

**Trifluoromethylation of α -Diazoesters and α -Diazoketones
with Fluoroform-Derived CuCF_3 : Synergistic Effects of Co-solvent and Pyridine as a Promoter**
Qiao Ma and Gavin Chit Tsui*

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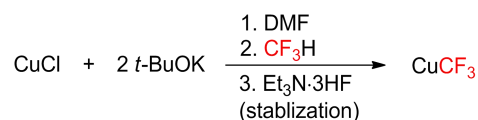
General Experimental. Reactions were monitored using thin-layer chromatography (TLC) on EM Science silica gel 60 F254 plates. Visualization of the developed plates was performed under UV light (254 nm) and/or with KMnO_4 or PMA stain followed by heating. Organic solvents were evaporated by rotary evaporation at 23–40 °C. Reaction products were purified by silica gel flash column chromatography using Grace Materials Technologies 230–400 mesh silica gel.

Materials. Fluoroform (Research Grade, Purity: 99.999% min., 9.1kg in 16 L size cylinder) was purchased from SynQuest Laboratories, USA. Copper(I) chloride (extra pure, 99.99%) was purchased from Acros. $\text{Et}_3\text{N}\cdot 3\text{HF}$ (97%) and Potassium *tert*-butoxide (97%) were purchased from Alfa Aesar. DMF from Solvent Purification System was further dried with 5 Å molecular sieves then bubbled with argon for 24 h. Other reagents and solvents were purchased from commercial sources and used as received. α -Diazoesters **1**¹ and ketones^{2,3} (for the synthesis of α -diazoketones **3**) were prepared according to literature procedures.

Instrumentation. Proton nuclear magnetic resonance (^1H NMR) spectra, carbon nuclear magnetic resonance (^{13}C NMR) spectra and fluorine nuclear magnetic resonance (^{19}F NMR) spectra were recorded at 23 °C on a Bruker 400 or 500 MHz NMR spectrometer. Chemical shifts of ^1H NMR spectra were reported using either residual solvent signal of CDCl_3 ($\delta = 7.26$ ppm) or TMS ($\delta = 0.00$ ppm) as internal standard. Chemical shifts of ^{13}C NMR spectra were reported using residual solvent signal of CDCl_3 ($\delta = 77.16$ ppm) as internal standard. Chemical shifts of ^{19}F NMR spectra were reported using benzotrifluoride ($\delta = -63.72$ ppm) as internal standard. Data are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), coupling constant (*J*, Hz), and integration. High resolution mass spectra (HRMS) were recorded on a Thermo Scientific Q Exactive Focus Mass Spectrometer.

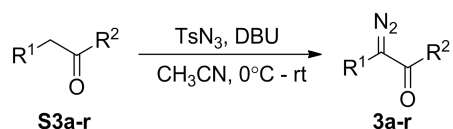
Experimental Procedures.

Procedure for the preparation of fluoroform-derived CuCF_3 reagent:⁴



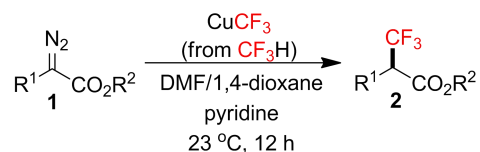
In a glove box, to a test tube (16*100 mm) was added CuCl (297.0 mg, 3.0 mmol), *t*-BuOK (673.3 mg, 6.0 mmol) and a stirrer bar. The tube was sealed with a septum, brought out of the glove box and put under an argon atmosphere. Degassed DMF (6.0 mL) was added *via* syringe and the mixture was stirred at room temperature for 30 min under argon. Then fluoroform was quickly bubbled into the mixture by using a needle connected to the fluoroform cylinder at room temperature for 2-3 min. The mixture was stirred for 5 min and Et₃N·3HF (246 μL, 1.50 mmol) was added under argon and the mixture was stirred for another 5 min. A colorless/slightly brown solution with some white solid was obtained as the [CuCF₃] solution in DMF (~0.42 M). The yield of [CuCF₃] was generally >90% determined by ¹⁹F NMR analysis (DMF, unlocked) using benzotrifluoride as the internal standard.

General experimental procedure for the synthesis of α -diazoketones (**3a-r**):



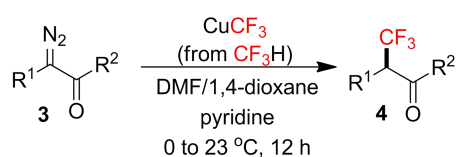
DBU (6.0 mmol) was added dropwise to a stirred solution of ketones **S3a-r** (5.0 mmol) and *p*-MeC₆H₄SO₂N₃ (6.0 mmol) in acetonitrile (50 mL) at 0 °C. The reaction was stirred at 0 °C for 1h and then at room temperature for 5 h. Sat. NaHCO₃/Et₂O (1:1 v/v, 50 mL) was then added and the layers were separated. The aq. layer was then extracted with Et₂O (2 x 25 mL) and the organic layers were combined. The organic layers were then dried over MgSO₄, filtered, and concentrated in vacuo. The crude residue was then purified by flash column chromatography quickly (SiO₂, hexanes/ethyl acetate = 15:1) to give pure α -diazoketones **3a-r**. α -Diazoketone **3s** was a known compound and prepared according to literature procedures.⁵

General procedure for trifluoromethylation of α -diazoesters (*cf.* Table 2):



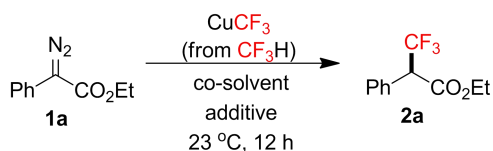
To a 25 mL flask equipped with a stir bar was added 1,4-dioxane (7 mL) and pyridine (100 μL, 1.25 mmol), the flask was sealed with a septum then charged with argon. CuCF₃ in DMF (3 mL, 1.25 mmol) was added via a syringe under argon followed by adding a solution of α -diazoesters **1** (0.5 mmol) in 1,4-dioxane (0.5 mL). The resulting mixture was stirred under argon for 12 h. The reaction mixture was extracted with DCM (3 × 20 mL), combined organic layer was washed with H₂O (2 × 20 mL), then brine (20 mL), dried over MgSO₄ and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel to afford α -trifluoromethyl esters **2**.

General procedure for trifluoromethylation of α -diazoketones (cf. Table 3):



To a 10 mL flask equipped with a stir bar was added 1,4-dioxane (4.5 mL), pyridine (36 μL , 0.45 mmol) and α -diazoketones **3** (0.3 mmol). The flask was sealed with a septum then charged with argon, after that the mixture was cooled to 0 $^\circ\text{C}$ with ice bath. CuCF_3 in DMF (1.1 mL, 0.45 mmol) was then added via a syringe under argon. The resulting mixture was kept stirring at 0 $^\circ\text{C}$ for \sim 3 h, then warmed up to room temperature naturally and stirred for another 9 h. The reaction mixture was extracted with DCM (3×10 mL), combined organic layers were washed with H_2O (2×10 mL), then brine (10 mL), dried over MgSO_4 and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel to afford α -trifluoromethyl ketones **4**.

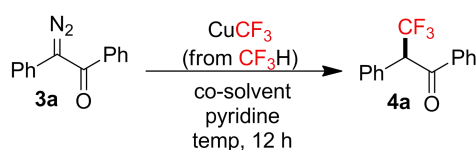
Table S1. Optimization studies for the trifluoromethylation of α -diazoester **1a (cf. Table 1).^a**



entry	co-solvent (mL)	additive (equiv)	yield (%) ^b
1	none	none	21
2 ^d	none	none	12
3	NMP	none	16
4	THF (0.6)	none	22
5	Et ₂ O (0.6)	none	22
6	toluene (0.6)	none	32
7	CH ₂ Cl ₂ (0.6)	none	32
8	CH ₃ CN (0.6)	none	52
9	CH ₃ CN (0.25)	none	42
10	CH ₃ CN (0.75)	none	56
11	CH₃CN (1.5)	none	66
12	CH ₃ CN (2.0)	none	67
13	toluene (1.5)	none	37
14	THF (1.5)	none	23
15	CH ₃ CN (1.5)	Et ₃ N (2.5)	55
16	CH ₃ CN (1.5)	TMEDA (2.5)	47
17	CH ₃ CN (1.5)	piperidine (2.5)	25
18	CH ₃ CN (1.5)	HTMP (2.5)	22
19	CH ₃ CN (1.5)	imidazole (2.5)	6
20	CH ₃ CN (1.5)	1,10-phenanthroline (2.5)	15
21	CH ₃ CN (1.5)	PPh ₃ (2.5)	6
22	CH ₃ CN (1.5)	K ₂ CO ₃ (2.5)	17

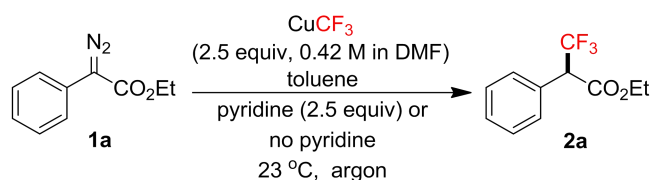
23	CH ₃ CN (1.5)	Na ₂ CO ₃ (2.5)	32
24	CH₃CN (1.5)	pyridine (2.5)	81
25	CH ₃ CN (1.5)	DMAP (2.5)	31
26	CH ₃ CN (1.5)	2-acetylpyridine (2.5)	60
27	CH ₃ CN (1.5)	3-acetylpyridine (2.5)	73
28	CH ₃ CN (1.5)	2-phenylpyridine (2.5)	56
29	CH ₃ CN (1.5)	4-methylpyridine (2.5)	81
30	toluene (1.5)	pyridine (2.5)	80
31	CH ₂ Cl ₂ (1.5)	pyridine (2.5)	69
32	THF (1.5)	pyridine (2.5)	76
33	Et ₂ O (1.5)	pyridine (2.5)	78
34	1,4-dioxane (1.5)	pyridine (2.5)	86, 83^e
35 ^e	none	pyridine (2.5)	24
36	1,4-dioxane (1.5)	pyridine (1.25)	60
37	1,4-dioxane (1.5)	pyridine (5.0)	86
38	1,4-dioxane (1.5)	none	37
39 ^f	1,4-dioxane (1.5)	pyridine (2.5)	62
40 ^g	1,4-dioxane (1.5)	pyridine (2.5)	64
41 ^h	1,4-dioxane (1.5)	pyridine (2.5)	62
42 ⁱ	1,4-dioxane (1.5)	none	19
43 ^j	1,4-dioxane (1.5)	pyridine (2.5)	0
44	pyridine (1.5)	none	3

^aUnless specified otherwise, reactions were carried out using **1a** (0.1 mmol), CuCF₃ (0.42 M in DMF solution, 0.6 mL, 2.5 equiv, prepared from CuCl/*t*-BuOK/CF₃H and stabilized with Et₃N·3HF), under argon. ^bYield was determined by ¹⁹F NMR analysis using benzotrifluoride as the internal standard. ^cIsolated yield. ^dAdded 0.6 mL DMF. ^eAdded 1.5 mL DMF. ^fAt 50 °C. ^gUsing 1.5 equiv of CuCF₃. ^hUsing 3.5 equiv of CuCF₃. ⁱCuCF₃ was stabilized with HF-pyridine (Olah's reagent). ^jReaction was open to air.

Table S2. Optimization studies for the trifluoromethylation of α -diazoketone 3a.^a

entry	equiv of CuCF ₃	co-solvent (mL)	equiv of pyridine	temp (°C)	yield (%) ^b
1	2.5	1,4-dioxane (1.5)	2.5	23	60
2	2.5	CH ₃ CN (1.5)	2.5	23	56
3 ^d	2.5	none	2.5	23	30
4	2.5	1,4-dioxane (0.75)	2.5	23	55
5	2.5	1,4-dioxane (2.25)	2.5	23	61
6	2.5	1,4-dioxane (1.5)	2.5	50	42
7	2.5	1,4-dioxane (1.5)	2.5	0 to 23	72
8	1.5	1,4-dioxane (1.5)	2.5	0 to 23	80
9	3.0	1,4-dioxane (1.5)	2.5	0 to 23	71
10	1.5	1,4-dioxane (1.5)	1.5	0 to 23	82, 80^c
11	1.5	1,4-dioxane (1.5)	0	0 to 23	60

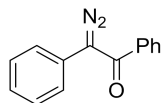
^aUnless specified otherwise, reactions were carried out using **3a** (0.1 mmol), CuCF₃ (0.42 M in DMF solution, prepared from CuCl/*t*-BuOK/CF₃H and stabilized with Et₃N·3HF), under argon. ^bYield was determined by ¹⁹F NMR analysis using benzotrifluoride as the internal standard. ^cIsolated yield. ^dAdded 1.5 mL DMF.

Table S3. Data for Figure 1.

time (min)	¹⁹ F NMR yield of 2a with pyridine (%)	¹⁹ F NMR yield of 2a without pyridine (%)	molar ratio of CuCF ₃ without pyridine	molar ratio of CuCF ₃ with pyridine
5	10	2	1.0	1.0
14	19	5	0.71	0.63
24	27	9	0.65	0.50
37	40	13	0.60	0.41
63	53	20	0.55	0.30
101	66	28	0.48	0.21
163	72	35	0.42	0.12

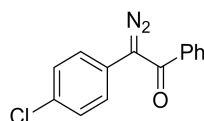
Characterization data of substrates

2-diazo-1,2-diphenylethanone (**3a**)



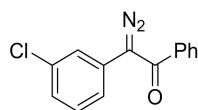
Following the general procedure, ketone **S3a** (1.0 g, 5.1 mmol) was converted to **3a** as a red solid (627 mg, 55% yield), $R_f = 0.44$ (hexanes/ethyl acetate = 5:1). $^1\text{H NMR}$ (400 MHz, CDCl_3): δ (ppm) 7.62 (d, $J = 8.0$ Hz, 2H), 7.53 – 7.39 (m, 7H), 7.28 – 7.26 (m, 1H). The spectral data are in full accordance with the literature report.⁶

2-(4-chlorophenyl)-2-diazo-1-phenylethanone (**3b**)



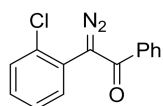
Following the general procedure, ketone **S3b** (461 mg, 2.0 mmol) was converted to **3b** as a red solid (430 mg, 84% yield), $R_f = 0.46$ (hexanes/ethyl acetate = 5:1). $^1\text{H NMR}$ (400 MHz, CDCl_3): δ (ppm) 7.62 – 7.60 (m, 2H), 7.52 (t, $J = 7.4$ Hz, 1H), 7.46 – 7.37 (m, 6H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3): δ (ppm) 188.3, 137.8, 132.8, 132.0, 129.4, 128.8, 127.8, 127.1, 124.8. **HRMS** m/z (APCI) calcd. for $\text{C}_{14}\text{H}_9\text{ClN}_2\text{O}$ $[\text{M}-\text{N}_2+\text{H}]^+$: 229.04147; found: 229.04233.

2-(3-chlorophenyl)-2-diazo-1-phenylethanone (**3c**)



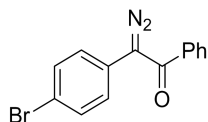
Following the general procedure, ketone **S3c** (461 mg, 2.0 mmol) was converted to **3c** as a yellow solid (450 mg, 88% yield), $R_f = 0.37$ (hexanes/ethyl acetate = 5:1). $^1\text{H NMR}$ (500 MHz, CDCl_3): δ (ppm) 7.63 – 7.61 (m, 2H), 7.56 (t, $J = 1.7$ Hz, 1H), 7.53 (t, $J = 7.3$ Hz, 1H), 7.45 (t, $J = 7.7$ Hz, 2H), 7.38 – 7.36 (m, 1H), 7.33 (t, $J = 7.8$ Hz, 1H), 7.23 (dt, $J = 7.8, 1.5$ Hz, 1H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3): δ (ppm) 188.1, 137.8, 135.2, 132.1, 130.3, 128.8, 128.3, 127.7, 127.1, 125.6, 123.8. **HRMS** m/z (APCI) calcd. for $\text{C}_{14}\text{H}_9\text{ClN}_2\text{O}$ $[\text{M}-\text{N}_2+\text{H}]^+$: 229.04147; found: 229.04219.

2-(2-chlorophenyl)-2-diazo-1-phenylethanone (**3d**)



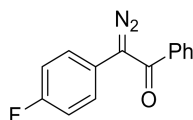
Following the general procedure, ketone **S3d** (461 mg, 2.0 mmol) was converted to **3d** as a yellow solid (370 mg, 72% yield), $R_f = 0.34$ (hexanes/ethyl acetate = 5:1). $^1\text{H NMR}$ (500 MHz, CDCl_3): δ (ppm) 7.52 – 7.43 (m, 4H), 7.36 – 7.24 (m, 5H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3): δ (ppm) 195.4, 138.8, 136.6, 133.9, 131.3, 130.20, 130.19, 129.3, 128.8, 126.8, 121.8. **HRMS** m/z (APCI) calcd. for $\text{C}_{14}\text{H}_9\text{ClN}_2\text{O}$ $[\text{M}-\text{N}_2+\text{H}]^+$: 229.04147; found: 229.04194.

2-(4-bromophenyl)-2-diazo-1-phenylethanone (**3e**)



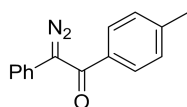
Following the general procedure, ketone **S3e** (550 mg, 2.0 mmol) was converted to **3e** as a yellow solid (480 mg, 80% yield), $R_f = 0.56$ (hexanes/ethyl acetate = 5:1). **¹H NMR** (500 MHz, CDCl₃): δ (ppm) 7.62 – 7.60 (m, 2H), 7.54 – 7.51 (m, 3H), 7.44 (t, $J = 7.8$ Hz, 2H), 7.38 (d, $J = 8.6$ Hz, 2H). **¹³C NMR** (126 MHz, CDCl₃): δ (ppm) 188.3, 137.8, 132.3, 132.1, 128.8, 127.8, 127.4, 125.4, 120.8. **HRMS** m/z (APCI) calcd. for C₁₄H₉BrN₂O [M-N₂+H]⁺: 272.99272; found: 272.99177.

2-diazo-2-(4-fluorophenyl)-1-phenylethanone (**3f**)



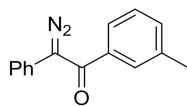
Following the general procedure, ketone **S3f** (428 mg, 2.0 mmol) was converted to **3f** as a yellow solid (140 mg, 30% yield), $R_f = 0.46$ (hexanes/ethyl acetate = 5:1). **¹H NMR** (500 MHz, CDCl₃): δ (ppm) 7.62 – 7.60 (m, 2H), 7.54 – 7.51 (m, 3H), 7.44 (t, $J = 7.8$ Hz, 2H), 7.38 (d, $J = 8.6$ Hz, 2H). **¹³C NMR** (126 MHz, CDCl₃): δ (ppm) 188.2, 137.8, 132.3, 132.1, 128.8, 127.8, 127.4, 125.4, 120.8. **HRMS** m/z (APCI) calcd. for C₁₄H₉FN₂O [M-N₂+H]⁺: 213.07102; found: 213.07144.

2-diazo-2-phenyl-1-(*p*-tolyl)ethenone (**3g**)



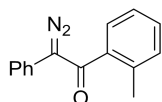
Following the general procedure, ketone **S3g** (210 mg, 1.0 mmol) was converted to **3g** as a red solid (126 mg, 53% yield), $R_f = 0.54$ (hexanes/ethyl acetate = 5:1). **¹H NMR** (500 MHz, CDCl₃): δ (ppm) 7.52 (d, $J = 8.1$ Hz, 2H), 7.47 (d, $J = 7.5$ Hz, 2H), 7.40 (t, $J = 7.5$ Hz, 2H), 7.27 – 7.24 (m, 1H), 7.21 (d, $J = 8.0$ Hz, 2H), 2.40 (s, 3H). **¹³C NMR** (126 MHz, CDCl₃): δ (ppm) 188.4, 142.5, 135.4, 129.3, 129.2, 128.0, 127.0, 126.5, 126.2, 21.7. **HRMS** m/z (APCI) calcd. for C₁₅H₁₂N₂O [M-N₂+H]⁺: 209.09609; found: 209.09627.

2-diazo-2-phenyl-1-(*m*-tolyl)ethenone (**3h**)



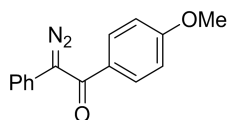
Following the general procedure, ketone **S3h** (210 mg, 1.0 mmol) was converted to **3h** as a red oil (113 mg, 48% yield), $R_f = 0.58$ (hexanes/ethyl acetate = 5:1). **¹H NMR** (500 MHz, CDCl₃): δ (ppm) 7.49 (d, $J = 7.5$ Hz, 2H), 7.45 (s, 1H), 7.42 – 7.38 (m, 3H), 7.31 – 7.27 (m, 2H), 7.18 – 7.16 (m, 1H), 2.38 (s, 3H). **¹³C NMR** (126 MHz, CDCl₃): δ (ppm) 188.8, 138.7, 138.1, 132.6, 129.2, 128.5, 128.4, 127.1, 126.3, 126.1, 124.9, 21.5. **HRMS** m/z (APCI) calcd. for C₁₅H₁₂N₂O [M-N₂+H]⁺: 209.09609; found: 209.09628.

2-diazo-2-phenyl-1-(*o*-tolyl)ethanone (**3i**)



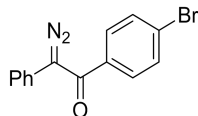
Following the general procedure, ketone **S3i** (210 mg, 1.0 mmol) was converted to **3i** as a red oil (65 mg, 28% yield), $R_f = 0.58$ (hexanes/ethyl acetate = 5:1). $^1\text{H NMR}$ (400 MHz, CDCl_3): δ (ppm) 7.53 (d, $J = 7.7$ Hz, 2H), 7.41 (t, $J = 7.6$ Hz, 2H), 7.36 – 7.33 (m, 2H), 7.25 – 7.21 (m, 3H), 2.41 (s, 3H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3): δ (ppm) 190.4, 138.4, 135.6, 131.2, 130.4, 129.2, 127.0, 126.7, 126.0, 125.7, 125.4, 19.2. **HRMS** m/z (APCI) calcd. for $\text{C}_{15}\text{H}_{12}\text{N}_2\text{O}$ $[\text{M}-\text{N}_2+\text{H}]^+$: 209.09609; found: 209.09648.

2-diazo-1-(4-methoxyphenyl)-2-phenylethanone (**3j**)



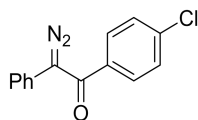
Following the general procedure, ketone **S3j** (226 mg, 1.0 mmol) was converted to **3j** as a yellow solid (88 mg, 35% yield), $R_f = 0.56$ (hexanes/ethyl acetate = 5:1). $^1\text{H NMR}$ (400 MHz, CDCl_3): δ (ppm) 7.61 (d, $J = 8.7$ Hz, 2H), 7.45 – 7.38 (m, 4H), 7.27 – 7.26 (m, 1H), 6.90 (d, $J = 8.8$ Hz, 2H), 3.85 (s, 3H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3): δ (ppm) 187.5, 162.6, 130.6, 130.2, 129.2, 127.0, 126.7, 126.3, 113.8, 55.6. **HRMS** m/z (APCI) calcd. for $\text{C}_{15}\text{H}_{12}\text{N}_2\text{O}_2$ $[\text{M}-\text{N}_2+\text{H}]^+$: 225.09101; found: 225.09116.

1-(4-bromophenyl)-2-diazo-2-phenylethanone (**3k**)



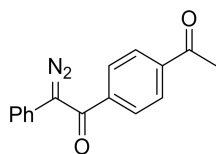
Following the general procedure, ketone **S3k** (275 mg, 1.0 mmol) was converted to **3k** as a red solid (90 mg, 30% yield), $R_f = 0.59$ (hexanes/ethyl acetate = 5:1). $^1\text{H NMR}$ (400 MHz, CDCl_3): δ (ppm) 7.55 (d, $J = 8.3$ Hz, 2H), 7.47 (d, $J = 8.4$ Hz, 2H), 7.42 – 7.38 (m, 4H), 7.30 – 7.27 (m, 1H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3): δ (ppm) 188.6, 138.1, 131.9, 129.3, 129.2, 128.7, 127.9, 127.2, 126.2. **HRMS** m/z (APCI) calcd. for $\text{C}_{14}\text{H}_9\text{BrN}_2\text{O}$ $[\text{M}-\text{N}_2+\text{H}]^+$: 272.99095; found: 272.99121.

1-(4-chlorophenyl)-2-diazo-2-phenylethanone (**3l**)



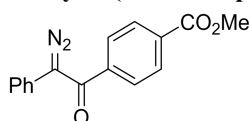
Following the general procedure, ketone **S3l** (1.3 g, 5.6 mmol) was converted to **3l** as a red solid (300 mg, 21% yield), $R_f = 0.57$ (hexanes/ethyl acetate = 5:1). $^1\text{H NMR}$ (500 MHz, CDCl_3): δ (ppm) 7.55 (d, $J = 8.5$ Hz, 2H), 7.42 – 7.37 (m, 6H), 7.30 – 7.26 (m, 1H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3): δ (ppm) 187.1, 138.1, 136.3, 129.5, 129.3, 128.9, 127.4, 126.5, 126.0. **HRMS** m/z (APCI) calcd. for $\text{C}_{14}\text{H}_9\text{ClN}_2\text{O}$ $[\text{M}-\text{N}_2+\text{H}]^+$: 229.04147; found: 229.04173.

1-(4-acetylphenyl)-2-diazo-2-phenylethanone (**3m**)



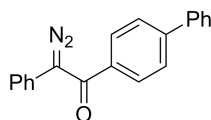
Following the general procedure, ketone **S3m** (1.17 g, 4.91 mmol) was converted to **3m** as a red solid (400 mg, 31% yield), $R_f = 0.27$ (hexanes/ethyl acetate = 5:1). **¹H NMR** (500 MHz, CDCl₃): δ (ppm) 7.99 (d, $J = 8.2$ Hz, 2H), 7.68 (d, $J = 8.2$ Hz, 2H), 7.45 – 7.39 (m, 4H), 7.32 – 7.27 (m, 1H), 2.63 (s, 3H). **¹³C NMR** (126 MHz, CDCl₃): δ (ppm) 197.5, 187.5, 141.8, 139.3, 129.3, 128.6, 128.2, 127.5, 126.5, 125.7, 26.9. **HRMS** m/z (APCI) calcd. for C₁₆H₁₂N₂O₂ [M-N₂+H]⁺: 237.09101; found: 237.09122.

methyl 4-(2-diazo-2-phenylacetyl)benzoate (**3n**)



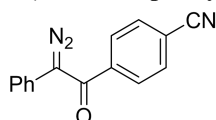
Following the general procedure, ketone **S3n** (1.4 g, 5.5 mmol) was converted to **3n** as a yellow solid (863 mg, 56% yield), $R_f = 0.60$ (hexanes/ethyl acetate = 5:1). **¹H NMR** (500 MHz, CDCl₃): δ (ppm) 8.08 (d, $J = 8.0$ Hz, 2H), 7.66 (d, $J = 8.0$ Hz, 2H), 7.44 – 7.39 (m, 4H), 7.31 – 7.26 (m, 1H), 3.94 (s, 3H). **¹³C NMR** (126 MHz, CDCl₃): δ (ppm) 187.7, 166.3, 141.8, 132.9, 129.9, 129.3, 127.9, 127.5, 126.4, 125.8, 52.6. **HRMS** m/z (APCI) calcd. for C₁₆H₁₂N₂O₃ [M-N₂+H]⁺: 253.08592; found: 253.08597.

1-([1,1'-biphenyl]-4-yl)-2-diazo-2-phenylethanone (**3o**)



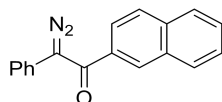
Following the general procedure, ketone **S3o** (200 mg, 0.73 mmol) was converted to **3o** as a yellow solid (103 mg, 47% yield), $R_f = 0.38$ (hexanes/ethyl acetate = 5:1). **¹H NMR** (500 MHz, CDCl₃): δ (ppm) 7.70 (d, $J = 8.4$ Hz, 2H), 7.65 – 7.61 (m, 4H), 7.51 – 7.38 (m, 7H), 7.28 (t, $J = 7.4$ Hz, 1H). **¹³C NMR** (126 MHz, CDCl₃): δ (ppm) 188.1, 144.7, 140.0, 136.8, 129.2, 129.1, 128.6, 128.3, 127.4, 127.3, 127.2, 126.34, 126.33. **HRMS** m/z (APCI) calcd. for C₂₀H₁₄N₂O [M-N₂+H]⁺: 271.11174; found: 271.11184.

4-(2-diazo-2-phenylacetyl)benzotrile (**3p**)



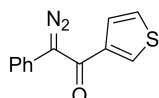
Following the general procedure, ketone **S3p** (180 mg, 0.81 mmol) was converted to **3p** as a yellow solid (125 mg, 62% yield), $R_f = 0.51$ (hexanes/ethyl acetate = 5:1). **¹H NMR** (500 MHz, CDCl₃): δ (ppm) 7.69 (q, $J = 8.2$ Hz, 4H), 7.44 – 7.38 (m, 4H), 7.32 – 7.29 (m, 1H). **¹³C NMR** (126 MHz, CDCl₃): δ (ppm) 186.5, 141.6, 132.5, 129.4, 128.6, 127.9, 126.8, 125.4, 118.0, 115.3. **HRMS** m/z (APCI) calcd. for C₁₅H₉N₃O [M-N₂+H]⁺: 220.07569; found: 220.07591.

2-diazo-1-(naphthalen-2-yl)-2-phenylethanone (**3q**)



Following the general procedure, ketone **S3q** (427 mg, 1.73 mmol) was converted to **3q** as a red solid (310 mg, 66% yield), $R_f = 0.44$ (hexanes/ethyl acetate = 5:1). **¹H NMR** (400 MHz, CDCl₃): δ (ppm) 8.14 (s, 1H), 7.88 (d, $J = 8.4$ Hz, 3H), 7.68 (dd, $J = 8.6, 1.7$ Hz, 1H), 7.61 – 7.54 (m, 2H), 7.52 – 7.49 (m, 2H), 7.42 (t, $J = 7.6$ Hz, 2H), 7.28 (t, $J = 7.3$ Hz, 1H). **¹³C NMR** (126 MHz, CDCl₃): δ (ppm) 188.4, 135.4, 134.9, 132.6, 129.23, 129.19, 128.61, 128.60, 128.1, 128.0, 127.2, 127.0, 126.4, 126.3, 124.5. **HRMS** m/z (APCI) calcd. for C₁₈H₁₂N₂O [M-N₂+H]⁺: 245.09609; found: 245.09621.

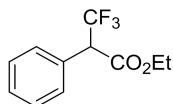
2-diazo-2-phenyl-1-(thiophen-3-yl)ethanone (**3r**)



Following the general procedure, ketone **S3r** (648 mg, 3.2 mmol) was converted to **3r** as a red oil (306 mg, 42% yield), $R_f = 0.34$ (hexanes/ethyl acetate = 5:1). **¹H NMR** (500 MHz, CDCl₃): δ (ppm) 7.70 (dd, $J = 2.9, 1.3$ Hz, 1H), 7.50 – 7.48 (m, 2H), 7.43 (t, $J = 7.5$ Hz, 2H), 7.34 – 7.29 (m, 3H). **¹³C NMR** (126 MHz, CDCl₃): δ (ppm) 181.7, 140.4, 130.1, 129.3, 127.6, 127.5, 127.0, 126.2, 126.1. **HRMS** m/z (APCI) calcd. for C₁₂H₈N₂OS [M-N₂+H]⁺: 201.03686; found: 201.03707.

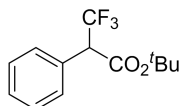
Characterization data of products

ethyl 3,3,3-trifluoro-2-phenylpropanoate (**2a**)



Following the general procedure, reaction was run using α -diazoester **1a** (190 mg, 1.0 mmol), pyridine (200 μ L, 2.5 mmol), 1,4-dioxane (15 mL) and CuCF₃ in DMF (6 mL, 2.5 mmol). The product was purified by flash column chromatography on silica gel (hexane/dichloromethane = 15:1) and obtained as a light green oil (197 mg, 85% yield), $R_f = 0.7$ (hexane/dichloromethane = 5:1). **¹H NMR** (400 MHz, CDCl₃): δ (ppm) 7.46 – 7.38 (m, 5H), 4.34 – 4.15 (m, 3H), 1.25 (t, $J = 7.1$ Hz, 3H). **¹³C NMR** (126 MHz, CDCl₃): δ (ppm) 166.2 (q, $J_{CF} = 2.8$ Hz), 129.61, 129.60, 129.3, 129.0, 123.9 (q, $J_{CF} = 279.5$ Hz), 62.2, 55.6 (q, $J_{CF} = 28.9$ Hz), 13.9. **¹⁹F NMR** (471 MHz, CDCl₃): δ (ppm) -68.7 (d, $J = 8.6$ Hz, 3F). The spectral data are in full accordance with the literature report.^{1a}

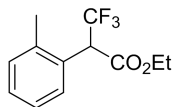
tert-butyl 3,3,3-trifluoro-2-phenylpropanoate (**2b**)



Following the general procedure, reaction was run using α -diazoester **1b** (109 mg, 0.5 mmol), pyridine (100 μ L, 1.25 mmol), 1,4-dioxane (7.5 mL) and CuCF₃ in DMF (3 mL, 1.25 mmol). The product was purified by flash column chromatography on silica gel (hexane/dichloromethane = 15:1) and obtained as a colorless oil (120 mg, 92% yield), $R_f = 0.71$ (hexane/dichloromethane = 2:1). **¹H NMR** (400 MHz,

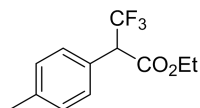
CDCl₃): δ (ppm) 7.44 – 7.38 (m, 5H), 4.21 (q, J = 8.7 Hz, 1H), 1.45 (s, 9H). ¹³C NMR (126 MHz, CDCl₃): δ (ppm) 165.3 (q, J_{CF} = 2.7 Hz), 130.0 (q, J_{CF} = 1.8 Hz), 129.5, 129.1, 128.9, 124.0 (q, J_{CF} = 279.6 Hz), 83.2, 56.6 (q, J_{CF} = 28.5 Hz), 27.9. ¹⁹F NMR (471 MHz, CDCl₃): δ (ppm) -68.6 (d, J = 8.7 Hz, 3F). HRMS m/z (ESI) calcd. for C₁₃H₁₅F₃O₂ [M+Na]⁺: 283.09164; found: 283.09155.

ethyl 3,3,3-trifluoro-2-(*o*-tolyl)propanoate (2c)



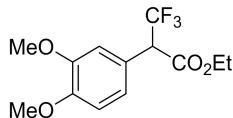
Following the general procedure, reaction was run using α -diazoester **1c** (102 mg, 0.5 mmol), pyridine (100 μ L, 1.25 mmol), 1,4-dioxane (7.5 mL) and CuCF₃ in DMF (3 mL, 1.25 mmol). The product was purified by flash column chromatography on silica gel (hexane/dichloromethane = 15:1) and obtained as a colorless oil (107 mg, 87% yield), R_f = 0.64 (hexane/dichloromethane = 2:1). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.53 (d, J = 7.7 Hz, 1H), 7.30 – 7.21 (m, 3H), 4.64 (q, J = 8.5 Hz, 1H), 4.29 – 4.13 (m, 2H), 2.43 (s, 3H), 1.24 (t, J = 7.2 Hz, 3H). ¹³C NMR (126 MHz, CDCl₃): δ (ppm) 166.7 (q, J_{CF} = 2.9 Hz), 137.5, 131.1, 129.2, 128.5, 128.4 (q, J_{CF} = 1.4 Hz), 126.7, 124.2 (q, J_{CF} = 279.7 Hz), 62.1, 50.7 (q, J_{CF} = 28.7 Hz), 20.0, 14.1. ¹⁹F NMR (471 MHz, CDCl₃): δ (ppm) -68.2 (d, J = 8.5 Hz, 3F). The spectral data are in full accordance with the literature report.^{1a}

ethyl 3,3,3-trifluoro-2-(*p*-tolyl)propanoate (2d)



Following the general procedure, reaction was run using α -diazoester **1d** (102 mg, 0.5 mmol), pyridine (100 μ L, 1.25 mmol), 1,4-dioxane (7.5 mL) and CuCF₃ in DMF (3 mL, 1.25 mmol). The product was purified by flash column chromatography on silica gel (hexane/dichloromethane = 15:1) and obtained as a yellow oil (108 mg, 88% yield), R_f = 0.4 (hexane/dichloromethane = 2:1). ¹H NMR (500 MHz, CDCl₃): δ (ppm) 7.32 (d, J = 7.9 Hz, 2H), 7.20 (d, J = 8 Hz, 2H), 4.29 – 4.15 (m, 3H), 2.36 (s, 3H), 1.25 (t, J = 7.1 Hz, 3H). ¹³C NMR (126 MHz, CDCl₃): δ (ppm) 166.4 (q, J_{CF} = 2.8 Hz), 139.3, 129.7, 129.4, 126.6 (q, J_{CF} = 1.8 Hz), 123.9 (q, J_{CF} = 279.6 Hz), 62.1, 55.3 (q, J_{CF} = 28.8 Hz), 21.3, 14.1. ¹⁹F NMR (471 MHz, CDCl₃): δ (ppm) -68.8 (d, J = 8.6 Hz, 3F). The spectral data are in full accordance with the literature report.^{1a}

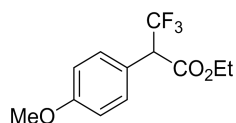
ethyl 2-(3,4-dimethoxyphenyl)-3,3,3-trifluoropropanoate (2e)



Following the general procedure, reaction was run using α -diazoester **1e** (125 mg, 0.5 mmol), pyridine (100 μ L, 1.25 mmol), 1,4-dioxane (7.5 mL) and CuCF₃ in DMF (3 mL, 1.25 mmol). The product was purified by flash column chromatography on silica gel (hexane/dichloromethane = 5:1) and obtained as a colorless oil (126 mg, 86% yield), R_f = 0.50 (hexane/dichloromethane = 2:1). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 6.98 (t, J = 2.7 Hz, 2H), 6.88 – 6.85 (m, 1H), 4.31 – 4.16 (m, 3H), 3.89 (d, J = 2.6 Hz, 6H), 1.26 (t, J = 7.1 Hz, 3H). ¹³C NMR (126 MHz, CDCl₃): δ (ppm) 166.4 (q, J_{CF} = 2.7 Hz), 149.8, 149.2, 123.8 (q, J_{CF} = 280.3 Hz), 122.3, 121.7 (q, J_{CF} = 1.7 Hz), 112.1, 111.2, 62.1, 56.0, 55.9, 55.0 (q,

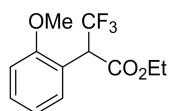
$J_{CF} = 28.8$ Hz), 14.0. ^{19}F NMR (471 MHz, CDCl_3): δ (ppm) -68.9 (d, $J = 8.6$ Hz, 3F). The spectral data are in full accordance with the literature report.^{1a}

ethyl 3,3,3-trifluoro-2-(4-methoxyphenyl)propanoate (**2f**)



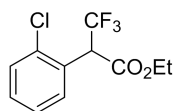
Following the general procedure, reaction was run using α -diazoester **1f** (110 mg, 0.5 mmol), pyridine (100 μL , 1.25 mmol), 1,4-dioxane (7.5 mL) and CuCF_3 in DMF (3 mL, 1.25 mmol). The product was purified by flash column chromatography on silica gel (hexane/dichloromethane = 10:1) and obtained as a colorless oil (111 mg, 84% yield), $R_f = 0.50$ (hexane/dichloromethane = 2:1). ^1H NMR (500 MHz, CDCl_3): δ (ppm) 7.36 (d, $J = 8.7$ Hz, 2H), 6.92 – 6.90 (m, 2H), 4.31 – 4.16 (m, 3H), 3.81 (s, 3H), 1.25 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3): δ (ppm) 166.5 (q, $J_{CF} = 2.7$ Hz), 160.4, 130.8, 123.9 (q, $J_{CF} = 280.0$ Hz), 121.5 (q, $J_{CF} = 1.8$ Hz), 114.4, 62.1, 55.4, 54.9 (q, $J_{CF} = 28.9$ Hz), 14.1. ^{19}F NMR (471 MHz, CDCl_3): δ (ppm) -69.1 (d, $J = 8.6$ Hz, 3F). The spectral data are in full accordance with the literature report.^{1a}

ethyl 3,3,3-trifluoro-2-(2-methoxyphenyl)propanoate (**2g**)

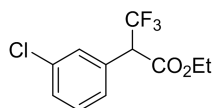


Following the general procedure, reaction was run using α -diazoester **1g** (110 mg, 0.5 mmol), pyridine (100 μL , 1.25 mmol), 1,4-dioxane (7.5 mL) and CuCF_3 in DMF (3 mL, 1.25 mmol). The product was purified by flash column chromatography on silica gel (hexane/dichloromethane = 15:1) and obtained as a colorless oil (77 mg, 59% yield), $R_f = 0.61$ (hexane/dichloromethane = 2:1). ^1H NMR (500 MHz, CDCl_3): δ (ppm) 7.50 (d, $J = 7.7$ Hz, 1H), 7.37 – 7.34 (m, 1H), 7.0 – 6.93 (m, 2H), 5.03 (q, $J = 8.9$ Hz, 1H), 4.27 – 4.15 (m, 2H), 3.86 (s, 3H), 1.24 (t, $J = 7.2$ Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3): δ (ppm) 166.9 (q, $J_{CF} = 2.7$ Hz), 157.5, 130.5, 129.8, 124.1 (q, $J_{CF} = 279.8$ Hz), 120.9, 118.4, 111.2, 61.9, 55.9, 47.1 (q, $J_{CF} = 29.0$ Hz), 14.1. ^{19}F NMR (471 MHz, CDCl_3): δ (ppm) -68.3 (d, $J = 8.9$ Hz, 3F). HRMS m/z (ESI) calcd. for $\text{C}_{12}\text{H}_{13}\text{F}_3\text{O}_3$ $[\text{M}+\text{Na}]^+$: 285.07090; found: 285.07073.

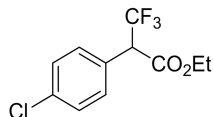
ethyl 2-(2-chlorophenyl)-3,3,3-trifluoropropanoate (**2h**)



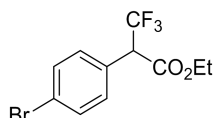
Following the general procedure, reaction was run using α -diazoester **1h** (112 mg, 0.5 mmol), pyridine (100 μL , 1.25 mmol), 1,4-dioxane (7.5 mL) and CuCF_3 in DMF (3 mL, 1.25 mmol). The product was purified by flash column chromatography on silica gel (hexane/dichloromethane = 15:1) and obtained as a colorless oil (95 mg, 71% yield), $R_f = 0.60$ (hexane/dichloromethane = 2:1). ^1H NMR (500 MHz, CDCl_3): δ (ppm) 7.65 (d, $J = 8.1$ Hz, 1H), 7.47 – 7.46 (m, 1H), 7.35 – 7.29 (m, 2H), 5.10 (q, $J = 8.5$ Hz, 1H), 4.30 – 4.17 (m, 2H), 1.25 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3): δ (ppm) 165.9 (q, $J_{CF} = 2.7$ Hz), 135.3, 130.5, 130.2, 130.1, 127.9 (q, $J_{CF} = 1.7$ Hz), 127.4, 123.8 (q, $J_{CF} = 279.8$ Hz), 62.4, 50.9 (q, $J_{CF} = 29.2$ Hz), 14.0. ^{19}F NMR (471 MHz, CDCl_3): δ (ppm) -68.0 (d, $J = 8.6$ Hz, 3F). The spectral data are in full accordance with the literature report.^{1a}

ethyl 2-(3-chlorophenyl)-3,3,3-trifluoropropanoate (2i)

Following the general procedure, reaction was run using α -diazoester **1i** (112 mg, 0.5 mmol), pyridine (100 μ L, 1.25 mmol), 1,4-dioxane (7.5 mL) and CuCF_3 in DMF (3 mL, 1.25 mmol). The product was purified by flash column chromatography on silica gel (hexane/dichloromethane = 15:1) and obtained as a colorless oil (97 mg, 73% yield), R_f = 0.60 (hexane/dichloromethane = 2:1). $^1\text{H NMR}$ (500 MHz, CDCl_3): δ (ppm) 7.46 (s, 1H), 7.40 – 7.37 (m, 1H), 7.34 – 7.33 (m, 2H), 4.31 – 4.15 (m, 3H), 1.27 (t, J = 7.1 Hz, 3H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3): δ (ppm) 165.7 (q, J_{CF} = 2.7 Hz), 134.9, 131.3 (q, J_{CF} = 1.8 Hz), 130.3, 129.8, 129.7, 127.8, 123.6 (q, J_{CF} = 279.8 Hz), 62.5, 55.2 (q, J_{CF} = 29.1 Hz), 14.0. $^{19}\text{F NMR}$ (471 MHz, CDCl_3): δ (ppm) -68.5 (d, J = 8.5 Hz, 3F). The spectral data are in full accordance with the literature report.^{1a}

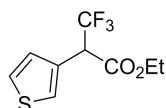
ethyl 2-(4-chlorophenyl)-3,3,3-trifluoropropanoate (2j)

Following the general procedure, reaction was run using α -diazoester **1j** (112 mg, 0.5 mmol), pyridine (100 μ L, 1.25 mmol), 1,4-dioxane (7.5 mL) and CuCF_3 in DMF (3 mL, 1.25 mmol). The product was purified by flash column chromatography on silica gel (hexane/dichloromethane = 15:1) and obtained as a light green oil (106 mg, 80% yield), R_f = 0.61 (hexane/dichloromethane = 2:1). $^1\text{H NMR}$ (500 MHz, CDCl_3): δ (ppm) 7.40 – 7.36 (m, 4H), 4.31 – 4.17 (m, 3H), 1.26 (t, J = 7.2 Hz, 3H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3): δ (ppm) 165.9 (q, J_{CF} = 2.7 Hz), 135.6, 130.9, 129.3, 128.0 (q, J_{CF} = 1.9 Hz), 123.6 (q, J_{CF} = 280.5 Hz), 62.4, 55.0 (q, J_{CF} = 29.1 Hz), 14.0. $^{19}\text{F NMR}$ (471 MHz, CDCl_3): δ (ppm) -68.7 (d, J = 8.4 Hz, 3F). The spectral data are in full accordance with the literature report.^{1a}

ethyl 2-(4-bromophenyl)-3,3,3-trifluoropropanoate (2k)

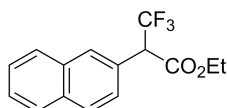
Following the general procedure, reaction was run using α -diazoester **1k** (135 mg, 0.5 mmol), pyridine (100 μ L, 1.25 mmol), 1,4-dioxane (7.5 mL) and CuCF_3 in DMF (3 mL, 1.25 mmol). The product was purified by flash column chromatography on silica gel (hexane/dichloromethane = 15:1) and obtained as a colorless oil (122 mg, 79% yield), R_f = 0.60 (hexane/dichloromethane = 2:1). $^1\text{H NMR}$ (500 MHz, CDCl_3): δ (ppm) 7.54 – 7.52 (m, 2H), 7.33 (d, J = 8.4 Hz, 2H), 4.30 – 4.17 (m, 3H), 1.26 (t, J = 7.1 Hz, 3H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3): δ (ppm) 165.8 (q, J_{CF} = 2.7 Hz), 132.3, 131.2, 128.5 (q, J_{CF} = 1.8 Hz), 123.8, 123.5 (q, J_{CF} = 279.8 Hz), 62.4, 55.1 (q, J_{CF} = 29.1 Hz), 14.0. $^{19}\text{F NMR}$ (471 MHz, CDCl_3): δ (ppm) -68.7 (d, J = 8.5 Hz, 3F). The spectral data are in full accordance with the literature report.^{1a}

ethyl 3,3,3-trifluoro-2-(thiophen-3-yl)propanoate (2l)



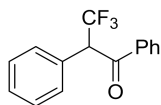
Following the general procedure, reaction was run using α -diazoester **1l** (98 mg, 0.5 mmol), pyridine (100 μ L, 1.25 mmol), 1,4-dioxane (7.5 mL) and CuCF_3 in DMF (3 mL, 1.25 mmol). The product was purified by flash column chromatography on silica gel (hexane/dichloromethane = 15:1) and obtained as a colorless oil (104 mg, 87% yield), R_f = 0.47 (hexane/dichloromethane = 2:1). $^1\text{H NMR}$ (500 MHz, CDCl_3): δ (ppm) 7.43 – 7.42 (m, 1H), 7.36 – 7.34 (m, 1H), 7.17 (d, J = 5.0 Hz, 1H), 4.47 (q, J = 8.5 Hz, 1H), 4.30 – 4.19 (m, 2H), 1.28 (t, J = 7.1 Hz, 3H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3): δ (ppm) 166.0 (q, J_{CF} = 2.8 Hz), 128.9 (q, J_{CF} = 2.0 Hz), 127.9, 126.5, 126.0, 123.6 (q, J_{CF} = 280.6 Hz), 62.3, 51.4 (q, J_{CF} = 29.7 Hz), 14.1. $^{19}\text{F NMR}$ (471 MHz, CDCl_3): δ (ppm) -69.0 (d, J = 8.5 Hz, 3F). The spectral data are in full accordance with the literature report.^{1b}

ethyl 3,3,3-trifluoro-2-(naphthalen-2-yl)propanoate (2m)



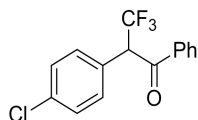
Following the general procedure, reaction was run using α -diazoester **1m** (120 mg, 0.5 mmol), pyridine (100 μ L, 1.25 mmol), 1,4-dioxane (7.5 mL) and CuCF_3 in DMF (3 mL, 1.25 mmol). The product was purified by flash column chromatography on silica gel (hexane/dichloromethane = 15:1) and obtained as a yellow solid (120 mg, 85% yield), R_f = 0.50 (hexane/dichloromethane = 2:1). $^1\text{H NMR}$ (500 MHz, CDCl_3): δ (ppm) 7.92 (s, 1H), 7.88 – 7.84 (m, 3H), 7.55 – 7.51 (m, 3H), 4.48 (q, J = 8.6 Hz, 1H), 4.32 – 4.18 (m, 2H), 1.25 (t, J = 7.1 Hz, 3H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3): δ (ppm) 166.3 (q, J_{CF} = 2.7 Hz), 133.5, 133.3, 129.5, 128.9, 128.3, 127.8, 127.0, 126.9 (q, J_{CF} = 1.7 Hz), 126.8, 126.4, 124.0 (q, J_{CF} = 279.9 Hz), 62.3, 55.8 (q, J_{CF} = 29.0 Hz), 14.1. $^{19}\text{F NMR}$ (471 MHz, CDCl_3): δ (ppm) -68.4 (d, J = 8.6 Hz, 3F). The spectral data are in full accordance with the literature report.^{1b}

3,3,3-trifluoro-1,2-diphenylpropan-1-one (4a)



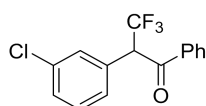
Following the general procedure, reaction was run using α -diazoketone **3a** (222 mg, 1.0 mmol), pyridine (120 μ L, 1.5 mmol), 1,4-dioxane (15 mL) and CuCF_3 in DMF (3.6 mL, 1.5 mmol). The product was purified by flash column chromatography on silica gel (hexane/dichloromethane = 15:1) and obtained as a white solid (219 mg, 83% yield), R_f = 0.71 (hexane/dichloromethane = 2:1). $^1\text{H NMR}$ (500 MHz, CDCl_3): δ (ppm) 7.90 (d, J = 7.6 Hz, 2H), 7.53 (t, J = 7.4 Hz, 1H), 7.46 (d, J = 6.8 Hz, 2H), 7.42 – 7.36 (m, 5H), 5.28 (q, J = 8.2 Hz, 1H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3): δ (ppm) 191.3, 135.5, 133.9, 130.0, 129.8 (q, J_{CF} = 1.9 Hz), 129.4, 129.3, 128.93, 128.90, 124.4 (q, J_{CF} = 280.6 Hz), 56.7 (q, J_{CF} = 26.5 Hz). $^{19}\text{F NMR}$ (471 MHz, CDCl_3): δ (ppm) -67.5 (d, J = 7.6 Hz, 3F). **HRMS** m/z (APCI) calcd. for $\text{C}_{15}\text{H}_{11}\text{F}_3\text{O}$ $[\text{M}+\text{H}]^+$: 265.08348; found: 265.08368.

2-(4-chlorophenyl)-3,3,3-trifluoro-1-phenylpropan-1-one (4b)



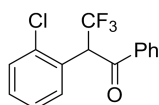
Following the general procedure, reaction was run using α -diazoketone **3b** (77 mg, 0.3 mmol), pyridine (36 μ L, 0.45 mmol), 1,4-dioxane (4.5 mL) and CuCF_3 in DMF (1.1 mL, 0.45 mmol). The product was purified by flash column chromatography on silica gel (hexane/dichloromethane = 15:1) and obtained as a colorless oil (76 mg, 85% yield), $R_f = 0.61$ (hexane/dichloromethane = 2:1). $^1\text{H NMR}$ (500 MHz, CDCl_3): δ (ppm) 7.88 (d, $J = 7.8$ Hz, 2H), 7.56 (t, $J = 7.3$ Hz, 1H), 7.44 – 7.35 (m, 6H), 5.27 (q, $J = 8.2$ Hz, 1H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3): δ (ppm) 190.9, 135.7, 135.3, 134.2, 131.3, 129.7, 129.1, 128.9, 128.3 (q, $J_{\text{CF}} = 1.9$ Hz), 124.1 (q, $J_{\text{CF}} = 280.4$ Hz), 55.8 (q, $J_{\text{CF}} = 26.8$ Hz). $^{19}\text{F NMR}$ (471 MHz, CDCl_3): δ (ppm) -67.5 (d, $J = 7.6$ Hz, 3F). **HRMS** m/z (APCI) calcd. for $\text{C}_{15}\text{H}_{10}\text{ClF}_3\text{O}$ $[\text{M}+\text{H}]^+$: 299.04450; found: 299.04488.

2-(3-chlorophenyl)-3,3,3-trifluoro-1-phenylpropan-1-one (4c)



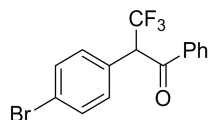
Following the general procedure, reaction was run using α -diazoketone **3c** (77 mg, 0.3 mmol), pyridine (36 μ L, 0.45 mmol), 1,4-dioxane (4.5 mL) and CuCF_3 in DMF (1.1 mL, 0.45 mmol). The product was purified by flash column chromatography on silica gel (hexane/dichloromethane = 15:1) and obtained as a colorless oil (75 mg, 83% yield), $R_f = 0.69$ (hexane/dichloromethane = 2:1). $^1\text{H NMR}$ (500 MHz, CDCl_3): δ (ppm) 7.81 (d, $J = 8.0$ Hz, 2H), 7.48 (t, $J = 7.3$ Hz, 1H), 7.40 (s, 1H), 7.35 (t, $J = 7.8$ Hz, 2H), 7.29 – 7.17 (m, 3H), 5.19 (q, $J = 8.1$ Hz, 1H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3): δ (ppm) 190.7, 135.3, 134.25, 134.24, 131.6 (q, $J_{\text{CF}} = 1.9$ Hz), 130.6, 130.0, 129.7, 129.1, 128.9, 128.2, 124.1 (q, $J_{\text{CF}} = 280.9$ Hz), 56.0 (q, $J_{\text{CF}} = 26.9$ Hz). $^{19}\text{F NMR}$ (471 MHz, CDCl_3): δ (ppm) -67.3 (d, $J = 7.5$ Hz, 3F). **HRMS** m/z (APCI) calcd. for $\text{C}_{15}\text{H}_{10}\text{ClF}_3\text{O}$ $[\text{M}+\text{H}]^+$: 299.04450; found: 299.04431.

2-(2-chlorophenyl)-3,3,3-trifluoro-1-phenylpropan-1-one (4d)



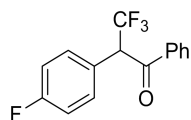
Following the general procedure, reaction was run using α -diazoketone **3d** (77 mg, 0.3 mmol), pyridine (36 μ L, 0.45 mmol), 1,4-dioxane (4.5 mL) and CuCF_3 in DMF (1.1 mL, 0.45 mmol). The product was purified by flash column chromatography on silica gel (hexane/dichloromethane = 15:1) and obtained as a colorless oil (52 mg, 58% yield), $R_f = 0.67$ (hexane/dichloromethane = 2:1). $^1\text{H NMR}$ (500 MHz, CDCl_3): δ (ppm) 7.92 (d, $J = 7.6$ Hz, 2H), 7.56 – 7.48 (m, 3H), 7.43 (t, $J = 7.8$ Hz, 2H), 7.30 (td, $J = 7.6, 1.3$ Hz, 1H), 7.24 (t, $J = 7.6$ Hz, 1H), 5.96 (q, $J = 7.9$ Hz, 1H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3): δ (ppm) 191.1, 135.1, 134.9, 134.2, 130.8, 130.7, 130.5, 129.1, 128.7, 127.9 (q, $J_{\text{CF}} = 1.7$ Hz), 127.7, 124.4 (q, $J_{\text{CF}} = 280.8$ Hz), 52.1 (q, $J_{\text{CF}} = 27.1$ Hz). $^{19}\text{F NMR}$ (471 MHz, CDCl_3): δ (ppm) -67.3 (d, $J = 7.5$ Hz, 3F). **HRMS** m/z (APCI) calcd. for $\text{C}_{15}\text{H}_{10}\text{ClF}_3\text{O}$ $[\text{M}+\text{H}]^+$: 299.04450; found: 299.04495.

2-(4-bromophenyl)-3,3,3-trifluoro-1-phenylpropan-1-one (4e)



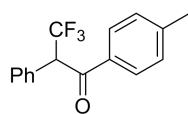
Following the general procedure, reaction was run using α -diazoketone **3e** (90 mg, 0.3 mmol), pyridine (36 μ L, 0.45 mmol), 1,4-dioxane (4.5 mL) and CuCF_3 in DMF (1.1 mL, 0.45 mmol). The product was purified by flash column chromatography on silica gel (hexane/dichloromethane = 15:1) and obtained as a white solid (93 mg, 91% yield), $R_f = 0.67$ (hexane/dichloromethane = 2:1). **^1H NMR** (500 MHz, CDCl_3): δ (ppm) 7.89 – 7.87 (m, 2H), 7.57 – 7.50 (m, 3H), 7.42 (t, $J = 8.1$ Hz, 2H), 7.34 (d, $J = 8.5$ Hz, 2H), 5.26 (q, $J = 8.1$ Hz, 1H). **^{13}C NMR** (126 MHz, CDCl_3): δ (ppm) 190.9, 135.2, 134.2, 132.7, 131.5, 129.1, 128.9, 128.8 (q, $J_{\text{CF}} = 1.8$ Hz), 124.1 (q, $J_{\text{CF}} = 280.4$ Hz), 123.9, 55.9 (q, $J_{\text{CF}} = 26.9$ Hz). **^{19}F NMR** (471 MHz, CDCl_3): δ (ppm) -67.5 (d, $J = 8.3$ Hz, 3F). **HRMS** m/z (APCI) calcd. for $\text{C}_{15}\text{H}_{10}\text{BrF}_3\text{O}$ $[\text{M}+\text{H}]^+$: 342.99399; found: 342.99319.

3,3,3-trifluoro-2-(4-fluorophenyl)-1-phenylpropan-1-one (4f)



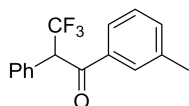
Following the general procedure, reaction was run using α -diazoketone **3f** (72 mg, 0.3 mmol), pyridine (36 μ L, 0.45 mmol), 1,4-dioxane (4.5 mL) and CuCF_3 in DMF (1.1 mL, 0.45 mmol). The product was purified by flash column chromatography on silica gel (hexane/dichloromethane = 15:1) and obtained as a colorless oil (74 mg, 88% yield), $R_f = 0.65$ (hexane/dichloromethane = 2:1). **^1H NMR** (500 MHz, CDCl_3): δ (ppm) 7.90 – 7.88 (m, 2H), 7.55 (t, $J = 7.6$ Hz, 1H), 7.46 – 7.41 (m, 4H), 7.08 (t, $J = 8.6$ Hz, 2H), 5.28 (q, $J = 8.2$ Hz, 1H). **^{13}C NMR** (126 MHz, CDCl_3): δ (ppm) 191.2, 164.3, 162.4, 135.4, 134.1, 131.8 (d, $J_{\text{CF}} = 8.5$ Hz), 129.0 (d, $J_{\text{CF}} = 17.5$ Hz), 125.6 (q, $J_{\text{CF}} = 1.5$ Hz), 124.2 (q, $J_{\text{CF}} = 280.8$ Hz), 116.6 (d, $J_{\text{CF}} = 21.7$ Hz), 55.7 (q, $J_{\text{CF}} = 26.9$ Hz). **^{19}F NMR** (471 MHz, CDCl_3): δ (ppm) -67.7 (d, $J = 8.3$ Hz, 3F). **HRMS** m/z (APCI) calcd. for $\text{C}_{15}\text{H}_{10}\text{F}_4\text{O}$ $[\text{M}+\text{H}]^+$: 283.07405; found: 283.07416.

3,3,3-trifluoro-2-phenyl-1-(*p*-tolyl)propan-1-one (4g)



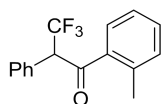
Following the general procedure, reaction was run using α -diazoketone **3g** (71 mg, 0.3 mmol), pyridine (36 μ L, 0.45 mmol), 1,4-dioxane (4.5 mL) and CuCF_3 in DMF (1.1 mL, 0.45 mmol). The product was purified by flash column chromatography on silica gel (hexane/dichloromethane = 15:1) and obtained as a green oil (74 mg, 89% yield), $R_f = 0.4$ (hexane/dichloromethane = 2:1). **^1H NMR** (500 MHz, CDCl_3): δ (ppm) 7.80 (d, $J = 8.3$ Hz, 2H), 7.46 – 7.45 (m, 2H), 7.39 – 7.35 (m, 3H), 7.20 (d, $J = 8.0$ Hz, 2H), 5.25 (q, $J = 8.3$ Hz, 1H), 2.36 (s, 3H). **^{13}C NMR** (126 MHz, CDCl_3): δ (ppm) 190.8, 145.0, 133.9, 133.0 (q, $J_{\text{CF}} = 1.7$ Hz), 130.0, 129.6, 129.4, 129.2, 129.1, 124.5 (q, $J_{\text{CF}} = 279.7$ Hz), 56.5 (q, $J_{\text{CF}} = 26.5$ Hz), 21.8. **^{19}F NMR** (471 MHz, CDCl_3): δ (ppm) -67.5 (d, $J = 8.5$ Hz, 3F). **HRMS** m/z (APCI) calcd. for $\text{C}_{16}\text{H}_{13}\text{F}_3\text{O}$ $[\text{M}+\text{H}]^+$: 279.09913; found: 279.09912.

3,3,3-trifluoro-2-phenyl-1-(*m*-tolyl)propan-1-one (4h)



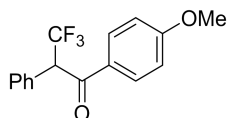
Following the general procedure, reaction was run using α -diazoketone **3h** (71 mg, 0.3 mmol), pyridine (36 μ L, 0.45 mmol), 1,4-dioxane (4.5 mL) and CuCF_3 in DMF (1.1 mL, 0.45 mmol). The product was purified by flash column chromatography on silica gel (hexane/dichloromethane = 15:1) and obtained as a colorless oil (60 mg, 72% yield), $R_f = 0.43$ (hexane/dichloromethane = 2:1). **$^1\text{H NMR}$** (500 MHz, CDCl_3): δ (ppm) 7.50 (d, $J = 7.8$ Hz, 1H), 7.45 – 7.44 (m, 2H), 7.38 – 7.32 (m, 4H), 7.22 – 7.16 (m, 2H), 5.16 (q, $J = 8.4$ Hz, 1H), 2.47 (s, 3H). **$^{13}\text{C NMR}$** (126 MHz, CDCl_3): δ (ppm) 194.6, 139.5, 136.6, 132.4, 132.2, 130.0, 129.6 (q, $J_{\text{CF}} = 1.8$ Hz), 129.33, 129.30, 128.5, 125.9, 124.4 (q, $J_{\text{CF}} = 280.5$ Hz), 58.9 (q, $J_{\text{CF}} = 26.5$ Hz), 21.3. **$^{19}\text{F NMR}$** (471 MHz, CDCl_3): δ (ppm) -67.5 (d, $J = 8.2$ Hz, 3F). **HRMS** m/z (APCI) calcd. for $\text{C}_{16}\text{H}_{13}\text{F}_3\text{O}$ $[\text{M}+\text{H}]^+$: 279.09913; found: 279.09910.

3,3,3-trifluoro-2-phenyl-1-(*o*-tolyl)propan-1-one (4i)



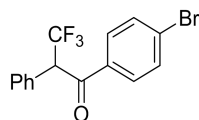
Following the general procedure, reaction was run using α -diazoketone **3i** (71 mg, 0.3 mmol), pyridine (36 μ L, 0.45 mmol), 1,4-dioxane (4.5 mL) and CuCF_3 in DMF (1.1 mL, 0.45 mmol). The product was purified by flash column chromatography on silica gel (hexane/dichloromethane = 15:1) and obtained as a colorless oil (50 mg, 60% yield), $R_f = 0.50$ (hexane/dichloromethane = 2:1). **$^1\text{H NMR}$** (500 MHz, CDCl_3): δ (ppm) 7.73 (s, 1H), 7.66 (d, $J = 7.7$ Hz, 1H), 7.46 (d, $J = 6.8$ Hz, 2H), 7.38 – 7.25 (m, 5H), 5.28 (q, $J = 8.2$ Hz, 1H), 2.35 (s, 3H). **$^{13}\text{C NMR}$** (126 MHz, CDCl_3): δ (ppm) 191.4, 138.9, 135.6, 134.7, 130.0, 129.9 (q, $J_{\text{CF}} = 1.8$ Hz), 129.41, 129.39, 129.3, 128.8, 126.1, 124.4 (q, $J_{\text{CF}} = 280.5$ Hz), 56.6 (q, $J_{\text{CF}} = 26.6$ Hz), 21.5. **$^{19}\text{F NMR}$** (471 MHz, CDCl_3): δ (ppm) -67.4 (d, $J = 8.5$ Hz, 3F). **HRMS** m/z (APCI) calcd. for $\text{C}_{16}\text{H}_{13}\text{F}_3\text{O}$ $[\text{M}+\text{H}]^+$: 279.09913; found: 279.09918.

3,3,3-trifluoro-1-(4-methoxyphenyl)-2-phenylpropan-1-one (4j)



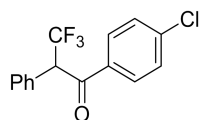
Following the general procedure, reaction was run using α -diazoketone **3j** (76 mg, 0.3 mmol), pyridine (36 μ L, 0.45 mmol), 1,4-dioxane (4.5 mL) and CuCF_3 in DMF (1.1 mL, 0.45 mmol). The product was purified by flash column chromatography on silica gel (hexane/dichloromethane = 15:1) and obtained as a colorless oil (72 mg, 81% yield), $R_f = 0.46$ (hexane/dichloromethane = 2:1). **$^1\text{H NMR}$** (500 MHz, CDCl_3): δ (ppm) 7.88 (d, $J = 8.9$ Hz, 2H), 7.46 (d, $J = 7.3$ Hz, 2H), 7.39 – 7.35 (m, 3H), 6.87 (d, $J = 9.0$ Hz, 2H), 5.23 (q, $J = 8.3$ Hz, 1H), 3.82 (s, 3H). **$^{13}\text{C NMR}$** (126 MHz, CDCl_3): δ (ppm) 189.7, 164.1, 131.3, 130.3 (q, $J_{\text{CF}} = 1.9$ Hz), 129.9, 129.4, 129.2, 128.4, 124.5 (q, $J_{\text{CF}} = 279.5$ Hz), 114.1, 56.3 (q, $J_{\text{CF}} = 26.4$ Hz), 55.6. **$^{19}\text{F NMR}$** (471 MHz, CDCl_3): δ (ppm) -67.4 (d, $J = 8.6$ Hz, 3F). **HRMS** m/z (APCI) calcd. for $\text{C}_{16}\text{H}_{13}\text{F}_3\text{O}_2$ $[\text{M}+\text{H}]^+$: 295.09404; found: 295.09419.

1-(4-bromophenyl)-3,3,3-trifluoro-2-phenylpropan-1-one (4k)



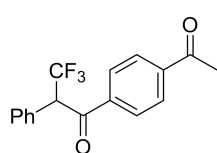
Following the general procedure, reaction was run using α -diazoketone **3k** (90 mg, 0.3 mmol), pyridine (36 μ L, 0.45 mmol), 1,4-dioxane (4.5 mL) and CuCF_3 in DMF (1.1 mL, 0.45 mmol). The product was purified by flash column chromatography on silica gel (hexane/dichloromethane = 15:1) and obtained as a light green solid (57 mg, 55% yield), $R_f = 0.53$ (hexane/dichloromethane = 2:1). $^1\text{H NMR}$ (500 MHz, CDCl_3): δ (ppm) 7.74 (d, $J = 8.5$ Hz, 2H), 7.54 (d, $J = 8.5$ Hz, 2H), 7.42 – 7.38 (m, 5H), 5.20 (q, $J = 8.1$ Hz, 1H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3): δ (ppm) 190.3, 134.2 (q, $J_{\text{CF}} = 1.7$ Hz), 132.32, 132.31, 130.4, 129.9, 129.6, 129.5, 129.3, 124.2 (q, $J_{\text{CF}} = 280.6$ Hz), 56.8 (q, $J_{\text{CF}} = 26.7$ Hz). $^{19}\text{F NMR}$ (471 MHz, CDCl_3): δ (ppm) -67.6 (d, $J = 8.3$ Hz, 3F). **HRMS** m/z (APCI) calcd. for $\text{C}_{15}\text{H}_{10}\text{BrF}_3\text{O}$ $[\text{M}+\text{H}]^+$: 342.99399; found: 342.99314.

1-(4-chlorophenyl)-3,3,3-trifluoro-2-phenylpropan-1-one (4l)



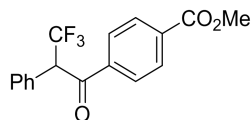
Following the general procedure, reaction was run using α -diazoketone **3l** (77 mg, 0.3 mmol), pyridine (36 μ L, 0.45 mmol), 1,4-dioxane (4.5 mL) and CuCF_3 in DMF (1.1 mL, 0.45 mmol). The product was purified by flash column chromatography on silica gel (hexane/dichloromethane = 15:1) and obtained as a yellow solid (78 mg, 87% yield), $R_f = 0.44$ (hexane/dichloromethane = 2:1). $^1\text{H NMR}$ (500 MHz, CDCl_3): δ (ppm) 7.82 (d, $J = 8.7$ Hz, 2H), 7.44 – 7.36 (m, 7H), 5.21 (q, $J = 8.1$ Hz, 1H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3): δ (ppm) 190.1, 140.5, 133.7, 130.3, 129.9, 129.6, 129.5, 129.3, 128.9 (q, $J_{\text{CF}} = 3.9$ Hz), 124.3 (q, $J_{\text{CF}} = 280.2$ Hz), 56.8 (q, $J_{\text{CF}} = 26.7$ Hz). $^{19}\text{F NMR}$ (471 MHz, CDCl_3): δ (ppm) -67.6 (d, $J = 8.3$ Hz, 3F). **HRMS** m/z (APCI) calcd. for $\text{C}_{15}\text{H}_{10}\text{ClF}_3\text{O}$ $[\text{M}+\text{H}]^+$: 299.04450; found: 299.04435.

1-(4-acetylphenyl)-3,3,3-trifluoro-2-phenylpropan-1-one (4m)



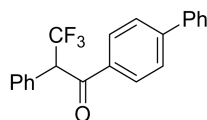
Following the general procedure, reaction was run using α -diazoketone **3m** (79 mg, 0.3 mmol), pyridine (36 μ L, 0.45 mmol), 1,4-dioxane (4.5 mL) and CuCF_3 in DMF (1.1 mL, 0.45 mmol). The product was purified by flash column chromatography on silica gel (hexanes/ethyl acetate = 15:1) and obtained as a yellow solid (73 mg, 79% yield), $R_f = 0.28$ (hexanes/ethyl acetate = 5:1). $^1\text{H NMR}$ (500 MHz, CDCl_3): δ (ppm) 7.89 (s, 4H), 7.38 – 7.31 (m, 5H), 5.20 (q, $J = 8.1$ Hz, 1H), 2.52 (s, 3H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3): δ (ppm) 197.2, 190.7, 140.7, 138.5, 135.3, 130.0, 129.61, 129.58, 129.1, 128.7, 124.2 (q, $J_{\text{CF}} = 280.8$ Hz), 57.2 (q, $J_{\text{CF}} = 26.8$ Hz), 27.0. $^{19}\text{F NMR}$ (471 MHz, CDCl_3): δ (ppm) -67.6 (d, $J = 8.3$ Hz, 3F). **HRMS** m/z (APCI) calcd. for $\text{C}_{17}\text{H}_{13}\text{F}_3\text{O}_2$ $[\text{M}+\text{H}]^+$: 307.09404; found: 307.09425.

methyl 4-(3,3,3-trifluoro-2-phenylpropanoyl)benzoate (4n)



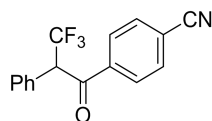
Following the general procedure, reaction was run using α -diazoketone **3n** (84 mg, 0.3 mmol), pyridine (36 μ L, 0.45 mmol), 1,4-dioxane (4.5 mL) and CuCF_3 in DMF (1.1 mL, 0.45 mmol). The product was purified by flash column chromatography on silica gel (hexane/dichloromethane = 15:1) and obtained as a white solid (83 mg, 86% yield), $R_f = 0.44$ (hexane/dichloromethane = 2:1). **$^1\text{H NMR}$** (500 MHz, CDCl_3): δ (ppm) 8.05 (d, $J = 8.7$ Hz, 2H), 7.93 (d, $J = 8.7$ Hz, 2H), 7.45 – 7.38 (m, 5H), 5.27 (q, $J = 8.1$ Hz, 1H), 3.92 (s, 3H). **$^{13}\text{C NMR}$** (126 MHz, CDCl_3): δ (ppm) 190.8, 166.0, 138.6, 134.6, 130.1, 130.0, 129.6, 129.5, 129.3 (q, $J_{\text{CF}} = 1.7$ Hz), 128.8, 124.2 (q, $J_{\text{CF}} = 280.4$ Hz), 57.1 (q, $J_{\text{CF}} = 26.8$ Hz), 52.7. **$^{19}\text{F NMR}$** (471 MHz, CDCl_3): δ (ppm) -67.6 (d, $J = 7.5$ Hz, 3F). **HRMS** m/z (APCI) calcd. for $\text{C}_{17}\text{H}_{13}\text{F}_3\text{O}_3$ $[\text{M}+\text{H}]^+$: 323.08896; found: 323.08827.

1-([1,1'-biphenyl]-4-yl)-3,3,3-trifluoro-2-phenylpropan-1-one (4o)



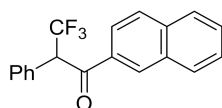
Following the general procedure, reaction was run using α -diazoketone **3o** (90 mg, 0.3 mmol), pyridine (36 μ L, 0.45 mmol), 1,4-dioxane (4.5 mL) and CuCF_3 in DMF (1.1 mL, 0.45 mmol). The product was purified by flash column chromatography on silica gel (hexanes/ethyl acetate = 15:1) and obtained as a yellow solid (87 mg, 85% yield), $R_f = 0.37$ (hexanes/ethyl acetate = 5:1). **$^1\text{H NMR}$** (500 MHz, CDCl_3): δ (ppm) 7.88 (d, $J = 8.5$ Hz, 2H), 7.52 (d, $J = 8.4$ Hz, 2H), 7.46 (d, $J = 7.4$ Hz, 2H), 7.40 (d, $J = 7.0$ Hz, 2H), 7.34 (t, $J = 7.2$ Hz, 2H), 7.32 – 7.27 (m, 4H), 5.23 (q, $J = 8.3$ Hz, 1H). **$^{13}\text{C NMR}$** (126 MHz, CDCl_3): δ (ppm) 190.8, 146.6, 139.5, 134.1, 130.0, 129.9 (q, $J_{\text{CF}} = 1.7$ Hz), 129.53, 129.46, 129.3, 129.1, 128.6, 127.5, 127.4, 124.5 (q, $J_{\text{CF}} = 280.1$ Hz), 56.7 (q, $J_{\text{CF}} = 26.6$ Hz). **$^{19}\text{F NMR}$** (471 MHz, CDCl_3): δ (ppm) -67.5 (d, $J = 8.5$ Hz, 3F). **HRMS** m/z (APCI) calcd. for $\text{C}_{21}\text{H}_{15}\text{F}_3\text{O}$ $[\text{M}+\text{H}]^+$: 341.11478; found: 341.11449.

4-(3,3,3-trifluoro-2-phenylpropanoyl)benzotrile (4p)



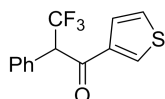
Following the general procedure, reaction was run using α -diazoketone **3p** (74 mg, 0.3 mmol), pyridine (36 μ L, 0.45 mmol), 1,4-dioxane (4.5 mL) and CuCF_3 in DMF (1.1 mL, 0.45 mmol). The product was purified by flash column chromatography on silica gel (hexanes/ethyl acetate = 15:1) and obtained as a yellow oil (53 mg, 61% yield), $R_f = 0.38$ (hexanes/ethyl acetate = 5:1). **$^1\text{H NMR}$** (500 MHz, CDCl_3): δ (ppm) 7.96 (d, $J = 8.5$ Hz, 2H), 7.70 (d, $J = 8.5$ Hz, 2H), 7.41 (s, 5H), 5.22 (q, $J = 7.9$ Hz, 1H). **$^{13}\text{C NMR}$** (126 MHz, CDCl_3): δ (ppm) 189.9, 138.3, 132.8, 129.9, 129.80, 129.76, 129.3, 128.9 (q, $J_{\text{CF}} = 1.7$ Hz), 124.0 (q, $J_{\text{CF}} = 280.2$ Hz), 117.7, 117.2, 57.2 (q, $J_{\text{CF}} = 27.2$ Hz). **$^{19}\text{F NMR}$** (471 MHz, CDCl_3): δ (ppm) -67.7 (d, $J = 8.0$ Hz, 3F). **HRMS** m/z (APCI) calcd. for $\text{C}_{16}\text{H}_{10}\text{F}_3\text{NO}$ $[\text{M}+\text{H}]^+$: 290.07873; found: 290.07859.

3,3,3-trifluoro-1-(naphthalen-2-yl)-2-phenylpropan-1-one (4q)



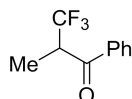
Following the general procedure, reaction was run using α -diazoketone **3q** (82 mg, 0.3 mmol), pyridine (36 μ L, 0.45 mmol), 1,4-dioxane (4.5 mL) and CuCF_3 in DMF (1.1 mL, 0.45 mmol). The product was purified by flash column chromatography on silica gel (hexanes/ethyl acetate = 15:1) and obtained as a yellow solid (78 mg, 83% yield), R_f = 0.39 (hexanes/ethyl acetate = 5:1). $^1\text{H NMR}$ (500 MHz, CDCl_3): δ (ppm) 8.33 (s, 1H), 7.89 (dd, J = 8.7, 1.8 Hz, 1H), 7.82 (d, J = 8.2 Hz, 1H), 7.76 (t, J = 8.4 Hz, 2H), 7.53 – 7.50 (m, 1H), 7.46 (t, J = 7.2 Hz, 3H), 7.33 – 7.27 (m, 3H), 5.37 (q, J = 8.3 Hz, 1H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3): δ (ppm) 191.2, 135.8, 132.8, 132.4, 131.0, 130.0, 129.83, 129.77, 129.4, 129.3, 129.2, 128.9, 127.9, 127.2, 124.5 (q, J_{CF} = 280.2 Hz), 124.1, 56.7 (q, J_{CF} = 26.6 Hz). $^{19}\text{F NMR}$ (471 MHz, CDCl_3): δ (ppm) -67.4 (d, J = 8.5 Hz, 3F). **HRMS** m/z (APCI) calcd. for $\text{C}_{19}\text{H}_{13}\text{F}_3\text{O}$ $[\text{M}+\text{H}]^+$: 315.09913; found: 315.09925.

3,3,3-trifluoro-2-phenyl-1-(thiophen-3-yl)propan-1-one (4r)



Following the general procedure, reaction was run using α -diazoketone **3r** (69 mg, 0.3 mmol), pyridine (36 μ L, 0.45 mmol), 1,4-dioxane (4.5 mL) and CuCF_3 in DMF (1.1 mL, 0.45 mmol). The product was purified by flash column chromatography on silica gel (hexanes/ethyl acetate = 15:1) and obtained as a green solid (45 mg, 55% yield), R_f = 0.41 (hexanes/ethyl acetate = 5:1). $^1\text{H NMR}$ (500 MHz, CDCl_3): δ (ppm) 7.92 (dd, J = 2.9, 1.3 Hz, 1H), 7.42 – 7.38 (m, 3H), 7.34 – 7.31 (m, 3H), 7.20 (t, J = 2.9 Hz, 1H), 4.99 (q, J = 8.2 Hz, 1H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3): δ (ppm) 185.3, 140.7, 133.9, 129.9, 129.44, 129.40, 128.9, 127.3, 126.9, 124.2 (q, J_{CF} = 280.4 Hz), 58.3 (q, J_{CF} = 26.6 Hz). $^{19}\text{F NMR}$ (471 MHz, CDCl_3): δ (ppm) -67.5 (d, J = 7.6 Hz, 3F). **HRMS** m/z (APCI) calcd. for $\text{C}_{13}\text{H}_9\text{F}_3\text{OS}$ $[\text{M}+\text{H}]^+$: 271.03990; found: 271.03999.

3,3,3-trifluoro-2-methyl-1-phenylpropan-1-one (4s)

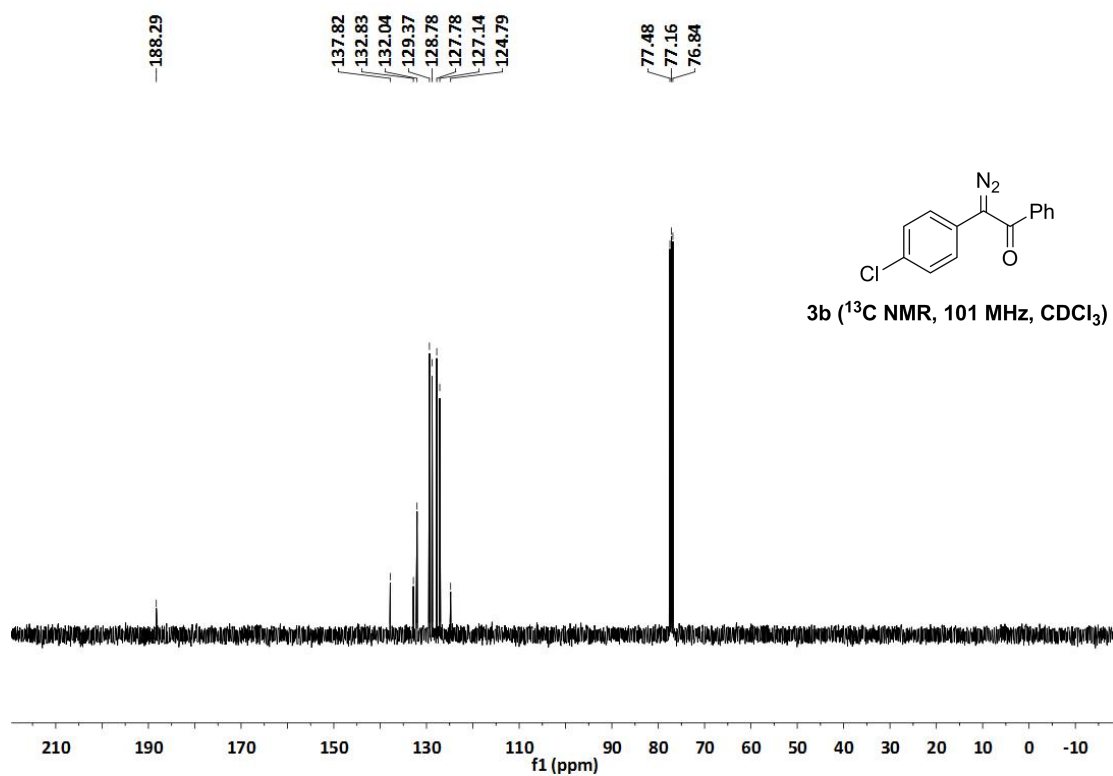
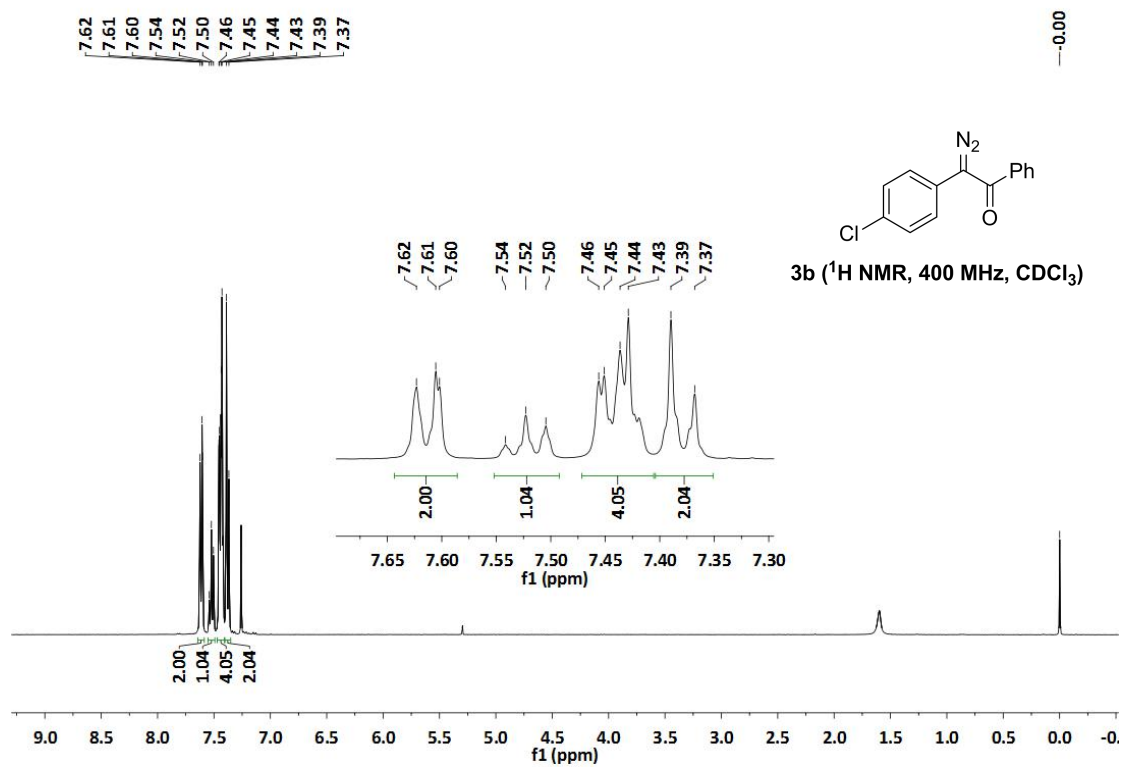


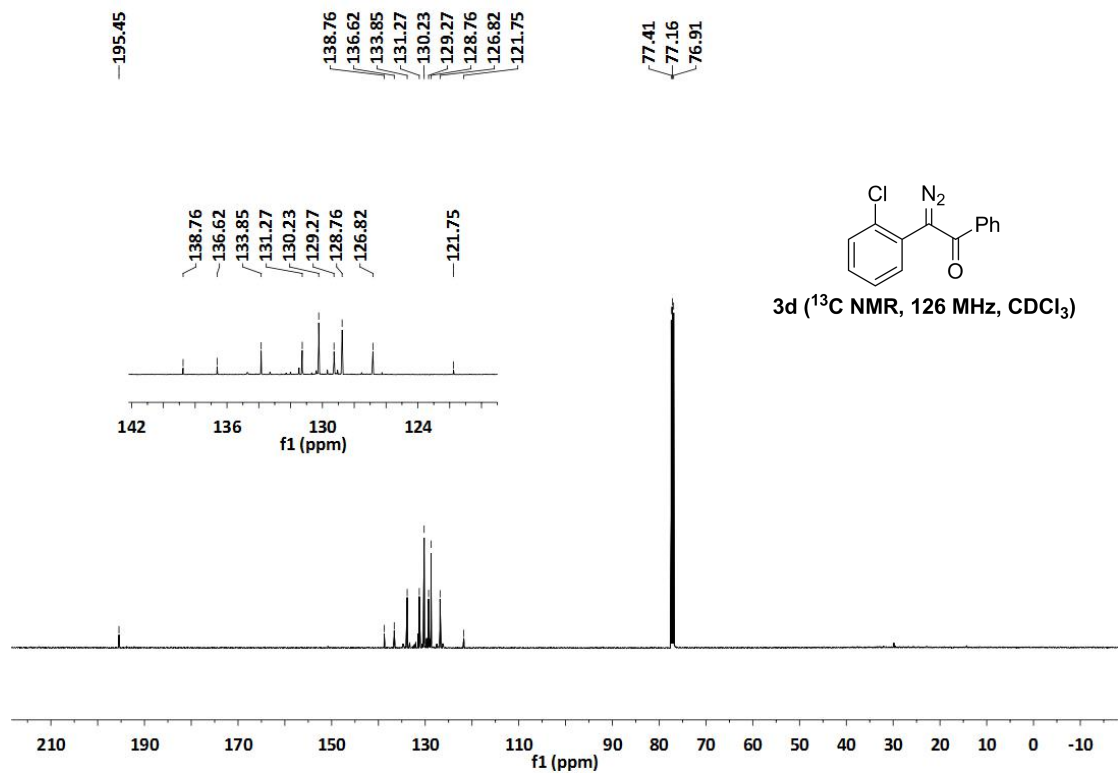
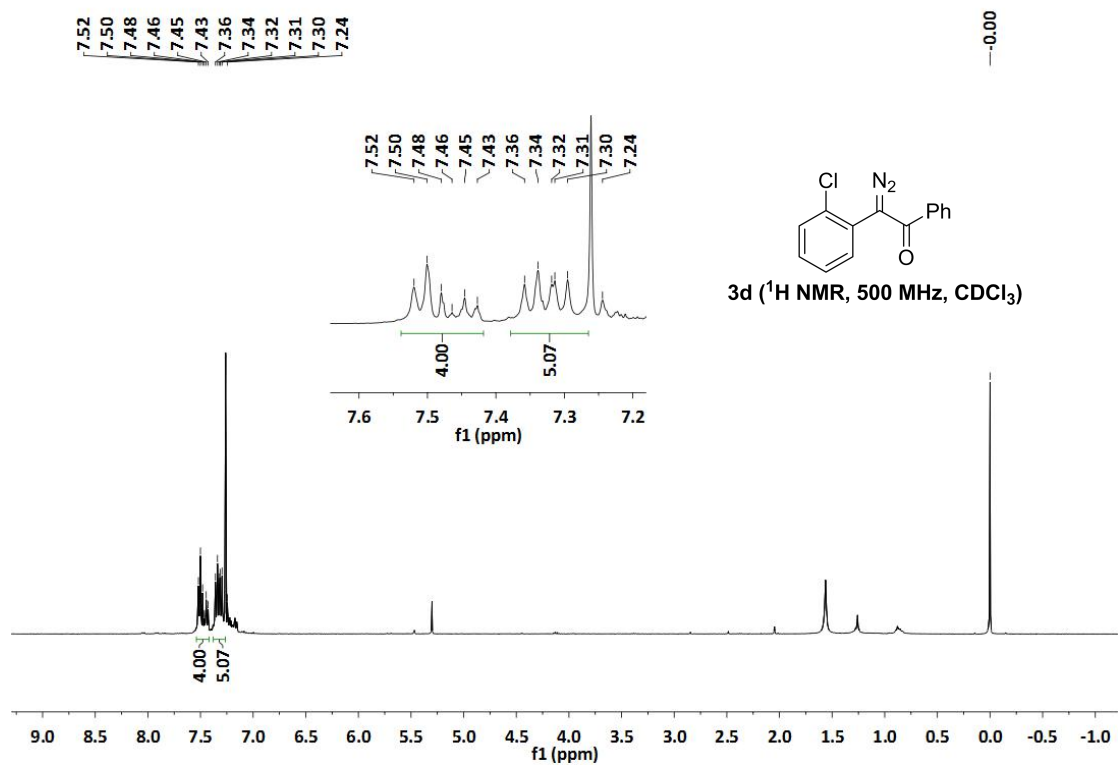
Following the general procedure, reaction was run using α -diazoketone **4s** (48 mg, 0.3 mmol), pyridine (60 μ L, 0.75 mmol), 1,4-dioxane (4.5 mL) and CuCF_3 in DMF (1.8 mL, 0.75 mmol). The yield (22%) was then determined through $^{19}\text{F NMR}$ with benzotrifluoride (δ = -63.72 ppm) as internal standard. $^1\text{H NMR}$ (500 MHz, CDCl_3): δ (ppm) 7.98 – 7.93 (m, 2H), 7.67 – 7.58 (m, 1H), 7.54 – 7.48 (m, 2H), 4.30 – 4.20 (m, 1H), 1.48 (d, J = 7.1 Hz, 3H). $^{19}\text{F NMR}$ (471 MHz, CDCl_3): δ (ppm) -68.3 (d, J = 8.6 Hz, 3F). **MS** (EI, m/z): 202 (M^+ , 1.47), 105 (100.00). The spectral data are in full accordance with the literature report.⁷

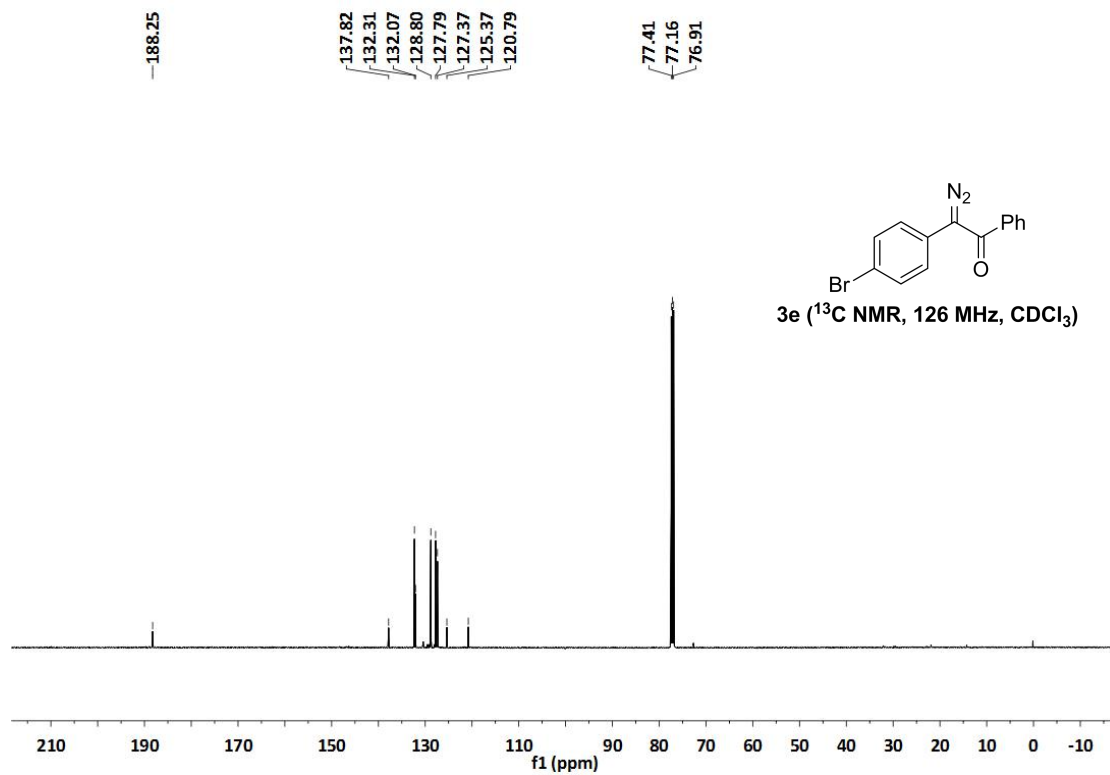
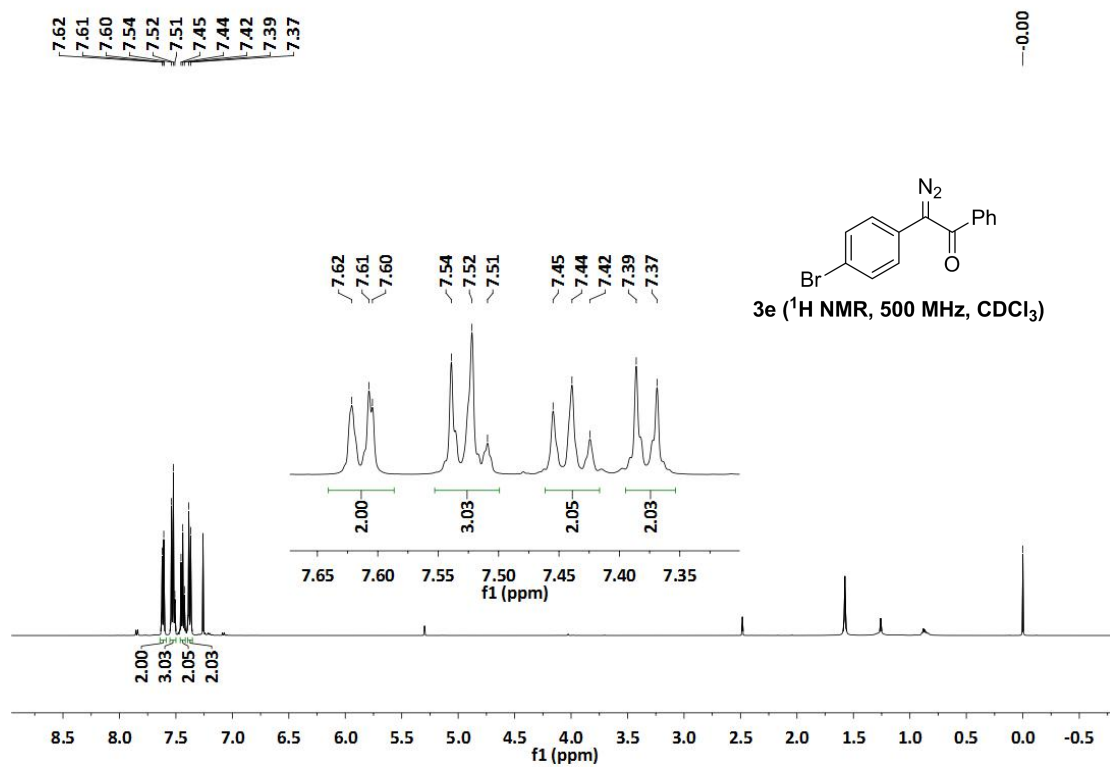
References

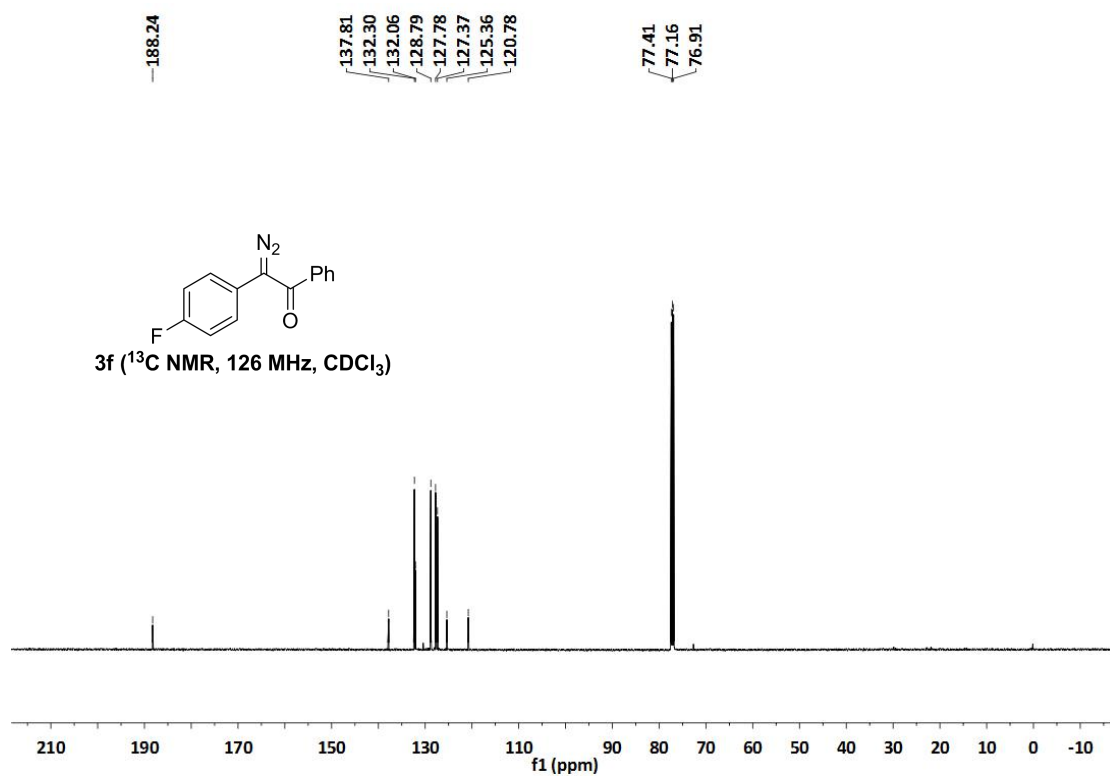
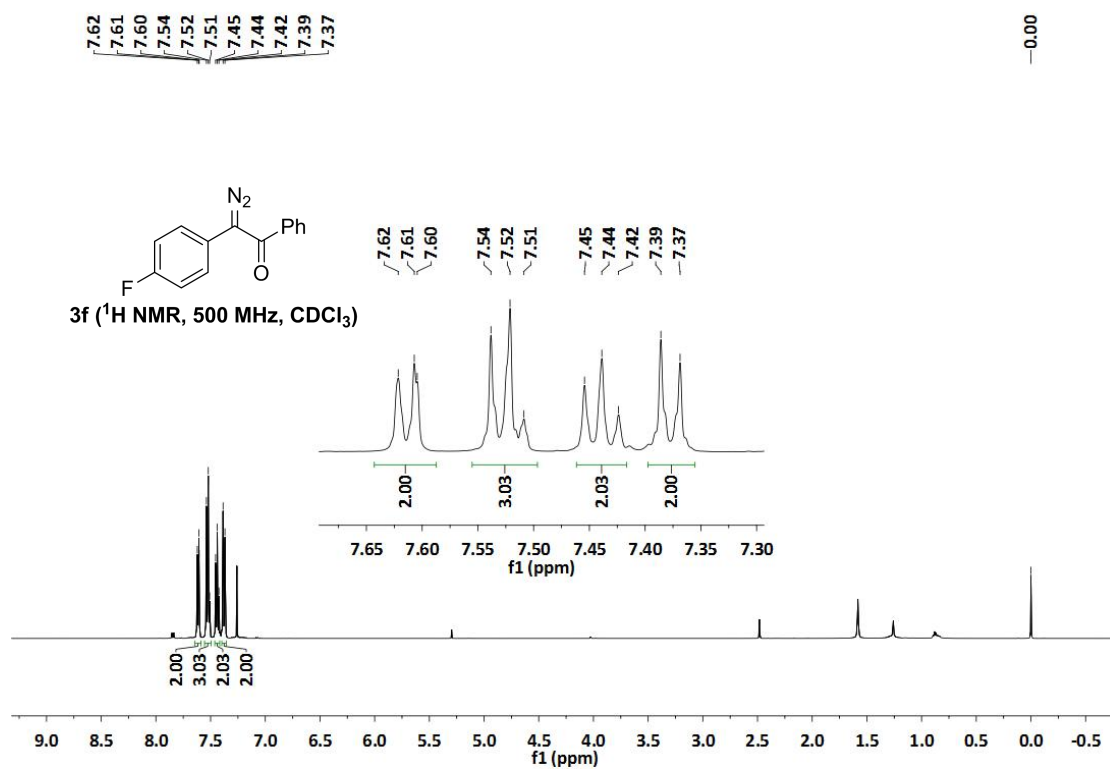
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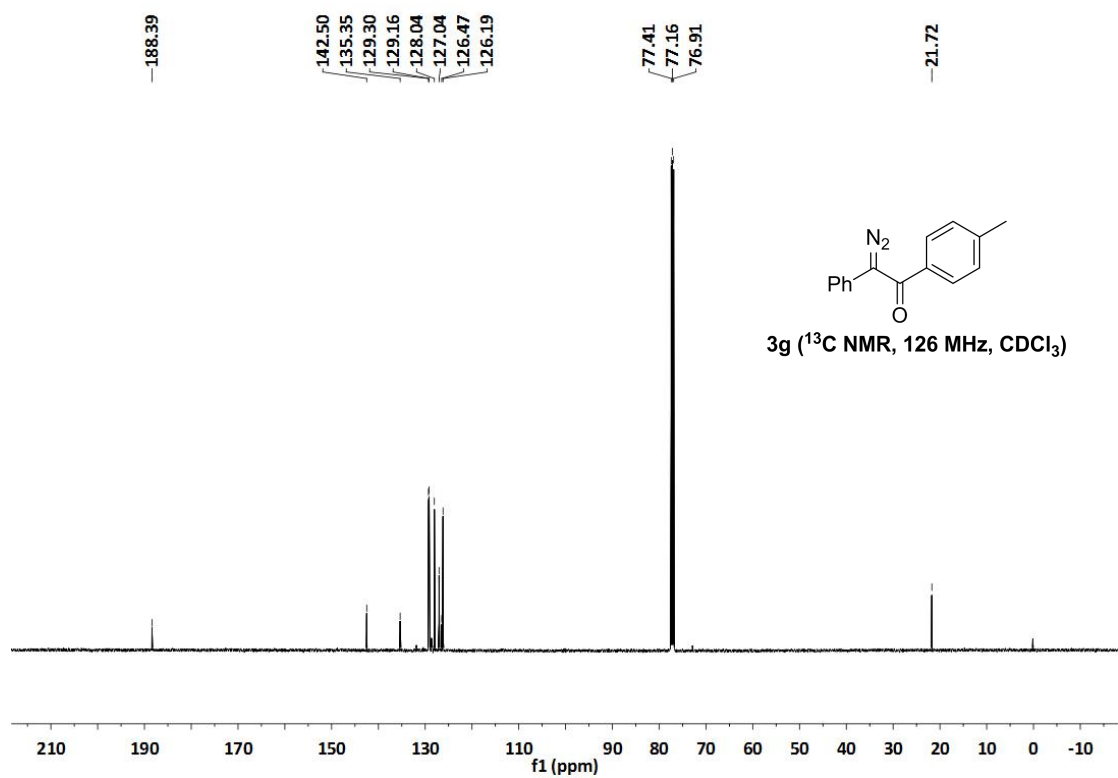
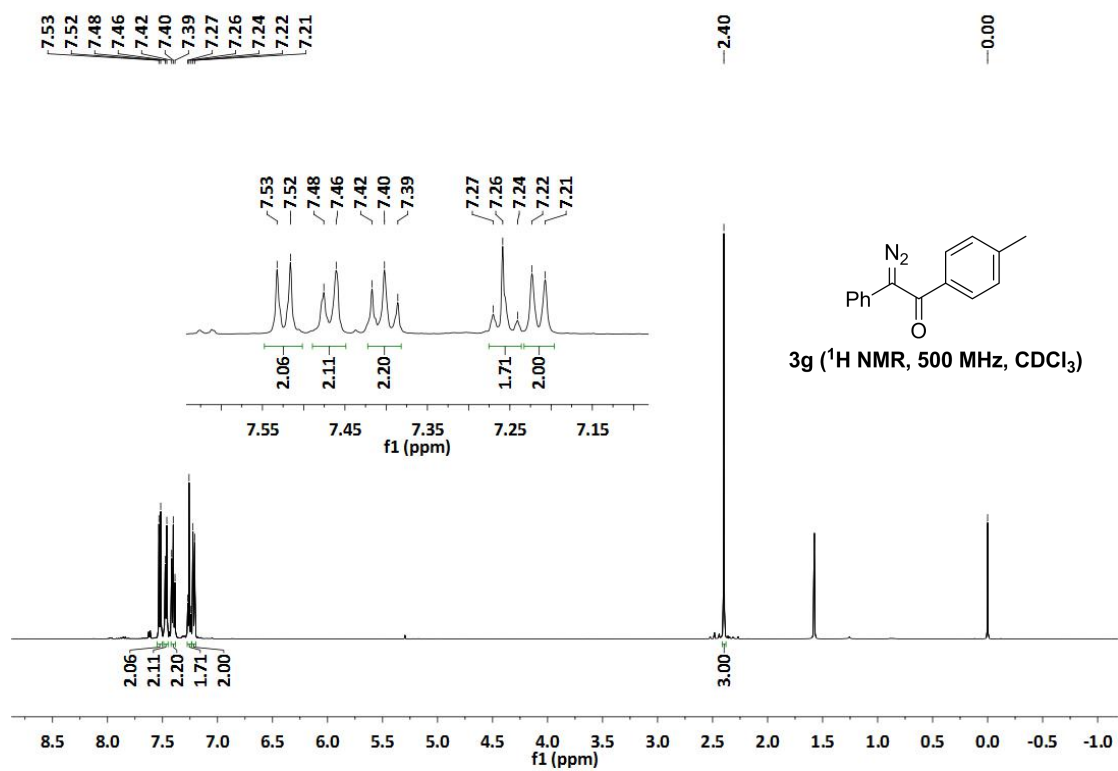
Spectra of substrates

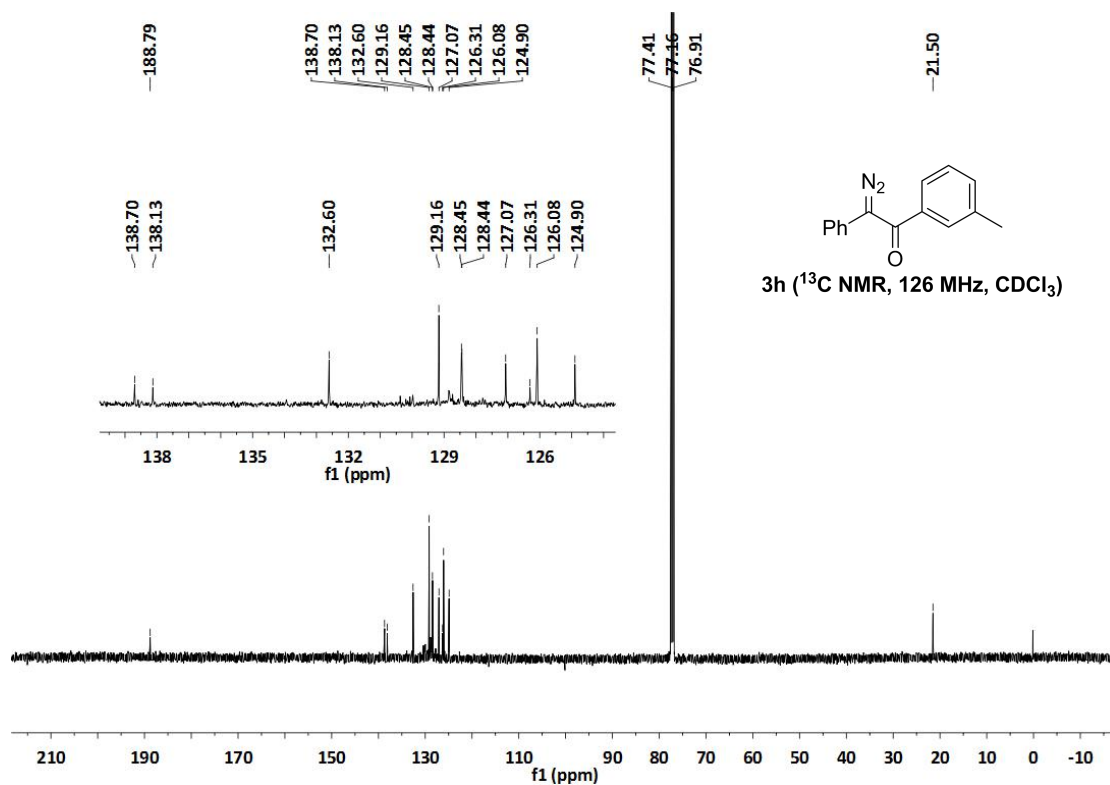
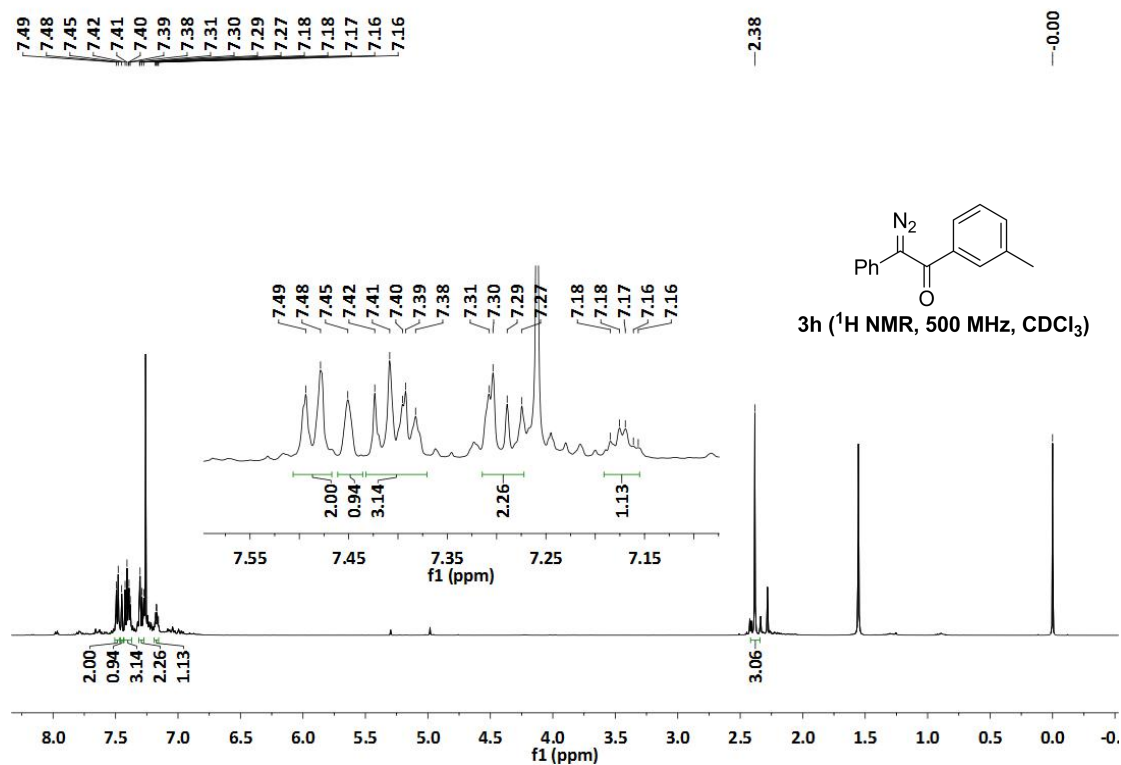


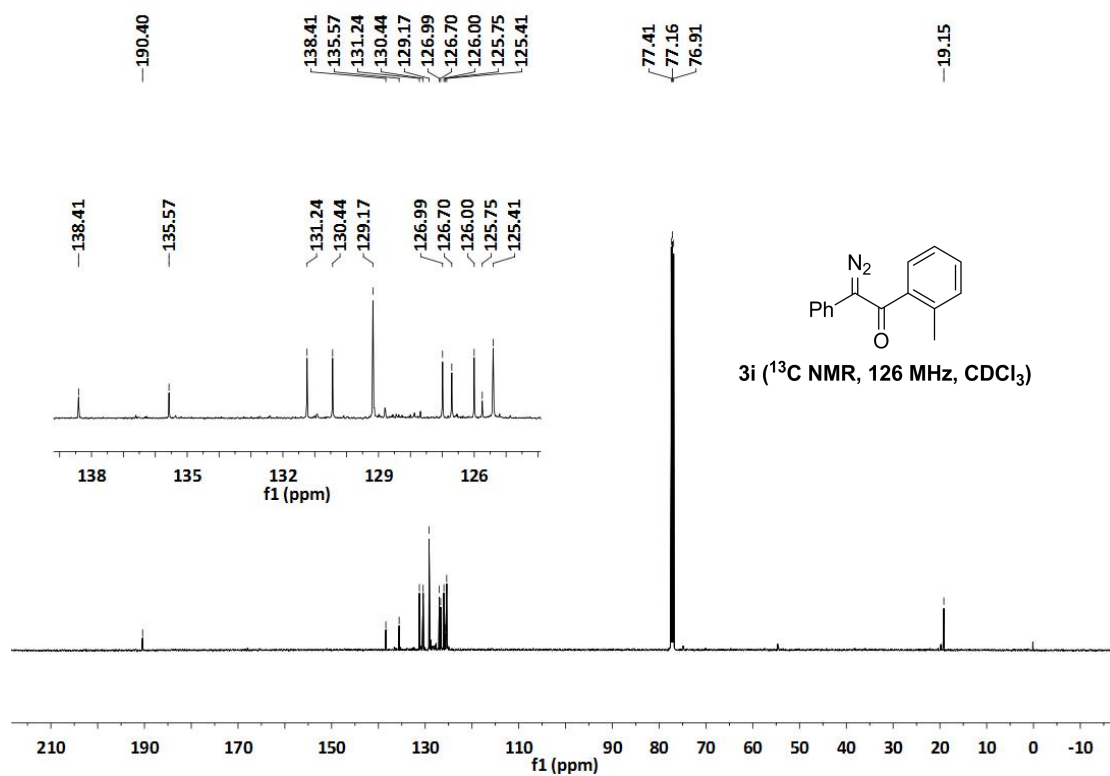
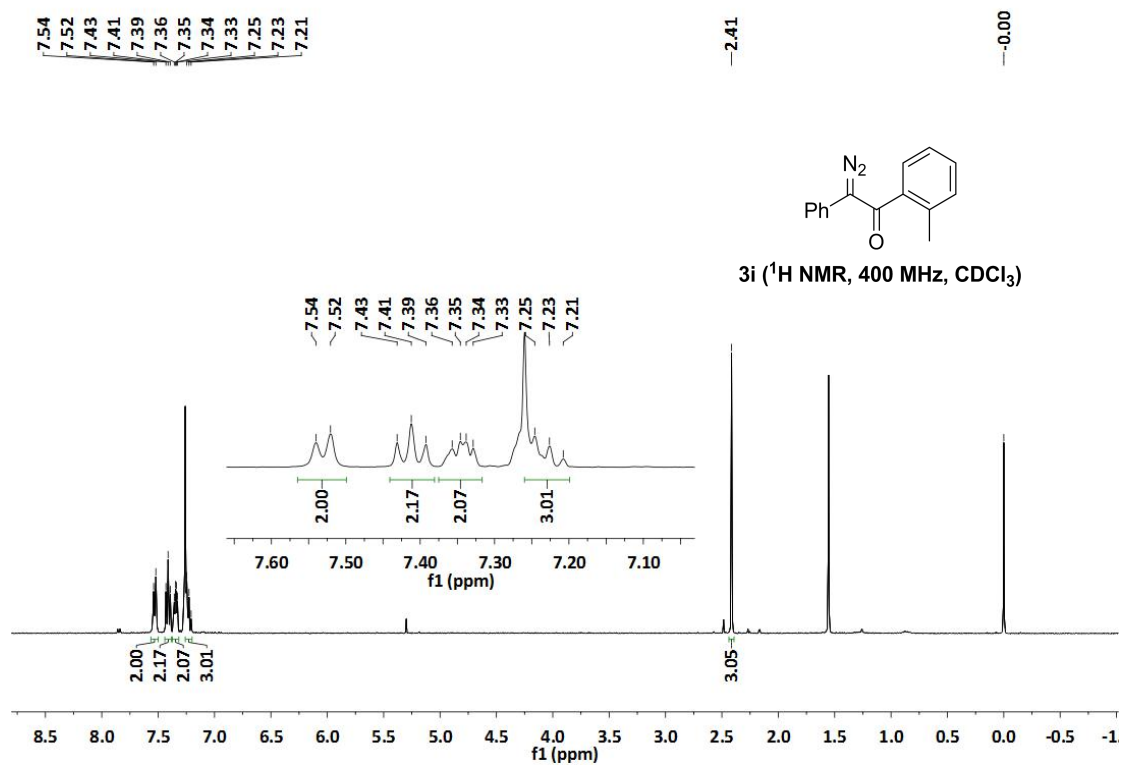


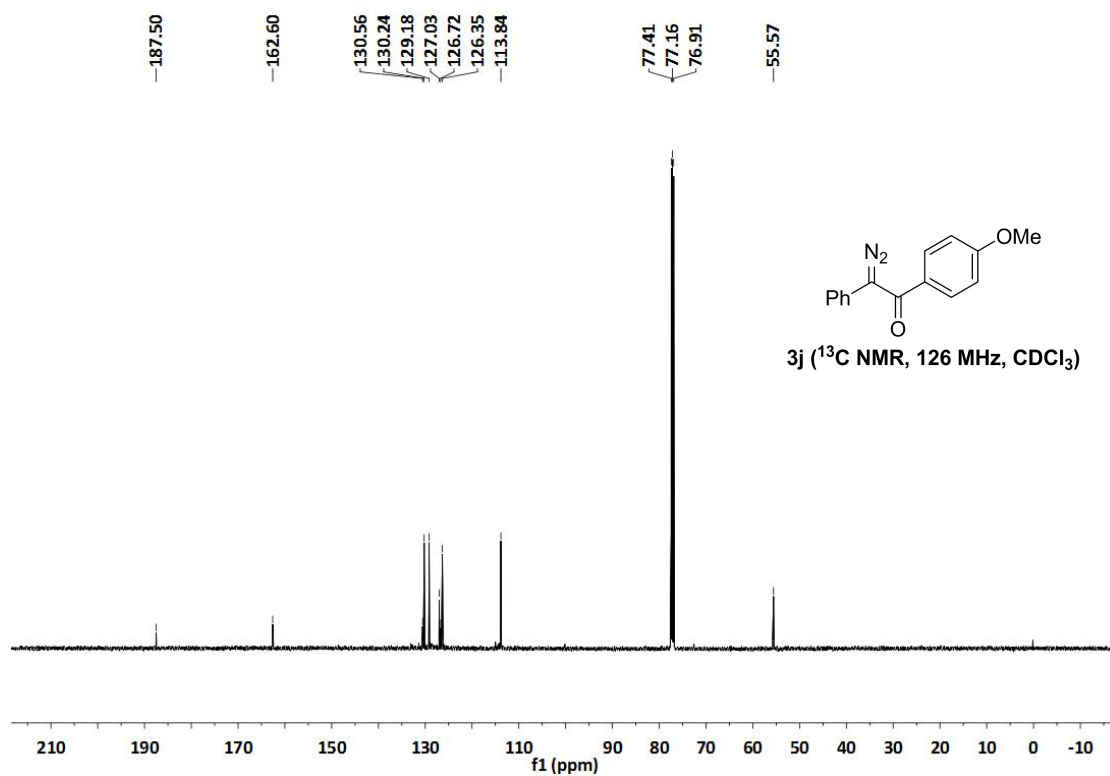
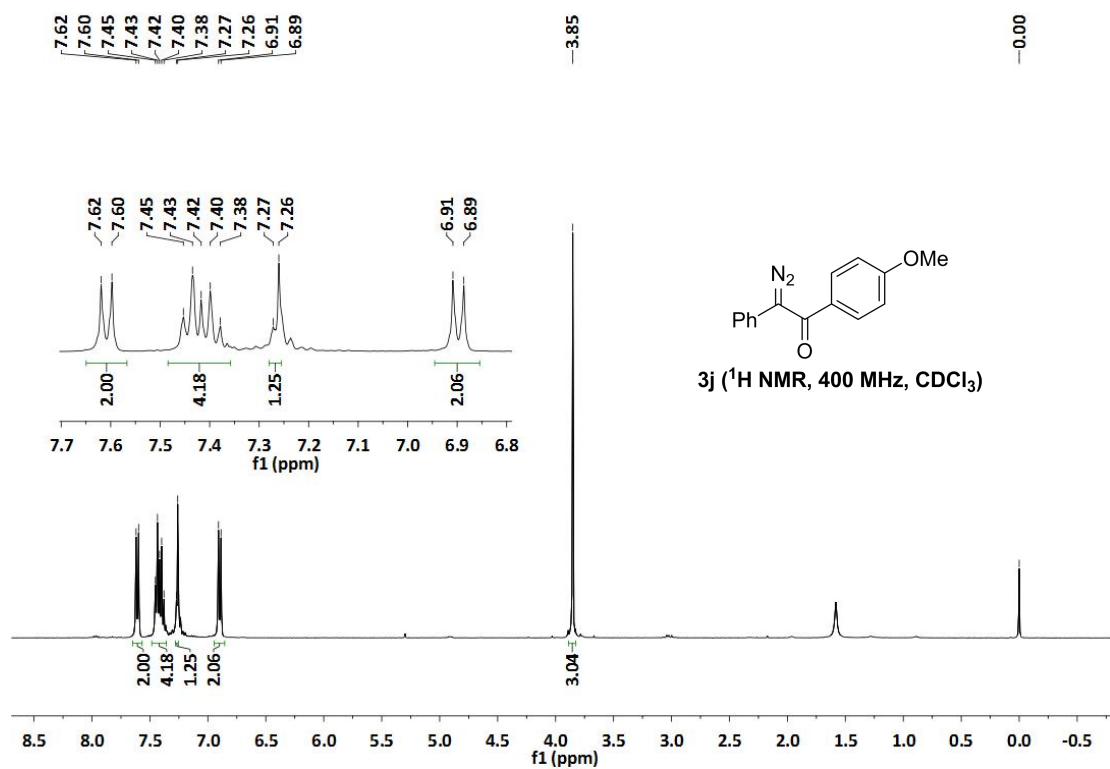


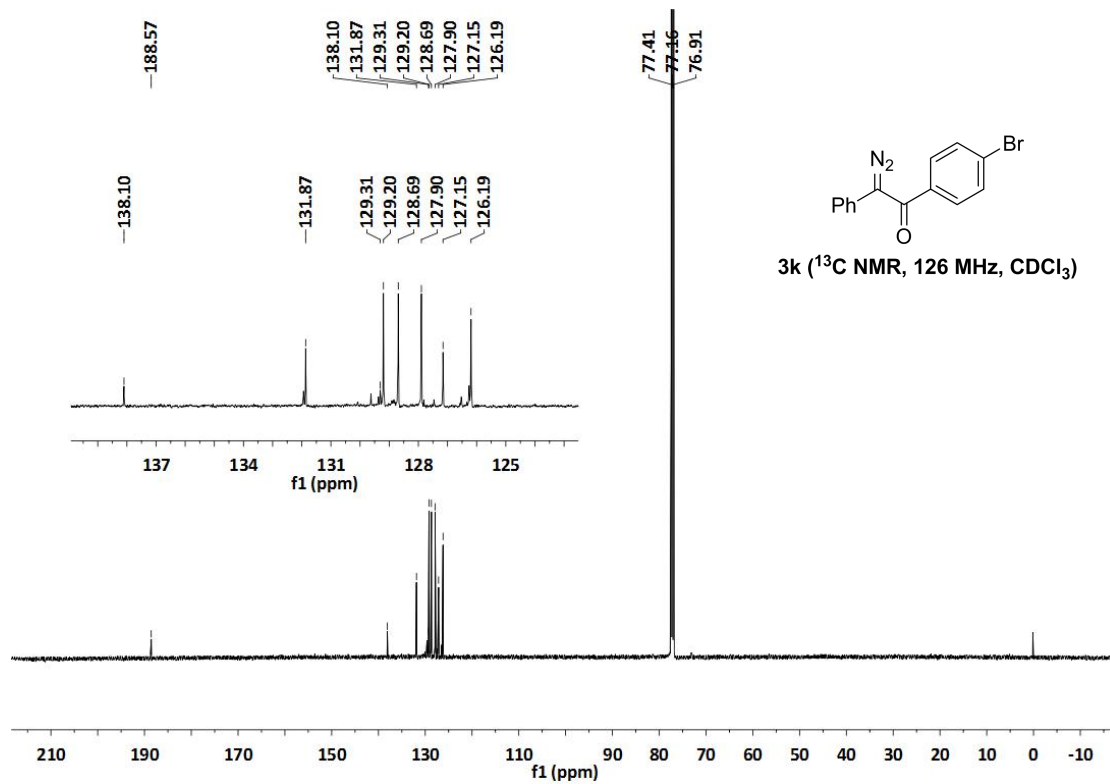
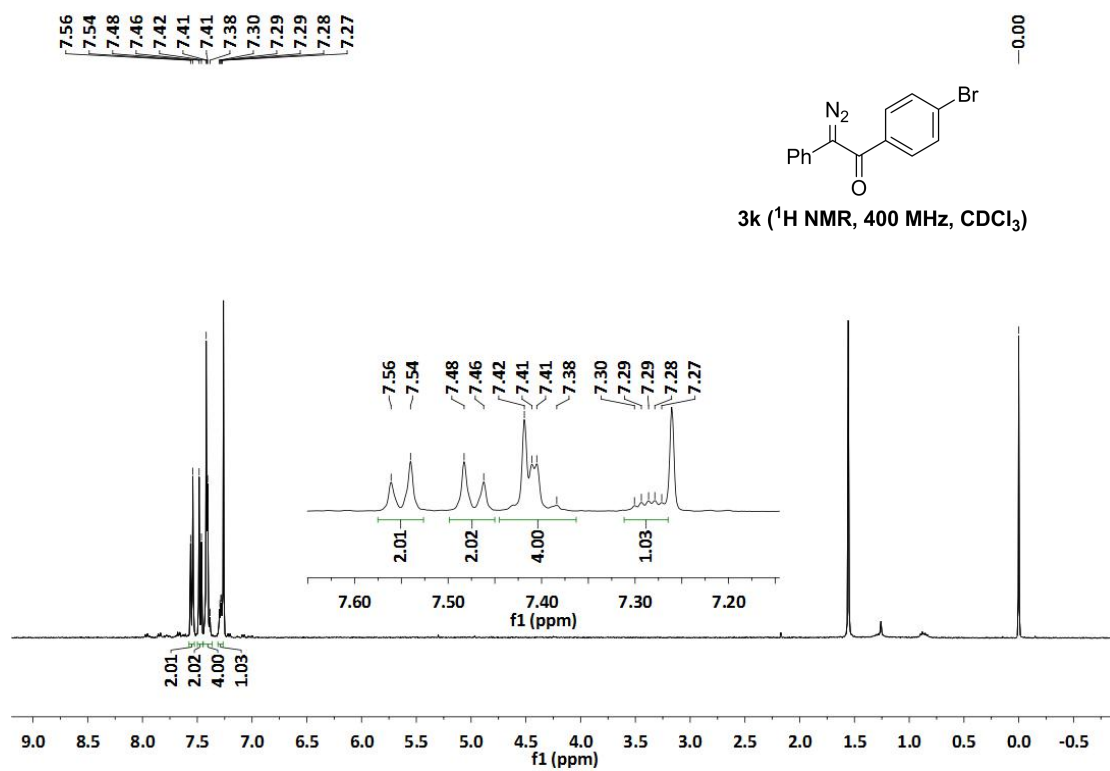


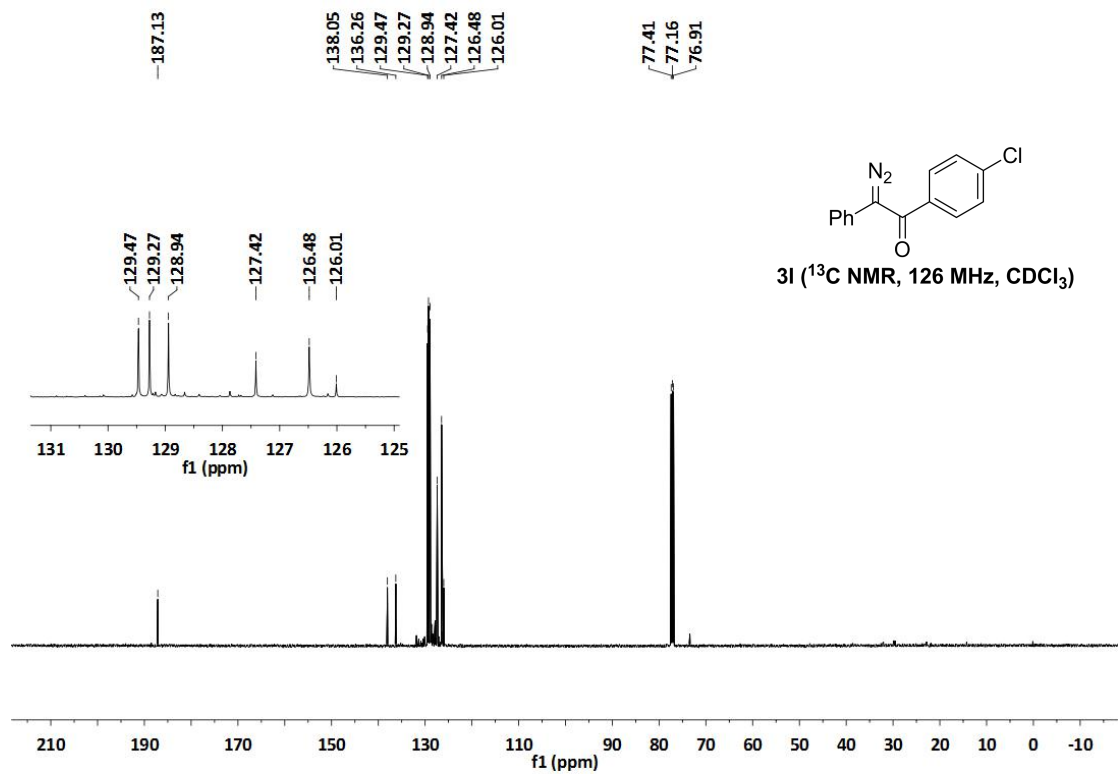
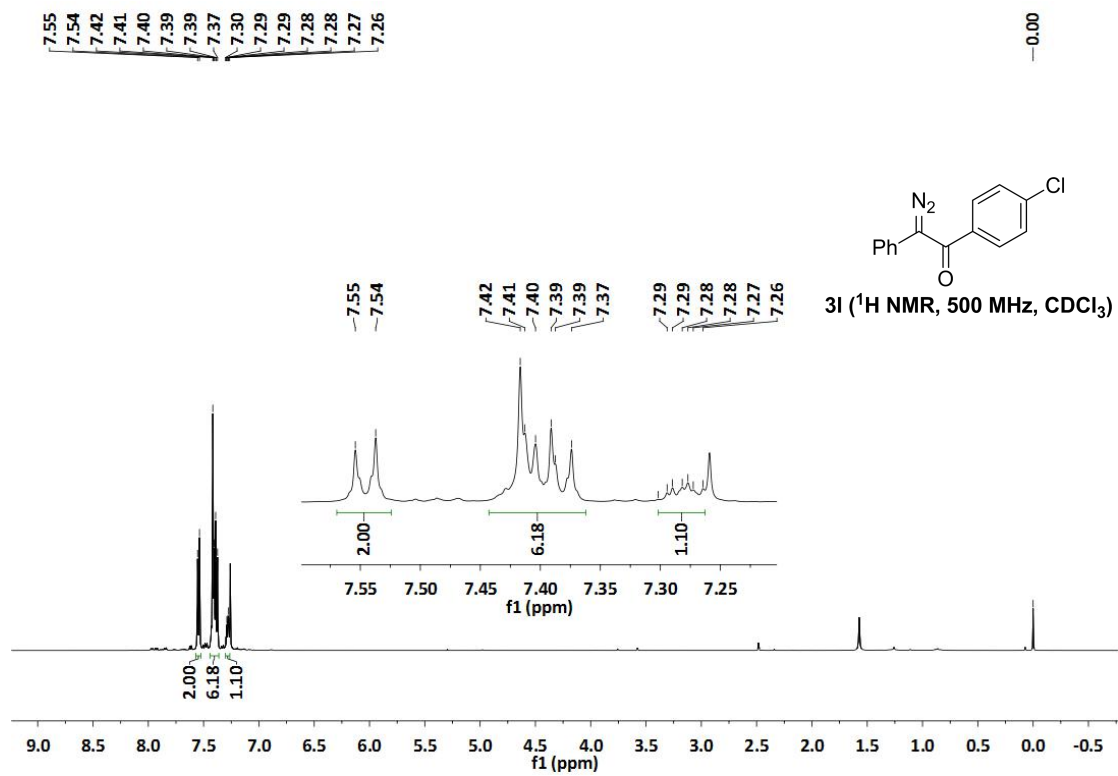


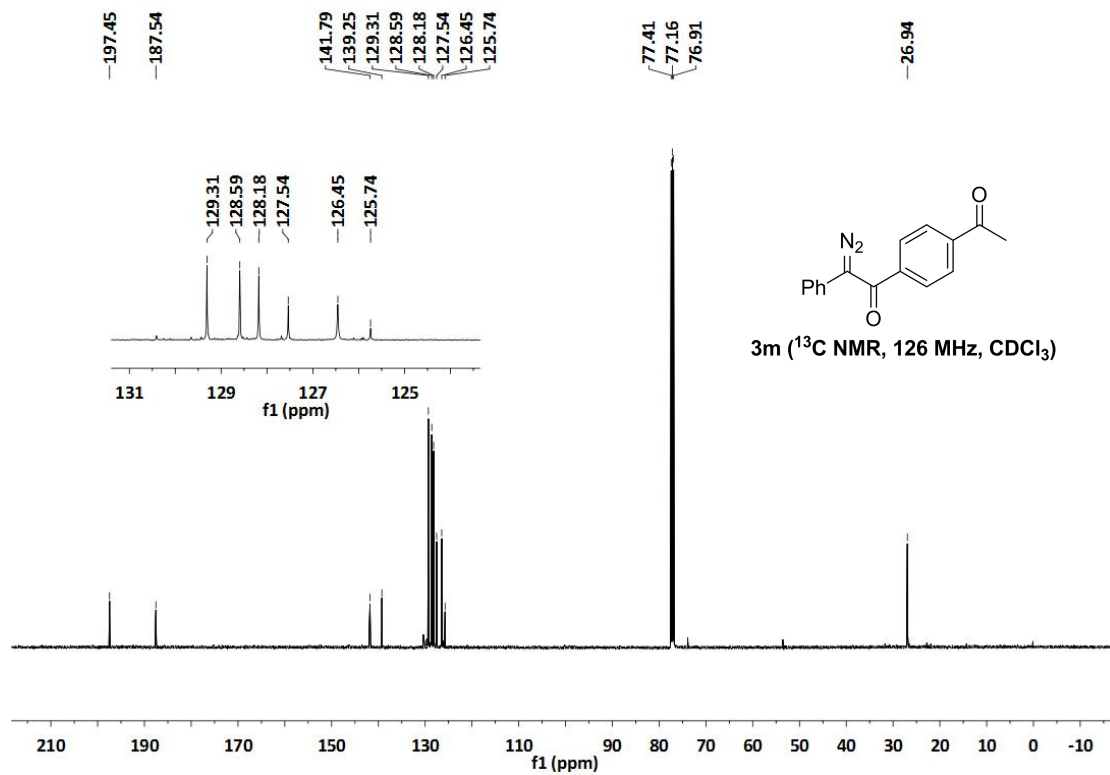
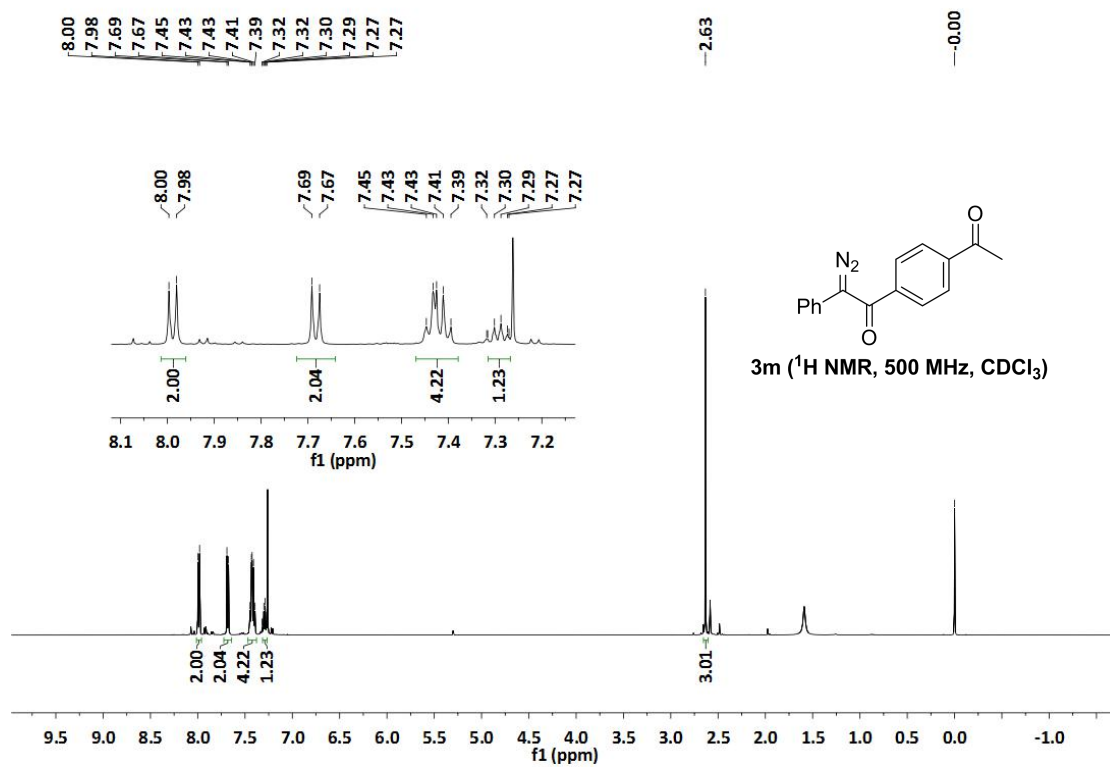


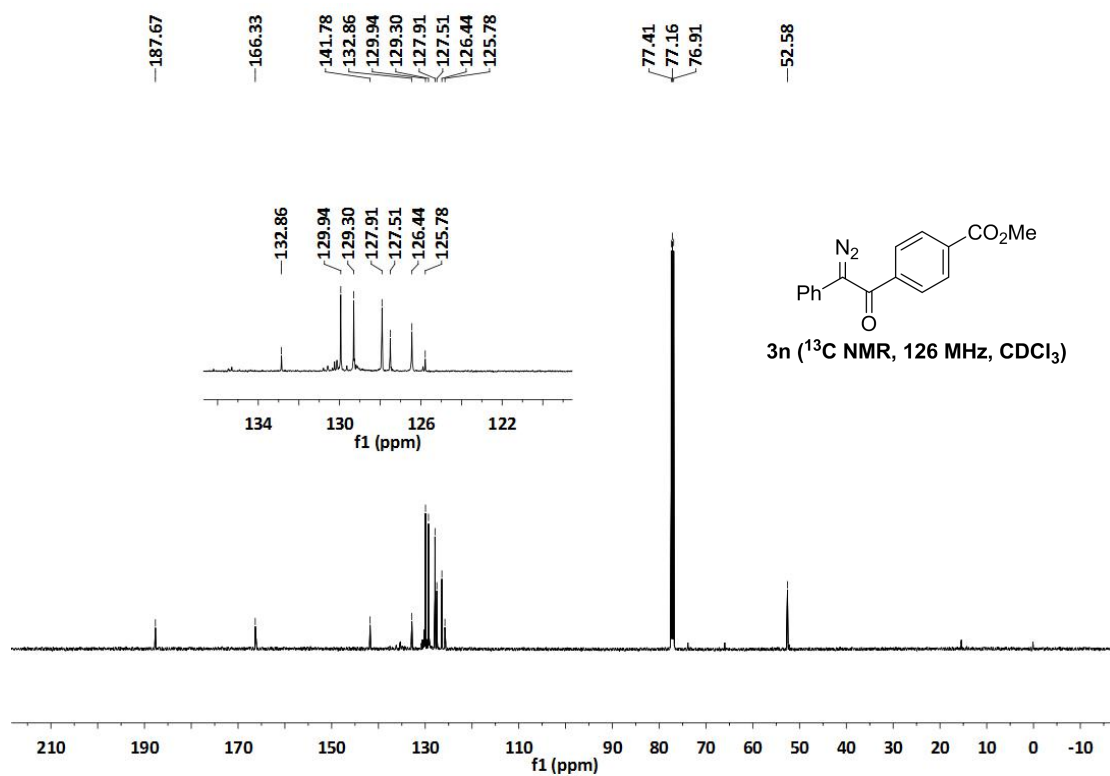
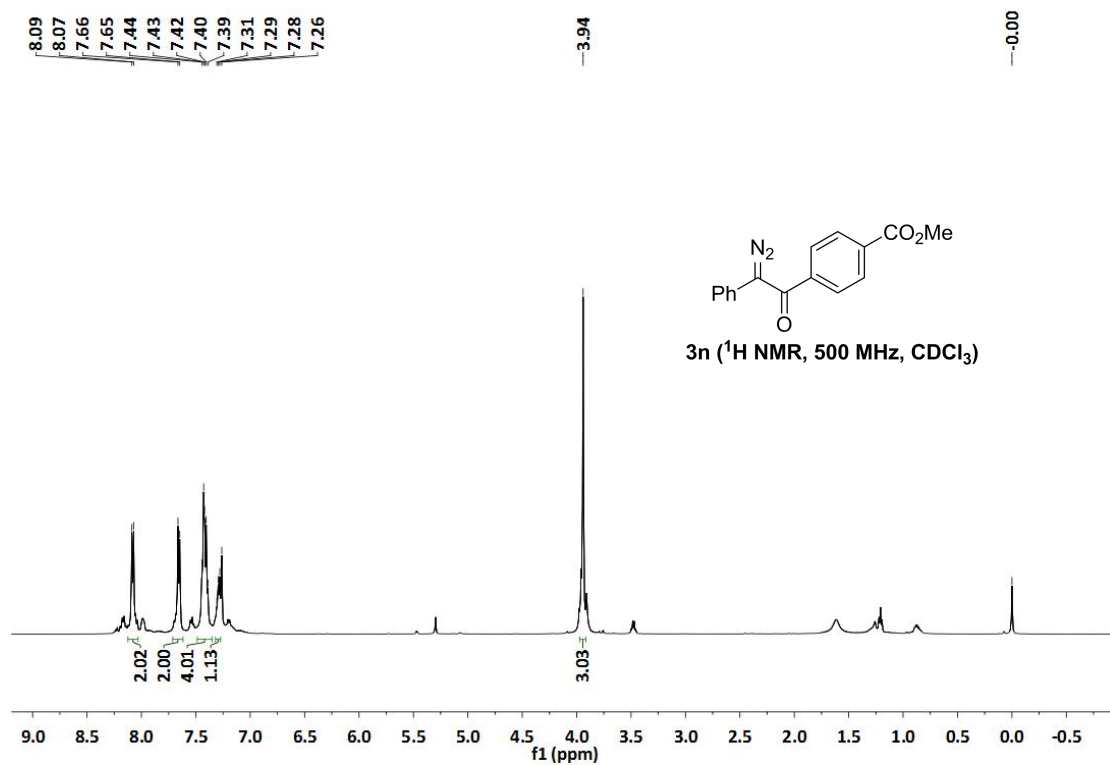


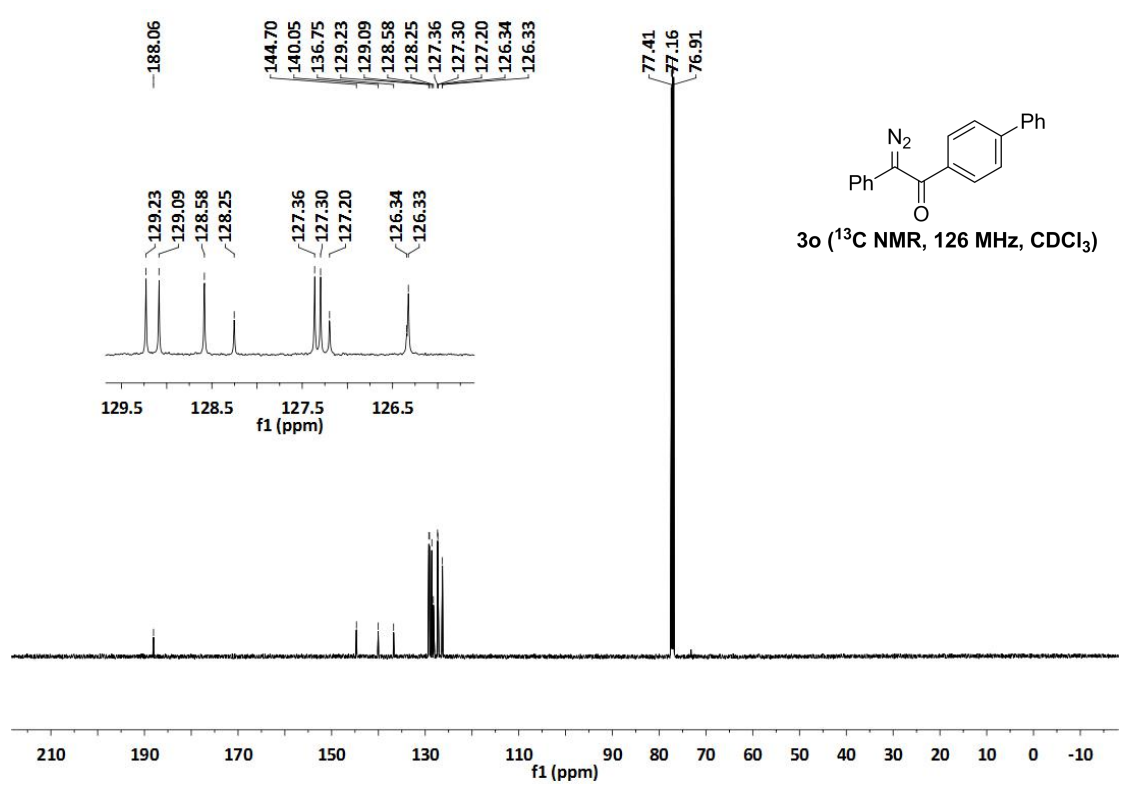
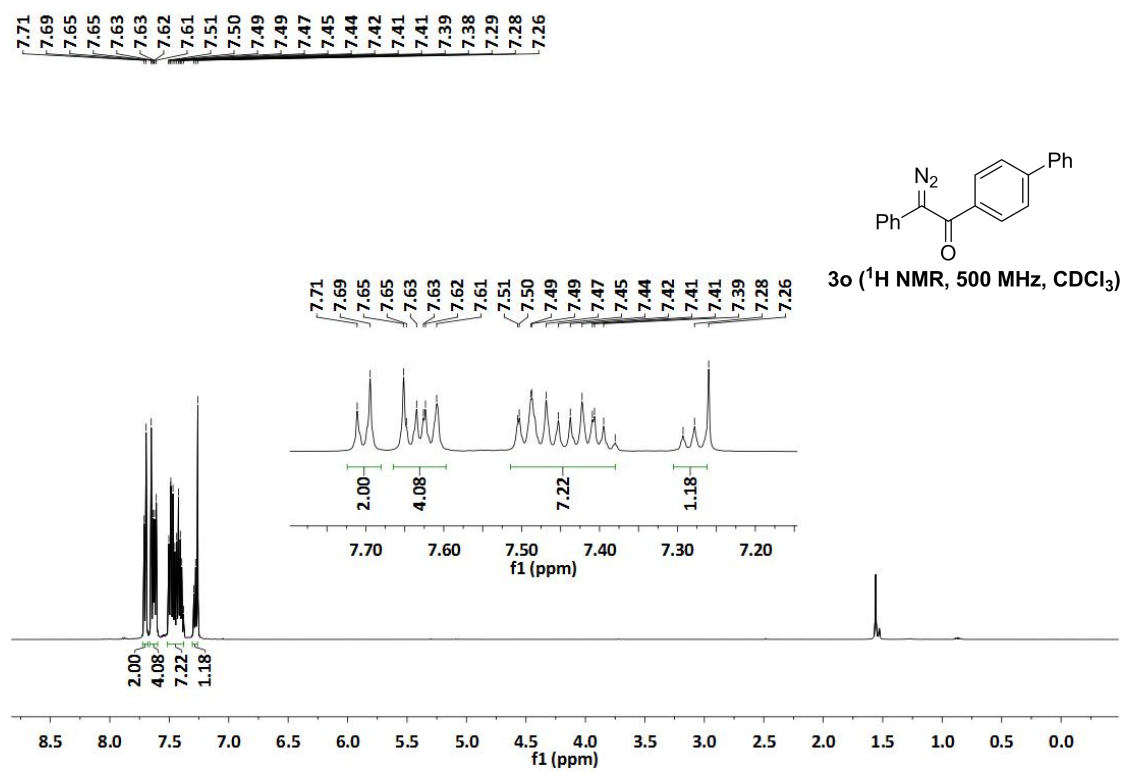


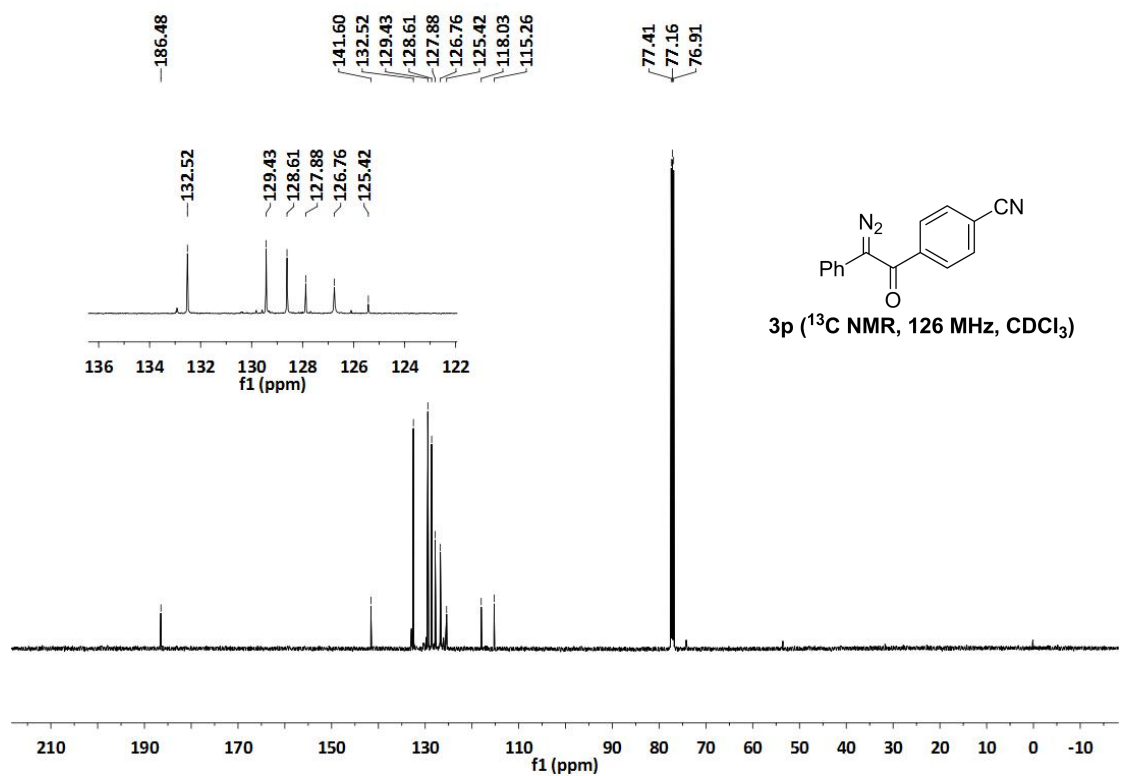
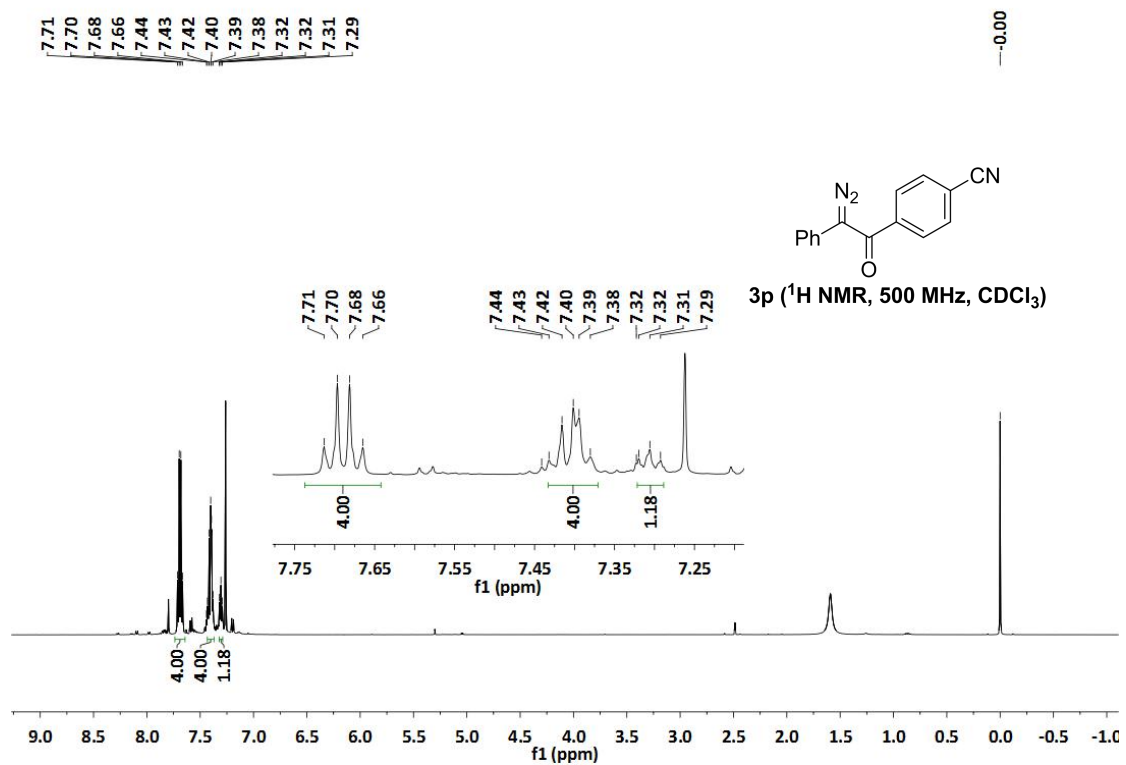


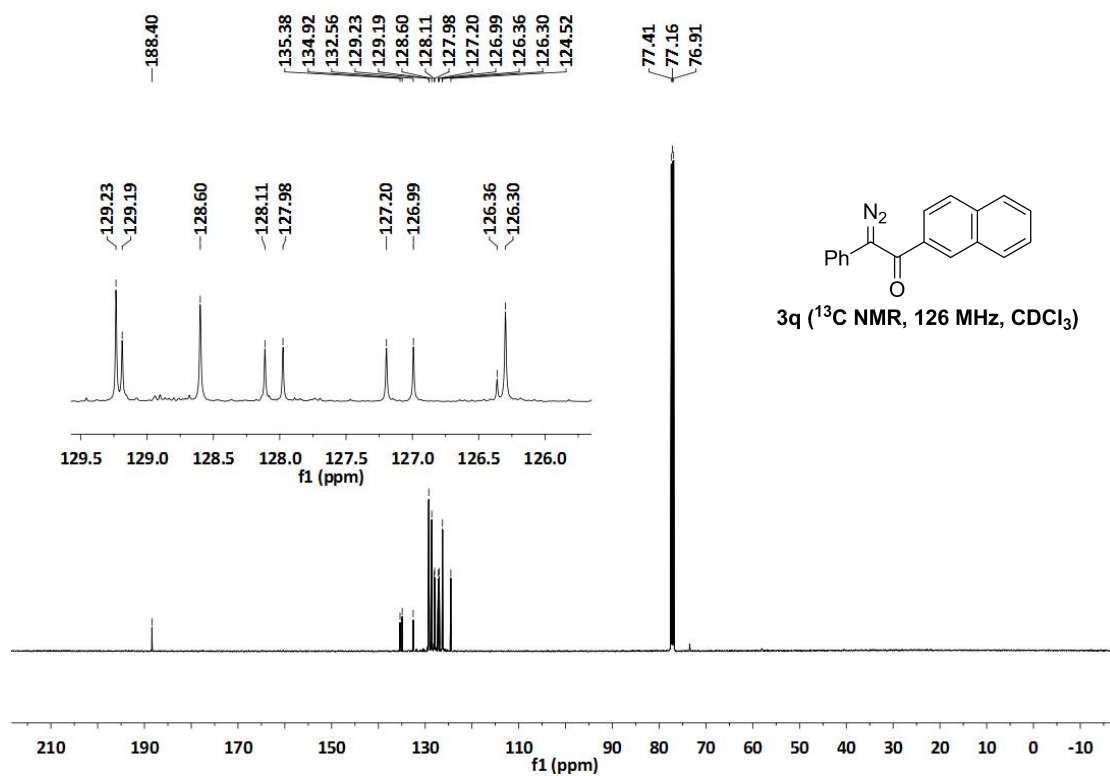
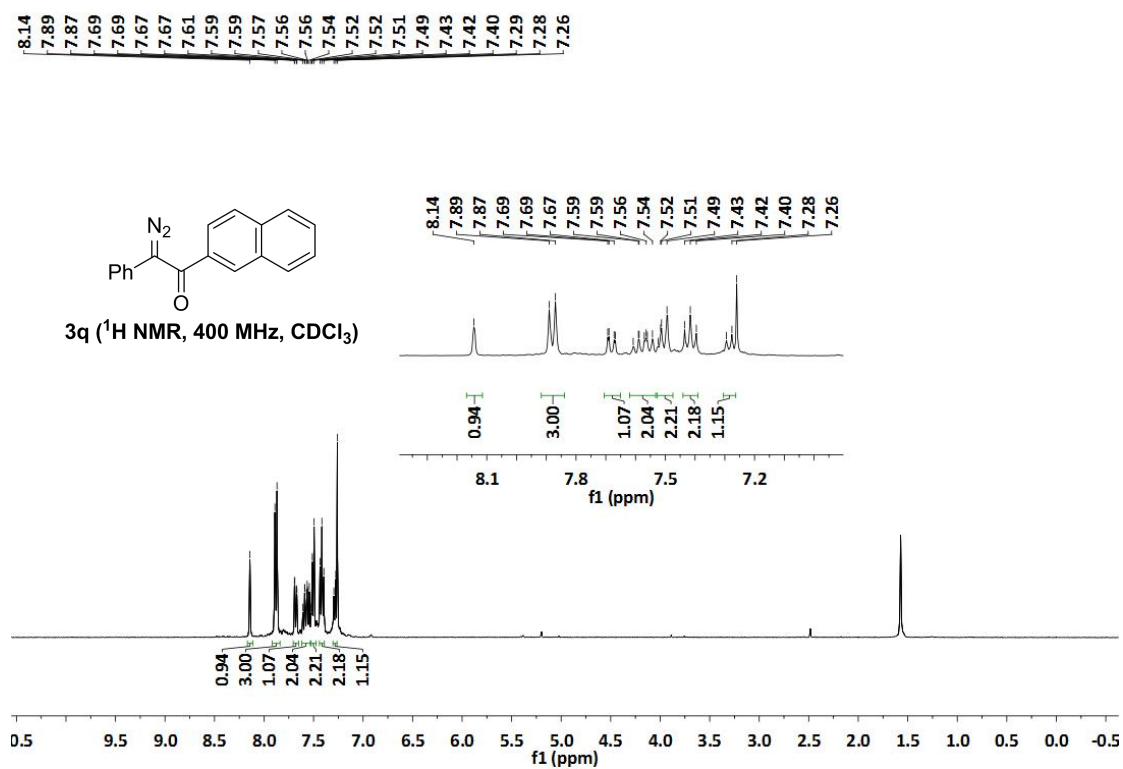


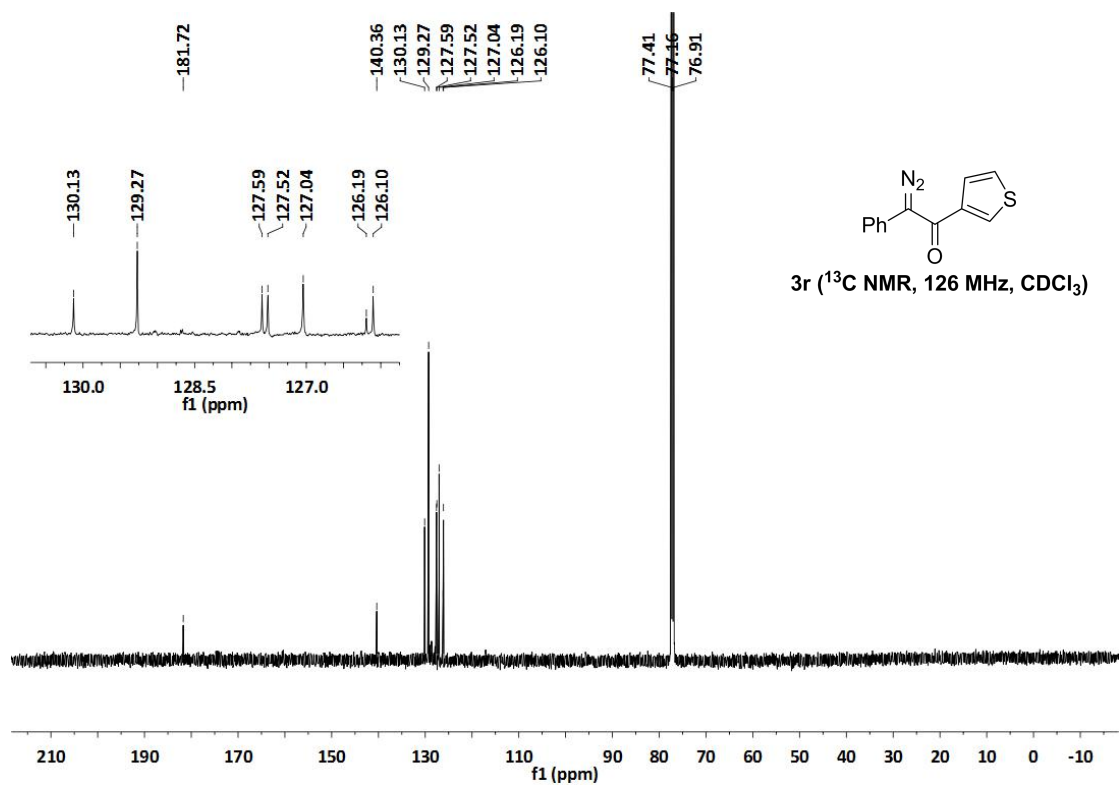
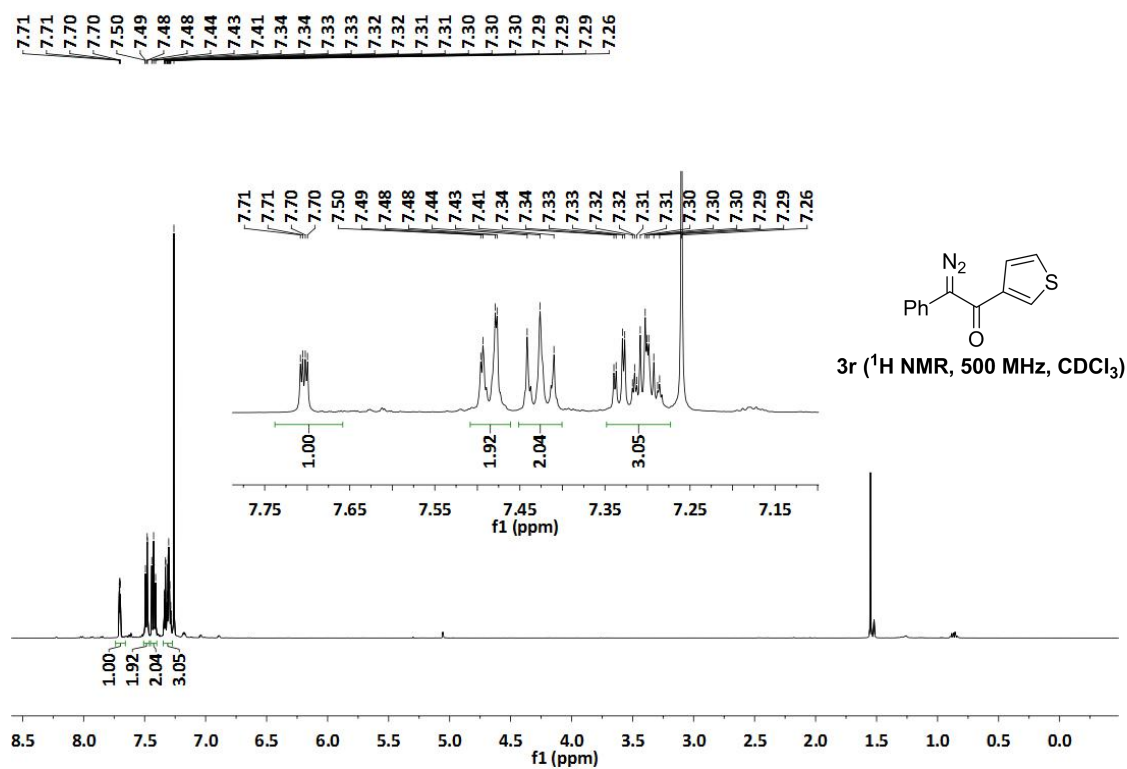












Spectra of products

