Supporting Information

Tandem Buildup of Complexity of Aromatic Molecules Through Multiple Successive Electrophile Generation in One Pot, Controlled by Varying the Reaction Temperature

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I. General Method

Melting points were determined with a Yanaco micro melting point apparatus without correction. ^{1}H-NMR (400 MHz) and ^{13}C-NMR spectra (100 MHz) were recorded on a Bruker Avance400. Chemical shifts were calibrated with tetramethylsilane as an internal standard or with the solvent peak, and are shown in ppm (δ) values, and coupling constants are shown in hertz (Hz). The following abbreviations are used: s = singlet, d = doublet, t = triplet, q = quartet, dd = double doublet, ddd = double double doublet, dt = double triplet, td = triple doublet, qd = quarto doublet, qt = quarto triplet m = multiplet, and brs = broad singlet. Electron spray ionization time-of-flight mass spectra (ESI-TOF MS) were recorded on a Bruker micrOTOF-05 to give

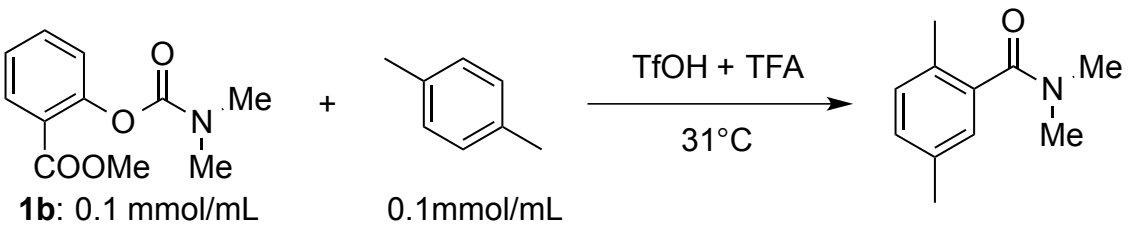
high-resolution mass spectra (HRMS). All of the reactions were performed in heat-gun-dried or oven-dried glassware. Trifluoromethanesulfonic acid (TfOH) was treated with trifluoromethanesulfonic anhydride (Tf_2O) before distillation, and purified prior to use by distillation under reduced pressure. Other commercially available compounds and solvents were used as received.

II. Kinetic Study

A weighed substrate (carbamate **1b** or **1f**) and *para*-xylene were stored in a dry flask, filled with dry argon gas and mixture of distilled TfOH and distilled TFA[S1] in specified weight ratios (total 0.7 mL for 0.07 mmol of carbamate **1b** or **1f**) was added and the solution was stirred at -40°C. An aliquot of the solution was transferred into an NMR tube, drying in a test tube filled with argon and the tube was shielded tightly. The NMR tube, containing the solution of the carbamate was heated in the NMR machine at specified temperature (at 31°C for **1b** and -6°C for **1f** in this case). Temperature of the sample in the NMR probe was calibrated by using methanol according to the Geet's method.[S2] Magnetic field locking was not used, but the shimming was maximized with using $CDCl_3$ before measurements. The peak of TfOH was used as an internal standard of integration.

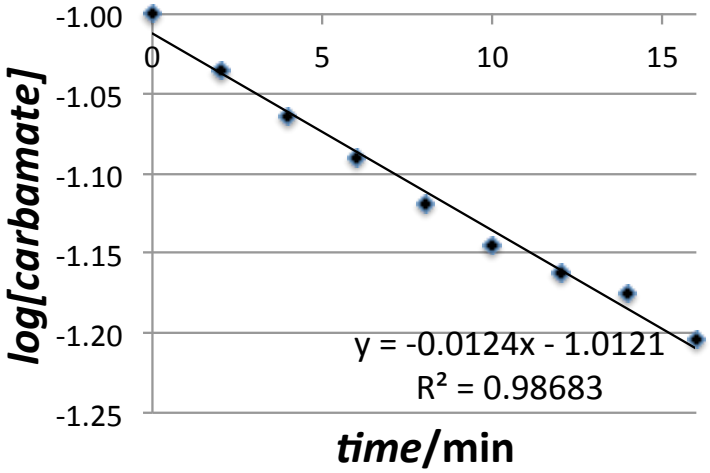
The integration value of protons of the carbamate (**1b** or **1f**), as compared with that of TfOH, was obtained and the concentrations of the carbamate (**1b** or **1f**) are calculated. The logarithms of the concentration of starting substrate (log[*C*]) were plotted against time (*t*, min) to give pseudo first order kinetics (regression coefficient r > 0.99 in all cases). The rate constants were obtained on the basis of the data.

[A] Kinetic study about the reaction of ortho ester carbamate 1b and *para*-xylene.



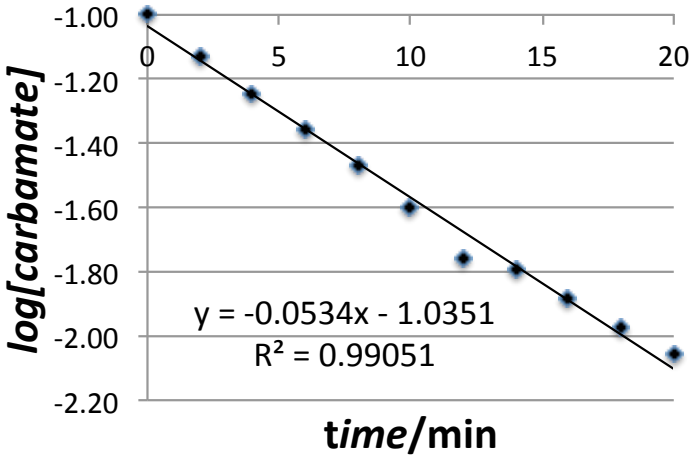
(a) $-H_0 = 7.7$ (TfOH/TFA = 0.9 (w/w%))

Time [min]	Concentration [mmol/mL]	log[*C*]
0	0.1000	-1.0000
2	0.0920	-1.0361
4	0.0861	-1.0650
6	0.0812	-1.0902
8	0.0759	-1.1197
10	0.0715	-1.1457
12	0.0688	-1.1626
14	0.0668	-1.1754
16	0.0626	-1.2036



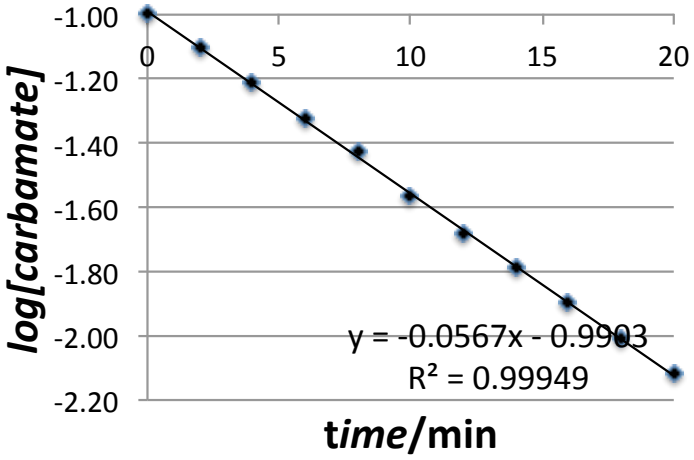
(b) $-H_0 = 9.7$ (TfOH/TFA = 11.4 (w/w%))

Time [min]	Concentration [mmol/mL]	log[*C*]
0	0.1000	-1.0000
2	0.0746	-1.1275
4	0.0570	-1.2443
6	0.0438	-1.3583
8	0.0342	-1.4660
10	0.0252	-1.5986
12	0.0174	-1.7592
14	0.0162	-1.7908
16	0.0131	-1.8819
18	0.0107	-1.9727
20	0.0088	-2.0579



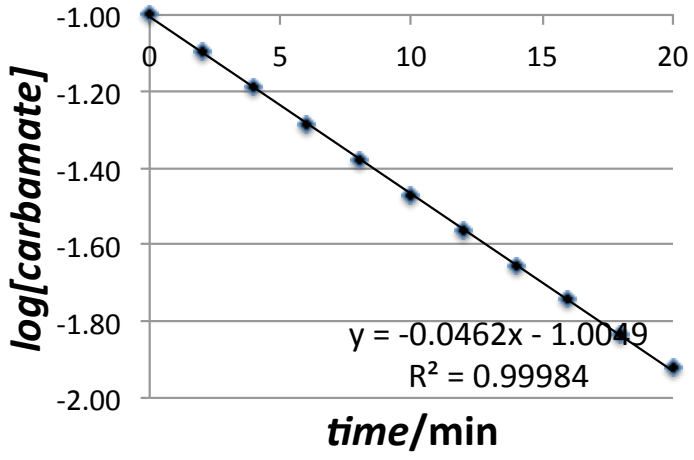
(c) $-H_0$ = 11.8 (TfOH/TFA = 53.4 (w/w%))

Time [min]	Concentration [mmol/mL]	log[*C*]
0	0.1000	-1.0000
2	0.0790	-1.1023
4	0.0612	-1.2130
6	0.0477	-1.3218
8	0.0374	-1.4275
10	0.0272	-1.5648
12	0.0208	-1.6826
14	0.0162	-1.7894
16	0.0126	-1.8990
18	0.0098	-2.0091
20	0.0076	-2.1187



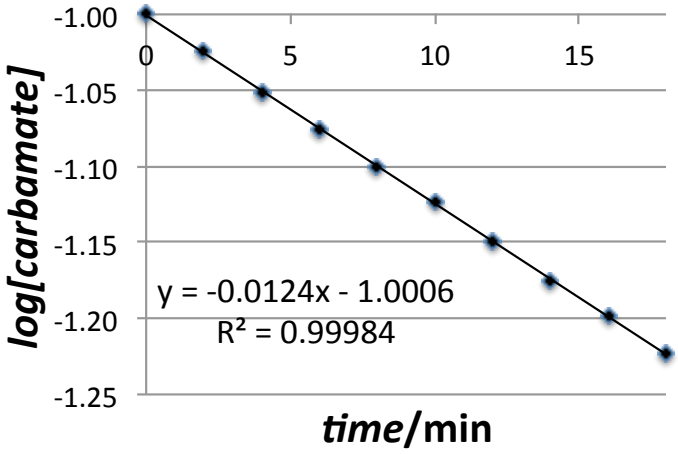
(d) $-H_0$ = 12.2 (TfOH/TFA = 62.4 (w/w%))

Time [min]	Concentration [mmol/mL]	log[*C*]
0	0.1000	-1.0000
2	0.0803	-1.0952
4	0.0647	-1.1893
6	0.0520	-1.2838
8	0.0418	-1.3793
10	0.0339	-1.4694
12	0.0273	-1.5634
14	0.0220	-1.6577
16	0.0180	-1.7436
18	0.0146	-1.8358
20	0.0119	-1.9230

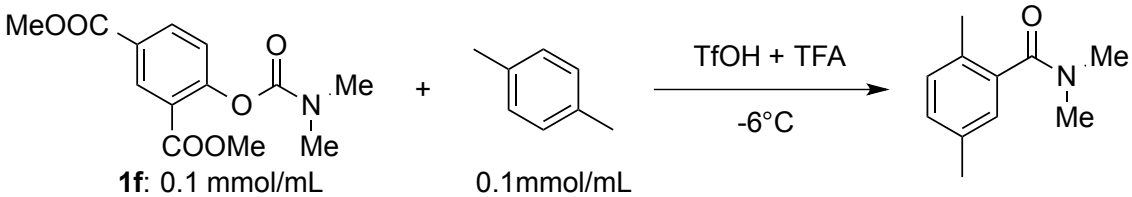


(e) $-H_0 = 13.5$ (TfOH/TFA = 98.2 (w/w%))

Time [min]	Concentration [mmol/mL]	log[*C*]
0	0.1000	-1.0000
2	0.0945	-1.0244
4	0.0889	-1.0509
6	0.0840	-1.0755
8	0.0792	-1.1010
10	0.0752	-1.1236
12	0.0709	-1.1493
14	0.0668	-1.1755
16	0.0634	-1.1980
18	0.0599	-1.2228



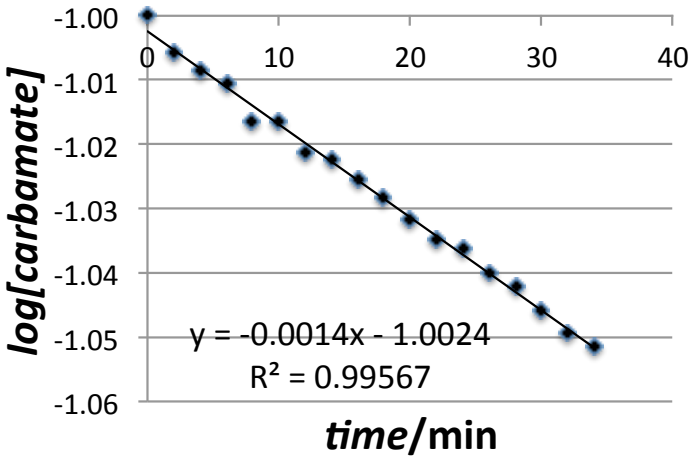
[B] Kinetic study about the reaction of *ortho*, *para*-diester carbamate 1f and *para*-xylene.



1f: 0.1 mmol/mL 0.1mmol/mL

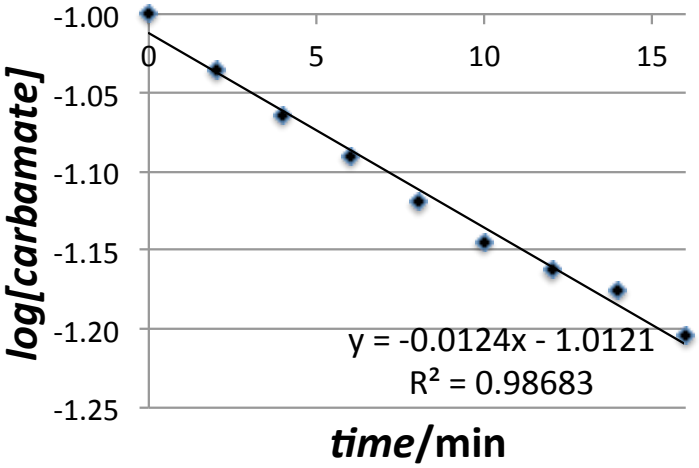
(a') $-H_0$ = 9.7 (TfOH/TFA = 11.4 (w/w%))

Time [min]	Concentration [mmol/mL]	log[*C*]
0	0.1000	-1.0000
2	0.0987	-1.0059
4	0.0981	-1.0085
6	0.0976	-1.0106
8	0.0963	-1.0165
10	0.0963	-1.0164
12	0.0952	-1.0213
14	0.0950	-1.0224
16	0.0943	-1.0253
18	0.0937	-1.0281
20	0.0930	-1.0317
22	0.0923	-1.0349
24	0.0920	-1.0363
26	0.0912	-1.0401
28	0.0907	-1.0422
30	0.0900	-1.0459
32	0.0893	-1.0492
34	0.0888	-1.0514



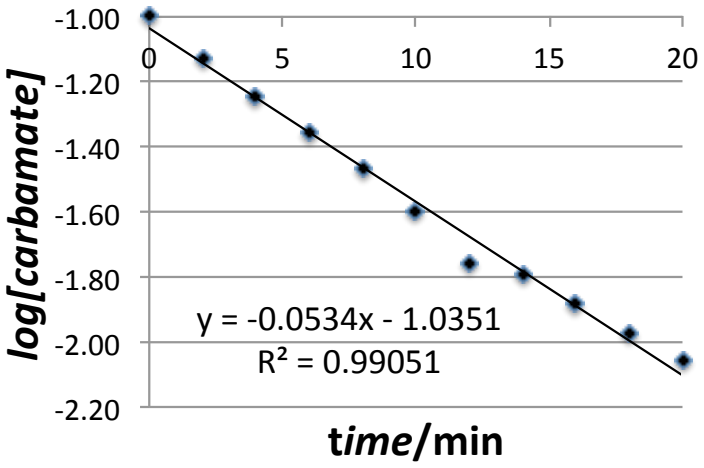
(b') $-H_0$ = 11.8 (TfOH/TFA = 53.4 (w/w%))

Time [min]	Concentration [mmol/mL]	log[*C*]
0	0.1000	-1.0000
2	0.0922	-1.0354
4	0.0861	-1.0649
6	0.0804	-1.0945
8	0.0758	-1.1205
10	0.0712	-1.1475
12	0.0658	-1.1815
14	0.0632	-1.1994
16	0.0592	-1.2277
18	0.0567	-1.2462
20	0.0530	-1.2756
22	0.0508	-1.2944
24	0.0477	-1.3211



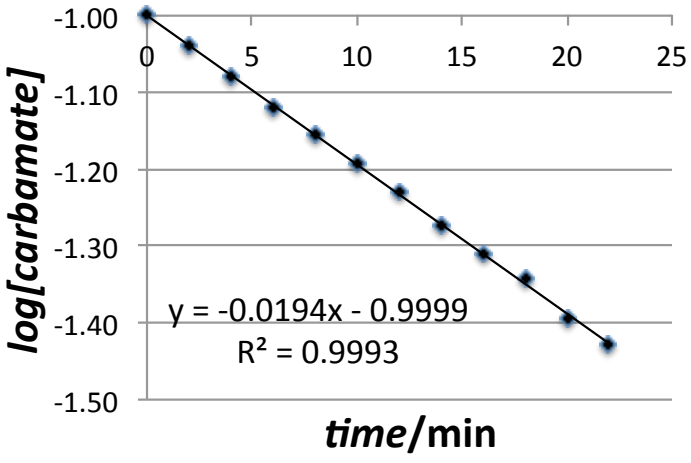
(c') $-H_0$ = 12.2 (TfOH/TFA = 62.4 (w/w%))

Time [min]	Concentration [mmol/mL]	log[*C*]
0	0.1000	-1.0000
2	0.0746	-1.1275
4	0.0570	-1.2443
6	0.0438	-1.3583
8	0.0342	-1.4660
10	0.0252	-1.5986
12	0.0174	-1.7592
14	0.0162	-1.7908
16	0.0131	-1.8819
18	0.0107	-1.9727
20	0.0088	-2.0579



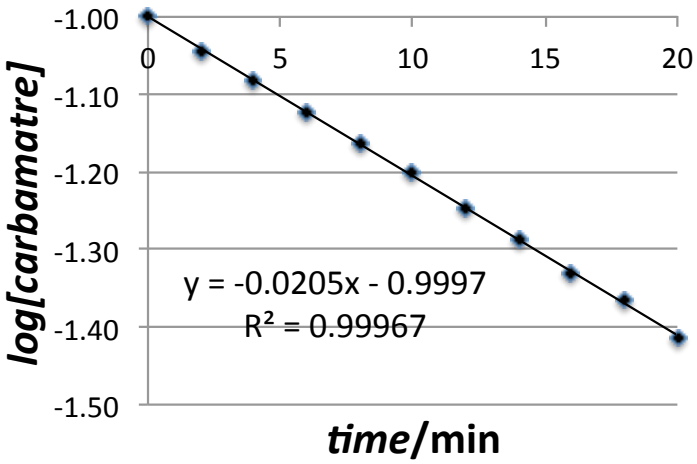
(d') $-H_0$ = 13.5 (TfOH/TFA = 98.2 (w/w%))

Time [min]	Concentration [mmol/mL]	log[*C*]
0	0.1000	-1.0000
2	0.0916	-1.0382
4	0.0834	-1.0788
6	0.0760	-1.1193
8	0.0700	-1.1552
10	0.0642	-1.1921
12	0.0591	-1.2286
14	0.0533	-1.2731
16	0.0490	-1.3101
18	0.0456	-1.3411
20	0.0403	-1.3951
22	0.0373	-1.4278



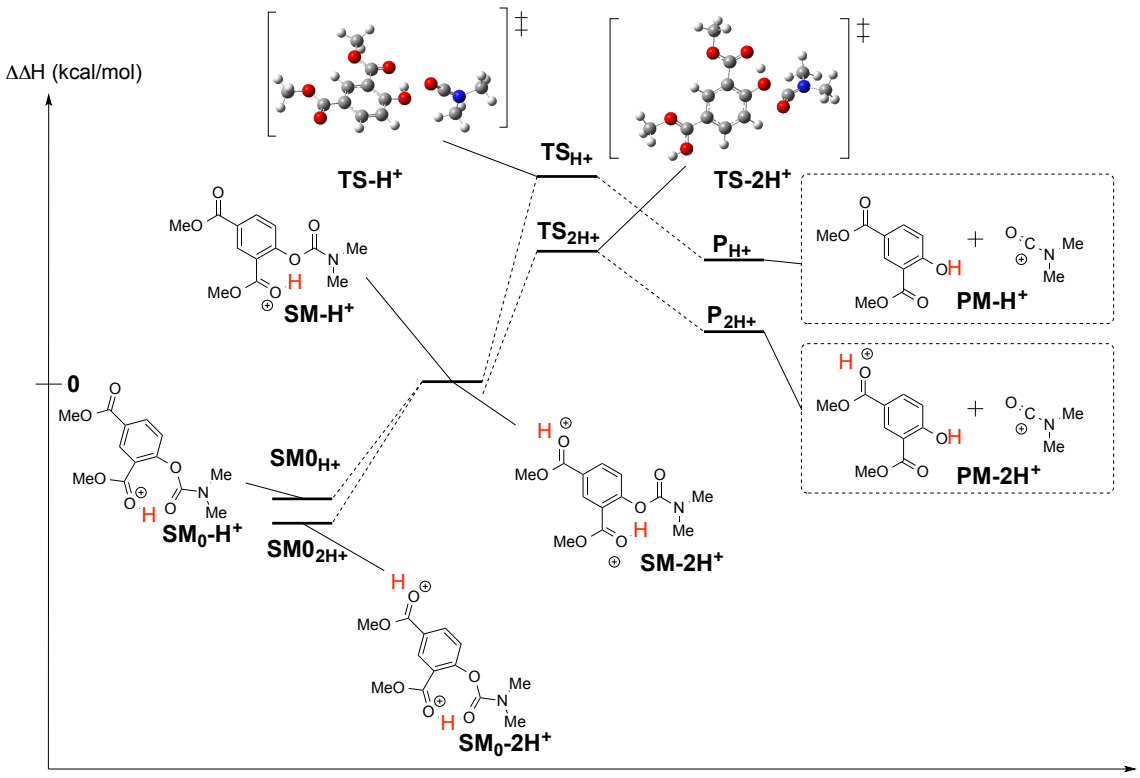
(e') $-H_0 = 14.1$ (only TfOH)

Time [min]	Concentration [mmol/mL]	log[C]
0	0.1000	-1.0000
2	0.0904	-1.0436
4	0.0829	-1.0812
6	0.0751	-1.1240
8	0.0687	-1.1627
10	0.0629	-1.2011
12	0.0567	-1.2465
14	0.0517	-1.2862
16	0.0468	-1.3294
18	0.0430	-1.3662
20	0.0384	-1.4152



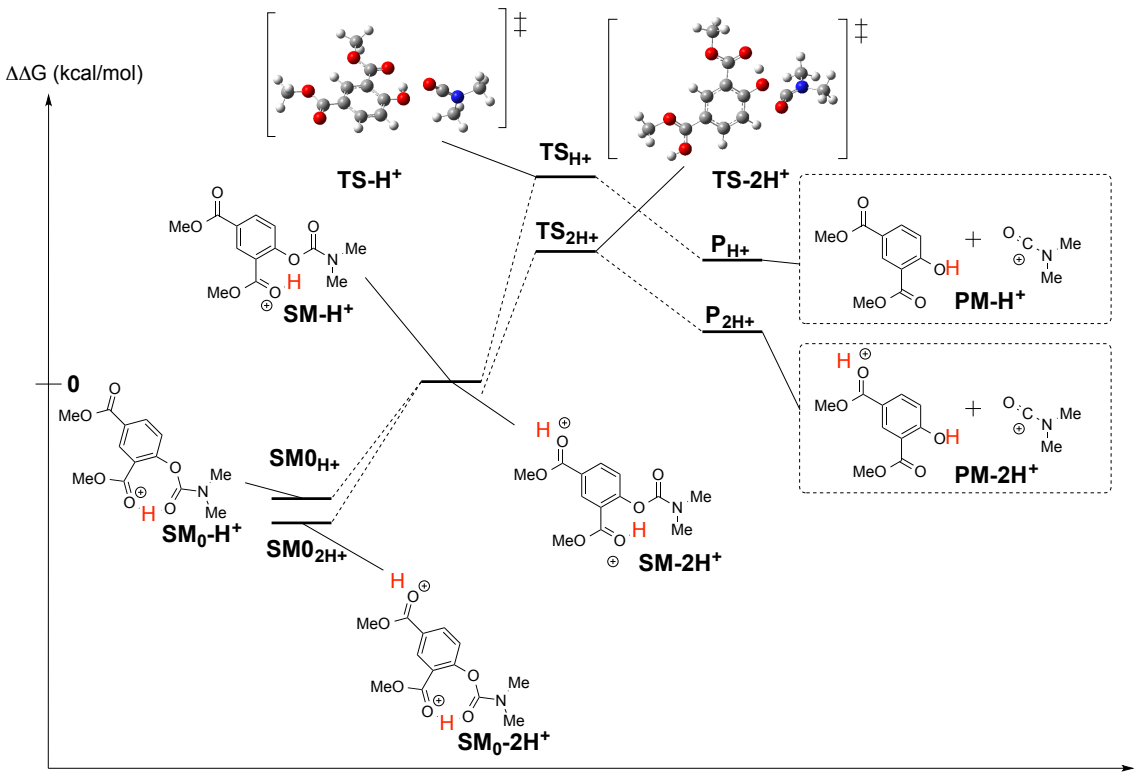
III. Computational Studies

We carried out computational studies by using the Gaussian 09 suites of programs.[S3] The geometries of the reactants (**SM**), transition states (**TS**), and products (**PM**) for dissociation step were fully optimized using the CPCM-B3LYP/6-31+G(d) level. Harmonic vibrational frequency computations characterized the optimized structures. Intrinsic reaction coordinate (IRC) computations of the transition structures verified the reactants, intermediates, and products on the potential energy surface (PES). Bulk solvation effects (self-consistent reaction field, SCRF) were simulated by the CPCM method in trifluoromethanesulfonic acid as a solvent (eps = 77.4,[S4] rsolv = 2.5985274,[S4] density = 1.696,[S5] epsinf = 1.882384 (the value of acetic acid was employed)). Single point energies were calculated with CPCM-M06-2X/6-311++G(d,p) (and some other calculation levels) on the basis of the optimized structures. The zero-point vibrational energy corrections were done without scaling.



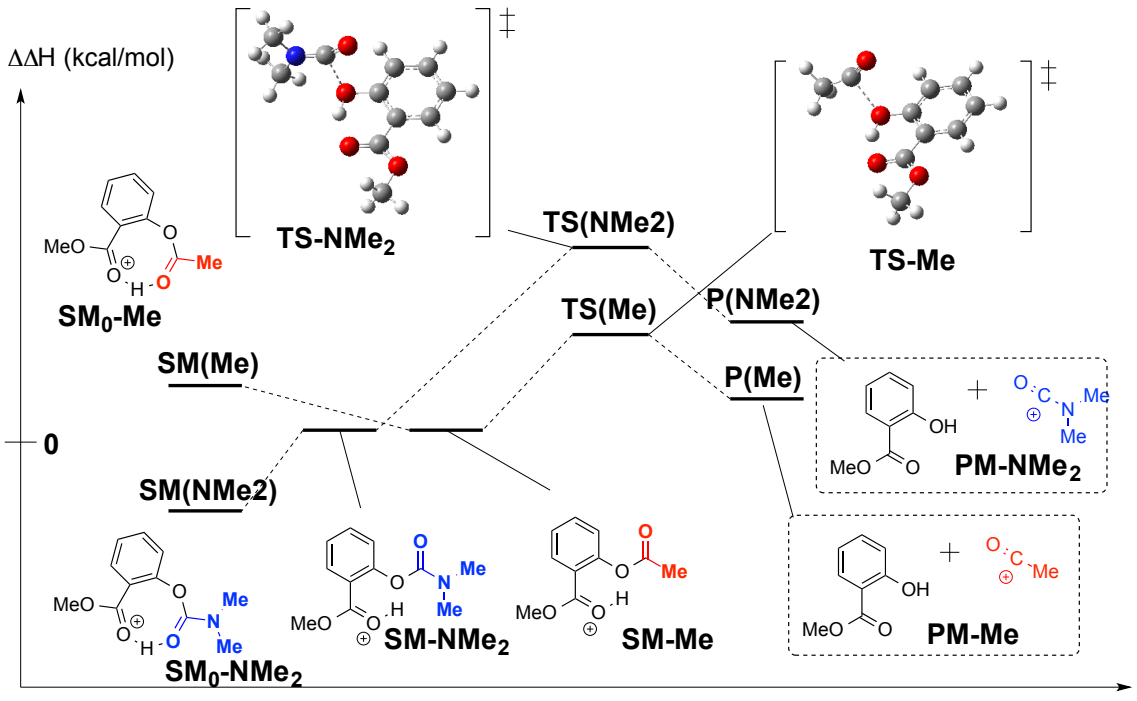
Energy Level	SM02H+	SM0H+	TS2H+	TSH+	ΔE(=EH+-E2H+)	P2H+	PH+
CPCM-M06/6-311++G(d,p)	-4.0	-4.4	12.5	13.4	**0.9**	4.7	9.2
CPCM-M06-2x/6-311++G(d,p)	-6.6	-6.8	12.5	15.4	**2.9**	7.7	12.2
CPCM-M06-HF/6-311++G(d,p)			12.2	16.5	**4.3**	11.5	15.5
CPCM-B3LYP/6-311++G(d,p)			9.5	11.2	**1.7**	1.3	6.6
CPCM-B3PW91/6-311++G(d,p)			10.6	13.2	**2.6**	4.0	9.4
CPCM-MP2/6-311++G(d,p)	-8.4	-8.2	6.5	8.7	**2.2**	1.8	6.2
CPCM-MP2/aug-ccVDZ			7.0	9.4	**2.4**	4.0	8.3

Figure SI-1. Calculated energy diagram (in ΔΔ*H*) of C-O bond cleavage step of 1f (structure was optimized at CPCM-B3LYP/6-31+G(d))



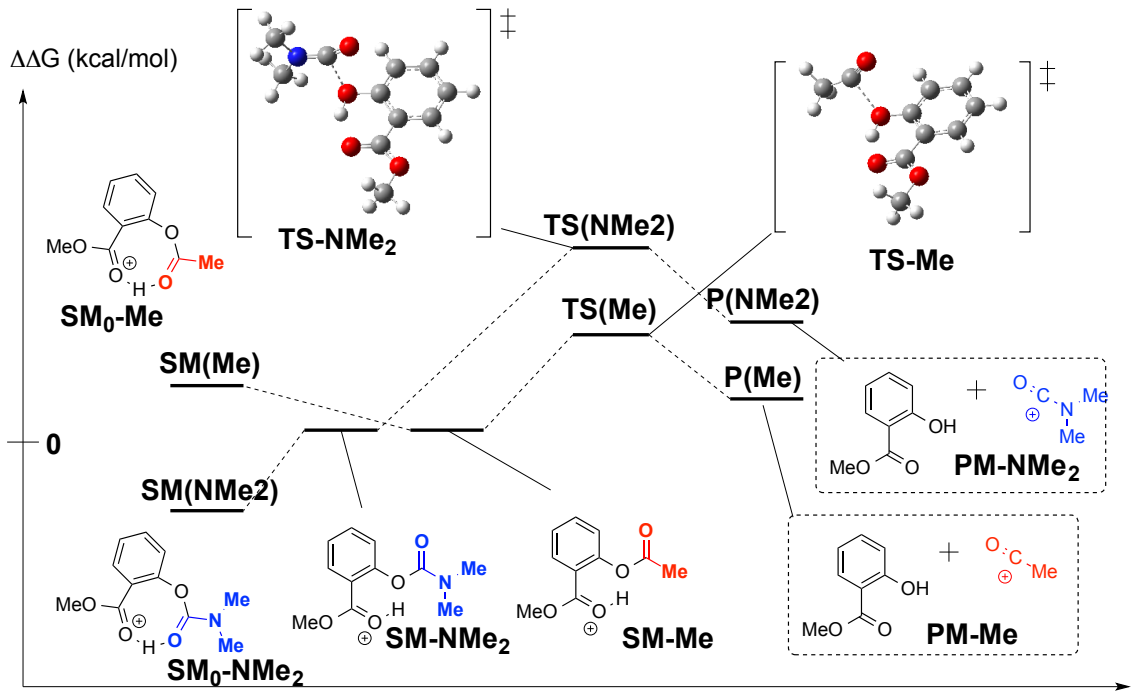
Energy Level	SM02H+	SM0H+	TS2H+	TSH+	ΔG(=GH+-G2H+)	P2H+	PH+
CPCM-M06/6-311++G(d,p)	-3.5	-4.3	12.6	13.6	**1.0**	1.5	6.4
CPCM-M06-2x/6-311++G(d,p)	-6.0	-6.7	12.6	15.4	**2.8**	4.7	9.3
CPCM-M06-HF/6-311++G(d,p)			12.2	16.6	**4.4**	8.5	12.7
CPCM-B3LYP/6-311++G(d,p)			9.6	11.3	**1.7**	-1.7	3.7
CPCM-B3PW91/6-311++G(d,p)			10.7	13.3	**2.6**	1.0	6.6
CPCM-MP2/6-311++G(d,p)	-7.8	-8.0	6.5	8.8	**2.3**	-1.2	3.4
CPCM-MP2/aug-ccVDZ			7.0	9.5	**2.5**	1.0	5.5

Figure SI-2. Calculated energy diagrams (in $\Delta\Delta G_{298K}$) of C-O bond cleavage steps of 1f (structure was optimized at CPCM-B3LYP/6-31+G(d))



Calculation Level	SM(NMe2)	SM(Me)	TS(NMe2)	TS(Me)	ΔE(=E(NMe2)-E(Me))	P(NMe2)	P(Me)
CPCM-M06/6-311++G(d,p)	-4.6	2.2	13.5	12.0	1.5	11.1	10.3
CPCM-M06-2X/6-311++G(d,p)	-7.4	2	17.1	13.7	3.4	14.5	12.3
CPCM-MP2/6-311++G(d,p)	-7.6	1.9	9.6	7.0	2.6	8.0	5.8

Figure SI-3. Calculated energy diagrams (in $\Delta\Delta H$) of C-O bond cleavage steps of 1b and 1e (structure was optimized at CPCM-B3LYP/6-31+G(d))

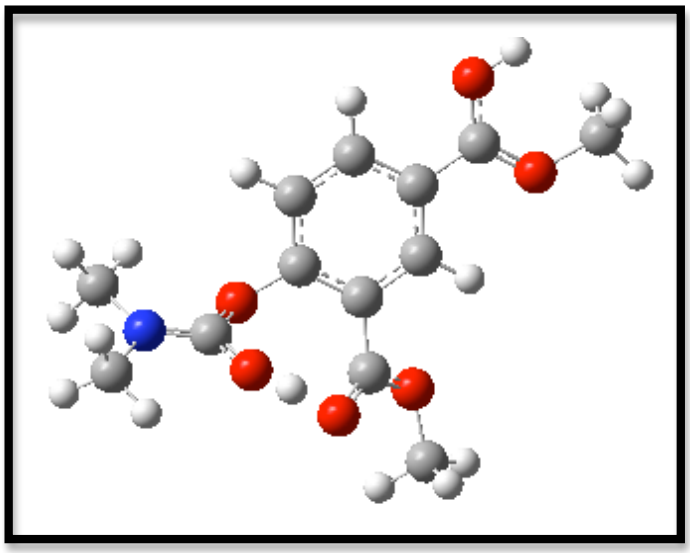


Calculation Level	SM(NMe2)	SM(Me)	TS(NMe2)	TS(Me)	ΔG(=G(NMe2)-G(Me))	P(NMe2)	P(Me)
CPCM-M06/6-311++G(d,p)	-4.2	2.4	17.8	11.4	6.4	4.3	8.7
CPCM-M06-2X/6-311++G(d,p)	-6.9	2.2	16.1	13.1	3.0	10.9	10.6
CPCM-MP2/6-311++G(d,p)	-7.2	2.2	8.6	6.4	2.2	4.4	4.2

Figure SI-4. Calculated energy diagrams (in $\Delta\Delta G_{298K}$) of C-O bond cleavage steps of 1b and 1e (structure was optimized at CPCM-B3LYP/6-31+G(d))

Calculation Coordinates

Diprotonation of carbamate 1f (SM_0-$2H^+$)



HF = -1011.027115 (M06/6-311++G(d,p))

HF = -1011.253772 (M06-2X/6-311++G(d,p))

HF = -1008.941968 (MP2/6-311++G(d,p))

ZPE = 0.298859 (Hartree/Particle)

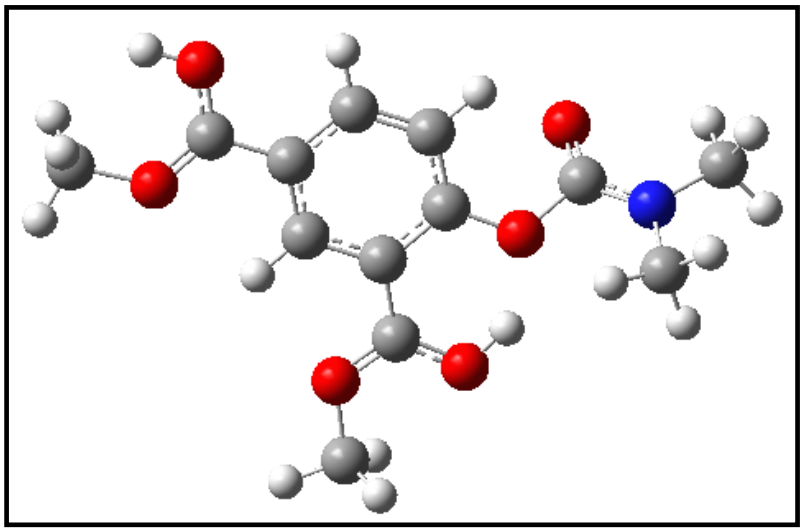
Thermal correction to Gibbs Free Energy = 0.248634 (Hartree/Particle)

NIMAG = 0

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	3.053131	-0.341351	0.115094
2	6	0	1.777956	-0.387476	-0.173143
3	8	0	1.346663	-1.014087	-1.225136
4	8	0	0.916936	0.185729	0.672576
5	6	0	-0.167558	0.972831	0.199595
6	6	0	-1.443913	0.423061	0.001851
7	6	0	0.062588	2.339277	0.103411
8	6	0	-2.501051	1.301725	-0.292293
9	6	0	-0.997343	3.191061	-0.218160
10	1	0	1.056417	2.731114	0.292195
11	6	0	-2.280061	2.672625	-0.410386

12	1	0	-3.493340	0.892422	-0.446674
13	1	0	-0.816931	4.258153	-0.302692
14	6	0	-1.698878	-1.040462	0.021309
15	8	0	-0.903061	-1.884681	-0.409712
16	8	0	-2.881217	-1.364106	0.507741
17	6	0	-3.257740	-2.769233	0.482509
18	1	0	-3.254925	-3.131472	-0.546834
19	1	0	-2.561190	-3.345827	1.093055
20	1	0	-4.260453	-2.794632	0.904217
21	6	0	4.036892	-1.107785	-0.668997
22	1	0	3.527950	-1.822009	-1.311994
23	1	0	4.627379	-0.414997	-1.274644
24	1	0	4.693006	-1.633089	0.028365
25	6	0	3.596905	0.461230	1.223068
26	1	0	4.394493	1.095067	0.828293
27	1	0	2.818047	1.075732	1.666571
28	1	0	4.007857	-0.214394	1.977907
29	1	0	0.395880	-1.363202	-1.039118
30	6	0	-3.454090	3.609128	-0.751293
31	8	0	-4.622731	2.935969	-0.901449
32	6	0	-5.686409	3.838267	-1.216646
33	1	0	-6.597586	3.289228	-1.331593
34	1	0	-5.796385	4.550245	-0.425512
35	1	0	-5.461153	4.350474	-2.128679
36	8	0	-3.476398	4.858173	-0.902816
37	1	0	-4.370140	5.139754	-1.111469

Diprotonation of carbamate 1f (SM-2H$^+$)

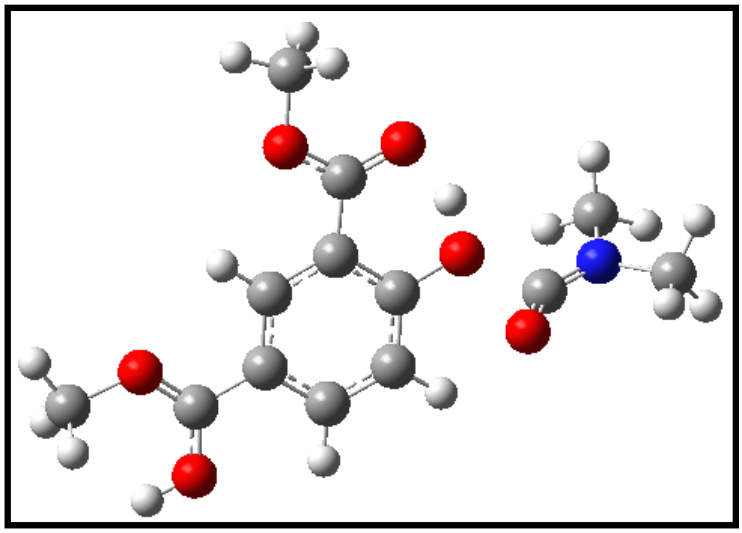


HF = -1011.3951975 (B3LYP/6-31+G(d))
HF = -1011.0208974 (M06/6-311++G(d,p))
HF = -1011.2434414 (M06-2X/6-311++G(d,p))
HF = -1011.3509331 (M06-HF/6-311++G(d,p))
HF = -1011.6562944 (B3LYP/6-311++G(d,p))
HF = -1011.2536199 (B3PW91/6-311++G(d,p))
HF = -1005.7768545 (MP2/6-311++G(d,p))
HF = -1005.6492891 (MP2/aug-ccVDZ)
ZPE = 0.299051 (Hartree/Particle)
Thermal correction to Gibbs Free Energy = 0.247918 (Hartree/Particle)
NIMAG = 0

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	4.120261	-0.951559	-0.124565
2	6	0	2.964332	-0.986969	0.537438
3	8	0	2.661553	-1.586290	1.548908
4	8	0	1.996594	-0.104957	-0.085467
5	6	0	0.668267	-0.387853	-0.020657
6	6	0	-0.232114	0.712055	0.012306
7	6	0	0.182850	-1.699446	-0.053171

8	6	0	-1.611534	0.468334	0.010239
9	6	0	-1.182113	-1.925842	-0.052033
10	1	0	0.872256	-2.532787	-0.089929
11	6	0	-2.088956	-0.843222	-0.018115
12	1	0	-2.300196	1.303560	0.033076
13	1	0	-1.551280	-2.944301	-0.088013
14	6	0	0.233220	2.095465	0.056573
15	8	0	1.478224	2.440061	0.041901
16	8	0	-0.648278	3.024134	0.116945
17	6	0	-0.238595	4.436688	0.170214
18	1	0	0.354675	4.594659	1.070449
19	1	0	0.327741	4.671425	-0.730521
20	1	0	-1.178774	4.979646	0.207856
21	6	0	5.282597	-1.631728	0.458787
22	1	0	5.038293	-1.984803	1.459205
23	1	0	5.567929	-2.480539	-0.171068
24	1	0	6.118002	-0.926968	0.511721
25	1	0	2.061311	1.639387	-0.008320
26	6	0	4.349862	-0.258536	-1.398906
27	1	0	3.411297	-0.086593	-1.921620
28	1	0	4.859078	0.695996	-1.226297
29	1	0	4.987104	-0.893863	-2.019405
30	6	0	-3.520455	-1.091989	-0.021809
31	8	0	-4.318961	-0.087207	-0.029063
32	6	0	-5.782496	-0.226317	-0.032913
33	1	0	-6.098669	-0.722407	0.886332
34	1	0	-6.142473	0.798546	-0.056281
35	1	0	-6.091493	-0.760311	-0.933414
36	8	0	-3.907535	-2.329628	-0.018572
37	1	0	-4.874942	-2.471239	-0.025652

TS-cleavage of C-O bond in deprotonated carbamate 1f (TS-2H$^+$)

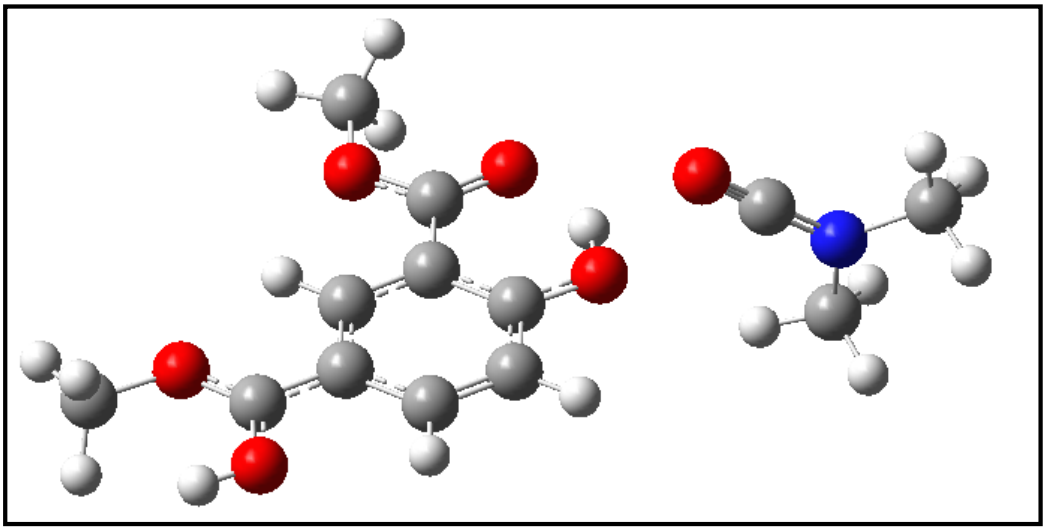


HF = -1011.3737261 (B3LYP/6-31+G(d))
HF = -1010.9976380 (M06/6-311++G(d,p))
HF = -1011.2201845 (M06-2X/6-311++G(d,p))
HF = -1011.3282710 (M06-HF/6-311++G(d,p))
HF = -1011.6378803 (B3LYP/6-311++G(d,p))
HF = -1011.2334248 (B3PW91/6-311++G(d,p))
HF = -1005.7399098 (MP2/6-311++G(d,p))
HF = -1005.6123368 (MP2/aug-ccVDZ)
ZPE = 0.295783 (Hartree/Particle)
Thermal correction to Gibbs Free Energy = 0.244747 (Hartree/Particle)
NIMAG = 1 (153.80*i*)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	-3.309015	-0.338827	0.027045
2	6	0	-2.352833	0.175698	0.734282
3	8	0	-2.074476	0.661231	1.767635
4	8	0	-0.871961	0.058244	-0.341596
5	6	0	0.184122	0.889534	-0.039619
6	6	0	1.450959	0.311233	0.207535
7	6	0	-0.009924	2.269617	-0.012621
8	6	0	2.530851	1.148534	0.473972

9	6	0	1.070972	3.094595	0.261697
10	1	0	-0.988945	2.688923	-0.214020
11	6	0	2.344542	2.538735	0.504008
12	1	0	3.507374	0.717636	0.657039
13	1	0	0.931945	4.169231	0.280972
14	6	0	1.583466	-1.163506	0.154781
15	8	0	0.611260	-1.886538	-0.133840
16	8	0	2.776509	-1.630149	0.426956
17	6	0	2.968400	-3.074862	0.381283
18	1	0	2.323158	-3.549401	1.121775
19	1	0	2.740540	-3.439346	-0.621222
20	1	0	4.018650	-3.219871	0.623854
21	6	0	-4.607695	-0.542255	0.727078
22	1	0	-4.505359	-0.288418	1.780878
23	1	0	-5.356801	0.098118	0.256246
24	1	0	-4.884884	-1.593241	0.621623
25	1	0	-0.466316	-0.921930	-0.324376
26	6	0	-3.251323	-0.772624	-1.385791
27	1	0	-2.514809	-0.190834	-1.932582
28	1	0	-3.016786	-1.839199	-1.432785
29	1	0	-4.240426	-0.596752	-1.809632
30	6	0	3.475052	3.406712	0.782148
31	8	0	4.624563	2.868045	0.977559
32	6	0	5.834580	3.649974	1.257854
33	1	0	5.687537	4.230990	2.169592
34	1	0	6.605151	2.898575	1.406974
35	1	0	6.067881	4.270983	0.391561
36	8	0	3.259111	4.685763	0.817556
37	1	0	4.043213	5.238773	1.008641

After cleavage of C-O bond to generate monoprotonated diester and dimethyl isocyanate cation (PM-2H$^+$)

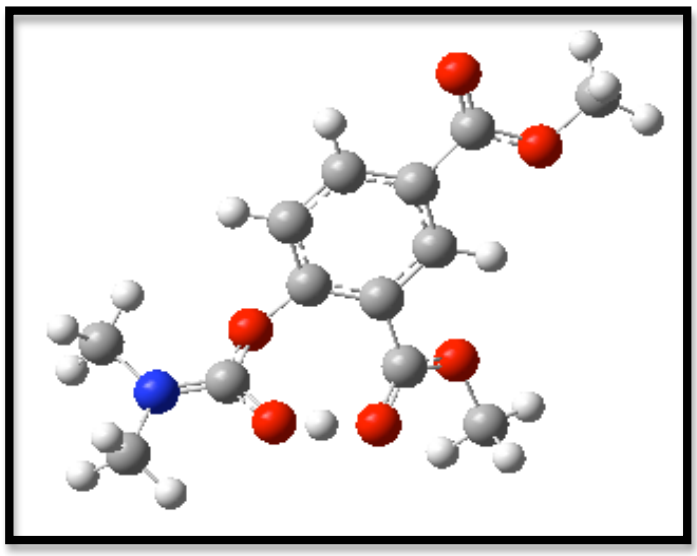


HF = -1011.3851069 (B3LYP/6-31+G(d))
HF = -1011.0110822 (M06/6-311++G(d,p))
HF = -1011.2284163 (M06-2X/6-311++G(d,p))
HF = -1011.3299912 (M06-HF/6-311++G(d,p))
HF = -1011.6514725 (B3LYP/6-311++G(d,p))
HF = -1005.6447781 (B3PW91/6-311++G(d,p))
HF = -1005.7734016 (MP2/6-311++G(d,p))
HF = -1011.2445806 (MP2/aug-ccVDZ)
ZPE = 0.296359 (Hartree/Particle)
Thermal correction to Gibbs Free Energy = 0.240461 (Hartree/Particle)
NIMAG = 0

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	5.073973	-0.884093	0.100600
2	6	0	4.156258	-0.913027	0.963025
3	8	0	3.335316	-0.943836	1.766114
4	8	0	1.637155	0.457775	-0.560830
5	6	0	0.373918	0.043167	-0.440767
6	6	0	-0.696911	0.943841	-0.167254
7	6	0	0.117733	-1.334970	-0.592399

8	6	0	-1.989593	0.442934	-0.049100
9	6	0	-1.166932	-1.817309	-0.473927
10	1	0	0.949353	-1.998947	-0.801942
11	6	0	-2.240218	-0.931554	-0.198219
12	1	0	-2.803811	1.125462	0.160506
13	1	0	-1.356270	-2.878342	-0.590165
14	6	0	-0.404204	2.388509	-0.013750
15	8	0	0.737207	2.850111	-0.115389
16	8	0	-1.470855	3.135095	0.240473
17	6	0	-1.258859	4.561204	0.404862
18	1	0	-0.588597	4.740575	1.247479
19	1	0	-0.838734	4.980886	-0.510993
20	1	0	-2.248340	4.969789	0.601492
21	6	0	6.491898	-1.153059	0.509208
22	1	0	6.536943	-1.326888	1.583468
23	1	0	6.824343	-2.036411	-0.037118
24	1	0	7.077129	-0.273504	0.239505
25	1	0	1.649023	1.446582	-0.431461
26	6	0	4.773919	-0.603566	-1.341314
27	1	0	3.710962	-0.397009	-1.455430
28	1	0	5.367675	0.265295	-1.627894
29	1	0	5.064449	-1.487562	-1.910271
30	6	0	-3.579554	-1.435671	-0.065573
31	8	0	-4.536400	-0.608526	0.199961
32	6	0	-5.927757	-1.035394	0.353322
33	1	0	-6.011962	-1.699814	1.215676
34	1	0	-6.471147	-0.111760	0.534957
35	1	0	-6.273027	-1.500772	-0.572025
36	8	0	-3.767766	-2.717150	-0.219543
37	1	0	-4.690069	-3.018379	-0.106589

Monoprotonation of carbamate 1f (SM_0-H^+)



HF = -1010.637221 (M06/6-311++G(d,p))

HF = -1010.865624 (M06-2X/6-311++G(d,p))

HF = -1008.554059 (MP2/6-311++G(d,p))

ZPE = 0.285978 (Hartree/Particle)

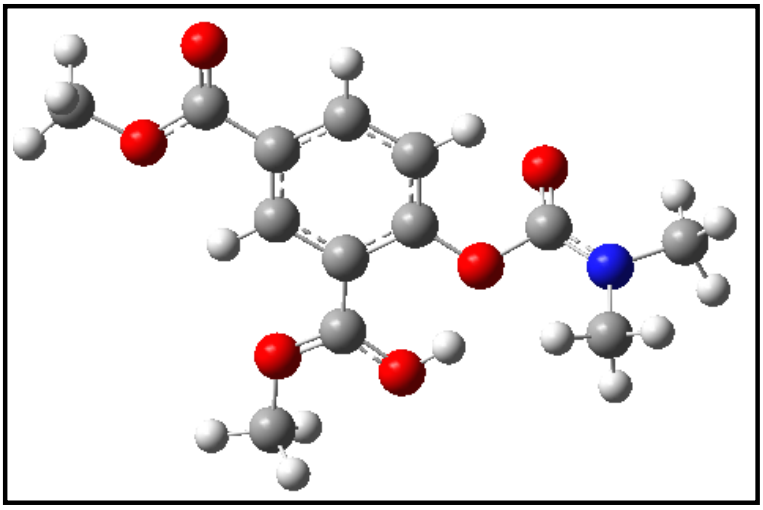
Thermal correction to Gibbs Free Energy = 0.234873 (Hartree/Particle)

NIMAG = 0

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	3.053131	-0.341351	0.115094
2	6	0	1.777956	-0.387476	-0.173143
3	8	0	1.346663	-1.014087	-1.225136
4	8	0	0.916936	0.185729	0.672576
5	6	0	-0.167558	0.972831	0.199595
6	6	0	-1.443913	0.423061	0.001851
7	6	0	0.062588	2.339277	0.103411
8	6	0	-2.501051	1.301725	-0.292293
9	6	0	-0.997343	3.191061	-0.218160
10	1	0	1.056417	2.731114	0.292195
11	6	0	-2.280061	2.672625	-0.410386
12	1	0	-3.493340	0.892422	-0.446674
13	1	0	-0.816931	4.258153	-0.302692

14	6	0	-1.698878	-1.040462	0.021309
15	8	0	-0.903061	-1.884681	-0.409712
16	8	0	-2.881217	-1.364106	0.507741
17	6	0	-3.257740	-2.769233	0.482509
18	1	0	-3.254925	-3.131472	-0.546834
19	1	0	-2.561190	-3.345827	1.093055
20	1	0	-4.260453	-2.794632	0.904217
21	6	0	4.036892	-1.107785	-0.668997
22	1	0	3.527950	-1.822009	-1.311994
23	1	0	4.627379	-0.414997	-1.274644
24	1	0	4.693006	-1.633089	0.028365
25	6	0	3.596905	0.461230	1.223068
26	1	0	4.394493	1.095067	0.828293
27	1	0	2.818047	1.075732	1.666571
28	1	0	4.007857	-0.214394	1.977907
29	1	0	0.395880	-1.363202	-1.039118
30	6	0	-3.454090	3.609128	-0.751293
31	8	0	-4.622731	2.935969	-0.901449
32	6	0	-5.686409	3.838267	-1.216646
33	1	0	-6.597586	3.289228	-1.331593
34	1	0	-5.796385	4.550245	-0.425512
35	1	0	-5.461153	4.350474	-2.128679
36	8	0	-3.476398	4.858173	-0.902816

Monoprotonation of carbamate 1f (SM-H$^+$)

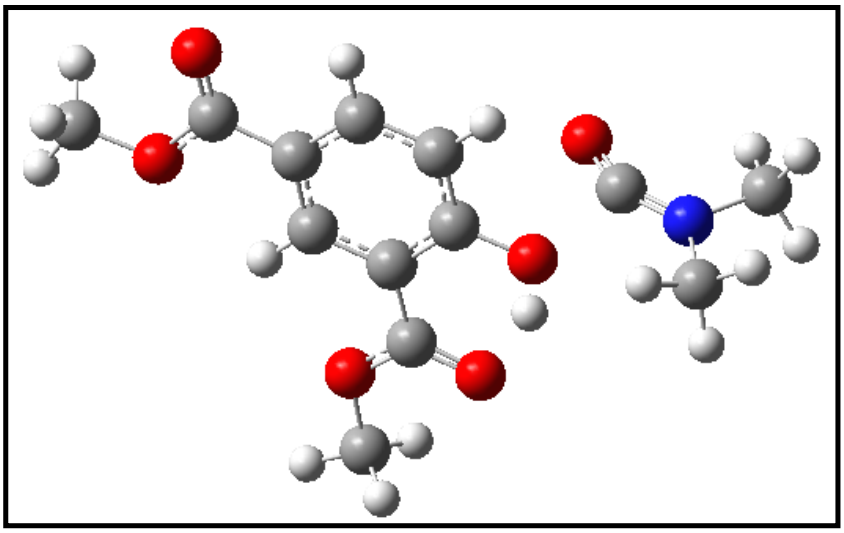


HF = -1011.0071535 (B3LYP/6-31+G(d))
HF = -1010.6306780 (M06/6-311++G(d,p))
HF = -1010.8552520 (M06-2X/6-311++G(d,p))
HF = -1010.9656815 (M06-HF/6-311++G(d,p))
HF = -1011.2635764 (B3LYP/6-311++G(d,p))
HF = -1010.8591816 (B3PW91/6-311++G(d,p))
HF = -1005.3768291 (MP2/6-311++G(d,p))
HF = -1005.2479501 (MP2/aug-ccVDZ)
ZPE = 0.286493 (Hartree/Particle)
Thermal correction to Gibbs Free Energy = 0.235224 (Hartree/Particle)
NIMAG = 0

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	4.143023	-0.892706	-0.049957
2	6	0	2.947083	-0.934048	0.544879
3	8	0	2.617178	-1.502417	1.568629
4	8	0	1.998094	-0.130785	-0.172554
5	6	0	0.657066	-0.419211	-0.080801
6	6	0	-0.249596	0.668838	-0.018772
7	6	0	0.182470	-1.728595	-0.121381
8	6	0	-1.634192	0.408475	0.005761

9	6	0	-1.187333	-1.961297	-0.092947
10	1	0	0.878577	-2.556090	-0.180040
11	6	0	-2.105733	-0.898616	-0.026478
12	1	0	-2.328708	1.237415	0.048056
13	1	0	-1.560599	-2.979196	-0.130034
14	6	0	0.204418	2.049144	0.018627
15	8	0	1.447844	2.405800	-0.044894
16	8	0	-0.677875	2.978463	0.120376
17	6	0	-0.267098	4.388063	0.156141
18	1	0	0.365211	4.549278	1.028987
19	1	0	0.259443	4.626414	-0.767745
20	1	0	-1.204046	4.932668	0.235040
21	6	0	5.290570	-1.498324	0.632749
22	1	0	4.991189	-1.838383	1.622656
23	1	0	5.661596	-2.347987	0.050130
24	1	0	6.087488	-0.753581	0.726180
25	1	0	2.029169	1.604974	-0.121907
26	6	0	4.426038	-0.240602	-1.333780
27	1	0	3.515254	-0.125068	-1.917692
28	1	0	4.888245	0.739768	-1.171260
29	1	0	5.123787	-0.872392	-1.889834
30	6	0	-3.565940	-1.216639	-0.000517
31	8	0	-4.329687	-0.118740	0.066937
32	6	0	-5.761818	-0.322486	0.100672
33	1	0	-6.035120	-0.904139	0.983768
34	1	0	-6.189965	0.677586	0.149363
35	1	0	-6.087004	-0.839486	-0.804664
36	8	0	-4.007716	-2.353954	-0.035731

TS-cleavage of C-O bond in monoprotonated carbamate 1f (TS-H$^+$)

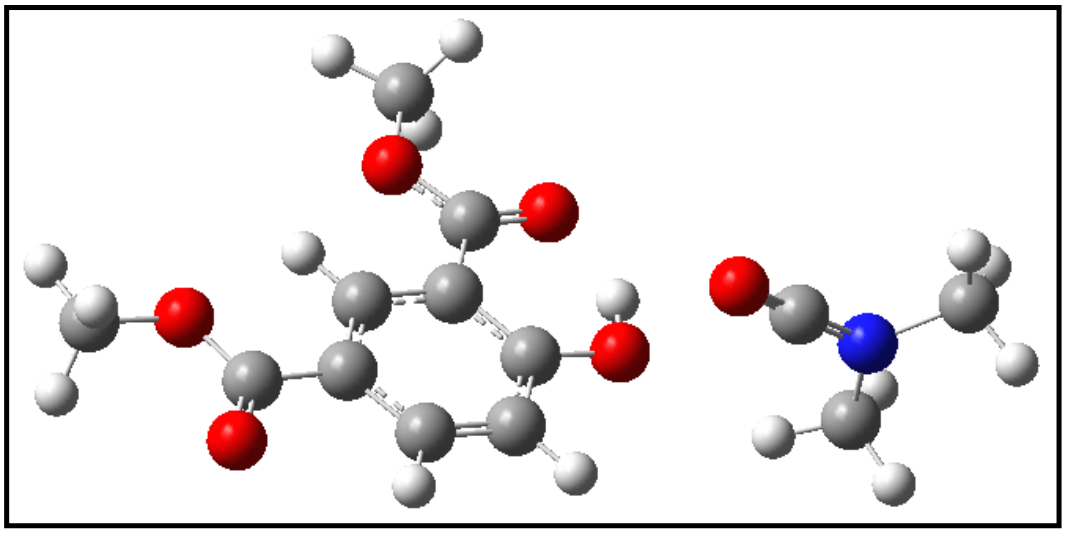


HF = -1010.9835863 (B3LYP/6-31+G(d))
HF = -1010.6068647 (M06/6-311++G(d,p))
HF = -1010.8285192 (M06-2X/6-311++G(d,p))
HF = -1010.9370624 (M06-HF/6-311++G(d,p))
HF = -1011.2434975 (B3LYP/6-311++G(d,p))
HF = -1010.8359288 (B3PW91/6-311++G(d,p))
HF = -1005.3418841 (MP2/6-311++G(d,p))
HF = -1005.2124406 (MP2/aug-ccVDZ)
ZPE = 0.284233 (Hartree/Particle)
Thermal correction to Gibbs Free Energy = 0.233094 (Hartree/Particle)
NIMAG = 1 (110.62*i*)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	4.217117	-0.932619	0.074151
2	6	0	3.052328	-0.995323	0.614810
3	8	0	2.355428	-1.293094	1.501831
4	8	0	1.865255	-0.111251	-0.753058
5	6	0	0.518162	-0.338655	-0.565946
6	6	0	-0.345490	0.734140	-0.250348
7	6	0	0.032304	-1.637283	-0.706871
8	6	0	-1.711104	0.472677	-0.083943

9	6	0	-1.326356	-1.875351	-0.531633
10	1	0	0.712061	-2.444705	-0.957829
11	6	0	-2.206882	-0.826369	-0.218597
12	1	0	-2.380796	1.290273	0.150186
13	1	0	-1.718327	-2.880939	-0.639944
14	6	0	0.215350	2.098222	-0.131977
15	8	0	1.415914	2.338709	-0.336454
16	8	0	-0.658406	3.030592	0.202426
17	6	0	-0.169237	4.393206	0.324639
18	1	0	0.592458	4.442414	1.104654
19	1	0	0.241124	4.724238	-0.630880
20	1	0	-1.044717	4.979303	0.597128
21	6	0	5.365129	-1.304222	0.958588
22	1	0	5.015976	-1.449655	1.979781
23	1	0	5.807768	-2.224740	0.573582
24	1	0	6.085135	-0.484720	0.923544
25	1	0	1.990339	0.897914	-0.659725
26	6	0	4.557847	-0.532251	-1.310756
27	1	0	3.700029	-0.664944	-1.962182
28	1	0	4.890314	0.508440	-1.310399
29	1	0	5.372264	-1.181690	-1.633795
30	6	0	-3.654984	-1.142714	-0.043531
31	8	0	-4.390356	-0.058011	0.243052
32	6	0	-5.808602	-0.264886	0.432871
33	1	0	-5.979433	-0.947156	1.268562
34	1	0	-6.213339	0.722124	0.652520
35	1	0	-6.253588	-0.670807	-0.478356
36	8	0	-4.121544	-2.267002	-0.148866

After cleavage of C-O bond to generate neutral diester and dimethyl isocyanate cation (PM-H$^+$)

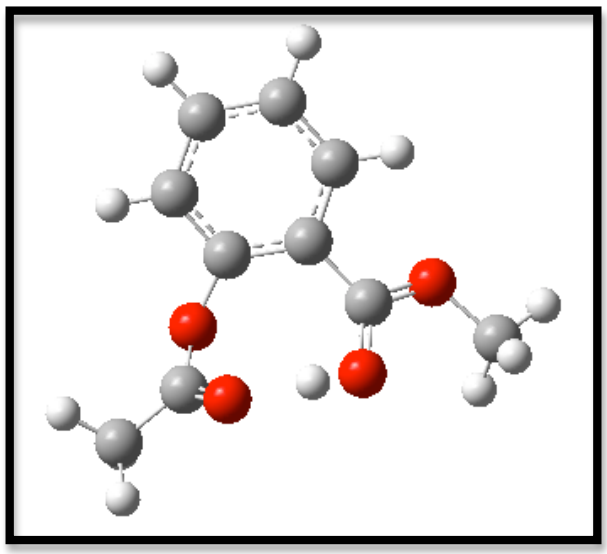


HF = -1010.9886583 (B3LYP/6-31+G(d))
HF = -1010.6134014 (M06/6-311++G(d,p))
HF = -1010.8332433 (M06-2X/6-311++G(d,p))
HF = -1010.9382821 (M06-HF/6-311++G(d,p))
HF = -1011.2505020 (B3LYP/6-311++G(d,p))
HF = -1010.8415436 (B3PW91/6-311++G(d,p))
HF = -1005.3657122 (MP2/6-311++G(d,p))
HF = -1005.2353747 (MP2/aug-ccVDZ)
ZPE = 0.283866 (Hartree/Particle)
Thermal correction to Gibbs Free Energy = 0.22811 (Hartree/Particle)
NIMAG = 0

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	4.871263	-0.843813	0.194768
2	6	0	3.845740	-1.085924	0.885992
3	8	0	2.937302	-1.319598	1.549322
4	8	0	1.654465	0.232423	-0.826804
5	6	0	0.370333	-0.129118	-0.618705
6	6	0	-0.635024	0.810048	-0.268408
7	6	0	0.039473	-1.486651	-0.757716

8	6	0	-1.947875	0.359943	-0.063417
9	6	0	-1.263566	-1.907448	-0.550364
10	1	0	0.819625	-2.190130	-1.030478
11	6	0	-2.274378	-0.989890	-0.198982
12	1	0	-2.712653	1.078014	0.203730
13	1	0	-1.518040	-2.956819	-0.657855
14	6	0	-0.275013	2.236093	-0.134271
15	8	0	0.871499	2.663439	-0.318946
16	8	0	-1.290351	3.029621	0.201782
17	6	0	-1.005290	4.442553	0.344961
18	1	0	-0.261063	4.595880	1.129009
19	1	0	-0.644159	4.848105	-0.602321
20	1	0	-1.956652	4.894323	0.621222
21	6	0	6.214882	-0.782522	0.860044
22	1	0	6.107063	-0.980987	1.925834
23	1	0	6.841567	-1.542309	0.391791
24	1	0	6.613345	0.219070	0.695328
25	1	0	1.710208	1.217111	-0.703185
26	6	0	4.788767	-0.649129	-1.288707
27	1	0	3.744161	-0.645483	-1.593783
28	1	0	5.254169	0.312029	-1.509837
29	1	0	5.334754	-1.469955	-1.755303
30	6	0	-3.654352	-1.497977	0.014242
31	8	0	-4.525010	-0.527004	0.344989
32	6	0	-5.892162	-0.932040	0.573669
33	1	0	-5.941306	-1.644591	1.400398
34	1	0	-6.423365	-0.014868	0.825534
35	1	0	-6.308668	-1.382135	-0.330527
36	8	0	-3.976283	-2.673653	-0.095713

Monoprotonation of ester 1e (SM_0-Me)



HF = -688.1694373 (M06/6-311++G(d,p))

HF = -688.3307554 (M06-2X/6-311++G(d,p))

HF = -686.7412388 (MP2/6-311++G(d,p))

ZPE = 0.197266 (Hartree/Particle)

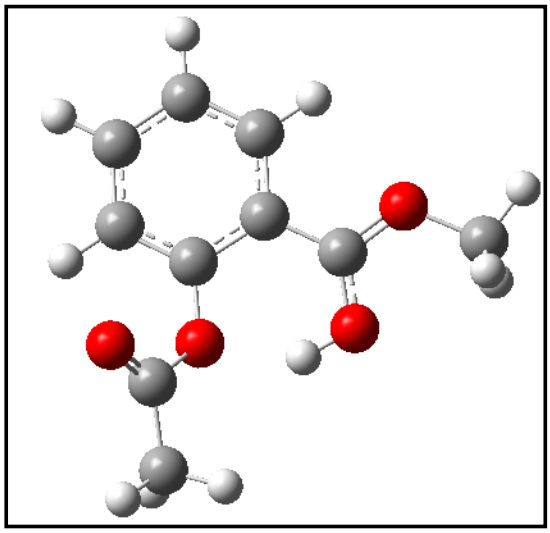
Thermal correction to Gibbs Free Energy = 0.157108 (Hartree/Particle)

NIMAG = 0

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.777956	-0.387476	-0.173143
2	8	0	1.346663	-1.014087	-1.225136
3	8	0	0.916936	0.185729	0.672576
4	6	0	-0.167558	0.972831	0.199595
5	6	0	-1.443913	0.423061	0.001851
6	6	0	0.062588	2.339277	0.103411
7	6	0	-2.501051	1.301725	-0.292293
8	6	0	-0.997343	3.191061	-0.218160
9	1	0	1.056417	2.731114	0.292195
10	6	0	-2.280061	2.672625	-0.410386
11	1	0	-3.493340	0.892423	-0.446674
12	1	0	-0.816930	4.258153	-0.302692
13	1	0	-3.107453	3.332621	-0.650639

14	6	0	-1.698878	-1.040462	0.021309
15	8	0	-0.903061	-1.884681	-0.409712
16	8	0	-2.881217	-1.364106	0.507741
17	6	0	-3.257740	-2.769233	0.482509
18	1	0	-3.254925	-3.131472	-0.546834
19	1	0	-2.561190	-3.345827	1.093055
20	1	0	-4.260453	-2.794631	0.904217
21	1	0	0.395880	-1.363202	-1.039118
22	6	0	3.098986	-0.339692	0.125459
23	1	0	3.545252	-1.290679	-0.077938
24	1	0	3.572618	0.411527	-0.471402
25	1	0	3.222109	-0.102197	1.161479

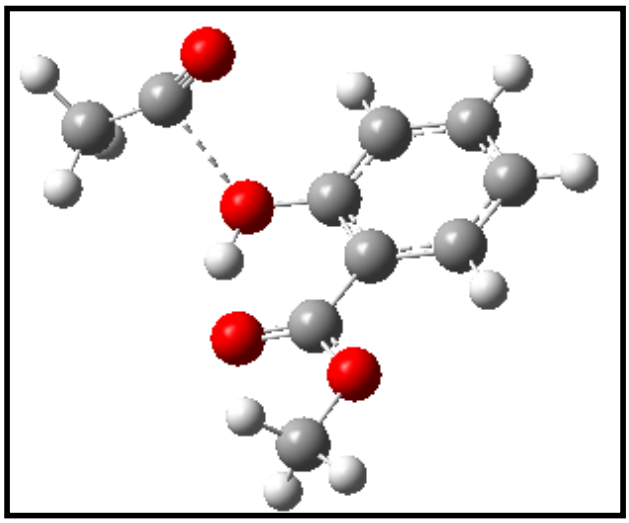
Monoprotonation of ester 1e (SM-Me)



HF = -688.44431060 (B3LYP/6-31+G(d))
HF = -688.17362201 (M06/6-311++G(d,p))
HF = -688.33463960 (M06-2X/6-311++G(d,p))
HF = -686.74500337 (MP2/6-311++G(d,p))
ZPE = 0.197989 (Hartree/Particle)
Thermal correction to Gibbs Free Energy = 0.157408 (Hartree/Particle)
NIMAG = 0

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.440291	-0.981320	0.247074
2	8	0	-2.856629	-0.287952	1.133903
3	8	0	-1.269400	-0.640516	-0.472309
4	6	0	-0.639354	0.582901	-0.264442
5	6	0	0.763195	0.584667	-0.068541
6	6	0	-1.348027	1.776462	-0.318761
7	6	0	1.428793	1.819845	0.093452
8	6	0	-0.666853	2.984679	-0.156053
9	1	0	-2.417285	1.765331	-0.489881
10	6	0	0.717576	3.009897	0.055270
11	1	0	2.502996	1.825374	0.235972
12	1	0	-1.225595	3.914412	-0.202279
13	1	0	1.235950	3.954929	0.177299
14	6	0	1.543478	-0.639665	-0.060198
15	8	0	1.061741	-1.811892	-0.332548
16	8	0	2.795865	-0.564556	0.223066
17	6	0	3.628581	-1.773893	0.226331
18	1	0	3.257447	-2.454758	0.992504
19	1	0	3.596987	-2.230384	-0.762650
20	1	0	4.623003	-1.407261	0.466212
21	1	0	0.093301	-1.743759	-0.533088
22	6	0	-3.004440	-2.267171	-0.270691
23	1	0	-3.164094	-2.198639	-1.351238
24	1	0	-2.304840	-3.090255	-0.088012
25	1	0	-3.946439	-2.474064	0.237633

TS-cleavage of C-O bond in monoprotonated ester 1e (TS-Me)

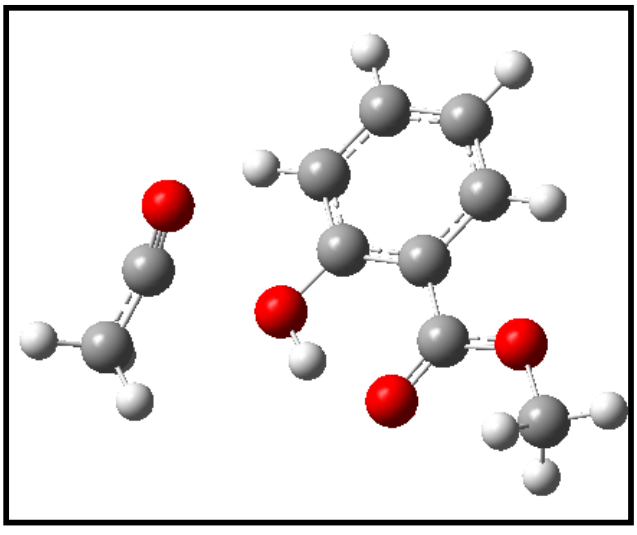


HF = -688.41991320 (B3LYP/6-31+G(d))
HF = -688.15138682 (M06/6-311++G(d,p))
HF = -688.30967320 (M06-2X/6-311++G(d,p))
HF = -686.73068812 (MP2/6-311++G(d,p))
ZPE = 0.194855 (Hartree/Particle)
Thermal correction to Gibbs Free Energy = 0.153271 (Hartree/Particle)
NIMAG = 1 (55.68*i*)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.790304	-0.952595	0.539401
2	8	0	-2.687251	-0.236698	1.417940
3	8	0	-1.225489	-0.468485	-0.794609
4	6	0	-0.494105	0.654192	-0.461611
5	6	0	0.870025	0.547508	-0.106513
6	6	0	-1.134676	1.892024	-0.485609
7	6	0	1.573361	1.718913	0.221647
8	6	0	-0.415549	3.039793	-0.150531
9	1	0	-2.179349	1.949774	-0.774199
10	6	0	0.936782	2.956824	0.204596
11	1	0	2.622254	1.645185	0.486324
12	1	0	-0.914517	4.004163	-0.171712

13	1	0	1.490536	3.854312	0.461336
14	6	0	1.515103	-0.781497	-0.120272
15	8	0	0.919334	-1.809920	-0.476779
16	8	0	2.780424	-0.787351	0.273701
17	6	0	3.472656	-2.062360	0.272143
18	1	0	2.974261	-2.755254	0.952628
19	1	0	3.492655	-2.472098	-0.739394
20	1	0	4.478917	-1.834099	0.618790
21	1	0	-0.566072	-1.235517	-0.796312
22	6	0	-3.385163	-2.005773	-0.257312
23	1	0	-3.596487	-1.618658	-1.258191
24	1	0	-2.683506	-2.843400	-0.329815
25	1	0	-4.303615	-2.316944	0.252887

After cleavage of C-O bond to generate neutral ester and acyl cation (PM-Me)



HF = -688.41991320 (B3LYP/6-31+G(d))

HF = -688.15401117 (M06/6-311++G(d,p))

HF = -688.31190150 (M06-2X/6-311++G(d,p))

HF = -686.73251818 (MP2/6-311++G(d,p))

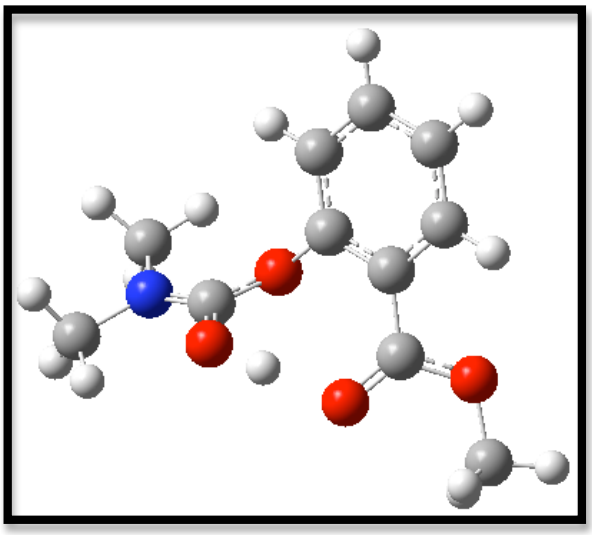
ZPE = 0.194803 (Hartree/Particle)

Thermal correction to Gibbs Free Energy = 0.151624 (Hartree/Particle)

NIMAG = 0

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-3.121662	-0.889466	0.581608
2	8	0	-2.931731	-0.157314	1.420121
3	8	0	-1.175063	-0.461934	-0.797210
4	6	0	-0.422189	0.632556	-0.468283
5	6	0	0.941334	0.513282	-0.104993
6	6	0	-1.037257	1.887911	-0.498833
7	6	0	1.659638	1.677751	0.224893
8	6	0	-0.304575	3.024985	-0.164599
9	1	0	-2.079360	1.961160	-0.793901
10	6	0	1.045618	2.925135	0.200163
11	1	0	2.704922	1.587706	0.498951
12	1	0	-0.789798	3.996545	-0.192236
13	1	0	1.611073	3.815090	0.458028
14	6	0	1.572034	-0.821012	-0.099869
15	8	0	0.969438	-1.854514	-0.422944
16	8	0	2.847783	-0.826728	0.277627
17	6	0	3.527648	-2.105944	0.293769
18	1	0	3.034178	-2.781722	0.995090
19	1	0	3.531263	-2.538934	-0.708508
20	1	0	4.541206	-1.880839	0.621573
21	1	0	-0.559185	-1.248755	-0.767431
22	6	0	-3.609526	-1.873672	-0.340684
23	1	0	-3.619522	-1.441418	-1.346276
24	1	0	-2.943944	-2.743869	-0.310351
25	1	0	-4.620629	-2.150206	-0.014728

Monoprotonation of carbamate 1b (SM_0-NMe_2)



HF = -782.8123796 (M06/6-311++G(d,p))

HF = -783.0881193 (M06-2X/6-311++G(d,p))

HF = -781.1794158 (MP2/6-311++G(d,p))

ZPE = 0.243337 (Hartree/Particle)

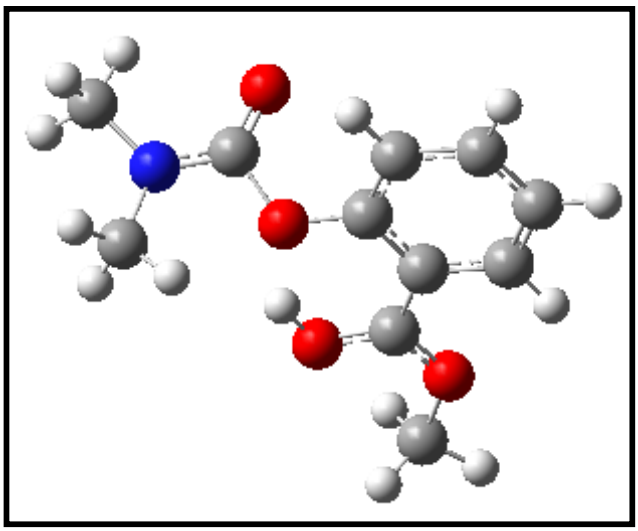
Thermal correction to Gibbs Free Energy = 0.19918 (Hartree/Particle)

NIMAG = 0

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	3.053131	-0.341351	0.115094
2	6	0	1.777956	-0.387476	-0.173143
3	8	0	1.346663	-1.014087	-1.225136
4	8	0	0.916936	0.185729	0.672576
5	6	0	-0.167558	0.972831	0.199595
6	6	0	-1.443913	0.423061	0.001851
7	6	0	0.062588	2.339277	0.103411
8	6	0	-2.501051	1.301725	-0.292293
9	6	0	-0.997343	3.191061	-0.218160
10	1	0	1.056417	2.731114	0.292195
11	6	0	-2.280061	2.672625	-0.410386
12	1	0	-3.493340	0.892422	-0.446674
13	1	0	-0.816931	4.258153	-0.302692

14	1	0	-3.107453	3.332621	-0.650639
15	6	0	-1.698878	-1.040462	0.021309
16	8	0	-0.903061	-1.884681	-0.409712
17	8	0	-2.881217	-1.364106	0.507741
18	6	0	-3.257740	-2.769233	0.482509
19	1	0	-3.254925	-3.131472	-0.546834
20	1	0	-2.561190	-3.345827	1.093055
21	1	0	-4.260453	-2.794632	0.904217
22	6	0	4.036892	-1.107785	-0.668997
23	1	0	3.527950	-1.822009	-1.311994
24	1	0	4.627379	-0.414997	-1.274644
25	1	0	4.693006	-1.633089	0.028365
26	6	0	3.596905	0.461230	1.223068
27	1	0	4.394493	1.095067	0.828293
28	1	0	2.818047	1.075732	1.666571
29	1	0	4.007857	-0.214394	1.977907
30	1	0	0.395880	-1.363202	-1.039118

Monoprotonation of carbamate 1b (SM-NMe$_2$)



HF = -728.8751510 (B3LYP/6-31+G(d))

HF = -782.8054535 (M06/6-311++G(d,p))

HF = -783.0764360 (M06-2X/6-311++G(d,p))

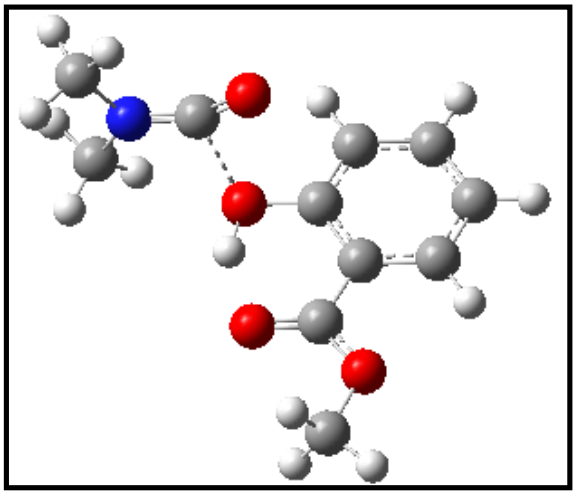
HF = -781.1681371 (MP2/6-311++G(d,p))

ZPE = 0.243816 (Hartree/Particle)
Thermal correction to Gibbs Free Energy = 0.198917 (Hartree/Particle)
NIMAG = 0

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	-3.071997	-0.504288	0.122317
2	6	0	-2.042734	0.140518	-0.439202
3	8	0	-2.021995	0.798465	-1.463658
4	8	0	-0.845887	-0.061765	0.316455
5	6	0	0.177284	0.863672	0.209433
6	6	0	1.501640	0.380380	0.073049
7	6	0	-0.069456	2.228658	0.307750
8	6	0	2.568198	1.307280	0.033441
9	6	0	0.999621	3.123545	0.260163
10	1	0	-1.085823	2.586527	0.422715
11	6	0	2.318275	2.667523	0.121888
12	1	0	3.582905	0.939152	-0.062731
13	1	0	0.799927	4.187803	0.339835
14	1	0	3.141294	3.373478	0.090975
15	6	0	1.794090	-1.036815	-0.020147
16	8	0	0.898371	-1.970118	0.066246
17	8	0	3.016030	-1.400882	-0.197654
18	6	0	3.357886	-2.825521	-0.281857
19	1	0	3.074048	-3.314148	0.650135
20	1	0	2.841489	-3.264775	-1.135201
21	1	0	4.435405	-2.829779	-0.422693
22	6	0	-4.345579	-0.566634	-0.599903
23	1	0	-4.231768	-0.117114	-1.584913
24	1	0	-4.648165	-1.613348	-0.707280
25	1	0	-5.116590	-0.028019	-0.038731
26	6	0	-3.023557	-1.212991	1.405840
27	1	0	-2.190929	-0.859670	2.010528
28	1	0	-3.957241	-1.016498	1.939933

29	1	0	-2.929186	-2.293028	1.243965
30	1	0	0.002443	-1.563848	0.203401

TS-cleavage of C-O bond in monoprotonated carbamate 1b (TS-NMe_2)

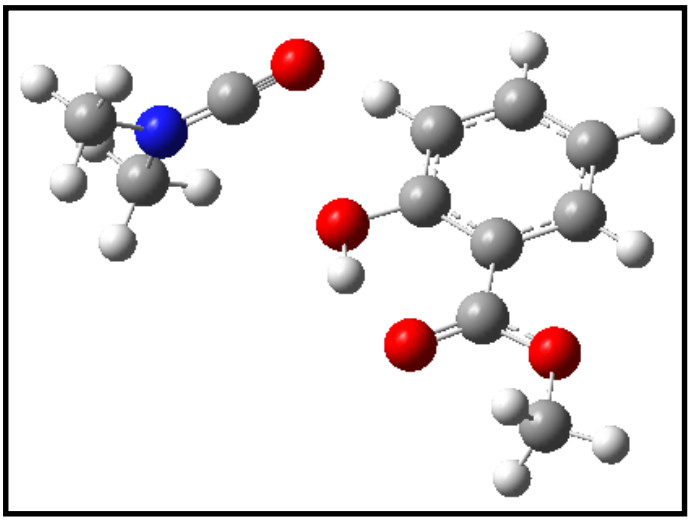


HF = -728.8522390 (B3LYP/6-31+G(d))
HF = -782.7813691 (M06/6-311++G(d,p))
HF = -783.0466561 (M06-2X/6-311++G(d,p))
HF = -781.1502918 (MP2/6-311++G(d,p))
ZPE = 0.241249 (Hartree/Particle)
Thermal correction to Gibbs Free Energy = 0.194782 (Hartree/Particle)
NIMAG = 1 (97.95*i*)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	-3.270849	-0.341600	0.021344
2	6	0	-2.309698	0.223678	0.647888
3	8	0	-1.795721	0.743375	1.550696
4	8	0	-0.707362	0.117854	-0.794229
5	6	0	0.379216	0.895764	-0.458031
6	6	0	1.611724	0.302169	-0.100955
7	6	0	0.233545	2.282458	-0.484761
8	6	0	2.693934	1.139099	0.222542

9	6	0	1.321123	3.090971	-0.155430
10	1	0	-0.721337	2.714267	-0.767479
11	6	0	2.552084	2.523309	0.199353
12	1	0	3.644003	0.689491	0.488834
13	1	0	1.206823	4.170751	-0.178812
14	1	0	3.394731	3.158977	0.452317
15	6	0	1.729089	-1.170343	-0.101562
16	8	0	0.799130	-1.916759	-0.443304
17	8	0	2.909281	-1.631736	0.289903
18	6	0	3.089645	-3.070917	0.303742
19	1	0	2.378763	-3.527228	0.995242
20	1	0	2.951134	-3.472282	-0.701903
21	1	0	4.112682	-3.220920	0.644058
22	6	0	-4.466830	-0.704139	0.850177
23	1	0	-4.271201	-0.488899	1.899728
24	1	0	-5.313123	-0.115350	0.492560
25	1	0	-4.647022	-1.771505	0.712312
26	1	0	-0.381289	-0.836768	-0.775868
27	6	0	-3.334376	-0.692584	-1.419066
28	1	0	-2.609200	-0.108882	-1.976317
29	1	0	-3.143312	-1.762332	-1.527986
30	1	0	-4.345078	-0.456783	-1.754010

After cleavage of C-O bond to generate neutral ester and dimethyl isocyanate cation (PM-NMe_2)



HF = -728.8552990 (B3LYP/6-31+G(d))
HF = -782.7848639 (M06/6-311++G(d,p))
HF = -783.0503338 (M06-2X/6-311++G(d,p))
HF = -781.1525106 (MP2/6-311++G(d,p))
ZPE = 0.240859 (Hartree/Particle)
Thermal correction to Gibbs Free Energy = 0.19023 (Hartree/Particle)
NIMAG = 0

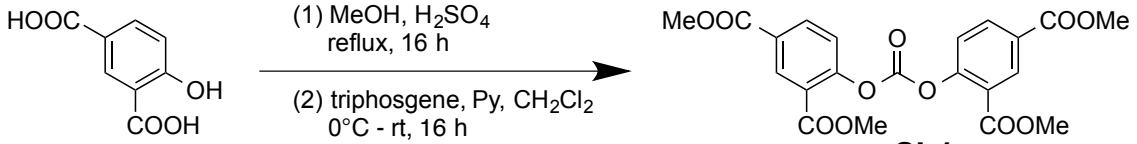
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	-3.728302	-0.363728	0.041683
2	6	0	-2.909642	0.167936	0.839750
3	8	0	-2.212517	0.643406	1.619709
4	8	0	-0.512314	0.051379	-0.813888
5	6	0	0.533128	0.841073	-0.451031
6	6	0	1.796322	0.306718	-0.092344
7	6	0	0.331406	2.227871	-0.437761
8	6	0	2.831618	1.190806	0.272937
9	6	0	1.370164	3.078466	-0.072136
10	1	0	-0.641938	2.618173	-0.719576

11	6	0	2.626754	2.564610	0.286152
12	1	0	3.797404	0.779422	0.545059
13	1	0	1.201300	4.151868	-0.066480
14	1	0	3.433032	3.233906	0.569774
15	6	0	1.994972	-1.153836	-0.116959
16	8	0	1.111199	-1.956330	-0.446830
17	8	0	3.216175	-1.549692	0.246898
18	6	0	3.477601	-2.973201	0.240933
19	1	0	2.808301	-3.480125	0.939212
20	1	0	3.344260	-3.374668	-0.765769
21	1	0	4.513976	-3.070275	0.560877
22	6	0	-4.873473	-1.159025	0.596887
23	1	0	-4.795943	-1.205556	1.682490
24	1	0	-5.793975	-0.655171	0.299692
25	1	0	-4.810354	-2.158785	0.166646
26	1	0	-0.193318	-0.888280	-0.788111
27	6	0	-3.634257	-0.173887	-1.440424
28	1	0	-2.712758	0.352926	-1.676770
29	1	0	-3.629152	-1.167969	-1.889145
30	1	0	-4.510630	0.395340	-1.752815

IV. Synthesis of Chemical Compounds and Acid-catalyzed Reactions

Preparation of Substrates

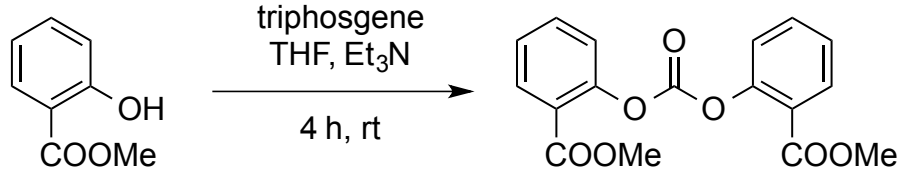
Preparation of tetramethyl 4,4'-(carbonylbis(oxy))diisophthalate SI-1



SI-1

To a solution of 4-hydroxyisophthalic acid (2000.1 mg, 11.0 mmol) in MeOH (40 mL), added conc. H_2SO_4 (10 mL) at room temperature, the whole was stirred for 16 hours at reflux. After the reaction completed, poured into ice-water and quenched with 2M aqueous solution of NaOH (30 mL). Then, The mixture was extracted with CH_2Cl_2 (30 mL x 3). The organic phase was washed with brine (30 mL), dried over Na_2SO_4, and the solvent was evaporated under reduced pressure to give a crude (2240.1 mg). This crude in CH_2Cl_2 (30 mL) was added to a solution of triphosgene (810.1 mg, 2.72 mmol) in CH_2Cl_2 (10 mL), then pyridine (4.0 mL) was added at 0°C. The whole was warmed up from 0°C to room temperature, and stirred for 16 hours. After the reaction completed, the reaction was quenched with 2M aqueous solution of HCl (30 mL). This reaction mixture was extracted with CH_2Cl_2 (30 mL x 4). The organic phase was washed with brine (40 mL), dried over Na_2SO_4, and the solvent was evaporated under reduced pressure to give a residue, which was column-chromatography on silica gel (eluent: EtOAc / n-Hexane = 2 / 3) to afford tetramethyl 4,4'-(carbonylbis(oxy))diisophthalate **SI-1** (1819.4 mg, 3.99 mmol, 74%) as a colorless solid. Mp. 176.9-177.6°C (colorless plates, recrystallized from CH_2Cl_2/n-Hexane). ^{1}H-NMR ($CDCl_3$, 400 MHz (ppm): δ (ppm): 8.700 (1H, d, *J* = 2.4 Hz), 8.275 (1H, dd, *J* = 8.4, 2.4 Hz), 7.484 (1H, d, *J* = 8.4 Hz), 3.970 (3H, s), 3.948 (3H, s). ^{13}C-NMR ($CDCl_3$, 100 MHz) δ (ppm): 165.85, 164.49, 154.31, 150.93, 135.70, 134.00, 129.43, 124.47, 123.84, 53.20, 53.11. HRMS (ESI-TOF, $[M+Na]^+$): Calcd. for $C_{21}H_{18}NaO_{11}^+$: 469.0741. Found: 469.0728. Anal. Calcd. for $C_{21}H_{18}O_{11}$: C, 56.51; H, 4.06. Found: C, 56.20; H, 4.11.

Preparation of dimethyl 2,2'-(carbonylbis(oxy))dibenzoate SI-2

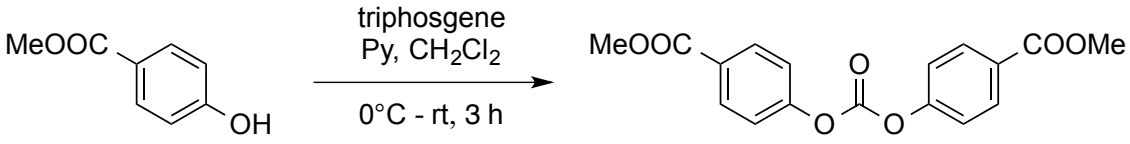


SI-2

To a solution of methyl 2-hydroxybenzoate (1019.5 mg, 66.7 mmol) and NEt_3 (15.0 mL, 107 mmol) in THF (30 mL) was added a solution of triphosgene (3000.1 mg, 10.1 mmol) in CH_2Cl_2 (25 mL) at 0°C. The whole was stirred at 0°C, for 20 min and then stirring was continued at room temperature for an additional 4 hours. The reaction was quenched with saturated aqueous solution of $NaHCO_3$ (30 mL). The whole was extracted with CH_2Cl_2 (20 mL x 5) and the organic phase was washed with brine (20 mL), dried over Na_2SO_4, and the solvent was evaporated to give a residue, which was recrystallized from $CHCl_3$ and n-Hexane to afford dimethyl 2,2'-(carbonylbis(oxy))dibenzoate **SI-2** (8863.4 mg, 26.9 mmol, 81%) as a colorless solid.

Mp. 109.5-110.2°C (colorless plates, recrystallized from $CHCl_3$/n-Hexane). ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm): 8.033 (1H, dd, *J* = 8.0, 1.6 Hz), 7.605 (1H, ddd, *J* = 10.0, 7.0, 2.0 Hz), 7.398-7.261 (2H, m), 3.945 (3H, s). ^{13}C-NMR (100 MHz, $CDCl_3$) δ (ppm): 165.36, 151.58, 151.23, 134.59, 132.38, 127.14, 124.06, 123.65, 52.93. HRMS (ESI-TOF, $[M+Na]^+$): Calcd. for $C_{17}H_{14}NaO_7^+$: 353.0632. Found: 353.0632. Anal. Calcd. for $C_{17}H_{14}O_7$: C, 61.82; H, 4.27. Found: C, 61.64; H, 4.50.

Preparation of dimethyl 4,4'-(carbonylbis(oxy))dibenzoate SI-3



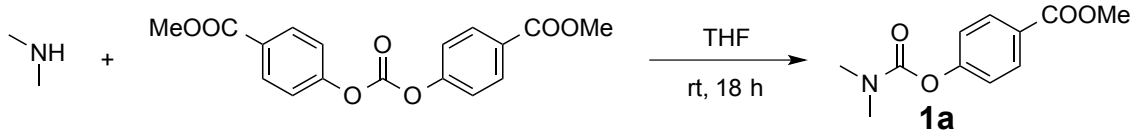
SI-3

Methyl 4-hydroxybenzoate (1791.1 mg, 11.8 mmol) in CH_2Cl_2 (30 mL) was added to a solution of triphosgene (940.5 mg, 3.17 mmol) in CH_2Cl_2 (30 mL), then pyridine (5.0 mL) was added at 0°C. The whole was warmed up from 0°C to room temperature, and stirred for 16 hours. After the reaction completed, the reaction was quenched with 2M aqueous solution of HCl (40 mL). This reaction mixture was extracted with CH_2Cl_2 (40 mL x 3). The organic phase was washed with brine (40 mL), dried over Na_2SO_4, and the solvent was evaporated under reduced pressure to give a residue, which was column-chromatography on silica gel (eluent : EtOAc / n-Hexane = 1 / 2) to afford dimethyl 4,4'-(carbonylbis(oxy))dibenzoate **SI-3** (2983.1 mg, 9.03 mmol, 90%) as a colorless solid. Mp. 189.1-190.1°C (colorless needles, recrystallized from $CHCl_3$/n-Hexane).

^{1}H-NMR ($CDCl_3$, 400 MHz) δ (ppm): 8.113 (4H, d, *J* = 8.0 Hz), 7.361 (4H, d, *J* = 7.6 Hz), 3.922 (6H, s). ^{13}C-NMR ($CDCl_3$, 100 MHz) δ (ppm): 166.58, 154.70, 151.39, 131.93, 128.95, 121.35, 52.83. HRMS (ESI-TOF, $[M+Na]^+$): Calcd. for $C_{17}H_{14}NaO_7^+$:

353.0632. Found: 353.0656. Anal. Calcd. for $C_{17}H_{14}O_7$: C, 61.82; H, 4.27. Found: C, 61.66; H, 4.40.

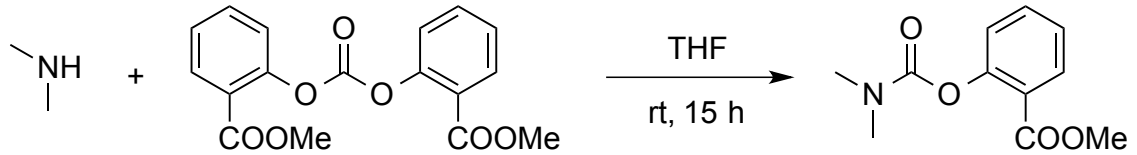
Preparation of methyl 4-((dimethylcarbamoyl)oxy)benzoate 1a



1a

To a solution of dimethyl 4,4'-(carbonylbis(oxy))dibenzoate **SI-3** (696.4 mg, 2.11 mmol) in THF (2.0 mL), 50%(w/w) aqueous solution of dimethyl amine (194.5 mg, 2.16 mmol) in THF (3.0 mL) was added at room temperature. After the reaction completed, added 2M aqueous solution of NaOH (40 mL), then extracted with CH_2Cl_2 (40 mL x 3). The organic phase was washed with brine (40 mL), dried over Na_2SO_4, and the solvent was evaporated under reduced pressure to give a residue, which was flash column-chromatographed on silica-gel (eluent: EtOAc / n-Hexane = 1 / 2) to afford methyl 4-((dimethylcarbamoyl)oxy)benzoate **1a** (400.4 mg, 1.79 mmol, 85%) as a colorless solid. Mp. 97.1-97.3°C (colorless needles, recrystallized from CH_2Cl_2/n-Hexane). ^{1}H-NMR ($CDCl_3$, 400 MHz) δ (ppm): 8.061 (2H, dt, *J* = 9.2, 2.8 Hz), 7.211 (2H, dt, *J* = 9.2, 2.8 Hz), 3.920 (3H, s), 3.123 (3H, s), 3.036 (3H, s). ^{13}C-NMR ($CDCl_3$, 100 MHz) δ (ppm): 167.01, 155.79, 154.64, 131.53, 127.48, 122.08, 52.62, 37.27, 37.03. HRMS (ESI-TOF, $[M+Na]^+$): Calcd. for $C_{11}H_{13}NNaO_4^+$: 246.0737. Found: 246.0751. Anal. Calcd. for $C_{11}H_{13}NO_4$: C, 59.19; H, 5.87; N, 6.27. Found: C, 59.15; H, 6.03; N, 6.24.

Preparation of methyl 2-((dimethylcarbamoyl)oxy)benzoate 1b

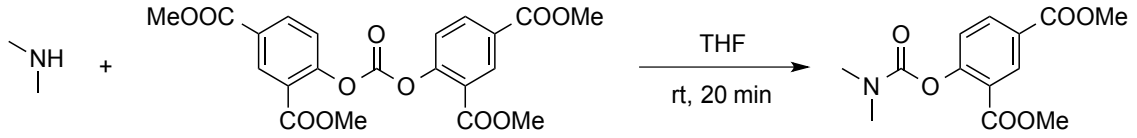


1b

To a solution of dimethyl 2,2'-(carbonylbis(oxy))dibenzoate **SI-2** (1413.7 mg, 4.28 mmol) in THF (5.0 mL), 50%(w/w) aqueous solution of dimethyl amine (411.9 mg, 4.57 mmol) in THF (5.0 mL) was added at room temperature. The whole reaction mixture was stirred for 15 hours at room temperature. The reaction mixture was column-chromatographed on silica-gel (eluent: EtOAc / n-Hexane = 1 / 2) to afford methyl 2-((dimethylcarbamoyl)oxy)benzoate **1b** (870.2 mg, 3.90 mmol, 91%) as a colorless oil. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.961 (1H, dd, *J* = 7.8, 1.6 Hz), 7.506 (1H, td, *J* = 7.8, 1.6 Hz), 7.242 (1H, td, *J* = 7.6, 1.2 Hz), 7.145 (1H, dd, *J* = 8.2,

1.2 Hz), 3.830 (3H, s), 3.115 (3H, s), 2.996 (3H, s). ^{13}C-NMR ($CDCl_3$, 100 MHz) δ (ppm):165.46, 154.92, 151.64, 133.81, 131.71, 125.60, 124.42, 123.90, 52.22, 36.93, 36.73. HRMS (ESI-TOF, $[M+Na]^+$): Calcd. for $C_{11}H_{13}NNaO_4^+$: 246.07368. Found: 246.07369. Anal. Calcd. for $C_{11}H_{13}NO_4$+0.02CH_2Cl_2: C, 58.85; H, 5.84; N, 6.23. Found: C, 58.62; H, 5.79; N, 6.12.

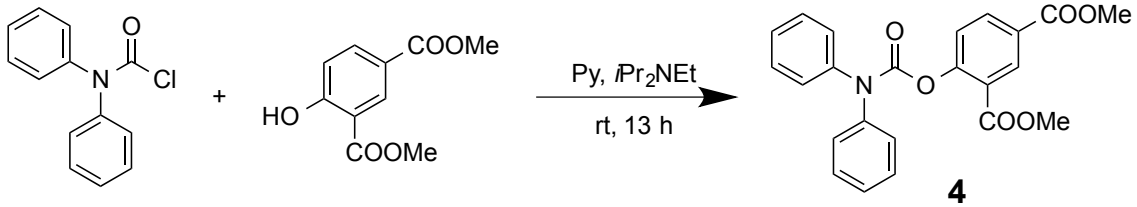
Preparation of dimethyl 4-((dimethylcarbamoyl)oxy)isophthalate 1f



1f

To a solution of tetramethyl 4,4'-(carbonylbis(oxy))diisophthalate **SI-1** (1511.9 mg, 3.39 mmol) in CH_2Cl_2 (5.0 mL), 50%(w/w) aqueous solution of dimethyl amine (307.1 mg, 3.41 mmol) in CH_2Cl_2 (10.0 mL) was added at room temperature. The whole mixture was stirred for 10 minutes at room temperature. The reaction mixture was purified by column-chromatography on silica gel (eluent : EtOAc / n-Hexane = 1 / 1) to afford dimethyl 4-((dimethylcarbamoyl)oxy)isophthalate **1f** (737.1 mg, 2.62 mmol, 77%) as a colorless solid. Mp. 90.6-91.2°C (colorless needles, recrystallized from CH_2Cl_2/n-Hexane). ^{1}H-NMR ($CDCl_3$, 400 MHz) δ (ppm): 8.635 (1H, d, *J* = 2.0 Hz), 8.189 (1H, dd, *J* = 8.6, 2.0 Hz), 7.242 (1H, d, *J* = 8.8 Hz), 3.926 (3H, s), 3.883 (3H, s), 3.148 (3H, s), 3.024 (3H, s). ^{13}C-NMR ($CDCl_3$, 100 MHz) δ (ppm): 166.19, 165.01, 155.41, 154.53, 135.08, 133.67, 127.88, 124.93, 124.36, 52.89, 52.79, 37.33, 37.13. HRMS (ESI-TOF, $[M+Na]^+$): Calcd. for $C_{13}H_{15}NNaO_6^+$: 304.0792. Found: 304.0794. Anal. Calcd. for $C_{13}H_{15}NO_6$: C, 55.51; H, 5.38; N, 4.98. Found: C, 55.38; H, 5.32; N, 5.01.

Preparation of dimethyl 4-((diphenylcarbamoyl)oxy)isophthalate 4

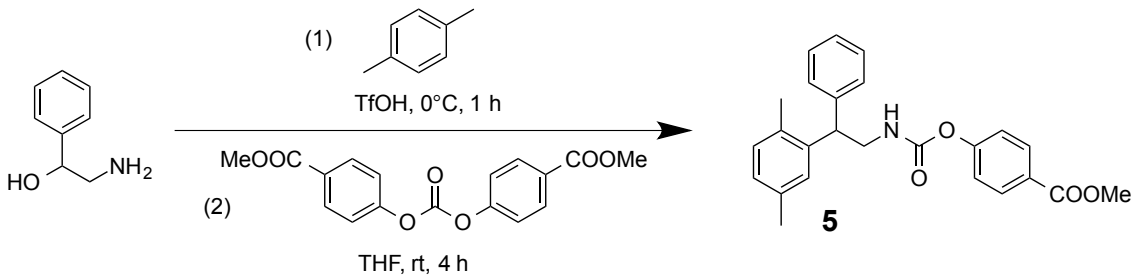


4

To a solution of dimethyl 4-hydroxyisophthalate (698.2 mg, 3.32 mmol) in *i*Pr_2NEt (0.65 mL), diphenylcarbamic chloride (717.8 mg, 3.10 mmol) was added at room temperature. The whole mixture was stirred for 13 hours at room temperature. After the reaction completed, added 2M aqueous solution of HCl (40 mL). then extracted with CH_2Cl_2 (40 mL x 3). The organic phase was washed with brine (40 mL), dried over Na_2SO_4, and the solvent was evaporated under reduced pressure to give a residue, which

was flash column-chromatographed on silica-gel (eluent: EtOAc / n-Hexane = 1 / 2) to afford dimethyl 4-((diphenylcarbamoyl)oxy)isophthalate **4** (1223.8 mg, 3.02 mmol, 97%) as a colorless solid. Mp. 158.9-159.7°C (colorless needles, recrystallized from CH_2Cl_2/n-Hexane). ^{1}H-NMR ($CDCl_3$, 400 MHz) δ (ppm): 8.649 (1H, d, *J* = 2.0 Hz), 8.173 (1H, dd, *J* = 8.4, 2.0 Hz), 7.448-7.352 (8H, m), 7.265-7.197 (3H, m), 3.933 (3H, s), 3.920 (3H, s). ^{13}C-NMR ($CDCl_3$, 100 MHz) δ (ppm): 166.10, 164.86, 154.82, 152.75, 142.75, 135.13, 133.67, 129.60, 128.27, 127.23 (br), 124.67, 124.56, 52.98, 52.92. HRMS (ESI-TOF, $[M+Na]^+$): Calcd. for $C_{23}H_{19}NNaO_6^+$: 428.1105. Found: 428.1105. Anal. Calcd. for $C_{23}H_{19}NO_6$: C, 68.14; H,4.72; N, 3.46. Found: C, 67.79; H, 4.90; N, 3.32.

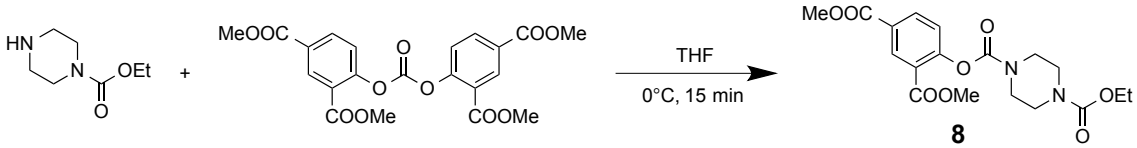
Preparation of methyl 4-(((2-(2,5-dimethylphenyl)-2-phenylethyl)- carbamoyl)oxy) benzoate 5



To a solution of *para*-xylene (5 mL) in TfOH (10 mL), 2-amino-1-phenylethanol (1011.2 mg, 7.37 mmol) was added at 0°C. The whole was warmed up from 0°C to 20°C, and stirred for 2 hours. After the reaction completed, the whole was poured into ice-water and added 2M aqueous solution of NaOH (50 mL). This reaction mixture was extracted with CH_2Cl_2 (30 mL x 4). The organic phase was washed with brine (30 mL), dried over Na_2SO_4, and the solvent was evaporated under reduced pressure to give a yellow crude (1784.3 mg). Then this crude was added to the solution of dimethyl 4,4'-(carbonylbis(oxy))dibenzoate **SI-3** (2109.0 mg, 6.39 mmol) in THF (20 mL) at rt. The whole was stirred for 4 hours at room temperature. After the reaction completed, added 2M aqueous solution of NaOH (40 mL). then extracted with CH_2Cl_2 (30 mL x 4). The organic phase was washed with brine (30 mL), dried over Na_2SO_4, and the solvent was evaporated under reduced pressure to give a residue, which was column-chromatographed on silica-gel (eluent: EtOAc / n-Hexane= 2 / 3) to afford methyl 4-(((2-(2,5-dimethylphenyl)- 2-phenylethyl)carbamoyl)oxy)benzoate **5** (222.0 mg, 4.99 mmol, 68% in two steps) as a colorless amorphous material. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ (ppm): 8.011 (2H, d, *J* = 8.4 Hz), 7.297 (2H, t, *J* = 7.6 Hz), 7.230-7.194 (3H, m), 7.135 (2H, td, *J* = 8.8, 2.0 Hz), 7.080-7.047 (2H, m), 6.990-6.971 (1H, m), 5.190-4.866 (1H, m), 4.419 (1H, t, *J* = 8.0 Hz), 3.878 (5H, m), 2.333 (3H, s), 2.229 (3H,

s.) ^{13}C-NMR ($CDCl_3$, 100 MHz) δ (ppm): 166.92, 155.23, 154.20, 141.77, 139.50, 136.17, 134.34, 131.55, 131.45, 129.23, 128.79, 128.08, 127.54, 127.31, 121.77, 52.60, 47.24, 46.00, 21.78, 19.80. HRMS (ESI-TOF, $[M+Na]^+$): Calcd. for $C_{25}H_{25}NNaO_4^+$: 426.1676. Found: 426.1652. Anal. Calcd. for $C_{25}H_{25}NO_4$+0.2H_2O: C, 73.76; H, 6.29; N, 3.44. Found: C, 73.46; H, 6.02; N, 3.25.

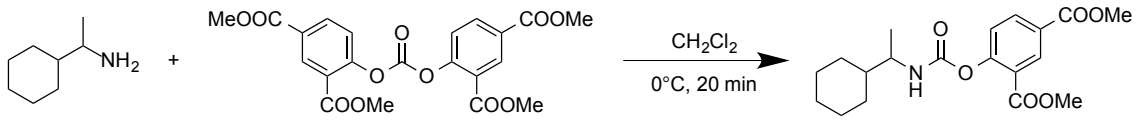
Preparation of 1-(2,4-bis(methoxycarbonyl)phenyl)-4-ethyl-piperazine-1,4-dicarboxylate 8



8

To a solution of tetramethyl 4,4'-(carbonylbis(oxy))diisophthalate **SI-1** (1349.5 mg, 3.02 mmol) in THF (10.0 mL), ethyl piperazine-1-carboxylate (490.1 mg, 3.10 mmol) in THF (5.0 mL) was added at 0°C. The whole mixture was stirred for 15 minutes at 0°C. The reaction mixture was purified by column-chromatography on silica gel (eluent : EtOAc / n-Hexane = 1 / 1) to afford 1-(2,4-bis(methoxycarbonyl)phenyl) 4-ethyl piperazine-1,4-dicarboxylate **8** (1147.7 mg, 2.91 mmol, 96%) as a colorless oil. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ (ppm): 8.603 (1H, d, *J* = 2.4 Hz), 8.160 (1H, dd, *J* = 8.4, 2.4 Hz), 7.203 (1H, d, *J* = 8.4 Hz), 4.138 (2H, q, *J* = 7.2 Hz), 3.888 (3H, s), 3.834 (3H, s), 3.664-3.528 (8H, m), 1.244 (3H, t, *J* = 7.2 Hz). ^{13}C-NMR ($CDCl_3$, 100 MHz) δ (ppm): 166.00, 164.59, 155.88, 155.07, 153.28, 135.11, 133.62, 128.09, 124.77, 124.07, 62.13, 52.84, 52.76, 45.17, 44.40, 43.83, 15.10. HRMS (ESI-TOF, $[M+Na]^+$): Calcd. for $C_{18}H_{22}N_2NaO_8^+$: 417.1268. Found: 417.1277. Anal. Calcd. for $C_{18}H_{22}N_2O_8$+0.6 H_2O: C, 53.36; H, 5.77; N, 6.91. Found: C, 53.11; H, 5.53; N, 6.78.

Preparation of dimethyl 4-(((1-cyclohexylethyl)carbamoyl)oxy)isophthalate 11

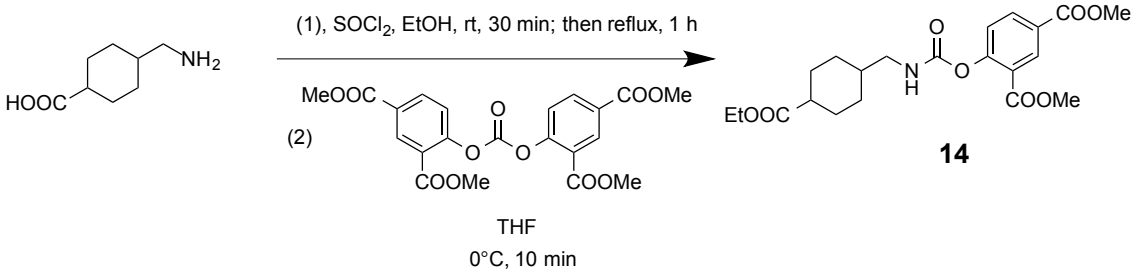


11

To a solution of tetramethyl 4,4'-(carbonylbis(oxy))diisophthalate **SI-1** (2234.9 mg, 5.01 mmol) in CH_2Cl_2 (5.0 mL), 1-cyclohexylethan-1-amine (647.6 mg, 5.09 mmol) in CH_2Cl_2 (5.0 mL) was added at 0°C. The whole mixture was stirred for 20 minutes at 0°C. The reaction mixture was purified by column-chromatography on silica gel (eluent: EtOAc / n-Hexane = 1 / 3) to afford dimethyl 4-(((1-cyclohexylethyl)carbamoyl)- oxy)isophthalate **11** (1787.2 mg, 4.92 mmol, 98%) as a colorless solid. Mp. 105.1-105.9°C (colorless powder, recrystallized from

CH_2Cl_2/n-Hexane). ^{1}H-NMR ($CDCl_3$, 400 MHz) δ (ppm) (presence of two amide conformers): 8.633-8.601 (1H, m), 8.177 (1H, dd, *J* = 8.4, 2.0 Hz), 7.237 (1H, d, *J* = 8.4 Hz), 5.071 (0.91H, d, *J* = 8.8 Hz), 4.707 (0.10H, d, *J* = 8.4 Hz), 3.925 (3H, s), 3.885 (3H, s), 3.647-3.559 (1H, m), 1.854-0.965 (14H, m). ^{13}C-NMR ($CDCl_3$, 100 MHz) δ (ppm): 166.23, 165.28, 154.63, 153.72, 134.99, 133.59, 127.95, 124.91, 124.88, 52.92, 52.90, 52.64, 43.67, 29.51, 29.44, 26.95, 26.72, 18.62. HRMS (ESI-TOF, $[M+Na]^+$): Calcd. for $C_{19}H_{25}NNaO_6^+$: 386.1574. Found: 386.1567. Anal. Calcd. for $C_{19}H_{25}NO_6$: C, 62.80; H, 6.93; N, 3.85. Found: C, 62.46; H, 6.81; N, 3.69.

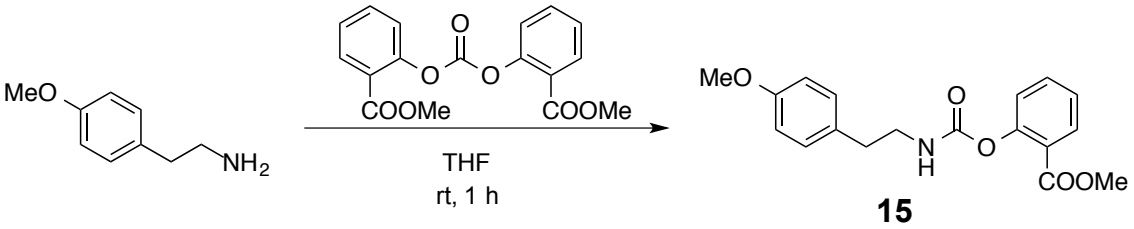
Preparation of dimethyl 4-((((4-(ethoxycarbonyl)cyclohexyl)methyl)carbamoyl)oxy)- isophthalate 14



To a solution of $SOCl_2$ (0.5 mL, 6.9 mmol) in EtOH (20 mL), added 4-(aminomethyl)cyclohexane-1-carboxylic acid (847.2 mg, 5.39 mmol) at 0°C, the whole was stirred for 30 minutes at room temperature, then for 1 hour at reflux. After the reaction completed, poured into ice-water and quenched with 2M aqueous solution of NaOH (50 mL). Then, EtOAc (100 mL) was added and the mixture was washed with 2M aqueous solution of NaOH (50 mL x 2). The organic phase was washed with brine (30 mL), dried over Na_2SO_4, and the solvent was evaporated under reduced pressure to give a crude (947.6 mg). To a solution of tetramethyl 4,4'-(carbonylbis(oxy))diisophthalate **SI-1** (1362.0 mg, 3.05 mmol) in THF (8.0 mL), crude (947.6 mg) in THF (2.0 mL) was added at 0°C. The whole mixture was stirred for 10 minutes at 0°C. The reaction mixture was purified by column-chromatography on silica gel (eluent : EtOAc / n-Hexane = 2 / 3) to afford dimethyl 4-((((4-(ethoxycarbonyl)cyclohexyl)methyl)carbamoyl)oxy)isophthalate **14** (947.6 mg, 2.25 mmol, 42% in two steps) as a colorless solid. Mp. 122.3-123.2°C (colorless needles, recrystallized from CH_2Cl_2/n-Hexane). ^{1}H-NMR ($CDCl_3$, 400 MHz) δ (ppm) (presence of two amide conformers): 8.646-8.607 (1H, m), 8.186 (1H, dd, *J* = 8.6, 2.0 Hz), 7.236 (1H, d, *J* = 8.4 Hz), 5.413 (0.89H, t, *J* = 13.2 Hz), 5.085 (0.11H, brs), 4.121 (2H, q, *J* = 6.8 Hz), 3.930 (3H, s), 3.883 (3H, s), 3.238 (0.24H, t, *J* = 6.4 Hz), 3.129 (1.84H, t, *J* = 6.4 Hz), 2.238 (1H, tt, *J* = 12.1, 3.6 Hz), 2.051-2.017 (2H, m), 1.929-1.850 (2H, m), 1.605-1.390 (3H, m), 1.250 (3H, t, *J* = 7.2 Hz), 1.015 (2H, qd, *J* =

13.2, 3.2 Hz). ^{13}C-NMR ($CDCl_3$, 100 MHz) δ (ppm): 176.33, 166.10, 165.05, 154.57, 154.35, 134.99, 133.49, 127.97, 124.78, 124.65, 60.69, 52.87, 52.81, 47.81, 43.72, 38.00, 30.06, 28.88, 14.70. HRMS (ESI-TOF, $[M+Na]^+$): Calcd. for $C_{21}H_{27}NNaO_8^+$: 444.16129. Found: 444.1619. Anal. Calcd. for $C_{21}H_{27}NO_8$: C, 59.85; H, 6.46; N, 3.32. Found: C, 59.73; H, 6.35; N, 3.29.

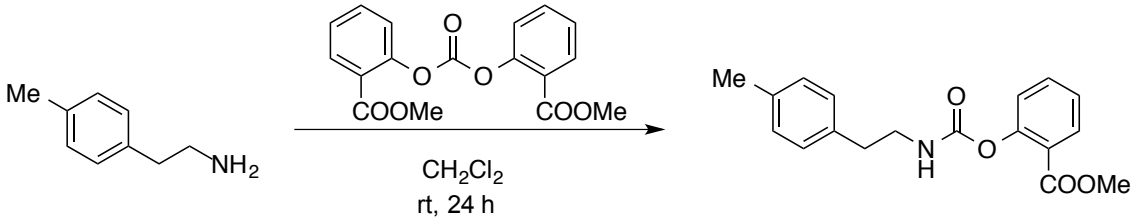
Preparation of methyl 2-(((4-methoxyphenethyl)carbamoyl)oxy)benzoate 15



15

To a solution of dimethyl 2,2'-carbonyldibenzoate **SI-2** (1660.9 mg, 5.03 mmol) in THF (10.0 mL), a solution of 2-(4-methoxyphenyl)ethan-1-amine (776.1 mg, 5.13 mmol) in THF (5.0 mL) was added at room temperature. The whole was stirred for 1 hour at room temperature. The reaction mixture was directly purified by column-chromatography on silica gel (eluent: EtOAc / n-Hexane = 1 / 1) to afford methyl 2-(((4-methoxyphenethyl)- carbamoyl)oxy)benzoate **15** (1630.2 mg, 4.95 mmol, 90%) as a colorless solid. Mp. 61.2-61.5°C (colorless cube, recrystallized from CH_2Cl_2/n-Hexane). ^{1}H-NMR ($CDCl_3$, 400 MHz) δ (ppm) (presence of two amide conformers): 7.954 (1H, dd, *J* = 8.0, 1.2 Hz), 7.519 (1H, td, *J* = 7.8, 1.6 Hz), 7.268 (1H, t, *J* = 7.2 Hz), 7.192-7.128 (3H, m), 5.196 (0.93H, brs), 4.828 (0.14H, brs), 3.845 (3H, s), 3.792 (3H, s), 3.495 (2H, q, *J* = 6.8 Hz), 2.839 (3H, t, *J* = 7.2 Hz) ^{13}C-NMR ($CDCl_3$, 100 MHz) δ (ppm): 165.89, 158.94, 154.94, 151.21, 134.06, 132.01, 131.22, 130.35, 126.11, 124.67, 124.55, 114.70, 55.84, 52.64, 43.32, 35.68. HRMS (ESI-TOF, $[M+Na]^+$): Calcd. for $C_{19}H_{18}NNaO_5^+$: 352.1152. Found: 352.1165. Anal. Calcd. for $C_{19}H_{18}NO_5$: C, 65.64; H, 5.82; N, 4.25. Found: C, 65.32; H, 5.79; N, 4.11.

Preparation of methyl 2-(((4-methylphenethyl)carbamoyl)oxy)benzoate 19

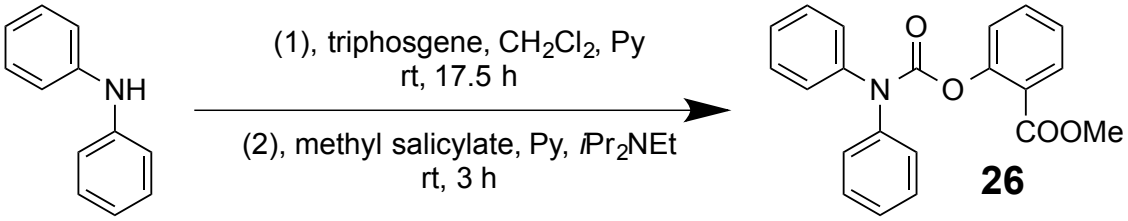


19

To a solution of dimethyl 2,2'-carbonyldibenzoate **SI-2** (2520.0 mg, 7.63 mmol) in CH_2Cl_2 (15.0 mL), a solution of 2-(*para*-tolyl)ethan-1-amine (1061.9 mg, 7.85 mmol) in CH_2Cl_2 (5.0 mL) was added at room temperature. The whole was stirred for 24 hours at

room temperature. The reaction mixture was directly purified by column-chromatography on silica gel (eluent: EtOAc / n-Hexane = 1 / 2) to afford methyl 2-(((4-methylphenethyl)carbamoyl)oxy)benzoate **19** (2318.8 mg, 7.40 mmol, 97%) as a colorless oil. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ (ppm) (presence of two amide conformers): 7.944 (1H, dd, *J* = 7.8, 1.2 Hz), 7.496 (1H, td, *J* = 8.0, 1.6 Hz), 7.246 (1H, t, *J* = 7.6 Hz), 7.136-7.096 (5H, m), 5.395 (0.88H, t, *J* = 5.6 Hz), 5.102 (0.17H, brs), 3.816 (3H, s), 3.474 (2H, q, *J* = 6.8 Hz), 2.827 (2H, t, *J* = 7.2 Hz), 2.315 (3H, s). ^{13}C-NMR ($CDCl_3$, 100 MHz) δ (ppm): 165.82, 154.87, 151.05, 136.43, 136.00, 133.96, 131.86, 129.74, 129.13, 125.96, 124.55, 124.42, 52.51, 43.09, 35.94, 21.43. HRMS (ESI-TOF, $[M+Na]^+$): Calcd. for $C_{18}H_{19}NNaO_4^+$: 336.1206. Found: 336.1202. Anal. Calcd. for $C_{18}H_{19}NO_4$+0.05 CH_2Cl_2: C, 68.26; H, 6.06; N, 4.41. Found: C, 68.13; H, 6.08; N, 4.43.

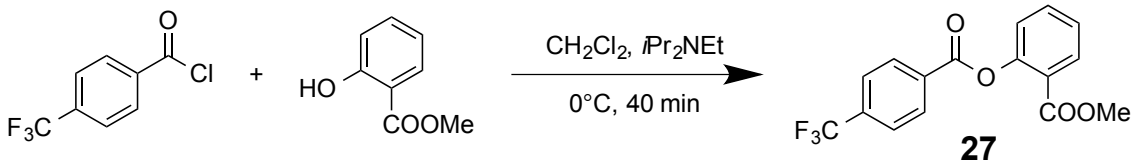
Preparation of methyl 2-((diphenylcarbamoyl)oxy)benzoate 26



To a solution of triphosgene (300.3 mg, 1.01 mmol) in CH_2Cl_2 (3.0 mL) was added a solution of diphenylamine (364.4 mg, 2.15 mmol) in CH_2Cl_2 (4.0 mL) and dry pyridine (1.0 mL) at 0°C. The resulting mixture was stirred at 0°C for 15 min and at room temperature for an additional 17.5 hours. The reaction was quenched with 2M aqueous solution of HCl (20 mL). The reaction mixture was extracted with CH_2Cl_2 (20 mL x 5). The organic phase was washed with brine (20 mL), dried over Na_2SO_4, and the solvent was evaporated to give the crude (498.9 mg). To a solution of methyl 2-hydroxybenzoate (518.3 mg, 3.41 mmol), pyridine (3.0 mL) and *i*Pr_2NEt (0.5 mL, 2.87 mmol), a solution of the above crude (498.9 mg) in CH_2Cl_2 (4.0 mL) was added at room temperature. The whole was stirred for 3 hours at room temperature. The crude reaction mixture was purified by column-chromatography on silica gel (eluent: EtOAc / n-Hexane = 1 / 2) to afford methyl 2-((diphenylcarbamoyl)oxy)benzoate **26** (636.2 mg, 1.83 mmol, 85%) as a colorless solid. Mp. 82.6-84.9°C (colorless needles, recrystallized from CH_2Cl_2/n-Hexane). ^{1}H-NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.976 (1H, d, *J* = 7.6 Hz), 7.519-7.340 (9H, m), 7.277-7.118 (4H, m), 3.907 (3H, s). ^{13}C-NMR ($CDCl_3$, 100 MHz) δ (ppm): 165.51, 153.24, 151.24, 142.89, 134.05, 131.97, 129.43, 127.51, 126.92, 126.16, 124.22, 124.19, 52.64. HRMS (ESI-TOF, $[M+Na]^+$): Calcd. for $C_{21}H_{17}NNaO_4^+$: 370.10498. Found: 370.10432. Anal. Calcd. for $C_{21}H_{17}NO_4$: C, 72.61; H, 4.93; N, 4.03.

Found: C, 72.77; H, 4.82; N, 4.12.

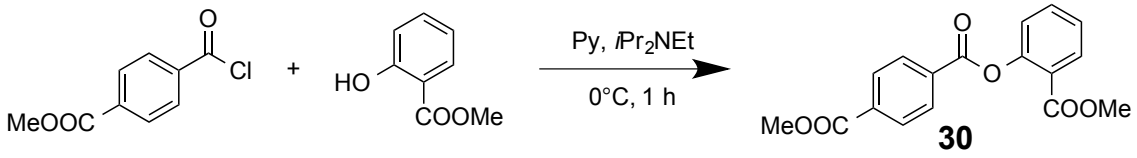
Preparation of methyl 2-((4-(trifluoromethyl)benzoyl)oxy)benzoate 27



27

To a solution of methyl salicyalate (15657.5 mg, 10.3 mmol) in CH_2Cl_2 (20 mL) and *i*Pr_2NEt (9.0 mL), 4-(trifluoromethyl)benzoyl chloride (1823.9 mg, 8.74 mmol) in CH_2Cl_2 (10 mL) was added at 0°C. The whole mixture was stirred for 40 minutes at 0°C. The reaction mixture was purified by column-chromatography on silica gel (eluent : EtOAc / n-Hexane = 1 / 4) to afford methyl 2-((4-(trifluoromethyl)benzoyl)oxy)benzoate **27** (1142.8 mg, 3.52 mmol, 40%) as a colorless solid. Mp. 68.7-69.2°C (colorless plates, recrystallized from CH_2Cl_2/n-Hexane). ^{1}H-NMR ($CDCl_3$, 400 MHz) δ (ppm): 8.339 (2H, d, *J* = 8.0 Hz), 8.091 (1H, dd, *J* = 7.8, 1.6 Hz), 7.788 (2H, d, *J* = 8.0 Hz), 7.627 (1H, td, *J* = 7.6, 2.0 Hz), 7.383 (1H, td, *J* = 7.8, 1.2 Hz), 7.252-7.230 (1H, m), 3.750 (3H, s). ^{13}C-NMR ($CDCl_3$, 100 MHz) δ (ppm): 165.33, 164.83, 151.14, 135.55 (q, *J* = 32 Hz), 134.60, 133.39, 132.60, 131.25, 126.98, 126.22 (q, *J* = 3 Hz), 124.39, 124.18 (q, *J* = 271 Hz), 123.73, 52.81. HRMS (ESI-TOF, $[M+Na]^+$): Calcd. for $C_{16}H_{11}F_3NaO_4^+$: 347.0507. Found: 347.0496. Anal. Calcd. for $C_{16}H_{11}F_3O_4$: C, 59.27; H, 3.42. Found: C, 59.08; H, 3.58.

Preparation of 2-(methoxycarbonyl)phenyl methyl terephthalate 30

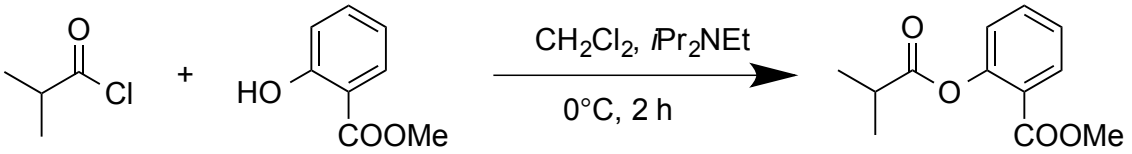


30

To a solution of methyl salicyalate (6.0 mL, 46.9 mmol) in *i*Pr_2NEt (7.0 mL), methyl 4-(chlorocarbonyl)benzoate (8010.1 mg, 40.3 mmol) was added at 20°C. The whole mixture was stirred for 1 hour at 20°C. After the reaction completed, added 2M aqueous solution of HCl (60 mL). then extracted with CH_2Cl_2 (50 mL x 4). The organic phase was washed with brine (40 mL), dried over Na_2SO_4, and the solvent was evaporated under reduced pressure to give a residue, which was column-chromatographed on silica-gel (eluent: EtOAc/n-Hexane = 1 / 2) to afford 2-(methoxycarbonyl)phenyl methyl terephthalate **30** (10901.6 mg, 34.7 mmol, 86%) as a colorless solid. Mp. 117.5-118.4°C (colorless cubes, recrystallized from CH_2Cl_2/n-Hexane). ^{1}H-NMR ($CDCl_3$, 400 MHz) δ (ppm): 8.287 (2H, dt, *J* = 8.4, 1.2 Hz), 8.180 (2H, dt, *J* = 8.4, 1.6

Hz), 8.084 (1H, dd, *J* = 7.8, 2.0 Hz), 7.617 (1H, td, *J* = 7.7, 2.0 Hz), 7.368 (1H, td, *J* = 7.6, 1.2 Hz), 7.245 (1H, dd, *J* = 8.2, 1.2 Hz), 3.966 (3H, s), 3.735 (3H, s). ^{13}C-NMR ($CDCl_3$, 100 MHz) δ (ppm): 166.74, 165.37, 165.16, 151.14, 134.97, 134.50, 133.85, 132.53, 130.76, 130.27, 126.84, 124.38, 123.79, 53.03, 52.74. HRMS (ESI-TOF, $[M+Na]^+$): Calcd. for $C_{17}H_{14}NaO_6^+$: 337.0688. Found: 337.0670. Anal. Calcd. for $C_{17}H_{14}O_6$: C, 64.97; H, 4.49. Found: C, 64.84; H, 4.71.

Preparation of methyl 2-(isobutyryloxy)benzoate 33



33

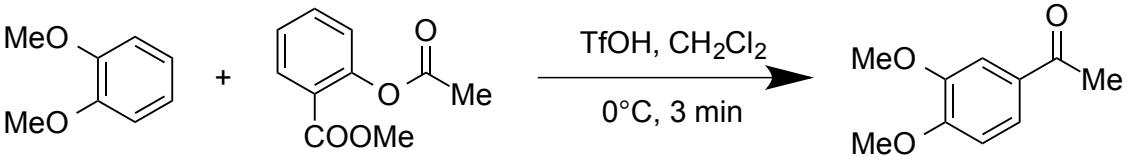
To a solution of methyl salicyalate (2399.7 mg, 15.8 mmol) in *i*Pr_2NEt (3.0 mL), isobutyryl chloride (1178.8 mg, 11.1 mmol) in CH_2Cl_2 (4.0 mL) was added at 0°C. The whole mixture was stirred for 2 hours at 0°C. The reaction mixture was purified by column-chromatography on silica gel (eluent : EtOAc / n-Hexane = 1 / 4) to afford methyl 2-(isobutyryloxy)benzoate **33** (2261.8 mg, 9.57 mmol, 87%) as a colorless oil. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ (ppm): 8.011 (1H, s), 7.547 (1H, s), 7.300 (1H, s), 7.091 (1H, s), 3.865 (3H, s), 2.894 (1H, d, *J* = 5.6 Hz), 1.371 (6H, s). ^{13}C-NMR ($CDCl_3$, 100 MHz) δ (ppm): 175.80, 165.47, 151.10, 134.07, 132.10, 126.24, 124.15, 124.01, 52.48, 34.56, 19.22. HRMS (ESI-TOF, $[M+Na]^+$): Calcd. for $C_{12}H_{14}NaO_4^+$: 245.0790. Found: 245.0788. Anal. Calcd. for $C_{12}H_{14}O_4$: C, 64.85; H, 6.35. Found: C, 64.65; H, 6.38.

Multiple Successive Electrophile Substitution Reactions in One Pot

General procedure for the acid-catalyzed amidation and acylation reactions are shown in Figure 1 and 2 of the main text.

(even though the reaction temperature is different, other procedures are same)

Acylation affording aromatic ketone 3c

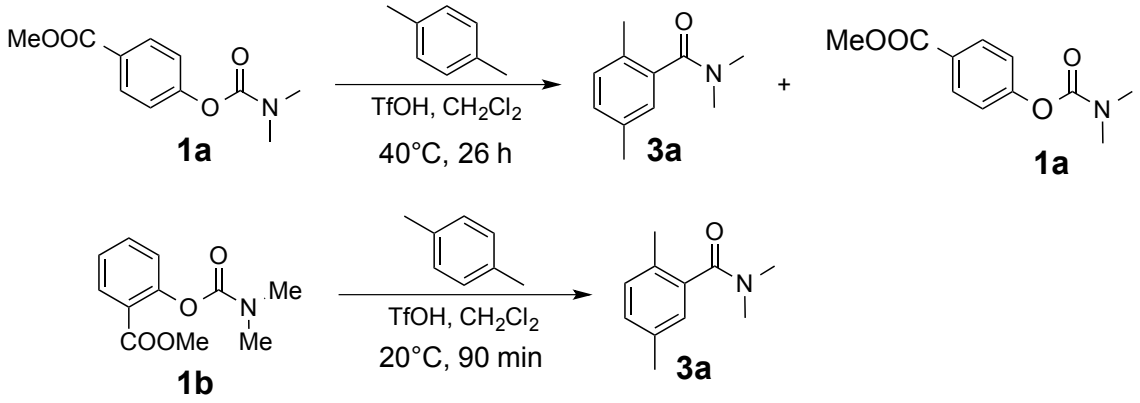


3c

To a solution of 1,2-dimethoxy benzene (141.2 mg, 1.02 mmol) in TfOH (1.0 mL), methyl 2-acetoxybenzoate (196.7 mg, 1.01 mmol) was added at 0°C. The whole was stirred for 3 minutes at 0°C. After the reaction completed, the whole was poured into

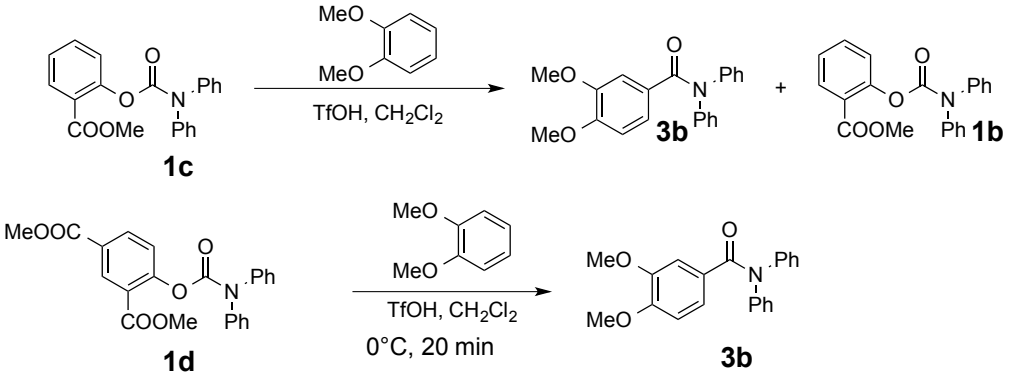
ice-water. This reaction mixture was extracted with CH_2Cl_2 (30 mL x 4). The organic phase was washed with brine (40 mL), dried over Na_2SO_4, and the solvent was evaporated under reduced pressure to give a residue, which was column-chromatographed on silica-gel (eluent: EtOAc / n-Hexane = 1 / 1) to afford 1-(3,4-dimethoxyphenyl)ethanone **3c** (149.8 mg, 0.83 mmol, 82%) as a colorless oil.
^{1}H-NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.567 (1H, dd, *J* = 8.4, 2.0 Hz), 7.519 (1H, d, *J* = 2.0 Hz), 6.884 (1H, d, *J* = 8.4 Hz), 3.938 (3H, s), 3.927 (3H, s), 2.557 (3H, s). ^{13}C-NMR ($CDCl_3$, 100 MHz) δ (ppm): 197.07, 153.71, 149.40, 130.89, 123.65, 110.52, 110.41, 56.43, 56.34, 26.54. HRMS (ESI-TOF, $[M+Na]^+$): Calcd. for $C_{10}H_{12}NaO_3^+$: 203.0679. Found: 203.0654. Anal. Calcd. for $C_{10}H_{12}O_3$: C, 66.65; H, 6.71. Found: C, 66.50; H, 6.61.

Aromatic Amidation to give amide 3a



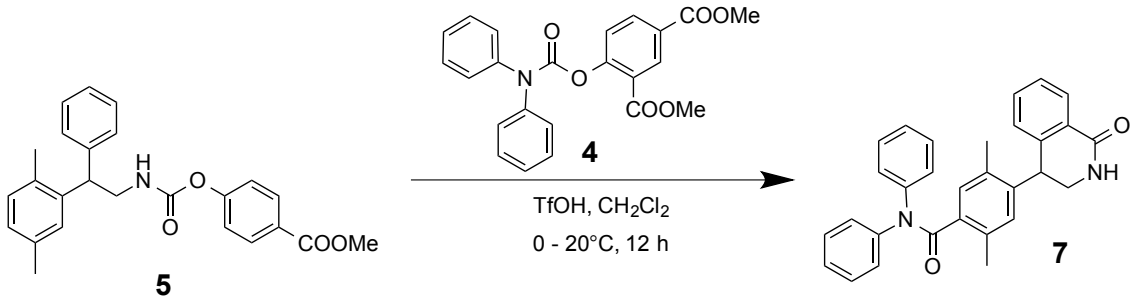
3a: colorless oil. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.087-7.039 (2H, m), 6.973 (1H, s), 3.115 (3H, s), 2.822 (3H, s), 2.297 (3H, s), 2.225 (3H, s). ^{13}C-NMR ($CDCl_3$, 100 MHz) δ (ppm): 172.09, 137.04, 135.87, 131.05, 130.57, 129.83, 126.68, 38.73, 34.87, 21.26, 18.77. HRMS (ESI-TOF, $[M+Na]^+$): Calcd. for $C_{11}H_{15}NNaO^+$: 200.10458. Found: 200.10426. Anal. Calcd. for $C_{11}H_{15}NO+0.23H_2O$: C, 72.84; H, 8.59; N, 7.72. Found: C, 72.59; H, 8.21; N, 7.63.

Aromatic Amidation to give amide 3b



3b: Mp. 159.2-160.0°C (colorless needles, recrystallized from CH_2Cl_2/n-Hexane). ^{1}H-NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.286 (4H, t, *J* = 8.0 Hz), 7.188-7.104 (7H, m), 6.993 (1H, d, *J* = 2.0 Hz), 6.675 (1H, d, *J* = 8.0 Hz), 3.820 (3H, s), 3.651 (3H, s). ^{13}C-NMR ($CDCl_3$, 100 MHz) δ (ppm): 170.52, 151.17, 148.43, 144.86, 129.58, 128.37, 127.87, 126.64, 123.91, 113.12, 110.44, 56.28, 56.17. HRMS (ESI-TOF, $[M+Na]^+$): Calcd. for $C_{21}H_{19}NNaO_3^+$: 356.12571. Found: 356.12513. Anal. Calcd. for $C_{21}H_{19}NO_3$: C 75.66; H, 5.74; N, 4.20. Found: C, 75.49; H, 5.97; N, 4.17.

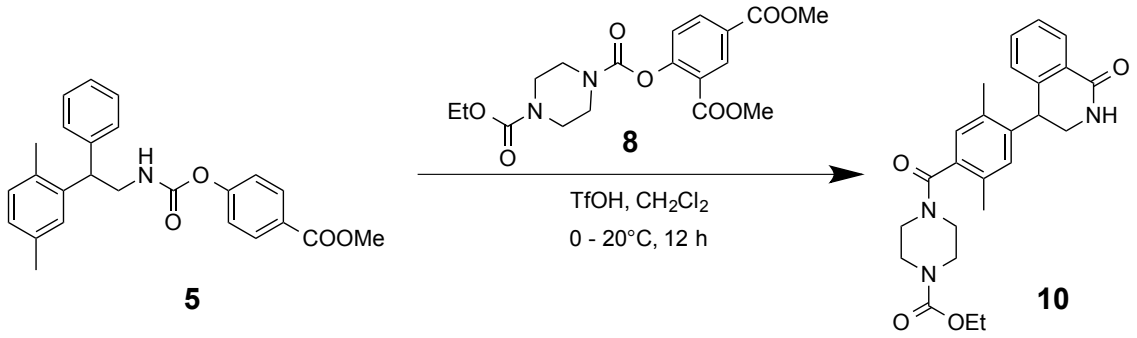
Dual amidation in one pot to give 7 (Table 1, Entry 1)



To TfOH (2.0 mL), methyl 4-(((2-(2,5-dimethylphenyl)-2-phenylethyl)carbamoyl)oxy)benzoate **5** (222.5 mg, 0.50 mmol) in CH_2Cl_2 (0.5 mL) was added at 0°C. Then, dimethyl 4-((diphenylcarbamoyl)oxy)isophthalate **4** (202.9 mg, 0.50 mmol) in CH_2Cl_2 (1.0 mL) was added at 0°C. The whole was warmed up from 0°C to 20°C, and stirred for 12 hours. After the reaction completed, the whole was poured into ice-water. Added 2M aqueous solution of NaOH (50 mL), and this reaction mixture was extracted with CH_2Cl_2 (40 mL x 3). The organic phase was washed with brine (40 mL), dried over Na_2SO_4, and the solvent was evaporated under reduced pressure to give a residue, which was column-chromatographed on silica-gel (eluent: Acetone / n-Hexane = 4 / 3) to afford 2,5-dimethyl-4-(1-oxo-1,2,3,4-tetrahydroisoquinolin-4-yl)-*N*,*N*-diphenyl-benzamide **7** (191.7 mg, 0.43 mmol, 86%) as a colorless solid. Mp. 240.7-241.3°C (colorless plates, recrystallized from CH_2Cl_2/n-Hexane). ^{1}H-NMR ($CDCl_3$, 400 MHz) δ (ppm): 8.133 (1H, dd, *J* = 9.2, 3.6 Hz), 7.394-6.969 (16H, m), 6.831-6.796 (2H, m), 6.760 (1H, s), 5.617 (1H, t, *J* = 6.0 Hz), 4.550 (1H, t, *J* = 7.2 Hz), 3.634 (2H, dd, *J* = 7.8, 2.8 Hz), 3.485 (2H, q, *J* = 6.4 Hz), 2.749 (2H, t, *J* = 6.8 Hz), 2.413 (3H, s), 2.342 (3H, s), 2.220 (3H, s). ^{13}C-NMR ($CDCl_3$, 100 MHz) δ (ppm): 171.33, 166.81, 143.51, 141.94, 139.49, 136.06, 133.96, 133.79, 132.91, 130.88, 130.66, 129.63, 129.45, 128.58, 127.89, 127.74, 127.49, 127.03, 46.13, 40.50, 19.81, 19.58. HRMS (ESI-TOF, $[M+Na]^+$): Calcd. for $C_{30}H_{26}N_2NaO_2^+$: 469.1886. Found: 469.1876. Anal. Calcd. for $C_{30}H_{26}N_2O_2$+0.2 H_2O:

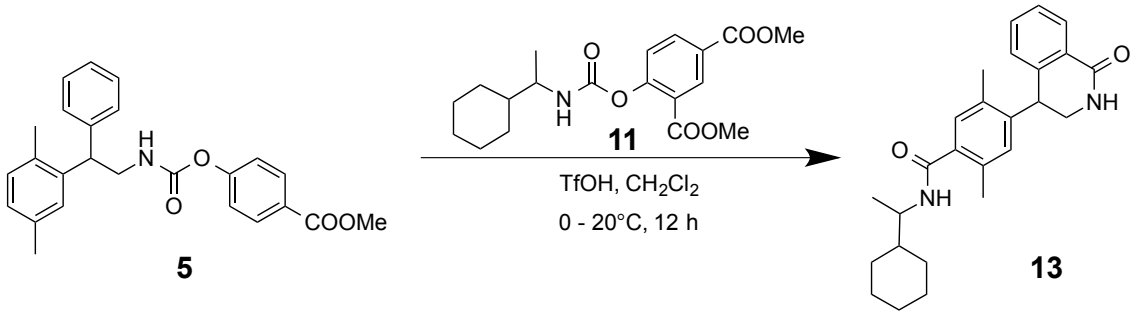
C, 80.05; H, 5.91; N, 6.22. Found: C, 80.13; H, 6.17; N, 6.07.

Dual amidation in one pot to give 10 (Table 1, Entry 2)



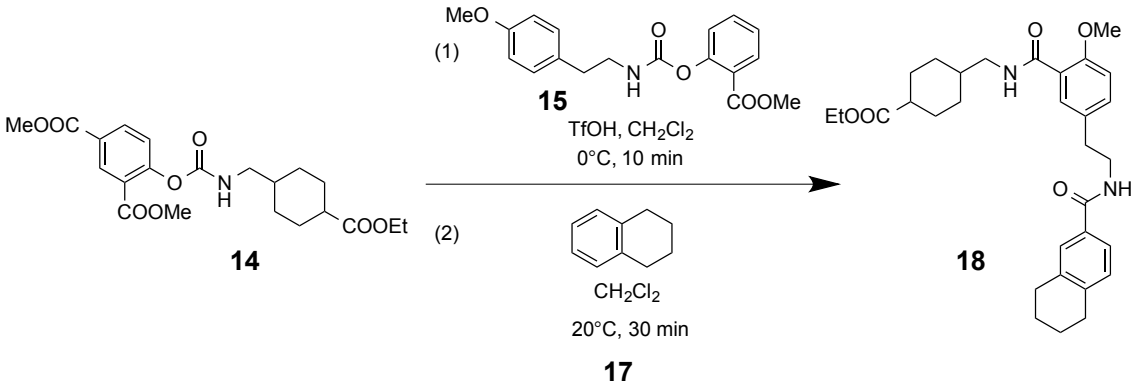
To TfOH (2.0 mL), methyl 4-(((2-(2,5-dimethylphenyl)-2-phenylethyl)carbamoyl)oxy)benzoate **5** (222.7 mg, 0.50 mmol) in CH_2Cl_2 (0.5 mL) was added at 0°C. Then, 1-(2,4-bis(methoxycarbonyl)phenyl) 4-ethyl piperazine-1,4-dicarboxylate **8** (203.7 mg, 0.52 mmol) in CH_2Cl_2 (0.5 mL) was added at 0°C. The whole was warmed up from 0°C to 20°C, and stirred for 12 hours. After the reaction completed, the whole was poured into ice-water. Added 2M aqueous solution of NaOH, (40 mL), and this reaction mixture was extracted with CH_2Cl_2 (40 mL x 3). The organic phase was washed with brine (40 mL), dried over Na_2SO_4, and the solvent was evaporated under reduced pressure to give a residue, which was column-chromatographed on silica-gel (eluent: EtOAc / n-Hexane = 2 / 1) to afford ethyl 4-(2,5-dimethyl-4-(1-oxo-1,2,3,4-tetrahydroisoquinolin-4-yl)benzoyl)piperazine-1-carb oxylate **10** (78.2 mg, 0.18 mmol, 36%) as a colorless solid. Mp. 195.9-196.6°C (colorless plates, recrystallized from CH_2Cl_2/n-Hexane). ^{1}H-NMR ($CDCl_3$, 400 MHz) δ (ppm): 8.080 (1H, s), 7.342 (2H, s), 6.979 (1H, s), 6.837-6.564 (3H, m), 4.514-4.480 (1H, m), 4.068 (2H, q, J = 6.8 Hz), 3.755-3.195 (10H, m), 2.301 (3H, s), 2.080 (3H, s), 1.211-1.179 (3H, m). ^{13}C-NMR ($CDCl_3$, 100 MHz) δ (ppm): 170.07, 166.42, 155.37, 141.13, 139.45, 134.71, 134.15, 132.69, 132.03, 130.99, 130.54, 129.14, 128.11, 127.47, 61.79, 46.61, 45.80, 44.13, 43.63, 41.35, 39.94, 19.29, 18.70, 14.62. HRMS (ESI-TOF, $[M+Na]^+$): Calcd. for $C_{25}H_{29}N_3NaO_4^+$: 458.2050. Found: 458.2030. Anal. Calcd. for $C_{25}H_{29}N_3O$+0.6 C_6H_{12}+1.1 CH_2Cl_2: C, 61.44; H, 6.87; N, 7.24. Found: C, 61.54; H, 6.57; N, 7.32.

Dual amidation in one pot to give 13 (Table 1, Entry 3)



To TfOH (2.0 mL), methyl 4-(((2-(2,5-dimethylphenyl)-2-phenylethyl)carbamoyl)oxy)benzoate **5** (223.4 mg, 0.50 mmol) in CH_2Cl_2 (2.0 mL) was added at 0°C. Then, dimethyl 4-(((1-cyclohexylethyl)carbamoyl)oxy)isophthalate **11** (182.6 mg, 0.50 mmol) was added at 0°C. The whole was warmed up from 0°C to 20°C, and stirred for 12 hours. After the reaction completed, the whole was poured into ice-water. Added 2M aqueous solution of NaOH (50 mL), and this reaction mixture was extracted with CH_2Cl_2 (50 mL x 3). The organic phase was washed with brine (40 mL), dried over Na_2SO_4, and the solvent was evaporated under reduced pressure to give a residue, which was column-chromatographed on silica-gel (eluent: EtOAc / n-Hexane = 4 / 1) to afford *N*-(1-cyclohexylethyl)-2,5-dimethyl-4-(1-oxo-1,2,3,4-tetrahydroisoquinolin-4-yl)benzamide **13** (110.5 mg, 0.27 mmol, 55%) as a colorless solid. Mp. 236.2-236.5°C (colorless plates, recrystallized from CH_2Cl_2/n-Hexane). ^{1}H-NMR ($CDCl_3$, 400 MHz) δ (ppm): 8.169-8.146 (1H, m), 7.431-7.380 (2H, m), 7.244 (1H, s), 6.968 (1H, brs), 6.853-6.798 (2H, m), 5.641 (1H, d, *J* = 8.8 Hz), 4.590 (1H, t, *J* = 7.2 Hz), 4.136-4.046 (1H, m), 3.725-3.678 (2H, m), 2.390 (3H, s), 2.312 (3H, s), 1.855-0.934 (14H, m). ^{13}C-NMR ($CDCl_3$, 100 MHz) δ (ppm): 169.70, 166.84, 141.77, 140.31, 136.70, 134.34, 133.97, 133.05, 131.40, 129.68, 129.51, 128.65, 127.89, 127.80, 50.26, 46.33, 43.66, 40.55, 29.70, 29.62, 26.91, 26.69, 19.94, 19.72, 18.63. HRMS (ESI-TOF, $[M+Na]^+$): Calcd. for $C_{26}H_{32}N_2NaO_2^+$: 427.2361. Found: 427.2340. Anal. Calcd. for $C_{26}H_{32}N_2O_2$+0.8 H_2O: C, 74.54; H, 8.08; N, 6.69. Found: C, 74.31; H, 7.97; N, 6.38.

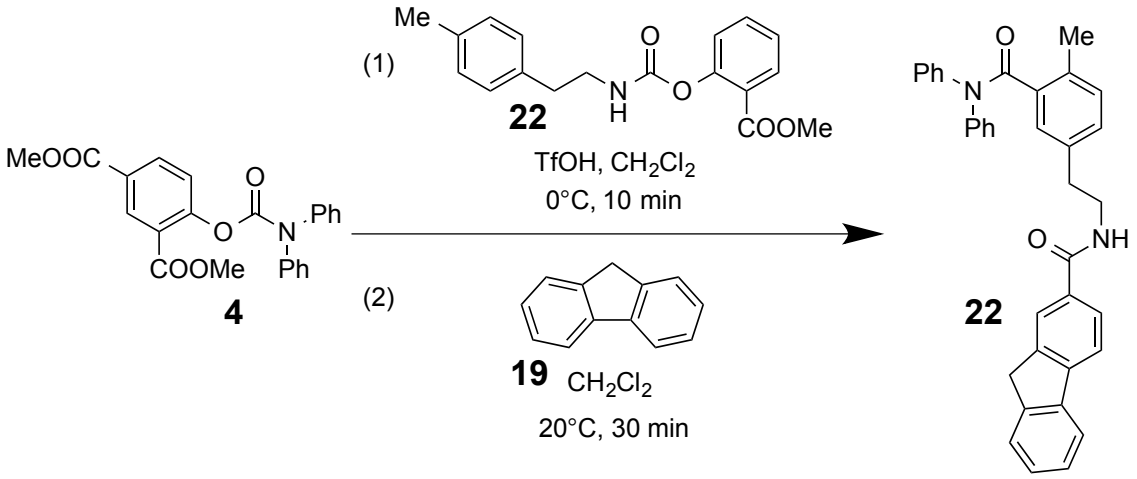
Dual amidation in one pot to give 18 (Table 1, Entry 4)



To TfOH (2.0 mL), methyl 2-(((4-methoxyphenethyl)carbamoyl)oxy)benzoate **15** (170.5 mg, 0.52 mmol) was added at 0°C. Then, dimethyl 4-((((4-(ethoxycarbonyl)cyclohexyl)methyl)carbamoyl)oxy)isophthalate **14** (210.7 mg, 0.50 mmol) in CH_2Cl_2 (1.0 mL) was added at 0°C. The whole was stirred for 15 minutes. Then, 1,2,3,4-tetrahydronaphthalene **17** (133.1 mg, 1.01 mmol) in CH_2Cl_2 (1.0 mL) was added at 0°C. The whole was warmed up from 0°C to 20°C, and stirred for 30 minutes. After the reaction completed, the whole was poured into ice-water. This reaction mixture was extracted with CH_2Cl_2 (40 mL x 3). The organic phase was washed with brine (40 mL), dried over Na_2SO_4, and the solvent was evaporated under reduced pressure to give a residue, which was column-chromatographed on silica-gel (eluent: EtOAc / n-Hexane = 2 / 1) to afford ethyl 4-((2-methoxy-5-(2-(5,6,7,8-tetrahydronaphthalene-2-carboxamido)ethyl)benzamido)methyl)cyclohexane-1-carboxylate **18** (175.2 mg, 0.34 mmol, 67%) as a yellow solid. Mp. 123.9-124.3°C (yellow plates, recrystallized from CH_2Cl_2/n-Hexane). ^{1}H-NMR ($CDCl_3$, 400 MHz) δ (ppm) (presence of two amide conformers): 8.068-8.055 (1H, m), 7.935 (1H, t, *J* = 6.0 Hz), 7.447 (0.66H, s), 7.407 (0.68H, dd, *J* = 8.0, 1.6 Hz), 7.358-7.285 (1H, m), 7.061-7.029 (1.65H, m), 6.925 (1H, t, *J* = 8.0 Hz), 6.462 (0.64H, t, *J* = 5.6 Hz), 5.984 (0.30H, t, *J* = 6.0 Hz), 4.111 (2H, q, *J* = 7.2 Hz), 3.950-3.943 (3H, m), 3.673 (2H, quintet, *J* = 6.4 Hz), 3.316 (2H, t, *J* = 6.0 Hz), 2.923-2.888 (2H, m), 2.756-2.743 (4H, m), 2.228 (1H, tt, *J* = 12.3, 3.6 Hz), 2.011 (2H, dd, *J* = 13.4, 2.8 Hz), 1.878 (2H, dd, *J* = 13.0, 2.4 Hz), 1.810-1.720 (4H, m), 1.626-1.534 (1H, m), 1.431 (2H, qd, *J* = 13.2, 3.2 Hz), 1.245 (3H, t, *J* = 7.2 Hz), 1.041 (2H, qd, *J* = 13.0, 3.2 Hz). ^{13}C-NMR ($CDCl_3$, 100 MHz) δ (ppm): 176.41, 171.00, 168.23, 165.77, 165.70, 156.63, 156.57, 141.40, 138.53, 137.85, 137.36, 135.22, 133.49, 133.45, 132.86, 132.74, 132.43, 132.24, 132.18, 131.16, 129.66, 128.33, 125.68, 124.36, 124.26, 122.05, 122.02, 112.23, 60.67, 56.65, 56.63, 46.09, 43.83, 41.48, 41.07, 37.95, 35.22, 35.19, 30.41, 30.29, 29.87, 29.80, 29.01, 27.15,

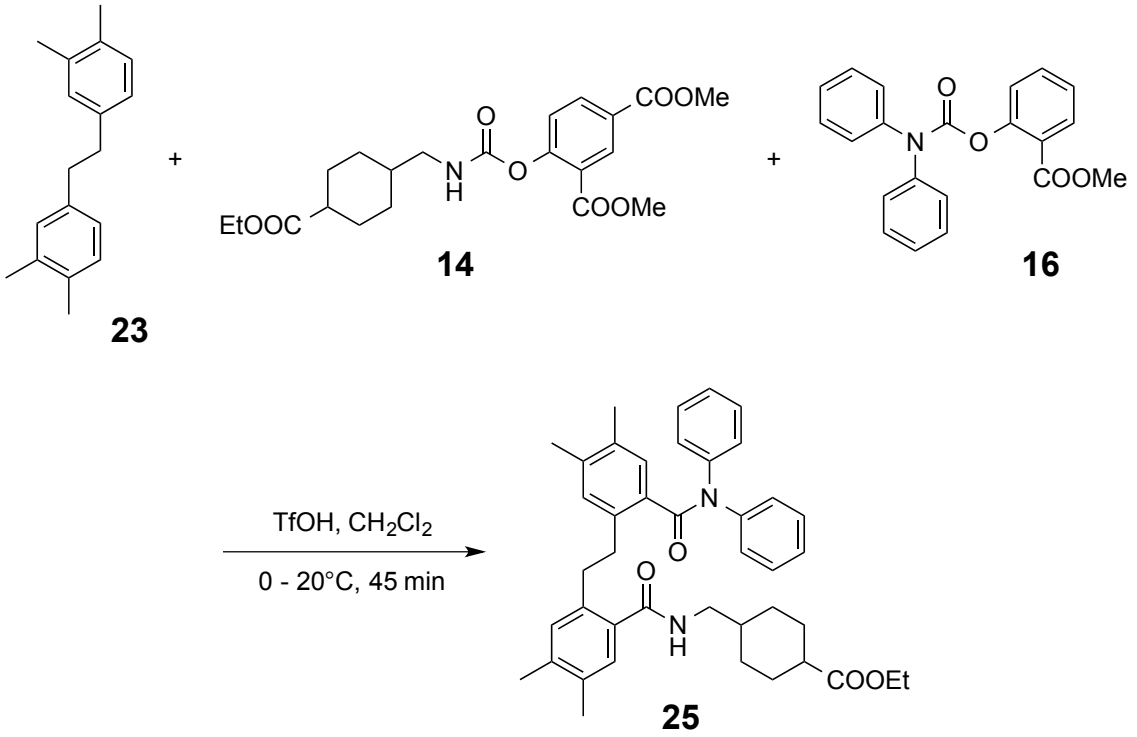
23.47, 23.41, 23.14, 14.72. HRMS (ESI-TOF, $[M+Na]^+$): Calcd. for $C_{31}H_{40}N_2NaO_5^+$: 543.2829. Found: 543.2829. Anal. Calcd. for $C_{31}H_{40}N_2O_5$+0.1 H_2O: C, 71.27; H, 7.76; N, 5.36. Found: C, 71.00; H, 7.88; N, 5.31.

Dual amidation in one pot to give 22 (Table 1, Entry 5)



To TfOH (2.0 mL), methyl 2-(((4-methylphenethyl)carbamoyl)oxy)benzoate **22** (157.0 mg, 0.50 mmol) was added at 0°C. Then, dimethyl 4-((diphenylcarbamoyl)oxy)isophthalate **4** (206.1 mg, 0.51 mmol) in CH_2Cl_2 (1.0 mL) was added at 0°C. The whole was stirred for 20 minutes. Then, 9H-fluorene **19** (169.8 mg, 1.02 mmol) in CH_2Cl_2 (1.0 mL) was added at 0°C. The whole was warmed up from 0°C to 20°C, and stirred for 30 minutes. After the reaction completed, the whole was poured into ice-water. This reaction mixture was extracted with CH_2Cl_2 (40 mL x 3). The organic phase was washed with brine (40 mL), dried over Na_2SO_4, and the solvent was evaporated under reduced pressure to give a residue, which was column-chromatographed on silica-gel (eluent: EtOAc / n-Hexane / CH_2Cl_2 = 1 / 1 / 1) to afford *N*-(3-(diphenylcarbamoyl)-4-methylphenethyl)-9H-fluorene-2-carboxamide **22** (161.1 mg, 0.31 mmol, 62%) as a yellow amorphous material. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.870 (1H, s), 7.799-7.744 (2H, m), 7.637 (1H, d, *J* = 8.0 Hz), 7.538 (1H, d, *J* = 7.6 Hz), 7.404-6.944 (15H, m), 6.158 (1H, t, *J* = 6.4 Hz), 3.882 (2H, s), 3.476 (2H, q, *J* = 6.8 Hz), 2.733 (2H, t, *J* = 6.8 Hz), 2.418 (3H, s). ^{13}C-NMR ($CDCl_3$, 100 MHz) δ (ppm): 171.38, 168.20, 145.34, 144.51, 143.92, 143.46, 141.12, 137.18, 136.40, 134.23, 133.29, 131.24, 130.25, 129.47, 128.74, 128.13, 127.82, 127.46, 127.07, 126.19, 125.69, 124.31, 121.01, 120.16, 41.48, 37.36, 35.35, 19.78. HRMS (ESI-TOF, $[M+Na]^+$): Calcd. for $C_{36}H_{30}N_2NaO_2^+$: 545.2199. Found: 545.2200. Anal. Calcd. for $C_{36}H_{30}N_2O_2$+0.7 H_2O: C, 80.78; H, 5.91; N, 5.23. Found: C, 80.58; H, 6.01; N, 5.15.

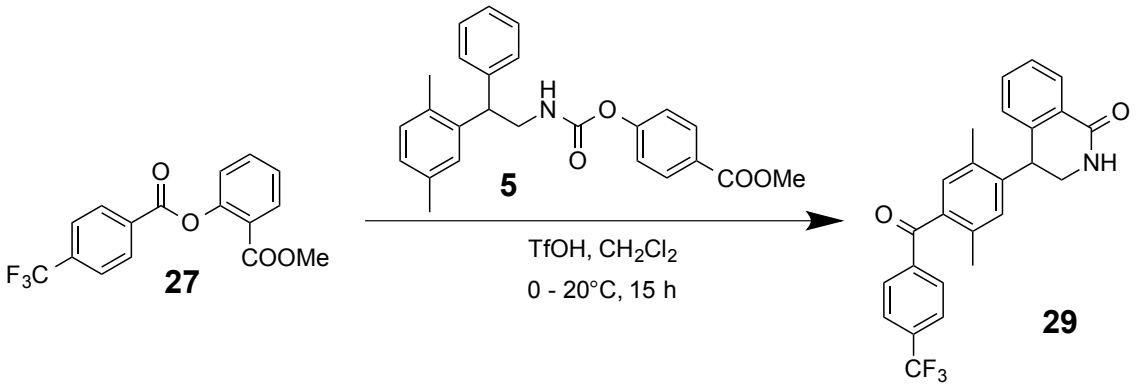
Dual amidation in one pot to 25 (Table 1, Entry 6)



To a solution of 1,2-bis(3,4-dimethylphenyl)ethane **14** (120.3 mg, 0.51 mmol), dimethyl 4-((((4-(ethoxycarbonyl)cyclohexyl)methyl)carbamoyl)oxy)isophthalate **23** (210.8 mg, 0.50 mmol) and methyl 2-((diphenylcarbamoyl)oxy)benzoate **26** (175.9 mg, 0.51 mmol) in CH_2Cl_2 (1.0 mL), TfOH (2.0 mL) was added at 0°C. The whole was stirred for 15 minutes. Then, the whole was warmed up from 0°C to 20°C, and stirred for 1 hour. After the reaction completed, the whole was poured into ice-water and added 2M aqueous solution of NaOH (30 mL). This reaction mixture was extracted with CH_2Cl_2 (40 mL x 3). The organic phase was washed with brine (40 mL), dried over Na_2SO_4, and the solvent was evaporated under reduced pressure to give a residue, which was column-chromatographed on silica-gel (eluent: EtOAc / n-Hexane = 1 / 2) to afford ethyl 4-((2-(2-(diphenylcarbamoyl)-4,5-dimethylphenethyl)-4,5-dimethylbenzamido)-methyl)cyclohexane-1-carboxylate **25** (155.3 mg, 0.24 mmol, 48 %) as a colorless oil.
^{1}H-NMR ($CDCl_3$, 400 MHz) δ (ppm) (presence of two amide conformers): 7.181-6.792 (14H, m), 6.101-6.032 (1H, m), 4.028 (2H, q, *J* = 7.2 Hz), 3.103 (2H, t, *J* = 6.4 Hz), 2.994-2.865 (5H, m), 2.157-2.122 (6H, m), 2.053 (3H, s), 1.954 (3H, m), 1.873-1.692 (5H, m), 1.411-1.337 (1H, m), 1.267 (2H, qd, *J* = 13.2, 3.2 Hz), 1.162 (3H, t, *J* = 7.2 Hz), 0.856 (2H, qd, *J* = 12.8, 3.6 Hz). ^{13}C-NMR ($CDCl_3$, 100 MHz) δ (ppm): 175.96, 175.88, 171.14, 171.10, 170.84, 170.34, 143.44, 143.34, 138.38, 138.03, 137.86, 137.80,

137.47, 137.25, 136.92, 135.70, 134.68, 134.33, 134.25, 133.55, 133.52, 133.33, 133.25, 132.55, 131.52, 131.06, 130.88, 130.13, 129.35, 129.05, 128.92, 128.53, 127.42, 126.90, 126.75, 126.31, 126.28, 60.39, 60.13, 53.45, 45.66, 45.45, 43.32, 43.28, 37.36, 37.18, 35.24, 34.99, 34.93, 34.78, 29.97, 29.86, 28.49, 28.44, 21.04, 19.90, 19.64, 19.57, 19.19, 19.03, 16.51, 14.25. HRMS (ESI-TOF, $[M+Na]^+$): Calcd. for $C_{40}H_{37}N_3NaO_3^+$: 630.2727. Found: 630.2731. Anal. Calcd. for $C_{40}H_{37}N_3O_3$+0.6 CH_2Cl_2: C, 74.03; H, 5.85; N, 6.38. Found: C, 74.06; H, 6.07; N, 6.18.

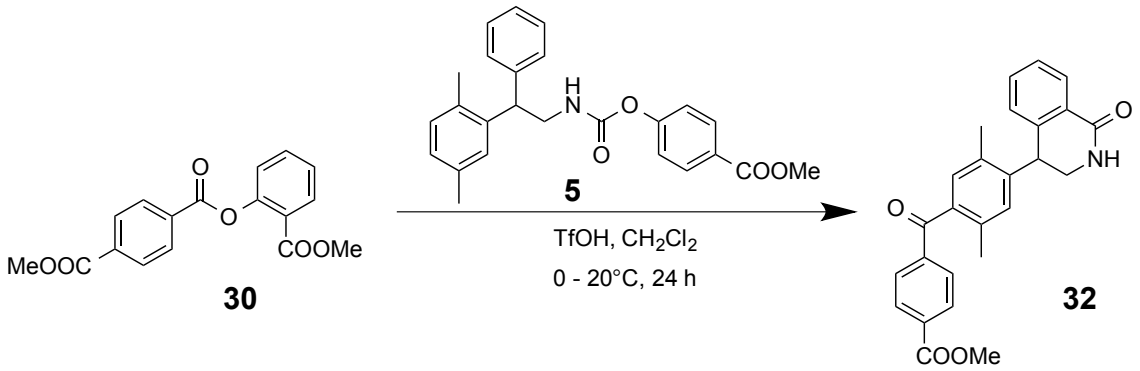
Sequential aromatic acylation-amidation reaction to 29 (Table 2, Entry 1)



To a mixture of TfOH (2.0 mL), methyl 4-(((2-(2,5-dimethylphenyl)-2-phenylethyl)carbamoyl)oxy)benzoate **5** (441.8 mg, 1.1 mmol) in CH_2Cl_2 (2.0 mL) was slowly added at 0°C. Then, methyl 2-((4-(trifluoromethyl)benzoyl)oxy)benzoate **27** (359.4 mg, 1.11 mmol) was added at 0°C. The whole was warmed up from 0°C to 20°C, and stirred for 15 hours. After the reaction completed, the whole was poured into ice-water. This reaction mixture was extracted with CH_2Cl_2 (30 mL x 4). The organic phase was washed with brine (40 mL), dried over Na_2SO_4, and the solvent was evaporated under reduced pressure to give a residue, which was column-chromatographed on silica-gel (eluent: EtOAc / n-Hexane = 1/1) to afford 4-(2,5-dimethyl-4-(4-(trifluoromethyl)benzoyl)phenyl)-3,4-dihydroisoquinolin-1(2H)-one **29** (367.5 mg, 0.87 mmol, 79%) as a colorless solid. Mp. 237.2-237.9°C (colorless needles, recrystallized from EtOAc). ^{1}H-NMR (DMSO-d_6, 400 MHz) δ (ppm): 8.002-7.888 (6H, m), 7.458 (2H, td, J = 24.5, 7.2 Hz), 7.276 (1H, s), 6.973 (1H, d, J = 7.2 Hz), 6.779 (1H, s), 4.619 (1H, t, J = 6.0 Hz), 3.699-3.524 (2H, m), 2.394(3H, s), 2.102 (3H, s). ^{13}C-NMR (DMSO-d_6, 100 MHz) δ (ppm): 196.52, 164.35, 142.46, 141.00, 140.68, 135.64, 134.06, 133.65, 132.53 (q, J = 32 Hz), 132.20, 131.02, 130.81, 130.32, 129.86, 127.46, 127.27, 127.23, 125.79 (q, J = 4 Hz), 123.76 (q, J = 271 Hz), 44.44, 39.16, 19.43, 18.68. HRMS (ESI-TOF, $[M+Na]^+$): Calcd. for $C_{25}H_{20}F_3NNaO_2^+$: 446.1338. Found: 446.1334. Anal. Calcd. for $C_{25}H_{20}F_3NO_2$+0.8 H_2O:

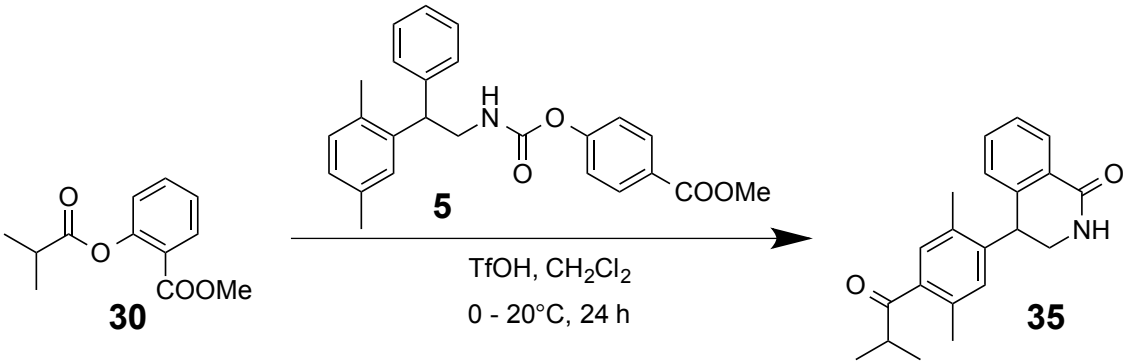
C, 68.58; H, 4.97; N, 3.20. Found: C, 68.74; H, 5.04; N, 3.09.

Sequential aromatic acylation-amidation reaction 32 (Table 2, Entry 2)



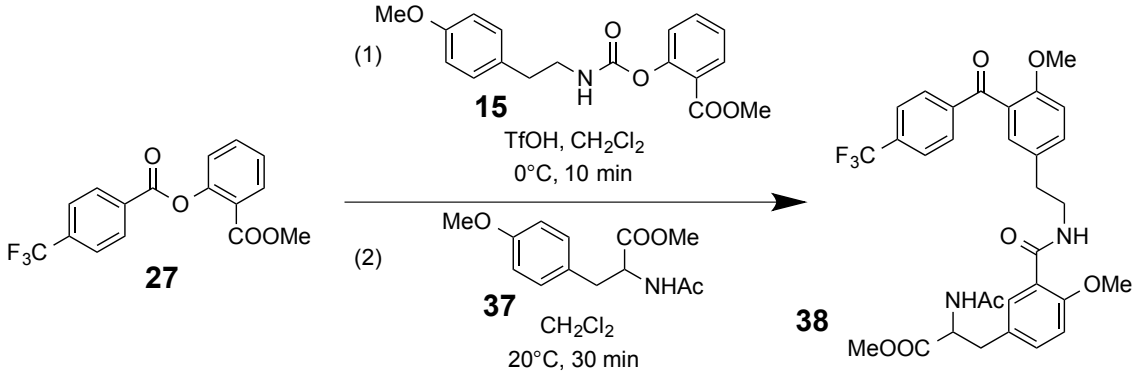
To a mixture of TfOH (1.0 mL), methyl 4-(((2-(2,5-dimethylphenyl)-2-phenylethyl)carbamoyl)oxy)benzoate **5** (224.0 mg, 0.50 mmol) in CH_2Cl_2 (1.0 mL) was slowly added at 0°C. Then, 2-(methoxycarbonyl)phenyl methyl terephthalate **30** (165.7 mg, 0.53 mmol) was added at 0°C. The whole was warmed up from 0°C to 20°C, and stirred for 11 hours. After the reaction completed, the whole was poured into ice-water. This reaction mixture was extracted with CH_2Cl_2 (30 mL x 4). The organic phase was washed with brine (40 mL), dried over Na_2SO_4, and the solvent was evaporated under reduced pressure to give a residue, which was column-chromatographed on silica-gel (eluent: EtOAc / n-Hexane = 4 / 1) to afford methyl 4-(2,5-dimethyl-4-(1-oxo-1,2,3,4-tetrahydroisoquinolin-4-yl)benzoyl)benzoate **32** (148.7 mg, 0.36 mmol, 72%) as a colorless solid. Mp. 231.8-232.7°C (colorless needles, recrystallized from EtOAc). ^{1}H-NMR (DMSO-d_6, 400 MHz) δ (ppm): 8.114 (2H, d, *J* = 8.0 Hz), 7.996-7.976 (2H, m), 7.829 (2H, d, *J* = 8.0 Hz), 7.499 (1H, t, *J* = 6.8 Hz), 7.434 (1H, t, *J* = 6.8 Hz), 7.254 (1H, s), 6.980 (1H, dd, *J* = 7.2 Hz), 6.762 (1H, s), 4.614 (1H, t, *J* = 6.4 Hz), 3.899 (3H, s), 3.684-3.524 (2H, m), 2.394 (3H, s), 2.087 (3H, s). ^{13}C-NMR (DMSO-d_6, 100 MHz) δ (ppm): 196.95, 165.54, 164.32, 142.29, 141.00, 140.89, 135.94, 133.85, 133.60, 133.24, 132.19, 130.89, 130.73, 129.83, 129.77, 129.53, 127.47, 127.24, 127.22, 52.51, 44.42, 19.43, 18.70. HRMS (ESI-TOF, $[M+Na]^+$): Calcd. for $C_{26}H_{23}NNaO_4^+$: 436.1519. Found: 436.1502. Anal. Calcd. for $C_{26}H_{23}NO_4$+0.3 H_2O: C, 74.55; H, 5.68; N, 3.34. Found: C, 74.43; H, 5.80; N, 3.35.

Sequential aromatic acylation-amidation reaction 35 (Table 2, Entry 3)



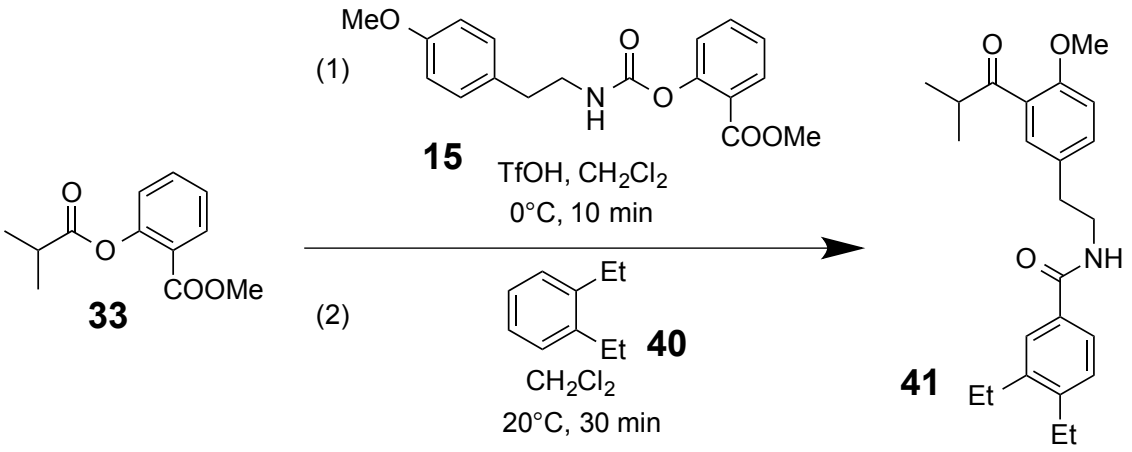
To TfOH (1.0 mL), methyl 4-(((2-(2,5-dimethylphenyl)-2-phenylethyl)carbamoyl)oxy)-benzoate **5** (221.9 mg, 0.50 mmol) was added at 0°C. Then, methyl 2-(isobutyryloxy)benzoate **30** (115.7 mg, 0.52 mmol) in CH_2Cl_2 (1.0 mL) was added at 0°C. The whole was warmed up from 0°C to 20°C, and stirred for 24 hours. After the reaction completed, the whole was poured into ice-water. Added 2M aqueous solution of NaOH (40 mL), and this reaction mixture was extracted with CH_2Cl_2 (40 mL x 3). The organic phase was washed with brine (40 mL), dried over Na_2SO_4, and the solvent was evaporated under reduced pressure to give a residue, which was column-chromatographed on silica-gel (eluent: EtOAc / n-Hexane = 2 / 1) to afford 4-(4-isobutyryl-2,5-dimethylphenyl)-3,4-dihydroisoquinolin-1(2H)-one **35** (117.9 mg, 0.37 mmol, 73%) as a colorless solid. Mp. 198.1-199.7°C (colorless needle, recrystallized from CH_2Cl_2/n-Hexane). ^{1}H-NMR ($CDCl_3$, 400 MHz) δ (ppm): 8.173-8.139 (1H, m), 7.437-7.371 (3H, m), 7.101 (1H, brs), 6.867-6.835 (2H, m), 4.604 (1H, t, J = 7.6 Hz), 3.717 (2H, dd, J = 6.4, 2.8 Hz), 3.394-3.325 (1H, m), 2.411 (3H, s), 2.284 (3H, s), 1.194-1.169 (6H, m). ^{13}C-NMR ($CDCl_3$, 100 MHz) δ (ppm): 209.50, 166.91, 141.67, 141.48, 138.23, 135.89, 134.06, 133.09, 132.15, 130.38, 129.80, 128.71, 127.96, 127.81, 46.27, 40.72, 39.25, 20.89, 19.89, 19.14, 19.12. HRMS (ESI-TOF, $[M+Na]^+$): Calcd. for $C_{21}H_{23}NNaO_2^+$: 344.1626. Found: 344.1623. Anal. Calcd. for $C_{21}H_{23}NO_2$+0.05 CH_2Cl_2: C, 77.64; H, 7.15; N, 4.30. Found: C, 77.62; H, 7.27; N, 4.33.

Sequential aromatic acylation-amidation reaction 38 (Table 2, Entry 4)



To TfOH (2.0 mL), methyl 2-(((4-methoxyphenethyl)carbamoyl)oxy)benzoate **15** (333.4 mg, 1.01 mmol) in CH_2Cl_2 (2.0 mL) was added at 0°C. Then, methyl 2-((4-(trifluoromethyl)benzoyl)oxy)benzoate **27** (332.1 mg, 1.02 mmol) was added at 0°C. The whole was stirred for 10 minutes. Then, methyl 2-acetamido-3-(4-methoxyphenyl)propanoate **37** (506.4 mg, 2.02 mmol) in CH_2Cl_2 (2.0 mL) was added at 0°C. The whole was warmed up from 0°C to 20°C, and stirred for 30 minutes. After the reaction completed, the whole was poured into ice-water. This reaction mixture was extracted with CH_2Cl_2 (40 mL x 3). The organic phase was washed with brine (40 mL), dried over Na_2SO_4, and the solvent was evaporated under reduced pressure to give a residue, which was column-chromatographed on silica-gel (eluent: EtOAc) to afford methyl 2-acetamido-3-(4-methoxy-3-((4-methoxy-3-(4-(trifluoromethyl)benzoyl)phenethyl)carbamoyl)phenyl)propanoate **38** (358.6 mg, 0.60 mmol, 60 %) as a colorless amorphous material. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.954-7.939 (2H, m), 7.863 (2H, d, *J* = 8.4 Hz), 7.654 (2H, d, *J* = 8.4 Hz), 7.420 (1H, dd, *J* = 8.6, 2.0 Hz), 7.305 (1H, d, *J* = 2.0 Hz), 7.208 (1H, dd, *J* = 8.4, 2.0 Hz), 6.980 (1H, d, *J* = 8.8 Hz), 6.868 (1H, d, *J* = 8.4 Hz), 6.454 (1H, d, *J* = 8.0 Hz), 4.854 (1H, q, *J* = 5.6 Hz), 3.814 (3H, s), 3.743-3.685 (8H, m), 3.079 (2H, ddd, *J* = 14.0, 6.4, 6.4 Hz), 2.920 (2H, t, *J* = 7.2 Hz), 2.634 (1H, brs), 1.974 (3H, s). ^{13}C-NMR ($CDCl_3$, 100 MHz) δ (ppm): 195.84, 172.55, 170.46, 165.56, 157.03, 156.72, 141.28, 134.38 (q, *J* = 33 Hz), 133.90, 133.56, 133.33, 132.16, 130.58, 130.25, 129.37, 128.33, 125.69 (q, *J* = 3 Hz), 124.17 (q, *J* = 270 Hz), 121.59, 112.33, 112.11, 56.36, 56.13, 53.74, 52.89, 41.40, 37.29, 35.08, 23.46. HRMS (ESI-TOF, $[M+Na]^+$): Calcd. for $C_{31}H_{31}N_2F_3NaO_7^+$: 623.1981. Found: 623.1973. Anal. Calcd. for $C_{31}H_{31}N_2F_3O_7$+0.6 H_2O: C, 60.90; H, 5.31; N, 4.58. Found: C, 60.67; H, 5.45; N, 4.34.

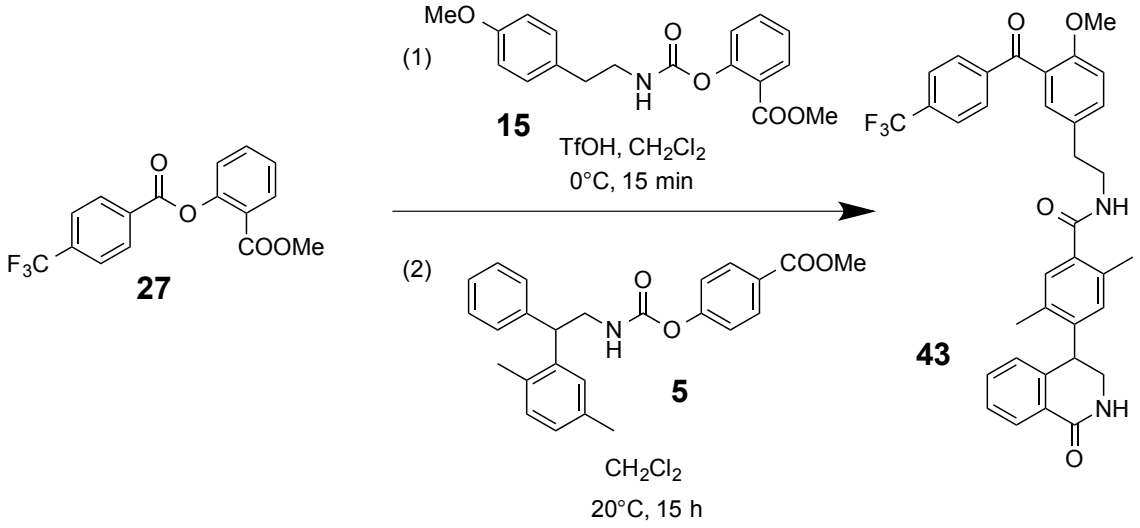
Sequential aromatic acylation-amidation reaction 41 (Table 2, Entry 5)



To TfOH (2.0 mL), methyl 2-(((4-methoxyphenethyl)carbamoyl)oxy)benzoate **15** (335.2 mg, 1.02 mmol) was added at 0°C. Then, methyl 2-(isobutyryloxy)benzoate **33** (228.6 mg, 1.03 mmol) in CH_2Cl_2 (2.0 mL) was added at 0°C. The whole was stirred for 10 minutes. Then, 1,2-diethylbenzene **40** (273.7 mg, 2.04 mmol) in CH_2Cl_2 (2.0 mL) was added at 0°C. The whole was warmed up from 0°C to 20°C, and stirred for 30 minutes. After the reaction completed, the whole was poured into ice-water. This reaction mixture was extracted with CH_2Cl_2 (40 mL x 3). The organic phase was washed with brine (40 mL), dried over Na_2SO_4, and the solvent was evaporated under reduced pressure to give a residue, which was column-chromatographed on silica-gel (eluent: EtOAc / n-Hexane = 1 / 2) to afford 3,4-diethyl-*N*-(3-isobutyryl-4-methoxyphenethyl)- benzamide **41** (299.7 mg, 0.79 mmol, 77%) as a colorless oil.

^{1}H-NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.571 (1H, d, *J* = 2.0 Hz), 7.449 (1H, t, *J* = 7.8 Hz), 7.375 (1H, t, *J* = 2.4 Hz), 7.294 (1H, d, *J* = 8.6 Hz), 7.173 (1H, d, *J* = 8.0 Hz), 6.893 (1H, d, *J* = 8.4 Hz), 6.334 (1H, t, *J* = 5.6 Hz), 3.855 (3H, s), 3.659 (2H, *J* = 6.8 Hz), 3.464 (1H, sep, *J* = 6.8 Hz), 2.877 (2H, t, *J* = 6.8 Hz), 2.667 (4H, qt, *J* = 7.4, 0.8 Hz), 1.214 (6H, qd, *J* = 7.4, 2.0 Hz), 1.128 (6H, d, *J* = 6.8 Hz). ^{13}C-NMR ($CDCl_3$, 100 MHz) δ (ppm): 208.70, 168.28, 156.96, 146.09, 142.63, 133.42, 132.69, 131.72, 130.58, 129.54, 128.94, 127.64, 124.69, 112.26, 56.17, 41.59, 40.57, 35.21, 25.99, 25.95, 19.06, 15.65, 15.56. HRMS (ESI-TOF, $[M+Na]^+$): Calcd. for $C_{24}H_{31}NNaO_3^+$: 404.2196. Found: 404.2192. Anal. Calcd. for $C_{24}H_{31}NO_3$+0.2 H_2O: C, 74.85; H, 8.22; N, 3.64. Found: C, 74.89; H, 8.14; N, 3.56.

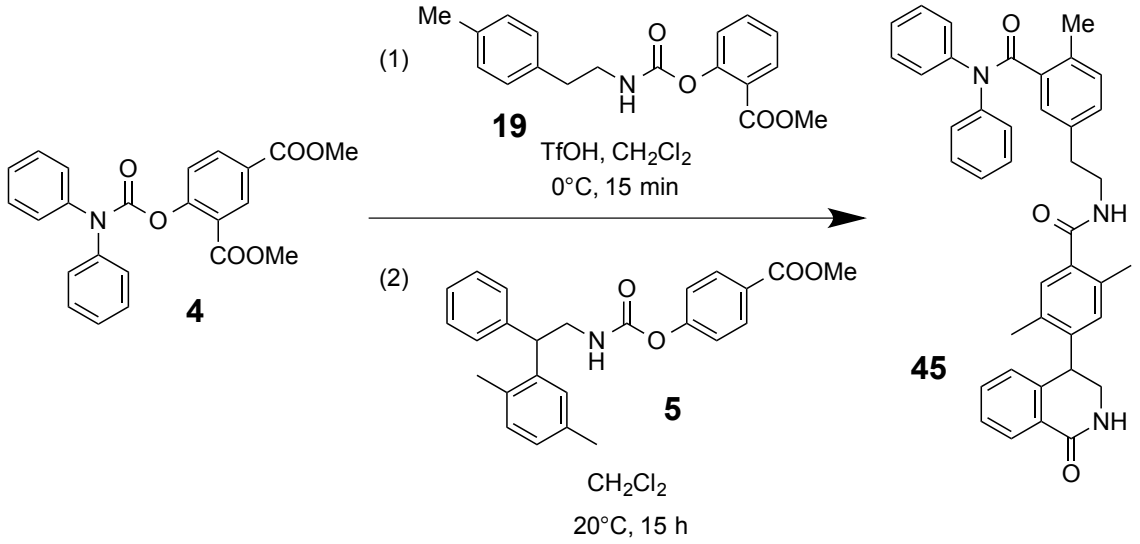
Formation of three bonds in a one-pot reaction 43 (Figure 8, Reaction (a))



To TfOH (2.0 mL), methyl 2-(((4-methoxyphenethyl)carbamoyl)oxy)benzoate **15** (166.1 mg, 0.50 mmol) was added at 0°C. Then, methyl 2-((4-(trifluoromethyl)benzoyl)oxy)benzoate **27** (164.0 mg, 0.51 mmol) was added at 0°C. The whole was stirred for 15 minutes. Then, methyl 4-(((2-(2,5-dimethylphenyl)-2-phenylethyl)carbamoyl)oxy)benzoate **5** (230.3 mg, 0.52 mmol) in CH_2Cl_2 (2.0 mL) was added at 0°C. The whole was warmed up from 0°C to 20°C, and stirred for 15 hours. After the reaction completed, the whole was poured into ice-water and added 2M aqueous solution of NaOH (30 mL). This reaction mixture was extracted with CH_2Cl_2 (40 mL x 3). The organic phase was washed with brine (40 mL), dried over Na_2SO_4, and the solvent was evaporated under reduced pressure to give a residue, which was column-chromatographed on silica-gel (eluent: EtOAc) to afford *N*-(4-methoxy-3-(4-(trifluoromethyl)benzoyl)phenethyl)-2,5-dimethyl-4-(1-oxo-1,2,3,4-tetrahydroisoquinolin-4-yl)benzamide **43** (172.7 mg, 0.29 mmol, 56%) as amorphous material. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ (ppm): 8.143-8.120 (1H, m), 7.869 (2H, d, *J* = 8.0 Hz), 7.673 (2H, d, *J* = 8.4 Hz), 7.424-7.373 (3H, m), 7.301 (1H, d, *J* = 2.4 Hz), 7.183 (1H, s), 6.961 (1H, d, *J* = 8.4 Hz), 6.818-6.796 (1H, m), 6.747 (1H, s), 6.608 (1H, brs), 5.956 (1H, t, *J* = 6.0 Hz), 4.546 (1H, t, *J* = 7.6 Hz), 3.725-3.630 (7H, m), 2.934 (2H, t, *J* = 7.6 Hz), 2.327 (3H, s), 2.232 (3H, s). ^{13}C-NMR ($CDCl_3$, 100 MHz) δ (ppm): 195.93, 170.41, 166.80, 156.86, 141.69, 141.30, 140.66, 135.88, 134.54 (q, *J* = 28 Hz), 134.37, 134.31, 133.62, 133.15, 131.79, 131.52, 131.02, 130.70, 130.35, 129.73, 128.72, 128.56, 127.97, 127.84, 125.79 (q, *J* = 3 Hz), 124.24 (q, *J* = 271 Hz), 112.43, 56.20, 46.31, 41.38, 40.56, 35.25, 19.94, 19.67. HRMS (ESI-TOF, $[M+Na]^+$): Calcd. for $C_{35}H_{31}F_3N_2NaO_4^+$: 623.2128. Found: 623.2128. Anal. Calcd. for $C_{35}H_{31}F_3N_2O_4$+0.5

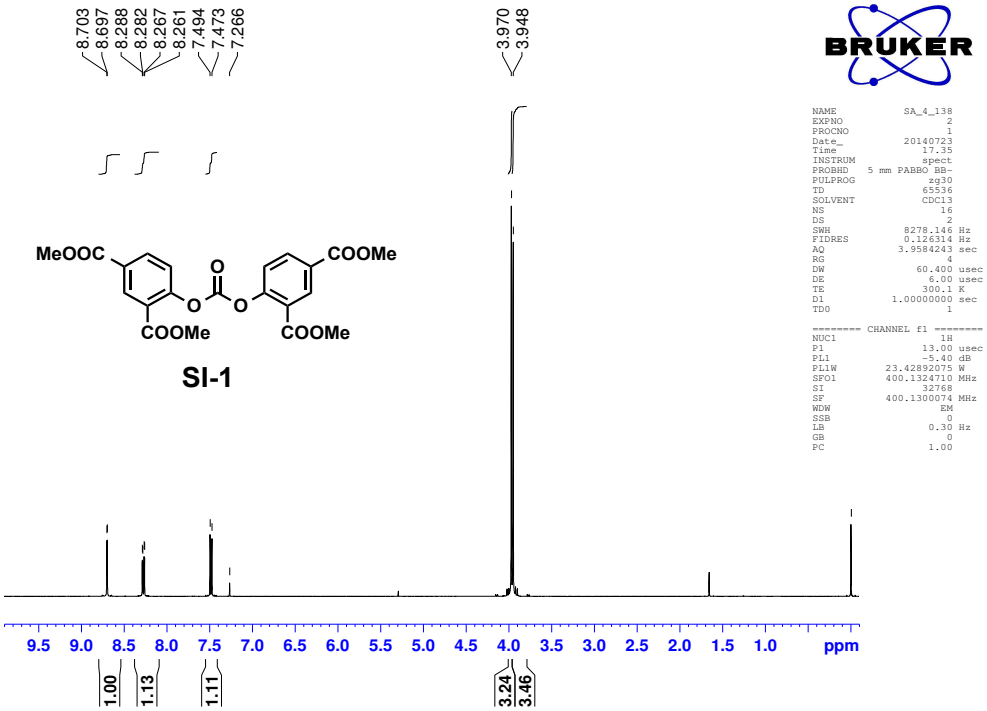
CH_2Cl_2: C, 66.30; H, 5.02; N, 4.36. Found: C, 66.05; H, 5.33; N, 4.35.

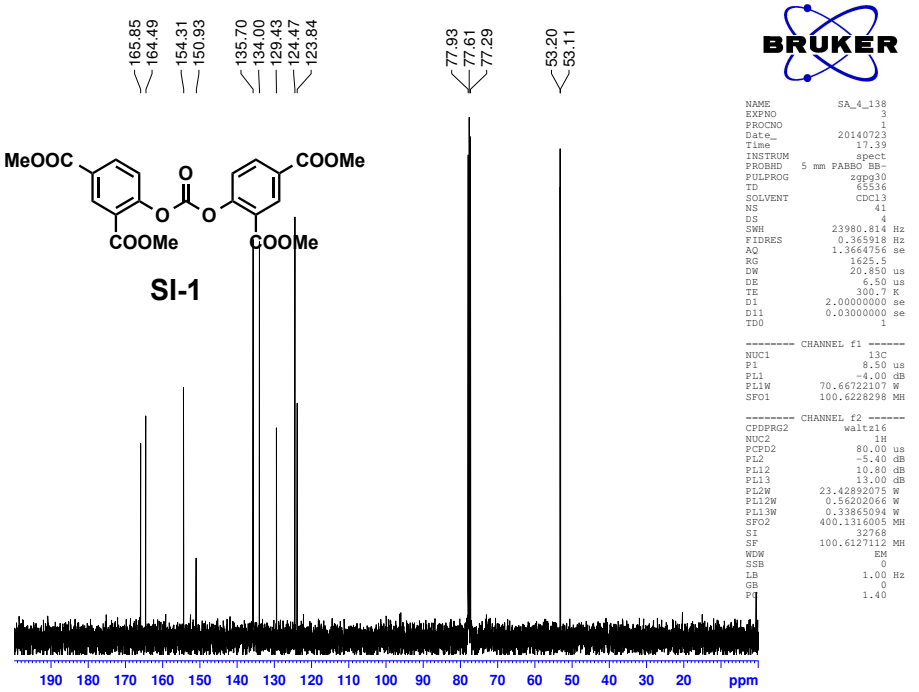
Formation of three bonds in a one-pot reaction 45 (Figure 8, Reaction (b))

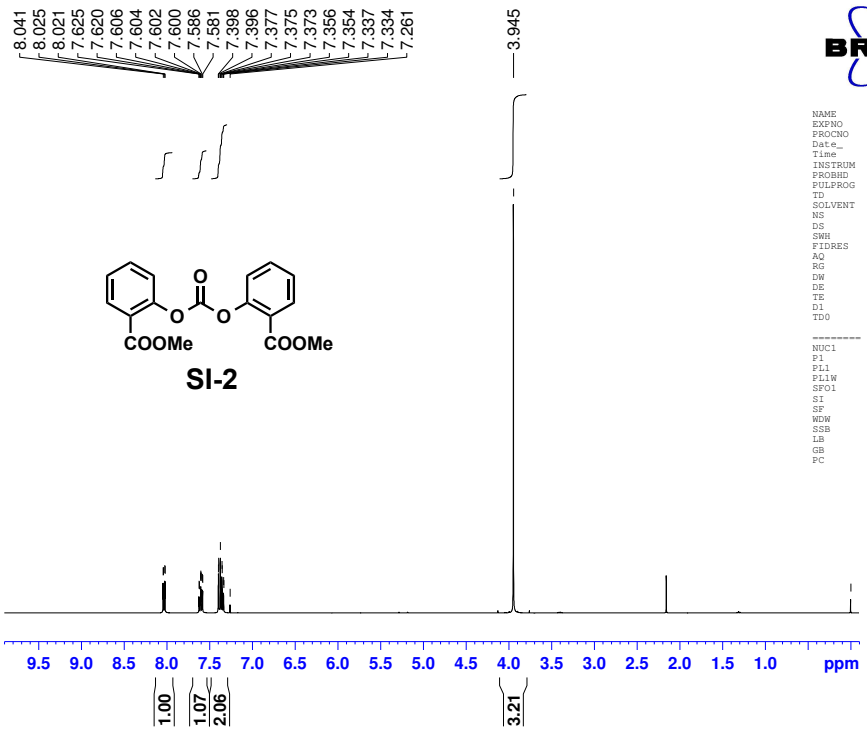


To TfOH (3.0 mL), methyl 2-(((4-methylphenethyl)carbamoyl)oxy)benzoate **19** (161.0 mg, 0.51 mmol) was added at 0°C. Then, dimethyl 4-((diphenylcarbamoyl)oxy)isophthalate **4** (203.7 mg, 0.50 mmol) was added at 0°C. The whole was stirred for 15 minutes. Then, methyl 4-(((2-(2,5-dimethylphenyl)-2-phenylethyl)carbamoyl)oxy)benzoate **5** (227.4 mg, 0.56 mmol) in CH_2Cl_2 (2.0 mL) was added at $0^{°C}$. The whole was warmed up from 0°C to 20°C, and stirred for 15 hours. After the reaction completed, the whole was poured into ice-water and added 2M aqueous solution of NaOH (30 mL). This reaction mixture was extracted with CH_2Cl_2 (40 mL x 3). The organic phase was washed with brine (40 mL), dried over Na_2SO_4, and the solvent was evaporated under reduced pressure to give a residue, which was column-chromatographed on silica-gel (eluent: EtOAc) to afford *N*-(3-(diphenylcarbamoyl)-4-methylphenethyl)-2,5-dimethyl-4-(1-oxo-1,2,3,4-tetrahydr oisoquinolin-4-yl)benzamide **45** (160.3 mg, 0.26 mmol, 53%) as a colorless amorphous material. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ (ppm): 8.153-8.112 (1H, m), 7.394-6.969 (16H, m), 6.831-6.796 (2H, m), 6.760 (1H, brs), 5.617 (1H, t, J = 6.0 Hz), 4.550 (1H, t, J = 7.2 Hz), 3.634 (2H, dd, J = 7.8, 2.8 Hz), 3.485 (2H, q, J = 6.4 Hz), 2.749 (2H, t, J = 6.8 Hz), 2.413 (3H, s), 2.342 (3H, s), 2.220 (3H, s). ^{13}C-NMR ($CDCl_3$, 100 MHz) δ (ppm): 171.30, 170.26, 166.74, 143.50, 141.70, 140.60, 137.20, 136.24, 135.94, 134.36, 134.28, 134.22, 133.08, 131.44, 131.29, 130.33, 129.77, 129.65, 129.49, 128.67, 128.61, 127.91, 127.77, 127.05, 46.28, 41.12, 40.54, 35.31, 19.97, 19.81, 19.69. HRMS (ESI-TOF, $[M+Na]^+$): Calcd. for $C_{40}H_{37}N_3NaO_3^+$: 630.2727. Found: 630.2731. Anal. Calcd. for $C_{40}H_{37}N_3O_3$+0.6 CH_2Cl_2: C, 74.03; H, 5.85; N, 6.38. Found: C, 74.06; H, 6.07; N, 6.18.

V. NMR spectra





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PROCNO                   1
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PULPROG               zg30
TD                   65536
SOLVENT              CDCl3
NS                      16
DS                       2
SWH              8278.146 Hz
FIDRES           0.126314 Hz
AQ               3.9584243 sec
RG                      57
DW                 60.400 usec
DE                  6.00 usec
TE                 296.2 K
D1              1.00000000 sec
TD0                      1

======== CHANNEL f1 =======
NUC1                    1H
P1                   13.00 usec
PL1                  -5.40 dB
PL1W           23.42892075 W
SFO1           400.1324710 MHz
SI                    32768
SF             400.1300090 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.00
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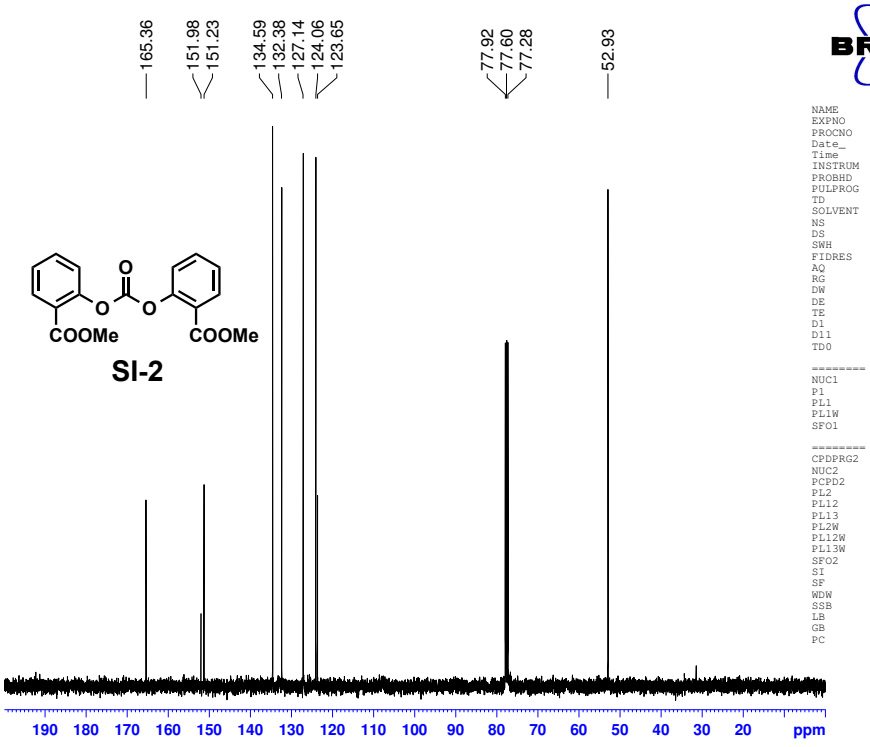


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PROCNO                   1
Date_             20130227
Time                11.03
INSTRUM             spect
PROBHD    5 mm PABBO BB-
PULPROG             zgpg30
TD                   65536
SOLVENT              CDCl3
NS                      97
DS                       4
SWH             26178.010 Hz
FIDRES           0.399445 Hz
AQ               1.2517875 se
RG                    2298.8
DW                 19.100 us
DE                  6.50 us
TE                 296.2 K
D1              2.00000000 se
D11             0.03000000 se
TD0                      1

======== CHANNEL f1 ======
NUC1                   13C
P1                    8.50 us
PL1                  -4.00 dB
PL1W           70.66722107 W
SFO1           100.6228298 MH

======== CHANNEL f2 ======
CPDPRG2             waltz16
NUC2                    1H
PCPD2                80.00 us
PL2                  -5.40 dB
PL12                 10.80 dB
PL13                 13.00 dB
PL2W           23.42892075 W
PL12W           0.56202066 W
PL13W           0.33865094 W
SFO2           400.1316005 MH
SI                    32768
SF             100.6127146 MH
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.40
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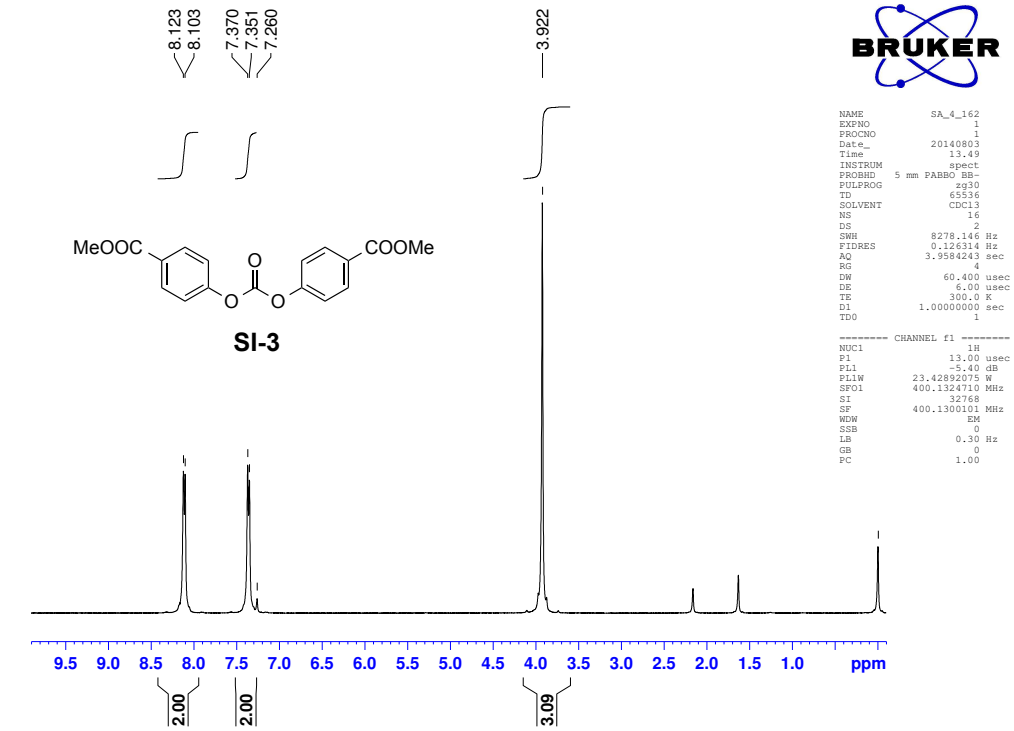


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EXPNO                  1
PROCNO                 1
Date_           20140803
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PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH           8278.146 Hz
FIDRES        0.126314 Hz
AQ            3.9584243 sec
RG                     4
DW               60.400 usec
DE                6.00 usec
TE               300.0 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 =======
NUC1                  1H
P1                 13.00 usec
PL1                -5.40 dB
PL1W        23.42892075 W
SFO1        400.1324710 MHz
SI                 32768
SF          400.1300101 MHz
WDW                   EM
SSB                    0
LB                 0.30 Hz
GB                     0
PC                 1.00
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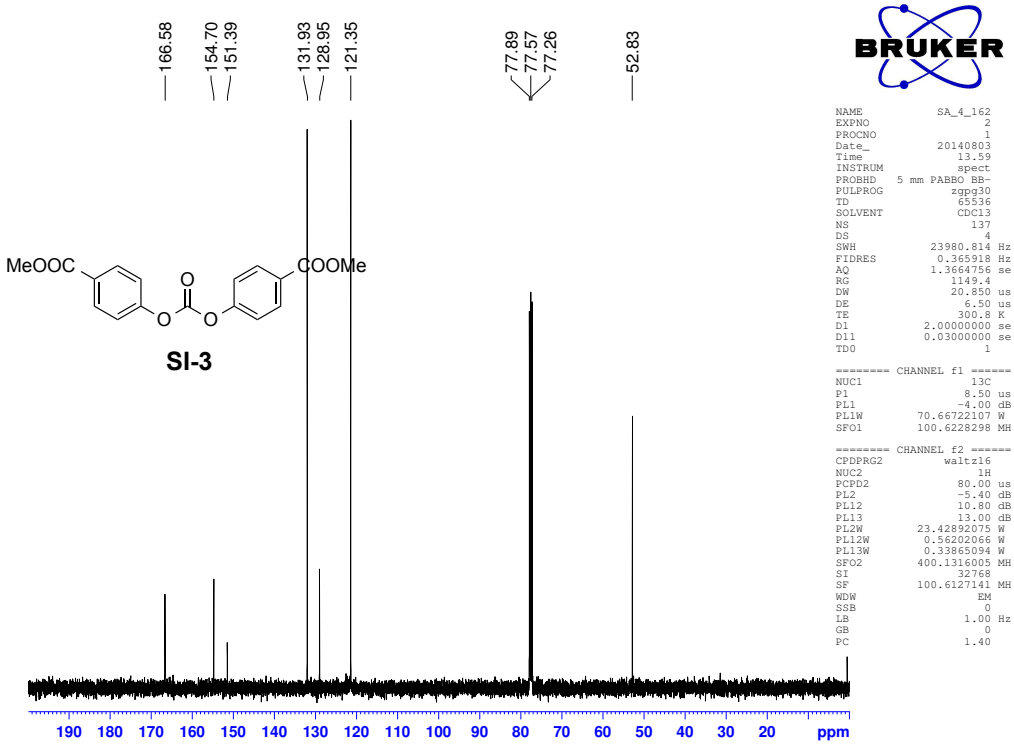


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PROCNO                 1
Date_           20140803
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INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   137
DS                     4
SWH          23980.814 Hz
FIDRES        0.365918 Hz
AQ            1.3664756 se
RG                1149.4
DW               20.850 us
DE                6.50 us
TE               300.8 K
D1            2.00000000 se
D11           0.03000000 se
TD0                    1

======== CHANNEL f1 ======
NUC1                  13C
P1                 8.50 us
PL1               -4.00 dB
PL1W        70.66722107 W
SFO1        100.6228298 MH

======== CHANNEL f2 ======
CPDPRG2          waltz16
NUC2                  1H
PCPD2             80.00 us
PL2               -5.40 dB
PL12              10.80 dB
PL13              13.00 dB
PL2W        23.42892075 W
PL12W        0.56202066 W
PL13W        0.33865094 W
SFO2        400.1316005 MH
SI                 32768
SF          100.6127141 MH
WDW                   EM
SSB                    0
LB                 1.00 Hz
GB                     0
PC                 1.40
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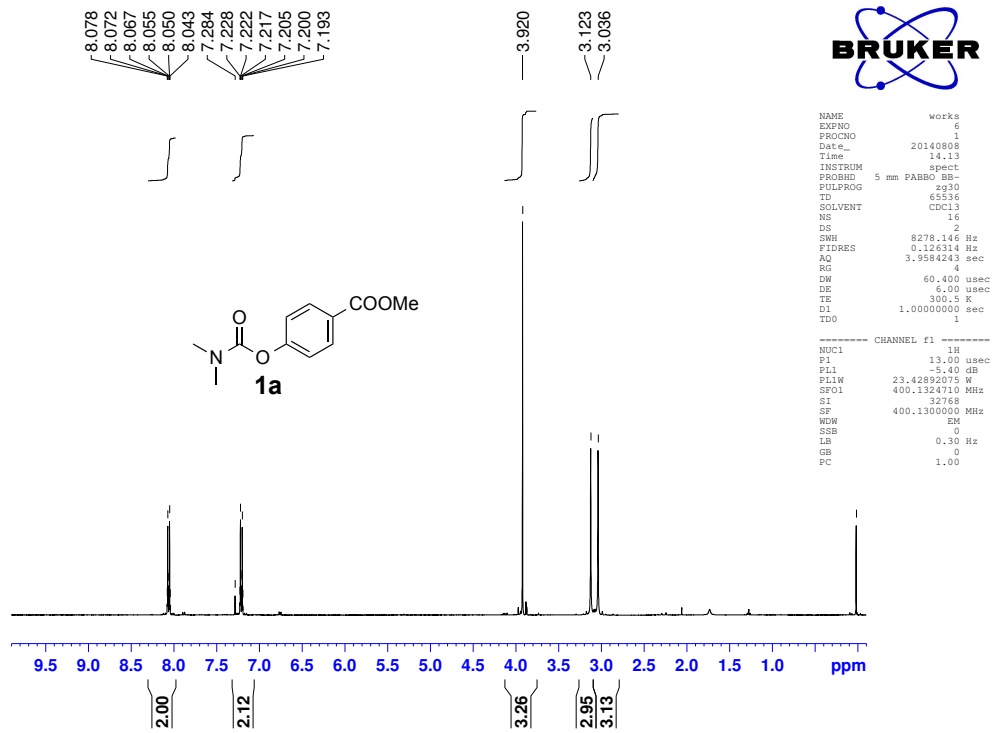

BRUKER

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PROCNO                1
Date_          20140808
Time              14.13
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH           8278.146 Hz
FIDRES        0.126314 Hz
AQ            3.9584243 sec
RG                     4
DW               60.400 usec
DE                6.00 usec
TE               300.5 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 =======
NUC1                  1H
P1                13.00 usec
PL1               -5.40 dB
PL1W        23.42892075 W
SFO1       400.1324710 MHz
SI                 32768
SF         400.1300000 MHz
WDW                   EM
SSB                    0
LB                0.30 Hz
GB                     0
PC                1.00
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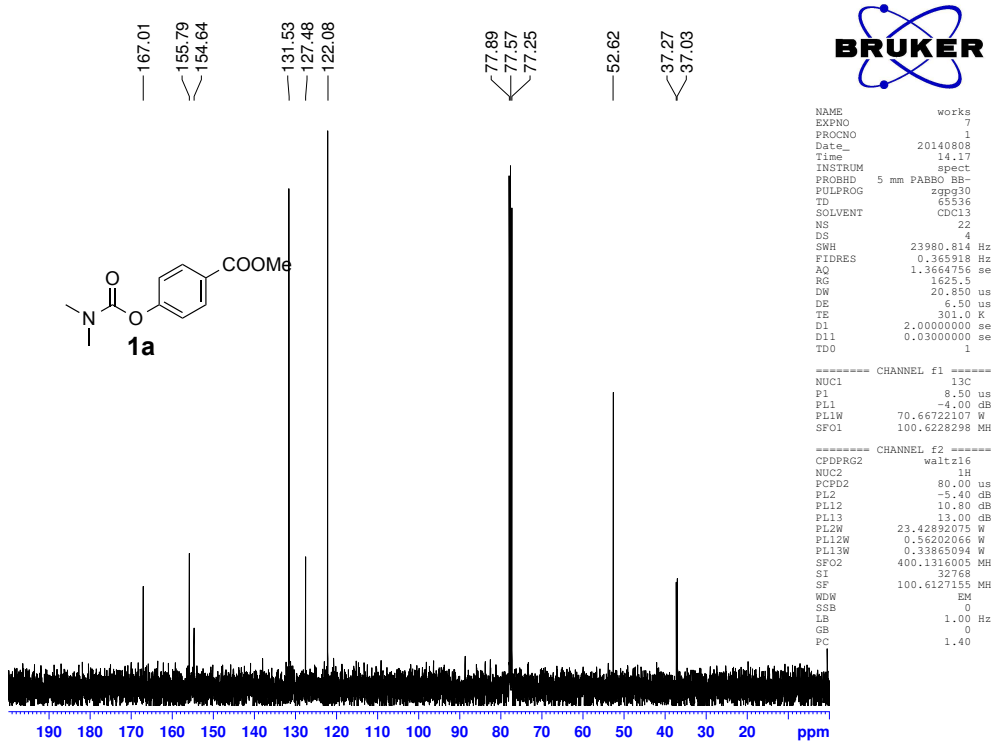

BRUKER

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EXPNO                 7
PROCNO                1
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Time              14.17
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                    22
DS                     4
SWH          23980.814 Hz
FIDRES        0.365918 Hz
AQ            1.3664756 se
RG                1625.5
DW               20.850 us
DE                6.50 us
TE               301.0 K
D1            2.00000000 se
D11           0.03000000 se
TD0                    1

======== CHANNEL f1 ======
NUC1                 13C
P1                8.50 us
PL1              -4.00 dB
PL1W        70.66722107 W
SFO1       100.6228298 MH

======== CHANNEL f2 ======
CPDPRG2          waltz16
NUC2                  1H
PCPD2            80.00 us
PL2               -5.40 dB
PL12              10.80 dB
PL13              13.00 dB
PL2W        23.42892075 W
PL12W        0.56202066 W
PL13W        0.33865094 W
SFO2       400.1316005 MH
SI                 32768
SF         100.6127155 MH
WDW                   EM
SSB                    0
LB                1.00 Hz
GB                     0
PC                1.40
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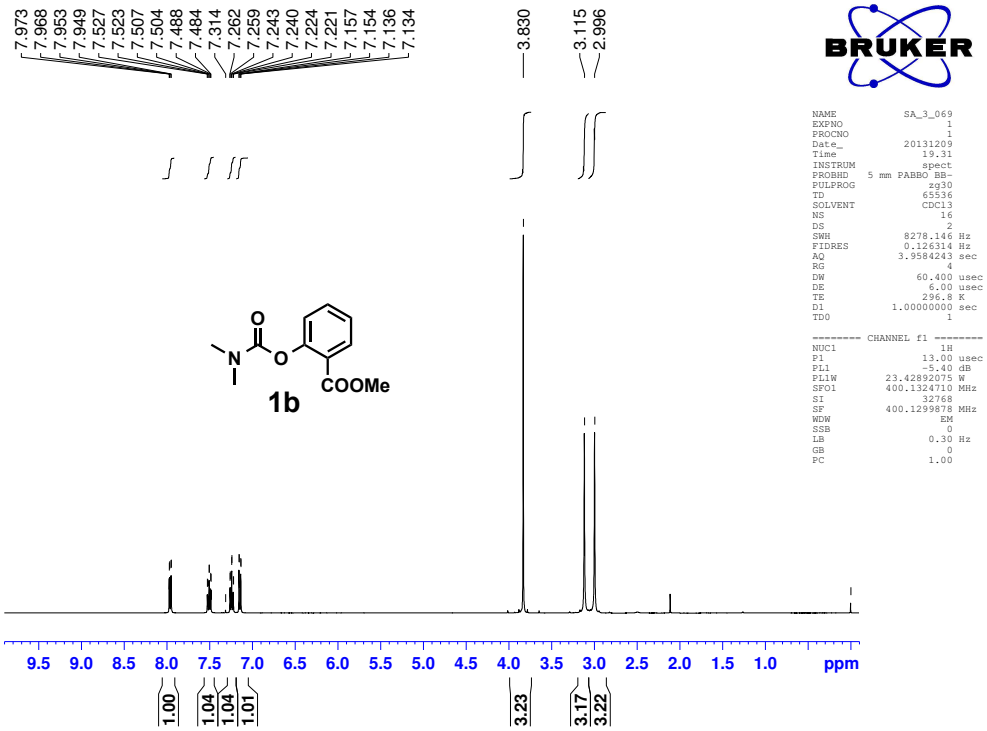
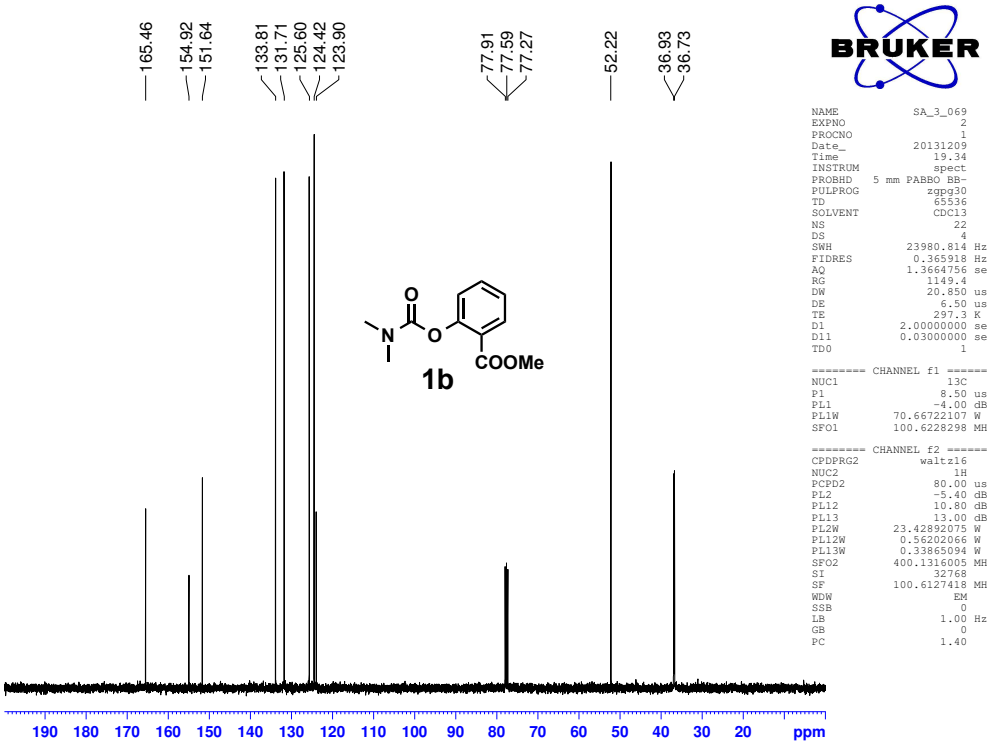
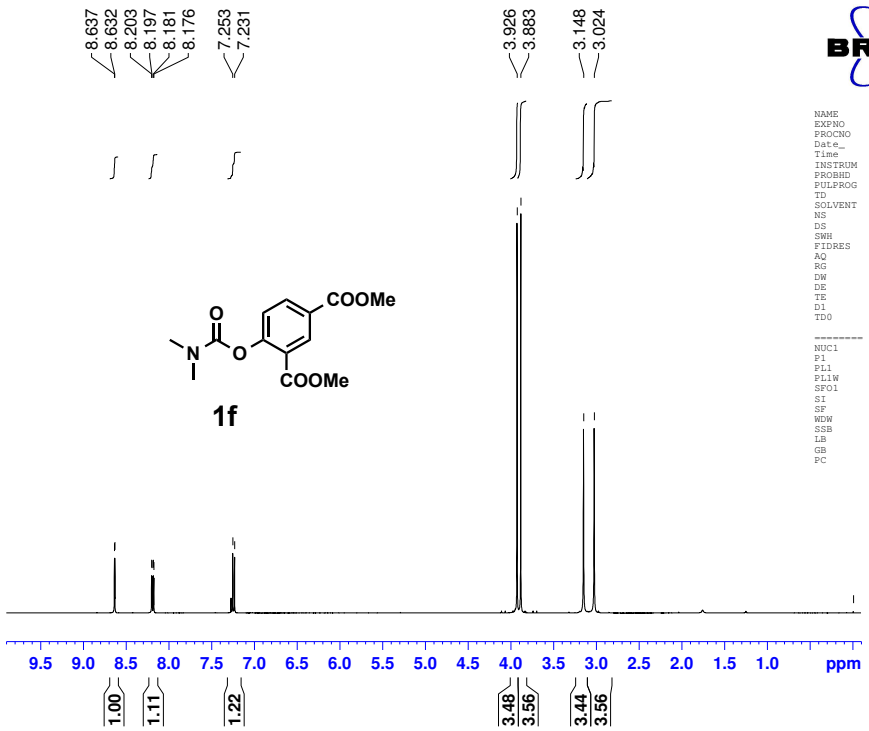
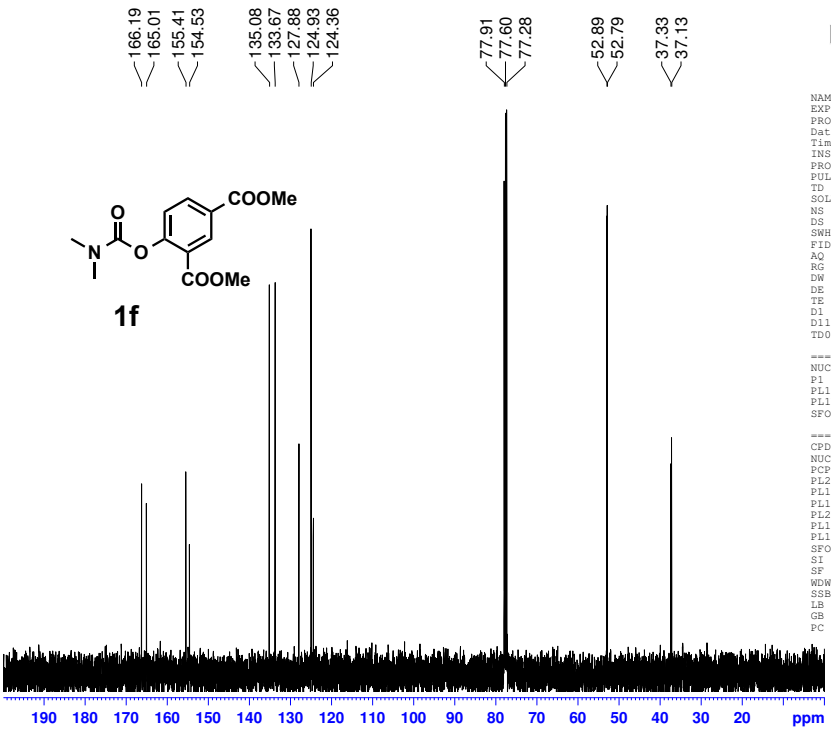

7.973
7.968
7.953
7.949
7.527
7.523
7.507
7.504
7.488
7.484
7.314
7.262
7.259
7.243
7.240
7.224
7.221
7.157
7.154
7.136
7.134
3.830
3.115
2.996
BRUKER
NAME SA_3_069
EXPNO 1
PROCNO 1
Date_ 20131209
Time 19.31
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 4
DW 60.400 usec
DE 6.00 usec
TE 296.8 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.00 usec
PL1 -5.40 dB
PL1W 23.42892075 W
SFO1 400.1324710 MHz
SI 32768
SF 400.1299878 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
O
N
O
COOMe
1b
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0
ppm
1.00
1.04
1.04
1.01
3.23
3.17
3.22


165.46
154.92
151.64
133.81
131.71
125.60
124.42
123.90
77.91
77.59
77.27
52.22
36.93
36.73
BRUKER
NAME SA_3_069
EXPNO 2
PROCNO 1
Date_ 20131209
Time 19.34
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 22
DS 4
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664756 se
RG 1149.4
DW 20.850 us
DE 6.50 us
TE 297.3 K
D1 2.00000000 se
D11 0.03000000 se
TD0 1
======== CHANNEL f1 ======
NUC1 13C
P1 8.50 us
PL1 -4.00 dB
PL1W 70.66722107 W
SFO1 100.6228298 MH
======== CHANNEL f2 ======
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 us
PL2 -5.40 dB
PL12 10.80 dB
PL13 13.00 dB
PL2W 23.42892075 W
PL12W 0.56202066 W
PL13W 0.33865094 W
SFO2 400.1316005 MH
SI 32768
SF 100.6127418 MH
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
O
N
O
COOMe
1b
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20
ppm



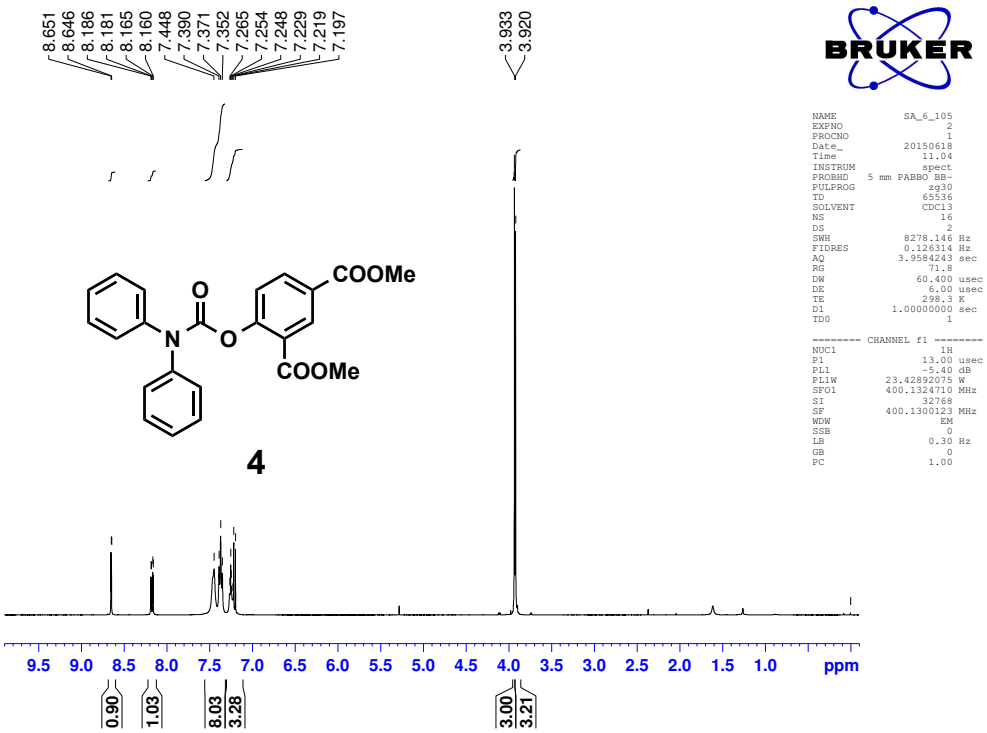
BRUKER

```
NAME                SA_4_159
EXPNO                      1
PROCNO                     1
Date_               20150827
Time                   21.35
INSTRUM                spect
PROBHD    5 mm PABBO BB-
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                        16
DS                         2
SWH                8278.146 Hz
FIDRES             0.126314 Hz
AQ                 3.9584243 sec
RG                      40.3
DW                    60.400 usec
DE                     6.00 usec
TE                    297.2 K
D1                 1.00000000 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                      1H
P1                     13.00 usec
PL1                    -5.40 dB
PL1W            23.42892075 W
SFO1           400.1324710 MHz
SI                        32768
SF             400.1300047 MHz
WDW                       EM
SSB                        0
LB                      0.30 Hz
GB                         0
PC                      1.00
```

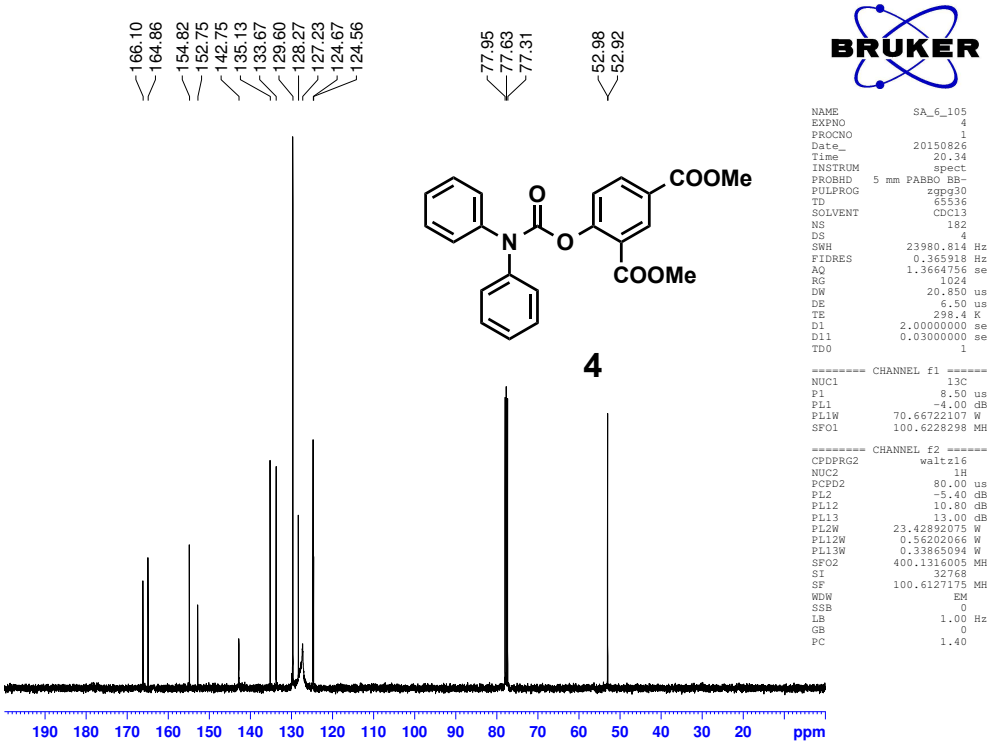


BRUKER

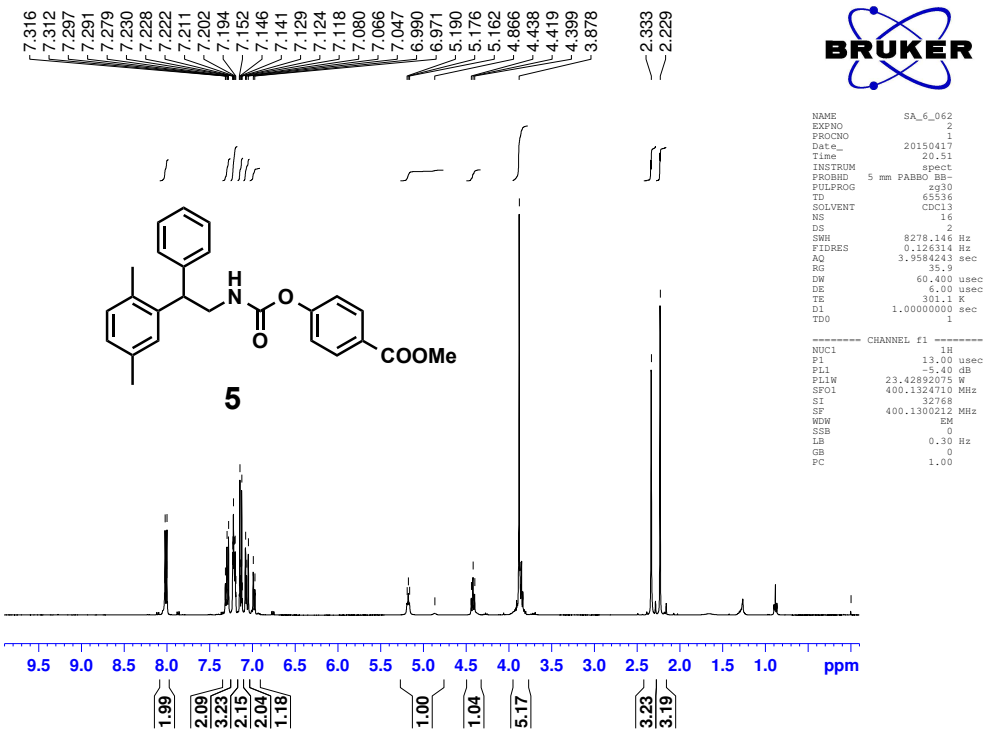
```
NAME                SA_4_159
EXPNO                      2
PROCNO                     1
Date_               20150827
Time                   21.38
INSTRUM                spect
PROBHD    5 mm PABBO BB-
PULPROG             zgpg30
TD                    65536
SOLVENT               CDCl3
NS                        18
DS                         4
SWH               23980.814 Hz
FIDRES             0.365918 Hz
AQ                 1.3664756 se
RG                     812.7
DW                    20.850 us
DE                     6.50 us
TE                    297.7 K
D1                 2.00000000 se
D11                0.03000000 se
TD0                        1

======== CHANNEL f1 ======
NUC1                      13C
P1                      8.50 us
PL1                    -4.00 dB
PL1W           70.66722107 W
SFO1          100.6228298 MH

======== CHANNEL f2 ======
CPDPRG2             waltz16
NUC2                      1H
PCPD2                 80.00 us
PL2                    -5.40 dB
PL12                   10.80 dB
PL13                   13.00 dB
PL2W           23.42892075 W
PL12W           0.56202066 W
PL13W           0.33865094 W
SFO2          400.1316005 MH
SI                        32768
SF            100.6127161 MH
WDW                       EM
SSB                        0
LB                      1.00 Hz
GB                         0
PC                      1.40
```

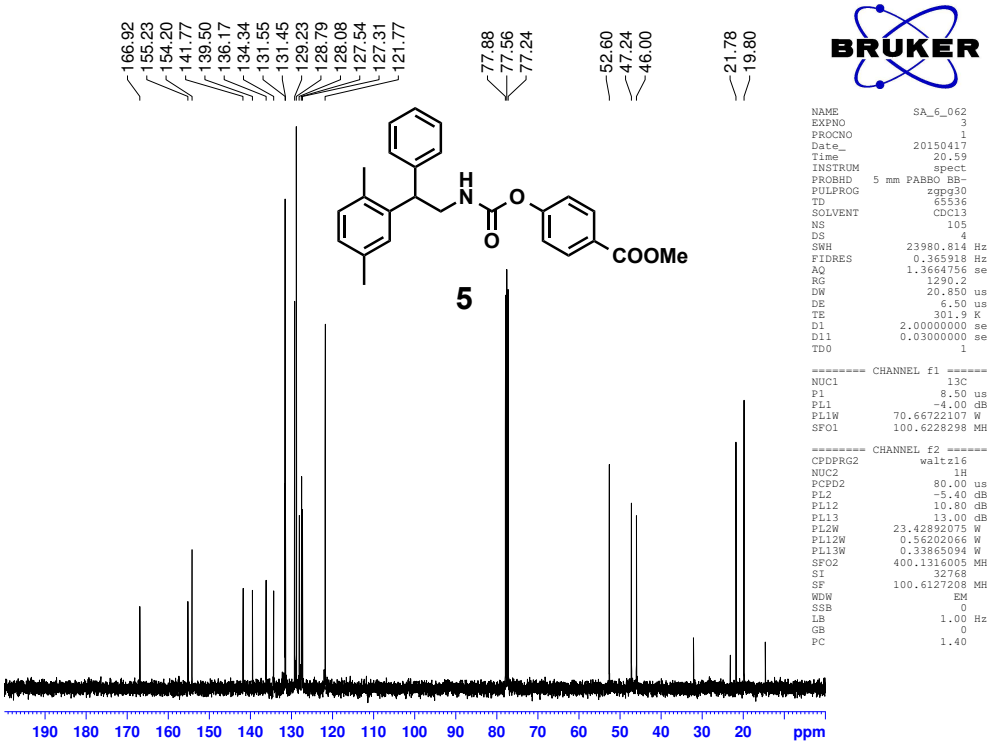


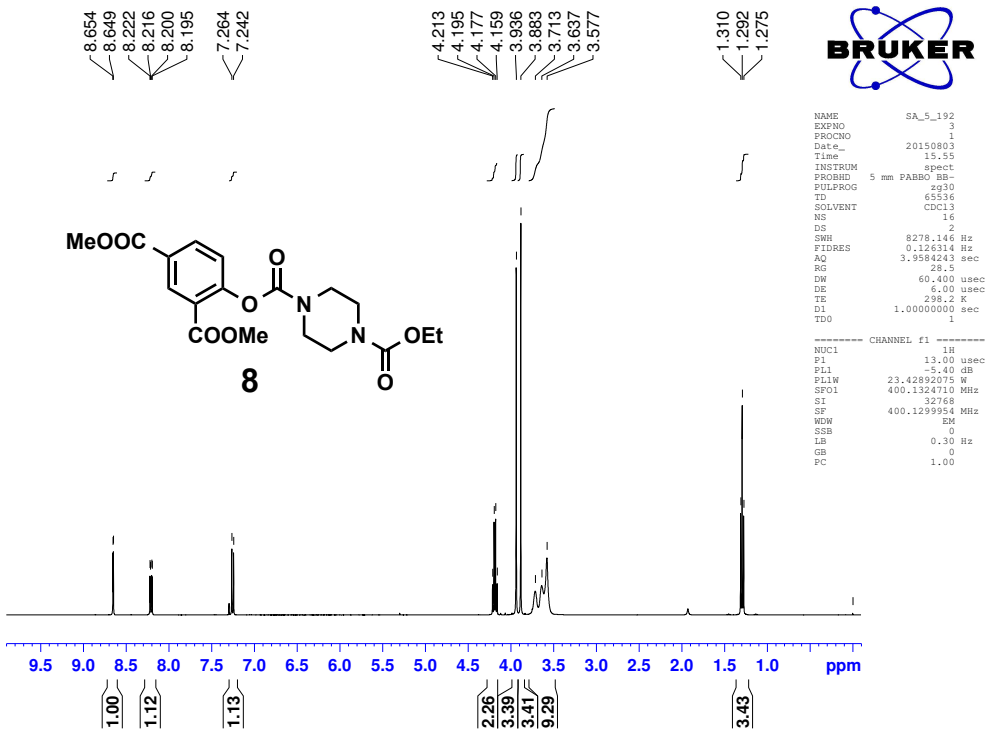

```
NAME            SA_6_105
EXPNO                  2
PROCNO                 1
Date_           20150618
Time               11.04
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH           8278.146 Hz
FIDRES        0.126314 Hz
AQ            3.9584243 sec
RG                  71.8
DW               60.400 usec
DE                6.00 usec
TE                298.3 K
D1           1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                   1H
P1                 13.00 usec
PL1                -5.40 dB
PL1W        23.42892075 W
SFO1       400.1324710 MHz
SI                 32768
SF         400.1300123 MHz
WDW                   EM
SSB                    0
LB                 0.30 Hz
GB                     0
PC                 1.00
```




```
NAME            SA_6_105
EXPNO                  4
PROCNO                 1
Date_           20150826
Time               20.34
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG            zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   182
DS                     4
SWH          23980.814 Hz
FIDRES        0.365918 Hz
AQ            1.3664756 se
RG                  1024
DW               20.850 us
DE                6.50 us
TE                298.4 K
D1           2.00000000 se
D11          0.03000000 se
TD0                    1

======== CHANNEL f1 ========
NUC1                  13C
P1                 8.50 us
PL1                -4.00 dB
PL1W        70.66722107 W
SFO1       100.6228298 MH

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2              80.00 us
PL2                -5.40 dB
PL12               10.80 dB
PL13               13.00 dB
PL2W        23.42892075 W
PL12W        0.56202066 W
PL13W        0.33865094 W
SFO2       400.1316005 MH
SI                 32768
SF         100.6127175 MH
WDW                   EM
SSB                    0
LB                 1.00 Hz
GB                     0
PC                 1.40
```


7.316
7.312
7.297
7.291
7.279
7.230
7.228
7.222
7.211
7.202
7.194
7.152
7.146
7.141
7.129
7.124
7.118
7.080
7.066
7.047
6.990
6.971
5.190
5.176
5.162
4.866
4.438
4.419
4.399
3.878
2.333
2.229
BRUKER
NAME SA_6_062
EXPNO 2
PROCNO 1
Date_ 20150417
Time 20.51
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDC13
NS 16
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 35.9
DW 60.400 usec
DE 6.00 usec
TE 301.1 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.00 usec
PL1 -5.40 dB
PL1W 23.42892075 W
SFO1 400.1324710 MHz
SI 32768
SF 400.1300212 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
H
N
O
O
O
COOMe
5
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
1.99
2.09
3.23
2.15
2.04
1.18
1.00
1.04
5.17
3.23
3.19


166.92
155.23
154.20
141.77
139.50
136.17
134.34
131.55
131.45
129.23
128.79
128.08
127.54
127.31
121.77
77.88
77.56
77.24
52.60
47.24
46.00
21.78
19.80
BRUKER
NAME SA_6_062
EXPNO 3
PROCNO 1
Date_ 20150417
Time 20.59
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDC13
NS 105
DS 4
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664756 se
RG 1290.2
DW 20.850 us
DE 6.50 us
TE 301.9 K
D1 2.00000000 se
D11 0.03000000 se
TD0 1
======== CHANNEL f1 ======
NUC1 13C
P1 8.50 us
PL1 -4.00 dB
PL1W 70.66722107 W
SFO1 100.6228298 MH
======== CHANNEL f2 ======
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 us
PL2 -5.40 dB
PL12 10.80 dB
PL13 13.00 dB
PL2W 23.42892075 W
PL12W 0.56202066 W
PL13W 0.33865094 W
SFO2 400.1316005 MH
SI 32768
SF 100.6127208 MH
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
H
N
O
O
O
COOMe
5
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm


8.654
8.649
8.222
8.216
8.200
8.195
7.264
7.242
4.213
4.195
4.177
4.159
3.936
3.883
3.713
3.637
3.577
1.310
1.292
1.275
MeOOC
COOMe
OEt
8
NAME SA_5_192
EXPNO 3
PROCNO 1
Date_ 20150803
Time 15.55
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 28.5
DW 60.400 usec
DE 6.00 usec
TE 298.2 K
D1 1.00000000 sec
TD0 1
CHANNEL f1
NUC1 1H
P1 13.00 usec
PL1 -5.40 dB
PL1W 23.42892075 W
SFO1 400.1324710 MHz
SI 32768
SF 400.1299954 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
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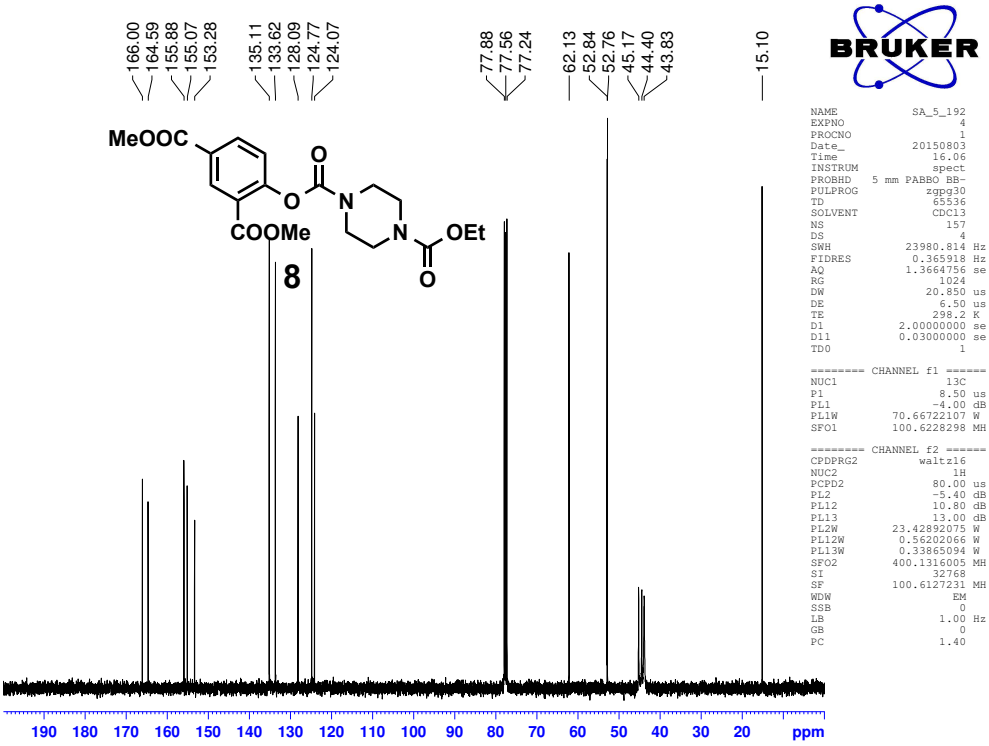
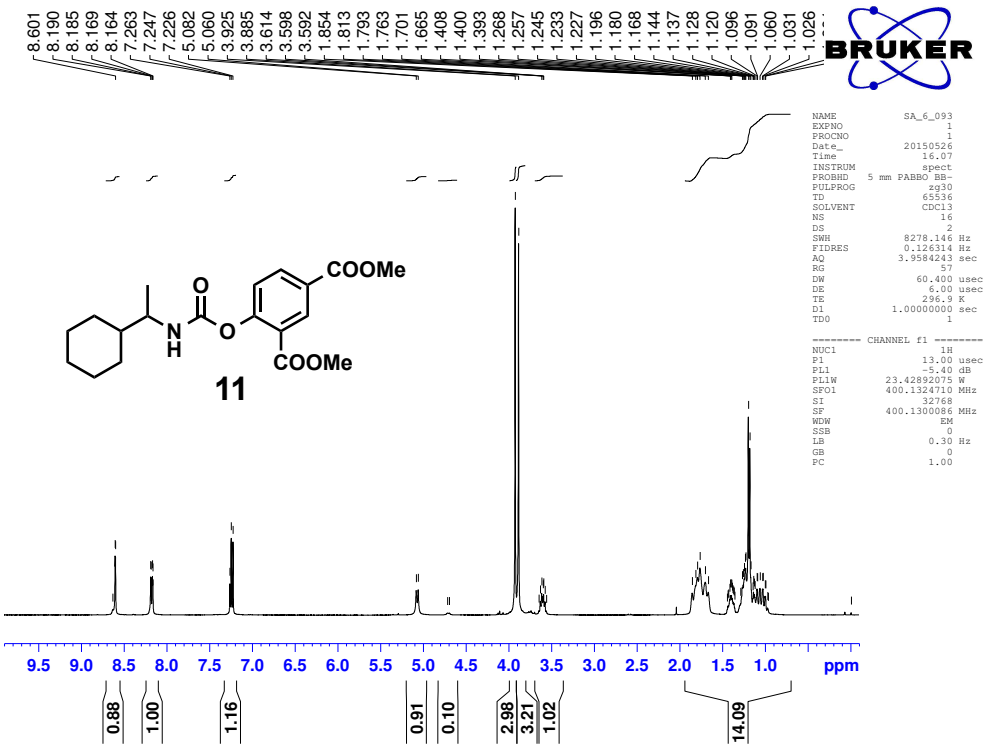
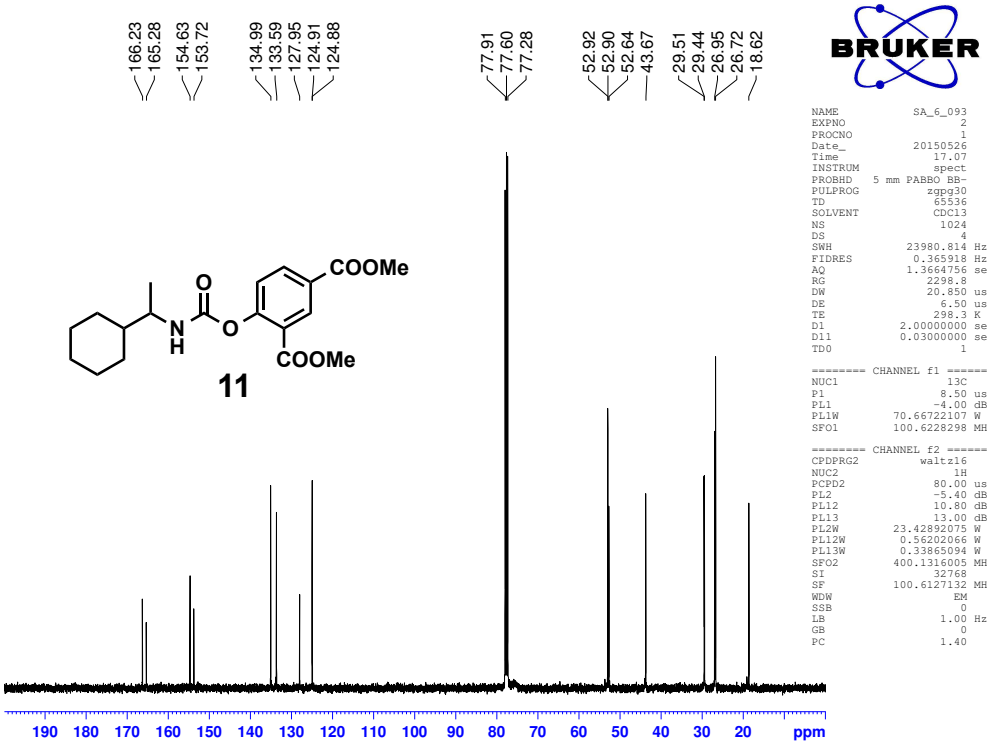
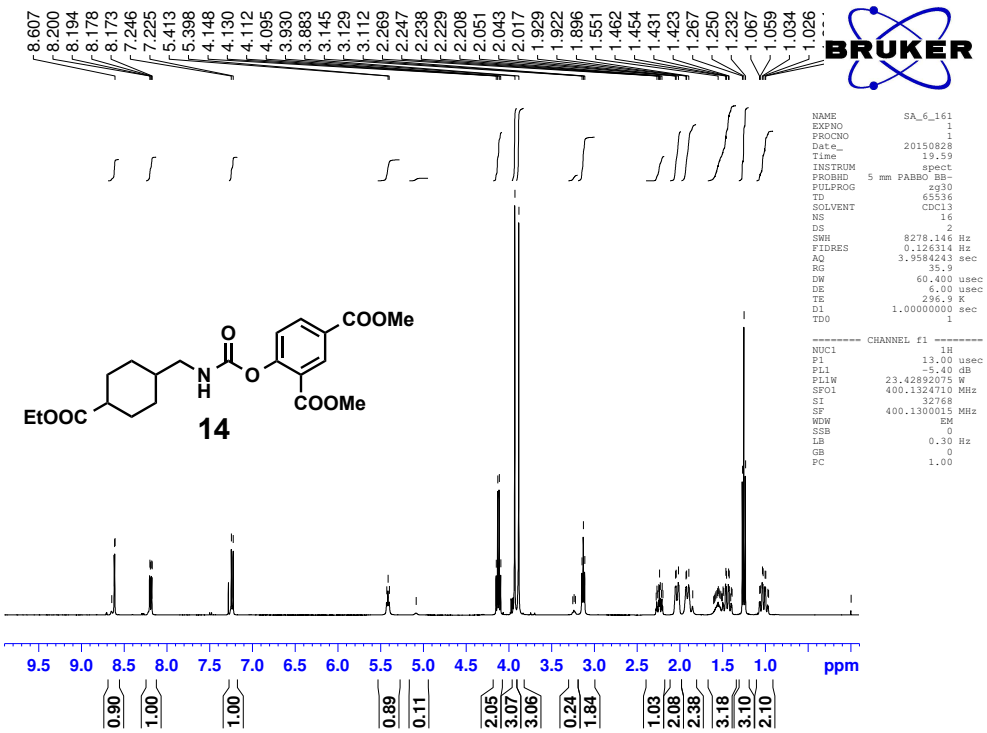
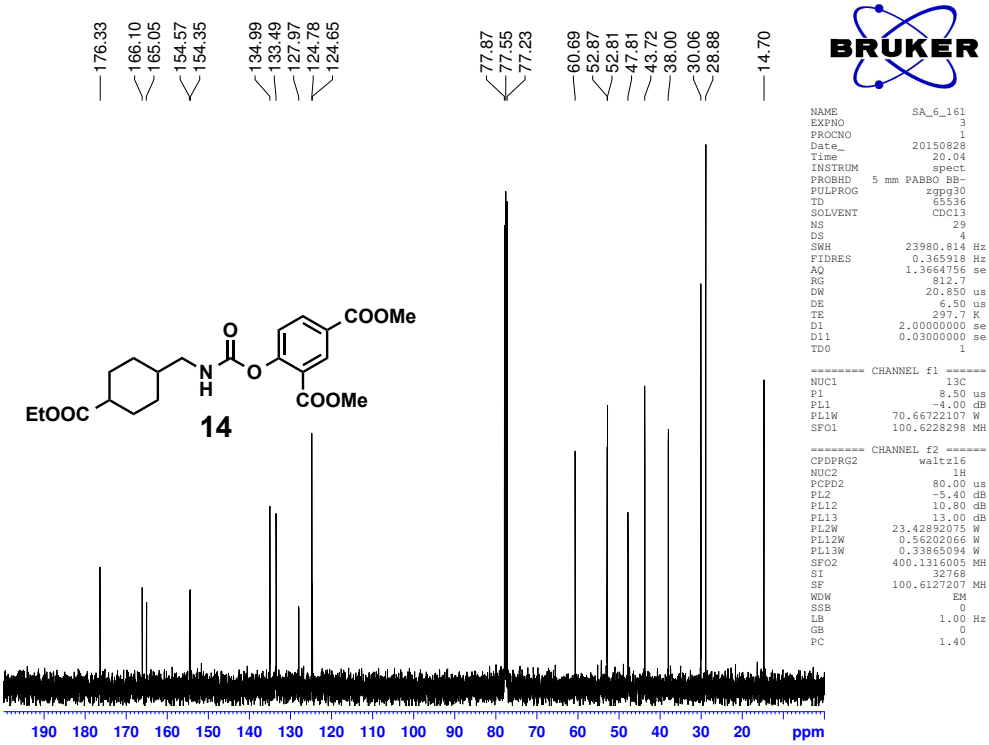
1.12
1.13
2.26
3.39
3.41
9.29
3.43

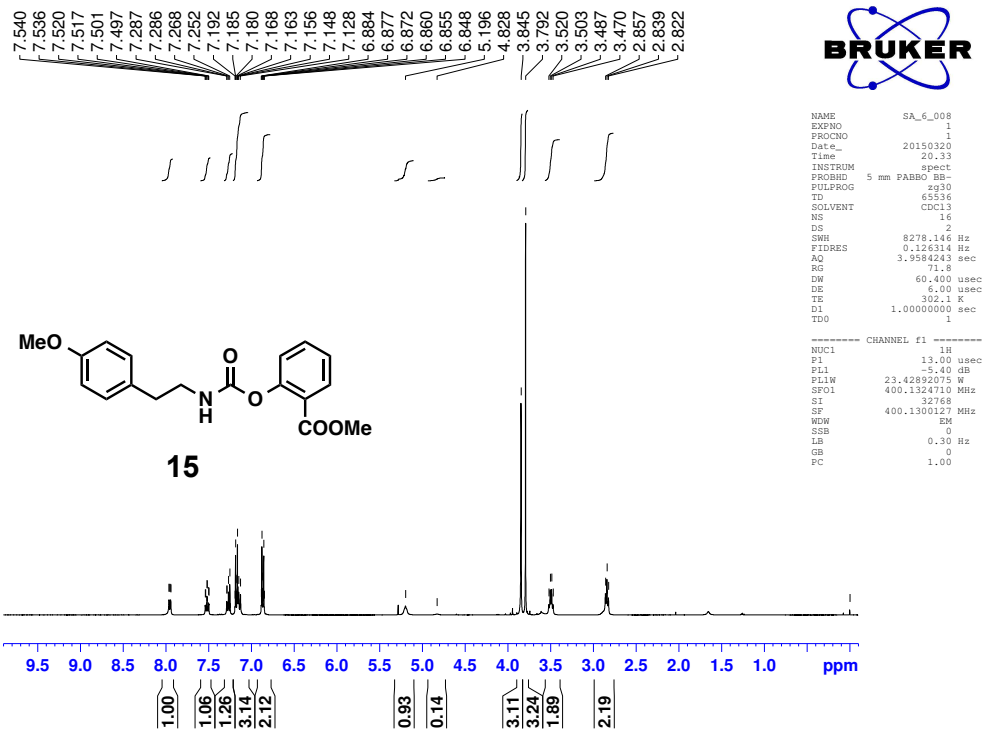

166.00
164.59
155.88
155.07
153.28
135.11
133.62
128.09
124.77
124.07
77.88
77.56
77.24
62.13
52.84
52.76
45.17
44.40
43.83
15.10
MeOOC
COOMe
OEt
8
NAME SA_5_192
EXPNO 4
PROCNO 1
Date_ 20150803
Time 16.06
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 157
DS 4
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664756 se
RG 1024
DW 20.850 us
DE 6.50 us
TE 298.2 K
D1 2.00000000 se
D11 0.03000000 se
TD0 1
CHANNEL f1
NUC1 13C
P1 8.50 us
PL1 -4.00 dB
PL1W 70.66722107 W
SFO1 100.6228298 MH
CHANNEL f2
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 us
PL2 -5.40 dB
PL12 10.80 dB
PL13 13.00 dB
PL2W 23.42892075 W
PL12W 0.56202066 W
PL13W 0.33865094 W
SFO2 400.1316005 MH
SI 32768
SF 100.6127231 MH
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

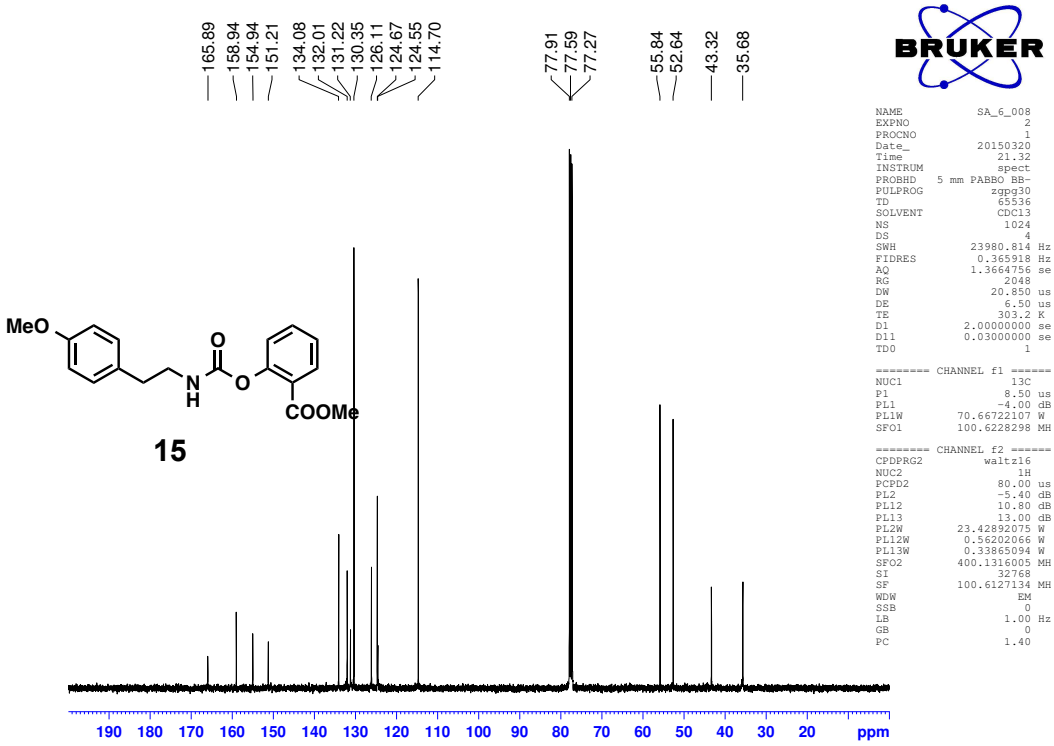

8.601
8.190
8.185
8.169
8.164
7.263
7.247
7.226
5.082
5.060
3.925
3.885
3.614
3.598
3.592
1.854
1.813
1.793
1.763
1.701
1.665
1.408
1.400
1.393
1.268
1.257
1.245
1.233
1.227
1.196
1.180
1.168
1.144
1.137
1.128
1.120
1.096
1.091
1.060
1.031
1.026
BRUKER
NAME SA_6_093
EXPNO 1
PROCNO 1
Date_ 20150526
Time 16.07
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 57
DW 60.400 usec
DE 6.00 usec
TE 296.9 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.00 usec
PL1 -5.40 dB
PL1W 23.42892075 W
SFO1 400.1324710 MHz
SI 32768
SF 400.1300086 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
COOMe
COOMe
11
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
0.88
1.00
1.16
0.91
0.10
2.98
3.21
1.02
14.09

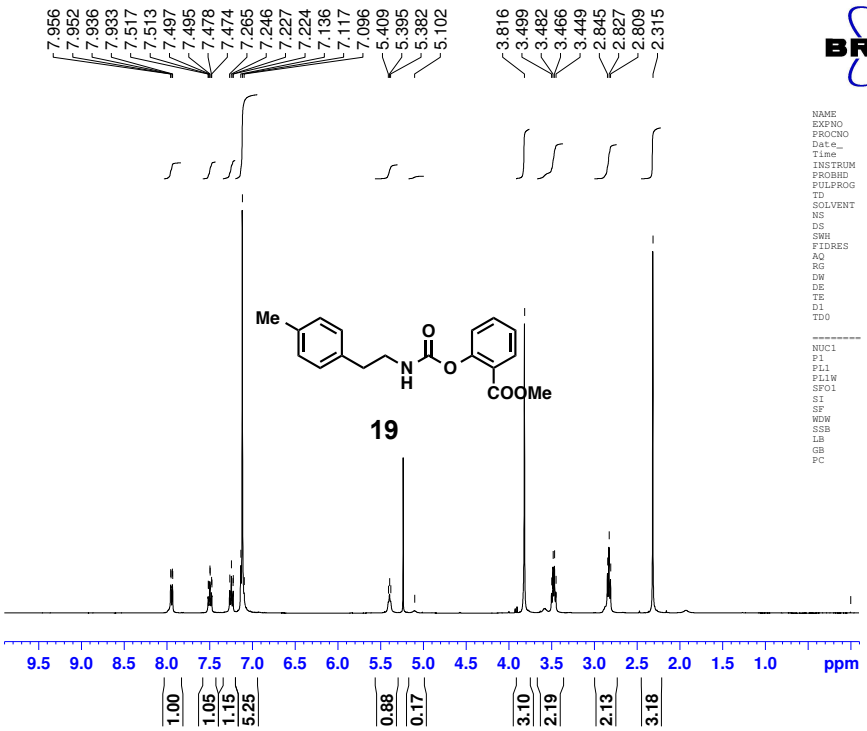

166.23
165.28
154.63
153.72
134.99
133.59
127.95
124.91
124.88
77.91
77.60
77.28
52.92
52.90
52.64
43.67
29.51
29.44
26.95
26.72
18.62
BRUKER
NAME SA_6_093
EXPNO 2
PROCNO 1
Date_ 20150526
Time 17.07
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1024
DS 4
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664756 se
RG 2298.8
DW 20.850 us
DE 6.50 us
TE 298.3 K
D1 2.00000000 se
D11 0.03000000 se
TD0 1
======== CHANNEL f1 ======
NUC1 13C
P1 8.50 us
PL1 -4.00 dB
PL1W 70.66722107 W
SFO1 100.6228298 MH
======== CHANNEL f2 ======
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 us
PL2 -5.40 dB
PL12 10.80 dB
PL13 13.00 dB
PL2W 23.42892075 W
PL12W 0.56202066 W
PL13W 0.33865094 W
SFO2 400.1316005 MH
SI 32768
SF 100.6127132 MH
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
COOMe
COOMe
11
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm


8.607
8.200
8.194
8.178
8.173
7.246
7.225
5.413
5.398
4.148
4.130
4.112
4.095
3.930
3.883
3.145
3.129
3.112
2.269
2.247
2.238
2.229
2.208
2.051
2.043
2.017
1.929
1.922
1.896
1.551
1.462
1.454
1.431
1.423
1.267
1.250
1.232
1.067
1.059
1.034
1.026
BRUKER
COOMe
COOMe
EtOOC
14
NAME SA_6_161
EXPNO 1
PROCNO 1
Date_ 20150828
Time 19.59
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 35.9
DW 60.400 usec
DE 6.00 usec
TE 296.9 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.00 usec
PL1 -5.40 dB
PL1W 23.42892075 W
SFO1 400.1324710 MHz
SI 32768
SF 400.1300015 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
0.90 1.00 1.00 0.89 0.11 2.05 3.07 3.06 0.24 1.84 1.03 2.08 2.38 3.18 3.10 2.10


176.33
166.10
165.05
154.57
154.35
134.99
133.49
127.97
124.78
124.65
77.87
77.55
77.23
60.69
52.87
52.81
47.81
43.72
38.00
30.06
28.88
14.70
BRUKER
COOMe
COOMe
EtOOC
14
NAME SA_6_161
EXPNO 3
PROCNO 1
Date_ 20150828
Time 20.04
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 29
DS 4
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664756 se
RG 812.7
DW 20.850 us
DE 6.50 us
TE 297.7 K
D1 2.00000000 se
D11 0.03000000 se
TD0 1
======== CHANNEL f1 ======
NUC1 13C
P1 8.50 us
PL1 -4.00 dB
PL1W 70.66722107 W
SFO1 100.6228298 MH
======== CHANNEL f2 ======
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 us
PL2 -5.40 dB
PL12 10.80 dB
PL13 13.00 dB
PL2W 23.42892075 W
PL12W 0.56202066 W
PL13W 0.33865094 W
SFO2 400.1316005 MH
SI 32768
SF 100.6127207 MH
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

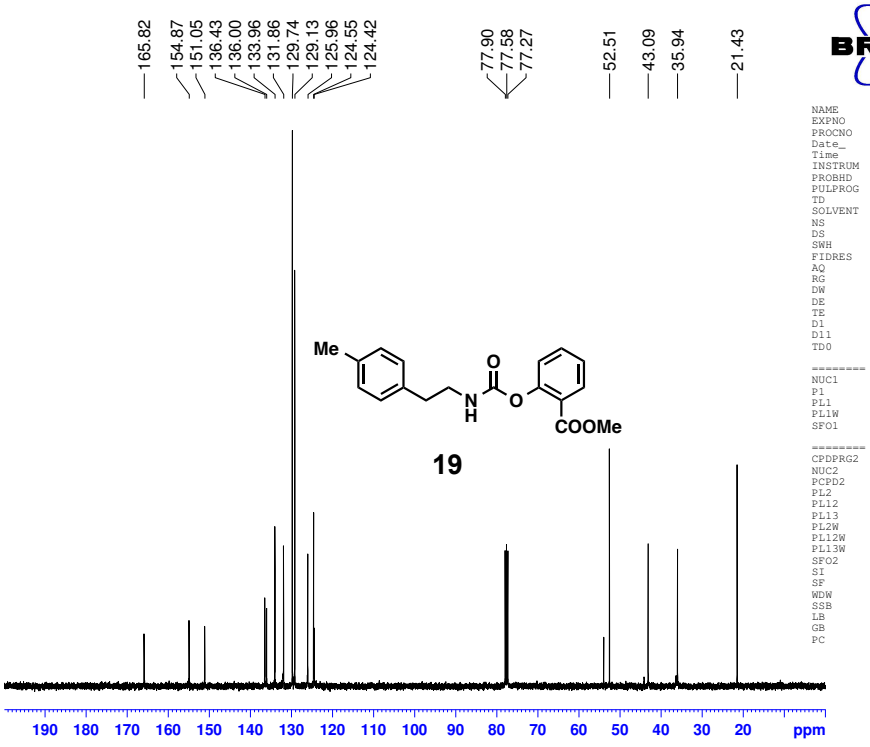

7.540
7.536
7.520
7.517
7.501
7.497
7.287
7.286
7.268
7.252
7.192
7.185
7.180
7.168
7.163
7.156
7.148
7.128
6.884
6.877
6.872
6.860
6.855
6.848
5.196
4.828
3.845
3.792
3.520
3.503
3.487
3.470
2.857
2.839
2.822
BRUKER
NAME SA_6_008
EXPNO 1
PROCNO 1
Date_ 20150320
Time 20.33
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDC13
NS 16
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 71.8
DW 60.400 usec
DE 6.00 usec
TE 302.1 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.00 usec
PL1 -5.40 dB
PL1W 23.42892075 W
SFO1 400.1324710 MHz
SI 32768
SF 400.1300127 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
MeO
O
N
H
O
O
COOMe
15
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
1.00
1.06
1.26
3.14
2.12
0.93
0.14
3.11
3.24
1.89
2.19


165.89
158.94
154.94
151.21
134.08
132.01
131.22
130.35
126.11
124.67
124.55
114.70
77.91
77.59
77.27
55.84
52.64
43.32
35.68
BRUKER
NAME SA_6_008
EXPNO 2
PROCNO 1
Date_ 20150320
Time 21.32
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDC13
NS 1024
DS 4
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664756 se
RG 2048
DW 20.850 us
DE 6.50 us
TE 303.2 K
D1 2.00000000 se
D11 0.03000000 se
TD0 1
======== CHANNEL f1 ======
NUC1 13C
P1 8.50 us
PL1 -4.00 dB
PL1W 70.66722107 W
SFO1 100.6228298 MH
======== CHANNEL f2 ======
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 us
PL2 -5.40 dB
PL12 10.80 dB
PL13 13.00 dB
PL2W 23.42892075 W
PL12W 0.56202066 W
PL13W 0.33865094 W
SFO2 400.1316005 MH
SI 32768
SF 100.6127134 MH
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
MeO
O
N
H
O
O
COOMe
15
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm



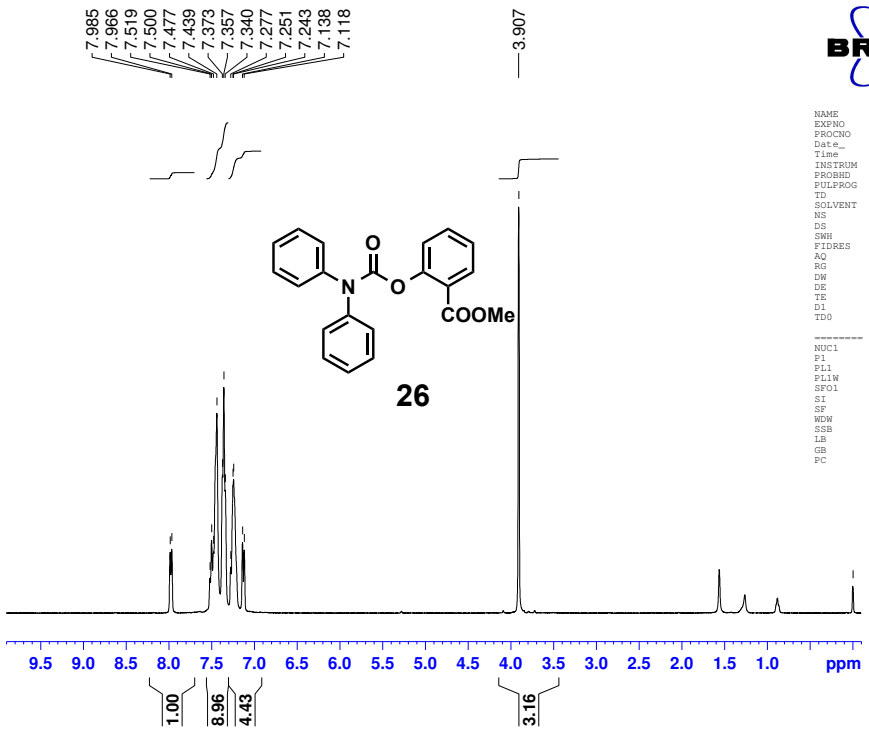
BRUKER

```
NAME              SA_6_116
EXPNO                    1
PROCNO                   1
Date_             20150826
Time                 20.13
INSTRUM              spect
PROBHD   5 mm PABBO BB-
PULPROG               zg30
TD                   65536
SOLVENT              CDCl3
NS                      16
DS                       2
SWH              8278.146 Hz
FIDRES           0.126314 Hz
AQ               3.9584243 sec
RG                      18
DW                 60.400 usec
DE                  6.00 usec
TE                 297.4 K
D1              1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                    1H
P1                   13.00 usec
PL1                  -5.40 dB
PL1W           23.42892075 W
SFO1          400.1324710 MHz
SI                   32768
SF            400.1300241 MHz
WDW                     EM
SSB                      0
LB                  0.30 Hz
GB                       0
PC                    1.00
```



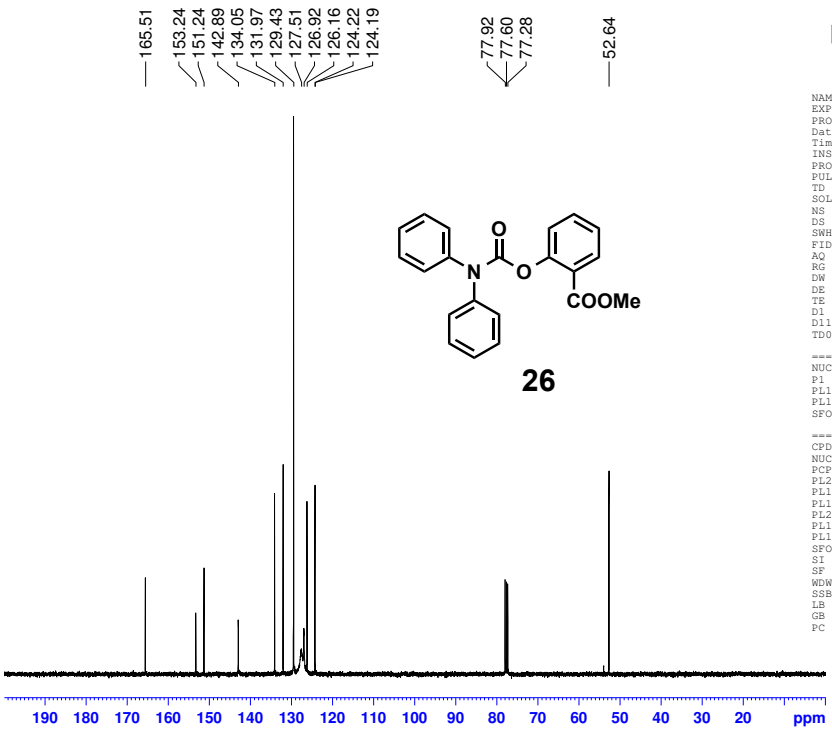
BRUKER

```
NAME              SA_6_116
EXPNO                    2
PROCNO                   1
Date_             20150826
Time                 20.18
INSTRUM              spect
PROBHD   5 mm PABBO BB-
PULPROG             zgpg30
TD                   65536
SOLVENT              CDCl3
NS                      66
DS                       4
SWH              23980.814 Hz
FIDRES           0.365918 Hz
AQ               1.3664756 se
RG                   812.7
DW                 20.850 us
DE                  6.50 us
TE                 298.1 K
D1              2.00000000 se
D11             0.03000000 se
TD0                      1

======== CHANNEL f1 ======
NUC1                   13C
P1                   8.50 us
PL1                 -4.00 dB
PL1W          70.66722107 W
SFO1         100.6228298 MH

======== CHANNEL f2 ======
CPDPRG2             waltz16
NUC2                   1H
PCPD2               80.00 us
PL2                 -5.40 dB
PL12                10.80 dB
PL13                13.00 dB
PL2W          23.42892075 W
PL12W          0.56202066 W
PL13W          0.33865094 W
SFO2         400.1316005 MH
SI                   32768
SF           100.6127315 MH
WDW                     EM
SSB                      0
LB                  1.00 Hz
GB                       0
PC                    1.40
```



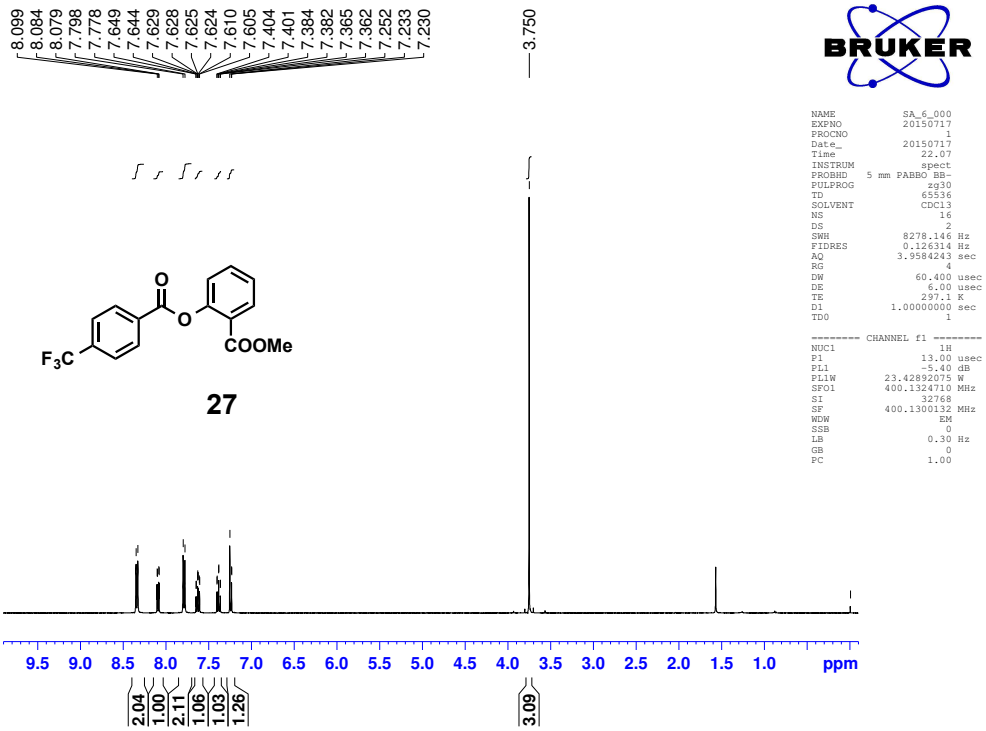
BRUKER

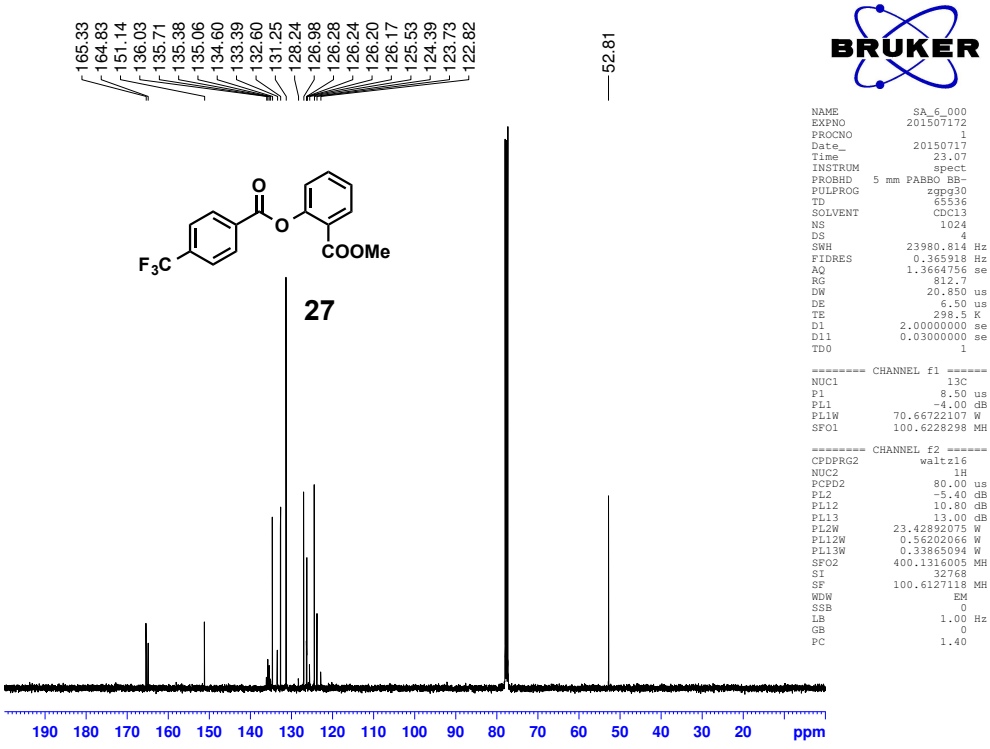
```
NAME            May17-2013
EXPNO                    1
PROCNO                   1
Date_             20130517
Time                 15.08
INSTRUM              spect
PROBHD   5 mm PABBO BB-
PULPROG               zg30
TD                   65536
SOLVENT              CDCl3
NS                      16
DS                       2
SWH              8278.146 Hz
FIDRES           0.126314 Hz
AQ               3.9584243 sec
RG                       4
DW                  60.400 usec
DE                   6.00 usec
TE                  296.4 K
D1               1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                    1H
P1                   13.00 usec
PL1                  -5.40 dB
PL1W           23.42892075 W
SFO1           400.1324710 MHz
SI                    32768
SF             400.1300158 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.00
```

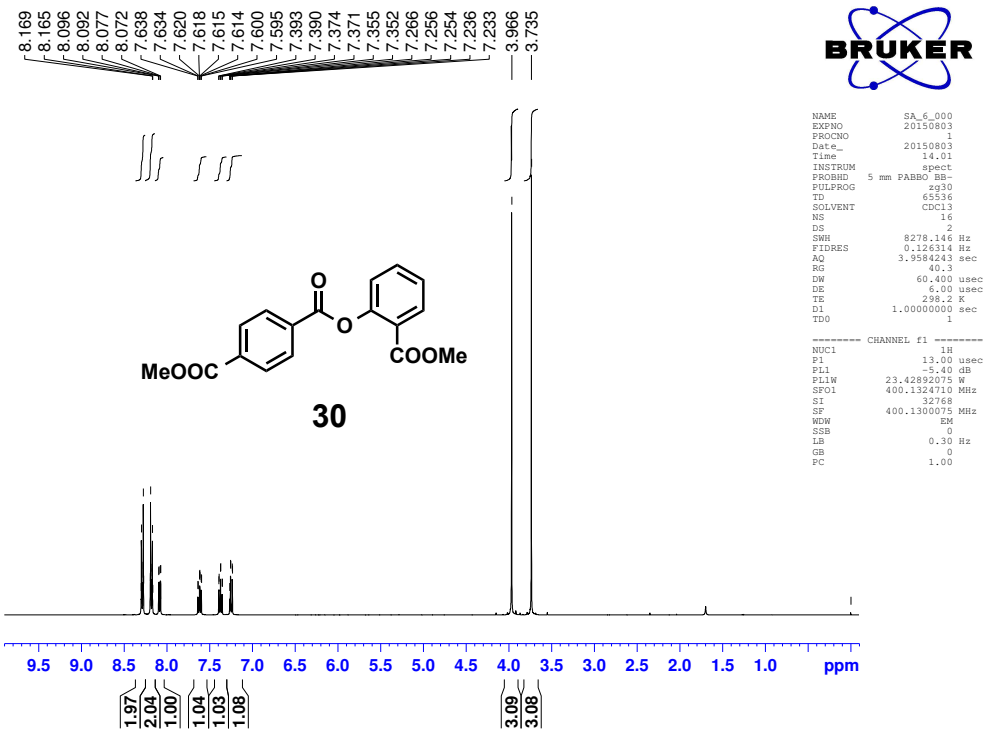


BRUKER

```
NAME            May18-2013
EXPNO                    2
PROCNO                   1
Date_             20130518
Time                 16.06
INSTRUM              spect
PROBHD   5 mm PABBO BB-
PULPROG             zgpg30
TD                   65536
SOLVENT              CDCl3
NS                      65
DS                       4
SWH             26178.010 Hz
FIDRES           0.399445 Hz
AQ               1.2517875 se
RG                  1625.5
DW                  19.100 us
DE                   6.50 us
TE                  297.6 K
D1               2.00000000 se
D11              0.03000000 se
TD0                      1

======== CHANNEL f1 ======
NUC1                   13C
P1                    8.50 us
PL1                  -4.00 dB
PL1W           70.66722107 W
SFO1           100.6228298 MH

======== CHANNEL f2 ======
CPDPRG2             waltz16
NUC2                    1H
PCPD2                80.00 us
PL2                  -5.40 dB
PL12                 10.80 dB
PL13                 13.00 dB
PL2W           23.42892075 W
PL12W           0.56202066 W
PL13W           0.33865094 W
SFO2           400.1316005 MH
SI                    32768
SF             100.6127339 MH
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.40
```

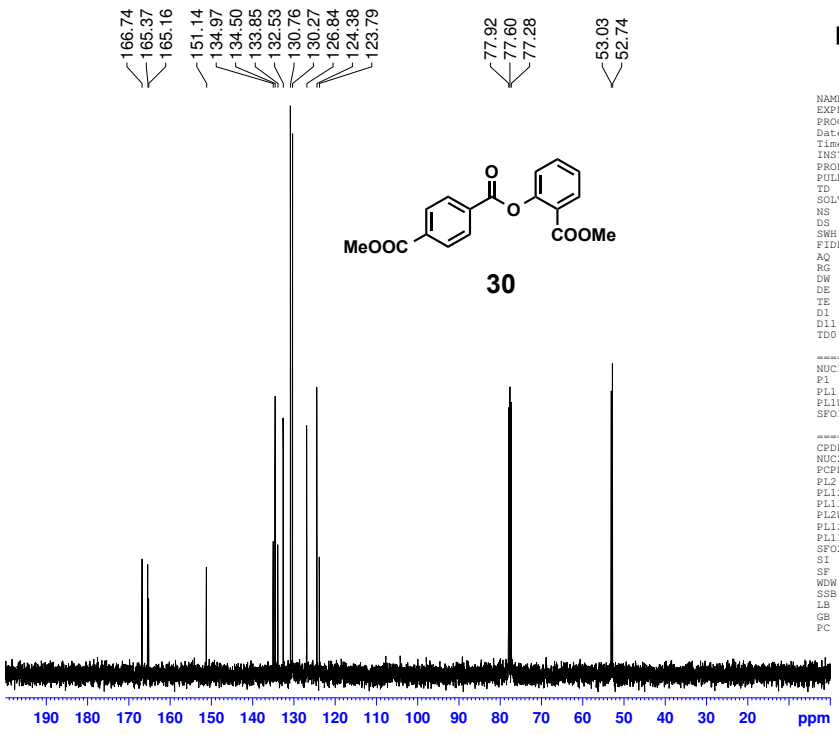

8.099
8.084
8.079
7.798
7.778
7.649
7.644
7.629
7.628
7.625
7.624
7.610
7.605
7.404
7.401
7.384
7.382
7.365
7.362
7.252
7.233
7.230
3.750
BRUKER
NAME SA_6_000
EXPNO 20150717
PROCNO 1
Date_ 20150717
Time 22.07
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 4
DW 60.400 usec
DE 6.00 usec
TE 297.1 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.00 usec
PL1 -5.40 dB
PL1W 23.42892075 W
SFO1 400.1324710 MHz
SI 32768
SF 400.1300132 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
O
O
F3C
COOMe
27
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
2.04
1.00
2.11
1.06
1.03
1.26
3.09


165.33
164.83
151.14
136.03
135.71
135.38
135.06
134.60
133.39
132.60
131.25
128.24
126.98
126.28
126.24
126.20
126.17
125.53
124.39
123.73
122.82
52.81
BRUKER
NAME SA_6_000
EXPNO 201507172
PROCNO 1
Date_ 20150717
Time 23.07
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1024
DS 4
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664756 se
RG 812.7
DW 20.850 us
DE 6.50 us
TE 298.5 K
D1 2.00000000 se
D11 0.03000000 se
TD0 1
======== CHANNEL f1 ======
NUC1 13C
P1 8.50 us
PL1 -4.00 dB
PL1W 70.66722107 W
SFO1 100.6228298 MH
======== CHANNEL f2 ======
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 us
PL2 -5.40 dB
PL12 10.80 dB
PL13 13.00 dB
PL2W 23.42892075 W
PL12W 0.56202066 W
PL13W 0.33865094 W
SFO2 400.1316005 MH
SI 32768
SF 100.6127118 MH
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
O
O
F3C
COOMe
27
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm



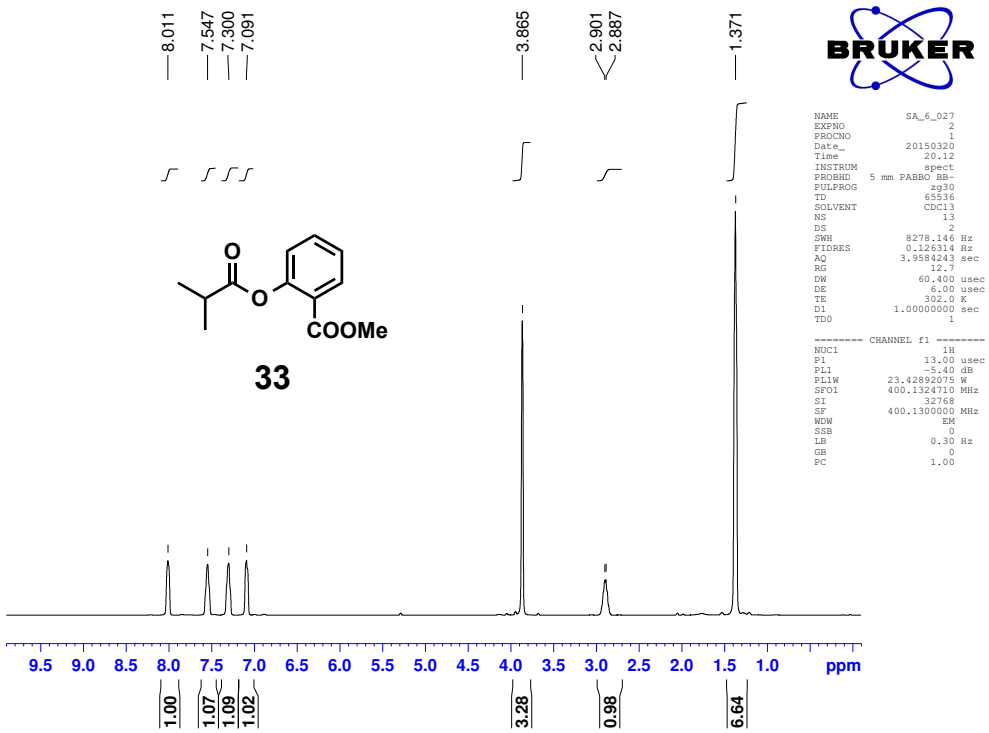
BRUKER

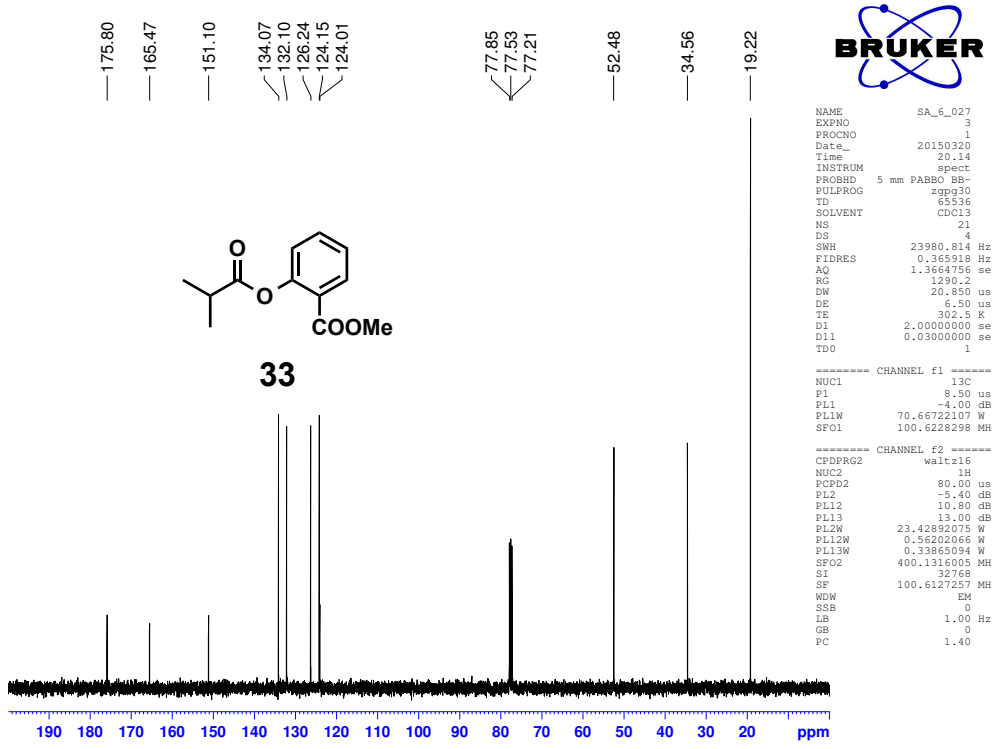
```
NAME            SA_6_000
EXPNO           20150803
PROCNO                1
Date_          20150803
Time              14.01
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH            8278.146 Hz
FIDRES         0.126314 Hz
AQ             3.9584243 sec
RG                  40.3
DW                60.400 usec
DE                 6.00 usec
TE                298.2 K
D1             1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 13.00 usec
PL1                -5.40 dB
PL1W         23.42892075 W
SFO1         400.1324710 MHz
SI                 32768
SF           400.1300075 MHz
WDW                   EM
SSB                    0
LB                 0.30 Hz
GB                     0
PC                 1.00
```

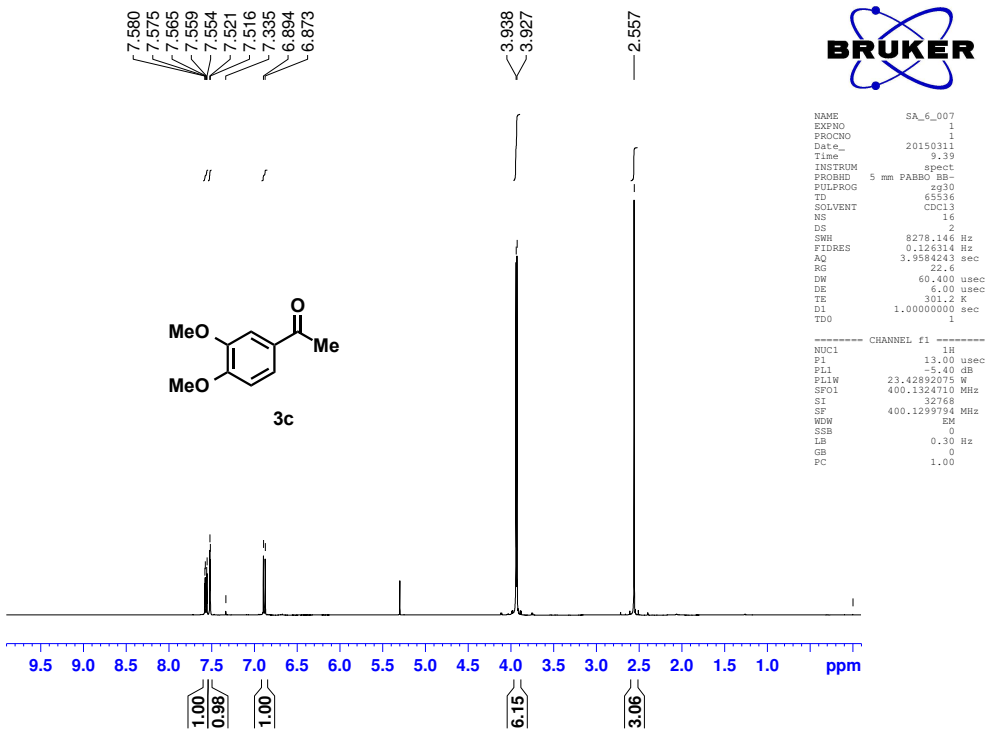


BRUKER

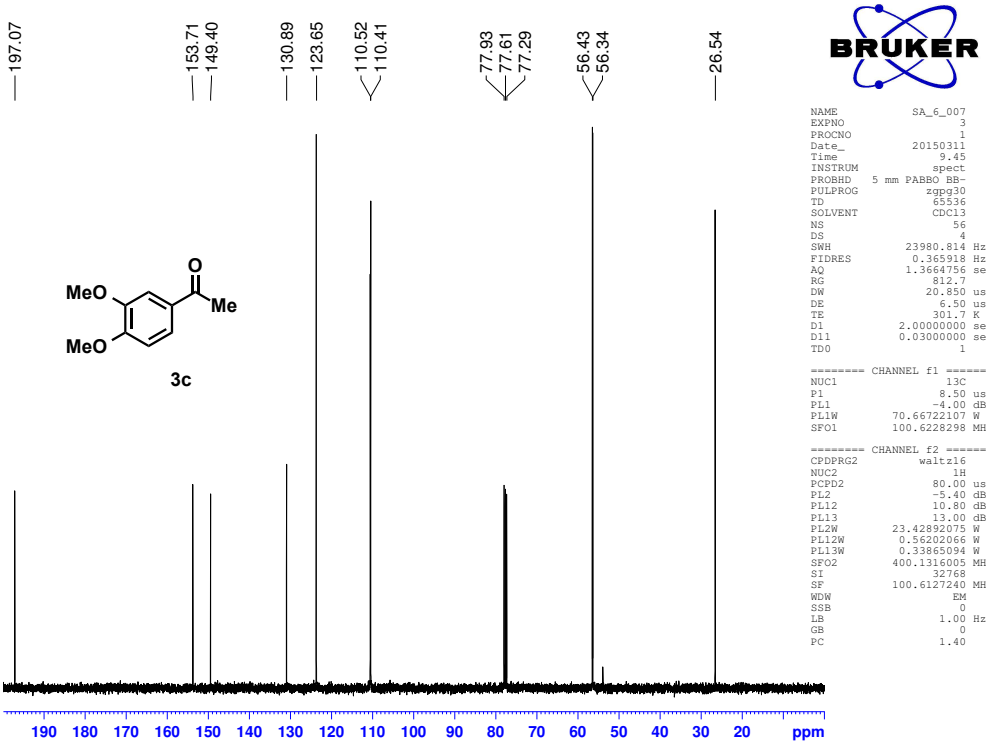
```
NAME            SA_6_000
EXPNO          201508032
PROCNO                1
Date_          20150803
Time              14.05
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                    22
DS                     4
SWH           23980.814 Hz
FIDRES         0.365918 Hz
AQ             1.3664756 se
RG                812.7
DW                20.850 us
DE                 6.50 us
TE                298.2 K
D1             2.00000000 se
D11            0.03000000 se
TD0                    1

======== CHANNEL f1 ======
NUC1                 13C
P1                 8.50 us
PL1                -4.00 dB
PL1W         70.66722107 W
SFO1         100.6228298 MH

======== CHANNEL f2 ======
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 us
PL2                -5.40 dB
PL12               10.80 dB
PL13               13.00 dB
PL2W         23.42892075 W
PL12W         0.56202066 W
PL13W         0.33865094 W
SFO2         400.1316005 MH
SI                 32768
SF           100.6127161 MH
WDW                   EM
SSB                    0
LB                 1.00 Hz
GB                     0
PC                 1.40
```


8.011
7.547
7.300
7.091
3.865
2.901
2.887
1.371
O
O
COOMe
33
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
1.00
1.07
1.09
1.02
3.28
0.98
6.64
BRUKER
NAME SA_6_027
EXPNO 2
PROCNO 1
Date_ 20150320
Time 20.12
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 13
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 12.7
DW 60.400 usec
DE 6.00 usec
TE 302.0 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.00 usec
PL1 -5.40 dB
PL1W 23.42892075 W
SFO1 400.1324710 MHz
SI 32768
SF 400.1300000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

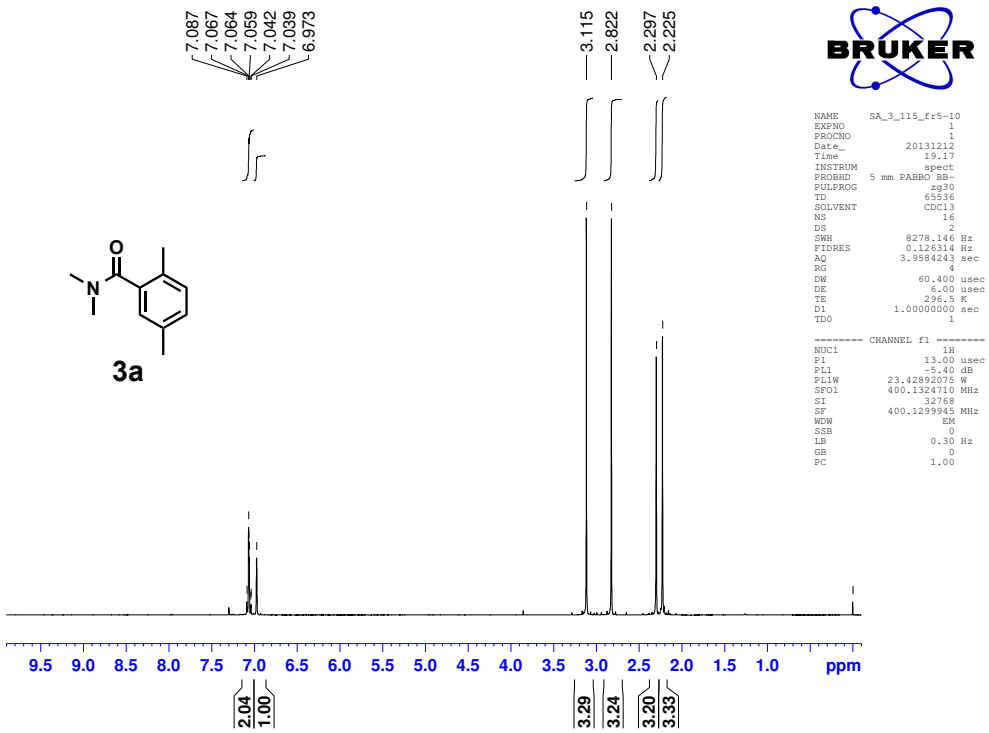

175.80
165.47
151.10
134.07
132.10
126.24
124.15
124.01
77.85
77.53
77.21
52.48
34.56
19.22
O
O
COOMe
33
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm
BRUKER
NAME SA_6_027
EXPNO 3
PROCNO 1
Date_ 20150320
Time 20.14
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 21
DS 4
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664756 se
RG 1290.2
DW 20.850 us
DE 6.50 us
TE 302.5 K
D1 2.00000000 se
D11 0.03000000 se
TD0 1
======== CHANNEL f1 ======
NUC1 13C
P1 8.50 us
PL1 -4.00 dB
PL1W 70.66722107 W
SFO1 100.6228298 MH
======== CHANNEL f2 ======
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 us
PL2 -5.40 dB
PL12 10.80 dB
PL13 13.00 dB
PL2W 23.42892075 W
PL12W 0.56202066 W
PL13W 0.33865094 W
SFO2 400.1316005 MH
SI 32768
SF 100.6127257 MH
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40



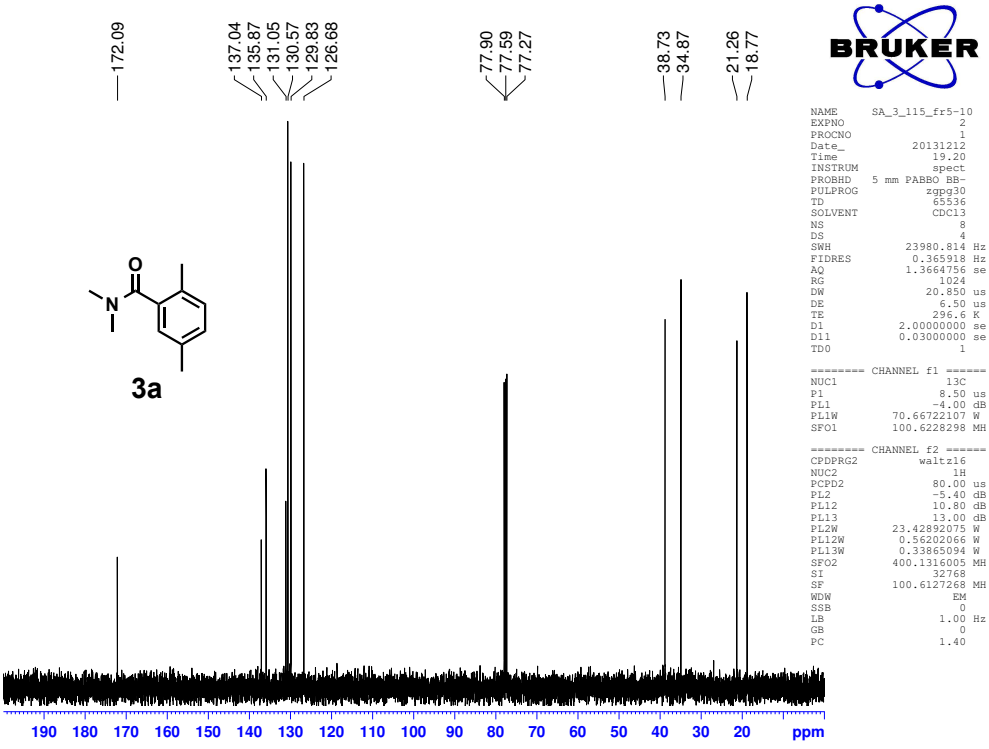

```
NAME              SA_6_007
EXPNO                    1
PROCNO                   1
Date_             20150311
Time                 9.39
INSTRUM             spect
PROBHD    5 mm PABBO BB-
PULPROG               zg30
TD                   65536
SOLVENT              CDCl3
NS                      16
DS                       2
SWH              8278.146 Hz
FIDRES           0.126314 Hz
AQ               3.9584243 sec
RG                    22.6
DW                  60.400 usec
DE                   6.00 usec
TE                  301.2 K
D1               1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                    1H
P1                   13.00 usec
PL1                  -5.40 dB
PL1W          23.42892075 W
SFO1          400.1324710 MHz
SI                   32768
SF            400.1299794 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.00
```



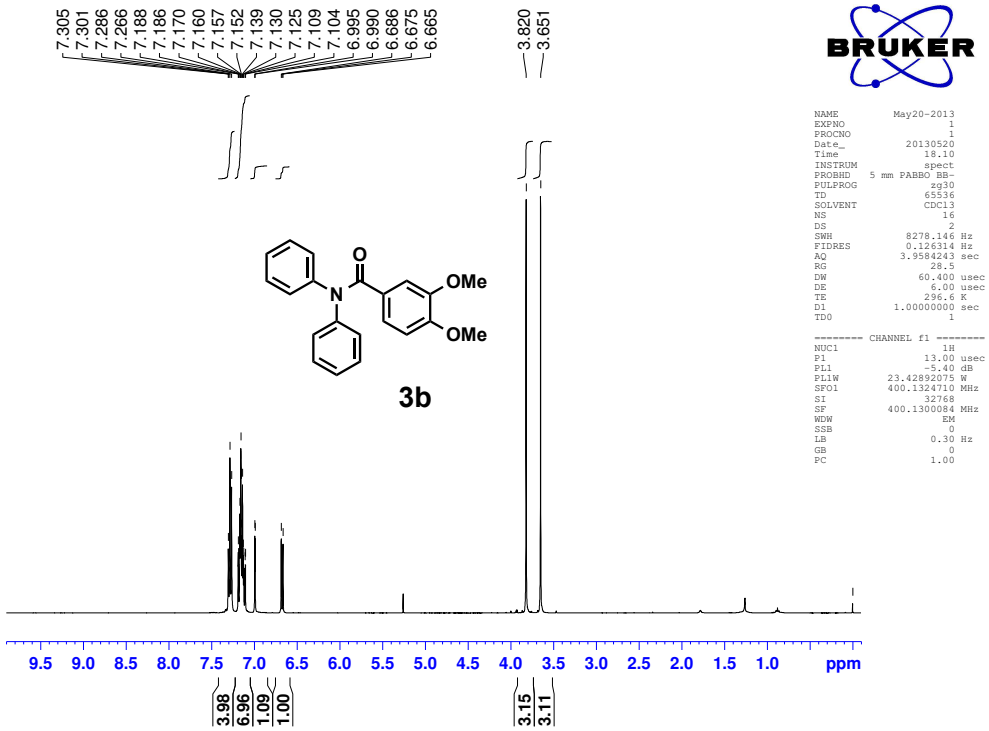

```
NAME              SA_6_007
EXPNO                    3
PROCNO                   1
Date_             20150311
Time                 9.45
INSTRUM             spect
PROBHD    5 mm PABBO BB-
PULPROG             zgpg30
TD                   65536
SOLVENT              CDCl3
NS                      56
DS                       4
SWH             23980.814 Hz
FIDRES           0.365918 Hz
AQ               1.3664756 se
RG                   812.7
DW                  20.850 us
DE                   6.50 us
TE                  301.7 K
D1               2.00000000 se
D11              0.03000000 se
TD0                      1

======== CHANNEL f1 ======
NUC1                   13C
P1                    8.50 us
PL1                  -4.00 dB
PL1W         70.66722107 W
SFO1         100.6228298 MH

======== CHANNEL f2 ======
CPDPRG2            waltz16
NUC2                    1H
PCPD2                80.00 us
PL2                  -5.40 dB
PL12                 10.80 dB
PL13                 13.00 dB
PL2W         23.42892075 W
PL12W         0.56202066 W
PL13W         0.33865094 W
SFO2         400.1316005 MH
SI                   32768
SF           100.6127240 MH
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.40
```




```
NAME        SA_3_115_fr5-10
EXPNO                     1
PROCNO                    1
Date_              20131212
Time                  19.17
INSTRUM               spect
PROBHD    5 mm PABBO BB-
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       16
DS                        2
SWH               8278.146 Hz
FIDRES            0.126314 Hz
AQ                3.9584243 sec
RG                        4
DW                   60.400 usec
DE                    6.00 usec
TE                   296.5 K
D1                1.00000000 sec
TD0                       1

======== CHANNEL f1 =======
NUC1                    1H
P1                   13.00 usec
PL1                  -5.40 dB
PL1W            23.42892075 W
SFO1           400.1324710 MHz
SI                    32768
SF             400.1299945 MHz
WDW                      EM
SSB                       0
LB                     0.30 Hz
GB                        0
PC                     1.00
```

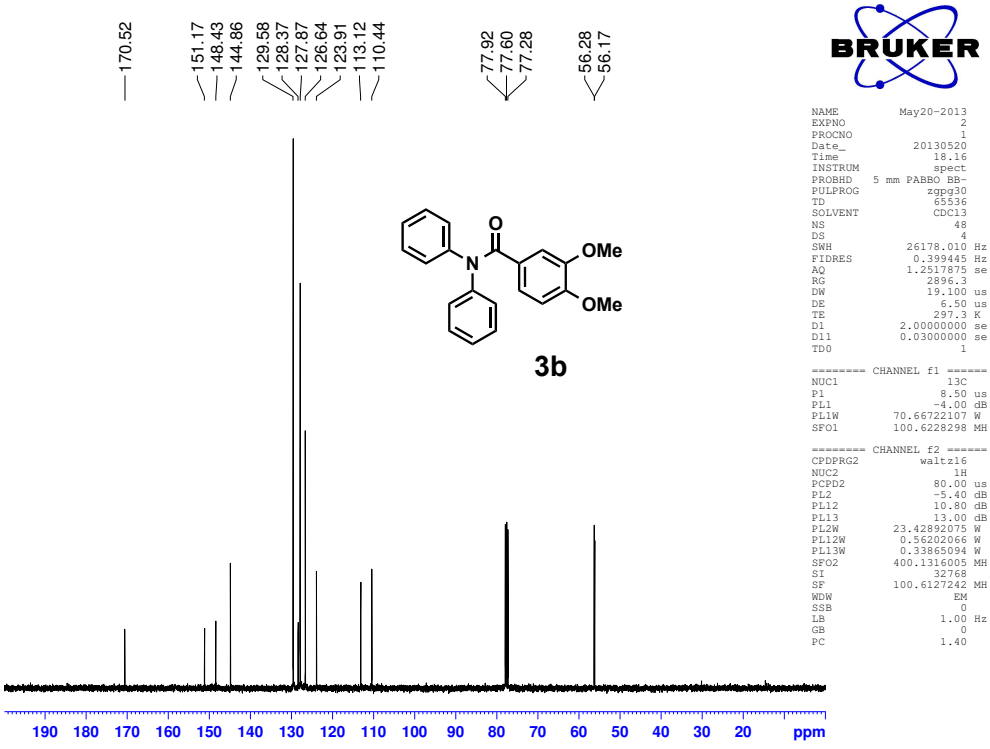



```
NAME        SA_3_115_fr5-10
EXPNO                     2
PROCNO                    1
Date_              20131212
Time                  19.20
INSTRUM               spect
PROBHD    5 mm PABBO BB-
PULPROG             zgpg30
TD                    65536
SOLVENT               CDCl3
NS                        8
DS                        4
SWH              23980.814 Hz
FIDRES            0.365918 Hz
AQ                1.3664756 se
RG                     1024
DW                   20.850 us
DE                    6.50 us
TE                   296.6 K
D1                2.00000000 se
D11               0.03000000 se
TD0                       1

======== CHANNEL f1 ======
NUC1                   13C
P1                    8.50 us
PL1                  -4.00 dB
PL1W           70.66722107 W
SFO1          100.6228298 MH

======== CHANNEL f2 ======
CPDPRG2            waltz16
NUC2                    1H
PCPD2                80.00 us
PL2                  -5.40 dB
PL12                 10.80 dB
PL13                 13.00 dB
PL2W           23.42892075 W
PL12W           0.56202066 W
PL13W           0.33865094 W
SFO2          400.1316005 MH
SI                    32768
SF            100.6127268 MH
WDW                      EM
SSB                       0
LB                     1.00 Hz
GB                        0
PC                     1.40
```



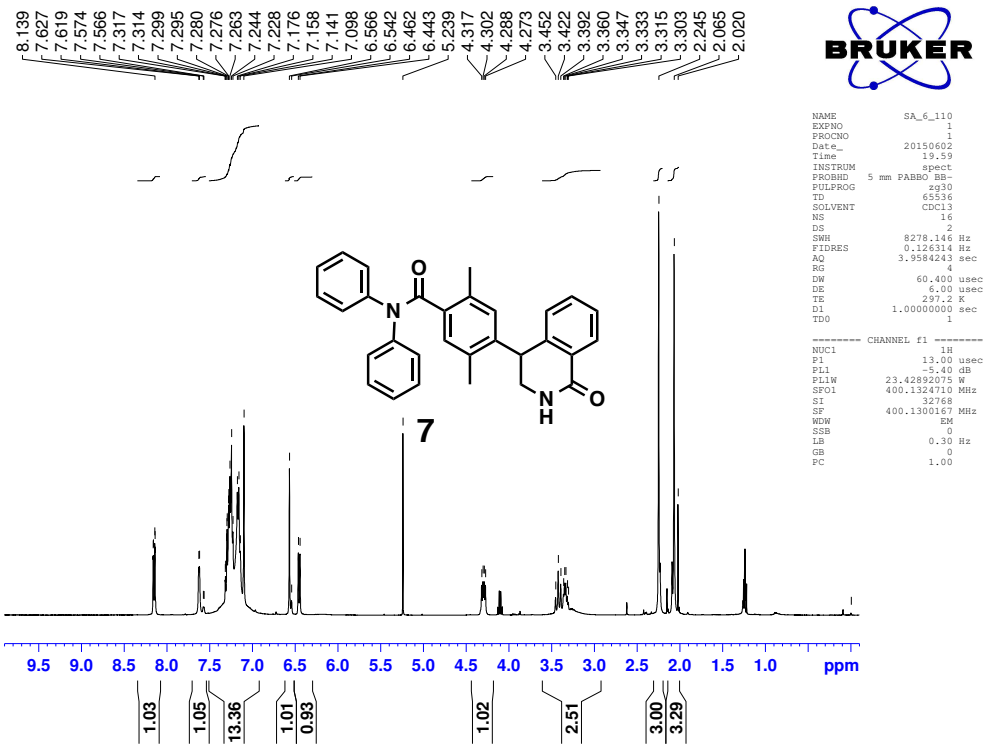
BRUKER

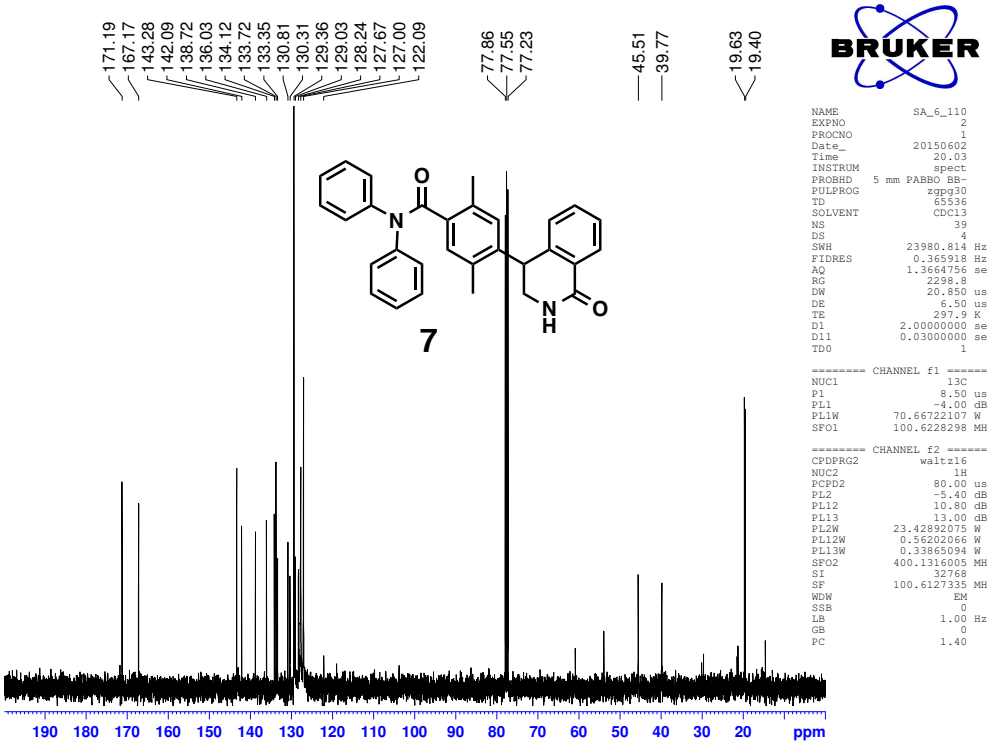
```
NAME            May20-2013
EXPNO                    1
PROCNO                   1
Date_             20130520
Time                 18.10
INSTRUM              spect
PROBHD    5 mm PABBO BB-
PULPROG               zg30
TD                   65536
SOLVENT              CDCl3
NS                      16
DS                       2
SWH             8278.146 Hz
FIDRES          0.126314 Hz
AQ              3.9584243 sec
RG                    28.5
DW                60.400 usec
DE                 6.00 usec
TE                296.6 K
D1             1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                   1H
P1                 13.00 usec
PL1                -5.40 dB
PL1W          23.42892075 W
SFO1         400.1324710 MHz
SI                   32768
SF           400.1300084 MHz
WDW                     EM
SSB                      0
LB                  0.30 Hz
GB                       0
PC                    1.00
```

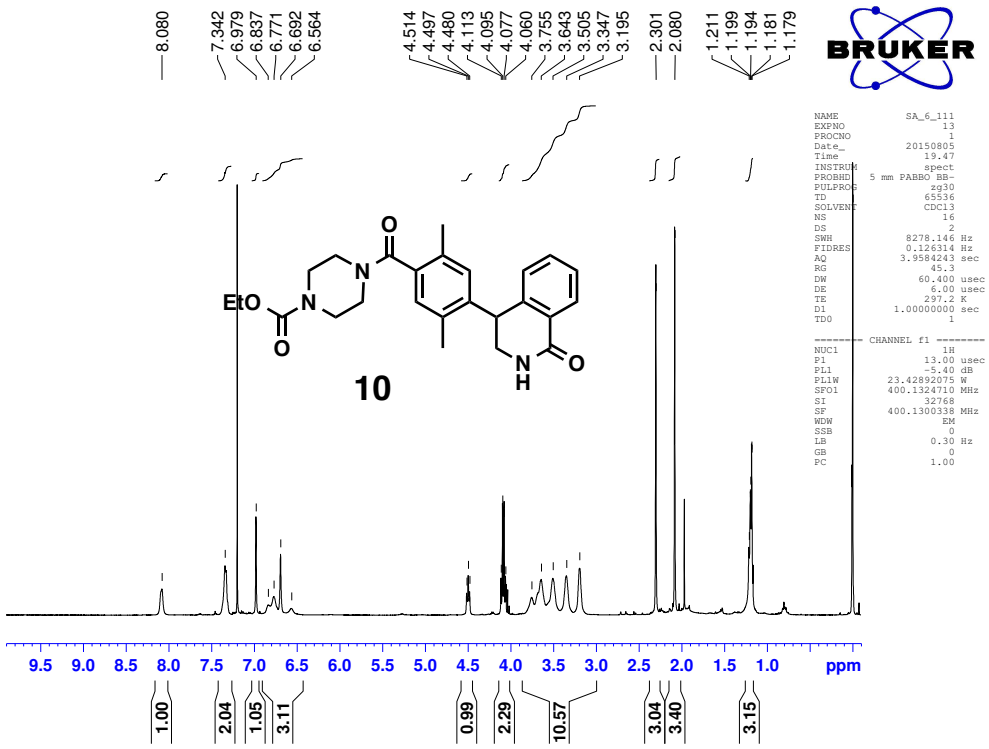


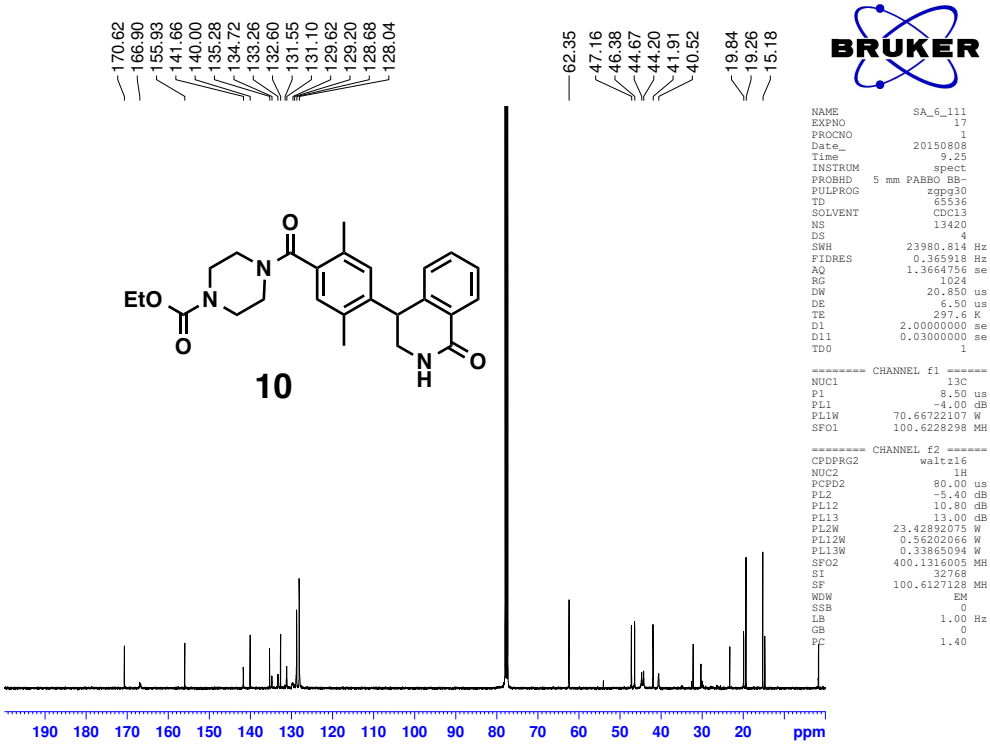
BRUKER

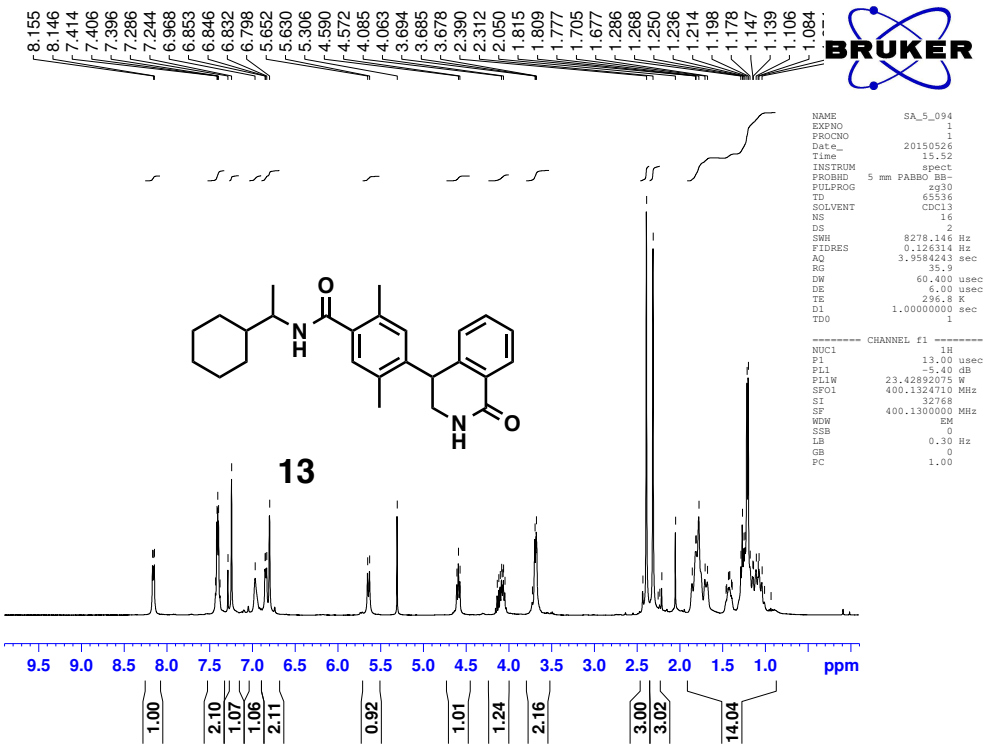
```
NAME            May20-2013
EXPNO                    2
PROCNO                   1
Date_             20130520
Time                 18.16
INSTRUM              spect
PROBHD    5 mm PABBO BB-
PULPROG             zgpg30
TD                   65536
SOLVENT              CDCl3
NS                      48
DS                       4
SWH            26178.010 Hz
FIDRES          0.399445 Hz
AQ              1.2517875 se
RG                  2896.3
DW                19.100 us
DE                 6.50 us
TE                297.3 K
D1             2.00000000 se
D11            0.03000000 se
TD0                      1

======== CHANNEL f1 ======
NUC1                   13C
P1                  8.50 us
PL1                -4.00 dB
PL1W          70.66722107 W
SFO1         100.6228298 MH

======== CHANNEL f2 ======
CPDPRG2            waltz16
NUC2                   1H
PCPD2              80.00 us
PL2                -5.40 dB
PL12               10.80 dB
PL13               13.00 dB
PL2W          23.42892075 W
PL12W          0.56202066 W
PL13W          0.33865094 W
SFO2         400.1316005 MH
SI                   32768
SF           100.6127242 MH
WDW                     EM
SSB                      0
LB                  1.00 Hz
GB                       0
PC                    1.40
```

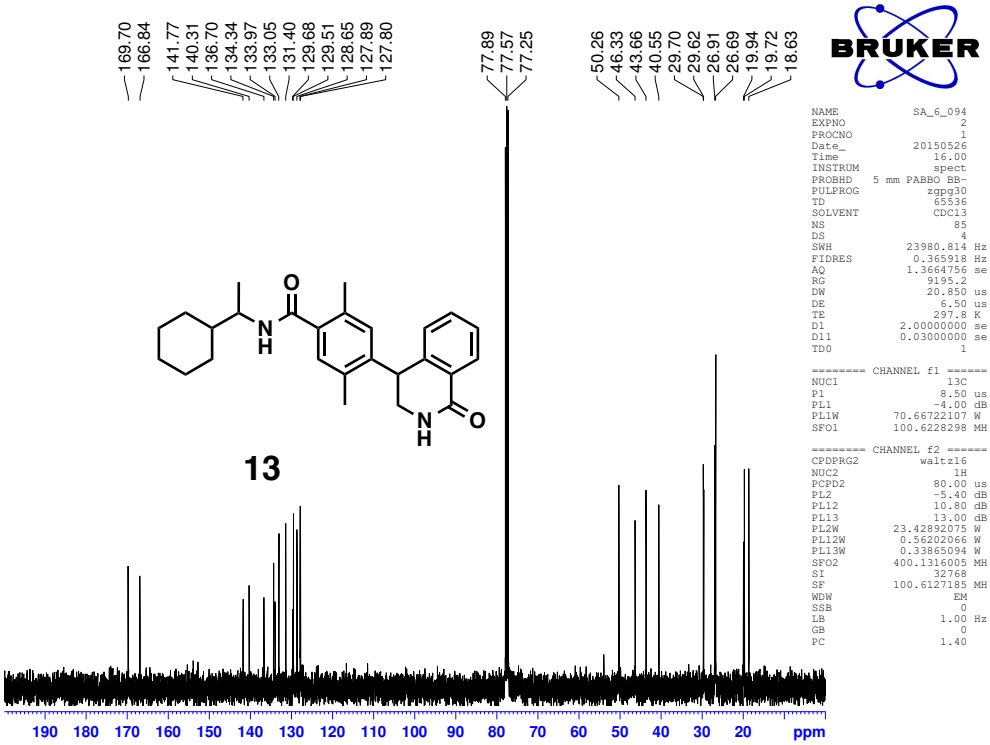

8.139
7.627
7.619
7.574
7.566
7.317
7.314
7.299
7.295
7.280
7.276
7.263
7.244
7.228
7.176
7.158
7.141
7.098
6.566
6.542
6.462
6.443
5.239
4.317
4.302
4.288
4.273
3.452
3.422
3.392
3.360
3.347
3.333
3.315
3.303
2.245
2.065
2.020
BRUKER
NAME SA_6_110
EXPNO 1
PROCNO 1
Date_ 20150602
Time 19.59
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 4
DW 60.400 usec
DE 6.00 usec
TE 297.2 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.00 usec
PL1 -5.40 dB
PL1W 23.42892075 W
SFO1 400.1324710 MHz
SI 32768
SF 400.1300167 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
O
N
H
O
7
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0
ppm
1.03
1.05
13.36
1.01
0.93
1.02
2.51
3.00
3.29

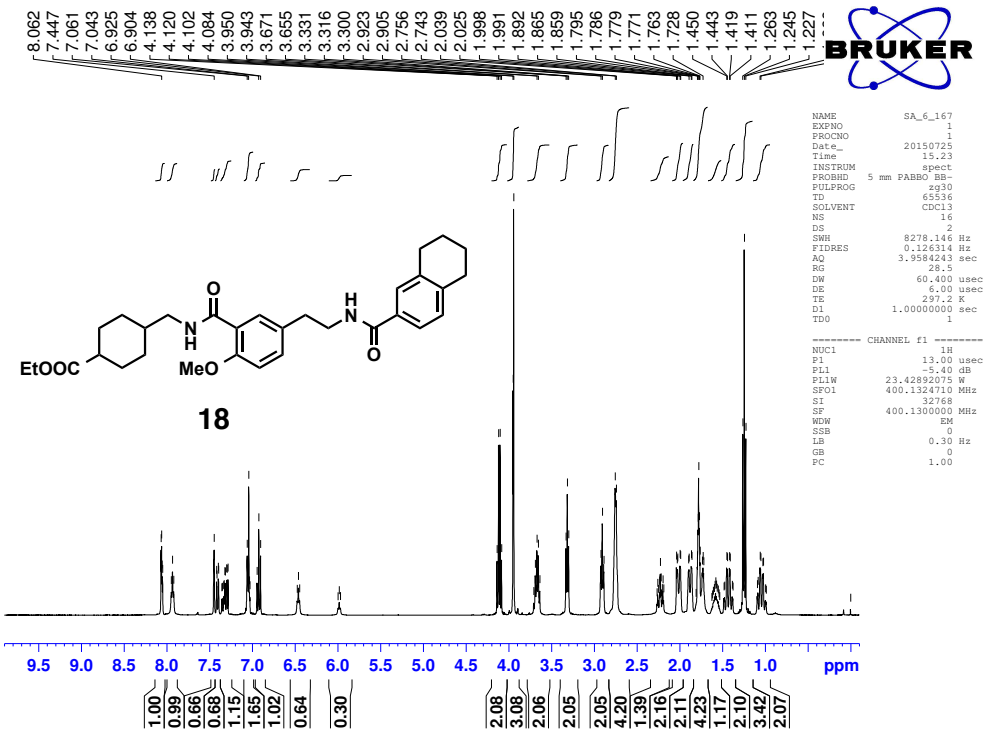

171.19
167.17
143.28
142.09
138.72
136.03
134.12
133.72
133.35
130.81
130.31
129.36
129.03
128.24
127.67
127.00
122.09
77.86
77.55
77.23
45.51
39.77
19.63
19.40
BRUKER
NAME SA_6_110
EXPNO 2
PROCNO 1
Date_ 20150602
Time 20.03
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 39
DS 4
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664756 se
RG 2298.8
DW 20.850 us
DE 6.50 us
TE 297.9 K
D1 2.00000000 se
D11 0.03000000 se
TD0 1
======== CHANNEL f1 ======
NUC1 13C
P1 8.50 us
PL1 -4.00 dB
PL1W 70.66722107 W
SFO1 100.6228298 MH
======== CHANNEL f2 ======
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 us
PL2 -5.40 dB
PL12 10.80 dB
PL13 13.00 dB
PL2W 23.42892075 W
PL12W 0.56202066 W
PL13W 0.33865094 W
SFO2 400.1316005 MH
SI 32768
SF 100.6127335 MH
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
O
N
H
O
7
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20
ppm

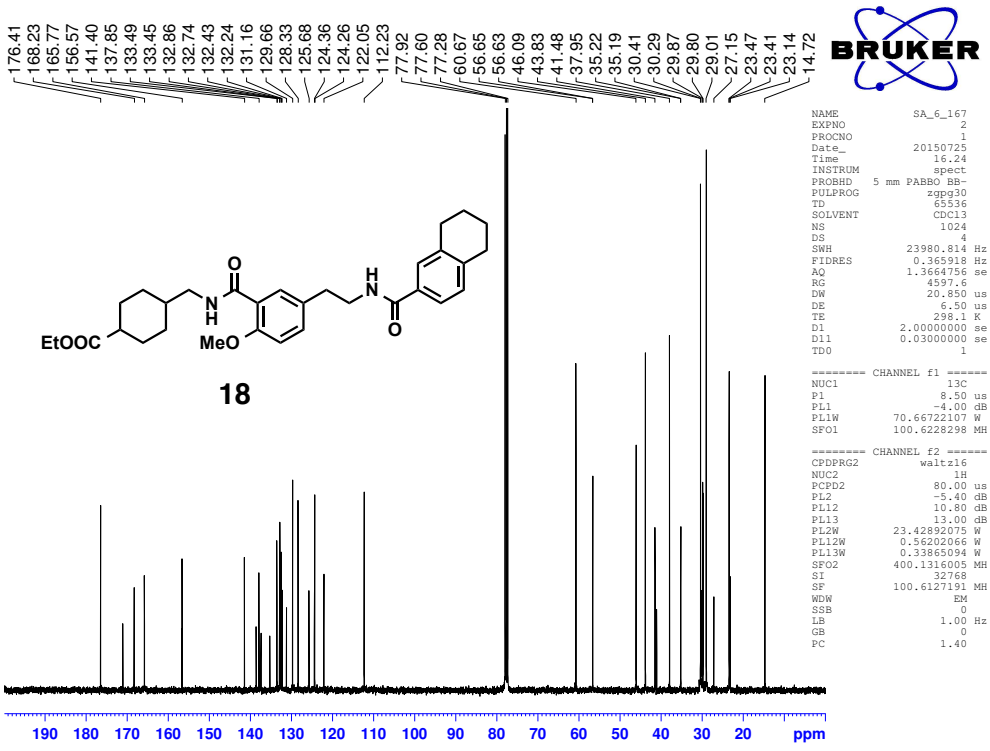

8.080
7.342
6.979
6.837
6.771
6.692
6.564
4.514
4.497
4.480
4.113
4.095
4.077
4.060
3.755
3.643
3.505
3.347
3.195
2.301
2.080
1.211
1.199
1.194
1.181
1.179
BRUKER
EtO
O
N
N
O
O
N
H
O
10
NAME SA_6_111
EXPNO 13
PROCNO 1
Date_ 20150805
Time 19.47
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 45.3
DW 60.400 usec
DE 6.00 usec
TE 297.2 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.00 usec
PL1 -5.40 dB
PL1W 23.42892075 W
SFO1 400.1324710 MHz
SI 32768
SF 400.1300338 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
1.00
2.04
1.05
3.11
0.99
2.29
10.57
3.04
3.40
3.15

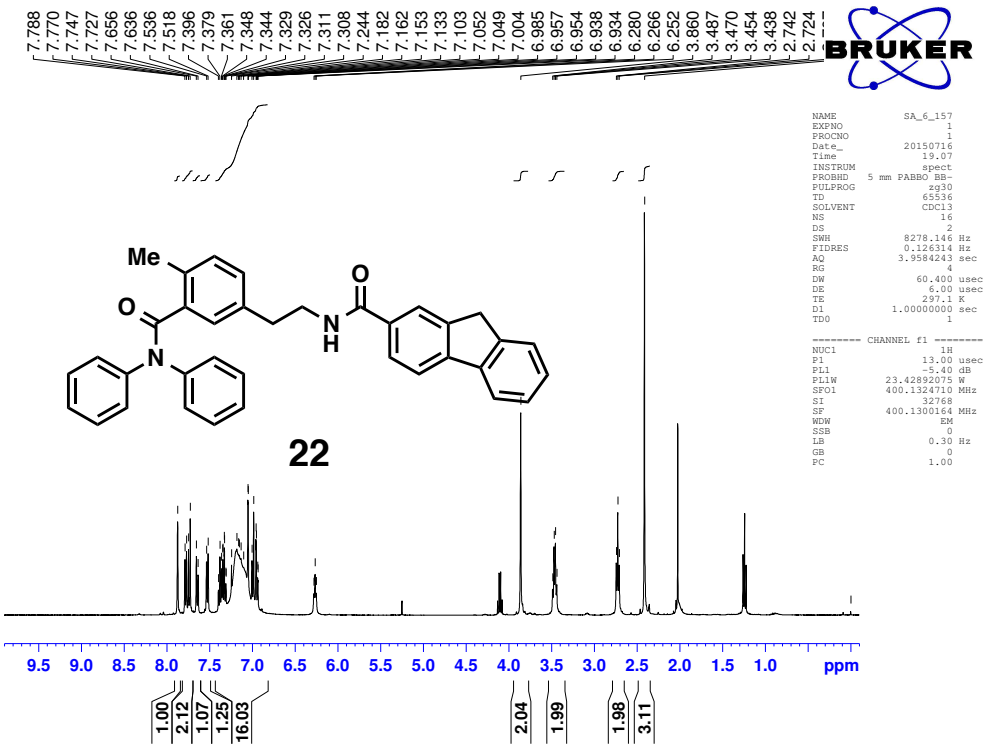

170.62
166.90
155.93
141.66
140.00
135.28
134.72
133.26
132.60
131.55
131.10
129.62
129.20
128.68
128.04
62.35
47.16
46.38
44.67
44.20
41.91
40.52
19.84
19.26
15.18
BRUKER
EtO
O
N
N
O
O
N
H
O
10
NAME SA_6_111
EXPNO 17
PROCNO 1
Date_ 20150808
Time 9.25
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 13420
DS 4
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664756 se
RG 1024
DW 20.850 us
DE 6.50 us
TE 297.6 K
D1 2.00000000 se
D11 0.03000000 se
TD0 1
======== CHANNEL f1 ======
NUC1 13C
P1 8.50 us
PL1 -4.00 dB
PL1W 70.66722107 W
SFO1 100.6228298 MH
======== CHANNEL f2 ======
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 us
PL2 -5.40 dB
PL12 10.80 dB
PL13 13.00 dB
PL2W 23.42892075 W
PL12W 0.56202066 W
PL13W 0.33865094 W
SFO2 400.1316005 MH
SI 32768
SF 100.6127128 MH
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

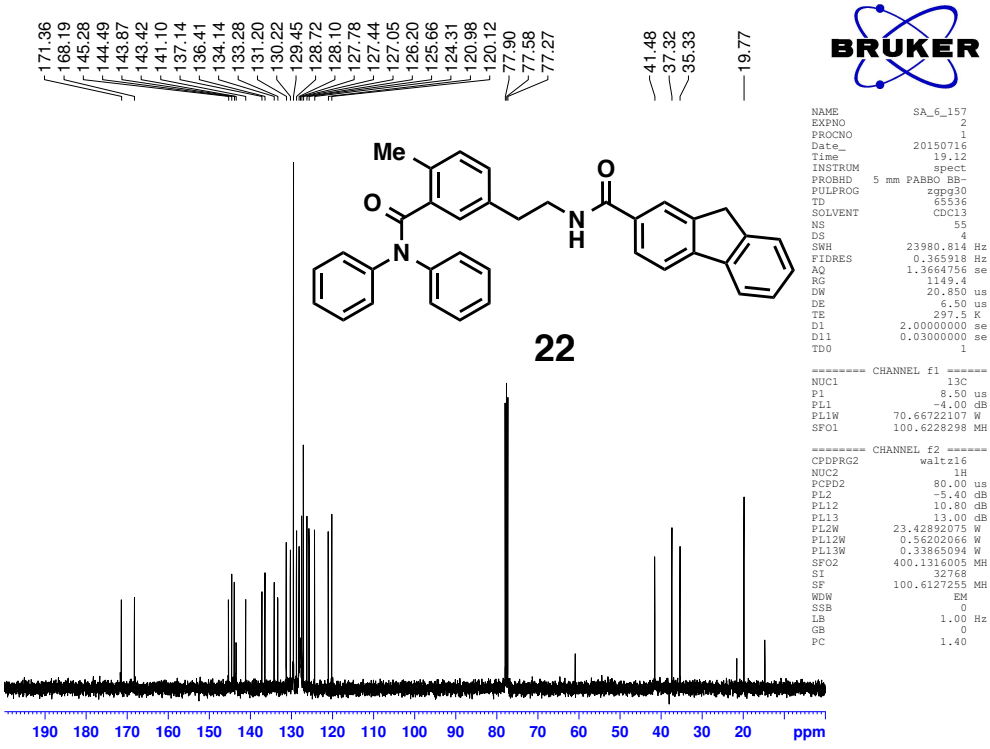

8.155
8.146
7.414
7.406
7.396
7.286
7.244
6.968
6.853
6.846
6.832
6.798
5.652
5.630
5.306
4.590
4.572
4.085
4.063
3.694
3.685
3.678
2.390
2.312
2.050
1.815
1.809
1.777
1.705
1.677
1.286
1.268
1.250
1.236
1.214
1.198
1.178
1.147
1.139
1.106
1.084
BRUKER
NAME SA_5_094
EXPNO 1
PROCNO 1
Date_ 20150526
Time 15.52
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 35.9
DW 60.400 usec
DE 6.00 usec
TE 296.8 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.00 usec
PL1 -5.40 dB
PL1W 23.42892075 W
SFO1 400.1324710 MHz
SI 32768
SF 400.1300000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
13
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
1.00
2.10
1.07
1.06
2.11
0.92
1.01
1.24
2.16
3.00
3.02
14.04

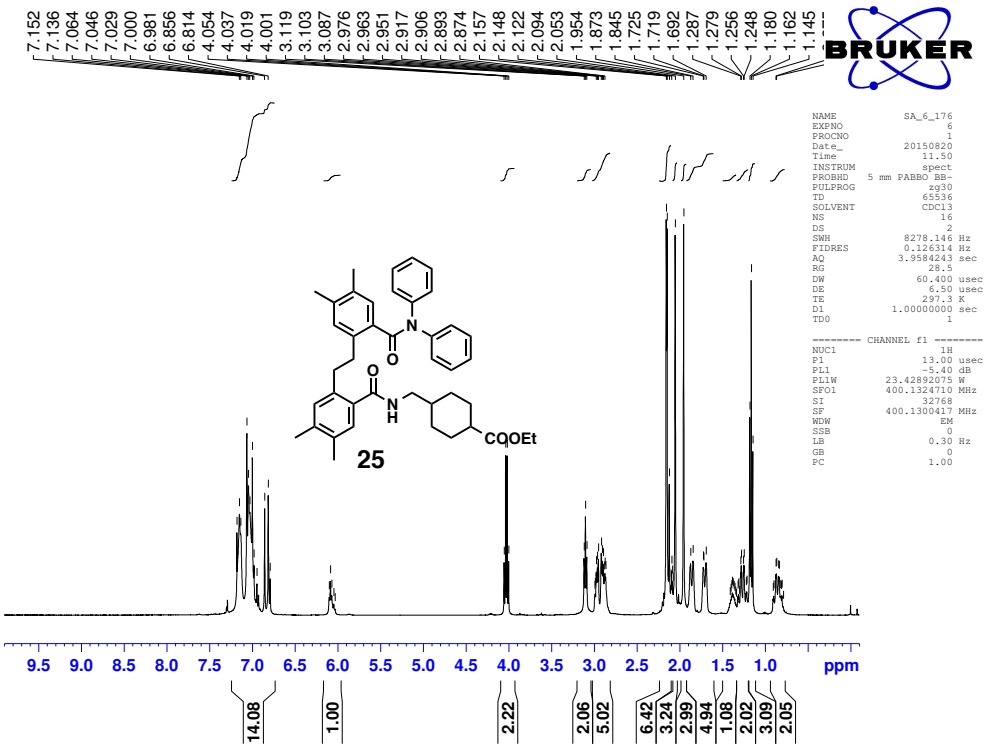

169.70
166.84
141.77
140.31
136.70
134.34
133.97
133.05
131.40
129.68
129.51
128.65
127.89
127.80
77.89
77.57
77.25
50.26
46.33
43.66
40.55
29.70
29.62
26.91
26.69
19.94
19.72
18.63
BRUKER
NAME SA_6_094
EXPNO 2
PROCNO 1
Date_ 20150526
Time 16.00
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 85
DS 4
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664756 se
RG 9195.2
DW 20.850 us
DE 6.50 us
TE 297.8 K
D1 2.00000000 se
D11 0.03000000 se
TD0 1
======== CHANNEL f1 ======
NUC1 13C
P1 8.50 us
PL1 -4.00 dB
PL1W 70.66722107 W
SFO1 100.6228298 MH
======== CHANNEL f2 ======
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 us
PL2 -5.40 dB
PL12 10.80 dB
PL13 13.00 dB
PL2W 23.42892075 W
PL12W 0.56202066 W
PL13W 0.33865094 W
SFO2 400.1316005 MH
SI 32768
SF 100.6127185 MH
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
13
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm


8.062
7.447
7.061
7.043
6.925
6.904
4.138
4.120
4.102
4.084
3.950
3.943
3.671
3.655
3.331
3.316
3.300
2.923
2.905
2.756
2.743
2.039
2.025
1.998
1.991
1.892
1.865
1.859
1.795
1.786
1.779
1.771
1.763
1.728
1.450
1.443
1.419
1.411
1.263
1.245
1.227
BRUKER
NAME SA_6_167
EXPNO 1
PROCNO 1
Date_ 20150725
Time 15.23
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 28.5
DW 60.400 usec
DE 6.00 usec
TE 297.2 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.00 usec
PL1 -5.40 dB
PL1W 23.42892075 W
SFO1 400.1324710 MHz
SI 32768
SF 400.1300000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
EtOOC
MeO
18
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
1.00 0.99 0.66 0.68 1.15 1.65 1.02 0.64 0.30 2.08 3.08 2.06 2.05 2.05 4.20 1.39 2.16 2.11 4.23 1.17 2.10 3.42 2.07


176.41
168.23
165.77
156.57
141.40
137.85
133.49
133.45
132.86
132.74
132.43
132.24
131.16
129.66
128.33
125.68
124.36
124.26
122.05
112.23
77.92
77.60
77.28
60.67
56.65
56.63
46.09
43.83
41.48
37.95
35.22
35.19
30.41
30.29
29.87
29.80
29.01
27.15
23.47
23.41
23.14
14.72
BRUKER
NAME SA_6_167
EXPNO 2
PROCNO 1
Date_ 20150725
Time 16.24
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1024
DS 4
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664756 se
RG 4597.6
DW 20.850 us
DE 6.50 us
TE 298.1 K
D1 2.00000000 se
D11 0.03000000 se
TD0 1
======== CHANNEL f1 ======
NUC1 13C
P1 8.50 us
PL1 -4.00 dB
PL1W 70.66722107 W
SFO1 100.6228298 MH
======== CHANNEL f2 ======
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 us
PL2 -5.40 dB
PL12 10.80 dB
PL13 13.00 dB
PL2W 23.42892075 W
PL12W 0.56202066 W
PL13W 0.33865094 W
SFO2 400.1316005 MH
SI 32768
SF 100.6127191 MH
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
EtOOC
MeO
18
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm


7.788
7.770
7.747
7.727
7.656
7.636
7.536
7.518
7.396
7.379
7.361
7.348
7.344
7.329
7.326
7.311
7.308
7.244
7.182
7.162
7.153
7.133
7.103
7.052
7.049
7.004
6.985
6.957
6.954
6.938
6.934
6.280
6.266
6.252
3.860
3.487
3.470
3.454
3.438
2.742
2.724
BRUKER
Me
O
N
O
N
H
22
NAME SA_6_157
EXPNO 1
PROCNO 1
Date_ 20150716
Time 19.07
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 4
DW 60.400 usec
DE 6.00 usec
TE 297.1 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.00 usec
PL1 -5.40 dB
PL1W 23.42892075 W
SFO1 400.1324710 MHz
SI 32768
SF 400.1300164 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
1.00
2.12
1.07
1.25
16.03
2.04
1.99
1.98
3.11


171.36
168.19
145.28
144.49
143.87
143.42
141.10
137.14
136.41
134.14
133.28
131.20
130.22
129.45
128.72
128.10
127.78
127.44
127.05
126.20
125.66
124.31
120.98
120.12
77.90
77.58
77.27
41.48
37.32
35.33
19.77
BRUKER
Me
O
N
O
N
H
22
NAME SA_6_157
EXPNO 2
PROCNO 1
Date_ 20150716
Time 19.12
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 55
DS 4
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664756 se
RG 1149.4
DW 20.850 us
DE 6.50 us
TE 297.5 K
D1 2.00000000 se
D11 0.03000000 se
TD0 1
======== CHANNEL f1 ======
NUC1 13C
P1 8.50 us
PL1 -4.00 dB
PL1W 70.66722107 W
SFO1 100.6228298 MH
======== CHANNEL f2 ======
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 us
PL2 -5.40 dB
PL12 10.80 dB
PL13 13.00 dB
PL2W 23.42892075 W
PL12W 0.56202066 W
PL13W 0.33865094 W
SFO2 400.1316005 MH
SI 32768
SF 100.6127255 MH
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm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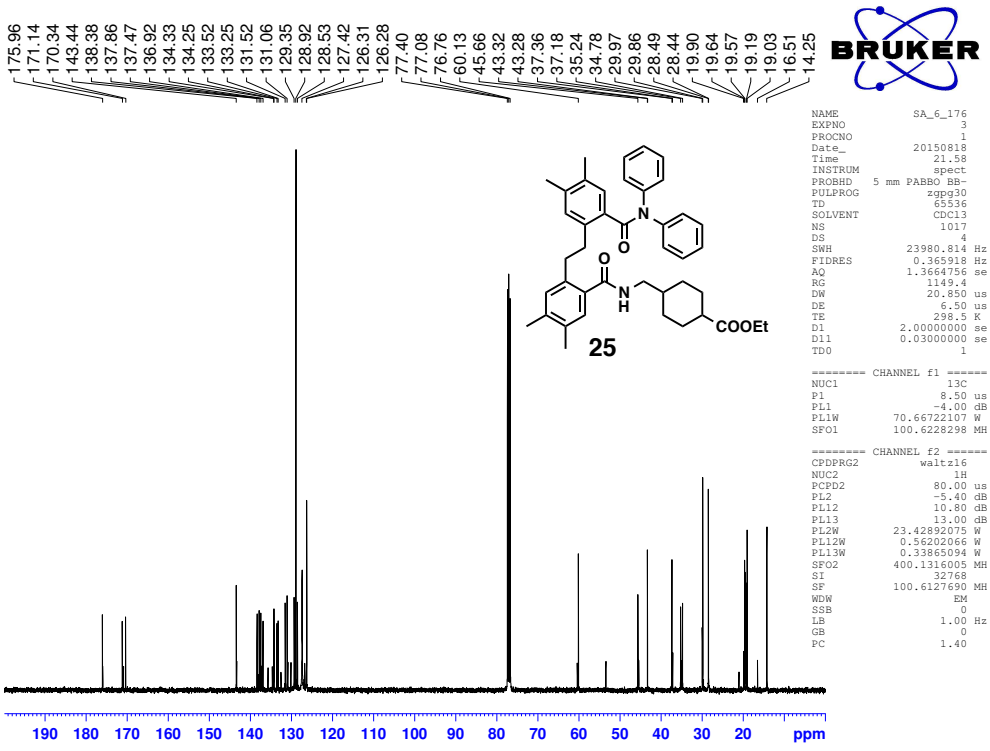
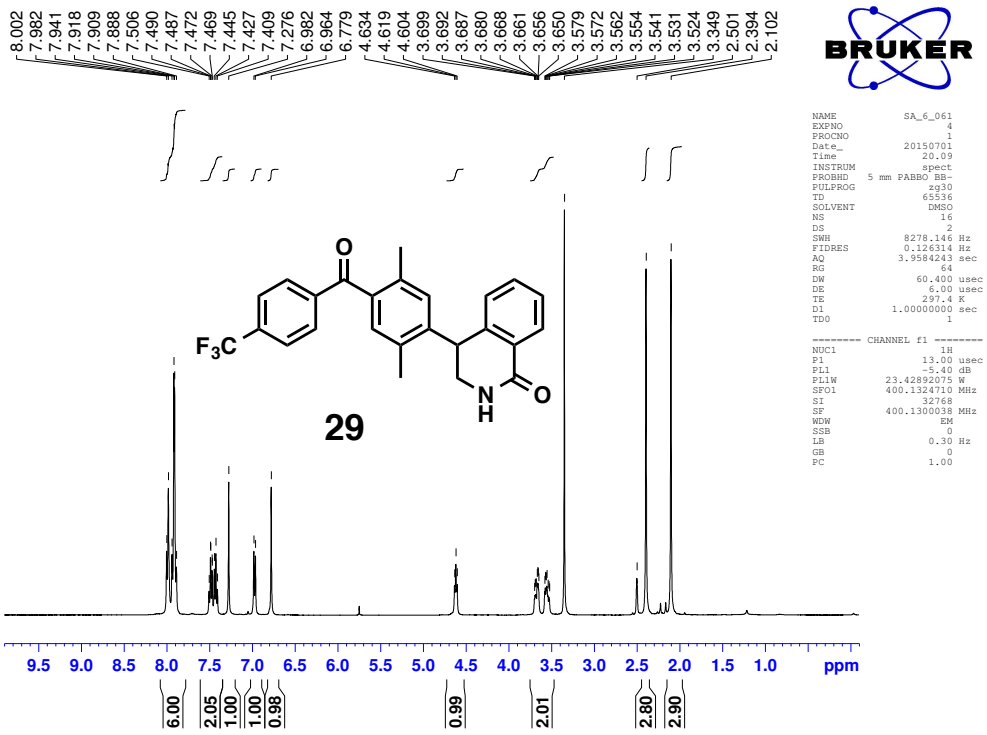
7.136
7.064
7.046
7.029
7.000
6.981
6.856
6.814
4.054
4.037
4.019
4.001
3.119
3.103
3.087
2.976
2.963
2.951
2.917
2.906
2.893
2.874
2.157
2.148
2.122
2.094
2.053
1.954
1.873
1.845
1.725
1.719
1.692
1.287
1.279
1.256
1.248
1.180
1.162
1.145
BRUKER
NAME SA_6_176
EXPNO 6
PROCNO 1
Date_ 20150820
Time 11.50
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 28.5
DW 60.400 usec
DE 6.50 usec
TE 297.3 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.00 usec
PL1 -5.40 dB
PL1W 23.42892075 W
SFO1 400.1324710 MHz
SI 32768
SF 400.1300417 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
CQOEt
25
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
14.08
1.00
2.22
2.06
5.02
6.42
3.24
2.99
4.94
1.08
2.02
3.09
2.05


175.96
171.14
170.34
143.44
138.38
137.86
137.47
136.92
134.33
134.25
133.52
133.25
131.52
131.06
129.35
128.92
128.53
127.42
126.31
126.28
77.40
77.08
76.76
60.13
45.66
43.32
43.28
37.36
37.18
35.24
34.78
29.97
29.86
28.49
28.44
19.90
19.64
19.57
19.19
19.03
16.51
14.25
BRUKER
NAME SA_6_176
EXPNO 3
PROCNO 1
Date_ 20150818
Time 21.58
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1017
DS 4
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664756 se
RG 1149.4
DW 20.850 us
DE 6.50 us
TE 298.5 K
D1 2.00000000 se
D11 0.03000000 se
TD0 1
======== CHANNEL f1 ======
NUC1 13C
P1 8.50 us
PL1 -4.00 dB
PL1W 70.66722107 W
SFO1 100.6228298 MH
======== CHANNEL f2 ======
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 us
PL2 -5.40 dB
PL12 10.80 dB
PL13 13.00 dB
PL2W 23.42892075 W
PL12W 0.56202066 W
PL13W 0.33865094 W
SFO2 400.1316005 MH
SI 32768
SF 100.6127690 MH
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
COOEt
25
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm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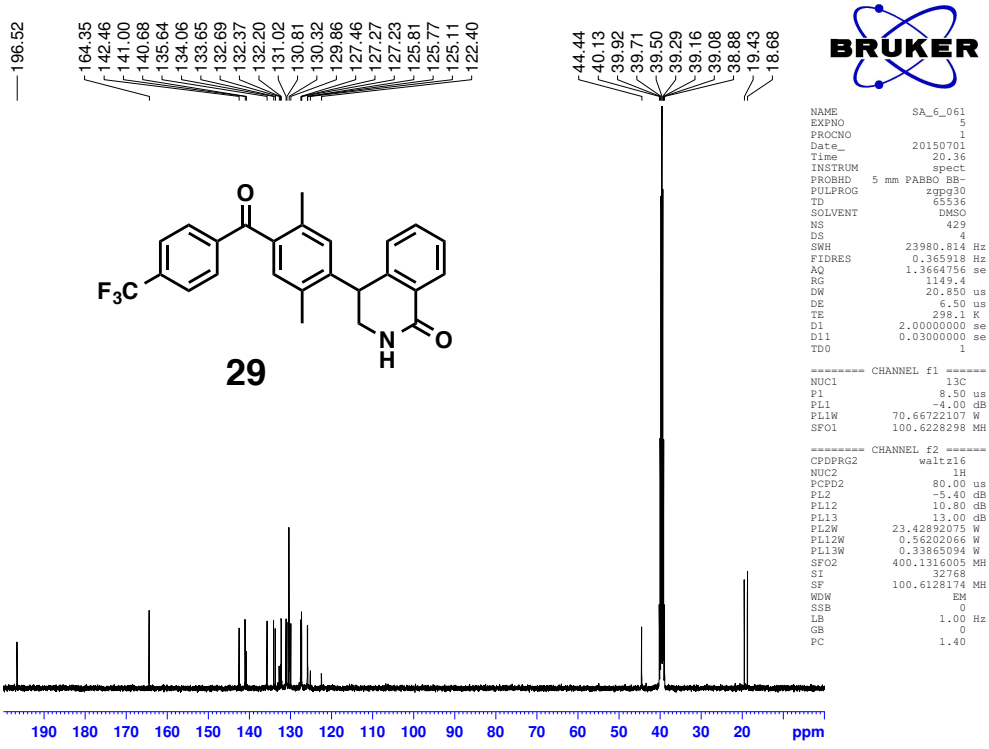
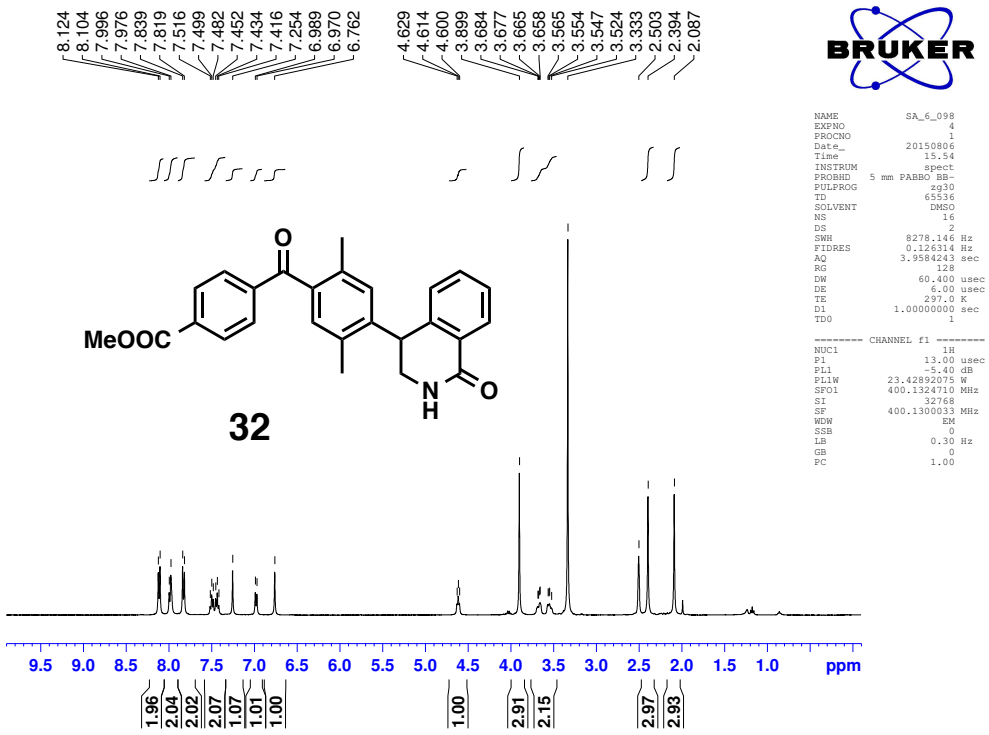
7.982
7.941
7.918
7.909
7.888
7.506
7.490
7.487
7.472
7.469
7.445
7.427
7.409
7.276
6.982
6.964
6.779
4.634
4.619
4.604
3.699
3.692
3.687
3.680
3.668
3.661
3.656
3.650
3.579
3.572
3.562
3.554
3.541
3.531
3.524
3.349
2.501
2.394
2.102
BRUKER
NAME SA_6_061
EXPNO 4
PROCNO 1
Date_ 20150701
Time 20.09
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT DMSO
NS 16
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 64
DW 60.400 usec
DE 6.00 usec
TE 297.4 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.00 usec
PL1 -5.40 dB
PL1W 23.42892075 W
SFO1 400.1324710 MHz
SI 32768
SF 400.1300038 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
O
F3C
N
H
O
29
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
6.00
2.05
1.00
1.00
0.98
0.99
2.01
2.80
2.90


196.52
164.35
142.46
141.00
140.68
135.64
134.06
133.65
132.69
132.37
132.20
131.02
130.81
130.32
129.86
127.46
127.27
127.23
125.81
125.77
125.11
122.40
44.44
40.13
39.92
39.71
39.50
39.29
39.16
39.08
38.88
19.43
18.68
BRUKER
NAME SA_6_061
EXPNO 5
PROCNO 1
Date_ 20150701
Time 20.36
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT DMSO
NS 429
DS 4
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664756 se
RG 1149.4
DW 20.850 us
DE 6.50 us
TE 298.1 K
D1 2.00000000 se
D11 0.03000000 se
TD0 1
======== CHANNEL f1 ======
NUC1 13C
P1 8.50 us
PL1 -4.00 dB
PL1W 70.66722107 W
SFO1 100.6228298 MH
======== CHANNEL f2 ======
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 us
PL2 -5.40 dB
PL12 10.80 dB
PL13 13.00 dB
PL2W 23.42892075 W
PL12W 0.56202066 W
PL13W 0.33865094 W
SFO2 400.1316005 MH
SI 32768
SF 100.6128174 MH
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
O
F3C
N
H
O
29
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm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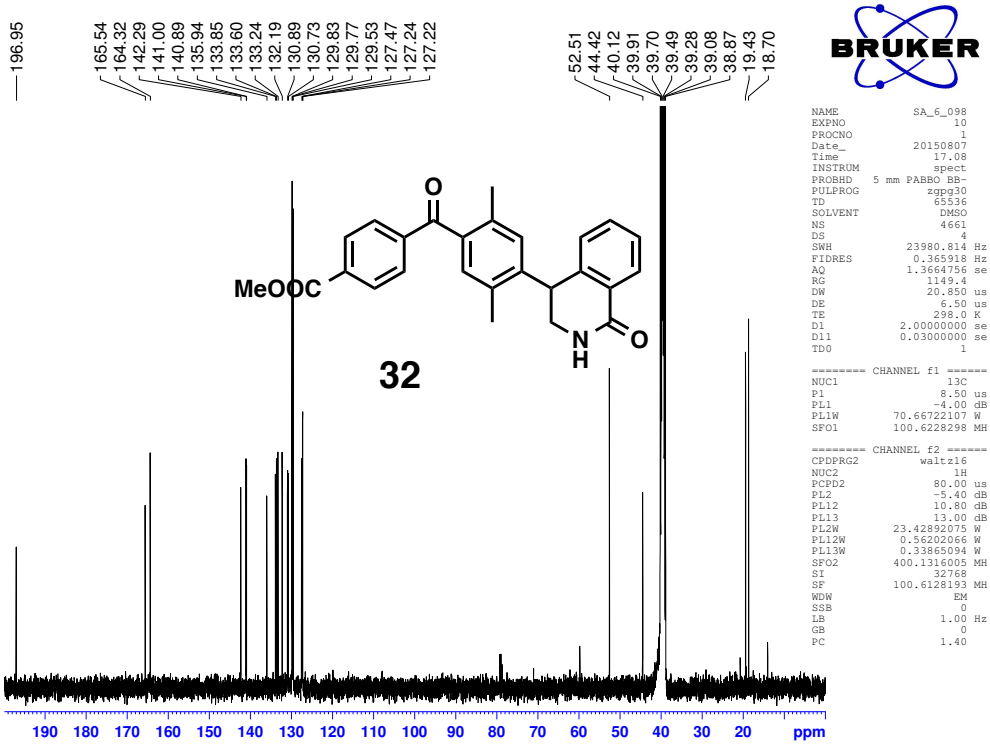
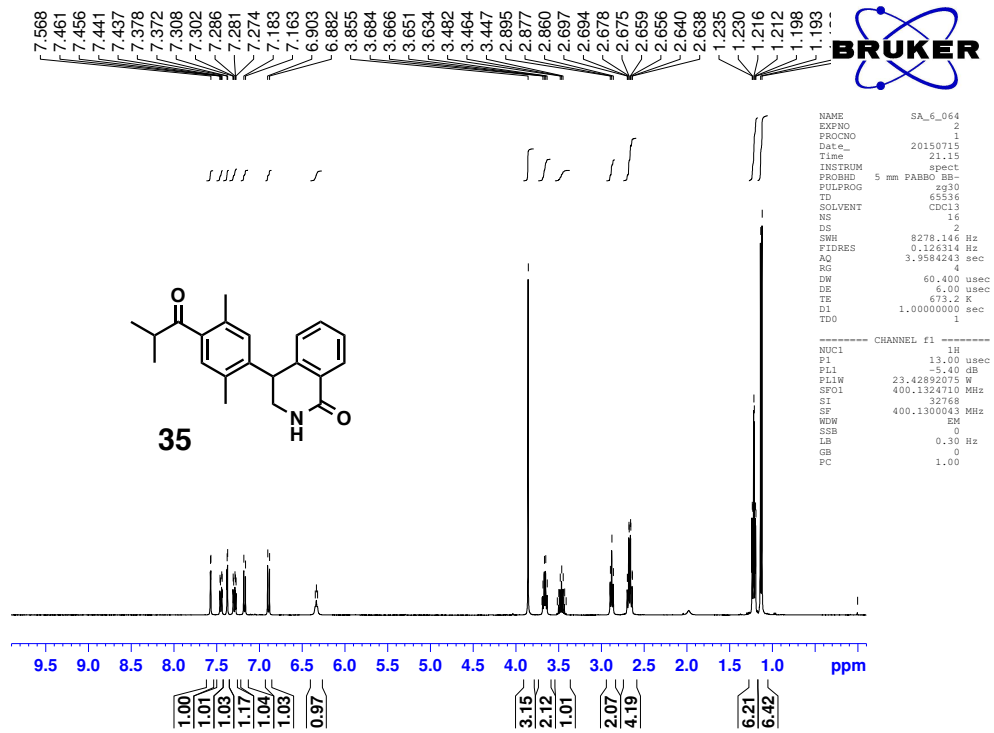
7.996
7.976
7.839
7.819
7.516
7.499
7.482
7.452
7.434
7.416
7.254
6.989
6.970
6.762
4.629
4.614
4.600
3.899
3.684
3.677
3.665
3.658
3.565
3.554
3.547
3.524
3.333
2.503
2.394
2.087
BRUKER
NAME SA_6_098
EXPNO 4
PROCNO 1
Date_ 20150806
Time 15.54
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT DMSO
NS 16
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 128
DW 60.400 usec
DE 6.00 usec
TE 297.0 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.00 usec
PL1 -5.40 dB
PL1W 23.42892075 W
SFO1 400.1324710 MHz
SI 32768
SF 400.1300033 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
MeOOC
O
N
H
O
32
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
1.96
2.04
2.02
2.07
1.07
1.01
1.00
1.00
2.91
2.15
2.97
2.93


196.95
165.54
164.32
142.29
141.00
140.89
135.94
133.85
133.60
133.24
132.19
130.89
130.73
129.83
129.77
129.53
127.47
127.24
127.22
52.51
44.42
40.12
39.91
39.70
39.49
39.28
39.08
38.87
19.43
18.70
BRUKER
NAME SA_6_098
EXPNO 10
PROCNO 1
Date_ 20150807
Time 17.08
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT DMSO
NS 4661
DS 4
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664756 se
RG 1149.4
DW 20.850 us
DE 6.50 us
TE 298.0 K
D1 2.00000000 se
D11 0.03000000 se
TD0 1
======== CHANNEL f1 ======
NUC1 13C
P1 8.50 us
PL1 -4.00 dB
PL1W 70.66722107 W
SFO1 100.6228298 MH
======== CHANNEL f2 ======
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 us
PL2 -5.40 dB
PL12 10.80 dB
PL13 13.00 dB
PL2W 23.42892075 W
PL12W 0.56202066 W
PL13W 0.33865094 W
SFO2 400.1316005 MH
SI 32768
SF 100.6128193 MH
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
MeOOC
O
N
H
O
32
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm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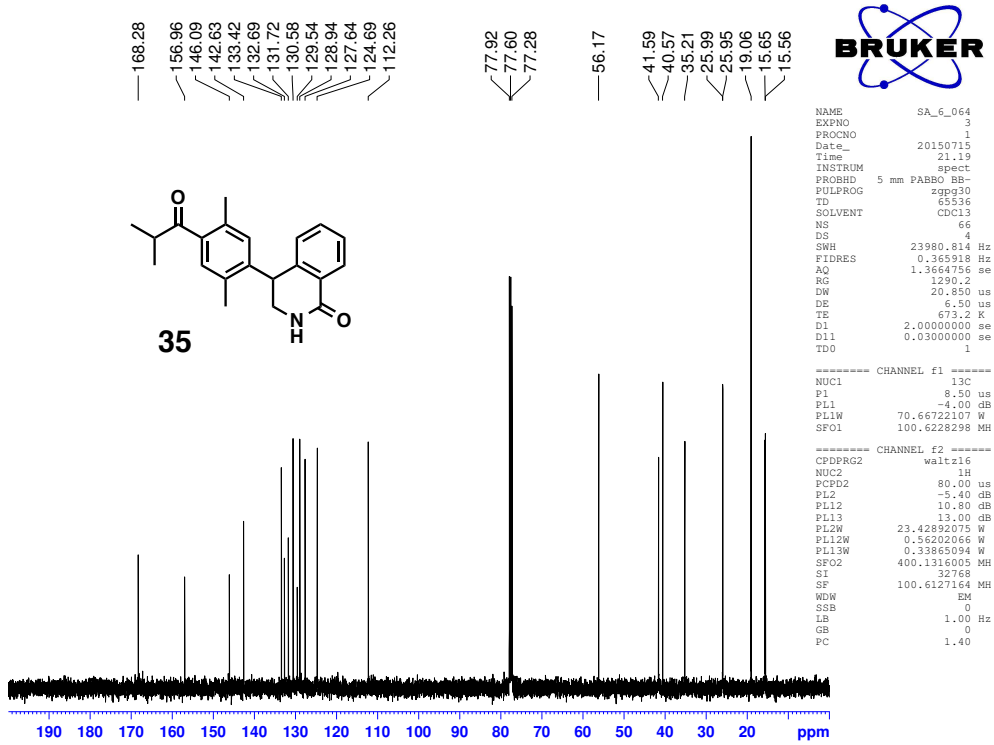
7.456
7.441
7.437
7.378
7.372
7.308
7.302
7.286
7.281
7.274
7.183
7.163
6.903
6.882
3.855
3.684
3.666
3.651
3.634
3.482
3.464
3.447
2.895
2.877
2.860
2.697
2.694
2.678
2.675
2.659
2.656
2.640
2.638
1.235
1.230
1.216
1.212
1.198
1.193
BRUKER
NAME SA_6_064
EXPNO 2
PROCNO 1
Date_ 20150715
Time 21.15
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 4
DW 60.400 usec
DE 6.00 usec
TE 673.2 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.00 usec
PL1 -5.40 dB
PL1W 23.42892075 W
SFO1 400.1324710 MHz
SI 32768
SF 400.1300043 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
35
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
1.00 1.01 1.03 1.17 1.04 1.03 0.97 3.15 2.12 1.01 2.07 4.19 6.21 6.42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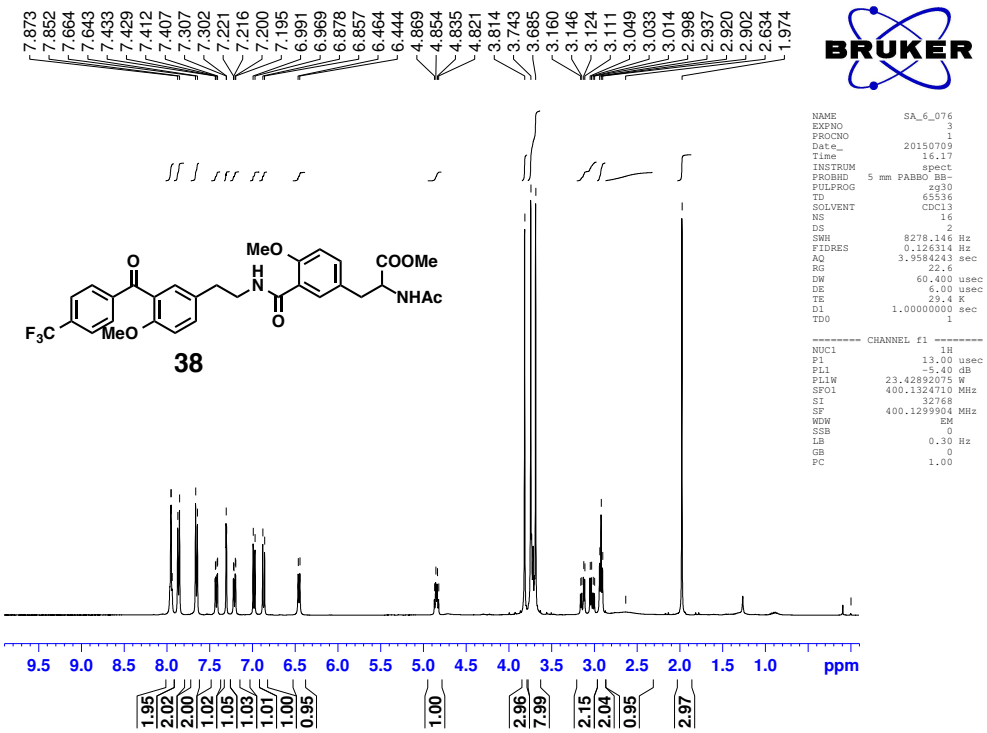
156.96
146.09
142.63
133.42
132.69
131.72
130.58
129.54
128.94
127.64
124.69
112.26
77.92
77.60
77.28
56.17
41.59
40.57
35.21
25.99
25.95
19.06
15.65
15.56
BRUKER
NAME SA_6_064
EXPNO 3
PROCNO 1
Date_ 20150715
Time 21.19
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 66
DS 4
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664756 se
RG 1290.2
DW 20.850 us
DE 6.50 us
TE 673.2 K
D1 2.00000000 se
D11 0.03000000 se
TD0 1
======== CHANNEL f1 ======
NUC1 13C
P1 8.50 us
PL1 -4.00 dB
PL1W 70.66722107 W
SFO1 100.6228298 MH
======== CHANNEL f2 ======
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 us
PL2 -5.40 dB
PL12 10.80 dB
PL13 13.00 dB
PL2W 23.42892075 W
PL12W 0.56202066 W
PL13W 0.33865094 W
SFO2 400.1316005 MH
SI 32768
SF 100.6127164 MH
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
35
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm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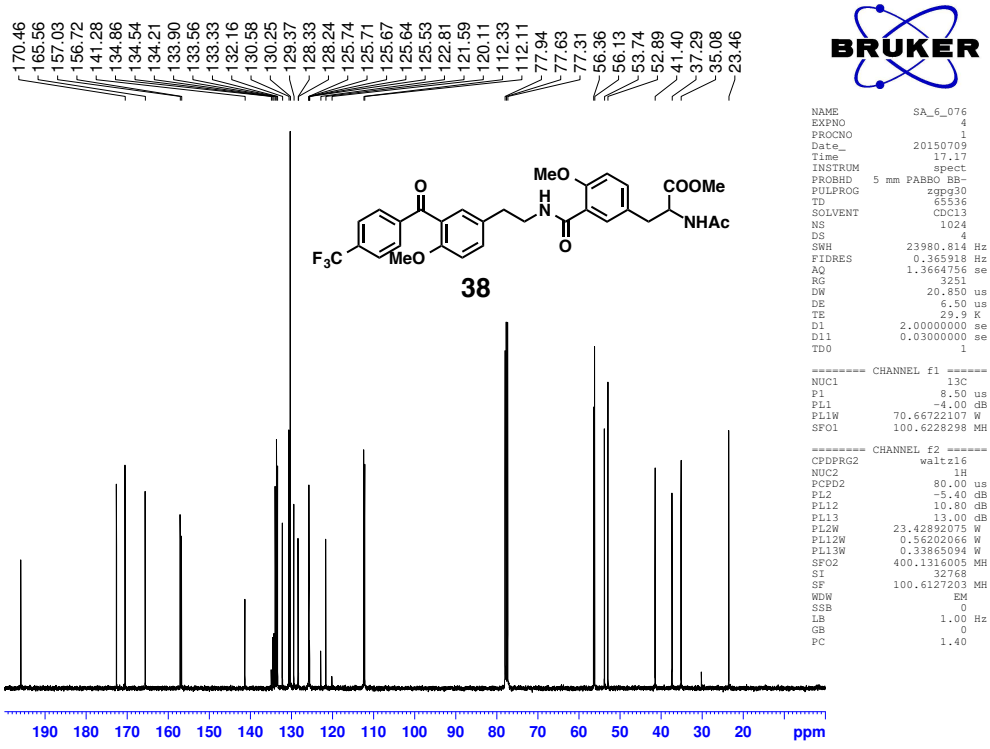
7.433
7.429
7.412
7.407
7.307
7.302
7.221
7.216
7.200
7.195
6.991
6.969
6.878
6.857
6.464
6.444
4.869
4.854
4.835
4.821
3.814
3.743
3.685
3.160
3.146
3.124
3.111
3.049
3.033
3.014
2.998
2.937
2.920
2.902
2.634
1.974
BRUKER
MeO
COOMe
NHAc
O
H
N
O
F3C
MeO
38
NAME SA_6_076
EXPNO 3
PROCNO 1
Date_ 20150709
Time 16.17
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 22.6
DW 60.400 usec
DE 6.00 usec
TE 29.4 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.00 usec
PL1 -5.40 dB
PL1W 23.42892075 W
SFO1 400.1324710 MHz
SI 32768
SF 400.1299904 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
1.95 2.02 2.00 1.02 1.05 1.03 1.01 1.00 0.95 1.00 2.96 7.99 2.15 2.04 0.95 2.97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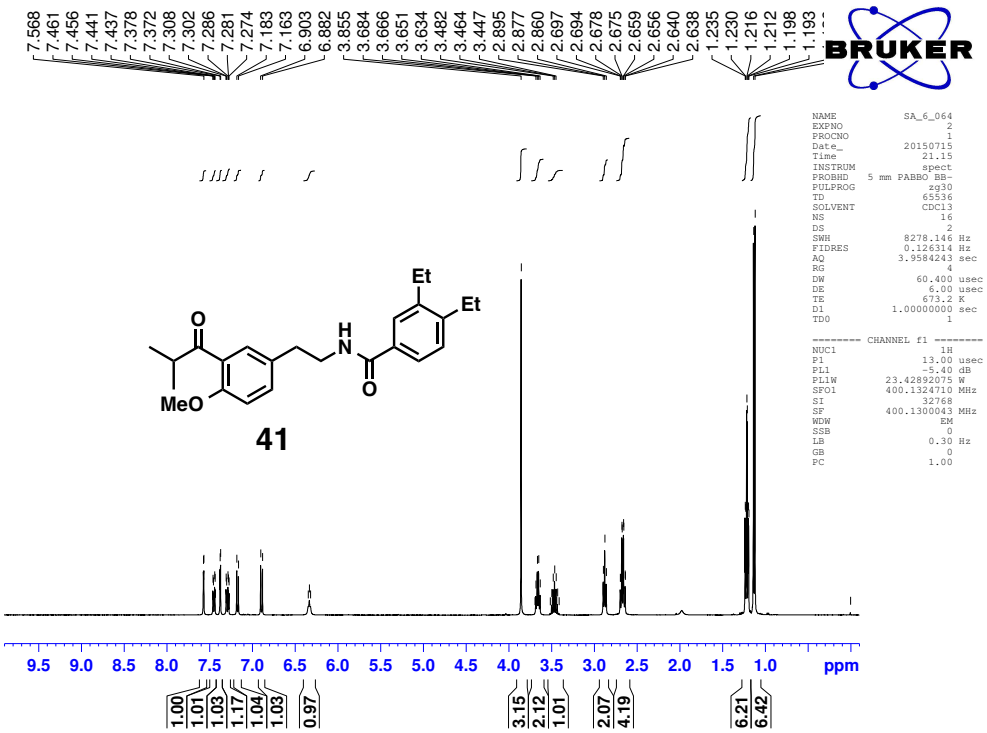
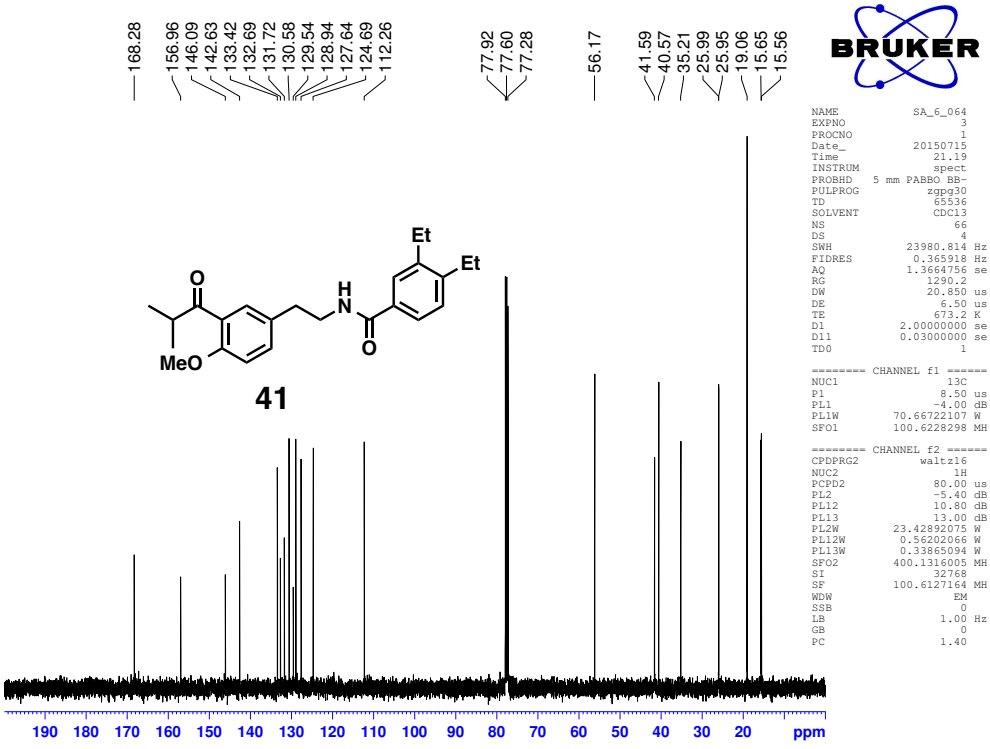
165.56
157.03
156.72
141.28
134.86
134.54
134.21
133.90
133.56
133.33
132.16
130.58
130.25
129.37
128.33
128.24
125.74
125.71
125.67
125.64
125.53
122.81
121.59
120.11
112.33
112.11
77.94
77.63
77.31
56.36
56.13
53.74
52.89
41.40
37.29
35.08
23.46
BRUKER
MeO
COOMe
NHAc
O
H
N
O
F3C
MeO
38
NAME SA_6_076
EXPNO 4
PROCNO 1
Date_ 20150709
Time 17.17
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1024
DS 4
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664756 se
RG 3251
DW 20.850 us
DE 6.50 us
TE 29.9 K
D1 2.00000000 se
D11 0.03000000 se
TD0 1
======== CHANNEL f1 ======
NUC1 13C
P1 8.50 us
PL1 -4.00 dB
PL1W 70.66722107 W
SFO1 100.6228298 MH
======== CHANNEL f2 ======
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 us
PL2 -5.40 dB
PL12 10.80 dB
PL13 13.00 dB
PL2W 23.42892075 W
PL12W 0.56202066 W
PL13W 0.33865094 W
SFO2 400.1316005 MH
SI 32768
SF 100.6127203 MH
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm


7.568
7.461
7.456
7.441
7.437
7.378
7.372
7.308
7.302
7.286
7.281
7.274
7.183
7.163
6.903
6.882
3.855
3.684
3.666
3.651
3.634
3.482
3.464
3.447
2.895
2.877
2.860
2.697
2.694
2.678
2.675
2.659
2.656
2.640
2.638
1.235
1.230
1.216
1.212
1.198
1.193
BRUKER
NAME SA_6_064
EXPNO 2
PROCNO 1
Date_ 20150715
Time 21.15
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 4
DW 60.400 usec
DE 6.00 usec
TE 673.2 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.00 usec
PL1 -5.40 dB
PL1W 23.42892075 W
SFO1 400.1324710 MHz
SI 32768
SF 400.1300043 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
Et
Et
O
H
N
O
MeO
41
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
1.00
1.01
1.03
1.17
1.04
1.03
0.97
3.15
2.12
1.01
2.07
4.19
6.21
6.42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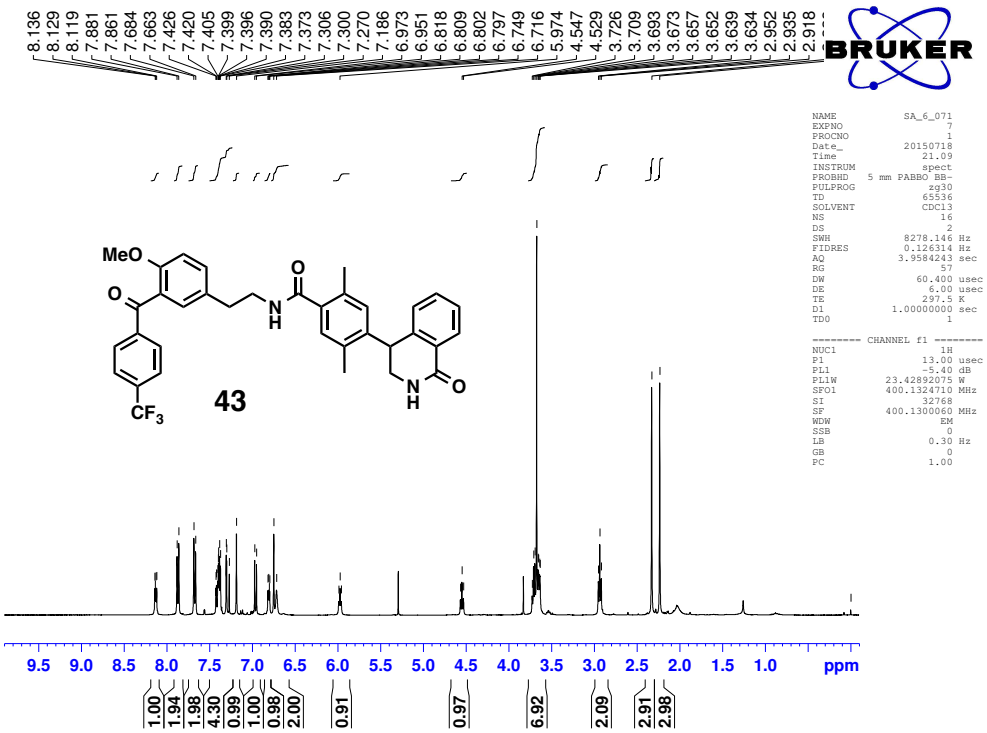
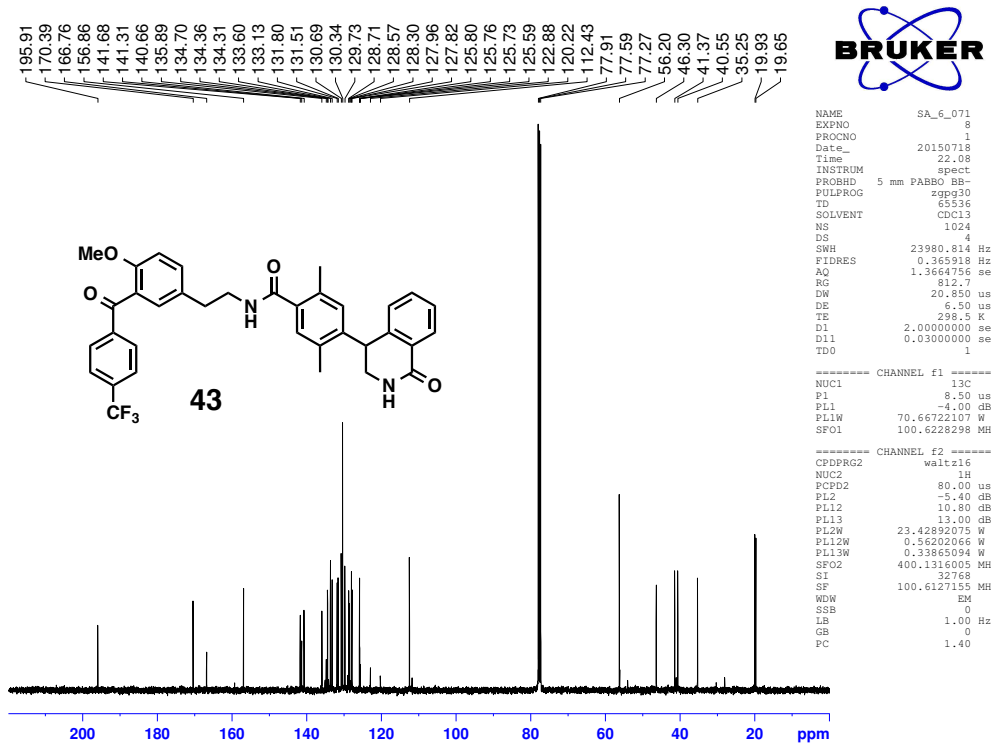
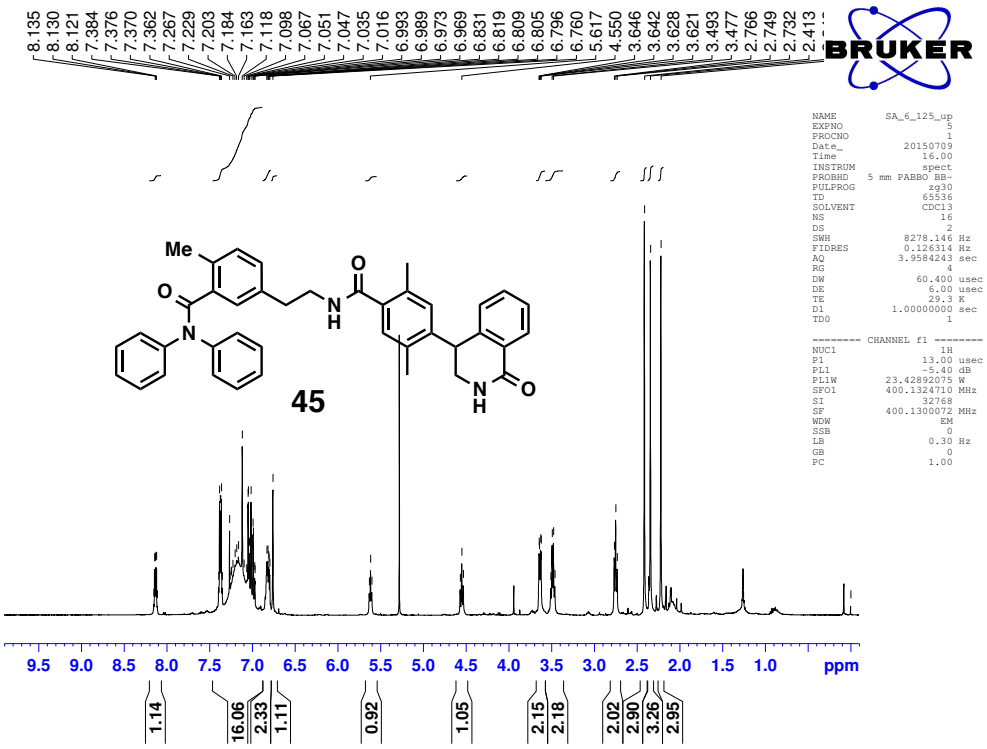
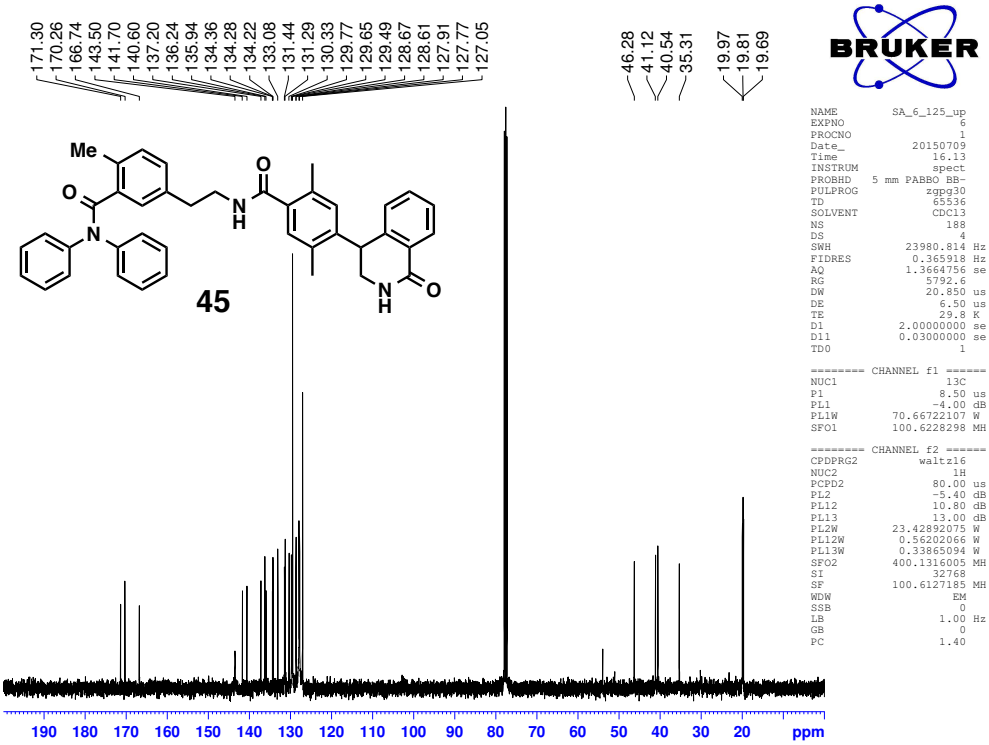
156.96
146.09
142.63
133.42
132.69
131.72
130.58
129.54
128.94
127.64
124.69
112.26
77.92
77.60
77.28
56.17
41.59
40.57
35.21
25.99
25.95
19.06
15.65
15.56
BRUKER
NAME SA_6_064
EXPNO 3
PROCNO 1
Date_ 20150715
Time 21.19
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 66
DS 4
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664756 se
RG 1290.2
DW 20.850 us
DE 6.50 us
TE 673.2 K
D1 2.00000000 se
D11 0.03000000 se
TD0 1
======== CHANNEL f1 ======
NUC1 13C
P1 8.50 us
PL1 -4.00 dB
PL1W 70.66722107 W
SFO1 100.6228298 MH
======== CHANNEL f2 ======
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 us
PL2 -5.40 dB
PL12 10.80 dB
PL13 13.00 dB
PL2W 23.42892075 W
PL12W 0.56202066 W
PL13W 0.33865094 W
SFO2 400.1316005 MH
SI 32768
SF 100.6127164 MH
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
Et
Et
O
H
N
O
MeO
41
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm


8.136
8.129
8.119
7.881
7.861
7.684
7.663
7.426
7.420
7.405
7.399
7.396
7.390
7.383
7.373
7.306
7.300
7.270
7.186
6.973
6.951
6.818
6.809
6.802
6.797
6.749
6.716
5.974
4.547
4.529
3.726
3.709
3.693
3.673
3.657
3.652
3.639
3.634
2.952
2.935
2.918
BRUKER
MeO
O
N
H
O
O
N
H
CF3
43
NAME SA_6_071
EXPNO 7
PROCNO 1
Date_ 20150718
Time 21.09
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 57
DW 60.400 usec
DE 6.00 usec
TE 297.5 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.00 usec
PL1 -5.40 dB
PL1W 23.42892075 W
SFO1 400.1324710 MHz
SI 32768
SF 400.1300060 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
1.00
1.94
1.98
4.30
0.99
1.00
0.98
2.00
0.91
0.97
6.92
2.09
2.91
2.98


195.91
170.39
166.76
156.86
141.68
141.31
140.66
135.89
134.70
134.36
134.31
133.60
133.13
131.80
131.51
130.69
130.34
129.73
128.71
128.57
128.30
127.96
127.82
125.80
125.76
125.73
125.59
122.88
120.22
112.43
77.91
77.59
77.27
56.20
46.30
41.37
40.55
35.25
19.93
19.65
BRUKER
MeO
O
N
H
O
O
N
H
CF3
43
NAME SA_6_071
EXPNO 8
PROCNO 1
Date_ 20150718
Time 22.08
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1024
DS 4
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664756 se
RG 812.7
DW 20.850 us
DE 6.50 us
TE 298.5 K
D1 2.00000000 se
D11 0.03000000 se
TD0 1
======== CHANNEL f1 ======
NUC1 13C
P1 8.50 us
PL1 -4.00 dB
PL1W 70.66722107 W
SFO1 100.6228298 MH
======== CHANNEL f2 ======
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 us
PL2 -5.40 dB
PL12 10.80 dB
PL13 13.00 dB
PL2W 23.42892075 W
PL12W 0.56202066 W
PL13W 0.33865094 W
SFO2 400.1316005 MH
SI 32768
SF 100.6127155 MH
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
200 180 160 140 120 100 80 60 40 20 ppm


8.135
8.130
8.121
7.384
7.376
7.370
7.362
7.267
7.229
7.203
7.184
7.163
7.118
7.098
7.067
7.051
7.047
7.035
7.016
6.993
6.989
6.973
6.969
6.831
6.819
6.809
6.805
6.796
6.760
5.617
4.550
3.646
3.642
3.628
3.621
3.493
3.477
2.766
2.749
2.732
2.413
BRUKER
NAME SA_6_125_up
EXPNO 5
PROCNO 1
Date_ 20150709
Time 16.00
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 4
DW 60.400 usec
DE 6.00 usec
TE 29.3 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.00 usec
PL1 -5.40 dB
PL1W 23.42892075 W
SFO1 400.1324710 MHz
SI 32768
SF 400.1300072 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
Me
O
N
O
N
H
O
N
H
O
45
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
1.14
16.06
2.33
1.11
0.92
1.05
2.15
2.18
2.02
2.90
3.26
2.95


171.30
170.26
166.74
143.50
141.70
140.60
137.20
136.24
135.94
134.36
134.28
134.22
133.08
131.44
131.29
130.33
129.77
129.65
129.49
128.67
128.61
127.91
127.77
127.05
46.28
41.12
40.54
35.31
19.97
19.81
19.69
BRUKER
NAME SA_6_125_up
EXPNO 6
PROCNO 1
Date_ 20150709
Time 16.13
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 188
DS 4
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664756 se
RG 5792.6
DW 20.850 us
DE 6.50 us
TE 29.8 K
D1 2.00000000 se
D11 0.03000000 se
TD0 1
======== CHANNEL f1 ======
NUC1 13C
P1 8.50 us
PL1 -4.00 dB
PL1W 70.66722107 W
SFO1 100.6228298 MH
======== CHANNEL f2 ======
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 us
PL2 -5.40 dB
PL12 10.80 dB
PL13 13.00 dB
PL2W 23.42892075 W
PL12W 0.56202066 W
PL13W 0.33865094 W
SFO2 400.1316005 MH
SI 32768
SF 100.6127185 MH
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
Me
O
N
O
N
H
O
N
H
O
45
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

VI. References in Supporting Information

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