

SUPPORTING INFORMATION

An efficient synthesis of 1-arylindazole-3-carboxamides using nitrile imines, isocyanides and 2-hydroxymethylbenzoic acid, followed by a chemoselective Buchwald-Hartwig intramolecular cyclization.

Mariateresa Giustiniano,^{a*} Valentina Mercalli,^b Ettore Novellino,^a and Gian Cesare Tron^{b*}

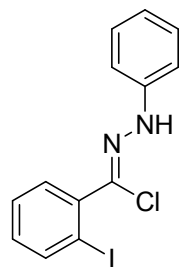
a) Dipartimento di Farmacia, Università degli Studi di Napoli “Federico II”, via D. Montesano 49, 80131 Napoli, Italy.

b) Dipartimento di Scienze del Farmaco, Università del Piemonte Orientale “A. Avogadro”, Largo Donegani 2, 28100 Novara, Italy.

Contents:

- Copies of ^1H and ^{13}C spectra.....S3

¹H NMR
400 MHz, CDCl₃



9

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8.0618
8.0421
7.6518
7.6325
7.4844
7.4656
7.4473
7.4291
7.4106
7.3509
7.3308
7.1435
7.1245
7.1045
7.0852
7.0673

1.0000
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0.9131
5.0755
2.0139

10

8

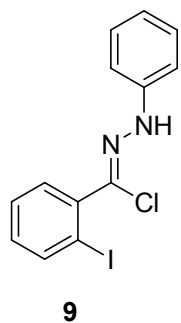
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[ppm]

¹³C NMR
100 MHz, CDCl₃



M 143.2761
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M 130.9493
M 130.7367
M 129.5991
M 128.3234
M 123.0131
M 121.6045
M 113.7534

M 96.7701

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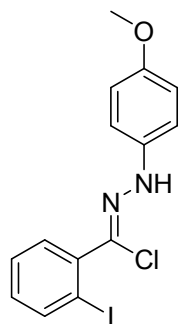
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[ppm]

34

¹H NMR
400 MHz, CDCl₃



14

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7.5799
7.5762
7.5605
7.5569
7.4270
7.4244
7.4082
7.3892
7.2117
7.2065
7.1940
7.1893
7.0669
7.0635
6.9213
6.9034
6.8990

3.8009

2.0242
0.9701
1.0945
1.9852
1.0643
2.0478

3.0000

10

8

S5

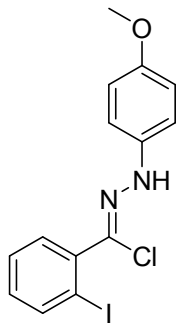
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[ppm]

¹³C NMR
100 MHz, CDCl₃



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— M 154.7146

— M 140.4572

— M 139.8834

— M 137.2292

— M 130.8447

— M 130.5040

— M 128.2085

— M 121.9855

— M 114.8478

— M 96.6092

— M 55.7381

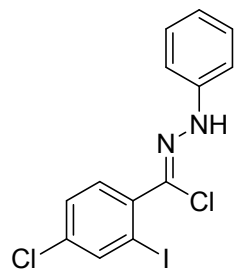
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100
S6

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[ppm]

¹H NMR
400 MHz, CDCl₃



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7.4805
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7.4032
7.3984
7.3823
7.3775
7.3282
7.3080
7.2890
7.2192
7.2001
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6.9653
6.9472

1.7670

1.8685

2.0228

2.0577

1.0000

10

8

6

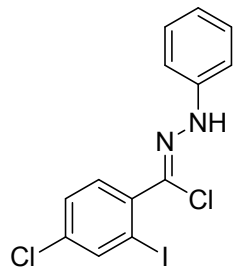
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[ppm]

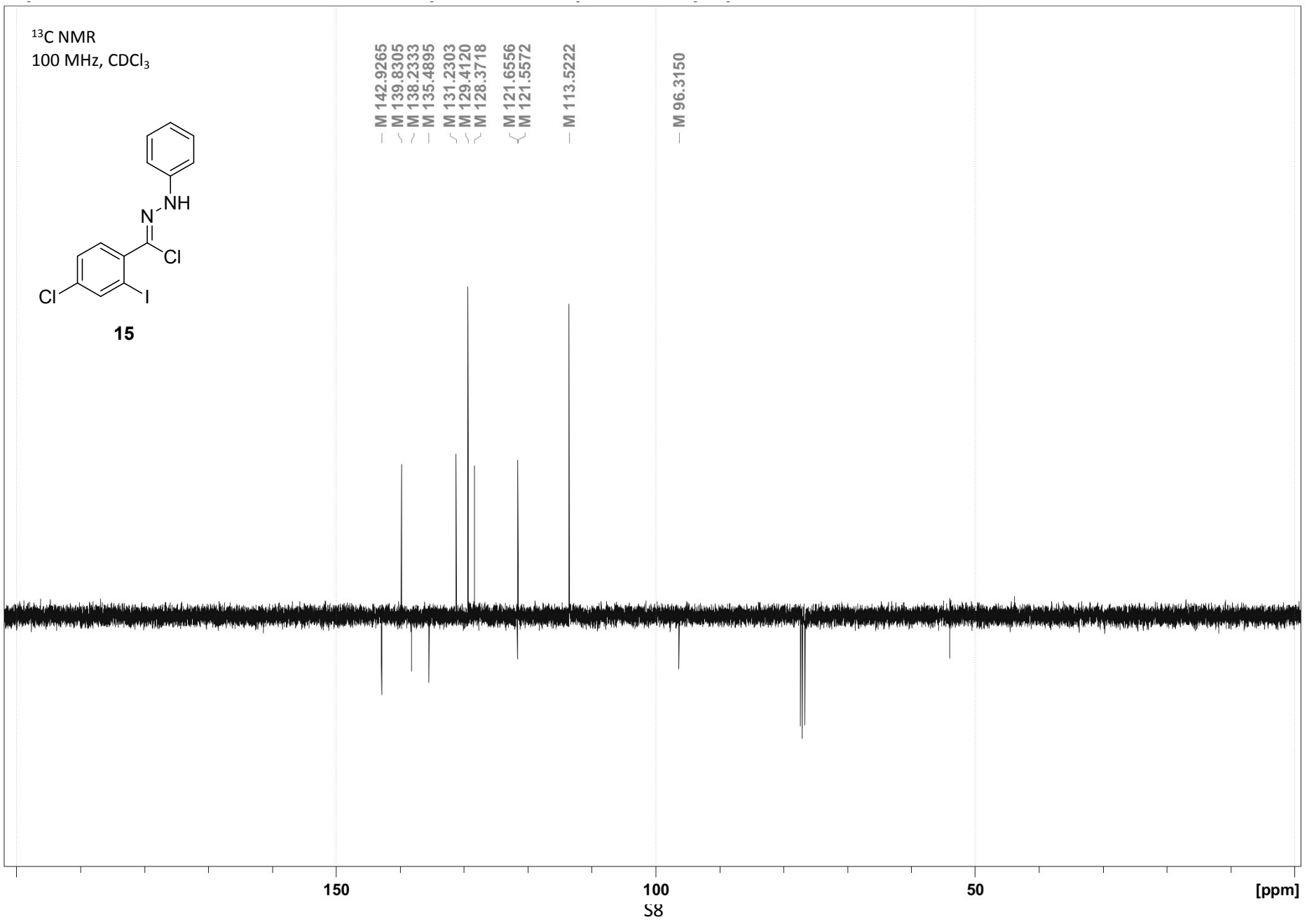
S/

¹³C NMR
100 MHz, CDCl₃

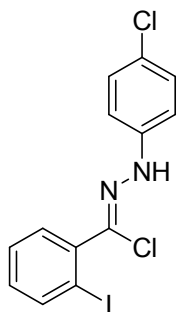


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- M 142.9265
- M 139.8305
- M 138.2333
- M 135.4895
- M 131.2303
- M 129.4120
- M 128.3718
- M 121.6556
- M 121.5572
- M 113.5222
- M 96.3150



¹H NMR
400 MHz, CDCl₃



16

8.0355
7.9784
7.9585
7.5575
7.5542
7.5382
7.5352
7.4291
7.4104
7.3915
7.2724
7.2505
7.1600
7.1380
7.0990
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7.0796
7.0608
7.0573

2.0000
0.9614
1.1768
5.0620

10

8

6

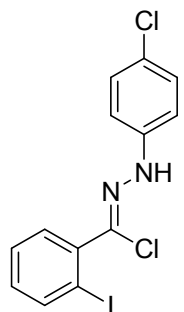
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[ppm]

S9

¹³C NMR
100 MHz, CDCl₃



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M 139.5925
M 130.7816
M 130.7377
M 129.3512
M 128.2235
M 126.0778
M 123.6864
— M 114.7789

— M 96.4769

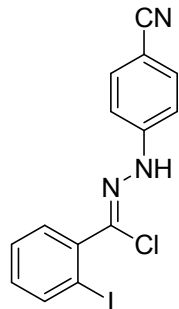
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100
S10

50

[ppm]

¹H NMR
400 MHz, CDCl₃



17

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7.9699
7.6591
7.6374
7.5981
7.5951
7.5790
7.5759
7.5091
7.5077
7.4894
7.4717
7.4700
7.4068
7.3849
7.2097
7.2063
7.1901
7.1876
7.1716
7.1681

3.3366

2.4786

1.0000

0.9136

6.2961

0.9658

10

8

6

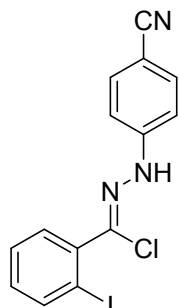
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[ppm]

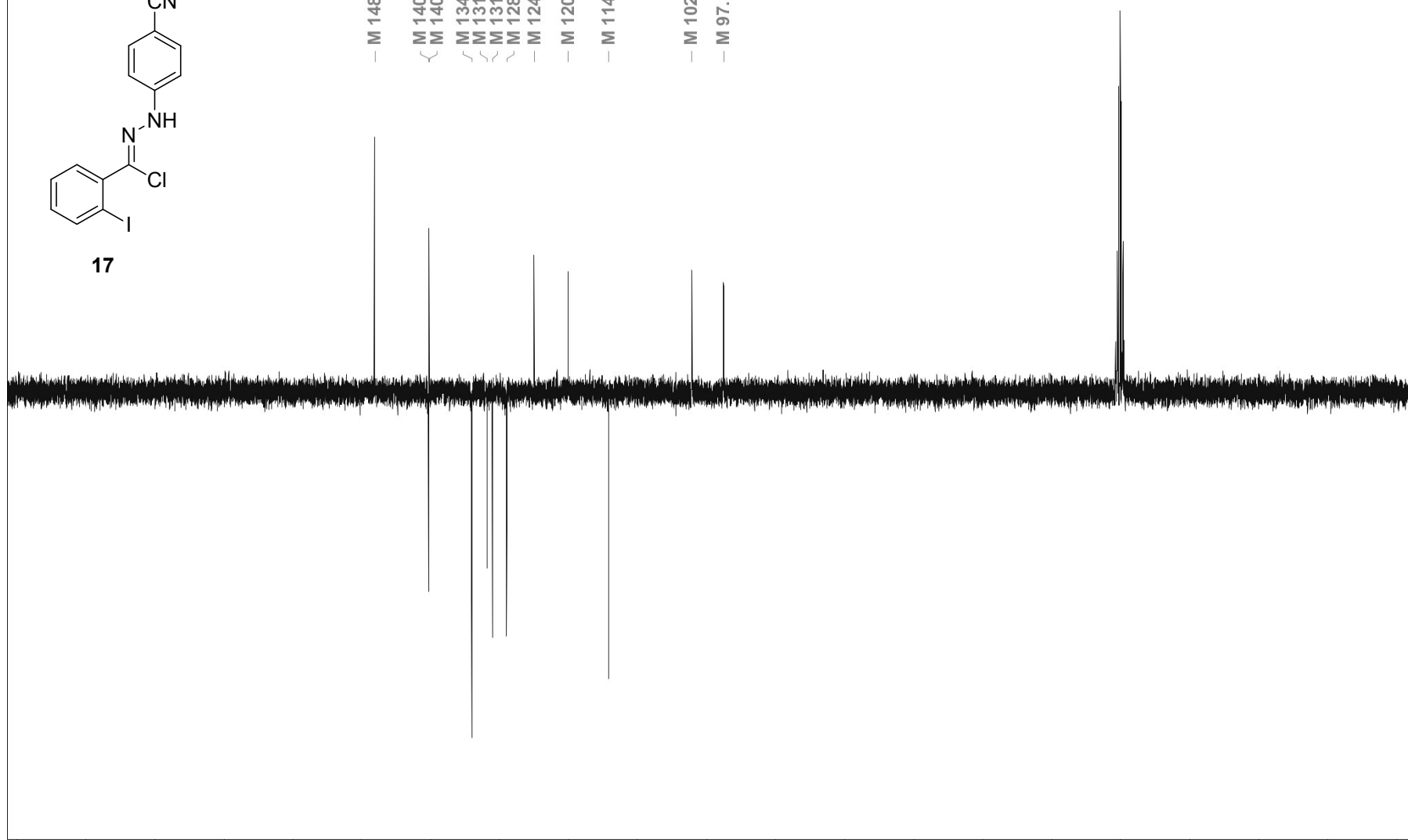
S11

¹³C NMR
100 MHz, CDCl₃



17

M 148.1153
M 140.3027
M 140.2254
M 134.0201
M 131.7714
M 131.0295
M 128.9972
M 124.9711
M 120.0563
M 114.2142
M 102.1746
M 97.5535



150

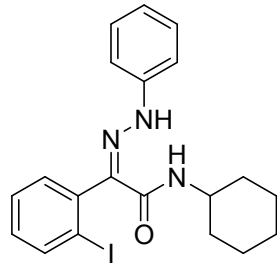
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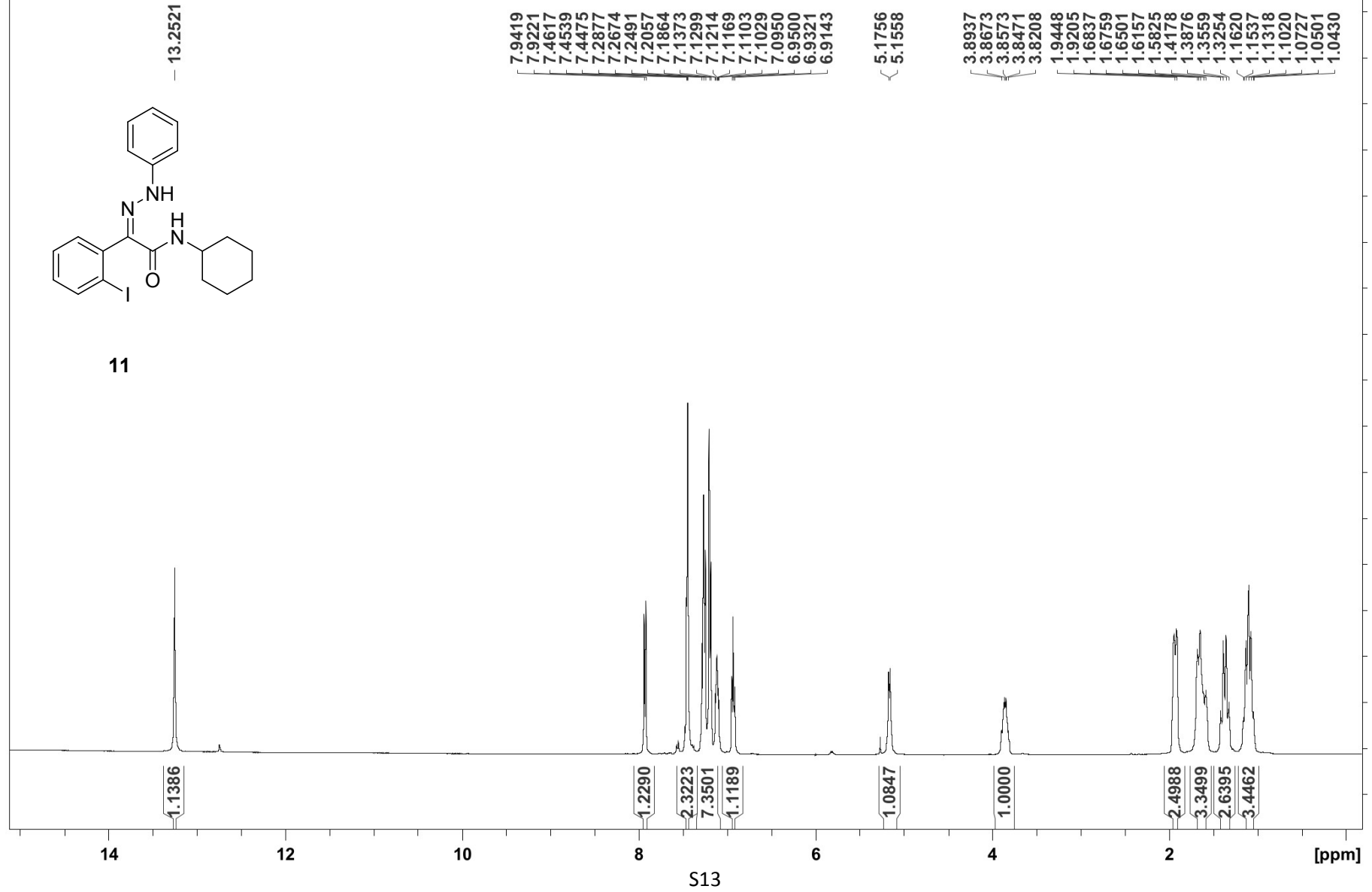
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S12

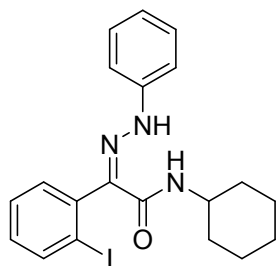
¹H NMR
400 MHz, CDCl₃



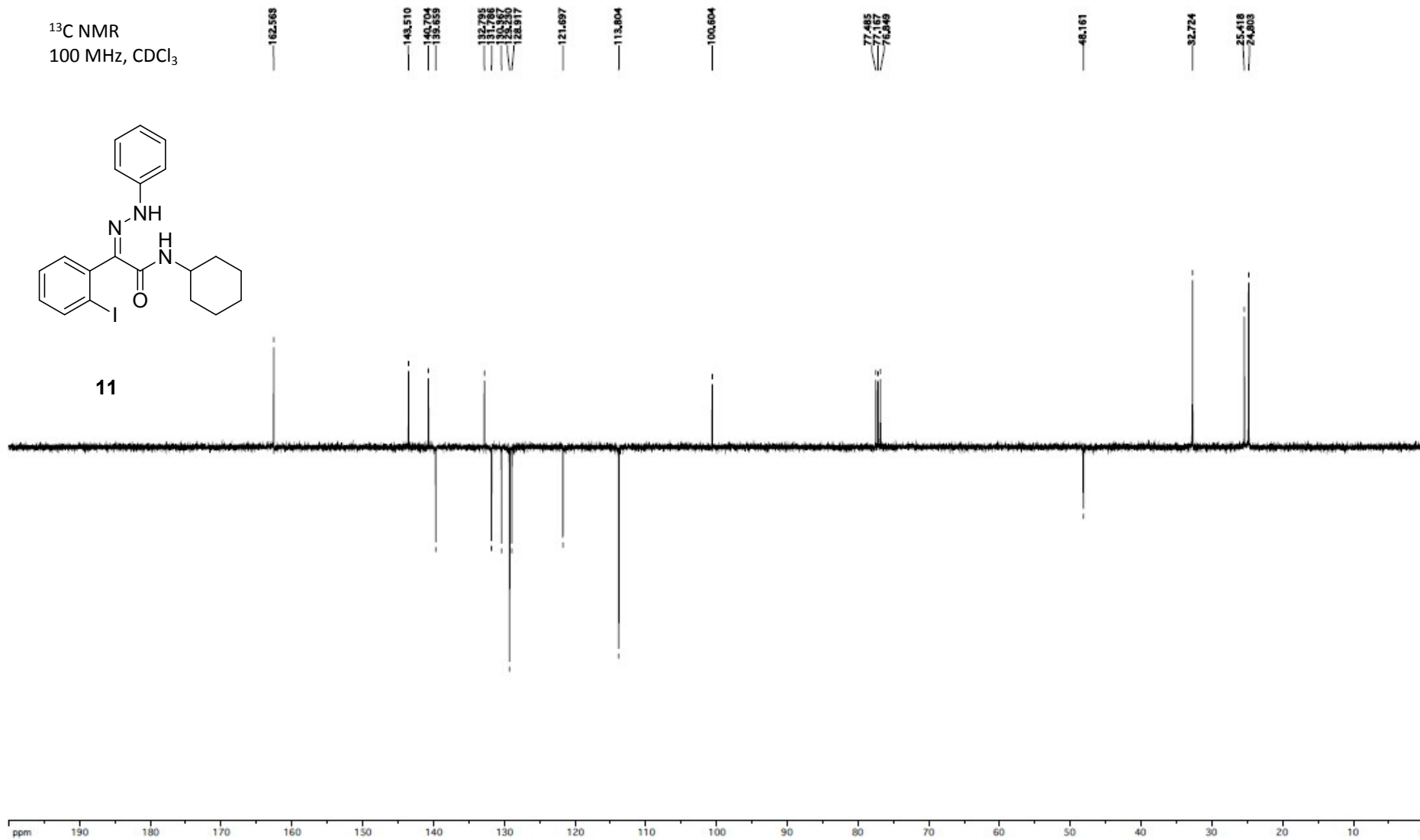
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¹³C NMR
100 MHz, CDCl₃

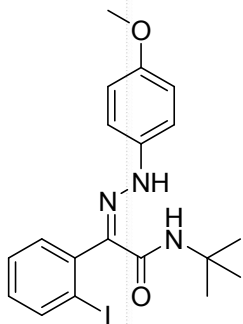


11



¹H NMR
400 MHz, CDCl₃

— 13.2035



23

7.9342
7.9143
7.4495
7.4453
7.4371
7.1478
M 7.1421
M 7.1319
7.1255
7.1160
7.1069
7.1007
7.0950
7.0866
7.0819
7.0728
6.8401
6.8178

— 5.0515

— 3.7627

— 1.3491

0.9685

0.8852

1.9787

3.0157

2.0832

0.9174

3.0741

9.0000

14

12

10

8

6

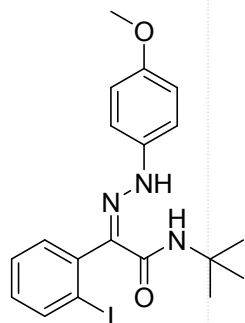
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[ppm]

S15

¹³C NMR
100 MHz, CDCl₃



23

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— M 154.8824

— M 141.2433

— M 139.6326

— M 137.6244

— M 132.2901

— M 131.8299

— M 130.1355

— M 128.8804

— M 114.9694

— M 114.5929

— M 100.7237

— M 55.6020

— M 51.6275

— M 28.6168

150

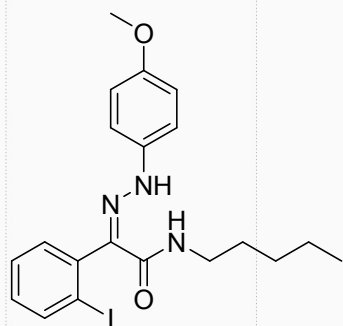
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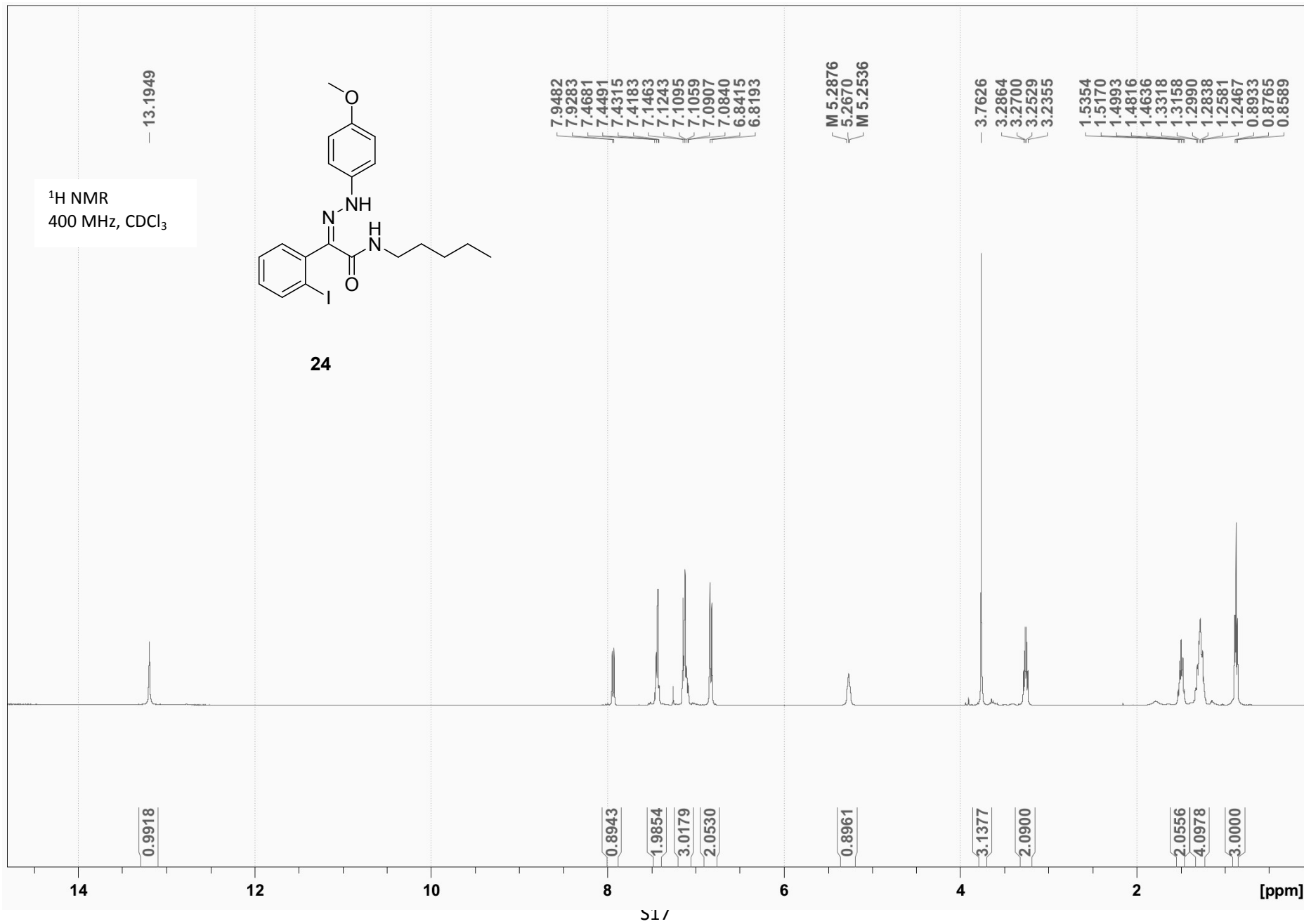
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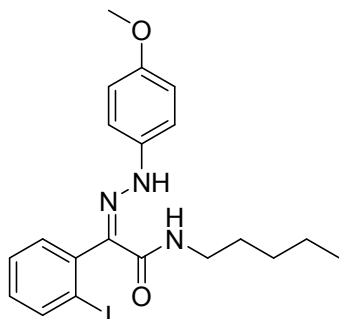
¹H NMR
400 MHz, CDCl₃



24



¹³C NMR
100 MHz, CDCl₃



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— M 140.9122

— M 139.6953

— M 137.4912

— M 131.7285

— M 131.5104

— M 130.2246

— M 128.8356

— M 114.9912

— M 114.6353

— M 101.0435

— M 55.6302

— M 39.2602

— M 29.1352

— M 29.0204

— M 22.3049

— M 14.0051

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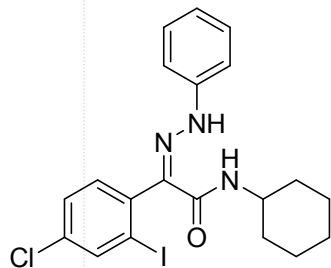
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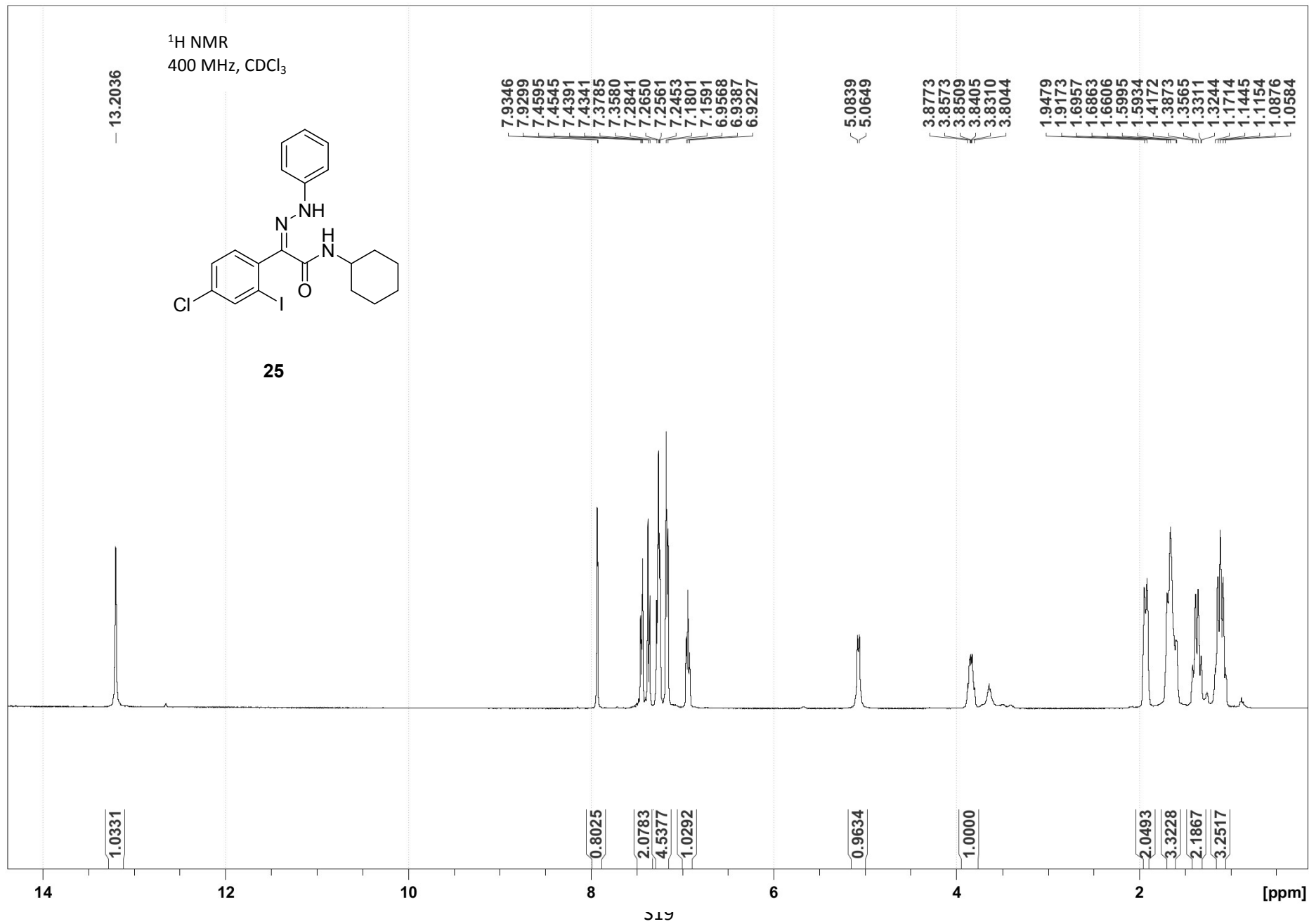
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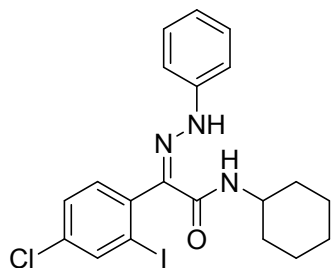
¹H NMR
400 MHz, CDCl₃



25

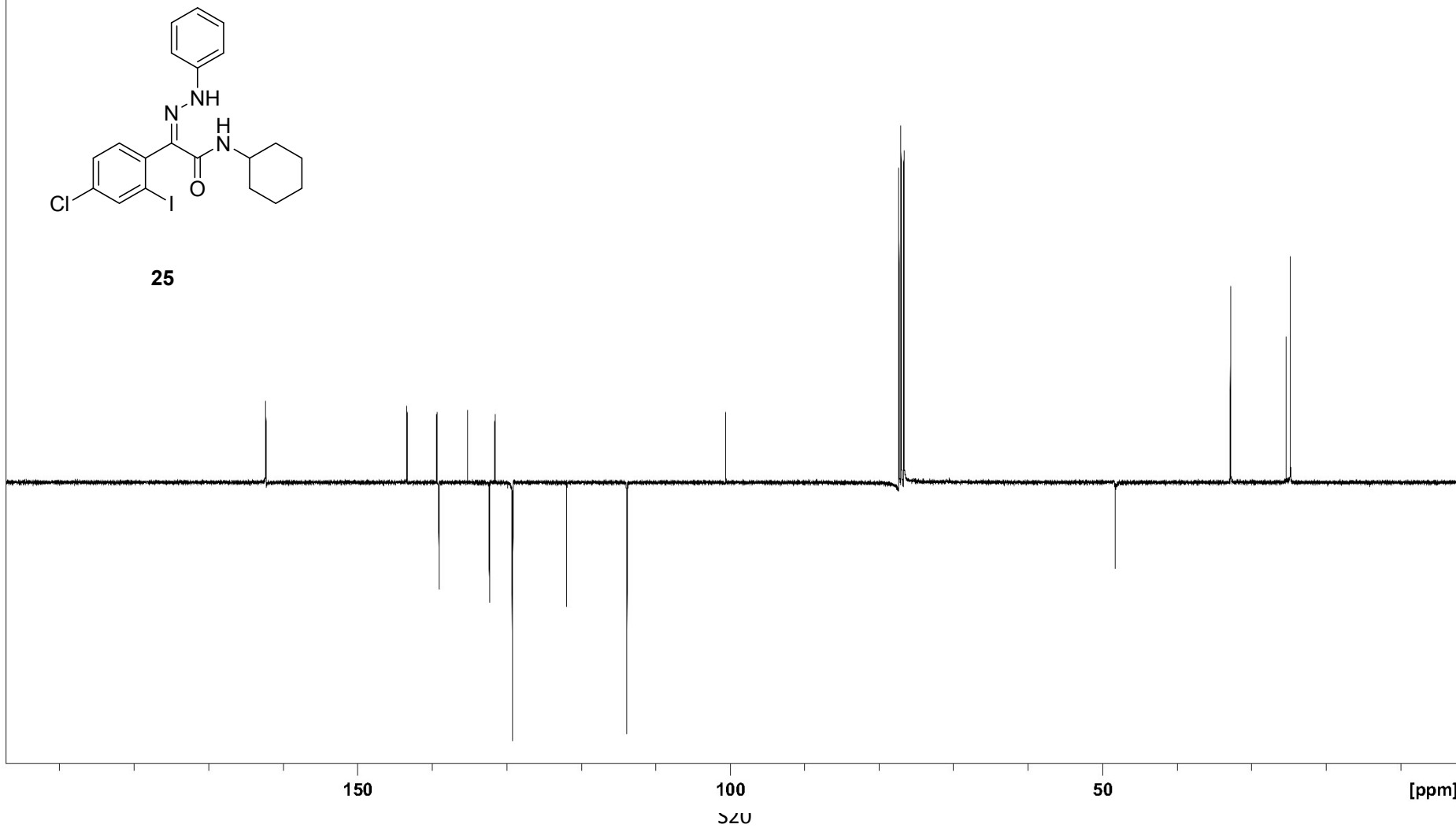


¹³C NMR
100 MHz, CDCl₃



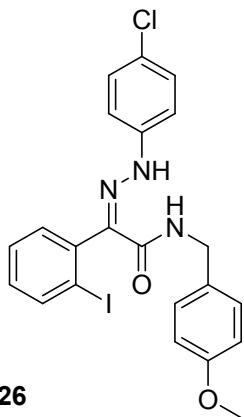
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— M 162.3351
— M 143.3331
— M 139.3757
— M 139.0418
— M 135.2180
— M 132.3126
— M 131.5445
— M 129.2402
— M 129.1567
— M 121.9266
— M 113.8783
— M 100.6371
— M 48.2564
— M 32.7776
— M 25.3805
— M 24.7961

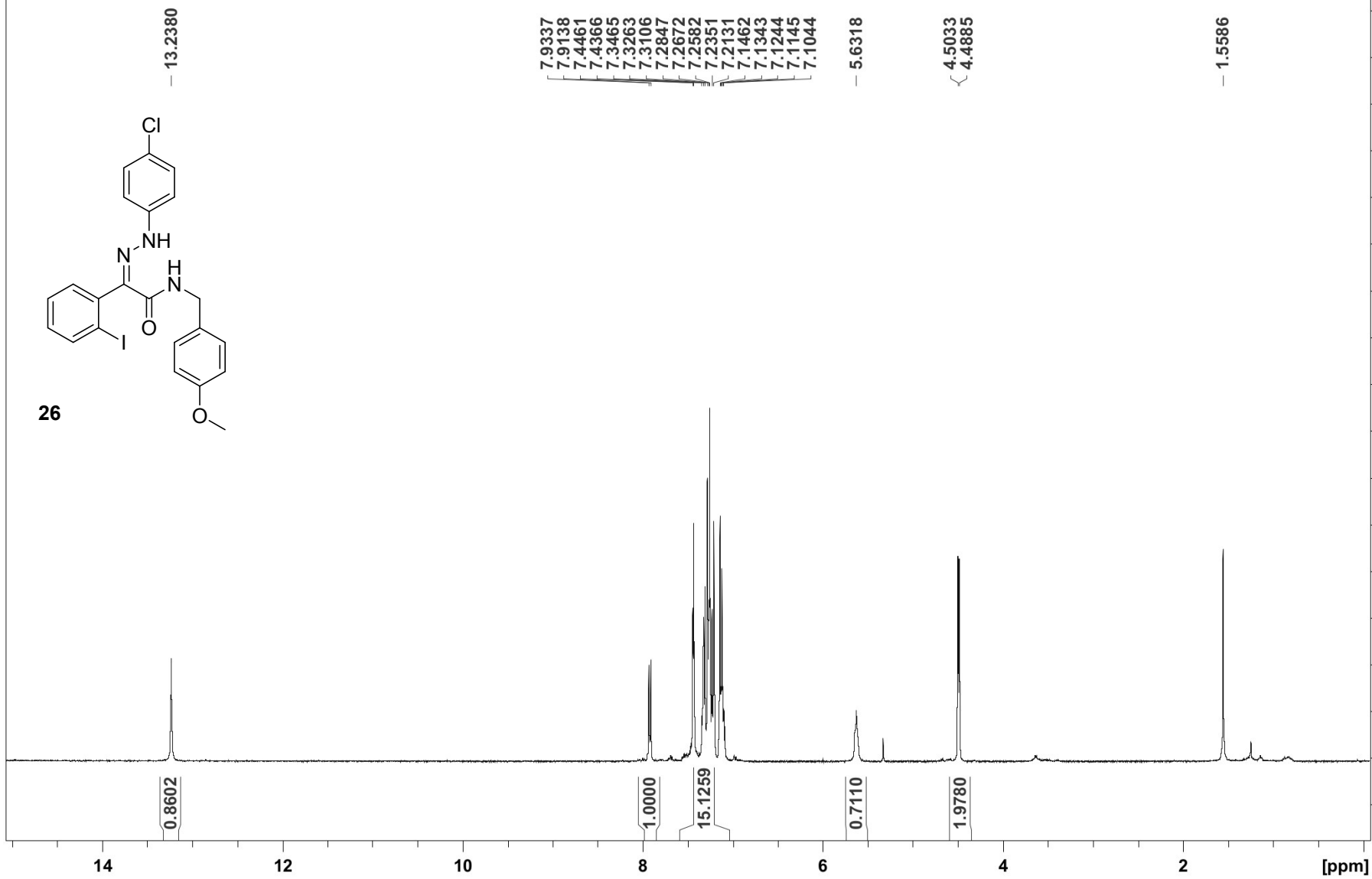


SZU

¹H NMR
400 MHz, CDCl₃

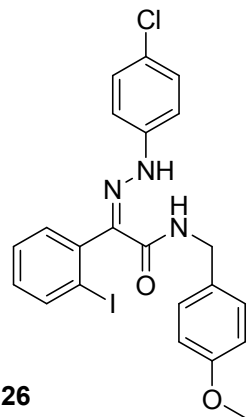


26



S21

¹³C NMR
100 MHz, CDCl₃



— M 163.4116

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M 140.3646
M 139.8196
M 137.3280
M 132.8705
M 131.5468
M 130.5346
M 129.1915
M 128.8606
M 128.7438
M 127.6538
M 126.6805

— M 115.1570

— M 100.5969

— M 43.3299

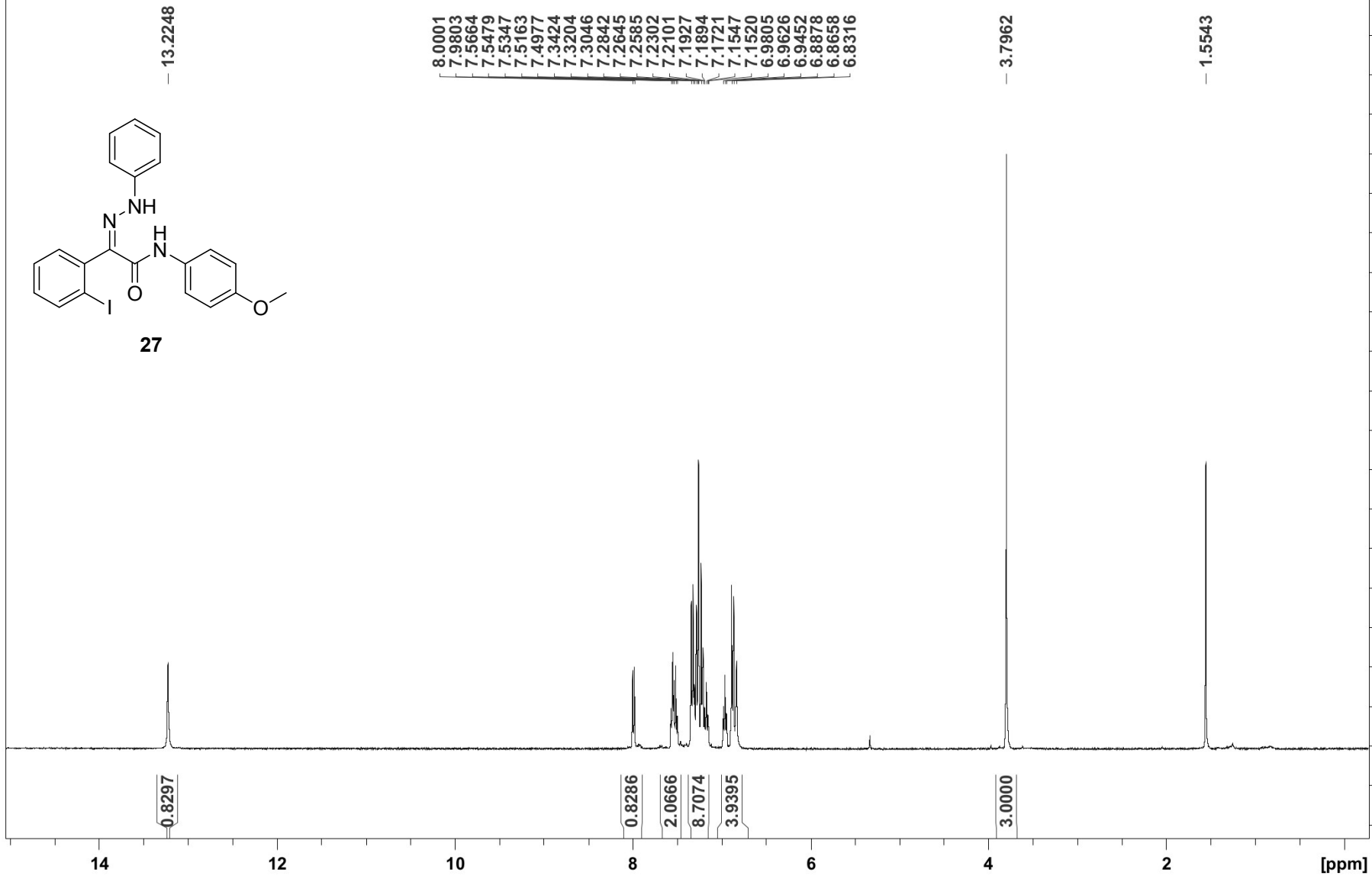
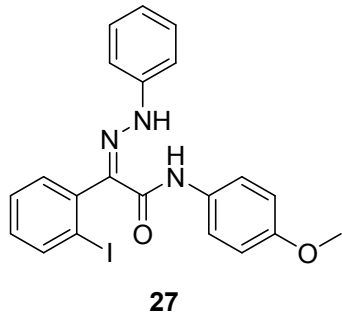
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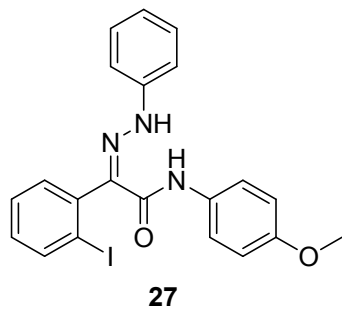
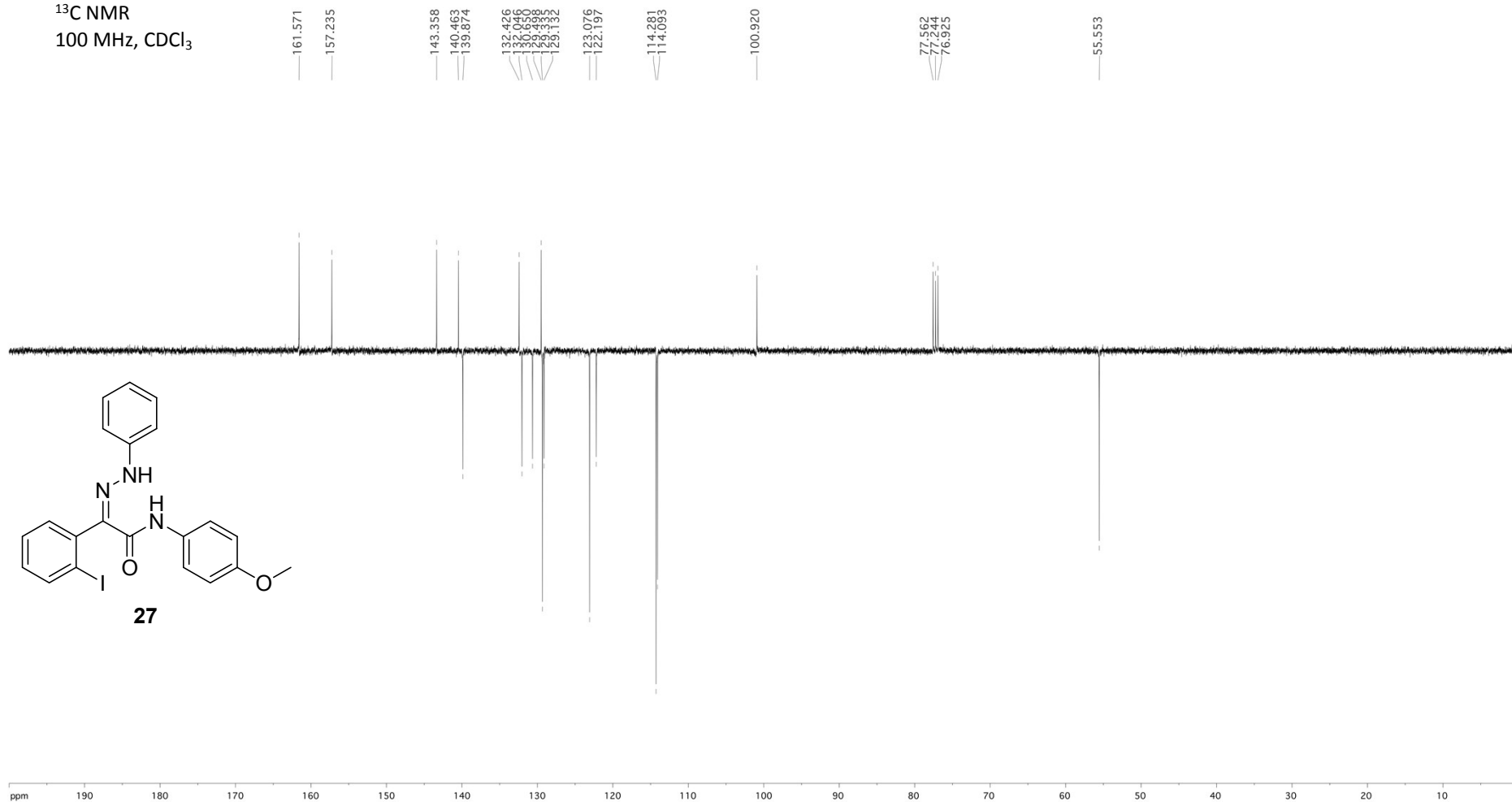
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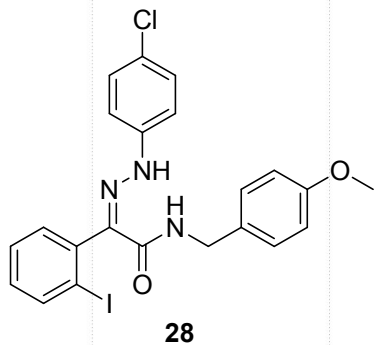
¹H NMR
400 MHz, CDCl₃



¹³C NMR
100 MHz, CDCl₃



¹H NMR
400 MHz, CDCl₃



13.241

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7.4361
7.4303
7.4229
7.2337
7.2113
7.1891
7.1448
7.1227
7.1149
7.1024
6.8579
6.8364

M 5.5975
5.5798
M 5.5671

4.4283
4.4142

3.7793

1.0000

1.0678

2.0947

7.3692

2.0679

0.8991

2.0537

3.0905

14

12

10

8

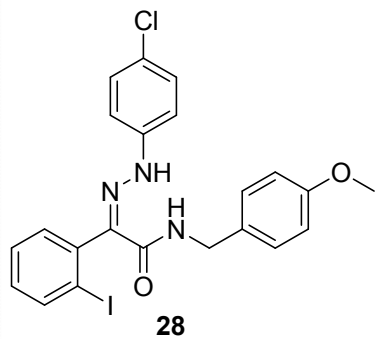
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4

2

[ppm]

¹³C NMR
100 MHz, CDCl₃



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M 159.1463

M 142.1051

M 140.2858

M 139.7684

M 132.8918

M 131.5899

M 130.5384

M 129.3033

M 129.1864

M 129.0635

M 128.8860

M 126.5698

M 115.0820

M 114.1077

M 100.5877

M 55.2861

M 42.8240

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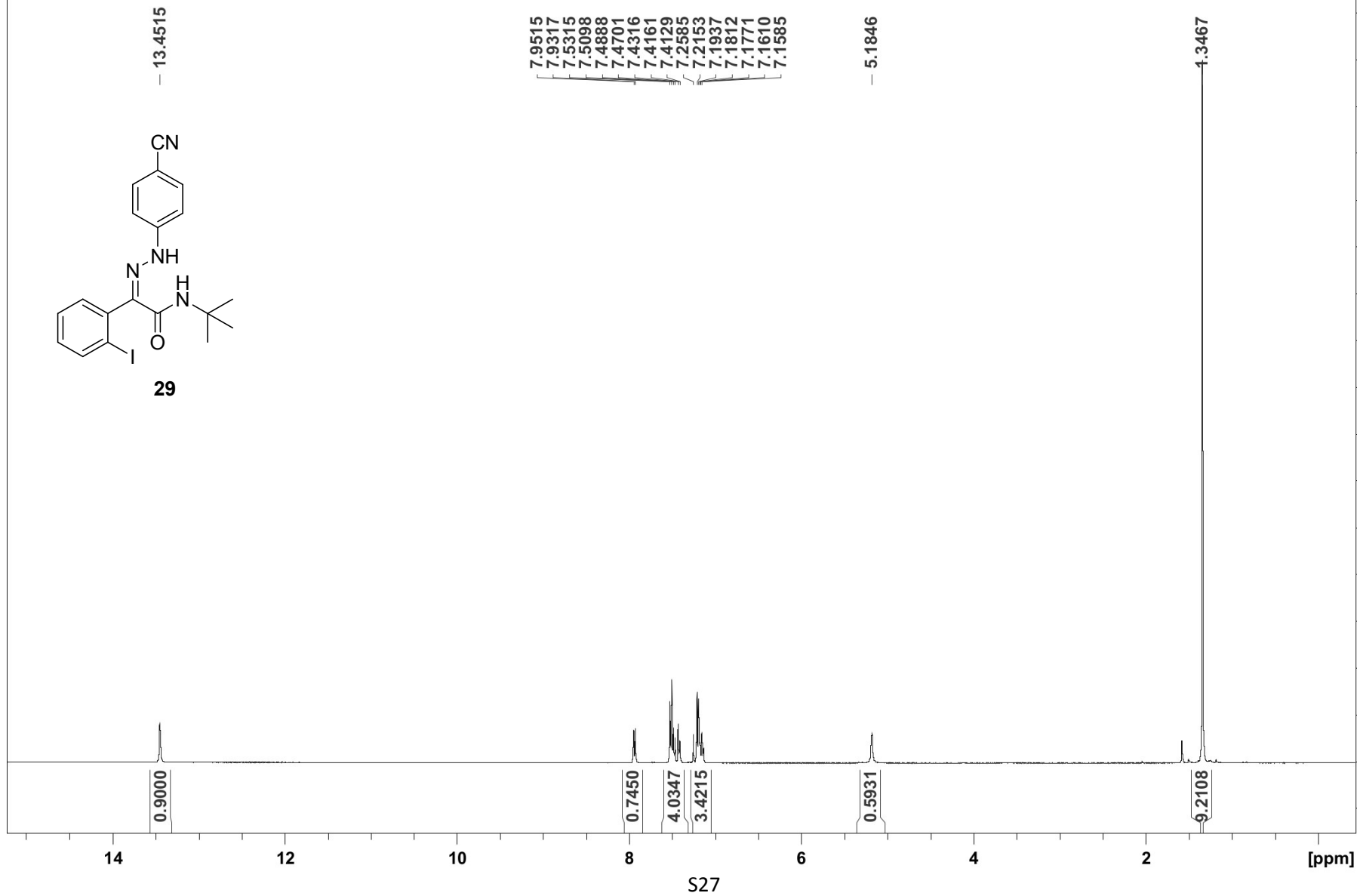
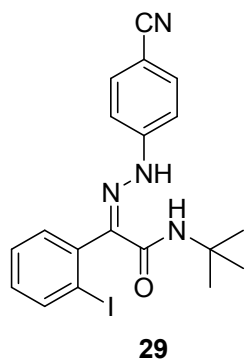
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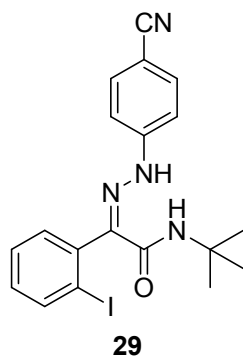
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SZb

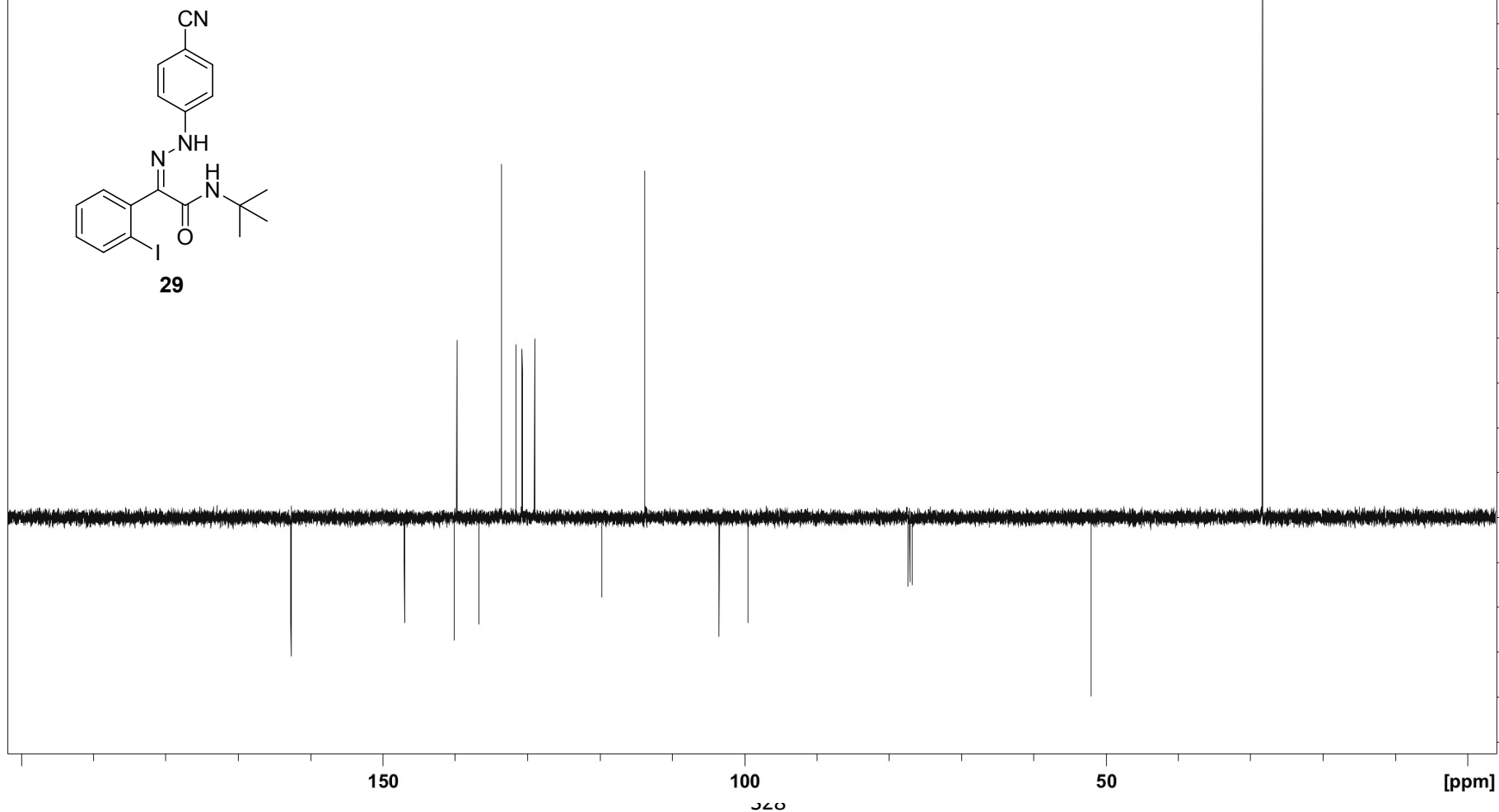
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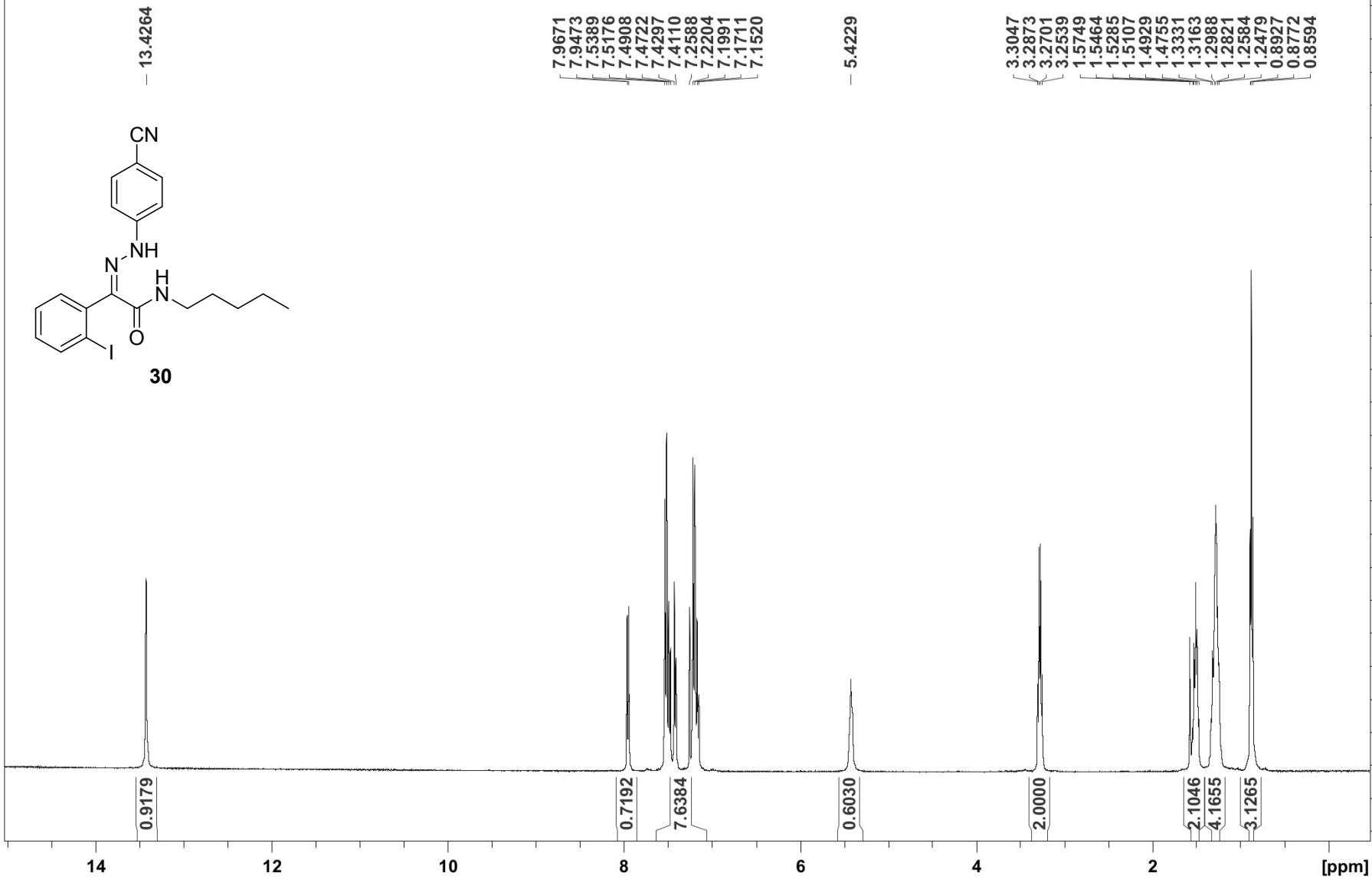
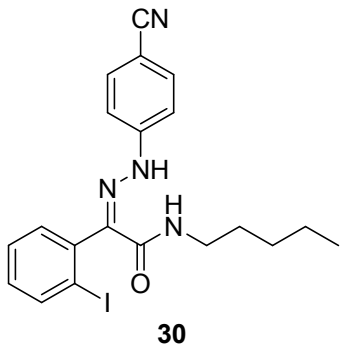
¹³C NMR
100 MHz, CDCl₃



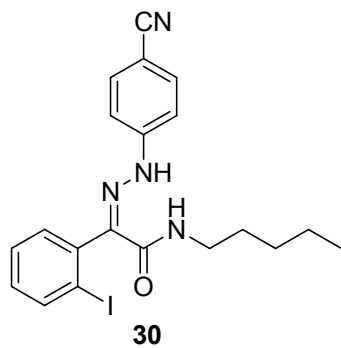
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- M 140.1570
- M 139.7168
- M 136.7258
- M 133.5389
- M 131.5449
- M 130.7780
- M 129.0113
- M 119.7345
- M 113.8037
- M 103.5271
- M 99.5676
- M 52.0817
- M 28.4268



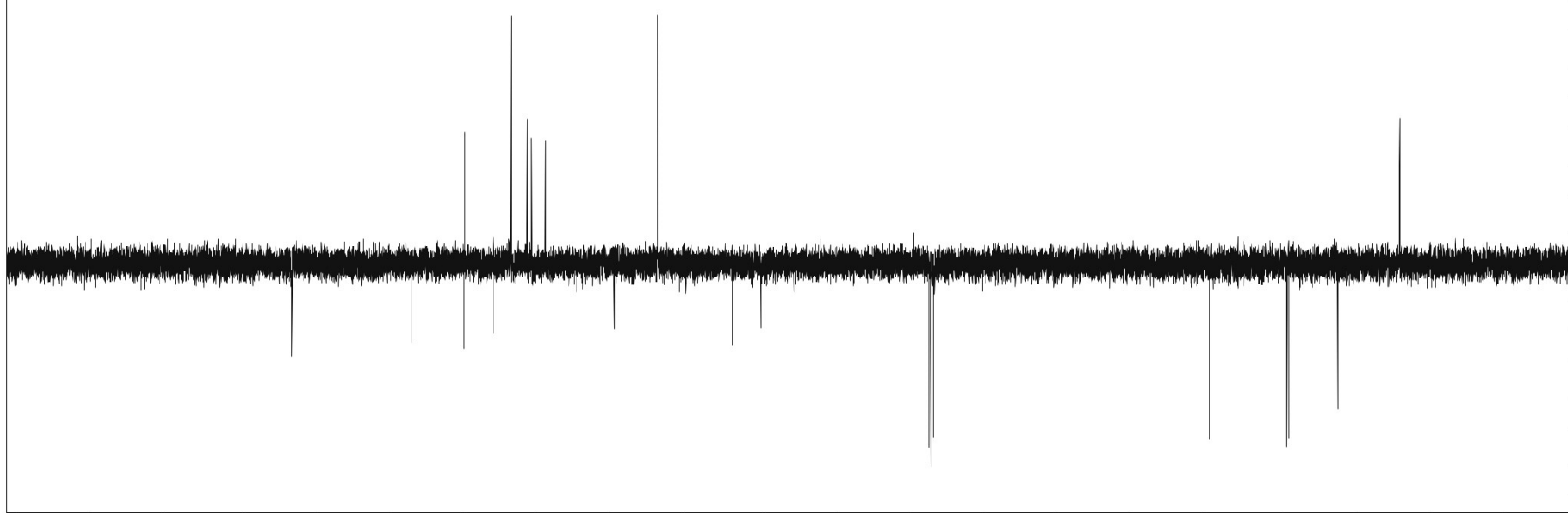
¹H NMR
400 MHz, CDCl₃



¹³C NMR
100 MHz, CDCl₃



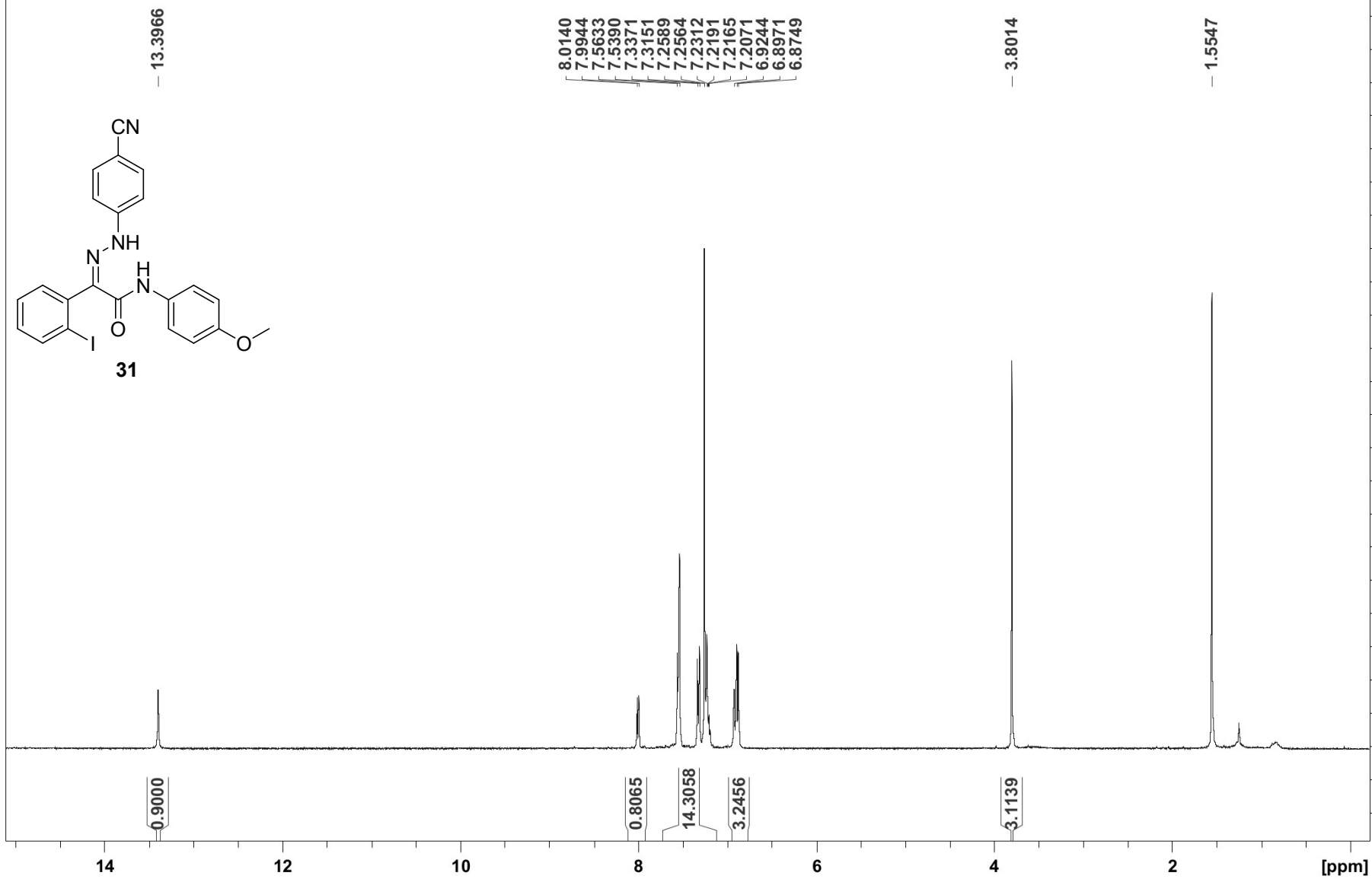
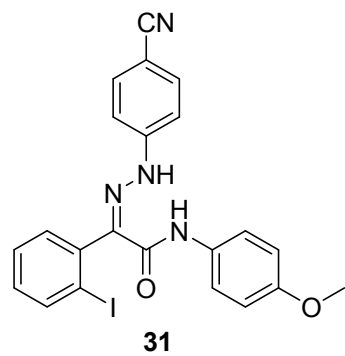
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- M 139.9306
- M 139.7985
- M 135.8616
- M 133.5629
- M 131.3963
- M 130.7886
- M 128.9655
- M 119.6914
- M 113.8786
- M 103.7590
- M 99.9014
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- M 29.0641
- M 28.7999
- M 22.2737
- M 13.9403



150
100
50
0 [ppm]

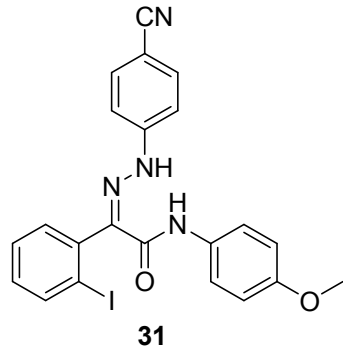
S30

¹H NMR
400 MHz, CDCl₃

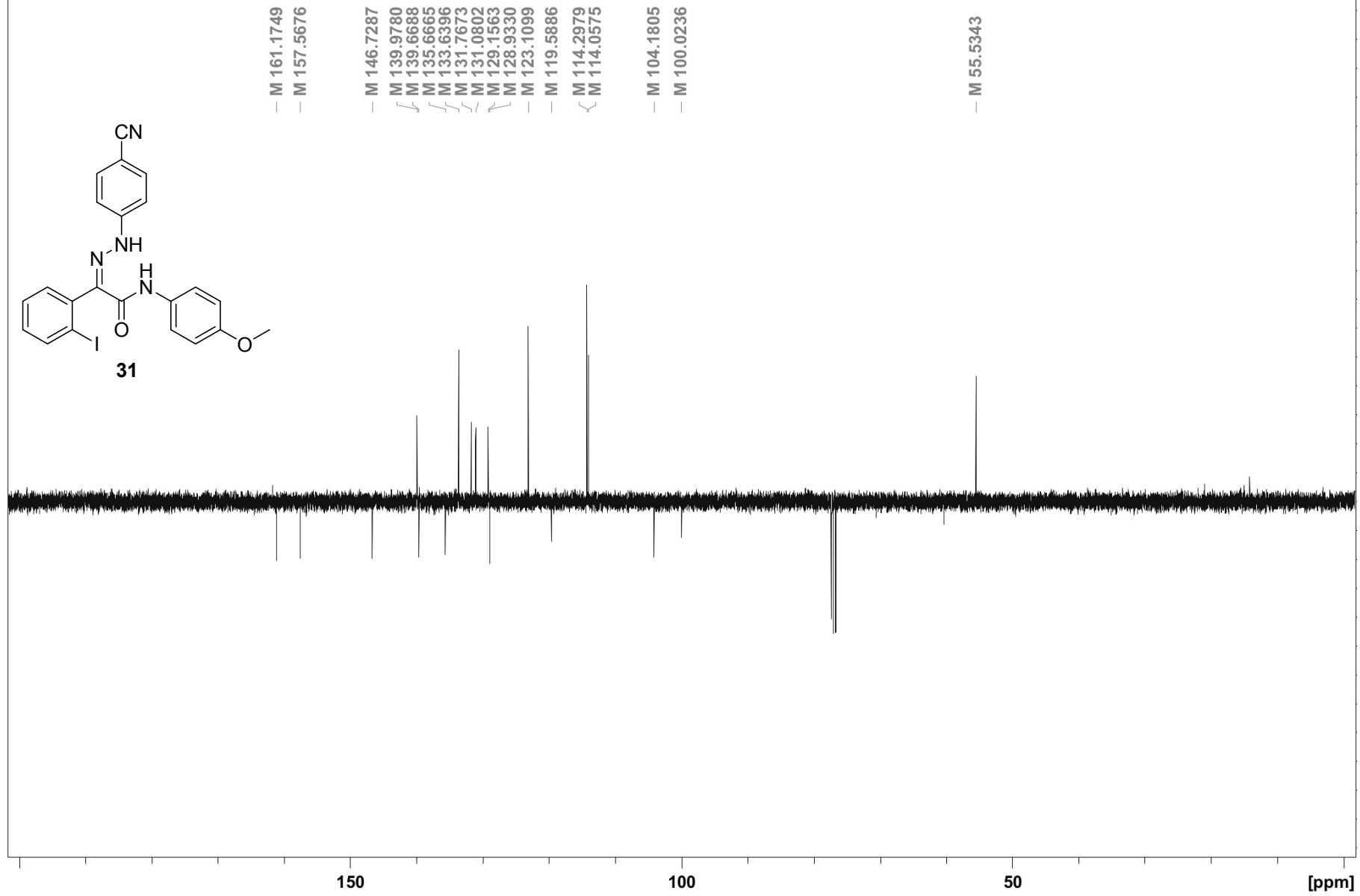


S31

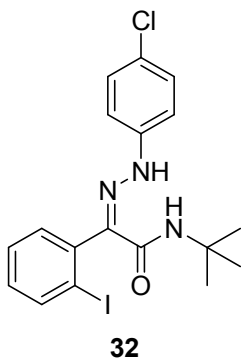
¹³C NMR
100 MHz, CDCl₃



- M 161.1749
- M 157.5676
- M 146.7287
- ✓ M 139.9780
- ✓ M 139.6688
- ✓ M 135.6665
- ✓ M 133.6396
- ✓ M 131.7673
- ✓ M 131.0802
- ✓ M 129.1563
- ✓ M 128.9330
- M 123.1099
- M 119.5886
- ✓ M 114.2979
- ✓ M 114.0575
- M 104.1805
- M 100.0236
- M 55.5343



¹H NMR
400 MHz, CDCl₃



13.2654

7.9378
7.9181
7.4623
7.4403
7.4349
7.4213
7.2170
7.1951
7.1286
7.1123
7.1066
7.0962

5.1116

1.3501

0.8881

0.8185

1.9474

5.0025

0.7974

9.0000

14

12

10

8

6

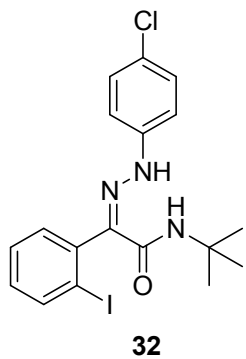
4

2

[ppm]

S33

¹³C NMR
100 MHz, CDCl₃



— M 163.1679

M 142.3065
M 140.7813
M 139.6989
M 134.0243
M 131.6791
M 130.4326
M 129.1370
M 128.9238
M 126.2177

— M 114.9342

— M 100.2230

— M 51.7926

— M 28.5531

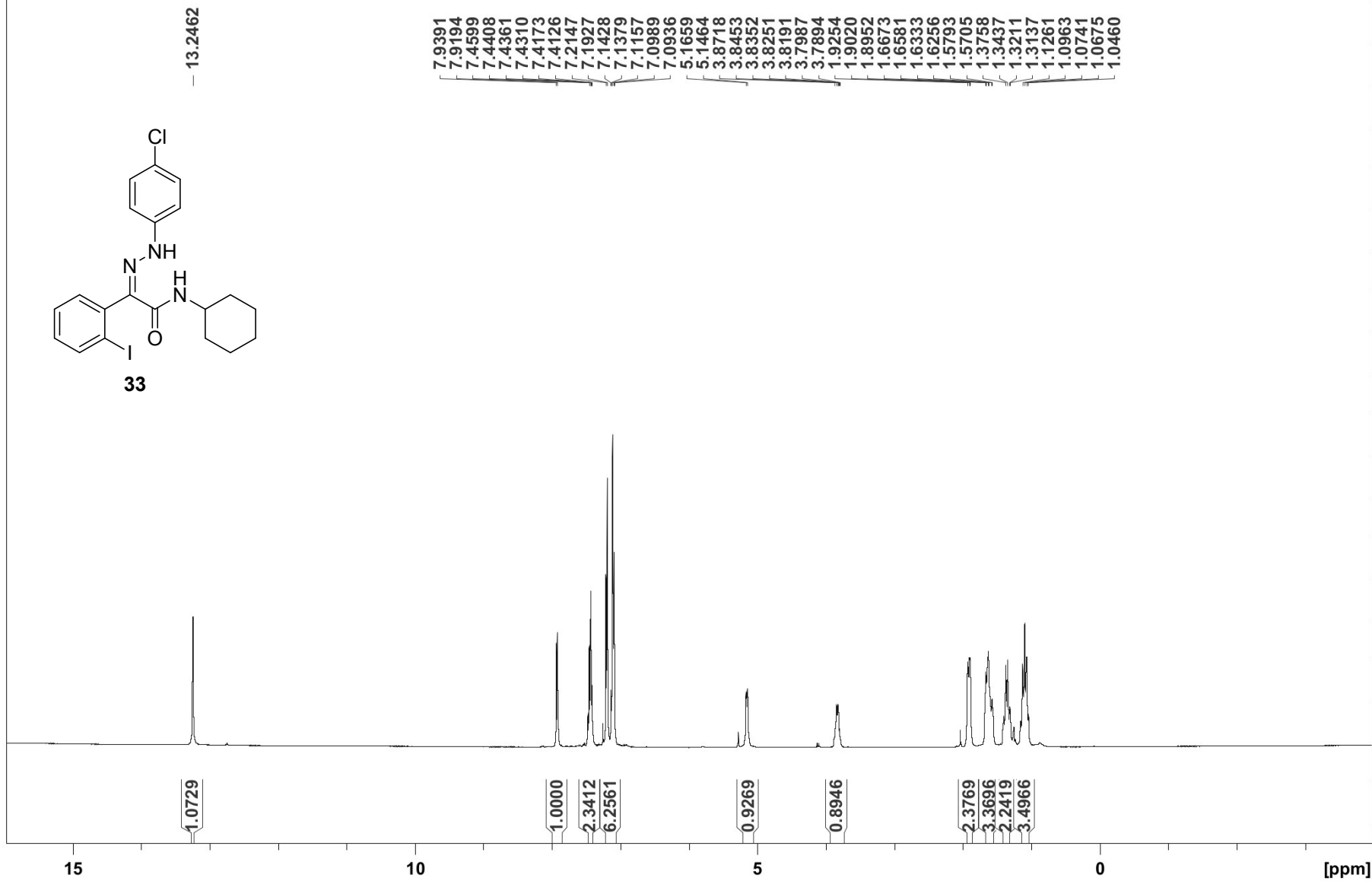
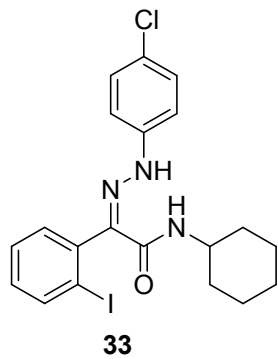
150

100
S34

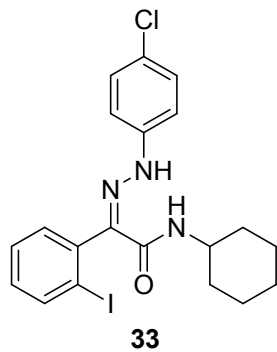
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[ppm]

¹H NMR
400 MHz, CDCl₃



¹³C NMR
100 MHz, CDCl₃



— M 162.4781

M 142.2045
M 140.5045
M 139.7268
M 133.4693
M 131.6789
M 130.4310
M 129.1650
M 128.8937
M 126.3256

— M 114.9319

— M 100.3913

— M 48.2153

— M 32.6982

M 25.3556
M 24.7407

200

150

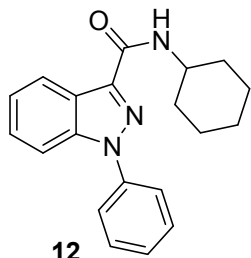
100

50

[ppm]

S36

¹H NMR
400 MHz, CDCl₃



8.5051
8.4848
7.7283
7.7263
7.7074
7.6866
7.6653
7.5774
7.5585
7.5383
7.4606
7.4405
7.4208
7.4012
7.3524
7.3330
7.3148
7.0538
7.0336

4.1030
4.0928
4.0663
4.0558
4.0451
4.0188
4.0096
2.0839
2.0597
2.0540
2.0339
1.7965
1.7873
1.7712
1.7630
1.6743
1.6650
1.6503
1.6420
1.4961
1.4885
1.4801
1.4586
1.4276
1.3961
1.3614
1.3548
1.3312
1.3041
1.2978
1.2664
1.2536
1.2276
1.1965

0.8303

3.0820

2.0707

3.1302

1.0000

1.0356

2.1784

3.2910

5.3218

10

8

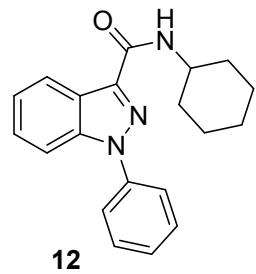
6

4

2

[ppm]

¹³C NMR
100 MHz, CDCl₃



— M 161.5590

M 140.3608
M 139.6590
M 139.4734

M 129.5790
M 127.6220
M 127.6027
M 123.8784
M 123.4259
M 123.3272
M 123.2510

— M 110.4088

— M 48.0232

— M 33.3043

M 25.6087
M 25.0296

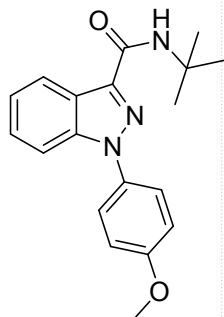
150

100
S38

50

[ppm]

¹H NMR
400 MHz, CDCl₃



34

8.4869
8.4667
7.6056
7.5833
7.5603
7.4371
7.4196
7.3988
7.3292
7.3105
7.2918
7.2568
7.0803
7.0584
7.0396

— 3.8881

1.5278

0.8446

3.0058

1.1564

1.0191

2.9588

3.0545

9.3463

10

8

6

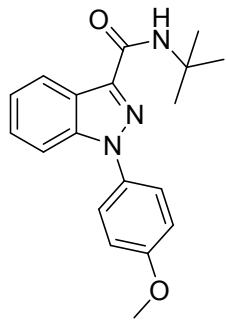
4

2

[ppm]

557

¹³C NMR
100 MHz, CDCl₃



34

— M 162.0542
— M 159.0482

— M 140.6754
— M 139.6360

— M 132.4302
— M 127.4015
— M 125.2243
— M 123.4123
— M 123.2718
— M 123.0190

— M 114.7035
— M 110.2648

— M 55.6662
— M 51.2837

— M 29.1043

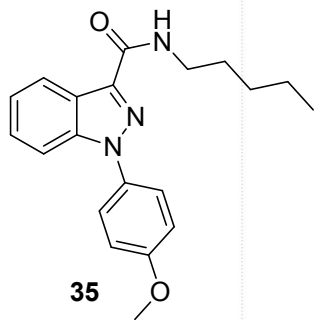
150

100
S4U

50

[ppm]

¹H NMR
400 MHz, CDCl₃



8.4826
8.4623
7.5933
7.5880
7.5824
7.5711
7.5614
7.4327
7.4150
7.3965
7.3944
7.3297
7.3111
7.2933
M 7.1592
M 7.1379
M 7.1223
7.0688
7.0466

3.8752
3.5187
3.5013
3.4846
3.4680

1.6645
1.6472
1.6297
M 1.6117
M 1.3907
1.3762
1.3674
M 1.3508
0.9186
0.9015
0.8844

0.8965

2.9249
1.0000
0.9970
0.9164
2.0100

2.9977
2.0556

2.0044
4.0211
2.9468

10

8

6

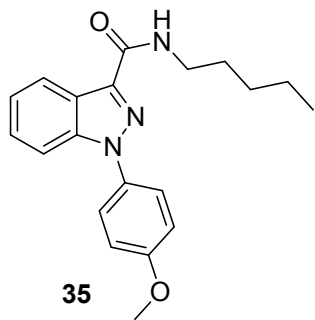
4

2

[ppm]

S41

¹³C NMR
100 MHz, CDCl₃



— M 162.4848
— M 159.0805

~ M 140.6172
~ M 139.0352

— M 132.4870
M 127.4306
M 125.0977
M 123.4856
M 123.1652
M 123.0651

— M 114.7146
— M 110.2790

— M 55.6301

— M 39.0793

M 29.5272
M 29.1668

— M 22.4082

— M 13.9976

150

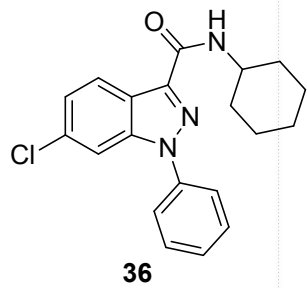
100

S42

50

[ppm]

¹H NMR
400 MHz, CDCl₃



8.4179
8.3964
7.6910
7.6691
7.6037
7.5848
7.5660
7.4770
7.4583
7.4405
7.3156
7.2940
6.9958
6.9764

M 4.0758
4.0465
4.0355
4.0263
M 4.0015

2.0775
2.0499
1.8012
1.7684
1.6606
1.4912
1.4613
1.4305
1.3988
1.3573
1.3295
1.3002
1.2667
1.2522
1.2346
1.2042
1.1734

0.9687

5.0835

1.0202

1.0444

1.0092

1.0092

2.0421

4.2921

5.0679

12

10

8

6

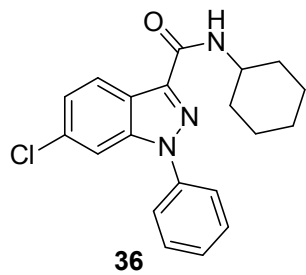
4

2

[ppm]

S43

¹³C NMR
100 MHz, CDCl₃



— M 161.0986

M 140.7443

M 139.7630

M 138.9831

— M 134.2530

M 129.7243

M 128.0134

M 124.3652

M 123.4846

M 122.3776

— M 110.2002

— M 48.0553

— M 33.2362

M 25.5624

M 24.9837

150

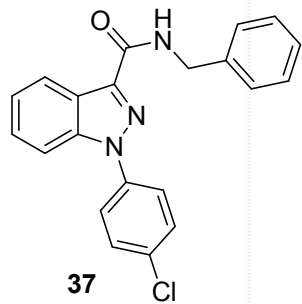
100

50

[ppm]

S44

¹H NMR
400 MHz, CDCl₃



8.5334
8.5131
7.6816
7.6713
7.6606
7.6498
7.5324
7.5109
7.4918
7.4721
7.4518
7.4245
7.4057
7.3793
7.3614
7.3429
7.3125
7.2951

4.7354
4.7205

0.8798

3.0728

10.0169

2.0000

10

8

6

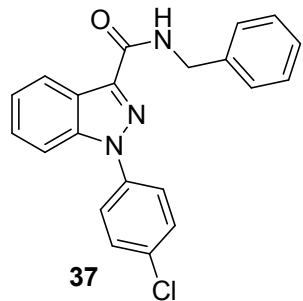
4

2

[ppm]

S45

¹³C NMR
100 MHz, CDCl₃



— M 162.1485

M 140.2269
M 139.5389
M 138.2805
M 137.9512
M 133.1764
M 129.7423
M 128.7486
M 128.0194
M 127.9371
M 127.5431
M 124.3678
M 123.9385
M 123.6151
M 123.3916

— M 110.2904

— M 43.1142

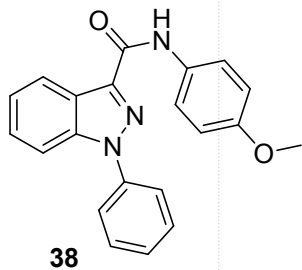
150

100
S46

50

[ppm]

¹H NMR
400 MHz, CDCl₃



8.8830
8.5385
8.5183
7.7329
7.7130
7.6888
7.6802
7.6679
7.6586
7.5755
7.5565
7.5372
7.4654
7.4450
7.4257
7.4066
7.3626
7.3436
7.3252
6.9176
6.8959

3.7849

1.0000

0.9970

5.1367

2.0781

2.4374

1.0935

2.0879

3.0995

10

8

6

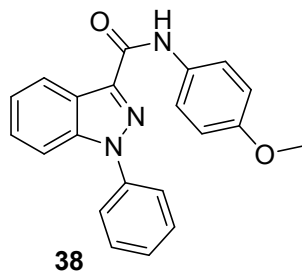
4

2

[ppm]

S47

¹³C NMR
100 MHz, CDCl₃



— M 160.0954

— M 156.3086

M 140.5209

M 139.4383

M 139.3279

M 131.0474

M 129.6334

M 127.7776

M 123.8804

M 123.5313

M 123.3988

M 123.1602

M 121.5120

M 114.2169

— M 110.6422

— M 55.4758

150

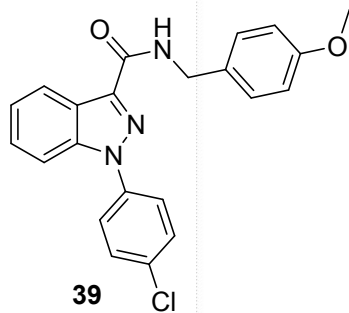
100

50

[ppm]

S48

¹H NMR
400 MHz, CDCl₃



8.5315
8.5114
7.6445
7.6273
7.6091
7.4857
7.4646
7.3666
7.3474
7.3286
7.3083
6.8745
6.8545

4.6479
4.6344

3.7706

0.9353

3.0474

4.0255

3.0805

2.0211

2.0000

3.0938

10

8

6

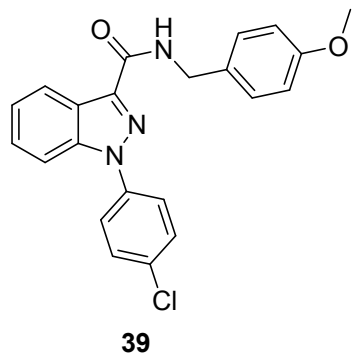
4

2

[ppm]

S49

¹³C NMR
100 MHz, CDCl₃



— M 162.0497
— M 159.0486

M 140.1945
M 139.6590
M 137.9759
M 133.0796
M 130.4115
M 129.6847
M 129.2927
M 127.9921
M 124.3007
M 123.9756
M 123.5548
M 123.4018
— M 114.0969
— M 110.2813

— M 55.2936

— M 42.5939

150

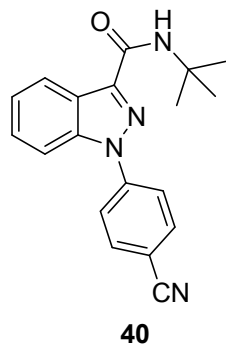
100

50

[ppm]

330

¹H NMR
400 MHz, CDCl₃



8.5110
8.4912
7.9192
7.8983
7.8482
7.8272
7.7394
7.7183
7.5131
7.4946
7.4748
7.3741
7.3547
7.3367
6.9857

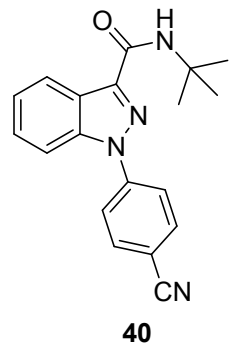
1.5314

0.8583
4.3766
1.0431
2.0000
0.7966

9.4292

12 10 8 6 4 2 [ppm]
S51

¹³C NMR
100 MHz, CDCl₃



— M 161.2710

— M 143.0442
— M 141.6905
— M 139.9952

— M 133.6213
— M 128.4616
— M 124.3691
— M 123.9213
— M 122.7495
— M 118.2158

— M 110.3448
— M 110.2646

— M 51.4675

— M 29.0020

150

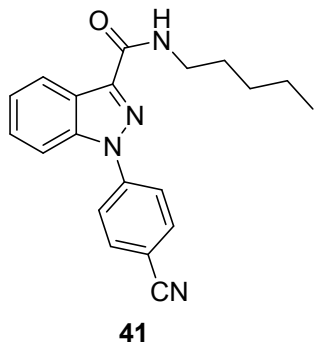
100

50

[ppm]

S52

¹H NMR
400 MHz, CDCl₃



8.5191
8.4987
7.9249
7.9032
7.8503
7.8286
7.7574
7.7360
7.5317
7.5296
7.5115
7.4929
7.4908
7.3935
7.3741
7.3558
7.2538
M 7.1386
M 7.1223
M 7.1080

3.5322
3.5152
3.4984
3.4811

1.7618
1.6858
1.6682
1.6504
1.3945
1.3859
1.3770
0.9252
0.9079
0.8905

1.0000
1.5410
1.0968
2.0807
0.9742

2.2056

2.1714
4.2337
3.2704

10

8

6

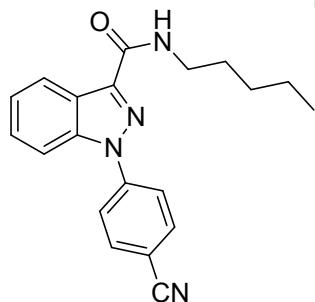
4

2

0 [ppm]

S53

¹³C NMR
100 MHz, CDCl₃



— M 161.7833

— M 143.1117
— M 141.0940
— M 139.9730

— M 133.6317
— M 128.5395
— M 124.4561
— M 124.0397
— M 123.8475
— M 122.6946
— M 118.1788

— M 110.3963
— M 110.3002

— M 39.2168

— M 29.4967
— M 29.1284

— M 22.4187

— M 14.0117

200

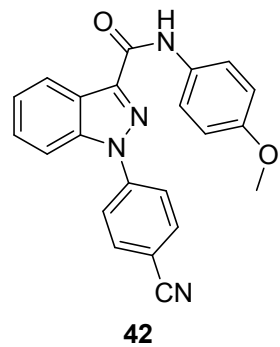
150

100
S54

50

[ppm]

¹H NMR
400 MHz, CDCl₃



8.7813
8.5669
8.5466
7.9713
7.9496
7.8929
7.8712
7.7950
7.7736
7.6702
7.6479
7.5754
7.5574
7.5385
7.5369
7.4443
7.4256
7.4066
7.2555
6.9424
6.9201

3.8228

0.8444

0.8573

3.9255

0.9564

1.9924

2.2603

2.0000

3.0121

10

8

6

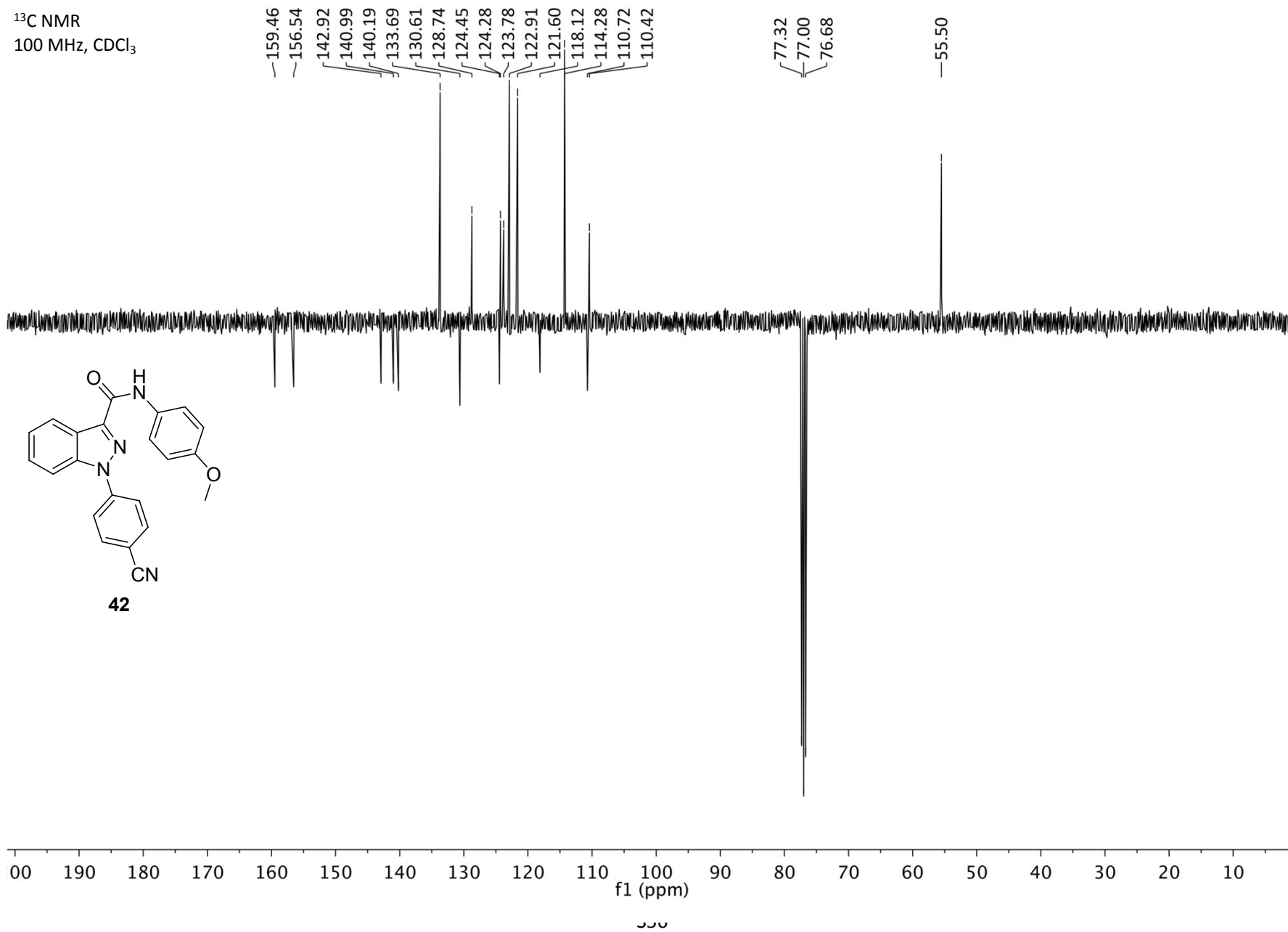
4

2

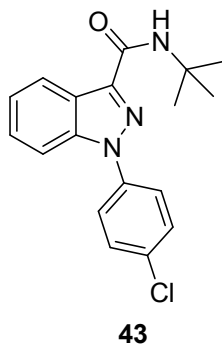
[ppm]

jjj

¹³C NMR
100 MHz, CDCl₃



¹H NMR
400 MHz, CDCl₃



8.5038
8.4835
7.6736
7.6518
7.6344
7.6130
7.5323
7.5105
7.4659
7.4640
7.4461
7.4274
7.3478
7.3285
7.3103
7.0088

1.5346

0.8992

3.0356

2.0550

1.0772

1.0000

0.9024

9.1817

10

8

6

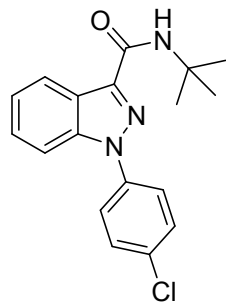
4

2

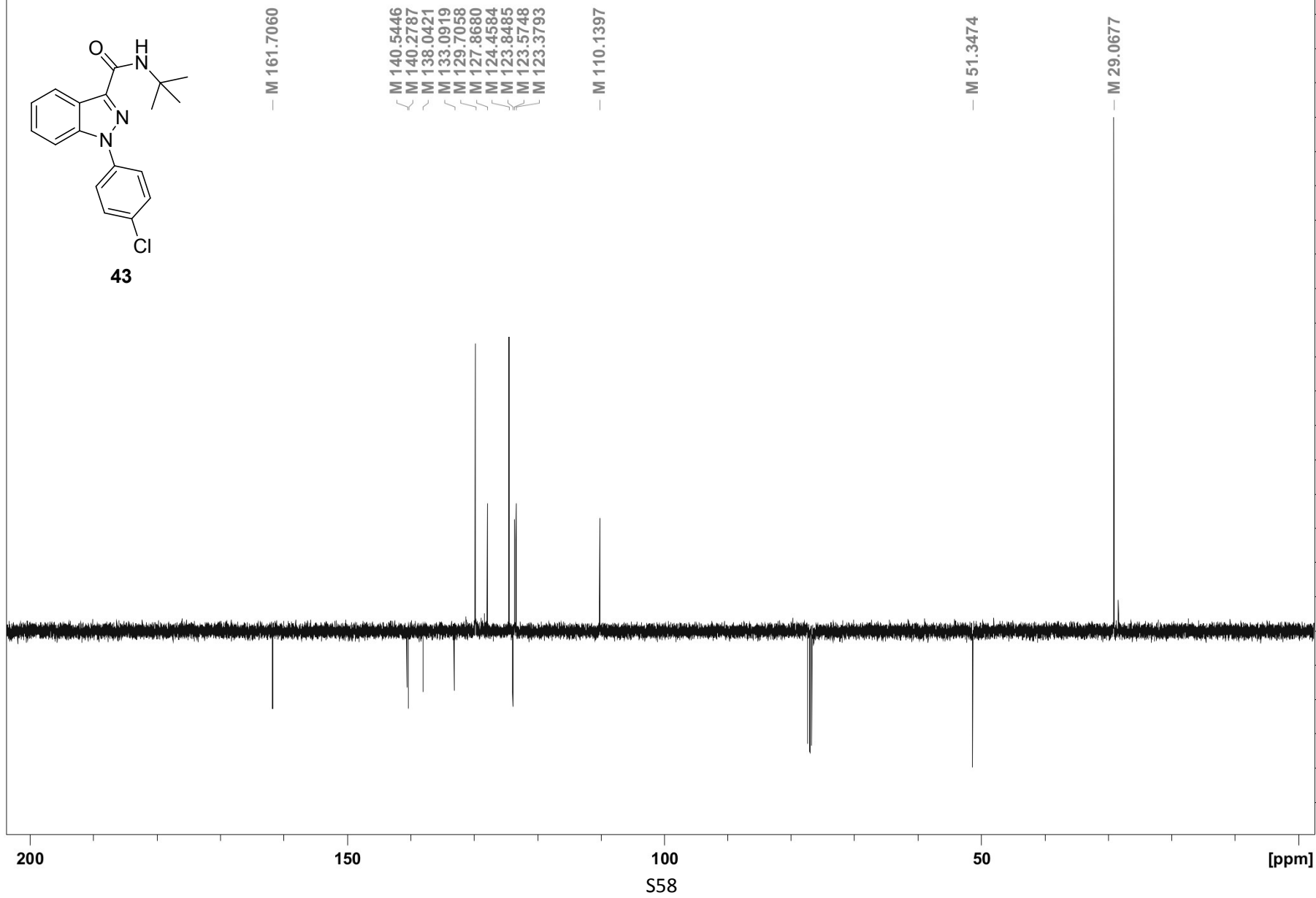
[ppm]

S57

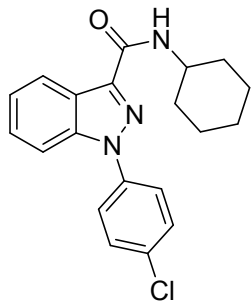
¹³C NMR
100 MHz, CDCl₃



43



¹H NMR
400 MHz, CDCl₃



44

8.4972
8.4769
7.6773
7.6556
7.6417
7.6204
7.5319
7.5102
7.4720
7.4529
7.4336
7.3558
7.3367
7.3183
7.0119
6.9930

4.1021
4.0842
4.0579
4.0474
4.0367
4.0105
2.0797
2.0564
2.0340
1.8352
1.7971
1.7878
1.7724
1.7638
1.6769
1.6676
1.6531
1.6447
1.4875
1.4784
1.4576
1.4267
1.3954
1.3651
1.3589
1.3354
1.3082
1.3019
1.2786
1.2672
1.2492
1.2310
1.2003

0.8385

3.1428
1.4677
1.0013
1.0104

0.9650

1.0000

2.1863

3.4137

5.5781

10

8

6

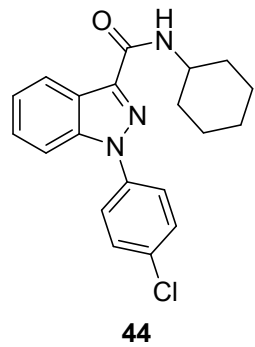
4

2

[ppm]

S59

¹³C NMR
100 MHz, CDCl₃



— M 161.3374

M 140.2385
M 140.0096
M 138.0370
M 133.1219
M 129.7217
M 127.9017
M 124.4360
M 123.9728
M 123.4988
M 123.4443

— M 110.1539

— M 48.0285

— M 33.2669

M 25.5999
M 25.0005

200

150

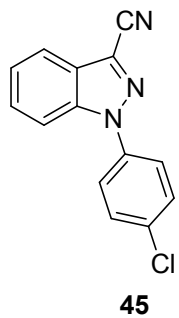
100

50

[ppm]

S60

¹H NMR
400 MHz, CDCl₃



7.9419
7.9215
7.7613
7.7397
7.6874
7.6655
7.5768
7.5720
7.5550
7.4637
7.4451
7.4269
7.2572

— 1.5540

1.0000
1.0000
2.0921
3.0905
1.0674

10

8

6

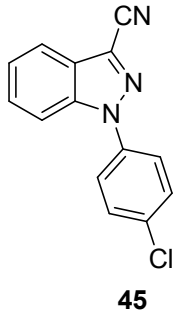
4

2

[ppm]

S61

¹³C NMR
100 MHz, CDCl₃



- M 139.0185
- M 137.3567
- M 134.3060
- M 130.0400
- M 128.9238
- M 126.1212
- M 124.6082
- M 124.4346
- M 120.6150
- M 120.0941
- M 113.1246
- M 111.2396

150

100

50

[ppm]

S62