Supporting Information

Reductive Arylation of Arylidene Malonates Using Photoredox Catalysis

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Table of Contents

General Information

All reactions were carried out under an argon or nitrogen atmosphere in flame-dried glassware with magnetic stirring. Solvents used in reactions were purified by passage through a bed of activated alumina. Unless stated otherwise, reagents were purified prior to use following the guidelines of Perrin and Armarego.[1] Purification of reaction products was carried out by flash chromatography on Biotage Isolera 4 systems with Ultra-grade silica cartridges. Analytical thin layer chromatography was performed on EM Reagent 0.25 mm silica gel 60-F plates. Visualization was accomplished with UV light. Infrared spectra were recorded on a Bruker Tensor 37 FT-IR spectrometer. ^{1}H NMR spectra were recorded on an AVANCE III 500 MHz spectrometer with direct cryoprobe (500 MHz) and Bruker Avance III 600 MHz (151 MHz) system. Spectra are reported in ppm using solvent as an internal standard ($CHCl_3$ at 7.26 ppm). Peak multiplicities are reported as (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, m = multiplet, br = broad; coupling constant(s) in Hz; integration.) Proton-decoupled ^{13}C NMR spectra were recorded on an AVANCE III 500 MHz with direct cryoprobe (125 MHz) spectrometer or Bruker Avance III 600 MHz (151 MHz) system. These are reported in ppm using solvent as an internal standard ($CDCl_3$ at 77.16 ppm). Low-resolution mass spectra were obtained on WATERS Acquity-H UPLC-MS with a single quad detector (ESI) Varian1200 Quadrupole Mass Spectrometer. High-resolution mass spectra were obtained using an Agilent 6120A LC-time of flight mass spectrometer. Gas chromatography experiments were run on Agilent 7890A/5975C GC/MS System. Blue light was generated by 3 40 W Kessil P160 LED lights. UV-Vis measurements were made on a Thermo Fisher Nanodrop One Spectrophotometer.

Iridium and Ruthenium photocatalysts were obtained from Strem Chemical and Sigma-Aldrich, respectively, and used as received. Photocatalysts DPAIPN and CZIPN were synthesized according literature precedent.[2]

Images of Setup for Photoredox Reactions

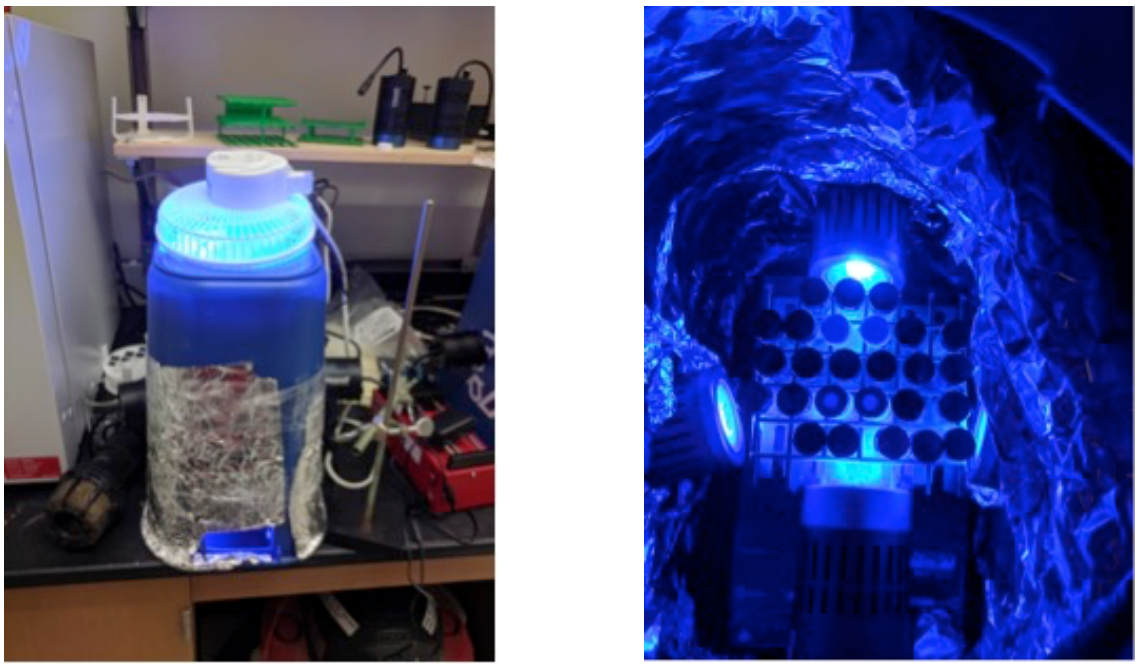


Figure S1: Images of setup for photoredox reactions

Equipment for 96-Well Plate Optimization of Reaction Conditions

Chemistry

96-well block photoredox plate assembly (Analytical Sales & Services, item #96973)

Replacement Rubber mats (Analytical Sales & Services, item #96965)

Replacement Films (Analytical Sales & Services, item #96967)

1 mL clear glass shell vials (Analytical Sales & Services, item #84001-case)

Stir Stix, stainless steel, PTFE encapsulated (V&P Scientific, item #VP 734-2)

Biotage SPE Dry 96-well plate evaporator (Biotage, item #SD-9600-DHS-NA)

Lumidox LED Controller (Analytical Sales & Services, item #LUMCON)

Lumidox 96-Well Blue LED Array (Analytical Sales & Services, item # LUM96B)

Magnetic Tumble Stirrer (V&P Scientific, item #VP 710E5)

Analytical

Sample Collection Plate (Waters, item #WAT058957)

Plate Sealing Cap (Waters, item #WAT058959)

Waters Acquity H-Class UPLC equipped with a single quad detector (ESI)

Selected Photos of Setup for 96-Well Plate Reaction Discovery

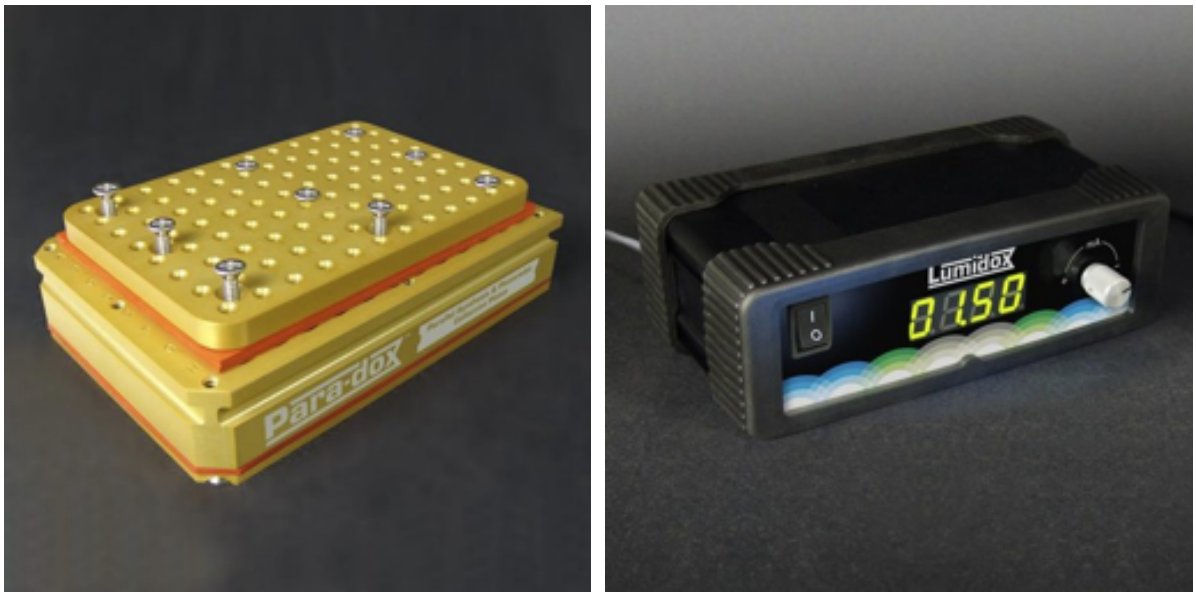


Figure S2: *96-well block photoredox plate assembly* (Analytical Sales & Services, item #96973) and Lumidox LED Controller (Analytical Sales & Services, item #LUMCON)

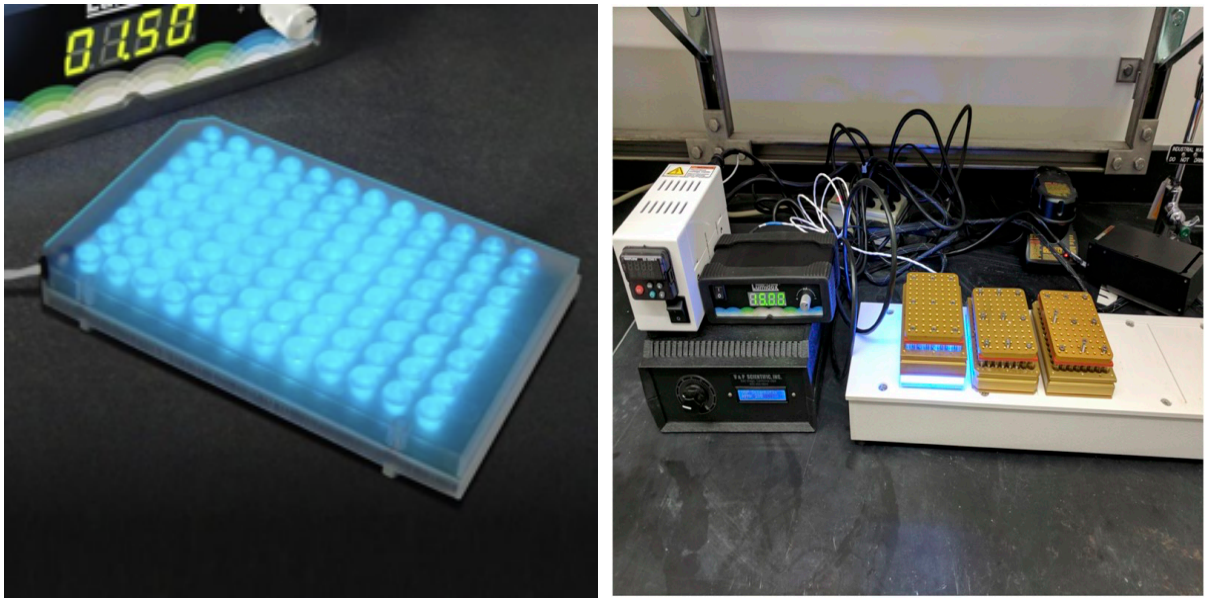


Figure S3: Lumidox 96-Well Blue LED Array (Analytical Sales & Services, item # LUM96B) and picture of full setup in use

Procedure for 96-Well Plate Optimization of Reaction Conditions

A 96-well plate photoredox plate assembly with 96 1 mL clear glass shell vial inserts equipped with Stir Stix was brought into an inert-air glovebox. Stock solutions were prepared and stored in the glovebox as follows:

1) Solution of arylidene malonate (1.0 equiv) and 4-CN pyridine (2.0 equiv) in CH_3CN
2) Solution of each photocatalyst in CH_3CN
    a. $Ir(ppy)_3$
    b. $Ru(bpy)_3$
    c. $Ir[(dF\text{-}CF_3)ppy)_2dtbpy]PF_6$
    d. $Ir[(ppy)_2dtbpy]PF_6$
    e. DPAIPN
    f. Ph-MesAcr-BF_4
3) Solution of $Sc(OTf)_3$ in CH_3CN
4) Solution of each terminal reductant in either CH_3CN or DMF
    a. NEt_3
    b. DIPEA
    c. NBu_3
    d. Hanztsch Ester (HE)

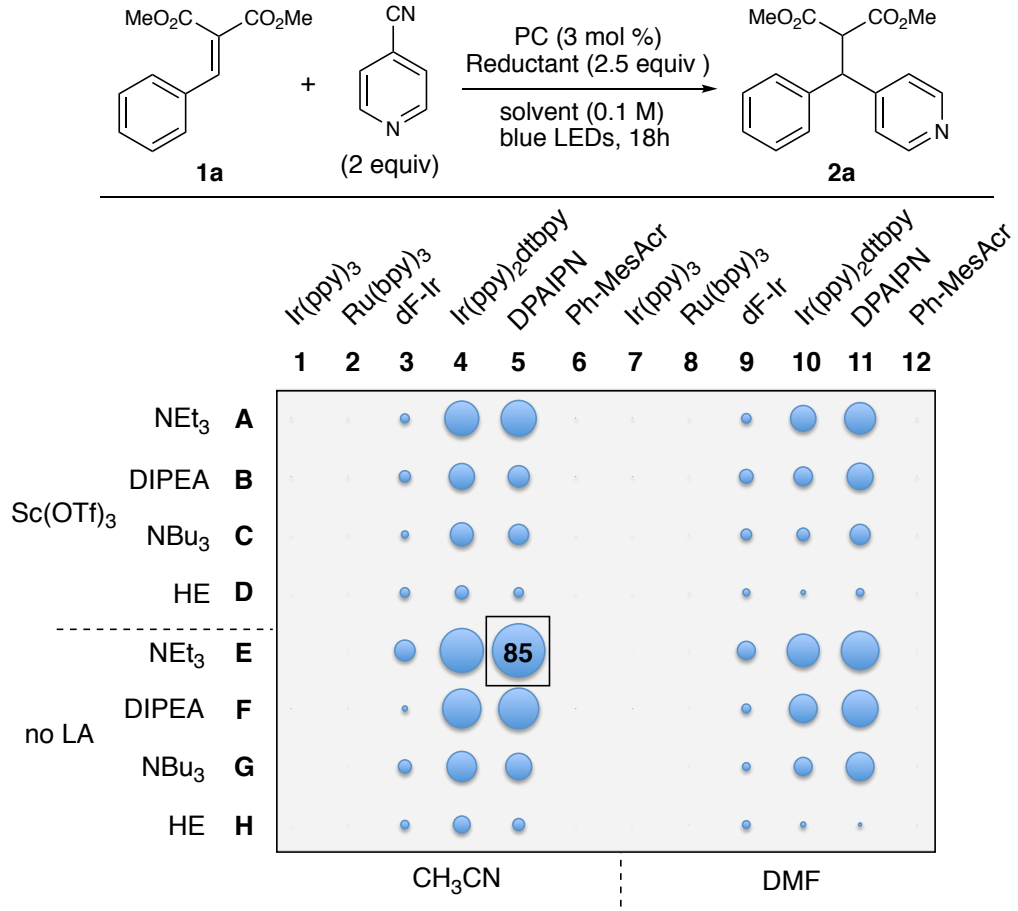
Dosing into the 96-well plate was as follows

1) Stock solution 1: A1-H12
2) Stock Solution 2
    a. Stock Solution 2a: A1-H1, A7-H7
    b. Stock Solution 2b: A2-H1, A8-H8
    c. Stock Solution 2c: A3-H3, A9-H9
    d. Stock Solution 2d: A4-H4, A10-H10
    e. Stock Solution 2e: A5-H5, A11-H11
    f. Stock Solution 2f: A6-H6, A12-H12
3) Stock Solution 3: A1-D12
4) CH_3CN Stock Solution: E1-H12
5) Evaporate solvent using Biotage SPE Dry 96-well plate evaporator
6) Stock Solution 4
    a. Stock Solution 4a: NEt_3 in CH_3CN: A1-A12
    b. Stock Solution 4b: DIPEA in CH_3CN: B1-B12
    c. Stock Solution 4c: NBu_3 in CH_3CN: C1-C12
    d. Stock Solution 4d: HE in CH_3CN: D1-D12
    e. Stock Solution 4a: NEt_3 in DMF: E1-E12
    f. Stock Solution 4a: DIPEA in DMF: F1-F12
    g. Stock Solution 4a: NBu_3 in DMF: G1-G12
    h. Stock Solution 4a: HE in DMF: H1-H12
7) The 96-well plate apparatus was sealed and removed from the glovebox. The 96-well plate was placed on the V&P Magnetic Tumble Stirrer on top of the Lumidox Blue LED array, and the reaction plate was irradiated at maximum irradiation for 18 hours.

8) Upon reaction completion, the reaction samples were then analyzed by UPLC-MS using naphthalene as an internal standard.

Results of 96-Well Plate Investigation of Reductive Arylation

Yields were obtained by UPLC-MS using naphthalene as an internal standard against an established calibration curve. Yields are representative of a single data run.



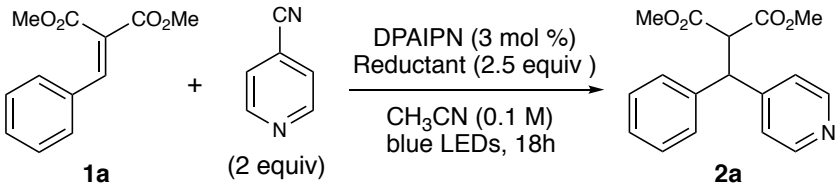
	1	2	3	4	5	6	7	8	9	10	11	12
A	0	0	14	55	57	0	0	0	15	41	50	0
B	0	0	18	41	34	0	0	0	22	30	42	0
C	0	0	11	37	32	0	0	0	17	20	32	0
D	0	0	15	21	15	0	0	0	11	7	12	0
E	0	0	33	70	85	0	0	0	29	52	61	0
F	0	0	8	62	65	0	0	0	14	45	58	0
G	0	0	21	48	42	0	0	0	12	29	45	0
H	0	0	13	27	19	0	0	0	12	8	5	0

Scheme S1: Results of 96-well plate reaction optimization

General Procedure for Optimization Scale Up

To a 2 dram vial was added arylidene malonate (1.0 equiv) and cyanoarene (2.0 equiv). The reaction vessel was equipped a stir bar, capped and was then taken into a glovebox. DPAIPN (3 mol %) was added to the vial, which was then removed from the glovebox. The vial was then charged with a

solution of terminal reductant (2.5 equiv) and sparged CH_3CN (0.1 M). The mixture was stirred until homogenous. The vial was then placed between 3 Kessil blue LED lights and irradiated for 18 hours (with a small fan placed for cooling to maintain temperature at 23 °C). Product yield was determined by GCMS using biphenyl as an internal standard.



1a **2a**

entry	PC	Terminal Reductant	Yield (%)[a]
1	DPAIPN	NEt_3	87 (85)[b]
2	DPAIPN	DIPEA	45
3	DPAIPN	NBu_3	29
4	DPAIPN	HE	N.D.
5[c]	DPAIPN	HE	24
6[d]	DPAIPN	NEt_3	55
7	DPAIPN	NPh_3	N.D.
8[e]	DPAIPN	NPh_3/NEt_3	<5
9[f]	DPAIPN	NPh_3/$NHEt_3Cl$	25
10	-	NEt_3	N.D.
11	DPAIPN	-	N.D.
12[g]	DPAIPN	NEt_3	N.D.

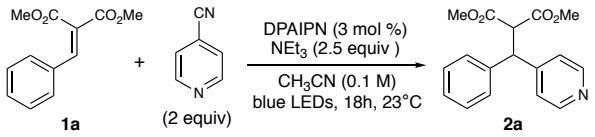
Table S1: Further Reaction Optimization

[a]Yield determined by GC with biphenyl as internal standard. [b]Yield of isolated product. [c]With inclusion of 10 mol % $Sc(OTf)_3$ [d]1.25 equiv NEt_3 used [e]1.25 equiv NEt_3 and 1.25 equiv of NPh_3 used [f]1.25 equiv $NHEt_3Cl$ and 1.25 equiv of NPh_3 used [g]Reaction performed in the absence of light. DIPEA = diisopropylethylamine, NEt_3 = triethylamine, NBu_3 = tributylamine, HE = Hanztsch Ester

Procedure for Determining Reaction-Condition-Based Sensitivity of Arylation Reaction

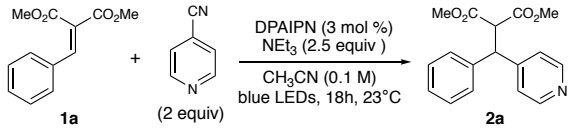
Following a procedure outlined by Glorius,[3] we conducted a "design of experiment" approach to determine the influence of several reaction parameters, with the end goal of determining fluctuation in yield based on parameter variations in positive and negative directions relative to the standard reaction conditions. Only one variable was intentionally changed per experiment while maintaining the others at the standard level. The assessed parameters are as follows: concentration, temperature,

light irradiation, oxygen levels, and water levels. Reactions were set up from single stock solutions of all reagents in order to minimize variability based on compounded weighing/dispensing of reagents. Reactions were set up in an inert-air glovebox except when otherwise noted. All reactions were run in triplicate to ensure reproducibility of results. All yields were determined by GCMS using biphenyl as an internal standard. Reaction was conducted per the General Procedure for Reductive Arylation, with variations from the standard conditions as noted. Variations in irradiation are based on irradiation control found on standard PR160 456 nm lights commercially available from Kessil.



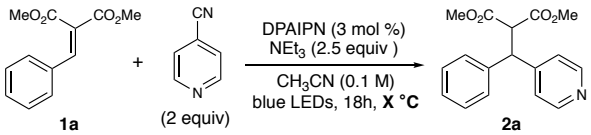
entry	Note	Yield 1 (%)	Yield 2 (%)	Yield 3 (%)	Average (%)	Std. Dev. (%)
1	**freeze-pump-thaw (low O_2)**	90	91	90	90	0.53
2	**N_2 bubbling (std. conditions)**	85	87	88	87	1.44
3	**not-degassed, prepared on benchtop (high O_2)**	76	75	77	76	1.07

Table S2: Effect of O_2 level on reaction yield



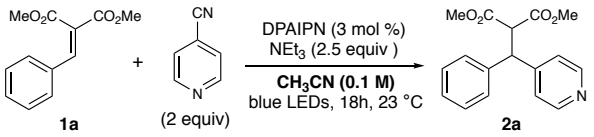
entry	Note	Water Content (ppm)	Yield 1 (%)	Yield 2 (%)	Yield 3 (%)	Average (%)	Std. Dev. (%)
1	**SDS CH_3CN, stored over 4 Å MS (low H_2O)**	5.5	91	90	90	90	0.52
2	**SDS CH_3CN (std. conditions)**	7.2	85	87	88	87	1.44
3	**10 equiv H_2O added (high H_2O)**	18,250	77	74	78	76	2.23

Table S3: Effect of H_2O level on reaction yield



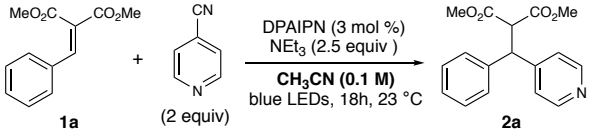
entry	Note	Yield 1 (%)	Yield 2 (%)	Yield 3 (%)	Average (%)	Std. Dev. (%)
1	**10 °C (low temp)**	79	80	78	79	1.03
2	**23 °C (std. conditions)**	85	87	88	87	1.44
3	**40 °C (high temp)**	86	85	85	85	0.55

Table S4: Effect of reaction temperature on reaction yield



entry	Note	Yield 1 (%)	Yield 2 (%)	Yield 3 (%)	Average (%)	Std. Dev. (%)
1	**0.05 M (low conc)**	85	84	85	85	0.56
2	**0.1 M (std. conditions)**	85	87	88	87	1.44
3	**0.3 M (high conc)**	79	82	78	80	2.13

Table S5: Effect of reaction concentration on reaction yield



entry	Note	Yield 1 (%)	Yield 2 (%)	Yield 3 (%)	Average (%)	Std. Dev. (%)
1	**Irradiation: 25 (low I)**	79	77	82	79	2.59
2	**Irradiation: 75 (std. conditions)**	85	87	88	87	1.44
3	**Irradiation: 100 (high I)**	88	90	86	88	1.86

Table S6: Effect of light irradiation power on reaction yield. Irradiation intensity is based on variable irradiation intensity control of PR160 456 nm lights from Kessil. See https://www.kessil.com/photoredox/Products.php for more information.

entry	Condition	Average Yield (%)	Difference (%)
1	**High Irradiation**	88	+1
2	**Low Irradiation**	79	-8
3	**High Concentration**	80	-7
4	**Low Concentration**	85	-2
5	**High Temperature**	85	-2
6	**Low Temperature**	79	-8
7	**High O_2**	76	-11
8	**Low O_2**	89	+2
9	**High H_2O**	77	-10
10	**Low H_2O**	91	+4
11	**std. conditions**	87	0

Table S7: Summary of differences in reaction yield based on positive/negative regulation of set reaction conditions

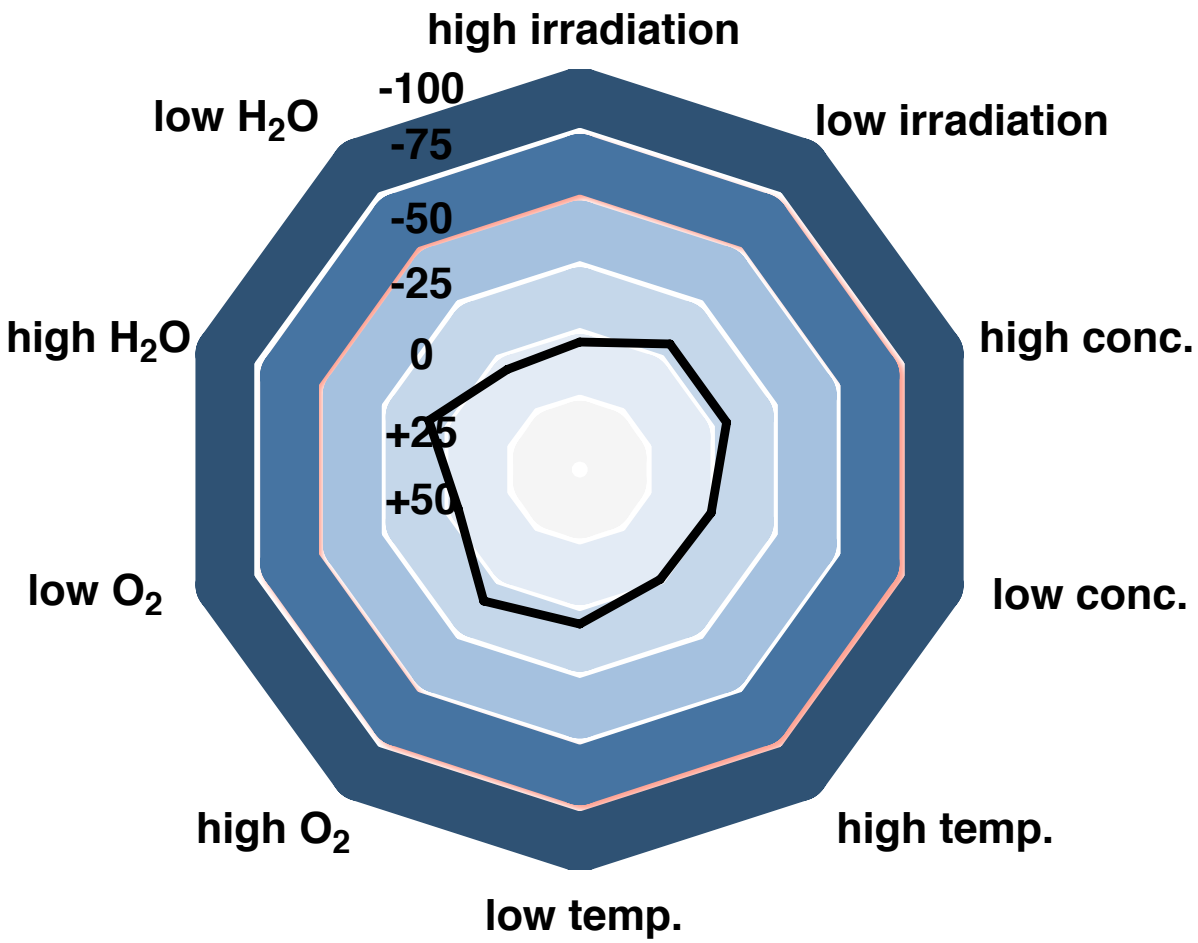


Figure S4: Radar graph plot outlining data in Table S7

Cyclic Voltammetry of Cyclohexyl Alkylidene Malonate (1u)

Cyclic voltammograms were collected with a Nuvant Ezstat Pro potentiostat/galvanostat. Samples were prepared with 0.05 mmol of substrate in 5 mL of 0.1 M tetra-n-butylammonium hexafluorophosphate in degassed acetonitrile. Measurements employed a platinum working electrode, platinum wire counter electrode, a Pt/Ag/AgCl pseudo reference electrode and a scan rate of 250 mV/s. Ferrocene was used as an internal standard. Two cycles were performed on each sample. Measurements reported are of the second scan cycle. No observable reduction of **1u** was observed.

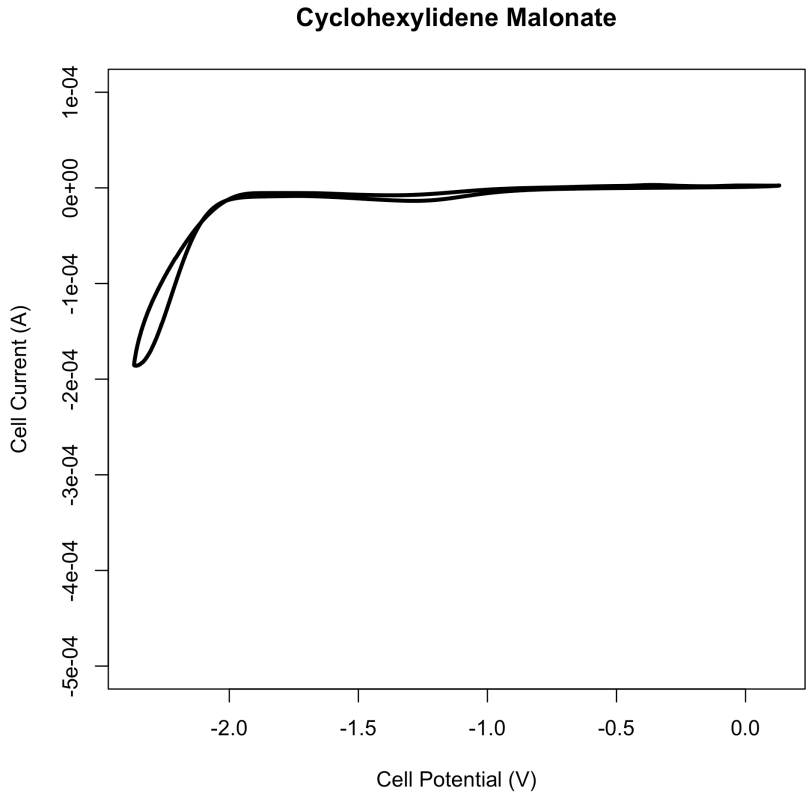
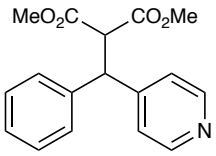


Figure S5: CV of Cyclohexylidene Malonate

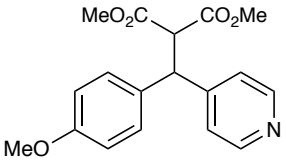
General Procedure for Reductive Arylation

To a 2 dram vial was added arylidene malonate (1.0 equiv) and cyanoarene (2.0 equiv). The reaction vessel was equipped with a stir bar, capped and and was then taken into a glovebox. DPAIPN (3 mol %) was added to the vial, which was then removed from the glovebox. The vial was then charged with NEt_3 (2.5 equiv) and sparged CH_3CN (0.1 M). The mixture was stirred until homogenous. The vial was then placed between 3 Kessil blue LED lights and irradiated for 18 hours (with a small fan placed for cooling to maintain temperature at 23 °C). Conversion of the malonate was monitored by UPLC/MS. Upon complete conversion, the reaction was concentrated under reduced pressure onto silica gel. This silica was loaded onto a column of silica gel and isolated via flash column chromatography (0–100% ethyl acetate/hexanes) to yield the desired product.

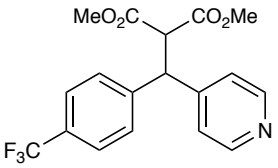
Analytical Data for Products



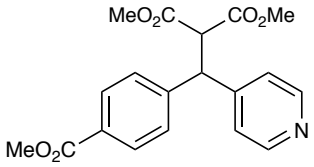
Prepared according to the general procedure for reductive arylation, 85% yield (**2a**)
^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.61 – 8.49 (m, 2H), 7.36 – 7.21 (m, 7H), 4.77 (d, *J* = 12.1 Hz, 1H), 4.36 (d, *J* = 12.0 Hz, 1H), 3.62 (s, 3H), 3.57 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.6, 167.5, 150.0, 149.9, 139.4, 128.9, 127.8, 127.6, 122.9, 56.4, 52.9, 52.8, 50.4. HRMS (ESI): Mass calcd for $C_{17}H_{18}NO_4$[M+H]+: 300.1158; found 300.1160



Prepared according to the general procedure for reductive arylation, 81% yield (**2b**)
^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.51 – 8.45 (m, 2H), 7.23 – 7.17 (m, 2H), 7.17 – 7.10 (m, 2H), 6.83 – 6.76 (m, 2H), 4.69 (d, *J* = 12.0 Hz, 1H), 4.27 (d, *J* = 12.0 Hz, 1H), 3.73 (s, 3H), 3.57 (s, 3H), 3.54 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.7, 167.5, 158.9, 151.1, 149.7, 131.3, 128.9, 122.9, 114.3, 56.5, 55.2, 52.9, 52.8, 49.6. HRMS (ESI): Mass calcd for $C_{18}H_{20}NO_5$ [M+H]+: 330.1263; found 330.1265

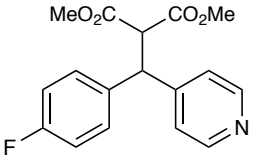


Prepared according to the general procedure for reductive arylation, 62% yield (**2c**)
^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.53 – 8.25 (m, 2H), 7.53 (d, *J* = 8.1 Hz, 2H), 7.37 (d, *J* = 8.1 Hz, 2H), 7.22 – 7.13 (m, 2H), 4.80 (d, *J* = 12.0 Hz, 1H), 4.32 (d, *J* = 12.0 Hz, 1H), 3.58 (s, 3H), 3.55 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.3, 167.2, 150.3, 149.1, 143.5, 129.9 (q, *J* = 32.6 Hz), 128.2, 125.9 (q, *J* = 3.7 Hz) 123.5 (q, *J* = 272 Hz), 122.8, 56.1, 53.0, 53.0, 50.0. HRMS (ESI): Mass calcd for $C_{18}H_{17}F_3NO_4$ [M+H]+: 368.1031; found 368.1035



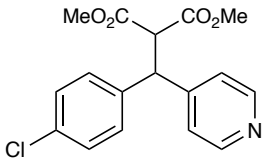
Prepared according to the general procedure for reductive arylation, 62% yield (**2d**)

^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.51 – 8.48 (m, 2H), 8.00 – 7.90 (m, 2H), 7.36 – 7.29 (m, 2H), 7.20 – 7.12 (m, 2H), 4.79 (d, *J* = 12.0 Hz, 1H), 4.33 (d, *J* = 12.0 Hz, 1H), 3.86 (s, 3H), 3.58 (s, 3H), 3.53 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.3, 167.3, 166.5, 150.2, 149.3, 144.5, 130.2, 129.5, 127.9, 122.9, 56.1, 53.0, 52.9, 52.2, 50.2. HRMS (ESI): Mass calcd for $C_{19}H_{20}NO_6$ [M+H]+: 358.1212; found 358.1210



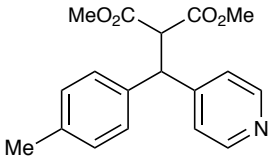
Prepared according to the general procedure for reductive arylation, 75% yield (**2e**)

^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.60 (d, *J* = 5.5 Hz, 2H), 7.54 – 7.41 (m, 2H), 7.23 – 7.19 (m, 2H), 7.06 – 6.92 (m, 2H), 4.82 (d, *J* = 11.8 Hz, 1H), 4.33 (d, *J* = 11.9 Hz, 1H), 3.61 (s, 3H), 3.55 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.3, 167.1, 162.2 (d, *J* = 248 Hz), 155.5, 146.5, 134.0 (d, *J* = 3.2 Hz), 129.6 (d, *J* = 8.2 Hz), 124.3, 116.2 (d, *J* = 21.5 Hz), 56.0, 53.2, 53.0, 49.9. HRMS (ESI): Mass calcd for $C_{17}H_{17}FNO_4$ [M+H]+: 318.1063; found 318.1063

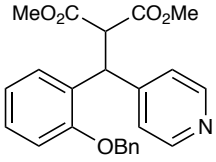


Prepared according to the general procedure for reductive arylation, 91% yield (**2f**)

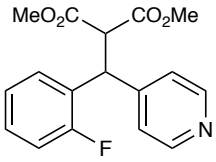
^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.60 – 8.52 (m, 2H), 7.39 – 7.29 (m, 3H), 7.29 – 7.17 (m, 3H), 4.79 (d, *J* = 12.0 Hz, 1H), 4.35 (d, *J* = 12.1 Hz, 1H), 3.65 (s, 3H), 3.54 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.4, 167.3, 150.2, 149.6, 138.0, 133.6, 129.2, 129.1, 122.8, 56.3, 52.9, 52.9, 49.7. HRMS (ESI): Mass calcd for $C_{17}H_{17}ClNO_4$ [M+H]+: 334.0768; found 334.0770



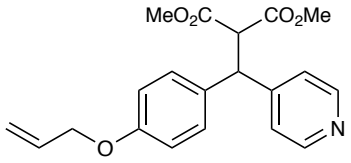
Prepared according to the general procedure for reductive arylation, 87% yield (**2g**)
^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.50 – 8.39 (m, 2H), 7.21 – 7.10 (m, 3H), 7.06 – 6.97 (m, 3H), 4.68 (d, *J* = 12.1 Hz, 1H), 4.31 (d, *J* = 12.0 Hz, 1H), 3.56 (s, 3H), 3.53 (s, 3H), 2.27 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.7, 167.5, 150.3, 150.1, 139.3, 138.6, 128.8, 128.7, 128.4, 124.6, 122.9, 56.4, 52.8, 52.8, 50.3, 21.4. HRMS (ESI): Mass calcd for $C_{18}H_{20}NO_4$ [M+H]+: 314.1314; found 314.1310



Prepared according to the general procedure for reductive arylation, 65% yield (**2h**)
^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.41 – 8.32 (m, 2H), 7.46 – 7.21 (m, 8H), 7.21 – 7.13 (m, 1H), 7.10 – 7.01 (m, 2H), 6.91 (td, *J* = 7.5, 1.1 Hz, 1H), 6.82 (dd, *J* = 8.3, 1.0 Hz, 1H), 5.04 (d, *J* = 12.2 Hz, 1H), 4.97 (s, 2H), 4.51 (d, *J* = 12.2 Hz, 1H), 3.54 (s, 3H), 3.53 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.1, 167.8, 156.2, 150.0, 136.5, 128.9, 128.6, 128.2, 128.1, 127.9, 127.7, 123.6, 120.9, 112.3, 70.3, 54.7, 52.7, 52.7, 45.2. HRMS (ESI): Mass calcd for $C_{24}H_{24}NO_5$ [M+H]+: 406.1576; found 406.1575

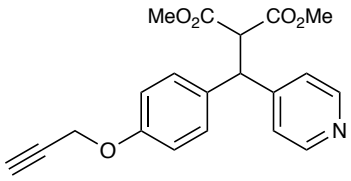


Prepared according to the general procedure for reductive arylation, 73% yield (**2i**)
^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.52 – 8.44 (m, 2H), 7.29 (td, *J* = 7.6, 1.7 Hz, 1H), 7.25 – 7.16 (m, 3H), 7.08 (td, *J* = 7.6, 1.2 Hz, 1H), 6.99 (ddd, *J* = 10.5, 8.3, 1.2 Hz, 1H), 4.99 (d, *J* = 12.2 Hz, 1H), 4.46 (d, *J* = 12.2 Hz, 1H), 3.58 (s, 3H), 3.55 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.5, 167.4, 161.4 (d, *J* = 247 Hz), 150.1, 149.0, 129.4 (d, *J* = 19.5 Hz), 128.7 (d, *J* = 3.7 Hz), 126.7 (d, *J* = 13.8 Hz), 124.5 (d, *J* = 3.4 Hz), 123.0, 116.1 (d, *J* = 22.3 Hz), 52.9, 52.9, 48.0, 44.3. HRMS (ESI): Mass calcd for $C_{17}H_{17}FNO_4$ [M+H]+: 318.1063; found 318.1063



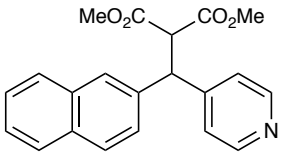
Prepared according to the general procedure for reductive arylation, 73% yield (**2j**)

^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.52 – 8.45 (m, 2H), 7.20 – 7.09 (m, 4H), 6.84 – 6.77 (m, 2H), 5.99 (ddt, *J* = 17.1, 10.5, 5.3 Hz, 1H), 5.35 (dq, *J* = 17.3, 1.6 Hz, 1H), 5.24 (dt, *J* = 10.5, 1.4 Hz, 1H), 4.67 (d, *J* = 12.0 Hz, 1H), 4.45 (dt, *J* = 5.4, 1.5 Hz, 2H), 4.26 (d, *J* = 12.0 Hz, 1H), 3.57 (s, 3H), 3.53 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.7, 167.6, 157.9, 150.6, 150.0, 133.1, 131.5, 128.9, 122.8, 117.8, 115.1, 68.8, 56.6, 52.8, 52.8, 46.8. HRMS (ESI): Mass calcd for $C_{20}H_{22}NO_5$ [M+H]+: 356.1420; found 356.1421



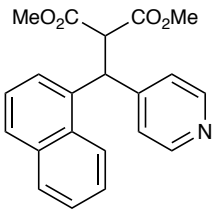
Prepared according to the general procedure for reductive arylation, 69% yield (**2k**)

^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.50 – 8.44 (m, 2H), 7.19 – 7.09 (m, 4H), 6.92 – 6.83 (m, 2H), 4.68 (d, *J* = 12.0 Hz, 1H), 4.61 (d, *J* = 2.4 Hz, 2H), 4.27 (d, *J* = 12.0 Hz, 1H), 3.56 (s, 3H), 3.54 (s, 3H), 2.48 (t, *J* = 2.3 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.6, 167.5, 156.9, 150.3, 150.1, 132.4, 129.0, 122.8, 115.2, 78.3, 75.6, 56.6, 55.8, 52.8, 52.8, 49.6. HRMS (ESI): Mass calcd for $C_{20}H_{20}NO_5$ [M+H]+: 354.1263; found 354.1260

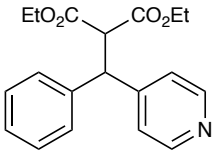


Prepared according to the general procedure for reductive arylation, 88% yield (**2l**)

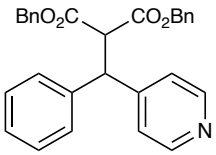
^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.52 – 8.45 (m, 2H), 7.86 – 7.62 (m, 5H), 7.44 (dtd, *J* = 7.9, 6.9, 5.4 Hz, 2H), 7.31 (dd, *J* = 8.5, 1.9 Hz, 1H), 7.27 – 7.21 (m, 1H), 4.91 (d, *J* = 12.0 Hz, 1H), 4.45 (d, *J* = 12.0 Hz, 1H), 3.60 (s, 3H), 3.49 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.6, 167.5, 150.1, 150.1, 150.0, 150.0, 136.9, 133.3, 132.6, 128.8, 127.9, 127.6, 126.5, 126.2, 125.8, 123.0, 56.4, 52.9, 52.8, 50.4. HRMS (ESI): Mass calcd for $C_{21}H_{20}NO_4$ [M+H]+: 350.1314; found 350.1310



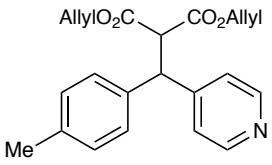
Prepared according to the general procedure for reductive arylation, 73% yield (**2m**)
^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.47 – 8.40 (m, 2H), 8.18 (d, *J* = 8.5 Hz, 1H), 7.81 (dd, *J* = 8.1, 1.4 Hz, 1H), 7.79 – 7.69 (m, 1H), 7.58 – 7.39 (m, 4H), 7.29 – 7.20 (m, 1H), 5.63 (d, *J* = 11.9 Hz, 1H), 4.48 (d, *J* = 11.8 Hz, 1H), 3.59 (s, 3H), 3.44 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.9, 167.4, 150.0, 149.8, 135.4, 134.2, 131.3, 129.0, 128.4, 126.7, 126.0, 125.2, 123.2, 123.1, 57.1, 52.9, 52.8, 45.0. HRMS (ESI): Mass calcd for $C_{21}H_{20}NO_4$ [M+H]+: 350.1314; found 350.1316



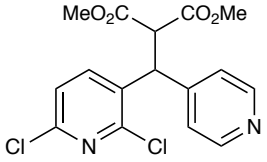
Prepared according to the general procedure for reductive arylation, 82% yield (**2n**)
^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.53 – 8.38 (m, 2H), 7.31 – 7.13 (m, 7H), 4.70 (d, *J* = 12.1 Hz, 1H), 4.27 (d, *J* = 12.1 Hz, 1H), 3.99 (dqd, *J* = 23.5, 7.2, 2.1 Hz, 4H), 1.05 (t, *J* = 7.1 Hz, 3H), 0.98 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.2, 167.1, 150.3, 150.0, 139.6, 128.8, 127.9, 127.5, 123.0, 61.9, 61.7, 56.7, 50.4, 13.8, 13.7. HRMS (ESI): Mass calcd for $C_{19}H_{22}NO_4$ [M+H]+: 328.1471; found 328.1476



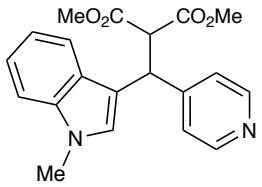
Prepared according to the general procedure for reductive arylation, 78% yield (**2o**)
^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.41 (s, 2H), 7.33 – 7.14 (m, 10H), 7.15 – 7.11 (m, 2H), 7.11 – 7.04 (m, 2H), 7.05 – 6.97 (m, 2H), 4.98 (d, *J* = 2.3 Hz, 2H), 4.95 – 4.88 (m, 2H), 4.73 (d, *J* = 12.1 Hz, 1H), 4.39 (d, *J* = 12.1 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.9, 166.8, 150.1, 149.8, 139.3, 134.8, 134.8, 128.9, 128.6, 128.5, 128.5, 128.3, 128.2, 127.9, 127.6, 123.0, 67.6, 67.5, 56.6, 50.4. HRMS (ESI): Mass calcd for $C_{29}H_{26}NO_4$ [M+H]+: 452.1784; found 452.177



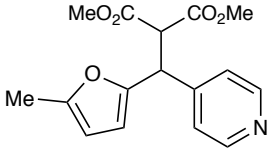
Prepared according to the general procedure for reductive arylation, 80% yield (**2p**)
^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.64 – 8.51 (m, 2H), 7.32 – 7.29 (m, 2H), 7.27 – 7.23 (m, 2H), 7.18 (d, *J* = 7.9 Hz, 2H), 5.85 – 5.65 (m, 2H), 5.31 – 5.20 (m, 4H), 4.82 (d, *J* = 12.0 Hz, 1H), 4.56 (ddq, *J* = 13.5, 5.7, 1.4 Hz, 4H), 4.46 (d, *J* = 12.1 Hz, 1H), 2.38 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.9, 166.7, 150.4, 150.1, 137.3, 136.4, 131.1, 131.0, 129.6, 127.7, 122.9, 119.1, 118.7, 66.3, 66.2, 56.6, 50.1, 21.0. HRMS (ESI): Mass calcd for $C_{22}H_{24}NO_4$ [M+H]+: 366.1627; found 366.1630



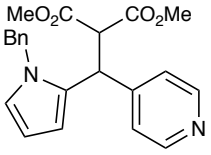
Prepared according to the general procedure for reductive arylation, 67% yield (**2q**)
^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.55 – 8.48 (m, 2H), 7.64 (d, *J* = 8.1 Hz, 1H), 7.27 (d, *J* = 8.1 Hz, 1H), 7.22 – 7.13 (m, 2H), 5.21 (d, *J* = 11.8 Hz, 1H), 4.29 (d, *J* = 11.8 Hz, 1H), 3.62 (s, 3H), 3.59 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.8, 166.8, 150.3, 150.2, 149.3, 147.3, 138.7, 132.9, 123.4, 123.1, 55.5, 53.2, 53.1, 46.8. HRMS (ESI): Mass calcd for $C_{16}H_{15}Cl_2N_2O_4$ [M+H]+: 369.0330; found 369.0325



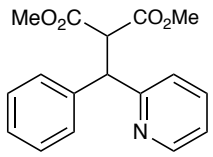
Prepared according to the general procedure for reductive arylation, 75% yield (**2r**)
^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.48 – 8.40 (m, 2H), 7.51 – 7.40 (m, 1H), 7.28 – 7.20 (m, 3H), 7.19 – 7.12 (m, 1H), 7.06 – 7.01 (m, 1H), 6.99 (s, 1H), 5.05 (d, *J* = 11.6 Hz, 1H), 4.29 (d, *J* = 11.6 Hz, 1H), 3.73 (s, 3H), 3.55 (s, 3H), 3.53 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.8, 167.8, 150.7, 149.9, 137.0, 126.7, 126.1, 123.2, 122.2, 119.4, 119.0, 113.3, 109.4, 57.2, 52.8, 52.7, 42.0, 32.9. HRMS (ESI): Mass calcd for $C_{20}H_{21}N_2O_4$ [M+H]+: 353.1423; found 353.1420



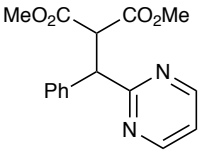
Prepared according to the general procedure for reductive arylation, 63% yield (**2s**)
^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.57 – 8.41 (m, 2H), 7.30 – 7.19 (m, 2H), 6.01 (d, *J* = 3.1 Hz, 1H), 5.83 (dd, *J* = 3.0, 1.3 Hz, 1H), 4.71 (d, *J* = 11.6 Hz, 1H), 4.18 (d, *J* = 11.7 Hz, 1H), 3.68 (s, 3H), 3.51 (s, 3H), 2.20 (d, *J* = 1.0 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.4, 167.2, 152.3, 150.0, 147.7, 123.4, 107.9, 106.3, 55.8, 52.9, 52.7, 44.4, 13.5. HRMS (ESI): Mass calcd for $C_{16}H_{18}NO_5$ [M+H]+: 304.1107; found 304.1110



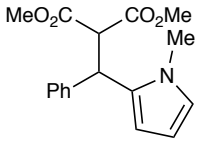
Prepared according to the general procedure for reductive arylation, 72% yield (**2t**)
^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.41 – 8.35 (m, 2H), 7.23 (dd, *J* = 4.7, 2.3 Hz, 3H), 6.99 – 6.94 (m, 2H), 6.87 (dd, *J* = 6.3, 2.9 Hz, 2H), 6.63 (dd, *J* = 2.6, 1.6 Hz, 1H), 6.26 (dd, *J* = 3.7, 1.7 Hz, 1H), 6.19 (t, *J* = 3.4 Hz, 1H), 5.19 – 4.90 (m, 2H), 4.69 – 4.62 (m, 1H), 4.14 (d, *J* = 11.4 Hz, 1H), 3.68 (s, 3H), 3.49 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.4, 167.4, 149.6, 148.6, 137.5, 130.3, 128.6, 127.5, 126.4, 123.6, 122.8, 107.6, 106.9, 57.7, 52.9, 52.6, 50.4, 46.8. HRMS (ESI): Mass calcd for $C_{22}H_{23}N_2O_4$ [M+H]+: 379.1580; found 379.1575



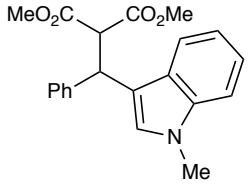
Prepared according to the general procedure for reductive arylation, 85% yield (**3a**). Product has been prepared previously and fully characterized.[4]



Prepared according to the general procedure for reductive arylation, 67% yield (**3b**).
^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.62 – 8.49 (m, 2H), 7.39 – 7.20 (m, 6H), 4.79 (d, *J* = 12.0 Hz, 1H), 4.38 (d, *J* = 12.0 Hz, 1H), 3.63 (s, 3H), 3.58 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.6, 167.5, 150.3, 150.0, 139.4, 128.9, 127.8, 127.6, 122.9, 56.4, 52.9, 52.8, 50.4. HRMS (ESI): Mass calcd for $C_{16}H_{17}N_2O_4$ [M+H]+: 301.1110; found 301.1104



Prepared according to the general procedure for reductive arylation, 74% yield (**3c**). Product has been prepared previously and fully characterized.[5]



Prepared according to the general procedure for reductive arylation, 68% yield (**3d**). Product has been prepared previously and fully characterized.[5]

Procedure for Gram-Scale Reductive Arylation and Catalyst Recovery

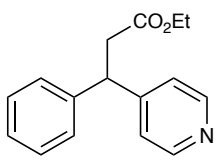
To a 250 mL flask was added arylidene malonate **1a** (1.0 equiv, 10 mmol, 2.2 g) and 4-CN pyridine (2.0 equiv, 20 mmol). The reaction vessel was equipped with a stir bar, capped and was then taken into a glovebox. DPAIPN (3 mol %, 0.3 mmol) was added to the vial, which was then removed from the glovebox. The vial was then charged with NEt_3 (2.5 equiv, 25 mmol) and sparged CH_3CN (0.1 M, 100 mL). The mixture was stirred until homogenous. The flask was then placed between 3 Kessil blue LED lights and irradiated for 18 hours (with a small fan placed for cooling to maintain temperature at 23 °C). Conversion of the malonate was monitored by UPLC/MS. Upon complete conversion, the reaction was concentrated under reduced pressure onto silica gel. This silica was loaded onto a column of silica gel and isolated via flash column chromatography (0-100% ethyl acetate/hexanes) to yield the desired product. Both the DPAIPN (91%) and **2a** (85%) were recovered from the column. The recovered DPAIPN was then utilized for an additional gram-scale experiment (2.0 g of **1a**), where similar yields to the initial experiment (83%) were obtained.

General Procedure for One-Pot Knoevenagel/Arylation

To a 2 dram vial was added benzaldehyde (1.0 equiv), diethyl malonate (1.0 equiv), piperidine (0.05 equiv), acetic acid (0.05 equiv) and cyanoarene (2.0 equiv) and 4 Å MS (200 wt %). The reaction vessel was equipped with a stir bar, capped and was then taken into a glovebox. DPAIPN (3 mol %) was added to the vial, which was then removed from the glovebox. The vial was then charged with NEt_3 (2.5 equiv) and sparged CH_3CN (0.1 M). The vial was then placed between 3 Kessil blue LED lights and irradiated for 24 hours (with a small fan placed for cooling to maintain temperature at 23 °C). Conversion to product was monitored by UPLC/MS. Upon complete conversion, the reaction was concentrated under reduced pressure onto silica gel. This silica was loaded onto a column of silica gel and isolated via flash column chromatography (0-100% ethyl acetate/hexanes) to yield the desired product.

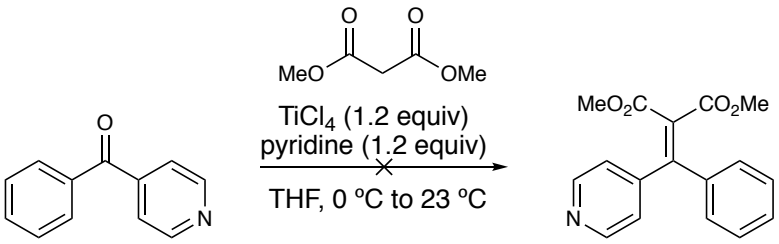
General Procedure for One-Pot Knoevenagel/Arylation/Krapcho

To a 2 dram vial was added benzaldehyde (1.0 equiv), diethyl malonate (1.0 equiv), piperidine (0.05 equiv), acetic acid (0.05 equiv) and cyanoarene (2.0 equiv) and 4 Å MS (200 wt %). The reaction vessel was equipped with a stir bar, capped and was then taken into a glovebox. DPAIPN (3 mol %) was added to the vial, which was then removed from the glovebox. The vial was then charged with NEt_3 (2.5 equiv) and sparged CH_3CN (0.1 M). The vial was then placed between 3 Kessil blue LED lights and irradiated for 24 hours (with a small fan placed for cooling to maintain temperature at 23 °C). Conversion to product was monitored by UPLC/MS. Upon complete conversion, the reaction was removed from stirring to allow the 4 Å MS to settle to the bottom of the vial. The resulting CH_3CN was removed by pipet and added to a separate 2 dram vial, and the 4 Å MS were subsequently rinsed with 2 aliquots of 1 volume CH_3CN. The combined CH_3CN aliquots were concentrated under reduced pressure. Subsequently, a 1/9 v/v mixture of H_2O/DMSO (0.2 M) was added to the 2 dram vial, and the resultant liquid was transferred to a 2-5 mL Biotage microwave vial. 3 equiv of LiCl and a stir bar were added, the microwave vial was crimped shut, and the vial was irradiated in an Initiator microwave for 1 hour at 150 °C. Upon reaction completion, the reaction was concentrated under reduced pressure onto silica gel. This silica was loaded onto a column of silica gel and isolated via flash column chromatography (0-100% ethyl acetate/hexanes) to yield the desired product.

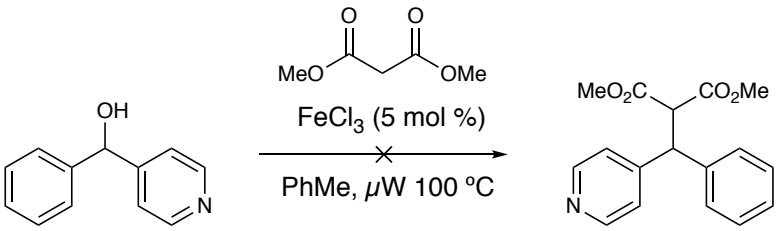


This product was been prepared previously and fully characterized.[6] Yield 64% (**4a**)

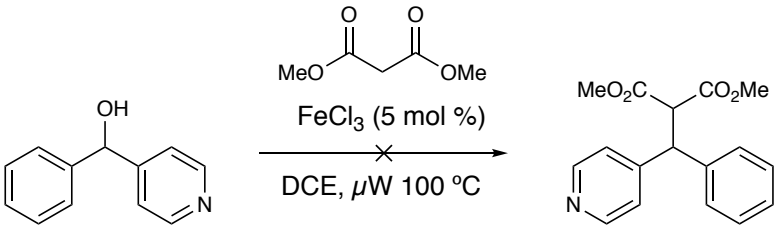
Procedures for Comparison to Known Methods to Synthesize Diarylmalonates



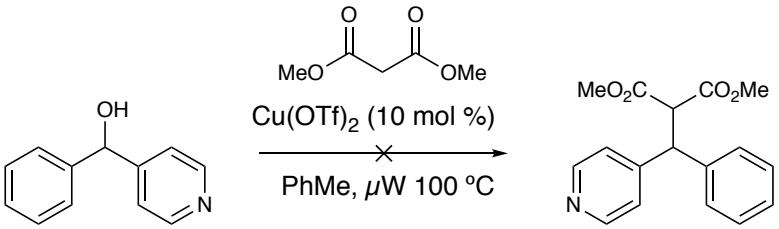
To an over dried 25 mL round bottom flask cooled to 0 °C was added THF (0.3 M relative to diarylketone). A solution of TiCl4 (1.2 equiv) in DCM (1.0 M) was added, followed by the addition of phenyl(pyridine-4-yl)methanone (1.0 equiv) over a period of 15 minutes and then followed by dimethyl malonate (1.1 equiv) over a period of 30 minutes. After stirring for 30 minutes, a solution of pyridine (1.2 equiv) in THF (0.3 M) was added dropwise over 30 minutes by sytringe pump. The reaction was allowed to warm up to room temperature overnight and was then analyzed by GC-MS, LC-MS and NMR, where no product formation was observed (complete decomposition of phenyl(pyridine-4-yl)methanone was observed).



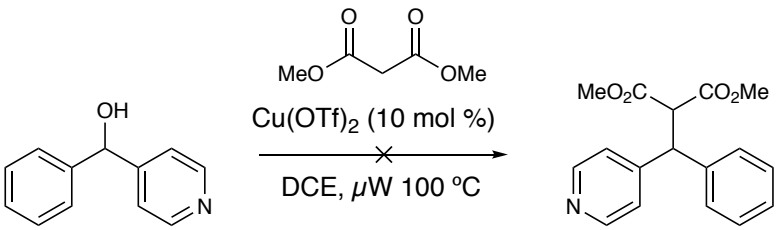
The following Lewis acid catalyzed dehydrative coupling is based off of a literature procedure.[7] To a dry Biotage microwave vial equipped with a magnetic stirrbar was added phenyl(pyridine-4-yl)methanol (1.0 equiv), dimethyl malonate (1.1 equiv mmol) and $FeCl_3$ (5 mol %) under an inert atmosphere. Toluene (0.2 M) was added by syringe, and the reaction was irradiated under microwave heat at 100 °C for 5 minutes. Upon reaction cooling, the reaction was analyzed by GC-MS, LC-MS and NMR, where no product formation was observed (complete decomposition of phenyl(pyridine-4-yl)methanol was observed).



The following Lewis acid catalyzed dehydrative coupling is based off of a literature procedure.[7] To a dry Biotage microwave vial equipped with a magnetic stirrbar was added phenyl(pyridine-4-yl)methanol (1.0 equiv), dimethyl malonate (1.1 equiv mmol) and $FeCl_3$ (5 mol %) under an inert atmosphere. Dichloroethane (0.2 M) was added by syringe, and the reaction was irradiated under microwave heat at 100 °C for 5 minutes. Upon reaction cooling, the reaction was analyzed by GC-MS, LC-MS and NMR, where no product formation was observed (complete decomposition of phenyl(pyridine-4-yl)methanol was observed).

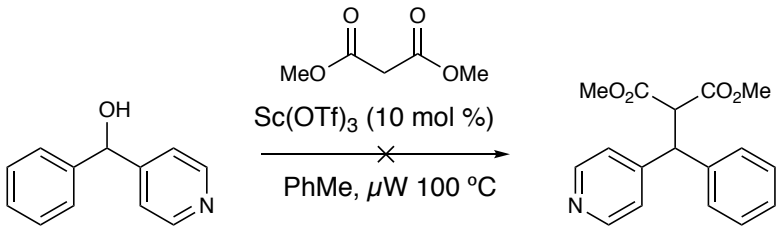


The following Lewis acid catalyzed dehydrative coupling is based off of a literature procedure.[7] To a dry Biotage microwave vial equipped with a magnetic stirrbar was added phenyl(pyridine-4-yl)methanol (1.0 equiv), dimethyl malonate (1.1 equiv mmol) and $Cu(OTf)_2$ (10 mol %) under an inert atmosphere. Toluene (0.2 M) was added by syringe, and the reaction was irradiated under microwave heat at 100 °C for 5 minutes. Upon reaction cooling, the reaction was analyzed by GC-MS, LC-MS and NMR, where no product formation was observed (complete decomposition of phenyl(pyridine-4-yl)methanol was observed).

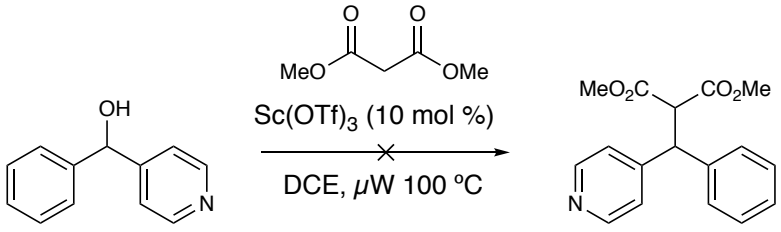


The following Lewis acid catalyzed dehydrative coupling is based off of a literature procedure.[7] To a dry Biotage microwave vial equipped with a magnetic stirrbar was added phenyl(pyridine-4-yl)methanol (1.0 equiv), dimethyl malonate (1.1 equiv mmol) and $Cu(OTf)_2$ (10 mol %) under an inert atmosphere. Dichloroethane (0.2 M) was added by syringe, and the reaction

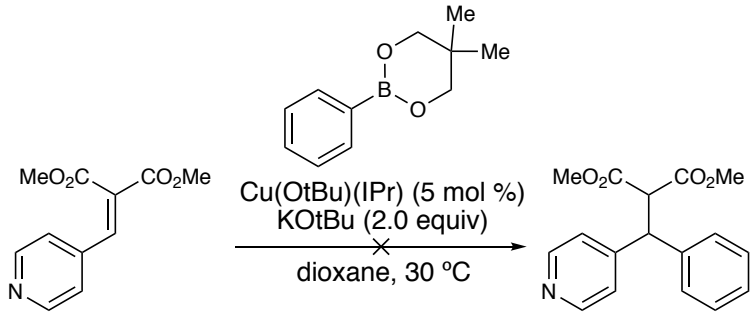
was irradiated under microwave heat at 100 °C for 5 minutes. Upon reaction cooling, the reaction was analyzed by GC-MS, LC-MS and NMR, where no product formation was observed (complete decomposition of phenyl(pyridine-4-yl)methanol was observed).



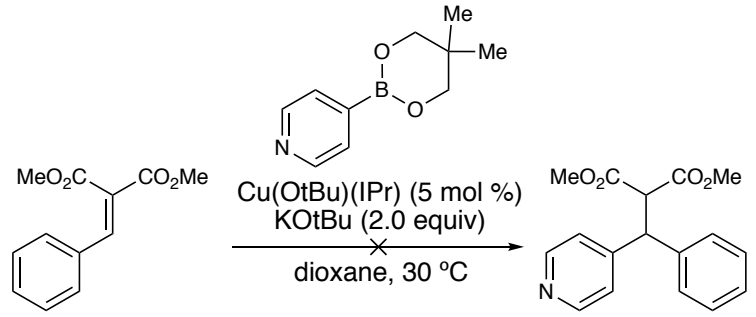
The following Lewis acid catalyzed dehydrative coupling is based off of a literature procedure.[7] To a dry Biotage microwave vial equipped with a magnetic stirrbar was added phenyl(pyridine-4-yl)methanol (1.0 equiv), dimethyl malonate (1.1 equiv mmol) and $Sc(OTf)_3$ (10 mol %) under an inert atmosphere. Toluene (0.2 M) was added by syringe, and the reaction was irradiated under microwave heat at 100 °C for 5 minutes. Upon reaction cooling, the reaction was analyzed by GC-MS, LC-MS and NMR, where no product formation was observed (complete decomposition of phenyl(pyridine-4-yl)methanol was observed)



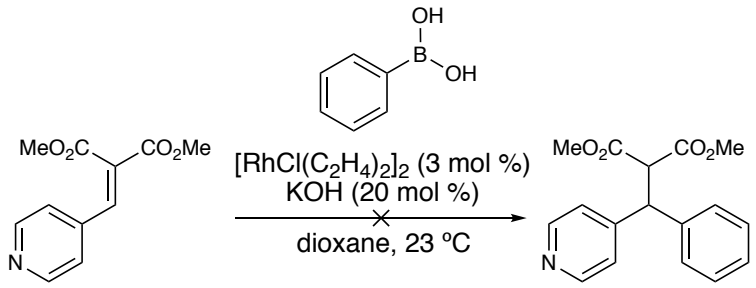
The following Lewis acid catalyzed dehydrative coupling is based off of a literature procedure.[7] To a dry Biotage microwave vial equipped with a magnetic stirrbar was added phenyl(pyridine-4-yl)methanol (1.0 equiv), dimethyl malonate (1.1 equiv mmol) and $Sc(OTf)_3$ (10 mol %) under an inert atmosphere. Dichloroethane (0.2 M) was added by syringe, and the reaction was irradiated under microwave heat at 100 °C for 5 minutes. Upon reaction cooling, the reaction was analyzed by GC-MS, LC-MS and NMR, where no product formation was observed (complete decomposition of phenyl(pyridine-4-yl)methanol was observed).



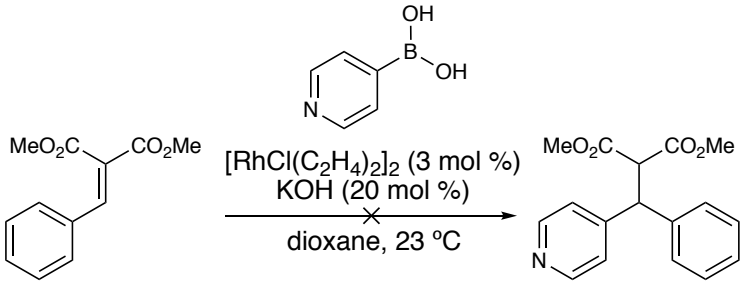
This procedure is based off of a literature precedent.[8] A solution of Cu(OtBu)(IPr) (5 mol %), dimethyl 2-(pyridin-4-ylmethylene)malonate (1.0 equiv), phenylboronic acid neopentylglycol ester (1.5 equiv), and KOtBu (2.0 equiv) in dioxane (1.0 M) was stirred for 20 h at 30 °C. The reaction mixture was diluted with EtOAc and passed through a pad of silica gel with EtOAc, and the solvent was removed under vacuum. The reaction was analyzed by GC-MS, LC-MS and NMR, where no product formation was observed (complete decomposition of dimethyl 2-(pyridin-4-ylmethylene)malonate was observed).



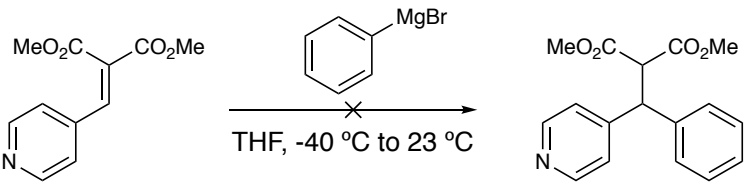
This procedure is based off of a literature precedent.[8] A solution of Cu(OtBu)(IPr) (5 mol %), dimethyl 2-benzylidenemalonate (1.0 equiv), pyridineboronic acid neopentylglycol ester (1.5 equiv), and KOtBu (2.0 equiv) in dioxane (1.0 M) was stirred for 20 h at 30 °C. The reaction mixture was diluted with EtOAc and passed through a pad of silica gel with EtOAc, and the solvent was removed under vacuum. The reaction was analyzed by GC-MS, LC-MS and NMR, where no product formation was observed (complete decomposition of dimethyl 2-benzylidenemalonate was observed).



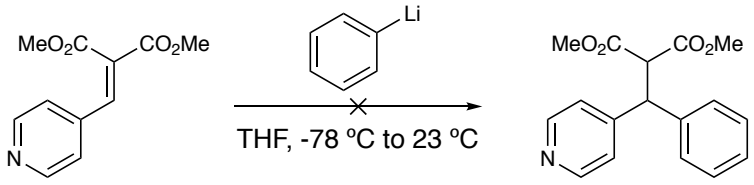
This procedure is based off of a literature precedent.[9] To a solution of $[RhCl(C_2H_4)_2]_2$ (3 mol %) in 1,4-dioxane (1.0 M) was added aq KOH solution (20 mol %) and the mixture was stirred for 10 min at 23 °C. Dimethyl 2-(pyridin-4-ylmethylene)malonate (0.20 mmol, 1.0 equiv.) and $PhB(OH)_2$ (1.5 equiv.) were added and the Schlenk tube was rinsed with 1,4-dioxane (0.2). After stirring for 1 h at 20 °C, water was added to quench the reaction mixture. The reaction was analyzed by GC-MS, LC-MS and NMR, where no product formation was observed (complete decomposition of dimethyl 2-(pyridin-4-ylmethylene)malonate was observed).



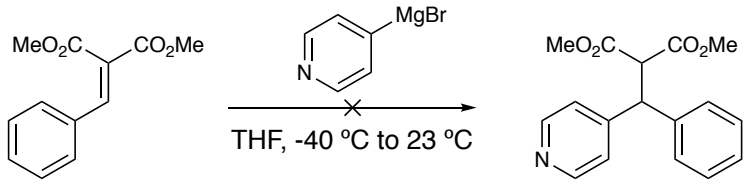
This procedure is based off of a literature precedent.[9] To a solution of $[RhCl(C_2H_4)_2]_2$ (3 mol %) in 1,4-dioxane (1.0 M) was added aq KOH solution (20 mol %) and the mixture was stirred for 10 min at 23 °C. Dimethyl 2-benzylidenemalonate (0.20 mmol, 1.0 equiv.) and 4-pyriidne boronic acid (1.5 equiv.) were added and the Schlenk tube was rinsed with 1,4-dioxane (0.2). After stirring for 1 h at 20 °C, water was added to quench the reaction mixture. The reaction was analyzed by GC-MS, LC-MS and NMR, where no product formation was observed (complete decomposition of dimethyl 2-benzylidenemalonate was observed).



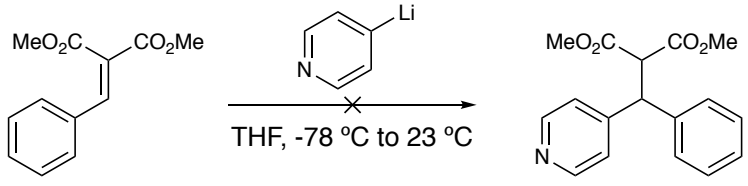
To an over dried 25 mL round bottom flask placed under N2 was added THF (0.2 M relative to arylidene malonate). Phenylmagnesium bromide (1.0 M in THF, 1.2 equiv) was added by syringe, and the reaction was cooled to -40 °C. A solution of dimethyl 2-(pyridin-4-ylmethylene)malonate (1y, 1.0 equiv) in THF (0.2 M) was slowly added by syringe pump over 30 minutes. Upon addition completion, the reaction was held at -40 °C for 1 hour before warming to room temperature slowly. Upon stirring at room temperature for 1 hour, the reaction was quenched by the addition of aqueous sat. NH4Cl, and analyzed by GC-MS, LC-MS and NMR, where no product formation was observed (complete decomposition of dimethyl 2-(pyridin-4-ylmethylene)malonate was observed).



To an over dried 25 mL round bottom flask placed under N2 was added THF (0.2 M relative to arylidene malonate). Phenyllithiuym (1.9 M in dibutylether, 1.2 equiv) was added by syringe, and the reaction was cooled to -78 °C. A solution of dimethyl 2-(pyridin-4-ylmethylene)malonate (1y, 1.0 equiv) in THF (0.2 M) was slowly added by syringe pump over 30 minutes. Upon addition completion, the reaction was held at -78 °C for 1 hour before warming to room temperature slowly. Upon stirring at room temperature for 1 hour, the reaction was quenched by the addition of aqueous sat. NH4Cl, and analyzed by GC-MS, LC-MS and NMR, where no product formation was observed (complete decomposition of dimethyl 2-(pyridin-4-ylmethylene)malonate was observed).

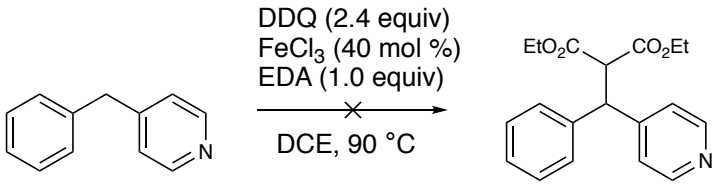


To an over dried 25 mL round bottom flask placed under N2 was added THF (0.2 M relative to arylidene malonate). Pyridin-4-ylmagnesium bromide (1.0 M in THF, 1.2 equiv, made fresh from Mg and 4-bromopyridine) was added by syringe, and the reaction was cooled to -40 °C. A solution of dimethyl 2-benzylidenemalonate (1a, 1.0 equiv) in THF (0.2 M) was slowly added by syringe pump over 30 minutes. Upon addition completion, the reaction was held at -40 °C for 1 hour before warming to room temperature slowly. Upon stirring at room temperature for 1 hour, the reaction was quenched by the addition of aqueous sat. NH4Cl, and analyzed by GC-MS, LC-MS and NMR, where no product formation was observed.

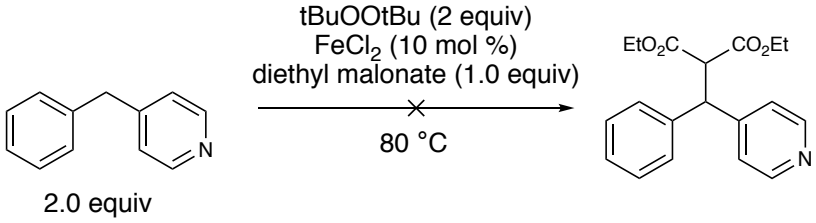


To an over dried 25 mL round bottom flask placed under N2 was added THF (0.2 M relative to arylidene malonate). Pyridin-4-yllithium (1.0 M in THF, 1.2 equiv, made fresh from nBuLi and 4-bromopyridine) was added by syringe, and the reaction was cooled to -78 °C. A solution of dimethyl 2-benzylidenemalonate (1a, 1.0 equiv) in THF (0.2 M) was slowly added by syringe pump over 30

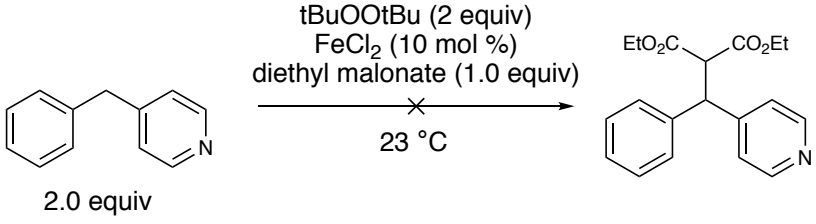
minutes. Upon addition completion, the reaction was held at -78 °C for 1 hour before warming to room temperature slowly. Upon stirring at room temperature for 1 hour, the reaction was quenched by the addition of aqueous sat. NH4Cl, and analyzed by GC-MS, LC-MS and NMR, where no product formation was observed.



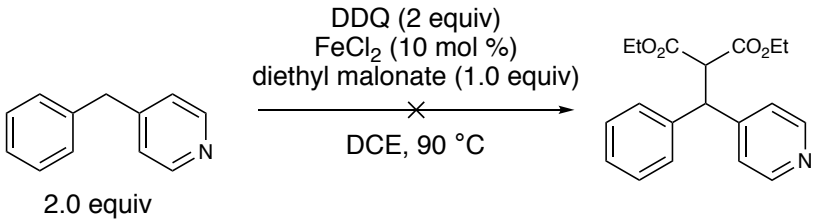
This procedure is based on literature precedent.[10] An oven-dried Schlenk tube was charged with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ, 2.4 equiv), $FeCl_3$ (40 mol %), 4-benzylpyridine (2.0 equiv), and ethyldiazoacetate (EDA) (1 equiv). Then dry dichloroethane（0.1 M）was added by syringe. The tube was degassed and refilled with N2 for three times. The sealed reaction mixture was stirred at 90 °C for 24 h. The mixture was cooled to room temperature and analyzed by GC-MS, LC-MS and NMR, where no product formation was observed. Complete decomposition of 4-benzylpyridine was observed.



This procedure is based on literature precedent.[11] 4-benzylpyridine (2.0 equiv) was added to a mixture of diethyl malonate (1.0 equiv) and $FeCl_2$ (10 mol %) under nitrogen at room temperature and *tert*-butyl peroxide (2.0 equiv) was then added dropwise. The resulting mixture was heated at 80 °C for 8 h. The mixture was cooled to room temperature and analyzed by GC-MS, LC-MS and NMR, where no product formation was observed. Complete decomposition of 4-benzylpyridine was observed.



This procedure is based on literature precedent.[11] 4-benzylpyridine (2.0 equiv) was added to a mixture of diethyl malonate (1.0 equiv) and $FeCl_2$ (10 mol %) under nitrogen at room temperature and *tert*-butyl peroxide (2.0 equiv) was then added dropwise. The resulting mixture was stirred at 23 °C for 36 h. The mixture was cooled to room temperature and analyzed by GC-MS, LC-MS and NMR, where no product formation was observed. Complete decomposition of 4-benzylpyridine was observed.



This procedure is based on literature precedent.[12] 4-benzylpyridine (2.0 equiv) was added to a mixture of diethyl malonate (1.0 equiv) and $FeCl_2$ (10 mol %) under nitrogen at room temperature and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ, 2 equiv) was then added, followed by addition of DCE (0.1 M). The resulting mixture was stirred at 90 °C for 12 h. The mixture was cooled to room temperature and analyzed by GC-MS, LC-MS and NMR, where no product formation was observed. Complete decomposition of 4-benzylpyridine was observed.

Stern-Volmer Fluorescence Quenching Experiments

Stern-Volmer fluorescence quenching experiments were run with freshly-prepared solutions of 2.0 x 10^{-6} M DPAIPN in acetonitrile at room temperature under an inert Ar atmosphere. The solutions were irradiated at 425 nm and fluorescence was measured at 523 nm. At the concentrations employed in these studies, neither arylidene malonate **1a** nor 4-CN pyridine measurably quench the excited state of DPAIPN; only NEt_3 is shown to reductively quench the excited state of DPAIPN. The data summarized in the tables is the fluorescence intensity measured three times for each sample. The data shown in the graphs is the average of three experiments.

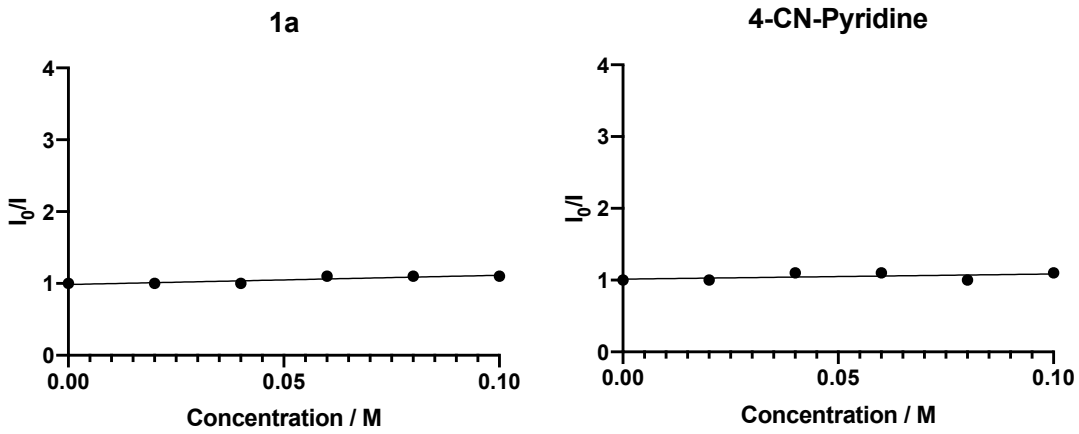
Stern-Volmer Fluorescence Quenching: Table Data and Individual Graphs

Vial	1	2	3	Average	I0/I	[1a] mol/L
0	516	506	509	510.3	1.0	0
1	515	505	520	513.3	1.0	0.02
2	510	513	517	513.3	1.0	0.04
3	512	520	518	516.7	1.0	0.06
4	513	515	517	515.0	1.0	0.08
5	507	515	517	513.0	1.0	0.1

Vial	1	2	3	Average	I0/I	[4-CN-Pyr] mol/L
0	520	519	516	518.3	1.0	0
1	512	520	505	512.3	1.0	0.02
2	505	516	507	509.3	1.0	0.04
3	506	519	520	515.0	1.0	0.06
4	516	509	510	511.7	1.0	0.08
5	516	510	509	511.7	1.0	0.1

Vial	1	2	3	Average	I0/I	[NEt3] mol/L
0	520	514	520	518.0	1.0	0
1	359	347	348	351.3	1.5	0.02
2	253	250	250	251.0	2.1	0.04
3	199	203	197	199.7	2.6	0.06
4	162	166	170	166.0	3.1	0.08
5	138	133	128	133.0	3.9	0.1

Table S8: Tabulated Stern-Volmer Measurements



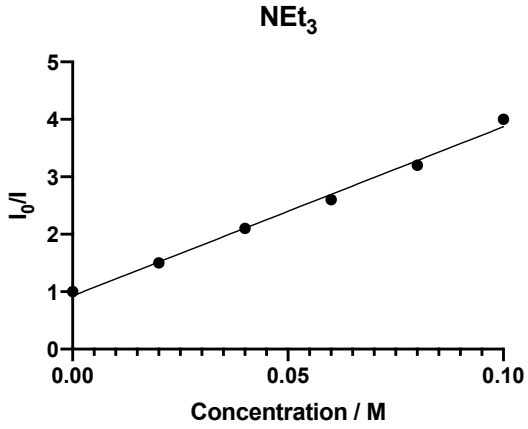


Figure S6: Individual Stern Volmer Measurement Graphs for Each Reaction Component

Procedure for Determination of Quantum Yield

The photon flux of the fluorimeter was determined using a ferrioxolate Hatchard – Parker actinometer as described by Yoon et al.[13] Based on the average of three experiments, the photon flux at 420 nm (10 nm slit width) was determined to be 5.27712E-09 einsteins s^{-1}. UV/Vis absorbance spectra of DPAIPN in MeCN (0.1 M) indicated that essentially all light was absorbed at 420 nm (f = 0.99148). A screw-top quartz cuvette with Teflon septa was charged with **1a** (0.1 mmol, 1 equiv), DPAIPN (3 mol %), 4-CN-pyridine (2 equiv), NEt_3 (2.5 equiv) and a small Teflon coated magnetic stirbar in a glovebox. The cuvette was sealed and removed from glovebox. The cuvette was then capped with a PTFE stopper, and 1 mL sparged MeCN added. The solution was stirred until homogenous. The sample was placed in the fluorimeter and irradiated (λ = 420 nm, slit width= 10.0 nm) for 10800 s (3 hours). ^{1}H NMR based on a trimethoxybenzene standard determined the yield of product formed was 16%, 14% and 18% when done in triplicate (16% average). The average quantum yield based on the three experiments was determined to be 0.28.

Procedure for Simple Luminescence Experiment

Simple luminescence experiments were done as described by Yoon et al.[13] Based on the average of three experiments, the luminescence intensity under the reaction conditions (λ = 523 nm, 10.0 nm slit width) was measured while being irradiated in the fluorometer. Luminescence intensity without NEt_3 quencher (I_0) was recorded, followed by luminescence intensity with 83 equiv of NEt_3 (2.5 equiv of NEt_3/0.03 equiv DPAIPN under the reaction conditions). The quenching fraction, Q, was determined by the below equation and averaged over the first 90 s of the reaction.

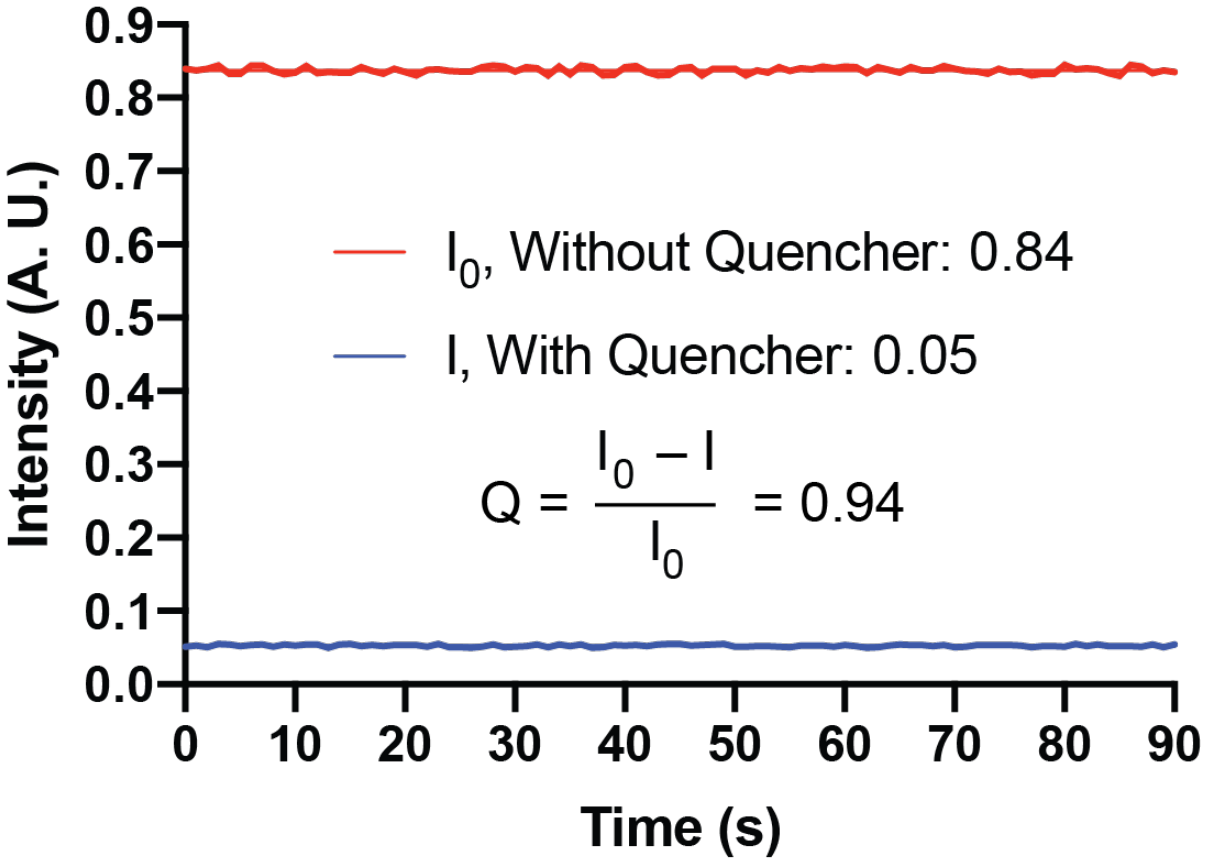


Figure S7: Simple Luminescence Quenching Experiment

General Procedure for Isolated Kinetic Isotope Effect Experiment

To a 2 dram vial was added arylidene malonate (either **protio-1a** or **deutero-1a** 1.0 equiv) and cyanoarene (2.0 equiv). The reaction vessel was equipped with a stir bar, capped and was then taken into a glovebox. DPAIPN (3 mol %) was added to the vial, which was then removed from the glovebox. The vial was then charged with NEt_3 (2.5 equiv) and sparged CH_3CN (0.1 M). The mixture was stirred until homogenous. The vial was then placed between 3 Kessil blue LED lights and irradiated (with a small fan placed for cooling to maintain temperature at 23 °C). 100 μL samples were taken upon set intervals and immediately diluted in 500 μL of CD_3CN containing CH_2Cl_2 as an internal standard. Conversion of starting material to arylation product **2a** was measured by NMR spectroscopy, where only initial rates were concerned (conversion < 15%) for determination of the KIE. KIE was determined as the average of three experiments.

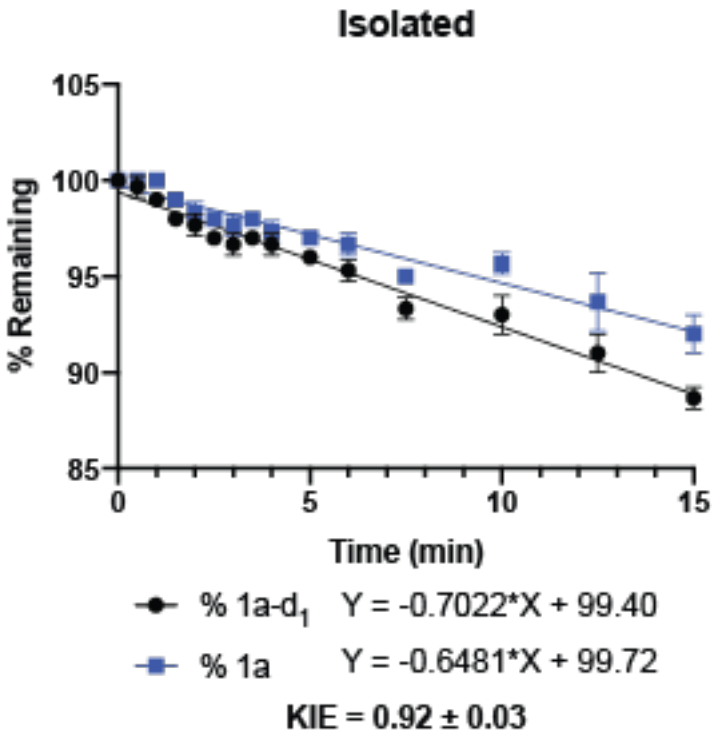


Figure S8: Isolated KIE Measurement

General Procedure for Combined Kinetic Isotope Effect Experiment

To a 2 dram vial was added arylidene malonate (both **protio-1a** and **deutero-1a** 1.0 equiv) and cyanoarene (2.0 equiv). The reaction vessel was equipped with a stir bar, capped and was then taken into a glovebox. DPAIPN (3 mol %) was added to the vial, which was then removed from the glovebox. The vial was then charged with NEt_3 (2.5 equiv) and sparged CH_3CN (0.1 M). The mixture was stirred until homogenous. The vial was then placed between 3 Kessil blue LED lights and irradiated (with a small fan placed for cooling to maintain temperature at 23 °C). 100 μL samples were taken upon set intervals and immediately diluted in 500 μL of CD_3CN containing CH_2Cl_2 as an internal standard. Conversion of starting material to arylation product **2a** was measured by NMR spectroscopy, where only initial rates were concerned (conversion < 15%) for determination of the KIE. KIE was determined as the average of three experiments.

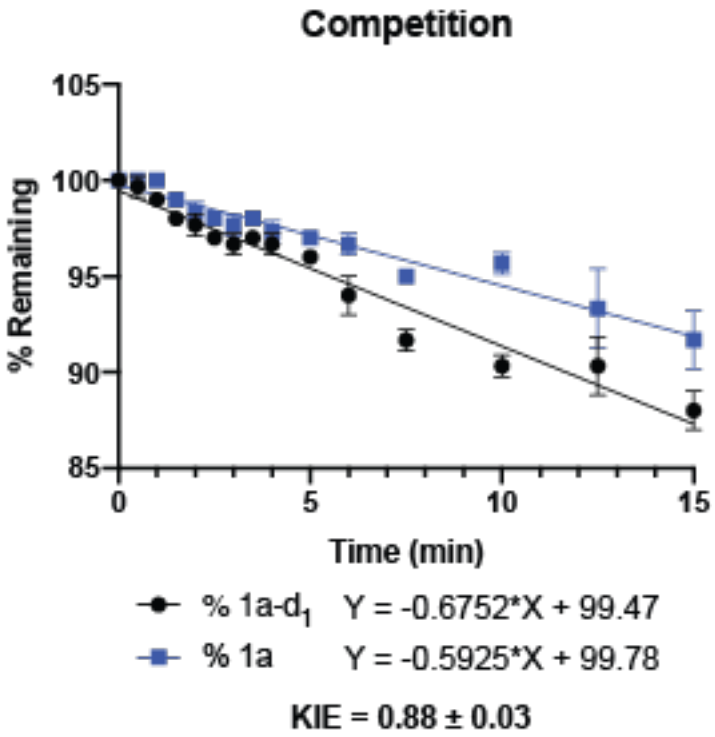


Figure S9: Competitive KIE Measurement

Cyclic Voltammetry of Additions of NEt_3 and $NHEt_3Cl$

Cyclic voltammograms were collected with a Nuvant Ezstat Pro potentiostat/galvanostat. Samples were prepared with 0.05 mmol of substrate in 5 mL of 0.1 M tetra-n-butylammonium hexafluorophosphate in degassed acetonitrile. Measurements employed a platinum working electrode, platinum wire counter electrode, a Pt/Ag/AgCl pseudo reference electrode and a scan rate of 250 mV/s. Ferrocene was used as an internal standard. Two cycles were performed on each sample. Measurements reported are of the second scan cycle.

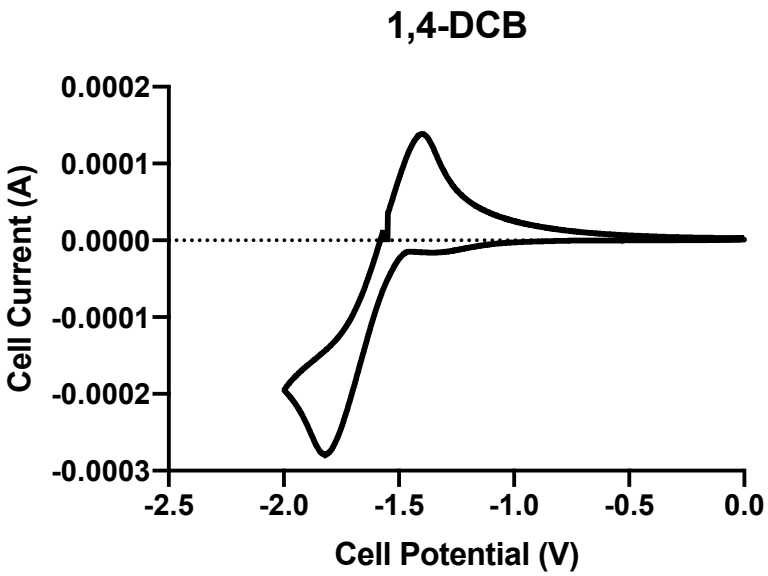


Figure S10: Cyclic Voltammetry Measurements for 1,4-dicyanobenzene: $E_{1/2}$ red = -1.67 V vs. SCE

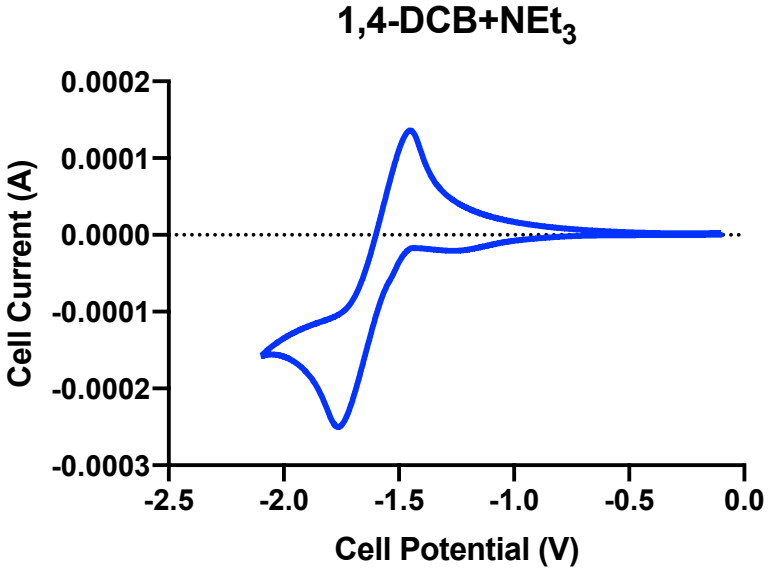


Figure S11: Cyclic Voltammetry Measurements for 1,4-dicyanobenzene + NEt_3: $E_{1/2}$ red = -1.63 V vs. SCE

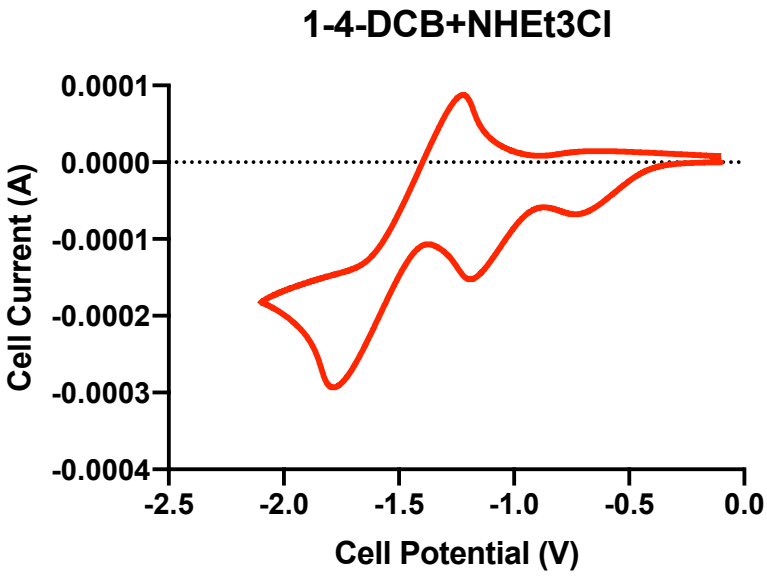


Figure S12: Cyclic Voltammetry Measurements for 1,4-dicyanobenzene + $NHEt_3Cl$: $E_{1/2}$ red = -1.60 V vs. SCE

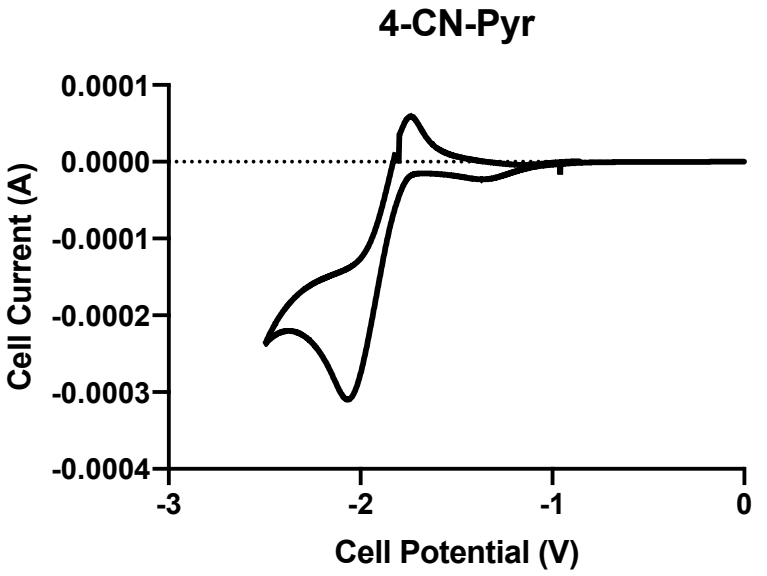


Figure S13: Cyclic Voltammetry Measurements for 4-cyanopyridine: $E_{1/2}$ red = -1.87 V vs. SCE

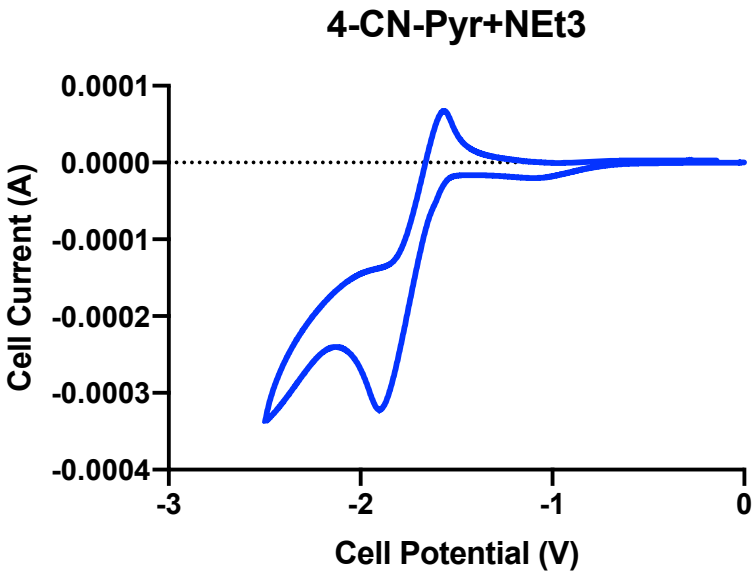


Figure S14: Cyclic Voltammetry Measurements for 4-cyanopyridine + NEt_3: $E_{1/2}$ red = -1.81 V vs. SCE

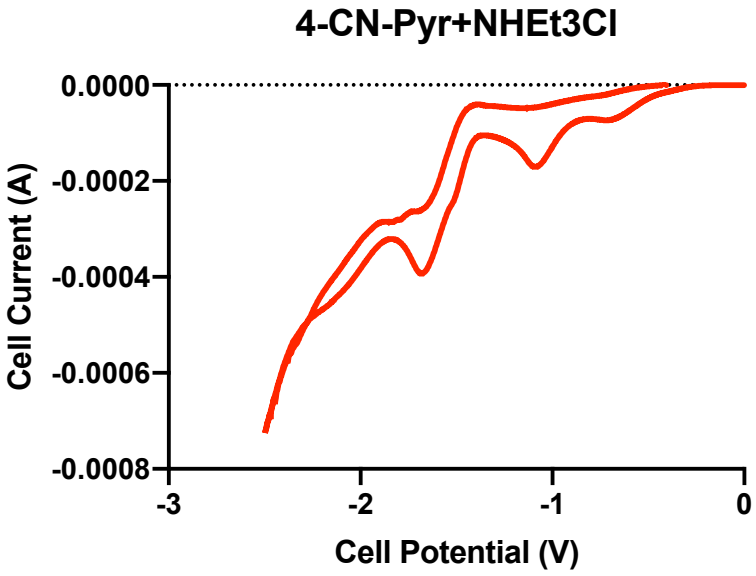


Figure S15: Cyclic Voltammetry Measurements for 4-cyanopyridine + $NHEt_3Cl$: $E_{1/2}$ red = -1.51 V vs. SCE

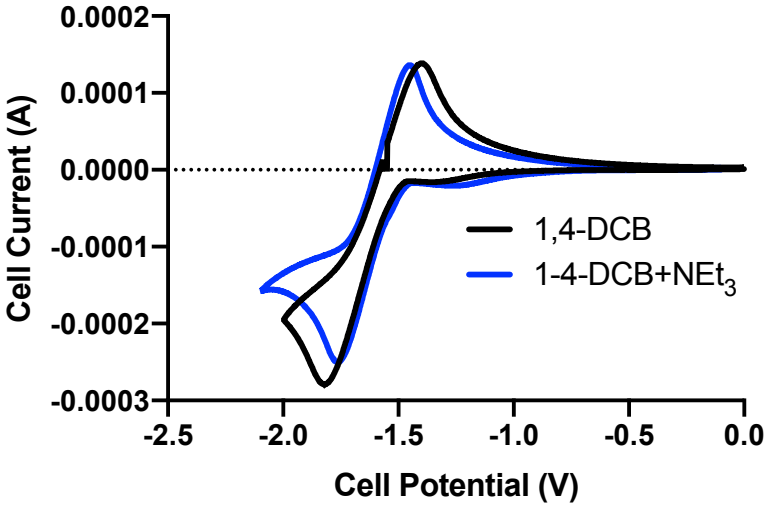


Figure S16: Cyclic Voltammetry Measurements for 1,4-dicyanobenezene and 1,4-dicyanobenzene + NEt_3

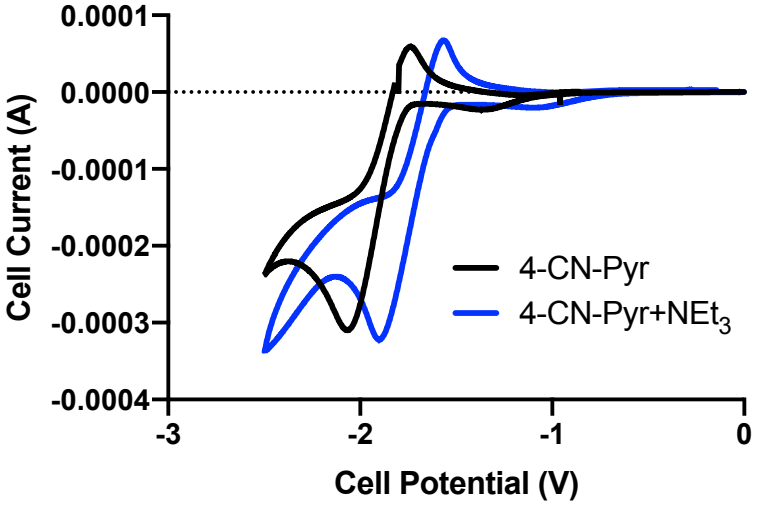


Figure S17: Cyclic Voltammetry Measurements for 4-cyanopyridine and 4-cyanopyridine + NEt_3

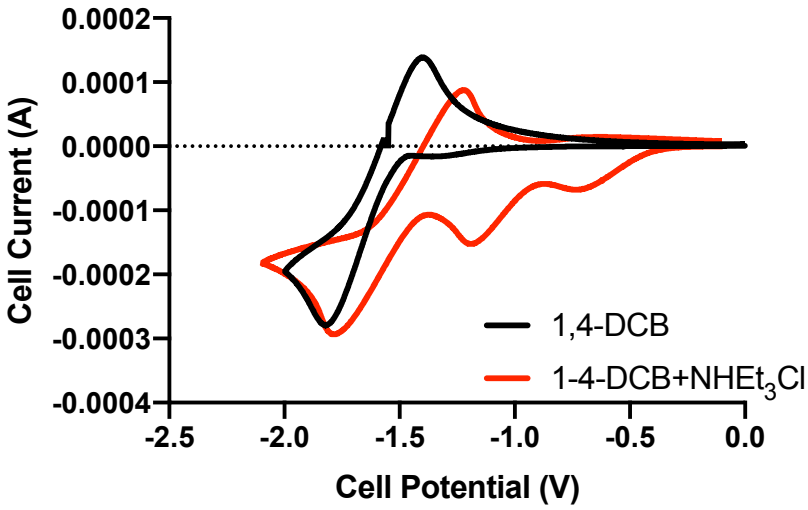


Figure S18: Cyclic Voltammetry Measurements for 1,4-dicyanobenezene and 1,4-dicyanobenzene + $NHEt_3Cl$

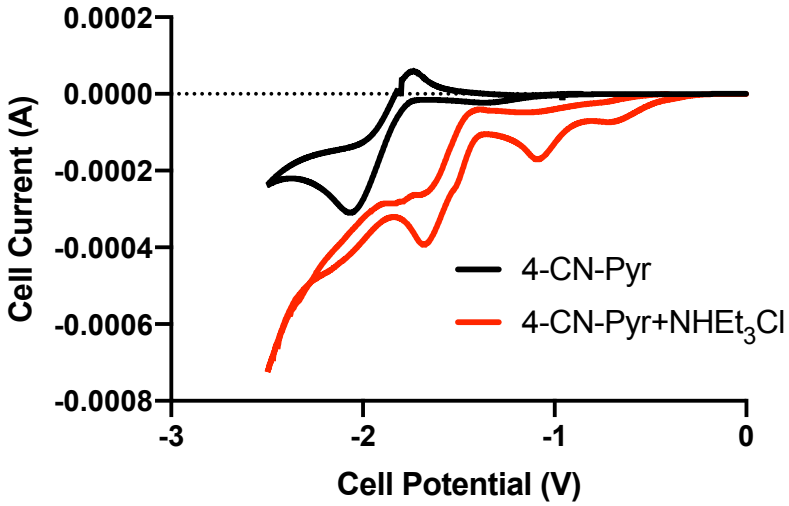


Figure S19: Cyclic Voltammetry Measurements for 4-cyanopyridine and 4-cyanopyridine + $NHEt_3Cl$

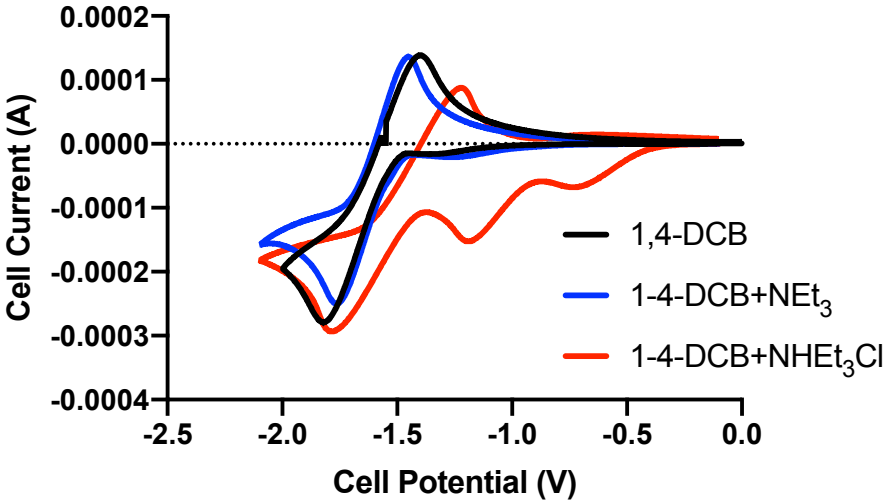


Figure S20: Compiled Cyclic Voltammetry Measurements for 1,4-dicyanobenezene

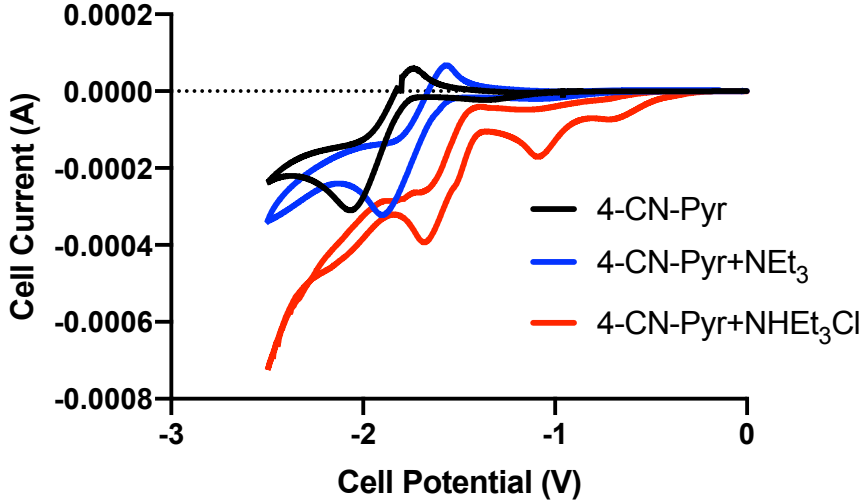


Figure S21: Compiled Cyclic Voltammetry Measurements for 4-cyanopyridine

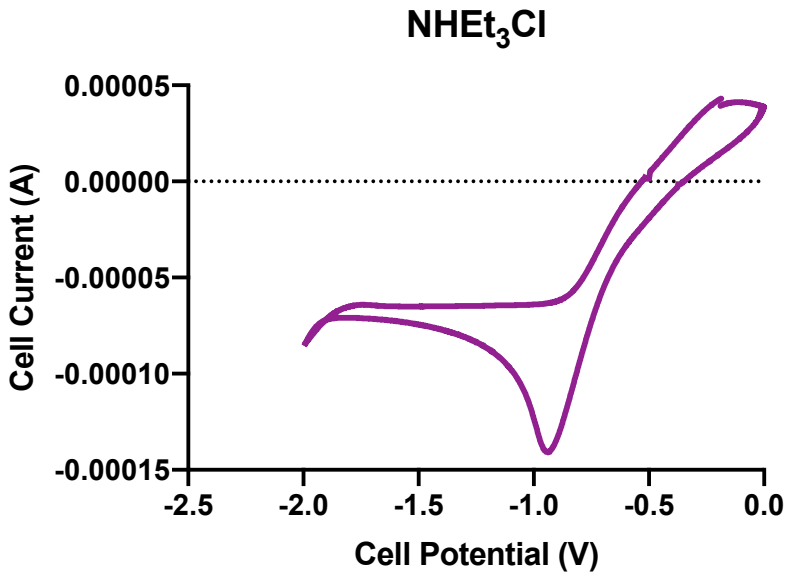


Figure S22: Cyclic Voltammetry Measurements for $NHEt_3Cl$: $E_{1/2}$ red = -0.79 V vs SCE

General Procedure for UV-Vis Experiments

A 1-dram vial equipped with a rubber septum and a stir bar was charged with **1a**, 4-CN-pyridine or 1,4-DCB in CH_3CN (0.1 M). The UV-Vis spectra were taken by removal of 1 μL of solution. NEt_3 or $NHEt_3Cl$ (0 or 100 mol %) were added to the reaction vial, and the vial stirred for 1 hour, followed by measurement of the UV-Vis spectra.

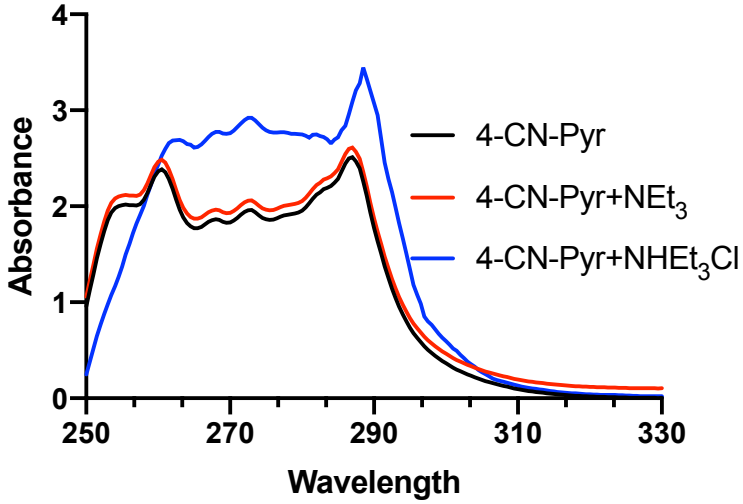


Figure S23: UV-Vis measurements for 4-cyanopyidine

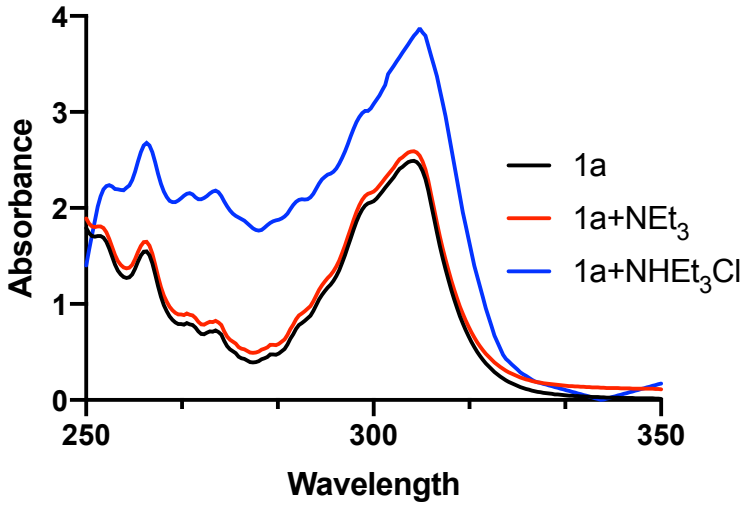


Figure S24: UV-Vis measurements for **1a**

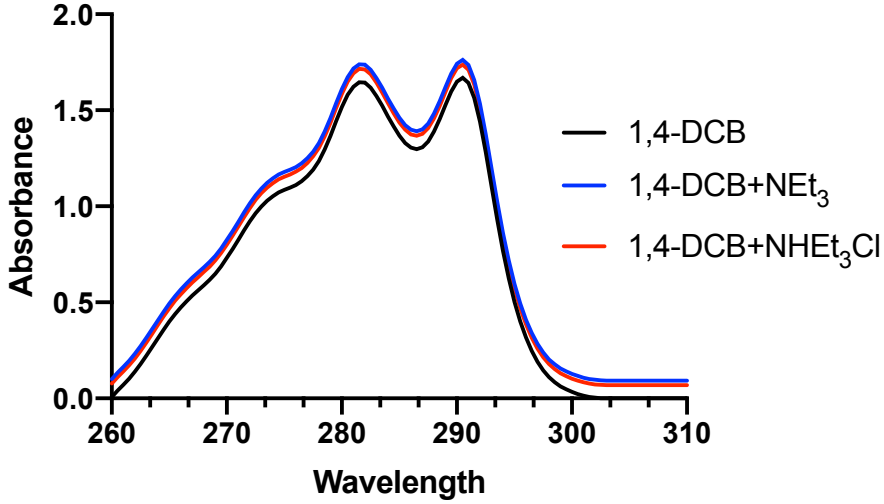
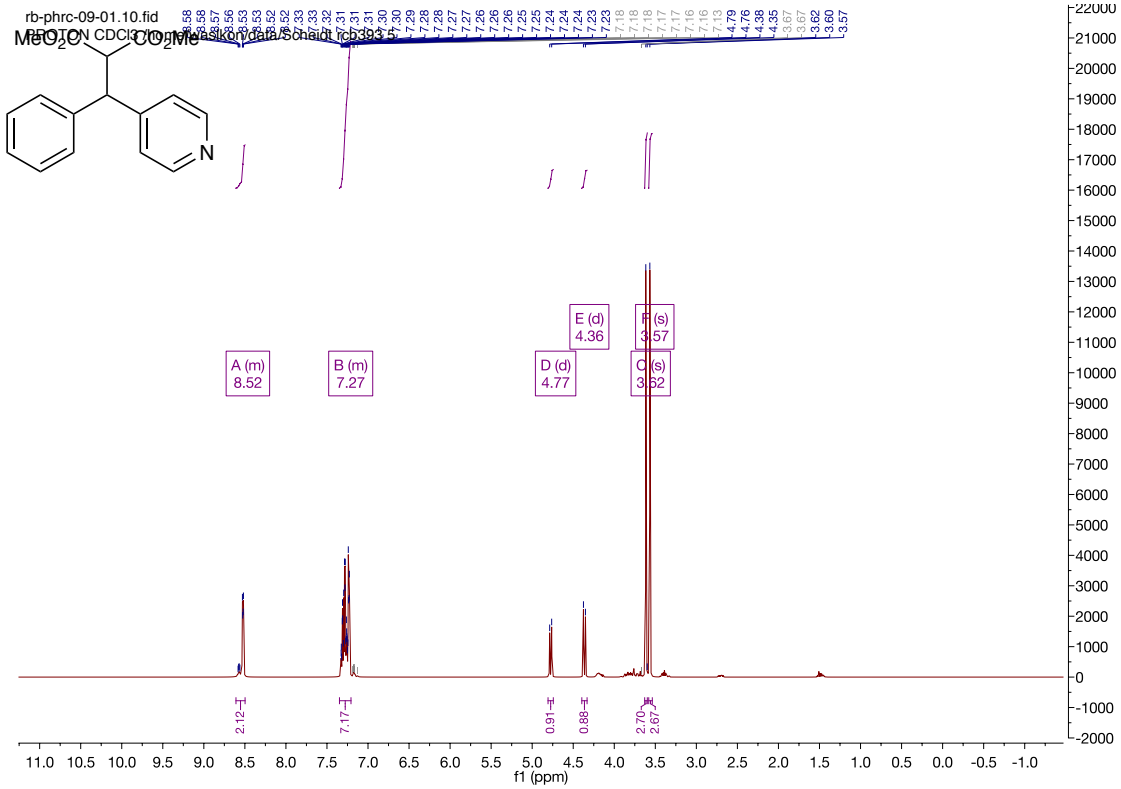
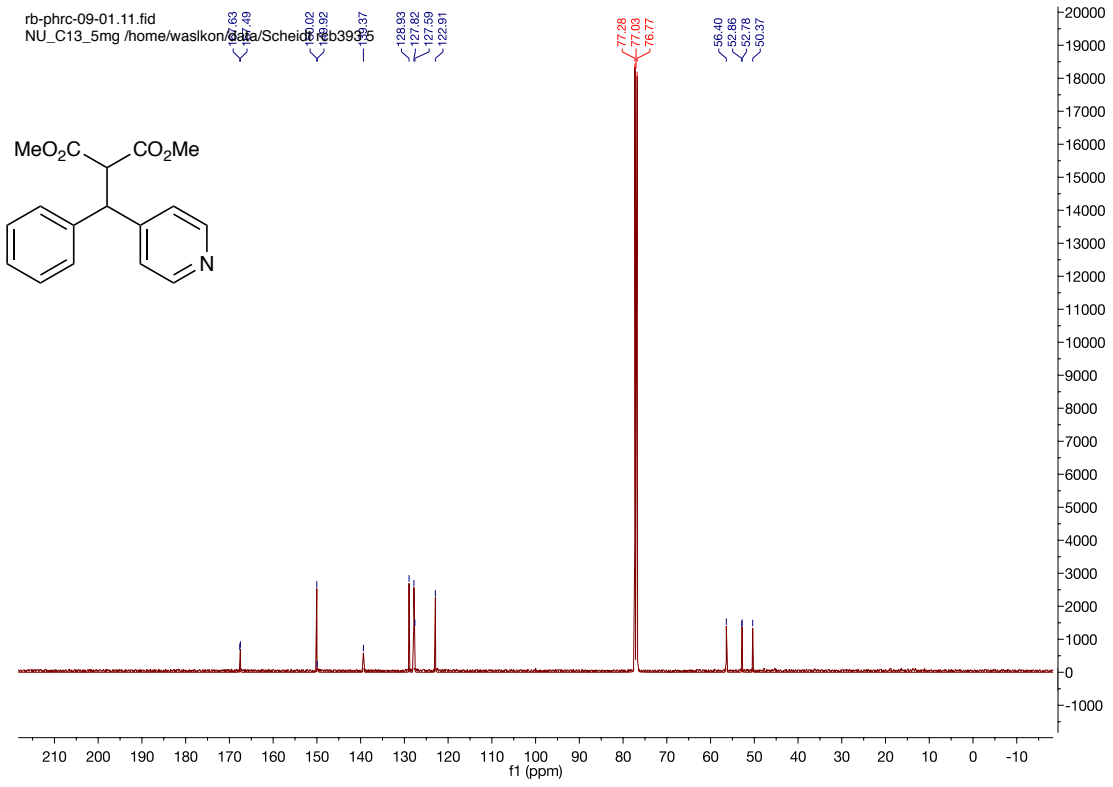
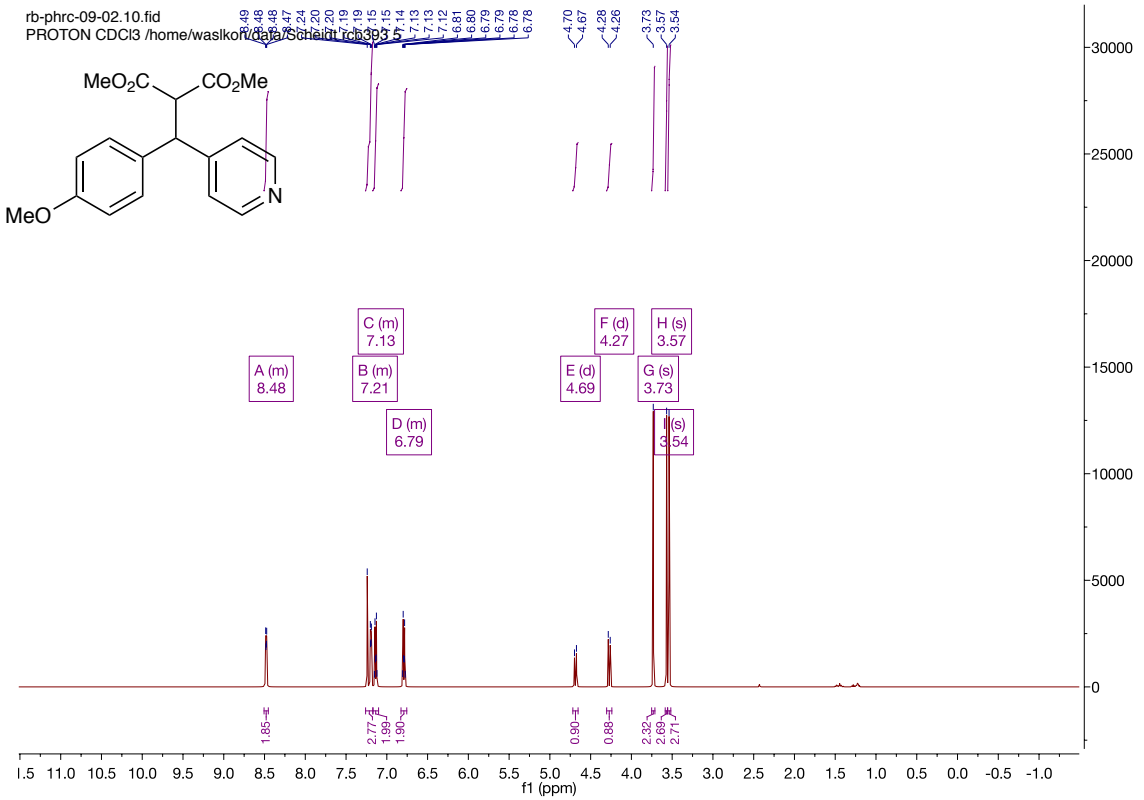


Figure S25: UV-Vis measurements for 1,4-dicyanobenzene

NMR Spectra for Arylation Products



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CO2Me
MeO
N
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B (m) 7.21
C (m) 7.13
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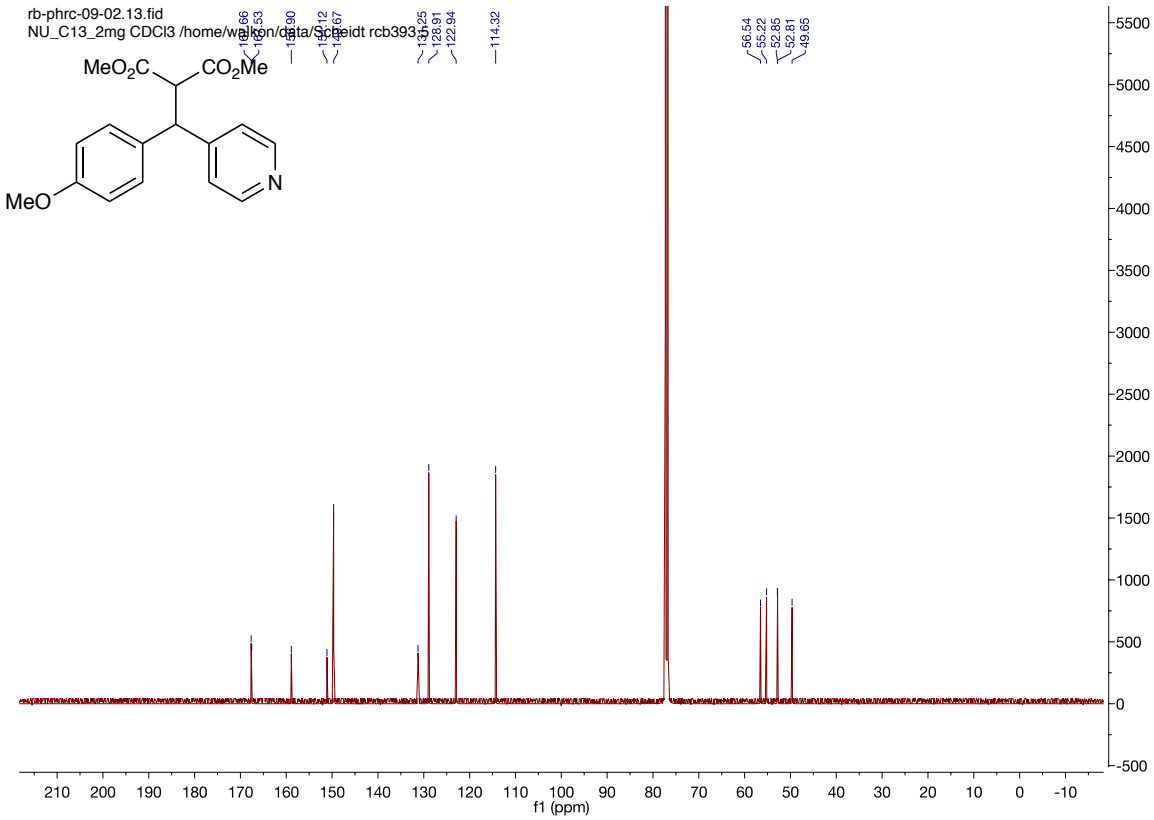
F (d) 4.27
G (s) 3.73
H (s) 3.57
I (s) 3.54
f1 (ppm)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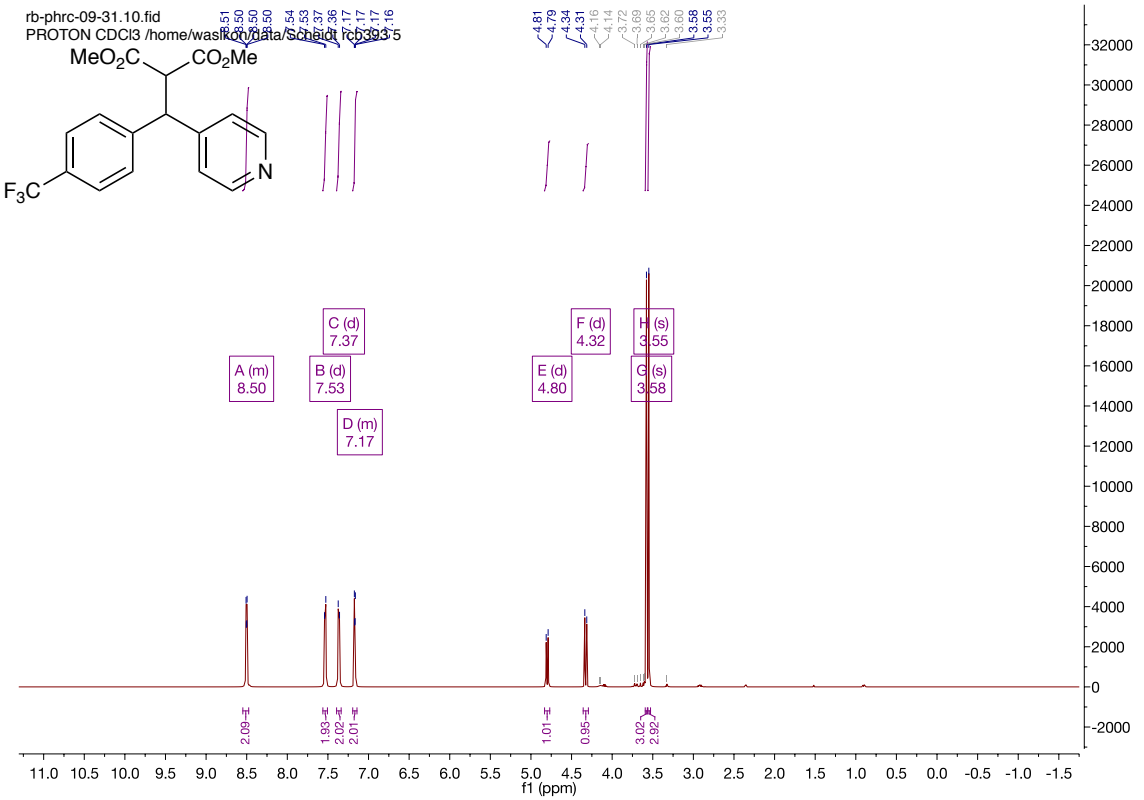
f1 (ppm)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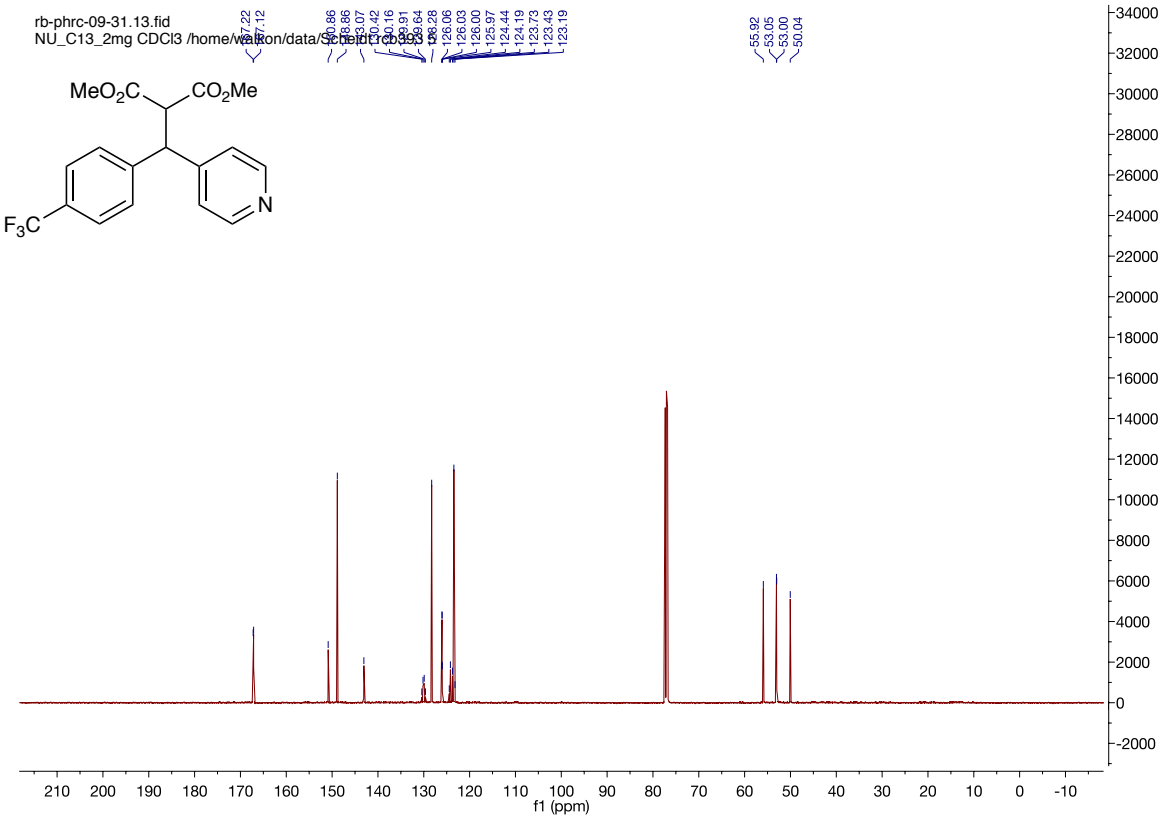
G (s) 3.58
H (s) 3.55
f1 (ppm)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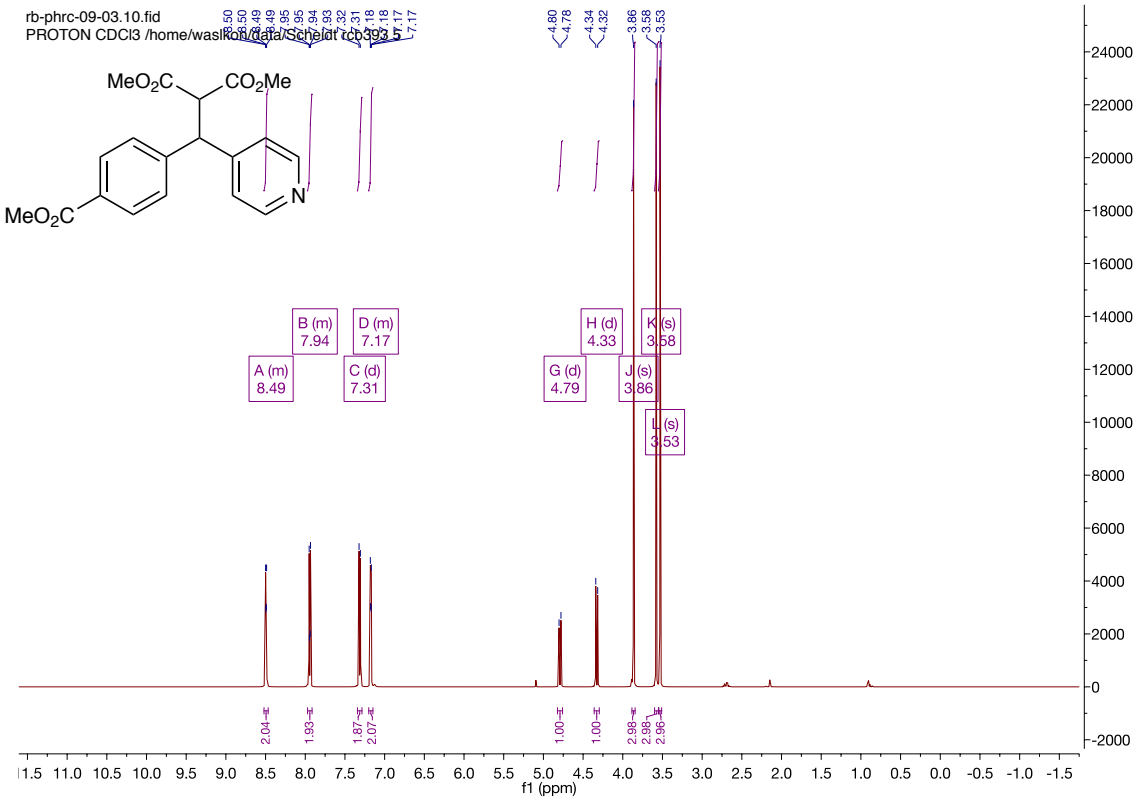
f1 (ppm)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CO2Me
MeO2C
N
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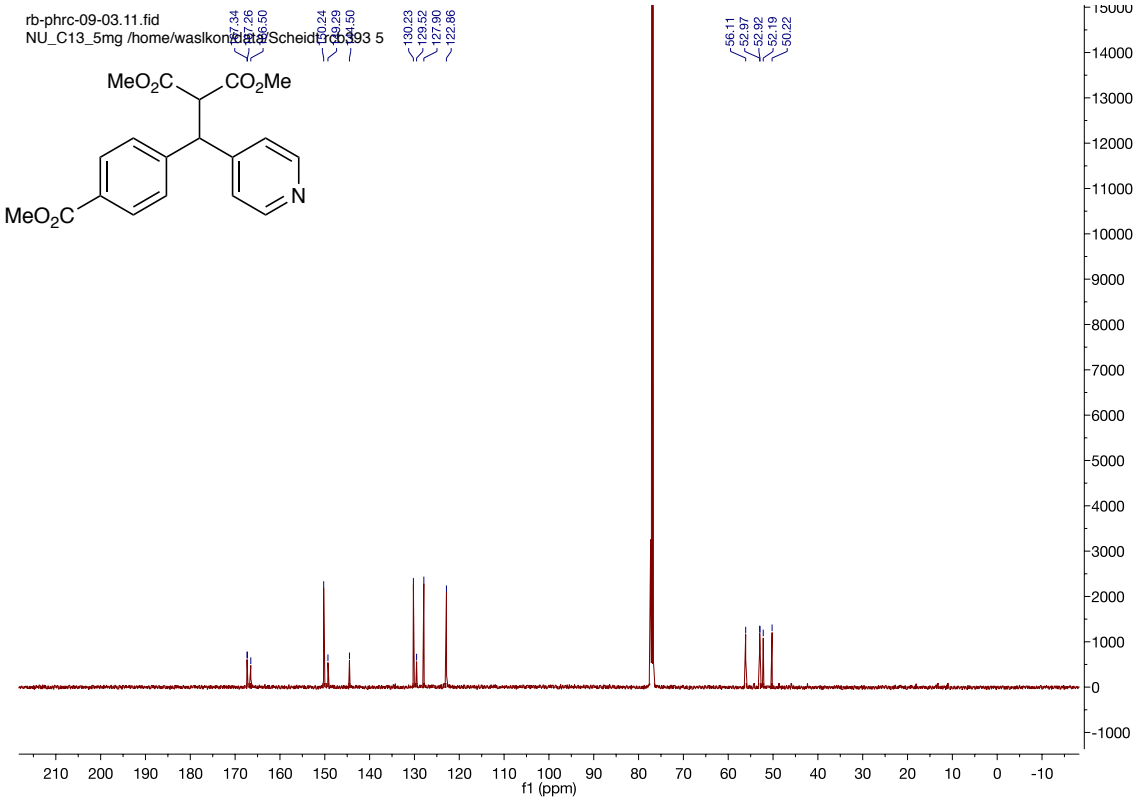
L (s) 3.53
f1 (ppm)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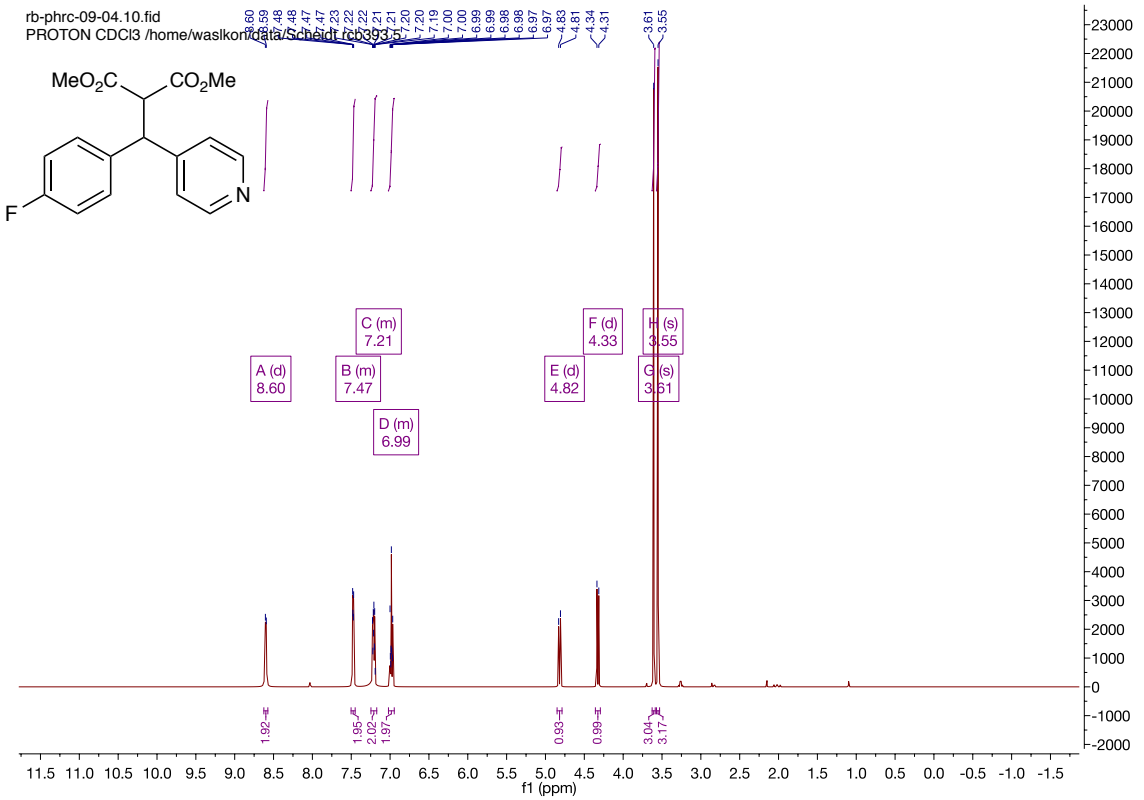
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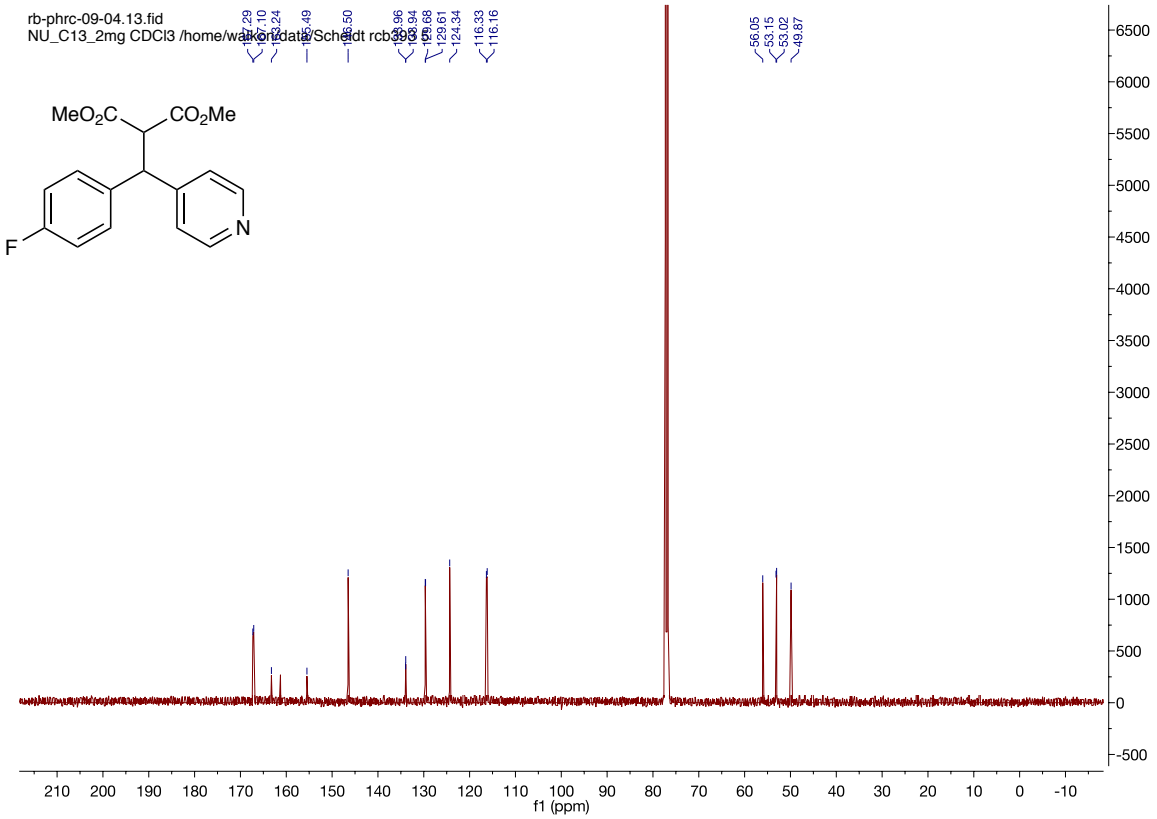
f1 (ppm)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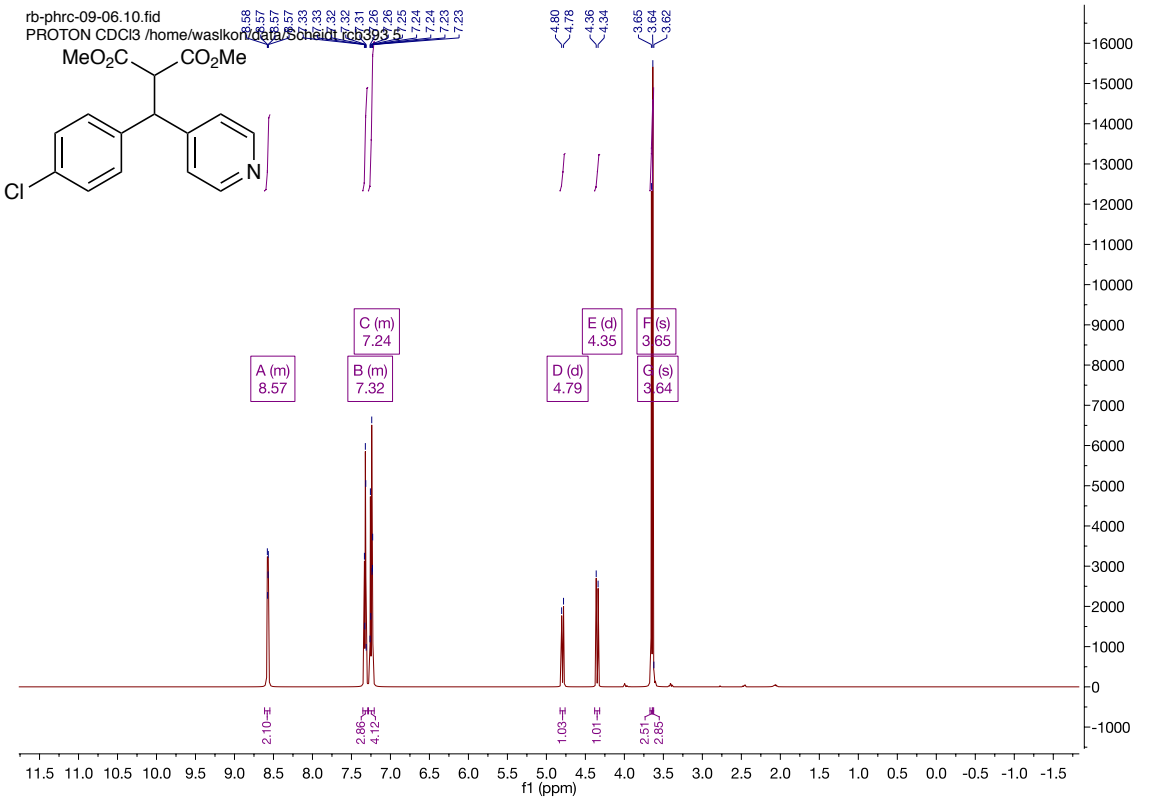
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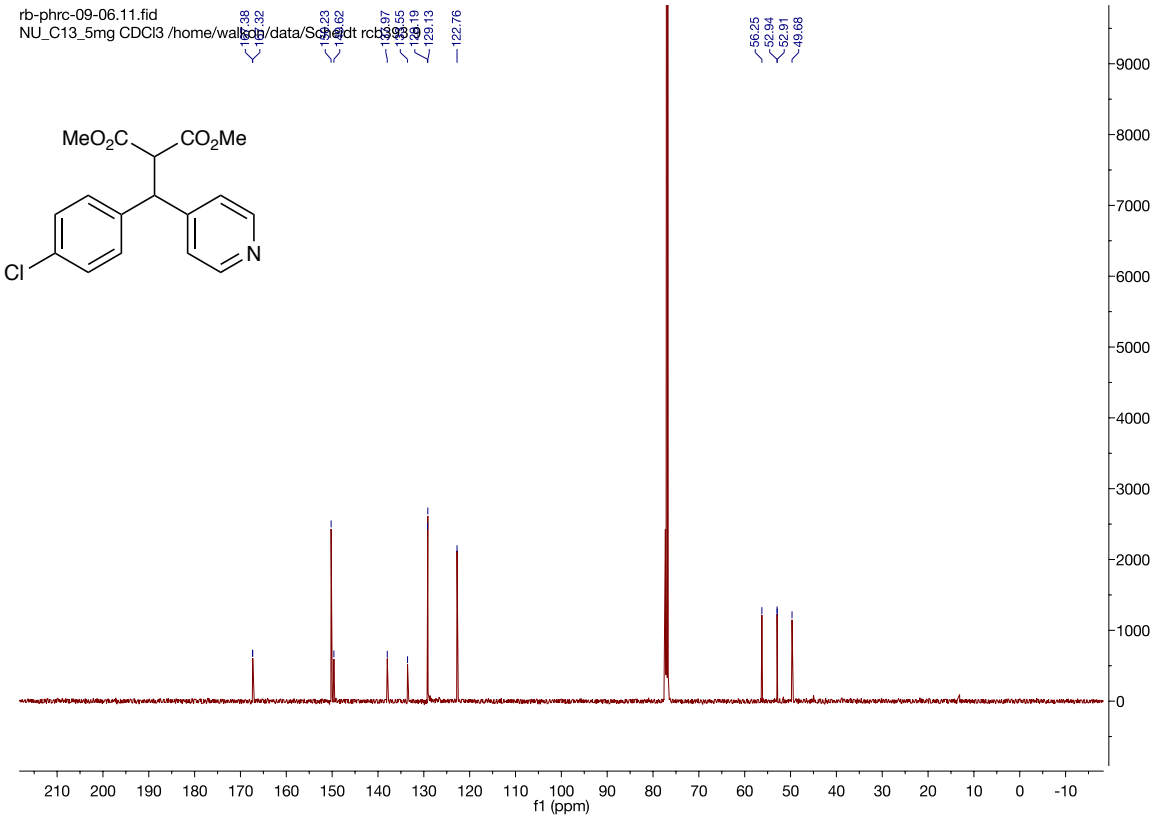
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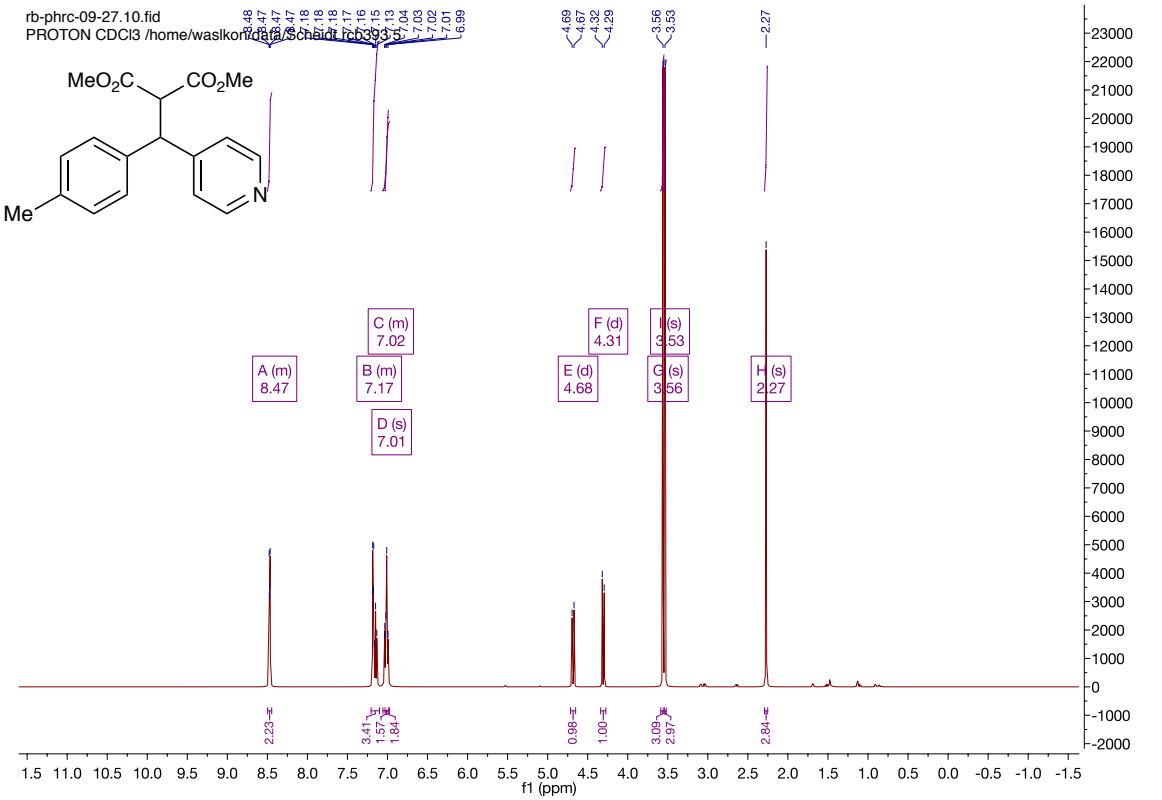
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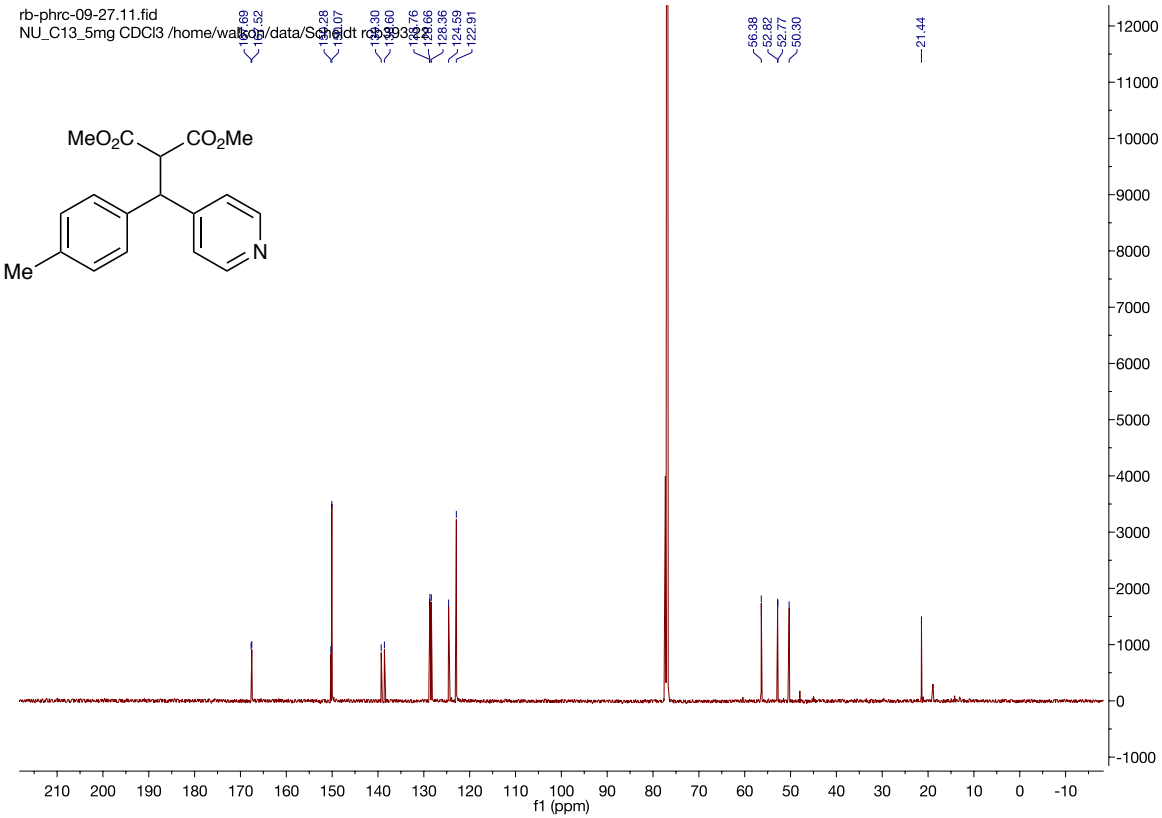
f1 (ppm)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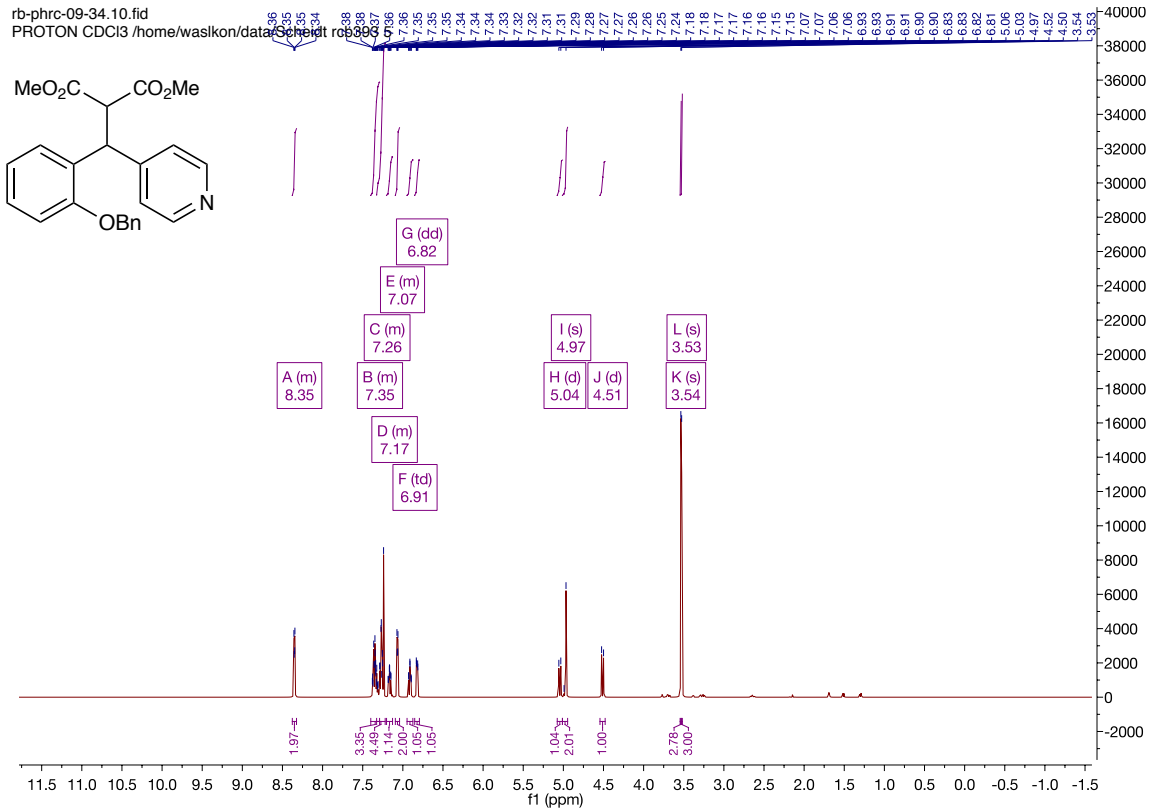
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L (s) 3.53
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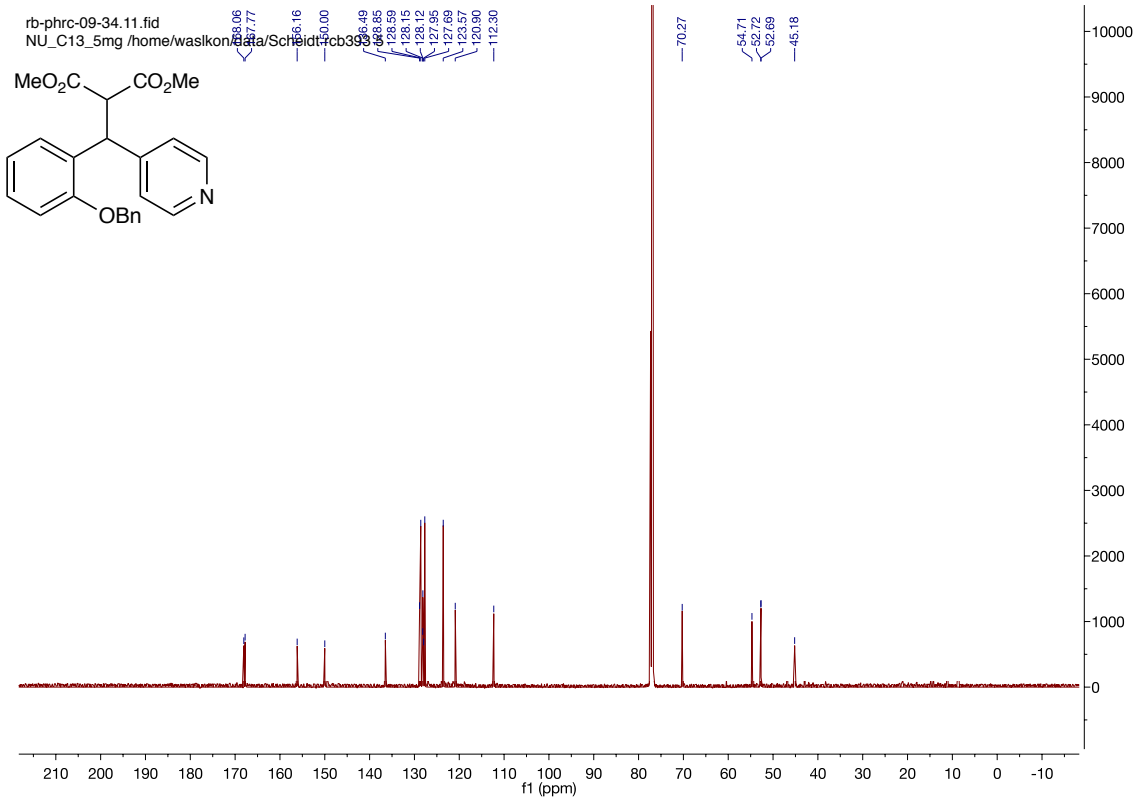
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45.18
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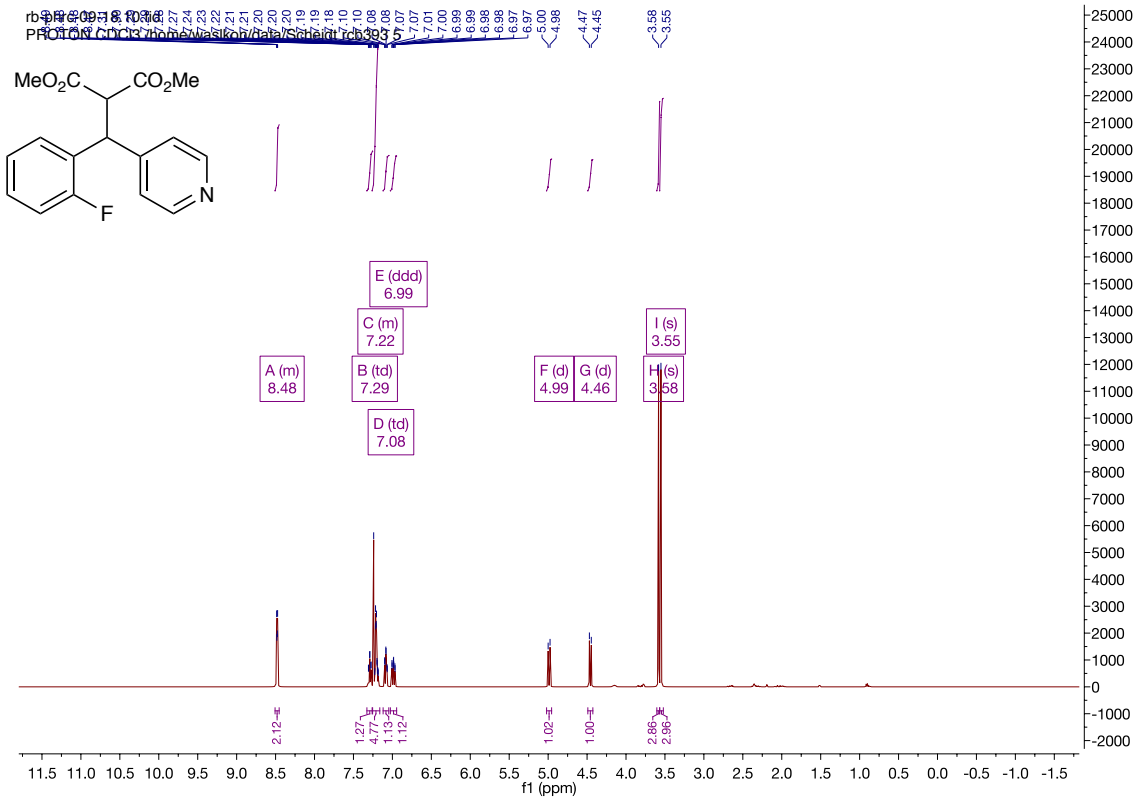
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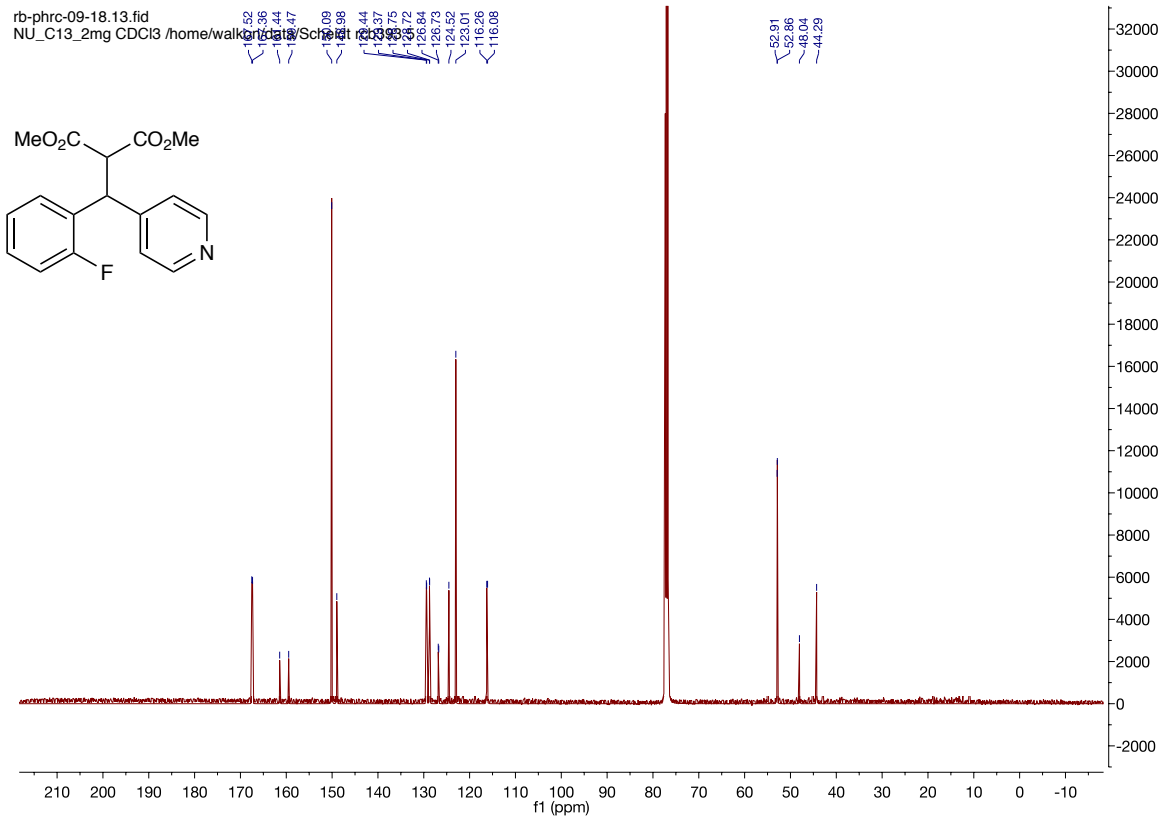
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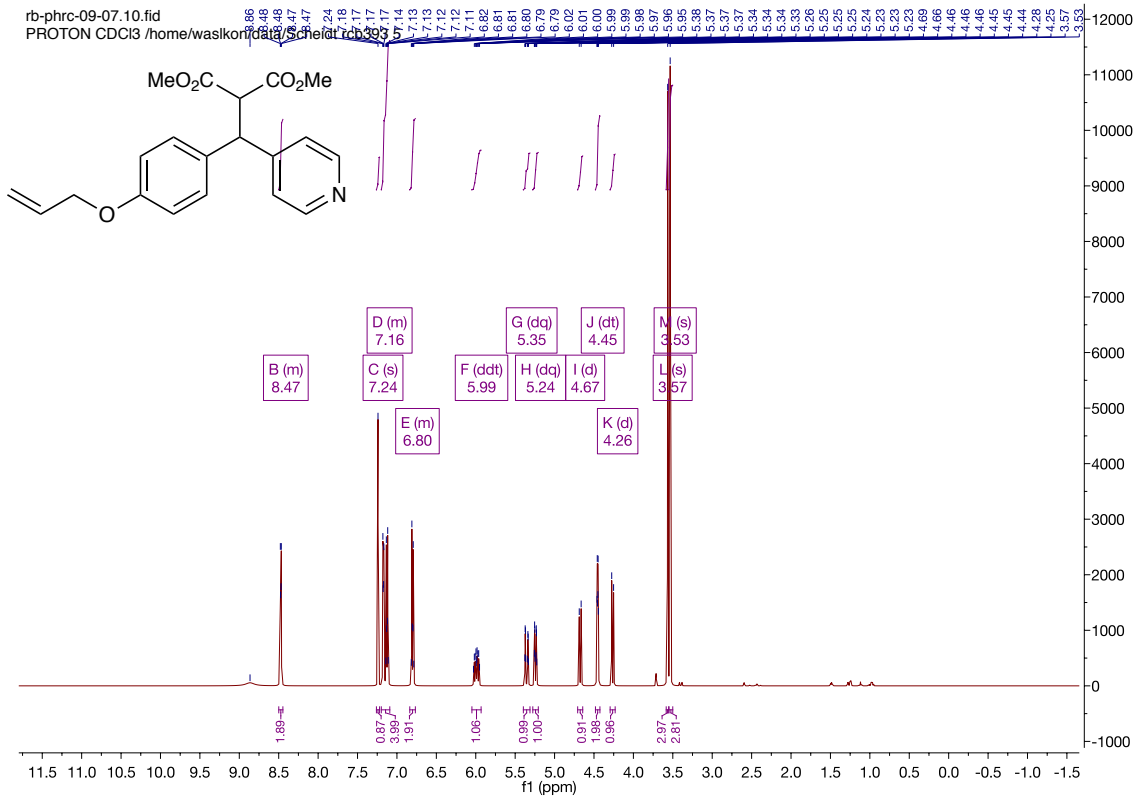
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C (s) 7.24
D (m) 7.16
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J (dt) 4.45
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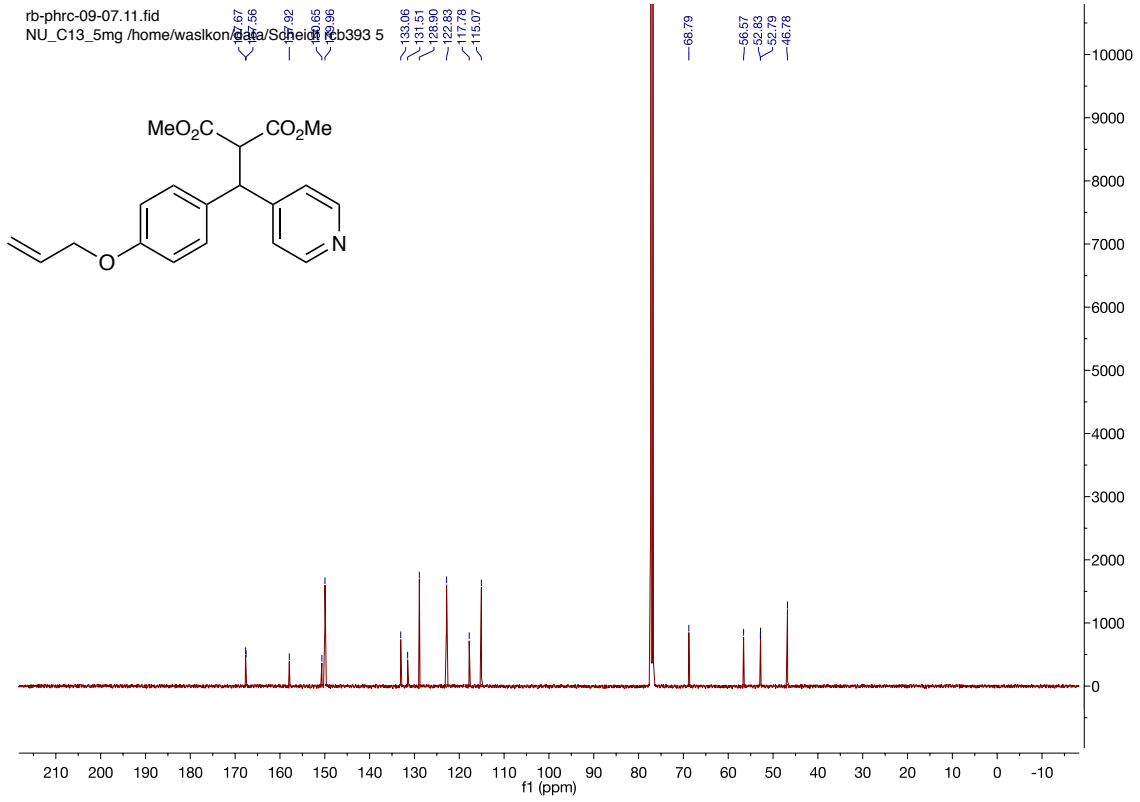
M (s) 3.53
f1 (ppm)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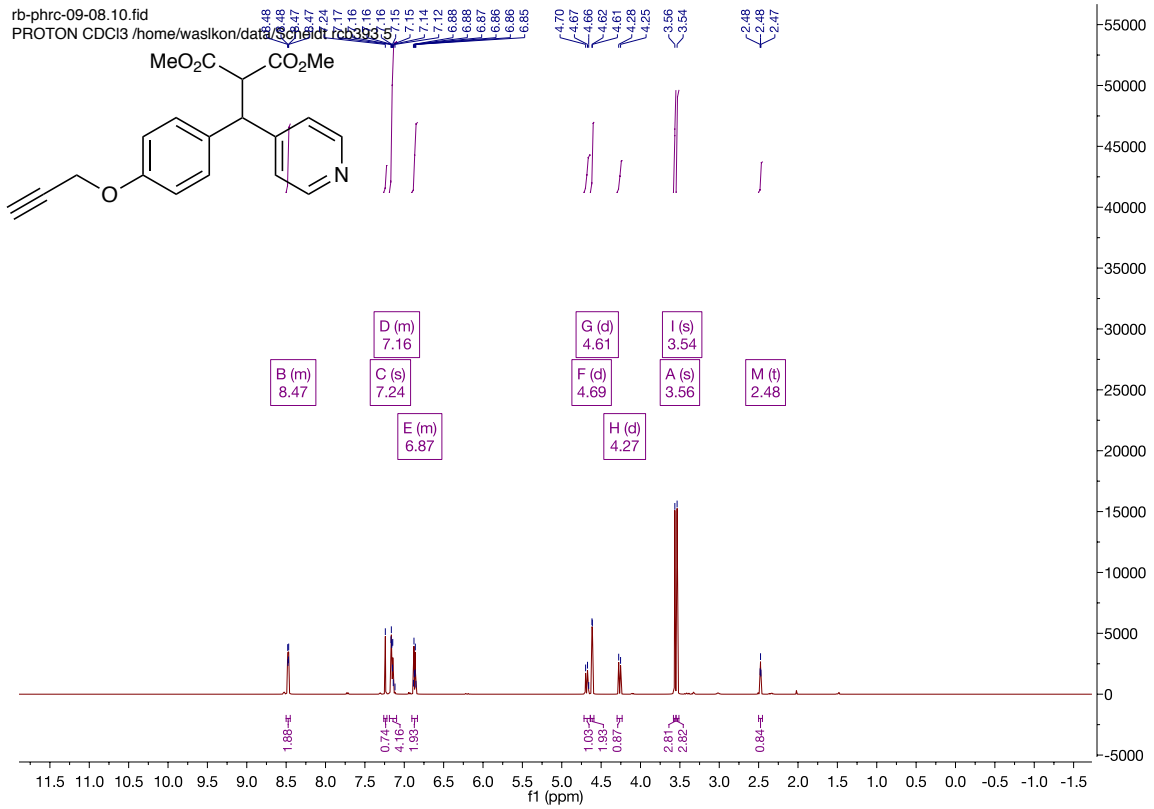
MeO2C
CO2Me
O
N
f1 (ppm)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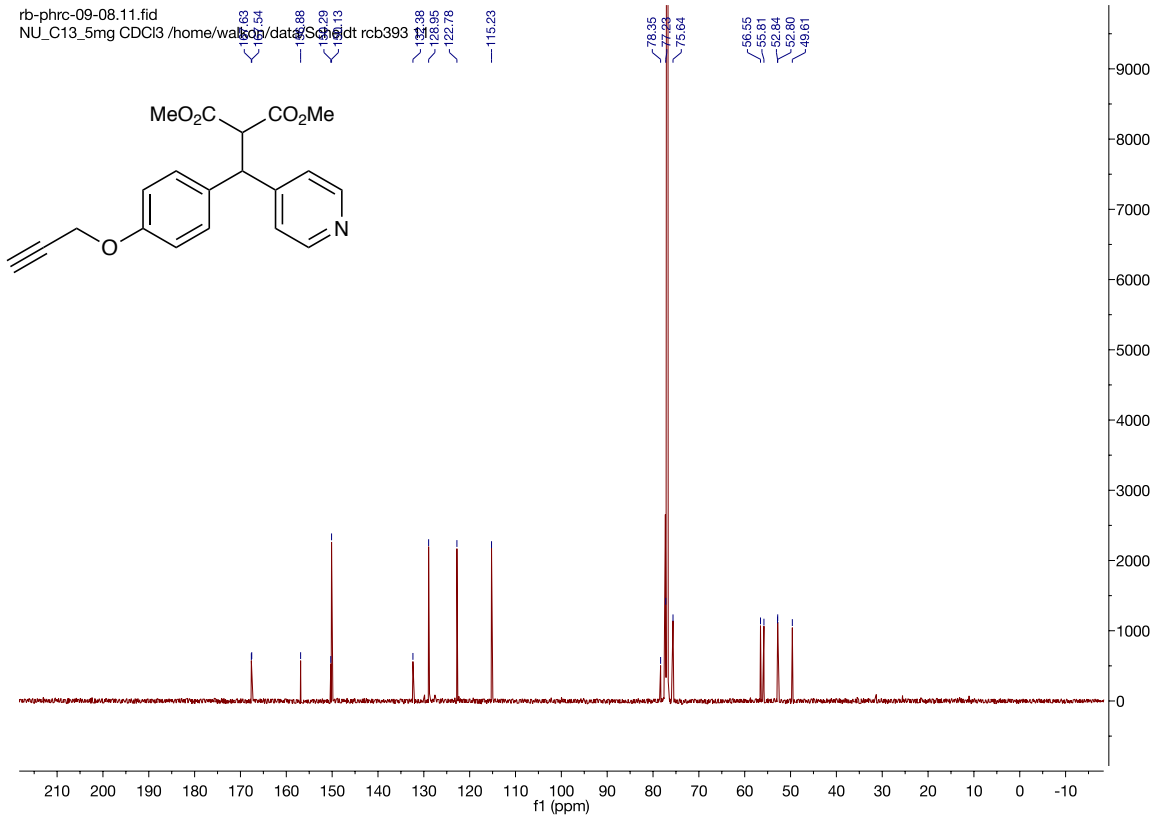
MeO2C
CO2Me
O
N
B (m) 8.47
C (s) 7.24
D (m) 7.16
E (m) 6.87
F (d) 4.69
G (d) 4.61
H (d) 4.27
A (s) 3.56
I (s) 3.54
M (t) 2.48
1.88
0.74
4.16
1.93
1.03
1.93
0.87
2.81
2.82
0.84
f1 (ppm)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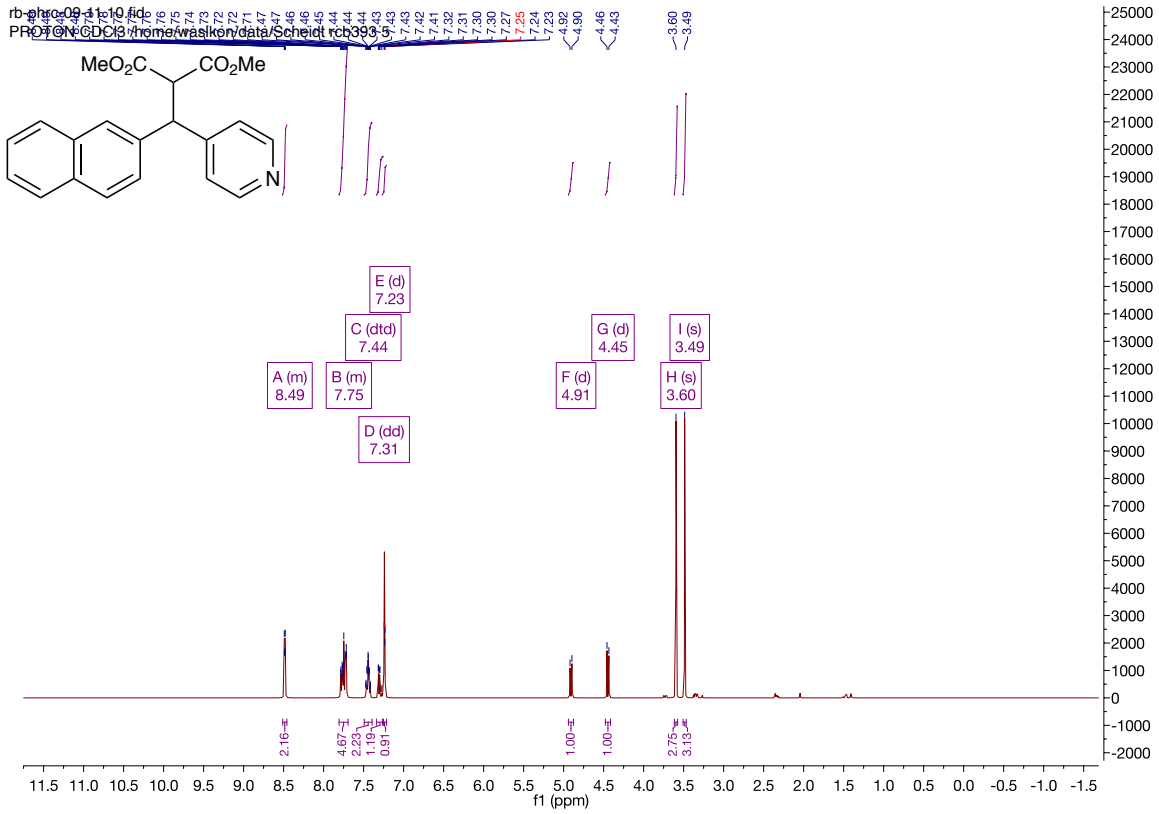
NU_C13_5mg CDCl3 /home/waslkon/data/Schmidt rcb393 11
MeO2C
CO2Me
O
N
165.63
154.54
138.88
136.29
136.13
123.38
123.95
122.78
115.23
78.35
77.03
75.64
56.55
55.81
52.84
52.80
49.61
f1 (ppm)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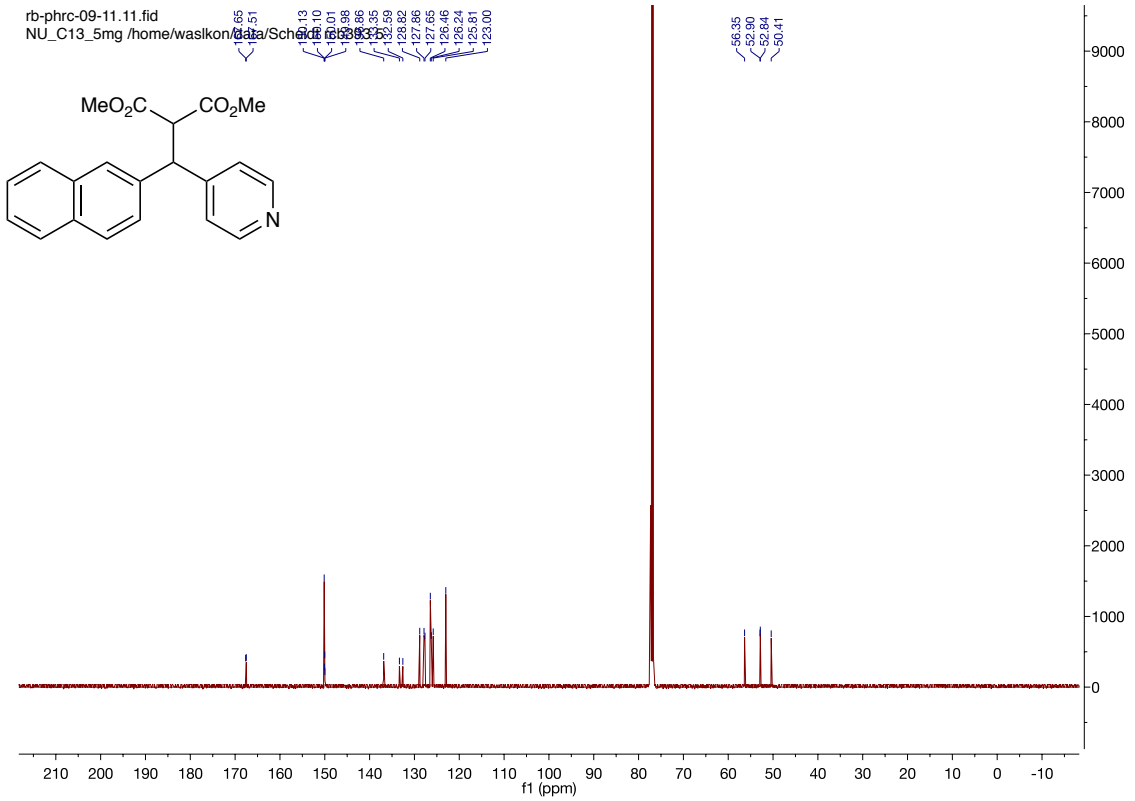
MeO2C
CO2Me
N
E (d) 7.23
C (dtd) 7.44
G (d) 4.45
I (s) 3.49
A (m) 8.49
B (m) 7.75
F (d) 4.91
H (s) 3.60
D (dd) 7.31
f1 (ppm)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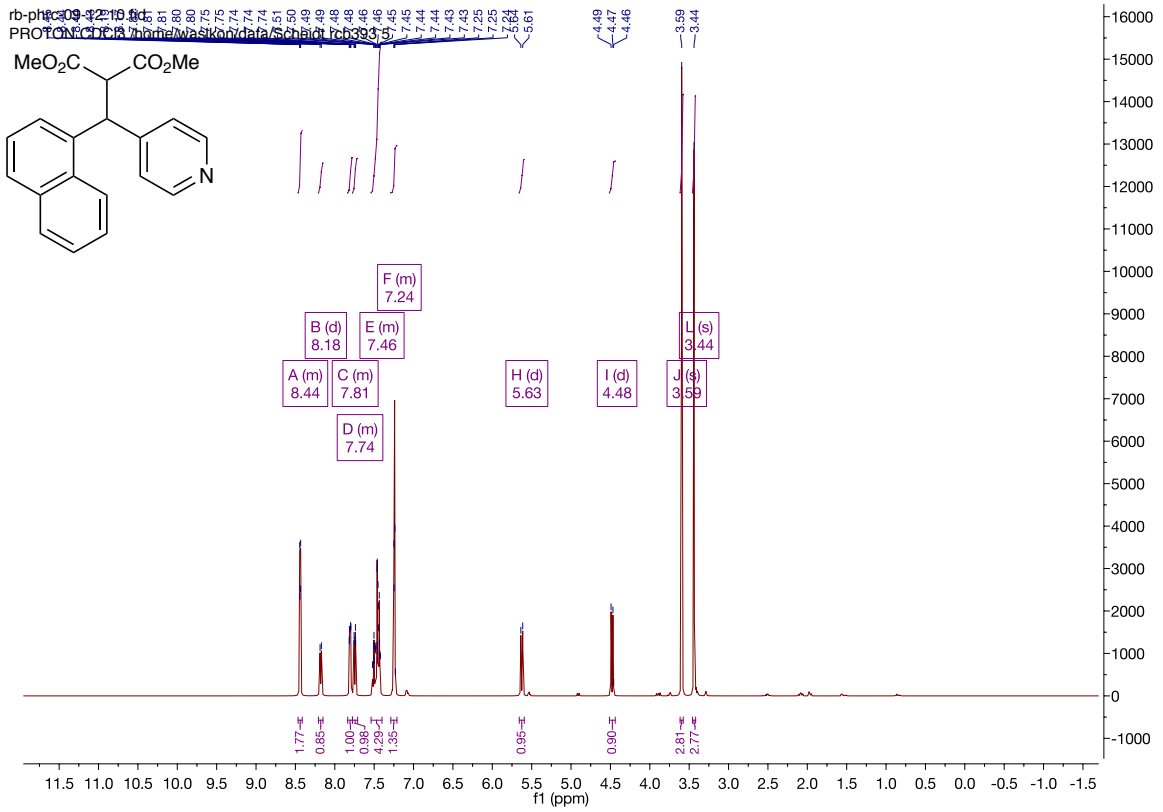
MeO2C
CO2Me
N
f1 (ppm)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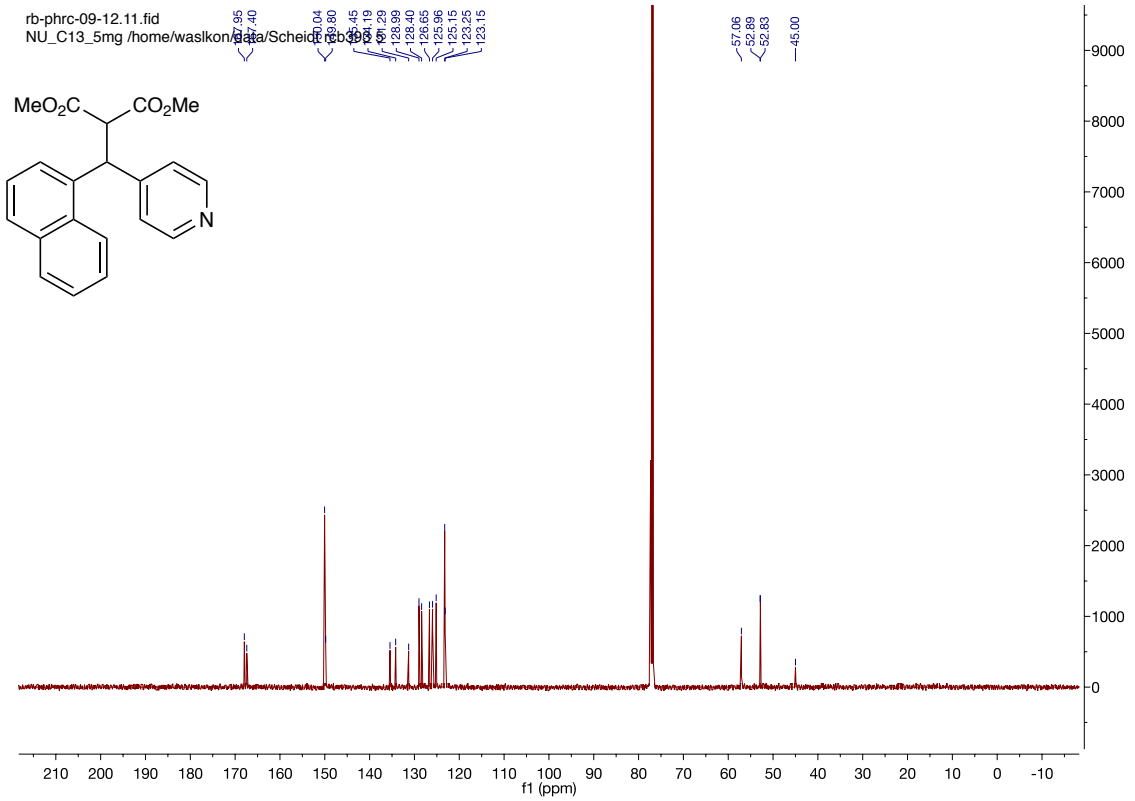
PROTON_CDCl3 /home/waslkon/data/Scheidt rcb393.5
MeO2C
CO2Me
N
F (m)
7.24
B (d)
8.18
E (m)
7.46
L (s)
3.44
A (m)
8.44
C (m)
7.81
H (d)
5.63
I (d)
4.48
J (s)
3.59
D (m)
7.74
f1 (ppm)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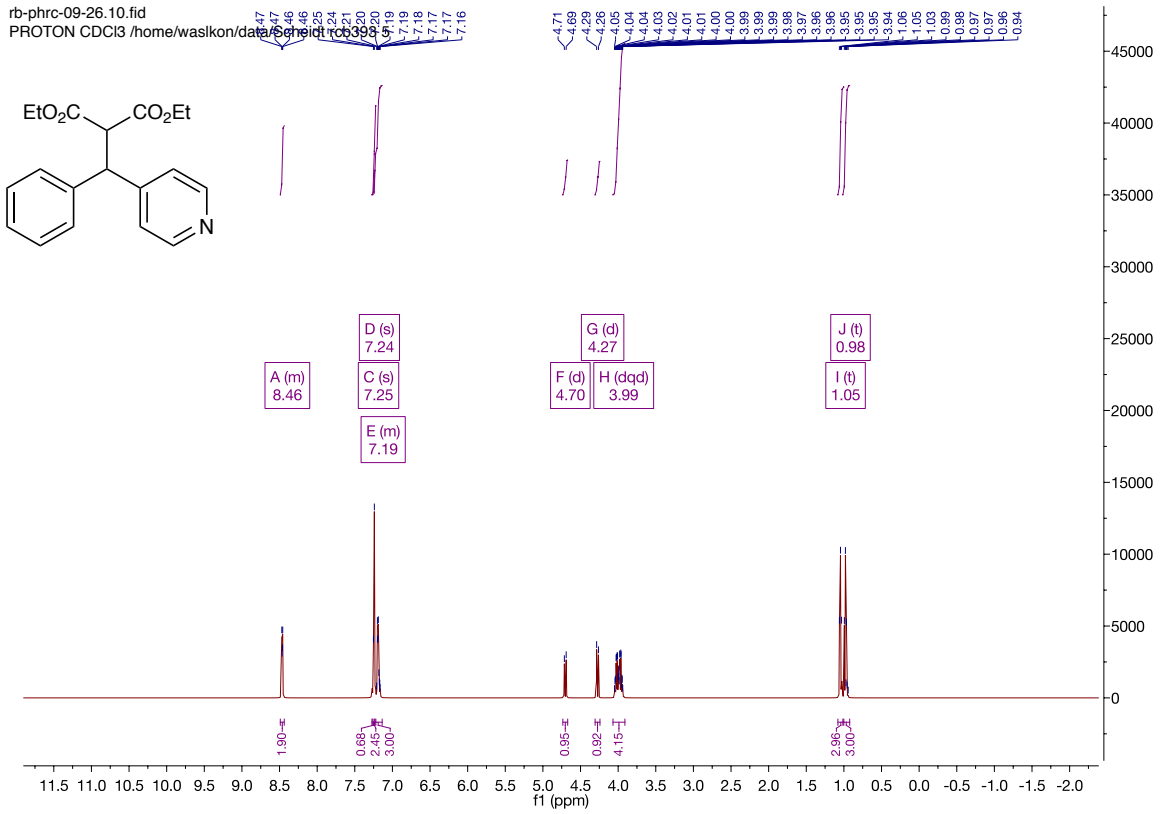
CO2Me
N
f1 (ppm)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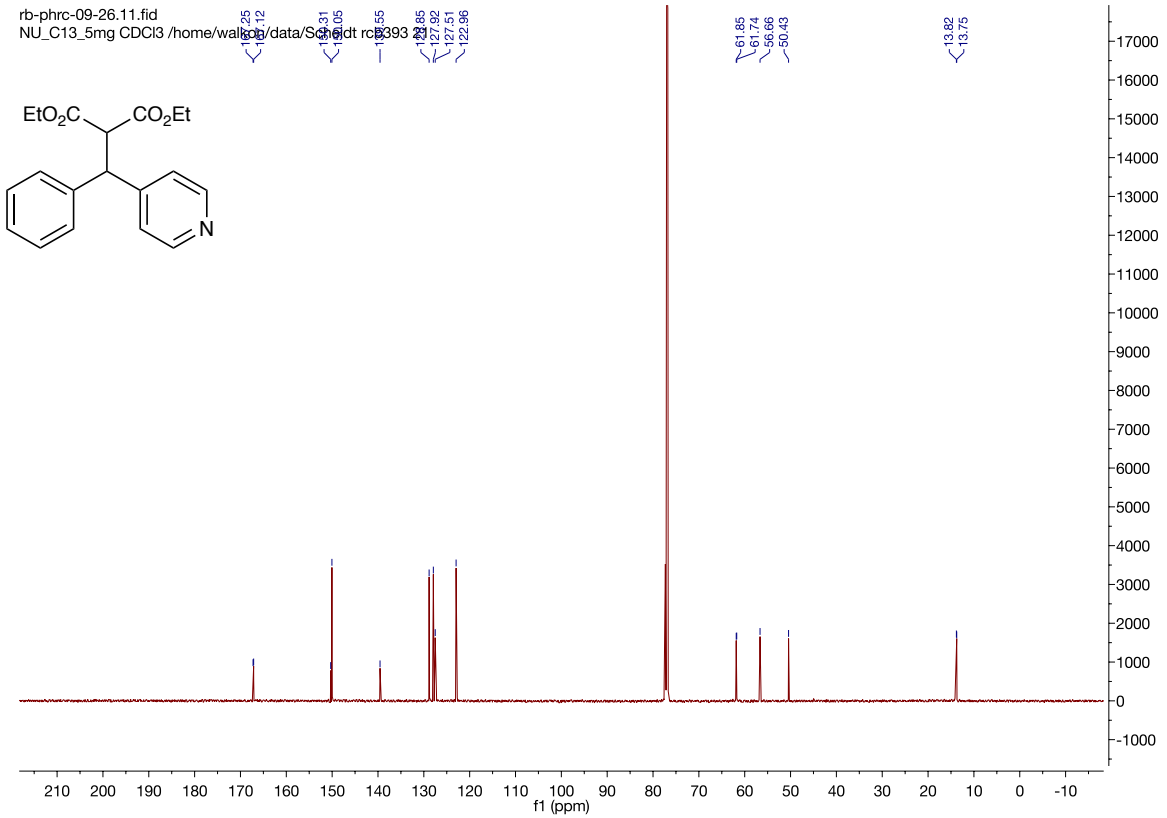
PROTON CDCl3 /home/waslkon/data/Schmidt rcb393 5
EtO2C
CO2Et
N
A (m) 8.46
C (s) 7.25
D (s) 7.24
E (m) 7.19
F (d) 4.70
H (dqd) 3.99
G (d) 4.27
I (t) 1.05
J (t) 0.98
f1 (ppm)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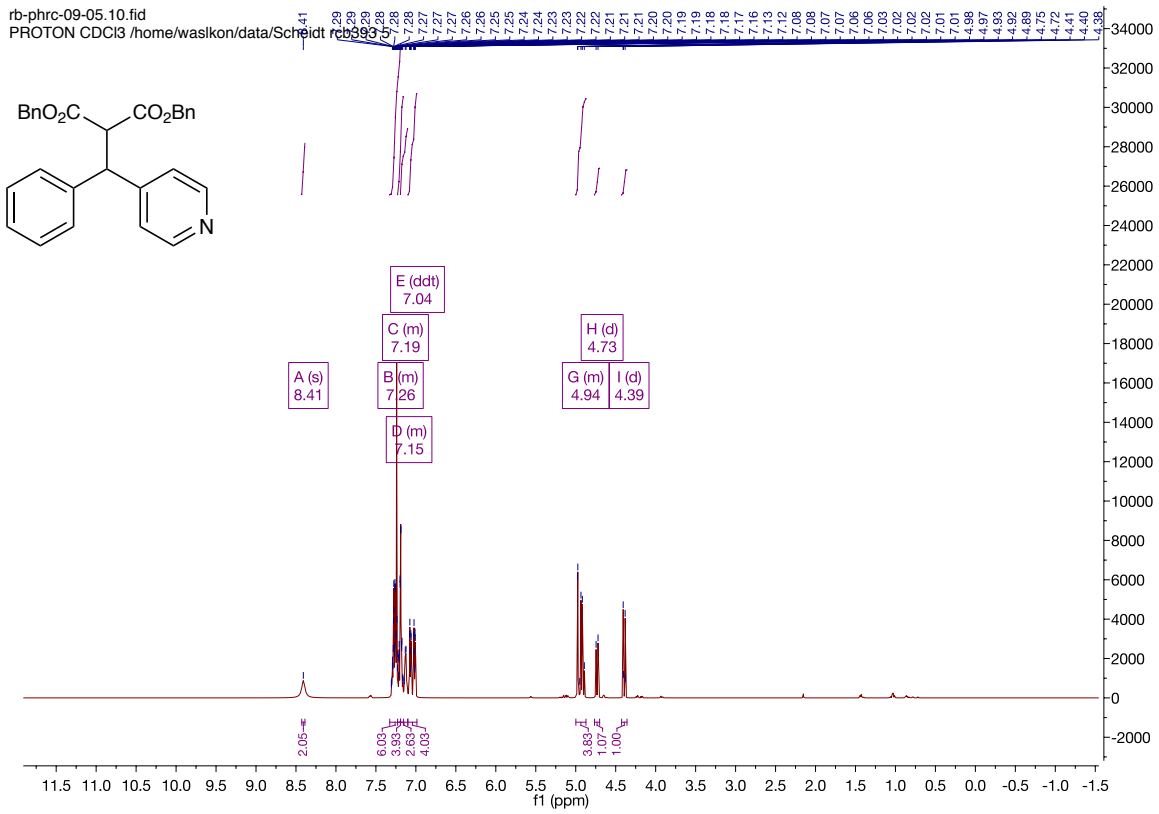
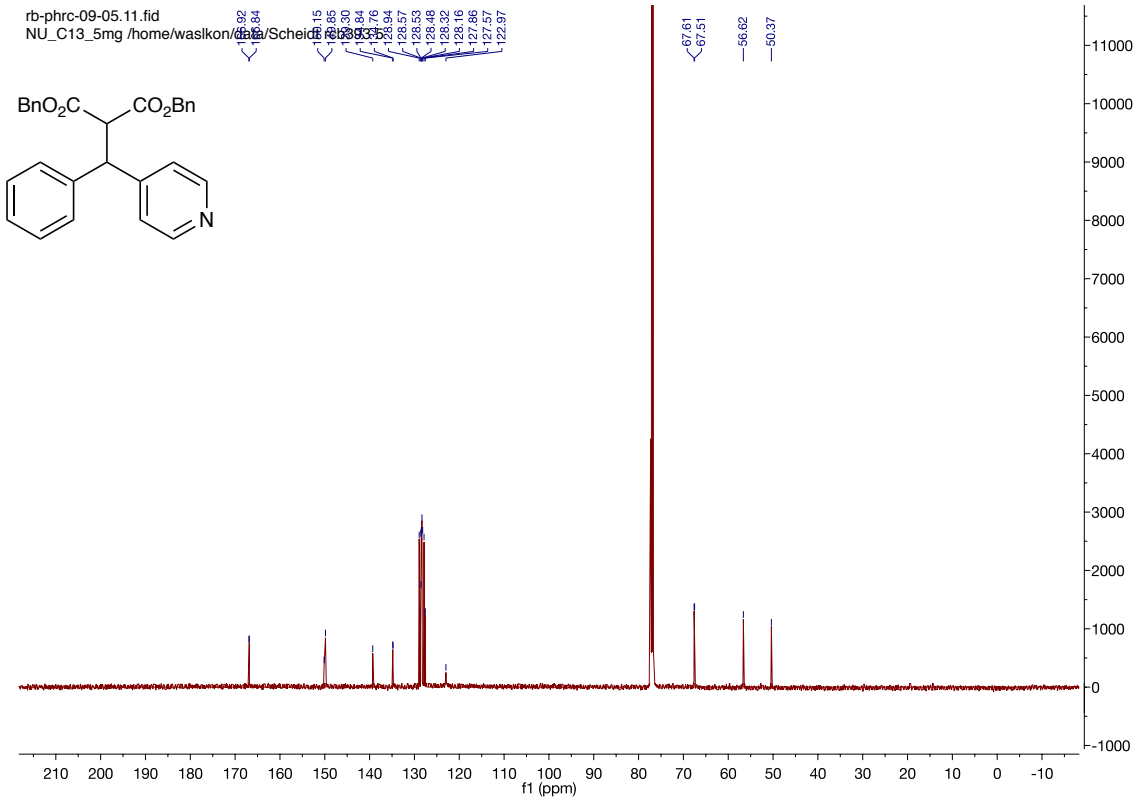
EtO2C
CO2Et
N
f1 (ppm)


rb-phrc-09-05.10.fid
PROTON CDCl3 /home/waslkon/data/Scheidt rcb393 5
BnO2C
CO2Bn
N
E (ddt)
7.04
C (m)
7.19
H (d)
4.73
A (s)
8.41
B (m)
7.26
G (m)
4.94
I (d)
4.39
D (m)
7.15
2.05
6.03
3.93
2.63
4.03
3.83
1.07
1.00
f1 (ppm)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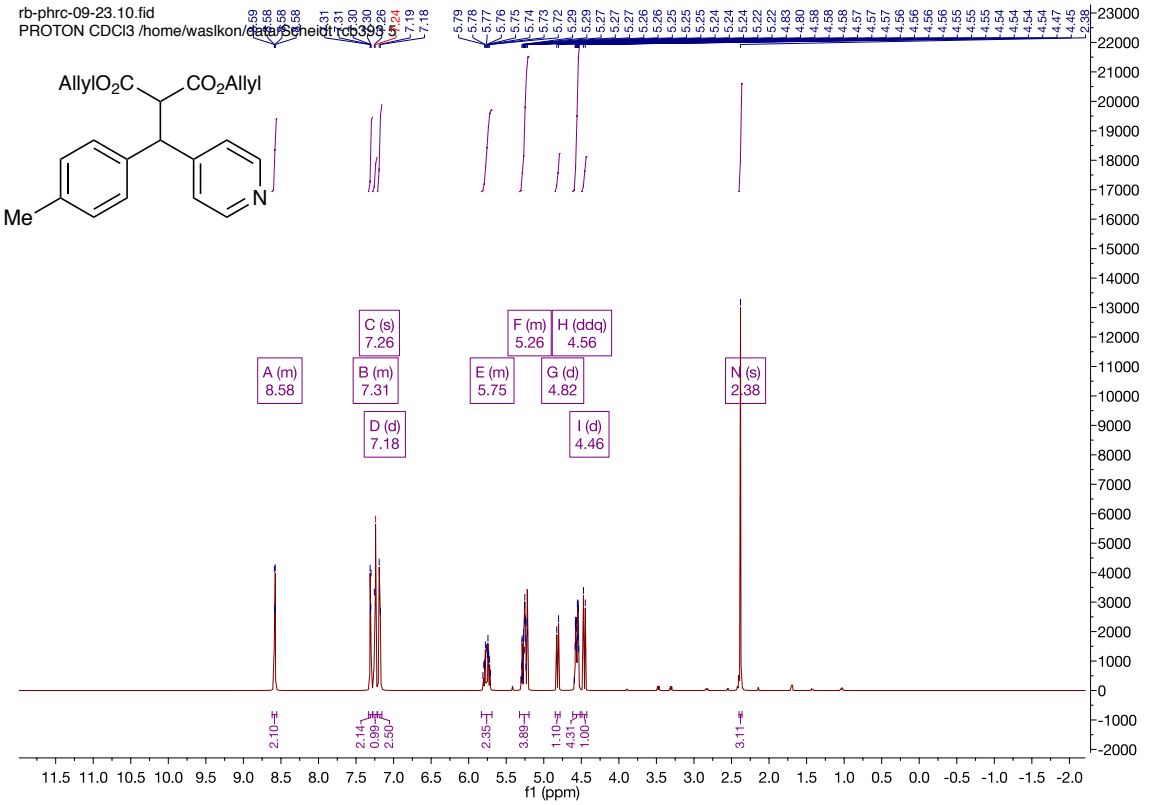
NU_C13_5mg /home/waslkon/data/Scheidt rcb393 5
BnO2C
CO2Bn
N
67.61
67.51
56.62
50.37
f1 (ppm)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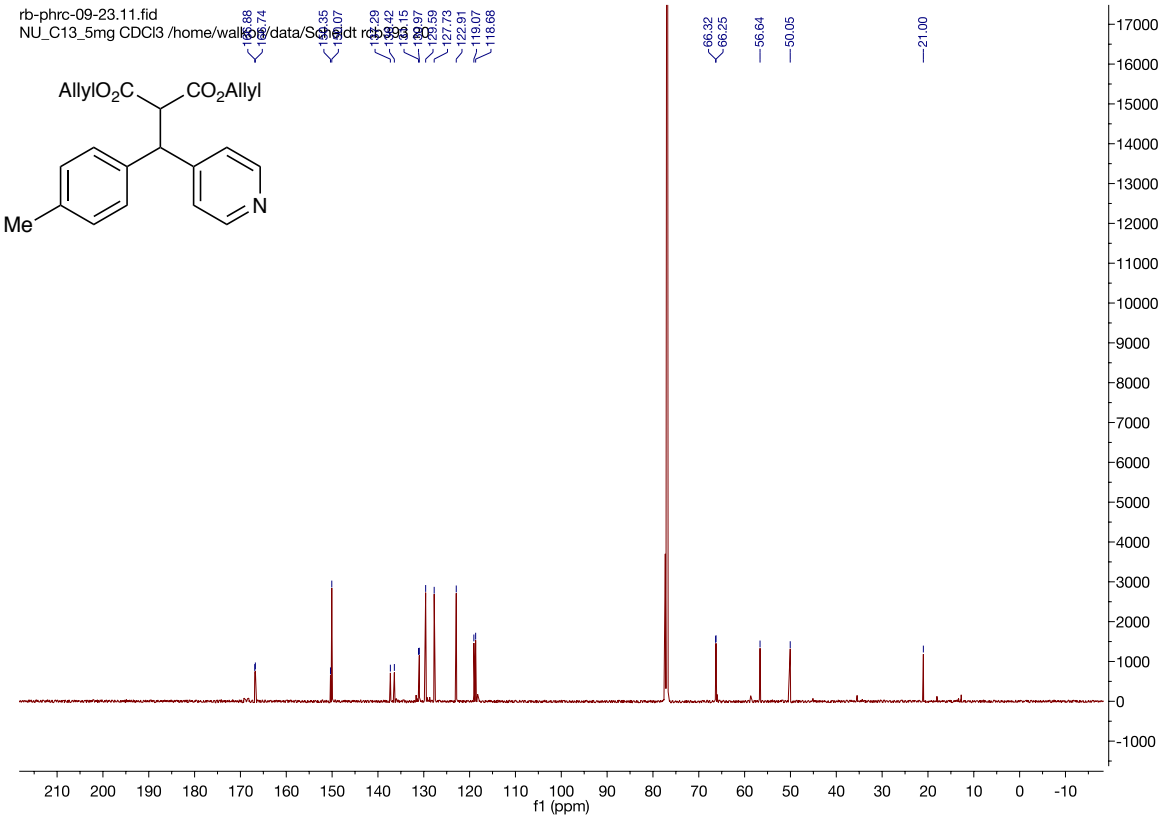
PROTON CDCl3 /home/waslkon/data/Scheidt rcb393 5
AllylO2C
CO2Allyl
Me
N
A (m) 8.58
B (m) 7.31
C (s) 7.26
D (d) 7.18
E (m) 5.75
F (m) 5.26
G (d) 4.82
H (ddq) 4.56
I (d) 4.46
N (s) 2.38
f1 (ppm)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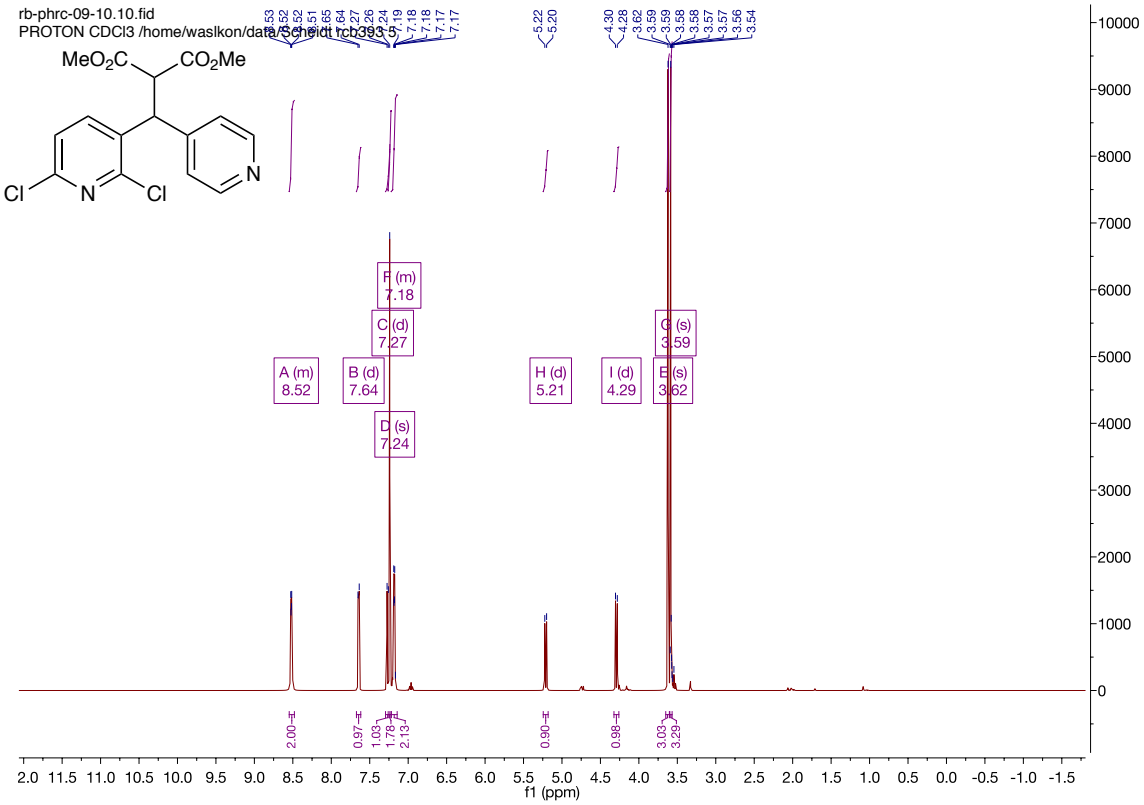
NU_C13_5mg CDCl3 /home/waslkon/data/Scheidt rcb393 20
AllylO2C
CO2Allyl
Me
N
66.32
66.25
56.64
50.05
21.00
f1 (ppm)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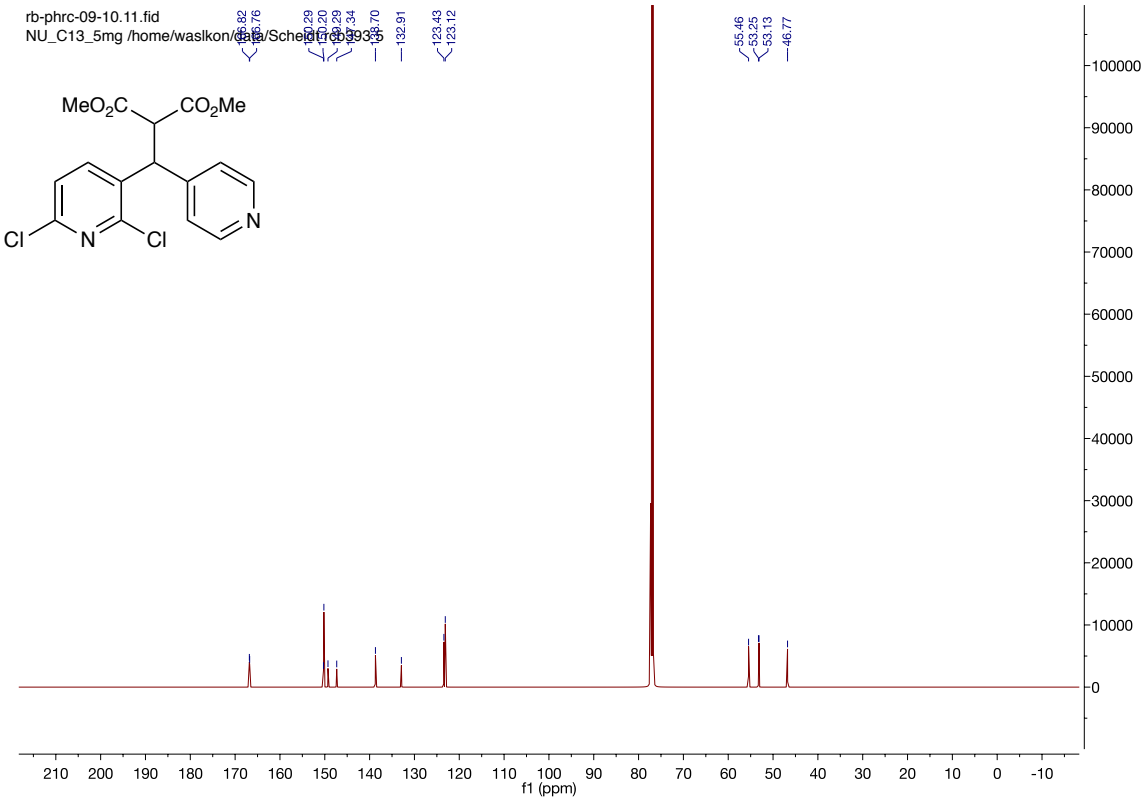
PROTON CDCl3 /home/waslkon/data/Scheidt/rcb393-5
MeO2C
CO2Me
Cl
N
Cl
N
F (m)
7.18
C (d)
7.27
G (s)
3.59
A (m)
8.52
B (d)
7.64
H (d)
5.21
I (d)
4.29
E (s)
3.62
D (s)
7.24
f1 (ppm)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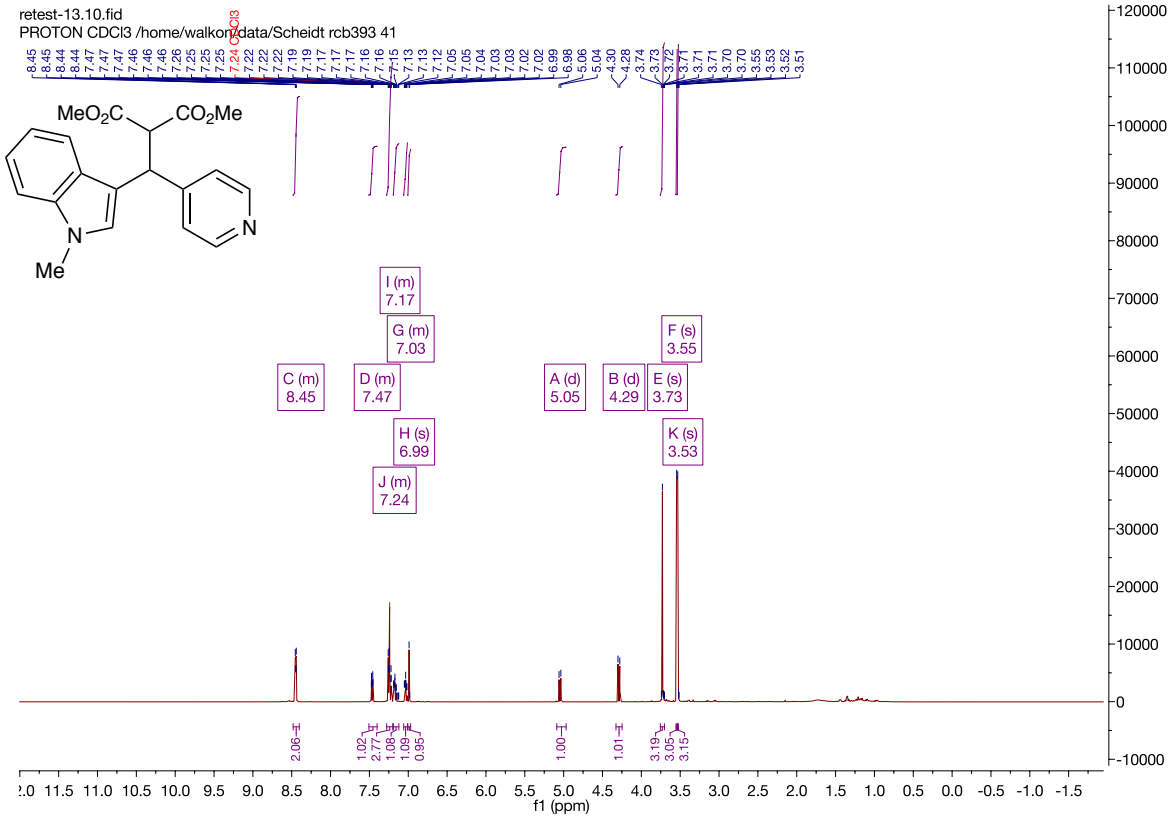
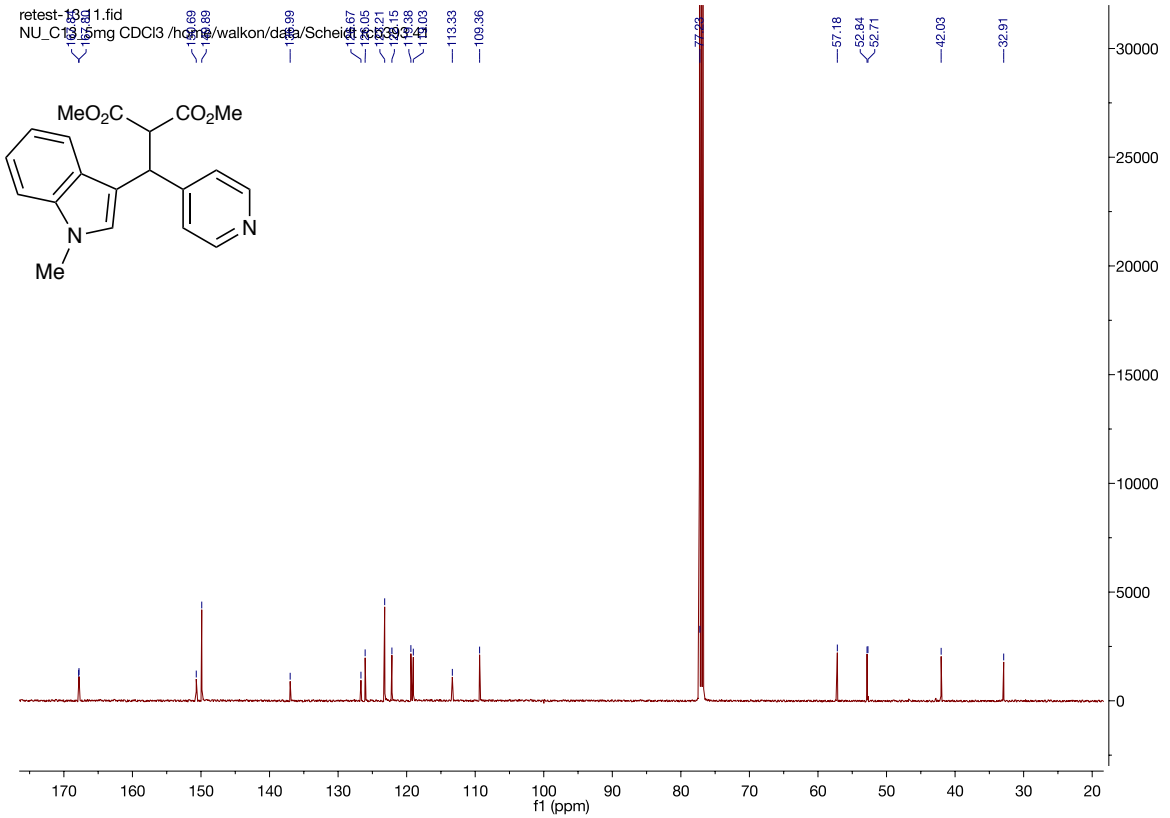
NU_C13_5mg /home/waslkon/data/Scheidt/rcb393-5
MeO2C
CO2Me
Cl
N
Cl
N
f1 (ppm)


retest-13.10.fid
PROTON CDCl3 /home/walkon/data/Scheidt rcb393 41
MeO2C
CO2Me
N
Me
I (m) 7.17
G (m) 7.03
F (s) 3.55
C (m) 8.45
D (m) 7.47
A (d) 5.05
B (d) 4.29
E (s) 3.73
H (s) 6.99
K (s) 3.53
J (m) 7.24
f1 (ppm)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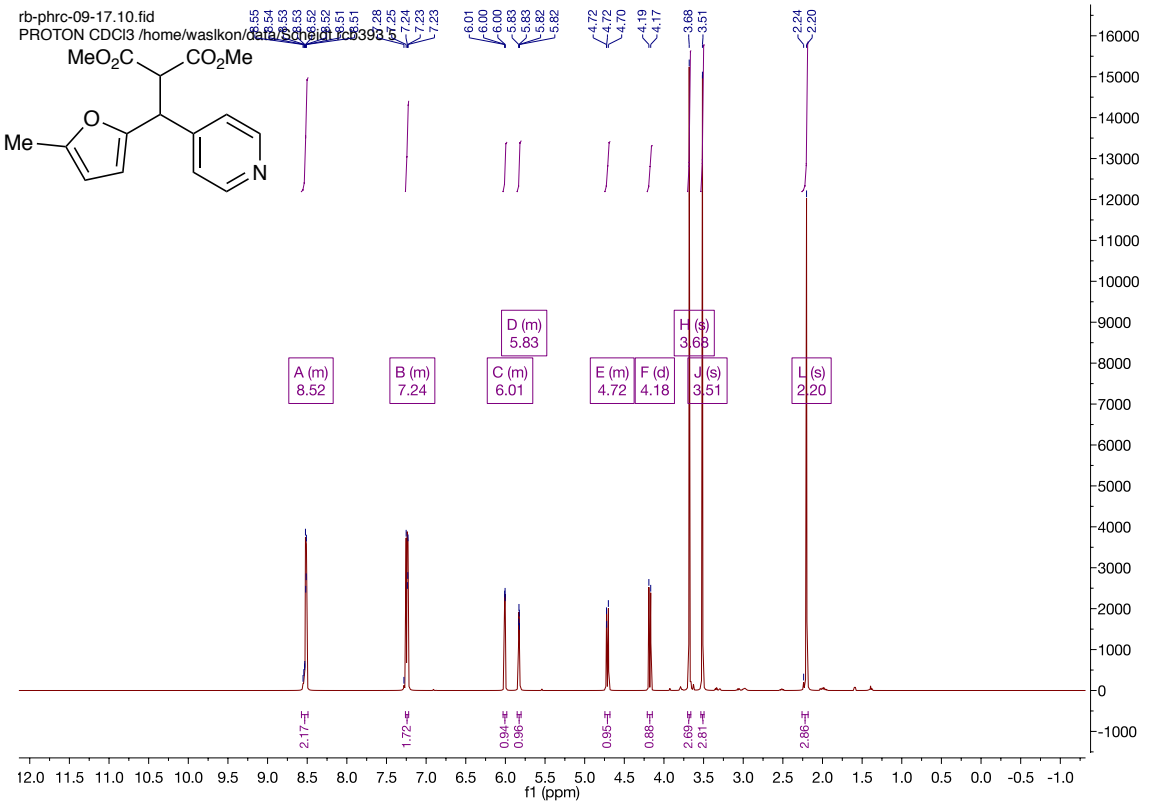
NU_C13 5mg CDCl3 /home/walkon/data/Scheidt rcb393 41
MeO2C
CO2Me
N
Me
f1 (ppm)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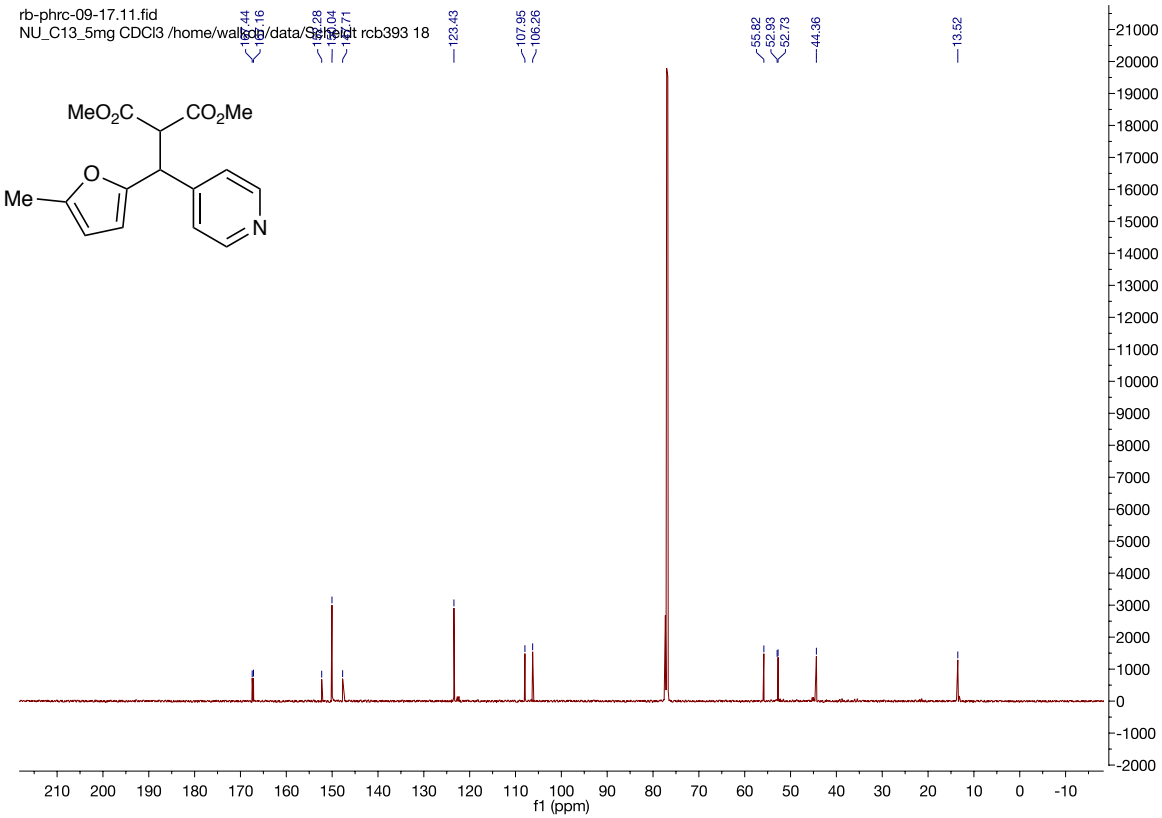
PROTON CDCl3 /home/waslkon/data/Schleidt rcb393
MeO2C
CO2Me
O
Me
N
A (m) 8.52
B (m) 7.24
C (m) 6.01
D (m) 5.83
E (m) 4.72
F (d) 4.18
H (s) 3.68
J (s) 3.51
L (s) 2.20
f1 (ppm)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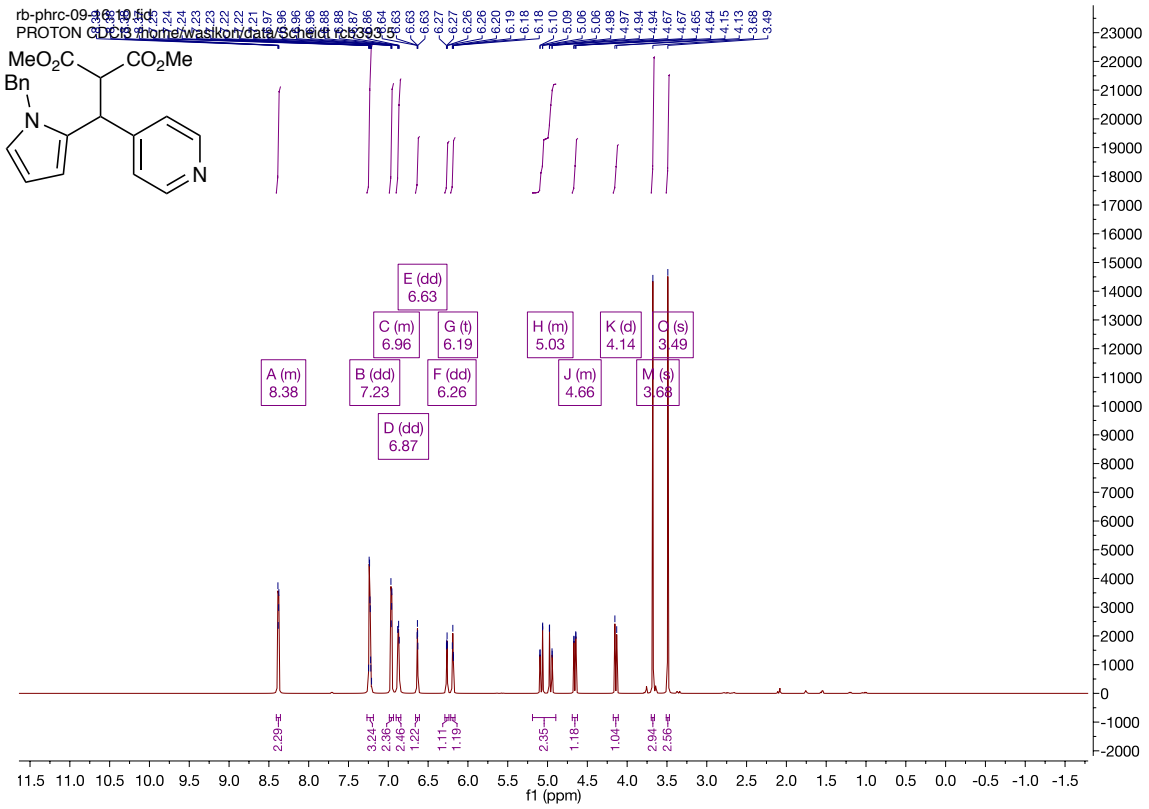
NU_C13_5mg CDCl3 /home/waslkon/data/Schleidt rcb393 18
MeO2C
CO2Me
O
Me
N
f1 (ppm)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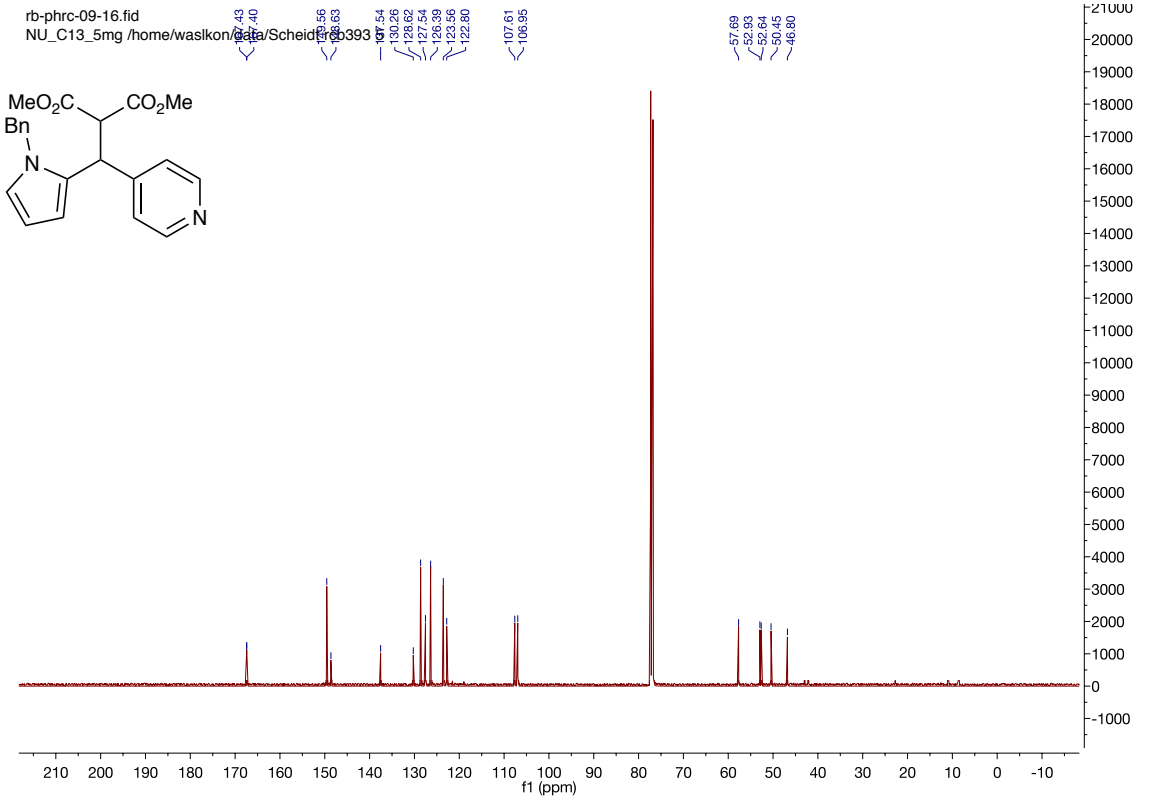
PROTON CDCl3 /home/waslkon/data/Scheidt/rcb393 5
MeO2C
CO2Me
Bn
N
N
E (dd)
6.63
C (m)
6.96
G (t)
6.19
H (m)
5.03
K (d)
4.14
O (s)
3.49
A (m)
8.38
B (dd)
7.23
F (dd)
6.26
J (m)
4.66
M (s)
3.68
D (dd)
6.87
f1 (ppm)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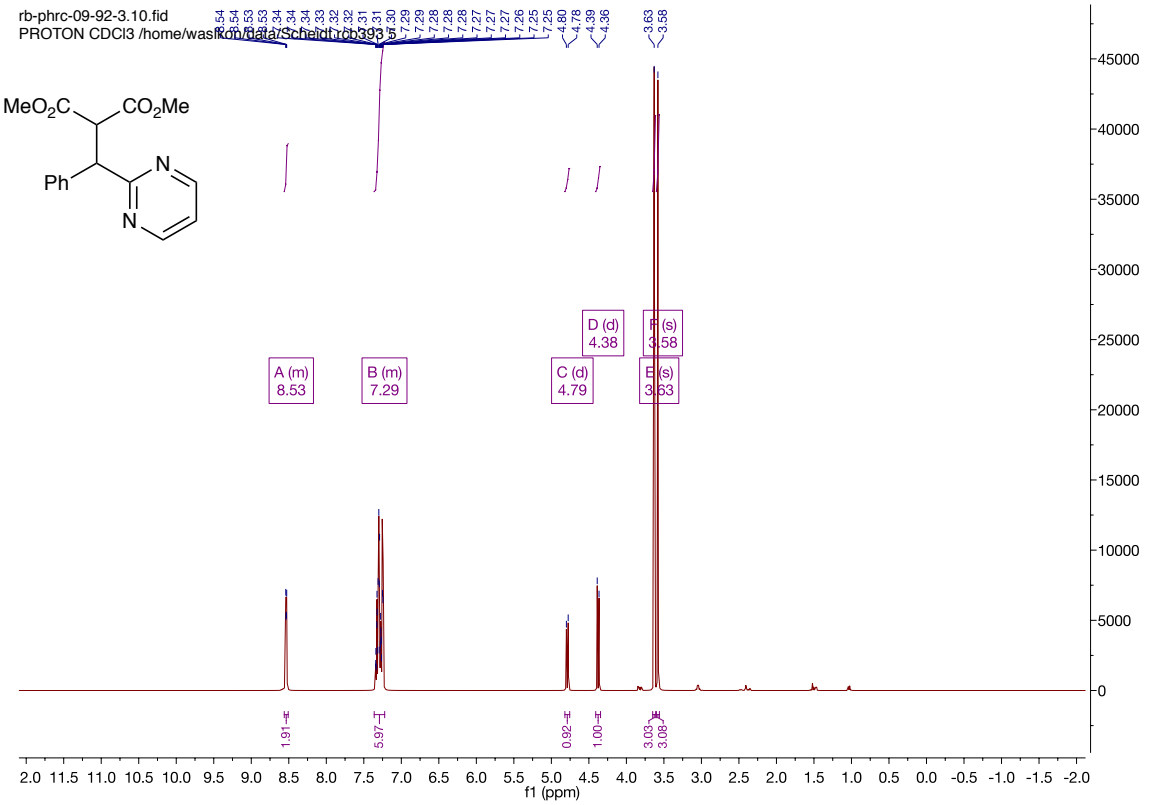
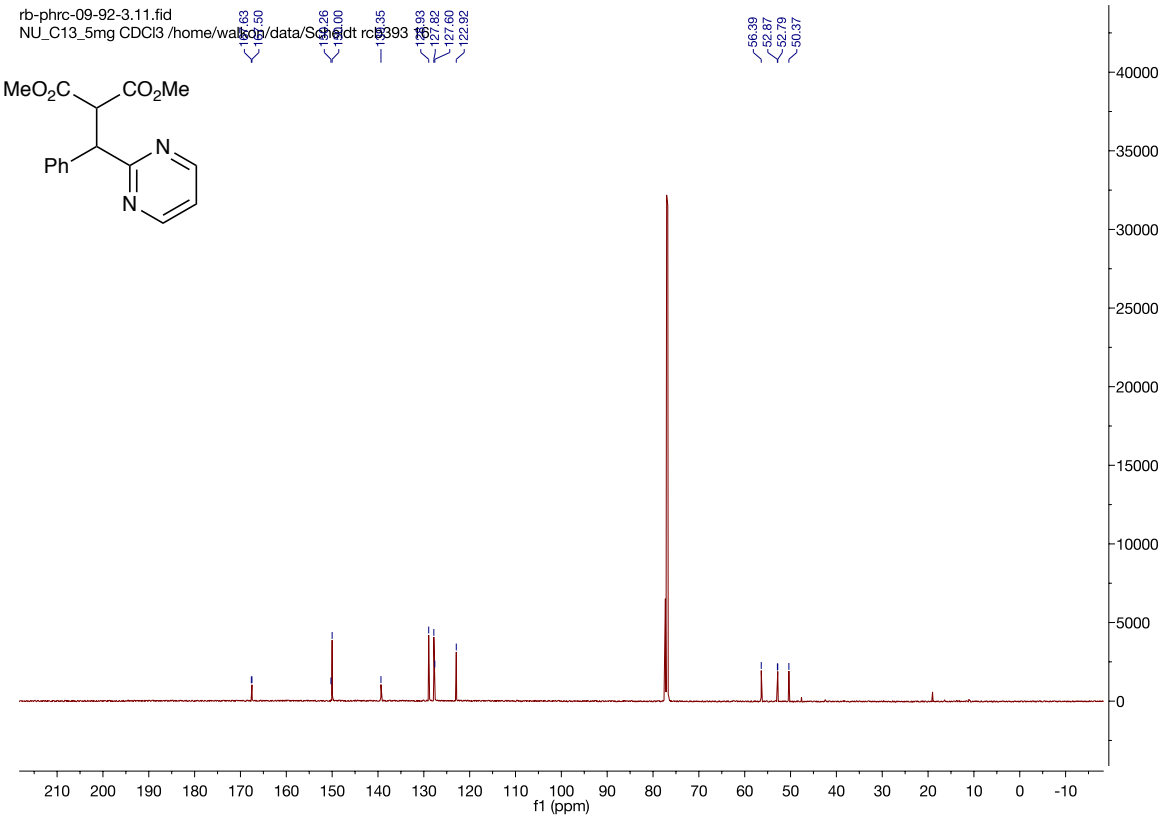
MeO2C
CO2Me
Bn
N
N
f1 (ppm)


rb-phrc-09-92-3.10.fid
PROTON CDCl3 /home/washkon/data/Schleidt/rcb393 15
MeO2C
CO2Me
Ph
N
N
A (m)
8.53
B (m)
7.29
C (d)
4.79
D (d)
4.38
E (s)
3.63
F (s)
3.58
1.91
5.97
0.92
1.00
3.03
3.08
f1 (ppm)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NU_C13_5mg CDCl3 /home/washkon/data/Schleidt rcb393 15
MeO2C
CO2Me
Ph
N
N
f1 (ppm)

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