Regioselective Umpolung Addition of Dicyanobenzene to α,β-Unsaturated Alkenes Enabled by Electrochemical Reduction

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Supporting Information

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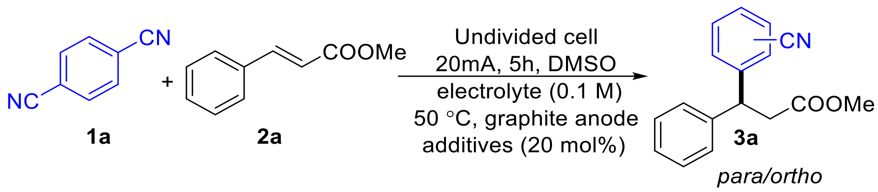
1. General Information

^{1}H NMR and ^{13}C NMR were recorded on a Bruker 400 MHz spectrometer (^{1}H NMR: 400MHz, ^{13}C NMR: 100MHz). The chemical shifts (δ) and coupling constants (*J*) were expressed in ppm and Hz respectively. ^{1}H NMR spectra were referenced to the solvent residual peak (TMS, δ 0 ppm) and $^{13}C\{1H\}$ NMR spectra were referenced to the solvent residual peak ($CDCl_3$, δ 77.0 ppm). High Resolution mass spectra were obtained using AB Sciex TripleTOF® 5600+ mass spectrometer. All solvents were purified and dried according to the standard procedures unless otherwise noted. Commercially substrates were purchased and used directly. α,β-Unsaturated esters[1] and enones[2] were prepared according to the literature procedures.

2. Optimization of reaction conditions

Table S1. Optimization of 'E-pinacol coupling'[a]

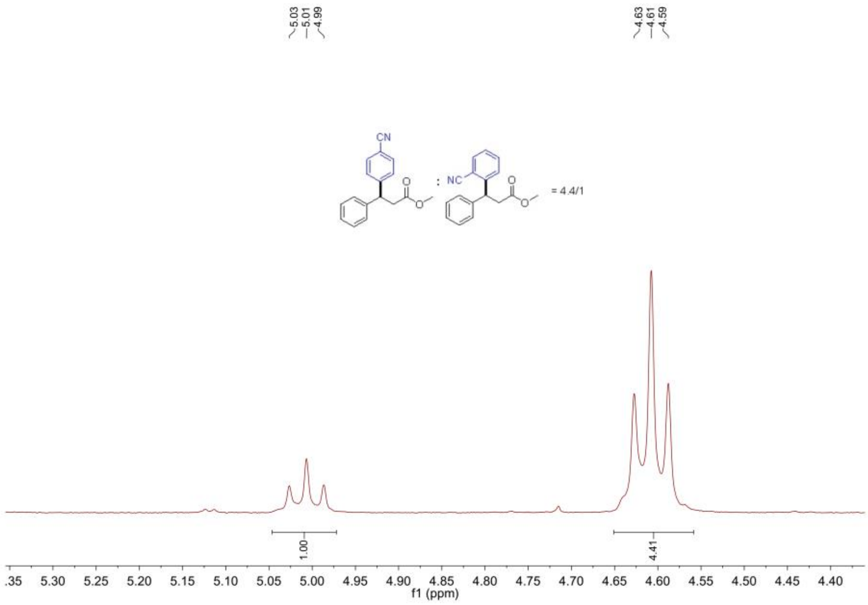


Entry	Solvent	Electrolyte	Cathode	Additives	Yield (%)[b]	*p/o*[c]
1	DMSO	$^{n}Bu_4NOAc$	Ni	none	83	4/1
2	DMSO	$^{n}Bu_4NOAc$	Zn	none	80	5/1
3	DMSO	$^{n}Bu_4NOAc$	Pt	none	81	6/1
4	DMSO	$^{n}Bu_4NClO_4$	Pt	none	48	29/1
5	DMSO	$^{n}Bu_4NPF_6$	Pt	none	46	10/1
6	DMSO	$^{n}Bu_4NOTf$	Pt	none	47	14/1
7	DMSO	$^{n}Bu_4NBr$	Pt	none	trace	n.d.
8	DMSO	$^{n}Bu_4NClO_4$	Pt	NH_4OAc	70	12/1
9	DMSO	**$^{n}Bu_4NClO_4$**	**Pt**	**NaOAc**	**78**	**15/1**
10[d]	DMSO	$^{n}Bu_4NClO_4$	Pt	NaOAc	83	6/1
11[e]	DMSO	$^{n}Bu_4NClO_4$	Pt	NaOAc	71	13/1
12	DMA	$^{n}Bu_4NClO_4$	Pt	NaOAc	73	10/1
13	CH_3CN	$^{n}Bu_4NClO_4$	Pt	NaOAc	trace	n.d.
14	CH_3CN/DCE (3/7)	$^{n}Bu_4NClO_4$	Pt	NaOAc	trace	n.d.

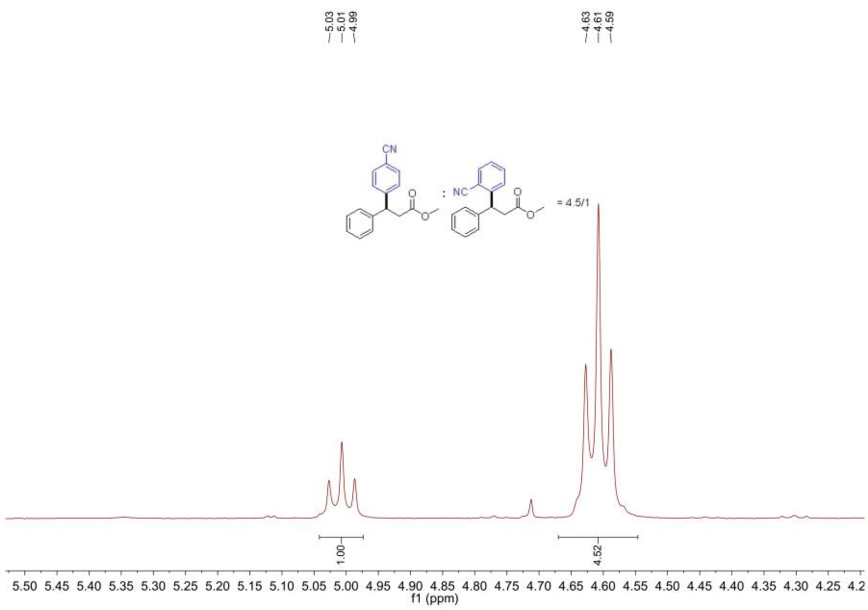
[a] Reaction conditions: **1a** (1 mmol), **2a** (2 mmol), electrolyte (1 mmol), additives (0.2 mmol), graphite rod anode (0.6*10 cm), metal plate cathode (1.5*1.5 cm), 20 mA, 5h (3.7 F/mol), 50 °C. [b] Isolated yield. [c] Ratio of *para*- and *ortho*-isomers was determined by ^{1}H NMR. [d] 0.5 mmol NaOAc was used. [e] 1 mol 2a was used in the reaction.

Initially, various cathodes were screened using $^{n}Bu_4NOAc$ as electrolyte (Entries 1-3). It was found that platinum cathode was the optimal one in terms of reaction selectivity (*para*/*ortho* = 6/1) (Entry 3), although nickel cathode gave the product **3a** with slightly higher yield (Entry 1). Subsequently, electrolytes were examined to access better regioselectivity (Entries 4-7). To our delight, $^{n}Bu_4NClO_4$ led to a significant increase of regioselectivity (29/1) albeit with low yield (Entry 4). However, halide electrolyte failed to afford the desired adduct (Entry 7). To access right balance for reaction efficiency and selectivity, 20 mol% acetate additives were introduced to the reaction, which was reported as a robust additive for the type of the photochemical reaction (Entries 8-10) . Upon treatment with NaOAc, the product **3a** was observed in 78% yield with 15/1 (*p/o*) regioselectivity (Entry 9). Increasing the amount of NaOAc, led to deteriorated regioselectivity (6/1) (Entry 10). Reducing amount of substrate 2a to 1 mmol led to slightly lower yield (71 %) and regioselectivity (13/1) (Entry 11). Varying reaction solvent resulted in lower reaction efficiency and regioselectivity (Entry 12-14). Acetonitrile and the mixed solvent of acetonitrile and DCM failed to give the desired product. Presumably, these two solvents are less liable to oxidation than the substrate **2a**, and the anodic oxidation of substrate **2a** led to side reaction.

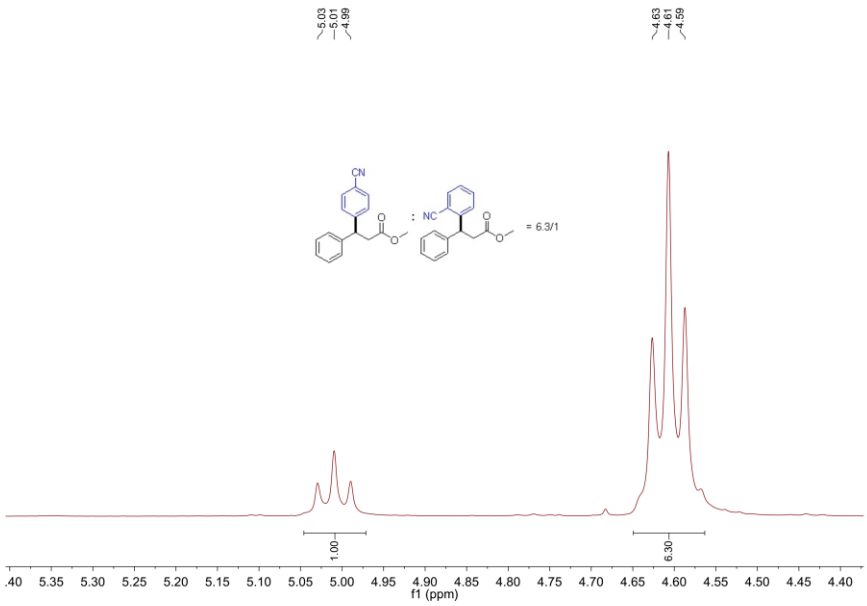
Entry 1 regioselectivity



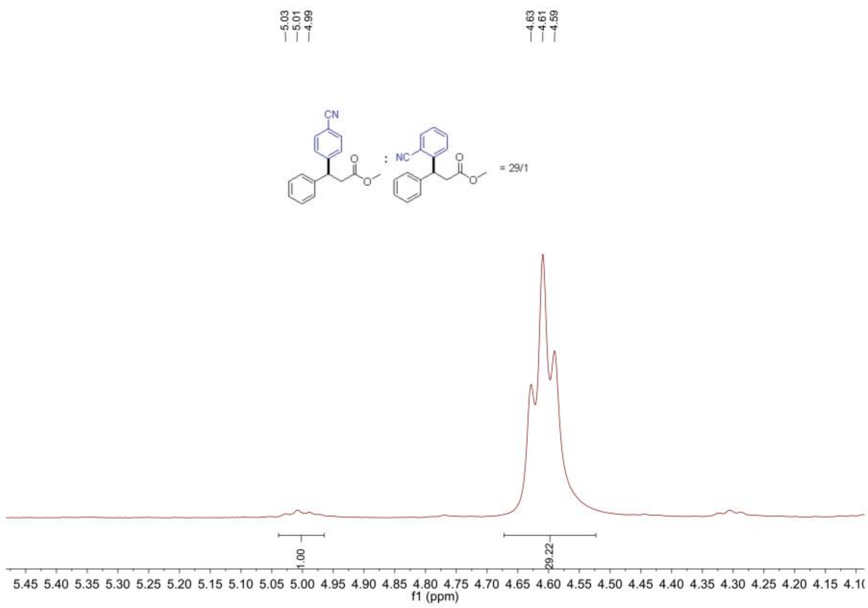
Entry 2 regioselectivity



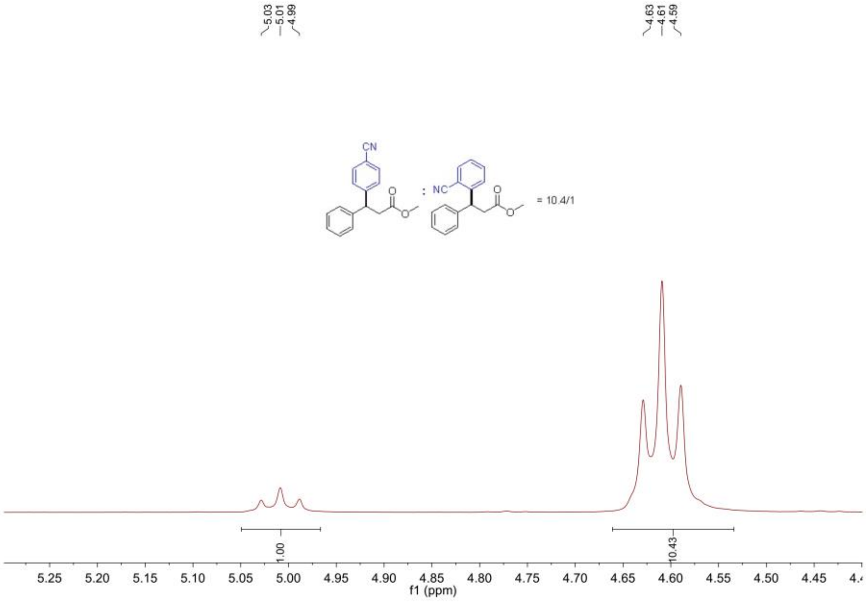
Entry 3 regioselectivity



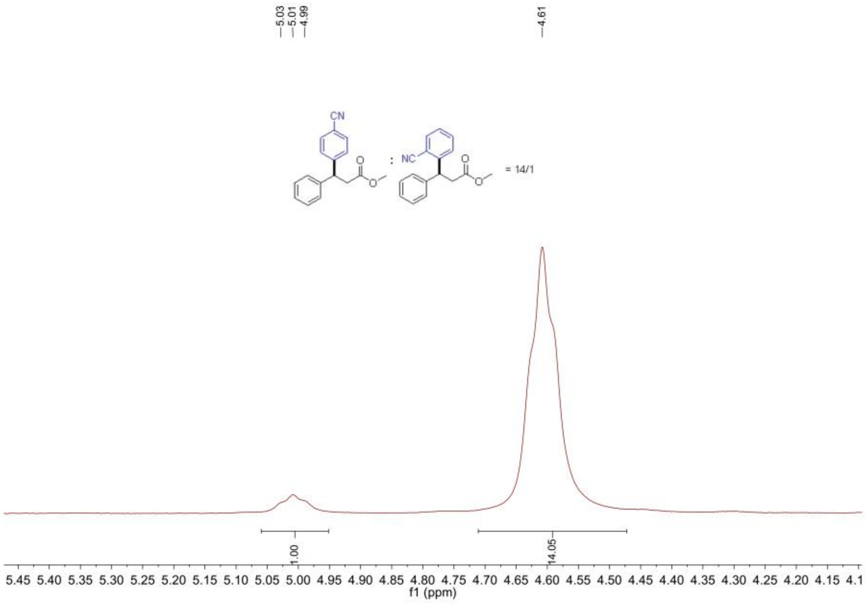
Entry 4 regioselectivity



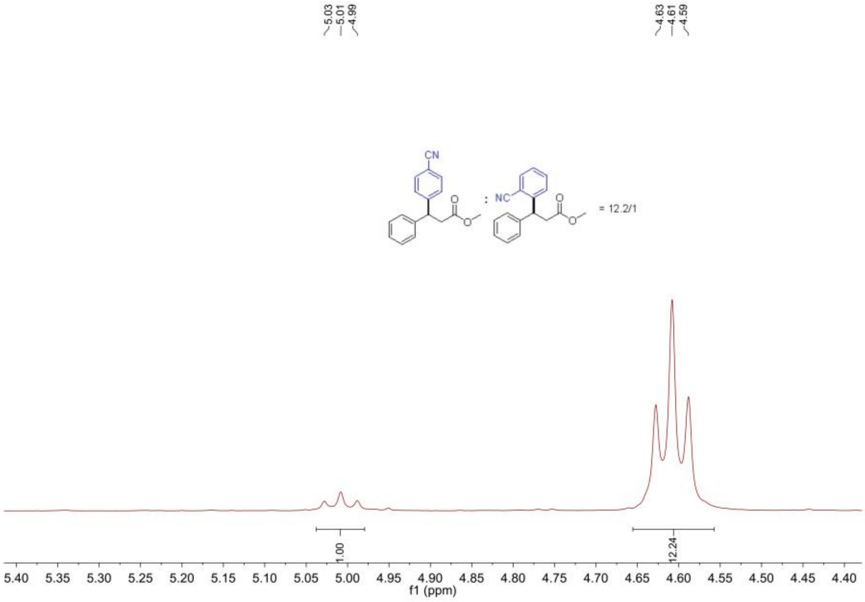
Entry 5 regioselectivity



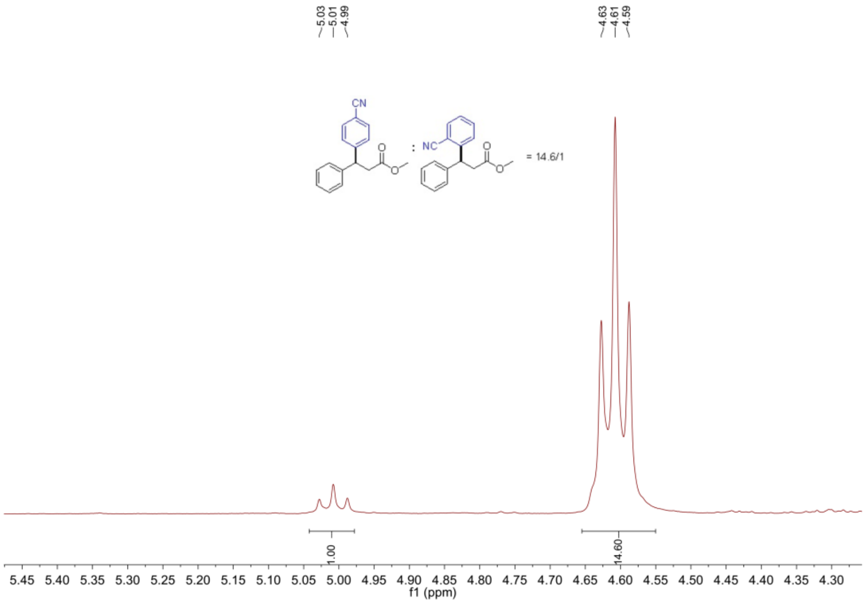
Entry 6 regioselectivity



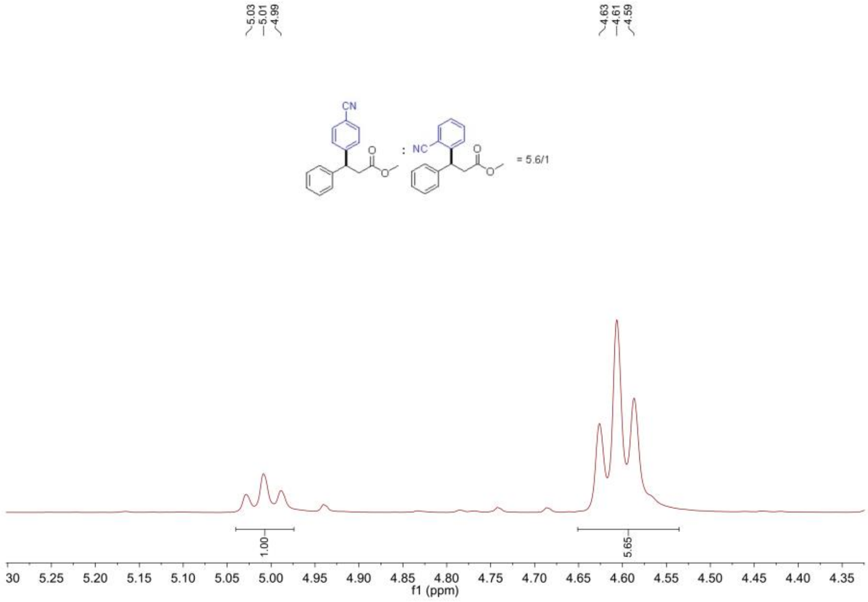
Entry 8 regioselectivity



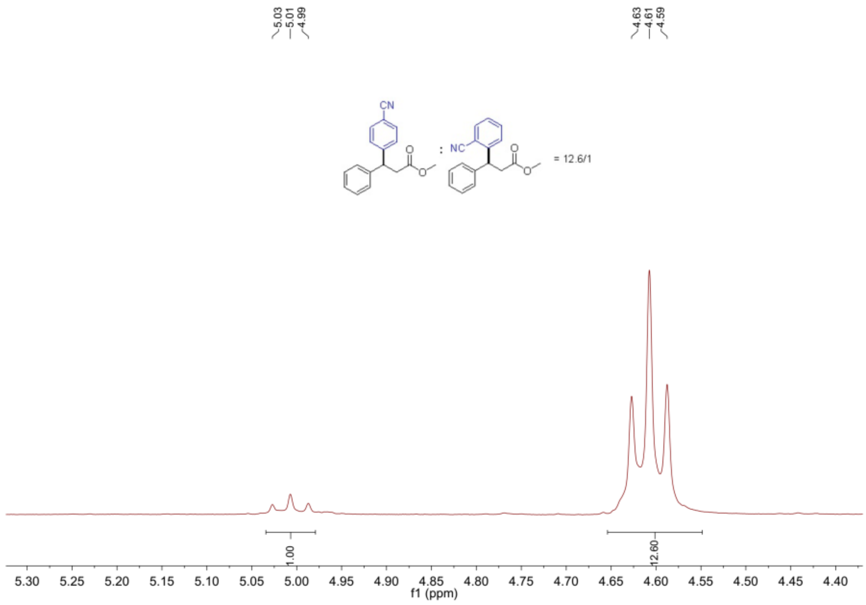
Entry 9 regioselectivity



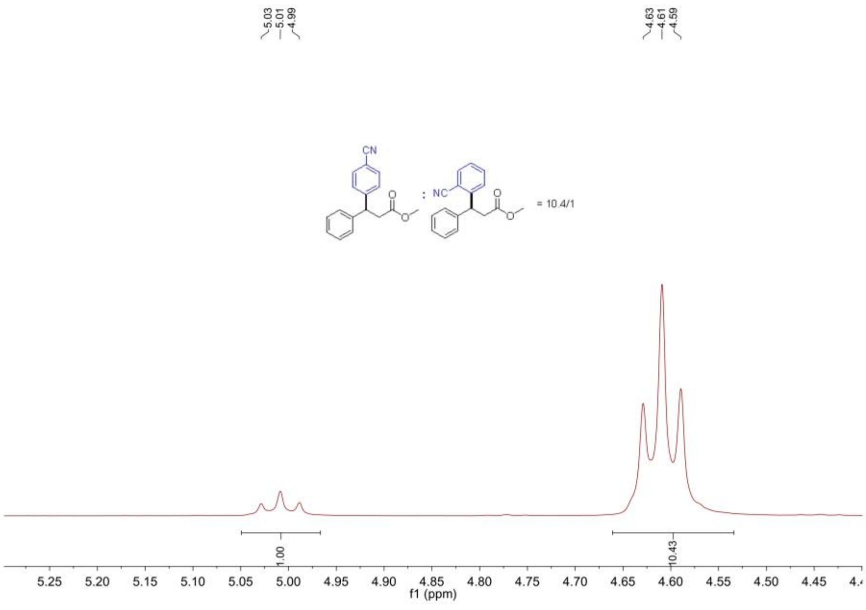
Entry 10 regioselectivity



Entry 11 regioselectivity



Entry 12 regioselectivity



3. General procedure for umpolung addition

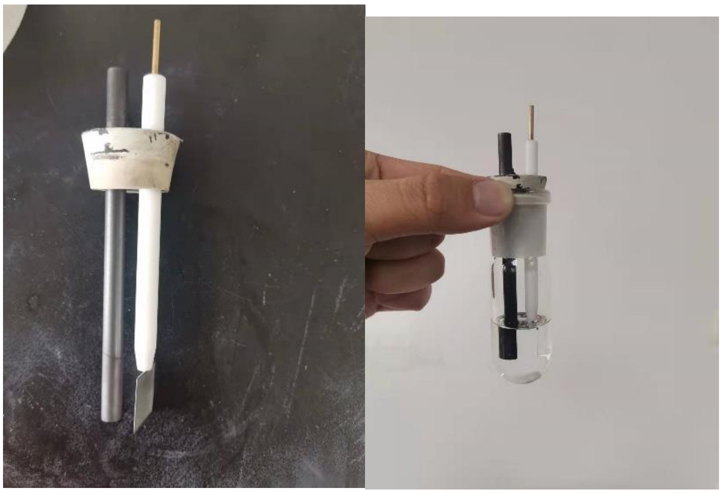
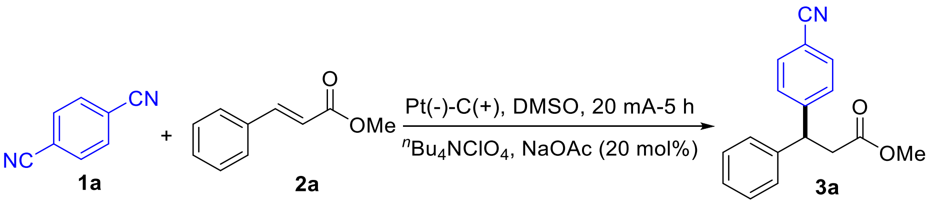


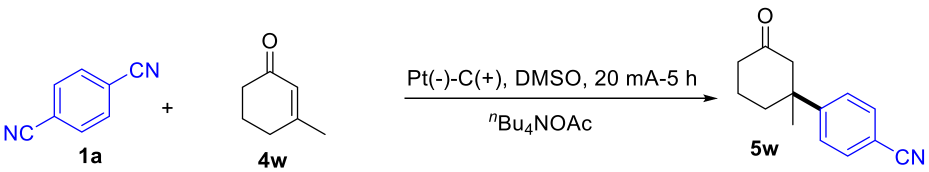
Fig. S1 Electrolysis setup (graphite rod: diameter 0.6 cm, length 10 cm; platinum plate: 1.5 cm *1.5 cm)

Condition I (3a as example)



An undivided cell was equipped with a magnet stirrer, platinum plate (1.8 *1.5 cm^2), graphite rod (0.6*10 cm), as cathode and anode, respectively (the electrolysis setup is shown in Fig. S1). The substrate 1,4-dicyanobenzene **1a** (128 mg, 1 mmol), methyl cinnamate **2a** (324 mg, 2 mmol), NaOAc (16 mg, 0.2 mmol) and $^{n}Bu_4NClO_4$ (342 mg, 1 mmol) were added to the solvent DMSO (10 mL). The resulting mixture was allowed to stir and electrolyze at constant current condition (20 mA, J = 8.9 mA·cm^{-2}) at 50 °C for 5 hours. Then the reaction mixture was poured into water (150 mL) and extracted with ethyl acetate (50 mL*3). The combined organic phase was condensed with a rotary evaporator. The residue was purified by column chromatography (PE/ EA= 10/1-6/1) on silica gel to afford the desired product **3a** (207 mg) in 78 % yield.

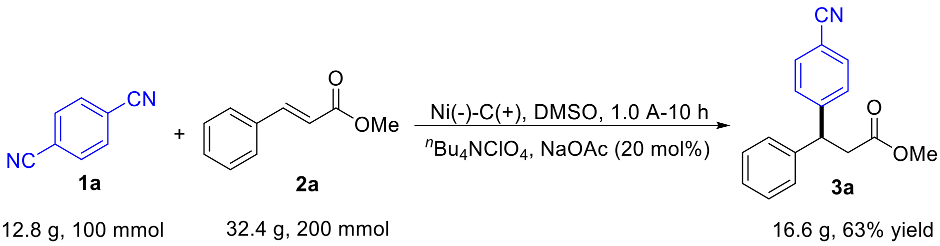
Condition II (5w as example)



An undivided cell was equipped with a magnet stirrer, platinum plate (1.8 *1.5 cm^2), graphite rod (0.6*10 cm), as cathode and anode, respectively (the electrolysis setup is shown in Fig. S1). The substrate 1,4-dicyanobenzene **1a** (128 mg, 1 mmol), 3-methylcyclohex-2-en-1-one **4w** (227 μL, 2 mmol), and $^{n}Bu_4NOAc$ (301 mg, 1 mmol) were added to the solvent DMSO (10 mL). The resulting mixture was allowed to stir and electrolyze at constant current condition (20 mA, J = 8.9 mA·cm^{-2}) at 50 °C for 5 hours. Then the reaction mixture was poured into water (150 mL) and extracted with ethyl acetate (50 mL*3). The combined organic phase was condensed with a rotary evaporator. The residue was purified by column chromatography (PE/ EA= 10/1-6/1) on silica gel to afford the desired product **3a** (173 mg) in 81 % yield.

4. Procedure for gram scale reaction

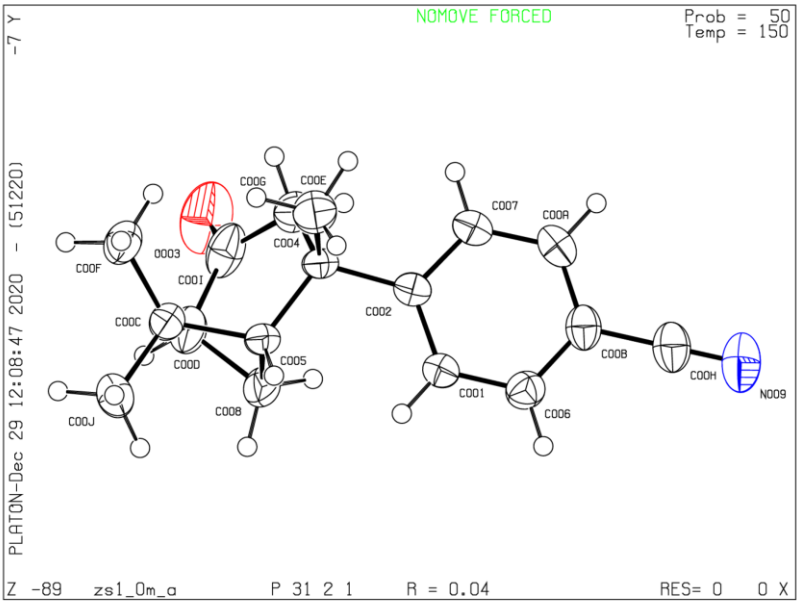
Fig. S2 Gram-scale electrolysis setup (graphite rods (*5): diameter 1.0 cm, length 10 cm, immergence depth 3.0 cm; nickel plate: width 23 cm, immergence depth 5.0 cm)



An undivided cell was equipped with a magnet stirrer, nickel plate (23*5.0 cm^2), 5 graphite rods (1.0*10 cm), as cathode and anode, respectively (the electrolysis setup is shown in **Fig. S2**). The substrate 1,4-dicyanobenzene **1a** (12.8 g, 0.1 mol), methyl cinnamate **2a** (32.4 g, 0.2 mol), NaOAc (656 mg, 8 mmol) and $^{n}Bu_4NClO_4$ (6.8 g, 10 mmol) were added to the solvent DMSO (200 mL). The resulting mixture was allowed to stir and electrolyze at constant current condition (1000 mA, J = 8.7 mA·cm^{-2}) at room temperature for 10 hours. Then the reaction mixture was poured into water (1000 mL) and extracted with ethyl acetate (200 mL*3). The combined organic phase was condensed with a rotary evaporator. The residue was purified by column chromatography (PE/ EA= 10/1-6/1) on silica gel to afford the desired product **3a** (16.6 g) in 63 % yield.

5. X-ray crystallographic data of 5y, 5z

5y



(CCDC number: 2122022)

Table S2. Crystal data and structure refinement for **5y**

Identification code	**5y**
Empirical formula	$C_{17}H_{19}NO$
Formula weight	253.33
Temperature/K	150.0
Crystal system	trigonal
Space group	$P3_121$
a/Å	10.9010(19)
b/Å	10.9010(19)
c/Å	20.449(5)
α/°	90
β/°	90
γ/°	120
Volume/Å^3	2104.4(9)
Z	6
ρ_{calc}g/cm^3	1.199
μ/mm^{-1}	0.370
F(000)	816.0
Radiation	GaKα (λ = 1.34139)
2Θ range for data collection/°	8.148 to 110.19
Index ranges	-13 ≤ h ≤ 13, -13 ≤ k ≤ 13, -24 ≤ l ≤ 24
Reflections collected	44884
Independent reflections	2673 [R_{int} = 0.0554, R_{sigma} = 0.0297]
Data/restraints/parameters	2673/0/175
Goodness-of-fit on F^2	0.997

Final R indexes [I>=2σ (I)]	R_1 = 0.0364, wR_2 = 0.1076
Final R indexes [all data]	R_1 = 0.0373, wR_2 = 0.1087
Largest diff. peak/hole / e Å^{-3}	0.15/-0.19
Flack parameter	0.15(10)

Table S3. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for **5y**. Ueq is defined as 1/3 of of the trace of the orthogonalised UIJ tensor.

Atom	x	y	z	U(eq)
C001	394.2(19)	2784.3(19)	7600.9(8)	36.0(4)
C002	1848.3(18)	3283.6(19)	7572.1(8)	33.6(4)
O003	4945(3)	6808(2)	6159.3(9)	90.9(8)
C004	2983.1(17)	4850.5(18)	7655.0(8)	33.9(4)
C005	2340.9(17)	5820.0(18)	7643.8(8)	33.9(4)
C006	-590(2)	1350(2)	7555.4(9)	40.6(4)
C007	2273(2)	2273(2)	7507.2(8)	42.2(4)
C008	1793(2)	5829(2)	6947.4(10)	46.7(5)
N009	-1946(3)	-2307(2)	7386.5(10)	66.7(6)
C00A	1306(2)	840(2)	7469.8(9)	45.6(5)
C00B	-132(2)	374.4(19)	7492.7(8)	41.1(4)
C00C	3421.4(18)	7442.5(19)	7545.4(8)	38.7(4)
C00D	3289(2)	7095(2)	6802.3(9)	47.3(5)
C00E	3641(3)	4945(3)	8338.1(11)	56.0(5)
C00F	4902(2)	8202(2)	7837.2(10)	49.7(5)
C00G	4095(2)	5315(2)	7093.3(11)	51.1(5)
C00H	-1148(2)	-1124(2)	7434.8(9)	50.1(5)
C00I	4191(2)	6468(2)	6638.8(9)	54.8(6)
C00J	2715(3)	8309(2)	7727.7(14)	58.1(6)

Table S4. Anisotropic Displacement Parameters (Å^2×10^3) for **5y**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	**U_{11}**	**U_{22}**	**U_{33}**	**U_{23}**	**U_{13}**	**U_{12}**
C001	35.0(9)	36.4(9)	40.1(8)	0.1(7)	0.7(7)	20.5(7)
C002	34.3(9)	38.1(9)	32.3(8)	0.7(6)	-0.5(6)	21.0(7)
O003	98.8(15)	74.7(13)	69.3(11)	2.1(9)	47.8(11)	20.9(11)
C004	26.5(8)	36.6(9)	40.8(8)	-2.6(7)	-2.3(6)	17.6(7)
C005	27.4(8)	34.7(8)	41.1(8)	-2.2(6)	-0.2(6)	16.5(7)
C006	37.1(9)	41.9(10)	41.0(9)	2.6(8)	1.8(7)	18.3(8)
C007	40.5(10)	43.8(10)	50.1(10)	-0.8(8)	-0.1(8)	26.9(9)
C008	41.2(10)	36.4(9)	55.7(11)	1.8(8)	-16.0(8)	14.2(8)
N009	81.7(15)	39.8(10)	62.4(11)	3.3(8)	-2.4(10)	18.3(10)
C00A	56.8(12)	41.2(10)	48.7(10)	0.0(8)	0.0(9)	31.9(9)
C00B	51.1(11)	33.6(9)	34.2(8)	2.0(6)	0.7(7)	17.8(8)
C00C	33.5(9)	34.5(9)	45.0(9)	-2.5(7)	0.2(7)	14.6(7)
C00D	51.6(12)	37.9(9)	41.1(9)	3.1(7)	-5.3(8)	14.0(9)

C00E	54.3(12)	51.0(11)	61.2(11)	-4.3(9)	-24.9(10)	25.2(10)
C00F	40.6(10)	39.6(10)	58.4(11)	-9.7(9)	-5.0(9)	12.3(8)
C00G	37.5(9)	43.5(10)	70.1(13)	-3.3(9)	17.5(9)	18.5(8)
C00H	62.9(13)	38.3(10)	43.1(9)	5.0(8)	1.5(9)	20.8(10)
C00I	53.4(12)	42.5(11)	45.9(10)	-7.5(8)	14.4(9)	7.0(9)
C00J	52.3(12)	37.6(10)	87.1(16)	-0.2(10)	7.0(12)	24.4(9)

Table S5. Bond Lengths for **5y**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C001	C002	1.396(2)	C007	C00A	1.382(3)
C001	C006	1.388(3)	C008	C00D	1.550(3)
C002	C004	1.537(2)	N009	C00H	1.144(3)
C002	C007	1.398(3)	C00A	C00B	1.387(3)
O003	C00I	1.212(2)	C00B	C00H	1.449(3)
C004	C005	1.532(2)	C00C	C00D	1.555(3)
C004	C00E	1.550(2)	C00C	C00F	1.520(3)
C004	C00G	1.559(2)	C00C	C00J	1.533(3)
C005	C008	1.546(2)	C00D	C00I	1.489(3)
C005	C00C	1.572(2)	C00G	C00I	1.524(3)
C006	C00B	1.388(3)			

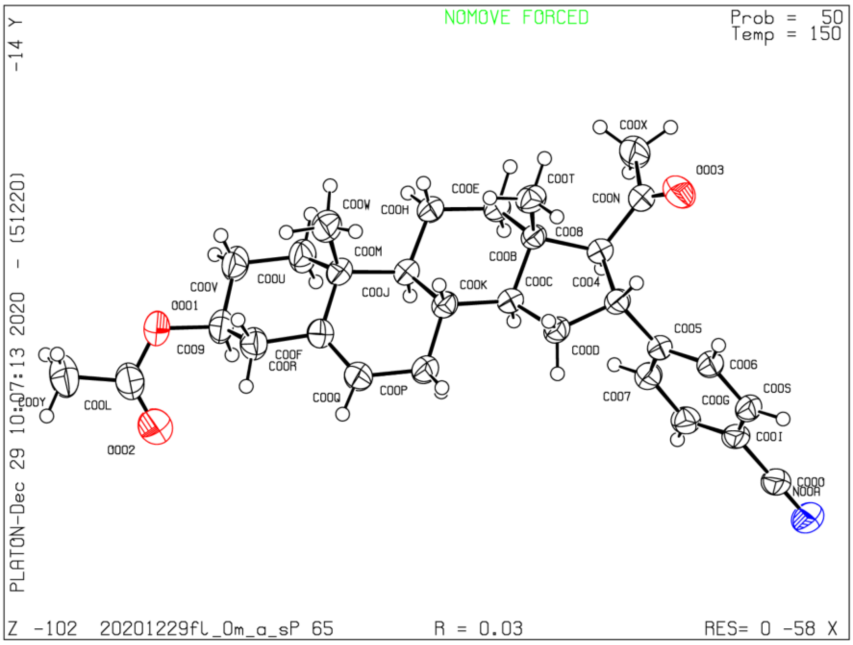
Table S6. Bond Angles for **5y**.

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom
C006	C001	C002	121.58(16)	C006	C00B	C00H
C001	C002	C004	123.67(15)	C00A	C00B	C006
C001	C002	C007	117.10(16)	C00A	C00B	C00H
C007	C002	C004	119.08(15)	C00D	C00C	C005
C002	C004	C00E	105.18(15)	C00F	C00C	C005
C002	C004	C00G	110.04(14)	C00F	C00C	C00D
C005	C004	C002	111.92(13)	C00F	C00C	C00J
C005	C004	C00E	108.87(15)	C00J	C00C	C005
C005	C004	C00G	108.30(14)	C00J	C00C	C00D
C00E	C004	C00G	112.55(17)	C008	C00D	C00C
C004	C005	C008	109.26(14)	C00I	C00D	C008
C004	C005	C00C	115.73(13)	C00I	C00D	C00C
C008	C005	C00C	87.10(13)	C00I	C00G	C004
C001	C006	C00B	119.85(18)	N009	C00H	C00B
C00A	C007	C002	121.98(18)	O003	C00I	C00D
C005	C008	C00D	86.78(14)	O003	C00I	C00G
C007	C00A	C00B	119.73(17)	C00D	C00I	C00G

Table S7. Hydrogen Atom Coordinates (Å×10[4]) and Isotropic Displacement Parameters (Å2×10[3]) for **5y.**

Atom	***x***	***y***	***z***	**U(eq)**
H001	70.68	3441.94	7652.93	43
H005	1627.94	5613.82	7996.44	41
H006	-1574.33	1036.9	7567.26	49
H007	3256.05	2581.07	7488.21	51
H00A	1027.91	6067.95	6932.12	56
H00B	1542.95	4968.07	6688.61	56
H00C	1625.98	177.55	7428.58	55
H00D	3341.35	7838.43	6498.48	57
H00E	4324.82	5936.62	8438.32	84
H00F	4123.74	4390.44	8338.6	84
H00G	2890.58	4567.67	8669.17	84
H00H	5421.76	9173.31	7668.58	74
H00I	5403.23	7698.83	7716.52	74
H00J	4836.06	8224.92	8314.51	74
H00K	5039.07	5652.6	7291.7	61
H00L	3870.93	4470.82	6826.36	61
H00M	3297.18	9281.55	7568.46	87
H00N	2623.7	8317.84	8204.13	87
H00O	1774.04	7880.31	7526.97	87

5z



(CCDC number: 2122023)

Table S8. Crystal data and structure refinement for **5z**.

Identification code	**5z**
Empirical formula	$C_{30}H_{37}NO_3$
Formula weight	459.60
Temperature/K	150.0
Crystal system	hexagonal
Space group	$P6_5$
a/Å	22.005(2)
b/Å	22.005(2)
c/Å	10.6121(15)
α/°	90
β/°	90
γ/°	120
Volume/Å^3	4450.2(11)
Z	6
ρ_{calc}g/cm^3	1.029
μ/mm^{-1}	0.327
F(000)	1488.0
Radiation	GaKα (λ = 1.34139)
2Θ range for data collection/°	4.034 to 110.098
Index ranges	-26 ≤ h ≤ 26, -26 ≤ k ≤ 26, -12 ≤ l ≤ 12
Reflections collected	120880
Independent reflections	5647 [R_{int} = 0.0514, R_{sigma} = 0.0211]
Data/restraints/parameters	5647/7/311
Goodness-of-fit on F^2	1.062
Final R indexes [I>=2σ (I)]	R_1 = 0.0295, wR_2 = 0.0895
Final R indexes [all data]	R_1 = 0.0301, wR_2 = 0.0902
Largest diff. peak/hole / e Å^{-3}	0.14/-0.13
Flack parameter	0.13(9)

Table S9. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for **5z** is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	***x***	***y***	***z***	**U(eq)**
O001	11808.6(7)	8421.0(7)	780.3(13)	59.4(4)
O002	10768.9(9)	8137.1(10)	-80.0(19)	78.9(5)
O003	10519.1(8)	5554.7(10)	11015.1(14)	68.7(4)
N00A	6262.8(8)	3340.1(10)	9983(2)	69.6(5)
C00B	10781.2(7)	6234.3(7)	7997.8(14)	34.3(3)
C00C	10271.8(7)	6403.8(7)	7290.4(14)	34.0(3)
C00D	9816.2(8)	6447.6(8)	8330.0(16)	38.6(3)

C00E	11154.1(8)	6030.9(8)	7013.4(15)	39.1(3)
C00F	10975.8(8)	7722.3(8)	3964.0(16)	41.1(3)
C00G	7925.3(8)	4320.5(9)	8611.4(17)	44.3(3)
C00H	11534.0(8)	6620.2(9)	6047.3(16)	41.3(3)
C00I	7568.5(8)	4286.3(8)	9715.5(18)	42.8(4)
C00J	11053.7(7)	6845.8(7)	5396.9(14)	34.9(3)
C00K	10622.9(7)	7006.2(8)	6348.9(15)	36.7(3)
C00L	11397.7(13)	8482.6(12)	-79(2)	61.7(5)
C00M	11455.5(7)	7456.6(8)	4448.3(15)	39.2(3)
C00N	10570.7(8)	5428.7(10)	9924.7(18)	48.8(4)
C00O	6838.0(9)	3753.9(9)	9860(2)	51.3(4)
C00P	10072.7(9)	7102.2(10)	5641.7(18)	49.2(4)
C00Q	10362.8(9)	7547.6(10)	4480.3(19)	50.3(4)
C00R	11239.5(10)	8207.0(9)	2831.7(18)	49.5(4)
C00S	7910.5(8)	4750.0(8)	10695.0(17)	42.8(3)
C00T	11312.5(8)	6845.7(9)	8816.5(17)	45.0(4)
C00U	11684.4(11)	7177.7(10)	3309.8(18)	52.2(4)
C00V	11984.7(11)	7695.1(11)	2212(2)	58.1(5)
C00W	12103.4(9)	8071.5(10)	5065(2)	56.8(5)
C00X	10965.5(13)	5059.5(14)	9570(3)	71.2(7)
C00Y	11827.1(18)	9030.5(19)	-1039(3)	98.4(10)
C004	9738.1(7)	5885.7(8)	9316.7(14)	37.2(3)
C005	8980.2(7)	5304.7(8)	9462.7(14)	35.9(3)
C006	8614.5(8)	5259.6(8)	10559.1(15)	39.1(3)
C007	8628.9(8)	4826.5(9)	8494.2(15)	42.1(3)
C008	10244.9(7)	5629.7(8)	8865.1(15)	37.4(3)
C009	11460.4(9)	7899.8(9)	1772.8(17)	49.8(4)

Table S10. Anisotropic Displacement Parameters (Å^2×10^3) for **5z**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	**U_{11}**	**U_{22}**	**U_{33}**	**U_{23}**	**U_{13}**	**U_{12}**
O001	55.1(7)	64.8(8)	48.9(7)	18.6(6)	11.5(6)	22.9(6)
O002	68.1(10)	84.4(11)	76.4(11)	19.8(9)	-2.5(8)	32.4(9)
O003	71.1(9)	100.2(12)	45.8(8)	12.8(7)	-1.0(6)	51.2(9)
N00A	39.8(8)	67.7(10)	86.1(13)	24.6(10)	2.4(8)	15.6(8)
C00B	29.4(6)	38.6(7)	34.0(7)	0.1(6)	2.0(5)	16.3(6)
C00C	30.0(6)	35.0(6)	36.6(7)	-1.5(5)	0.9(5)	15.9(5)
C00D	34.0(7)	40.4(7)	43.4(8)	4.7(6)	7.2(6)	20.1(6)
C00E	38.5(7)	46.2(8)	39.0(8)	1.8(6)	5.3(6)	26.0(6)
C00F	42.4(8)	38.4(7)	40.8(8)	2.6(6)	2.3(6)	19.0(6)

C00G	38.9(7)	41.7(7)	49.7(9)	1.9(6)	-3.7(6)	18.1(6)
C00H	36.2(7)	49.6(8)	42.5(8)	6.0(7)	7.2(6)	24.7(6)
C00I	33.0(7)	41.1(7)	57.6(10)	12.6(7)	2.6(7)	21.1(6)
C00J	32.0(6)	34.5(6)	36.6(7)	-0.4(6)	3.0(5)	15.4(5)
C00K	34.1(6)	36.4(7)	40.2(7)	1.2(6)	4.7(6)	18.1(5)
C00L	72.2(13)	65.0(11)	51.0(11)	14.5(9)	10.0(9)	36.6(10)
C00M	33.1(7)	38.5(7)	41.3(8)	1.7(6)	4.1(6)	14.3(6)
C00N	37.4(8)	59.1(10)	49.7(10)	16.3(8)	6.2(7)	24.1(7)
C00O	38.9(9)	50.6(9)	64.6(11)	15.5(8)	0.5(8)	22.7(8)
C00P	41.4(8)	58.6(9)	54.9(10)	17.1(8)	13.4(7)	30.4(7)
C00Q	48.2(9)	55.4(9)	55.4(10)	15.4(8)	7.3(8)	32.0(8)
C00R	52.3(9)	46.3(8)	48.7(10)	9.5(7)	7.5(7)	23.8(7)
C00S	37.6(7)	48.4(8)	48.2(9)	10.6(7)	10.4(6)	25.8(7)
C00T	34.9(7)	47.3(8)	44.4(9)	-6.1(7)	-3.6(6)	14.4(6)
C00U	59.3(10)	60.7(10)	45.9(9)	11.1(8)	17.0(8)	37.1(9)
C00V	60.0(10)	70.0(12)	49.2(10)	15.6(9)	20.4(8)	36.3(9)
C00W	42.1(9)	48.9(9)	57.9(11)	7.6(8)	-4.0(8)	6.6(7)
C00X	70.2(12)	92.3(16)	76.4(14)	37.6(13)	21.8(11)	59.7(12)
C00Y	100(2)	113(2)	89(2)	58.2(18)	28.7(16)	57.9(18)
C004	31.6(6)	43.0(7)	34.9(7)	0.5(6)	1.5(5)	17.2(6)
C005	32.7(7)	40.6(7)	36.5(7)	5.2(6)	3.1(5)	19.9(6)
C006	37.7(7)	43.2(8)	39.7(8)	2.5(6)	3.9(6)	22.7(6)
C007	37.3(7)	48.1(8)	38.9(8)	1.4(6)	1.6(6)	20.0(6)
C008	31.6(6)	40.8(7)	39.4(8)	3.3(6)	1.6(6)	17.8(6)
C009	49.4(9)	48.7(9)	41.7(9)	10.7(7)	10.7(7)	17.4(7)

Table S11. Bond Lengths for **5z**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O001	C00L	1.338(3)	C00I	C00O	1.448(2)
O001	C009	1.4605(19)	C00I	C00S	1.386(3)
O002	C00L	1.200(3)	C00J	C00K	1.5423(19)
O003	C00N	1.208(3)	C00J	C00M	1.553(2)
N00A	C00O	1.138(2)	C00K	C00P	1.526(2)
C00B	C00C	1.5419(19)	C00L	C00Y	1.498(3)
C00B	C00E	1.5270(19)	C00M	C00U	1.549(2)
C00B	C00T	1.536(2)	C00M	C00W	1.537(2)
C00B	C008	1.562(2)	C00N	C00X	1.504(3)
C00C	C00D	1.526(2)	C00N	C008	1.513(2)
C00C	C00K	1.526(2)	C00P	C00Q	1.504(2)
C00D	C004	1.563(2)	C00R	C009	1.512(3)

C00E	C00H	1.532(2)	C00S	C006	1.393(2)
C00F	C00M	1.529(2)	C00U	C00V	1.529(3)
C00F	C00Q	1.323(2)	C00V	C009	1.507(3)
C00F	C00R	1.516(2)	C004	C005	1.5192(19)
C00G	C00I	1.391(3)	C004	C008	1.555(2)
C00G	C007	1.389(2)	C005	C006	1.390(2)
C00H	C00J	1.537(2)	C005	C007	1.396(2)

Table S12. Bond Angles for **5z.**

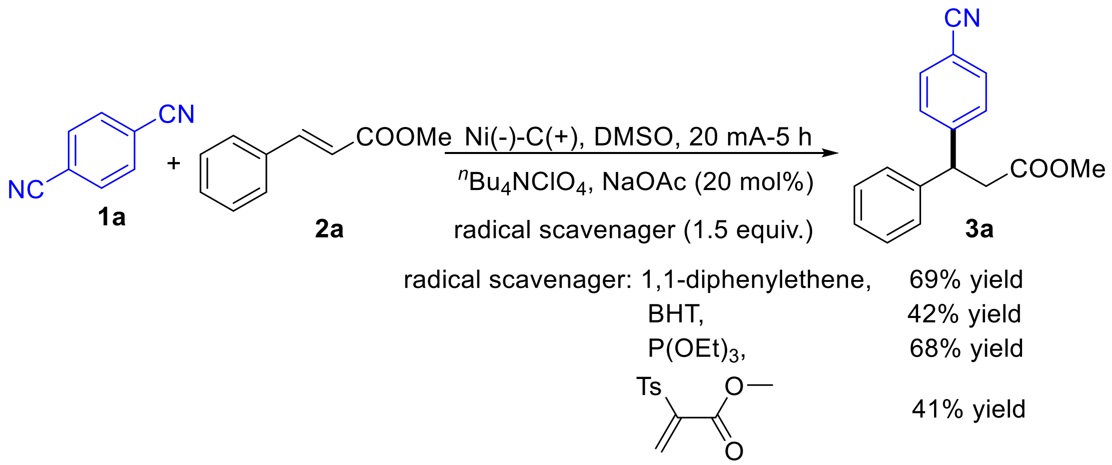
Atom	**Atom**	**Atom**	**Angle/˚**	**Atom**	**Atom**	**Atom**	**Angle/˚**
C00L	O001	C009	117.09(15)	C00F	C00M	C00U	108.23(14)
C00C	C00B	C008	99.31(10)	C00F	C00M	C00W	108.69(14)
C00E	C00B	C00C	107.46(12)	C00U	C00M	C00J	108.64(12)
C00E	C00B	C00T	111.01(12)	C00W	C00M	C00J	111.22(14)
C00E	C00B	C008	116.18(12)	C00W	C00M	C00U	109.79(15)
C00T	C00B	C00C	112.99(12)	O003	C00N	C00X	120.64(18)
C00T	C00B	C008	109.44(13)	O003	C00N	C008	122.13(16)
C00D	C00C	C00B	104.09(12)	C00X	C00N	C008	117.23(17)
C00K	C00C	C00B	114.54(11)	N00A	C00O	C00I	179.3(3)
C00K	C00C	C00D	118.81(12)	C00Q	C00P	C00K	112.69(13)
C00C	C00D	C004	104.49(11)	C00F	C00Q	C00P	124.60(15)
C00B	C00E	C00H	110.82(12)	C009	C00R	C00F	111.71(14)
C00Q	C00F	C00M	123.26(15)	C00I	C00S	C006	119.41(15)
C00Q	C00F	C00R	120.58(15)	C00V	C00U	C00M	113.84(15)
C00R	C00F	C00M	116.16(14)	C009	C00V	C00U	110.36(15)
C007	C00G	C00I	119.44(16)	C005	C004	C00D	111.98(12)
C00E	C00H	C00J	113.66(12)	C005	C004	C008	114.26(12)
C00G	C00I	C00O	120.09(18)	C008	C004	C00D	105.37(12)
C00S	C00I	C00G	120.52(14)	C006	C005	C004	119.89(14)
C00S	C00I	C00O	119.38(16)	C006	C005	C007	118.69(14)
C00H	C00J	C00K	112.35(12)	C007	C005	C004	121.38(13)
C00H	C00J	C00M	112.62(11)	C005	C006	C00S	121.01(15)
C00K	C00J	C00M	112.05(12)	C00G	C007	C005	120.92(15)
C00C	C00K	C00J	109.41(11)	C00N	C008	C00B	114.84(12)
C00C	C00K	C00P	110.49(12)	C00N	C008	C004	114.02(13)
C00P	C00K	C00J	109.30(14)	C004	C008	C00B	104.26(11)
O001	C00L	C00Y	111.0(2)	O001	C009	C00R	110.16(15)
O002	C00L	O001	124.02(19)	O001	C009	C00V	106.16(14)
O002	C00L	C00Y	125.0(2)	C00V	C009	C00R	111.66(16)
C00F	C00M	C00J	110.23(12)				

Table S13. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for **5z**

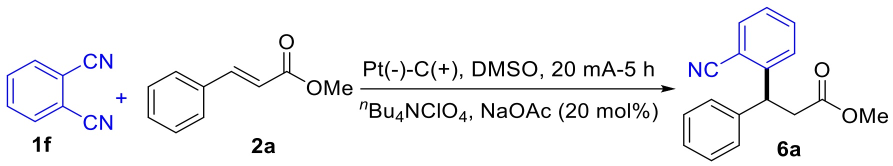
Atom	***x***	***y***	***z***	**U(eq)**
H00C	9956.95	5976.22	6785.91	41
H00A	9352.33	6338.47	7995.8	46
H00B	10046.23	6921.68	8711.11	46
H00D	10806.57	5597.56	6576.29	47
H00E	11497.69	5933.87	7436.21	47
H00G	7689.56	4000.31	7943.4	53
H00F	11746.73	6461.98	5396.7	50
H00H	11919.4	7032.51	6476.21	50
H00J	10707.69	6433.58	4891.08	42
H00K	10943.65	7448.73	6811.3	44
H00I	9680.44	6635.75	5396.79	59
H00L	9882.76	7323.07	6211.58	59
H00Q	10086.25	7715.21	4090.01	60
H00M	10863.86	8293.32	2528.22	59
H00N	11643.99	8663.29	3087.17	59
H00S	7667.13	4720.67	11452.39	51
H00O	11578.09	7262.59	8289.02	67
H00P	11635.89	6717.73	9209.82	67
H00R	11062.4	6946.84	9473.14	67
H00T	12042.64	7061.56	3595.43	63
H00U	11274.06	6738.73	3005.79	63
H00V	12421.25	8119.3	2483.06	70
H00W	12102.05	7477.19	1507.2	70
H00X	12291.72	8481.56	4508.8	85
H00Y	12461.92	7938.8	5205.77	85
H00Z	11969.56	8186.04	5873.25	85
H010	10701.74	4704.54	8925.74	107
H011	11024.42	4831.87	10316.2	107
H012	11427.44	5401.45	9235.54	107
H00$	11519.13	9132.2	-1554.43	148
H00:	12069.45	8858.18	-1580.29	148
H00	12173.67	9459.52	-609.68	148
H004	9907.3	6123.05	10150.6	45
H006	8848.09	5581.28	11226.19	47
H007	8874.47	4847.54	7744.34	50
H008	9969.81	5205.22	8326.65	45
H009	11038.46	7479.41	1418.79	60

6. Control experiments

Radical suppression experiment



An undivided cell was equipped with a magnet stirrer, platinum plate (1.8 *1.5 cm^2), graphite rod (0.6*10 cm), as cathode and anode, respectively (the electrolysis setup is shown in Fig. S1). The substrate 1,4-dicyanobenzene **1a** (128 mg, 1 mmol), methyl cinnamate **2a** (324 mg, 2 mmol), NaOAc (16 mg, 0.2 mmol), radical scavenger (1.5 mmol) and ^{n}Bu$_4$NClO$_4$ (342 mg, 1 mmol) were added to the solvent DMSO (10 mL). The resulting mixture was allowed to stir and electrolyze at constant current condition (20 mA, J = 8.9 mA·cm^{-2}) at 50 °C for 5 hours. Then the reaction mixture was poured into water (150 mL) and extracted with ethyl acetate (50 mL*3). The combined organic phase was condensed with a rotary evaporator. The residue was purified by column chromatography (PE/ EA= 10/1-6/1) on silica gel to afford the desired product **3a**.



An undivided cell was equipped with a magnet stirrer, platinum plate (1.8 *1.5 cm^2), graphite rod (0.6*10 cm), as cathode and anode, respectively (the electrolysis setup is shown in Fig. S1). The substrate 1,2-dicyanobenzene **1f** (128 mg, 1 mmol), methyl cinnamate **2a** (324 mg, 2 mmol), NaOAc (16 mg, 0.2 mmol) and ^{n}Bu$_4$NClO$_4$ (342 mg, 1 mmol) were added to the solvent DMSO (10 mL). The resulting mixture was allowed to stir and electrolyze at constant current condition (20 mA, J = 8.9 mA·cm^{-2}) at 50 °C for 5 hours. Then the reaction mixture was poured into water (150 mL) and extracted with ethyl acetate (50 mL*3). The combined organic phase was condensed with a rotary evaporator. The residue was purified by column chromatography (PE/ EA= 10/1-6/1) on silica gel to afford the desired product **6a** (29 mg) in 11 % yield.

7. Cyclic voltammetric experiments

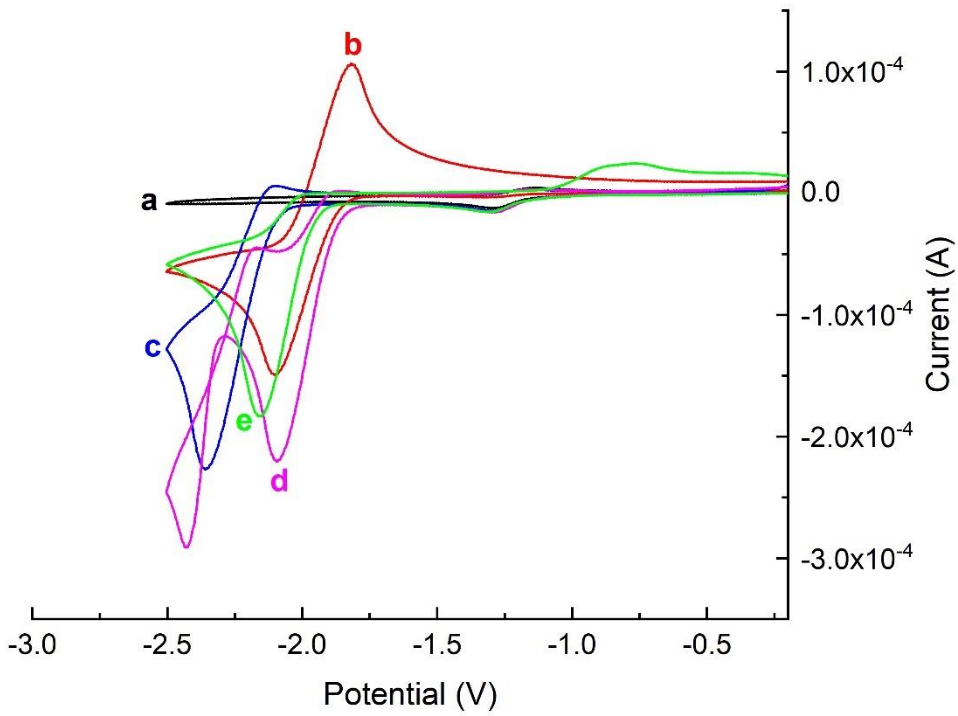


Fig S3. Cyclic voltammograms of substrates in 0.1 M $^{n}Bu_4NClO_4$ (DMSO), using a glassy carbon working electrode and Pt wire and $Ag/AgNO_3$ (0.1 M in CH_3CN) as counter and reference electrodes at a 100 mV·s^{-1} scan rate: a. blank; b. 1,4-dicyanobenzene; c. methyl cinnamate; d. methyl (*E*)-3-(4-(trifluoromethyl)phenyl)acrylate; e. (*E*)-4-phenylbut-3-en-2-one.

As shown in the Figure 2c, substrate 1,4-DCB (**1a**)， with reductive peak at -2.10 V, is more susceptible to cathodic reaction when compared to methyl cinnamate (**2a**) (-2.36 V) and enone (**4a**) (-2.16 V). This result indicates that the electroreductive addition is initiated by the reduction of 1,4-DCB. Further investigation of failed substrate **2x** showed that its reductive potential (-2.09) is slightly less negative than **1a**. This confirmed that more reducible cinnamate was unfavored for the reductive addition.

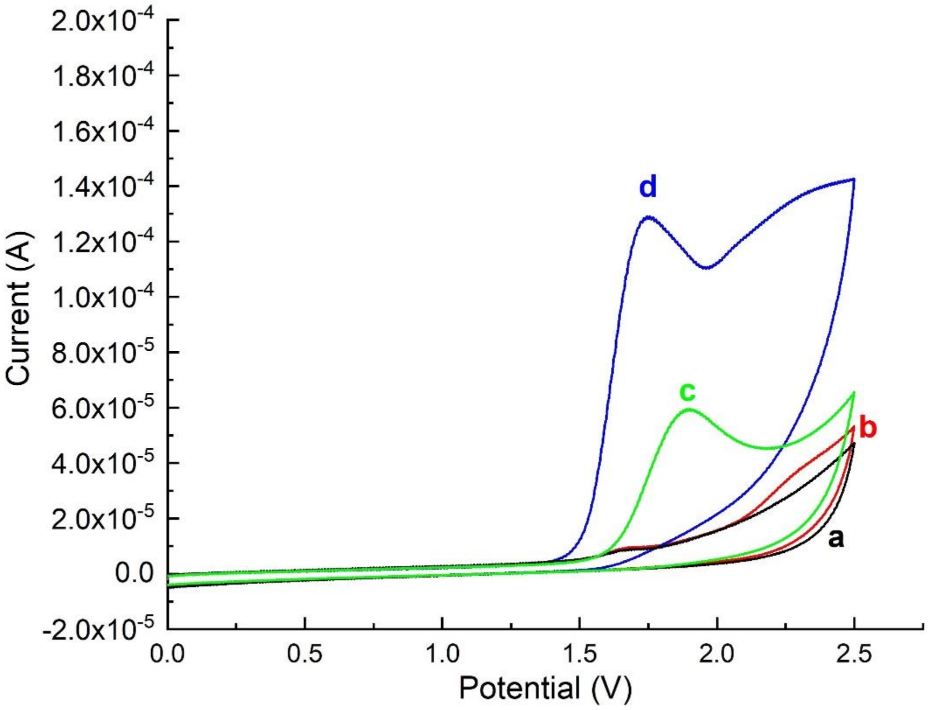
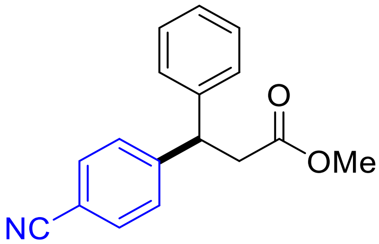


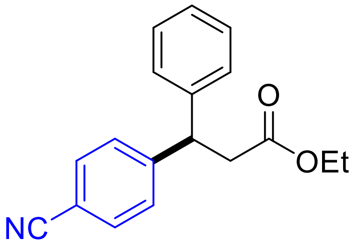
Fig S4. Cyclic voltammograms of substrates in 0.1 M $LiClO_4$ (CH_3CN), using a glassy carbon working electrode and Pt wire and Ag/$AgNO_3$ (0.1 M in CH_3CN) as counter and reference electrodes at a 100 mV·s^{-1} scan rate: a. blank; b. 1,4-dicyanobenzene; c. methyl cinnamate; d. DMSO

The anodic process in the reaction was further studied. It was found that solvent DMSO and substrate **2a** could be oxidized at the anode with anodic peaks at 1.74 V and 1.90 V, respectively. As DMSO is excessive in the reaction, oxidation of DMSO preferentially occurs at the anode.

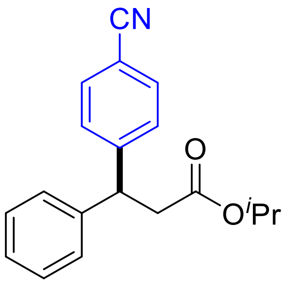
8. Experimental data for products



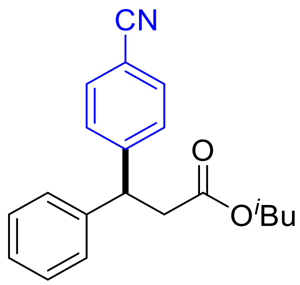
Methyl 3-(4-cyanophenyl)-3-phenylpropanoate (**3a**): 207 mg, 78% yield, colorless oil; regioselectivity: 14/1 *rr*; ^{1}H NMR (400 MHz, $CDCl_3$): 7.56 (d, J = 8.0 Hz, 2H), 7.35 (d, J = 8.0 Hz, 2H), 7.28 (m, 3H), 7.20 (m, 2H), 4.61 (t, J = 8.0 Hz, 1H), 3.58 (s, 3H), 3.07 (d, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): 171.7, 149.0, 142.0, 132.5, 128.9, 128.6, 127.6, 127.2, 118.8, 110.5, 51.9, 47.0, 40.0; These data are in accordance with the literature.[3]



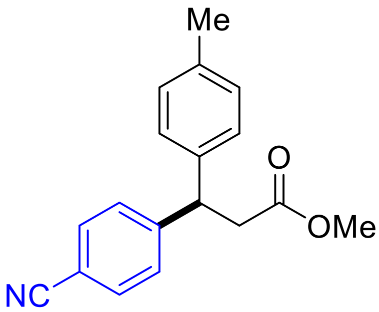
Ethyl 3-(4-cyanophenyl)-3-phenylpropanoate (**3b**): 226 mg, 81% yield, colorless oil; regioselectivity: 7/1 *rr*; ^{1}H NMR (400 MHz, $CDCl_3$): 7.56 (d, J = 8.0 Hz, 2H), 7.35 (d, J = 8.0 Hz, 2H), 7.30 (m, 2H), 7.21 (m, 3H), 4.60 (t, J = 8.0 Hz, 1H), 4.04 (q, J = 8.0 Hz, 2H), 3.05 (d, J = 8.0 Hz, 2H), 1.12 (t, J = 8.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 171.1, 148.9, 141.9, 132.3, 128.8, 128.5, 127.5, 127.0, 118.7, 110.5, 60.6, 47.0, 40.2, 14.0; HRMS (ESI): cacld. for $C_{18}H_{17}NO_2$ $[M+H]^+$: 280.1332, found 280.1328.



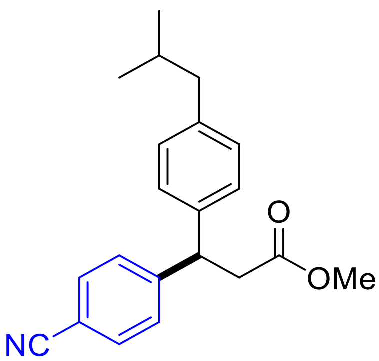
Isopropyl 3-(4-cyanophenyl)-3-phenylpropanoate (**3c**): 214mg, 73% yield, colorless oil; regioselectivity: 21/1 *rr*; ^{1}H NMR (400 MHz, $CDCl_3$): 7.57 (d, J = 8.0 Hz, 2H), 7.35 (d, J = 8.0 Hz, 2H), 7.29 (t, J = 8.0 Hz, 2H), 7.21 (m, 3H), 4.90 (m, 1H), 4.58 (t, J = 8.0 Hz, 1H), 3.02 (d, J = 8.0 Hz, 2H), 1.08 (d, J = 4.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): 170.7, 148.9, 141.9, 132.3, 128.8, 128.5, 127.6, 127.0, 118.7, 110.4, 68.1, 47.2, 40.5, 21.6, 21.6; HRMS (ESI): cacld. for $C_{19}H_{19}NO_2$ $[M+H]^+$: 294.1489, found 294.1487.



Isobutyl 3-(4-cyanophenyl)-3-phenylpropanoate (**3d**): 213mg, 69% yield, colorless oil; regioselectivity: 19/1 *rr*; ^{1}H NMR (400 MHz, $CDCl_3$): 7.56 (d, *J* = 8.0 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.29 (t, *J* = 8.0 Hz, 2H), 7.20 (t, *J* = 8.0 Hz, 3H), 4.59 (t, *J* = 8.0 Hz, 1H), 3.76 (d, *J* = 8.0 Hz, 1H), 3.06 (d, *J* = 8.0 Hz, 2H), 1.78 (m, 1H), 0.80 (d, *J* = 4.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): 171.2, 148.9, 141.9, 132.3, 128.8, 128.5, 127.5, 127.0, 118.7, 110.4, 70.8, 47.0, 40.2, 27.5, 18.8; HRMS (ESI): cacld. for $C_{20}H_{21}NO_2$ $[M+H]^+$: 308.1645, found 308.1648.

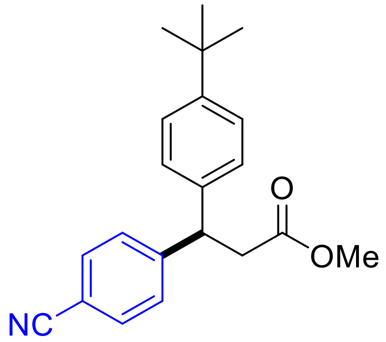


Methyl 3-(4-cyanophenyl)-3-(*p*-tolyl)propanoate (**3e**): 142 mg, 51% yield, colorless oil; regioselectivity: 8/1 *rr*; ^{1}H NMR (400 MHz, $CDCl_3$): 7.56 (d, *J* = 8.0 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.10 (m, 4H), 4.57 (t, *J* = 8.0 Hz, 1H), 3.59 (s, 3H), 3.05 (d, *J* = 8.0 Hz, 2H), 2.30 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 171.7, 149.1, 138.9, 136.7, 132.3, 129.5, 128.4, 127.3, 118.7, 110.3, 51.8, 46.5, 39.9, 20.9; HRMS (ESI): cacld. for $C_{18}H_{17}NO_2$ $[M+H]^+$: 280.1332, found 280.1324.

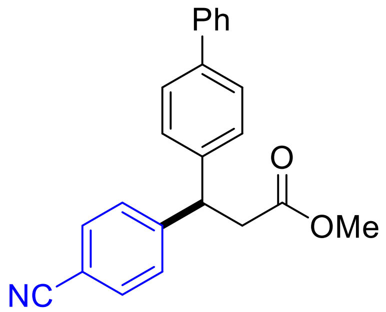


Methyl 3-(4-cyanophenyl)-3-(4-isobutylphenyl)propanoate (**3f**): 170 mg, 53% yield, colorless oil; regioselectivity: 6/1 *rr*; ^{1}H NMR (400 MHz, $CDCl_3$): 7.57 (d, *J* = 8.0 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.08 (s, 4H), 4.57 (t, *J* = 8.0 Hz, 1H), 3.59 (s, 3H), 3.06 (d, *J* = 8.0 Hz, 2H), 2.42 (d, *J* = 8.0 Hz, 2H), 1.82 (m, 1H), 0.87 (d, *J* = 8.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): 171.7, 149.1, 140.5, 139.1, 132.3, 129.5, 128.4, 127.1, 118.8, 110.3, 51.8, 46.5, 44.8, 40.0, 30.0, 22.3; HRMS (ESI): cacld. for $C_{21}H_{23}NO_2$

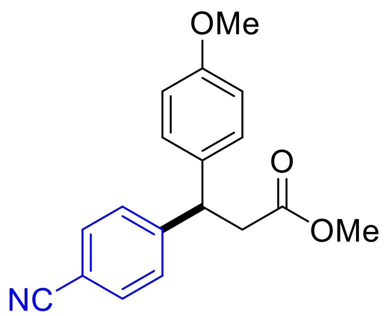
[M+H]$^+$: 322.1802, found 322.1788.



Methyl 3-(4-(tert-butyl)phenyl)-3-(4-cyanophenyl)propanoate (**3g**): 145 mg, 45% yield, colorless oil; regioselectivity: 7/1 *rr*; ^{1}H NMR (400 MHz, $CDCl_3$): 7.57 (d, *J* = 8.0 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.11 (d, *J* = 8.0 Hz, 2H), 4.58 (t, *J* = 8.0 Hz, 1H), 3.59 (s, 3H), 3.06 (d, *J* = 8.0 Hz, 2H), 1.28 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): 171.7, 149.8, 149.1, 138.8, 132.3, 128.5, 127.0, 125.7, 118.8, 110.3, 51.8, 46.4, 39.9, 34.3, 31.2; HRMS (ESI): cacld. for $C_{21}H_{23}NO_2$ [M+H]$^+$: 322.1802, found 322.1790.

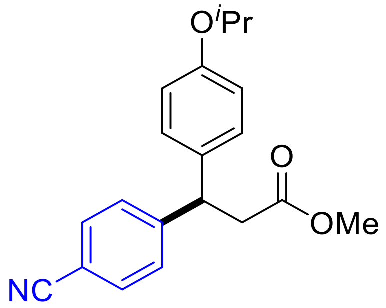


Methyl 3-([1,1'-biphenyl]-4-yl)-3-(4-cyanophenyl)propanoate (**3h**): 154 mg, 45% yield, colorless oil; regioselectivity: 24/1 *rr*; ^{1}H NMR (400 MHz, $CDCl_3$): 7.54 (m, 6H), 7.37 (m, 5H), 7.25 (d, *J* = 8.0 Hz, 2H), 4.64 (t, *J* = 8.0 Hz, 1H), 3.59 (s, 3H), 3.09 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): 171.5, 148.7, 140.9, 140.3, 139.9, 132.4, 128.7, 128.4, 127.9, 127.4, 127.3, 126.8, 118.6, 110.4, 51.8, 46.5, 39.8; HRMS (ESI): cacld. for $C_{23}H_{19}NO_2$ [M+H]$^+$: 342.1489, found 342.1497.

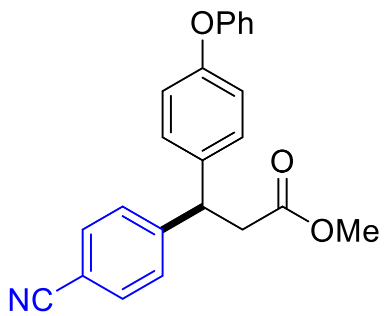


Methyl 3-(4-cyanophenyl)-3-(4-methoxyphenyl)propanoate (**3i**): 210 mg, 71% yield, colorless oil; regioselectivity: 5/1 *rr*; ^{1}H NMR (400 MHz, $CDCl_3$): 7.57 (d, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.11 (d, *J* = 8.0 Hz, 2H), 6.83 (d, *J* = 8.0 Hz, 2H), 4.56 (t, *J* = 8.0 Hz, 1H), 3.76 (s, 3H), 3.59 (s, 3H), 3.04

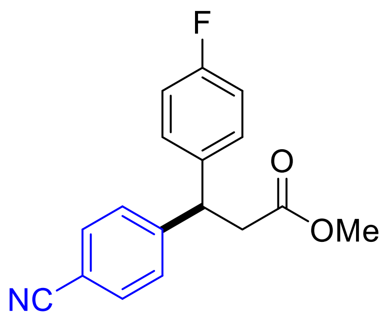
(d, J = 4.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): 171.7, 158.4, 149.2, 133.9, 132.3, 128.5, 128.3, 118.7, 114.1, 110.3, 55.1, 51.8, 46.1, 40.0; HRMS (ESI): cacld. for $C_{18}H_{17}NO_3$ $[M+H]^+$: 296.1281, found 296.1278.



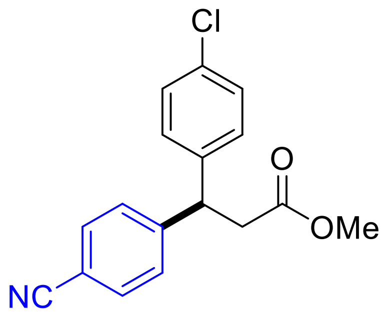
Methyl 3-(4-cyanophenyl)-3-(4-isopropoxyphenyl)propanoate (**3j**): 110 mg, 34% yield, colorless oil; regioselectivity: 9/1 *rr*; ^{1}H NMR (400 MHz, $CDCl_3$): 7.57 (d, J = 8.0 Hz, 2H), 7.34 (d, J = 8.0 Hz, 2H), 7.08 (d, J = 8.0 Hz, 2H), 6.81 (d, J = 8.0 Hz, 2H), 4.52 (m, 2H), 3.59 (s, 3H), 3.03 (d, J = 8.0 Hz, 2H), 1.31 (d, J = 4.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): 171.7, 156.8, 149.3, 133.7, 132.4, 128.5, 128.4, 118.8, 115.9, 110.3, 69.8, 51.8, 46.1, 40.1, 22.0; HRMS (ESI): cacld. for $C_{20}H_{21}NO_3$ $[M+H]^+$324.1594: , found 324.1586.



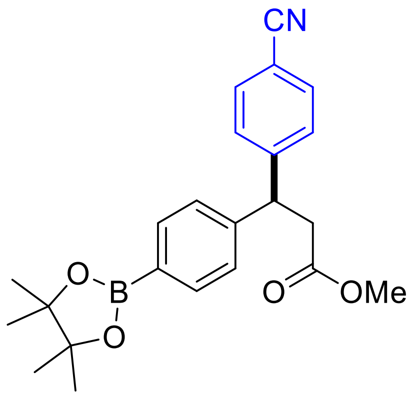
Methyl 3-(4-cyanophenyl)-3-(4-phenoxyphenyl)propanoate (**3k**): 197 mg, 55% yield, colorless oil; regioselectivity: 9/1 *rr*; ^{1}H NMR (400 MHz, $CDCl_3$): 7.58 (d, J = 8.0 Hz, 2H), 7.33 (q, J = 8.0 Hz, 4H), 7.12 (m, 3H), 6.98 (d, J = 12.0 Hz, 2H), 6.93 (d, J = 8.0 Hz, 2H), 4.59 (t, J = 8.0 Hz, 1H), 3.60 (s, 3H), 3.05 (d, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): 171.6, 156.7, 156.3, 148.9, 136.5, 132.4, 129.7, 128.8, 128.4, 123.4, 119.0 118.8, 118.7, 110.5, 51.8, 46.2, 40.0; HRMS (ESI): cacld. for $C_{23}H_{19}NO_3$ $[M+H]^+$ 358.1438, found 358.1431.



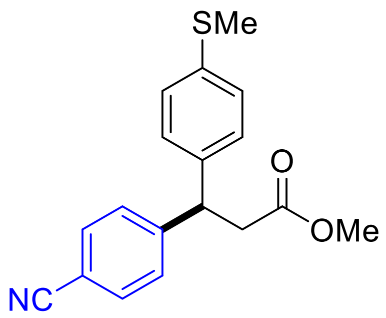
Methyl 3-(4-cyanophenyl)-3-(4-fluorophenyl)propanoate (**3l**): 156 mg, 55% yield, colorless oil; regioselectivity: 7/1 *rr*; ^{1}H NMR (400 MHz, $CDCl_3$): 7.58 (d, J = 8.0 Hz, 2H), 7.33 (d, J = 8.0 Hz, 2H), 7.17 (t, *J* = 8.0 Hz, 2H), 6.99 (t, *J* = 8.0 Hz, 2H), 4.60 (t, *J* = 8.0 Hz, 1H), 3.60 (s, 3H), 3.05 (d, *J* = 8.0 Hz, 2H); ^{19}F NMR (376 MHz, $CDCl_3$): -115.3; ^{13}C NMR (100 MHz, $CDCl_3$): 171.4, 161.6 (d, J_{F-C} = 244 Hz), 148.6, 137.6 (d, J_{F-C} = 3 Hz), 132.4, 129.0 (d, J_{F-C} = 8 Hz), 128.3, 118.6, 115.7 (d, J_{F-C} = 22 Hz), 110.6, 51.8, 46.1, 39.9; HRMS (ESI): cacld. for $C_{17}H_{14}FNO_2$ $[M+H]^+$: 284.1081, found 284.1080.



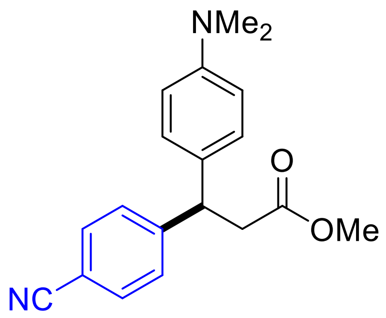
Methyl 3-(4-chlorophenyl)-3-(4-cyanophenyl)propanoate (**3m**): 78 mg, 26% yield, colorless oil; regioselectivity: 17/1 *rr*; ^{1}H NMR (400 MHz, $CDCl_3$): 7.58 (d, *J* = 8.0 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 7.13 (d, *J* = 8.0 Hz, 2H), 4.59 (t, *J* = 8.0 Hz, 1H), 3.60 (s, 3H), 3.04 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): 171.5, 148.4, 140.4, 133.0, 132.6, 129.1, 129.0, 128.5, 118.7, 110.8, 52.0, 46.3, 39.8; HRMS (ESI): cacld. for $C_{17}H_{14}ClNO_2$ $[M+H]^+$: 300.0786, found 300.0784.



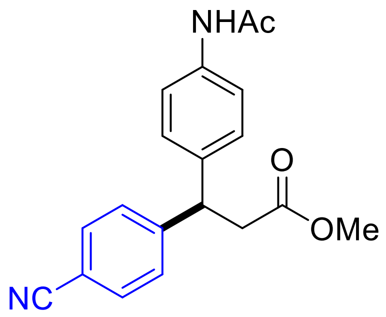
Methyl 3-(4-cyanophenyl)-3-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)propanoate (**3n**): 141 mg, 36% yield, colorless oil; regioselectivity: 10/1 *rr*; ^{1}H NMR (400 MHz, $CDCl_3$): 7.75 (d, *J* = 8.0 Hz, 2H), 7.57 (d, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.20 (d, *J* = 8.0 Hz, 2H), 4.62 (t, *J* = 8.0 Hz, 1H), 3.59 (s, 3H), 3.07 (d, *J* = 8.0 Hz, 2H), 1.32 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): 171.6, 148.7, 145.0, 135.4, 132.4, 128.5, 127.0, 118.7, 110.6, 83.8, 51.9, 47.0, 39.7, 24.8 (signal of boron-bonded carbon atom is invisible in the spectra); HRMS (ESI): cacld. for $C_{23}H_{26}BNO_4$ $[M+H]^+$: 392.2028, found 392.2030.



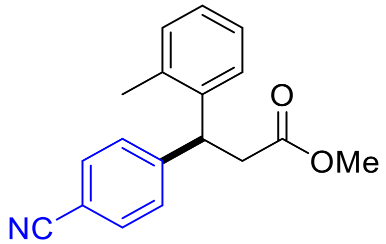
Methyl 3-(4-cyanophenyl)-3-(4-(methylthio)phenyl)propanoate (**3o**): 44 mg, 14% yield, colorless oil; regioselectivity (**3m**): 14/1 *rr*; ^{1}H NMR (400 MHz, $CDCl_3$): 7.58 (d, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.19 (d, *J* = 12.0 Hz, 2H), 7.11 (d, *J* = 8.0 Hz, 2H), 4.57 (t, *J* = 8.0 Hz, 1H), 3.60 (s, 3H), 3.04 (d, *J* = 8.0 Hz, 2H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 171.6, 148.8, 138.7, 137.3, 132.4, 128.4, 128.0, 126.8, 118.7, 110.5, 51.9, 46.3, 39.8, 15.6; HRMS (ESI): cacld. for $C_{18}H_{17}SNO_2$ $[M+H]^+$: 312.1053, found 312.1058.



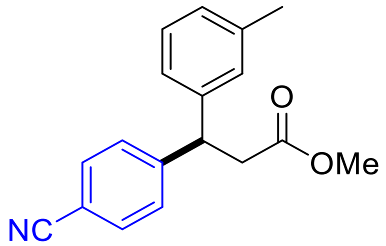
Methyl 3-(4-cyanophenyl)-3-(4-(dimethylamino)phenyl)propanoate (**3p**): 49 mg, 16% yield; white solid, m.p. 105-106 °C; regioselectivity: 11/1 *rr*; ^{1}H NMR (400 MHz, $CDCl_3$): 7.55 (d, *J* = 8.0 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.04 (d, *J* = 8.0 Hz, 2H), 6.66 (d, *J* = 12.0 Hz, 2H), 4.51 (t, *J* = 8.0 Hz, 1H), 3.59 (s, 3H), 3.02 (d, *J* = 8.0 Hz, 2H), 2.91 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): 172.0, 149.9, 149.5, 132.4, 129.7, 128.4, 128.2, 119.0, 112.7, 110.2, 51.8, 46.1, 40.5, 40.2; HRMS (ESI): cacld. for $C_{19}H_{20}N_2O_2$ $[M+H]^+$: 309.1598, found 309.1590.



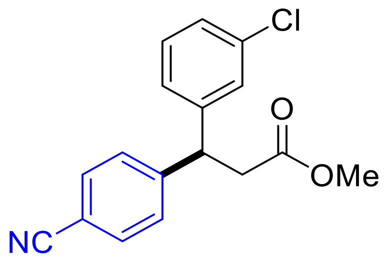
Methyl 3-(4-acetamidophenyl)-3-(4-cyanophenyl)propanoate (**3q**): 168 mg, 52% yield, colorless oil; regioselectivity: 7/1 *rr*; ^{1}H NMR (400 MHz, $CDCl_3$): 7.98 (br, 1H), 7.57 (d, *J* = 8.0 Hz, 2H), 7.46 (d, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.12 (d, *J* = 8.0 Hz, 2H), 4.56 (t, *J* = 8.0 Hz, 1H), 3.60 (s, 3H), 3.04 (d, *J* = 8.0 Hz, 2H), 2.13 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 171.7, 168.8, 148.9, 137.5, 136.9, 132.4, 128.4, 128.0, 120.3, 118.7, 110.2, 51.9, 46.2, 39.8, 24.3; HRMS (ESI): cacld. for $C_{19}H_{18}N_2O_3$ $[M+H]^+$: 323.1390, found 323.1380.



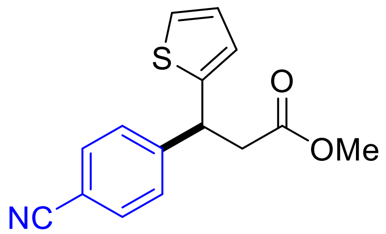
Methyl 3-(4-cyanophenyl)-3-(o-tolyl)propanoate (**3r**): 142 mg, 51% yield; white solid, m.p. 82-83 °C; regioselectivity: 14/1 *rr*; ^{1}H NMR (400 MHz, $CDCl_3$): 7.55 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.19 (m, 4H), 4.79 (t, *J* = 8.0 Hz, 1H), 3.60 (s, 3H), 3.04 (m, 2H), 2.26 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 171.7, 148.6, 139.7, 136.2, 132.3, 131.0, 128.7, 127.1, 126.4, 126.1, 118.8, 110.3, 51.8, 42.9, 40.2, 19.7; HRMS (ESI): cacld. for $C_{18}H_{17}NO_2$ [M+H]$^+$: 280.1332, found 280.1335.



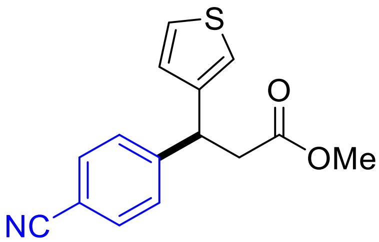
Methyl 3-(4-cyanophenyl)-3-(m-tolyl)propanoate (**3s**): 159 mg, 57% yield, colorless oil; regioselectivity: 13/1 *rr*; ^{1}H NMR (400 MHz, $CDCl_3$): 7.57 (d, *J* = 8.0 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.19 (t, *J* = 8.0 Hz, 1H), 7.02 (m, 3H), 4.57 (t, *J* = 8.0 Hz, 1H), 3.59 (s, 3H), 3.06 (d, *J* = 8.0 Hz, 2H), 2.30 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 171.6, 149.0, 141.9, 138.5, 132.7, 132.3, 128.7, 128.4, 127.8, 124.4, 118.7, 110.4, 51.8, 46.8, 39.8, 21.4; HRMS (ESI): cacld. for $C_{18}H_{17}NO_2$ [M+H]$^+$: 280.1332, found 280.1330.



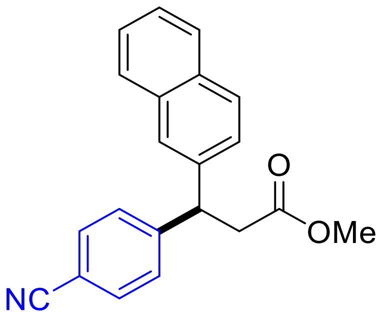
Methyl 3-(3-chlorophenyl)-3-(4-cyanophenyl)propanoate (**3t**): 159 mg, 53% yield, colorless oil; regioselectivity: 24/1 *rr*; ^{1}H NMR (400 MHz, $CDCl_3$): 7.60 (d, *J* = 8.0 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.22 (m, 3H), 7.09 (d, *J* = 8.0 Hz, 1H), 4.59 (t, *J* = 8.0 Hz, 1H), 3.61 (s, 3H), 3.05 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): 171.3, 148.0, 143.9, 134.7, 132.6, 130.1, 128.4, 127.7, 127.4, 125.7, 118.6, 110.8, 52.0, 46.5, 39.6; HRMS (ESI): cacld. for $C_{17}H_{14}ClNO_2$ [M+H]$^+$: 300.0786, found 300.0784.



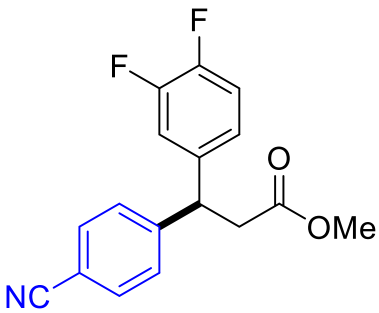
Methyl 3-(4-cyanophenyl)-3-(thiophen-2-yl)propanoate (**3u**): 60 mg, 22% yield, colorless oil; regioselectivity: 16/1 *rr*; ^{1}H NMR (400 MHz, $CDCl_3$): 7.61 (d, *J* = 8.0 Hz, 2H), 7.40 (d, *J* = 8.0 Hz, 2H), 7.20 (d, *J* = 4.0 Hz, 1H), 6.93 (m, 1H), 6.85 (s, 1H), 4.83 (t, *J* = 8.0 Hz, 1H), 3.62 (s, 3H), 3.16 (dd, *J* = 16.0 Hz, *J* = 8.0 Hz, 1H), 3.05 (dd, *J* = 16.0 Hz, *J* = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): 171.1, 148.3, 145.6, 132.5, 128.3, 126.9, 124.7, 124.5, 118.7, 110.9, 52.0, 42.5, 41.3; HRMS (ESI): cacld. for $C_{15}H_{13}NO_2S$ $[M+H]^+$: 272.0740, found 272.0729.



Methyl 3-(4-cyanophenyl)-3-(thiophen-3-yl)propanoate (**3v**): 95 mg, 35% yield, colorless oil; regioselectivity: 8/1 *rr*; ^{1}H NMR (400 MHz, $CDCl_3$): 7.59 (d, *J* = 8.0 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.26 (s, 1H), 7.02 (s, 1H), 6.85 (d, *J* = 4.0 Hz, 1H), 4.66 (t, *J* = 8.0 Hz, 1H), 3.61 (s, 3H), 3.10 (dd, *J* = 16.0 Hz, *J* = 8.0 Hz, 1H), 2.98 (dd, *J* = 16.0 Hz, *J* = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): 171.5, 148.5, 142.6, 132.4, 128.5, 127.1, 126.5, 120.9, 118.7, 110.6, 51.9, 42.7, 40.4; HRMS (ESI): cacld. for $C_{15}H_{13}NO_2S$ $[M+H]^+$: 272.0740, found 272.0736.

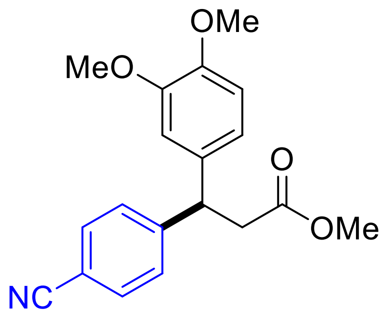


Methyl 3-(4-cyanophenyl)-3-(naphthalen-2-yl)propanoate (**3w**): 224 mg, 71% yield, colorless oil; regioselectivity: 33/1 *rr*; ^{1}H NMR (400 MHz, $CDCl_3$): 7.78 (m, 3H), 7.68 (s, 1H), 7.57 (d, *J* = 8.0 Hz, 2H), 7.47 (m, 2H), 7.38 (d, *J* = 8.0 Hz, 2H), 7.25 (d, *J* = 8.0 Hz, 1H), 4.77 (t, *J* = 8.0 Hz, 1H), 3.60 (s, 3H), 3.16 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): 171.6, 148.7, 139.3, 133.3, 132.4, 132.3, 128.7, 128.6, 127.7, 127.6, 126.4, 126.00, 125.98, 125.7, 118.2, 110.5, 51.9, 46.97, 39.8; HRMS (ESI): cacld. for $C_{21}H_{17}NO_2$ $[M+H]^+$: 316.1332, found 316.1329.

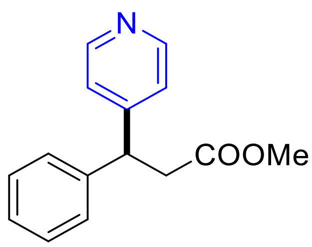


Methyl 3-(4-cyanophenyl)-3-(3,4-difluorophenyl)propanoate (**3x**): 148 mg, 49% yield, colorless oil;

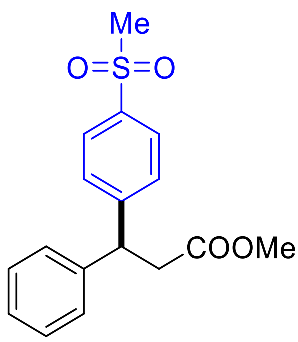
regioselectivity: 20/1 *rr*; ^{1}H NMR (400 MHz, $CDCl_3$): 7.61 (d, *J* = 12 Hz, 2H), 7.33 (d, *J* = 8 Hz, 2H), 7.04 (m, 3H), 4.59 (t, *J* = 8 Hz, 1H), 3.62 (s, 3H), 3.04 (d, *J* = 8 Hz, 2H); ^{19}F NMR (376 MHz, $CDCl_3$): -136.54 (*J* = 22.6 Hz), -139.71 (*J* = 22.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): 171.1, 150.2 (dd, J_{F-C} = 247 Hz, J_{F-C} = 12 Hz), 149.2 (dd, J_{F-C} = 246 Hz, J_{F-C} = 12 Hz), 147.8, 138.9 (t, J_{F-C} = 4.5 Hz), 132.5, 128.3, 123.5 (dd, J_{F-C} = 6 Hz, J_{F-C} = 4 Hz), 118.4, 117.5 (d, J_{F-C} = 17 Hz), 116.5 (d, J_{F-C} = 17 Hz), 110.9, 51.9, 46.0, 39.7; HRMS (ESI): cacld. for $C_{17}H_{13}F_2NO_2$ $[M+H]^+$: 302.0987, found 302.0988.



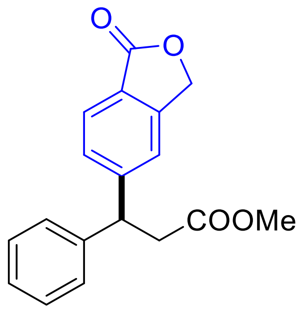
Methyl 3-(4-cyanophenyl)-3-(3,4-dimethoxyphenyl)propanoate (**3y**): 130 mg, 40% yield, colorless oil; regioselectivity: 54/1 *rr*; ^{1}H NMR (400 MHz, $CDCl_3$): 7.58 (d, *J* = 8 Hz, 2H), 7.35 (d, *J* = 8 Hz, 2H), 6.81 (d, *J* = 8 Hz, 1H), 6.75 (d, *J* = 12 Hz, 1H), 6.68 (s, 1H), 4.56 (t, *J* = 8 Hz, 1H), 3.84 (s, 3H), 3.83 (s, 3H), 3.60 (s, 3H), 3.04 (d, *J* = 8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): 171.6, 149.1, 149.0, 148.0, 134.4, 132.3, 128.3, 119.3, 118.7, 111.2, 111.0, 110.4, 55.8, 55.8, 51.8, 46.4, 40.1; HRMS (ESI): cacld. for $C_{19}H_{19}NO_4$ $[M+H]^+$: 326.1387, found 326.1380.



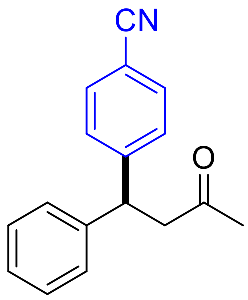
Methyl 3-phenyl-3-(pyridin-4-yl)propanoate (**3z**): 56 mg, 23% yield, colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): 8.50 (d, *J* = 8.0 Hz, 2H), 7.31 (t, *J* = 6.0 Hz, 2H), 7.21 (t, *J* = 8.0 Hz, 3H), 7.16 (d, *J* = 4.0 Hz, 2H), 4.53 (t, *J* = 8.0 Hz, 1H), 3.60 (s, 3H), 3.06 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): 171.6, 152.2, 150.0, 141.7, 128.8, 127.6, 127.1, 122.9, 51.8, 46.3, 39.6. These data are in accordance with the literature.[4]



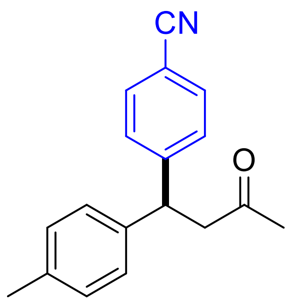
Methyl 3-(4-(methylsulfonyl)phenyl)-3-phenylpropanoate (**3aa**): 175 mg, 55% yield; white solid, 113-115 ºC; ^{1}H NMR (500 MHz, $CDCl_3$): 7.85 (d, *J* = 10.0 Hz, 2H), 7.45(d, *J* = 5.0 Hz, 2H), 7.31 (t, *J* = 7.5 Hz, 2H), 7.22 (m, 3H), 4.65 (t, *J* = 7.5 Hz, 1H), 3.60 (s, 3H), 3.10 (d, *J* = 5.0 Hz, 2H), 3.02 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): 171.6, 149.8, 142.0, 138.7, 128.9, 128.7, 127.7, 127.6, 127.1, 51.9, 46.8, 44.4, 40.0; HRMS (ESI): cacld. for $C_{17}H_{18}O_4S$ $[M+H]^+$: 319.0999, found 319.0996.



Methyl 3-(1-oxo-1,3-dihydroisobenzofuran-5-yl)-3-phenylpropanoate (**3ab**): 130 mg, 44% yield; white solid, 121-123 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): 7.84 (d, *J* = 5.0 Hz, 1H), 7.44 (d, *J* = 5.0 Hz, 1H), 7.35 (s, 1H), 7.32 (t, *J* = 7.5 Hz, 2H), 7.22 (d, *J* = 10.0 Hz, 3H), 5.26 (s, 2H), 4.70 (t, *J* = 7.5 Hz, 1H), 3.60 (s, 3H), 3.12 (d, *J* = 5.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): 171.7, 170.7, 150.5, 147.2, 142.1, 128.89, 128.86, 127.5, 127.1, 126.0, 124.3, 121.3, 69.5, 51.9, 47.1, 40.1; HRMS (ESI): cacld. for $C_{18}H_{16}O_4$ $[M+H]^+$: 297.1121, found 297.1124.

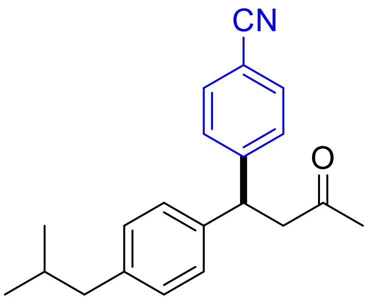


4-(3-Oxo-1-phenylbutyl)benzonitrile (**5a**): 135 mg, 54% yield, colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): 7.55 (d, *J* = 8 Hz, 2H), 7.30 (m, 4H), 7.20 (m, 3H), 4.65 (t, *J* = 12 Hz, 1H), 3.20 (d, *J* = 8 Hz, 2H), 2.11 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 205.7, 149.4, 142.4, 132.3, 128.8, 128.5, 127.6, 127.0, 118.7, 110.3, 49.0, 45.7, 30.5; These data are in accordance with the literature.[5]

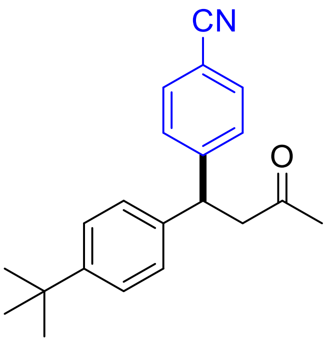


4-(3-Oxo-1-(*p*-tolyl)butyl)benzonitrile (**5b**): 140 mg, 53% yield, colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): 7.54 (d, *J* = 8.0 Hz, 2H), 7.32 (d, *J* = 8 Hz, 2H), 7.09 (m, 4H), 4.60 (t, *J* = 8 Hz, 1H), 3.18 (d, *J* =

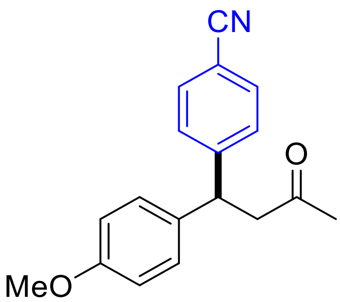
8 Hz, 2H), 2.29 (s, 3H), 2.11 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 205.9, 149.7, 139.3, 136.6, 132.3, 129.5, 128.4, 127.4, 118.8, 110.1, 49.0, 45.3, 30.5, 20.9; HRMS (ESI): cacld. for $C_{18}H_{17}NO$ $[M+H]^+$: 264.1383, found 264.1384.



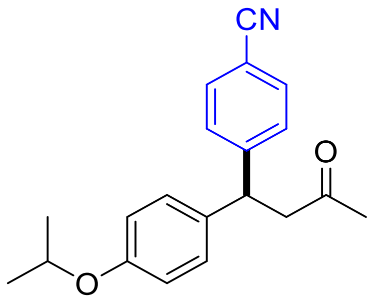
4-(1-(4-Isobutylphenyl)-3-oxobutyl)benzonitrile (**5c**): 229 mg, 75% yield, colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): 7.55 (d, *J* = 8 Hz, 2H), 7.33 (d, *J* = 8 Hz, 2H), 7.07 (s, 4H), 4.61 (t, *J* = 8 Hz, 1H), 3.19 (d, *J* = 8 Hz, 2H), 2.41 (d, *J* = 8 Hz, 2H), 2.11 (s, 3H), 1.81 (m, 1H), 0.87 (d, *J* = 8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): 206.0, 149.7, 140.3, 139.5, 132.3, 129.5, 128.5, 127.2, 118.8, 110.1, 49.0, 45.3, 44.8, 30.5, 30.0, 22.3; HRMS (ESI): cacld. for $C_{21}H_{23}NO$ $[M+H]^+$: 306.1852, found 306.1845.



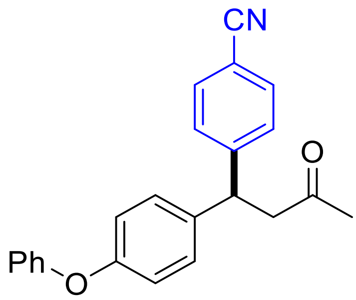
4-(1-(4-(*tert*-Butyl)phenyl)-3-oxobutyl)benzonitrile (**5d**): 238 mg, 78% yield, colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): 7.55 (d, *J* = 8 Hz, 2H), 7.34 (d, *J* = 8 Hz, 2H), 7.30 (d, *J* = 8 Hz, 2H), 7.10 (d, *J* = 8 Hz, 2H), 4.61 (t, *J* = 8 Hz, 1H), 3.20 (d, *J* = 8 Hz, 2H), 2.11 (s, 3H), 1.27 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): 206.0, 149.7, 149.6, 139.2, 132.3, 128.5, 127.1, 125.7, 118.8, 110.1, 49.0, 45.2, 34.3, 31.2, 30.5; HRMS (ESI): cacld. for $C_{21}H_{23}NO$ $[M+H]^+$: 306.1852, found 306.1856.



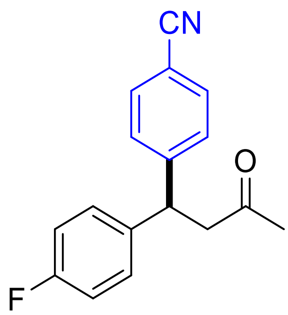
4-(1-(4-Methoxyphenyl)-3-oxobutyl)benzonitrile (**5e**): 226 mg, 81% yield, colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): 7.55 (d, *J* = 8 Hz, 2H), 7.32 (d, *J* = 8 Hz, 2H), 7.10 (d, *J* = 8 Hz, 2H), 6.83 (d, *J* = 8 Hz, 2H), 4.59 (t, *J* = 8 Hz, 1H), 3.76 (s, 3H), 3.17 (d, *J* = 8 Hz, 2H), 2.11 (s, 3H); ^{13}C NMR (100 MHz, CDCl3): 206.0, 158.3, 149.8, 134.3, 132.3, 128.6, 128.4, 118.8, 114.1, 110.0, 55.1, 49.1, 44.9, 30.6; HRMS (ESI): cacld. for $C_{18}H_{17}NO_2$ [M+H]$^+$: 280.1332, found 280.1341.



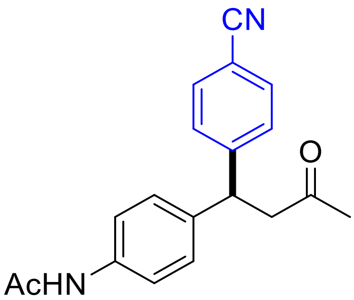
4-(1-(4-Isopropoxyphenyl)-3-oxobutyl)benzonitrile (**5f**): 157 mg, 51% yield, colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): 7.55 (d, *J* = 8 Hz, 2H), 7.32 (d, *J* = 8 Hz, 2H), 7.07 (d, *J* = 8 Hz, 2H), 6.80 (d, *J* = 8 Hz, 2H), 4.58 (t, *J* = 8 Hz, 1H), 4.49 (m, 1H), 3.16 (d, *J* = 8 Hz, 2H), 2.11 (s, 3H), 1.31 (d, *J* = 4 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): 206.0, 156.7, 149.9, 134.1, 132.3, 128.6, 128.4, 118.8, 116.0, 110.1, 69.8, 49.2, 45.0, 30.6, 22.0; HRMS (ESI): cacld. for $C_{20}H_{21}NO_2$ [M+H]$^+$: 308.1645, found 308.1650.



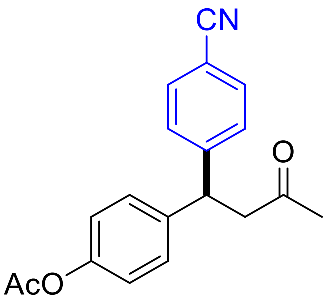
4-(3-Oxo-1-(4-phenoxyphenyl)butyl)benzonitrile (**5g**): 160 mg, 47% yield, colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): 7.56 (d, *J* = 8 Hz, 2H), 7.32 (m, 4H), 7.12 (m, 3H), 6.97 (d, *J* = 8 Hz, 2H), 6.92 (d, *J* = 8 Hz, 2H), 4.63 (t, *J* = 8 Hz, 1H), 3.19 (d, *J* = 8 Hz, 2H), 2.12 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 206.0, 156.9, 156.3, 149.6, 137.1, 132.5, 129.8, 129.0, 128.6, 123.5, 119.1, 119.0, 118.9, 110.3, 49.1, 45.1, 30.7; HRMS (ESI): cacld. for $C_{23}H_{19}NO_2$ [M+H]$^+$: 342.1489, found 342.1497.



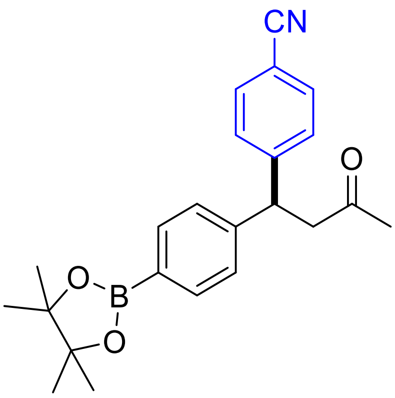
4-(1-(4-Fluorophenyl)-3-oxobutyl)benzonitrile (**5h**): 112 mg, 42% yield, colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): 7.57 (d, *J* = 8 Hz, 2H), 7.31 (d, *J* = 8 Hz, 2H), 7.15 (m, 2H), 6.98 (t, *J* = 8 Hz, 2H), 4.64 (t, *J* = 8 Hz, 1H), 3.19 (d, *J* = 8 Hz, 2H), 2.12 (s, 3H); ^{19}F NMR (376 MHz, $CDCl_3$): -115.5; ^{13}C NMR (100 MHz, $CDCl_3$): 205.6, 161.6 (d, J_{F-C} = 245 Hz), 149.2, 138.1 (d, J_{F-C} = 3 Hz), 132.4, 129.1 (d, J_{F-C} = 8 Hz), 128.4, 118.7, 115.6 (d, $J_{F\text{-}C}$ = 21 Hz), 110.4, 49.0, 44.8, 30.5; HRMS (ESI): cacld. for $C_{17}H_{14}FNO_2$ $[M+H]^+$: 268.1132, found 268.1131.



N-(4-(1-(4-cyanophenyl)-3-oxobutyl)phenyl)acetamide (**5i**): 52 mg, 17% yield, colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): 7.56 (d, *J* = 8 Hz, 2H), 7.43 (d, *J* = 8 Hz, 2H), 7.34 (br, 1H), 7.31 (d, *J* = 8 Hz, 2H), 7.13 (d, *J* = 8 Hz, 2H), 4.61 (t, *J* = 8 Hz, 1H), 3.18 (d, *J* = 8 Hz, 2H), 2.16 (s, 3H), 2.12 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 206.0, 168.5, 149.4, 138.3, 136.7, 132.5, 128.6, 128.2, 120.3, 110.3, 100.0, 49.0, 45.2, 30.7, 24.6; HRMS (ESI): cacld. for $C_{19}H_{18}N_2O_2$ $[M+H]^+$: 307.1441, found 307.1431.

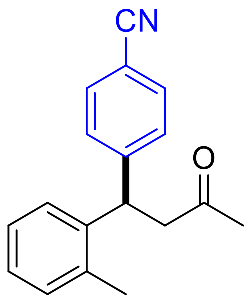


4-(1-(4-Cyanophenyl)-3-oxobutyl)phenyl acetate (**5j**): 98 mg, 32% yield, colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): 7.57 (d, *J* = 8 Hz, 2H), 7.32 (d, *J* = 8 Hz, 2H), 7.18 (d, *J* = 8 Hz, 2H), 7.02 (d, *J* = 8 Hz, 2H), 4.66 (t, *J* = 8 Hz, 1H), 3.19 (d, *J* = 8 Hz, 2H), 2.28 (s, 3H), 2.12 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 205.6, 169.4, 149.4, 149.0, 139.9, 132.4, 128.6, 128.5, 121.9, 118.7, 110.3, 48.9, 45.0, 30.5, 21.1; HRMS (ESI): cacld. for $C_{19}H_{17}NO_3$ $[M+H]^+$: 308.1281, found 308.1282.

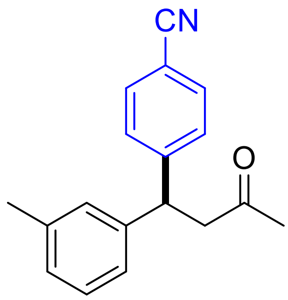


4-(3-Oxo-1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)butyl)benzonitrile (**5k**): 98 mg, 22% yield, colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): 7.75 (d, *J* = 8 Hz, 2H), 7.55 (d, *J* = 8 Hz, 2H), 7.32

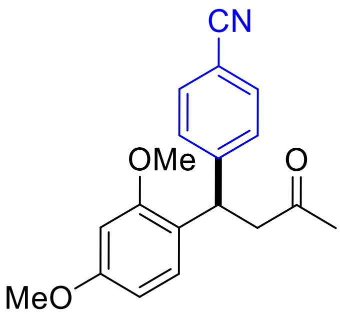
(d, J = 8 Hz, 2H), 7.20 (d, J = 8 Hz, 2H), 4.66 (t, J = 8 Hz, 1H), 3.21 (d, J = 8 Hz, 2H), 2.11 (s, 3H), 1.32 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): 205.7, 149.1, 145.4, 135.3, 132.3, 128.5, 127.0, 118.7, 110.2, 83.8, 48.7, 45.8, 30.6, 24.8 (signal of boron-bonded carbon atom is invisible in the spectra); HRMS (ESI): cacld. for $C_{23}H_{26}BNO_3$ $[M+H]^+$: 376.2079, found 376.2086.



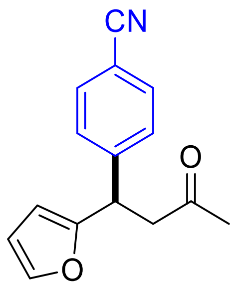
4-(3-Oxo-1-(o-tolyl)butyl)benzonitrile (**5l**): 79 mg, 30% yield, colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): 7.54 (d, J = 8 Hz, 2H), 7.29 (d, J = 8 Hz, 2H), 7.17 (m, 4H), 4.85 (t, J = 8 Hz, 1H), 3.17 (d, J = 8 Hz, 2H), 2.26 (s, 3H), 2.12 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 205.9, 149.2, 140.2, 136.3, 132.3, 131.0, 128.8, 127.0, 126.3, 126.2, 118.8, 110.1, 49.3, 41.6, 30.6, 19.8; HRMS (ESI): cacld. for $C_{18}H_{17}NO$ $[M+H]^+$: 264.1383, found 264.1383.



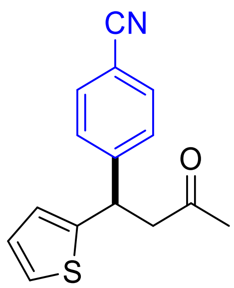
4-(3-Oxo-1-(m-tolyl)butyl)benzonitrile (**5m**): 129 mg, 49% yield, colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): 7.55 (d, J = 8 Hz, 2H), 7.33 (d, J = 8 Hz, 2H), 7.18 (t, J = 8 Hz, 1H), 7.01 (m, 3H), 4.60 (t, J = 8 Hz, 1H), 3.20 (d, J = 4 Hz, 2H), 2.30 (s, 3H), 2.12 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 205.9, 149.5, 142.2, 138.5, 132.3, 128.7, 128.5, 128.4, 127.7, 124.5, 118.8, 110.1, 48.9, 45.6, 30.5, 21.4; HRMS (ESI): cacld. for $C_{18}H_{17}NO$ $[M+H]^+$: 264.1383, found 264.1379.



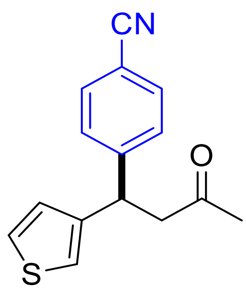
4-(1-(2,4-Dimethoxyphenyl)-3-oxobutyl)benzonitrile (**5n**): 96 mg, 31% yield, colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): 7.52 (d, J = 8 Hz, 2H), 7.32 (d, J = 8 Hz, 2H), 7.00 (d, J = 8 Hz, 1H), 6.43 (m, 2H), 4.88 (t, J = 8 Hz, 1H), 3.77 (s, 3H), 3.73 (s, 3H), 3.15 (d, J = 4 Hz, 2H), 2.11 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 206.5, 159.8, 157.6, 149.7, 132.0, 128.6, 128.1, 123.1, 119.0, 109.7, 104.1, 98.9, 55.3, 55.2, 48.1, 39.2, 30.2; HRMS (ESI): cacld. for $C_{19}H_{19}NO_3$ $[M+H]^+$: 310.1438, found 310.1443.



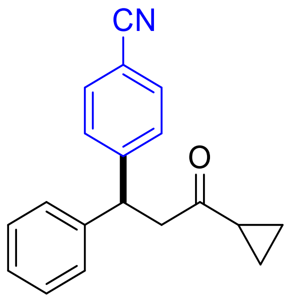
4-(1-(Furan-2-yl)-3-oxobutyl)benzonitrile (**5o**): 29 mg, 12% yield, colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): 7.59 (d, *J* = 8 Hz, 2H), 7.37 (d, *J* = 8 Hz, 2H), 7.32 (s, 1H), 6.30 (s, 1H), 6.04 (s, 1H), 4.66 (t, *J* = 8 Hz, 1H), 3.27 (dd, *J* = 16 Hz, *J* = 8 Hz, 1H), 3.04 (dd, *J* = 16 Hz, *J* = 8 Hz, 1H), 2.14 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 205.3, 154.8, 147.2, 142.0, 132.4, 128.7, 118.8, 110.8, 110.3, 106.3, 47.7, 39.9, 30.4; These data are in accordance with the literature.[6]



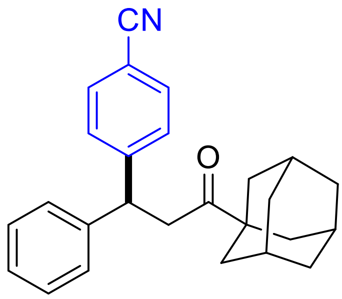
4-(3-Oxo-1-(thiophen-2-yl)butyl)benzonitrile (**5p**): 69 mg, 27% yield, colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): 7.60 (d, *J* = 8 Hz, 2H), 7.39 (d, *J* = 8 Hz, 2H), 7.18 (d, *J* = 4 Hz, 1H), 6.92 (s, 1H), 6.81 (s, 1H), 4.89 (t, *J* = 8 Hz, 1H), 3.29 (dd, *J* = 16 Hz, *J* = 8 Hz, 1H), 3.18 (dd, *J* = 16 Hz, *J* = 8 Hz, 1H), 2.14 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 205.3, 149.0, 146.1, 132.6, 128.5, 127.0, 124.6, 124.5, 118.8, 110.8, 50.4, 41.3, 30.6; HRMS (ESI): cacld. for $C_{15}H_{13}NOS$ $[M+H]^+$: 256.0791, found 256.0790.



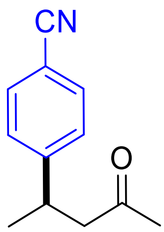
4-(3-Oxo-1-(thiophen-3-yl)butyl)benzonitrile (**5q**): 133 mg, 52% yield, colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): 7.57 (d, *J* = 8 Hz, 2H), 7.33 (d, *J* = 8 Hz, 2H), 7.26 (s, 1H), 6.98 (s, 1H), 6.84 (d, *J* = 8 Hz, 1H), 4.70 (t, *J* = 8 Hz, 2H), 3.18 (m, 2H), 2.12 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 205.9, 149.2, 143.1, 132.5, 128.7, 127.3, 126.6, 120.9, 118.9, 110.4, 49.5, 41.5, 30.6; HRMS (ESI): cacld. for $C_{15}H_{13}NOS$ $[M+H]^+$: 256.0791, found 256.0795.



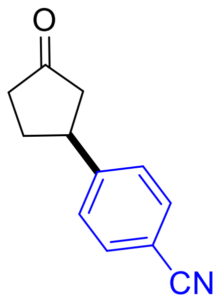
4-(3-Cyclopropyl-3-oxo-1-phenylpropyl)benzonitrile (**5r**): 160 mg, 58% yield, colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): 7.56 (d, *J* = 8 Hz, 2H), 7.32 (m, 4H), 7.21 (m, 3H), 4.68 (t, *J* = 8 Hz, 1H), 3.34 (d, *J* = 8 Hz, 2H), 1.92 (m, 1H), 0.88 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): 208.1, 149.6, 142.6, 132.4, 128.9, 128.7, 127.7, 127.0, 118.9, 110.2, 49.0, 45.9, 21.1, 11.1; HRMS (ESI): cacld. for $C_{19}H_{17}NO$ $[M+H]^+$: 276.1383, found 276.1385.



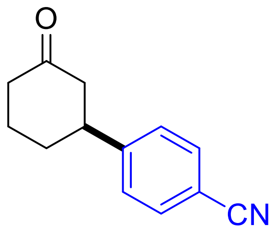
4-(3-(adamantan-1-yl)-3-oxo-1-phenylpropyl)benzonitrile (**5s**): 111 mg, 30% yield, colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): 7.55 (d, *J* = 8 Hz, 2H), 7.33 (d, *J* = 8 Hz, 2H), 7.28 (d, *J* = 8 Hz, 2H), 7.20 (m, 3H), 4.69 (t, *J* = 8 Hz, 1H), 3.22 (m, 2H), 2.01 (s, 3H), 1.69 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): 212.4, 149.9, 142.9, 132.3, 128.7, 128.6, 127.7, 126.8, 118.9, 110.0, 46.3, 45.3, 41.9, 37.9, 36.4, 27.7; HRMS (ESI): cacld. for $C_{26}H_{27}NO$ $[M+H]^+$: 370.2165, found 370.2166.



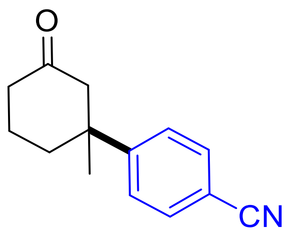
4-(4-Oxopentan-2-yl)benzonitrile (**5t**): 107 mg, 57% yield; white solid, m.p. 65-66 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): 7.58 (d, *J* = 8 Hz, 2H), 7.33 (d, *J* = 8 Hz, 2H), 3.39 (m, 1H), 2.74 (m, 2H), 2.09 (s, 3H), 1.27 (d, *J* = 8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 206.5, 151.7, 132.3, 127.7, 118.8, 110.1, 51.1, 35.1, 30.4, 21.5; These data are in accordance with the literature.[6]



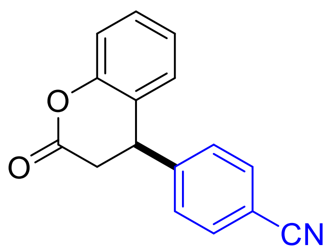
4-(3-Oxocyclopentyl)benzonitrile (**5u**): 54 mg, 29% yield; white solid, m.p. 50-51 °C; ^{1}H NMR (400 MHz, $CDCl_3$): 7.64 (d, *J* = 8 Hz, 2H), 7.38 (d, *J* = 8 Hz, 2H), 3.49 (m, 1H), 2.71 (dd, *J* = 20 Hz, *J* = 8 Hz, 1H), 2.50 (m, 2H), 2.33 (dd, *J* = 16 Hz, *J* = 8 Hz, 2H), 1.99 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): 216.7, 148.5, 132.5, 127.6, 118.7, 110.7, 45.2, 42.2, 38.6, 30.8; These data are in accordance with the literature.[5]



4-(3-Oxocyclohexyl)benzonitrile (**5v**): 70 mg, 35% yield; white solid, m.p. 97-98 °C; ^{1}H NMR (400 MHz, $CDCl_3$): 7.64 (d, *J* = 8 Hz, 2H), 7.35 (d, *J* = 8 Hz, 2H), 3.09 (t, *J* = 12 Hz, 1H), 2.49 (m, 4H), 2.14 (m, 2H), 1.86 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): 216.7, 148.5, 132.5, 127.6, 118.7, 110.7, 45.2, 42.2, 38.6, 30.8; These data are in accordance with the literature.[7]

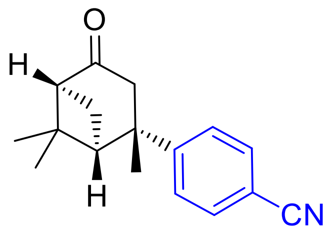


4-(3-Oxocyclohexyl)benzonitrile (**5w**): 173 mg, 81% yield; white solid, m.p. 114-115 °C; ^{1}H NMR (400 MHz, $CDCl_3$): 7.62 (d, *J* = 8 Hz, 2H), 7.44 (d, *J* = 8 Hz, 2H), 2.86 (d, *J* = 16 Hz, 1H), 2.48 (d, *J* = 16 Hz, 1H), 2.33 (m, 2H), 2.21 (m, 1H), 1.95 (m, 2H), 1.62 (m, 1H), 1.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 210.2, 152.8, 132.4, 126.5, 118.7, 110.2, 52.6, 43.3, 40.6, 37.6, 29.6, 21.9; HRMS (ESI): cacld. for $C_{14}H_{15}NO$ $[M+H]^+$: 214.1226, found 214.1224.

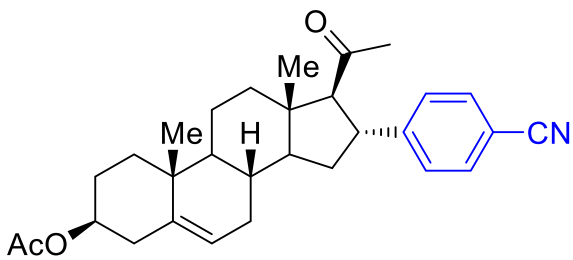


(R)-4-(2-oxochroman-4-yl)benzonitrile (**5x**): 82 mg, 33% yield; white solid, m.p. 154-155 °C; ^{1}H NMR

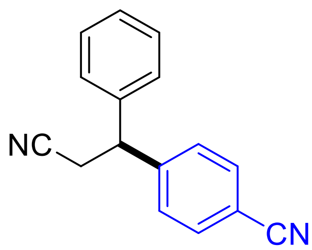
(400 MHz, $CDCl_3$): 7.65 (d, *J* = 8 Hz, 2H), 7.36 (t, *J* = 8 Hz, 1H), 7.29 (d, *J* = 8 Hz, 2H), 7.15 (m, 2H), 7.00 (d, *J* = 8 Hz, 1H), 4.44 (t, *J* = 8 Hz, 1H), 3.13 (dd, *J* = 16 Hz, *J* = 8 Hz, 1H), 3.03 (dd, *J* = 16 Hz, *J* = 4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): 166.6, 151.6, 145.7, 132.9, 129.4, 128.3, 128.1, 124.9, 124.0, 118.3, 117.4, 111.6, 40.6, 36.5; HRMS (ESI): cacld. for $C_{16}H_{11}NO_2$ [M+H]$^+$: 250.0863, found 250.0864.



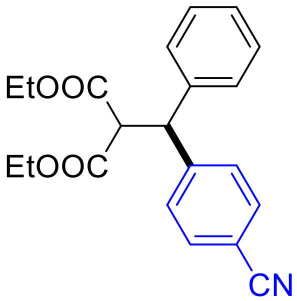
4-((1R,2S,5S)-2,6,6-Trimethyl-4-oxobicyclo[3.1.1]heptan-2-yl)benzonitrile (**5y**): 114 mg, 45% yield; white solid, m.p. 142-143 °C; ^{1}H NMR (400 MHz, $CDCl_3$): 7.64 (d, *J* = 8 Hz, 2H), 7.36 (d, *J* = 8 Hz, 2H), 3.10 (d, *J* = 20 Hz, 1H), 2.89 (d, *J* = 20 Hz, 1H), 2.64 (m, 3H), 1.49 (s, 3H), 1.46 (s, 3H), 1.31 (m, 1H), 1.16 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 211.9, 157.2, 132.3, 126.6, 118.7, 109.6, 56.2, 50.1, 48.1, 41.0, 39.9, 31.4, 27.5, 26.6, 25.4; HRMS (ESI): cacld. for $C_{17}H_{19}NO$ [M+H]$^+$: 254.1539, found 254.1537.



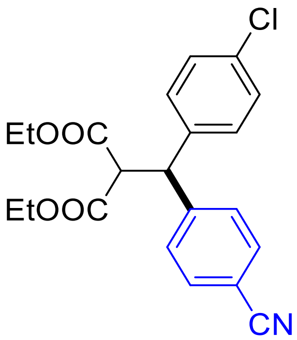
(3S,8S,10R,13S,16R,17S)-17-Acetyl-16-(4-cyanophenyl)-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl acetate (**5z**): 372 mg, 81% yield; white solid, m.p. 183-185 °C; ^{1}H NMR (400 MHz, $CDCl_3$): 7.48 (d, *J* = 8.0 Hz, 2H), 7.23 (d, *J* = 8.0 Hz, 2H), 5.32 (s, 1H), 4.55 (m, 1H), 3.84 (d, *J* = 8.0 Hz, 1H), 2.55 (d, *J* = 12.0 Hz,1H), 2.28 (m, 2H), 1.98 (s, 7 H), 1.66 (m, 12 H), 1.13 (m, 2H), 0.98 (s, 3H), 0.69 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 207.3, 170.5, 152.8, 139.6, 132.3, 128.0, 121.9, 119.0, 109.5, 74.0, 73.6, 57.4, 49.7, 45.7, 42.0, 38.7, 37.9, 36.9, 36.5, 33.8, 31.8, 31.7, 31.6, 27.6, 21.4, 20.8, 19.2, 13.8; HRMS (ESI): cacld. for $C_{30}H_{37}NO_3$ [M+H]$^+$: 460.2846, found 460.2859.



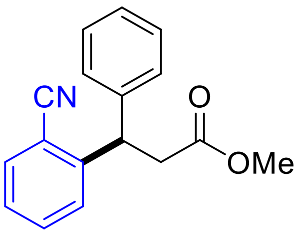
4-(2-Cyano-1-phenylethyl)benzonitrile (**5aa**): 188 mg, 81% yield, colorless oil; white solid, m.p. 113-114 °C; ^{1}H NMR (400 MHz, $CDCl_3$): 7.63 (d, *J* = 8 Hz, 2H), 7.34 (m, 5H), 7.19 (d, *J* = 8 Hz, 2H), 4.43 (t, *J* = 8 Hz, 1H), 3.05 (d, *J* = 8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): 146.4, 139.7, 132.7, 129.2, 128.4, 127.9, 127.4, 118.3, 117.7, 111.5, 47.0, 23.7; These data are in accordance with the literature.[8]



Diethyl 2-((4-cyanophenyl)(phenyl)methyl)malonate (**5ab**): 249 mg, 71% yield, colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): 7.56 (d, *J* = 8 Hz, 2H), 7.42 (d, *J* = 8 Hz, 2H), 7.24 (m, 5H), 4.81 (d, *J* = 12 Hz, 1H), 4.31 (d, *J* = 12 Hz, 1H), 4.02 (m, 4H), 1.04 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): 167.2, 167.1, 146.9, 139.8, 132.4, 128.8, 128.6, 127.8, 127.4, 118.5, 110.8, 61.8, 61.7, 56.9, 51.0, 13.8, 13.9; HRMS (ESI): cacld. for $C_{21}H_{21}NO_4$ $[M+H]^+$: 352.1543, found 352.1534.



Diethyl 2-((4-chlorophenyl)(4-cyanophenyl)methyl)malonate (**5ac**): 293 mg, 76% yield; white solid, m.p. 70-71 °C; ^{1}H NMR (400 MHz, $CDCl_3$): 7.58 (d, *J* = 12 Hz, 2H), 7.39 (d, *J* = 8 Hz, 2H), 7.26 (d, *J* = 8 Hz, 2H), 7.20 (d, *J* = 8 Hz, 2H), 4.80 (d, *J* = 12 Hz, 1H), 4.27 (d, *J* = 12 Hz, 1H), 4.03 (m, 4H), 1.06 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): 167.0, 166.9, 146.3, 138.4, 133.4, 132.5, 129.1, 129.0, 128.5, 118.4, 111.1, 61.9, 56.7, 50.2, 13.8; HRMS (ESI): cacld. for $C_{21}H_{20}ClNO_4$ $[M+H]^+$: 386.1154, found 386.1149.



Methyl 3-(2-cyanophenyl)-3-phenylpropanoate (**6a**): 29 mg, 11% yield, colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): 7.60 (d, *J* = 8.0 Hz, 1H), 7.54 (t, *J* = 6.0 Hz, 1H), 7.42 (d, *J* = 8.0 Hz, 1H), 7.29 (m, 4H), 7.21 (m, 2H), 5.01 (t, *J* = 8.0 Hz, 1H), 3.59 (s, 3H), 3.14 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): 171.1, 146.8, 141.3, 133.3, 133.0, 128.7, 127.6, 127.2, 127.07, 127.06, 117.8, 112.8, 51.8, 44.8, 39.8; HRMS (ESI): cacld. for $C_{17}H_{15}NO_2$ $[M+H]^+$: 266.1176, found 266.1178.

11. References

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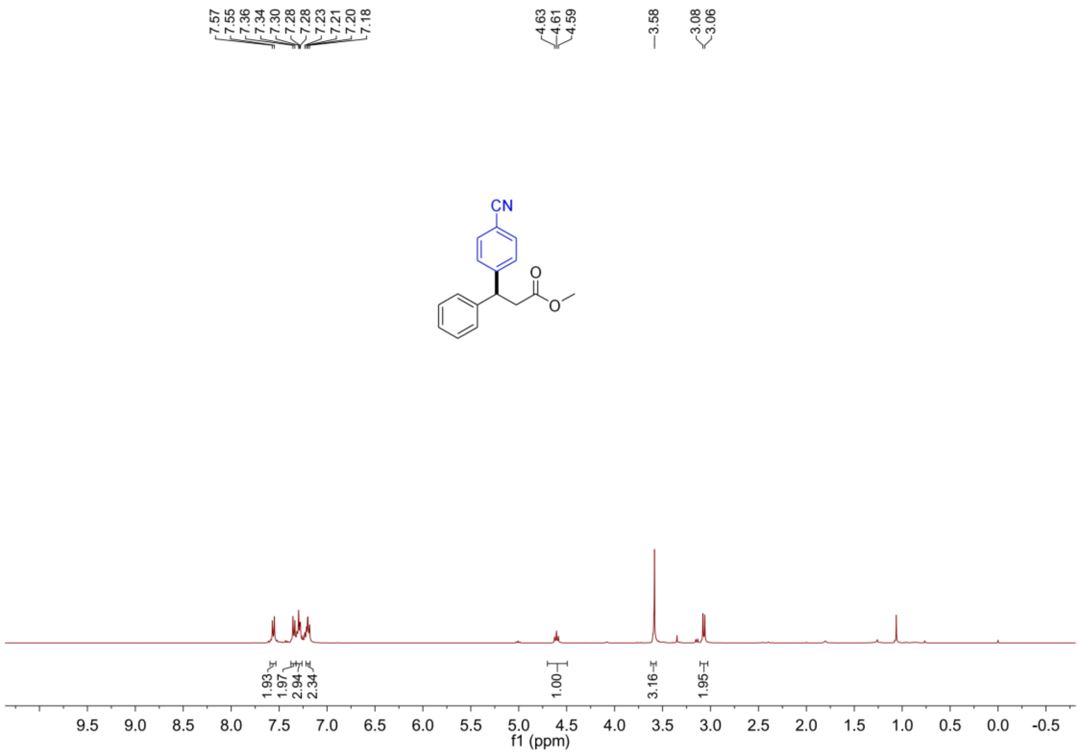
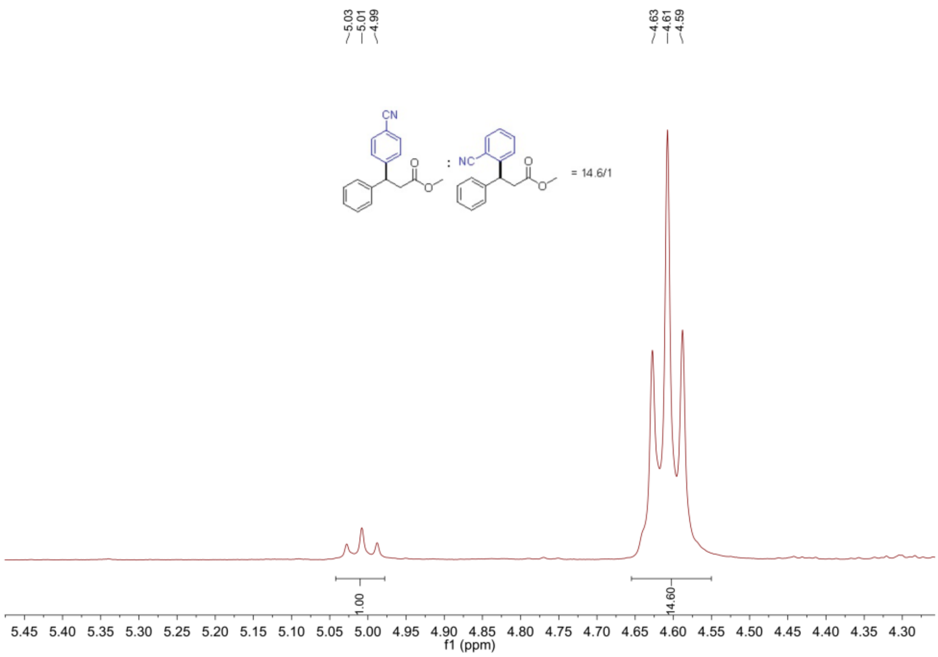
NMR spectra

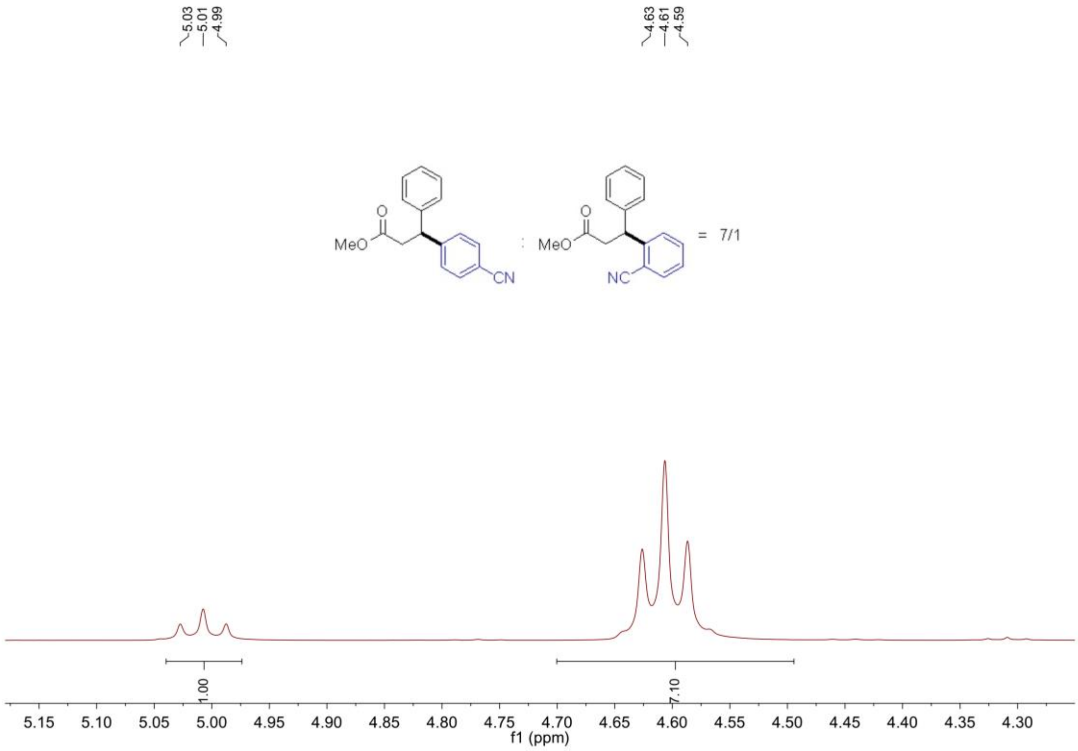
3a ^{1}HNMR



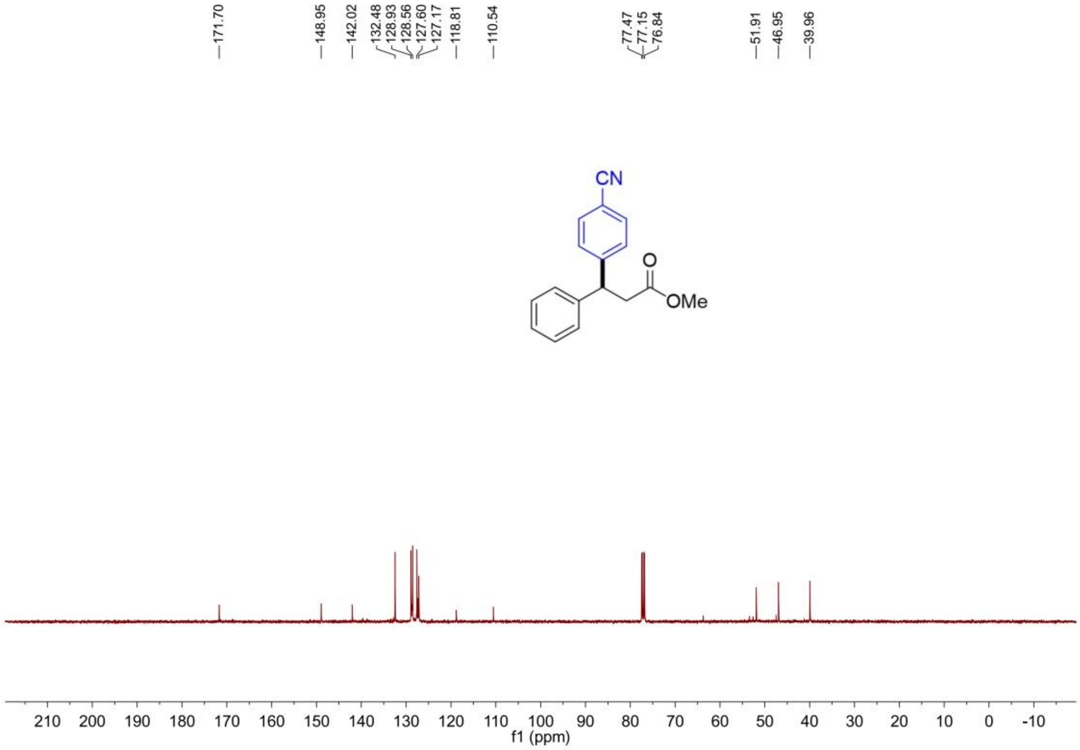
3a Regioselectivity



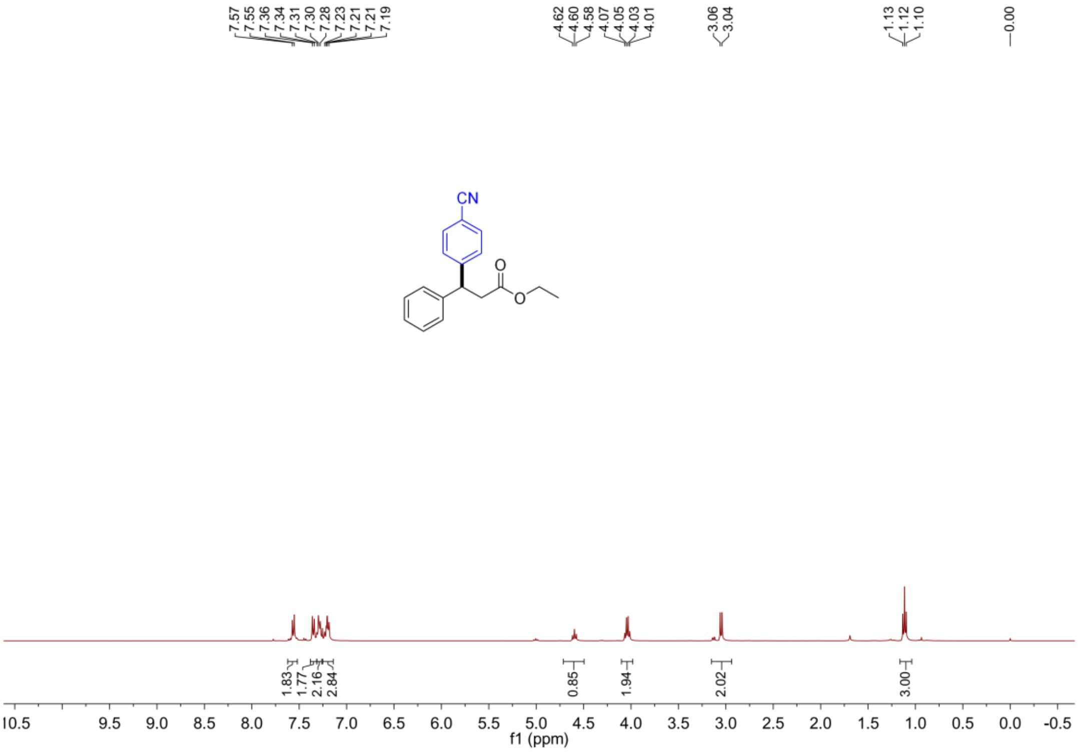
3a Regioselectivity (gram-scale reaction)



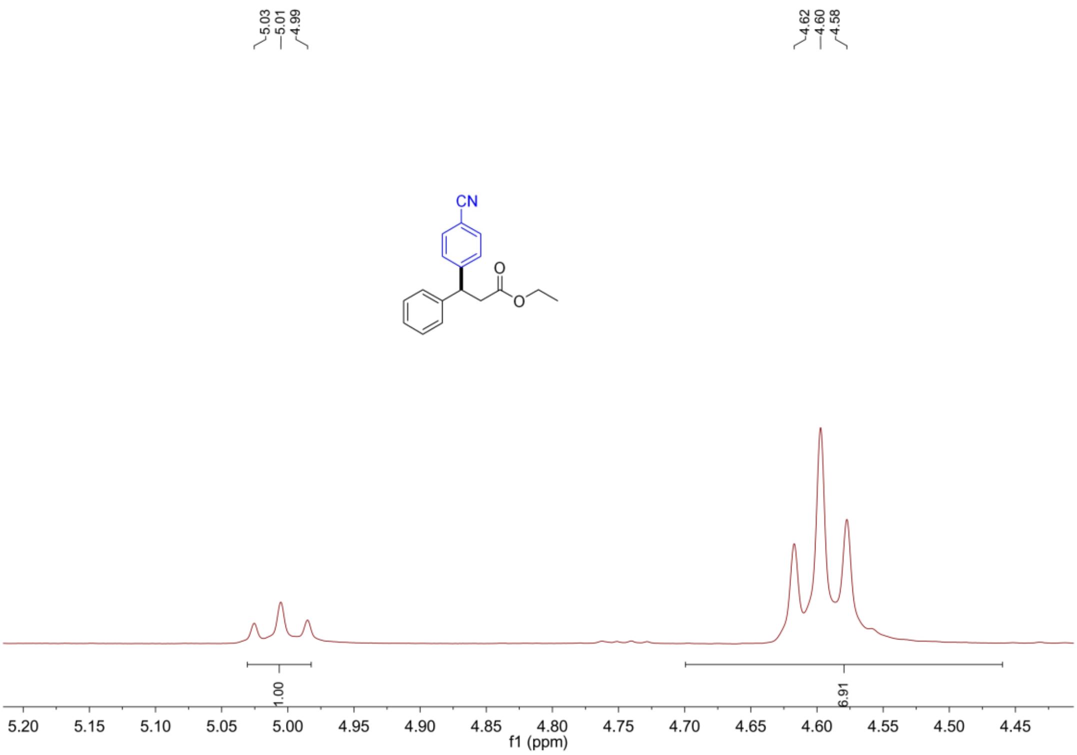
3a ^{13}CNMR



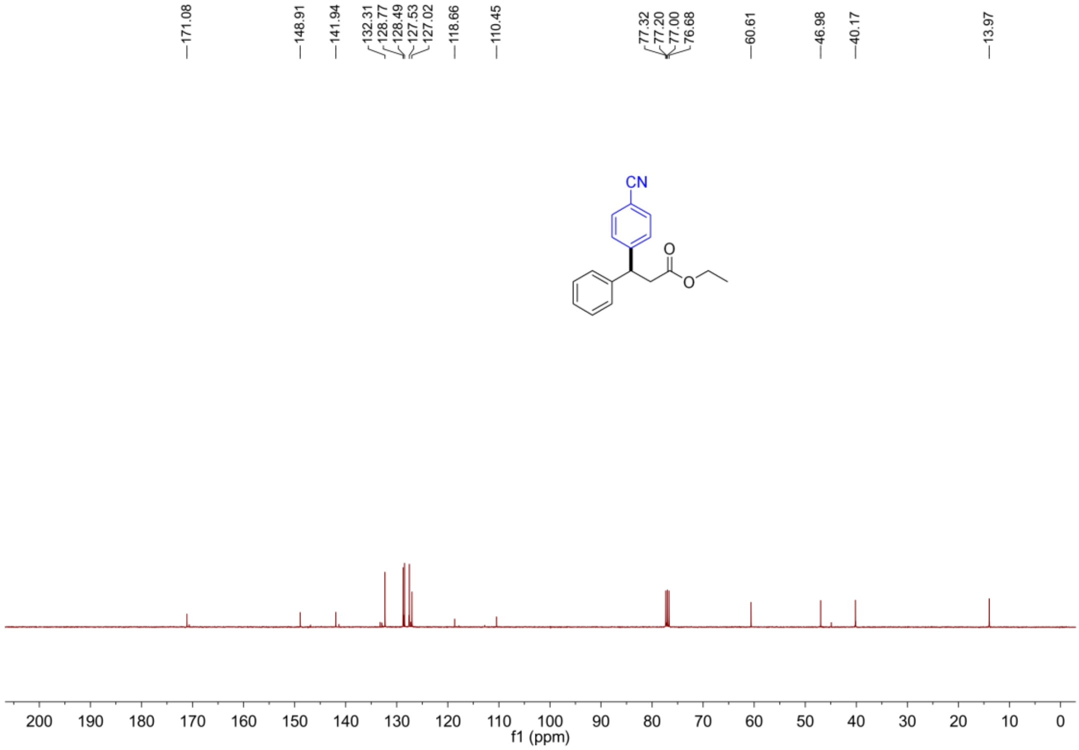
3b ^{1}HNMR



3b Regioselectivity



3b ^{13}CNMR



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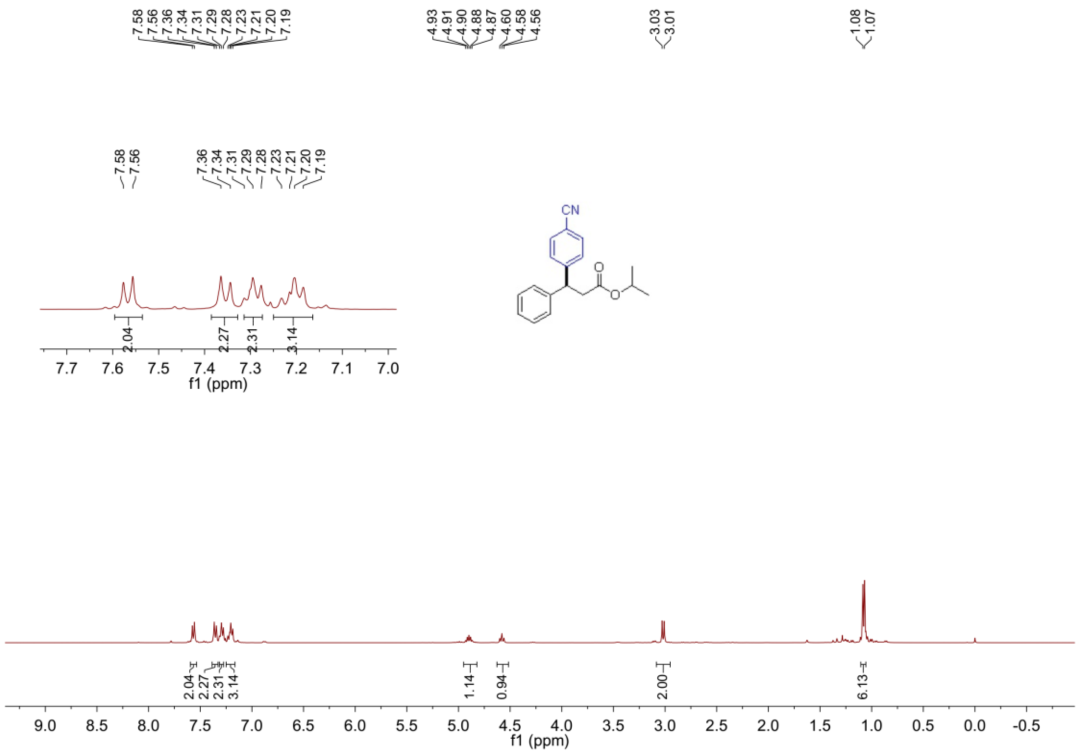

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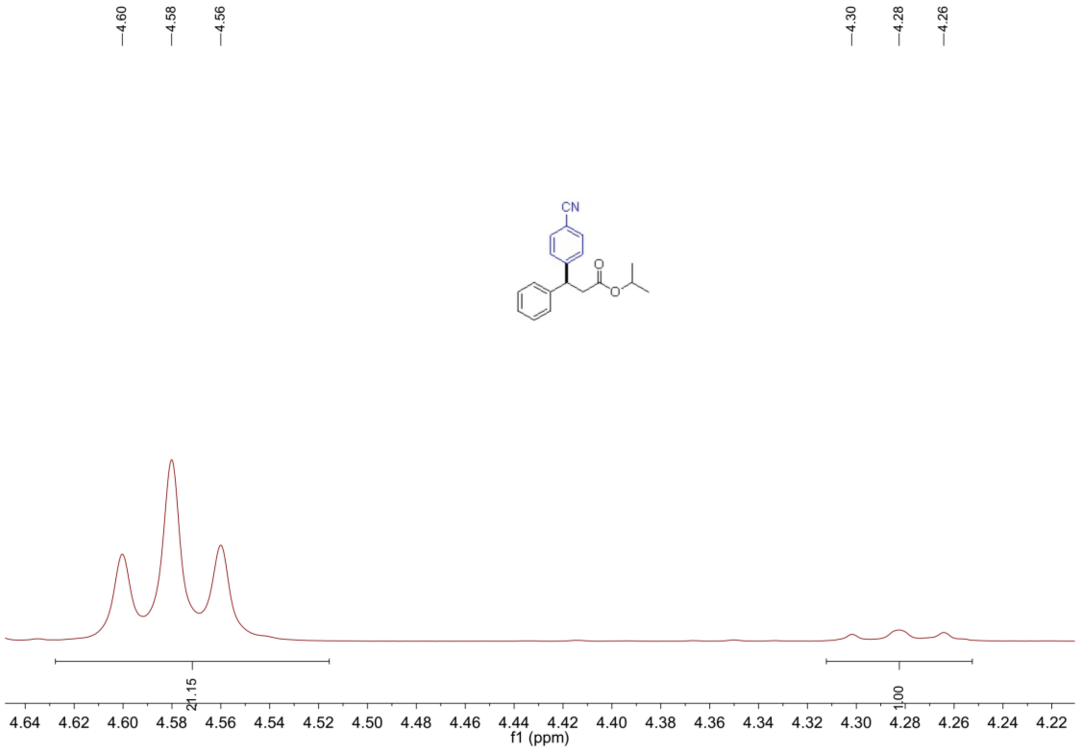

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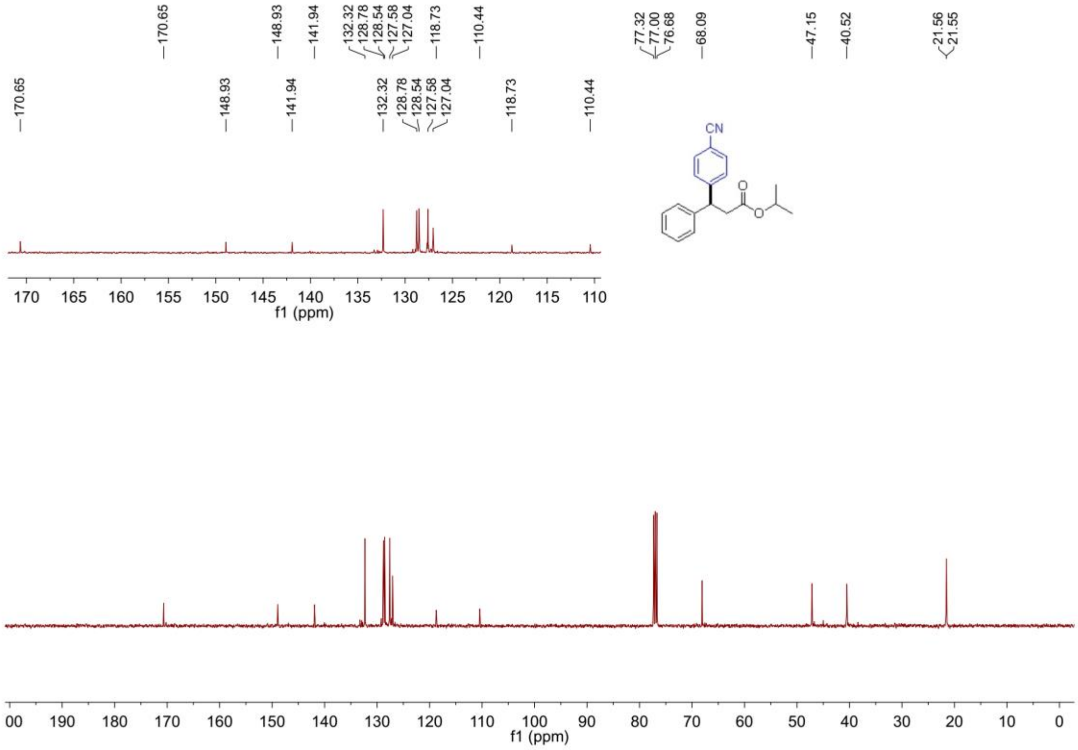

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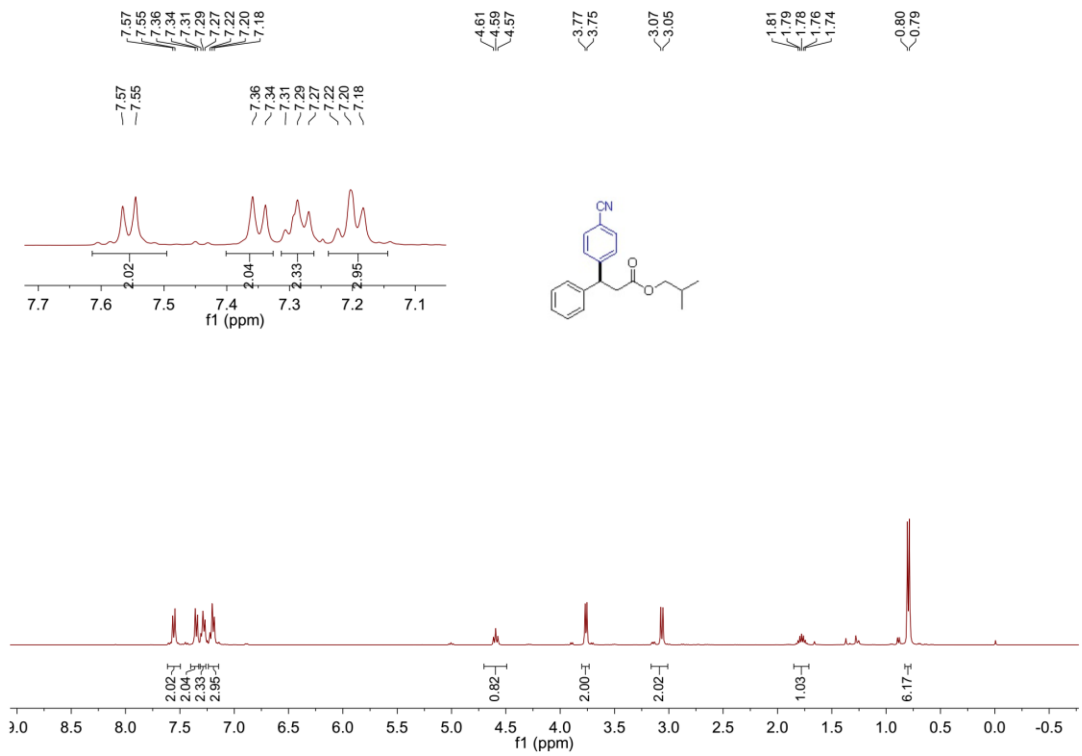

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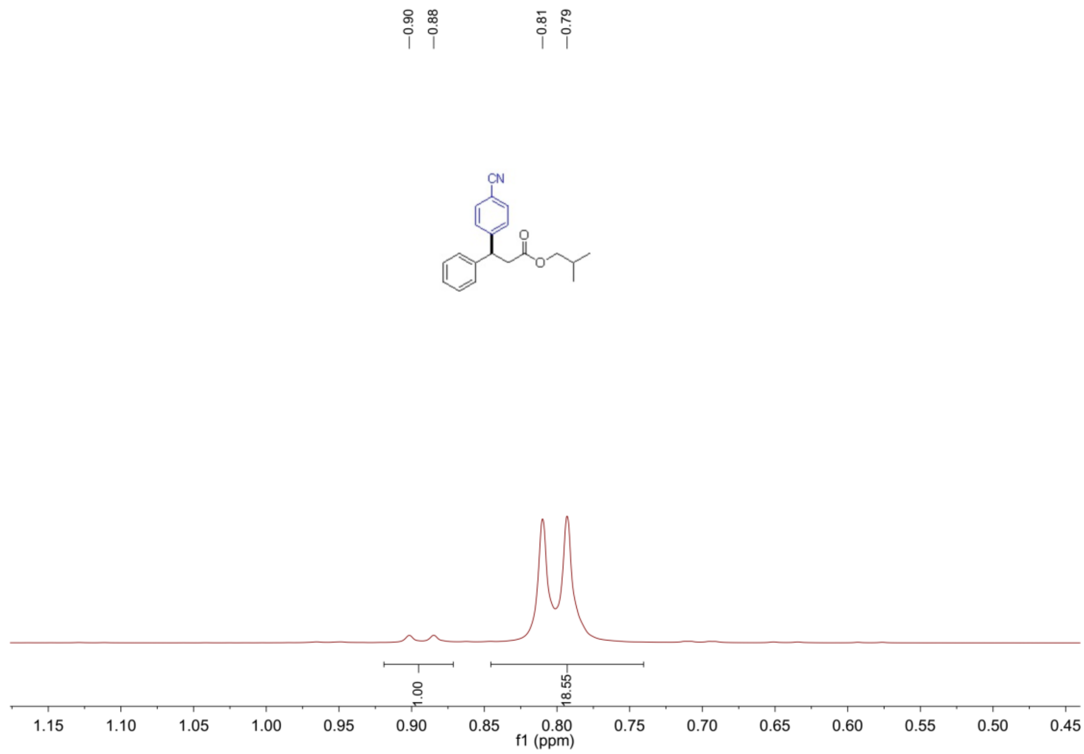

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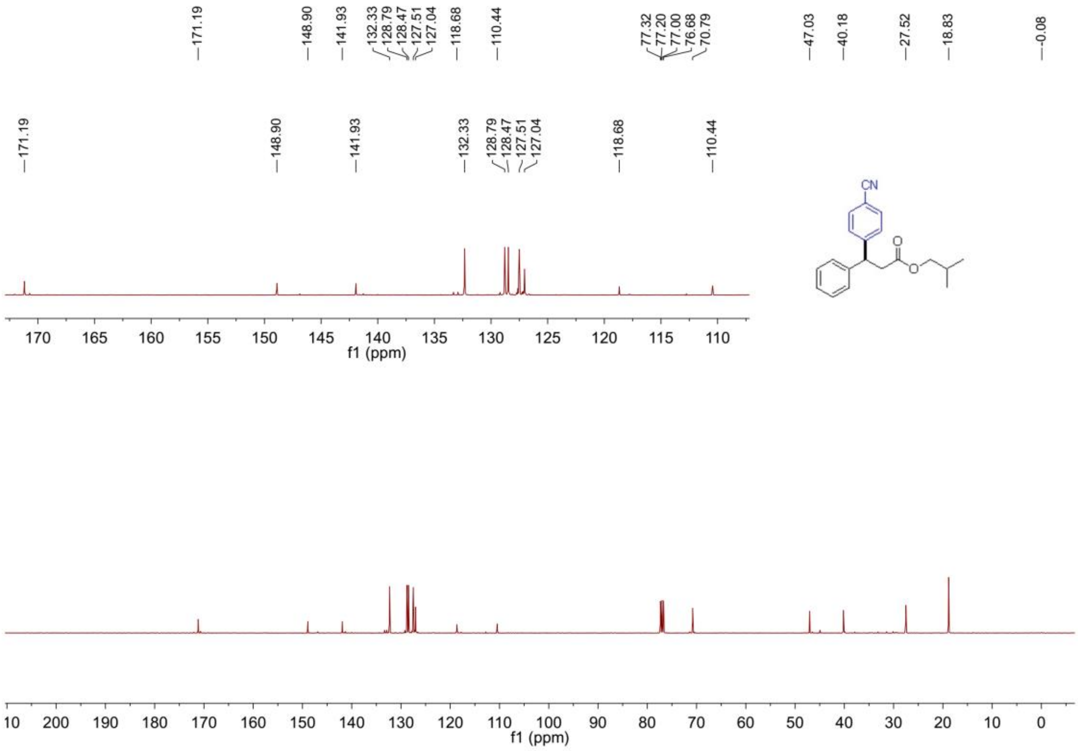

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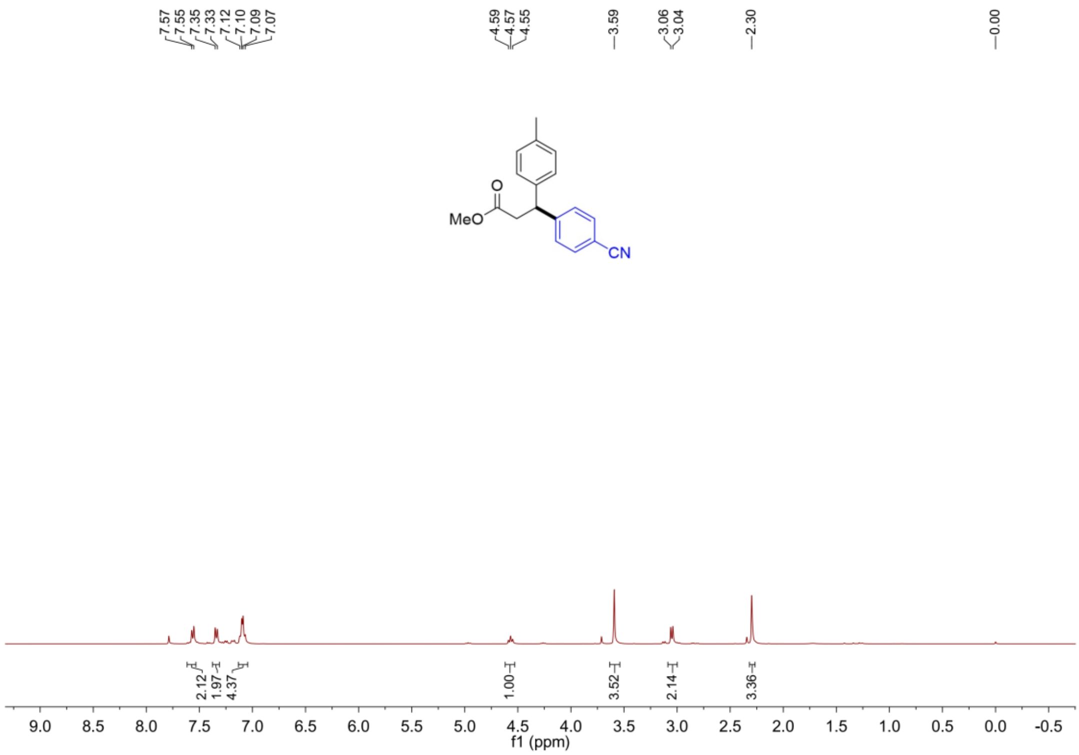

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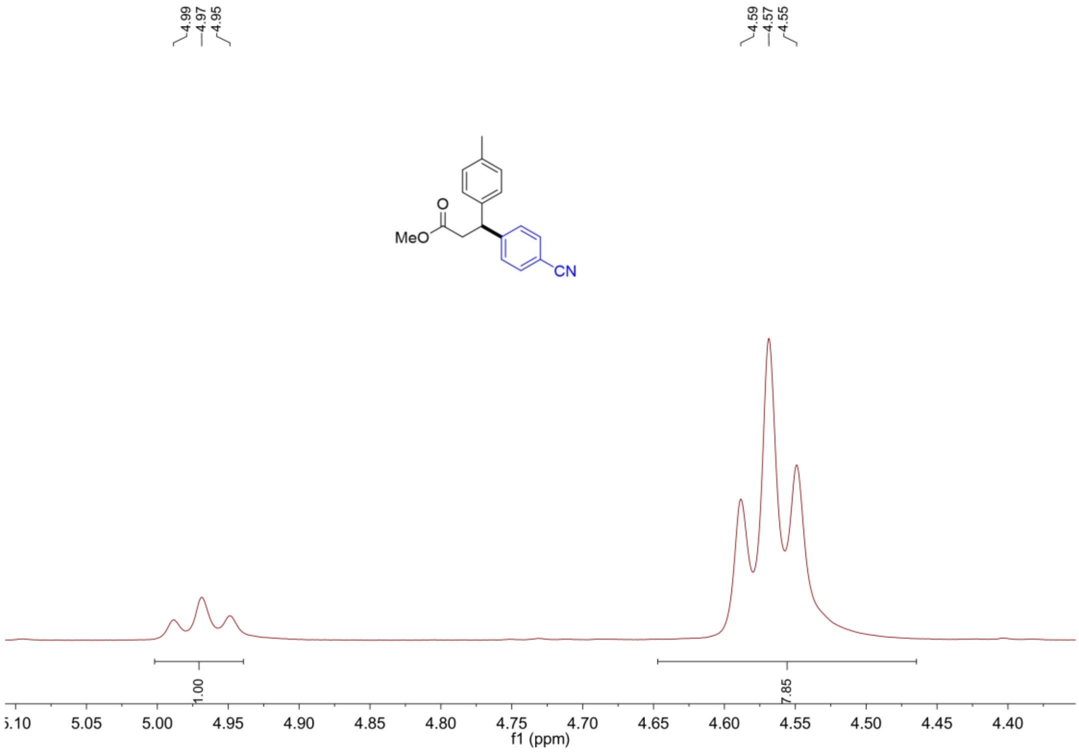

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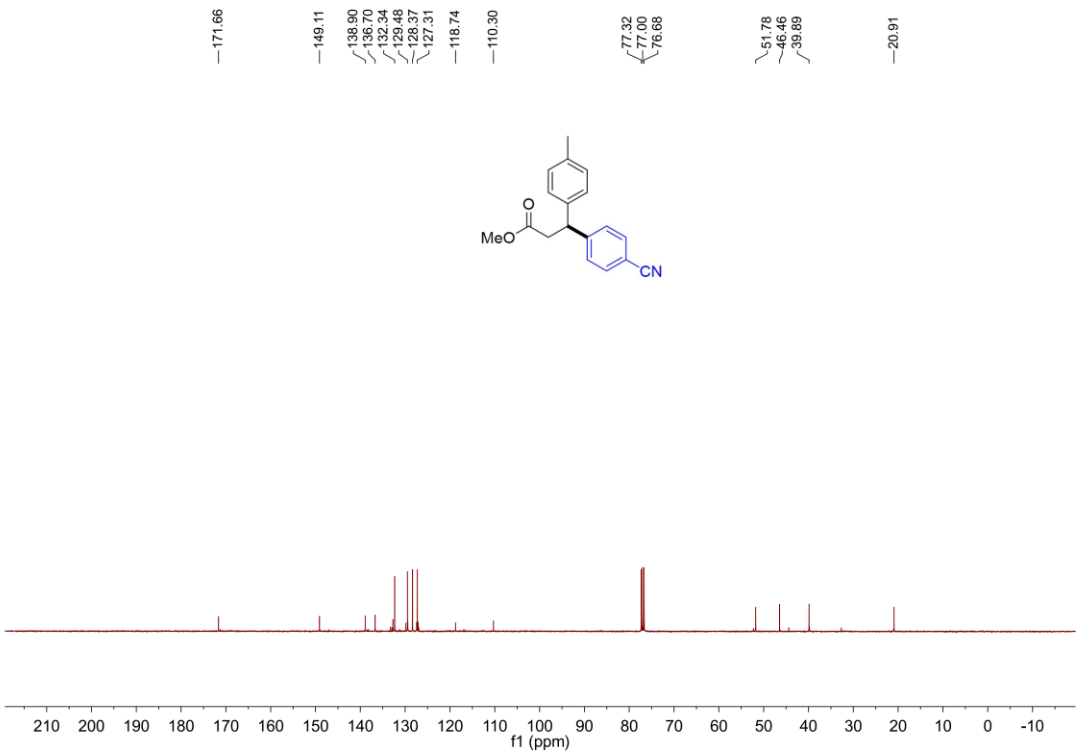

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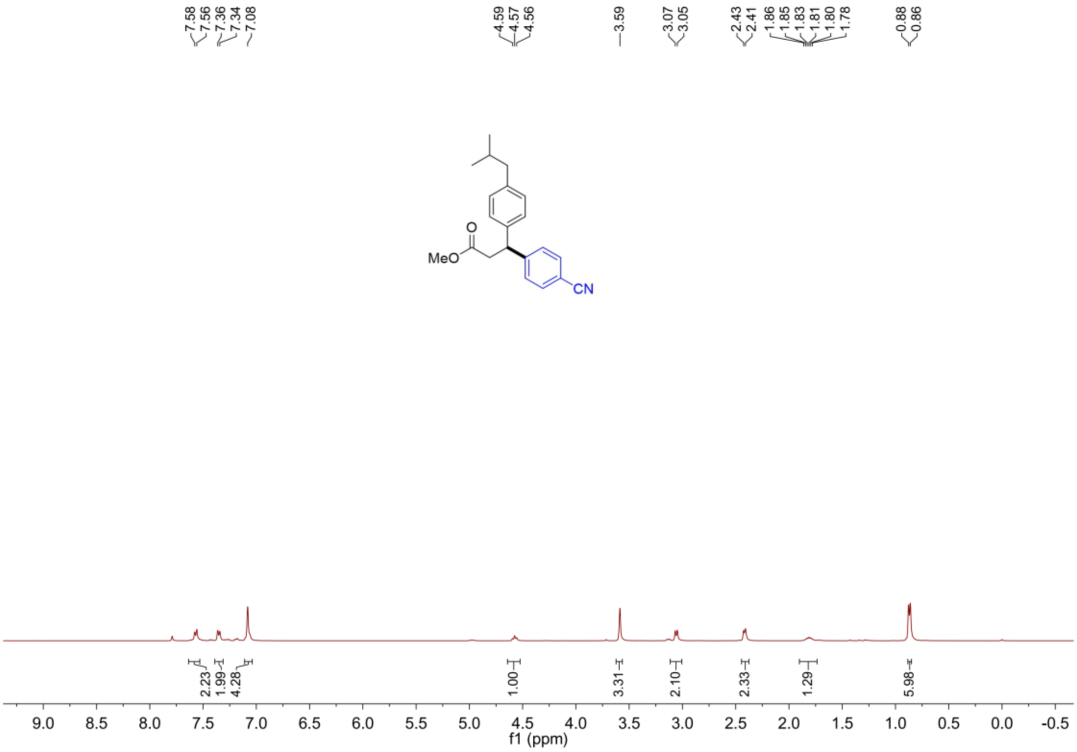

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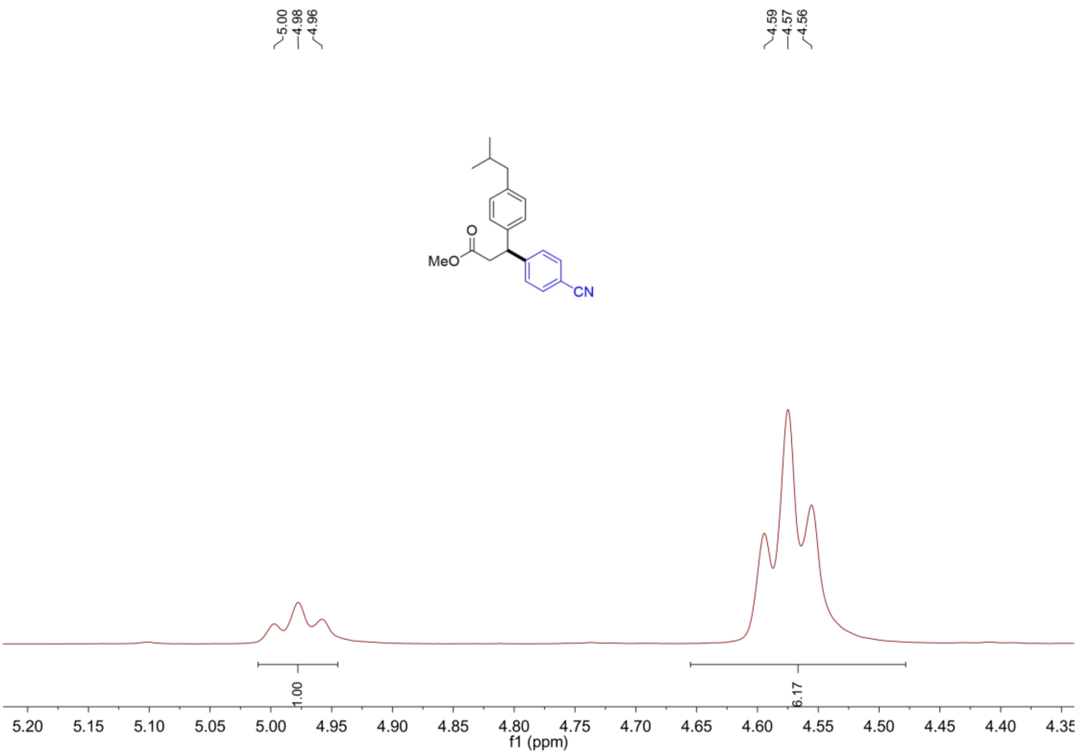

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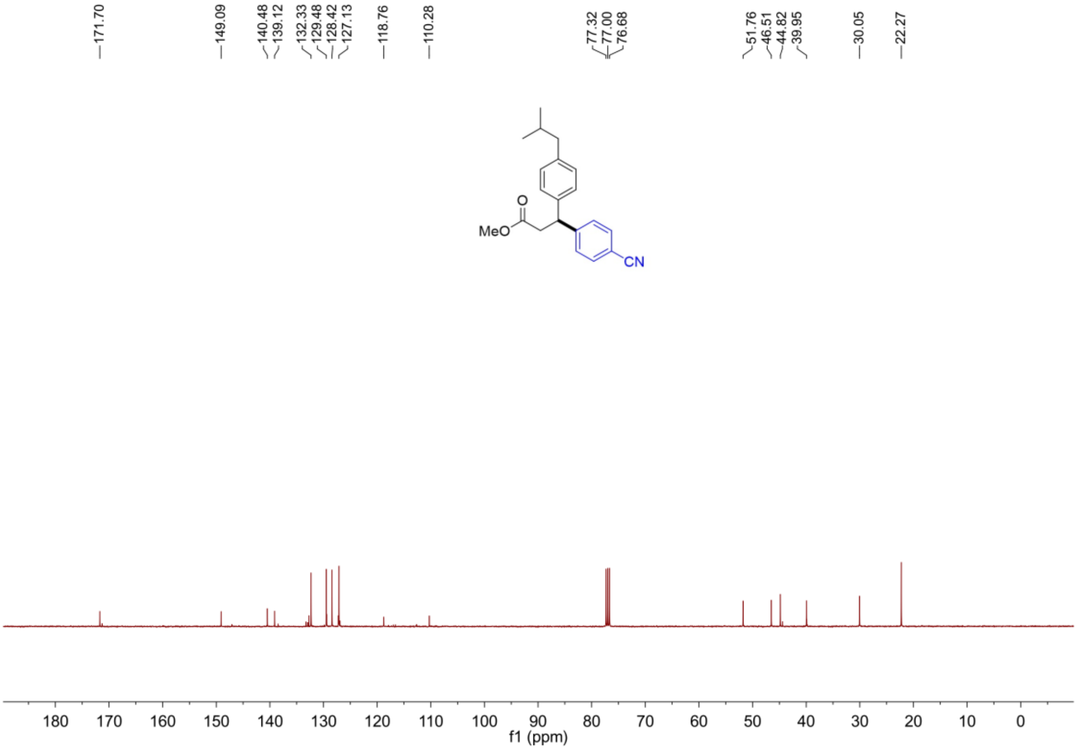

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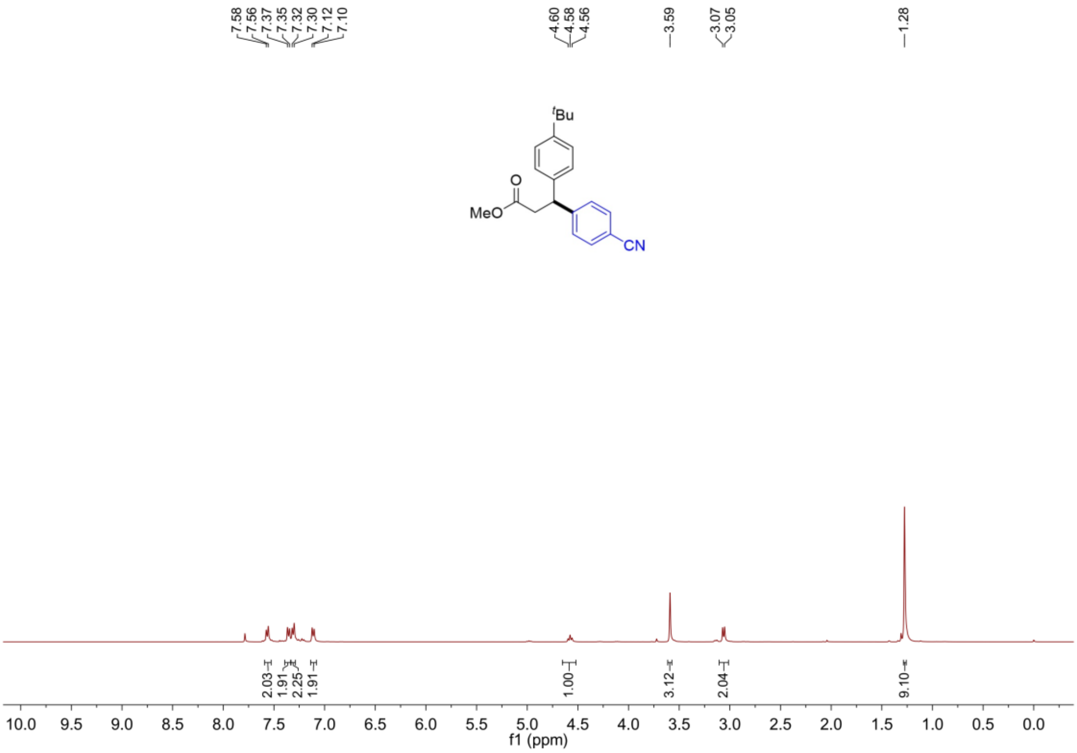
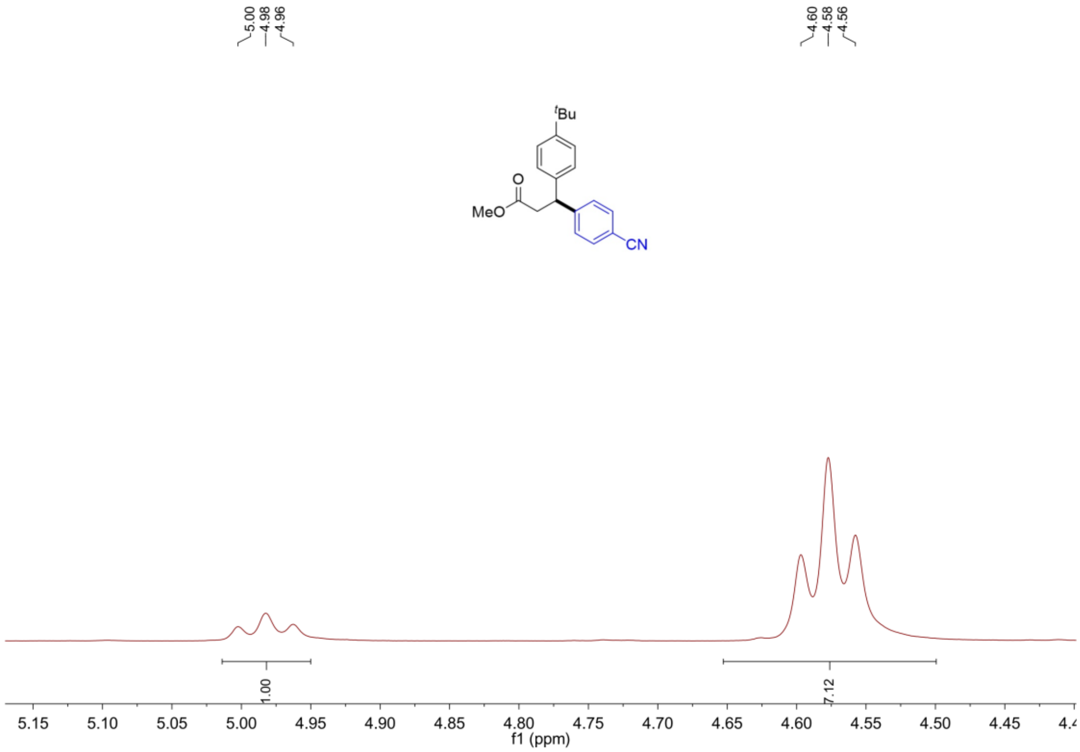


3g Regioselectivity



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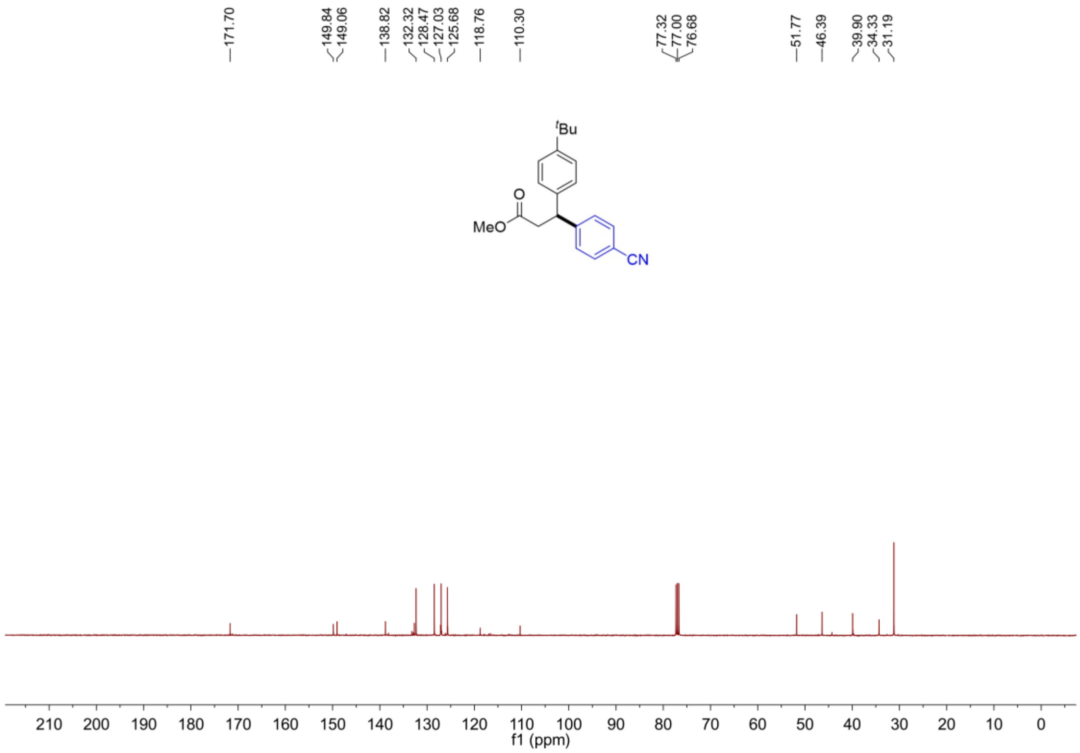

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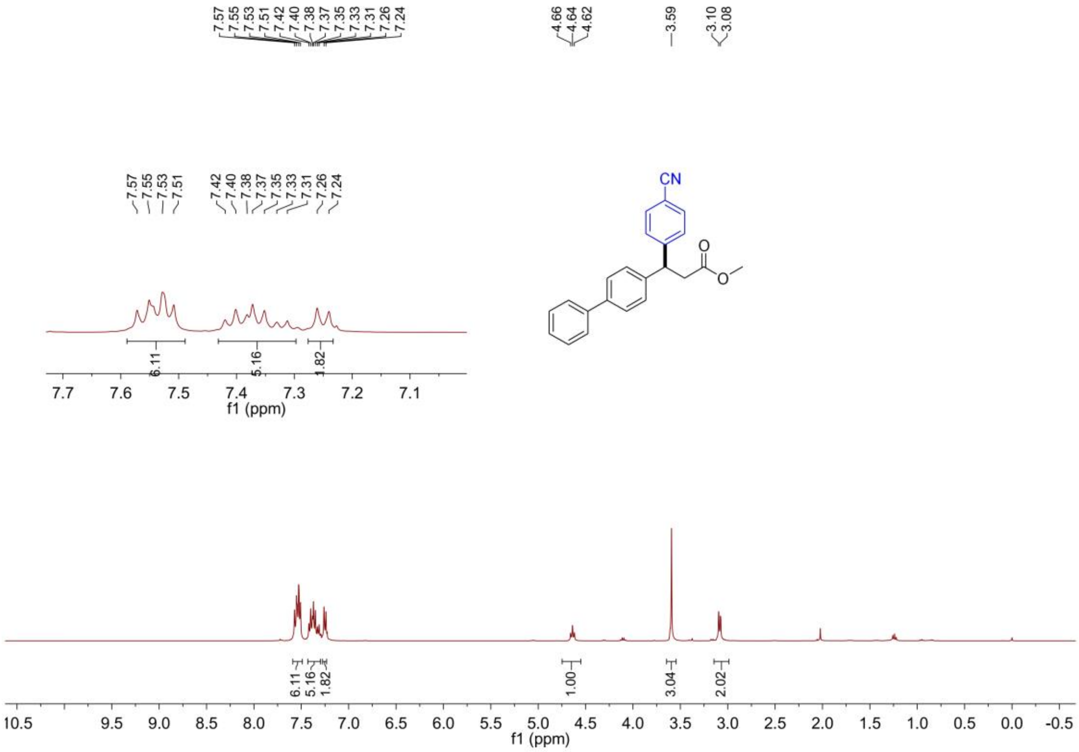

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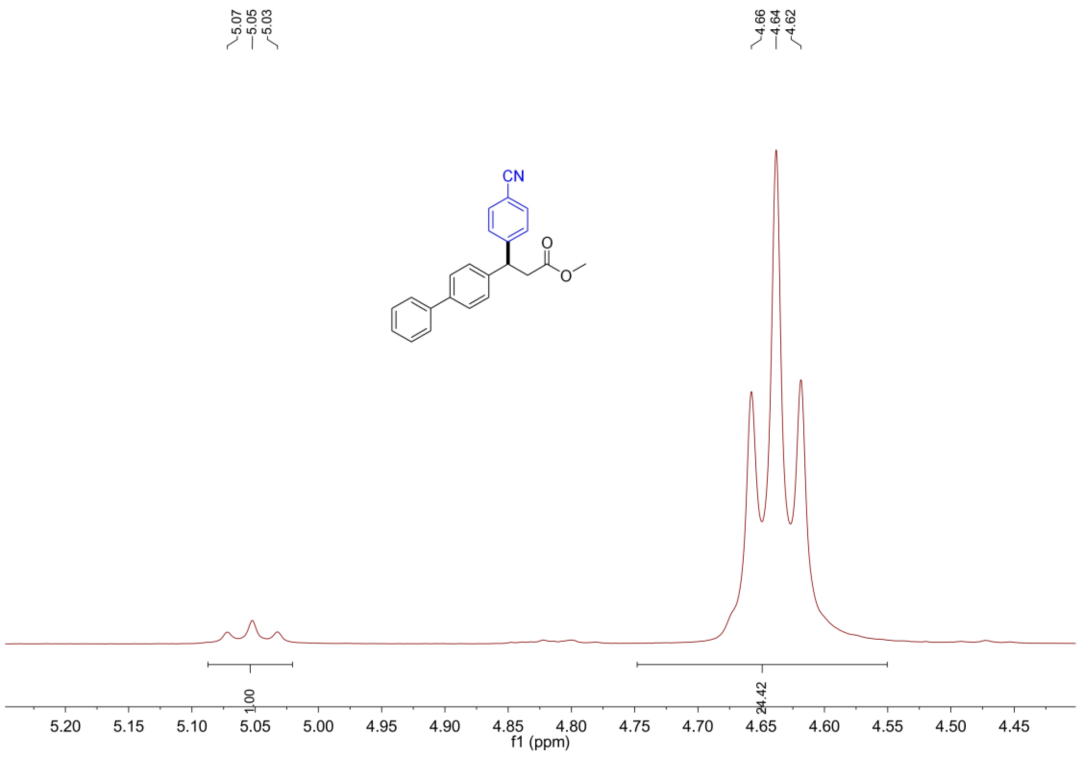

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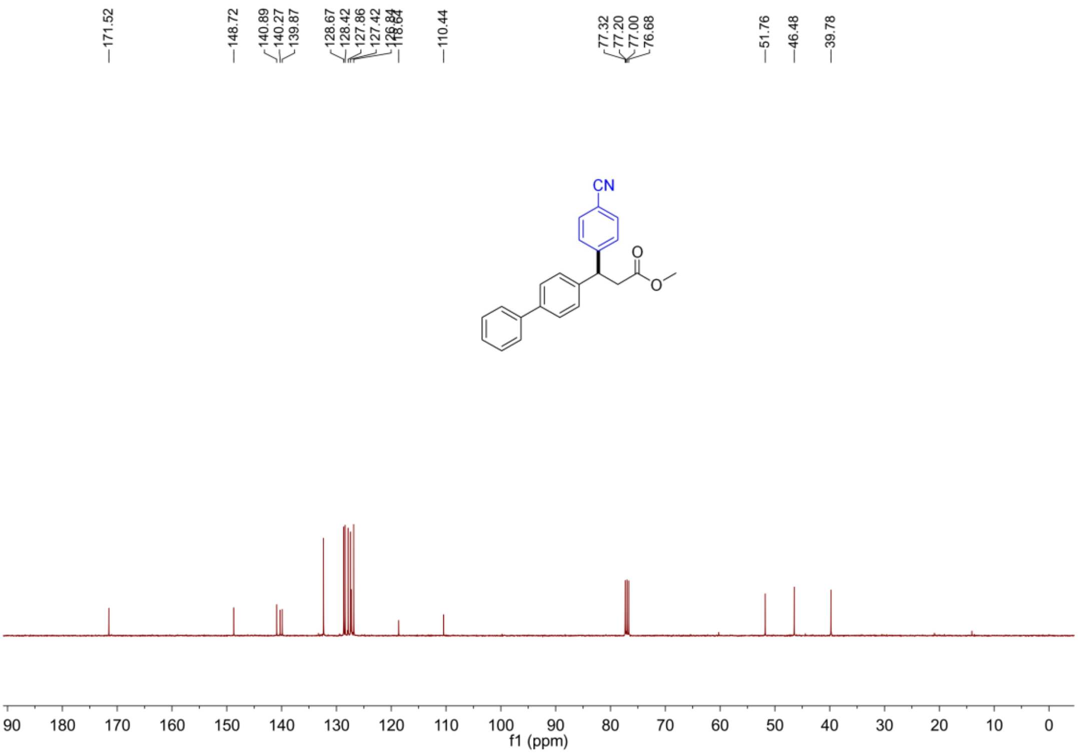

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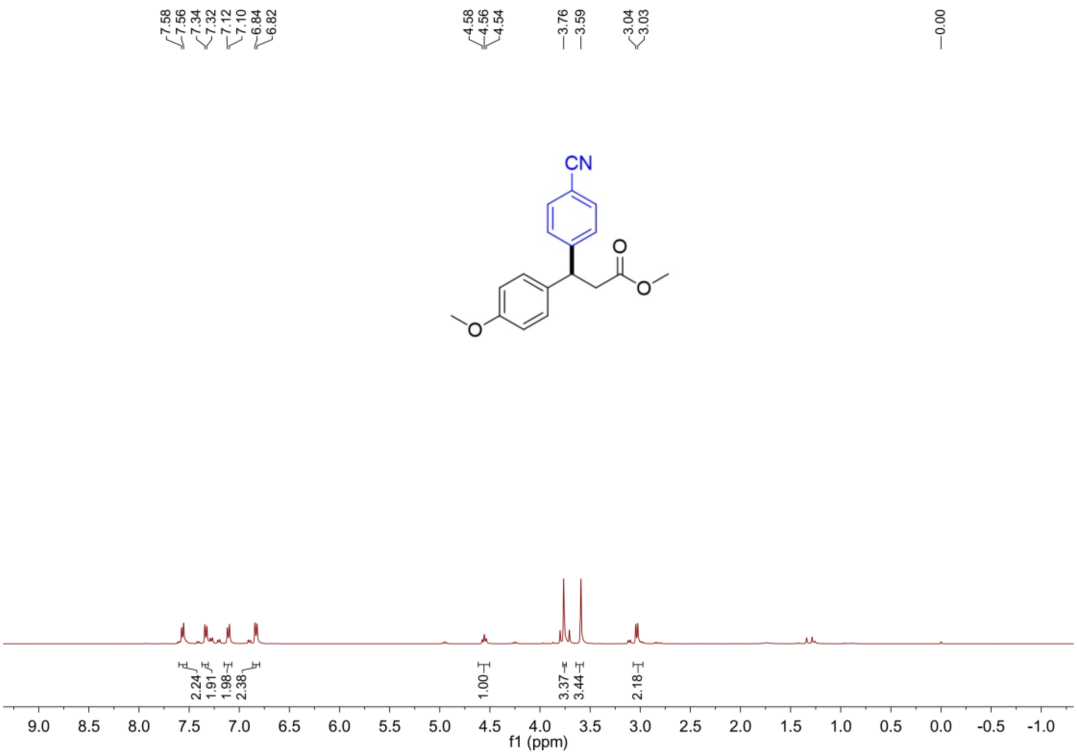
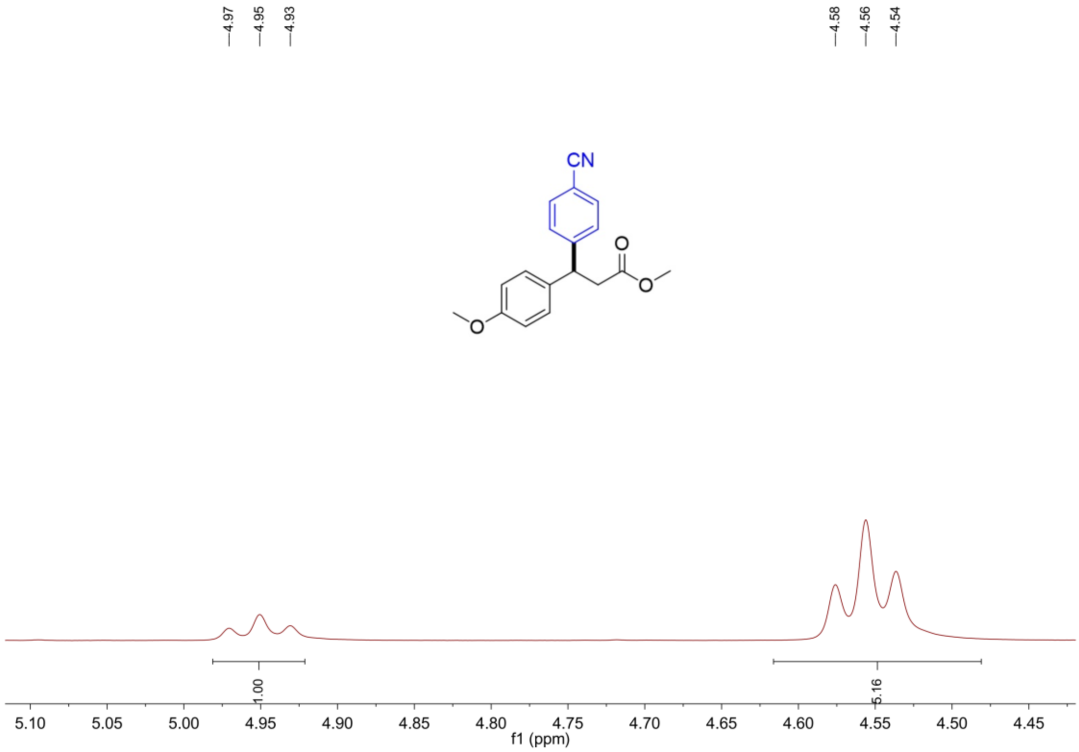


3i Regioselectivity



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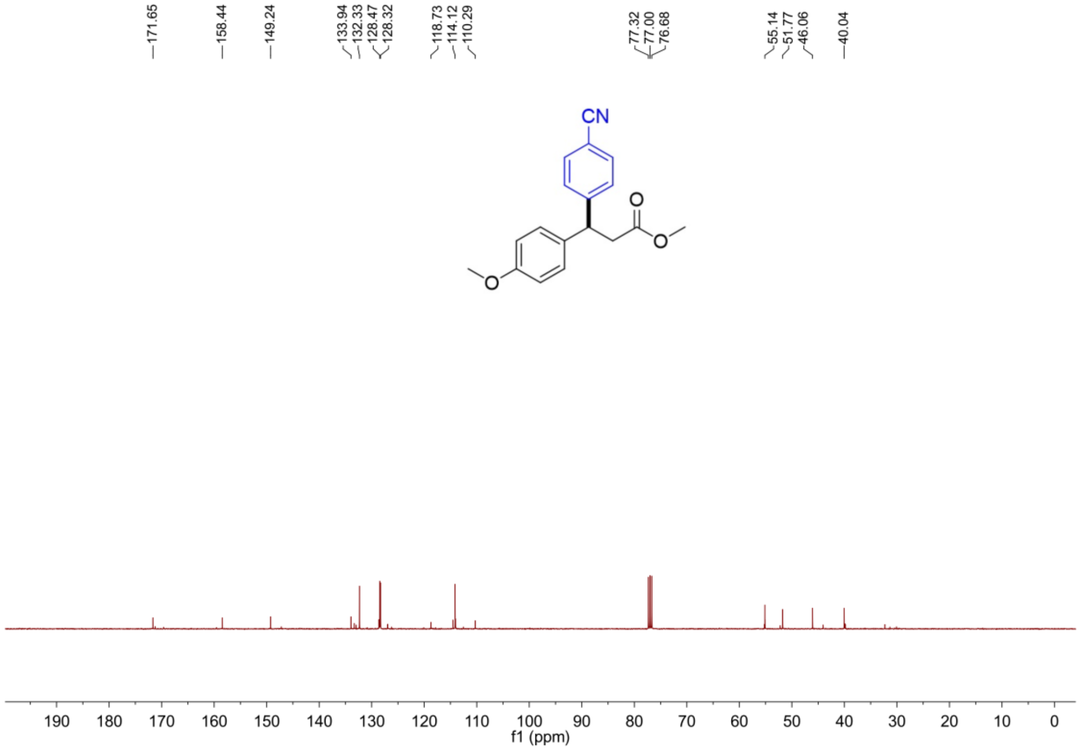

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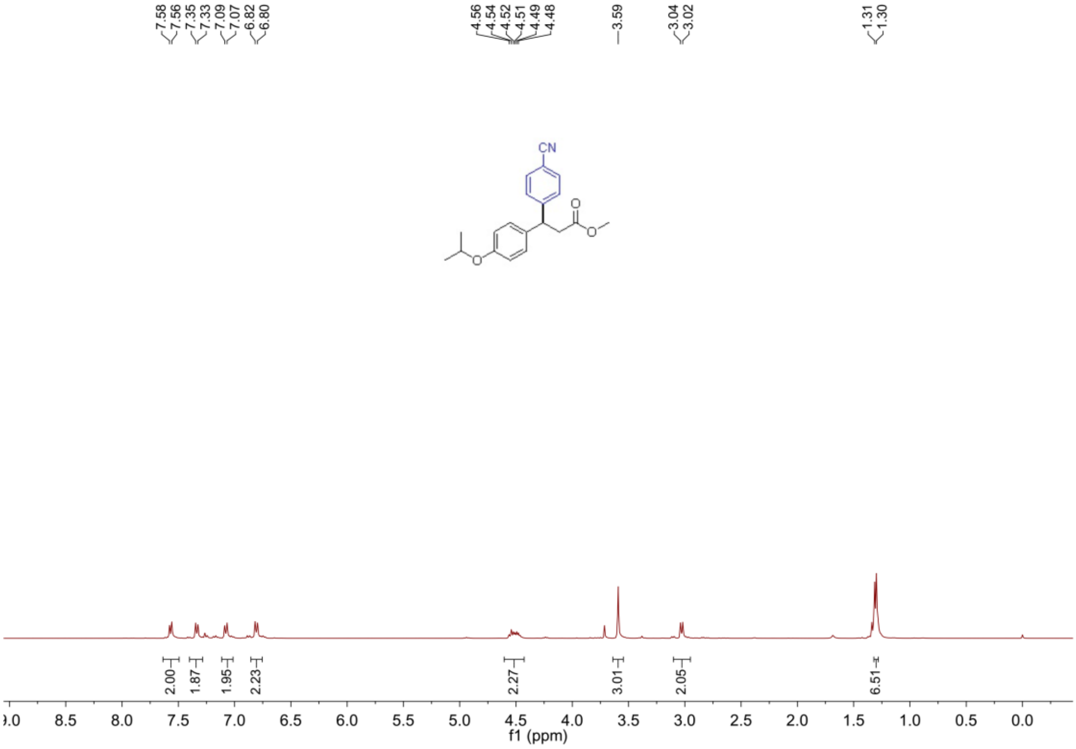

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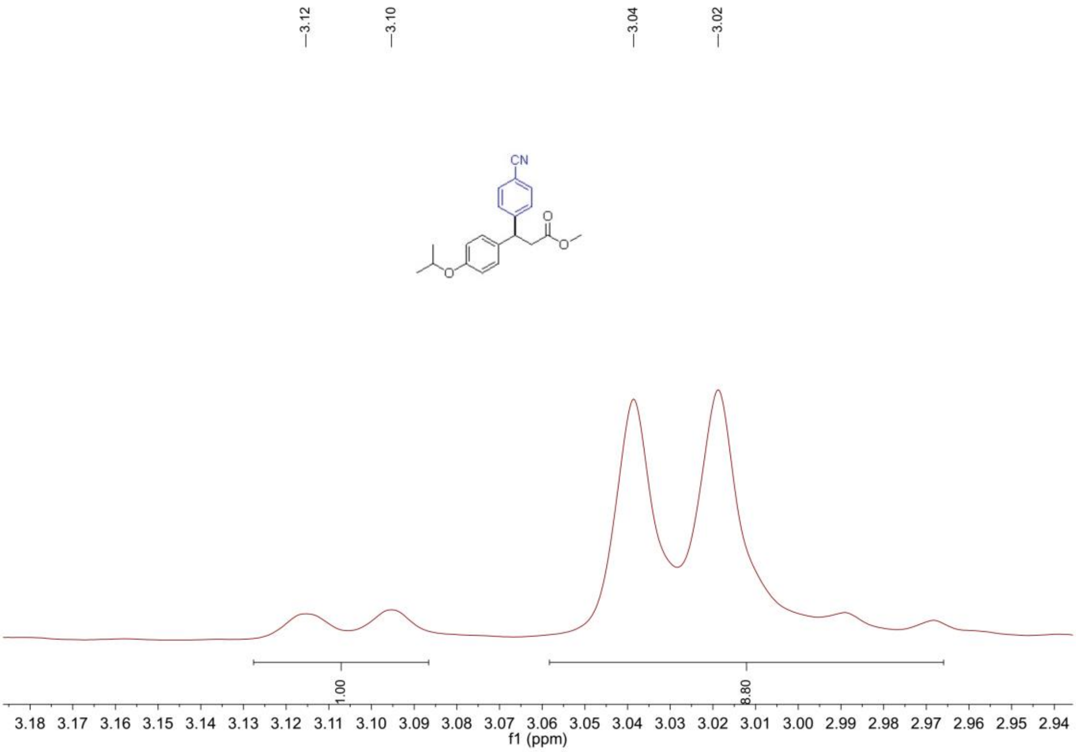

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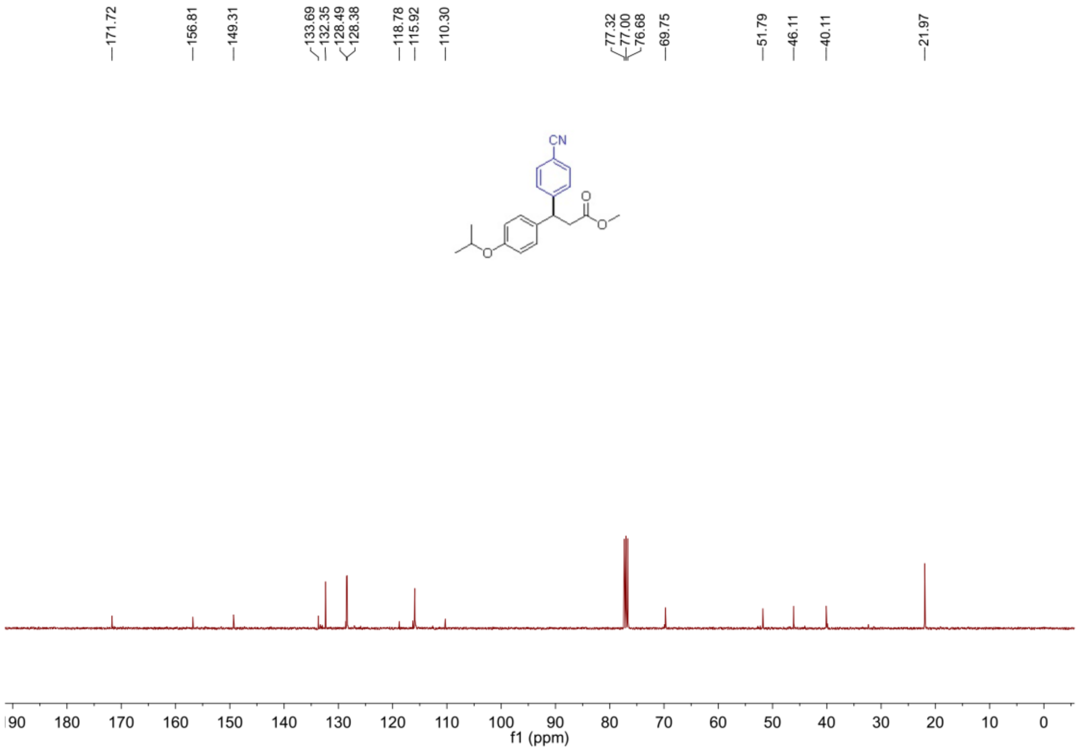

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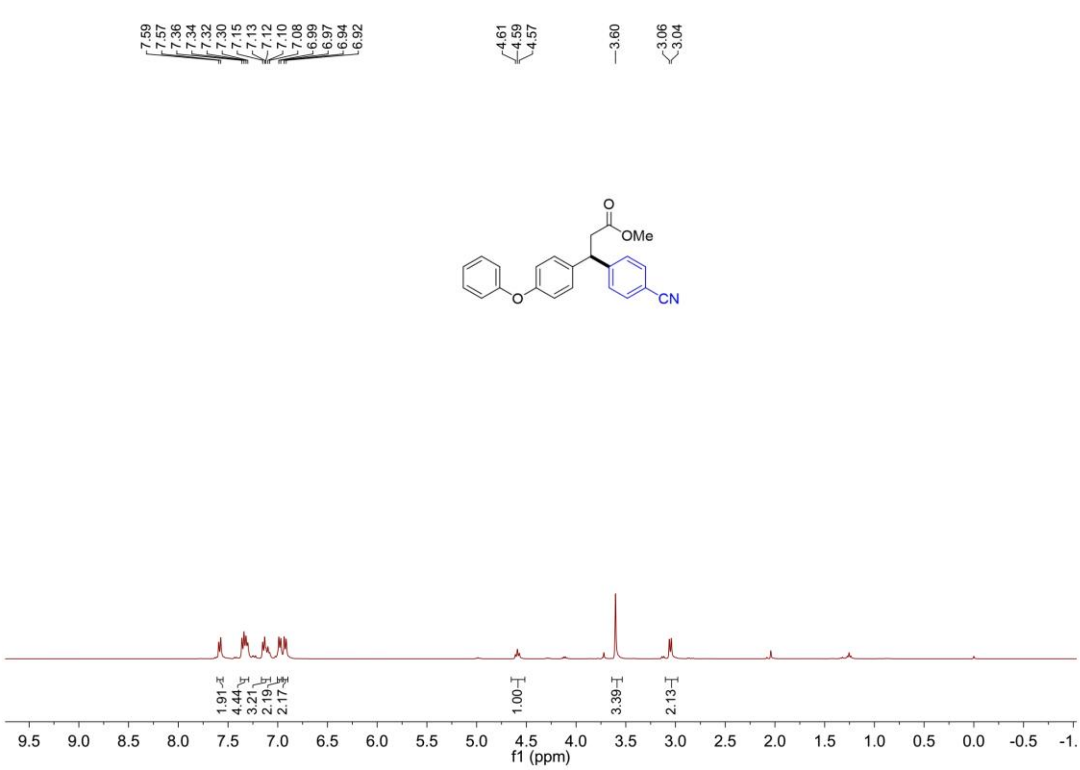

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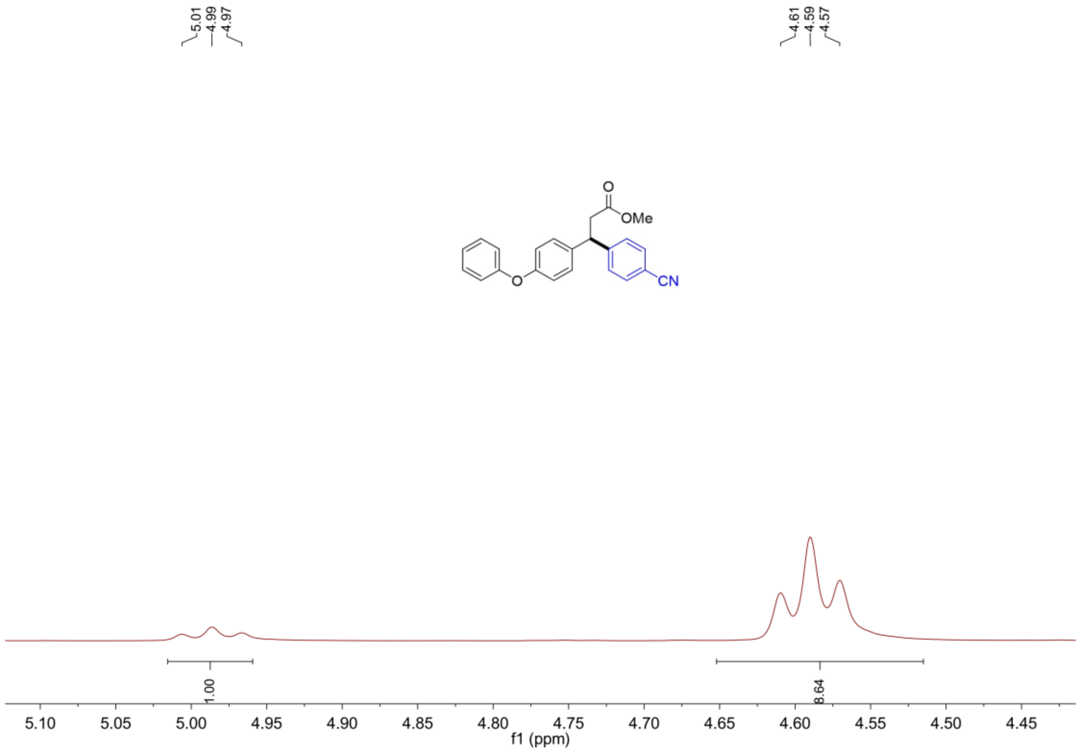

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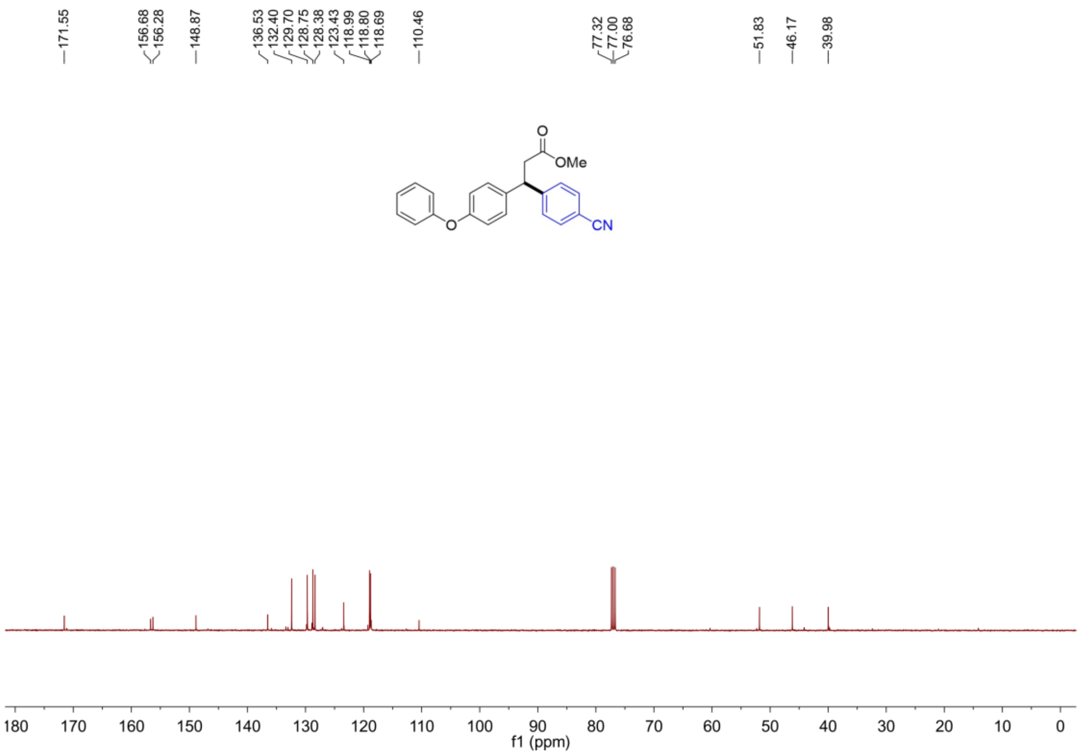
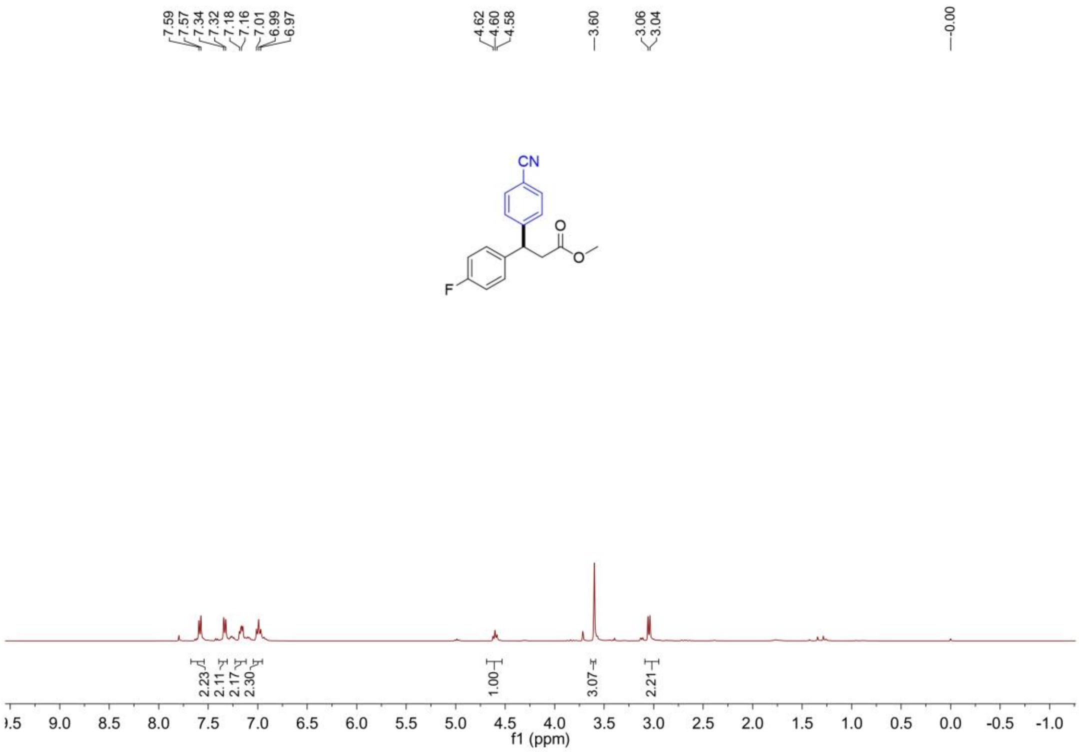
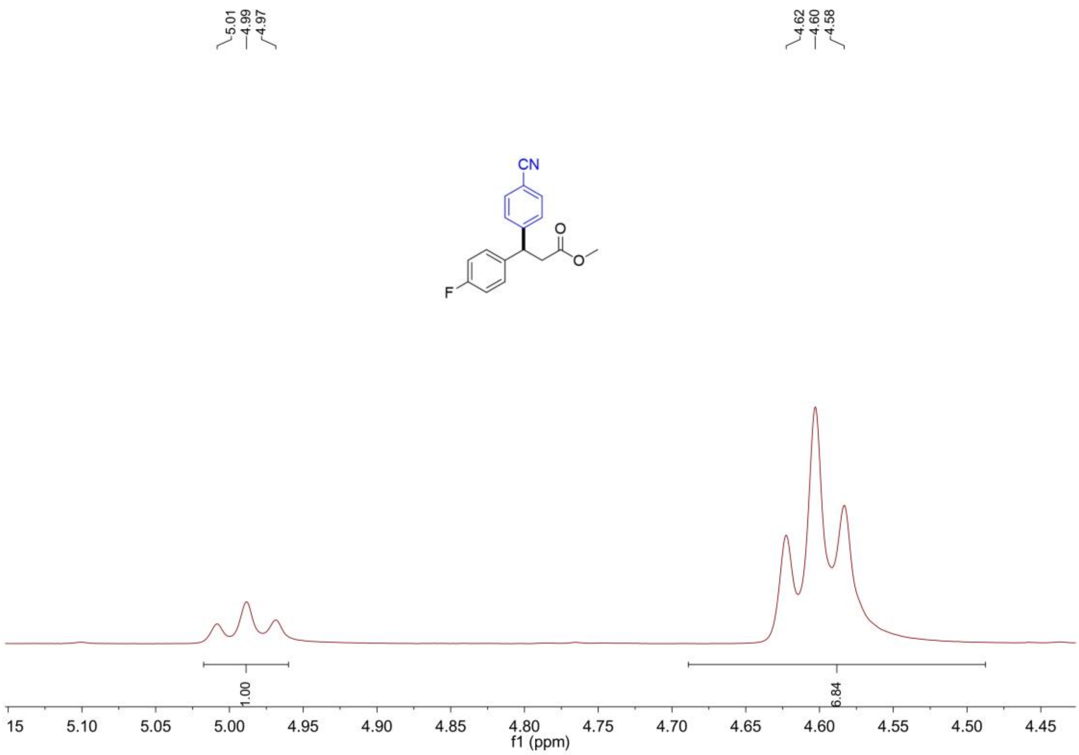


3l ¹HNMR



3l Regioselectivity



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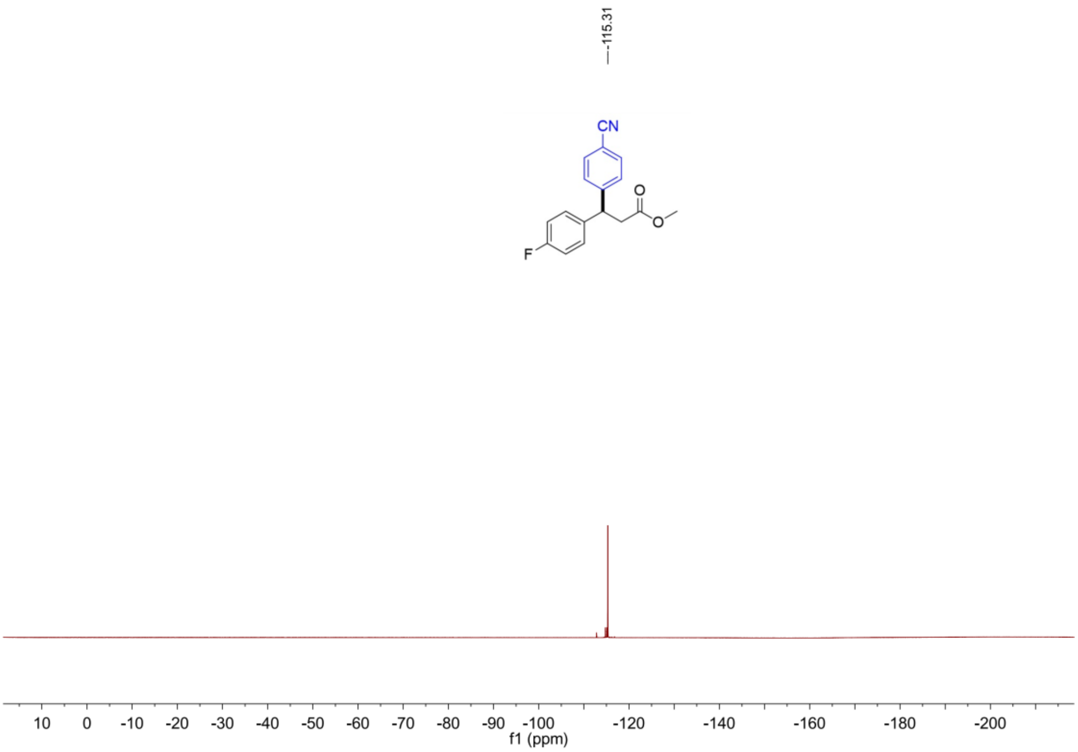

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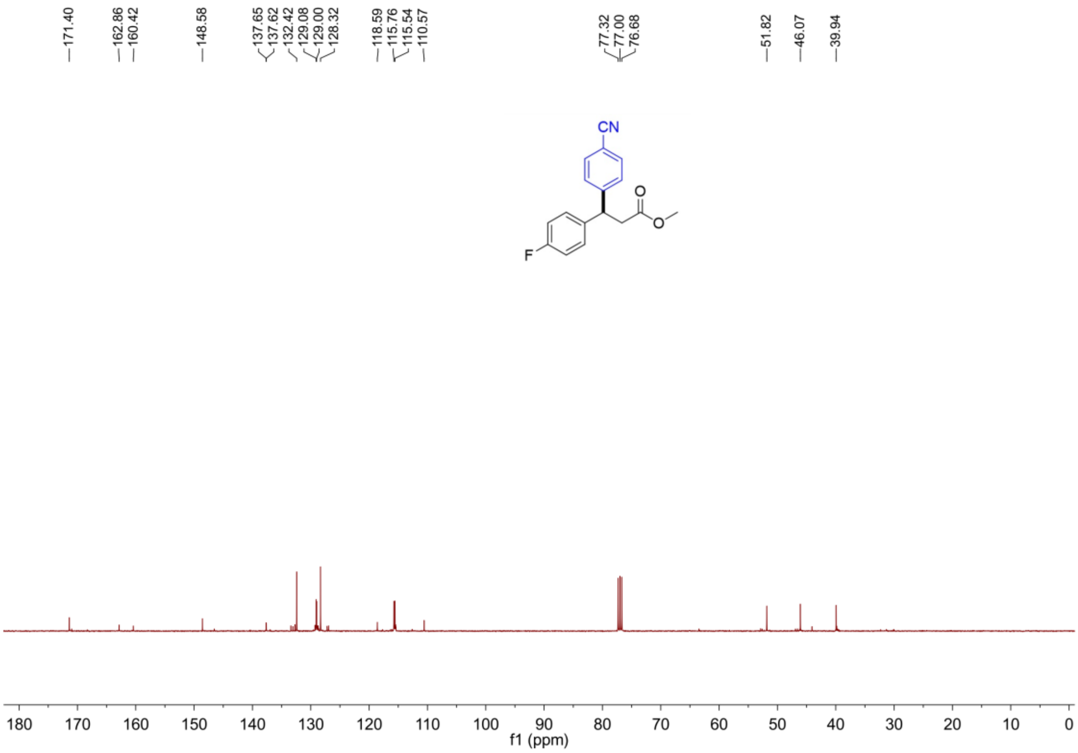

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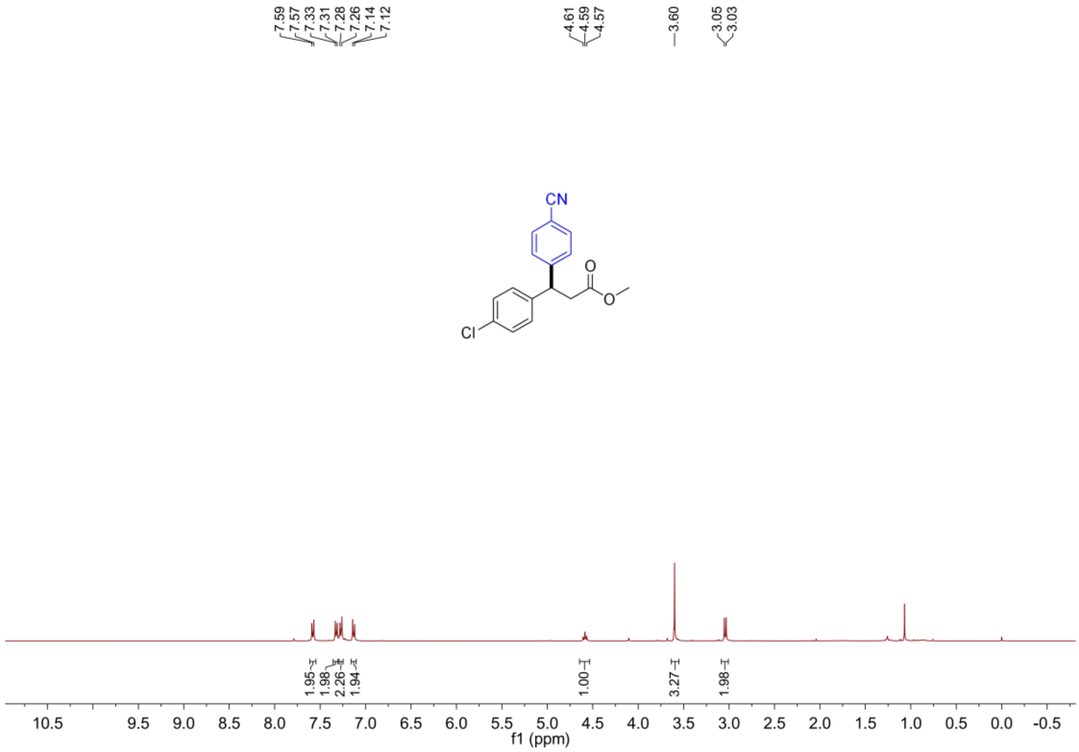
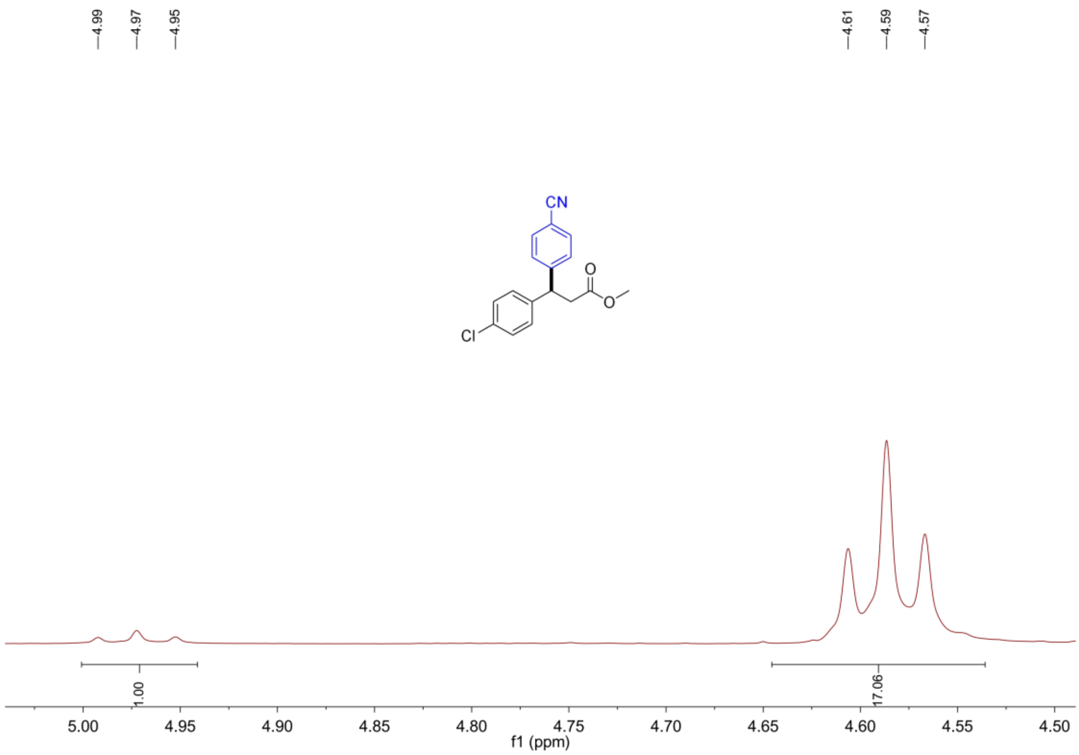


3m Regioselectivity



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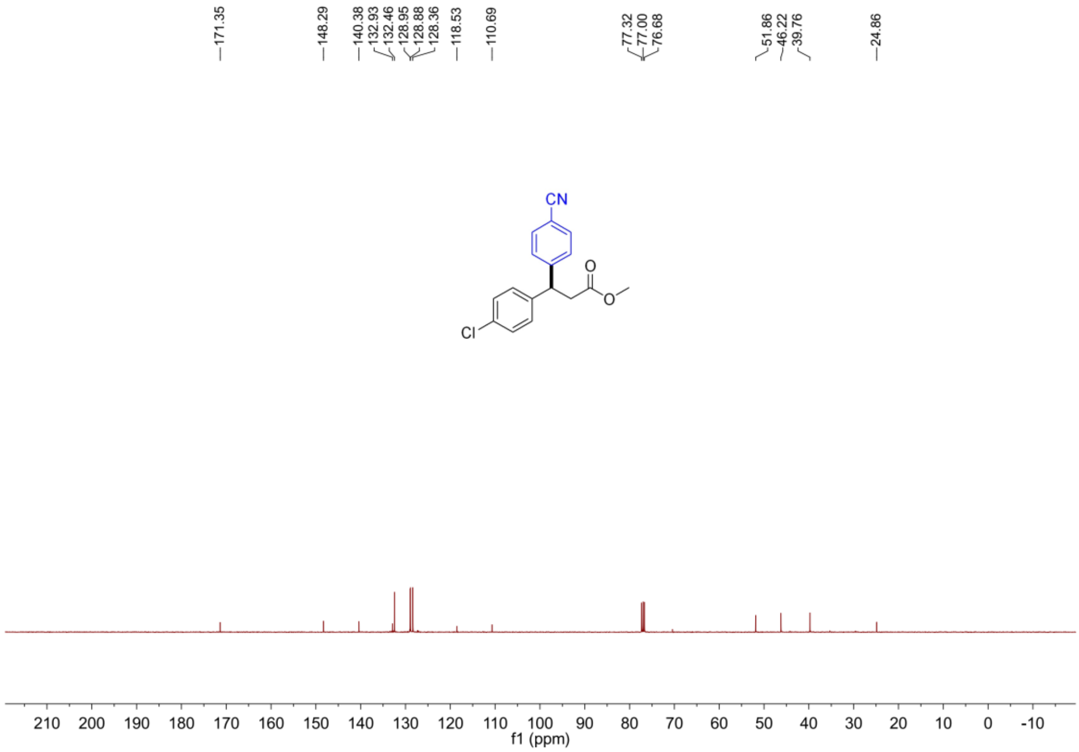

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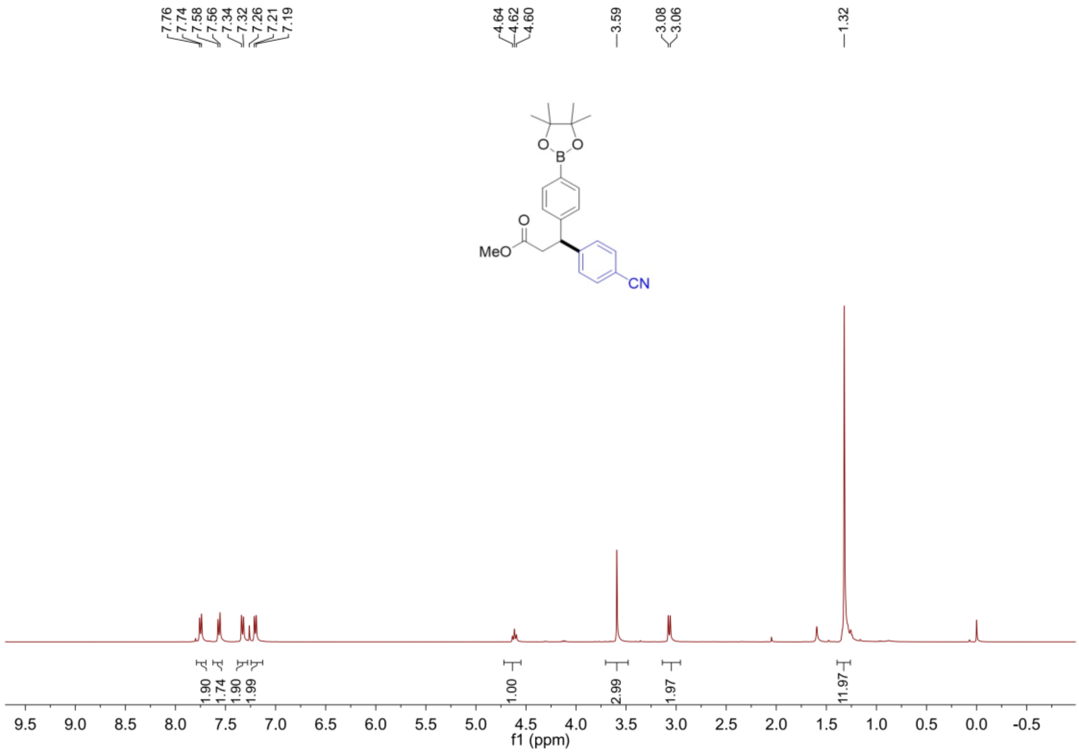
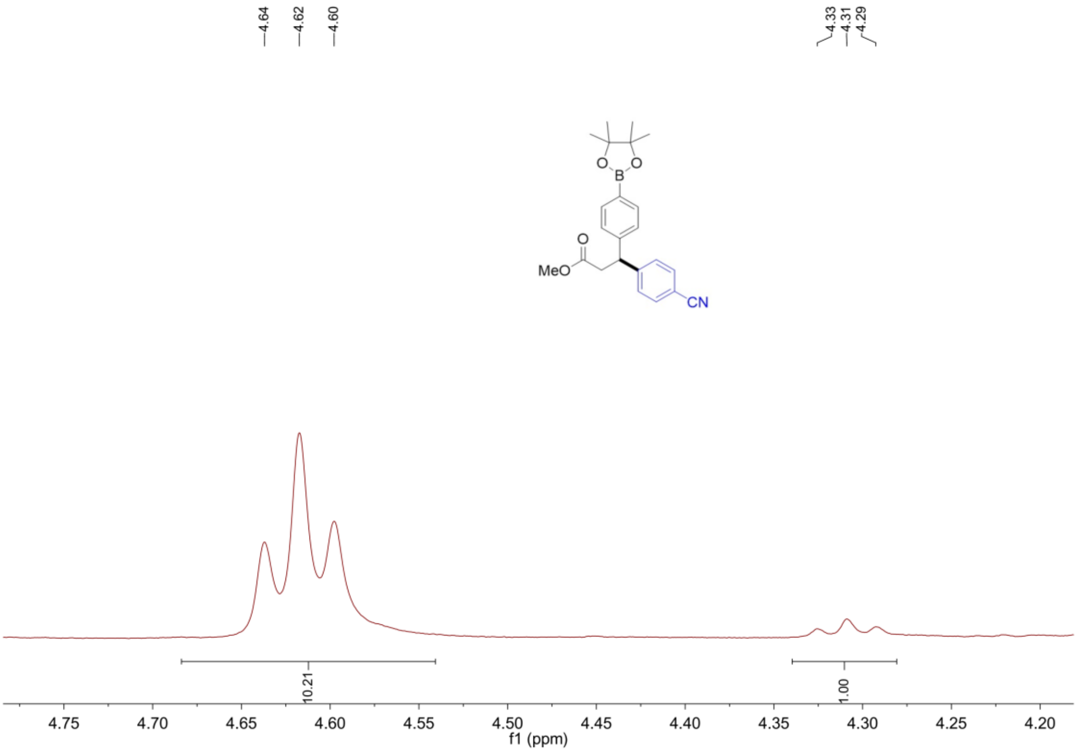


3n Regioselectivity



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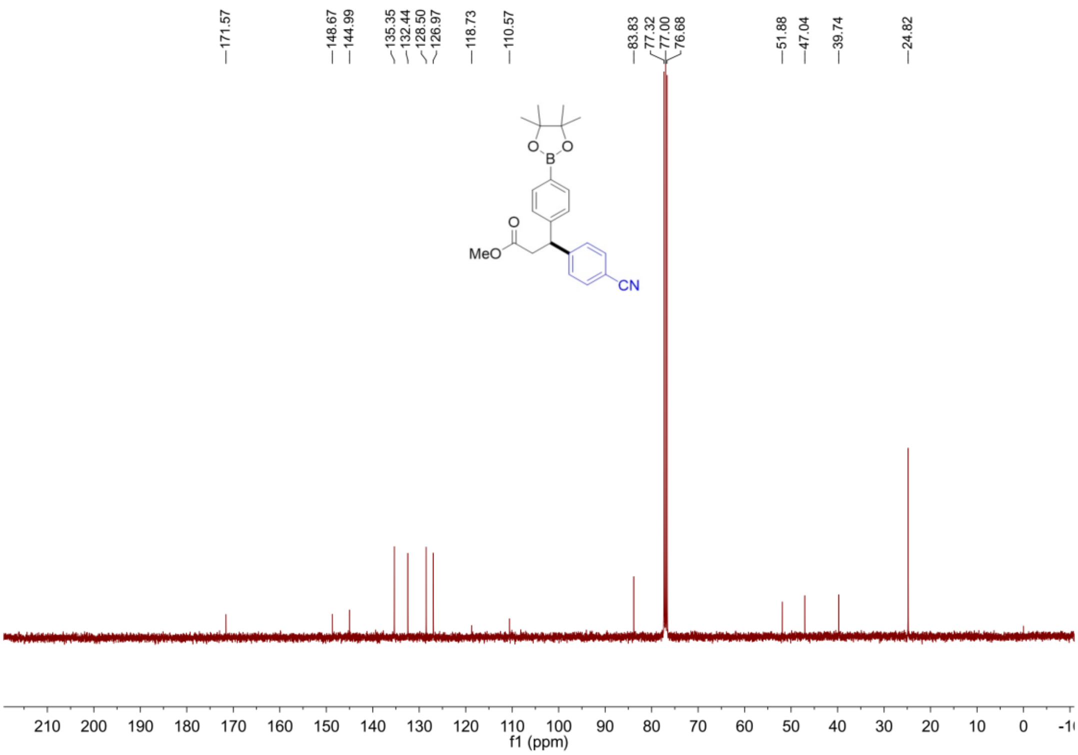

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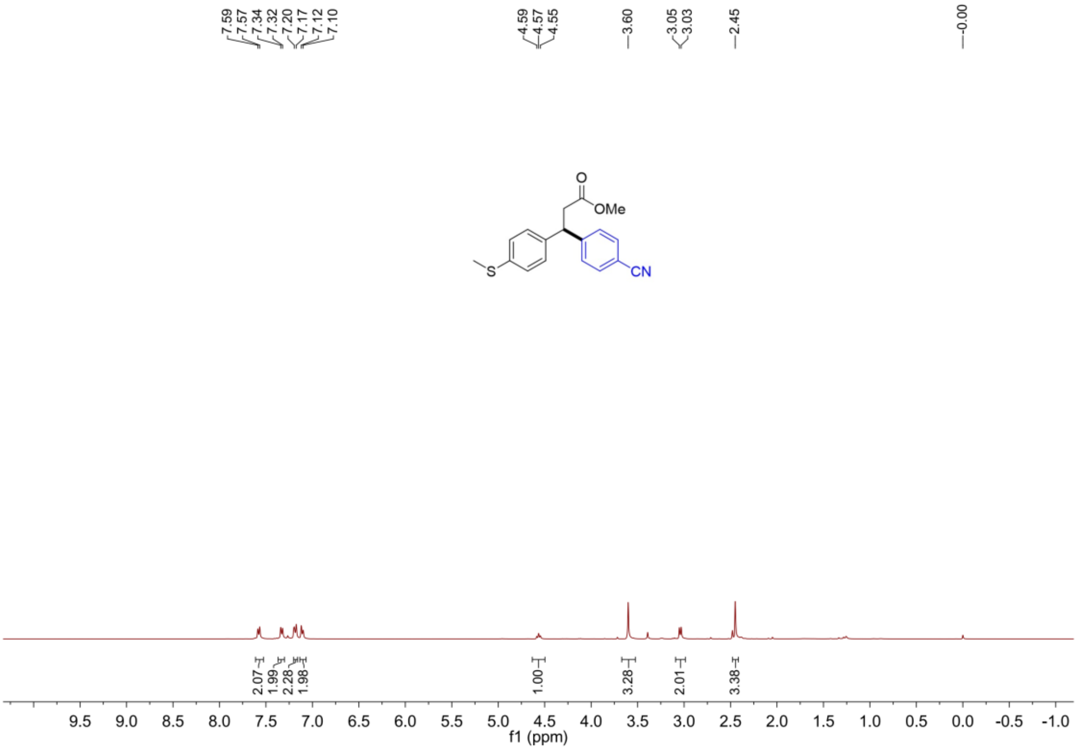

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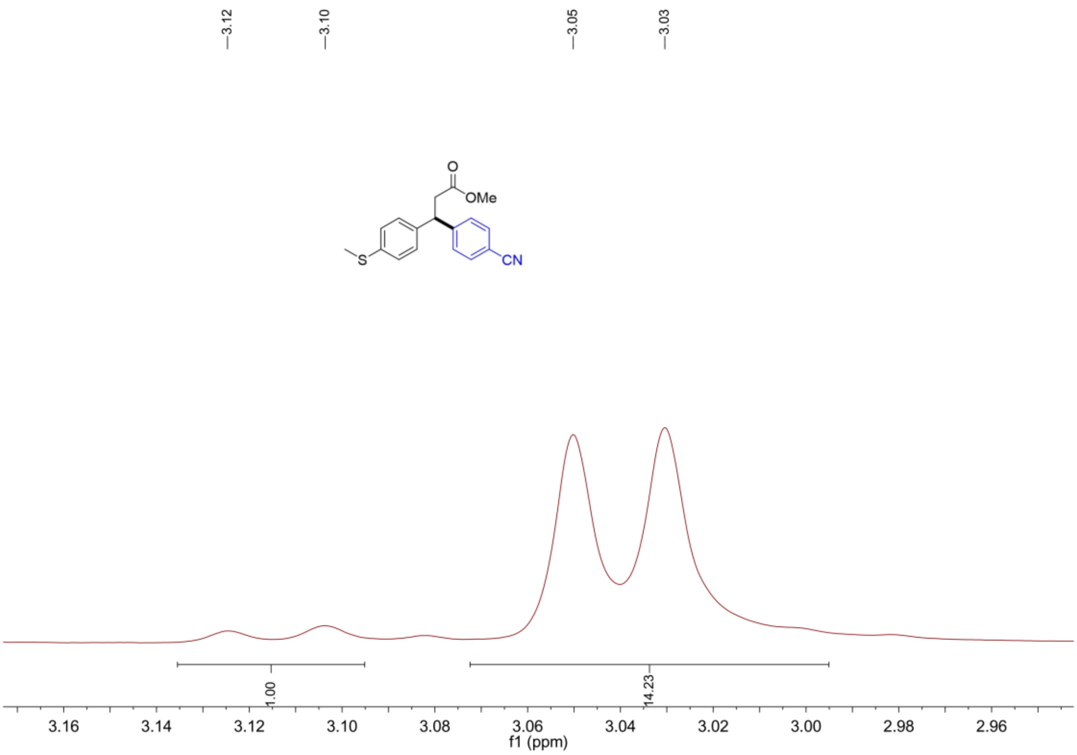

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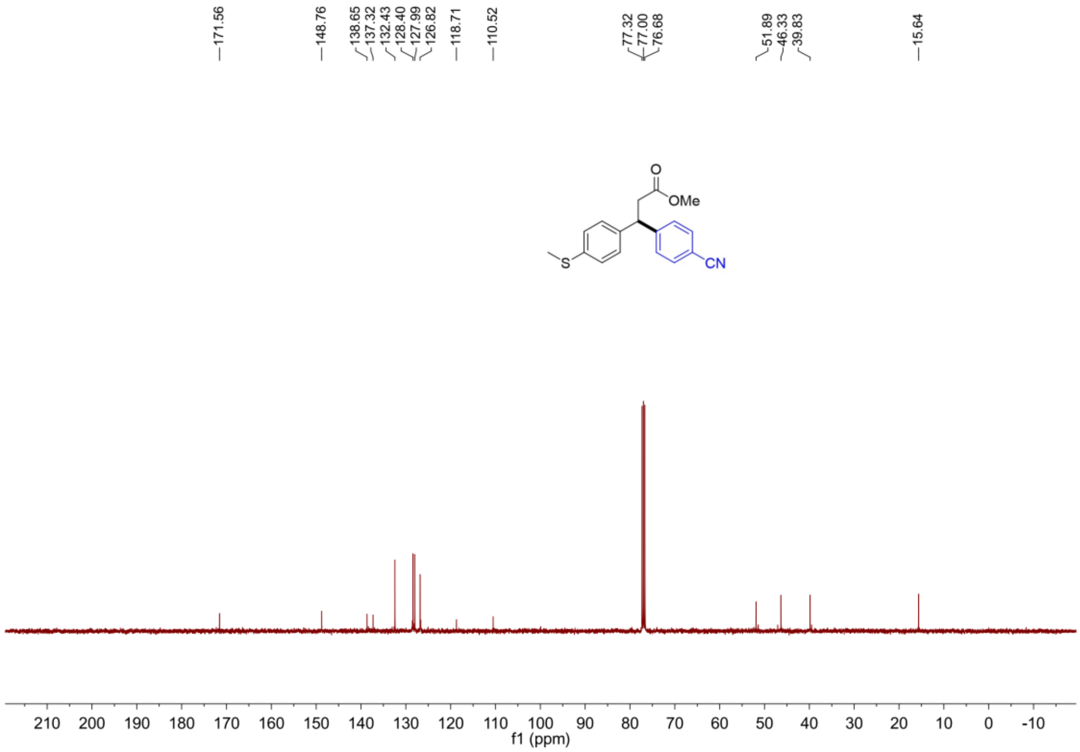

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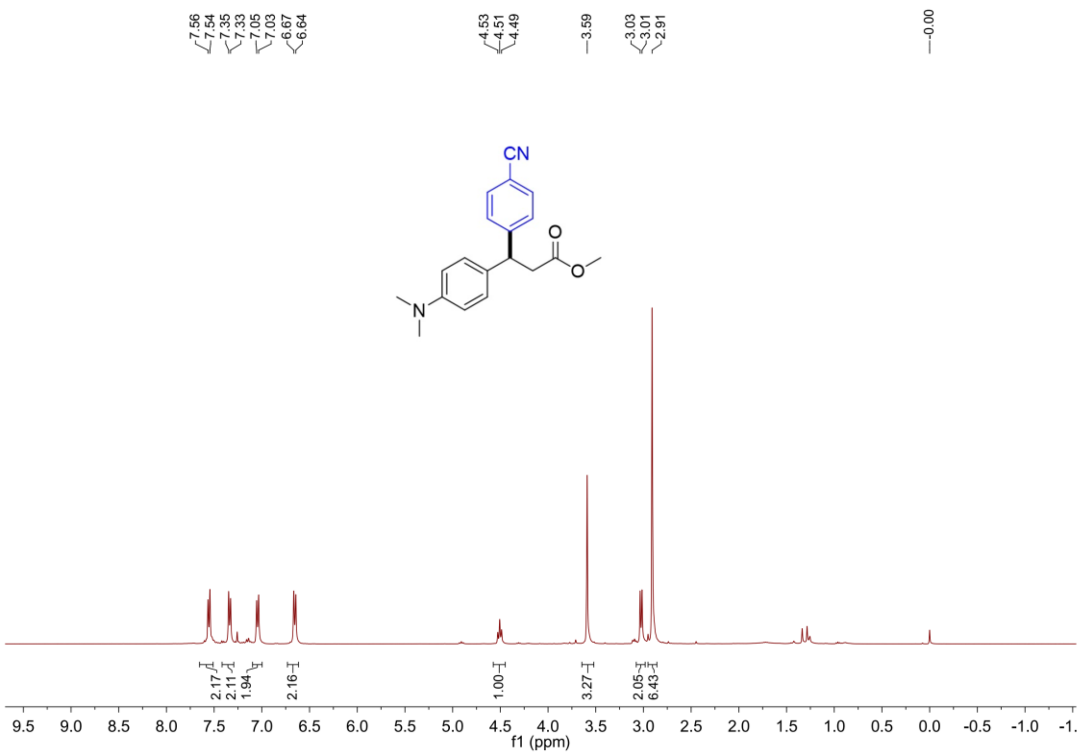
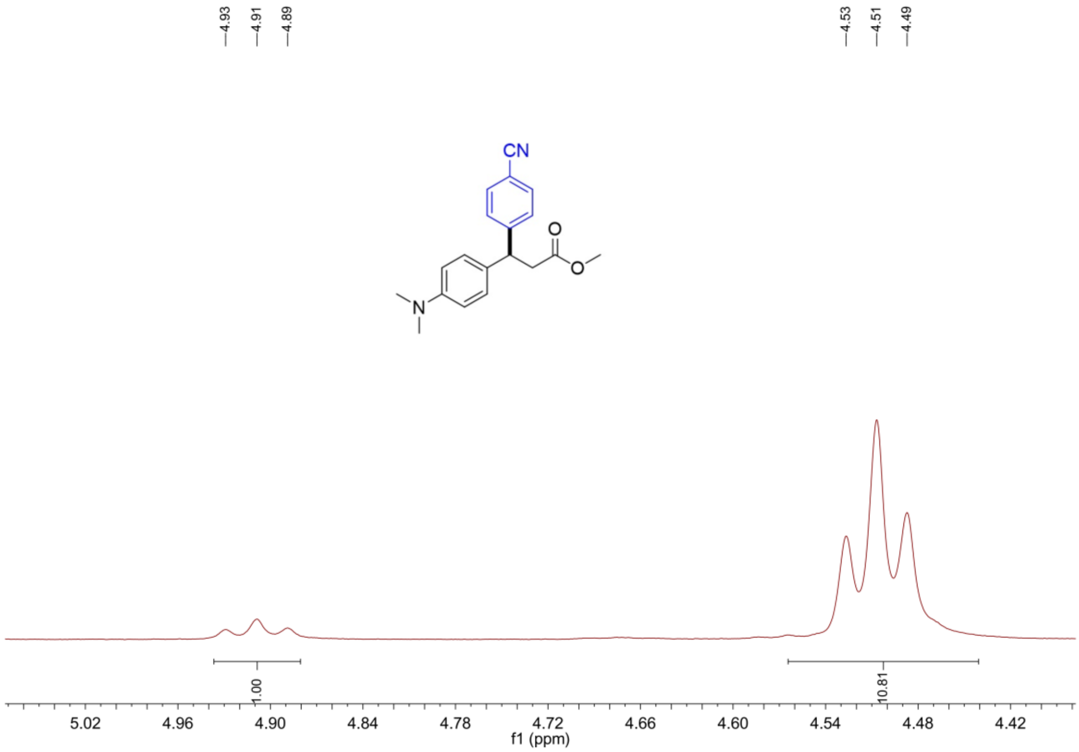
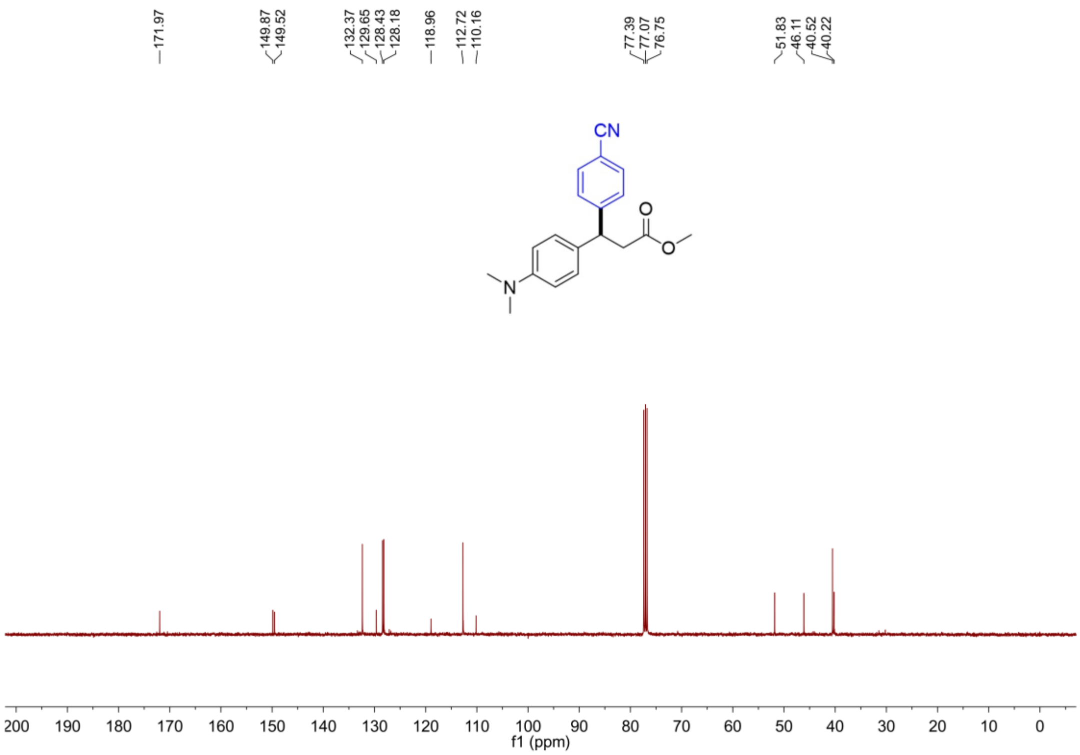


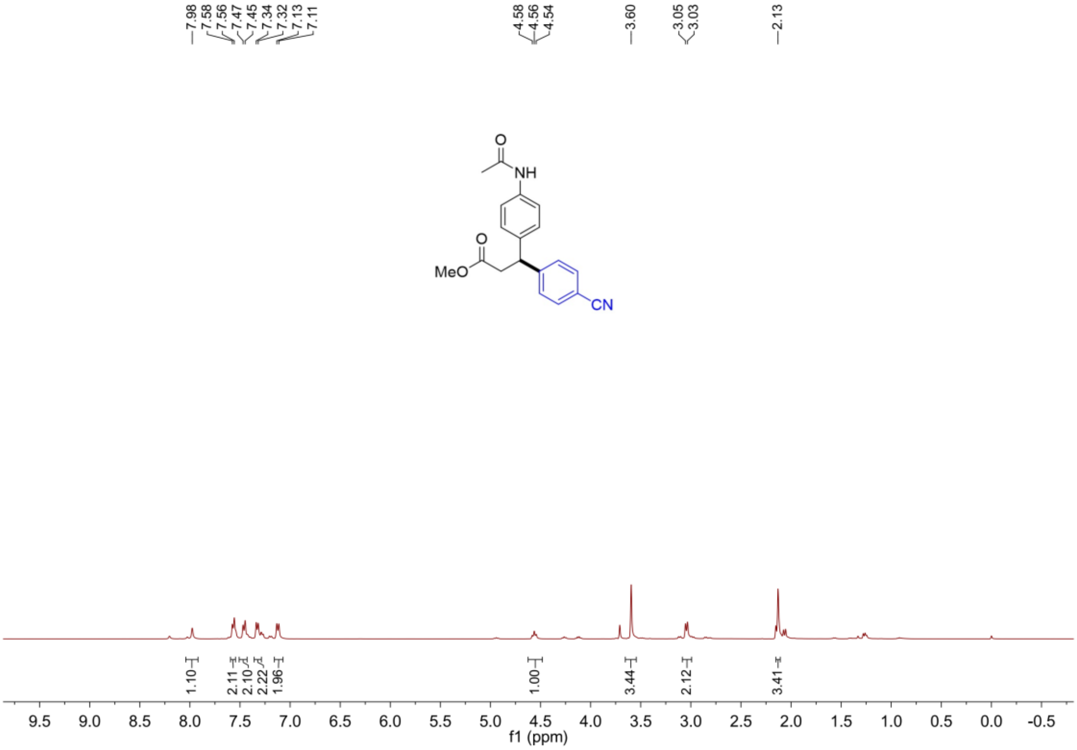
3p Regioselectivity



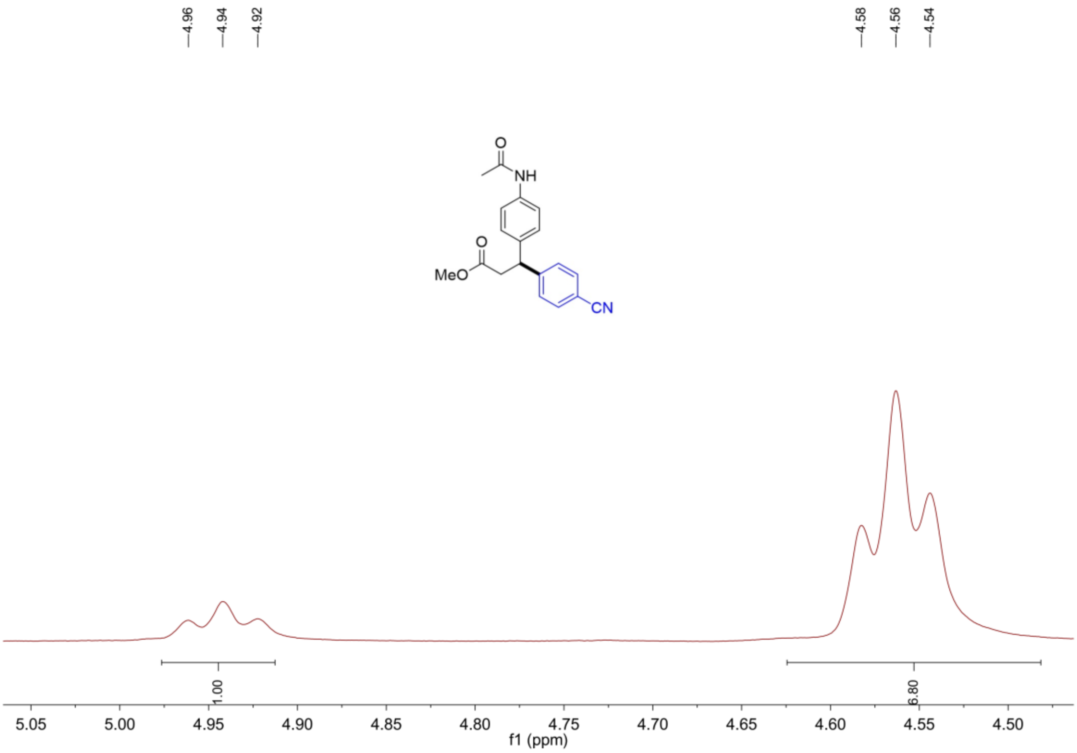
3p ^{13}CNMR



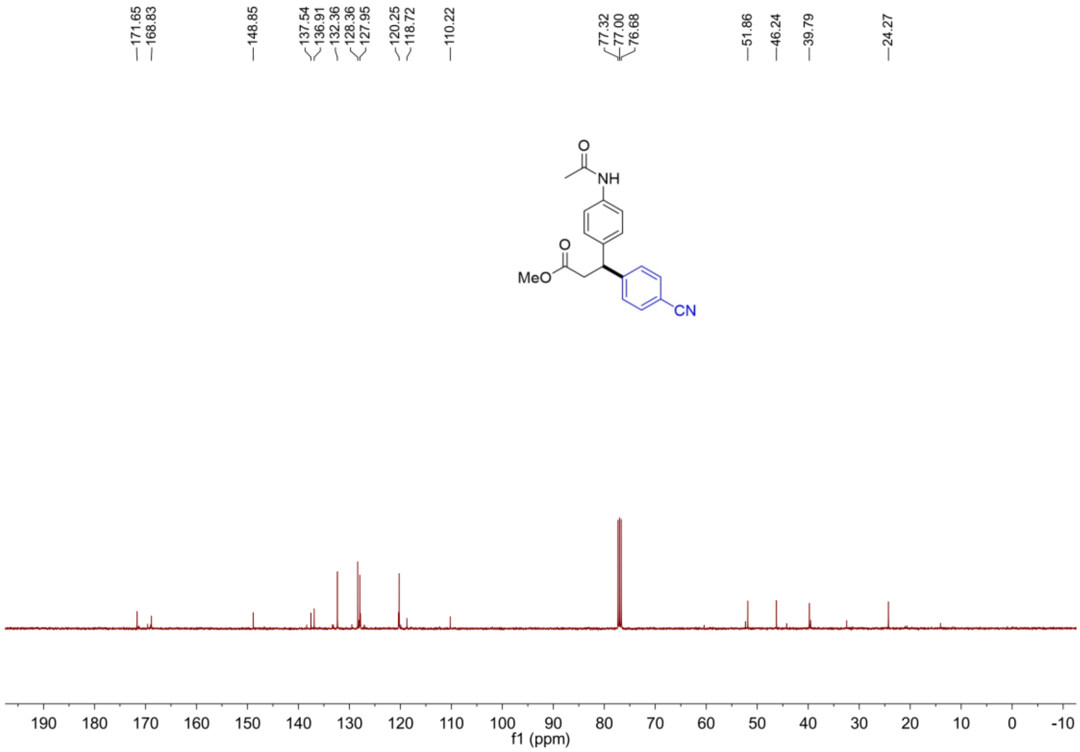
3q ¹HNMR



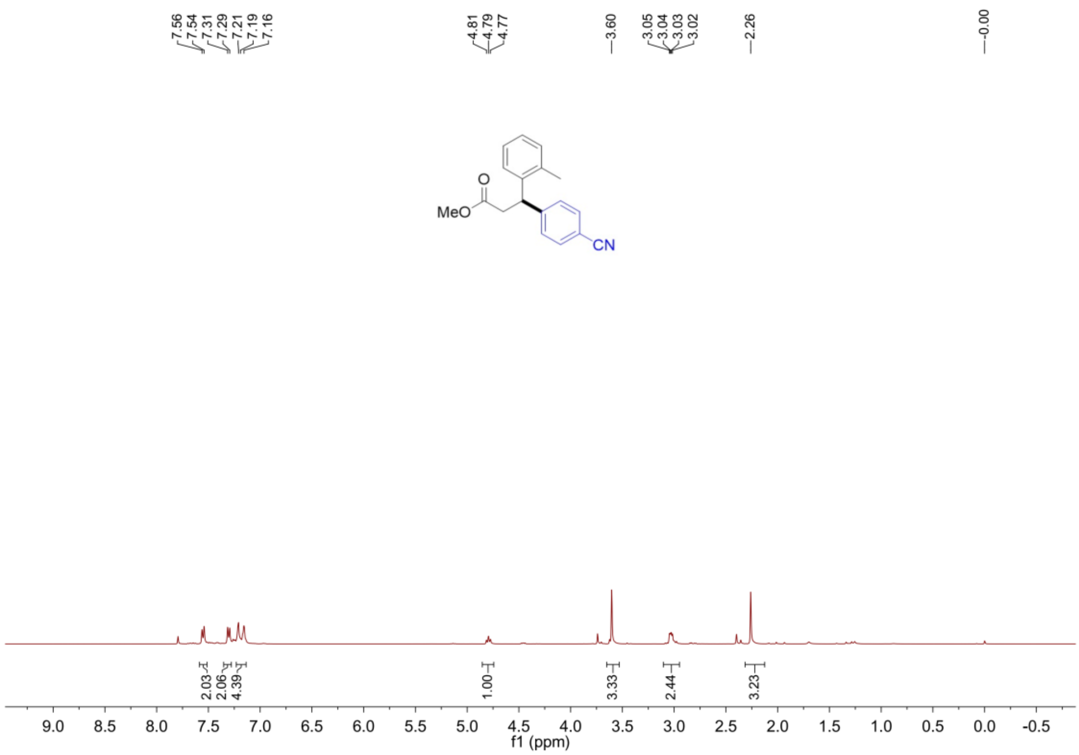
3q Regioselectivity



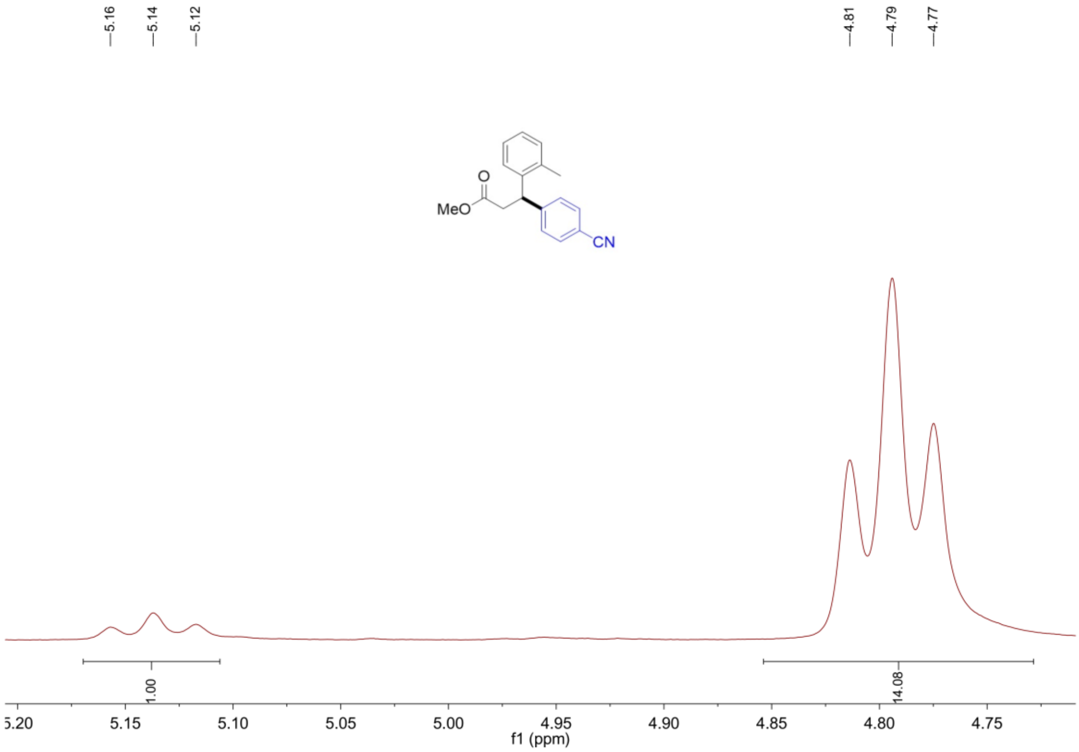
3q ^{13}CNMR



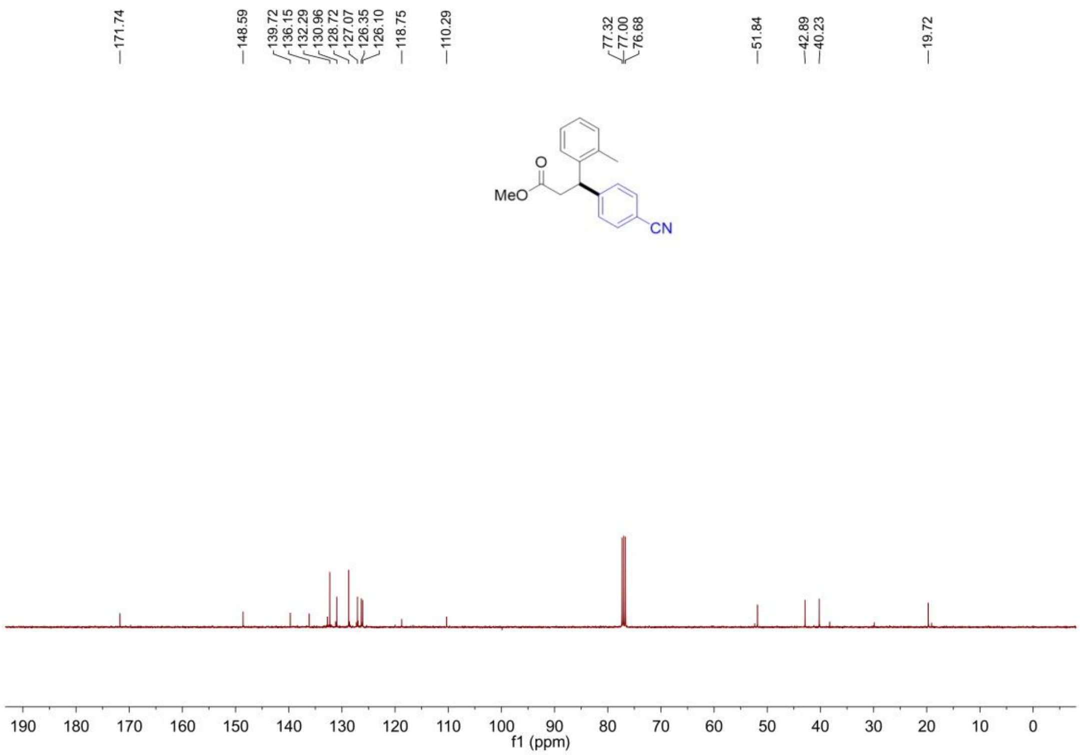
3r ^{1}HNMR



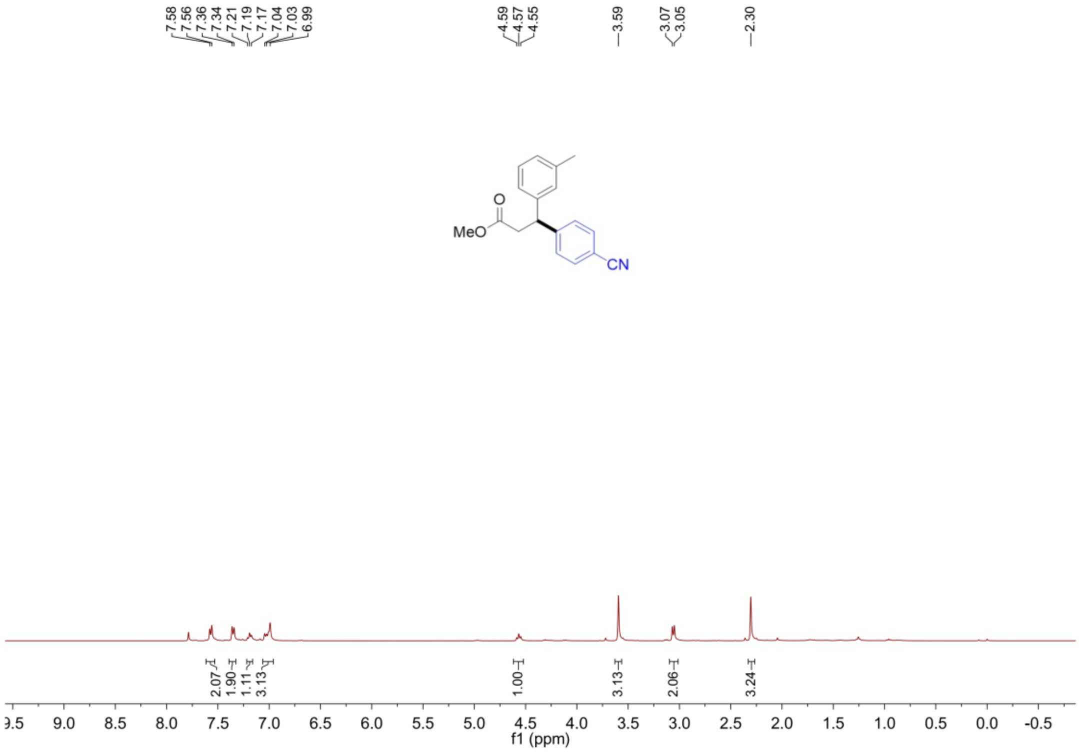
3r Regioselectivity



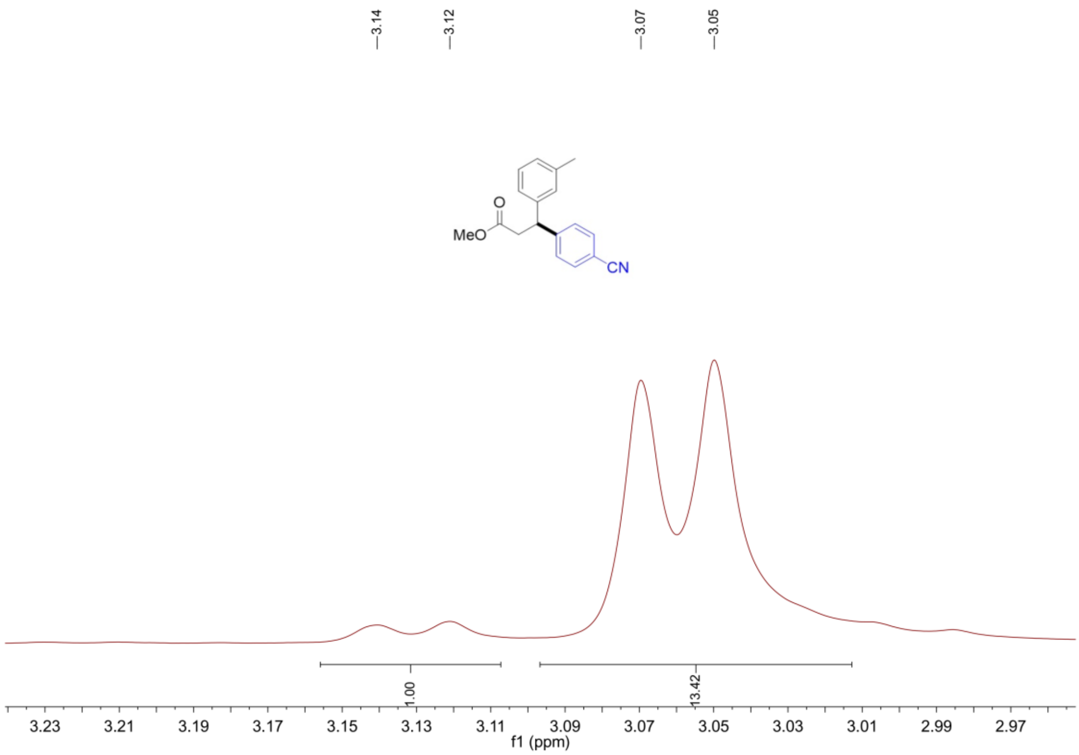
3r ^{13}CNMR



3s ^{1}HNMR



3s Regioselectivity



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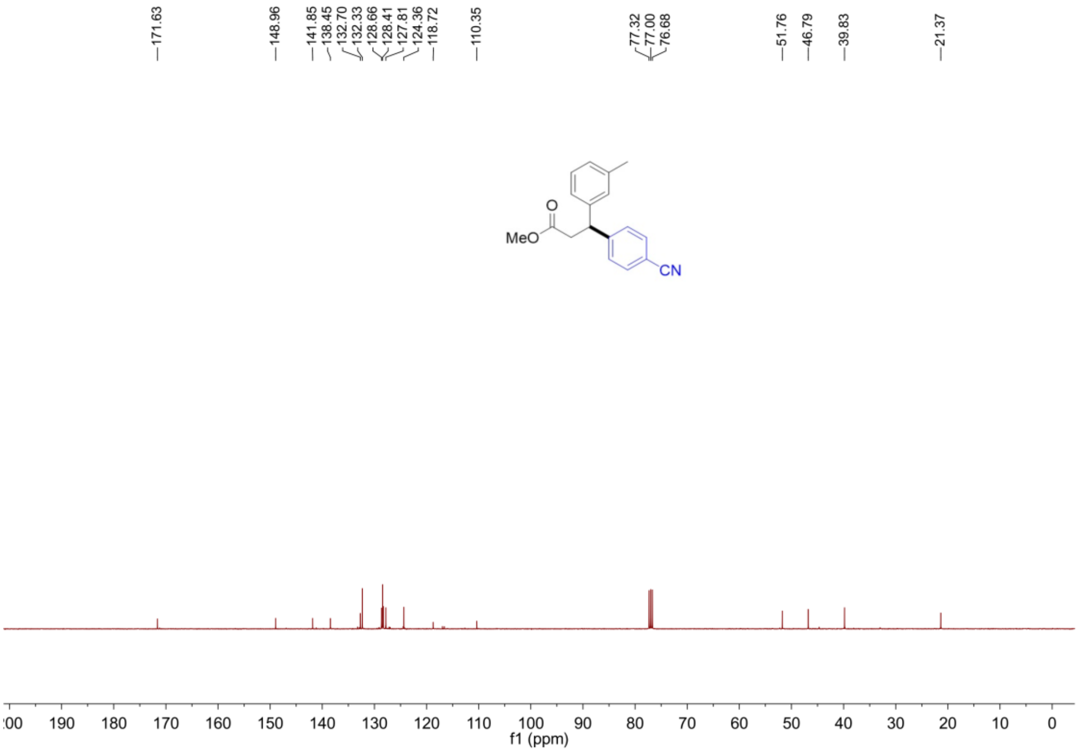

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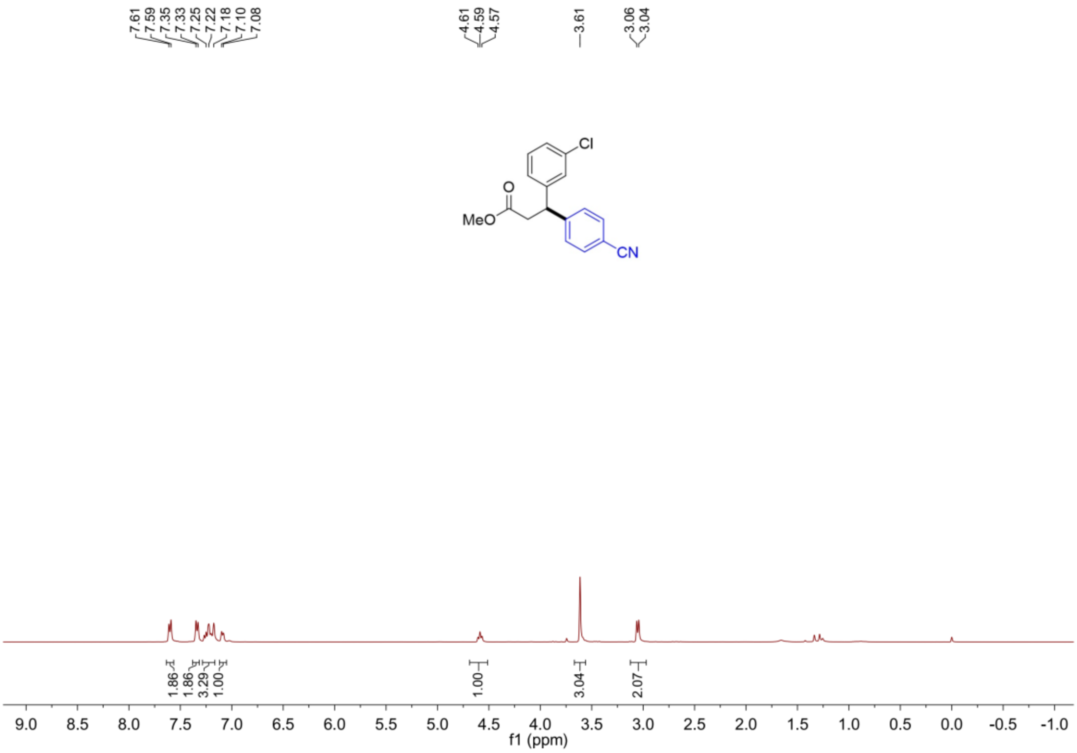
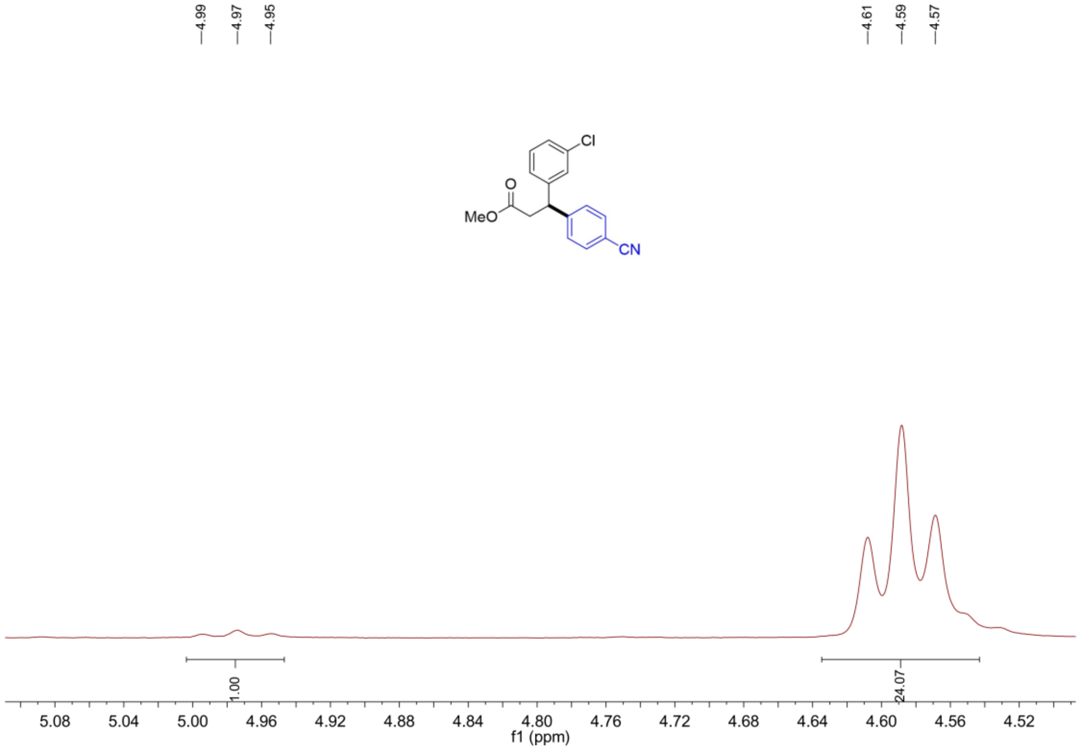
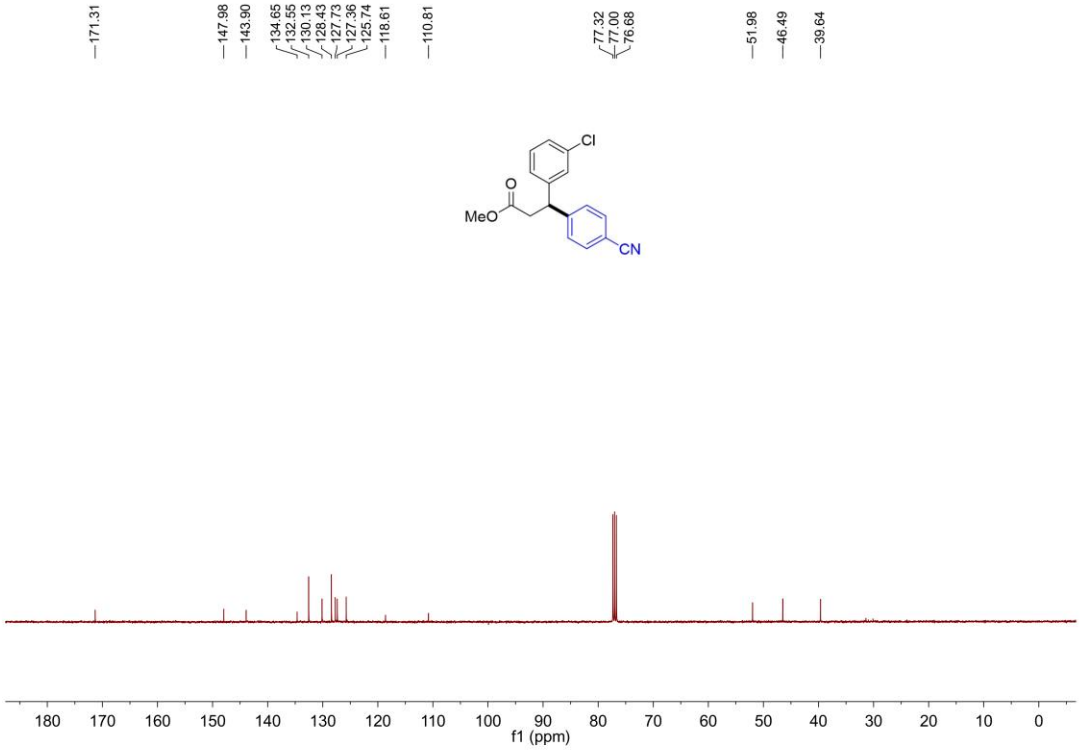


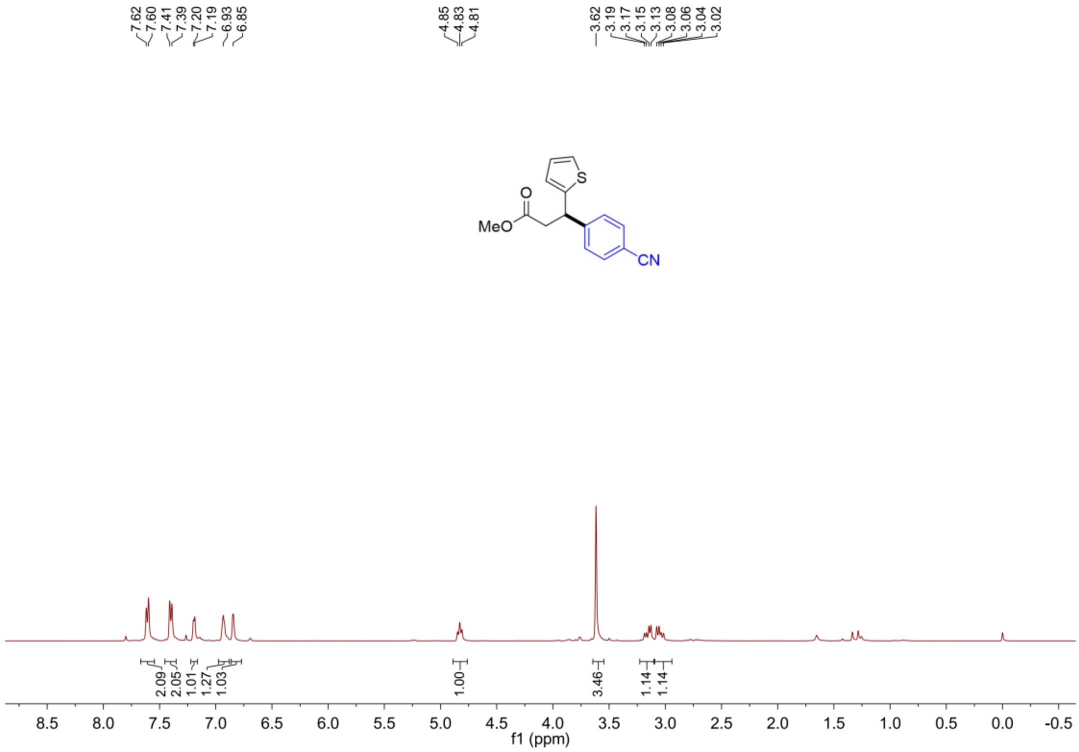
3t Regioselectivity



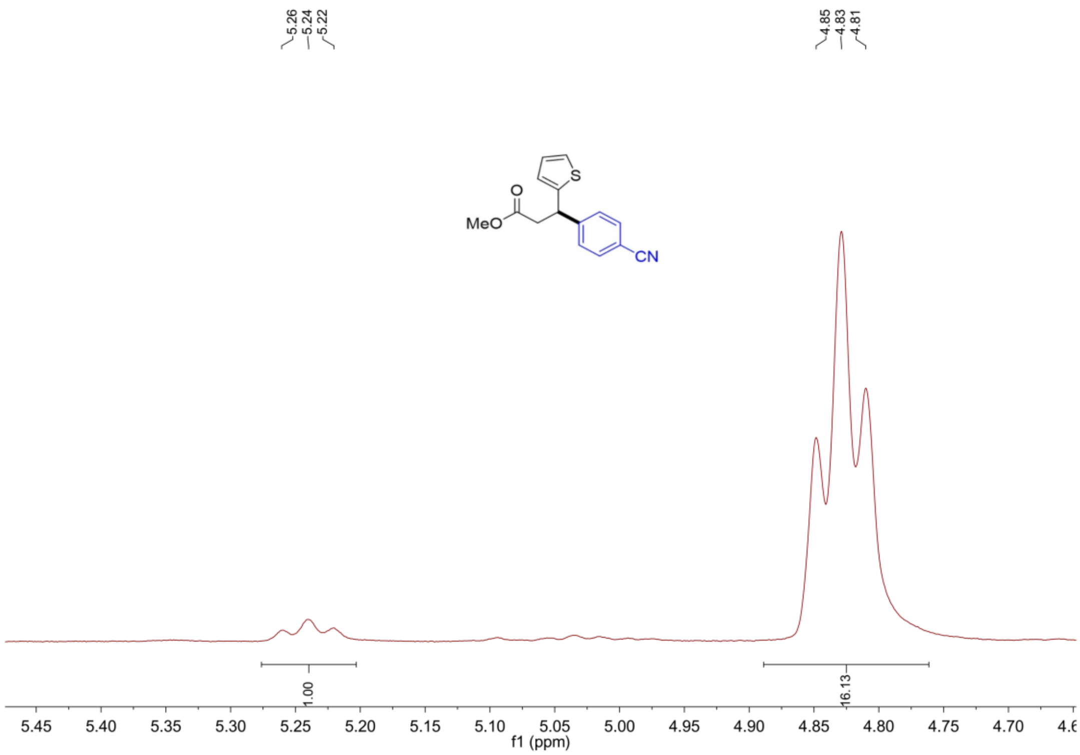
3t ^{13}CNMR



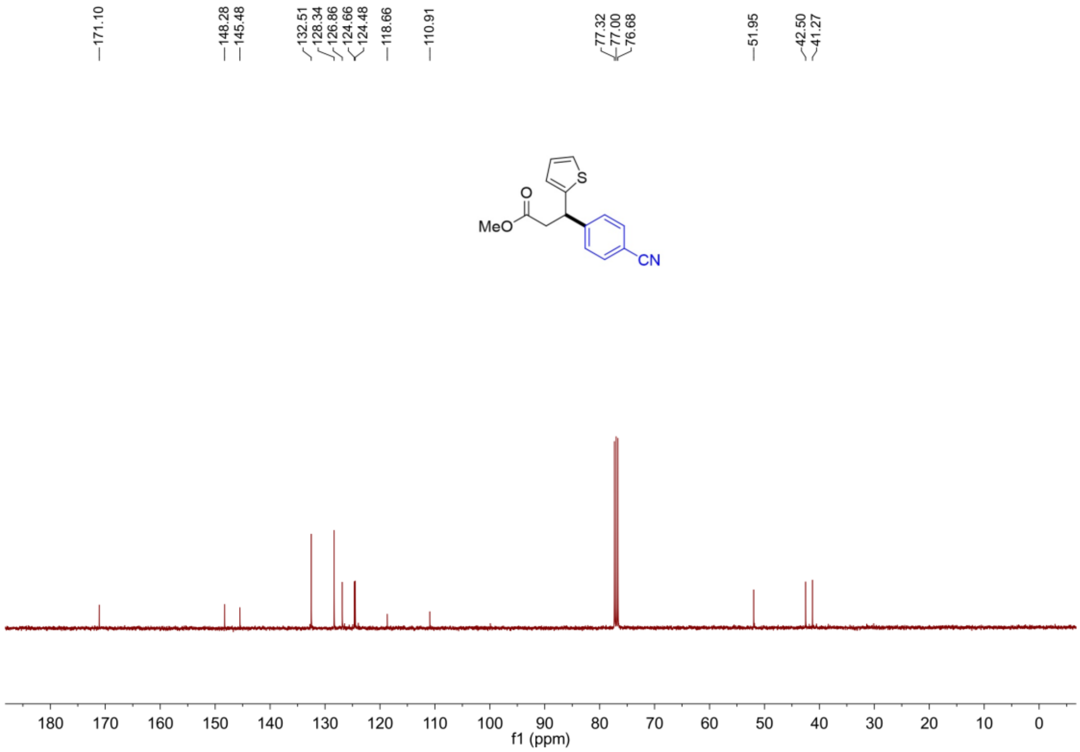
3u ¹HNMR



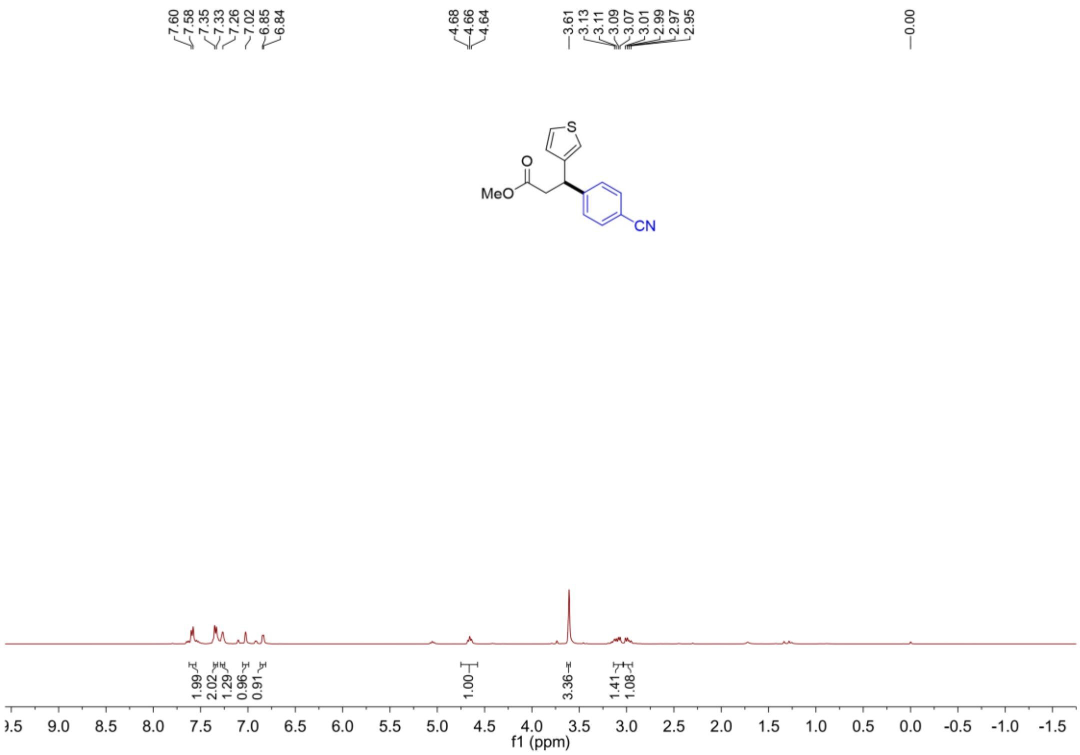
3u Regioselectivity



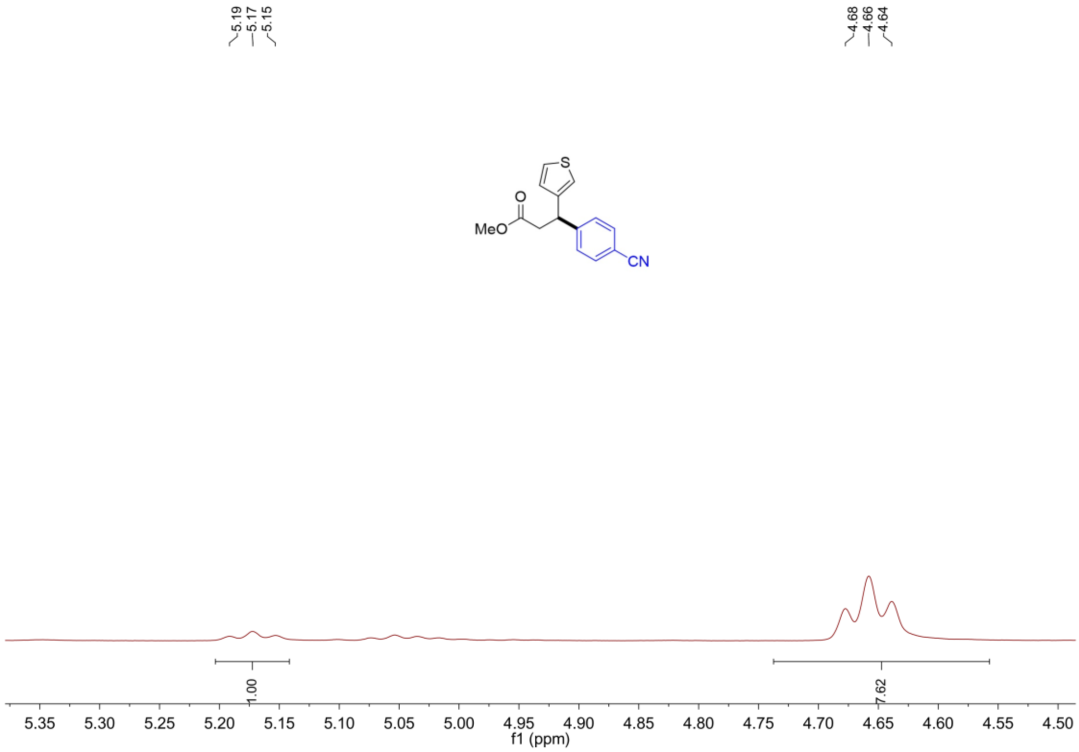
3u ^{13}CNMR



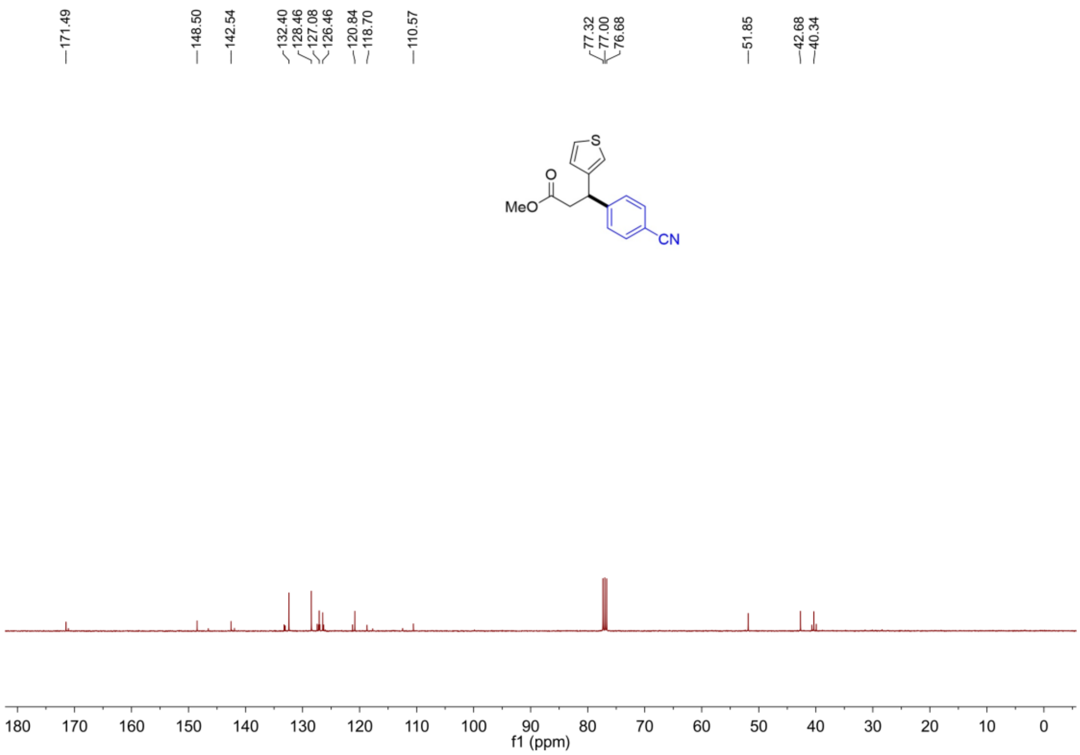
3v ^{1}HNMR



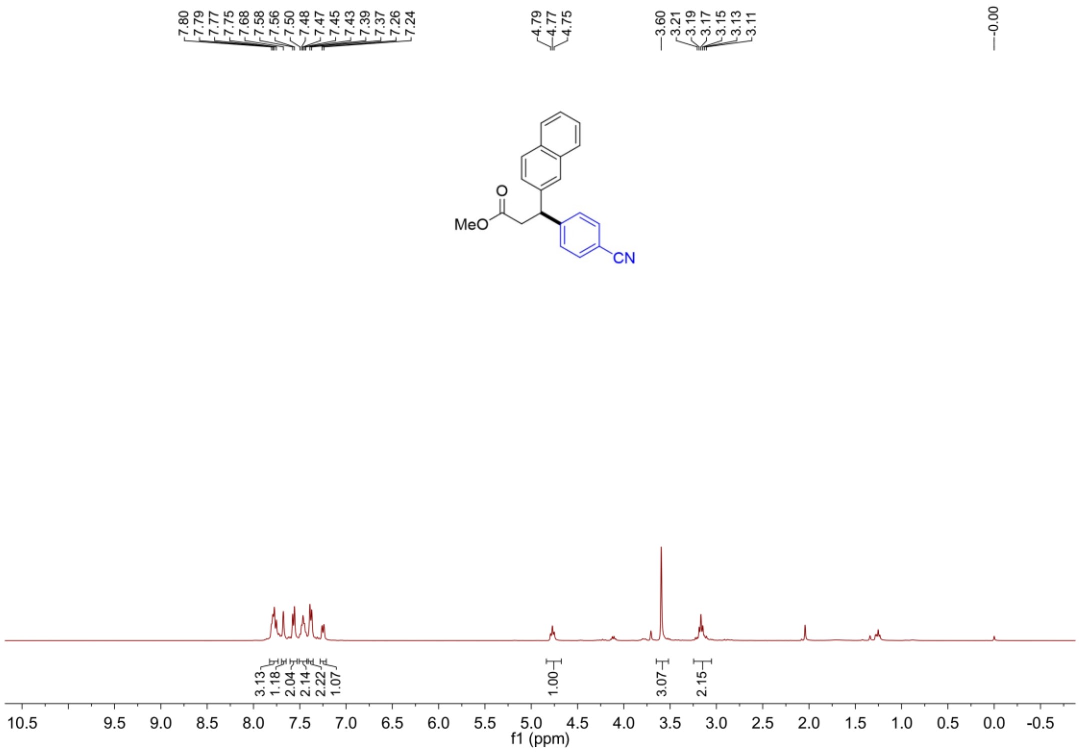
3v Regioselectivity



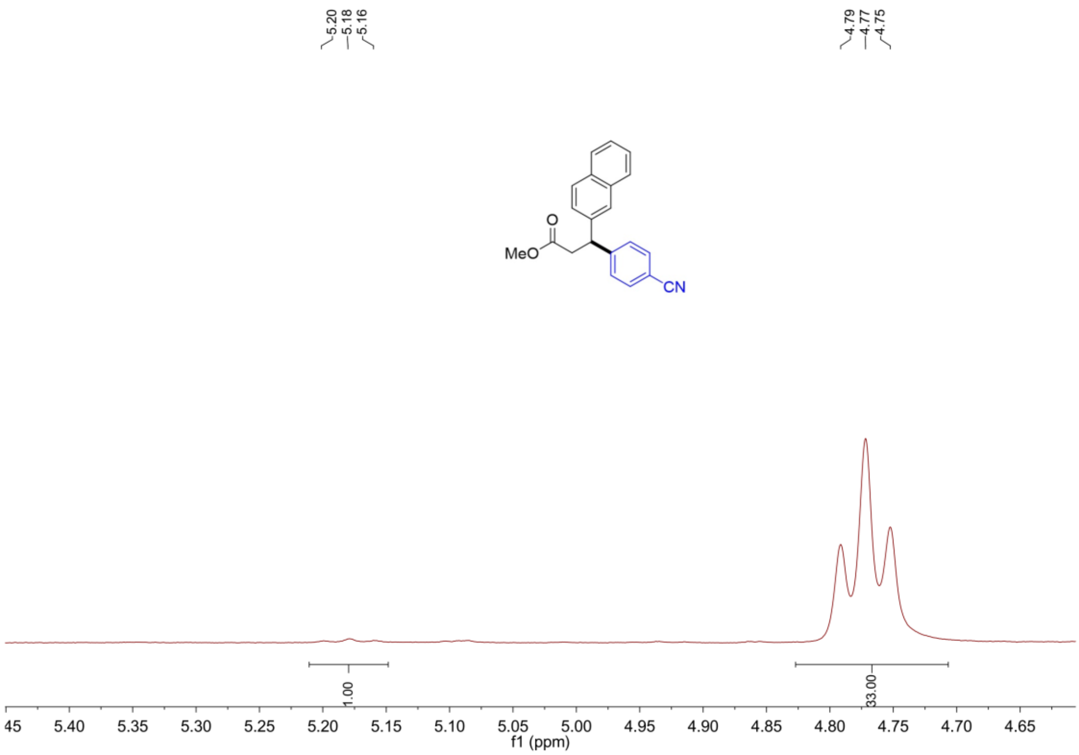
3v ^{13}CNMR



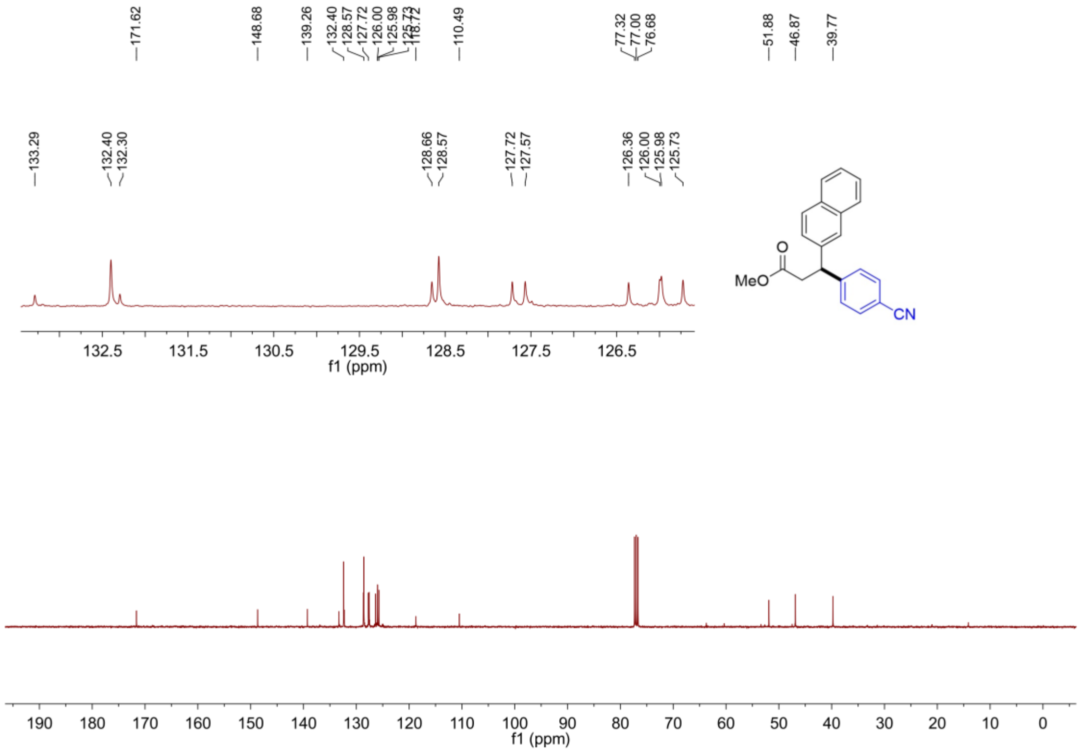
3w ^{1}HNMR



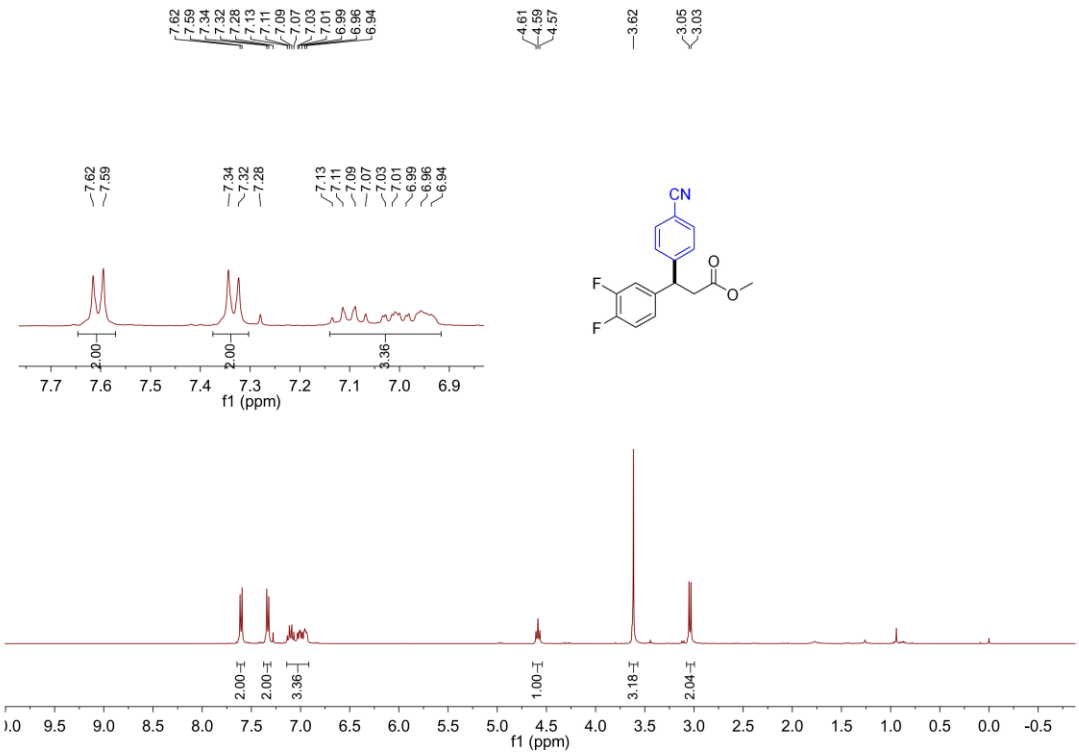
3w Regioselectivity



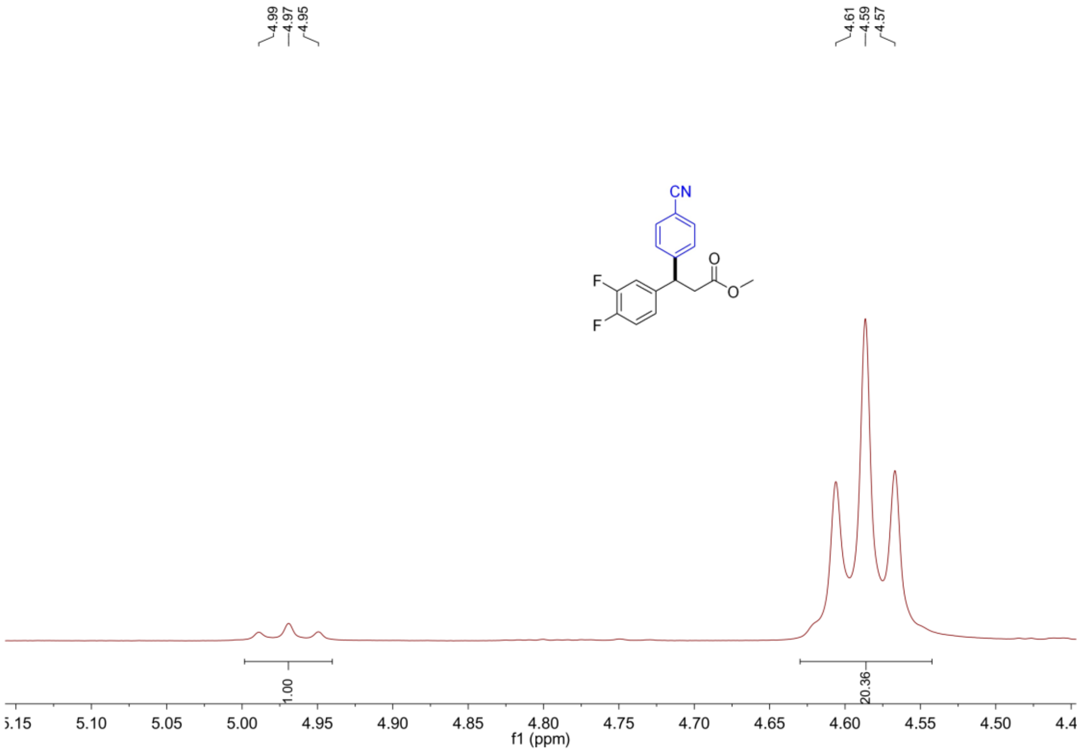
3w ^{13}CNMR



3x ^{1}HNMR



3x Regioselectivity



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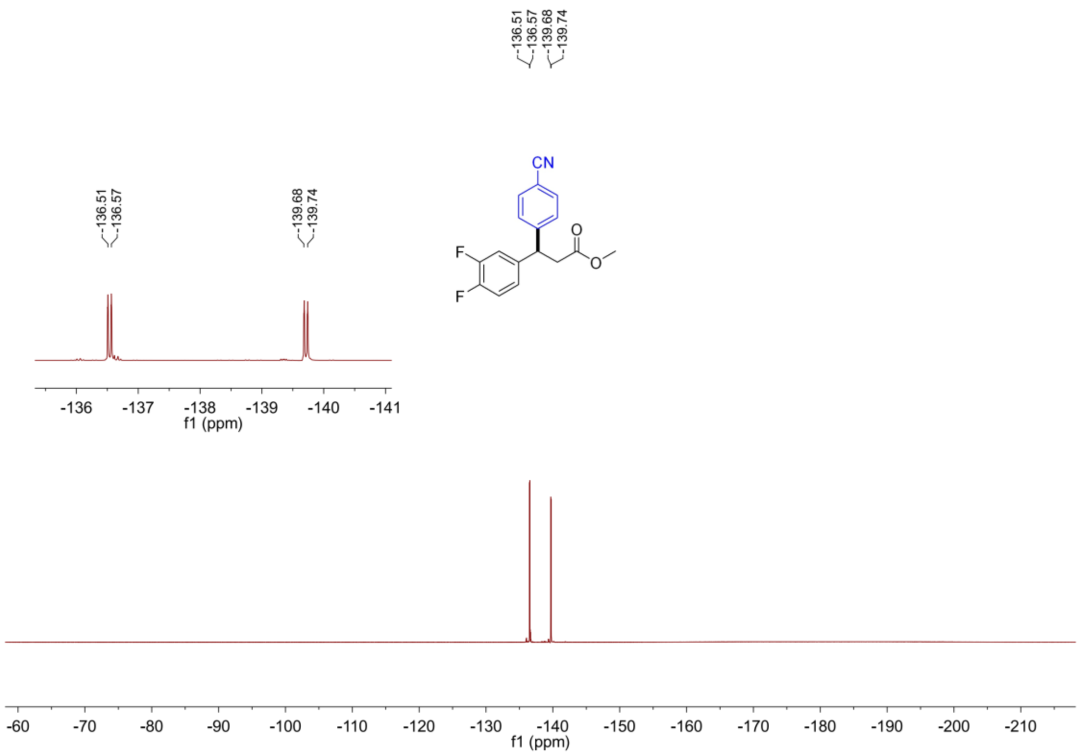

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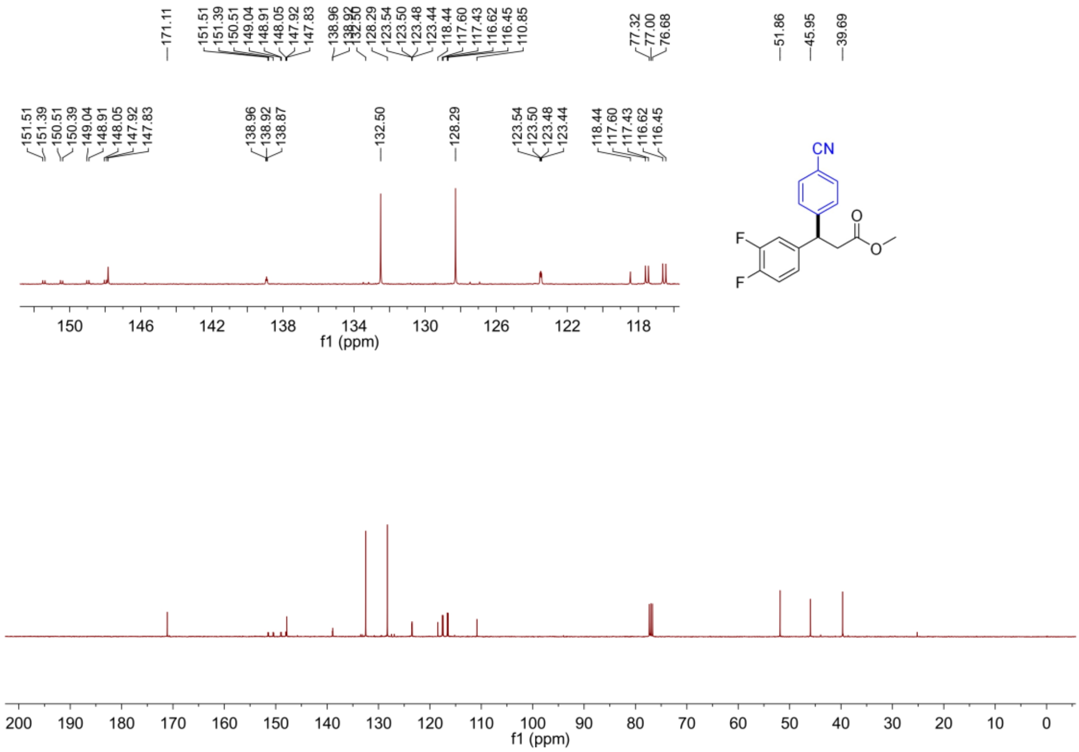
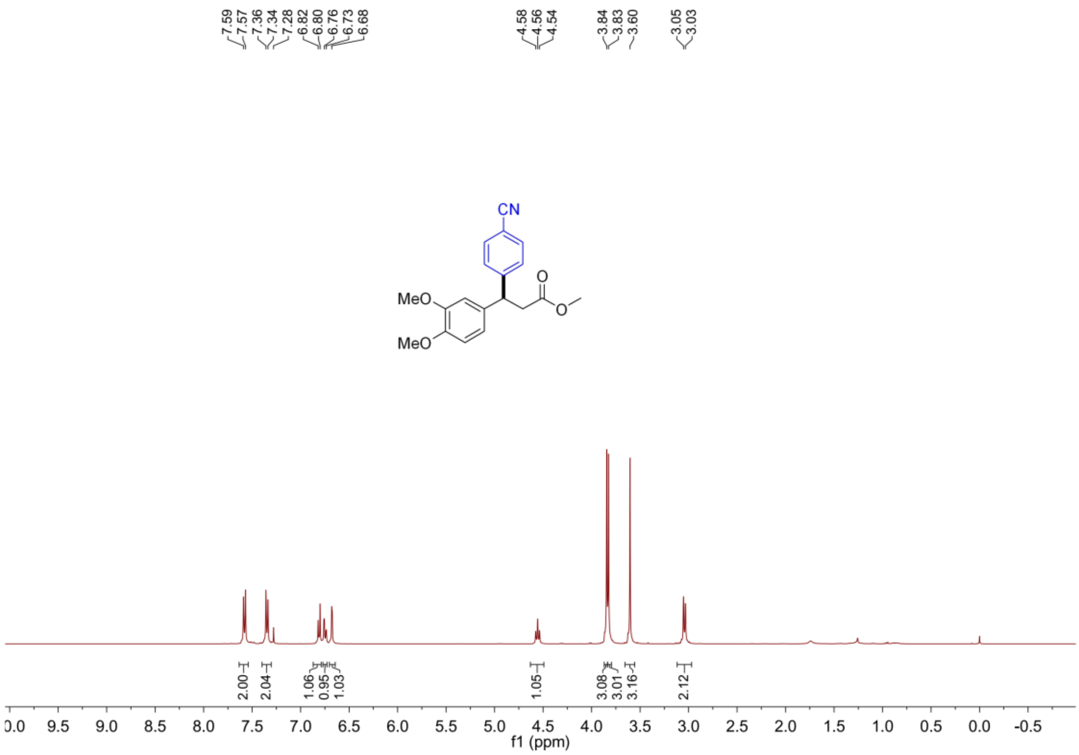
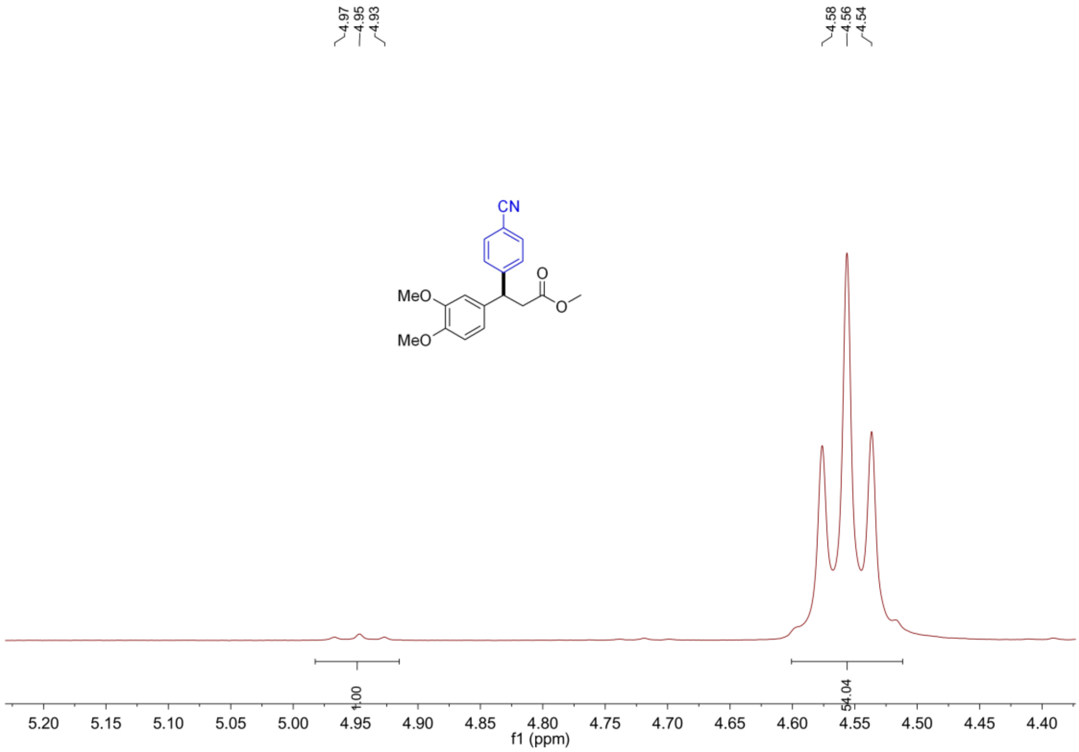


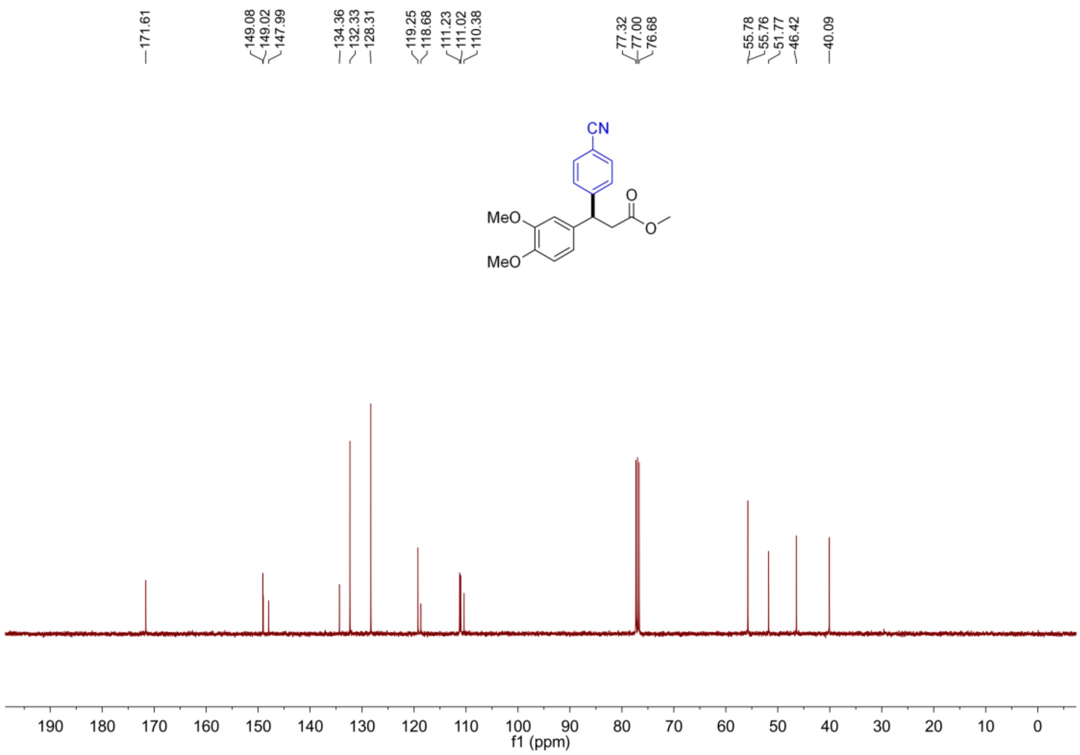
3y ^{1}HNMR



3y Regioselectivity



3y ^{13}CNMR



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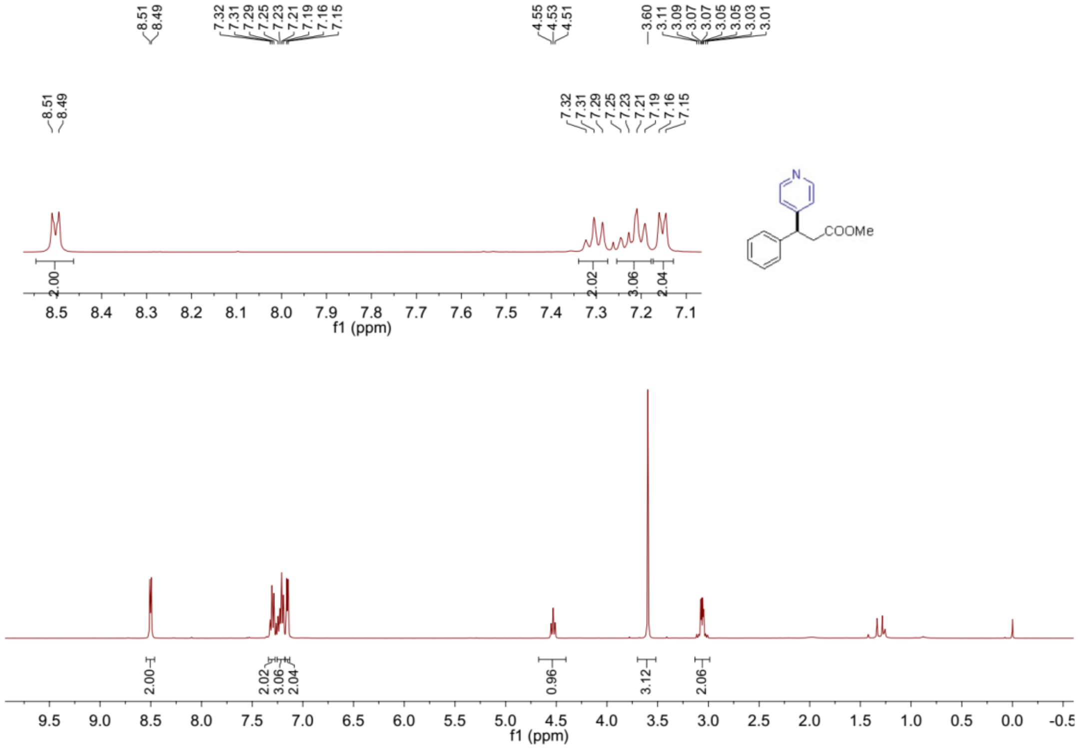

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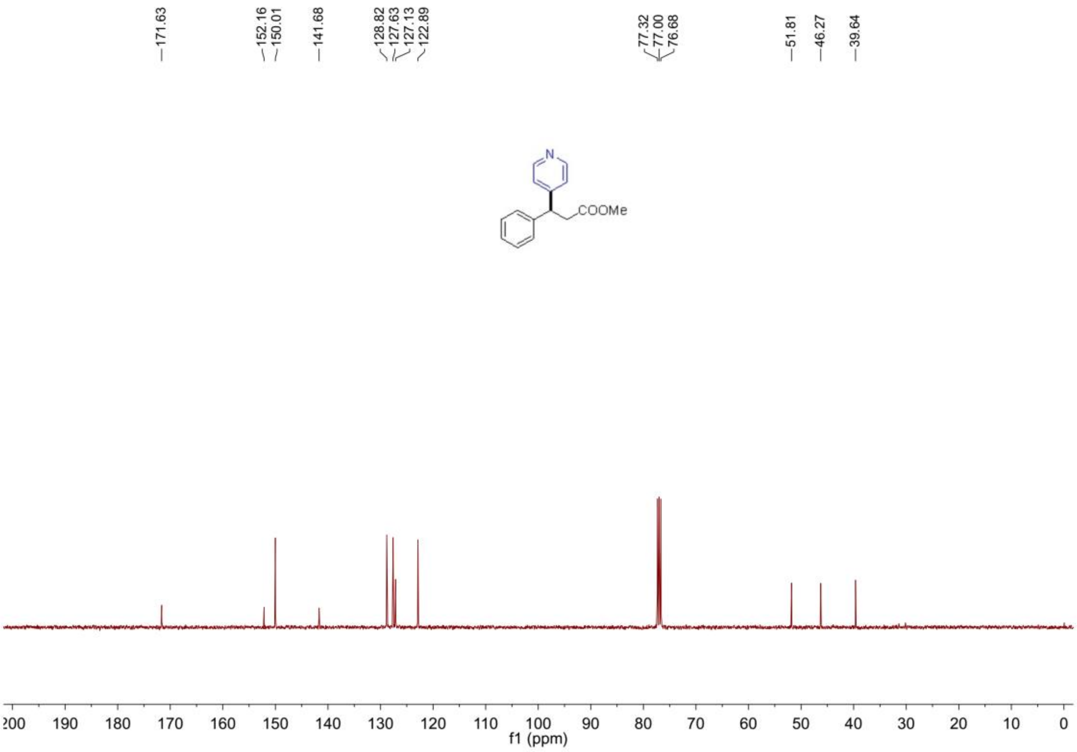

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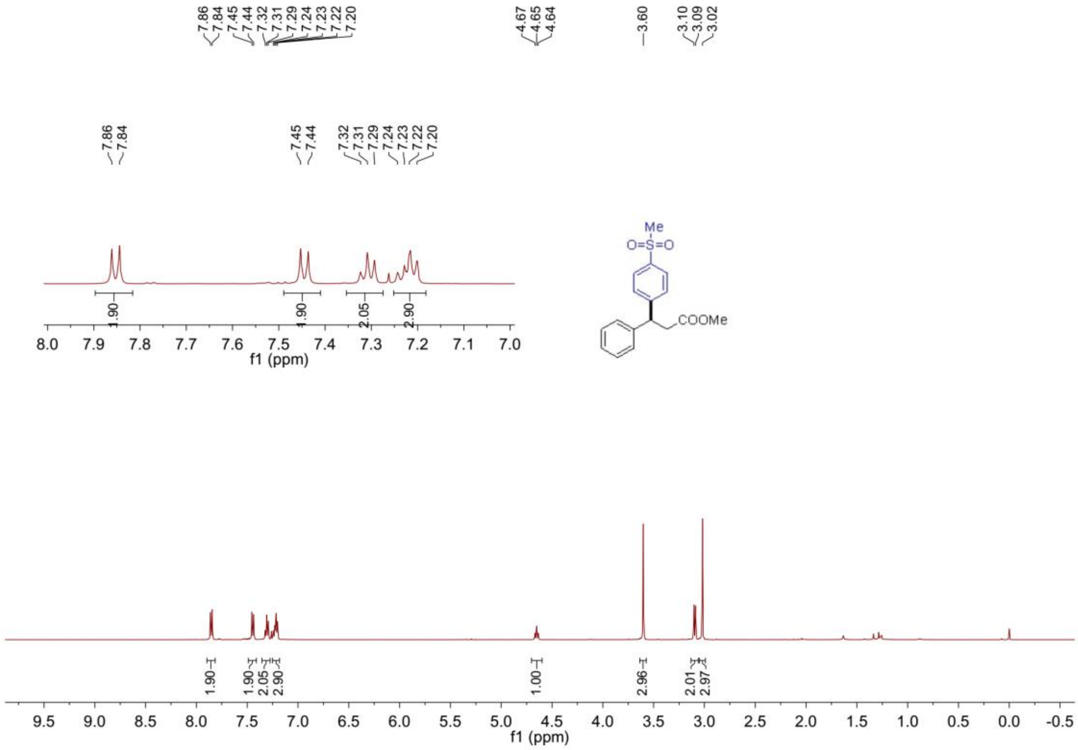

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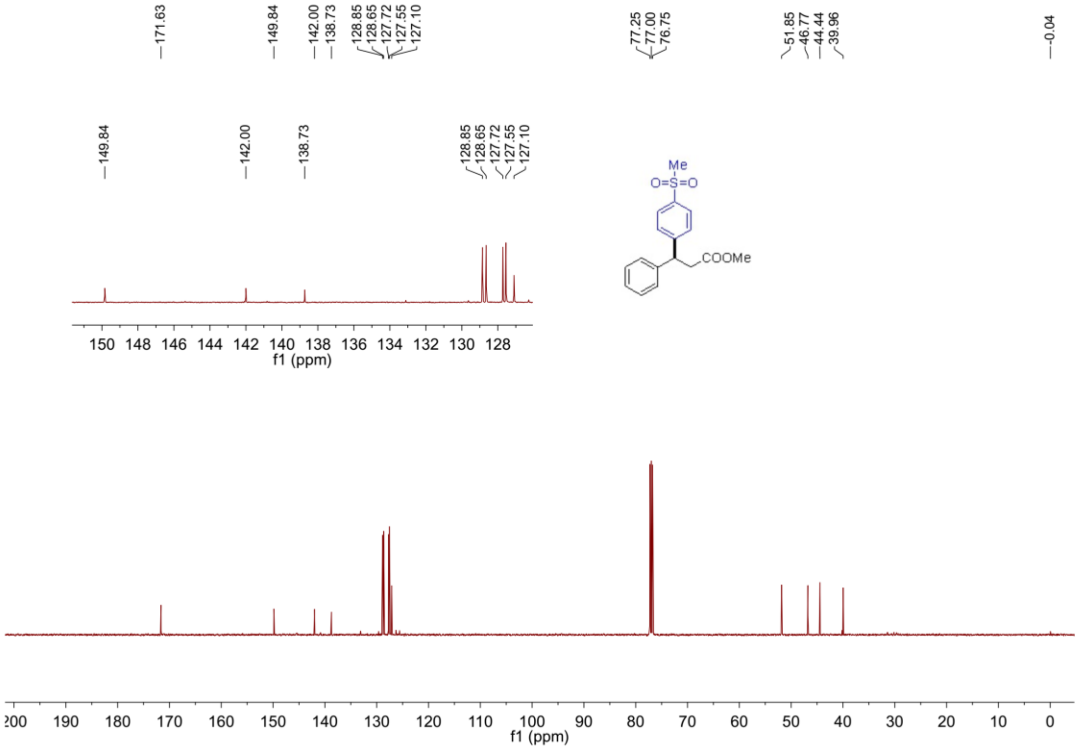

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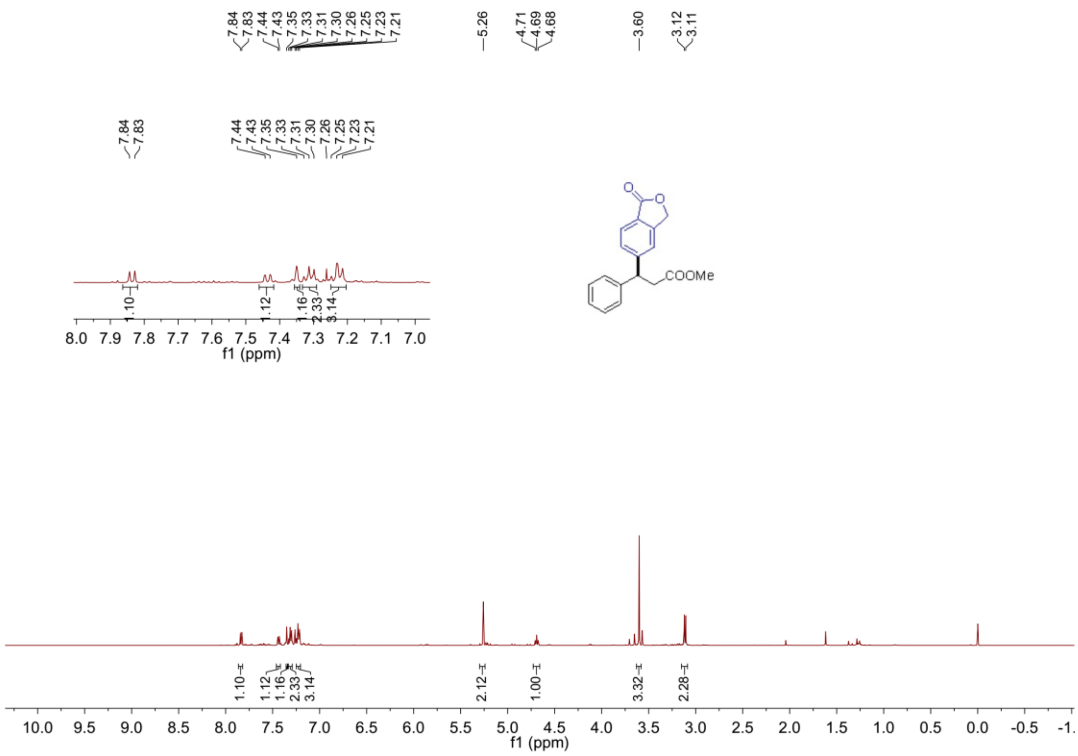

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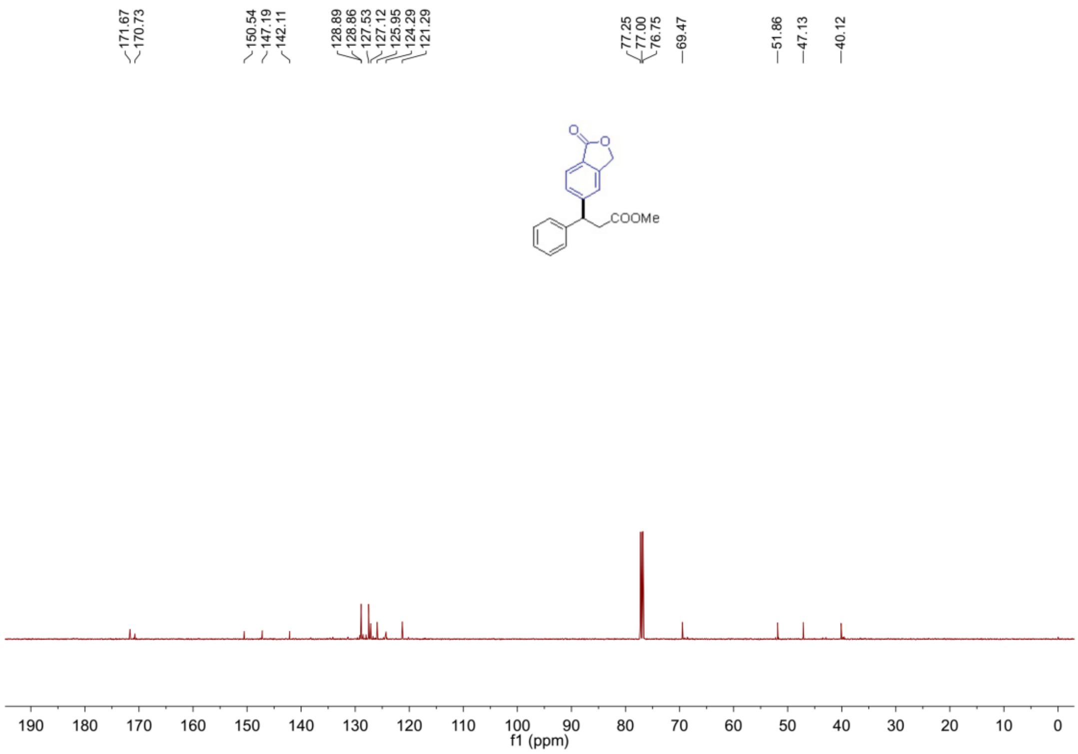

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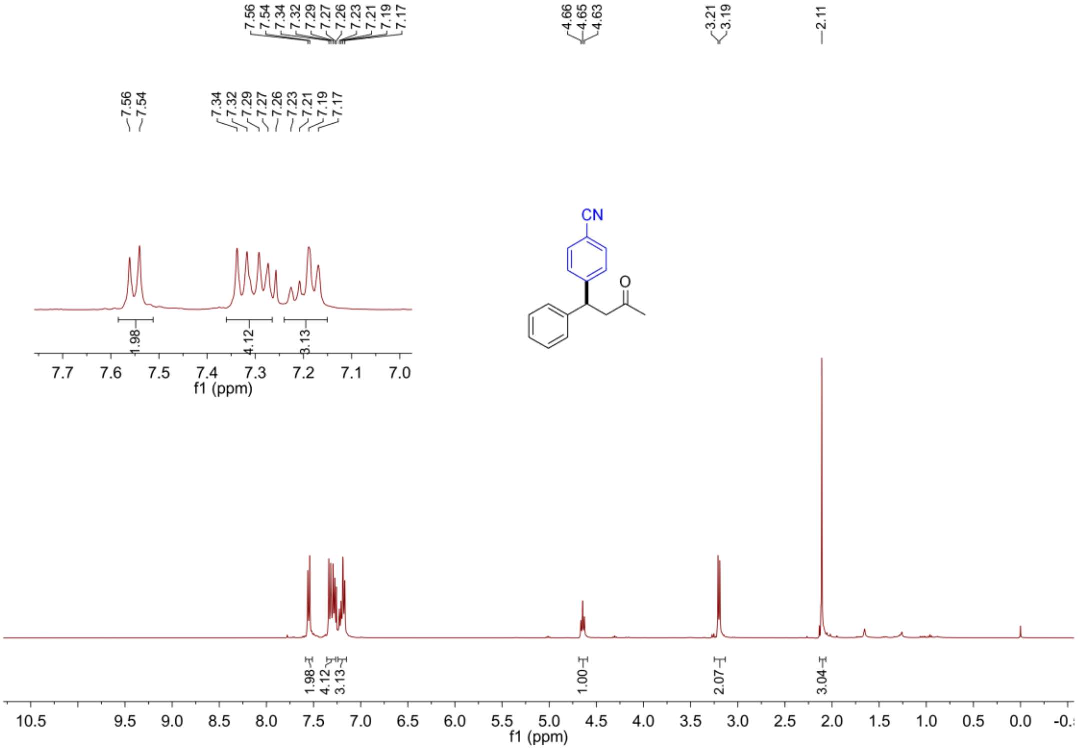

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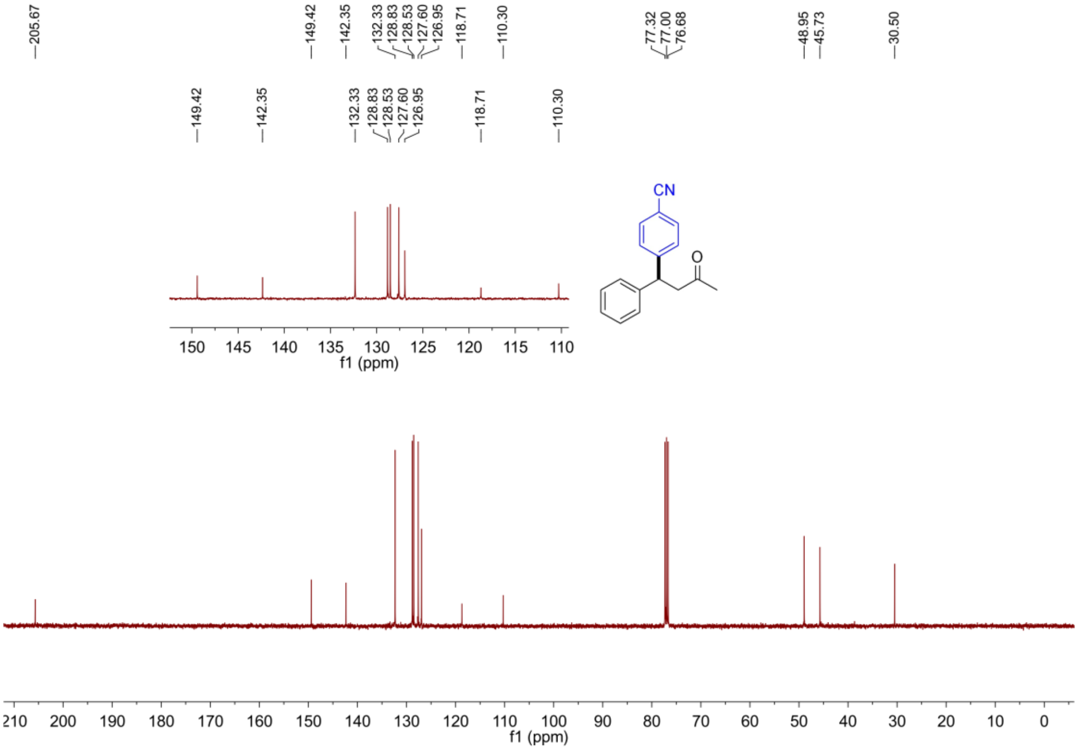

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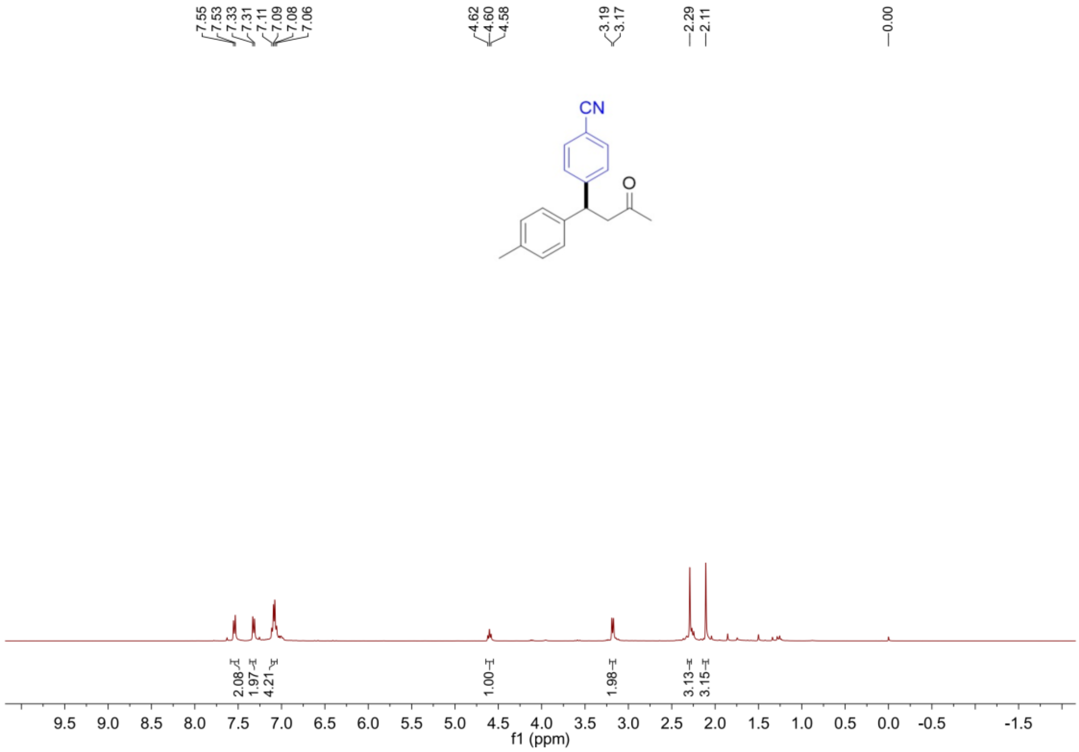

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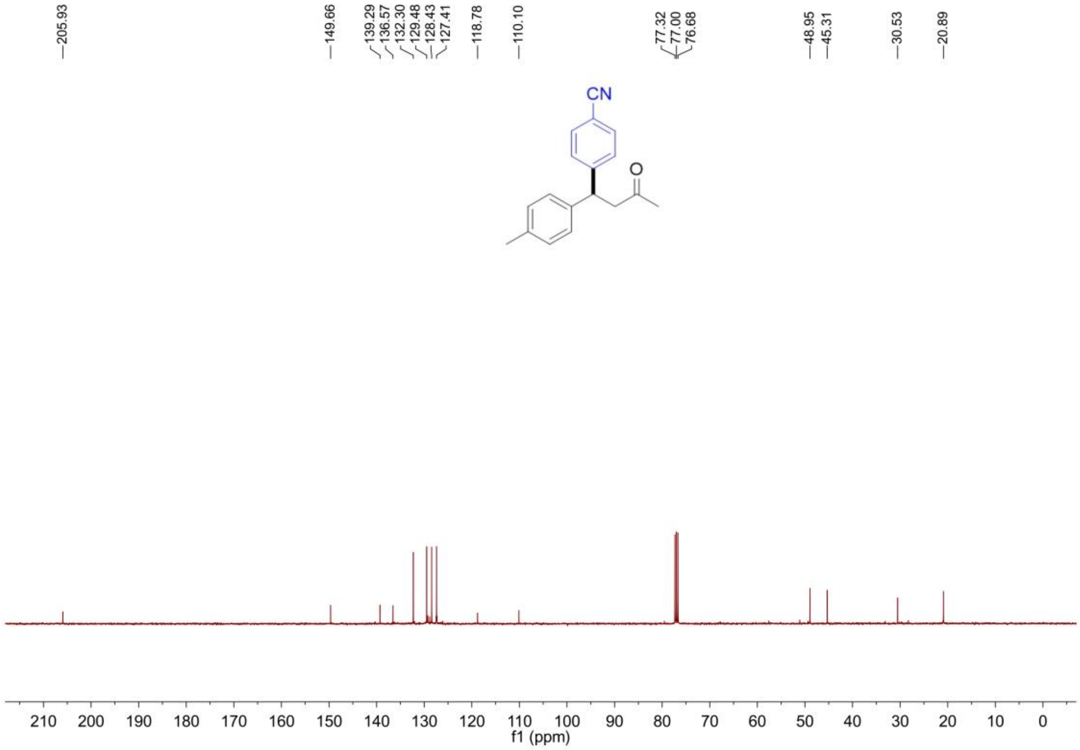

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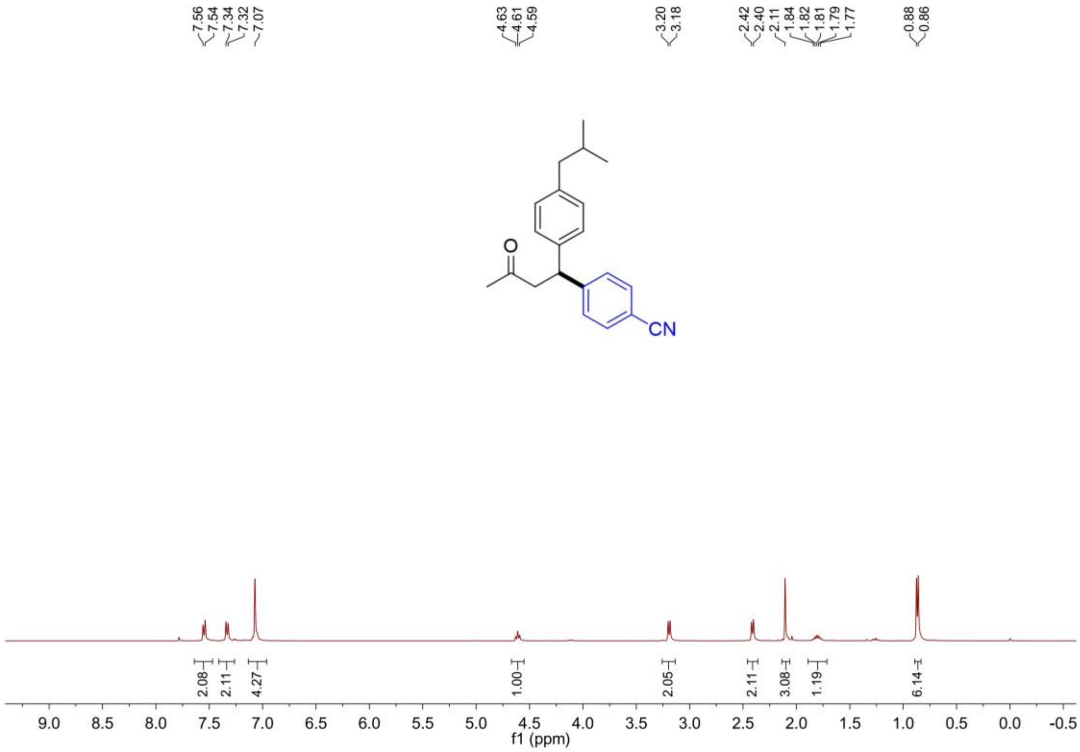

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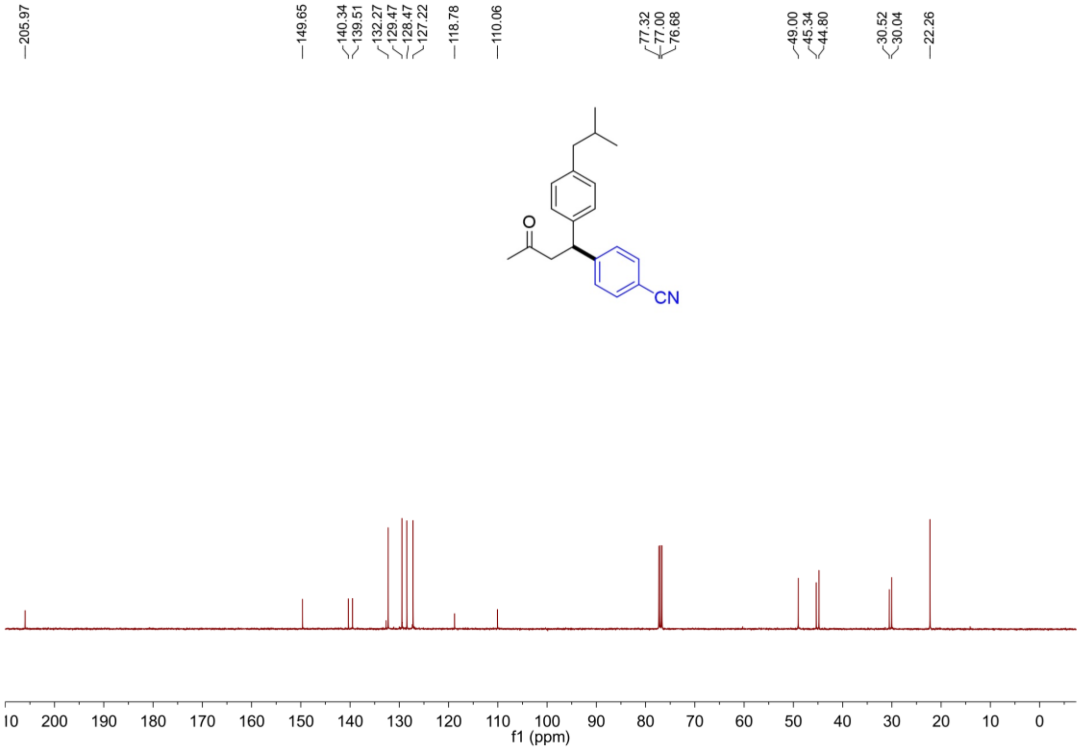

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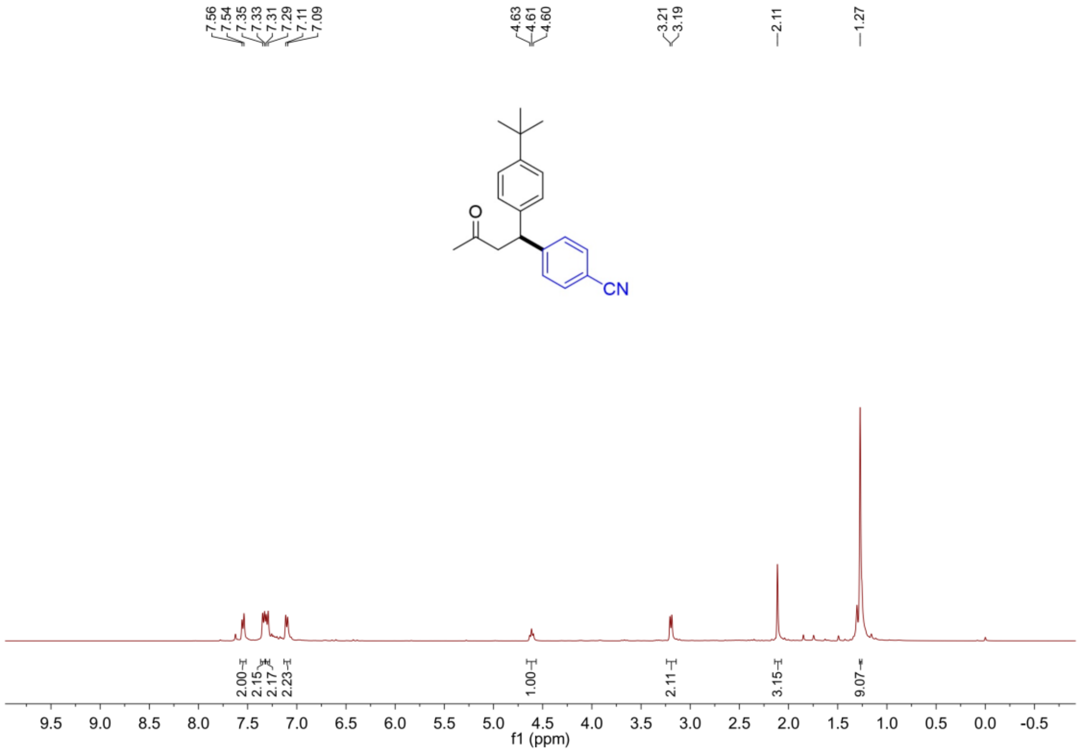

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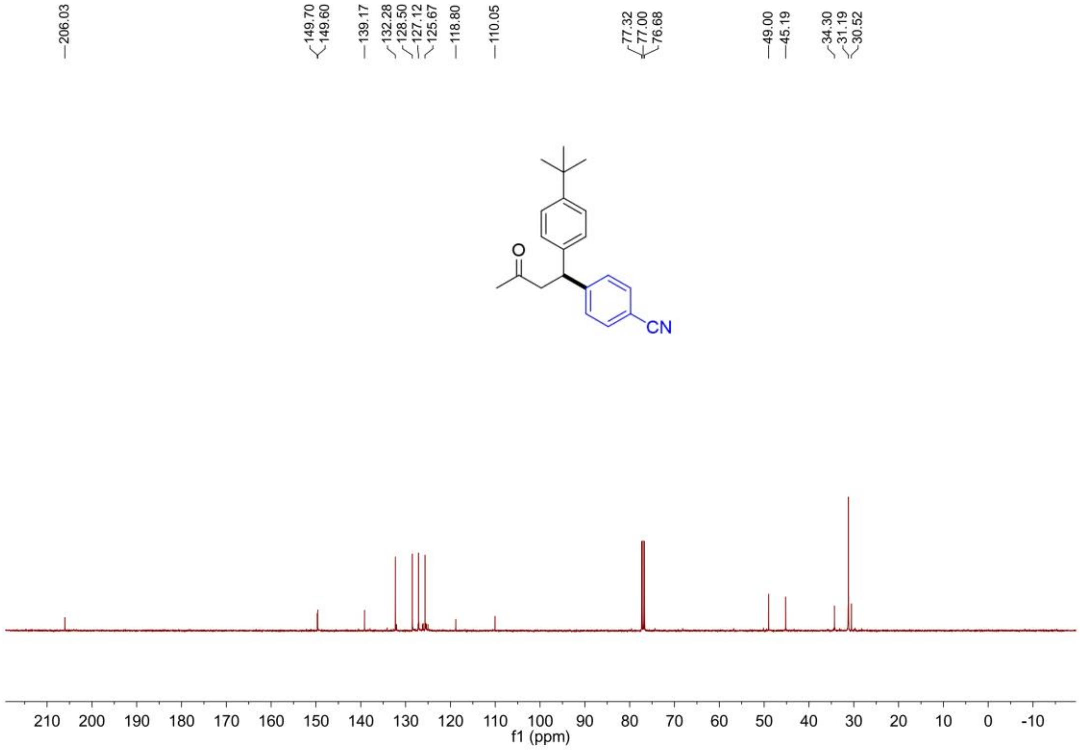

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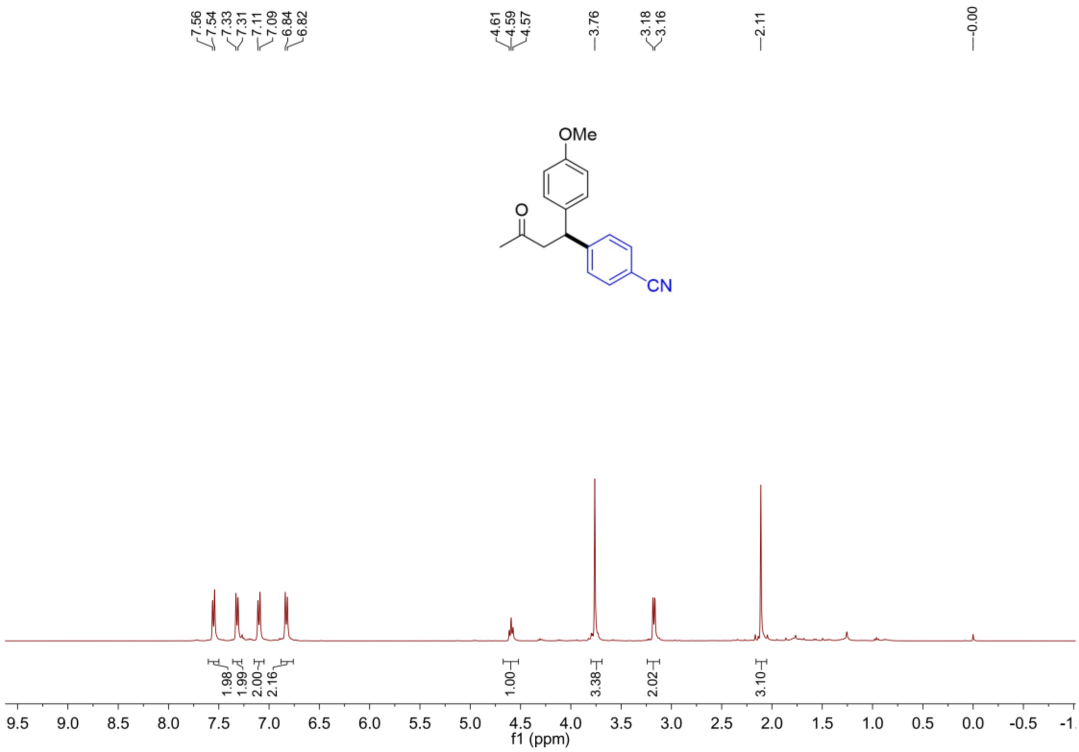

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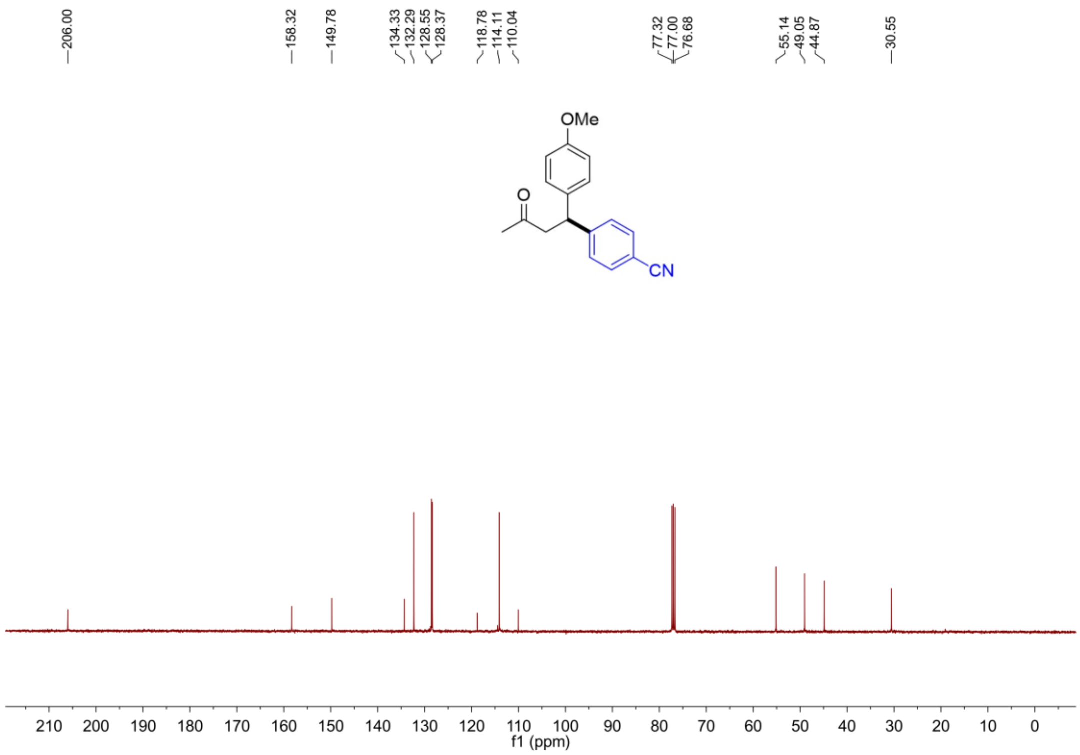

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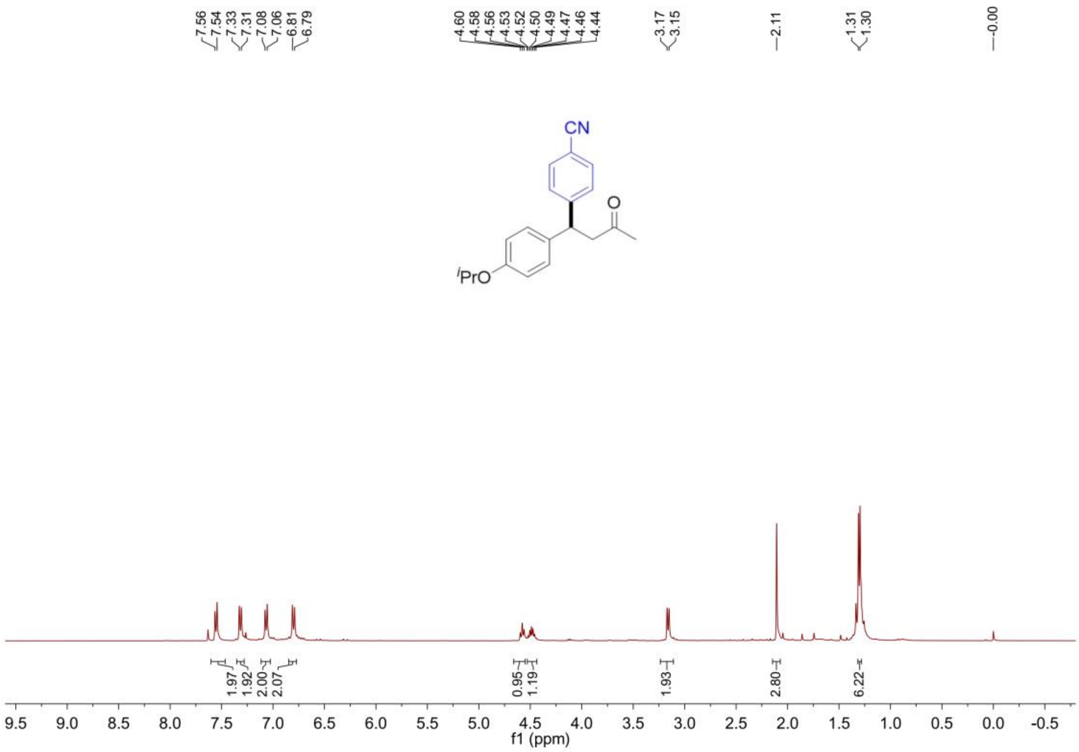

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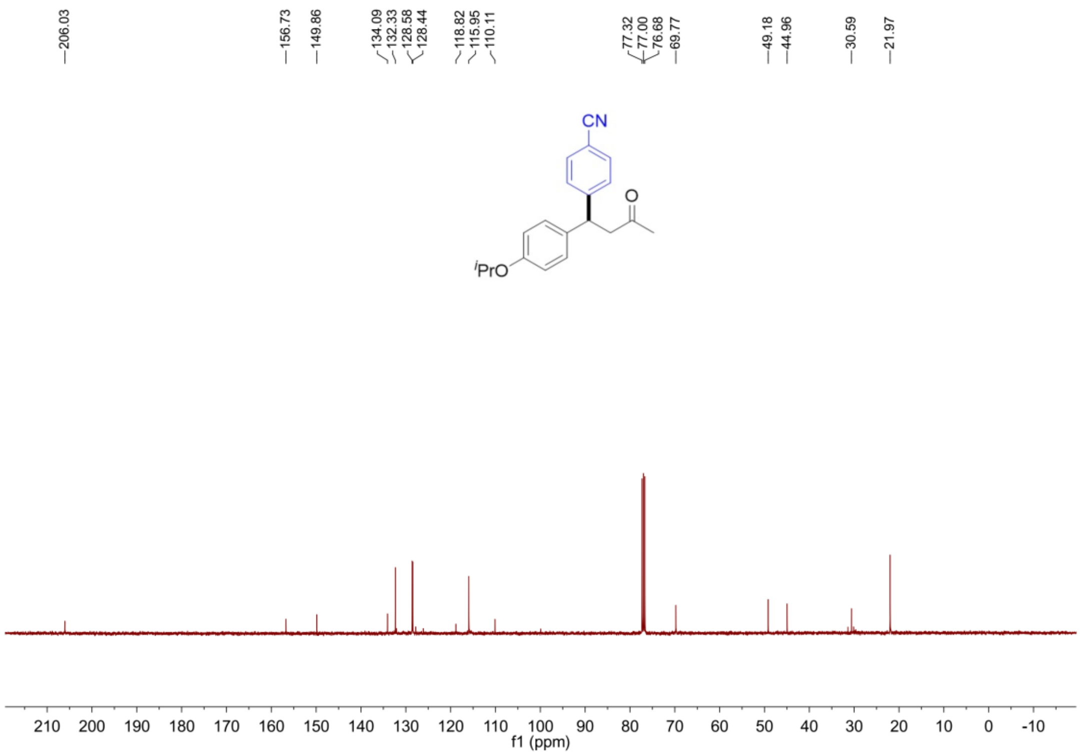

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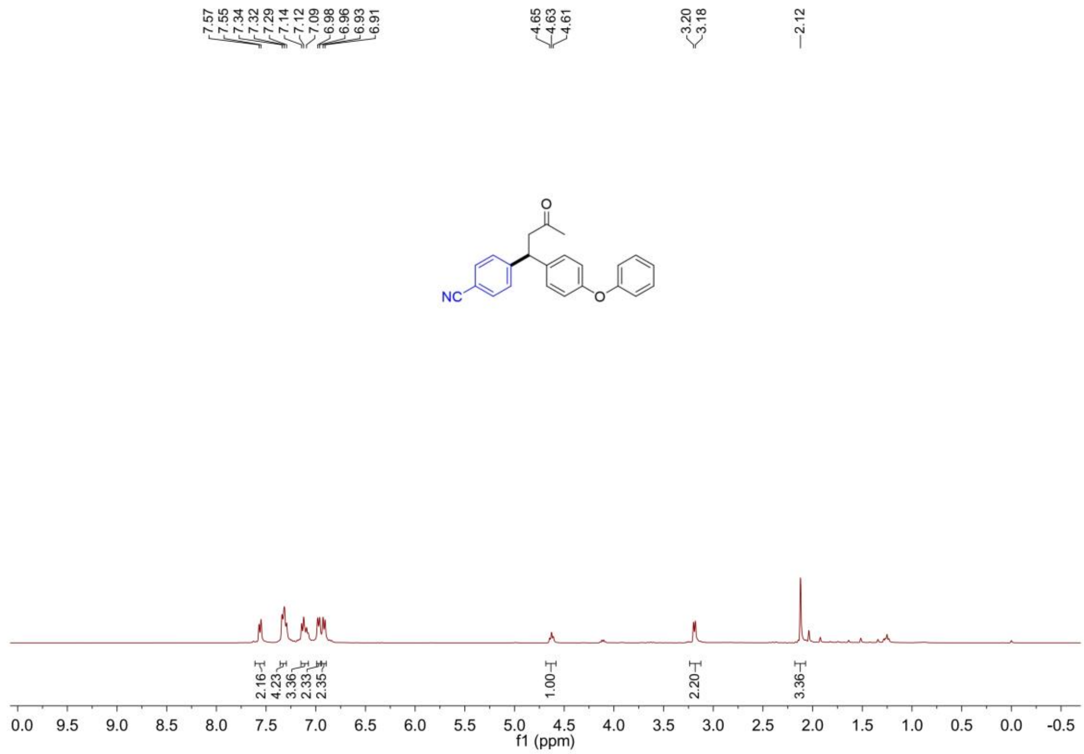

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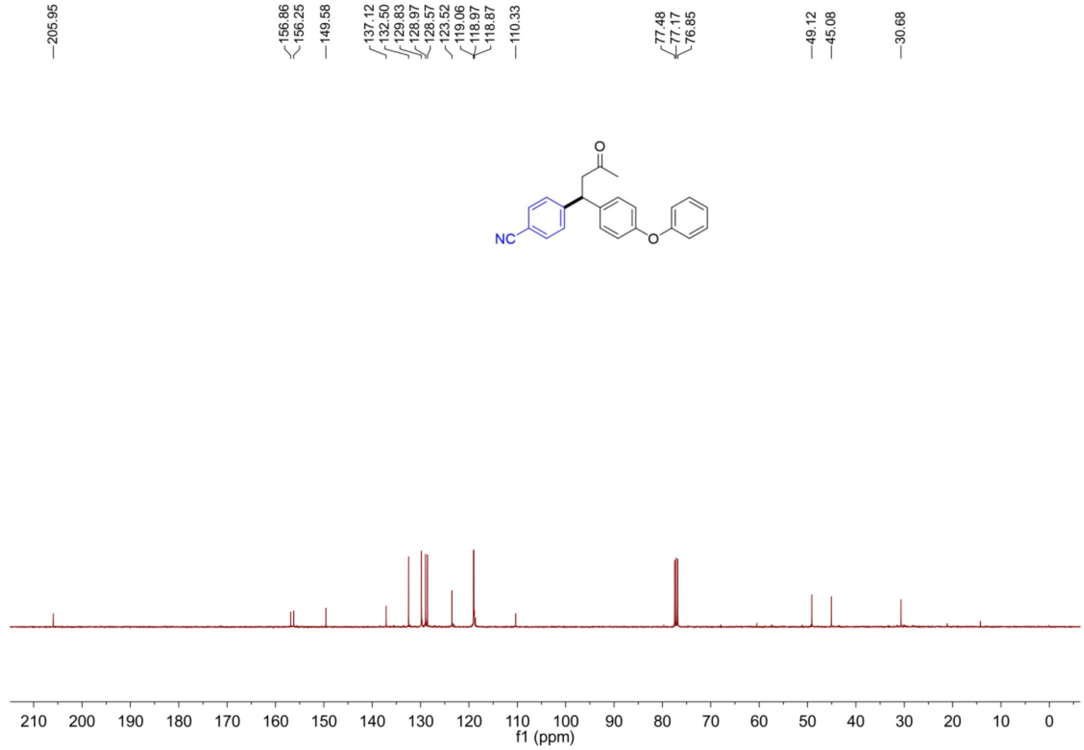

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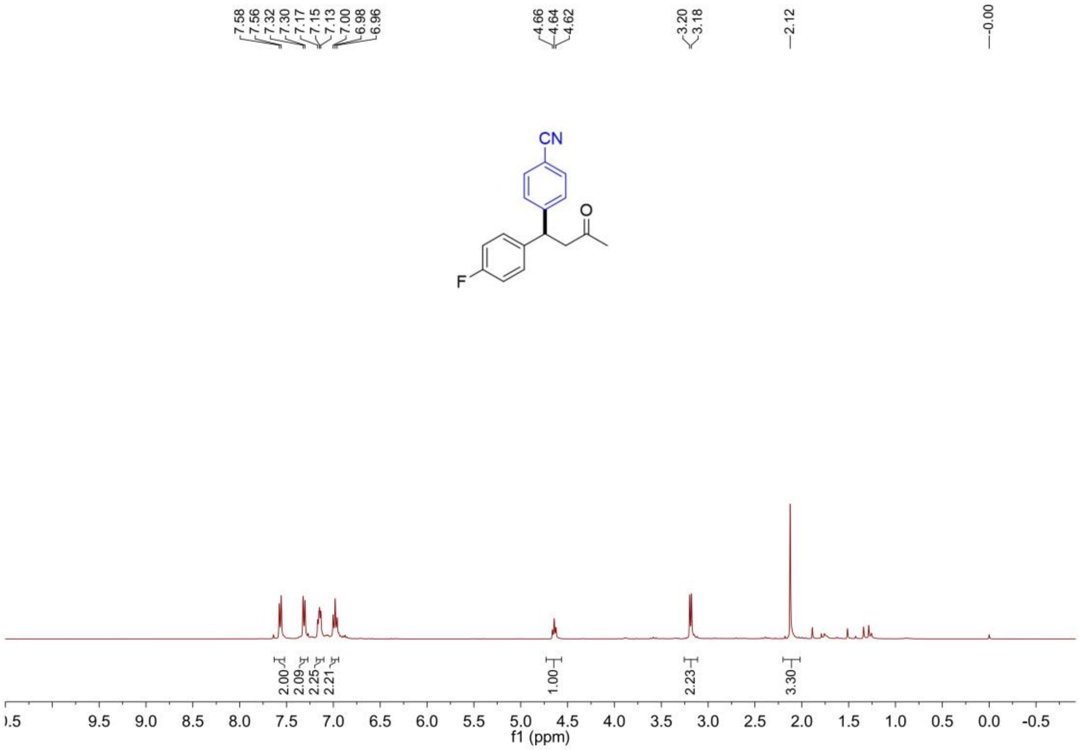

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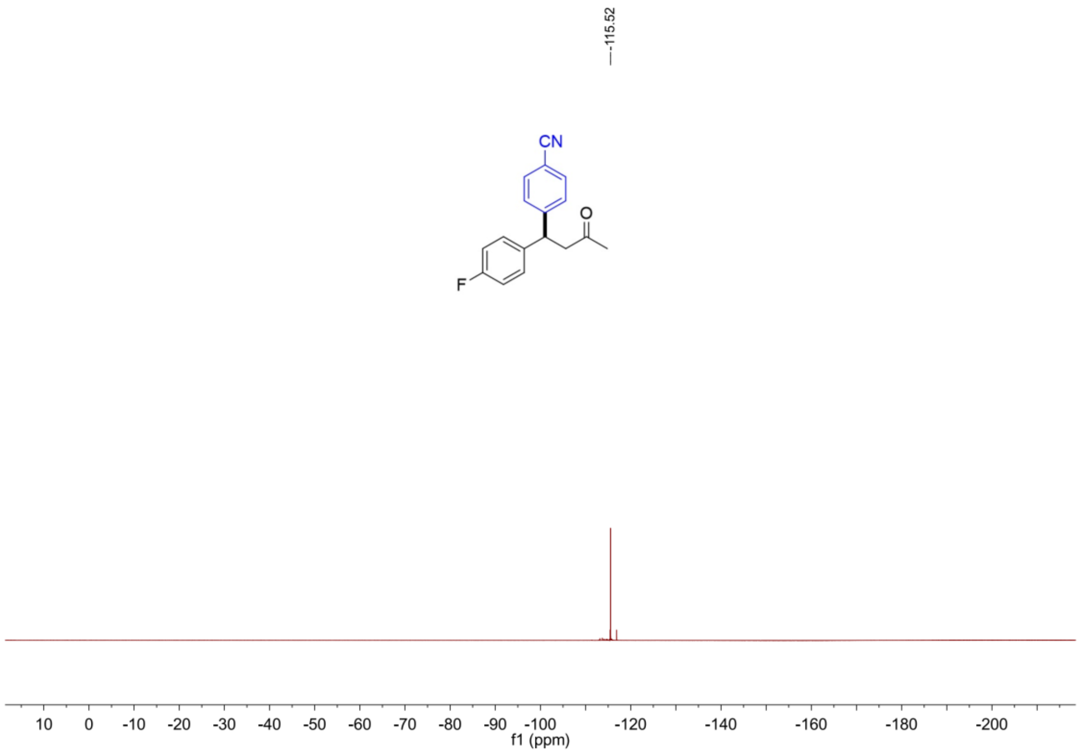

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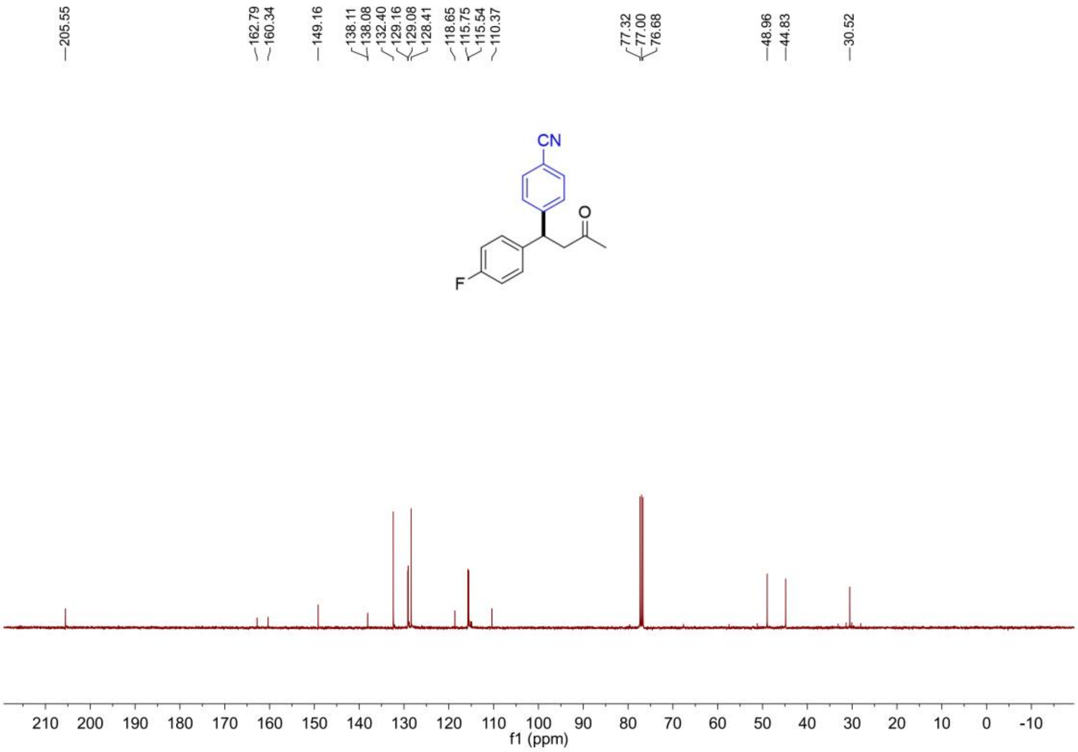

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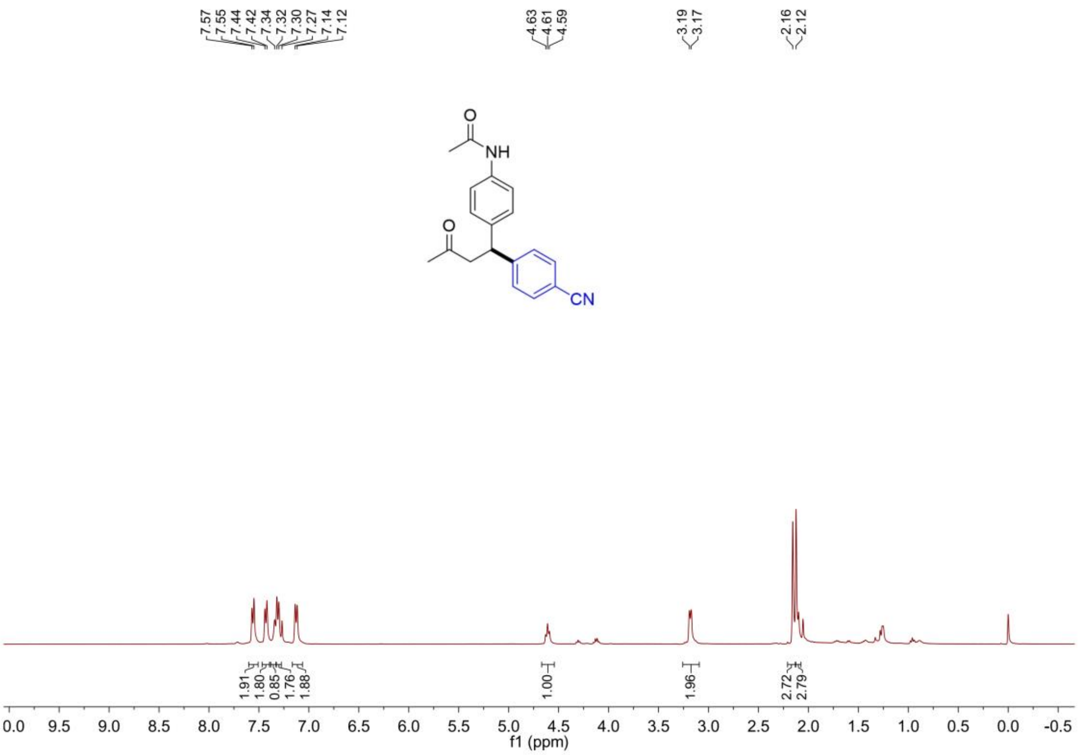

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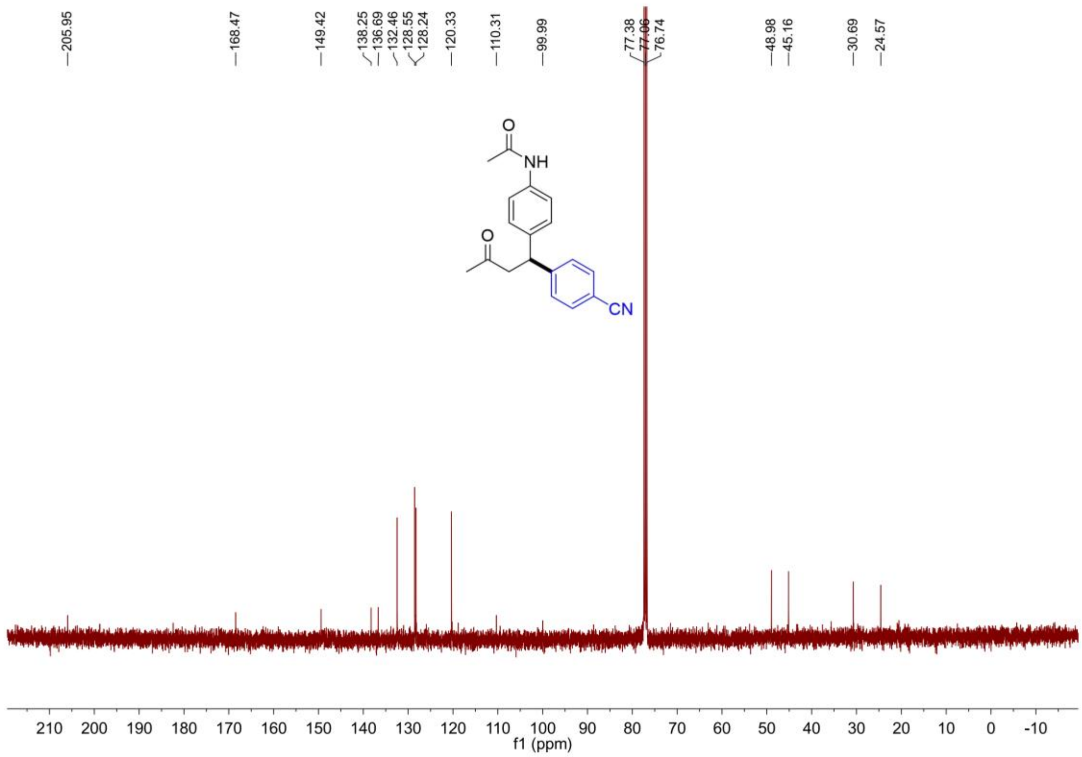

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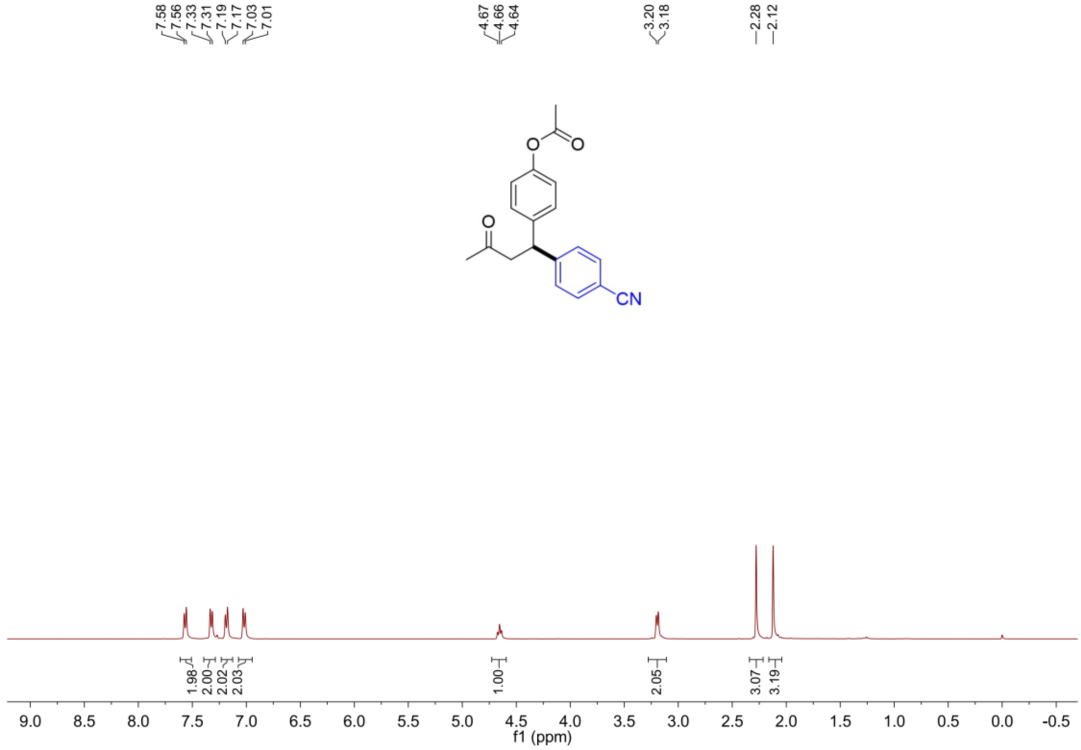

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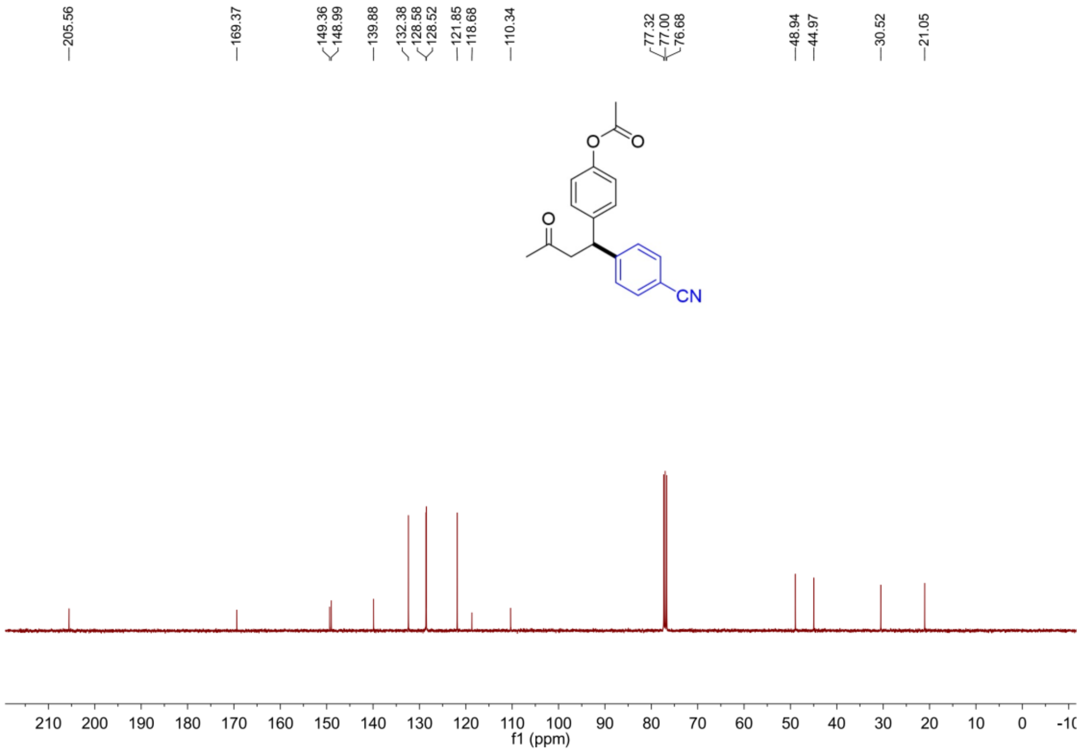

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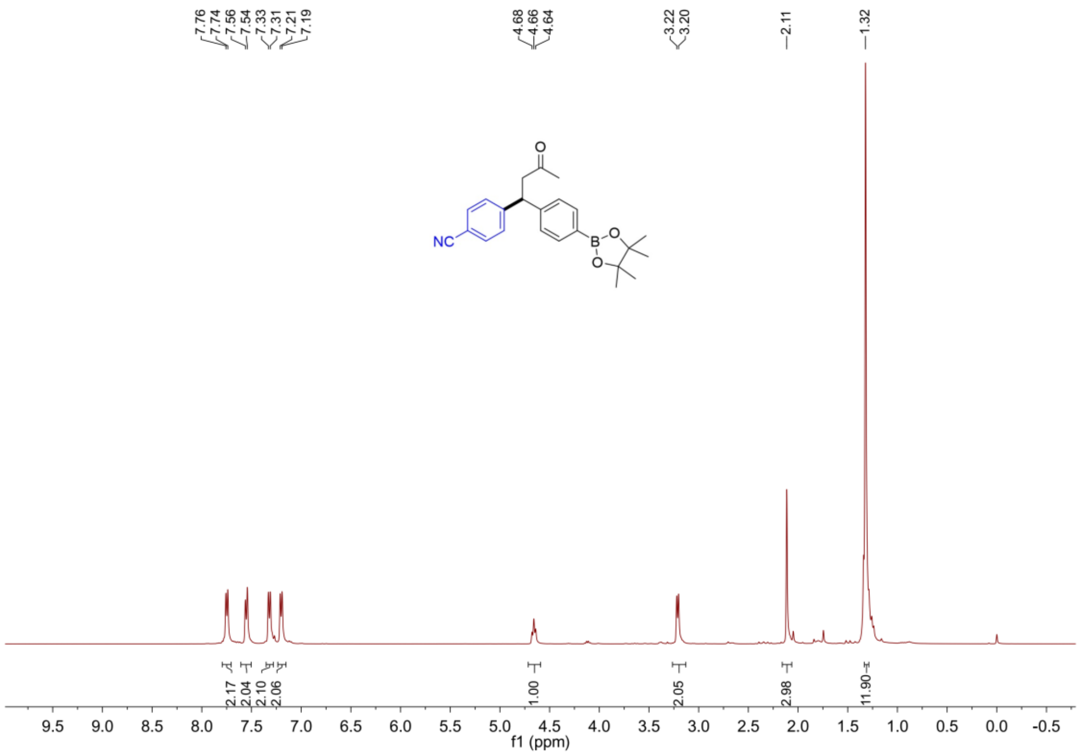

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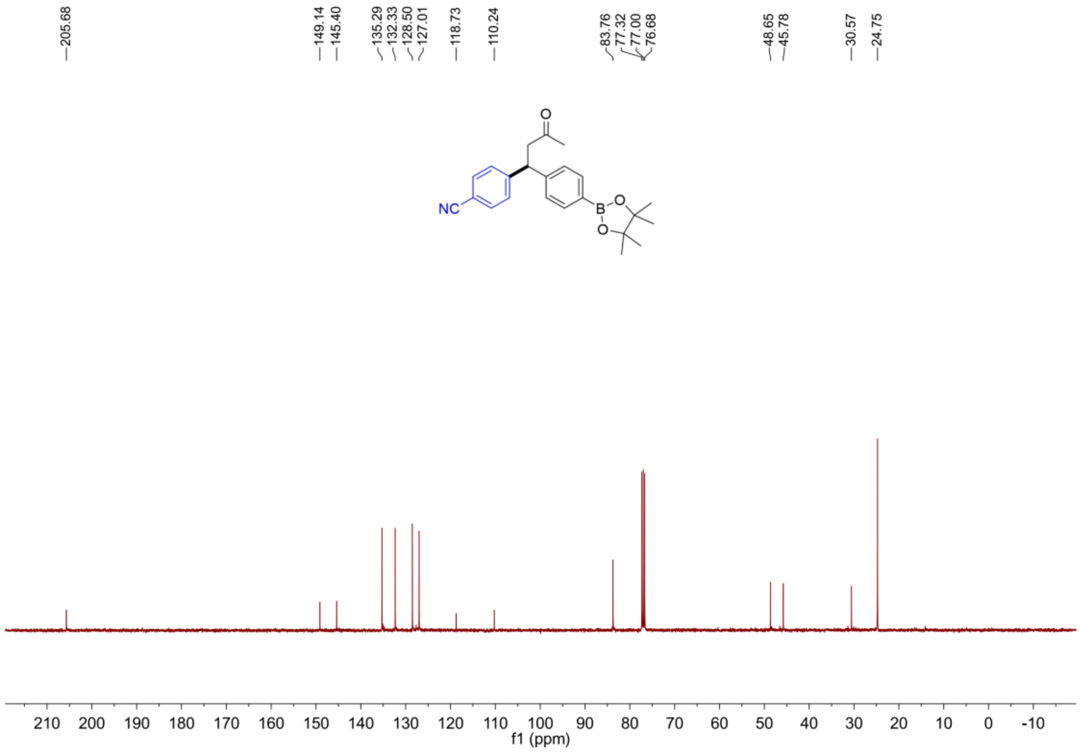

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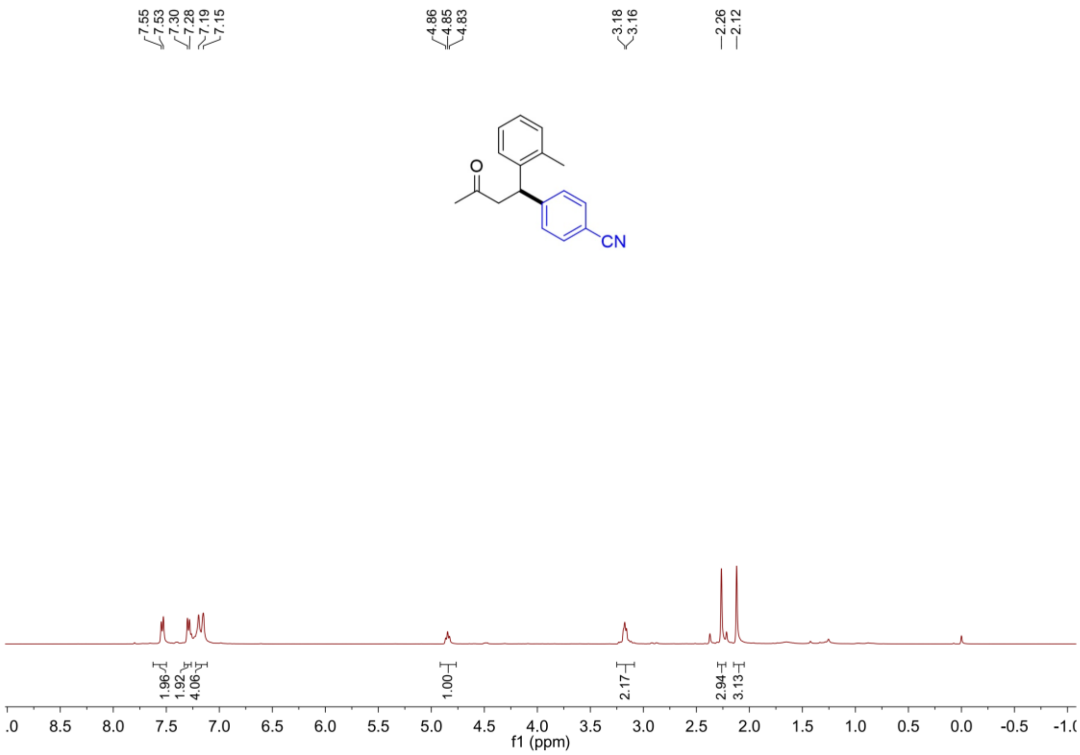

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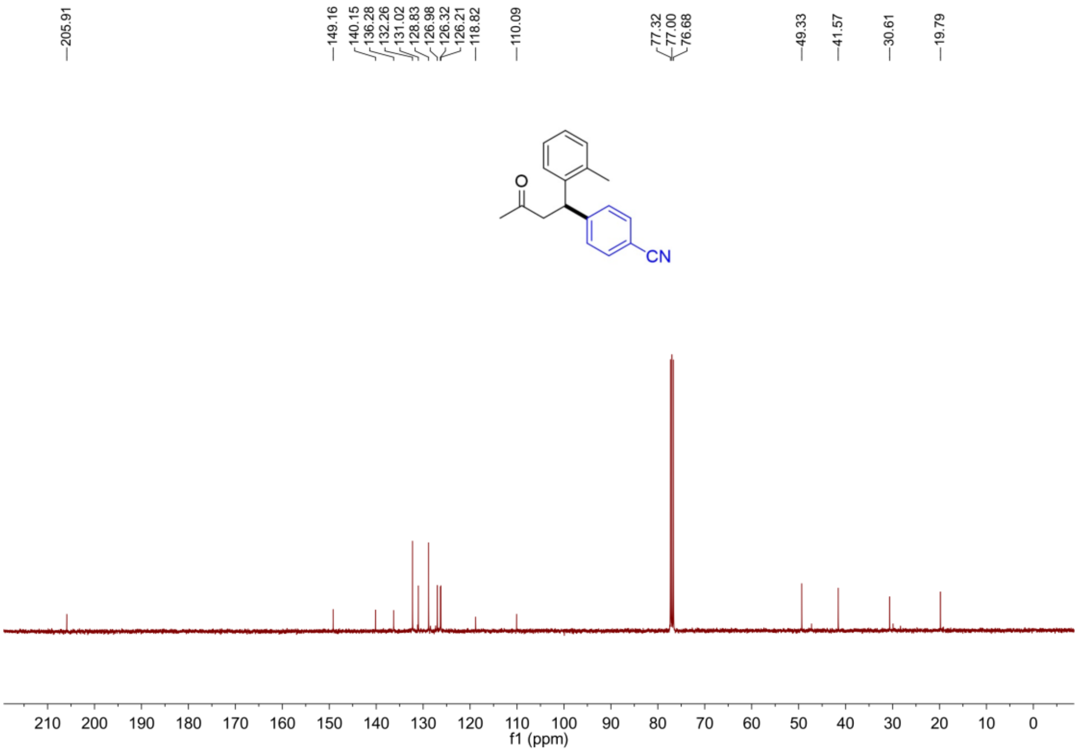

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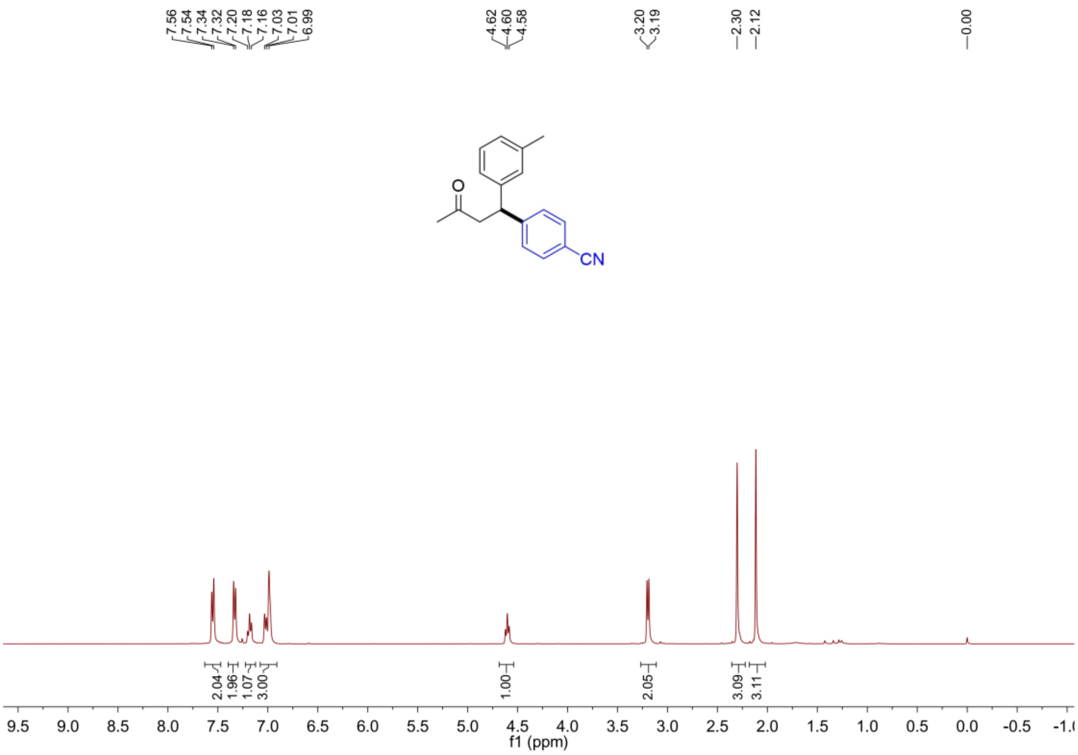

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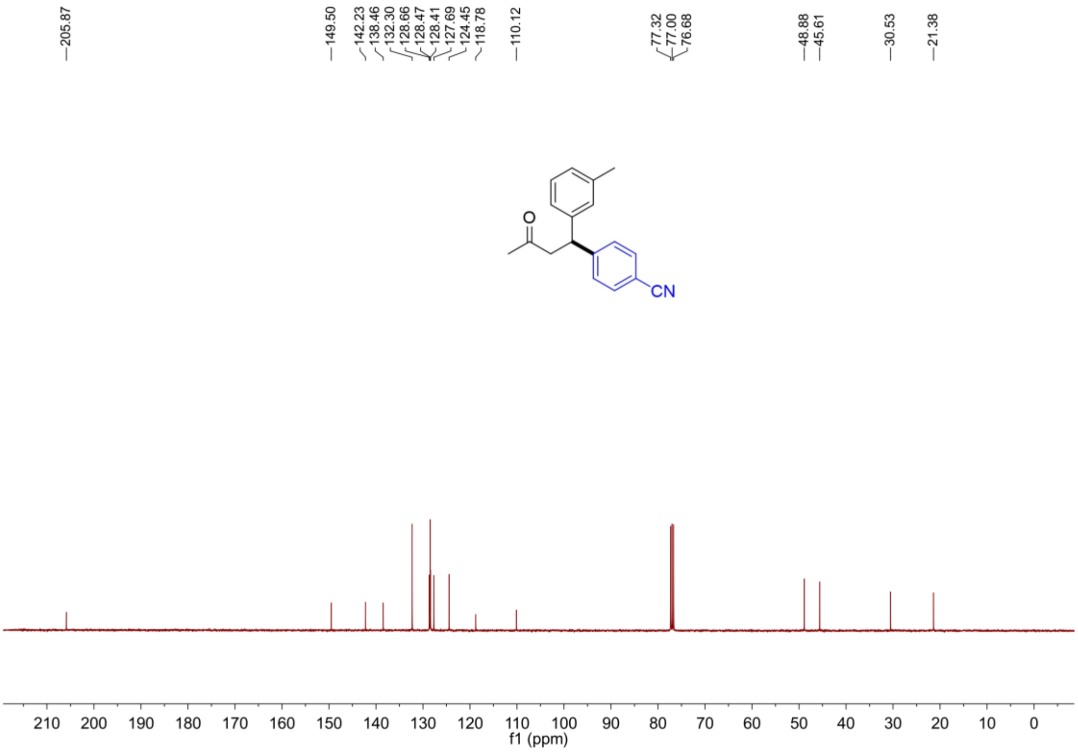

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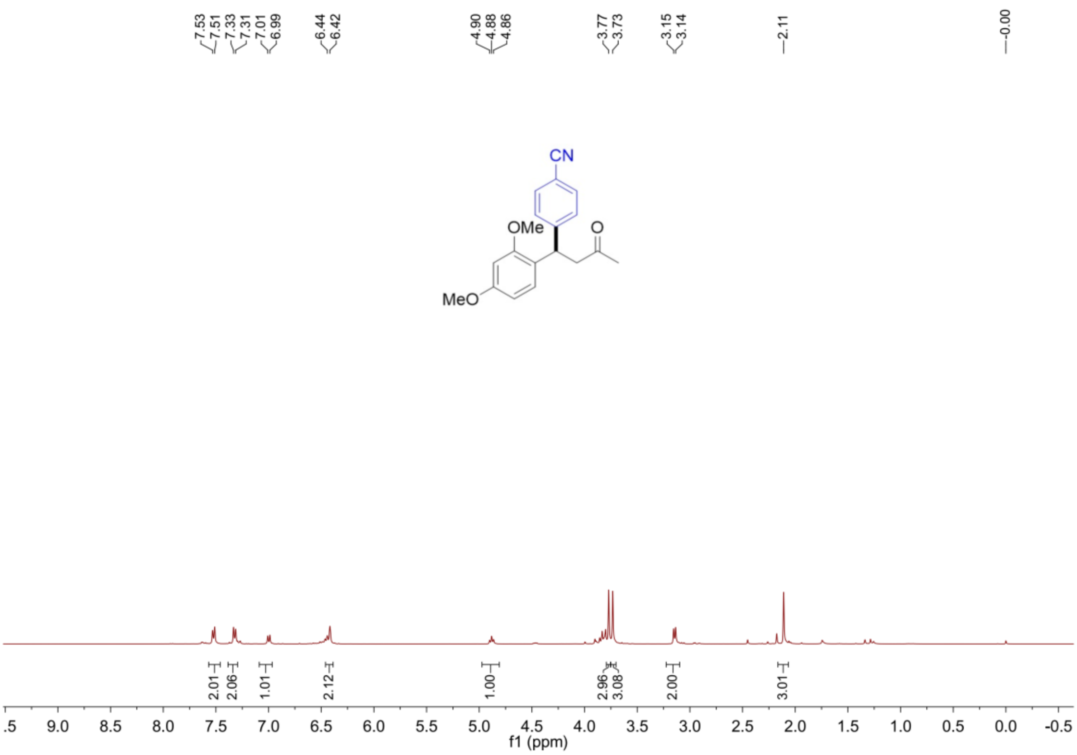

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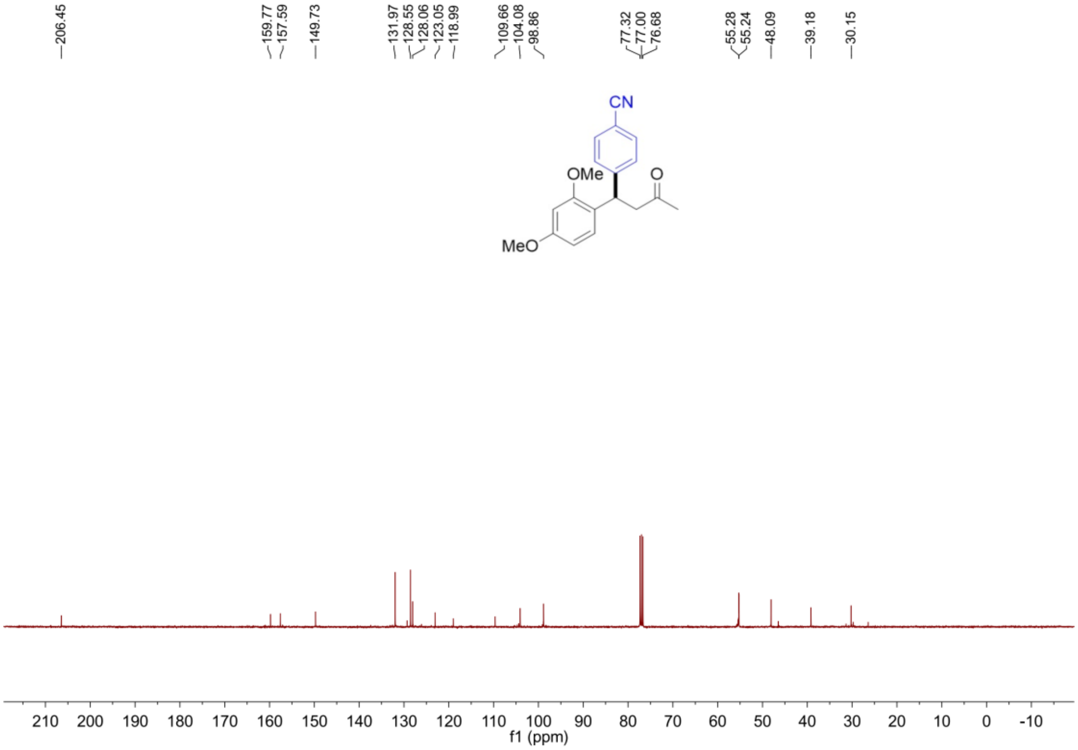

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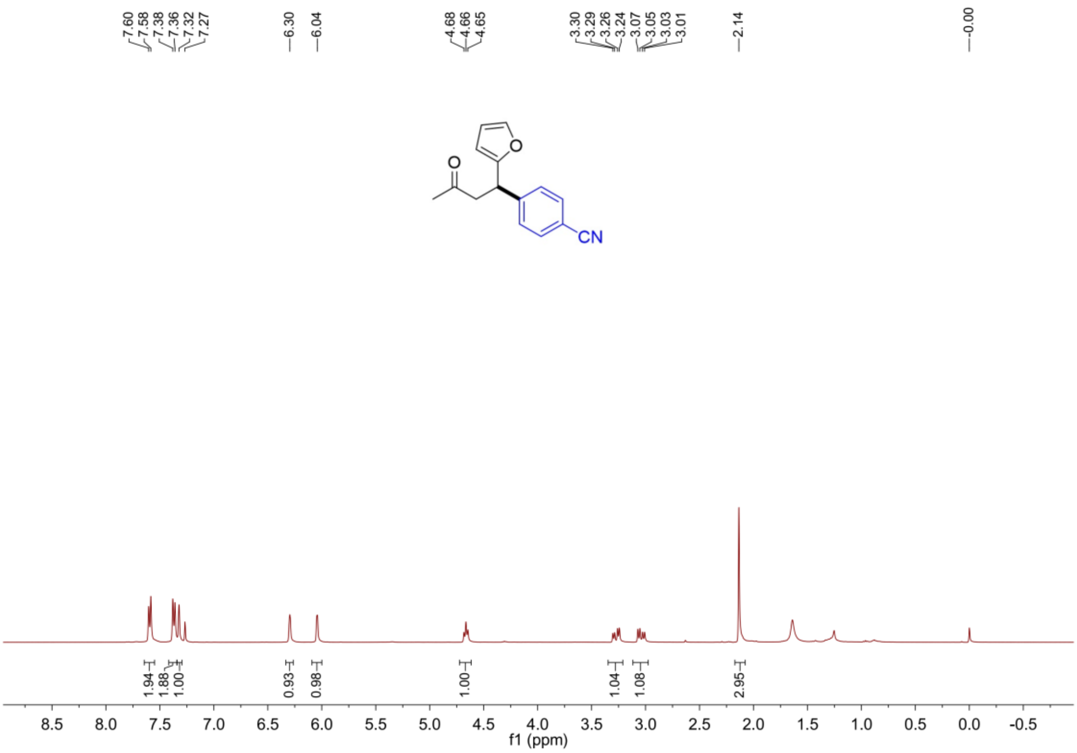

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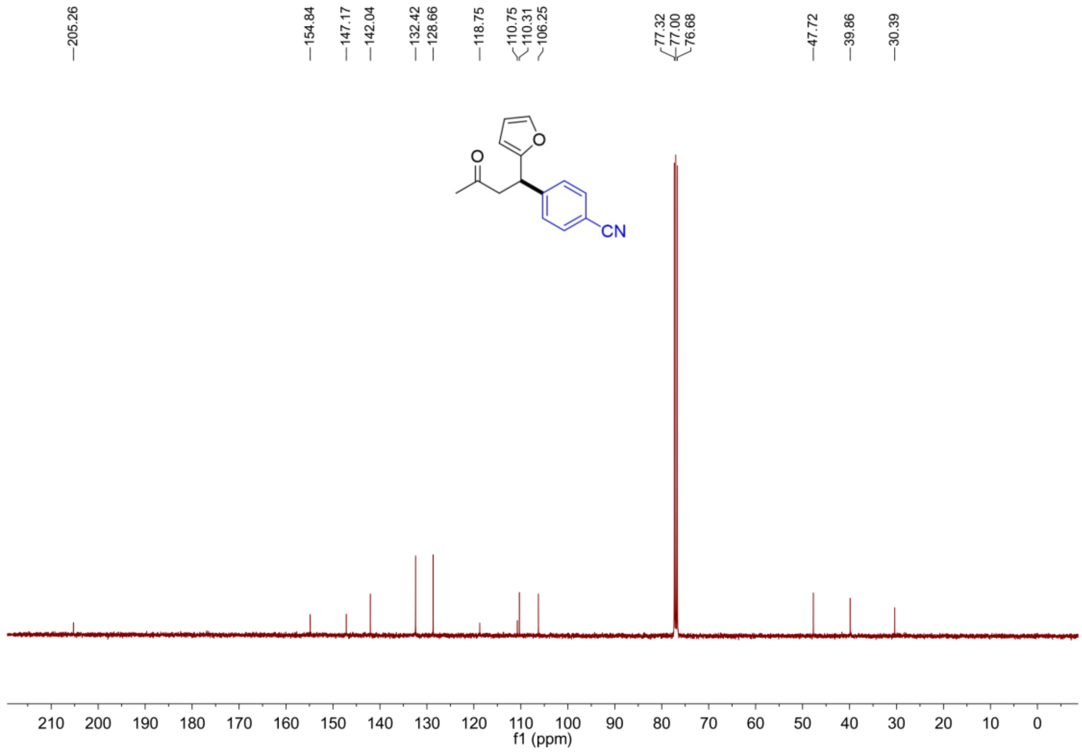

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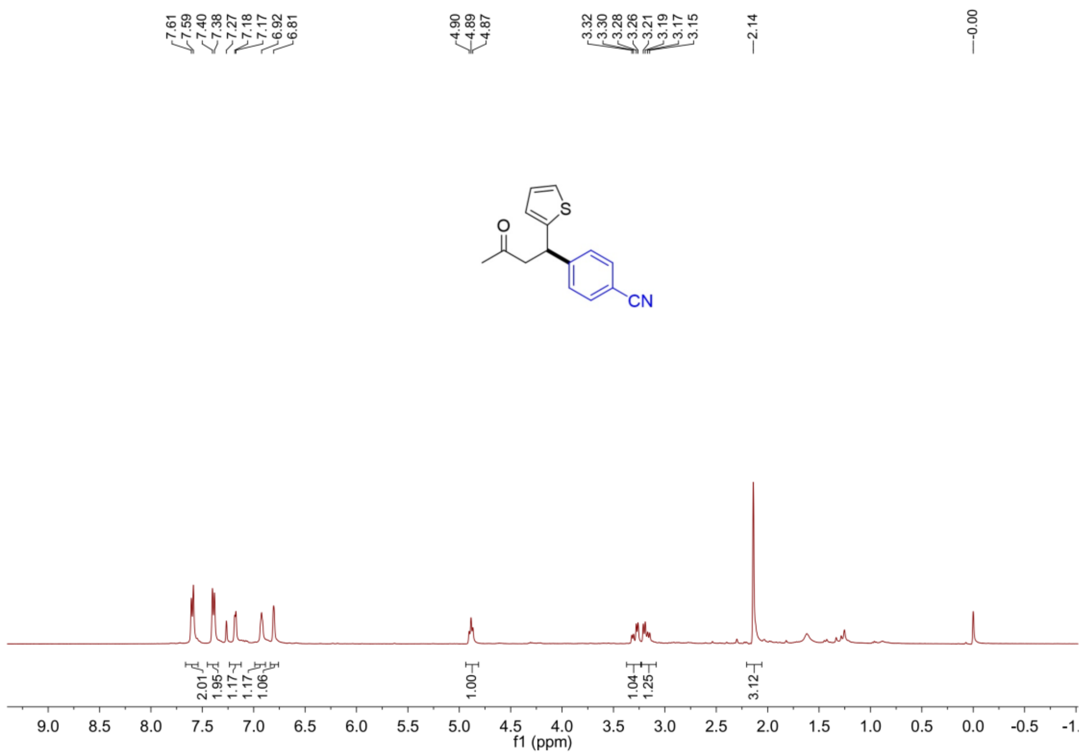

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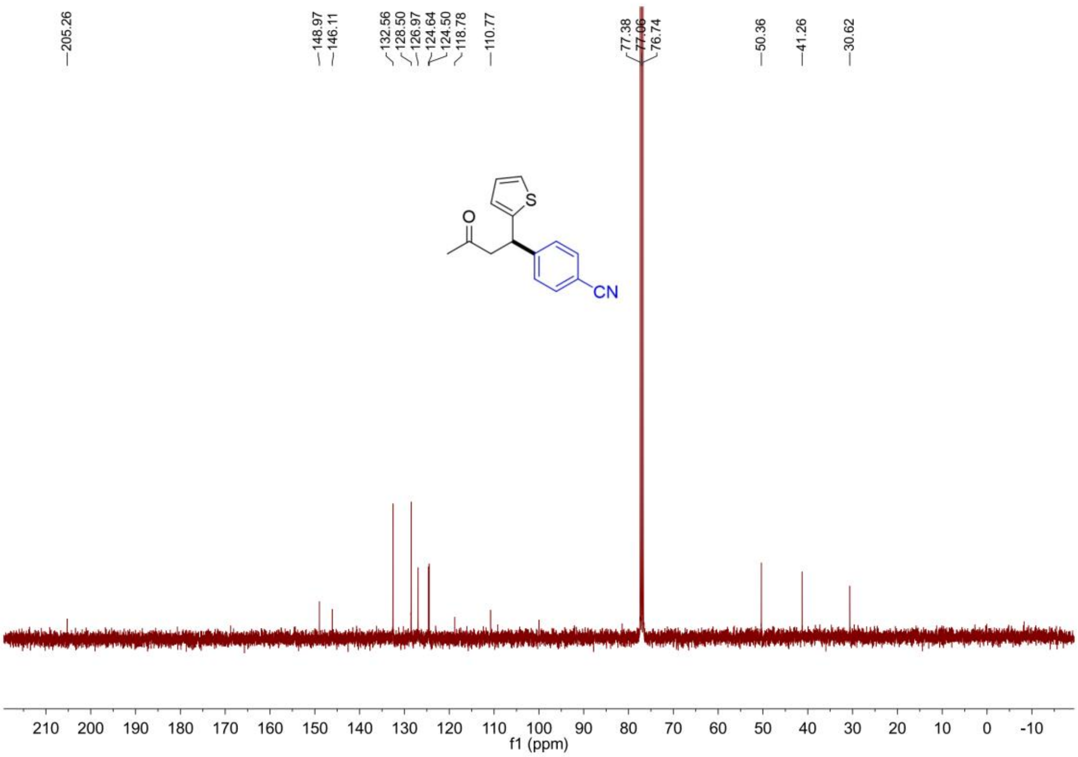

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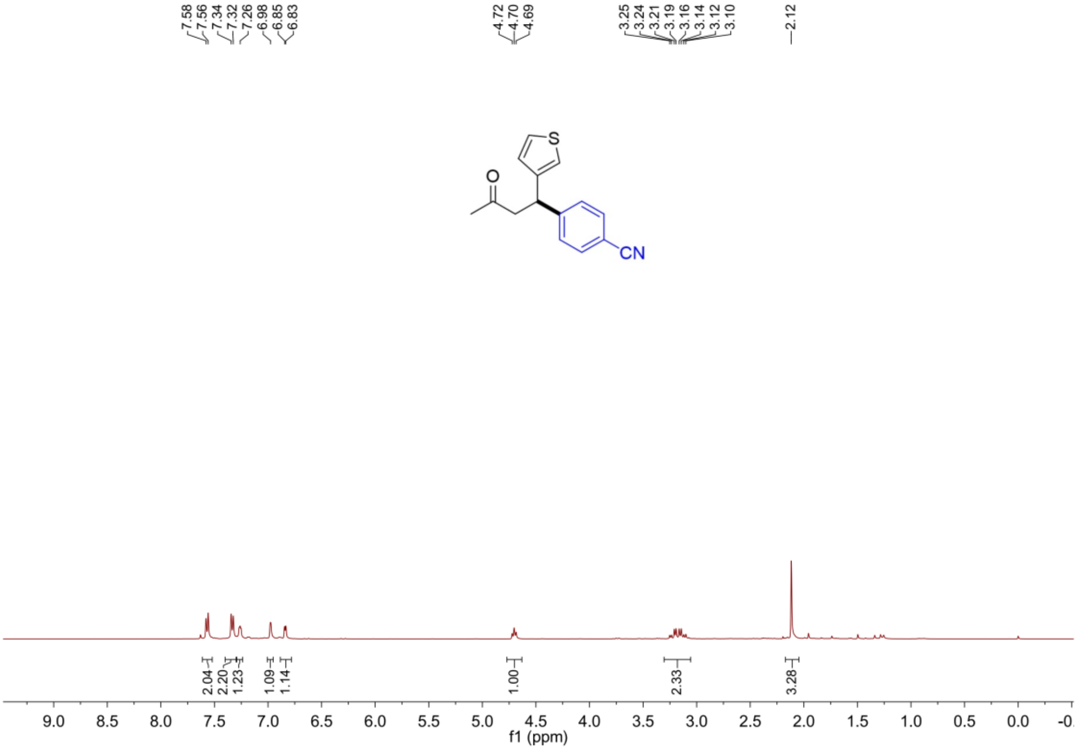

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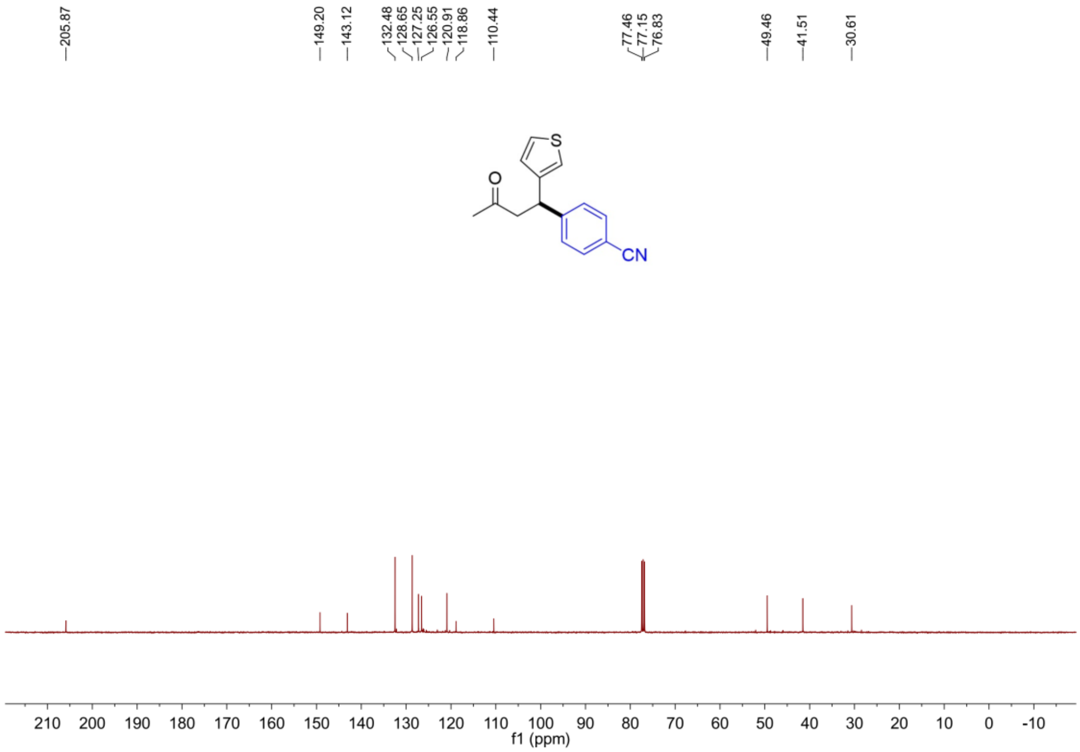

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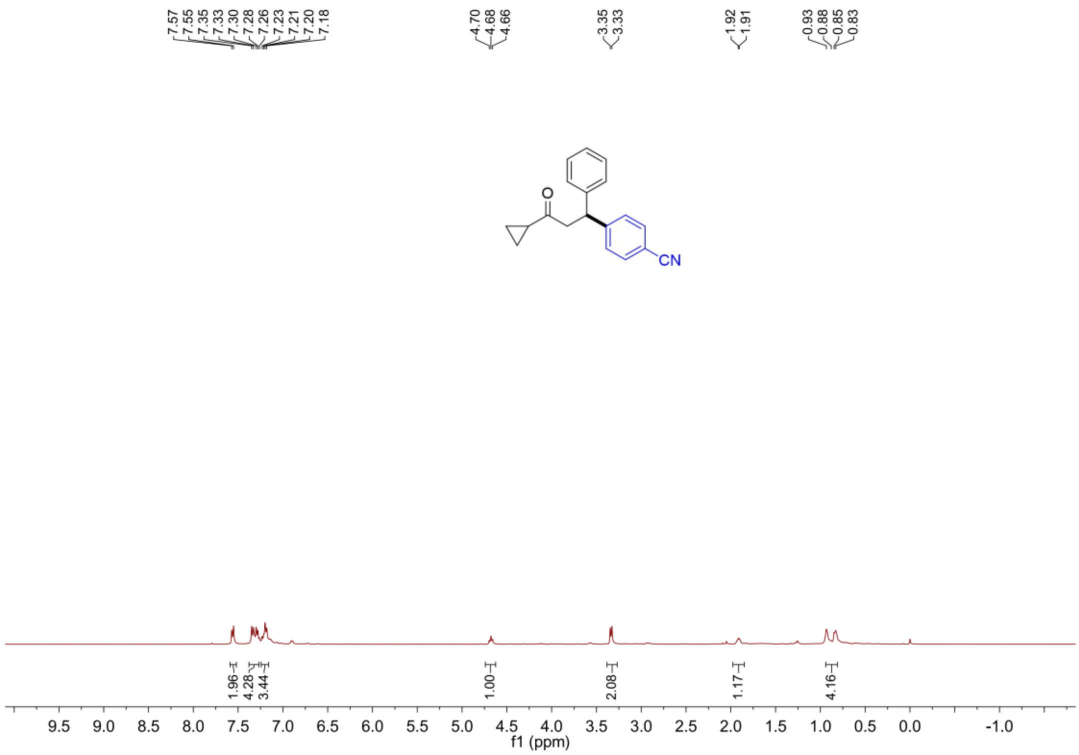

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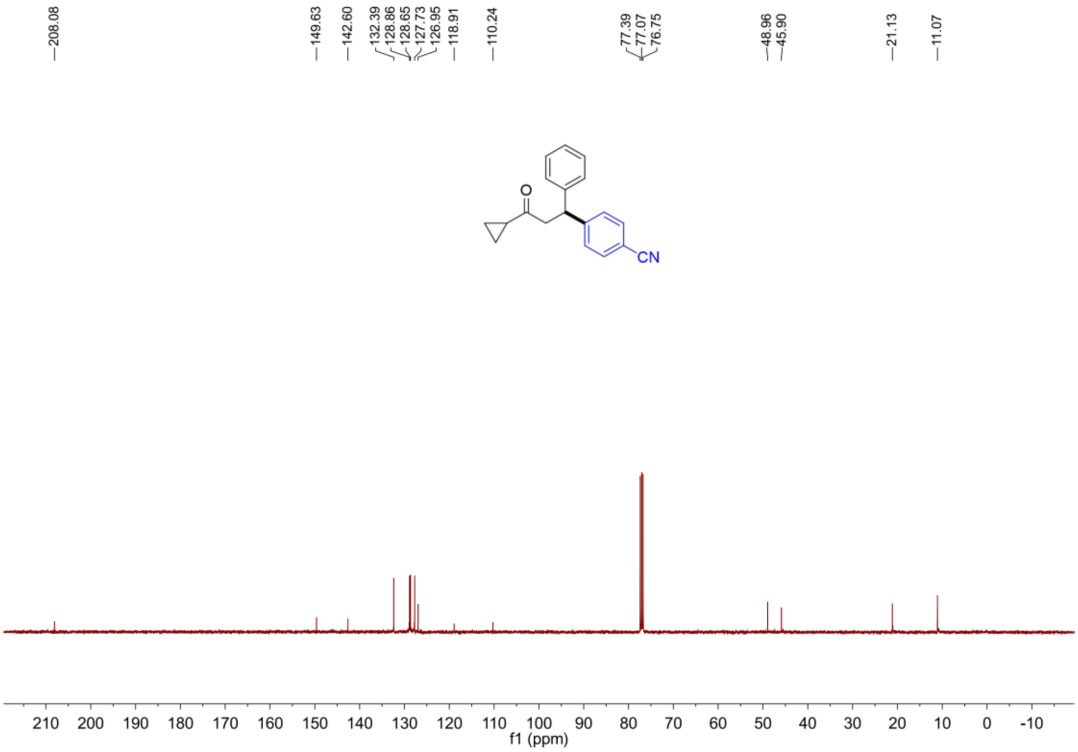

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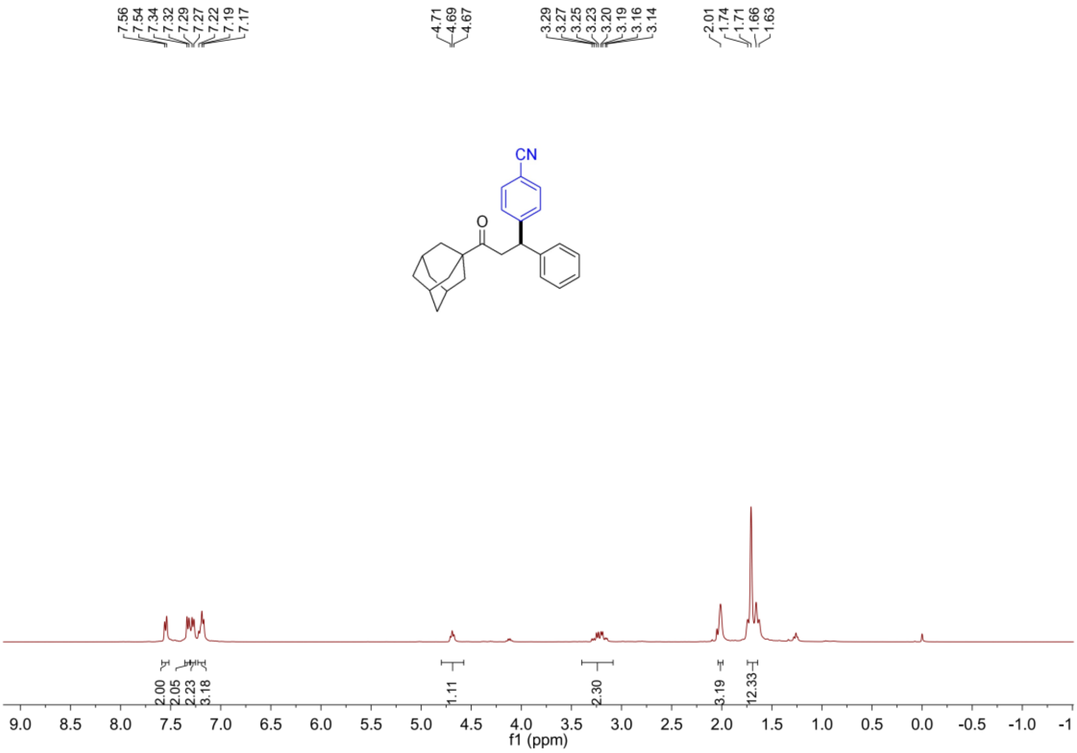

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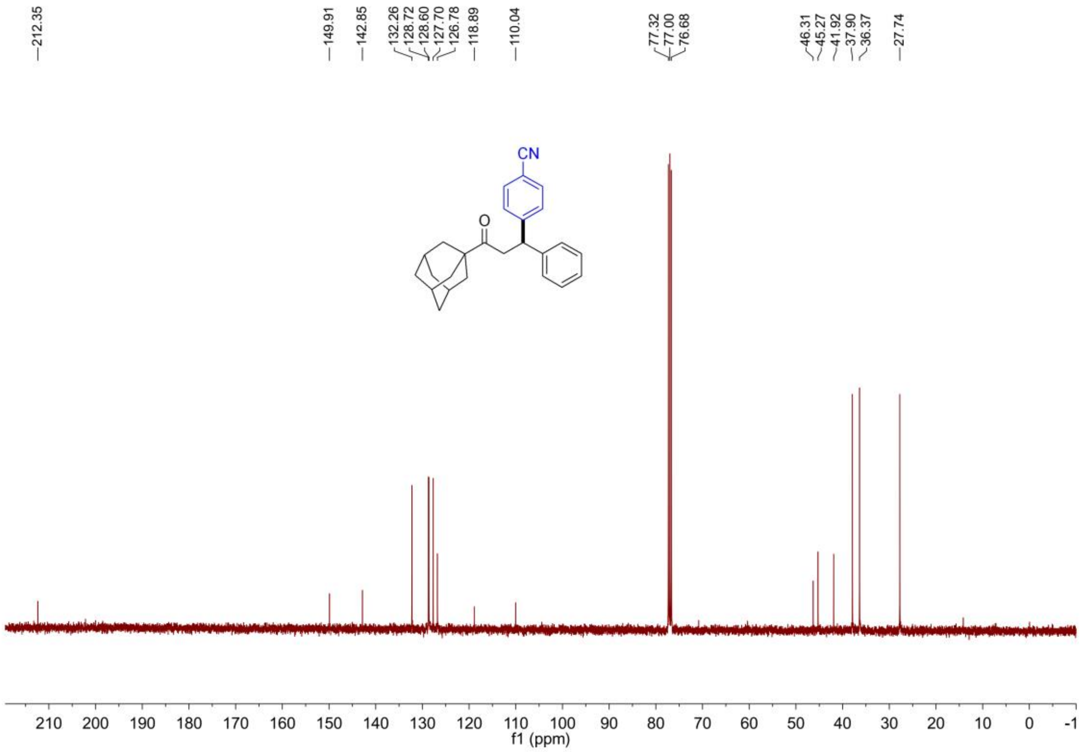

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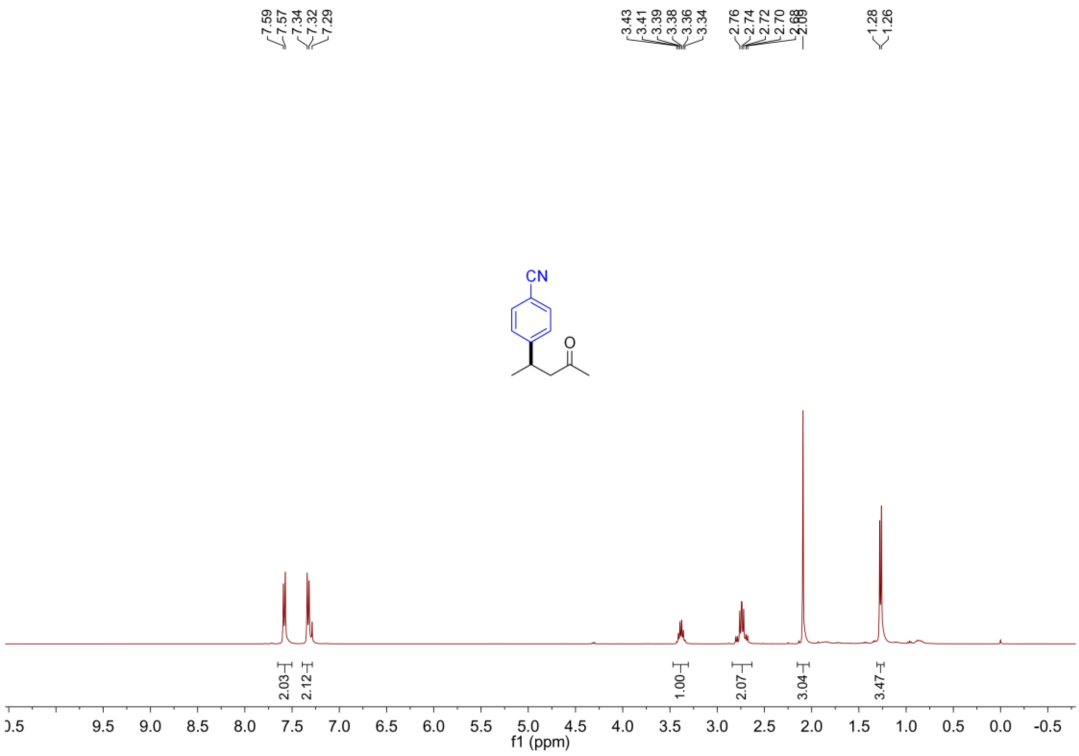

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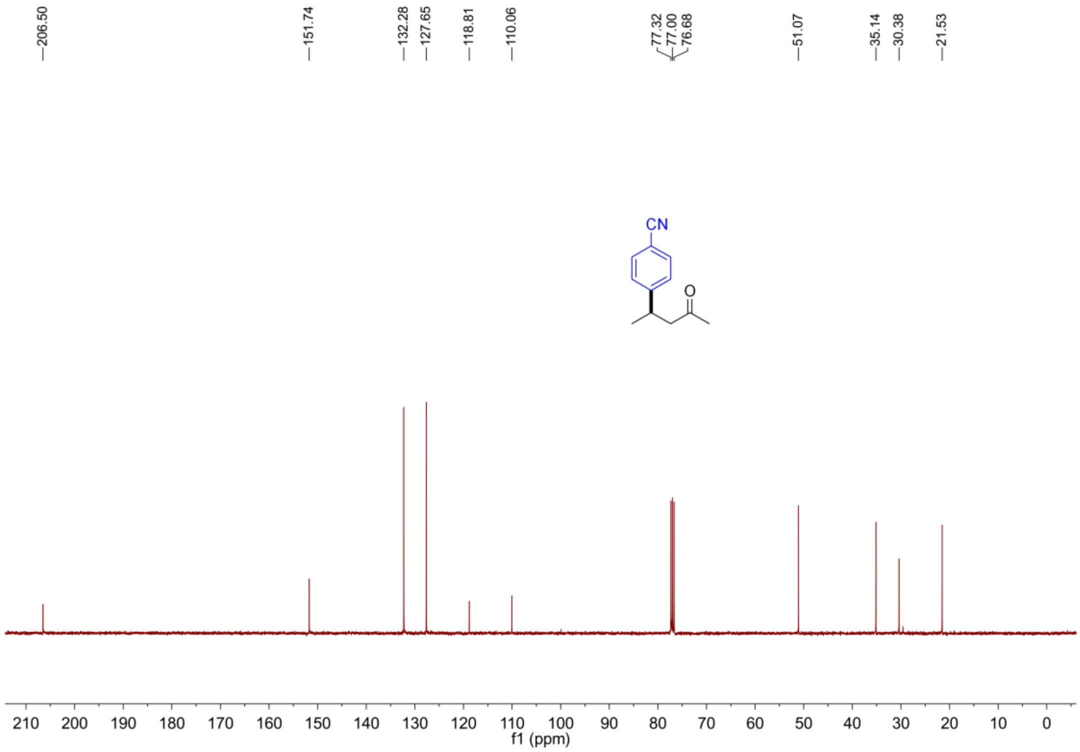

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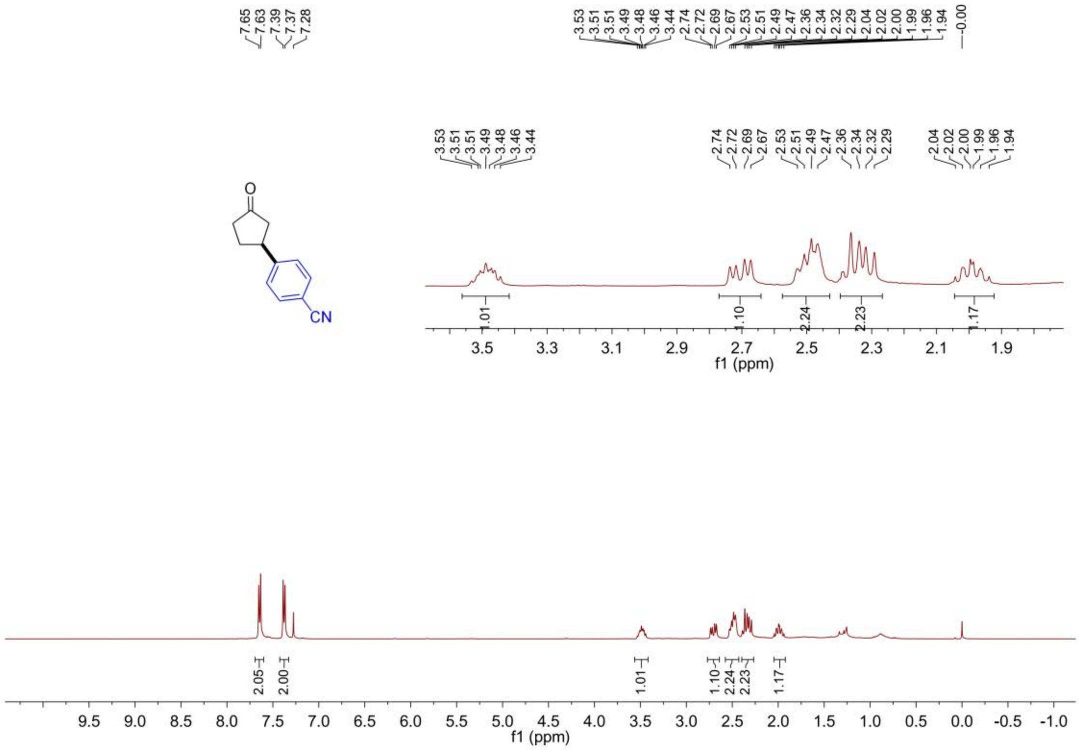

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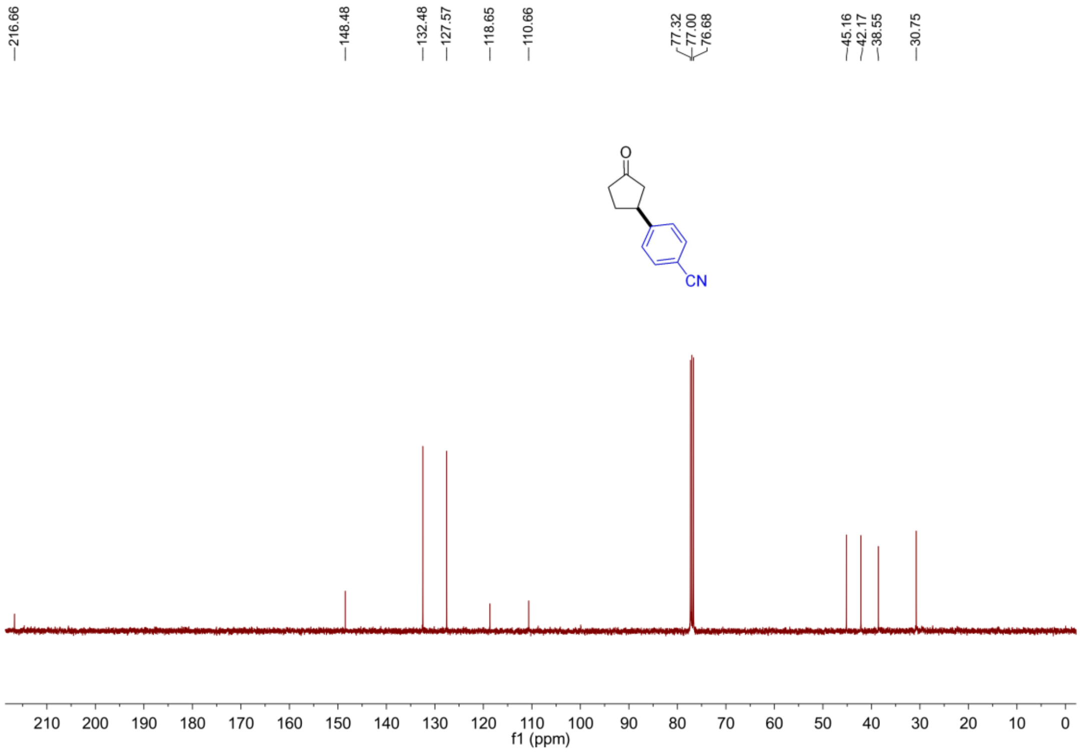

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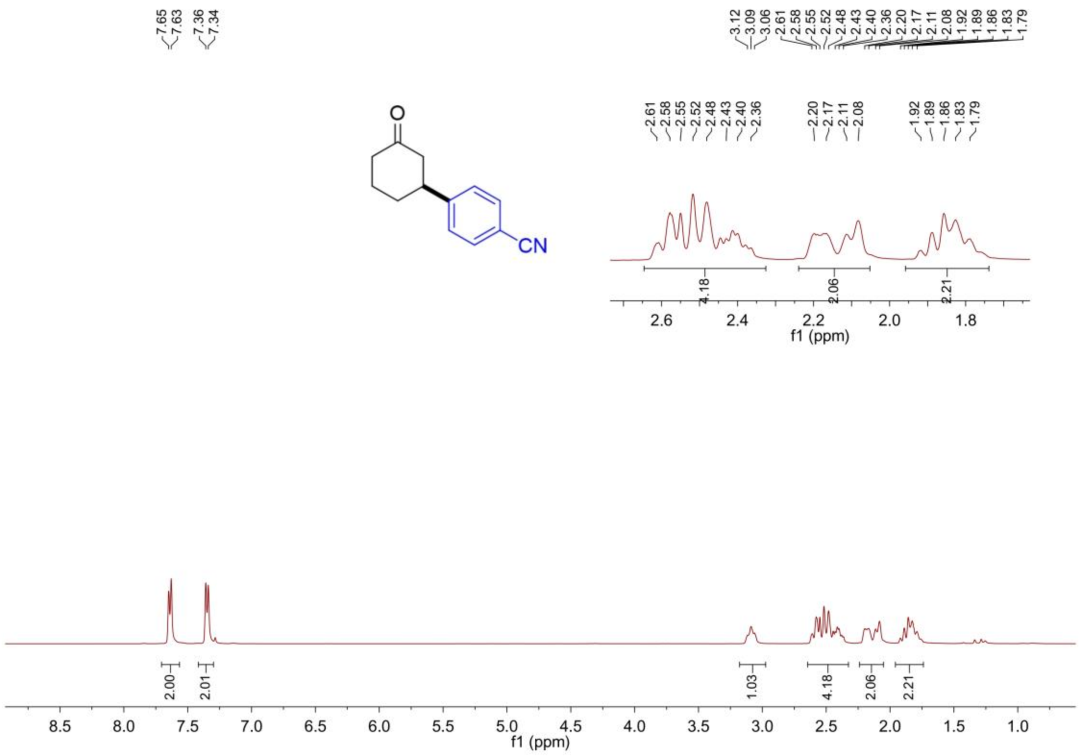

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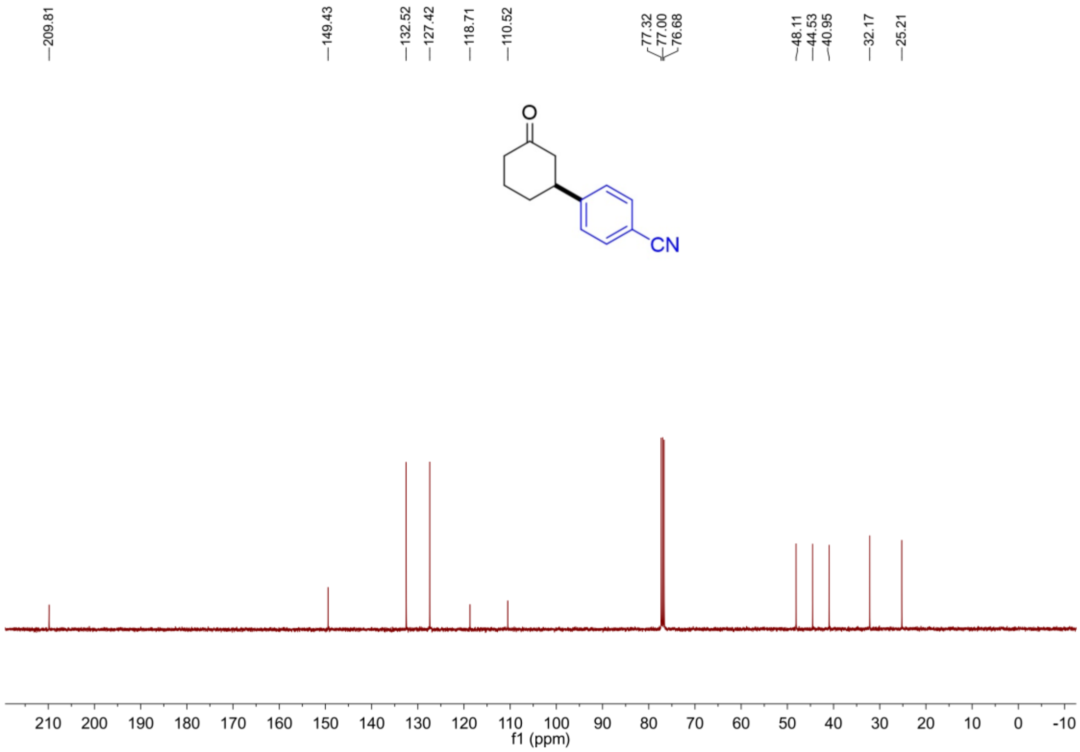

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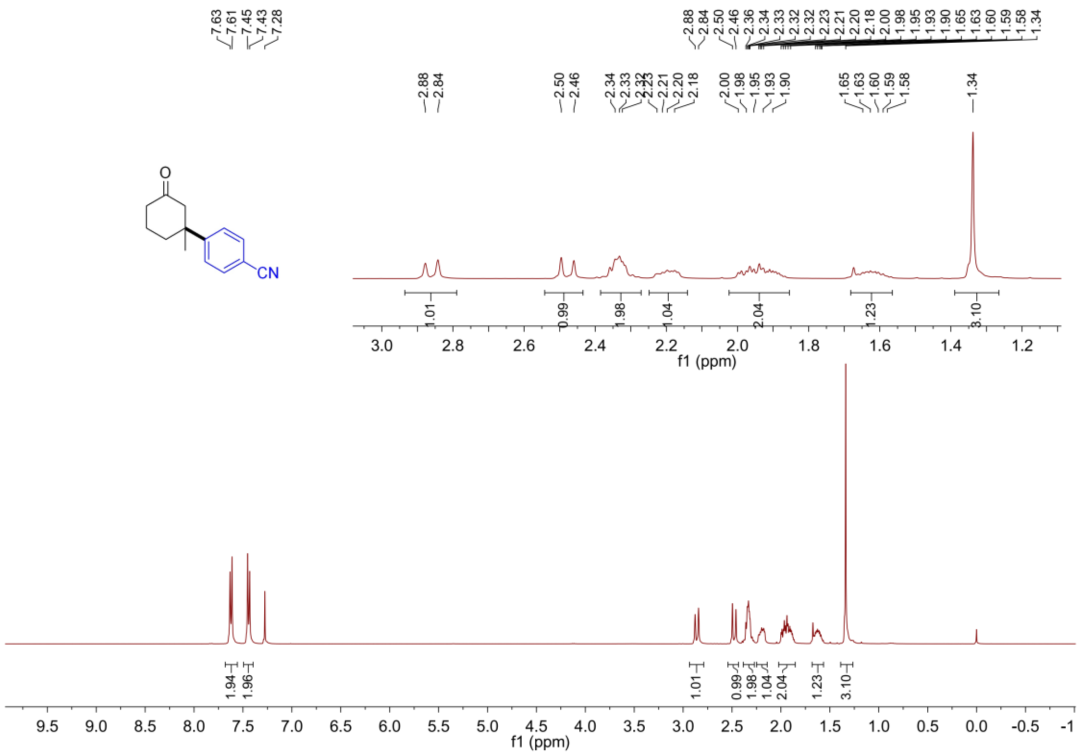

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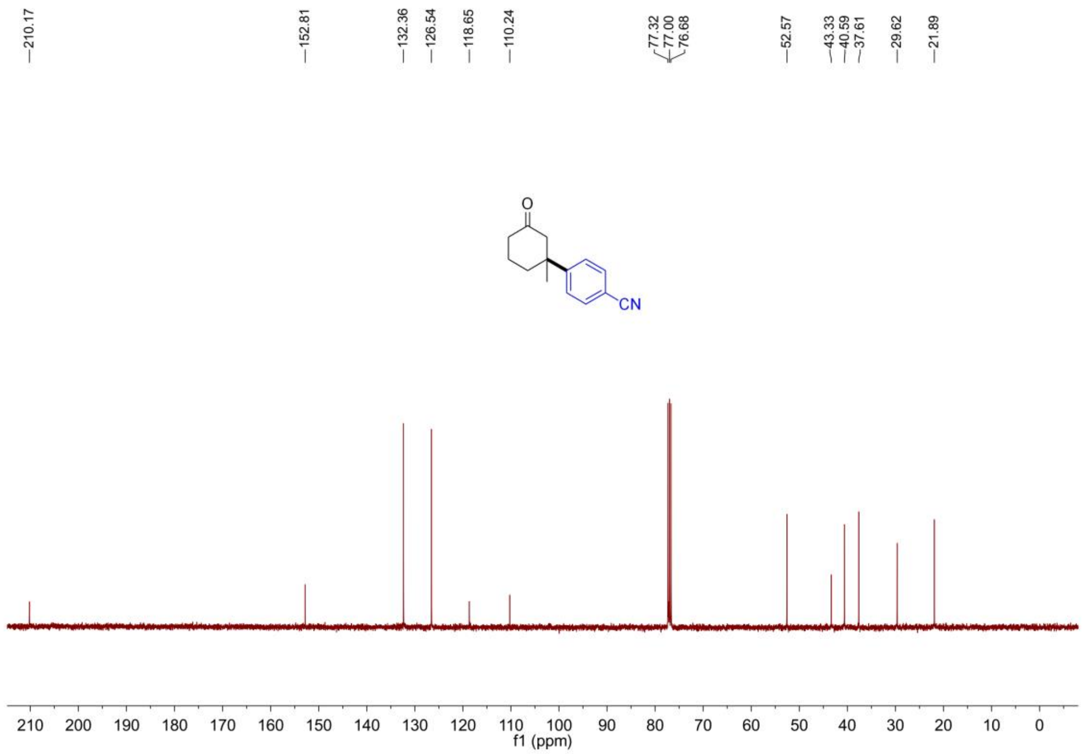

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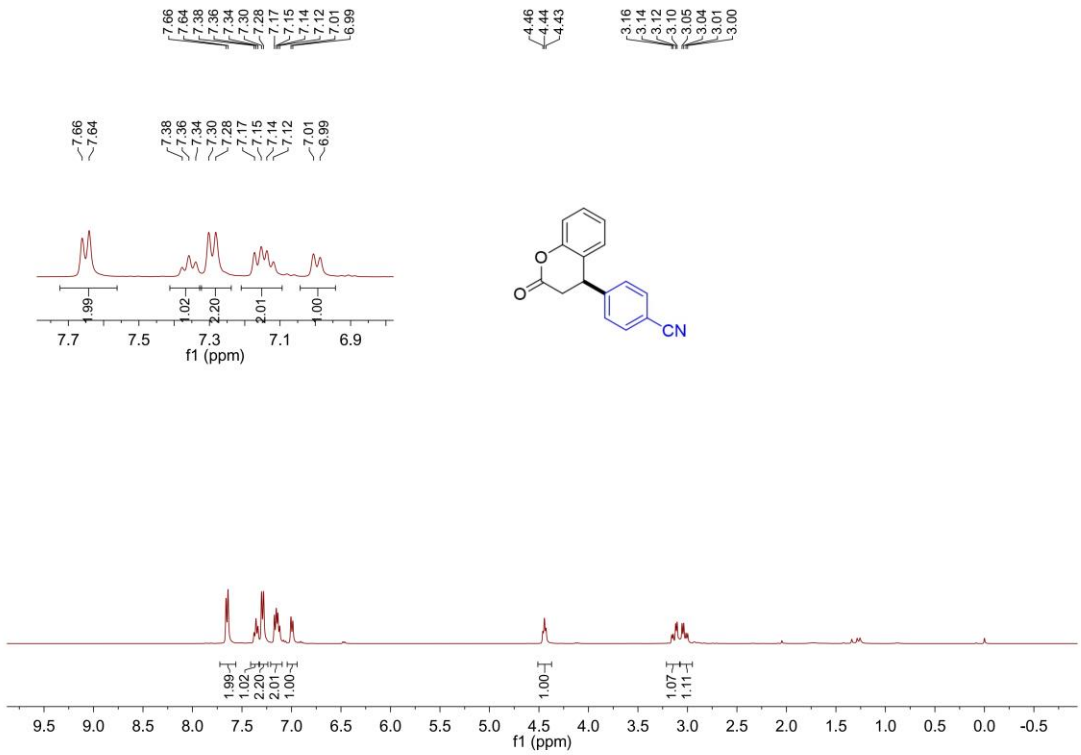

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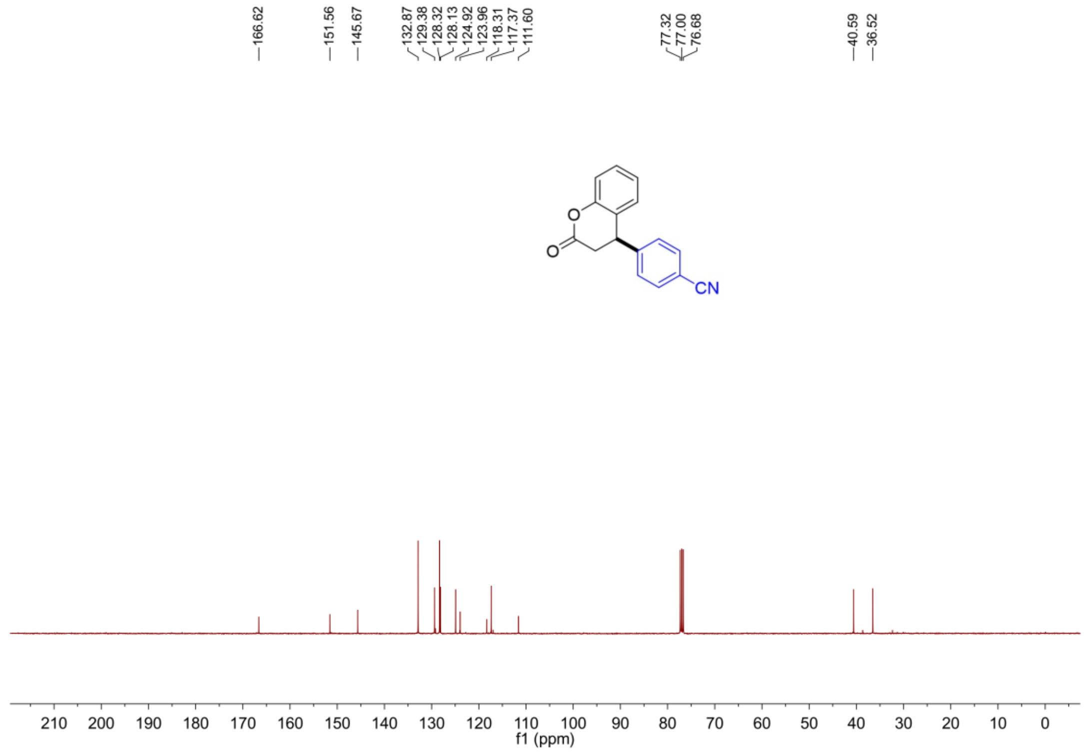

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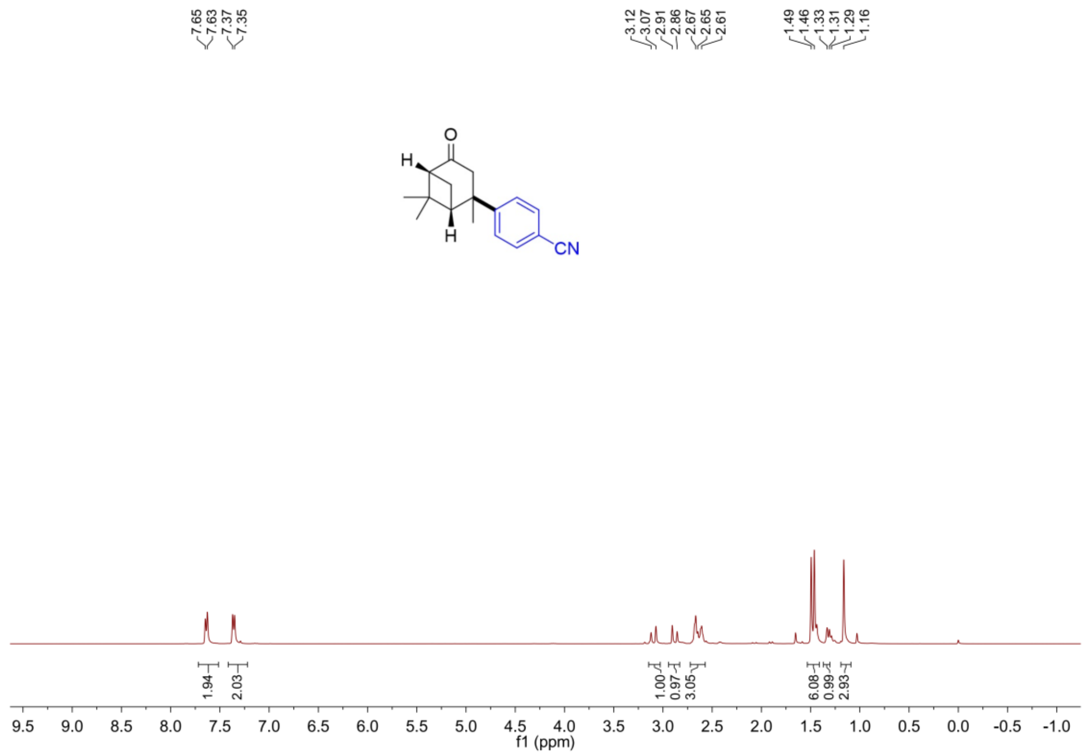

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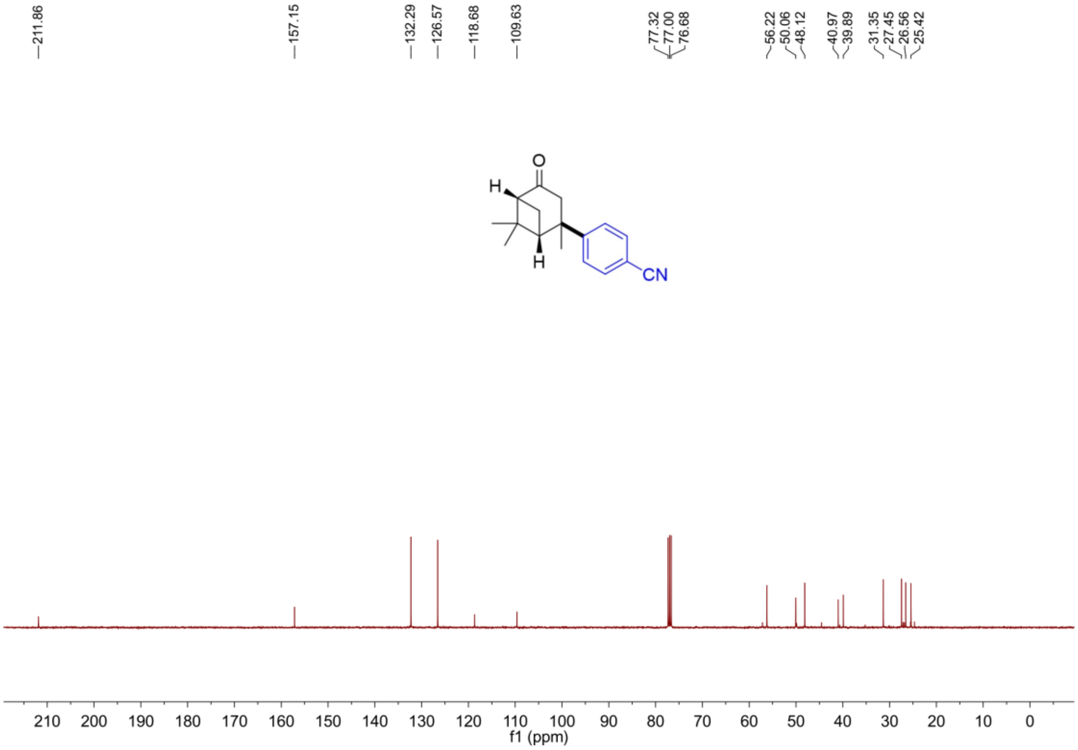

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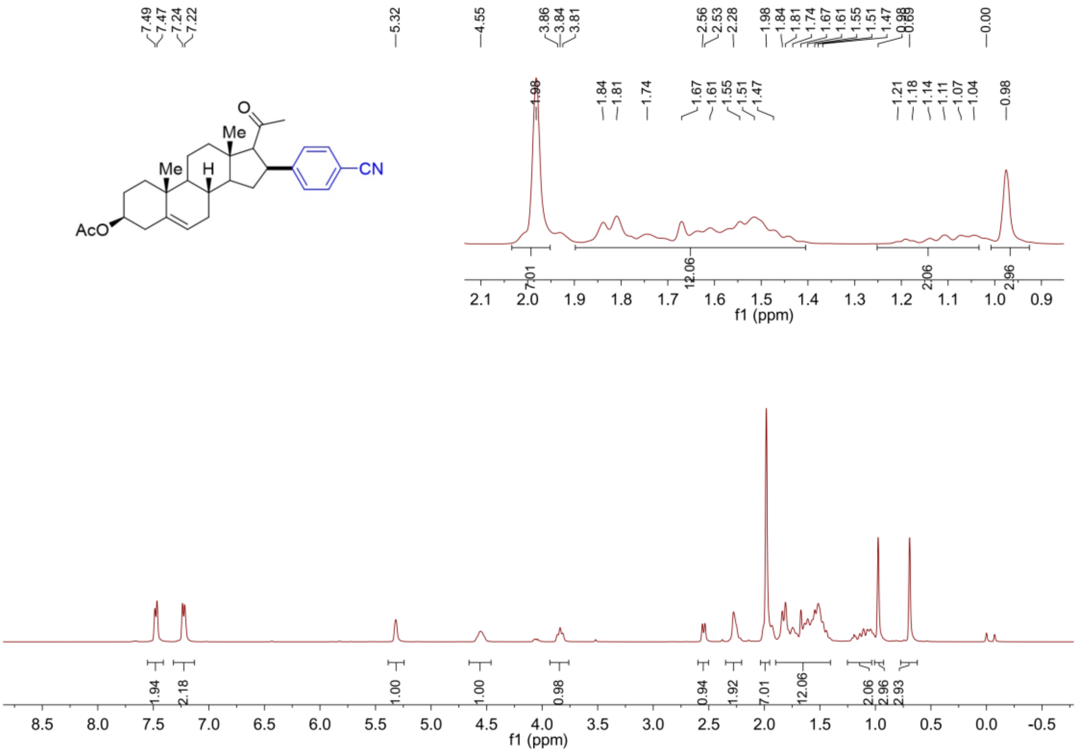

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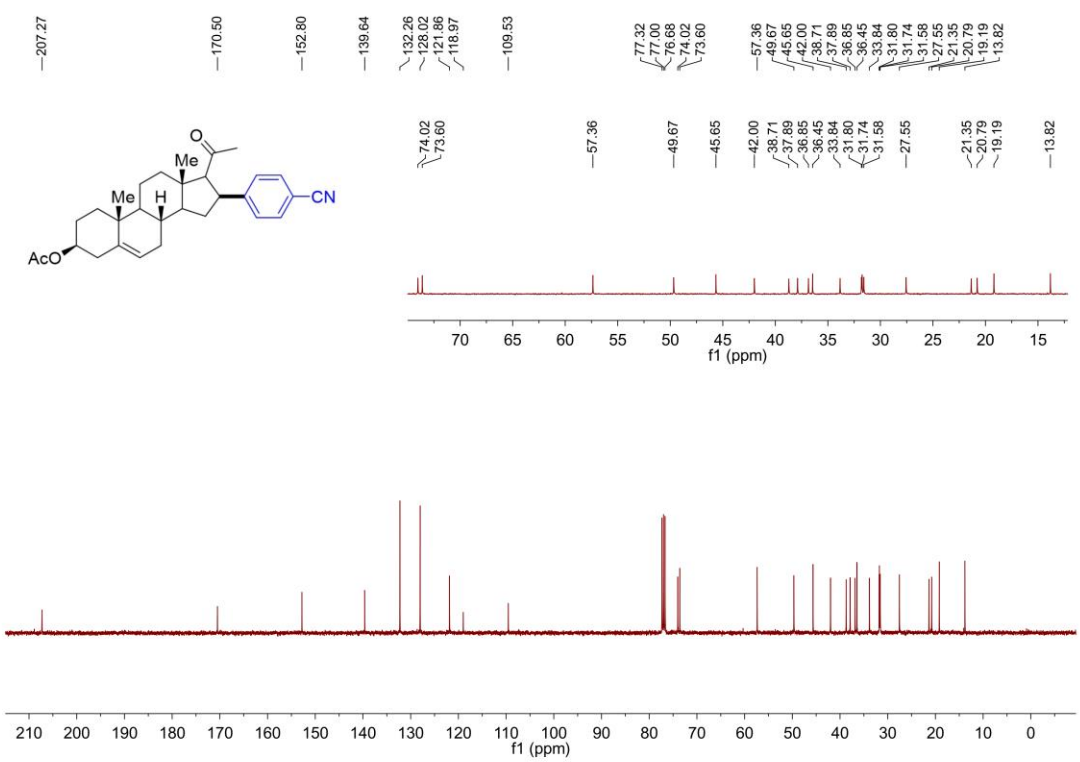

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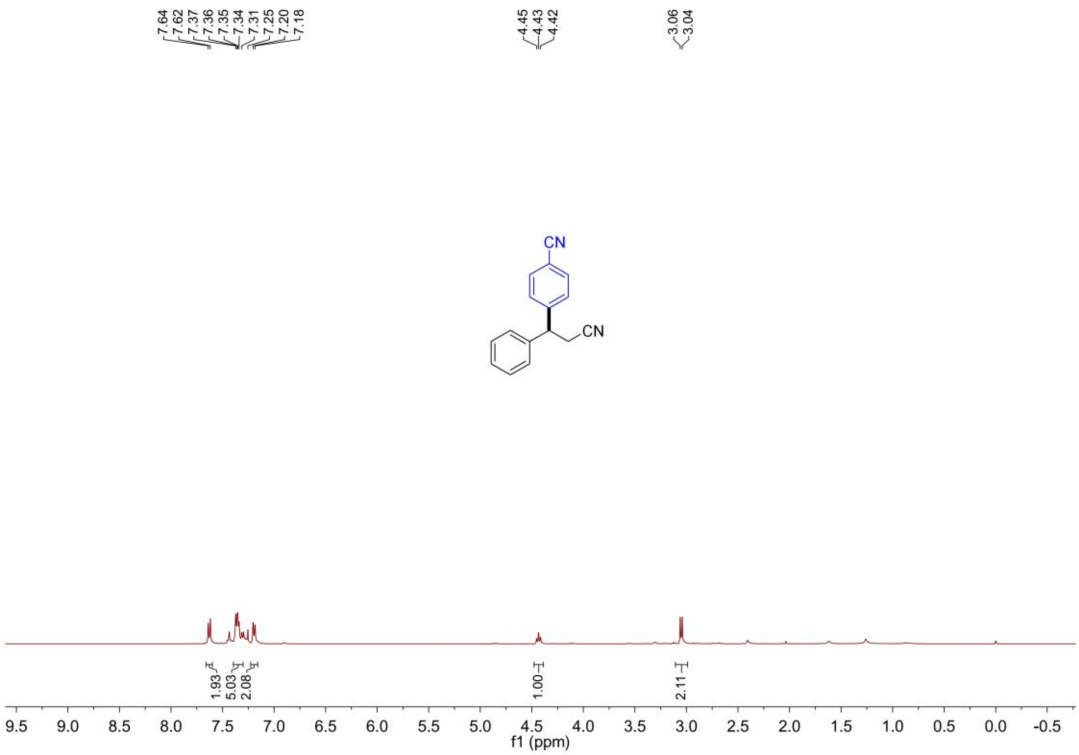

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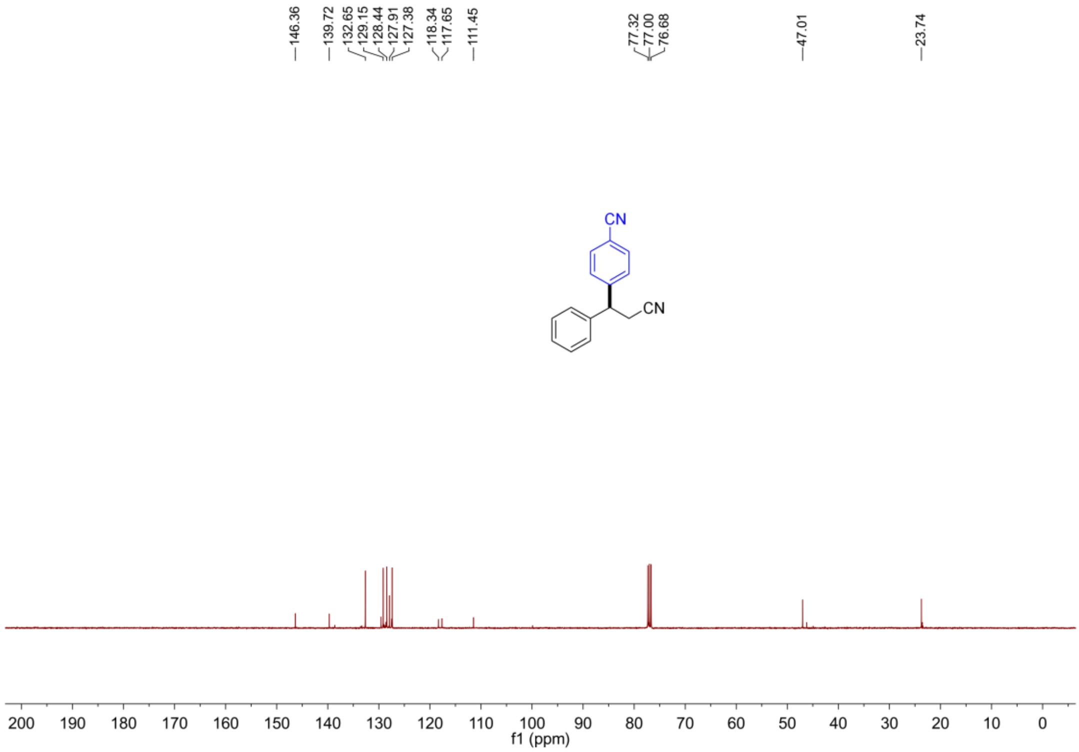

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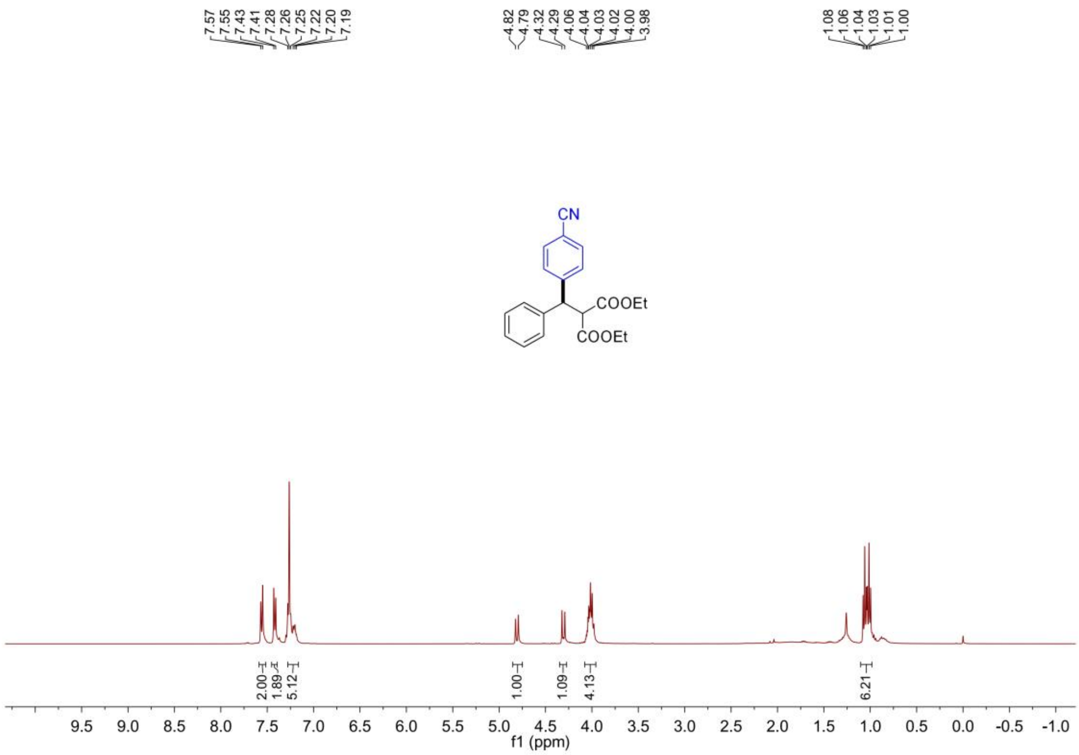

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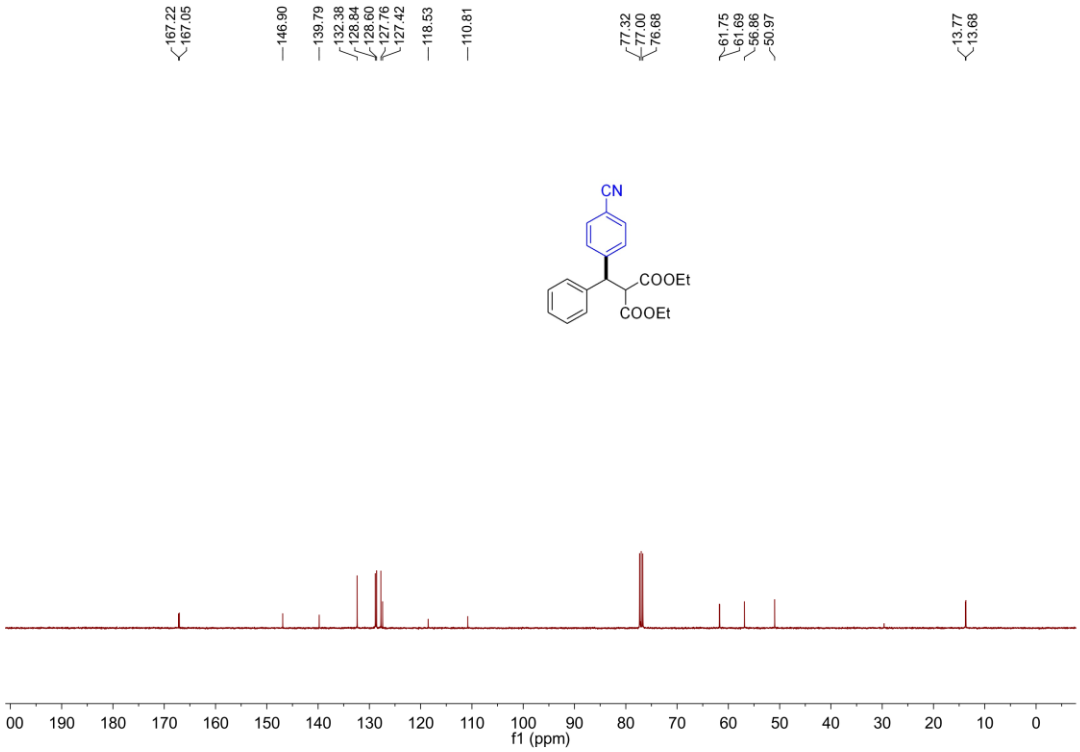

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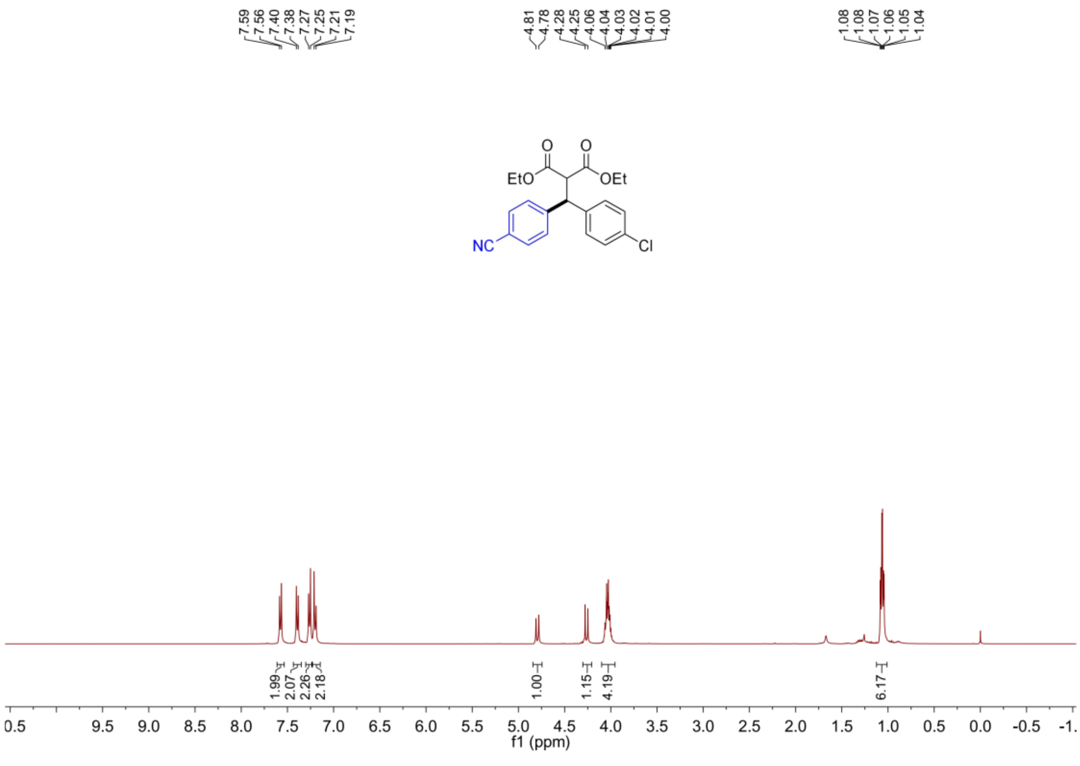

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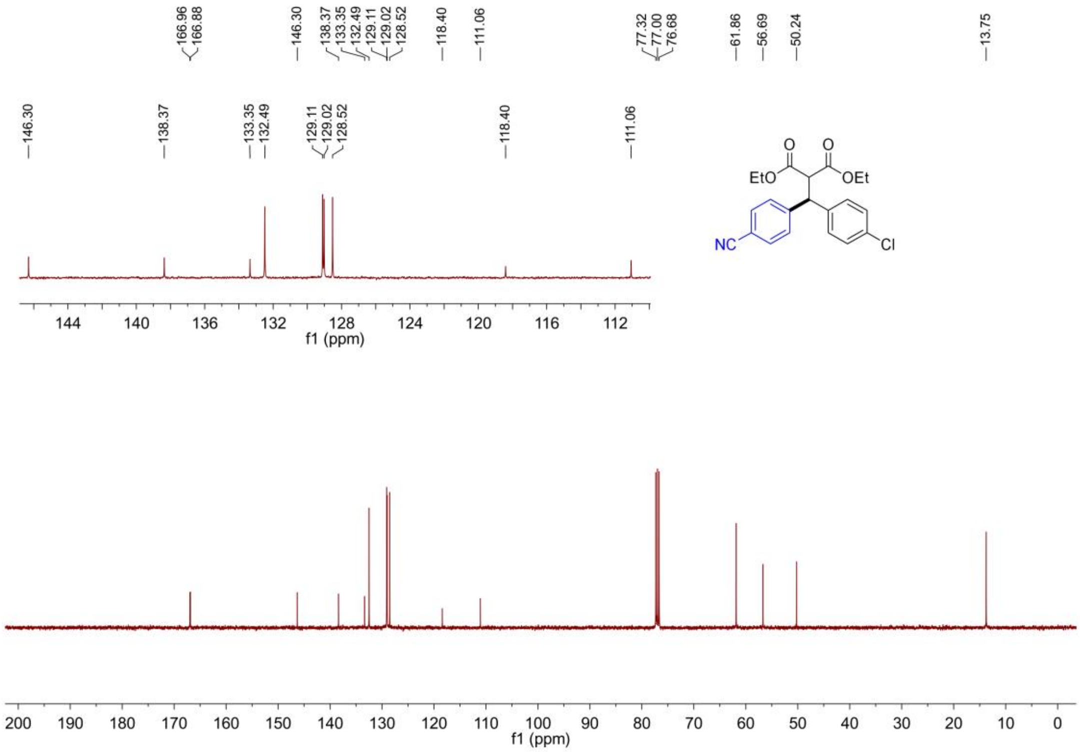

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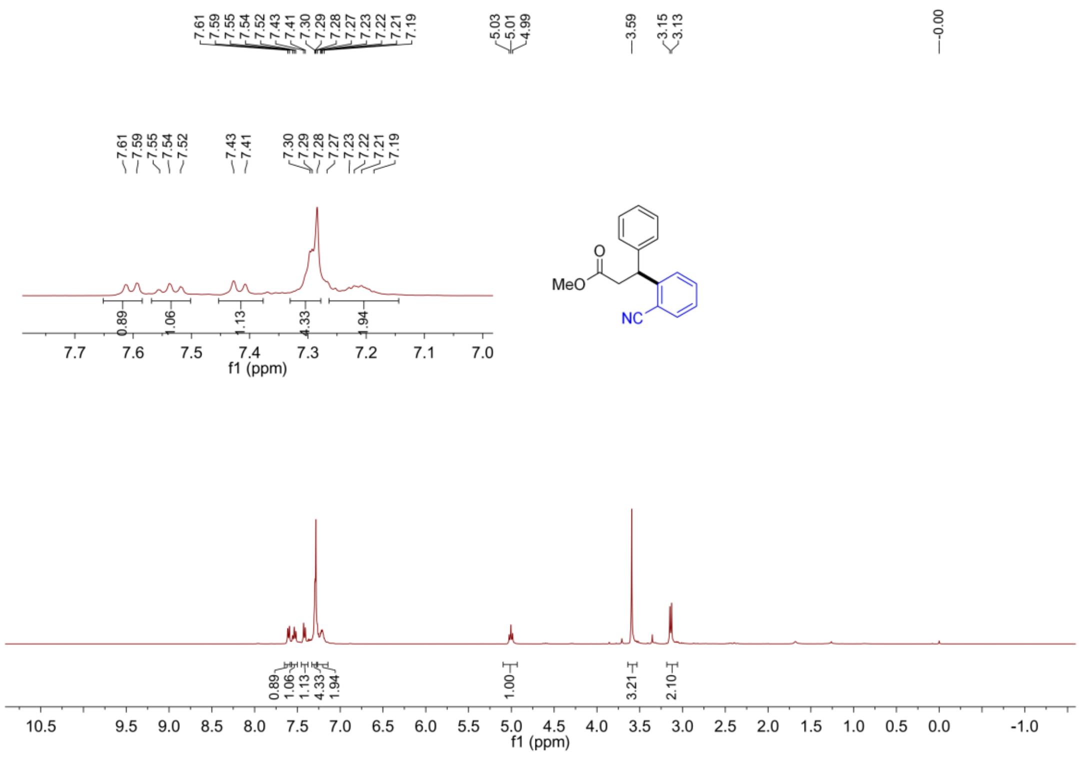

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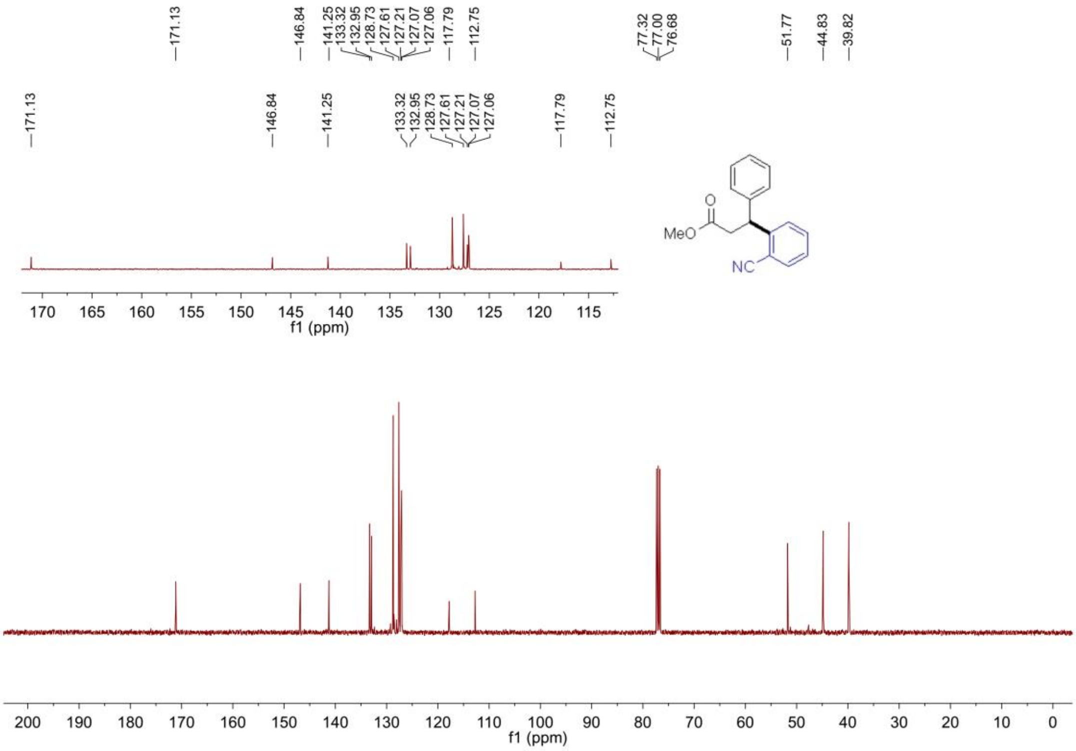
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