

Supporting Information for

TEMPO–Me: An Electrochemically Activated Methylating Agent

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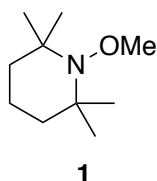
Appendix S1. Synthetic methods and characterisation

1.1 General experimental

Water is deionized water. Brine refers to a saturated aqueous solution of NaCl. Petrol refers to the fraction of petroleum ether boiling in the range 40-60 °C. All synthetic reactions were conducted open to the air. All compounds, reagents and solvents were purchased from commercial sources and used as supplied unless otherwise stated. Flash column chromatography was carried out using Merck silica gel 60 (0.04-0.063 mm, 230-400 mesh). Thin layer chromatography was carried out using Merck F₂₅₄ aluminium-backed silica plates and visualized using UV light (254 and 365 nm), ethanolic anisaldehyde or potassium permanganate solution. ¹H (400 or 600 MHz) and ¹³C (100 or 150 MHz) NMR spectra were recorded on a Bruker AVANCE 400 or 600 instrument. Chemical shifts are quoted as parts per million (ppm) and referenced to CHCl₃ (δ_H 7.26) or CDCl₃ (δ_C 77.16). ¹³C NMR spectra were recorded with broadband proton decoupling, and assigned using DEPT experiments where necessary. Coupling constants (*J*) are quoted in Hertz. Electrospray high resolution mass spectra were recorded on an Orbitrap QE plus or LCT Premier.

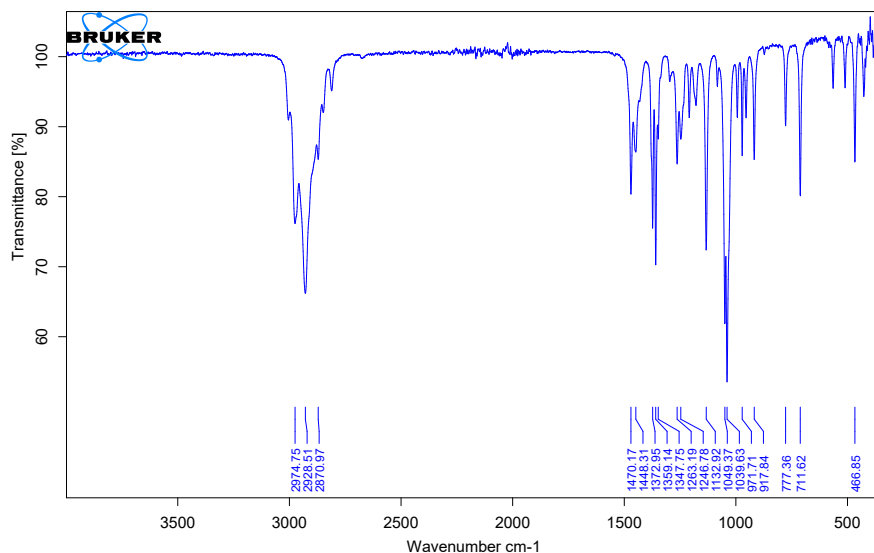
1.2 Synthesis of TEMPO-Me

1-methoxy-2,2,6,6-tetramethylpiperidine (TEMPO-Me, **1**)

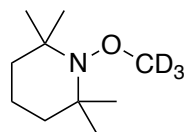


To a solution of 2,2,6,6-tetramethyl-1-piperidinyloxy (5.0 g, 32 mmol) in DMSO (125 mL) at 10 °C was added iron(II) sulfate heptahydrate (12.2 g, 43.9 mmol, 1.4 eq.), then H₂O₂ solution (30% v/v, 18.2 mL, 5 eq.) was added dropwise *via* syringe pump over 3 hours, maintaining the temperature between 5-10 °C. The reaction mixture was stirred for a further hour, then diluted with H₂O (100 mL), extracted with Et₂O (3 × 100 mL), washed with brine (50 mL), dried over Na₂SO₄ and concentrated under reduced pressure. Purified by flash chromatography, eluting with 5% EtOAc-petrol, to give 1-methoxy-2,2,6,6-tetramethylpiperidine (**1**) (5.2 g, 94%) as a colourless oil; ¹H NMR (400 MHz; CDCl₃) 3.56 (s, 3H), 1.50-1.26 (m, 6H), 1.13 (s, 6H), 1.04

(s, 6H); ^{13}C NMR (100 MHz, CDCl_3) 65.4 (CH_3), 59.8 (C), 39.8 (CH_2), 33.1 (CH_3), 20.1 (CH_3), 17.2 (CH_2); HRMS (ESI) m/z calculated for $\text{C}_{10}\text{H}_{22}\text{NO}^+$ ($\text{M} + \text{H}$) $^+$ 172.1696, found 172.1696 (+0.227 ppm error).



1-(d_3 -methoxy)-2,2,6,6-tetramethylpiperidine (d_3 -1)



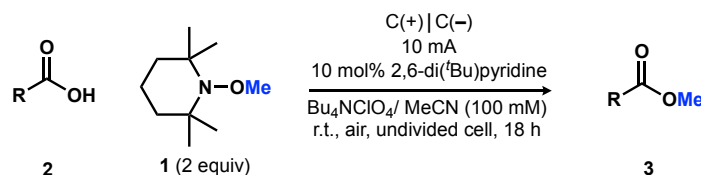
d_3 -1

To a solution of 2,2,6,6-tetramethyl-1-piperidinyloxy (780 mg, 5.0 mmol) in d_6 -DMSO (10 g) at 10 °C was added iron(II) sulfate heptahydrate (1.9 g, 6.8 mmol, 1.4 eq.), then H_2O_2 solution (30% v/v, 2.9 mL, 5 eq.) was added dropwise via syringe pump over 1 hour, maintaining the temperature between 5-10 °C. The reaction mixture was stirred for a further hour, then diluted with H_2O (50 mL), extracted with Et_2O (3×50 mL), washed with brine (20 mL), dried over Na_2SO_4 and concentrated under reduced pressure. Purified by flash chromatography, eluting with 5% EtOAc-petrol, to give 1-(d_3 -methoxy)-2,2,6,6-tetramethylpiperidine (d_3 -1) (509 mg, 59%) as a colourless oil; ^1H NMR (400 MHz; CDCl_3) 1.46-1.22 (m, 6H), 1.08 (s, 6H), 0.99 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3) 64.4 (sept, $J = 21.5$ Hz, CD_3), 59.7 (C), 39.7 (CH_2), 33.1 (CH_3), 20.0 (CH_3), 17.2 (CH_2); HRMS (ESI) m/z calculated for $\text{C}_{10}\text{H}_{19}\text{D}_3\text{NO}^+$ ($\text{M} + \text{H}$) $^+$ 175.1884, found 175.1893 (+5.1 ppm error).

1.3 General procedures for the electrochemical methylation of carboxylic acids

General Procedure A – Undivided Cell: Figure 2 of main text

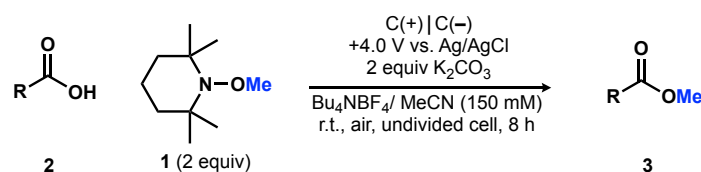
ElectraSyn 2.0 (IKA); constant current



The carboxylic acid (0.5 mmol, 1 eq.), TEMPO-Me (**1**) (171 mg, 1.0 mmol, 2 eq.), and 2,6-di(*tert*-butyl)pyridine (12 μL , 0.05 mmol, 10 mol%) were added to a solution of Bu_4NClO_4 (342 mg, 1.0 mmol) in CH_3CN (10 mL) in a 10 mL ElectraSyn vial, fitted with two graphite electrodes. A constant current of 10 mA was applied for 18 hours with stirring at 500 rpm. H_2O (10 mL) was then added and the mixture was extracted with Et_2O (3 x 10 mL). The combined organic layers were dried over MgSO_4 , concentrated under reduced pressure and purified by flash column chromatography with 5% EtOAc/hexane as eluent to give the desired compound.

General Procedure B – Alternative Procedure; Undivided Cell: Figure 2 of main text

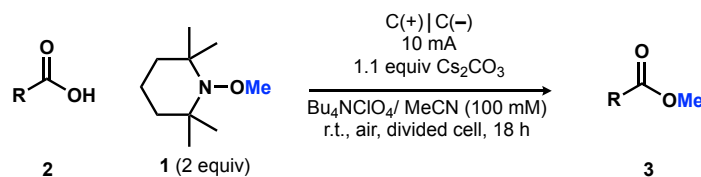
ElectraSyn 2.0 (IKA); constant voltage



The carboxylic acid (1.0 mmol, 1 eq.), TEMPO-Me (**1**) (342 mg, 2.0 mmol, 2 eq.), and K_2CO_3 (272 mg, 2.0 mmol, 2.0 eq.) were added to a solution of Bu_4NBF_4 (979 mg, 3.0 mmol) in CH_3CN (20 mL) in a 20 mL ElectraSyn vial, fitted with two graphite electrodes. A voltage of 4.0 V vs. Ag/AgCl with a variable current (alternating direction, every 2 min) was applied for 8 hours with stirring at 500 rpm. H_2O (15 mL) was then added and the mixture was extracted with Et_2O (3 x 10 mL). The combined organic layers were dried over MgSO_4 , concentrated under reduced pressure and purified by flash column chromatography with 5% EtOAc/hexane as eluent to give the desired compound.

General Procedure C – Divided Cell: Figure 2 of main text

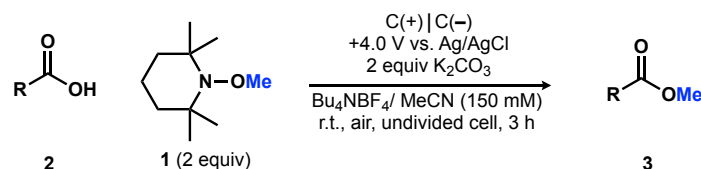
Custom H-cell with ElectraSyn 2.0 (IKA) as power source



The carboxylic acid (1.0 mmol, 1 eq.), TEMPO-Me (**1**) (342 mg, 2.0 mmol, 2 eq.), and cesium carbonate (358 mg, 1.1 mmol, 1.1 eq.) were added to a solution of Bu_4NClO_4 (684 mg, 2.0 mmol) in CH_3CN (20 mL) in the anodic chamber of a glass H-cell described in Appendix S3. A solution of Bu_4NClO_4 (684 mg, 2.0 mmol) in CH_3CN (20 mL) was added to the cathodic chamber. Using two cylindrical graphite electrodes (see Appendix S3) connected to an Electrasyn 2.0 as the power source, a constant current of 10 mA was applied for 18 hours. The solution in the anodic chamber was diluted with H_2O (20 mL) and the mixture was extracted with Et_2O (3 x 20 mL). The combined organic layers were dried over MgSO_4 , concentrated under reduced pressure and purified by flash column chromatography with 5% EtOAc/hexane as eluent to give the desired compound.

General Procedure D – Undivided Cell: Table S1

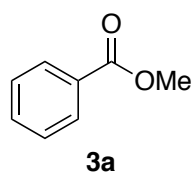
ElectraSyn 2.0 (IKA); potentiostatic operation: 0.2 mmol-scale



Benzoic acid (24.4 mg, 200 μmol , 1 eq.), TEMPO-Me (**1**) (68.4 mg, 400 μmol , 2 eq.), and K_2CO_3 (55.2 mg, 400 μmol , 2.0 eq.) were added to a solution of Bu_4NBF_4 (200 mg, 600 μmol) in CH_3CN (2 mL) in a 10 mL ElectraSyn vial, fitted with two graphite electrodes. A voltage of 4.0 V vs. Ag/AgCl with a variable current (alternating direction, every 0.25 min) was applied for 3 hours with stirring at 600 rpm. After this time, the vial was removed from the ElectraSyn unit, uncapped, and a solution of anthracene (35.6 mg, 200 μmol ; internal standard) in CH_2Cl_2 (2 mL) was added. An aliquot (500 μL) was then obtained from this mixture and analyzed by GC.

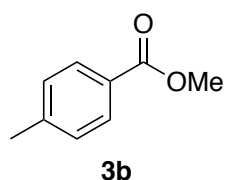
1.4 Characterisation data of methylation products

Methyl benzoate **3a**



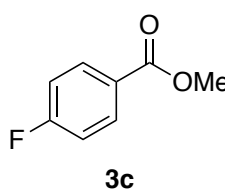
Using General Procedure A, benzoic acid (61 mg, 0.5 mmol) gave methyl benzoate (**3a**) (62 mg, 91%) as a colourless oil; $^1\text{H NMR}$ (400 MHz; CDCl_3) 8.04 (d, $J = 7.7$ Hz, 2H), 7.55 (t, $J = 7.5$ Hz, 1H), 7.44 (app t, $J = 7.7$ Hz, 2H), 3.92 (s, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) 167.2 (C), 133.0 (CH), 130.3 (C), 129.7 (CH), 128.5 (CH), 52.2 (CH_3).

Methyl *p*-toluate **3b**



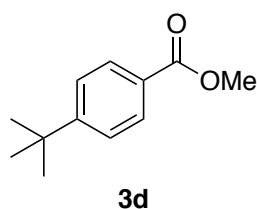
Using General Procedure A, *p*-toluic acid (68 mg, 0.5 mmol) gave methyl *p*-toluate (**3b**) (73 mg, 97%) as a colourless oil; $^1\text{H NMR}$ (400 MHz; CDCl_3) 7.93 (d, $J = 8.1$ Hz, 2H), 7.23 (d, $J = 8.1$ Hz, 2H), 3.90 (s, 3H), 2.40 (s, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) 167.3 (C), 143.7 (C), 129.7 (CH), 129.2 (CH), 127.6 (C), 52.1 (CH_3), 21.8 (CH_3).

Methyl 4-fluorobenzoate **3c**



Using General Procedure B, 4-fluorobenzoic acid (140 mg, 1.0 mmol) gave methyl 4-fluorobenzoate (**3c**) (128 mg, 83%) as a colourless oil; $^1\text{H NMR}$ (600 MHz; CDCl_3) 8.05 (dd, $J = 8.7, 5.6$ Hz, 2H), 7.10 (dd, $J = 8.7, 8.7$ Hz, 2H), 3.91 (s, 3H); $^{13}\text{C NMR}$ (150 MHz, CDCl_3) 166.3 (C), 165.9 (d, $^1J_{\text{C-F}} = 252.3$ Hz, C), 132.3 (d, $^3J_{\text{C-F}} = 9.3$ Hz, CH), 126.6 (C), 115.6 (d, $^2J_{\text{C-F}} = 21.9$ Hz, CH), 52.3 (CH_3).

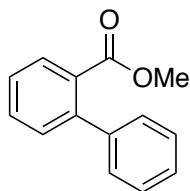
Methyl 4-(*tert*-butyl)benzoate **3d**



Using General Procedure A, 4-(*tert*-butyl)benzoic acid (89 mg, 0.5 mmol) gave methyl 4-(*tert*-butyl)benzoate (**3d**) (83 mg, 86%) as a colourless oil; $^1\text{H NMR}$ (400 MHz; CDCl_3) 7.97 (d, $J = 8.6$ Hz, 2H), 7.45 (d, $J = 8.6$ Hz, 2H), 3.90 (s, 3H), 1.34 (s, 9H); $^{13}\text{C NMR}$ (100 MHz,

CDCl₃) 167.3 (C), 156.7 (C), 129.6 (CH), 127.5 (C), 125.5 (CH), 52.1 (CH₃), 35.2 (C), 31. (CH₃).

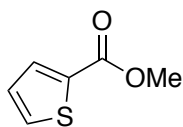
Methyl 2-phenylbenzoate **3e**



3e

Using General Procedure A, 2-phenylbenzoic acid (99 mg, 0.5 mmol) gave methyl 2-phenylbenzoate (**3e**) (77 mg, 73%) as a colourless oil; ¹H NMR (400 MHz; CDCl₃) 7.85 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.54 (td, *J* = 7.6, 1.5 Hz, 1H), 7.45-7.33 (m, 7H), 3.65 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) 169.2 (C), 142.5 (C), 141.4 (C), 131.3 (CH), 131.0 (C), 130.8 (CH), 129.8 (CH), 128.4 (CH), 128.1 (CH), 127.3 (CH), 127.2 (CH), 52.0 (CH₃).

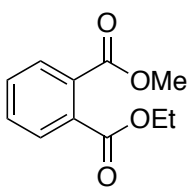
Methyl thiophene-2-carboxylate **3f**



3f

Using General Procedure A, thiophene-2-carboxylic acid (64 mg, 0.5 mmol) gave methyl thiophene-2-carboxylate (**3f**) (65 mg, 92%) as a colourless oil; ¹H NMR (400 MHz; CDCl₃) 7.80 (dd, *J* = 3.7, 1.2 Hz, 1H), 7.55 (dd, *J* = 5.0, 1.2 Hz, 1H), 7.10 (dd, *J* = 5.0, 3.7 Hz, 1H), 3.89 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) 162.8 (C), 133.7 (C), 133.6 (CH), 132.5 (CH), 127.9 (CH), 52.3 (CH₃).

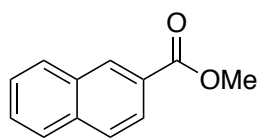
Methyl ethyl phthalate **3g**



3g

Using General Procedure A, monoethyl phthalate (97 mg, 0.5 mmol) gave methyl ethyl phthalate (**3g**) (59 mg, 57%) as a colourless oil; ¹H NMR (400 MHz; CDCl₃) 7.75-7.68 (m, 2H), 7.54-7.52 (m, 2H), 4.36 (q, *J* = 7.2 Hz, 2H), 3.90 (s, 3H), 1.36 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) 168.3 (C), 167.7 (C), 132.3 (C), 132.1 (C), 131.1 (2 CH), 129.0 (CH), 128.9 (CH), 61.8 (CH₂), 52.7 (CH₃), 14.2 (CH₃).

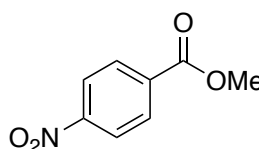
Methyl naphthalene-2-carboxylate **3h**



3h

Using General Procedure A, naphthalene-2-carboxylic acid (86 mg, 0.5 mmol) gave methyl naphthalene-2-carboxylate (**3h**) (60 mg, 65%) as a colourless solid; $^1\text{H NMR}$ (400 MHz; CDCl_3) 8.62 (s, 1H), 8.07 (dd, $J = 8.6, 1.7$ Hz, 1H), 7.95 (d, $J = 8.1$ Hz, 1H), 7.89-7.86 (m, 2H), 7.60-7.52 (m, 2H), 3.98 (s, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) 167.3 (C), 135.6 (C), 132.6 (C), 131.2 (CH), 129.4 (CH), 128.3 (CH), 128.2 (CH), 127.8 (CH), 127.5 (C), 126.7 (CH), 125.3 (CH), 52.3 (CH_3).

Methyl 4-nitrobenzoate **3i**

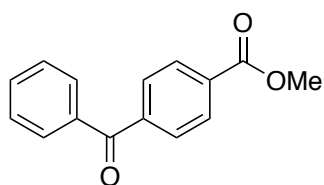


3i

Using General Procedure C, 4-nitrobenzoic acid (167 mg, 1.0 mmol) gave methyl 4-nitrobenzoate (**3i**) (119 mg, 65%) as a colourless solid; $^1\text{H NMR}$ (400 MHz; CDCl_3) 8.28 (d, $J = 8.9$ Hz, 2H), 8.20 (d, $J = 8.9$ Hz, 2H), 3.97 (s, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) 165.3 (C), 150.7 (C), 135.6 (C), 130.8 (CH), 123.7 (CH), 52.9 (CH_3).

The analogous reaction with TEMPO- CD_3 (***d*₃-1**) gave *d*₃-methyl 4-nitrobenzoate (***d*₃-3i**; $^1\text{H NMR}$ (400 MHz; CDCl_3) 8.28-8.24 (m, 2H), 8.20-8.17 (m, 2H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) 165.2 (C), 150.6 (C), 135.6 (C), 130.8 (CH), 123.6 (CH), 52.2 (sept, $J = 22.5$ Hz, CD_3); **HRMS** (EI) *m/z* calculated for $\text{C}_8\text{H}_4\text{D}_3\text{NO}_4^+$ (M^+) 184.0563, found 184.0562 (-0.5 ppm error).

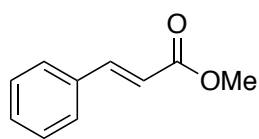
Methyl 4-benzoylbenzoate **3j**



3j

Using General Procedure C, 4-benzoylbenzoic acid (226 mg, 1.0 mmol) gave methyl 4-benzoylbenzoate (**3j**) (141 mg, 59%) as a colourless solid; $^1\text{H NMR}$ (400 MHz; CDCl_3) 8.15 (d, $J = 8.4$ Hz, 2H), 7.84 (d, $J = 8.4$ Hz, 2H), 7.80 (d, $J = 7.6$ Hz, 2H), 7.62 (t, $J = 7.4$ Hz, 1H), 7.50 (dd, $J = 7.7, 7.7$ Hz, 2H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) 196.1 (C), 166.4 (C), 141.5 (C), 137.1 (C), 133.4 (C), 133.1 (CH), 130.2 (CH), 129.9 (CH), 129.6 (CH), 128.6 (CH), 52.6 (CH_3).

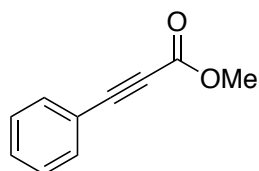
Methyl *trans*-cinnamate **3k**



3k

Using General Procedure C, *trans*-cinnamic acid (148 mg, 1.0 mmol) gave methyl *trans*-cinnamate (**3k**) (96 mg, 59%) as a colourless oil; $^1\text{H NMR}$ (400 MHz; CDCl_3) 7.70 (d, $J = 16.0$ Hz, 1H), 7.53-7.50 (m, 2H), 7.39-7.36 (m, 3H), 6.44 (d, $J = 16.0$ Hz, 1H), 3.80 (s, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) 167.2 (C), 144.7 (CH), 134.3 (C), 130.2 (CH), 128.8 (CH), 127.9 (CH), 117.7 (CH), 51.5 (CH_3).

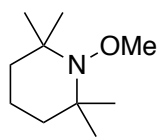
Methyl phenylpropiolate **3l**



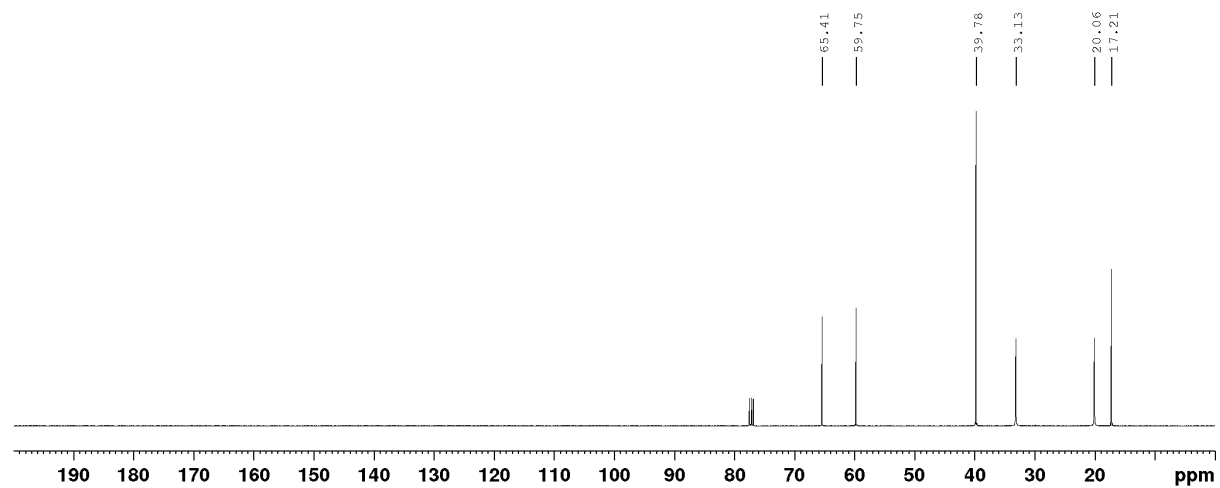
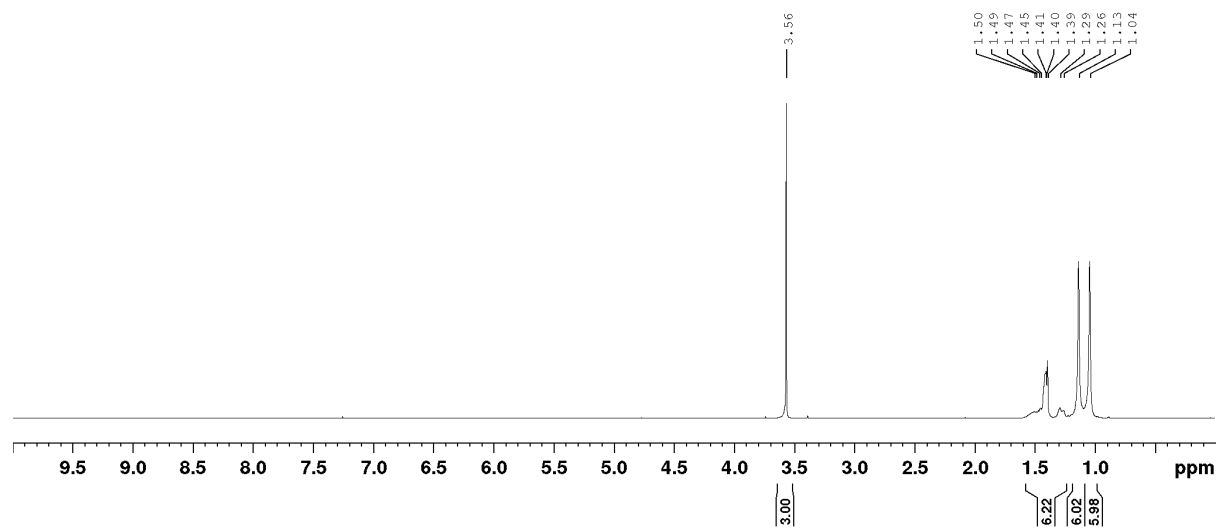
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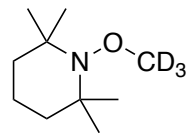
Using General Procedure C, phenylpropionic acid (146 mg, 1.0 mmol) gave methyl phenylpropiolate (**3l**) (145 mg, 91%) as a colourless oil; $^1\text{H NMR}$ (400 MHz; CDCl_3) 7.59 (d, $J = 7.3$ Hz, 2H), 7.46 (t, $J = 7.5$ Hz, 1H), 7.38 (t, $J = 7.5$ Hz, 2H), 3.84 (s, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) 154.6 (C), 133.2 (CH), 130.8 (CH), 128.7 (CH), 119.7 (C), 86.7 (C), 80.5 (C), 52.9 (CH_3).

1.5 ¹H and ¹³C NMR spectra of synthesised compounds

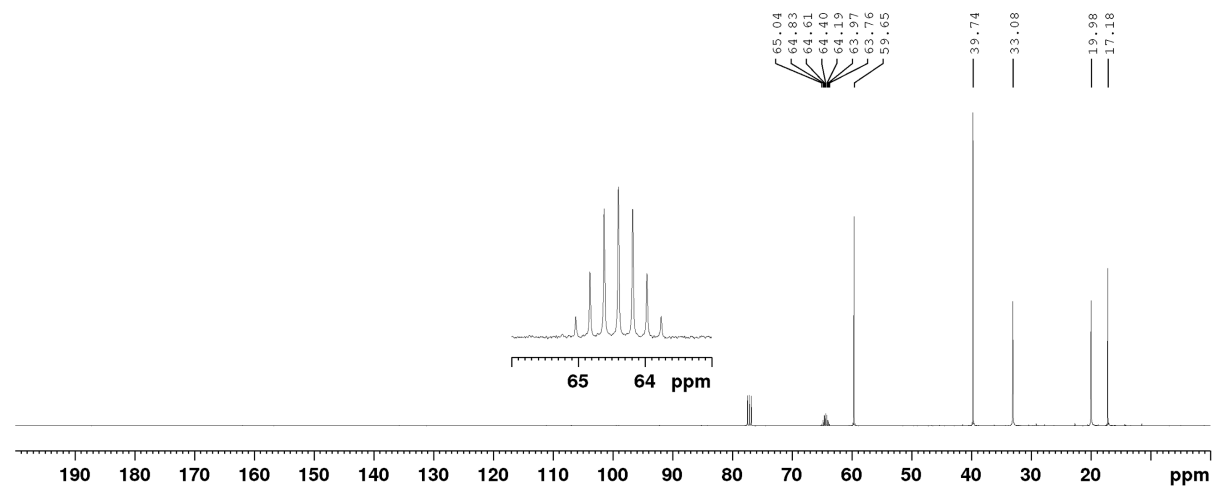
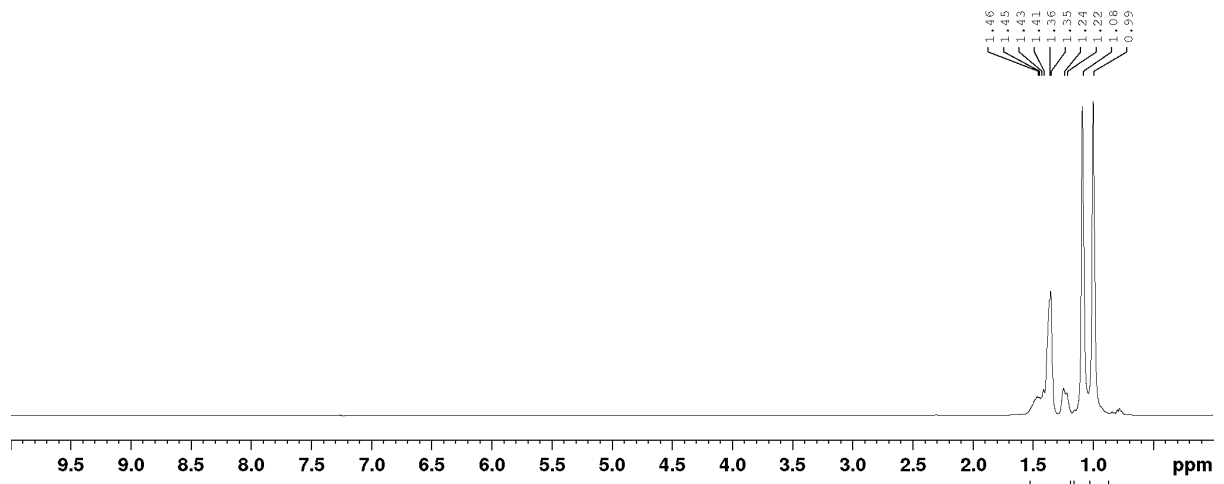


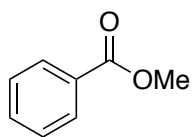
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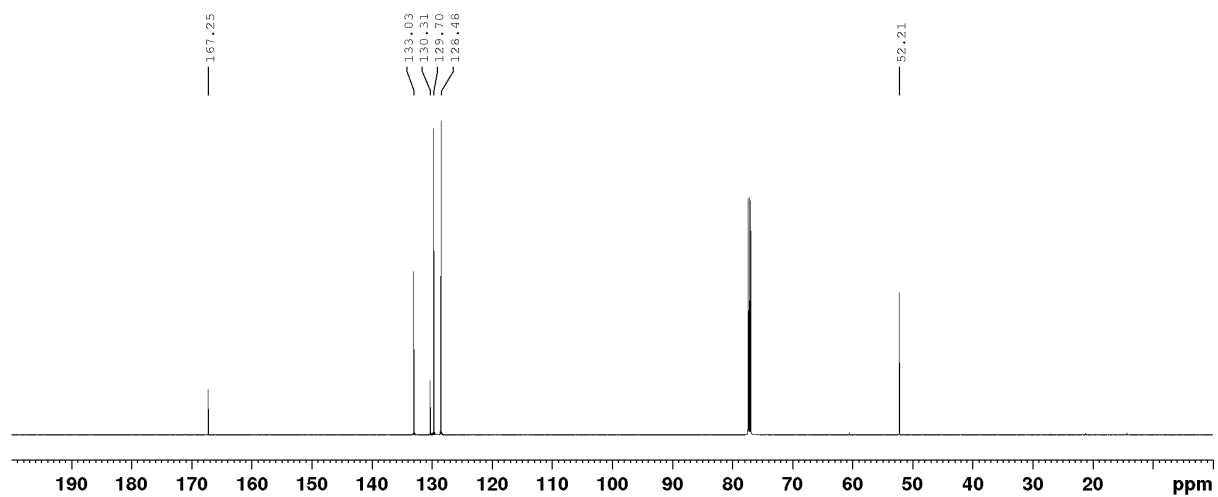
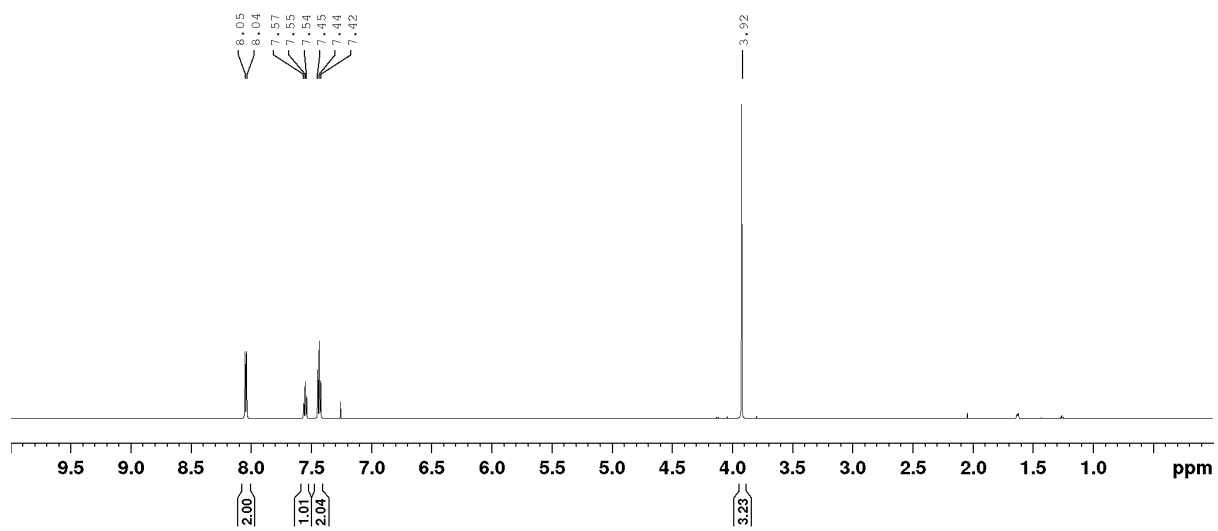


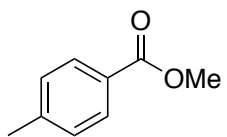
d₃-1



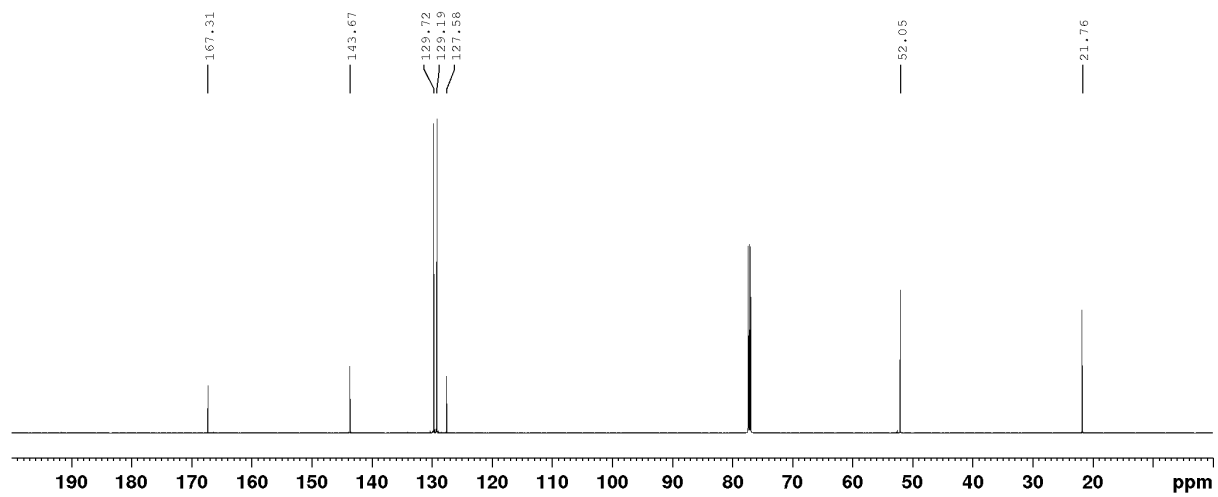
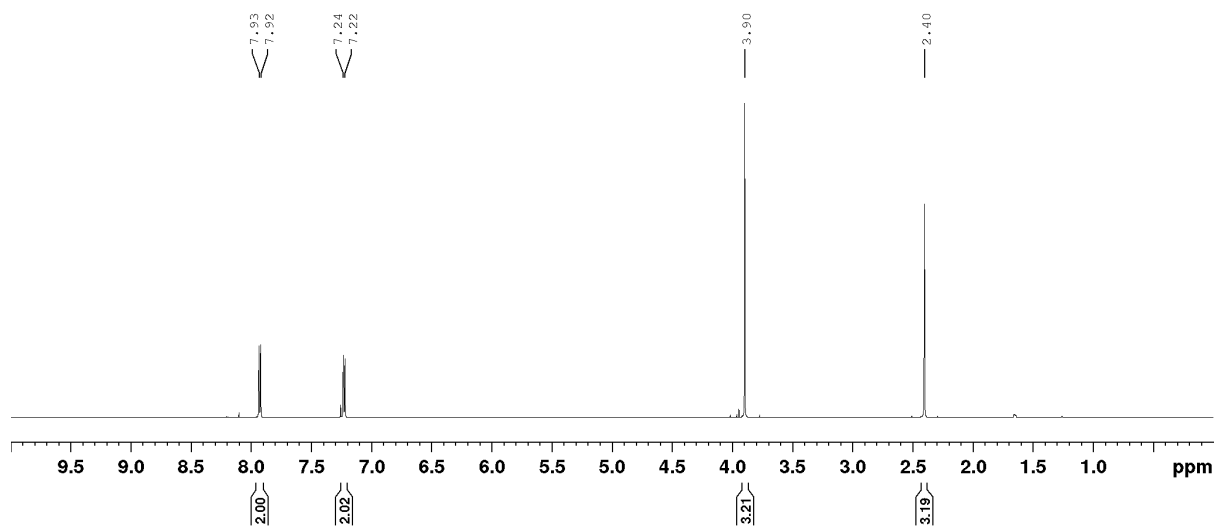


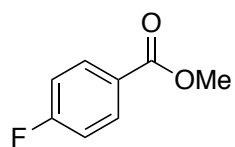
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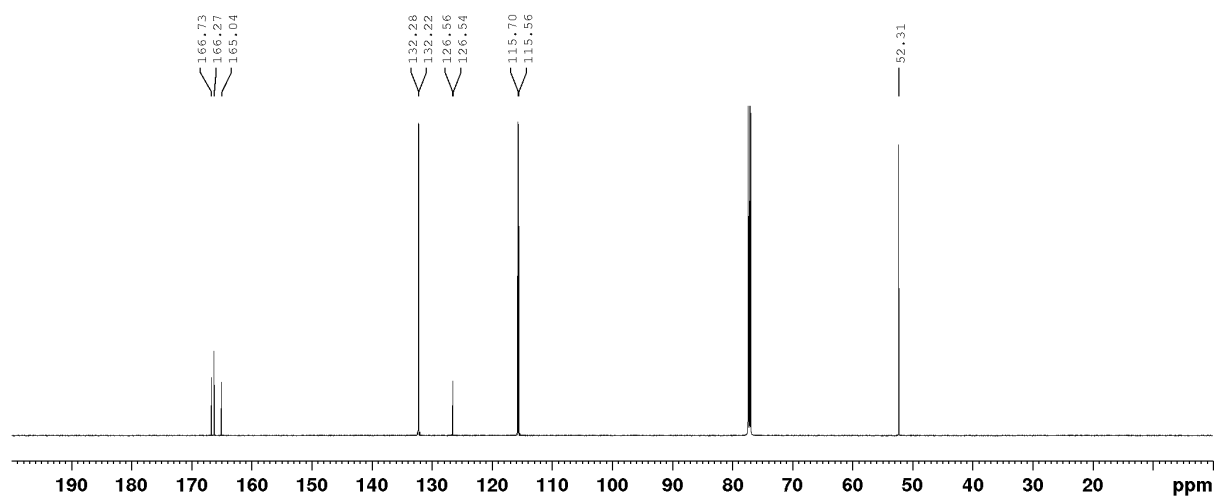
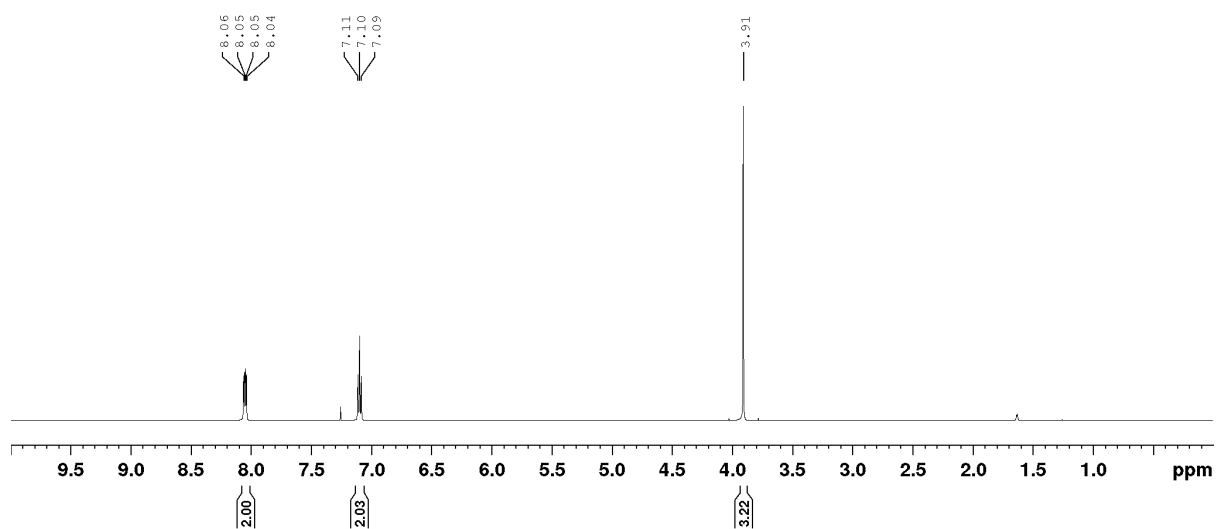


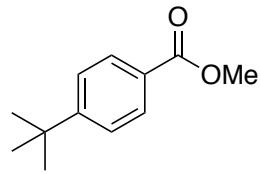
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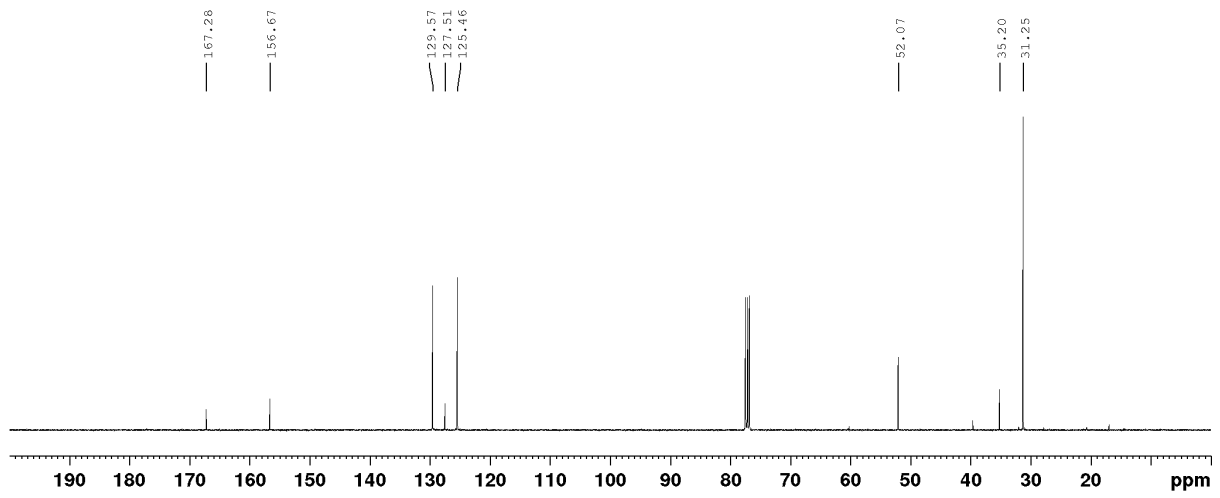
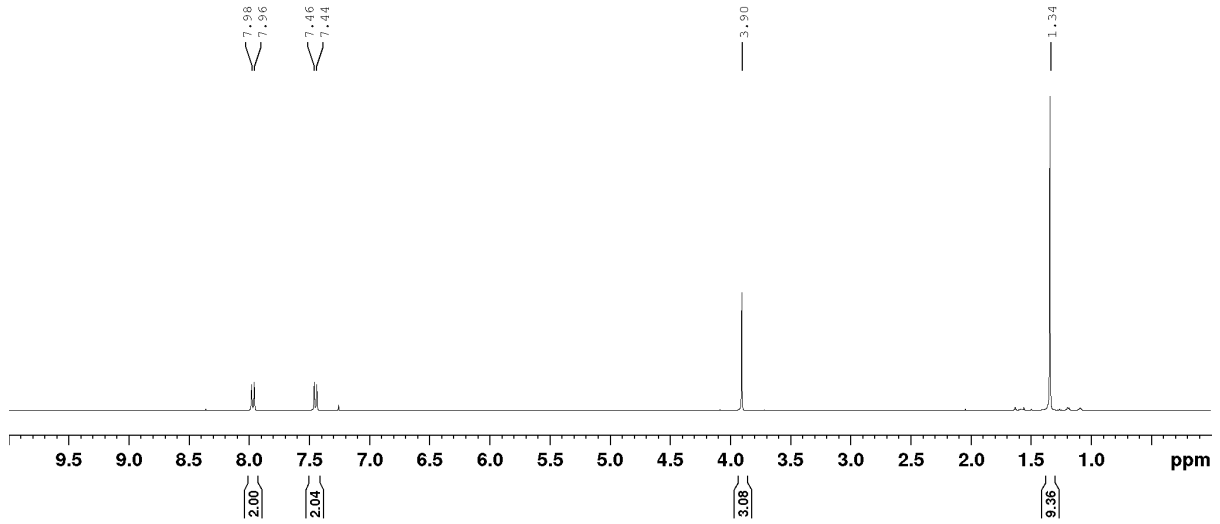


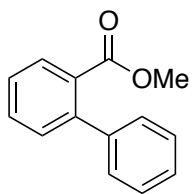
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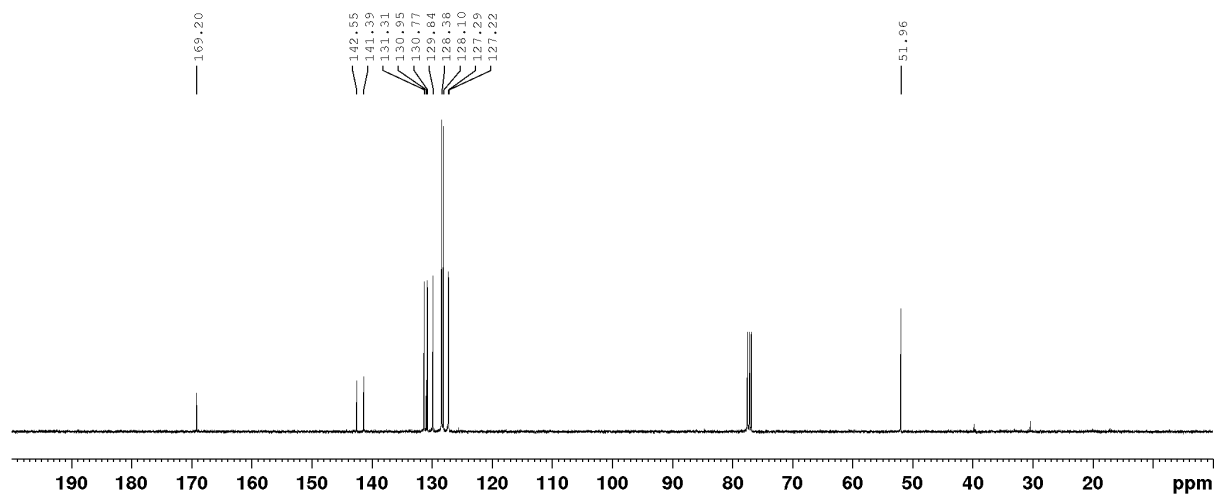
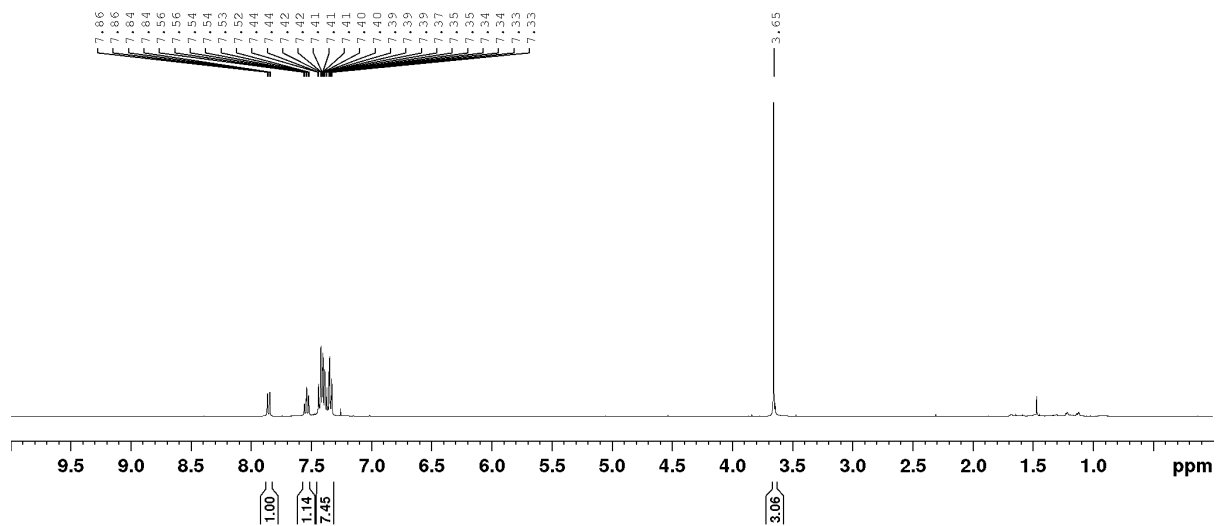


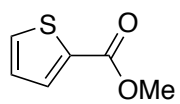
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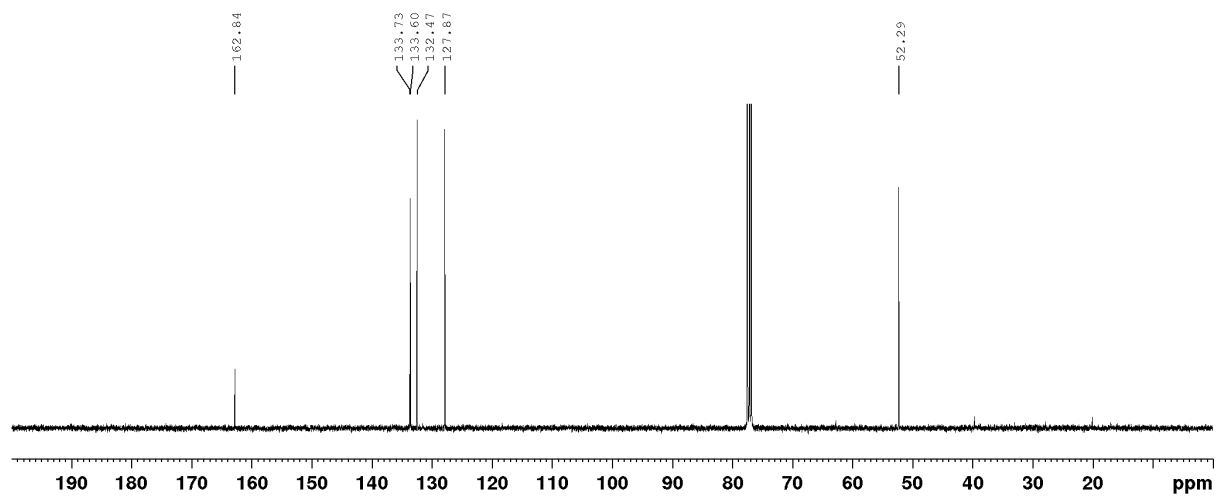
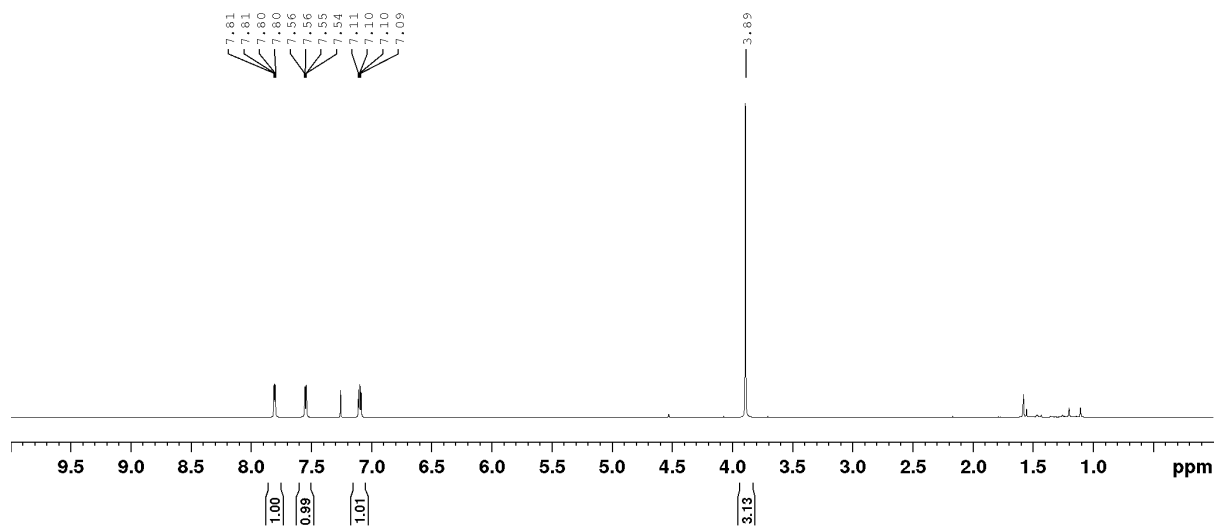


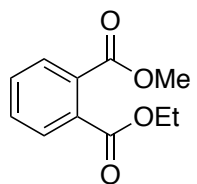
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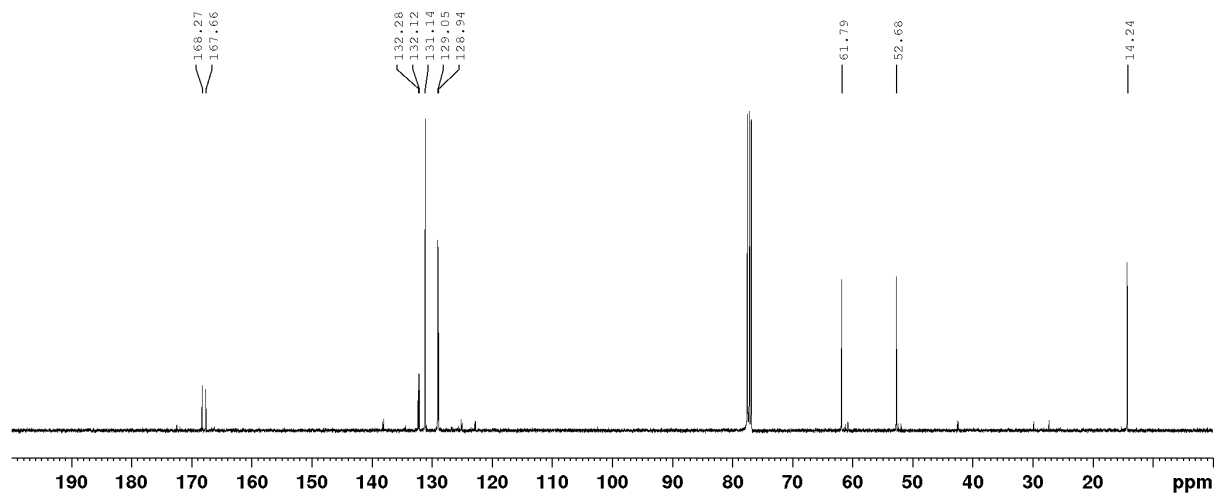
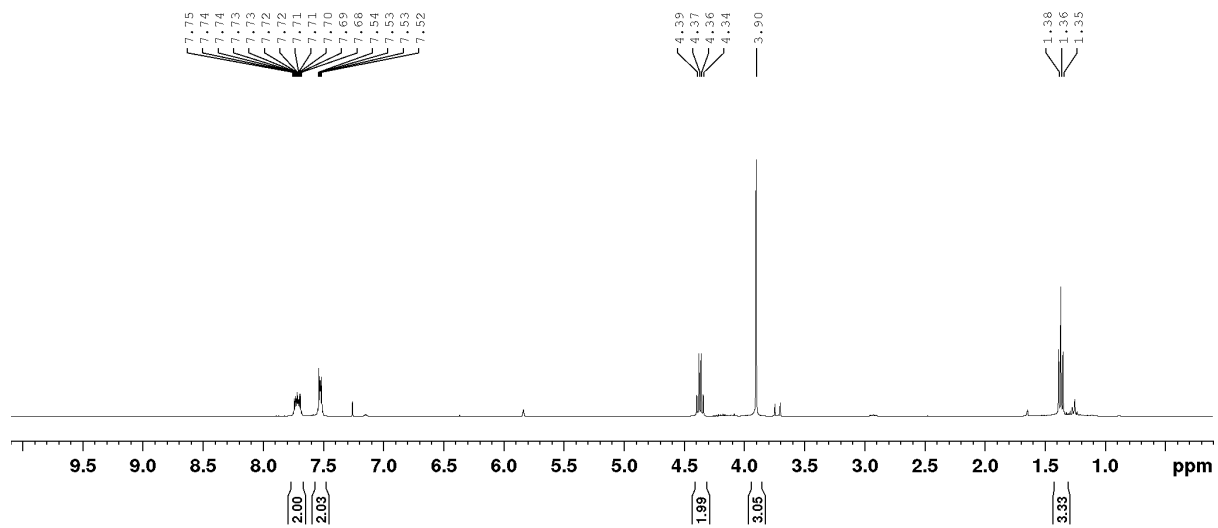


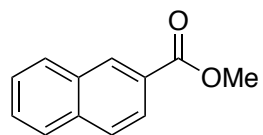
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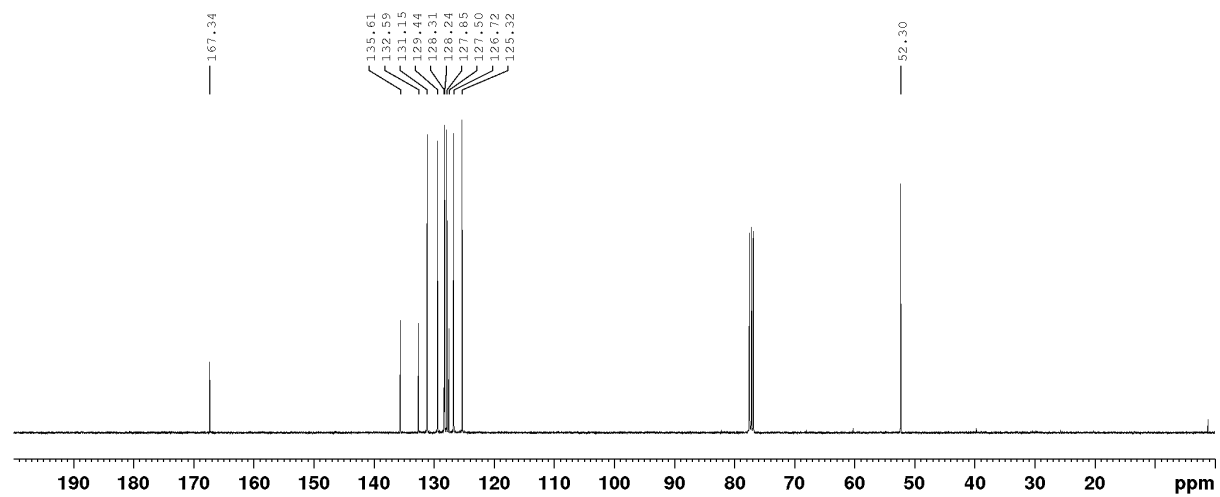
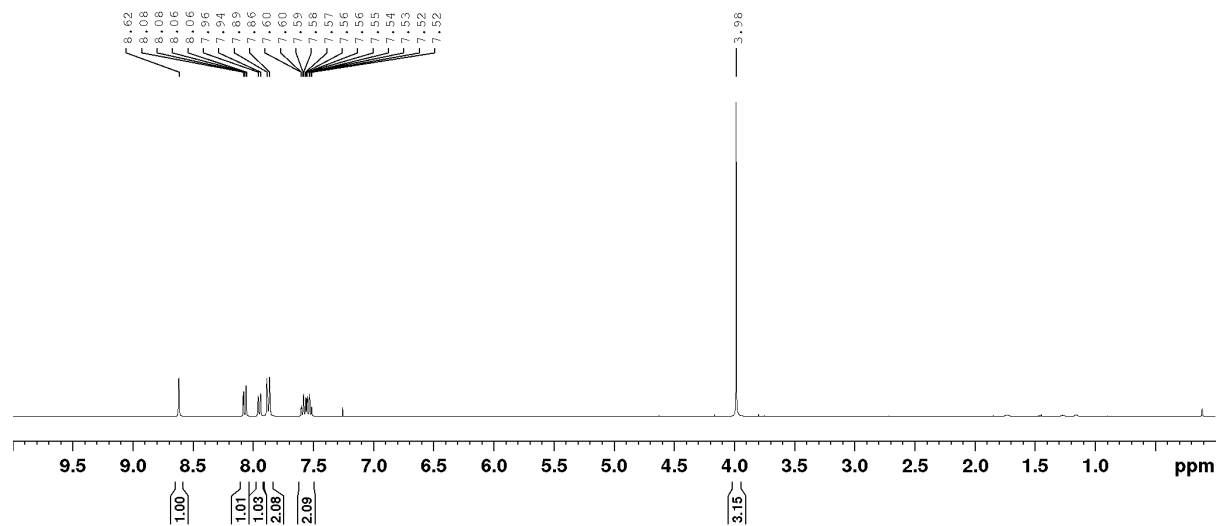


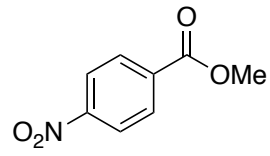
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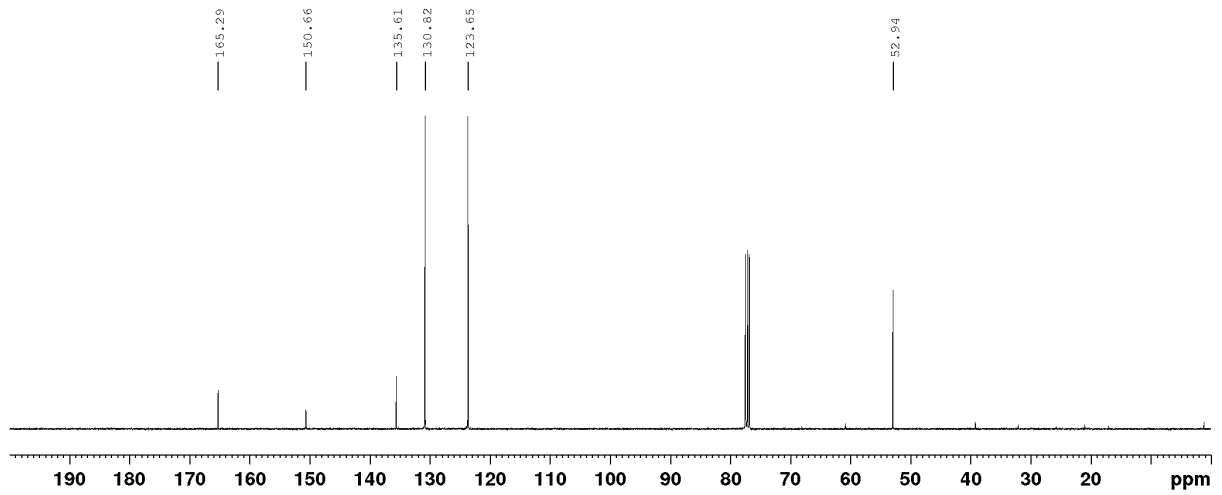
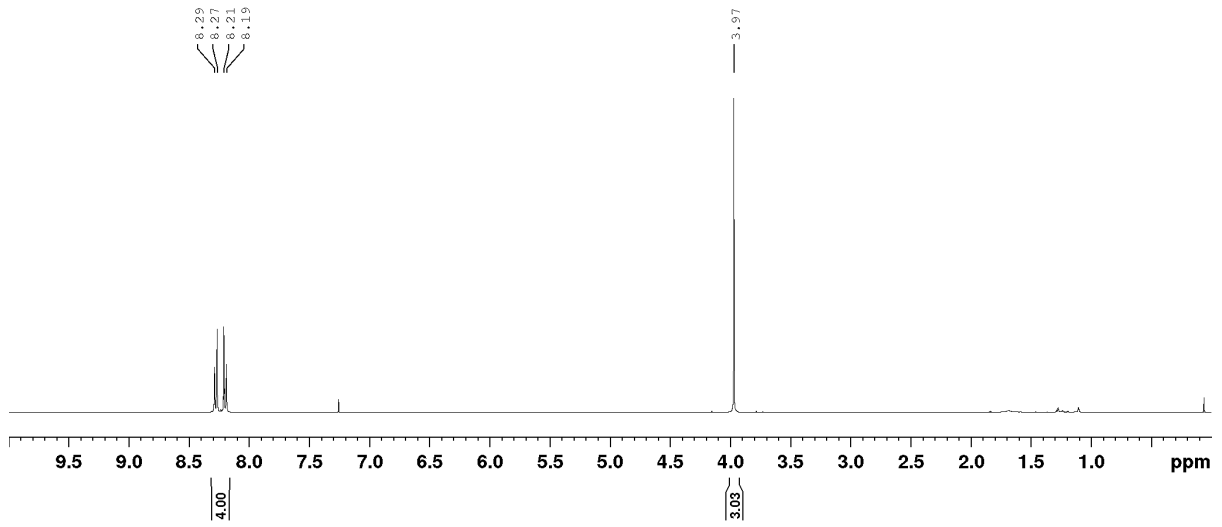


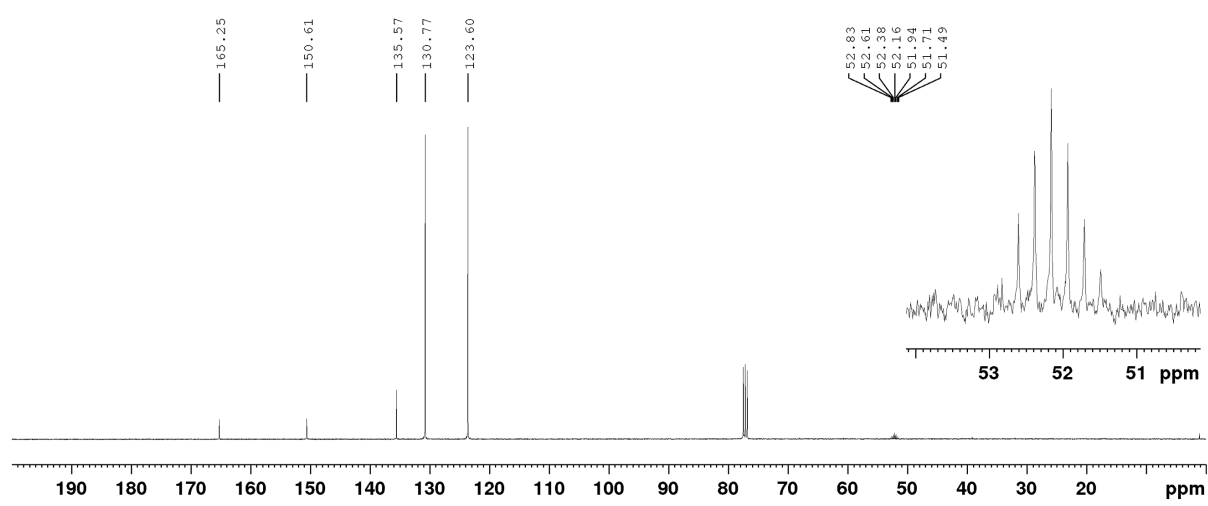
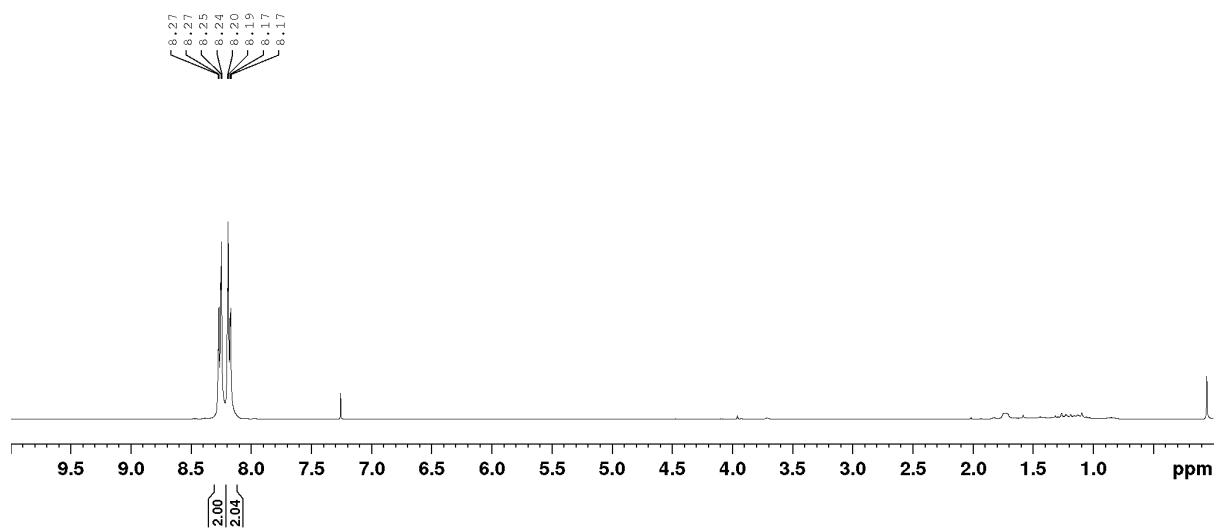
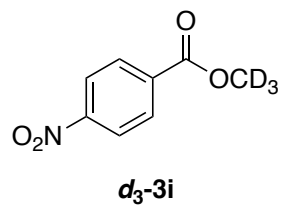
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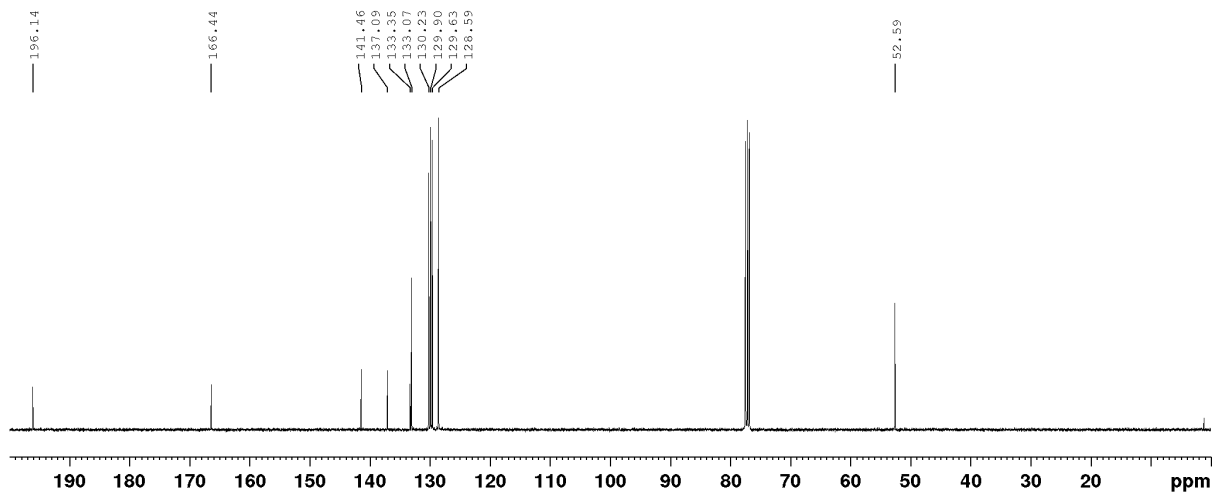
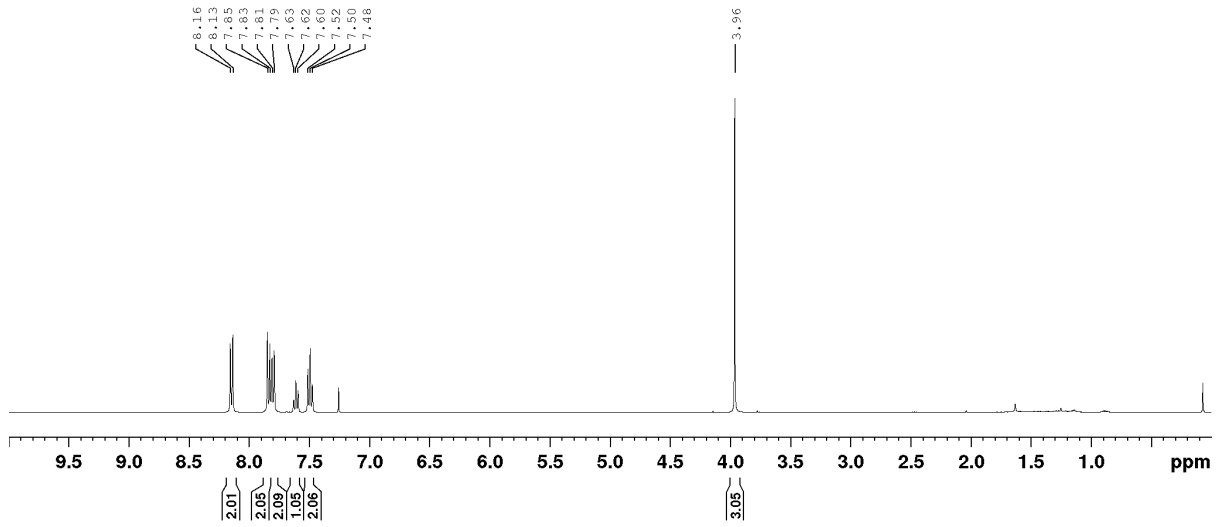
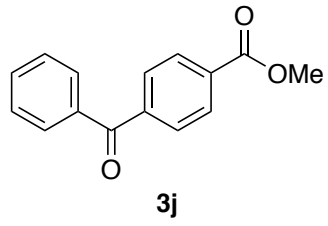


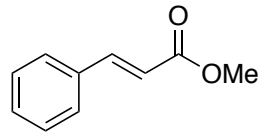


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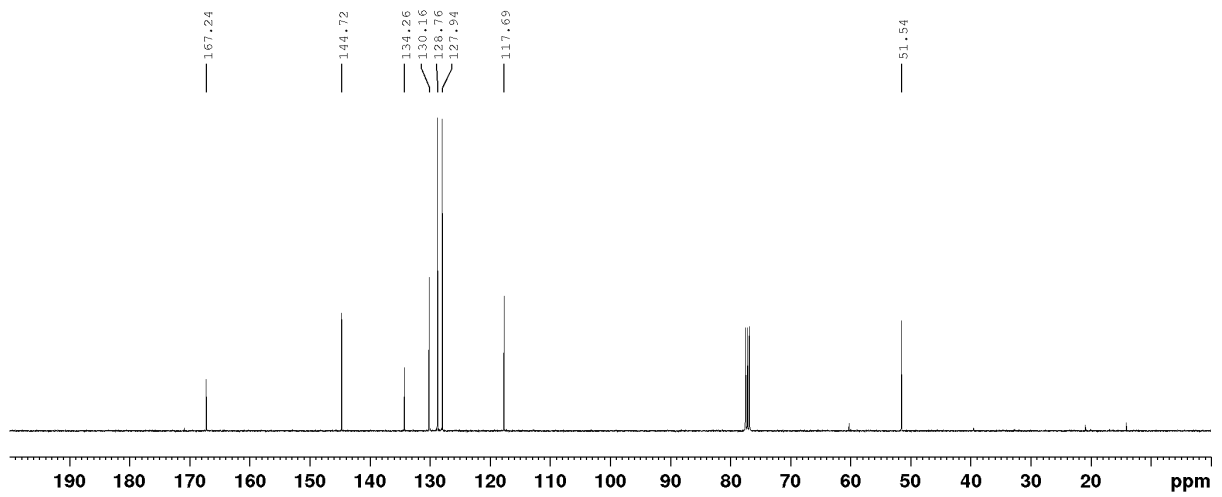
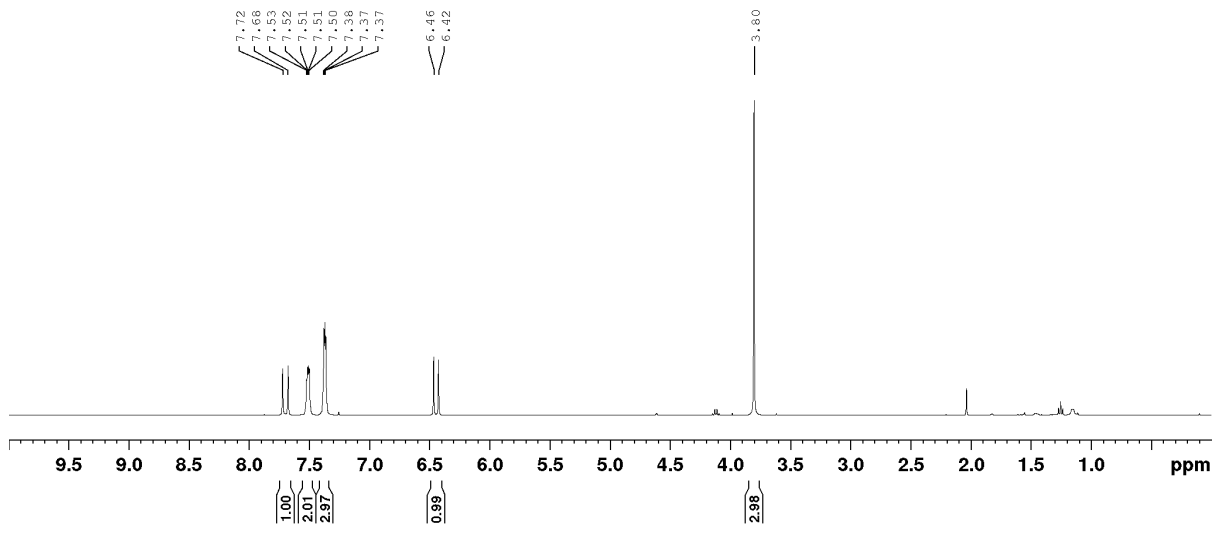


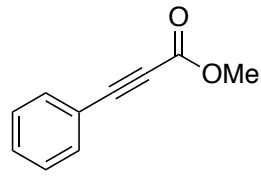




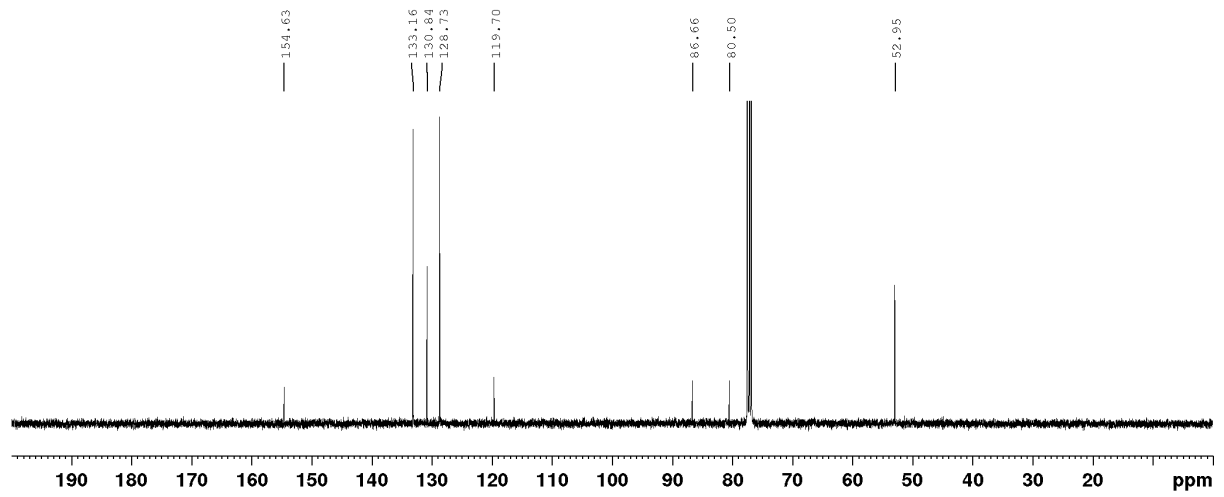
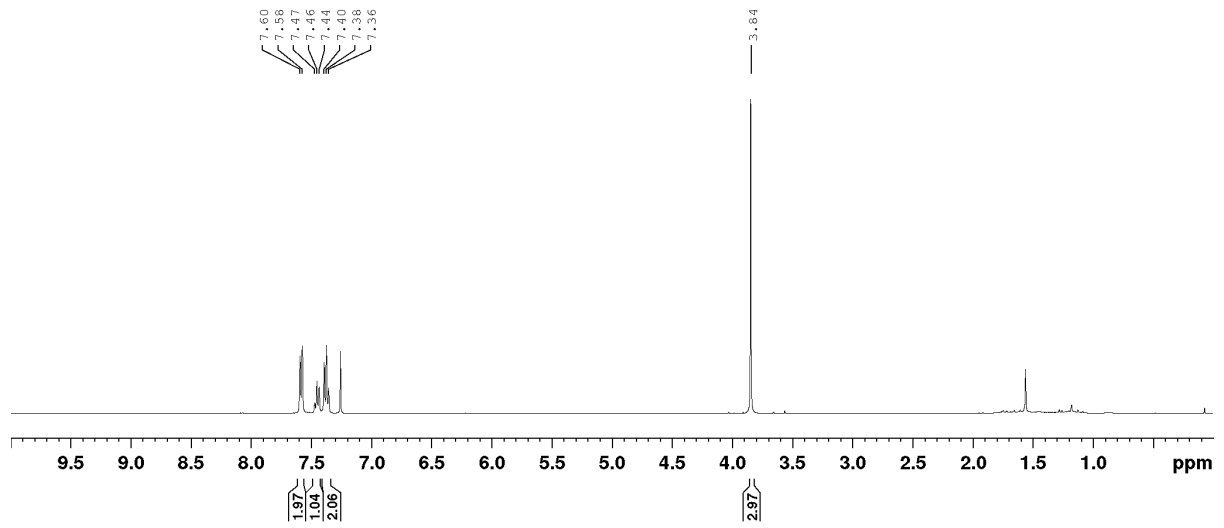


3k





3I



Appendix S2. Benzoic Acid Methylation: Influence of Other Electrochemical Parameters

Table S1. Electrochemical Methylation of Benzoic Acid Using TEMPO–Me: Influence of Reaction Parameters.^a

Entry	Variation from the "standard" conditions	Yield (%) ^b
1	none	87
2	1 h rxn time	53
3	2 h rxn time	68
4	+ 3.0 V	41
5	+ 4.5 V	30
6	+ 5.0 V	5
7	constant current: 5 mA	7
8	constant current: 10 mA	49
9	1.1 equiv TEMPO–Me	64
10	1.5 equiv TEMPO–Me	73
11	3.0 equiv TEMPO–Me	56
12	2 equiv Cs ₂ CO ₃ , instead K ₂ CO ₃	46
13	2 equiv K ₃ PO ₄ , instead K ₂ CO ₃	21
14	no K ₂ CO ₃	12
15	1 equiv TEMPO added	<2
16	8 mL MeCN, instead of 4 mL MeCN	56
17	SS(+) SS(-)	32
18	Ni(+) Ni(-)	0
19	RVC(+) RVC(-)	19

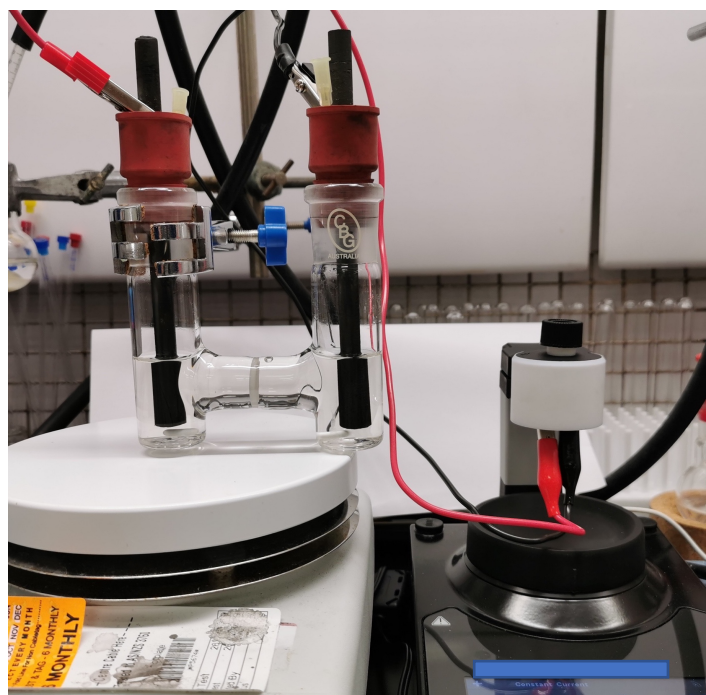
^aReactions were performed using **2a** (0.20 mmol), **1** (0.40 mmol), K₂CO₃ (0.40 mmol), Bu₄NBF₄ (0.60 mmol), MeCN (4 mL), and a constant cell potential of +4.0 V vs. Ag/AgCl in an undivided cell at r.t for 3 h using an IKA Electrasyn 2.0. ^bYields determined by gas chromatography (GC) with the aid of a calibrated internal standard (average of 2 experiments). SS = stainless steel; RVC = reticulated vitreous carbon.

Appendix S3. Details of divided cell setup

A glass H-cell was used, comprising of two cylindrical chambers (height: 85 mm, OD: 25 mm) connected by a porosity 4 glass frit in a channel 48 mm long (OD: 22 mm), raised 15 mm from the base of the unit. Two cylindrical graphite rods (10 mm diameter, 150 mm height) were positioned 5 mm from the base of each chamber, which could each hold up to ~30 mL of solvent.



Under General Procedure C, the electrodes were connected to the terminals on an Electrasyn 2.0 vial lid. The applied voltage was controlled by the Electrasyn, while the solutions in both chambers of the reaction were stirred at ~800 rpm using a separate magnetic stirrer.



Appendix S4. Cyclic voltammetry data

3.1 General conditions

Electrochemical experiments were carried out using a PalmSens4 Potentiostat/Galvanostat/Impedance Analyzer and a single compartment three-electrode glass cell. Electrochemical experiments were performed at room temperature (23 ± 2 °C) under argon. Glassy carbon disks (0.065 cm^2) served as the working electrode, a platinum coil was used as counter electrode, and silver/silver chloride as the reference electrode. Alkoxyamine (2 mM) was dissolved in $1.0 \times 10^{-1} \text{ M MeCN/Bu}_4\text{NClO}_4$. The solution was stirred and bubbled briefly under argon prior to measurement. All cyclic voltammograms were obtained after bubbling, with no stirring. The cell iR drop was not compensated during measurement.

3.2 Reactivity of $1^{+\bullet}$ with benzoic acid and tetra-*n*-butylammonium benzoate

Figure S1: TEMPO-Me (2 mM) in MeCN/ Bu_4NClO_4 (100 mM). (a) $50 \text{ mV}\cdot\text{s}^{-1}$, (b) $100 \text{ mV}\cdot\text{s}^{-1}$, (c) $200 \text{ mV}\cdot\text{s}^{-1}$, (d) $500 \text{ mV}\cdot\text{s}^{-1}$. *Solid line* = scan 1, *dotted line* = scan 2.

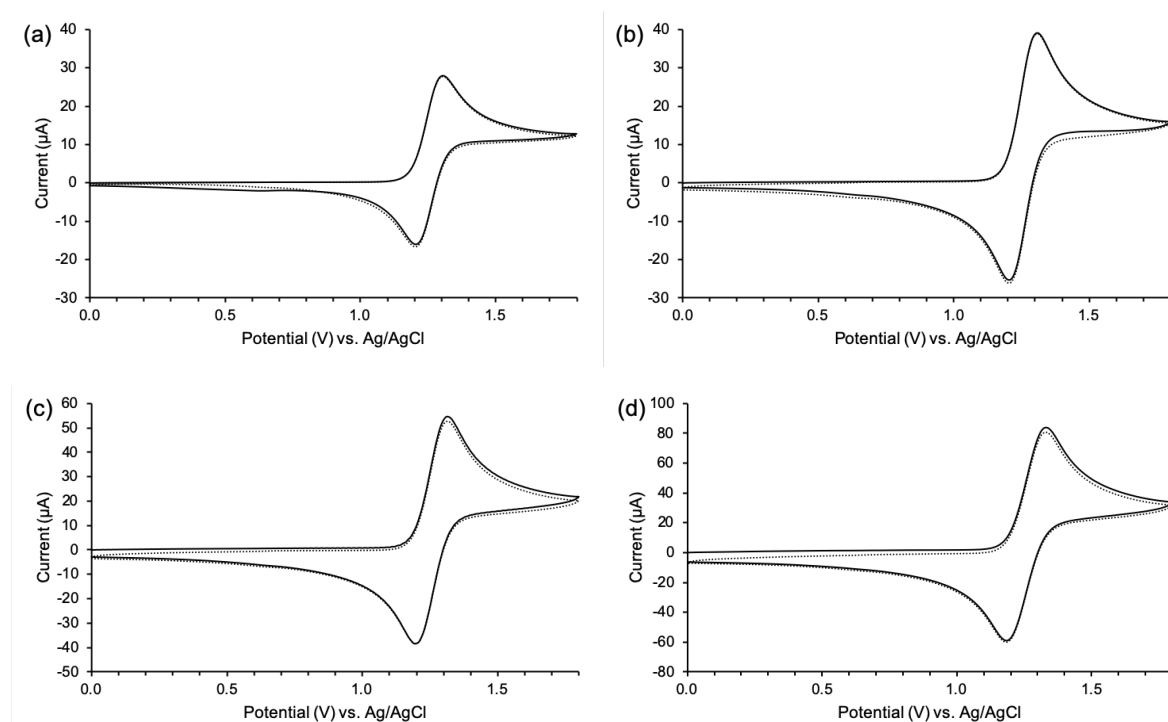


Figure S2: TEMPO-Me (2 mM) and benzoic acid (4 mM) in MeCN/Bu₄NClO₄ (100 mM).

(a) 50 mV.s⁻¹, (b) 100 mV.s⁻¹, (c) 200 mV.s⁻¹, (d) 500 mV.s⁻¹. *Solid line* = scan 1, *dotted line* = scan 2.

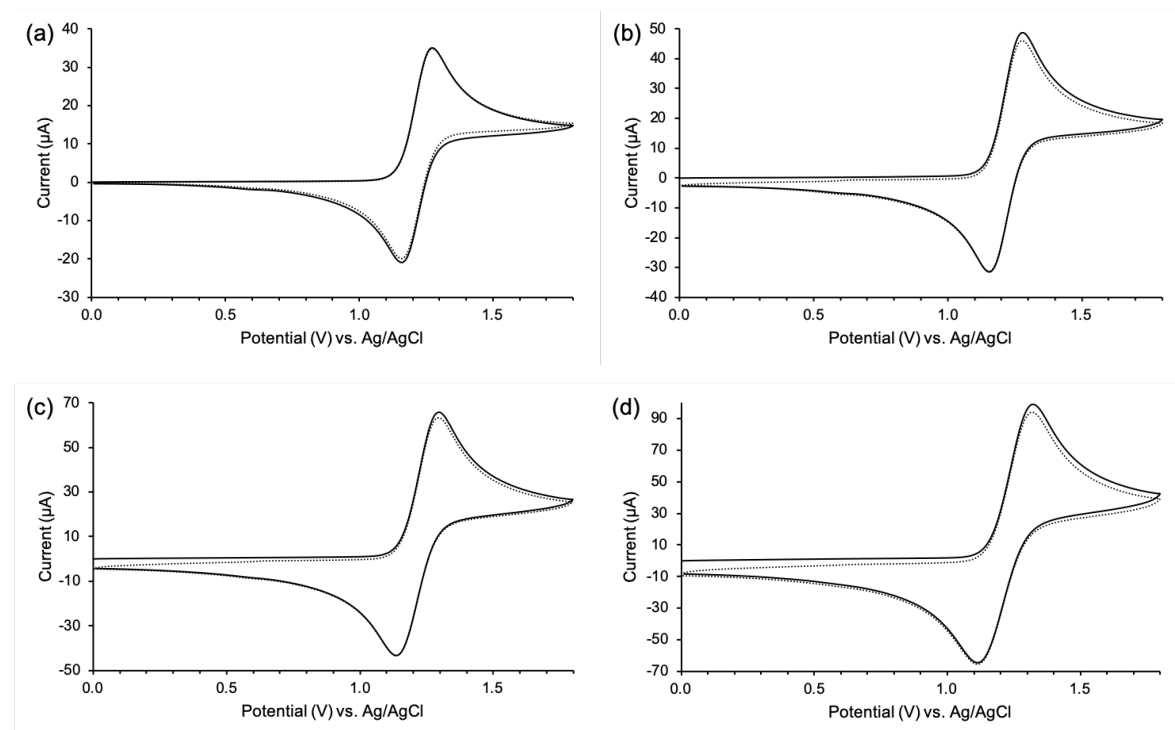
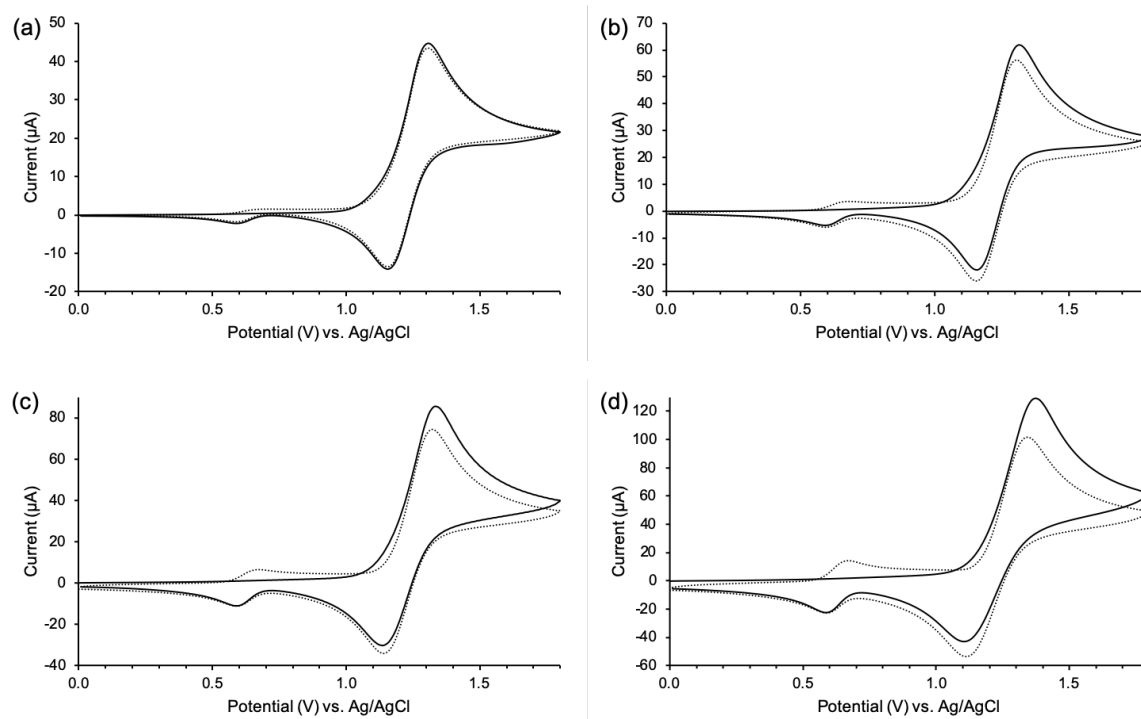


Figure S3: TEMPO-Me (2 mM) and tetra-*n*-butylammonium benzoate (1 mM) in MeCN/Bu₄NClO₄ (100 mM). (a) 50 mV.s⁻¹, (b) 100 mV.s⁻¹, (c) 200 mV.s⁻¹, (d) 500 mV.s⁻¹. Solid line = scan 1, dotted line = scan 2.



3.3 Reactivity of $1^{+\bullet}$ with 2,6-di(*tert*-butyl)pyridine and other pyridine nucleophiles

Figure S4: TEMPO-Me (2 mM) and pyridine (4 mM) in MeCN/ Bu_4NClO_4 (100 mM). (a) $50 \text{ mV}\cdot\text{s}^{-1}$, (b) $100 \text{ mV}\cdot\text{s}^{-1}$, (c) $200 \text{ mV}\cdot\text{s}^{-1}$, (d) $500 \text{ mV}\cdot\text{s}^{-1}$. *Solid line* = scan 1, *dotted line* = scan 2.

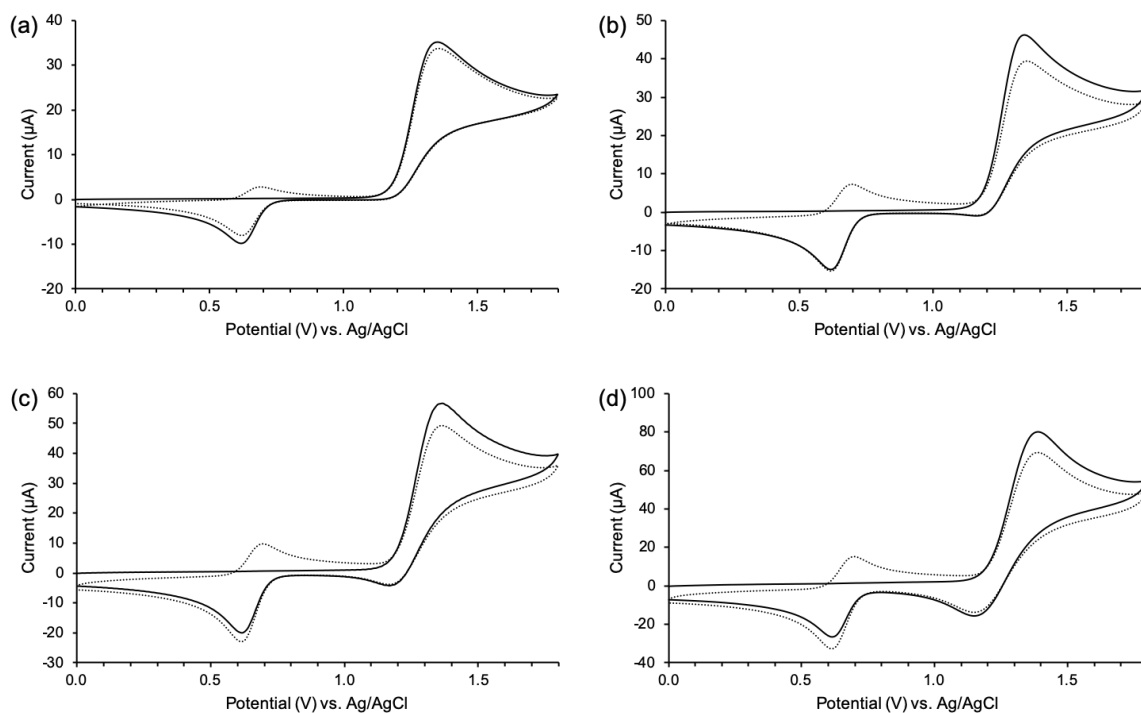


Figure S5: TEMPO-Me (2 mM) and 2,6-lutidine (4 mM) in MeCN/ Bu_4NClO_4 (100 mM). (a) $50 \text{ mV}\cdot\text{s}^{-1}$, (b) $100 \text{ mV}\cdot\text{s}^{-1}$, (c) $200 \text{ mV}\cdot\text{s}^{-1}$, (d) $500 \text{ mV}\cdot\text{s}^{-1}$. *Solid line* = scan 1, *dotted line* = scan 2.

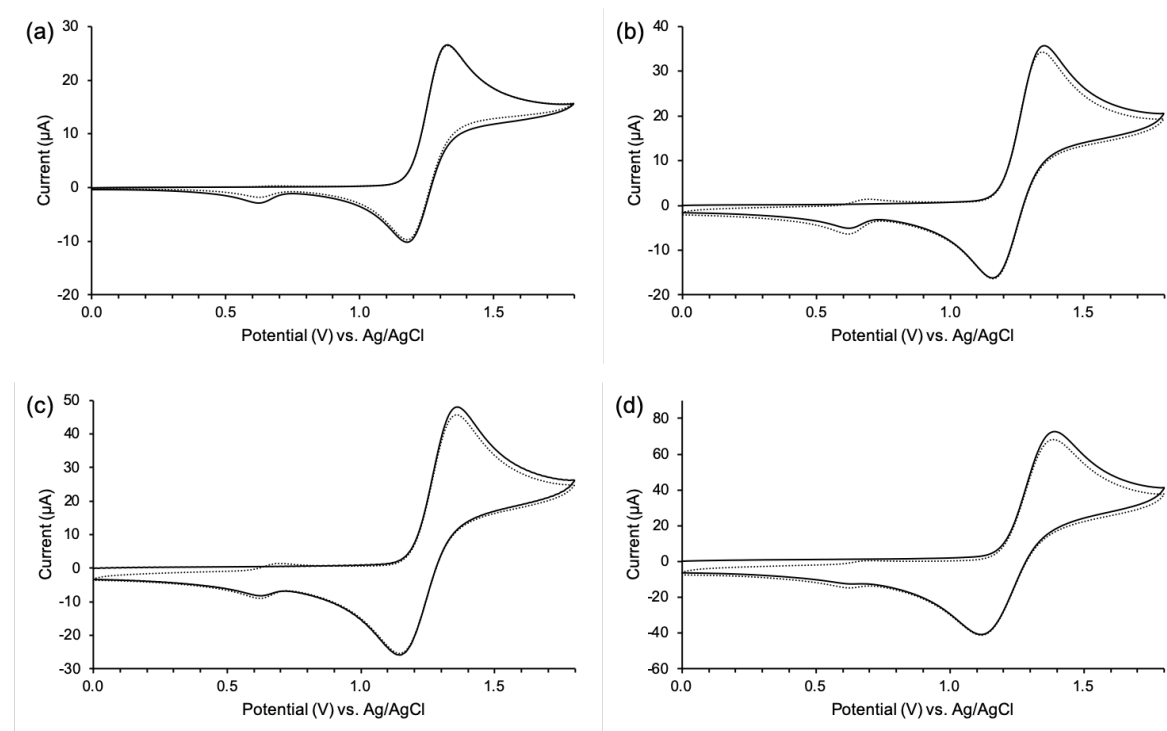
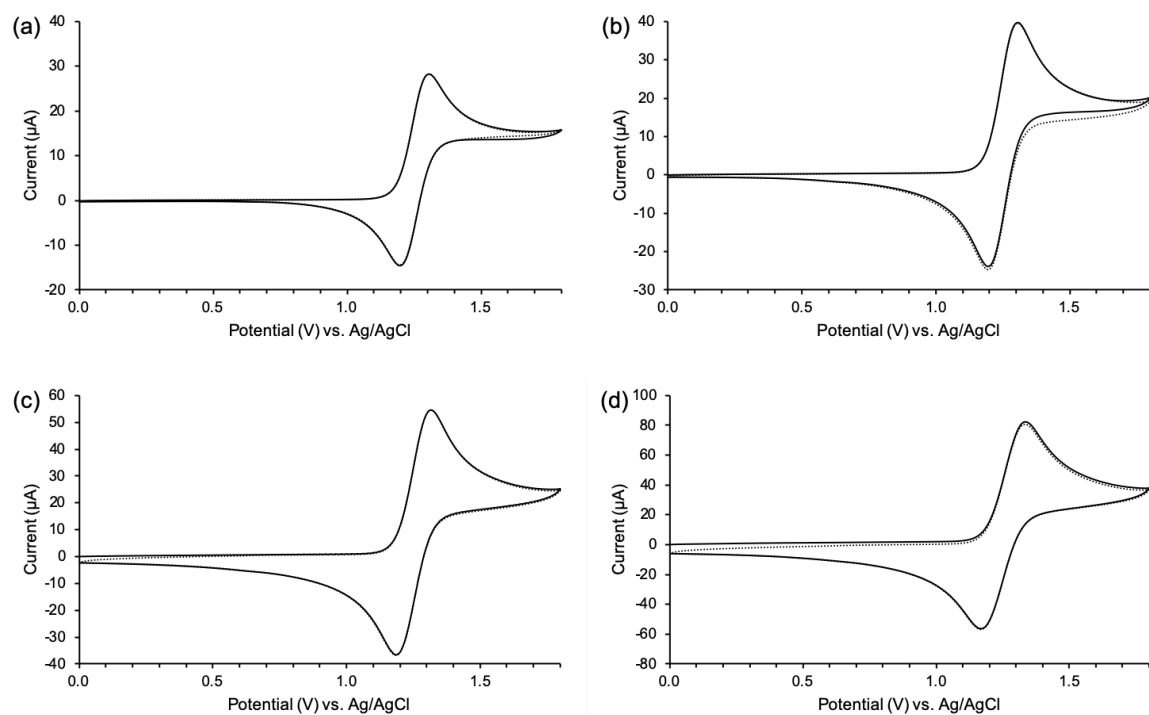


Figure S6: TEMPO-Me (2 mM) and 2,6-di(*tert*-butyl)pyridine (4 mM) in MeCN/Bu₄NClO₄ (100 mM). (a) 50 mV.s⁻¹, (b) 100 mV.s⁻¹, (c) 200 mV.s⁻¹, (d) 500 mV.s⁻¹. *Solid line* = scan 1, *dotted line* = scan 2.



Appendix S5. Computational methods

Theoretical Methodology

All standard ab initio molecular orbital theory and density functional theory (DFT) calculations were carried out using Gaussian 09¹ and Molpro² software packages. Procedures were chosen based on benchmarking against experiment in previous studies of similar systems.³⁻⁴ Geometries were optimized at the M06-2X/6-31+G(d,p)⁵ level of theory, and frequencies were also calculated at this level. Single point energies were calculated using the high-level composite ab initio method G3(MP2)CC(+), which is a variant of G3(MP2)CC⁶ where the calculations with the 6-31G(d) basis set are replaced with corresponding 6-31+G(d) calculations to allow for better treatment of the anionic species. Gibbs free energies in solution were calculated via a thermocycle in which Gibbs free energies in the gas phase, as calculated via standard ideal gas partition functions, were combined with Gibbs free energies of solvation and the necessary phase change correction term.⁷ The SMD solvent model⁸ was used to correct for implicit solvent effects. For this purpose, geometries were fully optimized in solution at the M06-2X/6-31+G(d,p) level.

Raw Energies of all the species investigated in this study

Note unless specified, units are in Hartrees.

Species	Corrections			Raw Electronic Energies					Thermochemistry		
	S (J/mol K)	TC	ZPVE	M06-2X/ 6-31+G(d,p)	UMP2/ 6-31+G(d)	UMP2/ GTMP2L	URCCSD(T)/ 6-31+G(d)	G3(MP2)CC(+)	G _{gas}	ΔG _{solv}	G _{sol}
Pyridine	281.38	0.005210	0.089597	-248.186196	-247.498035	-247.744992	-247.565532	-247.953685	-247.890831	-0.008220	-247.899051
Methylpyridinium ⁺	329.58	0.007036	0.131331	-287.847034	-287.028289	-287.327616	-287.114720	-287.583481	-287.482541	-0.091604	-287.574146
TEMPO [•]	431.72	0.012692	0.264452	-483.523430	-482.091358	-482.662112	-482.254390	-483.130329	-482.902210	-0.008901	-482.911112
TEMPO-Me ^{••}	485.25	0.014883	0.304399	-523.145627	-521.577375	-522.200367	-521.765152	-522.721569	-522.457392	-0.081244	-522.538636
TEMPO-Me ^{••} Pyridine TS	622.31	0.020395	0.394389	-771.332436	-769.081983	-769.951357	-769.335449	-770.679442	-770.335327	-0.077033	-770.412360
OTf ⁻	345.84	0.008008	0.027999	-961.320764	-959.658416	-960.371245	-959.701494	-960.649648	-960.652916	-0.075708	-960.728623
MeOTf	406.16	0.010232	0.068547	-1001.089404	-999.290084	-1000.057667	-999.354408	-1000.385555	-1000.352899	-0.005273	-1000.358173
MeOTf Pyridine TS	535.58	0.015511	0.158689	-1249.247028	-1246.763751	-1247.778956	-1246.895618	-1248.315582	-1248.202202	-0.027155	-1248.229357
MeN ₂ ⁺	243.57	0.004605	0.045951	-149.021546	-148.655953	-148.803088	-148.689551	-148.911990	-148.889093	-0.106742	-148.995835
MeN ₂ ⁺ Pyridine TS	417.84	0.010384	0.135712	-397.234418	-396.181400	-396.574656	-396.283320	-396.893076	-396.794429	-0.088450	-396.882879
N ₂	191.46	0.003305	0.005793	-109.492041	-109.259371	-109.351750	-109.273867	-109.413311	-109.425956	0.008212	-109.417744
O [•] Me ₃	296.73	0.006773	0.122798	-194.562241	-193.990311	-194.236146	-194.056086	-194.424290	-194.328416	-0.095335	-194.423751
O [•] Me ₃ Pyridine TS	450.33	0.012277	0.212389	-442.756829	-441.498899	-441.991738	-441.632338	-442.388741	-442.215213	-0.081791	-442.297004
OMe ₂	263.70	0.005234	0.080676	-154.955408	-154.514366	-154.709942	-154.560385	-154.850092	-154.794127	-0.000739	-154.794866

Gas-phases geometries of all the species investigated in this study

MeN₂⁺

1\1\GINC-R51\FOpt\RM062X\6-31+G(d,p)\C1H3N2(1+)\ROOT\22-Feb-2019\0\#M062X/6-31+G(d,p) SCF=Tight INT(grid=ultrafine) OPT IOP(2/17=4) maxdisk=5GB\CH3N2+.freq\1,1\C,-0.0000004348,0.,-1.28438\N,-0.0000004348,0.,0.17391\H,0.5248510308,-0.9090694049,-1.58792\H,0.5248510308,0.9090694049,-1.58792\H,-1.049703366,0.,-1.58792\N,-0.000004348,0.,1.27027\Version=ES64L-G09RevD.01\State=1-A1\HF=-149.0215457\RMSD=6.321e-10\RMSF=1.435e-04\Dipole=0.,0.,-0.840382\Quadrupole=-1.269915,-1.269915,2.5398301,0.,0.,0.\PG=C03V [C3(C1N1N1),3SGV(H1)]\@

MeN₂⁺ Pyridine TS

1\1\GINC-R40\FTS\RM062X\6-31+G(d,p)\C6H8N3(1+)\ROOT\21-Feb-2019\0\#M062X/6-31+G(d,p) SCF=Tight INT(grid=ultrafine) OPT=(TS,calcf, noeigentest,maxstep=10) IOP(2/17=4) maxdisk=8GB\Pyridine_CH3N2+.TS.freq\1,1\C,-3.4395967448,1.0781540665,-0.0637414583\N,-1.8952230478,1.5782899322,0.2040990732\H,-3.6823021837,0.6638879854,0.9081844061\H,-3.2732171913,0.3683442011,-0.8660309017\H,-3.9063110176,2.0183834751,-0.3343312915\N,-0.8677389936,1.9144764165,0.384323214\N,-5.70497334,0.3709494005,-0.4305713328\C,-6.6729689692,0.8454294086,0.3643433189\H,-6.3665899786,1.538009055,1.1457869147\C,-8.0105885209,0.49180166,0.2250093233\H,-8.7543780553,0.9055205221,0.8961372316\C,-8.3597514855,-0.3969492423,-0.7882952891\H,-9.3932762068,-0.6961923294,-0.9278082081\C,-7.3602496329,-0.8951243809,-1.6196307169\H,-7.5850014649,-1.5889099811,-2.4214443523\C,-6.0498343285,-0.4830809579,-1.4026519878\H,-5.2467188387,-0.8542392311,-2.0354379432\Version=ES64L-G09RevD.01\State=1-A\HF=-397.234418\RMSD=6.066e-09\RMSF=4.842e-06\Dipole=2.5172674,0.7830053,0.4010575\Quadrupole=20.1288534,-9.8679941,-10.2608593,9.5276043,3.7292789,5.2317777\PG=C01 [X(C6H8N3)]\@

N₂

1\1\GINC-R39\FOpt\RM062X\6-31+G(d,p)\N2\ROOT\21-Feb-2019\0\#M062X/6-31+G(d,p) SCF=Tight INT(grid=ultrafine) OPT IOP(2/17=4) maxdisk=5GB\N2.freq\0,1\N,-4.043231887,1.2845555445,0.\N,-2.945748113,1.2426644555,0.\Version=ES64L-G09RevD.01\State=1-SGG\HF=-109.4920406\RMSD=5.661e-09\RMSF=1.615e-04\Dipole=0.,0.,0.\Quadrupole=-0.7422595,0.3703181,0.3719414,0.0425292,0.,0.\PG=D*H [C*(N1.N1)]\@

TEMPO-Me⁺

1\1\GINC-R270\FOpt\UM062X\6-31+G(d,p)\C10H21N1O1(1+,2+)\ROOT\24-Oct-2017\0\#M062X/6-31+G(d,p) SCF=Tight INT(grid=ultrafine) OPT IOP(2/17=4) maxdisk=16GB\TEMPO-CH3.freq\1,2\C,-4.7522891336,1.1649458547,0.3741039439\C,-4.5204671498,-0.2396614614,-0.2018555803\C,-3.1811987961,-0.848846535,0.196084032\C,-2.0549363051,0.0497695857,-0.3005045022\C,-2.113282251,1.4786675633,0.2596433569\N,-3.5168755559,1.9734414423,0.1932453268\C,-5.9074691701,1.860008002,-0.3528974628\O,-3.6479975436,3.2750839386,0.4689660521\C,-5.0523109473,1.1266442527,1.8915587842\H,-4.5841644089,-0.1857657393,-1.2959194746\H,-5.3567413333,-0.8597736601,0.1347799309\H,-3.0827550015,-1.8389813295,-0.2554592722\H,-3.1205270487,-0.9978559041,1.2795309215\H,-2.0898107408,0.1006087255,-1.3958414034\H,-1.0739666377,-0.3542529352,-0.0327931823\C,-1.2144901205,2.4116063496,-0.5581128481\C,-1.6916339722,1.5370218235,1.7476659466\H,-5.6693473338,2.0436614915,-1.404489608\H,-6.1940770024,2.7929330258,0.1365746243\H,-6.7675468278,1.1868879813,-0.3198144677\C,-3.8341346017,4.1807583385,-0.6678704319\H,-4.3486650786,0.4971200382,2.4365070209\H,-6.0534917793,0.7043325323,2.0098195908\H,-5.0455151937,2.1334121548,2.3145226064\H,-1.5131928746,2.4394432842,-1.6093657124\H,-0.2005223288,2.0068903531,-0.5159373738\H,-1.1898007555,3.4233592571,-0.1481907537\H,-2.2023855793,0.7867326637,2.3514774108\H,-1.8769772112,2.5289606548,2.1649160488\H,-0.6181931597,1.3356305802,1.7860727189\H,-3.3364900086,5.1001740841,-0.3651403187\H,-4.8993863866,4.3434876516,-0.82151573

17\H,-3.3646177624,3.7639659356,-1.557710192\\Version=ES64L-G09RevD.01\State=2-A\HF=-523.1456267\S2=0.754276\S2-1=0.\S2A=0.750016\RMSD=8.422e-09\RMSF=1.942e-06\Dipole=-0.0664919,0.4043827,-0.4274358\Quadrupole=2.2141217,2.7295035,-4.9436253,-0.1438838,0.121849,-3.3965918\PG=C01 [X(C10H21N1O1)]\@

TEMPO-Me* Pyrdine TS

1\1\GINC-R295\FTS\UM062X\6-31+G(d,p)\C15H26N2O1(1+,2)\ROOT\06-Aug-2018\0\#M062X\6-31+G(d,p) SCF=Tight INT(grid=ultrafine) OPT=(TS,calcfc,noeigentest,maxstep=10) IOP(2/17=4) maxdisk=30GB\TEMPO-CH3.radcat.Pyrdine.freq\1,2\C,0.7705152551,-1.3276945945,0.1449816598\C,1.8274043984,-1.2997040501,-0.9676550222\C,2.7297666251,-0.0720076232,-0.9182347038\C,1.8751117097,1.1831588927,-1.0529921441\C,0.8228829044,1.3286281247,0.0547285653\N,0.1251431337,0.0188505586,0.2500428352\C,-0.3186394094,-2.3476570273,-0.1921385091\O,-0.9578204728,0.0636836616,0.9498638181\C,1.3838877236,-1.667071057,1.5151120929\H,1.3176077415,-1.3284701147,-1.9396375605\H,2.4085079152,-2.2237980453,-0.886012366\H,3.4516152989,-0.1141521606,-1.7380205563\H,3.3155961652,-0.0515277366,0.0073537953\H,1.3643733882,1.1645989162,-2.0247110721\H,2.4916220423,2.0875091681,-1.0353180821\C,-0.2261593209,2.3654223535,-0.3508951014\C,1.4526209173,1.735557819,1.3988207199\H,-0.8491285636,-2.0710276288,-1.1090112305\H,-1.0314358717,-2.4600699438,0.6273987156\H,0.1592402883,-3.3153766207,-0.3638120724\C,-2.5435035872,0.0631840819,0.1196966834\H,2.2638183543,-1.0618752356,1.7379355157\H,1.6891703266,-2.7168620799,1.5052561209\H,0.6443538999,-1.5260377061,2.3071596726\H,-0.7763803657,2.0462676552,-1.2416268272\H,0.2896862336,3.297586266,-0.5944198874\H,-0.9266532934,2.5666130338,0.4622397714\H,2.3086062865,1.1129850605,1.663253913\H,0.7098709653,1.6785223569,2.1983339477\H,1.7988587976,2.7693961642,1.3171095281\H,-2.8270245786,1.0232899511,0.5243069751\H,-2.874956724,-0.8373901422,0.6138575945\H,-2.1580913123,0.0092231348,-0.8886310731\N,-4.4646195601,0.0502514895,-0.8065592598\C,-5.3078503054,1.0810896682,-0.7031822413\C,-6.5693004572,1.0708309906,-1.2892444659\C,-6.9602129725,-0.0567077722,-2.0064450231\C,-6.0796147213,-1.1308555652,-2.1122319789\C,-4.8385472112,-1.0332180956,-1.4937052166\H,-4.9618457976,1.9392518352,-0.13221707\H,-7.2241490691,1.9276058163,-1.1808931525\H,-7.9376935579,-0.098737351,-2.4753769346\H,-6.3446660865,-2.0280125984,-2.6595274672\H,-4.1180771324,-1.84685385,-1.5456829069\\Version=ES64L-G09RevD.01\State=2-A\HF=-771.332436\S2=0.754085\S2-1=0.\S2A=0.750015\RMSD=6.569e-09\RMSF=7.936e-07\Dipole=-0.9133094,-0.0081777,-0.5491946\Quadrupole=28.130142,-9.4335049,-18.6966371,-1.2530509,10.6074915,2.4453801\PG=C01 [X(C15H26N2O1)]\@

TEMPO*

1\1\GINC-R3523\FOpt\UM062X\6-31+G(d,p)\C9H18N1O1(2)\ROOT\18-Nov-2014\0\#M062X\6-31+G(d,p) INT(grid=ultrafine) OPT IOP(2/17=4) Freq=norman maxdisk=268435456\TEMPO.freq\0,2\C,-3.1795695774,0.6943840806,-0.1543978295\N,-3.0111091496,-0.6645227138,-0.7474070193\C,-2.1216419643,-1.7186166351,-0.1778452386\C,-0.8388983908,-1.0785296864,0.3680998261\C,-1.098476247,0.1548451927,1.2268757815\C,-1.835785072,1.1952442897,0.3901943528\C,-3.6560721161,1.6204220309,-1.274930014\C,-4.2509331437,0.638971433,0.9459956346\C,-2.8804531409,-2.4869222357,0.9156209616\C,-1.7714822058,-2.6780921076,-1.3166991768\O,-3.9914971532,-1.0875822902,-1.4441355913\H,-0.2044304603,-0.7887816971,-0.4802770318\H,-0.2927318602,-1.8456082837,0.9290419387\H,-0.1493419719,0.5675071656,1.5834918306\H,-1.6779759482,-0.1079021929,2.1199763312\H,-1.1988640854,1.4793971645,-0.4582368735\H,-2.0258390315,2.107392652,0.9674537094\H,-2.9604672147,1.5864125622,-2.1183802738\H,-3.7017280578,2.6464577713,-0.8968153984\H,-4.6440264258,1.3242459484,-1.6301073411\H,-3.9056557026,0.1110272116,1.8382430558\H,-5.1406851559,0.1331938842,0.5613572075\H,-4.5251846193,1.6569024339,1.2404806744\H,-3.0283905726,-1.8899049507,1.8187997648\H,-2.3155619

019,-3.3829709303,1.1915076377\H,-3.858031528,-2.7923787955,0.5329290769\H,-1.3312005709,-2.1297411036,-2.154490572\H,-2.6612429111,-3.1982355339,-1.6740528207\H,-1.0451436066,-3.4128794674,-0.9556946844\\Version=ES64L-G09RevD.01\State=2-A\HF=-483.5234304\S2=0.754861\S2-1=0.\S2A=0.750014\RMSD=3.991e-09\RMSF=5.988e-06\Dipole=0.8207978,0.3514986,0.8605761\Quadrupole=-0.7073146,2.3702525,-1.6629378,-1.6385592,-2.2349817,-0.9337956\PG=CS [SG(C1H2N1O1),X(C8H16)]\@

O⁺Me₃

1\1\GINC-R37\FOpt\RM062X\6-31+G(d,p)\C3H9O1(1+)\ROOT\07-Aug-2018\0\#M062X\6-31+G(d,p) SCF=Tight INT(grid=ultrafine) OPT IOP(2/17=4) maxdisk=5GB\OMe3+.freq\1,1\O,-2.6957046907,1.5673254486,-0.0378172135\C,-1.2316850606,1.6103252687,0.0877903027\C,-3.235545522,0.2096097093,-0.1995563808\C,-3.2350171011,2.536735914,-1.0023716099\H,-0.9752632652,0.9461148384,0.9101306448\H,-0.9748785917,2.640188074,0.3257069079\H,-0.7917465054,1.2842770562,-0.8570383941\H,-2.8599246119,-0.3712795228,0.6398767035\H,-2.8970436708,-0.1873436248,-1.1589307513\H,-4.3182860815,0.3031177127,-0.1537262024\H,-2.8590429505,3.5114914246,-0.6996070089\H,-4.3177890936,2.4918154246,-0.908786178\H,-2.8964885009,2.2575832035,-2.0023850031\\Version=ES64L-G09RevD.01\State=1-A\HF=-194.5622407\RMSD=4.750e-09\RMSF=1.794e-05\Dipole=0.0781678,-0.0701329,-0.2032432\Quadrupole=1.1746184,1.2980967,-2.4727151,0.5680838,1.6462917,-1.4770672\PG=C03V [C3(O1),3SGV(C1H1),X(H6)]\@

O⁺Me₃ Pyridine TS

1\1\GINC-R357\FTS\RM062X\6-31+G(d,p)\C8H14N1O1(1+)\ROOT\07-Aug-2018\0\#M062X\6-31+G(d,p) SCF=Tight INT(grid=ultrafine) OPT=(TS,calcfc,noeigentest,maxstep=10) IOP(2/17=4) maxdisk=20GB\OCH3+.Pyrdine.freq\1,1\C,3.5322549249,-0.4208624963,1.1547517\O,2.9282107955,-0.3264074346,-0.148547974\C,1.1674089388,-0.1651656093,-0.072885439\H,1.0304640919,-1.063939478,0.5111561025\H,1.0373559389,-0.2105500537,-1.144646142\H,1.1630653131,0.7980443598,0.4235801469\N,-0.9452017297,-0.0238238523,-0.0088174457\C,-1.6642325969,-1.0264510268,-0.5246627053\C,-3.054099675,-1.0204796209,-0.5273104793\C,-3.7147972658,0.0723337883,0.0289932128\C,-2.9647962854,1.1156236259,0.5657412993\C,-1.5778617565,1.0253567436,0.5252607011\H,-1.1052499035,-1.858222424,-0.9478990809\H,-3.5992372036,-1.8534646235,-0.9556677136\H,-4.7989679419,0.110127697,0.0438776291\H,-3.4387122048,1.9841481186,1.0080624663\H,-0.9539386379,1.8173352435,0.9329237754\C,3.5411639278,0.6768031503,-0.9793533457\H,3.0391365026,-1.2379563152,1.6795102673\H,3.4046441082,0.5228339872,1.6949504099\H,4.5910813522,-0.6489844488,1.0265992223\H,3.0545427177,0.6298891831,-1.9525831169\H,4.5999588501,0.4364680801,-1.0831228471\H,3.4136287394,1.665559406,-0.5268596435\\Version=ES64L-G09RevD.01\State=1-A\HF=-442.7568293\RMSD=4.977e-09\RMSF=1.519e-06\Dipole=1.5496157,0.2041122,0.1112543\Quadrupole=23.2666116,-10.3953784,-12.8712332,1.5150631,0.9321953,1.7107289\PG=C01 [X(C8H14N1O1)]\@

OMe₂

1\1\GINC-R37\FOpt\RM062X\6-31+G(d,p)\C2H6O1\ROOT\21-Feb-2019\0\#M062X\6-31+G(d,p) SCF=Tight INT(grid=ultrafine) OPT IOP(2/17=4) maxdisk=5GB\OMe2.freq\0,1\O,-2.509372905,1.6389066432,-0.0746687658\C,-1.104076492,1.6603731491,-0.0983322938\C,-3.007878593,0.755550583,0.8985017427\H,-0.7998800583,2.3644406015,-0.8739881563\H,-0.6950844609,0.6662558642,-0.3320492442\H,-0.6950721251,1.9889558869,0.8685782929\H,-4.0969157261,0.7974618086,0.8523453589\H,-2.6773968508,1.046818428,1.9065269101\H,-2.6774091867,-0.2758815947,0.705899373\\Version=ES64L-G09RevD.01\State=1-A\HF=-154.9554085\RMSD=4.489e-09\RMSF=6.092e-05\Dipole=0.3343888,-0.3178294,0.3501409\Quadrupole=0.7962862,-0.4075104,-0.3887758,1.0433013,-1.1493911,-0.0964766\PG=C02V [C2(O1),SGV(C2H2),X(H4)]\@

MeOTf

1\1\GINC-R75\FOpt\RM062X\6-31+G(d,p)\C2H3F3O3S1\ROOT\14-Jan-2019\0\#\M062X\6-31+G(d,p) SCF=Tight INT(grid=ultrafine) OPT IOP(2/17=4) maxdisk=8GB\CH3.OTf.retry.freq\0,1\C,2.1402070726,-1.0709252363,0.9696257224\O,1.4651186466,-0.6636770136,-0.2471100818\S,0.5161818618,0.6147049059,-0.1999790373\O,0.8085695084,1.4084690496,0.9695504344\O,0.4433703114,1.1519123628,-1.5297963165\C,-1.1006704809,-0.2274041492,0.1228027773\F,-2.0473485158,0.687758817,0.2622223901\F,-1.4043748799,-1.0356324748,-0.8801281397\F,-1.0061253188,-0.9396470031,1.2453293856\H,2.8244372998,-1.8522082628,0.6460772619\H,1.4167404501,-1.4636461499,1.6848298162\H,2.6833640448,-0.2269148457,1.3926557873\Version=ES64L-G09RevD.01\State=1-A\HF=-1001.0894036\RMSD=5.450e-09\RMSF=6.898e-06\Dipole=0.5471475,-1.1078907,0.7817563\Quadrupole=4.2789763,-1.3452412,-2.9337351,-3.0193653,2.3938478,-1.2878991\PG=C01 [X(C2H3F3O3S1)]\@

MeOTf Pyridine TS

1\1\GINC-R105\FTS\RM062X\6-31+G(d,p)\C7H8F3N1O3S1\ROOT\03-Aug-2018\0\#\M062X\6-31+G(d,p) SCF=Tight INT(grid=ultrafine) OPT=(TS,calcfc,noeigentest,maxstep=10) IOP(2/17=4) maxdisk=12GB\MeOTf.Pyridine.freq\0,1\C,-0.6823439376,0.5225382094,0.721673954\O,1.1401530503,0.8557037929,1.1002216207\S,2.0621954005,0.8410443782,-0.1061977189\O,1.3115950485,0.9741663795,-1.3529383558\O,3.2702611113,1.6127721175,0.0896480341\C,2.6071601715,-0.9248853781,-0.1017874433\F,3.3721939247,-1.1878762554,-1.1565292884\F,3.2843950274,-1.216993556,1.0045250082\F,1.5291187476,-1.7268546889,-0.1541130444\H,-0.469734483,-0.5137440658,0.5077270134\H,-0.6581038347,1.2516286246,-0.072843704\N,-2.5875168583,0.1918808866,0.321190901\H,-0.9046338576,0.8261012656,1.7344319622\C,-2.8910799759,-0.0146774175,-0.9626473677\C,-4.1917398503,-0.2813734943,-1.3744958494\C,-5.1973703177,-0.3317583193,-0.4120585312\C,-4.8709723254,-0.115537929,0.9242721917\C,-3.5439857524,0.1445896852,1.2494068236\H,-2.0611075302,0.038044456,-1.6644621102\H,-4.4043039744,-0.443834755,-2.4246563992\H,-6.2231590712,-0.5371474448,-0.700079464\H,-5.6239622933,-0.1462668067,1.7031163721\H,-3.2311694197,0.3199313151,2.2755163953\Version=ES64L-G09RevD.01\State=1-A\HF=-1249.2470284\RMSD=3.181e-09\RMSF=1.804e-06\Dipole=-5.2939764,-0.967222,0.3514084\Quadrupole=10.5651496,-9.1990485,-1.3661011,-4.1185462,-0.4416082,1.4462282\PG=C01 [X(C7H8F3N1O3S1)]\@

OTf

1\1\GINC-R87\FOpt\RM062X\6-31+G(d,p)\C1F3O3S1(1-)\ROOT\19-Mar-2016\0\#\M062X\6-31+G(d,p) INT(grid=ultrafine) OPT IOP(2/17=4) Freq=noraman maxdisk=268435456\OTf.anion.C3V.freq\0,1\S,0.000000137,0,-0.95104\O,0.7175822598,1.2428886953,-1.26131\O,0.7175822598,-1.2428886953,-1.26131\O,-1.4351641086,0,-1.26131\C,0.000000137,0,0.90693\F,1.24769,0,1.40615\F,-0.6238447945,-1.0805311174,1.40615\F,-0.6238447945,1.0805311174,1.40615\Version=ES64L-G09RevD.01\State=1-A\HF=-961.3207645\RMSD=9.845e-09\RMSF=6.784e-05\Dipole=0,0,1.6114666\Quadrupole=0.2894337,0.2894337,-0.5788675,0,0,0\PG=C03V [C3(C1S1),3SGV(F1O1)]\@

Pyridine

1\1\GINC-R121\FOpt\RM062X\6-31+G(d,p)\C5H5N1\ROOT\03-Aug-2018\0\#\M062X\6-31+G(d,p) SCF=Tight INT(grid=ultrafine) OPT IOP(2/17=4) maxdisk=5GB\Pyridine.freq\0,1\C,-1.1399524933,0.6879130296,0\C,-1.1963865301,-0.7052924301,0\C,0,-1.4163694077,0\C,1.1963865301,-0.7052924301,0\C,1.1399524933,0.6879130296,0\N,0,1.3832232945,0\H,-2.0553316643,1.2748227612,0\H,-2.1547794403,-1.2131517559,0\H,0,-2.5020870964,0\H,2.1547794403,-1.2131517559,0\H,2.0553316643,1.2748227612,0\Version=ES64L-G09RevD.01\State=1-A\HF=-248.1861963\RMSD=5.864e-09\RMSF=3.953e-05\Dipole=0,,

-0.9256658,0.\Quadrupole=4.0664884,-1.3989628,-2.6675256,0.,0.,0.\PG=C02V [C2(H1C1 N1),SGV(C4H4)]\@

Methylpyridinium⁺

1\1\GINC-R111\FOpt\RM062X\6-31+G(d,p)\C6H8N1(1+)\ROOT\03-Aug-2018\0\#M062X\6-31+G(d,p) SCF=Tight INT(grid=ultrafine) OPT IOP(2/17=4) maxdisk=5GB\Pyridine.CH3.freq\1,1\C,-3.0080098039,2.1040174798,0.0000203922\C,-2.7365896029,0.7498707132,0.000203922\C,-1.4080983637,0.3238698599,0.0000203922\C,-0.3875476272,1.2711896675,0.0000203922\C,-0.7151162615,2.615682989,0.0000203922\N,-2.0047662196,3.0084304647,0.0000203922\C,-2.3494236951,4.4481692364,0.0000203922\H,-4.0148681394,2.506916131,0.0000203922\H,-3.5599349504,0.045755923,0.0000203922\H,-1.1727131345,-0.7351570142,0.0000203922\H,0.6568324265,0.9832366314,0.0000203922\H,0.0297043988,3.4025616236,0.0000203922\H,-1.4313189724,5.0315119282,0.0000203922\H,-2.9291100273,4.6727571833,0.895639433\H,-2.9291100273,4.6727571833,-0.8955986487\Version=E S64L-G09RevD.01\State=1-A\HF=-287.8470344\RMSD=5.323e-09\RMSF=9.346e-05\Dipole=-0.0981475,0.3981333,0.\Quadrupole=2.123117,6.9362874,-9.0594045,-1.1920312,0.,0.\PG=CS [SG(C6H6N1),X(H2)]\@

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