J = 14.1, 8.5 Hz, 1H), 1.85-2.52 (m, 4H), 3.53-3.73 (m, 2H), 3.86-4.10 (m, 2H), 4.25-4.36 (m, 1H), 6.93-7.10 (m, 4H), 7.17-7.25 (m, 2H), 7.29-7.47 (m, 6H), 7.60-7.72 (m, 2H) ppm. ¹³C{¹H, ¹⁹F} NMR (151 MHz, CDCl₃): δ = 29.5, 29.5, 31.0, 31.1, 39.1, 39.5, 44.8, 45.1, 47.0, 47.1, 61.1, 61.3, 64.1, 64.6, 66.1, 66.1, 115.3, 115.3, 127.9, 128.0, 128.2, 128.2, 128.3, 128.5, 128.6, 128.6, 128.7, 128.9, 130.2, 130.3, 136.8, 137.0, 139.8, 139.9, 140.0, 140.7, 161.8, 161.9, 167.6, 168.1, 177.5, 177.5 ppm. HRMS (ESI): m/z calculated for [C₃₀H₃₄NO₃FNa] [M+Na⁺]: 498.2415, found: 498.2406.

2-Hydroxyethyl 2-(2-(4-(*tert*-butyl)phenyl)-2-((diphenylmethylene)amino)ethyl)-4,4-dimethylpentanoate (33)

Following the general procedure, benzophenone *O*-pivaloyl oxime **1a** (84.3 mg, 0.3 mmol), 1-(*tert*-butyl)-4-vinylbenzene **2j** (32.0 mg, 0.2 mmol), and 2-hydroxyethyl acrylate **3b** (46.4 mg, 0.4 mmol) were used. Purification by column chromatography using pre-basified silica with pentane/EtOAc (10:1 to 8:1, v/v) as eluent afforded **33** as colorless oil in 55:45 diastereomeric ratio (64 mg, 62% yield). Combined NMR data

for both the isomers are reported here. 1 H NMR (400 MHz, CDCl₃): δ = 0.78-0.84 (m, 9H), 1.31 (s, 9H), 1.65-2.11 (m, 4H), 2.18-2.52 (m, 2H), 3.57-3.68 (m, 2H), 3.85-3.93 (m, 1H), 3.96-4.03 (m, 1H), 4.31-4.37 (m, 1H), 7.04-7.12 (m, 2H), 7.18-7.21 (m, 2H), 7.28-7.46 (m, 8H), 7.63-7.67 (m, 2H) ppm. 13 C NMR (101 MHz, CDCl₃): δ = 29.51, 29.52, 31.0, 31.1, 31.5, 34.56, 34.58, 39.2, 39.6, 44.7, 44.9, 46.98, 47.00, 61.1, 61.4, 64.6, 65.1, 66.0, 125.33, 125.36, 126.8, 127.0, 128.07, 128.08, 128.10, 128.18, 128.3, 128.4, 128.5, 128.72, 128.75, 130.02, 130.07, 136.9, 137.2, 140.0, 140.2, 141.2, 141.7, 149.7, 149.8, 167.2, 167.5, 177.6, 177.7 ppm. HRMS (ESI): m/z calculated for [C₃₄H₄₃NNaO₃] [M+Na⁺]: 536.3141, found: 536.3138.

34, 58:42 d.r.

2-Hydroxyethyl 2-(2-(2,5-dimethylphenyl)-2-((diphenylmethylene)amino)ethyl)-4,4-dimethylpentanoate (34 and 34')

Following the general procedure, benzophenone O-pivaloyl oxime **1a** (84.3 mg, 0.3 mmol), 1,4-dimethyl-2-vinylbenzene **2k** (26.4 mg, 0.2 mmol), and 2-hydroxyethyl acrylate **3b** (46.4 mg, 0.4 mmol) were used. Purification by column chromatography using pre-basified silica with pentane/EtOAc (10:1 to 8:1, v/v) as eluent afforded two separable diastereomers (**34** and **34'**) as colorless oils in 58:42 diastereomeric ratio (**34**: 11 mg, **34'**: 15 mg, 27% combined yield). Diastereomer **34**: ¹H NMR (400 MHz, CDCl₃): δ = 0.81 (s, 9H), 1.21 (dd, J = 14.1, 2.9 Hz, 1H), 1.64-1.83 (m, 5H), 2.08 (s, 1H), 2.28 (s, 3H), 2.35-2.56 (m, 2H), 3.61-3.73 (m, 2H), 3.91-4.01 (m, 1H), 4.05-4.15 (m, 1H), 4.54 (dd, J = 9.3, 3.9 Hz, 1H), 6.86-7.05 (m, 4H), 7.30-7.42 (m, 7H), 7.64-7.71 (m, 2H) ppm. ¹³C NMR (101 MHz, CDCl₃): δ = 18.5, 21.3, 29.6, 31.0, 40.1, 43.7, 46.0, 60.9, 61.3, 66.3, 127.3, 127.8, 128.2, 128.2, 128.5, 128.8, 130.1, 130.8, 135.8, 137.5, 140.0, 143.6, 168.3, 177.8 ppm. HRMS (ESI): m/z calculated for [C₃₂H₃₉NO₃Na] [M+Na⁺]: 508.2822, found: 508.2823. Diastereomer **34'**: ¹H NMR (400 MHz, CDCl₃):

 δ = 0.90 (s, 9H), 1.32 (dd, J = 14.1, 3.6 Hz, 1H), 1.71 (dd, J = 14.1, 8.5 Hz, 1H), 1.79 (s, 3H), 1.92 (t, J = 6.1 Hz, 1H), 2.01 (ddd, J = 13.6, 10.7, 2.8 Hz, 1H), 2.16 (ddd, J = 13.7, 10.2, 3.4 Hz, 1H), 2.27 (s, 3H), 2.60-2.71 (m, 1H), 3.61-3.71 (m, 2H), 3.89-4.14 (m, 2H), 4.35 (dd, J = 10.2, 2.8 Hz, 1H), 6.86-6.99 (m, 4H), 7.28-7.46 (m, 7H), 7.63-7.78 (m, 2H) ppm. ¹³C NMR (101 MHz, CDCl₃): δ = 18.3, 21.3, 29.6, 31.2, 39.8, 44.7, 47.5, 60.8, 61.5, 66.4, 127.1, 127.7, 128.0, 128.2, 128.2, 128.4, 128.7, 130.1, 130.1, 130.8, 135.7, 137.4, 140.2, 144.2, 168.5, 177.9 ppm. HRMS (ESI): m/z calculated for [C₃₂H₃₉NO₃Na] [M+Na⁺]: 508.2822, found: 508.2820.

35, 55:45 d.r.

2-Hydroxyethyl 2-(2-(4-acetoxyphenyl)-2-((diphenylmethylene)amino)ethyl)-4,4-dimethylpentanoate (35)

Following the general procedure, benzophenone *O*-pivaloyl oxime **1a** (84.3 mg, 0.3 mmol), 4-vinylphenyl acetate **2l** (32.4 mg, 0.2 mmol), and 2-hydroxyethyl acrylate **3b** (46.4 mg, 0.4 mmol) were used. Purification by column chromatography using prebasified silica with pentane/EtOAc (8:1 to 4:1, v/v) as eluent afforded **35** as colorless oil in 55:45 diastereomeric ratio (54 mg, 52% yield). Combined NMR data for both the isomers are reported here. 1 H NMR (400 MHz, CDCl₃): δ = 0.79-0.84 (m, 9H), 1.17-1.26 (m, 1H), 1.66-1.73 (m, 2H), 1.91-2.08 (m, 2H), 2.19-2.50 (m, 5H), 3.60-3.64 (m, 2H), 3.85-3.91 (m, 1H), 3.95-4.01 (m, 1H), 4.33-4.39 (m, 1H), 6.99-7.09 (m, 4H), 7.25-7.45 (m, 8H), 7.62-7.67 (m, 2H) ppm. 13 C NMR (101 MHz, CDCl₃): δ = 21.3, 29.5, 31.0, 31.1, 39.2, 39.4, 44.7, 45.0, 47.0, 47.1, 61.1, 61.3, 64.5, 64.7, 66.1, 121.49, 121.50, 127.9, 128.0, 128.1, 128.2, 128.3, 128.36, 128.40, 128.5, 128.6, 128.71, 128.73, 130.20, 130.24, 136.8, 137.0, 139.8, 139.9, 141.8, 142.3, 149.5, 149.6, 167.7, 167.9, 169.7,

169.8, 177.4, 177.5 ppm. HRMS (ESI): m/z calculated for [C₃₂H₃₇NNaO₅] [M+Na⁺]: 538.2569, found: 538.2569.

2-Tosylethyl 4-(1-((diphenylmethylene)amino)-3-((2-hydroxyethoxy)carbonyl)-5,5-dimethylhexyl)benzoate (36)

Following the general procedure, benzophenone *O*-pivaloyl oxime **1a** (84.3 mg, 0.3 mmol), 2-tosylethyl 4-vinylbenzoate **2m** (66.1 mg, 0.2 mmol), and 2-hydroxyethyl acrylate **3b** (46.4 mg, 0.4 mmol) were used. Purification by column chromatography using pre-basified silica with pentane/EtOAc (10/1 to 1/3, v/v) as eluent afforded **36** as a white solid in 55:45 diastereomeric ratio (35 mg, 26% yield). Combined NMR data for both the isomers are reported here. ¹H NMR (400 MHz, CDCl₃): δ = 0.75-0.88 (m, 9H), 1.13-1.27 (m, 1H), 1.65-1.73 (m, 1H), 1.74-2.58 (m, 7H), 3.53-3.72 (m, 4H), 3.85-4.09 (m, 2H), 4.30-4.43 (m, 1H), 4.55-4.67 (m, 2H), 6.92-7.07 (m, 2H), 7.22-7.48 (m, 10H), 7.60-7.70 (m, 4H), 7.77-7.84 (m, 2H) ppm. ¹³C NMR (101 MHz, CDCl₃): δ = 21.7, 21.7, 29.5, 29.5, 31.0, 31.1, 39.1, 39.5, 44.5, 44.8, 47.0, 47.0, 55.4, 58.4, 61.1, 61.3, 64.6, 65.0, 66.1, 66.1, 127.0, 127.3, 127.6, 127.8, 127.9, 128.2, 128.4, 128.6, 128.7, 130.0, 130.2, 130.4, 136.6, 136.6, 145.1, 145.1, 165.8, 177.3, 177.3 ppm. HRMS (ESI): m/z calculated for [C₄₀H₄₅NO₇SNa] [M+Na⁺]: 706.2809, found: 706.2813.

tert-Butyl 2-(2-((diphenylmethylene)amino)-2,2-diphenylethyl)-4,4-dimethylpentanoate (37)

Following the general procedure, benzophenone O-pivaloyl oxime 1a (84.3 mg, 0.3

mmol), ethene-1,1-diyldibenzene **2a** (36.0 mg, 0.2 mmol), and *tert*-butyl acrylate **3c** (51.2 mg, 0.4 mmol) were used. Purification by column chromatography using prebasified silica with pentane/EtOAc (400:1 to 200:1, v/v) as eluent afforded **37** as colorless oil (76 mg, 70% yield). 1 H NMR (400 MHz, CDCl₃): δ = 0.63 (s, 9H), 1.11-1.15 (m, 1H), 1.24 (s, 9H), 1.51-1.59 (m, 1H), 2.32-2.37 (m, 1H), 2.47-2.53 (m, 1H), 2.88-2.92 (m, 1H), 6.68-6.69 (m, 2H), 6.97-7.03 (m, 5H), 7.06-7.14 (m, 4H), 7.16-7.20 (m, 2H), 7.31-7.44 (m, 5H), 7.67-7.70 (m, 2H) ppm. 13 C NMR (101 MHz, CDCl₃): δ = 27.9, 29.5, 30.9, 38.7, 46.1, 47.7, 69.3, 79.7, 125.8, 125.9, 126.5, 127.2, 127.4, 127.6, 127.7, 127.9, 128.4, 128.6, 128.8, 129.8, 139.2, 142.3, 149.3, 149.8, 167.3, 177.4 ppm. HRMS (ESI): m/z calculated for [C₃₈H₄₃NNaO₂] [M+Na⁺]: 568.3191, found: 568.3189.

Butyl 2-(2-((diphenylmethylene)amino)-2,2-diphenylethyl)-2,4,4-trimethylpentanoate (38)

Following the general procedure, benzophenone *O*-pivaloyl oxime **1a** (84.3 mg, 0.3 mmol), ethene-1,1-diyldibenzene **2a** (36.0 mg, 0.2 mmol), and butyl methacrylate **3d** (56.8 mg, 0.4 mmol) were used. Purification by column chromatography using prebasified silica with pentane/EtOAc (400:1 to 200:1, v/v) as eluent afforded **38** as colorless oil (46 mg, 41% yield). 1 H NMR (400 MHz, CDCl₃): δ = 0.83 (s, 9H), 0.85-0.89 (m, 3H), 1.08 (s, 3H), 1.19-1.29 (m, 2H), 1.31-1.44 (m, 2H), 1.96 (d, J = 14.4 Hz, 1H), 2.57 (d, J = 14.0 Hz, 1H), 3.11-3.23 (m, 2H), 3.38-3.44 (m, 1H), 6.64 (m, 2H), 6.93-7.01 (m, 5H), 7.05-7.13 (m, 5H), 7.30-7.37 (m, 6H), 7.66-7.68 (m, 2H) ppm. 13 C NMR (101 MHz, CDCl₃): δ = 14.0, 19.4, 22.4, 30.4, 31.2, 31.9, 45.8, 52.5, 56.3, 64.5, 68.5, 125.6, 125.7, 126.7, 127.2, 127.66, 127.7, 128.0, 128.7, 129.8, 138.9, 142.4, 148.9, 151.4, 177.3 ppm. HRMS (ESI): m/z calculated for [C₃₉H₄₅NNaO₂] [M+Na⁺]: 582.3348, found: 582.3347.

Benzyl 2-(2-((diphenylmethylene)amino)-2,2-diphenylethyl)-4,4-dimethylpentanoate (39)

Following the general procedure, benzophenone *O*-pivaloyl oxime **1a** (84.3 mg, 0.3 mmol), ethene-1,1-diyldibenzene **2a** (36.0 mg, 0.2 mmol), and benzyl acrylate **3e** (64.8 mg, 0.4 mmol) were used. Purification by column chromatography using pre-basified silica with pentane/EtOAc (400:1 to 200:1, v/v) as eluent afforded **39** as colorless oil (76 mg, 66% yield). 1 H NMR (400 MHz, CDCl₃): δ = 0.58 (s, 9H), 1.12 (dd, J = 14.0 Hz, 3.6 Hz, 1H), 1.58-1.63 (m, 1H), 2.20-2.24 (m, 1H), 2.47-2.53 (m, 1H), 2.98-3.04 (m, 1H), 4.24-4.27 (m, 1H), 4.56-4.59 (m, 1H), 6.61 (m, 2H), 6.84-6.92 (m, 7H), 6.98-7.03 (m, 1H), 7.08-7.14 (m, 3H), 7.16-7.30 (m, 8H), 7.40-7.62 (m, 4H) ppm. 13 C NMR (101 MHz, CDCl₃): δ = 29.3, 31.0, 37.7, 46.9, 49.6, 66.1, 69.2, 125.8, 126.0, 126.5, 127.2, 127.3, 127.5, 127.79, 127.82, 127.95, 128.00, 128.2, 128.4, 128.7, 129.9, 136.2, 138.9, 142.2, 148.6, 149.8, 167.6, 177.5 ppm. HRMS (ESI): m/z calculated for [C₄₁H₄₁NNaO₂] [M+Na⁺]: 602.3035, found: 602.3027.

2,2,2-Trifluoroethyl 2-(2-((diphenylmethylene)amino)-2,2-diphenylethyl)-4,4-dimethylpentanoate (40)

Following the general procedure, benzophenone *O*-pivaloyl oxime **1a** (84.3 mg, 0.3 mmol), ethene-1,1-diyldibenzene **2a** (36.0 mg, 0.2 mmol), and 2,2,2-trifluoroethyl acrylate **3f** (61.6 mg, 0.4 mmol) were used. Purification by column chromatography using pre-basified silica with pentane/EtOAc (400:1 to 200:1, v/v) as eluent afforded **40** as colorless oil (80 mg, 70% yield). ¹H NMR (400 MHz, CDCl₃): $\delta = 0.65$ (s, 9H),

1.19-1.28 (m, 1H), 1.65 (dd, J = 14.2, 8.2 Hz, 1H), 2.29 (dd, J = 13.4, 2.5 Hz, 1H), 2.48-2.59 (m, 1H), 3.06 (dd, J = 13.3, 10.7 Hz, 1H), 3.37 (dq, J = 12.7, 8.7 Hz, 1H), 3.91 (dq, J = 12.7, 8.6 Hz, 1H), 6.67 (s, 2H), 6.89-7.02 (m, 6H), 7.07 (tt, J = 7.4, 1.3 Hz, 1H), 7.19 (qt, J = 7.2, 1.5 Hz, 2H), 7.26-7.41 (m, 5H), 7.44-7.71 (m, 4H) ppm. ¹³C NMR (101 MHz, CDCl₃): $\delta = 29.2$, 31.1, 37.3, 47.3, 49.6, 60.6 (q, J = 36.0 Hz), 69.3, 125.9, 126.2, 126.7, 127.2, 127.3, 127.6, 127.9, 128.1, 128.6, 130.1, 138.8, 142.2, 148.1, 149.5, 168.1, 176.2 ppm. HRMS (ESI): m/z calculated for [C₃₆H₃₆F₃NNaO₂] [M+Na⁺]: 594.2596, found: 594.2590.

Prop-2-yn-1-yl 2-(2-((diphenylmethylene)amino)-2,2-diphenylethyl)-4,4-dimethylpentanoate (41)

Following the general procedure, benzophenone *O*-pivaloyl oxime **1a** (84.3 mg, 0.3 mmol), ethene-1,1-diyldibenzene **2a** (36.0 mg, 0.2 mmol), and prop-2-yn-1-yl acrylate **3g** (44.0 mg, 0.4 mmol) were used. Purification by column chromatography using prebasified silica with pentane/EtOAc (400:1 to 200:1, v/v) as eluent afforded **41** as colorless oil (63 mg, 60% yield). 1 H NMR (400 MHz, CDCl₃): δ = 0.68 (s, 9H), 1.17-1.21 (m, 1H), 1.65-1.71 (m, 1H), 2.27-2.31 (m, 1H), 2.36 (t, J = 2.4 Hz, 1H), 2.50-2.56 (m, 1H), 3.02-3.08 (m, 1H), 3.82-3.87 (m, 1H), 4.07-4.12 (m, 1H), 6.69 (m, 2H), 6.92-7.00 (m, 7H), 7.06-7.10 (m, 1H), 7.15-7.20 (m, 1H), 7.24-7.40 (m, 5H), 7.48-7.64 (m, 2H), 7.63-7.69 (m, 2H) ppm. 13 C NMR (101 MHz, CDCl₃): δ = 29.4, 31.1, 37.5, 47.0, 49.6, 51.8, 69.2, 74.5, 78.1, 125.8, 126.1, 126.6, 127.26, 127.32, 127.5, 127.9, 128.0, 128.2, 128.4, 128.6, 130.0, 138.8, 142.0, 148.4, 149.8, 167.6, 176.8 ppm. HRMS (ESI): m/z calculated for [C₃₇H₃₇NNaO₂] [M+Na⁺]: 550.2722, found: 550.2716.

42

Methyl 2-(2-((diphenylmethylene)amino)-2,2-diphenylethyl)-2-fluoro-4,4-dimethylpentanoate (42)

Following the general procedure, benzophenone *O*-pivaloyl oxime **1a** (84.3 mg, 0.3 mmol), ethene-1,1-diyldibenzene **2a** (36.0 mg, 0.2 mmol), and methyl 2-fluoroacrylate **3h** (41.6 mg, 0.4 mmol) were used. Purification by column chromatography using prebasified silica with pentane/EtOAc (400:1 to 200:1, v/v) as eluent afforded **42** as colorless oil (75 mg, 72% yield). 1 H NMR (400 MHz, CDCl₃): δ = 0.86 (s, 9H), 1.73-1.78 (m, 1H), 1.84-1.97 (m, 1H), 2.88-2.93 (m, 1H), 3.04-3.15 (m, 1H), 3.17 (s, 3H), 6.60-6.62 (m, 2H), 7.02-7.12 (m, 5H), 7.13-7.21 (m, 4H), 7.27-7.41 (m, 7H), 7.71-7.74 (m, 2H) ppm. 13 C NMR (101 MHz, CDCl₃): δ = 30.3, 30.4, 31.2, 48.4, 48.6, 52.0, 52.8, 53.0, 66.9, 94.9, 96.8, 125.91, 125.94, 127.0, 127.3, 127.5, 127.7, 127.8, 128.0, 128.5, 128.8, 129.9, 139.1, 142.5, 148.5, 150.8, 167.1, 171.9, 172.1 ppm. HRMS (ESI): m/z calculated for [C₃₅H₃₆FNNaO₂] [M+Na⁺]: 544.2628, found: 544.2625.

43, 50:50 d.r.

Dimethyl 2-(tert-butyl)-3-(2-((diphenylmethylene)amino)-2,2-diphenylethyl)succinate (43)

Following the general procedure, benzophenone *O*-pivaloyl oxime **1a** (84.3 mg, 0.3 mmol), ethene-1,1-diyldibenzene **2a** (36.0 mg, 0.2 mmol), and dimethyl maleate **3i** (57.6 mg, 0.4 mmol) were used. Purification by column chromatography using prebasified silica with pentane/EtOAc (200:1 to 100:1, v/v) as eluent afforded **43** as colorless oil in 50:50 diastereomeric ratio (57 mg, 51% yield). Combined NMR data for both the isomers are reported here. ¹H NMR (400 MHz, CDCl₃): $\delta = 0.75$ (s, 9H),

2.34-2.37 (m, 1H), 2.47-2.49 (m, 1H), 2.68-2.78 (m, 1H), 3.01-3.07 (m, 4H), 3.58 (s, 3H), 6.75-6.77 (m, 3H), 6.81-7.06 (m, 7H), 7.13-7.39 (m, 8H), 7.62-7.65 (m, 2H) ppm. 13 C NMR (101 MHz, CDCl₃): δ = 28.1, 33.4, 40.0, 43.2, 51.2, 51.7, 59.0, 69.4, 125.8, 126.1, 126.4, 127.23, 127.25, 127.4, 127.6, 127.9, 128.5, 128.8, 129.9, 139.0, 142.4, 148.2, 149.3, 167.9, 173.3, 175.6 ppm. HRMS (ESI): m/z calculated for [C₃₇H₃₉NNaO₄] [M+Na⁺]: 584.2777, found: 584.2777.

3-(2-((Diphenylmethylene)amino)-2,2-diphenylethyl)-3-neopentyldihydrofuran-2(3*H*)-one (44)

Following the general procedure, benzophenone O-pivaloyl oxime 1a (84.3 mg, 0.3 ethene-1,1-diyldibenzene 2a (36.0)mg, 0.2 mmol). methylenedihydrofuran-2(3H)-one **3j** (39.2 mg, 0.4 mmol) were used. Purification by column chromatography using pre-basified silica with pentane/EtOAc (200:1 to 100:1, v/v) as eluent afforded **44** as colorless oil (44 mg, 43% yield). ¹H NMR (400 MHz, CDCl₃): $\delta = 0.96$ (s, 9H), 1.61-1.64 (m, 1H), 1.72-1.85 (m, 2H), 2.05-2.12 (m, 1H), 2.94-2.98 (m, 1H), 3.08-3.12 (m, 1H), 3.98-4.05 (m, 1H), 4.12-4.17 (m, 1H), 6.74 (m, 2H), 6.93-6.99 (m, 5H), 7.03-7.07 (m, 2H), 7.10-7.17 (m, 1H), 7.18-7.23 (m, 3H), 7.30-7.40 (m, 5H), 7.62-7.64 (m, 2H) ppm. 13 C NMR (101 MHz, CDCl₃): $\delta = 30.2, 31.5,$ 32.0, 45.5, 48.2, 53.0, 65.5, 68.6, 125.9, 126.1, 126.7, 127.3, 127.6, 127.7, 128.0, 128.1, 128.4, 128.6, 130.1, 130.2, 138.5, 141.7, 148.2, 150.3, 168.0, 182.0 ppm. HRMS (ESI): m/z calculated for $[C_{36}H_{37}NNaO_2]$ $[M+Na^+]$: 538.2722, found: 538.2722.

45

2-Hydroxyethyl 2-(2-((diphenylmethylene)amino)-2,2-diphenylethyl)-4,4-dimethylpentanoate (45)

Following the general procedure, benzophenone *O*-pivaloyl oxime **1a** (84.3 mg, 0.3 mmol), ethene-1,1-diyldibenzene **2a** (36.0 mg, 0.2 mmol), and 2-hydroxyethyl acrylate **3b** (46.4 mg, 0.4 mmol) were used. Purification by column chromatography using prebasified silica with pentane/EtOAc (20:1 to 10:1, v/v) as eluent afforded **45** as colorless oil (72 mg, 68% yield). ¹H NMR (400 MHz, CDCl₃): δ = 0.67 (s, 9H), 1.20 (dd, J = 14.0 Hz, 3.2 Hz, 1H), 1.66-1.76 (m, 2H), 2.30-2.34 (m, 1H), 2.52-2.58 (m, 1H), 3.03-3.09 (m, 1H), 3.40-3.45 (m, 1H), 3.48-3.60 (m, 2H), 3.66-3.72 (m, 1H), 6.68 (m, 2H), 6.92-7.00 (m, 7H), 7.06-7.10 (m, 1H), 7.15-7.20 (m, 1H), 7.24-7.29 (m, 2H), 7.31-7.40 (m, 3H), 7.54-7.63 (m, 2H), 7.65-7.68 (m, 2H) ppm. ¹³C NMR (101 MHz, CDCl₃): δ = 29.3, 31.0, 37.5, 47.0, 49.8, 61.1, 66.0, 69.2, 125.8, 126.1, 126.6, 127.2, 127.3, 127.5, 127.8, 128.0, 128.1, 128.3, 128.6, 130.0, 138.8, 142.3, 148.4, 149.6, 167.8, 178.3 ppm. HRMS (ESI): m/z calculated for [C₃₆H₃₉NNaO₃] [M+Na⁺]: 556.2828, found: 556.2822.

Dimethyl (1-((diphenylmethylene)amino)-5,5-dimethyl-1,1-diphenylhexan-3-yl)phosphonate (46)

Following the general procedure, benzophenone *O*-pivaloyl oxime **1a** (84.3 mg, 0.3 mmol), ethene-1,1-diyldibenzene **2a** (36.0 mg, 0.2 mmol), and dimethyl vinylphosphonate **3k** (54.4 mg, 0.4 mmol) were used. Purification by column chromatography using pre-basified silica with pentane/EtOAc (6:1 to 2:1, v/v) as eluent afforded **46** as colorless oil (64 mg, 58% yield). ¹H NMR (400 MHz, CDCl₃): δ = 0.69 (s, 9H), 1.46-1.72 (m, 2H), 2.10-2.21 (m, 1H), 2.43-2.51 (m, 1H), 3.08-3.17 (m, 1H), 3.48-3.54 (m, 6H), 6.64-6.66 (m, 2H), 6.96-7.00 (m, 2H), 7.02-7.18 (m, 9H), 7.25-7.38 (m, 5H), 7.66-7.68 (m, 2H) ppm. ¹³C NMR (101 MHz, CDCl₃): δ = 28.0, 29.4, 30.0, 30.6 (d, J = 2.0 Hz), 43.2 (d, J = 2.0 Hz), 44.3 (d, J = 4.0 Hz), 52.1 (d, J = 7.0 Hz), 52.3

(d, J = 6.0 Hz), 69.6 (d, J = 11.0 Hz), 125.94, 125.96, 126.5, 127.25, 127.32, 127.6, 127.7, 127.9, 128.6, 128.7, 129.9, 139.0, 142.2, 148.8, 149.1, 167.2 ppm. HRMS (ESI): m/z calculated for [C₃₅H₄₀NNaO₃P] [M+Na⁺]: 576.2644, found: 576.2647.

$\hbox{$2$-(2-((Bis(4-fluor ophenyl)methylene)amino)-2,2-diphenylethyl)-4,4-dimethylpentanenitrile~(47)}$

Following the general procedure, oxime ester **1al** (95.2 mg, 0.3 mmol), ethene-1,1-diyldibenzene **2a** (36.0 mg, 0.2 mmol), and acrylonitrile **3a** (21.2 mg, 0.4 mmol) were used. Purification by column chromatography using pre-basified silica with pentane/EtOAc (500:1 to 200:1, v/v) as eluent afforded **47** as a white solid (46 mg, 45% yield). 1 H NMR (400 MHz, CDCl₃): δ = 0.72 (s, 9H), 1.09 (dd, J = 13.9, 2.9 Hz, 1H), 1.69 (dd, J = 13.9, 10.3 Hz, 1H), 2.29 (dd, J = 13.6, 3.3 Hz, 1H), 2.54 (ddt, J = 10.2, 8.4, 3.1 Hz, 1H), 2.93 (dd, J = 13.6, 8.5 Hz, 1H), 6.55 (s, 2H), 6.71 (t, J = 8.6 Hz, 2H), 6.91-6.98 (m, 2H), 6.99-7.11 (m, 5H), 7.17-7.23 (m, 1H), 7.26-7.32 (m, 2H), 7.42-7.57 (m, 2H), 7.64-7.71 (m, 2H) ppm. 13 C{ 1 H, 19 F} NMR (126 MHz, CDCl₃): δ = 22.3, 29.2, 31.0, 46.3, 48.7, 68.9, 114.6, 115.0, 115.7, 124.6, 126.6, 126.7, 128.0, 128.1, 128.3, 129.0, 130.8, 132.6, 134.3, 137.7, 147.9, 148.0, 161.7, 164.4, 166.9 ppm. HRMS (ESI): m/z calculated for [C₃₄H₃₂N₂F₂Na] [M+Na⁺]: 529.2426, found: 529.2421.

2-(2-(((4-Methoxyphenyl)(phenyl)methylene)amino)-2,2-diphenylethyl)-4,4dimethylpentanenitrile (48)

Following the general procedure, oxime ester 1am (93.4 mg, 0.3 mmol), ethene-1,1diyldibenzene 2a (36.0 mg, 0.2 mmol), and acrylonitrile 3a (21.2 mg, 0.4 mmol) were used. Purification by column chromatography using pre-basified silica with pentane/EtOAc (500:1 to 25:1, v/v) as eluent afforded 48 as a white solid (41 mg, 41%) yield) with an E/Z-ratio of 70:30. Combined NMR data for both the isomers are reported here. ${}^{1}H$ NMR (400 MHz, CDCl₃): $\delta = 0.69-0.76$ (m, 9H), 1.06-1.17 (m, 1H), 1.58-1.71 (m, 1H), 2.28-2.38 (m, 1H), 2.52-2.63 (m, 1H), 2.91-3.02 (m, 1H), 3.76-3.84 (m, 3H), 6.37-6.69 (m, 2H), 6.81-7.20 (m, 9H), 7.20-7.29 (m, 2H), 7.32-7.40 (m, 1H), 7.48 (s, 2H), 7.62-7.75 (m, 2H) ppm. 13 C NMR (101 MHz, CDCl₃): $\delta = 22.4, 22.4, 29.3, 31.0,$ 31.0, 45.8, 46.2, 48.4, 55.3, 55.4, 68.4, 68.6, 112.9, 113.3, 124.5, 124.6, 126.3, 126.4, 126.5, 126.8, 127.2, 127.4, 127.9, 128.0, 128.0, 128.1, 128.2, 128.6, 128.8, 130.2, 130.4, 130.9, 134.6, 138.8, 142.0, 148.2, 148.3, 148.4, 148.5, 158.4, 161.4, 168.0, 169.0 ppm. HRMS (ESI): m/z calculated for [C₃₅H₃₆N₂ONa] [M+Na⁺]: 523.2720, found: 523.2717.

49, 52:48 E/Z

2-(2-(((4-bromophenyl)(phenyl)methylene)amino)-2,2-diphenylethyl)-4,4-dimethylpentanenitrile (49)

Following the general procedure, oxime ester **1an** (108 mg, 0.3 mmol), ethene-1,1-diyldibenzene **2a** (36.0 mg, 0.2 mmol), and acrylonitrile **3a** (21.2 mg, 0.4 mmol) were used. Purification by column chromatography using pre-basified silica with pentane/EtOAc (500:1 to 150:1, v/v) as eluent afforded **49** as a white solid (56 mg, 51% yield) with an E/Z-ratio of 52:48. Combined NMR data for both the isomers are reported here. 1 H NMR (400 MHz, CDCl₃): δ = 0.73 (s, 9H), 1.05-1.14 (m, 1H), 1.62-1.74 (m, 1H), 2.25-2.39 (m, 1H), 2.47-2.63 (m, 1H), 2.85-3.09 (m, 1H), 6.32-6.73 (m, 2H), 6.91-7.23 (m, 8H), 7.23-7.31 (m, 2H), 7.32-7.62 (m, 6H), 7.66-7.72 (m, 1H) ppm. 13 C NMR (101 MHz, CDCl₃): δ = 22.3, 22.3, 29.2, 31.0, 31.0, 46.0, 46.4, 48.6, 68.8, 68.9, 121.3, 124.5, 124.6, 125.1, 126.5, 126.6, 126.7, 126.7, 127.1, 127.6, 128.0, 128.0, 128.1, 128.1, 128.2, 128.2, 128.6, 128.7, 128.9, 130.1, 130.3, 130.5, 130.6, 131.2, 131.7, 131.8, 137.6, 138.1, 140.5, 141.0, 147.8, 147.9, 147.9, 148.2, 167.7, 168.0 ppm. HRMS (ESI): m/z calculated for [C₃₄H₃₃N₂BrNa] [M+Na⁺]: 571.1719, found: 571.1720.

(*E*)-2-(2,2-Diphenyl-2-((1-phenylethylidene)amino)ethyl)-4,4-dimethylpentanenitrile (50)

Following the general procedure, (*E*)-1-phenylethan-1-one *O*-pivaloyl oxime **1ao** (65.8 mg, 0.3 mmol), ethene-1,1-diyldibenzene **2a** (36.0 mg, 0.2 mmol), and acrylonitrile **3a** (21.2 mg, 0.4 mmol) were used. Purification by column chromatography using pre-basified silica with pentane/EtOAc (500:1 to 50:1, v/v) as eluent afforded **50** as a colorless oil (26 mg, 32% yield) in >95:5 *E/Z* ratio. ¹H NMR (400 MHz, CDCl₃): δ = 0.73 (s, 9H), 1.19 (dd, J = 13.9, 2.8 Hz, 1H), 1.62-1.74 (m, 1H), 1.83 (s, 3H), 2.51-2.64 (m, 2H), 3.04-3.14 (m, 1H), 7.17-7.25 (m, 2H), 7.28-7.36 (m, 4H), 7.37-7.48 (m, 5H), 7.52-7.60 (m, 2H), 7.94-8.03 (m, 2H) ppm. ¹³C NMR (101 MHz, CDCl₃): δ = 20.8, 22.6, 29.3, 31.0, 47.1, 48.7, 68.6, 124.6, 126.7, 126.8, 127.2,

127.5, 127.8, 128.3, 128.5, 128.6, 130.0, 142.1, 146.9, 147.1, 167.9 ppm. HRMS (ESI): m/z calculated for [C₂₉H₃₂N₂Na] [M+Na⁺]: 431.2458, found: 431.2457.

51

Benzyl (3-cyano-5-((diphenylmethylene)amino)-5,5-diphenylpentyl)carbamate (51)

Following the general procedure, benzyl (2-(((diphenylmethylene)amino)oxy)-2-oxoethyl)carbamate **1s** (116.4 mg, 0.3 mmol), ethene-1,1-diyldibenzene **2a** (36.0 mg, 0.2 mmol), and acrylonitrile **3a** (21.2 mg, 0.4 mmol) were used. Purification by column chromatography using pre-basified silica with pentane/EtOAc (10:1 to 8:1, v/v) as eluent afforded **51** as a white solid (69 mg, 60% yield). 1 H NMR (400 MHz, CDCl₃): δ = 1.60-1.74 (m, 2H), 2.35-2.39 (m, 1H), 2.66-2.73 (m, 1H), 2.89-2.95 (m, 1H), 3.06-3.22 (m, 2H), 4.22-4.57 (m, 1H), 5.02-5.10 (m, 2H), 6.55-6.57 (m, 2H), 7.00-7.19 (m, 9H), 7.21-7.27 (m, 2H), 7.30-7.42 (m, 8H), 7.46-7.51 (m, 2H), 7.71-7.74 (m, 2H) ppm. 13 C NMR (101 MHz, CDCl₃): δ = 24.0, 33.9, 38.4, 43.3, 66.8, 68.4, 122.2, 126.57, 126.65, 127.0, 127.1, 127.5, 127.98, 128.04, 128.08, 128.11, 128.22, 128.27, 128.6, 128.7, 130.3, 136.6, 138.4, 141.4, 147.6, 148.2, 156.2, 169.1 ppm. HRMS (ESI): m/z calculated for [C₃₉H₃₅N₃NaO₂] [M+Na⁺]: 600.2627, found: 600.2615.

(2R)-Methyl

2-(((benzyloxy)carbonyl)amino)-5-cyano-7-

((diphenylmethylene)amino)-7,7-diphenylheptanoate (52)

Following the general procedure, (*R*)-methyl 2-(((benzyloxy)carbonyl)amino)-4-(((diphenylmethylene)amino)oxy)-4-oxobutanoate **1t** (138.0 mg, 0.3 mmol), ethene-1,1-diyldibenzene **2a** (36.0 mg, 0.2 mmol), and acrylonitrile **3a** (21.2 mg, 0.4 mmol) were used. Purification by column chromatography using pre-basified silica with

pentane/EtOAc (6:1 to 4:1, v/v) as eluent afforded **52** as a white solid in 50:50 diastereomeric ratio (83 mg, 64% yield). Combined NMR data for both the isomers are reported here. 1 H NMR (400 MHz, CDCl₃): δ = 1.30-1.62 (m, 2H), 1.65-2.00 (m, 2H), 2.31-2.36 (m, 1H), 2.59-2.66 (m, 1H), 2.84-2.92 (m, 1H), 3.69-3.75 (m, 3H), 4.23-4.38 (m, 1H), 5.09-5.16 (m, 3H), 6.52-6.54 (m, 2H), 7.00-7.12 (m, 7H), 7.13-7.20 (m, 2H), 7.21-7.25 (m, 2H), 7.30-7.45 (m, 10H), 7.69-7.72 (m, 2H) ppm. 13 C NMR (101 MHz, CDCl₃): δ = 26.6, 26.7, 29.9, 30.2, 43.6, 52.60, 52.63, 53.4, 67.2, 68.27, 68.30, 122.0, 122.1, 126.57, 126.63, 127.07, 127.14, 127.49, 127.54, 127.90, 127.92, 127.97, 128.04, 128.09, 128.22, 128.25, 128.4, 128.66, 128.67, 128.70, 129.0, 129.4, 130.4, 136.2, 138.41, 138.42, 141.43, 141.44, 147.66, 147.70, 148.09, 148.17, 155.9, 168.9, 172.3 ppm. HRMS (ESI): m/z calculated for [C₄₂H₃₉N₃NaO₄] [M+Na⁺]: 672.2838, found: 672.2839.

53

tert-Butyl (2-((3-cyano-5-((diphenylmethylene)amino)-5,5-diphenylpentyl)amino)-2-oxoethyl)carbamate (53)

Following the general procedure, *tert*-butyl (2-((2-(((diphenylmethylene)amino)oxy)-2-oxoethyl)amino)-2-oxoethyl)carbamate **1u** (123.3 mg, 0.3 mmol), ethene-1,1-diyldibenzene **2a** (36.0 mg, 0.2 mmol), and acrylonitrile **3a** (21.2 mg, 0.4 mmol) were used. Purification by column chromatography using pre-basified silica with pentane/EtOAc (2:1 to 1:1, v/v) as eluent afforded **53** as a white solid (61 mg, 51% yield). 1 H NMR (400 MHz, CDCl₃): δ = 1.45-1.46 (m, 9H), 1.62-1.74 (m, 2H), 2.34-2.38 (m, 1H), 2.59-2.66 (m, 1H), 2.87-2.93 (m, 1H), 3.08-3.29 (m, 2H), 3.62-3.63 (m, 2H), 5.01 (s, 1H), 5.95-5.97 (m, 1H), 6.53-6.55 (m, 2H), 6.99-7.14 (m, 7H), 7.17-7.30 (m, 4H), 7.32-7.47 (m, 5H), 7.68-7.71 (m, 2H) ppm. 13 C NMR (101 MHz, CDCl₃): δ = 24.2, 28.4, 33.4, 36.9, 43.2, 44.3, 68.4, 80.4, 122.4, 126.58, 126.61, 127.06, 127.11, 127.5, 128.02, 128.06, 128.09, 128.3, 128.7, 130.4, 138.4, 141.4, 147.6, 148.4, 169.1, 169.6 ppm. HRMS (ESI): m/z calculated for [C₃₈H₄₀N₄NaO₃] [M+Na⁺]: 623.2998,

found: 623.3009.

Benzyl (2-((2-((3-cyano-5-((diphenylmethylene)amino)-5,5-

diphenylpentyl)amino)-2-oxoethyl)amino)-2-oxoethyl)carbamate (54)

Following the general procedure, benzyl (4,7,10-trioxo-1,1-diphenyl-3-oxa-2,6,9-triazaundec-1-en-11-yl)carbamate **1v** (150.6 mg, 0.3 mmol), ethene-1,1-diyldibenzene **2a** (36.0 mg, 0.2 mmol), and acrylonitrile **3a** (21.2 mg, 0.4 mmol) were used. Purification by column chromatography using pre-basified silica with pentane/EtOAc (1:1, v/v) as eluent afforded **54** as a white solid (91 mg, 66% yield). ¹H NMR (400 MHz, CDCl₃): $\delta = 1.56$ -1.70 (m, 2H), 2.32-2.36 (m, 1H), 2.60-2.66 (m, 1H), 2.86-2.91 (m, 1H), 3.12-3.26 (m, 2H), 3.75-3.78 (m, 4H), 5.07-5.09 (m, 2H), 5.72 (t, J = 5.6 Hz, 1H), 6.48-6.53 (m, 2H), 6.85 (t, J = 5.6 Hz, 1H), 6.98-7.18 (m, 10H), 7.21-7.25 (m, 2H), 7.27-7.39 (m, 8H), 7.42-7.44 (m, 2H), 7.67-7.70 (m, 2H) ppm. ¹³C NMR (101 MHz, CDCl₃): $\delta = 24.4$, 33.2, 36.9, 43.0, 43.3, 44.7, 67.4, 68.4, 122.6, 126.56, 126.60, 127.1, 127.5, 127.96, 127.99, 128.04, 128.07, 128.2, 128.3, 128.4, 128.67, 128.72, 130.4, 136.2, 138.4, 141.4, 147.5, 148.2, 157.0, 168.8, 169.1, 169.8 ppm. HRMS (ESI): m/z calculated for [C₄₃H₄₁N₅NaO₄] [M+Na⁺]: 714.3056, found: 714.3048.

2-(2-((Diphenylmethylene)amino)-2,2-diphenylethyl)icosanenitrile (55)

Following the general procedure, benzophenone *O*-stearoyl oxime **1w** (138.9 mg, 0.3 mmol), ethene-1,1-diyldibenzene **2a** (36.0 mg, 0.2 mmol), and acrylonitrile **3a** (21.2 mg, 0.4 mmol) were used. Purification by column chromatography using pre-basified silica with pentane/EtOAc (400:1 to 200:1, v/v) as eluent afforded **55** as a white solid

(74 mg, 57% yield). 1 H NMR (400 MHz, CDCl₃): δ = 0.90 (t, J = 7.2 Hz, 3H), 1.11-1.48 (m, 35H), 2.34-2.39 (m, 1H), 2.57-2.63 (m, 1H), 2.86-2.92 (m, 1H), 6.56-6.58 (m, 2H), 7.01-7.20 (m, 9H), 7.22-7.27 (m, 2H), 7.33-7.42 (m, 3H), 7.43-7.53 (m, 2H), 7.71-7.74 (m, 2H) ppm. 13 C NMR (101 MHz, CDCl₃): δ = 14.3, 22.8, 26.6, 26.8, 29.0, 29.4, 29.5, 29.6, 29.7, 29.78, 29.79, 29.82, 29.84, 32.1, 34.0, 43.6, 68.4, 122.9, 126.46, 126.48, 127.0, 127.3, 127.4, 127.98, 128.02, 128.06, 128.2, 128.7, 129.1, 130.2, 138.6, 141.6, 148.1, 148.5, 168.7 ppm. HRMS (ESI): m/z calculated for [C₄₇H₆₀N₂Na] [M+Na⁺]: 675.4654, found: 675.4651.

56

(Z)-2-(2-((Diphenylmethylene)amino)-2,2-diphenylethyl)icos-11-enenitrile (56)

Following the general procedure, (*Z*)-benzophenone *O*-oleoyl oxime **1x** (138.3 mg, 0.3 mmol), ethene-1,1-diyldibenzene **2a** (36.0 mg, 0.2 mmol), and acrylonitrile **3a** (21.2 mg, 0.4 mmol) were used. Purification by column chromatography using pre-basified silica with pentane/EtOAc (400:1 to 200:1, v/v) as eluent afforded **56** as a white solid (78 mg, 60% yield). 1 H NMR (400 MHz, CDCl₃): δ = 0.87-0.90 (m, 3H), 1.06-1.46 (m, 26H), 1.99-2.05 (m, 4H), 2.33-2.37 (m, 1H), 2.55-2.61 (m, 1H), 2.85-2.90 (m, 1H), 5.30-5.40 (m, 2H), 6.54-6.56 (m, 2H), 7.00-7.18 (m, 9H), 7.22-7.26 (m, 2H), 7.32-7.40 (m, 3H), 7.42-7.52 (m, 2H), 7.70-7.72 (m, 2H) ppm. 13 C NMR (101 MHz, CDCl₃): δ = 14.3, 22.8, 26.7, 26.8, 27.35, 27.37, 29.0, 29.34, 29.37, 29.46, 29.52, 29.7, 29.88, 29.91, 32.0, 34.0, 43.6, 68.4, 122.9, 126.47, 126.49, 127.0, 127.3, 127.5, 127.99, 128.03, 128.07, 128.2, 128.7, 130.0, 130.1, 130.3, 132.4, 138.6, 141.6, 148.1, 148.5, 168.7 ppm. HRMS (ESI): m/z calculated for [C₄₇H₅₈N₂Na] [M+Na⁺]: 673.4498, found: 673.4505.

(Z)-2-(2-((Diphenylmethylene)amino)-2,2-diphenylethyl)tetracos-15-enenitrile (57)

Following the general procedure, (*Z*)-benzophenone *O*-docos-13-enoyl oxime **1y** (155.1 mg, 0.3 mmol), ethene-1,1-diyldibenzene **2a** (36.0 mg, 0.2 mmol), and acrylonitrile **3a** (21.2 mg, 0.4 mmol) were used. Purification by column chromatography using pre-basified silica with pentane/EtOAc (400:1 to 200:1, v/v) as eluent afforded **57** as a white solid (79 mg, 56% yield). 1 H NMR (400 MHz, CDCl₃): δ = 0.89 (t, J = 6.8 Hz, 3H), 1.07-1.46 (m, 34H), 2.00-2.05 (m, 4H), 2.33-2.37 (m, 1H), 2.55-2.61 (m, 1H), 2.84-2.90 (m, 1H), 5.32-5.50 (m, 2H), 6.54-6.56 (m, 2H), 6.99-7.18 (m, 9H), 7.21-7.25 (m, 2H), 7.32-7.40 (m, 3H), 7.41-7.47 (m, 2H), 7.69-7.72 (m, 2H) ppm. 13 C NMR (101 MHz, CDCl₃): δ = 14.3, 22.8, 26.7, 26.8, 27.4, 29.0, 29.38, 29.47, 29.48, 29.63, 29.67, 29.72, 29.74, 29.79, 29.92, 29.94, 32.0, 34.1, 43.6, 68.4, 122.9, 126.48, 126.49, 127.0, 127.3, 127.5, 128.00, 128.03, 128.07, 128.2, 128.7, 130.04, 130.06, 130.3, 138.6, 141.6, 148.1, 148.5, 168.7 ppm. HRMS (ESI): m/z calculated for [C₅₁H₆₆N₂Na] [M+Na⁺]: 729.5124, found: 729.5118.

$(11Z,14Z)-2-(2-((diphenylmethylene)amino)-2,2-diphenylethyl)icosa-11,14-dienenitrile \ (58)$

Following the general procedure, benzophenone O-((9Z,12Z)-octadeca-9,12-dienoyl) oxime $\mathbf{1z}$ (137.7 mg, 0.3 mmol), ethene-1,1-diyldibenzene $\mathbf{2a}$ (36.0 mg, 0.2 mmol), and

acrylonitrile **3a** (21.2 mg, 0.4 mmol) were used. Purification by column chromatography using pre-basified silica with pentane/EtOAc (400:1 to 200:1, v/v) as eluent afforded **58** as a white solid (78 mg, 60% yield). 1 H NMR (400 MHz, CDCl₃): δ = 0.88-0.92 (m, 3H), 1.06-1.46 (m, 20H), 2.03-2.09 (m, 4H), 2.33-2.38 (m, 1H), 2.55-2.62 (m, 1H), 2.76-2.81 (m, 2H), 2.85-2.90 (m, 1H), 5.31-5.44 (m, 4H), 6.55-6.57 (m, 2H), 7.00-7.12 (m, 7H), 7.13-7.19 (m, 2H), 7.22-7.26 (m, 2H), 7.32-7.41 (m, 3H), 7.41-7.51 (m, 2H), 7.70-7.72 (m, 2H) ppm. 13 C NMR (101 MHz, CDCl₃): δ = 14.2, 22.7, 25.8, 26.7, 26.8, 27.35, 27.37, 29.0, 29.33, 29.37, 29.49, 29.52, 29.8, 31.7, 34.0, 43.6, 68.4, 122.9, 126.47, 16.49, 127.0, 127.3, 127.5, 127.99, 128.02, 128.07, 128.15, 128.16, 128.7, 130.24, 130.27, 130.35, 138.6, 141.6, 148.1, 148.5, 168.7 ppm. HRMS (ESI): m/z calculated for [C₄₇H₅₆N₂Na] [M+Na⁺]: 671.4341, found: 671.4341.

59, 50:50 d.r.

4-((Diphenylmethylene)amino)-4,4-diphenyl-2-((4,7,7-trimethyl-3-oxo-2-oxabicyclo[2.2.1]heptan-1-yl)methyl)butanenitrile (59)

Following the general procedure, 1-((((diphenylmethylene)amino)oxy)carbonyl)-4,7,7-trimethyl-2-oxabicyclo[2.2.1]heptan-3-one **1aa** (113.1 mg, 0.3 mmol), ethene-1,1-diyldibenzene **2a** (36.0 mg, 0.2 mmol), and acrylonitrile **3a** (21.2 mg, 0.4 mmol) were used. Purification by column chromatography using pre-basified silica with pentane/EtOAc (40:1 to 30:1, v/v) as eluent afforded **59** as a white solid in 50:50 diastereomeric ratio (76 mg, 67% yield). Combined NMR data for both the isomers are reported here. 1 H NMR (400 MHz, CDCl₃): δ = 0.67 (s, 3H), 0.73 (s, 3H), 1.02 (s, 3H), 1.39-1.45 (m, 2H), 1.55-1.73 (m, 2H), 1.76-1.87 (m, 2H), 2.64-2.68 (m, 1H), 2.87-2.95 (m, 2H), 6.56-6.58 (m, 2H), 6.99-7.02 (m, 2H), 7.04-7.10 (m, 5H), 7.12-7.16 (m, 1H), 7.21-7.28 (m, 3H), 7.29-7.43 (m, 3H), 7.42-7.53 (m, 2H), 7.71-7.74 (m, 2H) ppm. 13 C NMR (101 MHz, CDCl₃): δ = 10.0, 16.2, 16.4, 23.0, 28.9, 29.2, 33.5, 44.1, 52.3, 53.5, 68.5, 92.5, 123.3, 126.55, 126.59, 127.0, 127.2, 127.5, 127.8, 128.04, 128.09, 128.13, 128.40, 128.48, 128.8, 129.0, 129.5, 130.3, 138.6, 141.5, 147.7, 148.1, 169.0, 179.5

ppm. HRMS (ESI): m/z calculated for $[C_{39}H_{38}N_2NaO_2]$ $[M+Na^+]$: 589.2831, found: 589.2833.

60, 50:50 d.r.

2-(((5R)-3,3-Dimethyl-4,4-dioxido-7-oxo-4-thia-1-azabicyclo[3.2.0]heptan-2-yl)methyl)-4-((diphenylmethylene)amino)-4,4-diphenylbutanenitrile (60)

Following the general procedure, (2S,5R)-2-((((diphenylmethylene)amino)oxy)carbonyl)-3,3-dimethyl-4-thia-1-

azabicyclo[3.2.0]heptan-7-one 4,4-dioxide **1ae** (123.6 mg, 0.3 mmol), ethene-1,1-diyldibenzene **2a** (36.0 mg, 0.2 mmol), and acrylonitrile **3a** (21.2 mg, 0.4 mmol) were used. Purification by column chromatography using pre-basified silica with pentane/EtOAc (6:1 to 4:1, v/v) as eluent afforded **60** as a white solid in 50:50 diastereomeric ratio (67 mg, 56% yield). Combined NMR data for both the isomers are reported here. 1 H NMR (400 MHz, CDCl₃): δ = 1.24-1.32 (m, 1H), 1.61-1.71 (m, 6H), 2.01-2.16 (m, 2H), 2.32-2.43 (m, 1H), 2.55-2.67 (m, 1H), 2.93-3.07 (m, 2H), 3.75-3.81 (m, 1H), 5.46-5.52 (m, 1H), 6.52-6.54 (m, 2H), 6.98-7.03 (m, 3H), 7.05-7.14 (m, 3H), 7.16-7.28 (m, 3H), 7.29-7.48 (m, 7H), 7.53-7.69 (m, 2H) ppm. 13 C NMR (101 MHz, CDCl₃): δ = 18.7, 22.7, 23.9, 28.8, 37.7, 42.1, 44.6, 51.1, 68.6, 115.6, 120.7, 121.9, 126.7, 126.9, 127.09, 127.12, 127.48, 127.55, 128.0, 128.17, 128.20, 128.4, 128.6, 128.7, 129.0, 129.1, 129.19, 129.25, 129.27, 130.5, 138.4, 141.3, 147.1, 147.6, 164.2, 169.3 ppm. HRMS (ESI): m/z calculated for [C₃₇H₃₅N₃NaO₃S] [M+Na⁺]: 624.2297, found: 624.2297.

86

7-(2,5-Dimethylphenoxy)-2-(2-((diphenylmethylene)amino)-2,2-diphenylethyl)-4,4-dimethylheptanenitrile (61)

Following the general procedure, benzophenone O-(5-(2,5-dimethylphenoxy)-2,2-dimethylpentanoyl) oxime **1ac** (128.7 mg, 0.3 mmol), ethene-1,1-diyldibenzene **2a** (36.0 mg, 0.2 mmol), and acrylonitrile **3a** (21.2 mg, 0.4 mmol) were used. Purification by column chromatography using pre-basified silica with pentane/EtOAc (40:1 to 30:1, v/v) as eluent afforded **61** as a white solid (62 mg, 50% yield). 1 H NMR (400 MHz, CDCl₃): δ = 0.78-0.79 (m, 3H), 0.82-0.83 (m, 3H), 1.14-1.34 (m, 3H), 1.44-1.52 (m, 1H), 1.58-1.64 (m, 1H), 1.71-1.78 (m, 1H), 2.18-2.20 (m, 3H), 2.34-2.41 (m, 4H), 2.63-2.68 (m, 1H), 3.02-3.08 (m, 1H), 3.75-3.86 (m, 2H), 6.60-6.70 (m, 4H), 7.02-7.18 (m, 10H), 7.24-7.28 (m, 2H), 7.34-7.40 (m, 3H), 7.49-7.55 (m, 2H), 7.73-7.76 (m, 2H) ppm. 13 C NMR (101 MHz, CDCl₃): δ = 15.9, 21.5, 22.0, 24.2, 26.8, 27.2, 33.2, 38.1, 46.2, 46.3, 68.3, 68.6, 112.1, 120.7, 123.6, 124.4, 126.4, 126.5, 126.9, 127.2, 127.4, 128.00, 128.04, 128.08, 128.2, 128.7, 130.2, 130.4, 136.5, 138.6, 141.6, 148.0, 148.4, 157.1, 168.9 ppm. HRMS (ESI): m/z calculated for [C44H46N2NaO] [M+Na⁺]: 641.3508, found: 641.3500.

62, 50:50 d.r.

4-(4-(2,2-Dichlorocyclopropyl)phenoxy)-2-(2-((diphenylmethylene)amino)-2,2-diphenylethyl)-4-methylpentanenitrile (62)

Following the general procedure, benzophenone O-(2-(4-(2,2-dichlorocyclopropyl)phenoxy)-2-methylpropanoyl) oxime **1ad** (93.4 mg, 0.2 mmol), ethene-1,1-diyldibenzene **2a** (72.0 mg, 0.4 mmol), and acrylonitrile **3a** (21.2 mg, 0.4 mmol) were used. Purification by column chromatography using pre-basified silica with pentane/EtOAc (40:1 to 30:1, v/v) as eluent afforded **62** as a white solid in 50:50 diastereomeric ratio (62 mg, 32% yield). Combined NMR data for both the isomers are reported here. ¹H NMR (400 MHz, CDCl₃): δ = 1.12 (s, 3H), 1.14 (s, 3H), 1.71 (dd, J = 14.4, 3.1 Hz, 1H), 1.78 (dd, J = 8.4, 7.4 Hz, 1H), 1.90-2.07 (m, 2H), 2.50-2.61 (m,

1H), 2.84 (dd, J = 10.7, 8.3 Hz, 1H), 2.89-3.03 (m, 2H), 6.57 (d, J = 5.3 Hz, 2H), 6.70-6.78 (m, 2H), 6.98-7.18 (m, 11H), 7.20-7.25 (m, 2H), 7.29-7.39 (m, 3H), 7.43-7.53 (m, 2H), 7.68-7.75 (m, 2H) ppm. ¹³C NMR (101 MHz, CDCl₃): $\delta = 22.3$, 25.9, 26.0, 26.9, 35.0, 45.2, 46.9, 61.0, 68.6, 79.4, 123.5, 123.5, 123.8, 126.5, 126.5, 126.9, 127.3, 127.4, 128.0, 128.1, 128.2, 128.8, 129.5, 129.6, 129.6, 130.3, 138.6, 141.6, 148.1, 148.5, 154.2, 168.8 ppm. HRMS (ESI): m/z calculated for [C₄₂H₃₈N₂OCl₂Na] [M+Na⁺]: 679.2253, found: 679.2257.

4-((Diphenylmethylene)amino)-4,4-diphenyl-2-(((3aS,3bR,7aS,8aS)-2,2,5,5-tetramethyltetrahydro-3aH-[1,3]dioxolo[4',5':4,5]furo[3,2-d][1,3]dioxin-8a-yl)methyl)butanenitrile (63)

Following the general procedure, benzophenone O-((3aS,3bR,7aS,8aR)-2,2,5,5-tetramethyltetrahydro-3aH-[1,3]dioxolo[4',5':4,5]furo[3,2-d][1,3]dioxine-8a-carbonyl) oxime **1af** (135.9 mg, 0.3 mmol), ethene-1,1-diyldibenzene **2a** (36.0 mg, 0.2 mmol), and acrylonitrile **3a** (21.2 mg, 0.4 mmol) were used. Purification by column chromatography using pre-basified silica with pentane/EtOAc (20:1 to 10:1, v/v) as eluent afforded **63** as a white solid in 50:50 diastereomeric ratio (90 mg, 70% yield). Combined NMR data for both the isomers are reported here. ¹H NMR (400 MHz, CDCl₃): δ = 1.13-1.29 (m, 6H), 1.36-1.44 (m, 6H), 1.98-2.03 (m, 1H), 2.26-2.37 (m, 1H), 2.60-2.69 (m, 1H), 2.90-2.99 (m, 1H), 3.02-3.10 (m, 1H), 3.75-4.01 (m, 3H), 4.17-4.21 (m, 2H), 6.57-6.63 (m, 2H), 6.98-7.04 (m, 2H), 7.09-7.22 (m, 9H), 7.30-7.42 (m, 5H), 7.71-7.74 (m, 2H) ppm. ¹³C NMR (101 MHz, CDCl₃): δ = 18.8, 19.0, 22.6, 22.7, 26.58, 26.64, 27.39, 27.43, 28.6, 28.9, 41.4, 42.1, 44.48, 44.53, 60.29, 60.31, 68.4, 68.5, 72.4, 73.4, 73.6, 86.3, 86.4, 97.4, 97.5, 111.5, 111.6, 113.7, 123.0, 123.1, 126.29, 126.39, 126.42, 126.5, 126.8, 127.0, 127.25, 127.28, 127.36, 127.44, 127.91, 127.96, 127.98, 128.04, 128.06, 128.09, 128.1, 128.80, 128.81, 130.1, 130.2, 138.6, 138.7,

141.6, 141.7, 148.0, 148.1, 148.3, 148.4, 168.6, 168.7 ppm. HRMS (ESI): m/z calculated for $[C_{41}H_{42}N_2NaO_5]$ $[M+Na^+]$: 665.2991, found: 665.2998.

the

Following

64, 50:50 d.r.

4-((Diphenylmethylene)amino)-2-(((6aS,6bR,8aR,10S,12aR,12bR,14bR)-10-hydroxy-2,2,6a,6b,9,9,12a-heptamethyl-

1,2,3,4,4a,5,6,6*a*,6*b*,7,8,8*a*,9,10,11,12,12*a*,12*b*,13,14*b*-icosahydropicen-4*a*-yl)methyl)-4,4-diphenylbutanenitrile (64)

procedure,

general

0-

benzophenone

((4aS,6aS,6bR,8aR,10S,12aR,12bR,14bS)-10-hydroxy-2,2,6a,6b,9,9,12aheptamethyl-1,2,3,4,4*a*,5,6,6*a*,6*b*,7,8,8*a*,9,10,11,12,12*a*,12*b*,13,14*b*icosahydropicene-4a-carbonyl) oxime **1ag** (190.5 mg, 0.3 mmol), ethene-1,1diyldibenzene 2a (36.0 mg, 0.2 mmol), and acrylonitrile 3a (21.2 mg, 0.4 mmol) were used. Purification by column chromatography using pre-basified silica with pentane/EtOAc (30:1 to 10:1, v/v) as eluent afforded 64 as a white solid in 50:50 diastereomeric ratio (79 mg, 48% yield). Combined NMR data for both the isomers are reported here. ¹H NMR (400 MHz, CDCl₃): $\delta = 0.69-0.75$ (m, 3H), 0.78-0.85 (m, 9H), 0.86-1.19 (m, 20H), 1.25-1.66 (m, 9H), 1.73-1.89 (m, 4H), 1.99-2.06 (m, 1H), 2.09-2.13 (m, 1H), 2.30-2.34 (m, 1H), 2.38-2.58 (m, 1H), 2.89-3.03 (m, 1H), 3.19-3.23 (m, 1H), 4.95-5.18 (m, 1H), 6.57 (m, 2H), 6.84-6.88 (m, 1H), 6.96-7.22 (m, 8H), 7.25-7.40 (m, 5H), 7.42-7.74 (m, 4H) ppm. 13 C NMR (101 MHz, CDCl₃): $\delta = 15.58$, 15.62, 15.69, 15.70, 16.93, 16.96, 18.4, 20.7, 20.8, 22.9, 23.0, 23.6, 23.7, 25.5, 25.9, 26.1, 26.3, 27.3, 28.17, 28.19, 30.78, 30.82, 32.2, 32.4, 33.2, 33.3, 34.2, 34.3, 35.6, 36.1, 36.96, 36.98, 38.7, 38.85, 38.87, 39.9, 40.0, 41.49, 41.54, 43.8, 45.0, 46.1, 46.4, 46.7, 47.0, 47.4, 47.55, 47.62, 55.2, 68.55, 68.64, 79.00, 79.05, 122.5, 122.9, 124.0, 124.4, 126.29, 128.03, 128.10, 128.13, 128.2, 128.7, 128.8, 130.1, 130.2, 138.6, 138.8, 141.6, 144.0, 144.3, 148.3, 148.5, 148.6, 149.2, 168.6, 169.0 ppm. HRMS (ESI): m/z calculated for [C₅₉H₇₂N₂NaO] [M+Na⁺]: 847.5542, found: 847.5537.

65, 50:50 d.r.

4-((Diphenylmethylene)amino)-2-(((1S,4aS,10aS)-7-isopropyl-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthren-1-yl)methyl)-4,4-diphenylbutanenitrile (65)

Following the general procedure, benzophenone O-((1R,4aS,10aR)-7-isopropyl-1,4adimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene-1-carbonyl) oxime **1ah** (143.7 mg, 0.3 mmol), ethene-1,1-diyldibenzene 2a (36.0 mg, 0.2 mmol), and acrylonitrile 3a (21.2 mg, 0.4 mmol) were used. Purification by column chromatography using prebasified silica with pentane/EtOAc (400:1 to 20:1, v/v) as eluent afforded 65 as a white solid in 50:50 diastereomeric ratio (76 mg, 57% yield). Combined NMR data for both the isomers are reported here. ¹H NMR (400 MHz, CDCl₃): $\delta = 0.67$ -0.93 (m, 3H), 1.00-1.10 (m, 1H), 1.13-1.17 (m, 3H), 1.19-1.35 (m, 3H), 1.47-1.67 (m, 4H), 1.75-1.85 (m, 1H), 2.17-2.22 (m, 1H), 2.34-2.49 (m, 1H), 2.58-2.72 (m, 1H), 2.74-2.93 (m, 2H), 2.98-3.08 (m, 1H), 6.59 (m, 2H), 6.83-6.86 (m, 1H), 6.97-7.16 (m, 11H), 7.17-7.25 (m, 2H), 7.29-7.40 (m, 3H), 7.41-7.52 (m, 2H), 7.69-7.73 (m, 2H) ppm. ¹³C NMR (101 MHz, CDCl₃): $\delta = 18.8$, 18.9, 19.0, 20.0, 21.0, 21.1, 21.5, 24.08, 24.13, 24.15, 25.4, 25.6, 29.7, 30.2, 33.5, 33.6, 36.5, 36.7, 36.86, 36.92, 37.6, 37.7, 38.1, 38.2, 46.2, 46.8, 47.1, 47.9, 48.6, 48.8, 68.57, 68.61, 123.8, 123.9, 124.1, 124.3, 124.4, 124.5, 126.40, 126.42, 126.44, 126.9, 127.0, 127.2, 127.4, 127.9, 128.01, 128.04, 128.09, 128.19, 128.21, 128.8, 130.22, 130.25, 134.6, 135.0, 138.6, 138.7, 141.5, 141.6, 145.6, 147.2, 147.4, 148.14, 148.16, 148.4, 148.5, 168.8, 168.9 ppm. HRMS (ESI): m/z calculated for [C₄₉H₅₂N₂Na] [M+Na⁺]: 691.4028, found: 691.4024.

1,2,3,4,4*a*,5,6,6*a*,6*b*,7,8,8*a*,9,10,11,12,12*a*,12*b*,13,14*b*-icosahydropicen-2-yl)methyl)-4,4-diphenylbutanenitrile (66)

Following the general procedure, (2S,4aS,6aS,6bR,8aR,10S,12aS,12bR,14bR)-2-((((diphenylmethylene)amino)oxy)carbonyl)-10-hydroxy-2,4a,6a,6b,9,9,12aheptamethyl-1,3,4,4*a*,5,6,6*a*,6*b*,7,8,8*a*,9,10,11,12,12*a*,12*b*,14*b*-octadecahydropicen-13(2H)-one **1ai** (194.7 mg, 0.3 mmol), ethene-1,1-diyldibenzene **2a** (36.0 mg, 0.2 mmol), and acrylonitrile **3a** (21.2 mg, 0.4 mmol) were used. Purification by column chromatography using pre-basified silica with pentane/EtOAc (8:1 to 3:1, v/v) as eluent afforded 66 as a white solid in 50:50 diastereomeric ratio (92 mg, 55% yield). Combined NMR data for both the isomers are reported here. ¹H NMR (400 MHz, CDCl₃): $\delta = 0.58-0.65$ (m, 3H), 0.71-0.76 (m, 6H), 0.85-0.96 (m, 6H), 1.00-1.09 (m, 9H), 1.15-1.36 (m, 12H), 1.48-1.61 (m, 4H), 1.65-1.95 (m, 3H), 2.21-2.31 (m, 2H), 2.41-2.62 (m, 1H), 2.67-2.77 (m, 1H), 2.87-3.01 (m, 1H), 3.12-3.18 (m, 1H), 5.42-5.49 (m, 1H), 6.48 (m, 2H), 6.88-7.10 (m, 9H), 7.12-7.19 (m, 2H), 7.23-7.33 (m, 3H), 7.34-7.45 (m, 2H), 7.60-7.64 (m, 2H) ppm. 13 C NMR (101 MHz, CDCl₃): $\delta = 15.7$, 16.4, 16.5, 17.6, 18.79, 18.82, 18.84, 20.7, 20.8, 21.2, 21.3, 23.4, 23.5, 26.4, 27.4, 28.2, 28.58, 28.62, 28.69, 29.8, 32.1, 32.5, 32.6, 32.9, 33.8, 34.2, 34.3, 35.75, 35.81, 37.2, 39.2, 39.3, 42.8, 42.9, 43.35, 43.37, 43.39, 44.0, 45.47, 45.51, 46.1, 46.2, 46.4, 46.9, 47.0, 50.1, 50.3, 55.0, 61.8, 61.9, 68.5, 68.6, 78.9, 124.2, 124.4, 126.4, 126.5, 126.6, 126.9, 127.0, 127.1, 127.2, 127.4, 127.99, 128.03, 128.05, 128.10, 128.15, 128.18, 128.29, 128.34, 128.68, 128.70, 128.73, 130.3, 138.5, 138.6, 141.5, 148.0, 148.3, 148.6, 168.84, 168.88, 169.2, 169.67, 169.70, 200.2, 200.3 ppm. HRMS (ESI): m/z calculated for

 $[C_{59}H_{70}N_2NaO_2]$ [M+Na⁺]: 861.5335, found: 861.5327.

67, 50:50 d.r.

(6R)-6-((5S,8R,9S,10S,13R,14S,17R)-10,13-Dimethyl-3,7,12-

trioxohexadecahydro-1*H*-cyclopenta[*a*]phenanthren-17-yl)-2-(2-

((diphenylmethylene)amino)-2,2-diphenylethyl)heptanenitrile (67)

Following (5*S*,8*R*,9*S*,10*S*,13*R*,14*S*,17*R*)-17-((*R*)-5the general procedure, (((diphenylmethylene)amino)oxy)-5-oxopentan-2-yl)-10,13-dimethyldecahydro-1*H*cyclopenta[a]phenanthrene-3,7,12(2H,4H,8H)-trione **1aj** (174.3 mg, 0.3 mmol), ethene-1,1-diyldibenzene 2a (36.0 mg, 0.2 mmol), and acrylonitrile 3a (21.2 mg, 0.4 mmol) were used. Purification by column chromatography using pre-basified silica with pentane/EtOAc (10:1 to 8:1, v/v) as eluent afforded 67 as a white solid in 50:50 diastereomeric ratio (71 mg, 46% yield). Combined NMR data for both the isomers are reported here. ¹H NMR (400 MHz, CDCl₃): $\delta = 0.75-0.77$ (m, 3H), 1.02-1.05 (m, 4H), 1.39 (m, 6H), 1.51-1.65 (m, 2H), 1.70-2.04 (m, 6H), 2.07-2.16 (m, 2H), 2.19-2.37 (m, 9H), 2.54-2.62 (m, 1H), 2.80-2.94 (m, 5H), 6.54 (m, 2H), 6.99-7.13 (m, 6H), 7.15-7.25 (m, 5H), 7.27-7.40 (m, 4H), 7.41-7.47 (m, 2H), 7.69-7.72 (m, 2H) ppm. ¹³C NMR (101 MHz, CDCl₃): δ = 11.90, 11.92, 18.90, 18.98, 22.0, 23.89, 24.02, 25.2, 26.6, 26.7, 27.9, 34.25, 34.32, 34.7, 35.3, 35.9, 36.0, 36.1, 36.6, 38.7, 42.9, 43.4, 43.6, 45.1, 45.6, 45.9, 46.0, 46.9, 51.9, 56.9, 68.33, 68.35, 122.8, 122.9, 126.4, 126.5, 127.0, 127.2, 127.4, 127.5, 127.9, 127.98, 128.03, 128.12, 128.14, 128.4, 128.7, 128.8, 129.4, 130.2, 138.46, 138.48, 141.50, 141.51, 148.02, 148.03, 148.40, 148.43, 168.61, 168.63, 208.88, 208.90, 209.2, 212.0 ppm. HRMS (ESI): m/z calculated for [C₅₃H₅₈N₂NaO₃] [M+Na⁺]: 793.4345, found: 793.4341.

68, 50:50 d.r.

(6R)-2-(2-((Diphenylmethylene)amino)-2,2-diphenylethyl)-6-

((3R,5R,8R,9S,10S,13R,14S,17R)-3-hydroxy-10,13-dimethylhexadecahydro-1H-cyclopenta[a]phenanthren-17-yl)heptanenitrile (68)

Following procedure, benzophenone O-((R)-4the general ((3R,5R,8R,9S,10S,13R,14S,17R)-3-hydroxy-10,13-dimethylhexadecahydro-1Hcyclopenta[a]phenanthren-17-yl)pentanoyl) oxime **1ak** (166.5 mg, 0.3 mmol), ethene-1,1-diyldibenzene 2a (36.0 mg, 0.2 mmol), and acrylonitrile 3a (21.2 mg, 0.4 mmol) were used. Purification by column chromatography using pre-basified silica with pentane/EtOAc (10:1 to 8:1, v/v) as eluent afforded 68 as a white solid in 50:50 diastereomeric ratio (64 mg, 43% yield). Combined NMR data for both the isomers are reported here. ¹H NMR (400 MHz, CDCl₃): $\delta = 0.61-0.62$ (m, 3H), 0.82-0.84 (m, 4H), 0.92-0.93 (m, 3H), 0.97-1.44 (m, 18H), 1.48-1.57 (m, 3H), 1.64-1.97 (m, 9H), 2.33-2.38 (m, 1H), 2.55-2.62 (m, 1H), 2.84-2.90 (m, 1H), 3.58-3.66 (m, 1H), 6.56 (m, 2H), 7.00-7.19 (m, 9H), 7.22-7.26 (m, 2H), 7.33-7.42 (m, 3H), 7.44-7.46 (m, 2H), 7.70-7.72 (m, 2H) ppm. 13 C NMR (101 MHz, CDCl₃): $\delta = 12.1, 18.5, 18.6, 20.9, 23.4, 23.5, 24.3,$ 26.5, 26.7, 26.8, 27.3, 28.4, 30.6, 34.4, 34.5, 34.7, 35.1, 35.3, 35.46, 35.53, 35.6, 36.0, 36.6, 40.3, 40.5, 42.2, 42.8, 43.5, 43.6, 56.3, 56.6, 68.36, 68.38, 72.0, 122.8, 122.9, 126.43, 126.45, 127.0, 127.2, 127.4, 127.9, 127.96, 127.99, 128.04, 128.1, 128.7, 130.2, 138.5, 141.5, 148.07, 148.10, 148.4, 168.6 ppm. HRMS (ESI): m/z calculated for $[C_{53}H_{64}N_2NaO]$ [M+Na⁺]: 767.4916, found: 767.4909.

5. Synthetic application

5.1. Large scale synthesis of product 57



Fig. S9. Reaction setup used for the large scale synthesis of **57** featuring two 18 W blue LEDs ($\lambda_{\text{max}} = 405 \text{ nm}$).

A 100 mL Schlenk tube was charged with a magnetic stirring bar, thioxanthone (106 mg, 0.499 mmol, 10 mol%), and oxime ester $\mathbf{1y}$ (2.59 g, 5.00 mmol, 1.0 equiv). The Schlenk tube was evacuated and backfilled with argon three times and was then charged with dry EtOAc (50 mL, 0.10 M), 1,1-diphenylethylene ($\mathbf{2a}$,1.81 g, 10.0 mmol, 2.0 equiv), and acrylonitrile ($\mathbf{3a}$, 531 mg, 10.0 mmol, 2.0 equiv). The reaction mixture was then irradiated at 405 nm for 12 h using the setup shown above. The solvent was removed under reduced pressure and column chromatography on silica gel (prebasified using n-pentane/CH₂Cl₂/NEt₃ = 5/1/0.03; n-pentane/CH₂Cl₂ = 5/1 to 4/1) gave $\mathbf{57}$ as colorless oil (1.48 g, 2.09 mmol, 42% yield).

5.2. Dihydroxylation of product 57

A 20 mL vial was charged with 57 (70.7 mg, 0.100 mmol, 1.0 equiv), 'BuOH/H₂O/THF $(1/1/1, 4.0 \text{ mL}, 25 \text{ mM}), \text{ K}_2\text{OsO}_4 \cdot \text{H}_2\text{O} (1.8 \text{ mg}, 0.0049 \text{ mmol}, 5 \text{ mol}\%), and NMO (35.1)$ mg, 0.300 mmol, 3.0 equiv). The resulting mixture was stirred at r.t. for 16 h and was then filtered through a short pad of silica which has been prebasified (EtOAc + 2% NEt₃), eluting with EtOAc (50 mL). Concentration under reduced pressure followed by column chromatography (silica prebasified with CH₂Cl₂ + 0.3% NEt₃; CH₂Cl₂ + 1% MeOH) gave dihydroxylated product 69 as a white solid in 50:50 diastereomeric ratio (57.5 mg, 0.0776 mmol, 78%). Combined NMR data for both the isomers are reported here. ¹H NMR (400 MHz, CDCl₃): $\delta = 0.86 - 0.92$ (m, 3H), 1.02-1.58 (m, 38H), 1.89 (s, 2H), 2.35 (dd, J = 13.6, 3.6 Hz, 1H), 2.58 (tt, J = 8.4, 4.0 Hz, 1H), 2.87 (dd, J = 13.6, 8.3 Hz, 1H), 3.60 (t, J = 5.3 Hz, 2H), 6.55 (d, J = 7.5 Hz, 2H), 6.97-7.20 (m, 9H), 7.20-7.26 (m, 2H), 7.31-7.51 (m, 5H), 7.67-7.74 (m, 2H) ppm. ¹³C NMR (101 MHz, CDCl₃): $\delta = 14.2, 22.8, 26.2, 26.7, 26.8, 28.9, 29.3, 29.4, 29.6, 29.7, 29.7, 29.7, 29.8, 31.3, 32.0,$ 34.0, 43.6, 68.4, 74.8, 122.9, 126.5, 126.5, 127.0, 127.2, 127.5, 128.0, 128.0, 128.1, 128.2, 128.7, 130.3, 138.6, 141.6, 148.1, 148.5, 168.7 ppm. HRMS (ESI): m/z calculated for $[C_{51}H_{68}N_2O_2Na]^+$ $[M+Na^+]$: 763.5173, found: 763.5173.

5.3. Deprotection of product 21 and 68

A 10 mL tube was charged with compound **21** (51.8 mg, 0.1 mmol) and 6 N HCl (2.0 mL), and the solution was stirred at 100 °C for 12 h. After cooling the mixture to room temperature, Et₂O (1 mL) was added into the tube. Then, stirring the resulting mixture and carefully remove the upper organic phase with a dropper. After repeating this

operation once, the water layer was combined and the tube was washed with MeOH (5 mL). Next, water and MeOH were combined, and the volatile was removed in vacuo, and the product **70** was obtained as a white solid (29 mg, 71% yield). *Note: the product* **70** *is slightly soluble in water and* Et_2O , *but soluble in methanol.* ¹H NMR (400 MHz, DMSO- d_6): $\delta = 1.18-1.46$ (m, 1H), 1.50-1.76 (m, 2H), 1.79-1.98 (m, 1H), 2.46-2.61 (m, 3H), 3.05-3.23 (m, 2H), 7.12-7.21 (m, 3H), 7.23-7.32 (m, 4H), 7.31-7.48 (m, 8H), 8.96-9.06 (m, 1H), 9.42 (s, 1H), 11.8 (s, 1H) ppm. ¹³C NMR (101 MHz, DMSO- d_6): $\delta = 28.1$, 29.3, 34.9, 41.3, 41.5, 72.6, 125.6, 125.76, 125.79, 127.4, 127.5, 128.18, 128.25, 128.57, 128.62, 141.6, 143.7, 144.5, 172.4 ppm.

A 10 mL tube was charged with compound **68** (51.8 mg, 0.1 mmol) and 6 N HCl (2.0 mL), and the solution was stirred at 100 °C for 12 h. After cooling the mixture to room temperature, Et₂O (1 mL) was added into the tube. Then, stirring the resulting mixture and carefully remove the upper organic phase with a dropper. After repeating this operation once, the water layer was combined and the tube was washed with MeOH (5 mL). Next, water and MeOH were combined, and the volatile was removed in vacuo, and the product **71** was obtained as a white solid in 50:50 diastereomeric ratio (42 mg, 66% yield). *Note: the product 71 is insoluble in water and Et₂O, but soluble in methanol*. Combined NMR data for both the isomers are reported here. ¹H NMR (400 MHz, CD₃OD): δ = 0.64-0.66 (m, 3H), 0.88-1.63 (m, 31H), 1.68-1.99 (m, 6H), 2.63 (m, 1H), 3.18 (m, 2H), 3.54 (m, 1H), 7.13-7.52 (m, 10H) ppm. ¹³C NMR (101 MHz, CD₃OD): δ = 12.53, 12.55, 19.1, 19.2, 21.9, 23.9, 24.2, 24.3, 25.2, 27.6, 28.3, 29.4, 31.1, 31.6, 31.7, 35.6, 36.4, 36.6, 36.77, 36.81, 37.08, 37.13, 41.5, 41.8, 43.4, 43.6, 43.8, 57.35, 57.39, 57.8, 72.3, 74.4, 127.3, 127.4, 129.02, 129.08, 129.87, 129.91, 144.2, 144.3, 145.0, 174.0 ppm.

6. X-Ray analysis

X-Ray diffraction: Data sets for compound **19** were collected with a Bruker D8 Venture Photon III Diffractometer. Programs used: data collection: *APEX4* Version 2021.4-0^[14] (Bruker AXS Inc., **2021**); cell refinement: *SAINT* Version 8.40B (Bruker AXS Inc., **2021**); data reduction: *SAINT* Version 8.40B (Bruker AXS Inc., **2021**); absorption correction, *SADABS* Version 2016/2 (Bruker AXS Inc., **2021**); structure solution *SHELXT*-Version 2018-3 ^[15] (Sheldrick, G. M. *Acta Cryst.*, **2015**, *A71*, 3-8); structure refinement *SHELXL*- Version 2018-3 ^[16] (Sheldrick, G. M. *Acta Cryst.*, **2015**, *C71* (1), 3-8) and graphics, *XP* ^[17] (Version 5.1, Bruker AXS Inc., Madison, Wisconsin, USA, **1998**). *R*-values are given for observed reflections, and *wR* ² values are given for all reflections.

X-ray crystal structure analysis of 19 (glo10386): A colorless, plate-like specimen of C₃₅H₃₄N₂O, approximate dimensions 0.052 mm x 0.065 mm x 0.202 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured on a single crystal diffractometer Bruker D8 Venture Photon III system equipped with a micro focus tube Mo ImS (MoK α , $\lambda = 0.71073$ Å) and a MX mirror monochromator. A total of 576 frames were collected. The total exposure time was 4.80 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 59448 reflections to a maximum θ angle of 26.74° (0.79 Å resolution), of which 5803 were independent (average redundancy 10.244, completeness = 99.7%, $R_{int} = 9.05\%$, $R_{sig} = 3.93\%$) and 4626 (79.72%) were greater than $2\sigma(F^2)$. The final cell constants of a = 9.3198(3) Å, b = 11.1833(4) Å, c = 26.6506(7) Å, β = 99.8120(10)°, volume = $2737.06(15) \text{ Å}^3$, are based upon the refinement of the XYZ-centroids of 7272 reflections above 20 $\sigma(I)$ with $4.784^{\circ} < 2\theta < 53.40^{\circ}$. Data were corrected for absorption effects using the Multi-Scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.923. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9860 and 0.9960. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group $P2_1/n$, with Z = 4 for the formula unit, $C_{35}H_{34}N_2O$. The final anisotropic fullmatrix least-squares refinement on F^2 with 343 variables converged at R1=4.23%, for the observed data and wR2 = 10.06% for all data. The goodness-of-fit was 1.059. The largest peak in the final difference electron density synthesis was 0.308 e⁻/Å³ and the largest hole was -0.221 e⁻/Å³ with an RMS deviation of 0.043 e⁻/Å³. On the basis of the final model, the calculated density was 1.210 g/cm³ and F(000), 1064 e⁻. CCDC Nr.: 2207448.

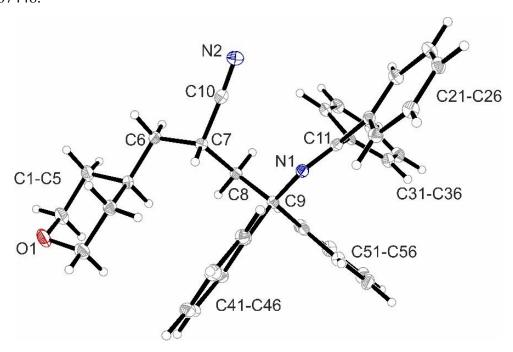
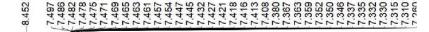


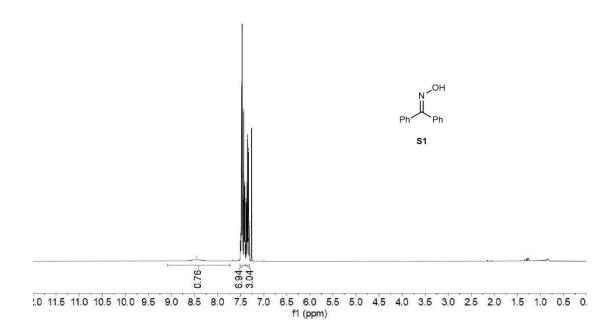
Fig. S10. Crystal structure of compound **19**. Thermal ellipsoids are shown at 50% probability.

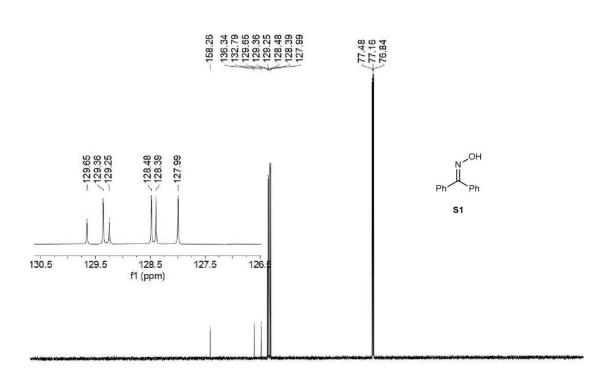
7. References

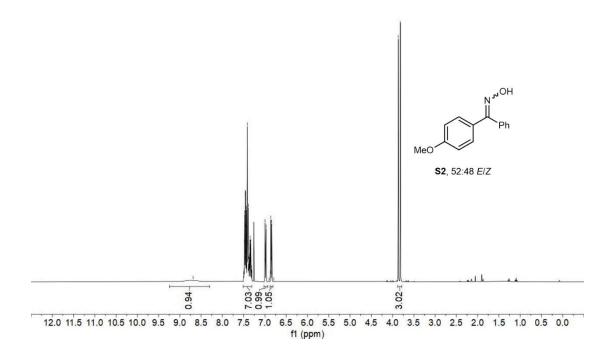
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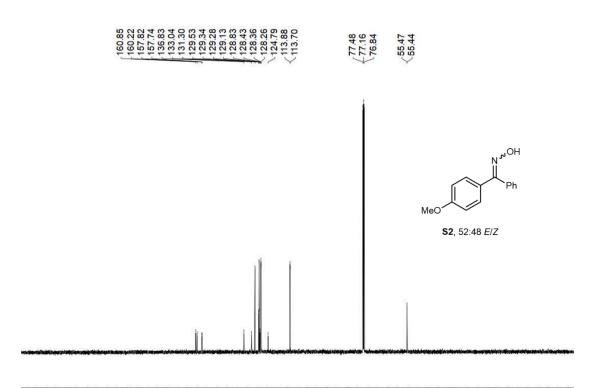
8. Copies of ¹H and ¹³C NMR spectra





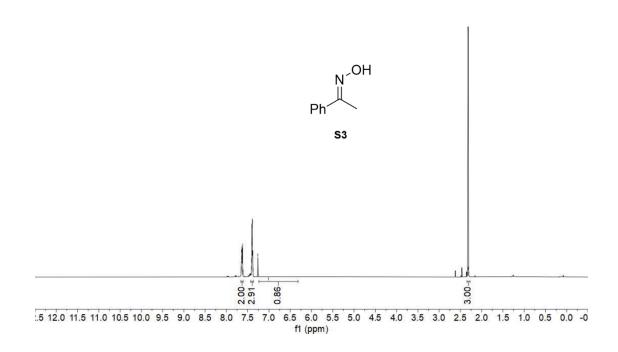


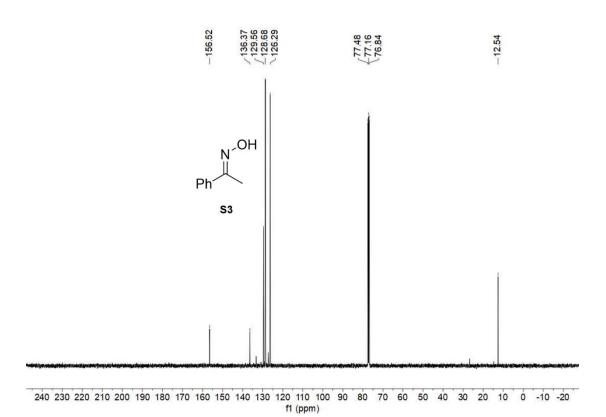


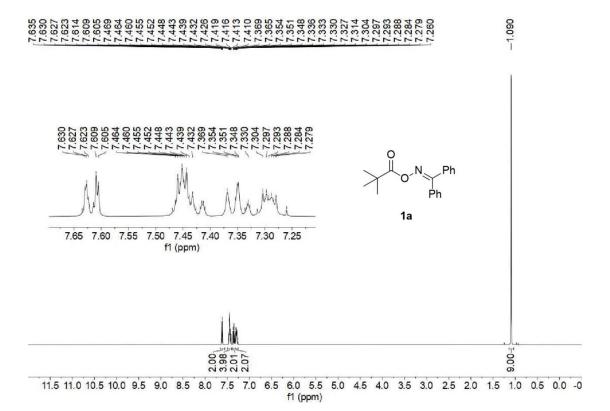


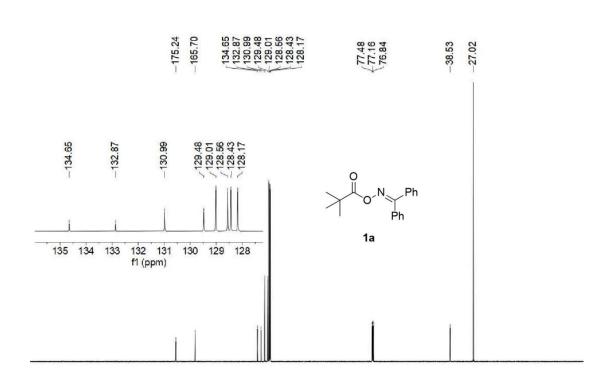


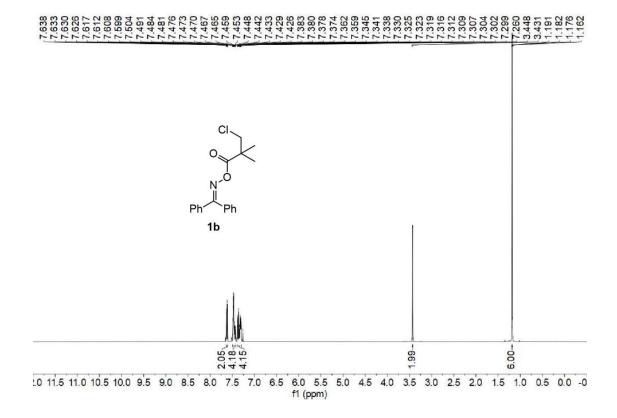


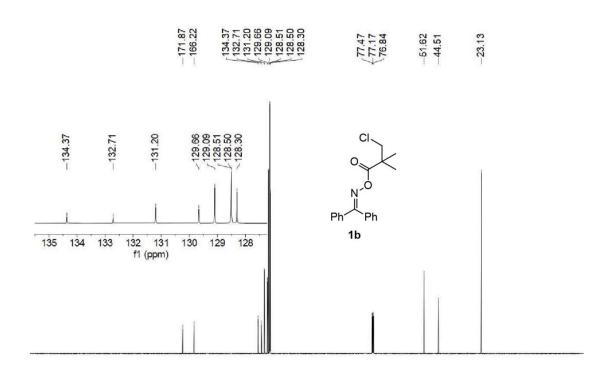


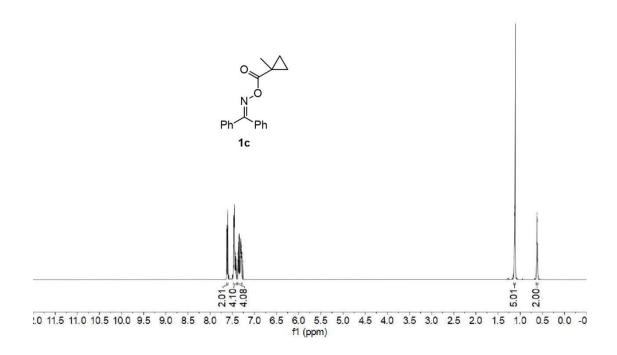


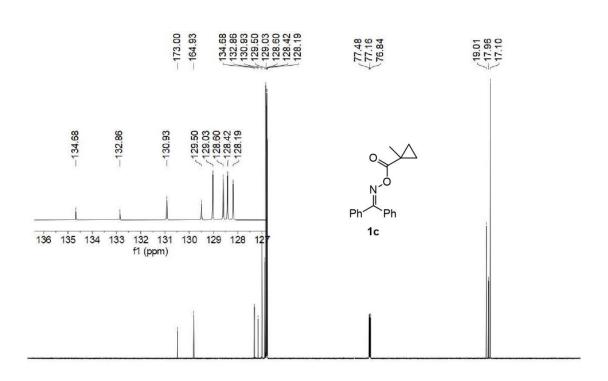


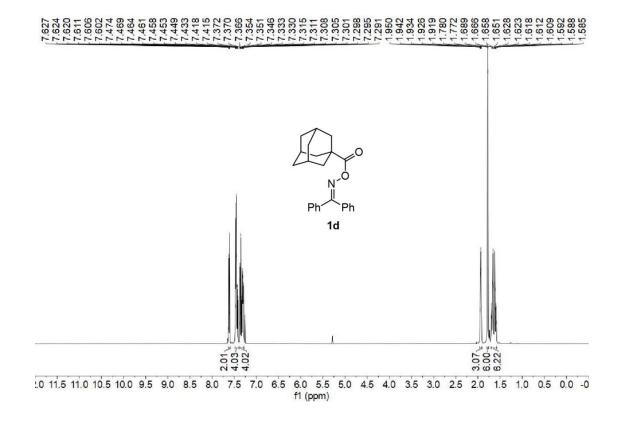


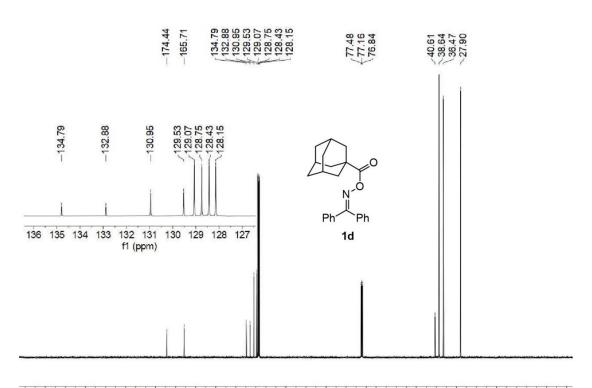


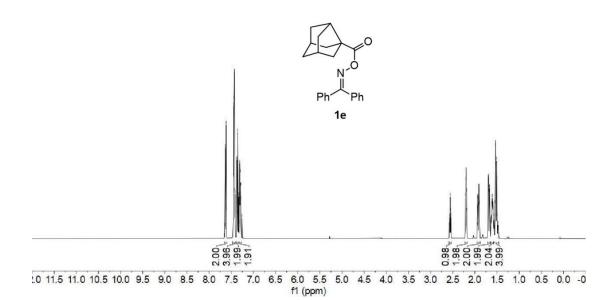


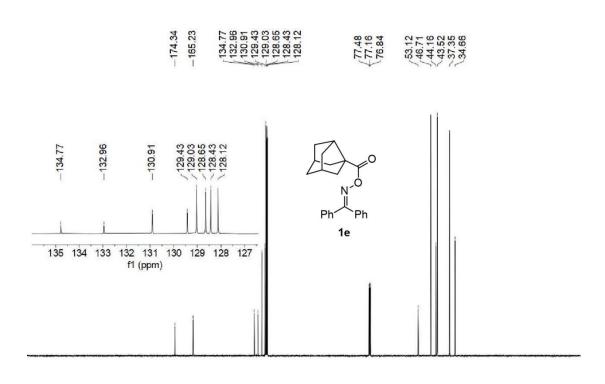


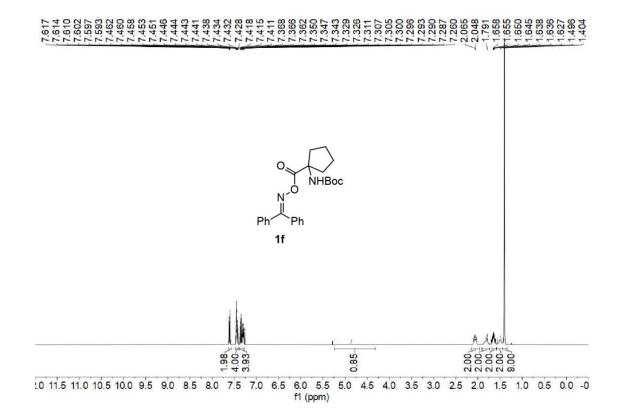


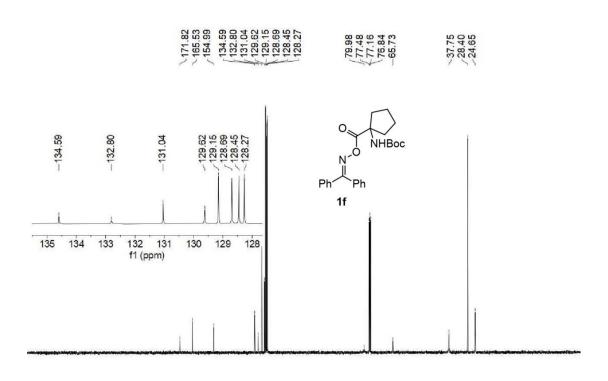


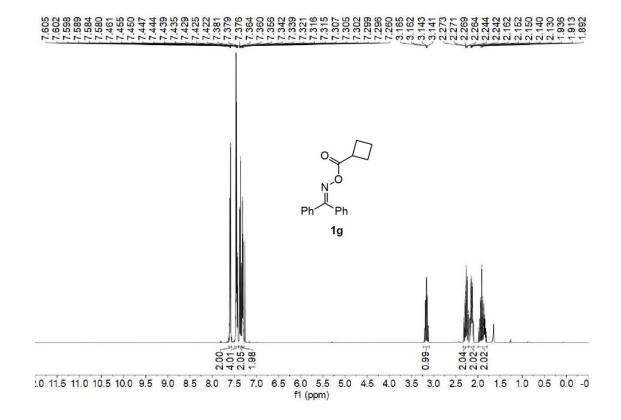


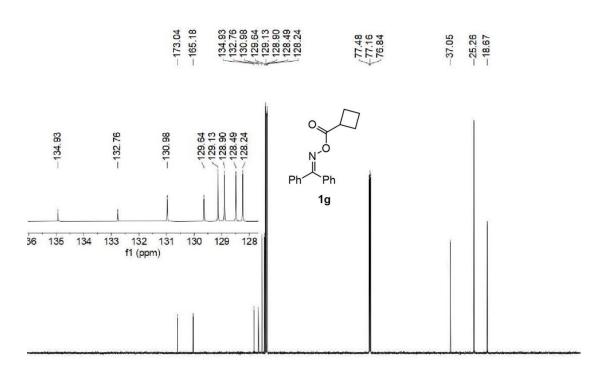


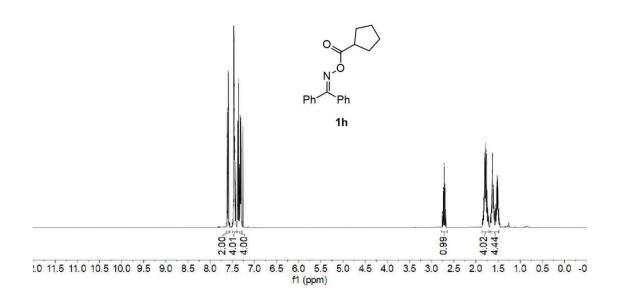


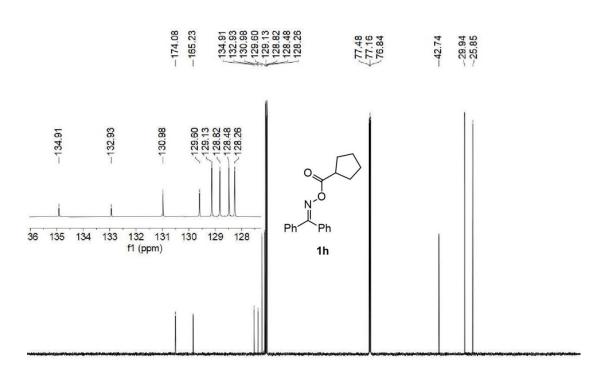


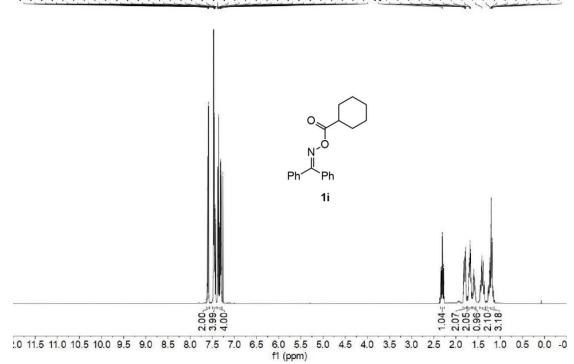


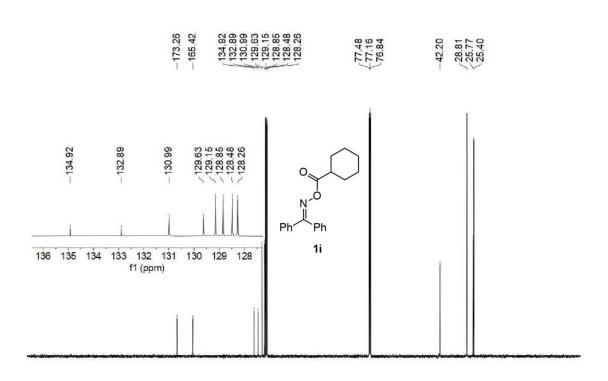


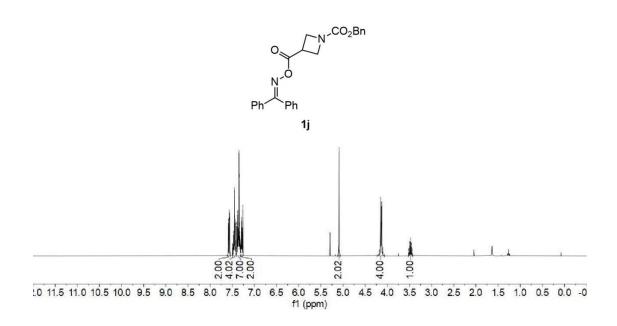


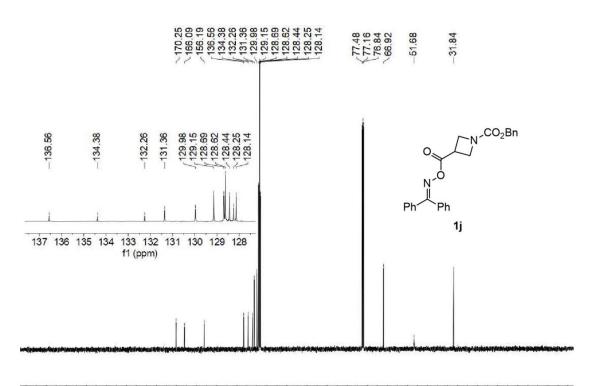


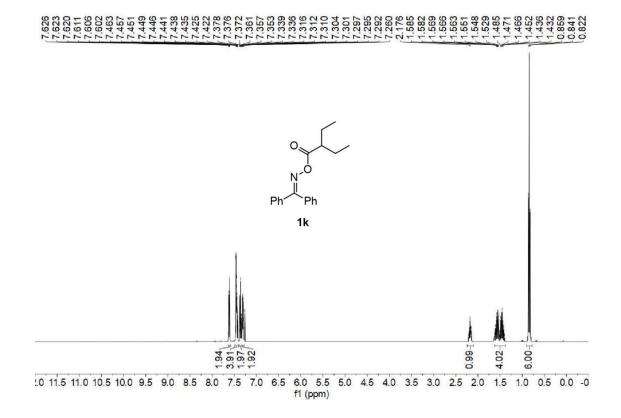


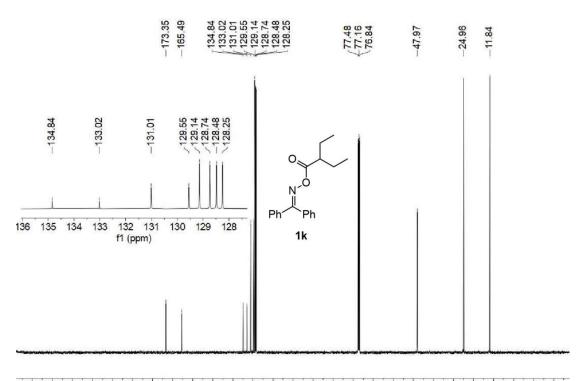


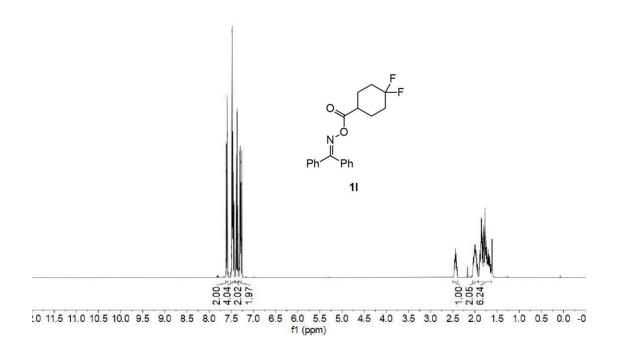


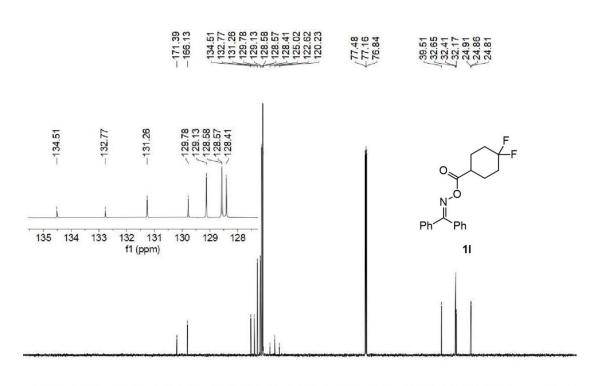


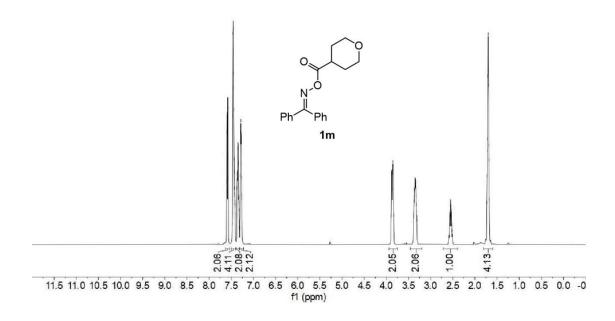


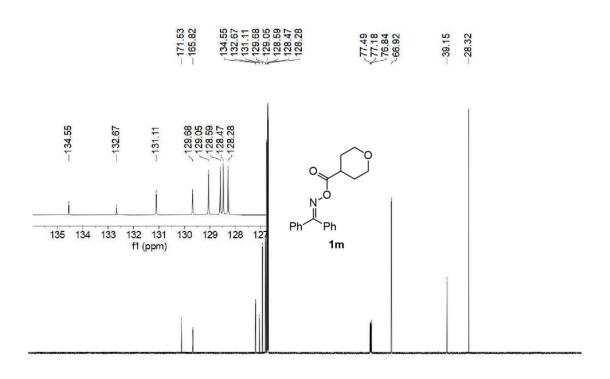


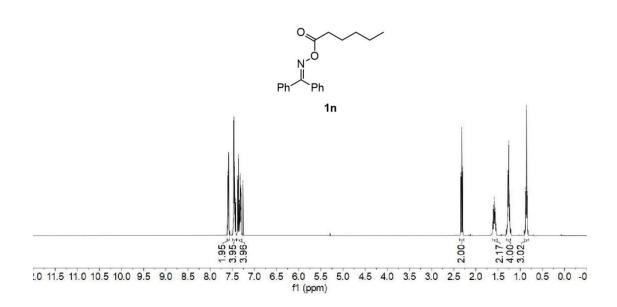


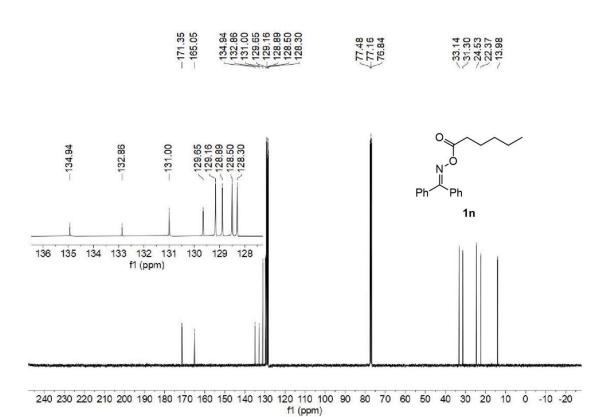


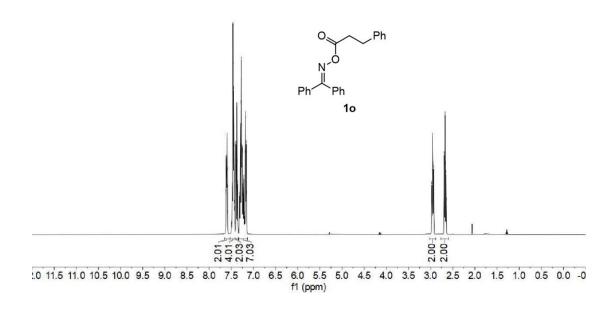


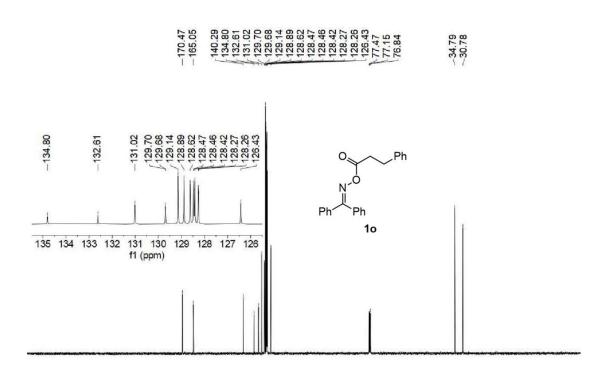


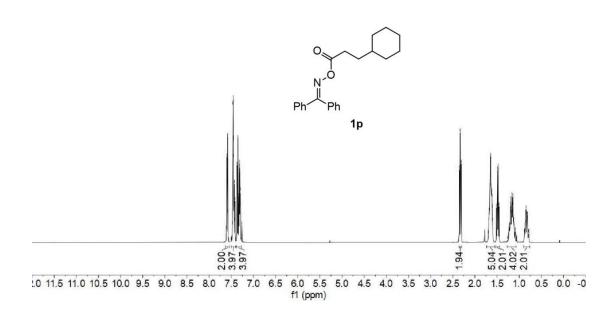


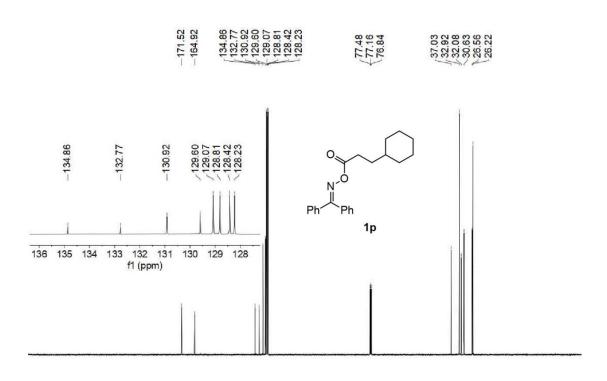


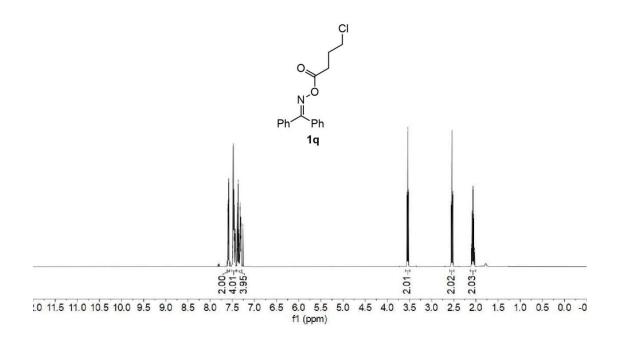


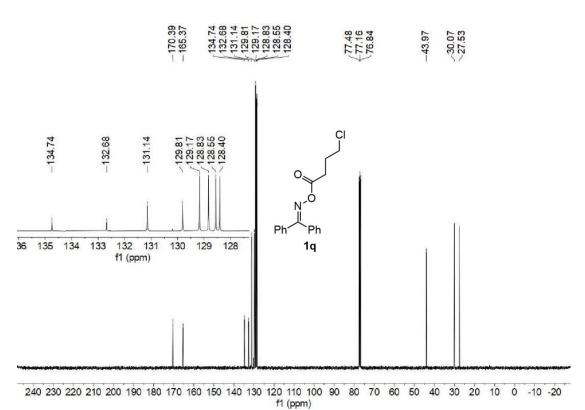


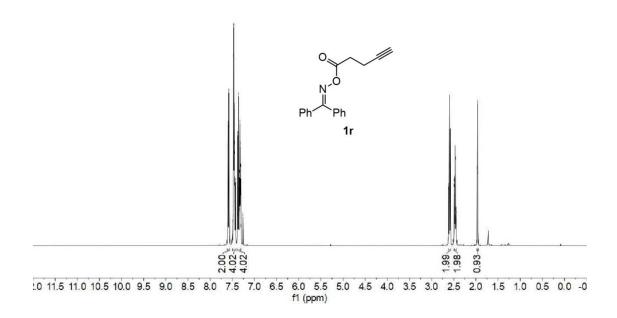


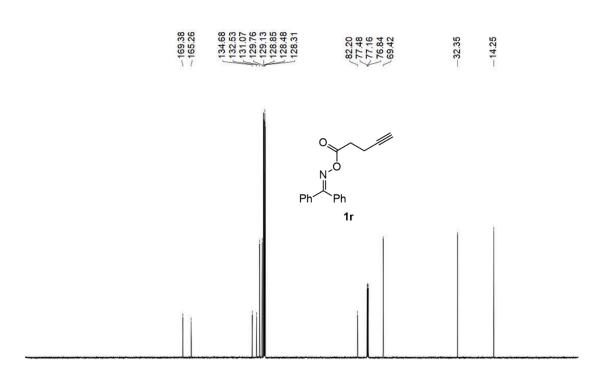


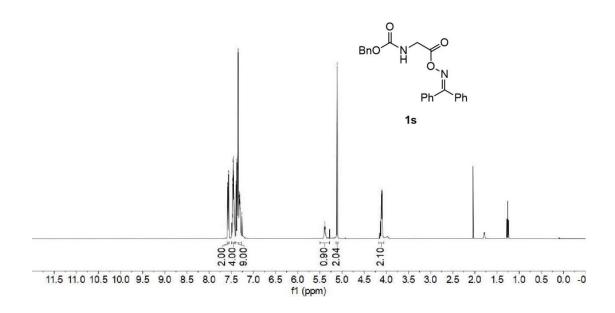


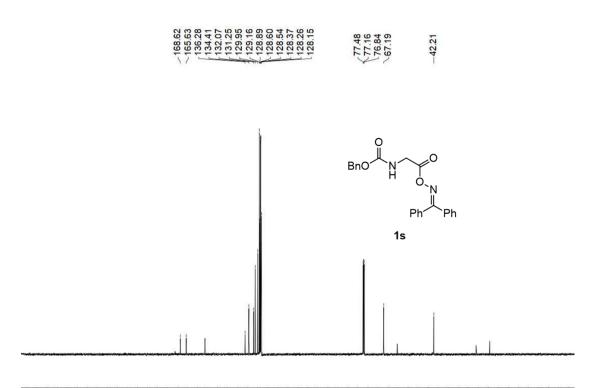


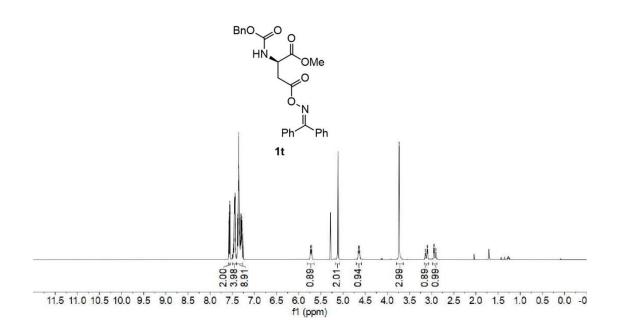


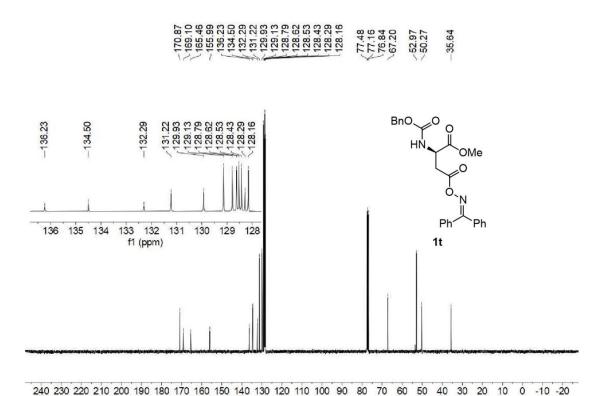


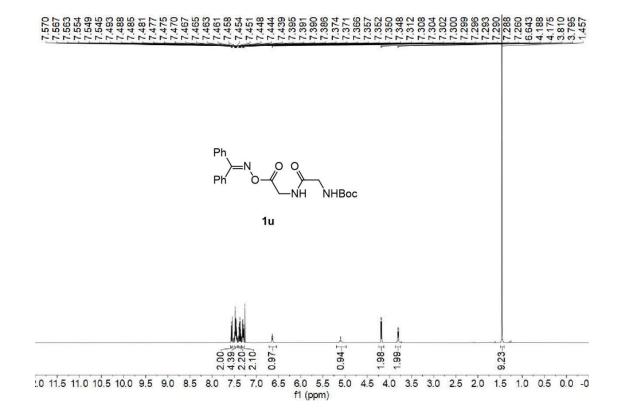


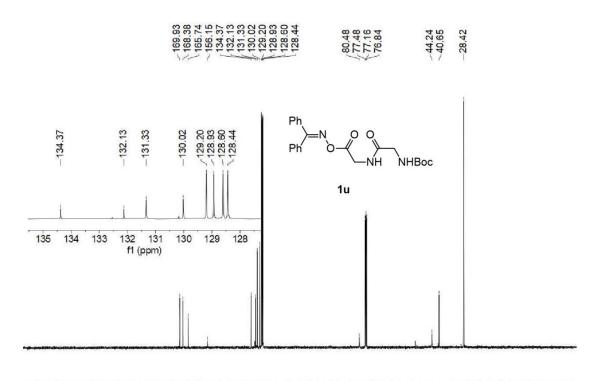


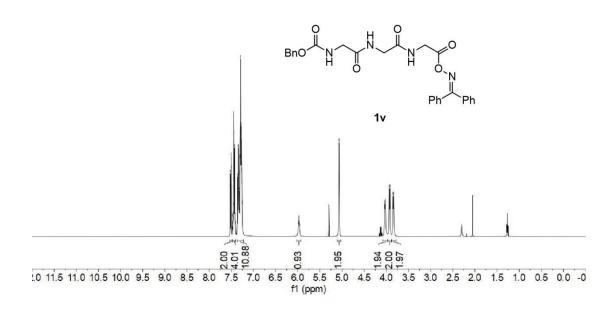


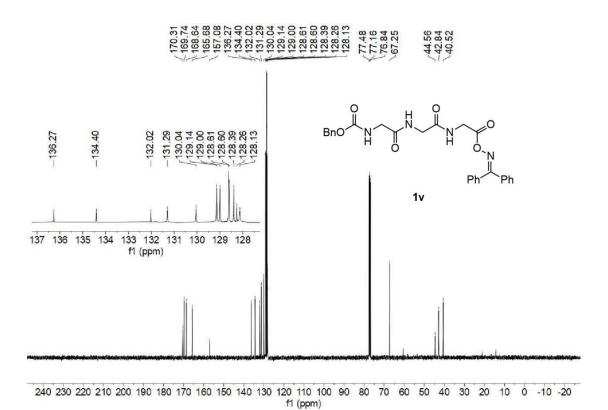


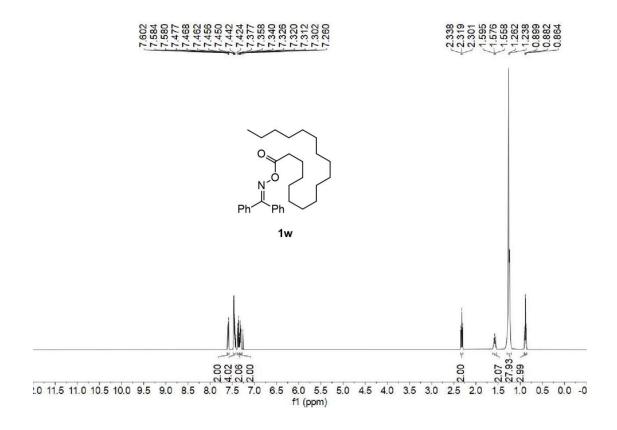


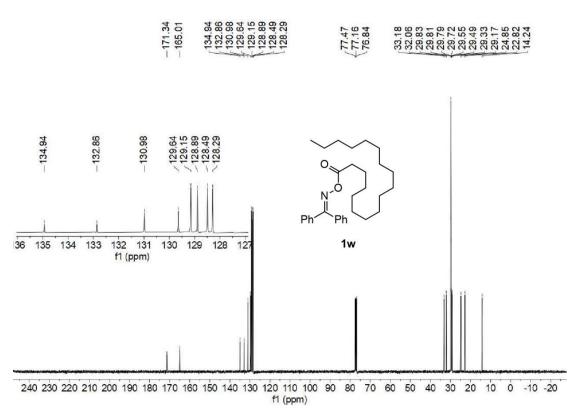


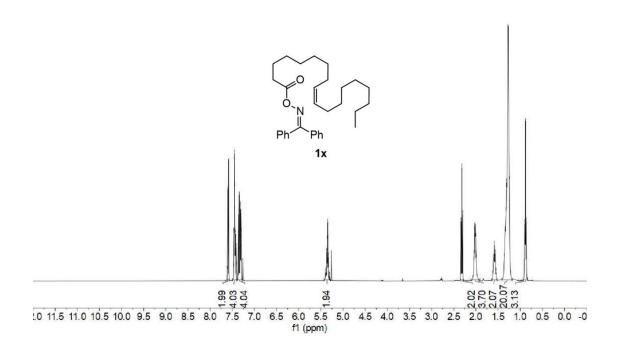


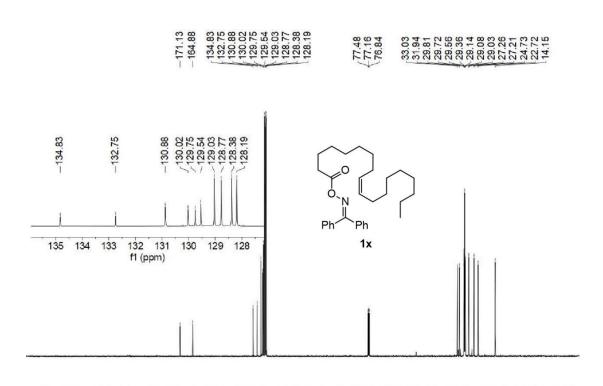


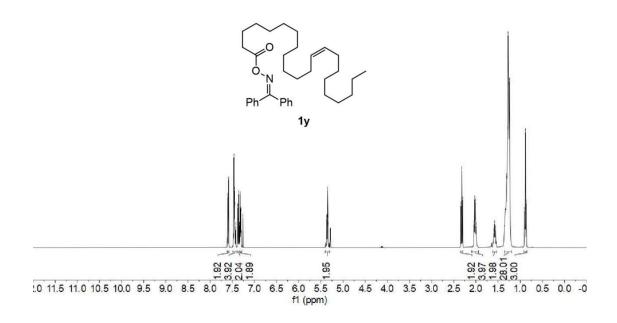


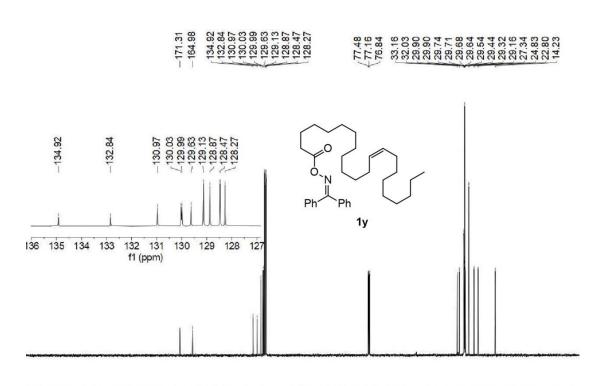


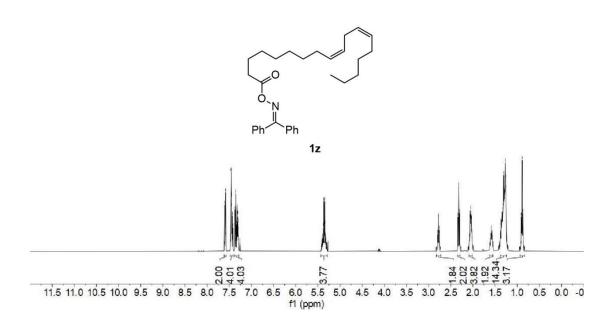


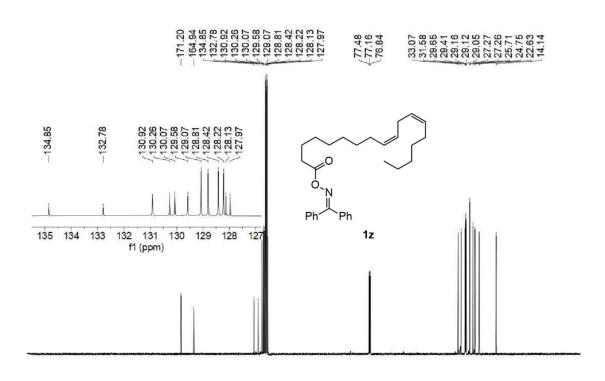


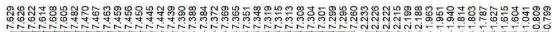


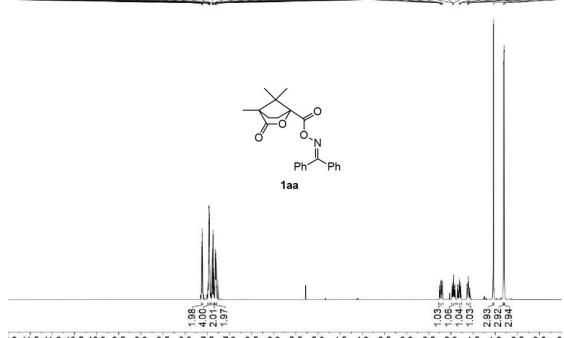




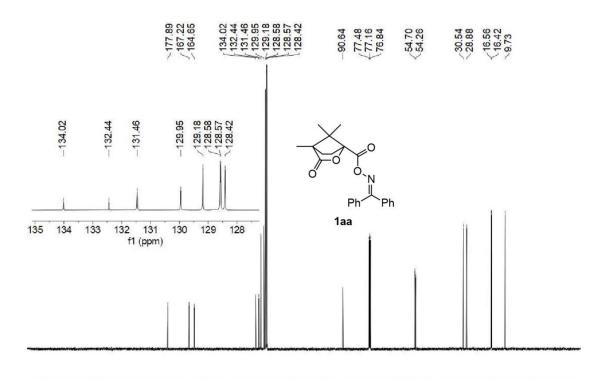


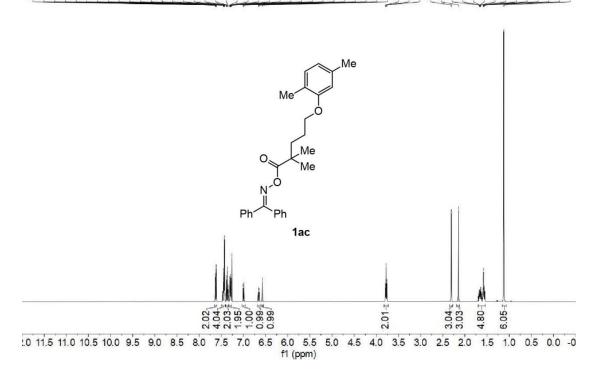


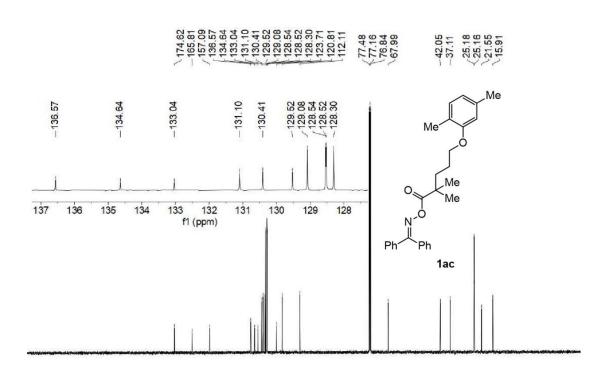


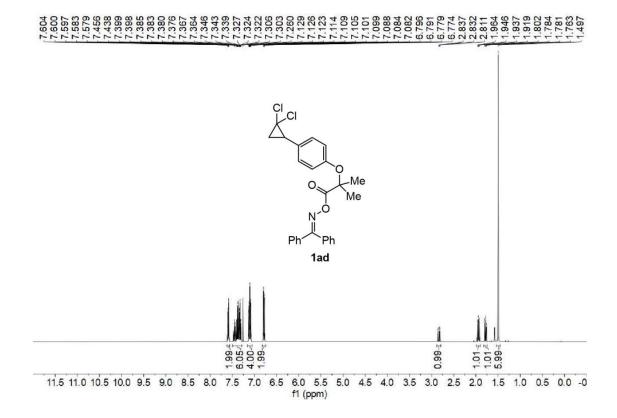


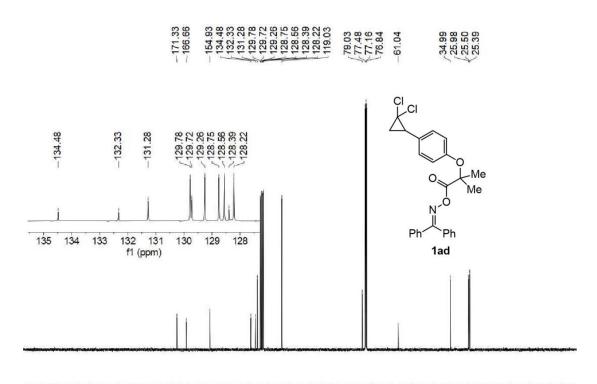
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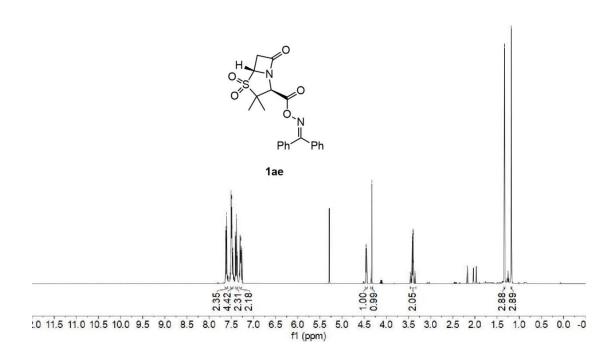


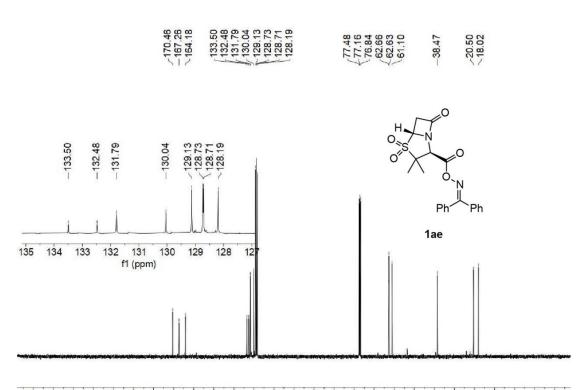


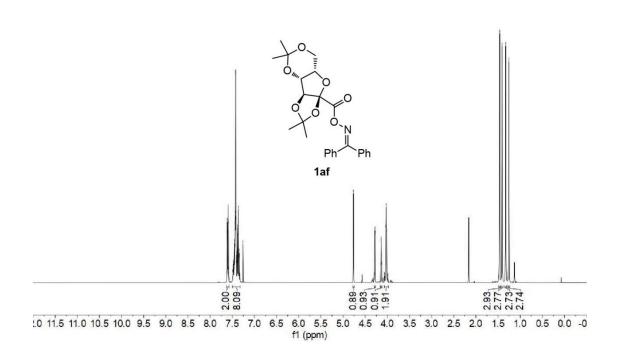


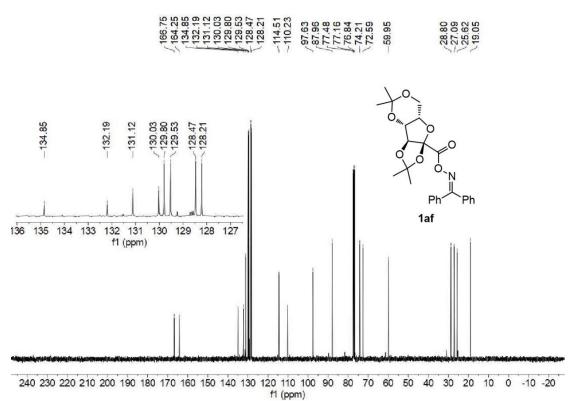


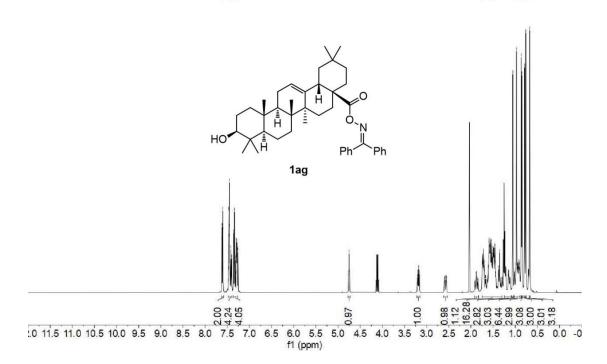




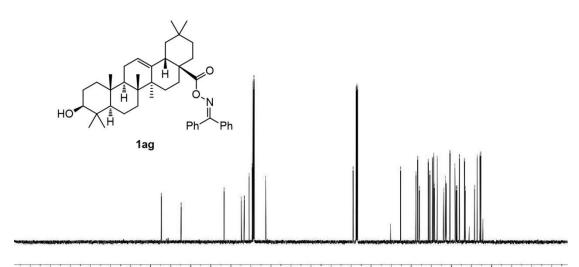


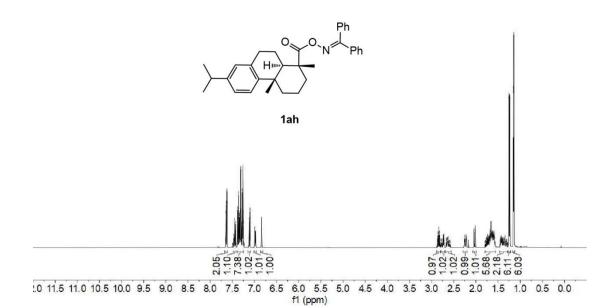


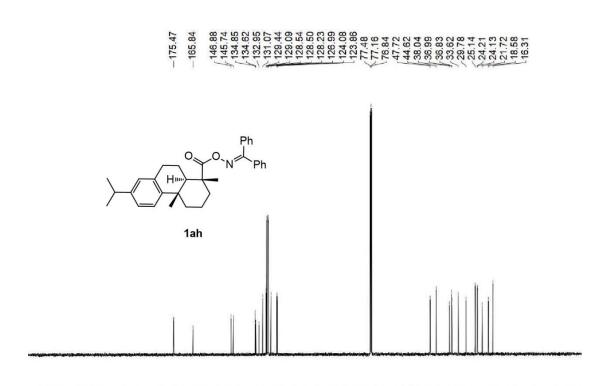


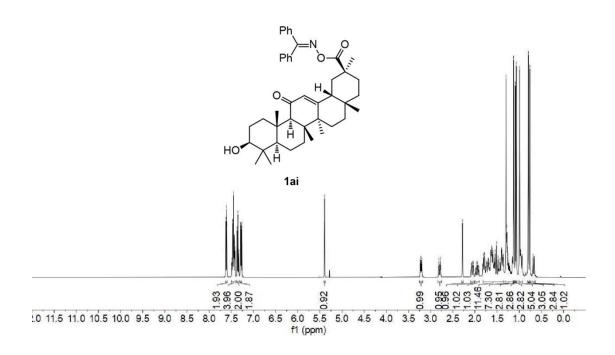


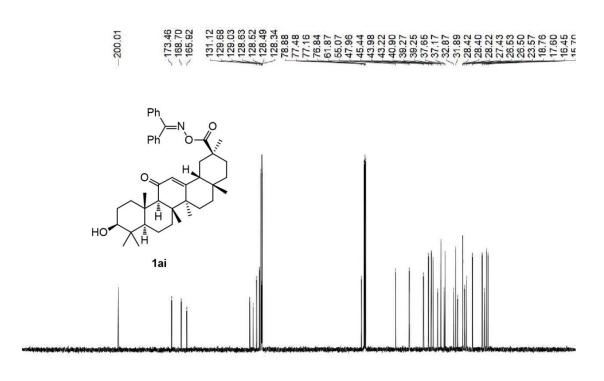


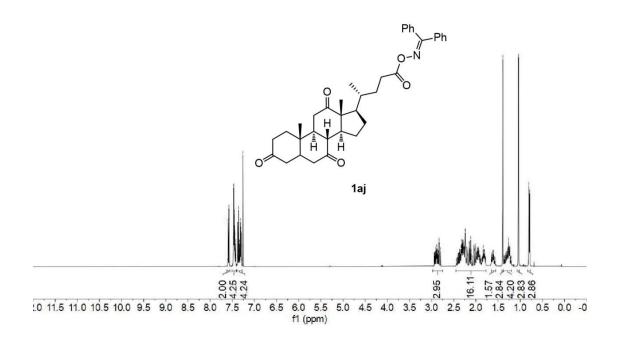


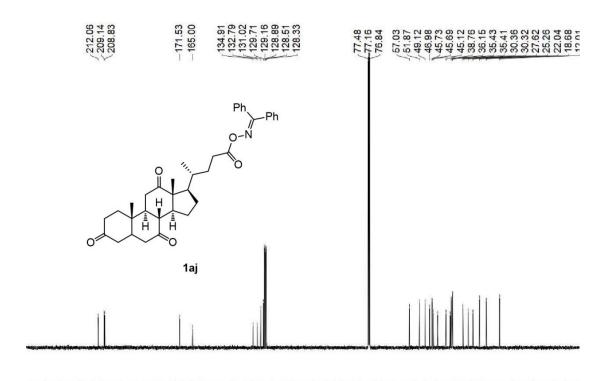


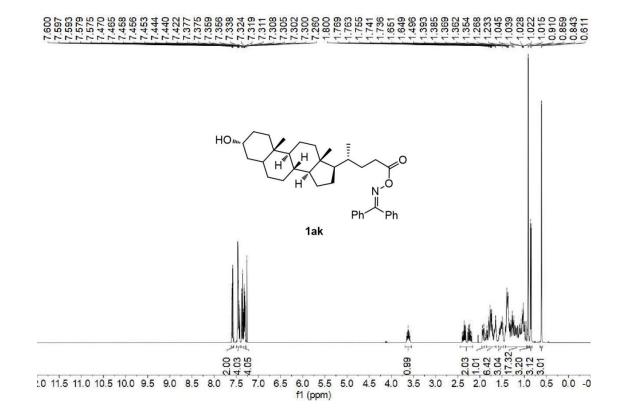


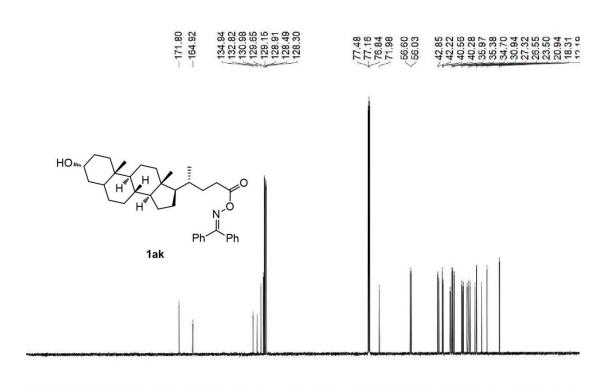


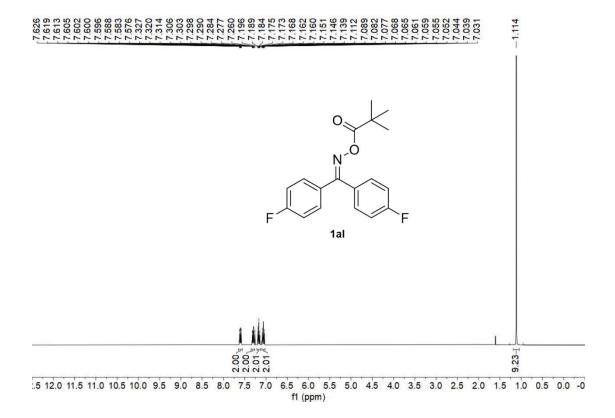


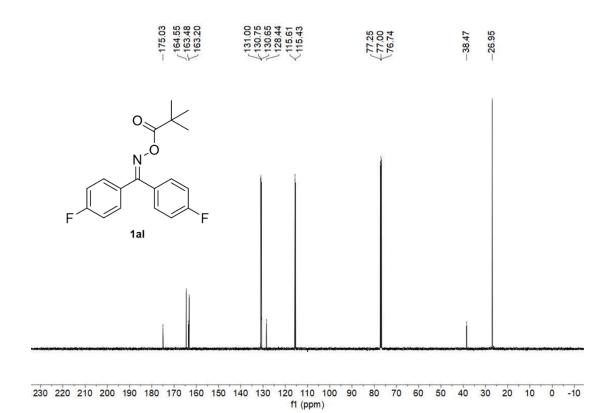


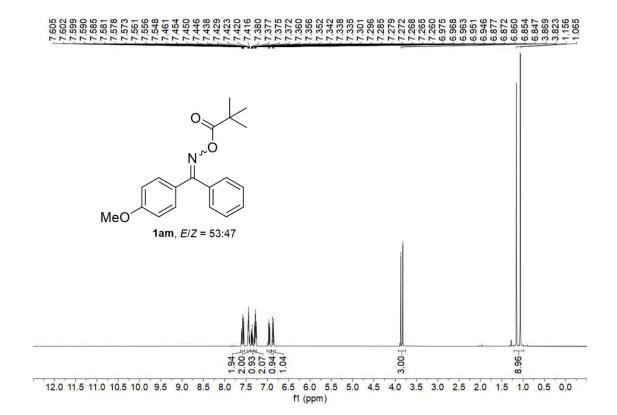


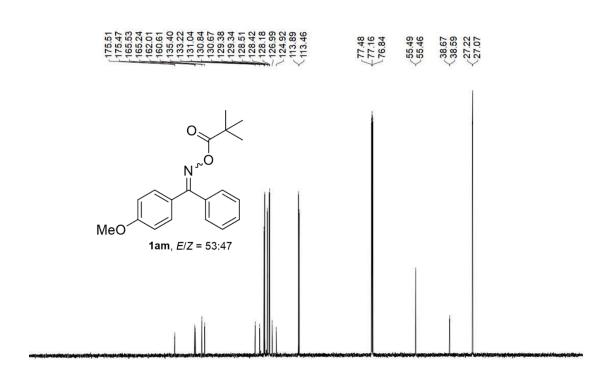


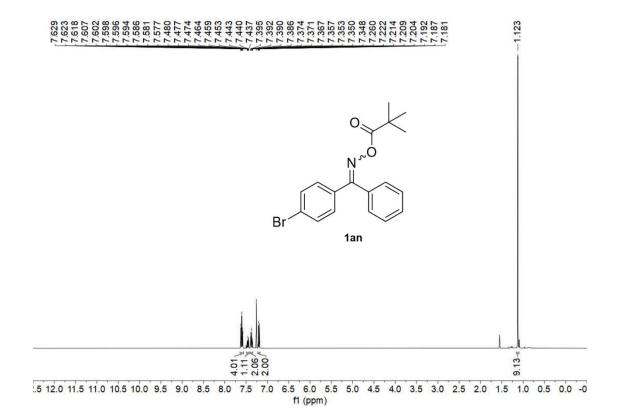


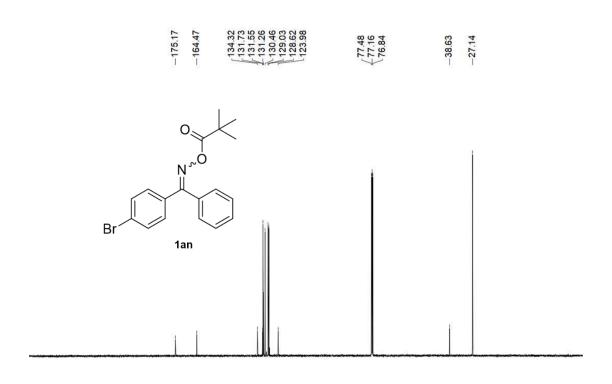


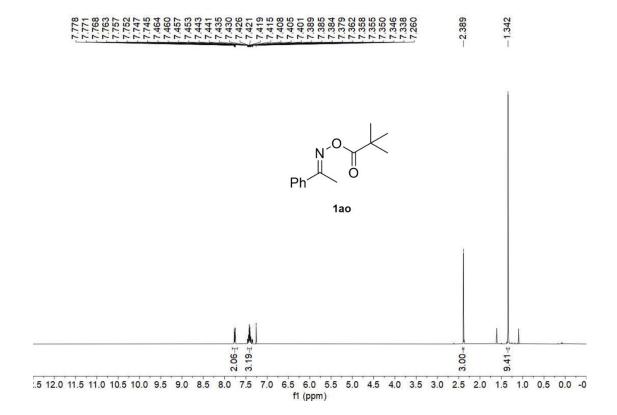


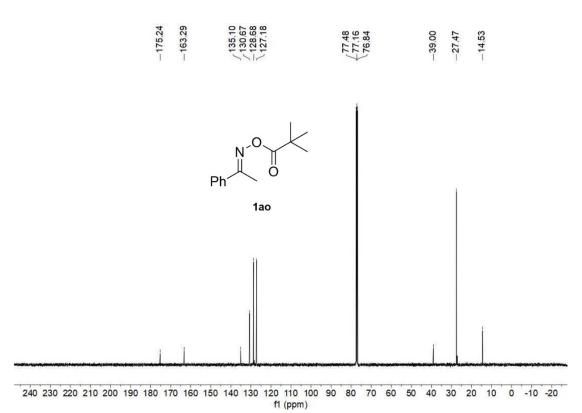


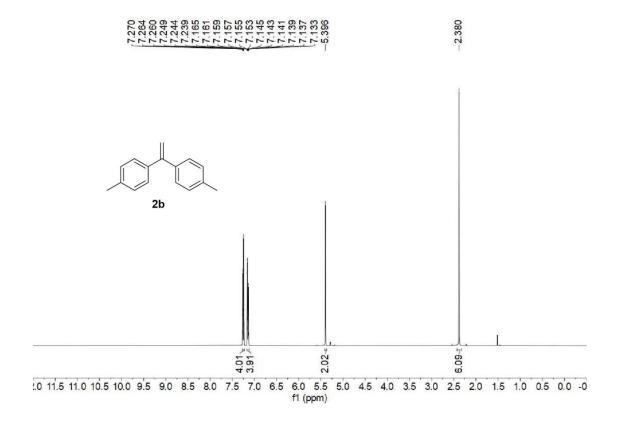


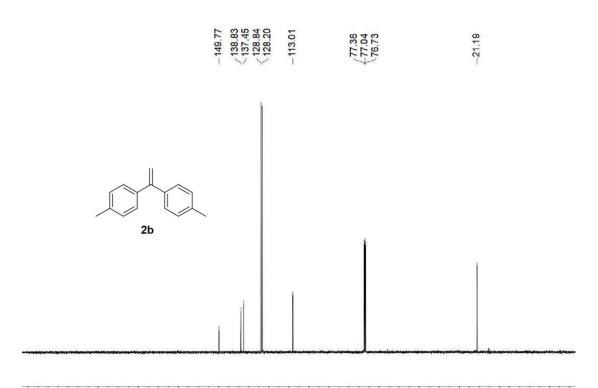


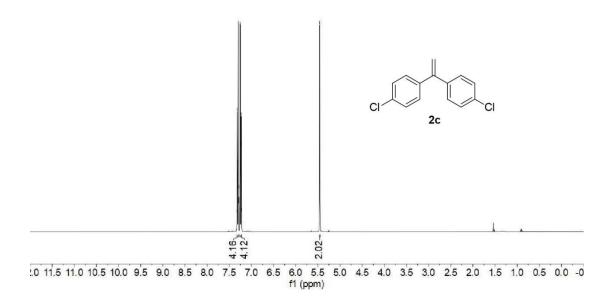


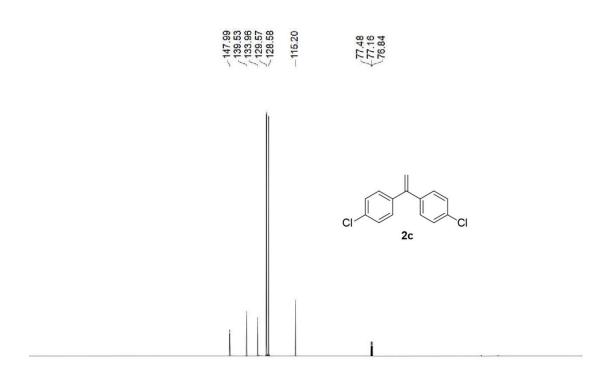


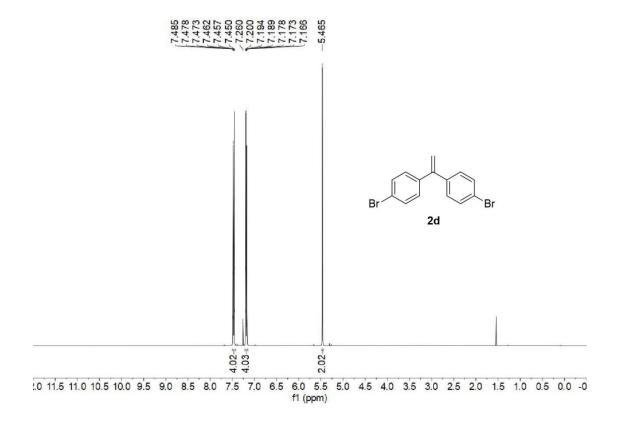


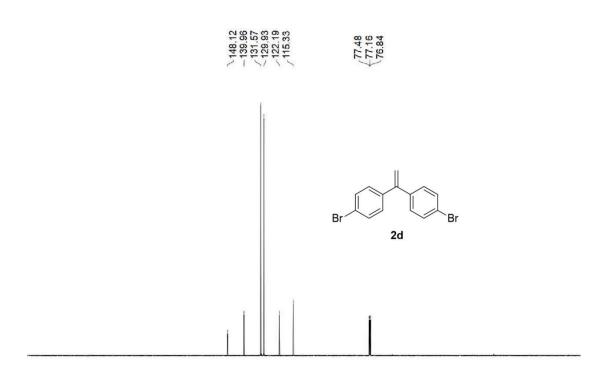


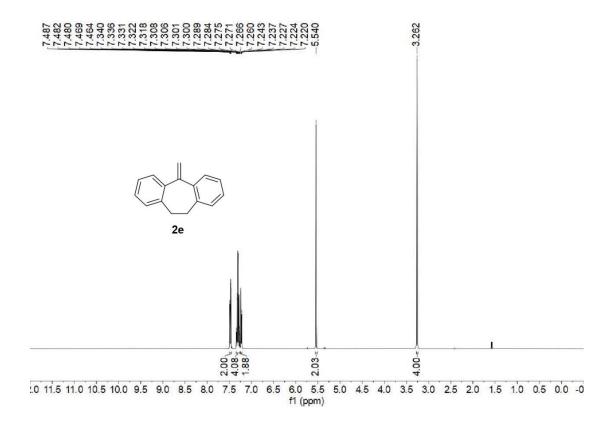


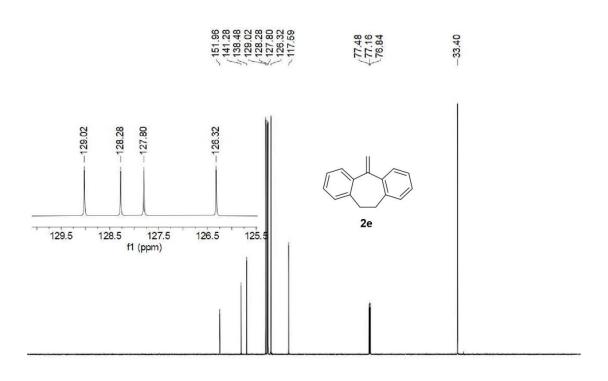


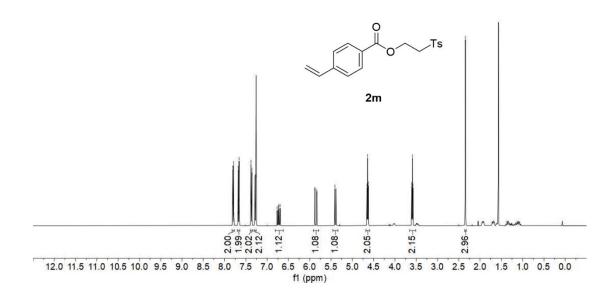


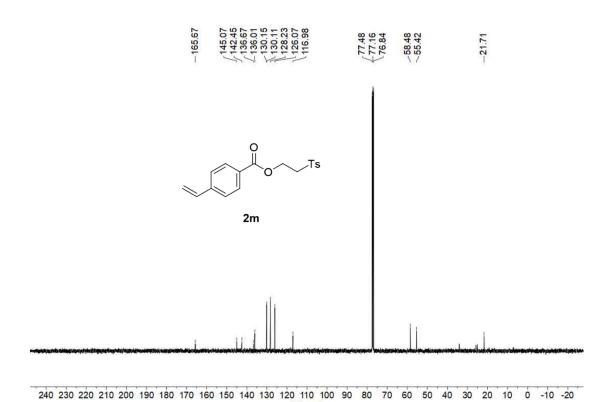


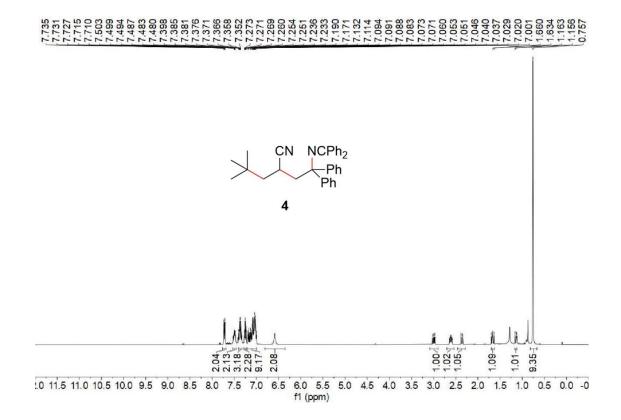


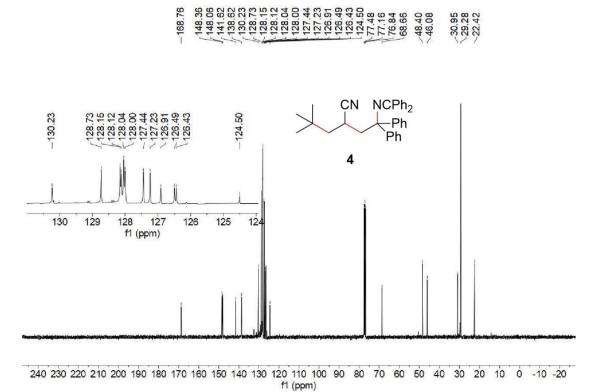


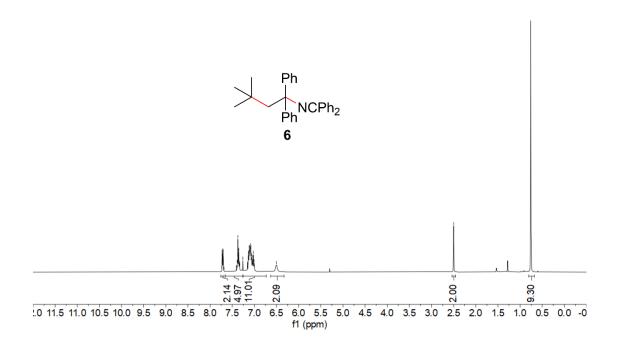


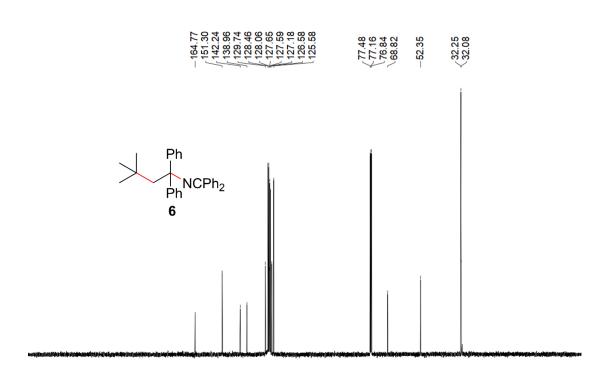


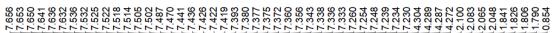


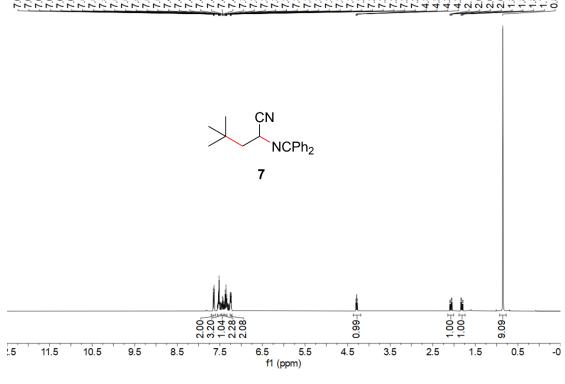




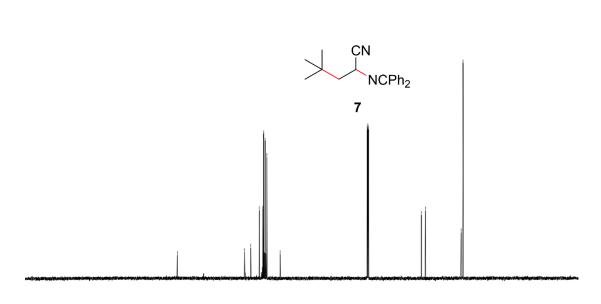


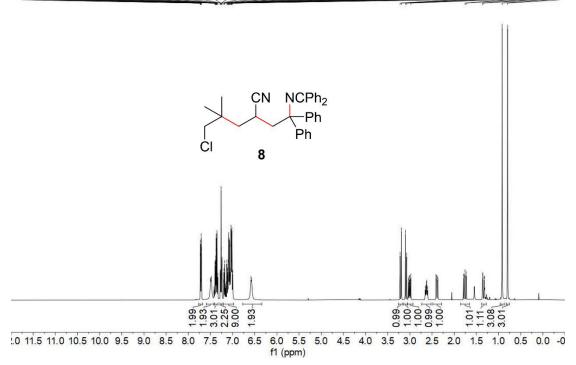


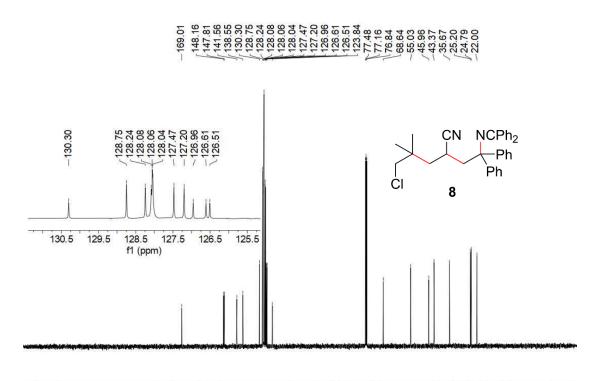


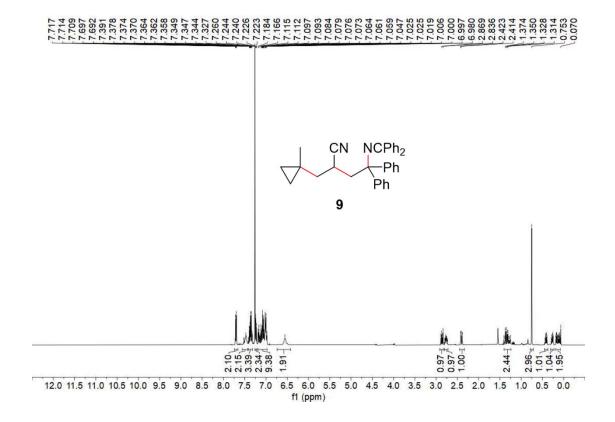


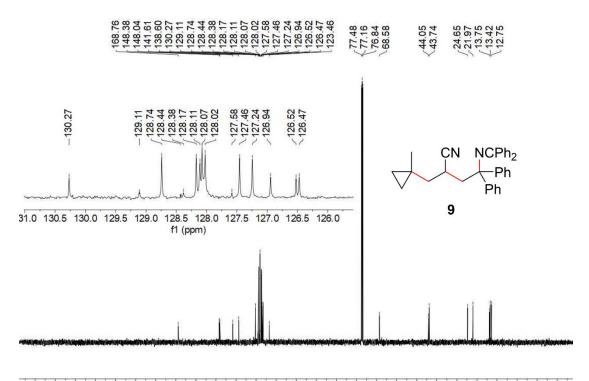


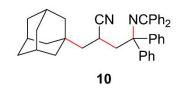


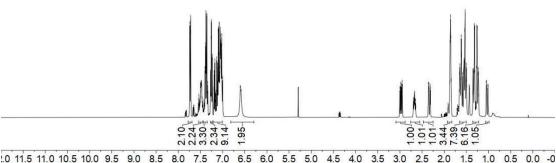




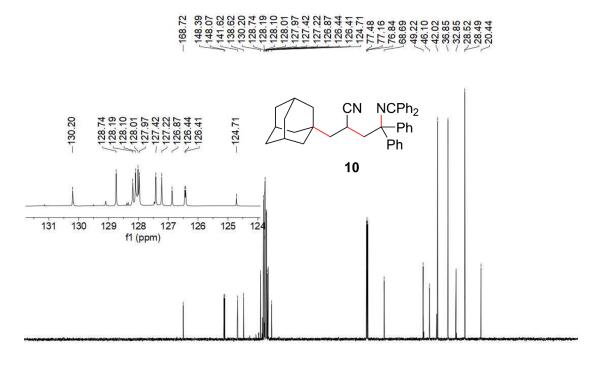


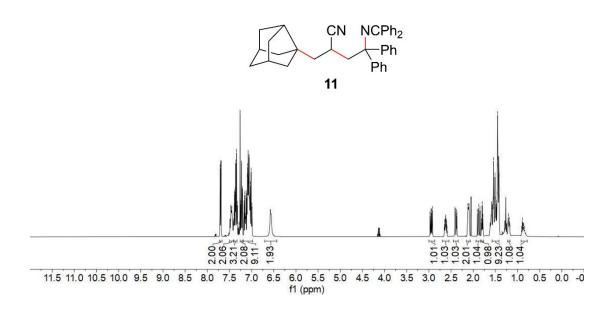


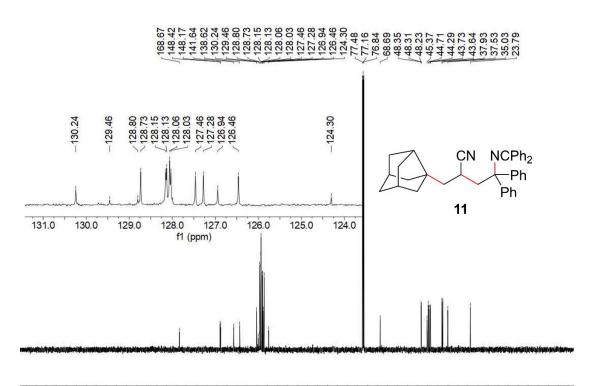


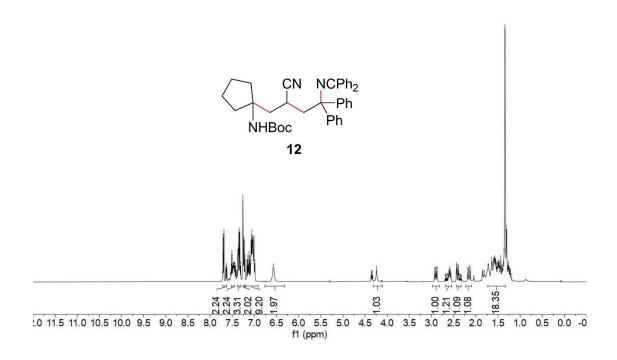


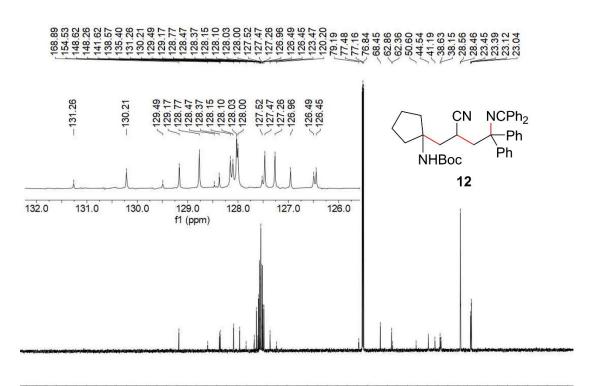
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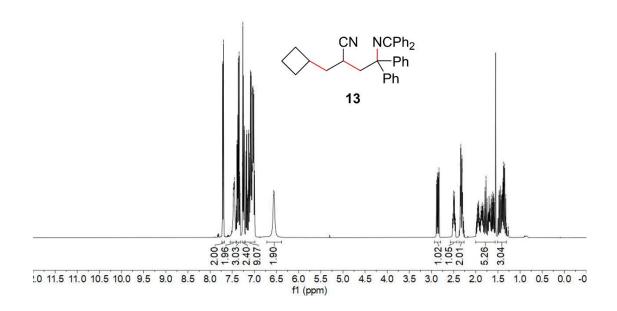


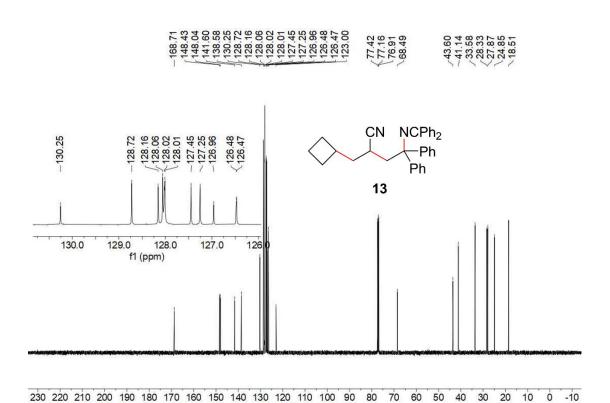


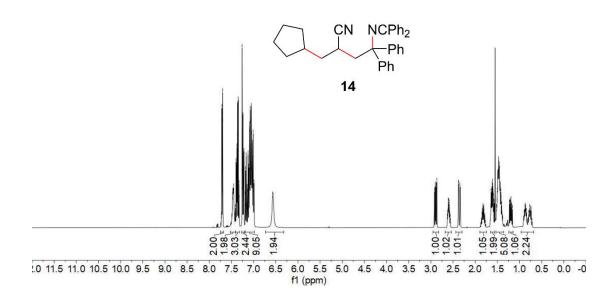


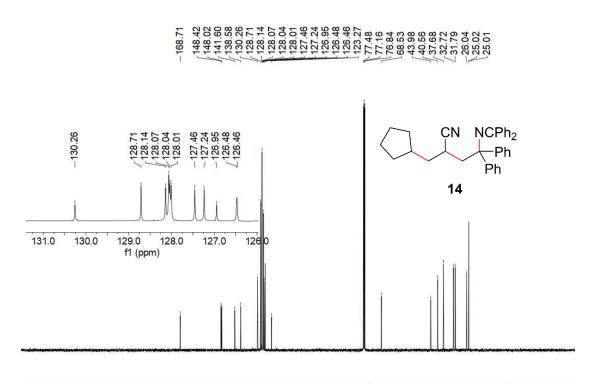


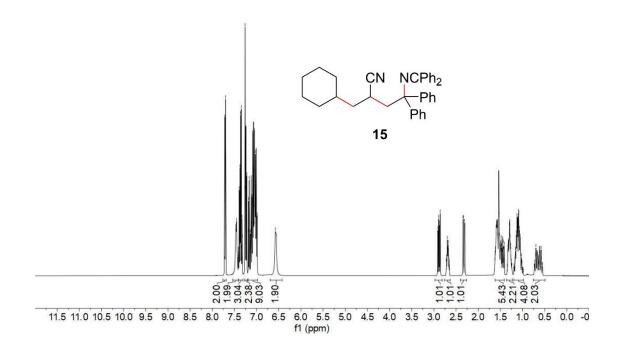


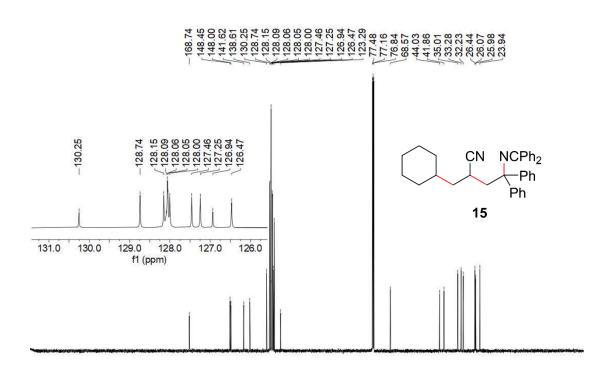


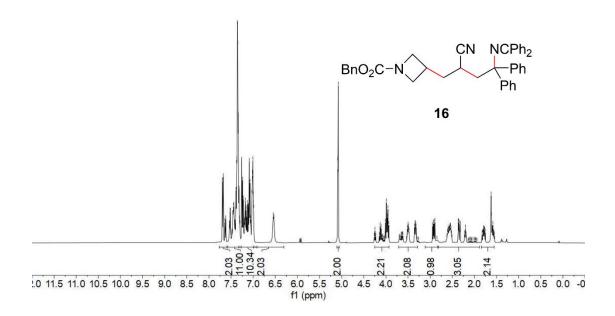




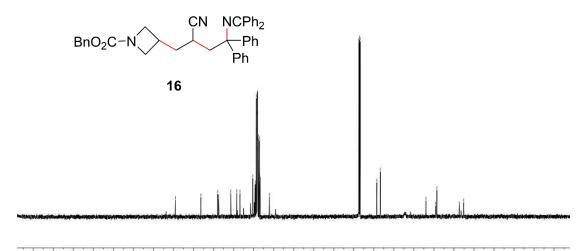


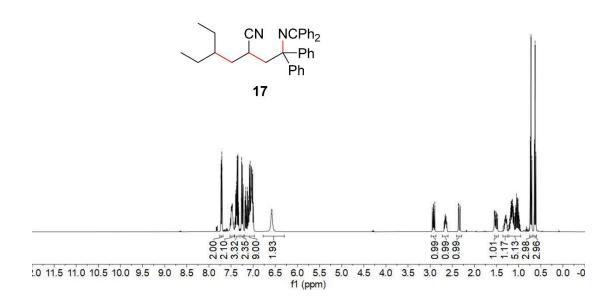


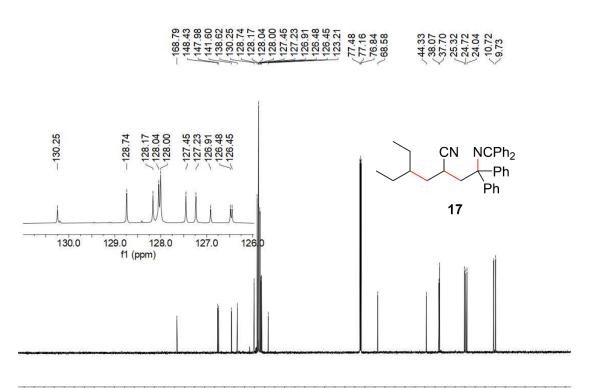


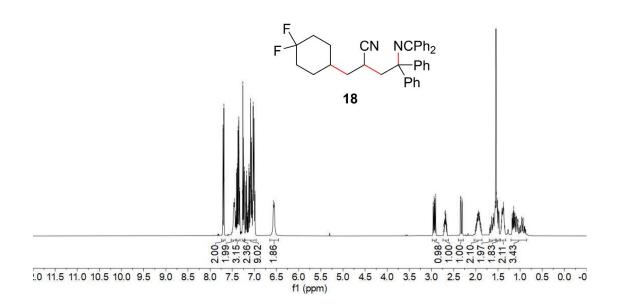


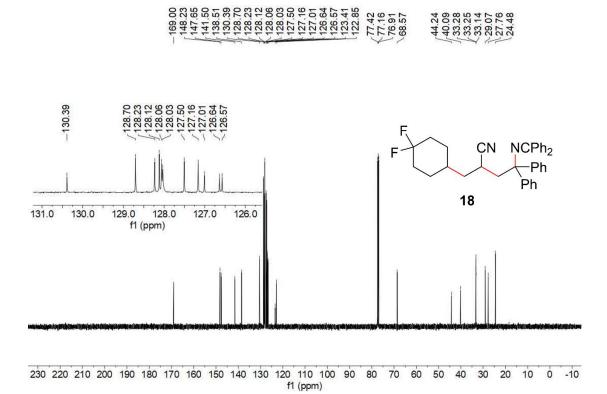


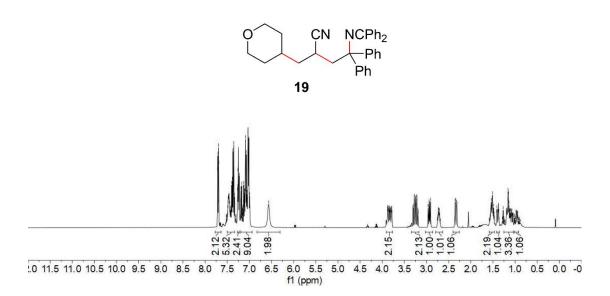


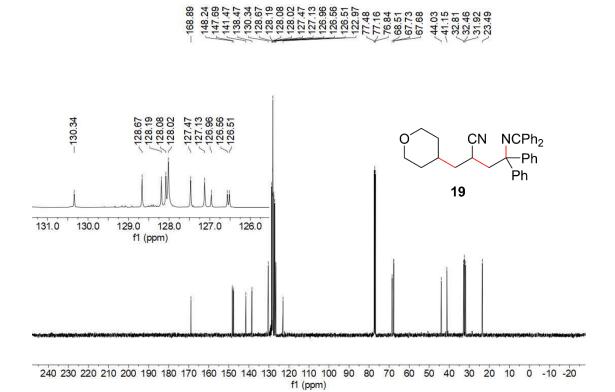


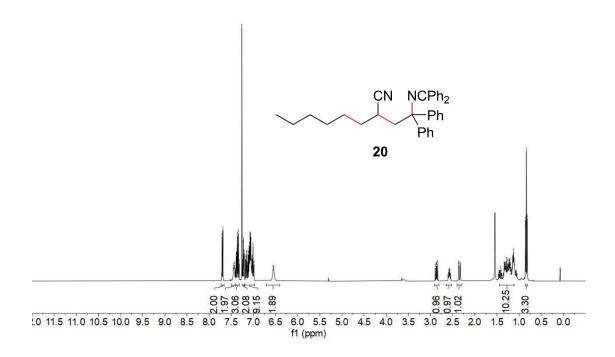


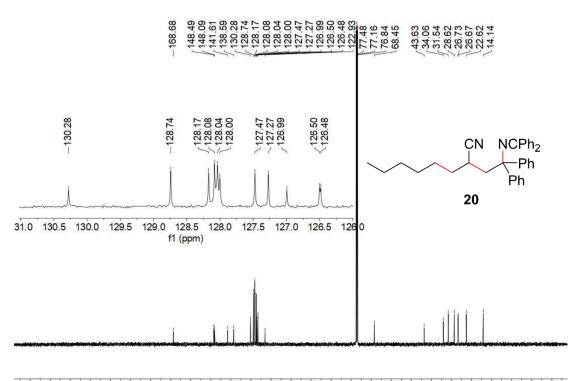


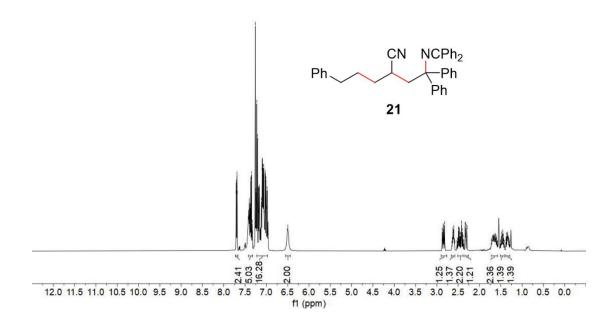


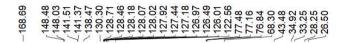


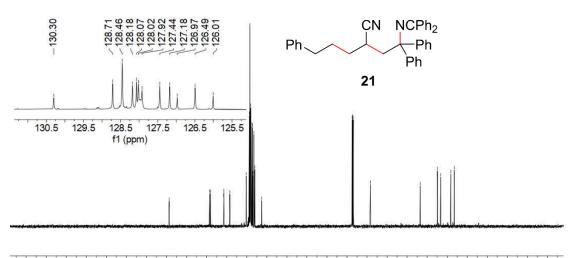


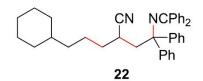


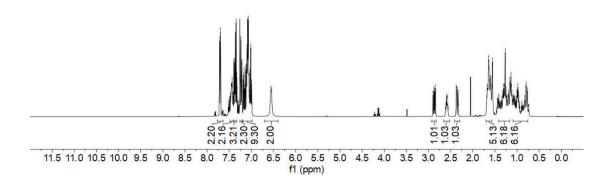




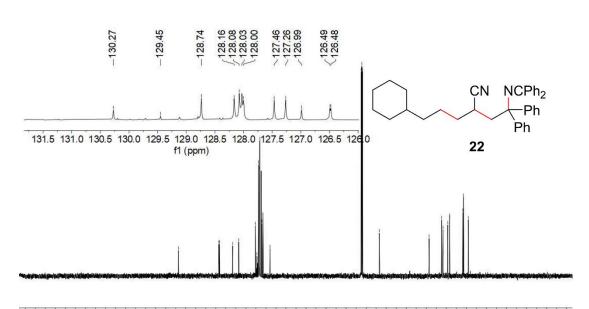


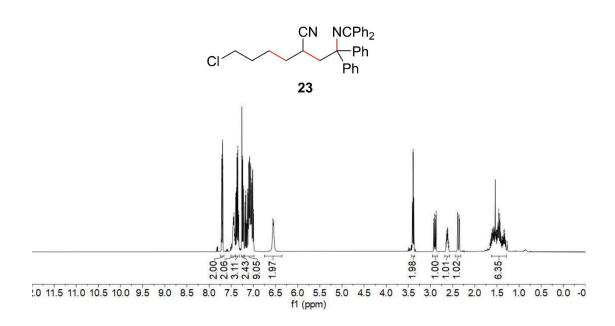


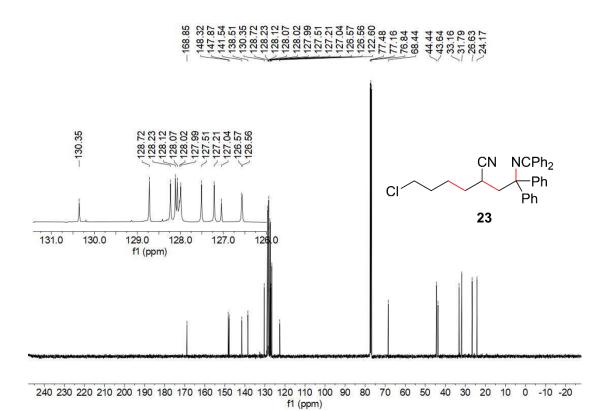


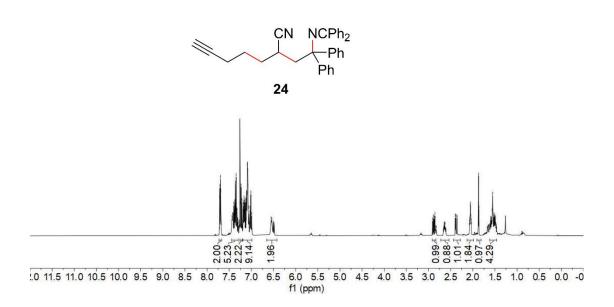


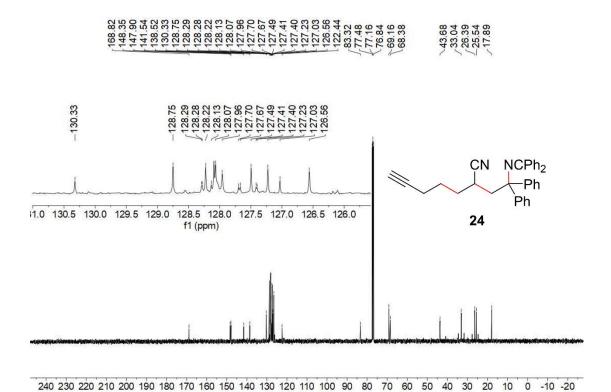


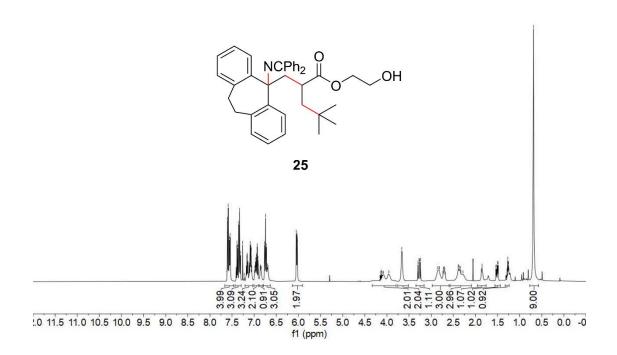


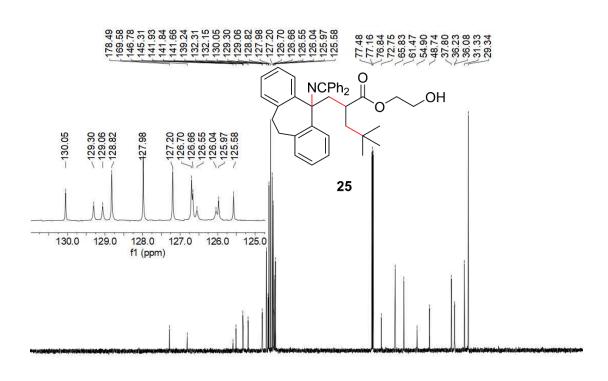


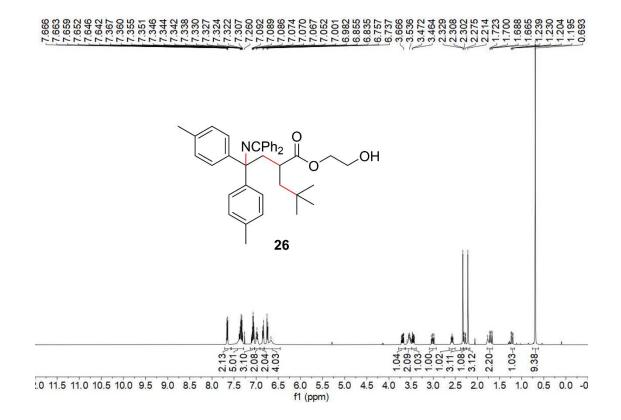


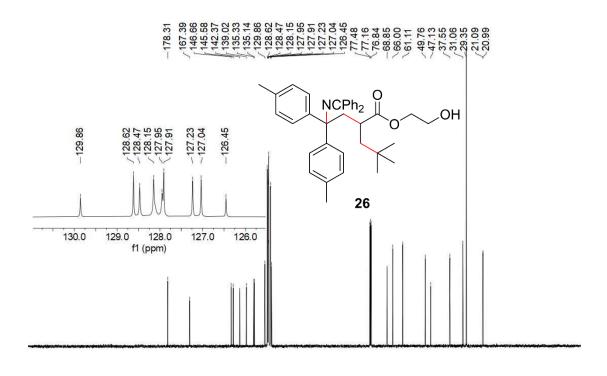


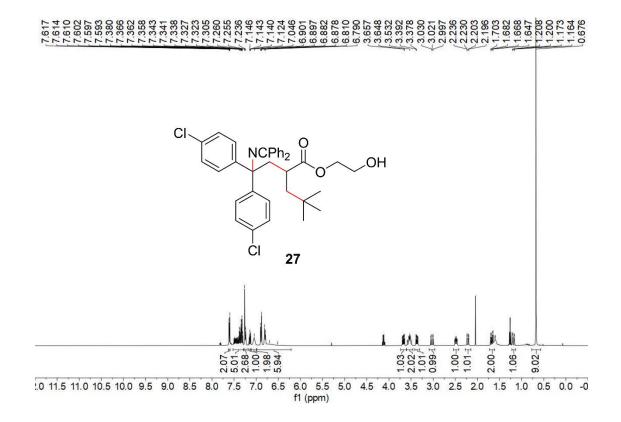


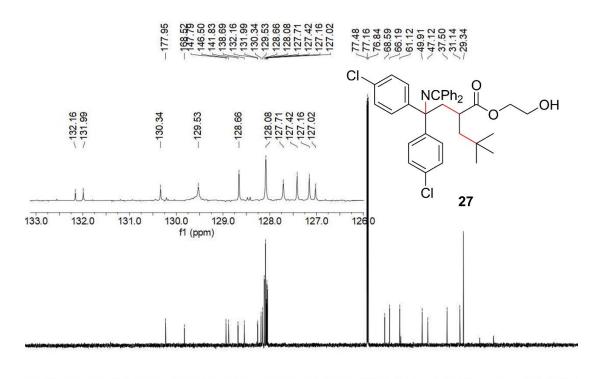


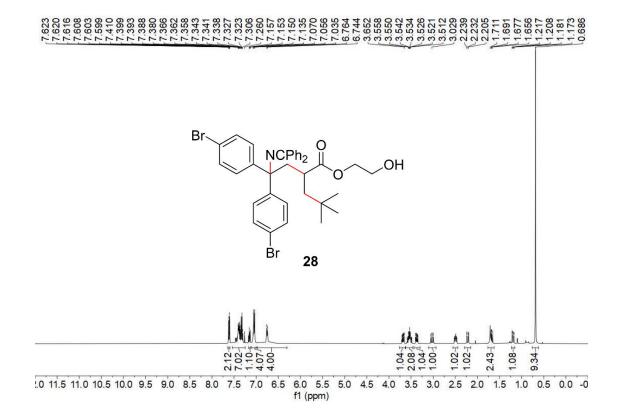


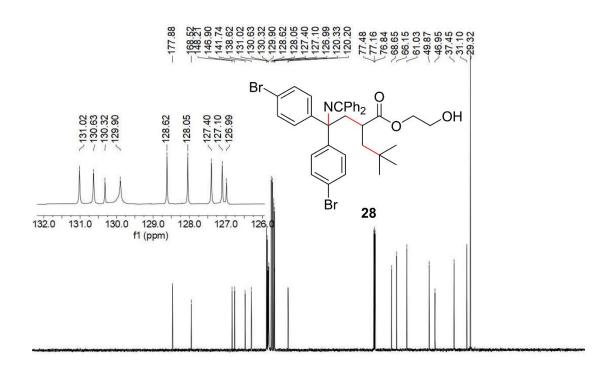


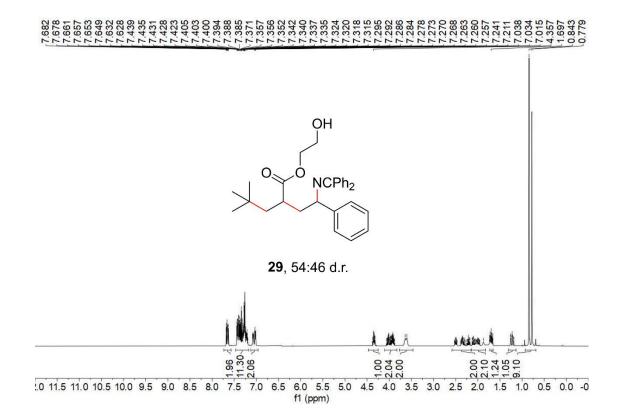


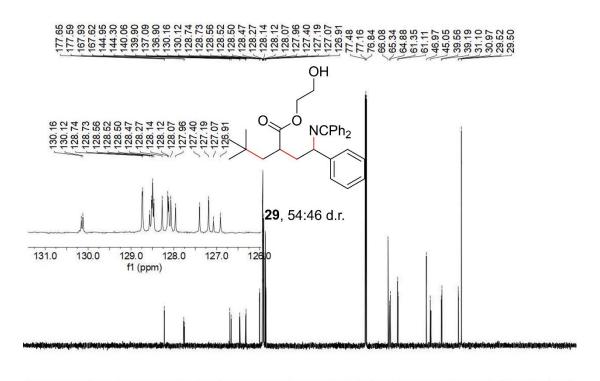


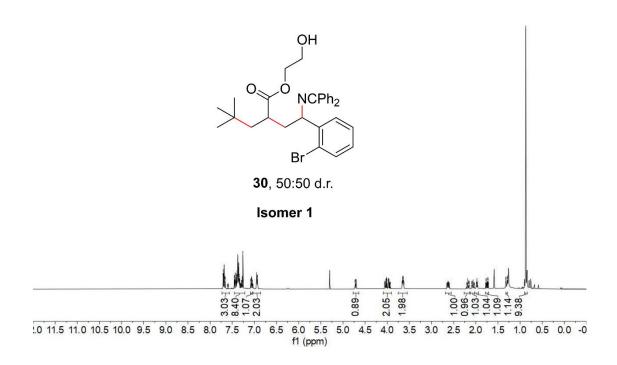


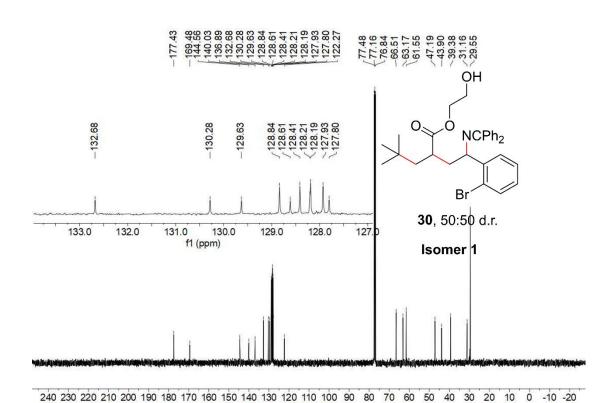


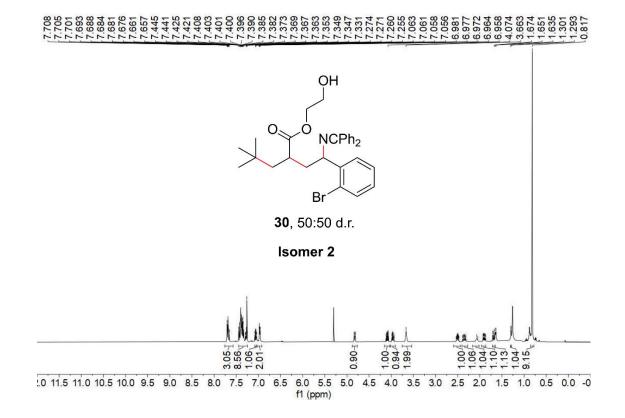


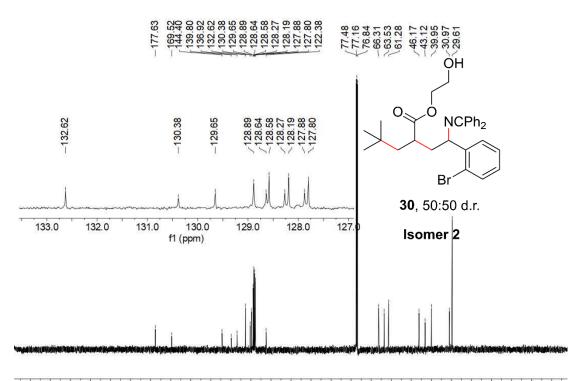


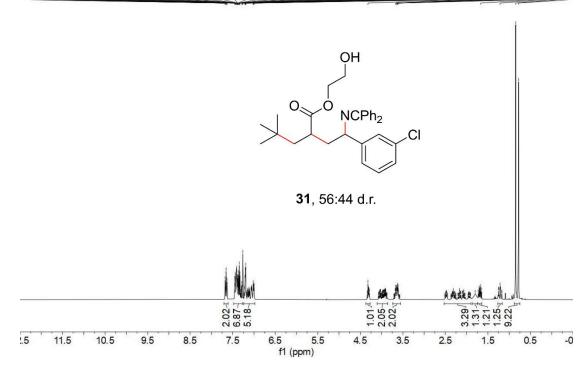


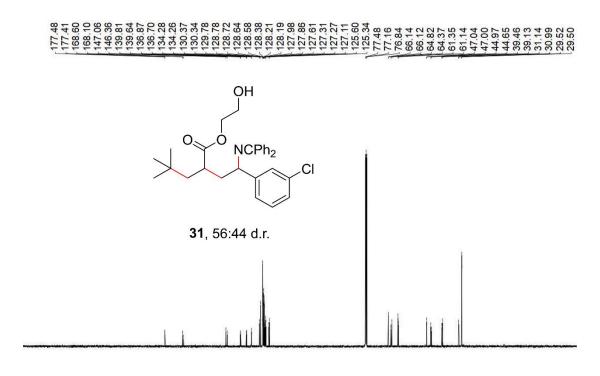


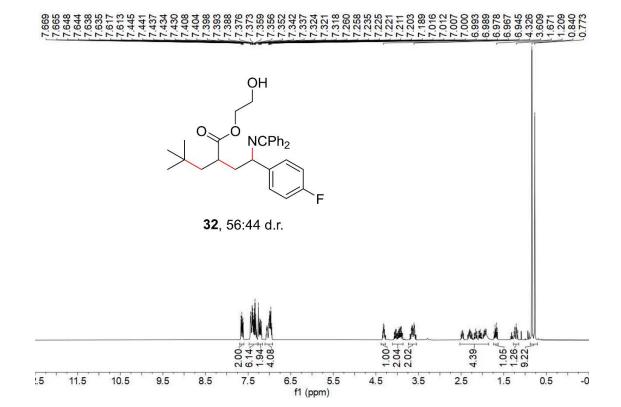


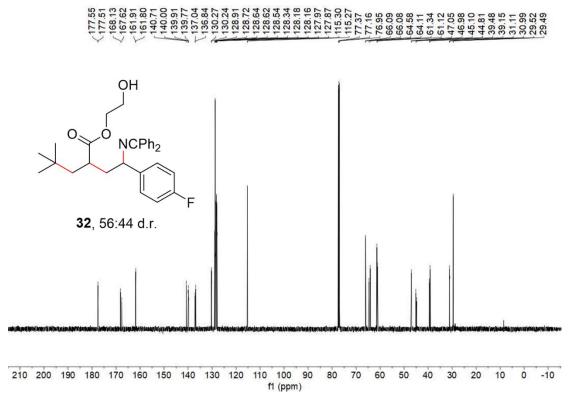


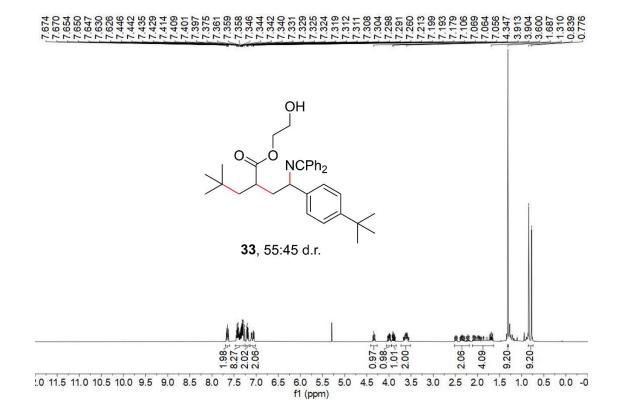


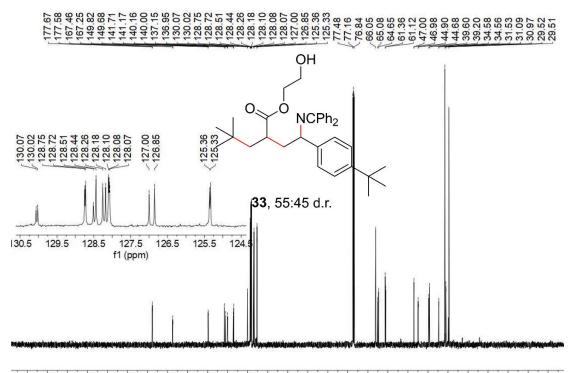


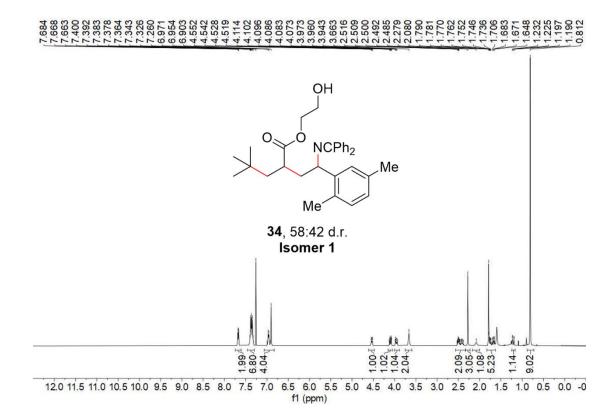


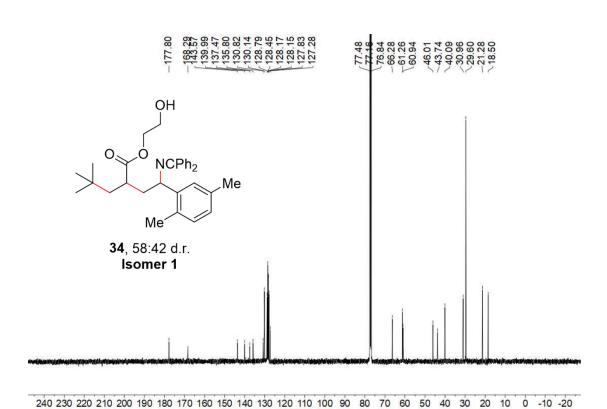


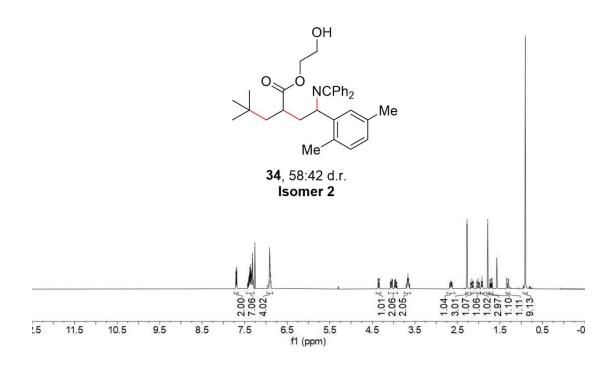


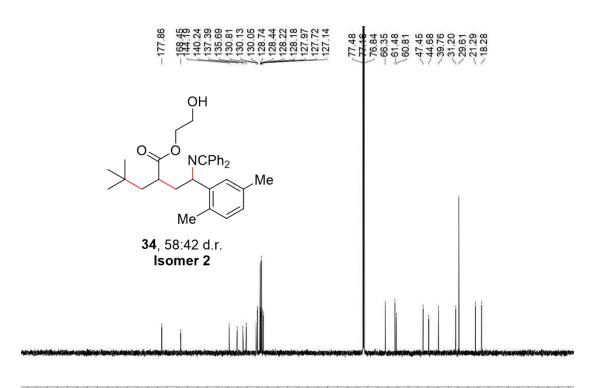


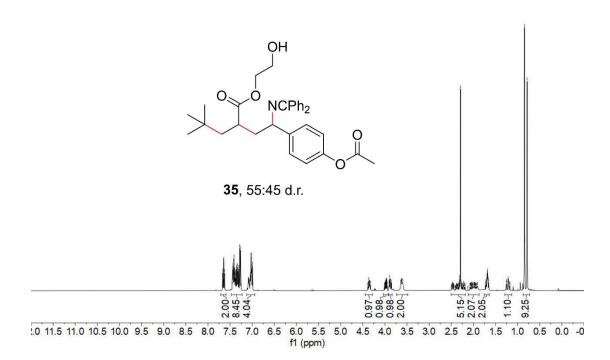


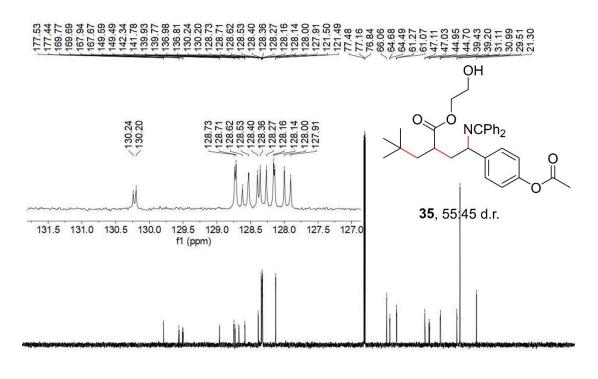


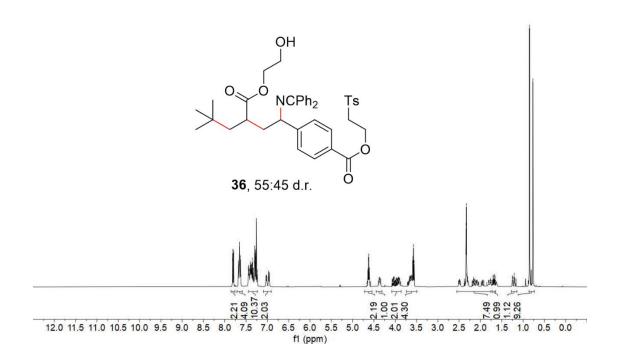


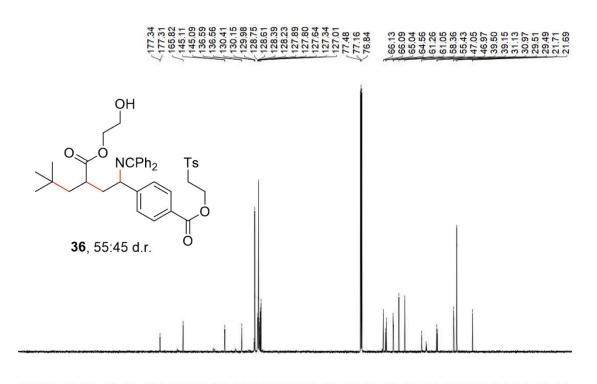


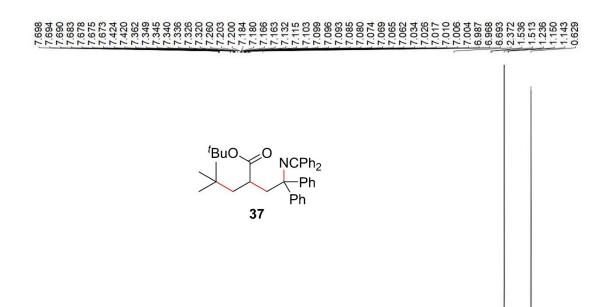










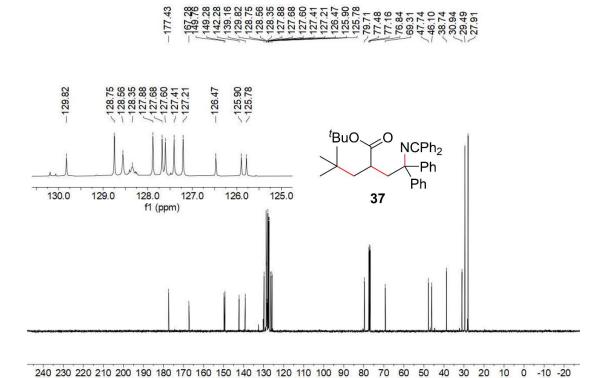


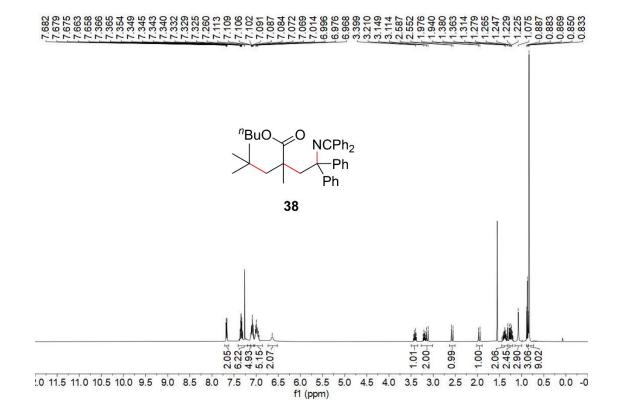
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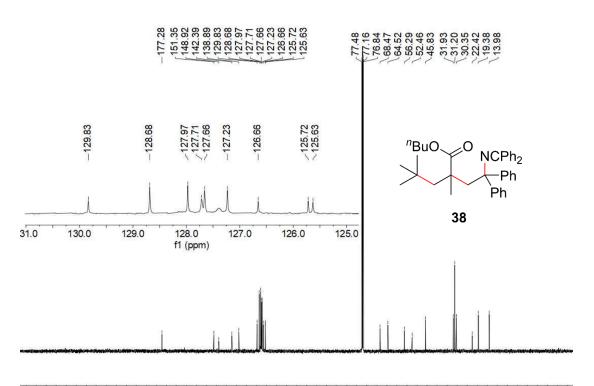
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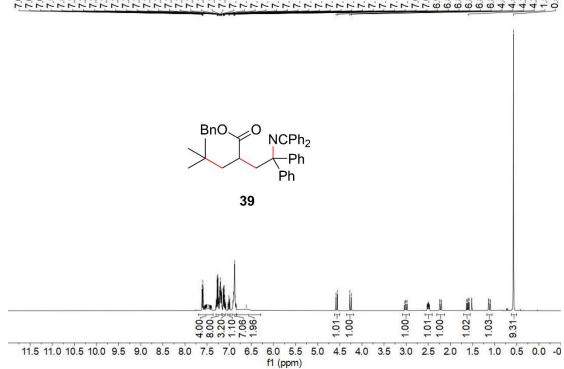
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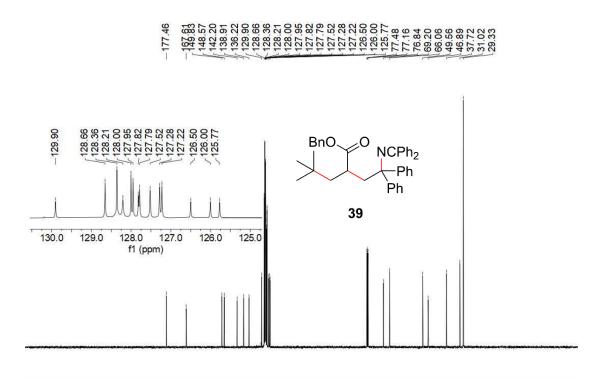
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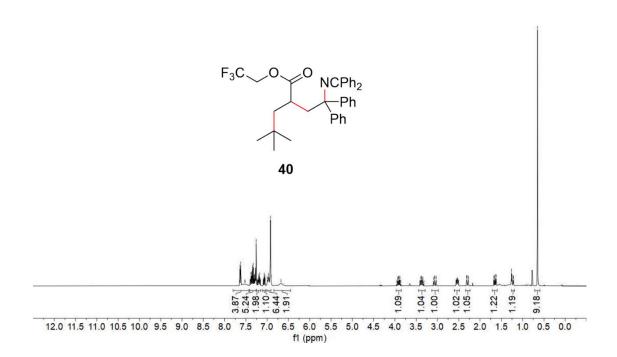


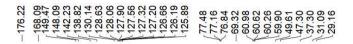


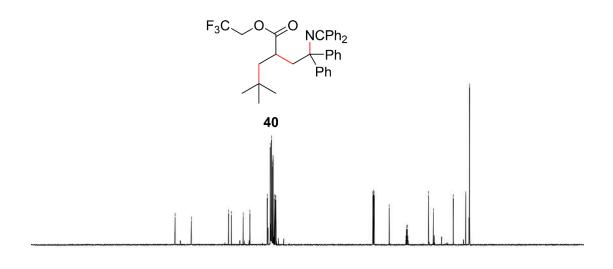


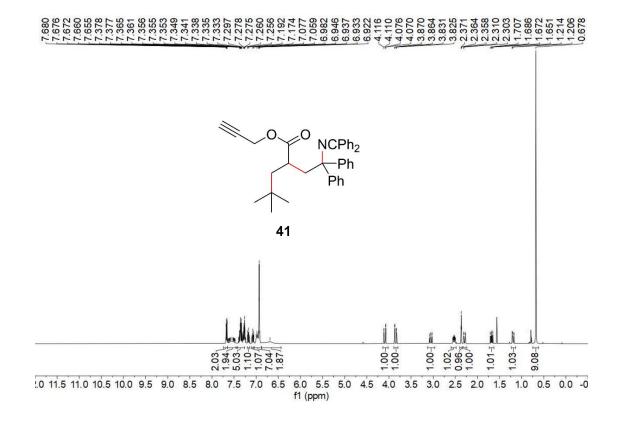


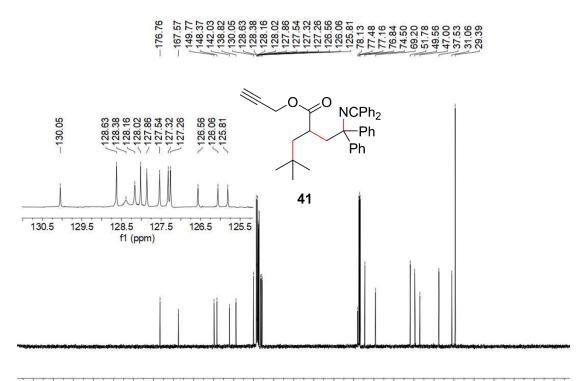


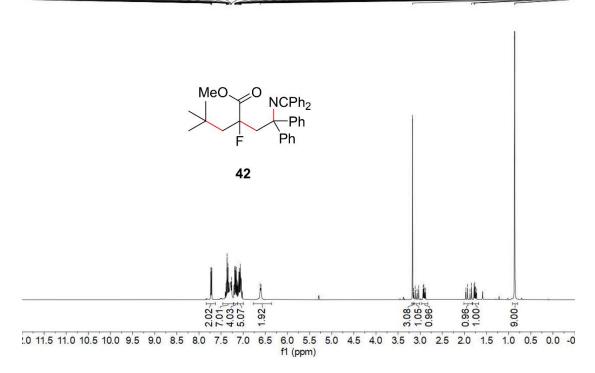


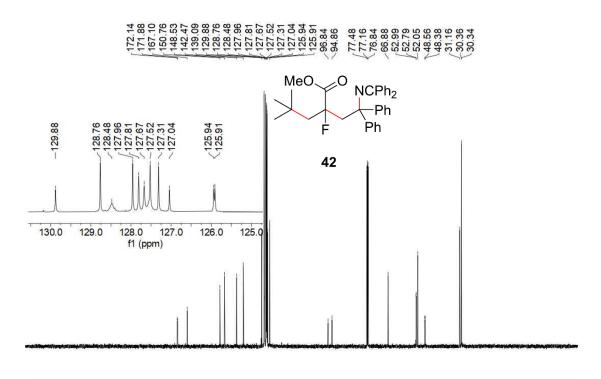


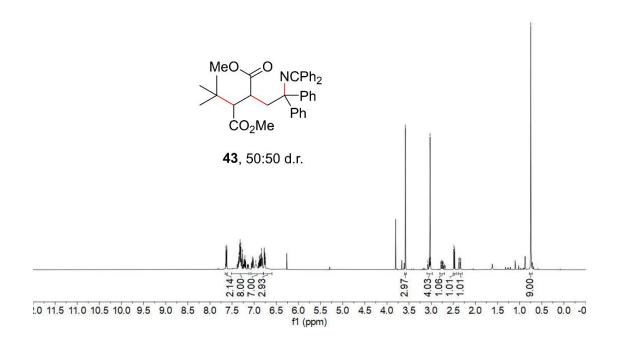


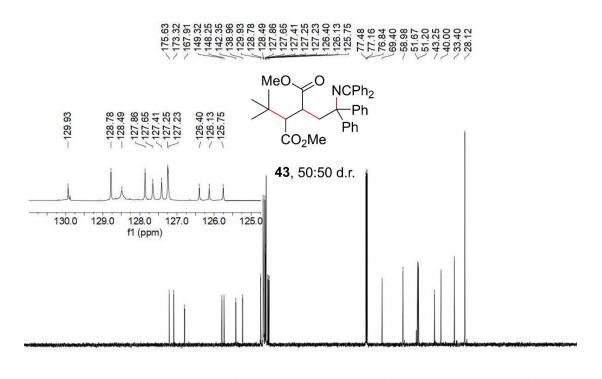


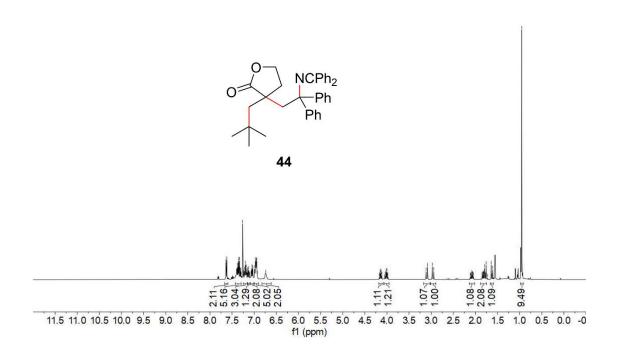


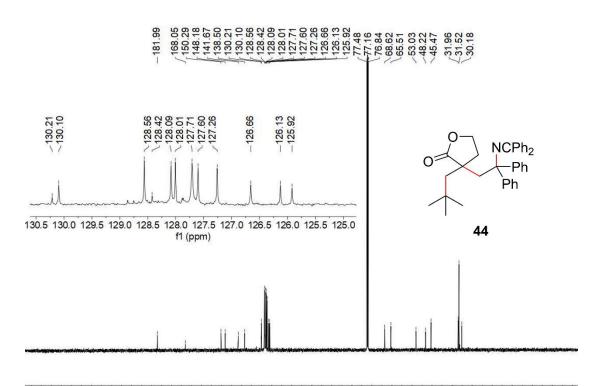


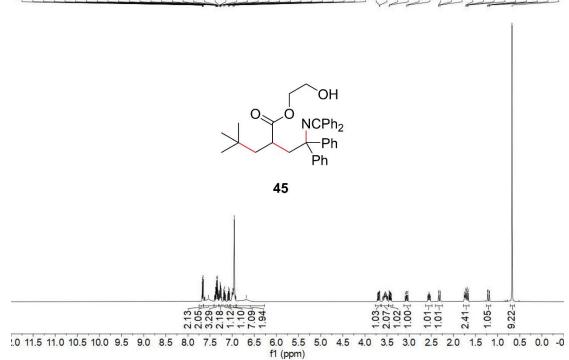




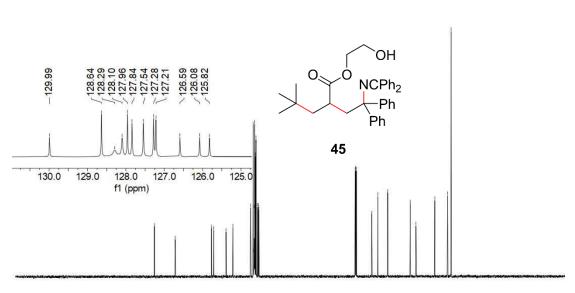


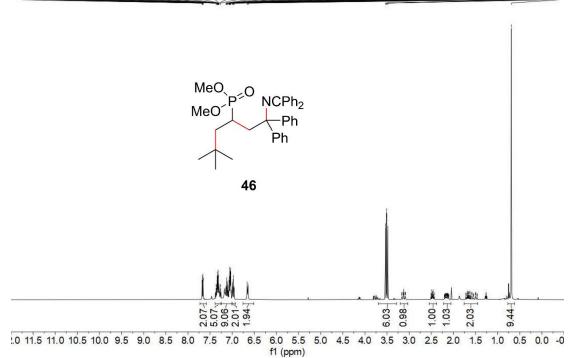




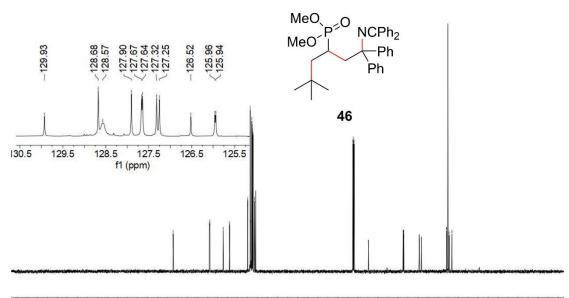


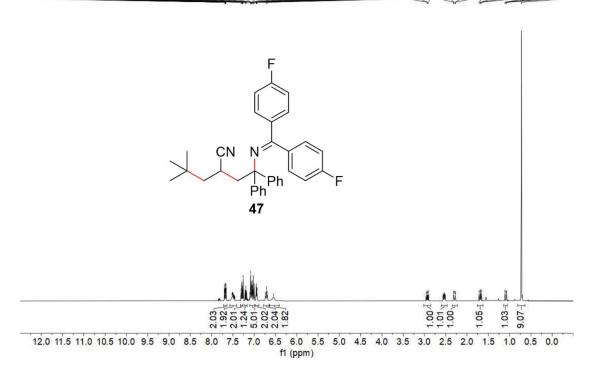


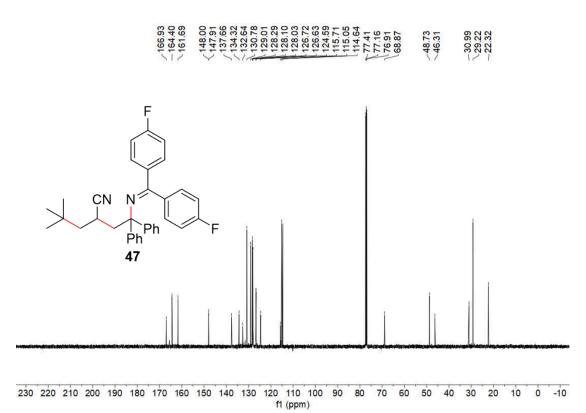


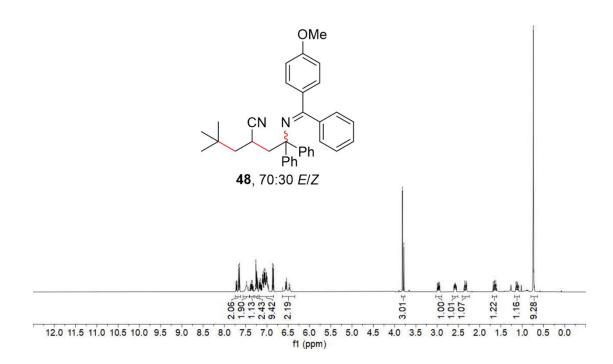


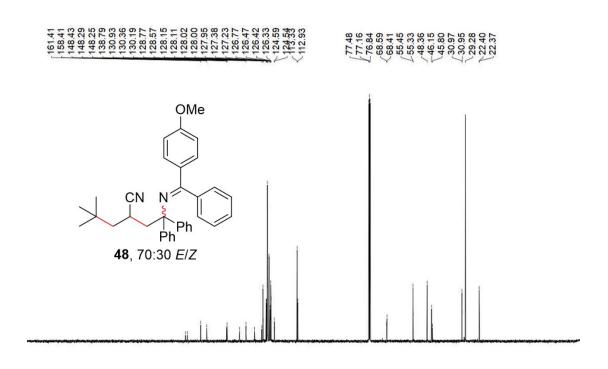


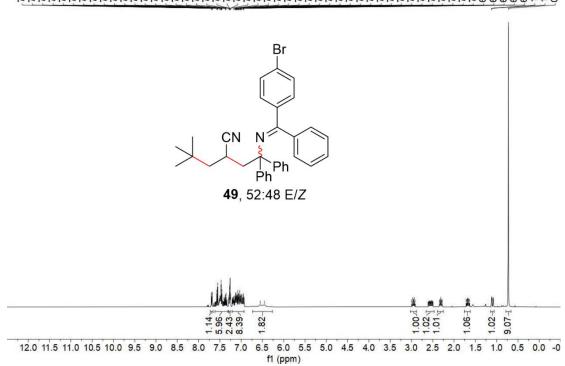


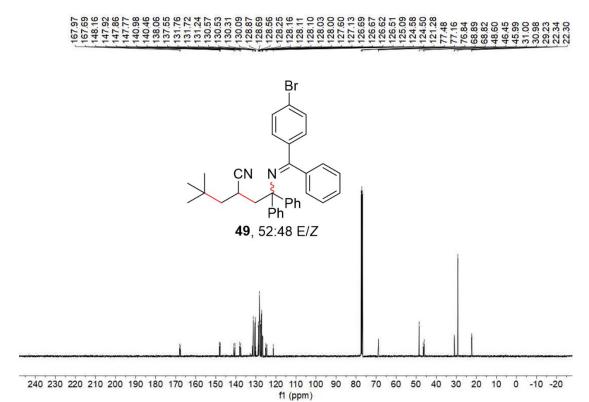


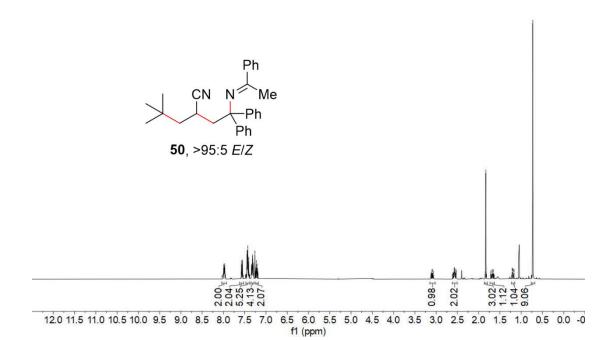




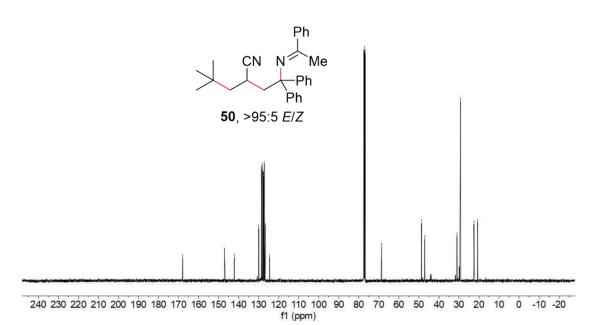


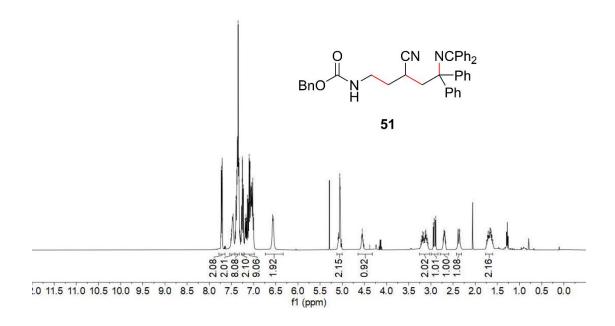


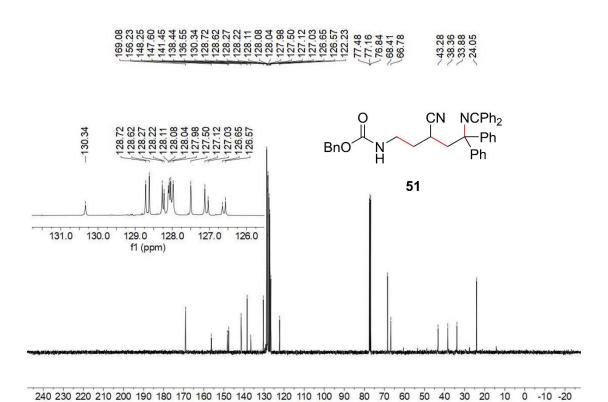


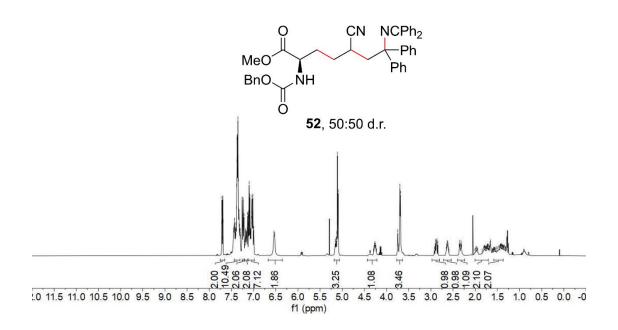




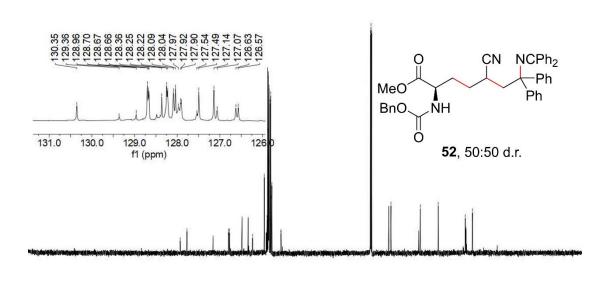


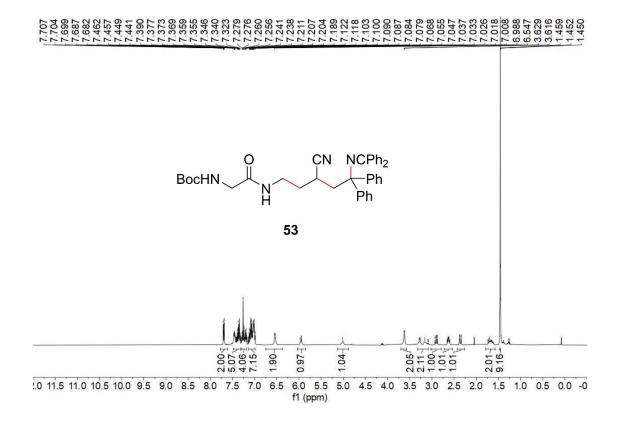


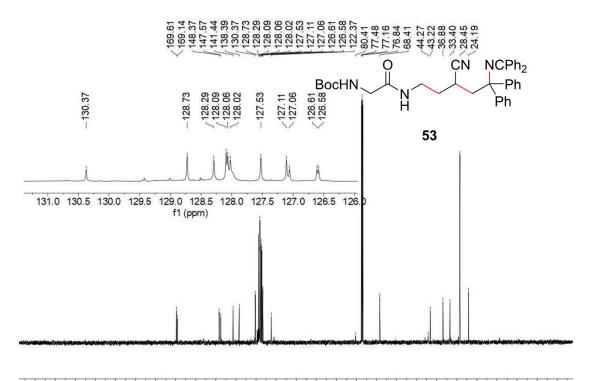


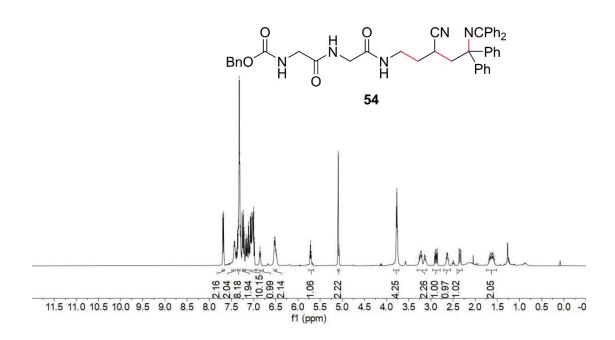


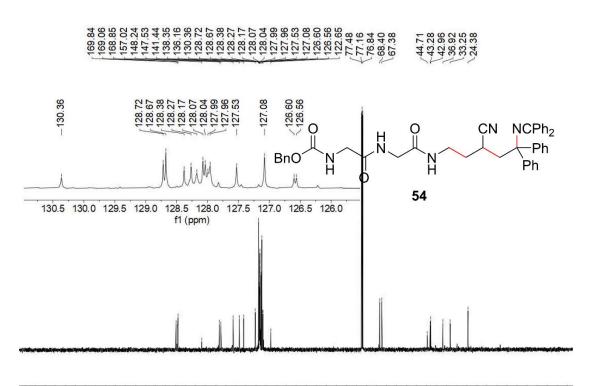


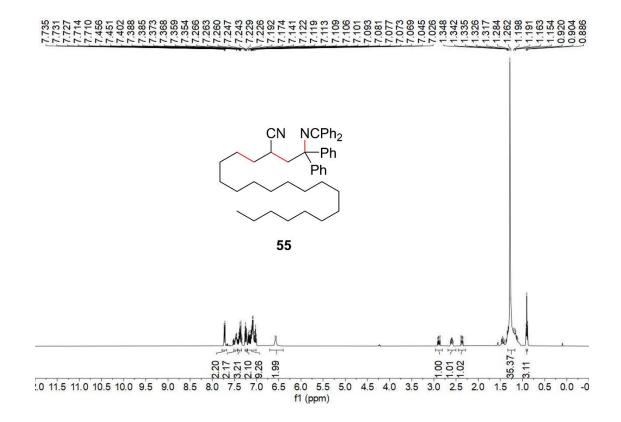


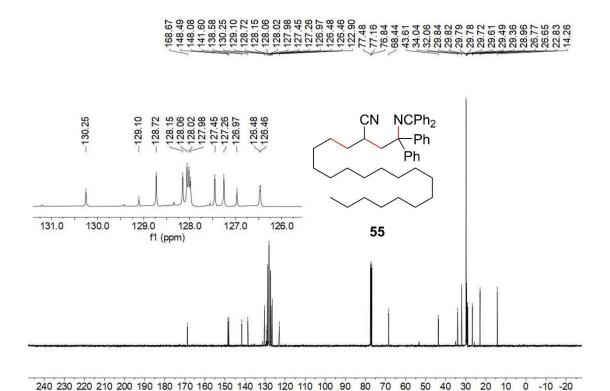


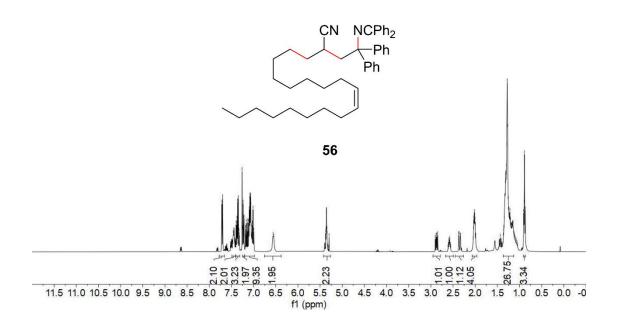


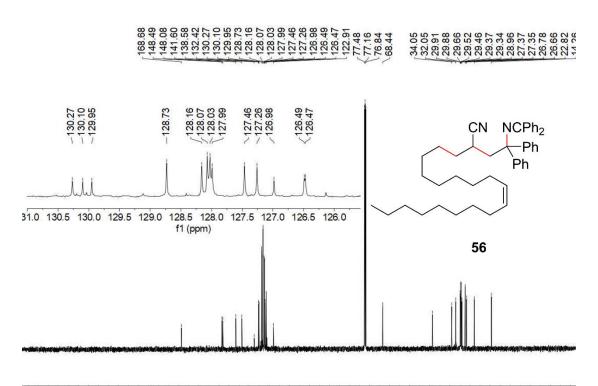


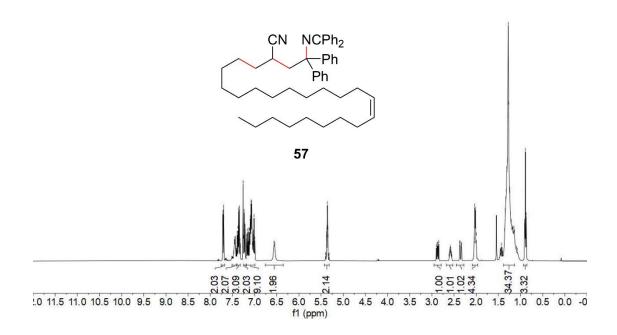


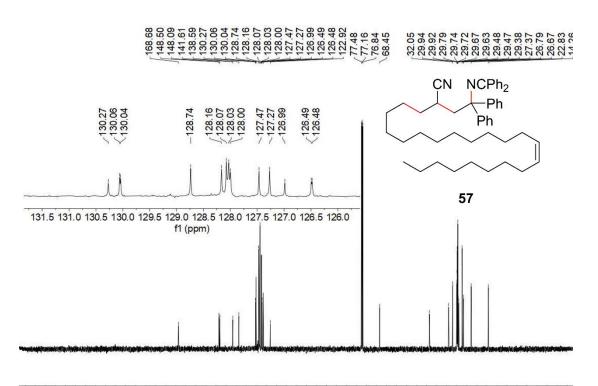


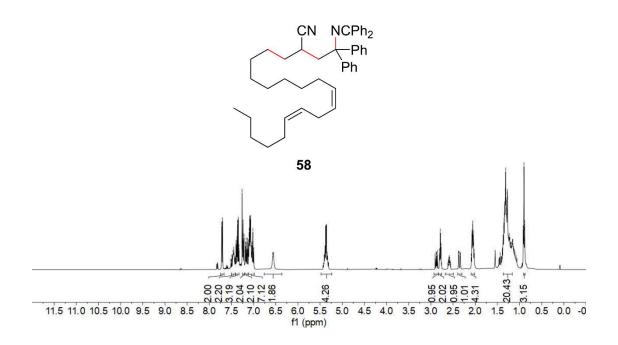


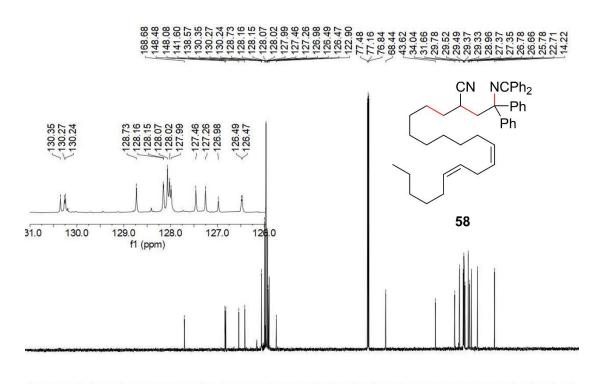


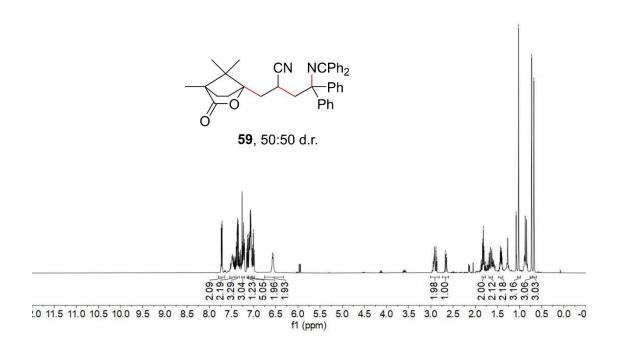


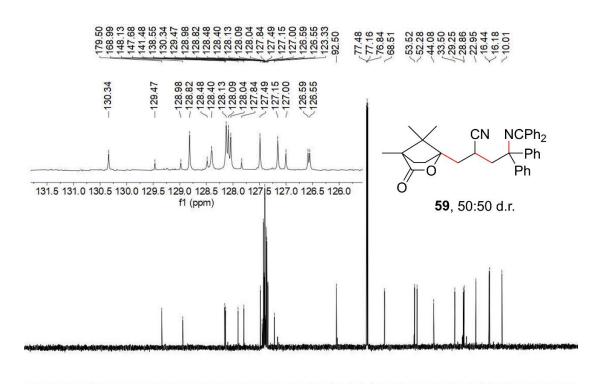


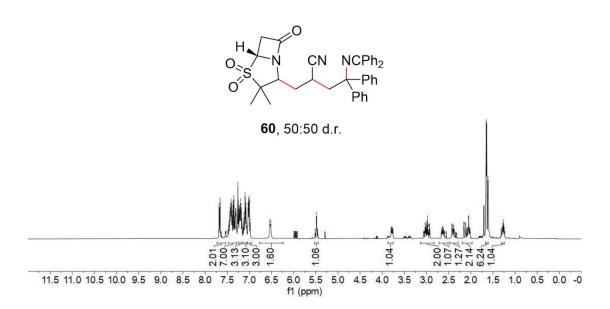




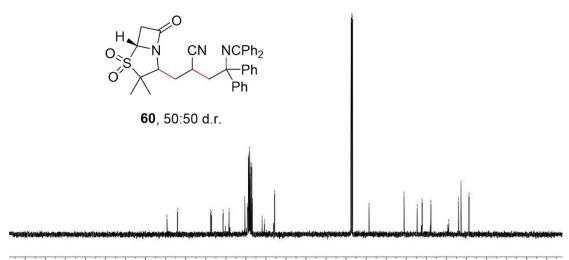


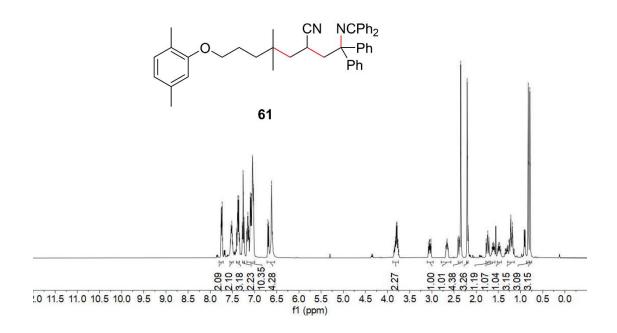


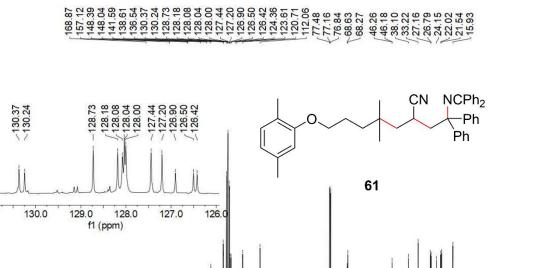


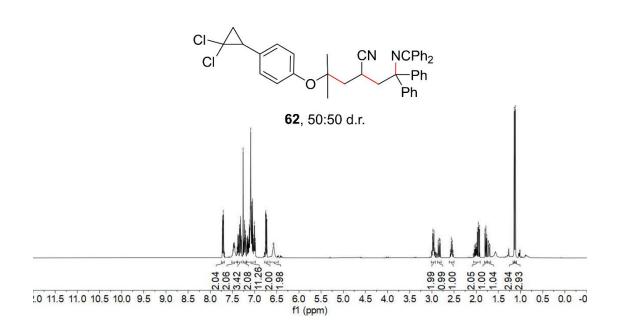


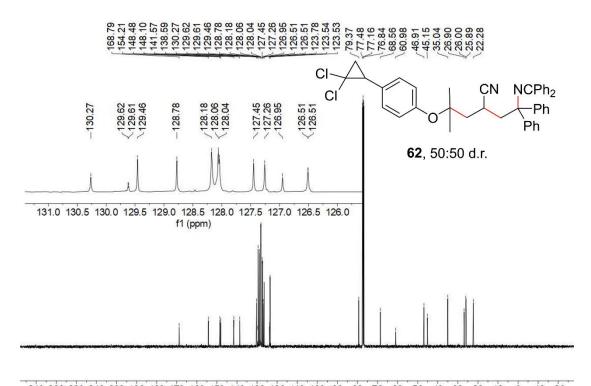


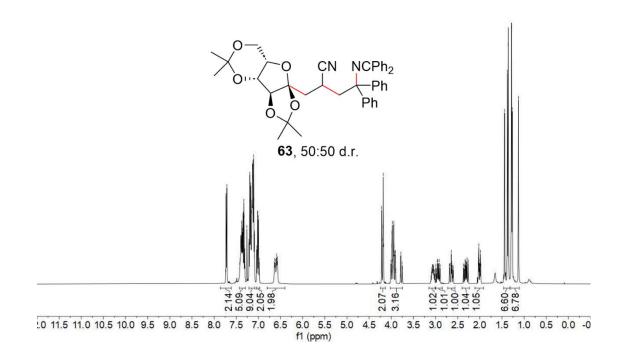


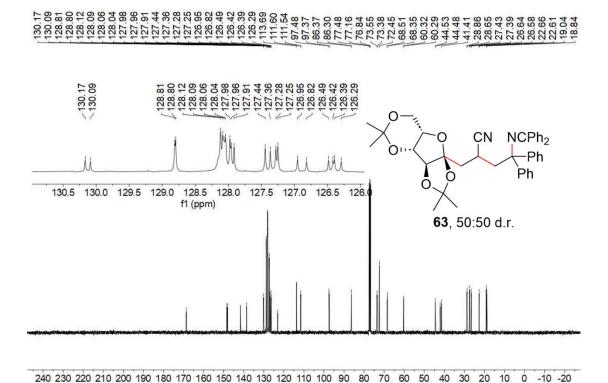


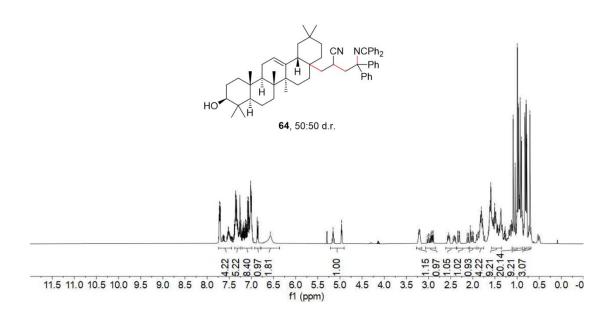


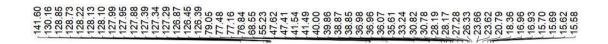


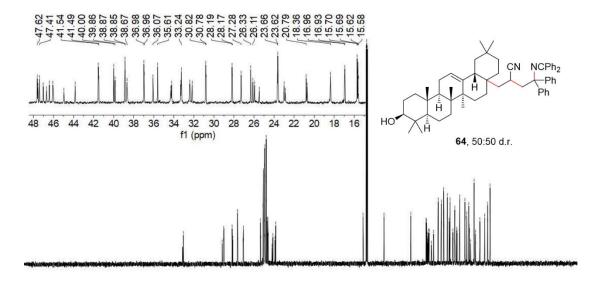


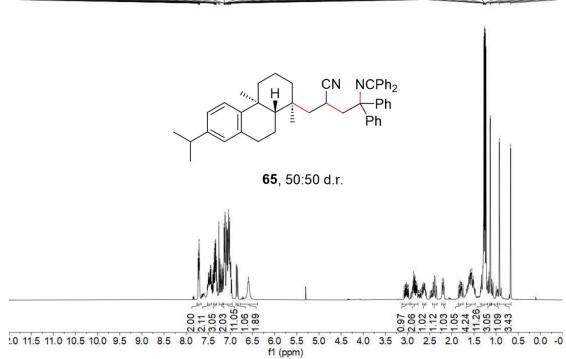




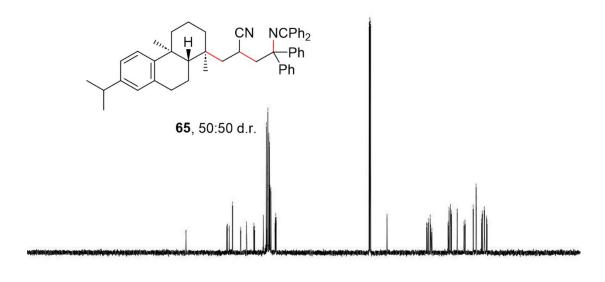


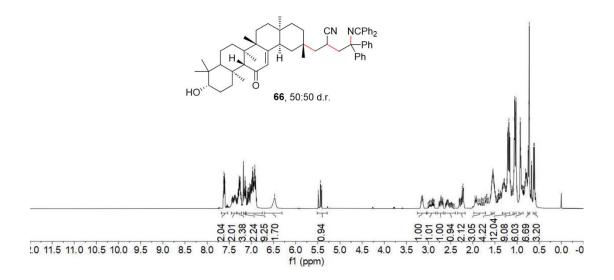


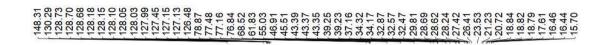


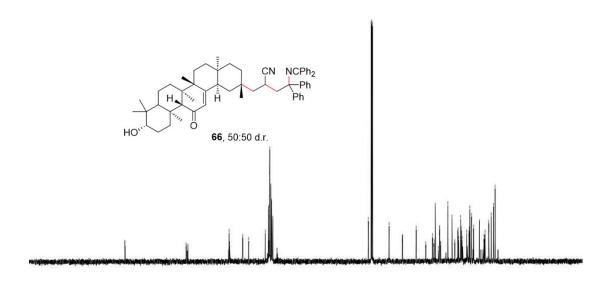


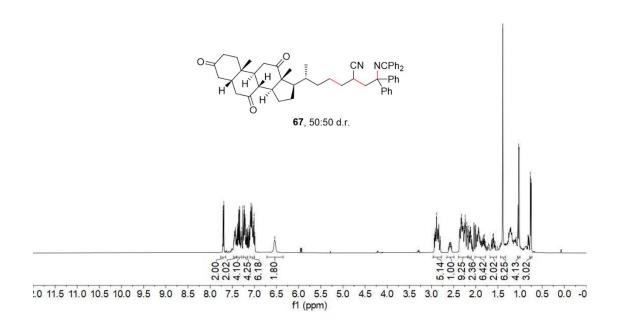
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212.05 208.30 208.30 208.30 208.30 208.30 208.30 20.30

