Cobalt-catalyzed, directed arylation of C–H bonds in *N*-aryl pyrazoles

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Supporting Information

1. Materials and instrumentation

All reagents and starting materials were obtained commercially from Sigma-Aldrich and were used as received without any further purification unless otherwise noted. Gas chromatographic (GC) analyses were performed using a Shimadzu GC 2010-Plus equipped with a flame ionization detector (FID) and an SPB-5 column (length = 30 m, inner diameter = 0.25 mm, and film thickness = 0.25 μm). GC-MS analyses were collected on a Shimadzu GCMS-QP2010Ultra with a ZB-5MS column (length = 30 m, inner diameter = 0.25 mm, and film thickness = 0.25 μm). The ^{1}H NMR and ^{13}C NMR were recorded on Bruker AV 500 spectrometers using residual solvent peak as a reference. Without notice, chemical shifts are reported in ppm and referenced to the residual peak for $CDCl_3$ (δ = 7.26 ppm for ^{1}H NMR and δ = 77.16 ppm for ^{13}C NMR).

Splitting is reported with the following symbols: s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, td = triplet of doublets, dt = doublet of triplets, and m = multiplet. Coupling constants (*J*) are reported in Hertz. HR-MS spectra were recorded by an Agilent HPLC 1200 Series coupled to Bruker micrOTOF-QII. *N*-aryl pyrazoles **1a-1h** were prepared following the known procedure.[1]

2. General procedures

2.1. Procedure for optimization (Table 1)

To a 10 mL Schlenk tube equipped with a magnetic stir bar was added pyrazole **1a** (0.1 mmol, 17 mg), phenylboronic acid **2a** (0.2 mmol, 24 mg), catalyst, additive, co-oxidant, and solvent (1 mL). The tube was then placed into a preheated bath. The reaction was monitored by TLC. Upon completion, the solvent was evaporated. To the crude mixture was added diphenyl ether internal standard (0.1 mmol, 17 mg), EtOAc (5 mL) and K Na tartrate aqueous solution (1M, 5 mL). The aqueous phase was futher extracted with EtOAc (3 mL x 2). Combined organic layers were dried over Na_2SO_4, filtered, concentrated, and analyzed by GC.

2.2. Procedure for isolation of products (Schemes 2 and 3)

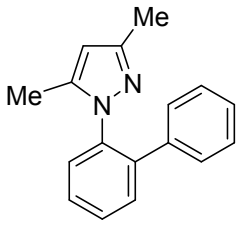
To a 25 mL Schlenk tube equipped with a magnetic stir bar was added a pyrazole derivative (0.5 mmol), an arylboronic acid (1 mmol), $Co(hfacac)_2$ (0.1 mmol, 47 mg), pivalic acid (0.25 mmol, 26 mg), $CeSO_4$ (1 mmol, 332 mg), and HFIP (2.5 mL). The tube was then placed into a preheated bath. The reaction was periodically stopped after 2 h, 4 h, 8 h, and 16 h for TLC check. After 24 h, the solvent was evaporated. To the crude

[1] S. H. Kwak, N. Gulia, O. Daugulis, *J. Org. Chem.* **2018**, *83*, 5844.

mixture was added EtOAc (10 mL) and K Na tartrate aqueous solution (1M, 10 mL). The aqueous phase was futher extracted with EtOAc (5 mL x 2). Combined organic layers were dried over Na_2SO_4, filtered, and concentrated under vacuum. The crude mixture was diluted with hexanes/EtOAc to obtain the pure product.

3. Characterization of arylation products

1-([1,1'-Biphenyl]-2-yl)-3,5-dimethyl-1*H*-pyrazole (3aa)

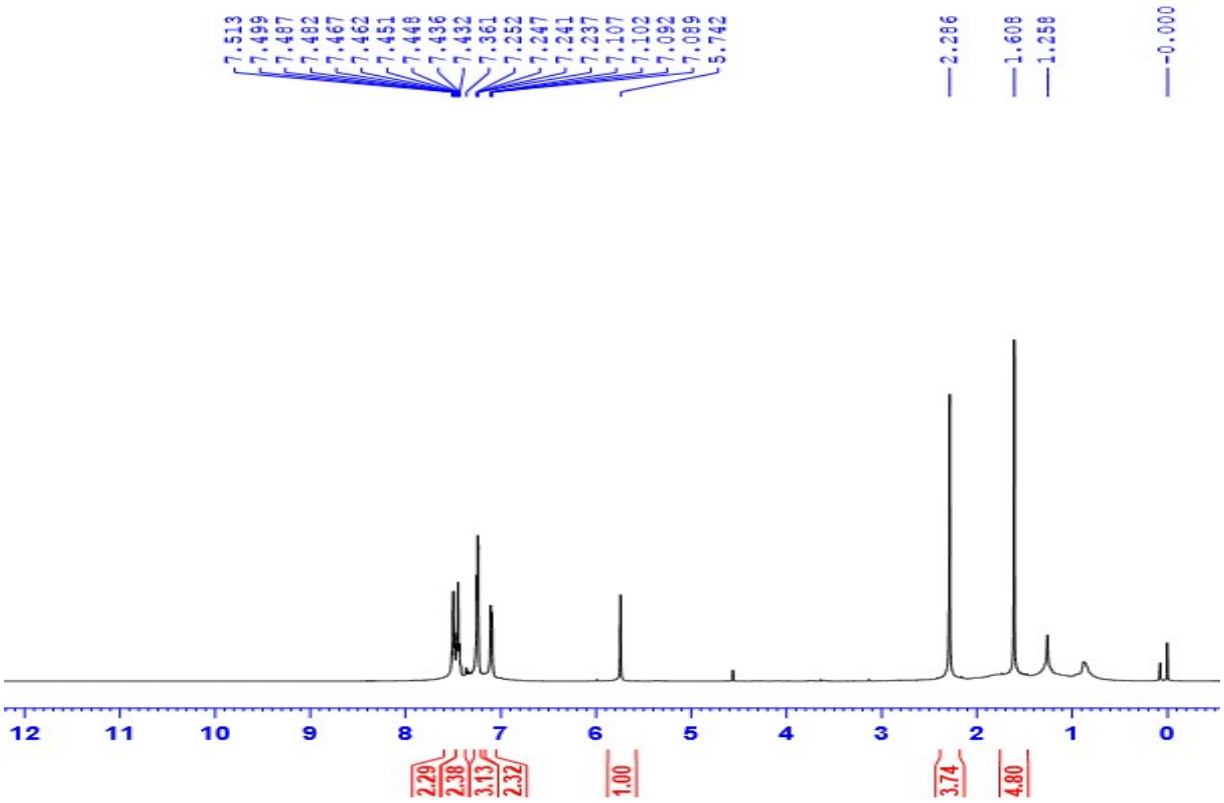


R_f = 0.40 (hexanes/EtOAc 20:1), yellow oil. This compound is known.[2]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 – 7.41 (m, 4H), 7.25 – 7.24 (m, 3H), 7.13 – 7.07 (m, 2H), 5.74 (s, 1H), 2.29 (s, 3H), 1.61 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 148.6, 140.6, 139.2, 138.5, 137.5, 130.4, 129.1, 128.9, 128.5, 128.3, 128.2, 127.3, 105.5, 29.7, 13.6, 11.1.

[2] C. J. Teskey, S. M. A. Sohel, D. L. Bunting, S. G. Modha, M. F. Greaney, *Angew. Chem. Int. Ed.* **2017**, *56*, 5263.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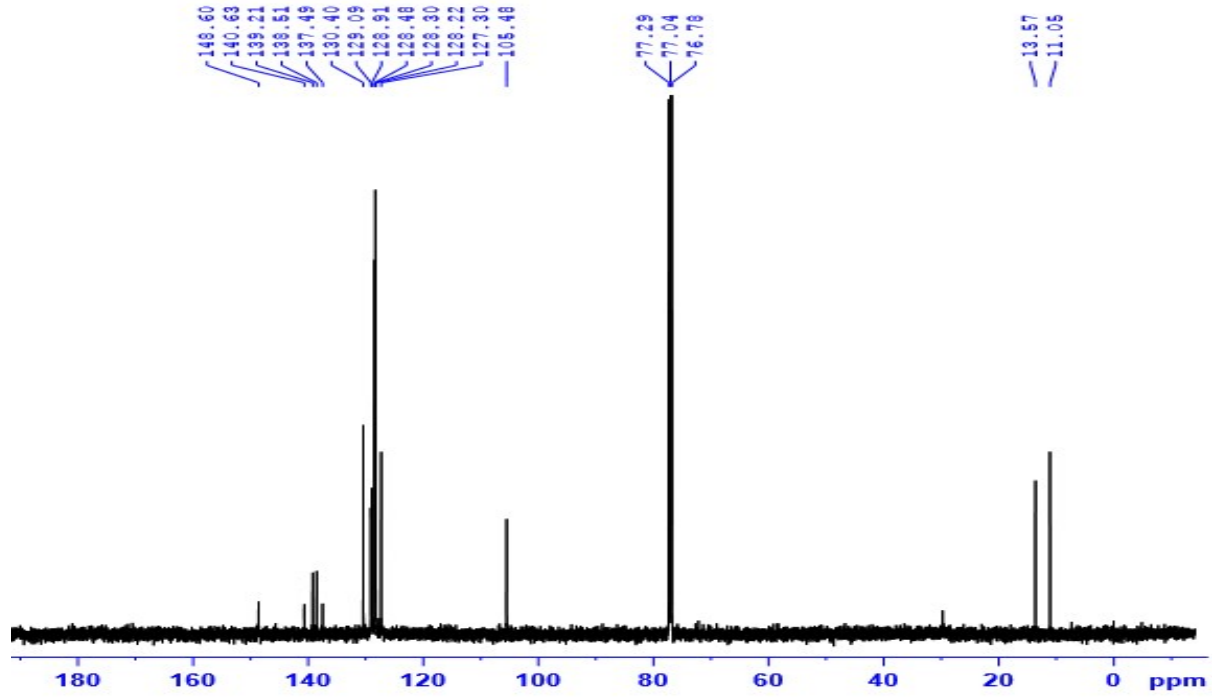
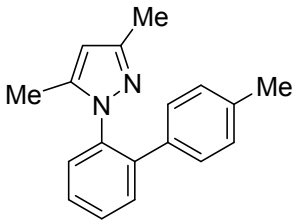
7.499
7.487
7.482
7.467
7.462
7.451
7.448
7.436
7.432
7.361
7.252
7.247
7.241
7.237
7.107
7.102
7.092
7.089
5.742
2.286
1.608
1.258
0.000
12
11
10
9
8
7
6
5
4
3
2
1
0
2.29
2.38
3.13
2.32
1.00
3.74
4.80


148.60
140.63
139.21
138.51
137.49
130.40
129.09
128.91
128.48
128.30
128.22
127.30
105.48
77.29
77.04
76.78
13.57
11.05
180
160
140
120
100
80
60
40
20
0
ppm

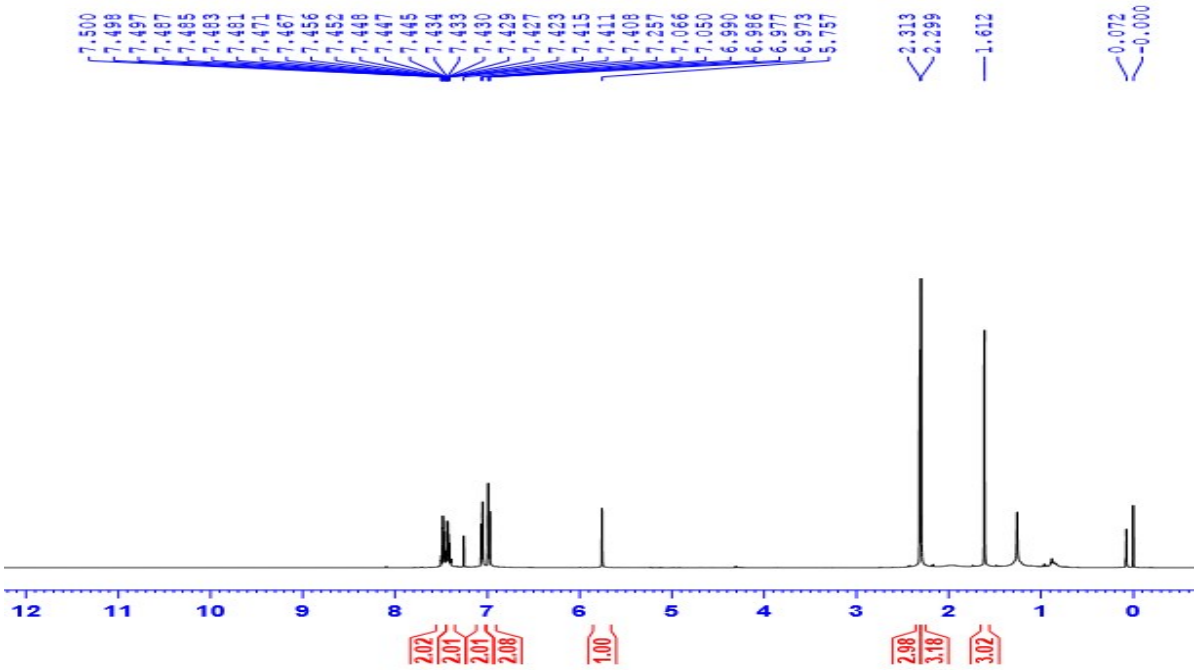
3,5-Dimethyl-1-(4'-methyl-[1,1'-biphenyl]-2-yl)-1*H*-pyrazole (3ab)

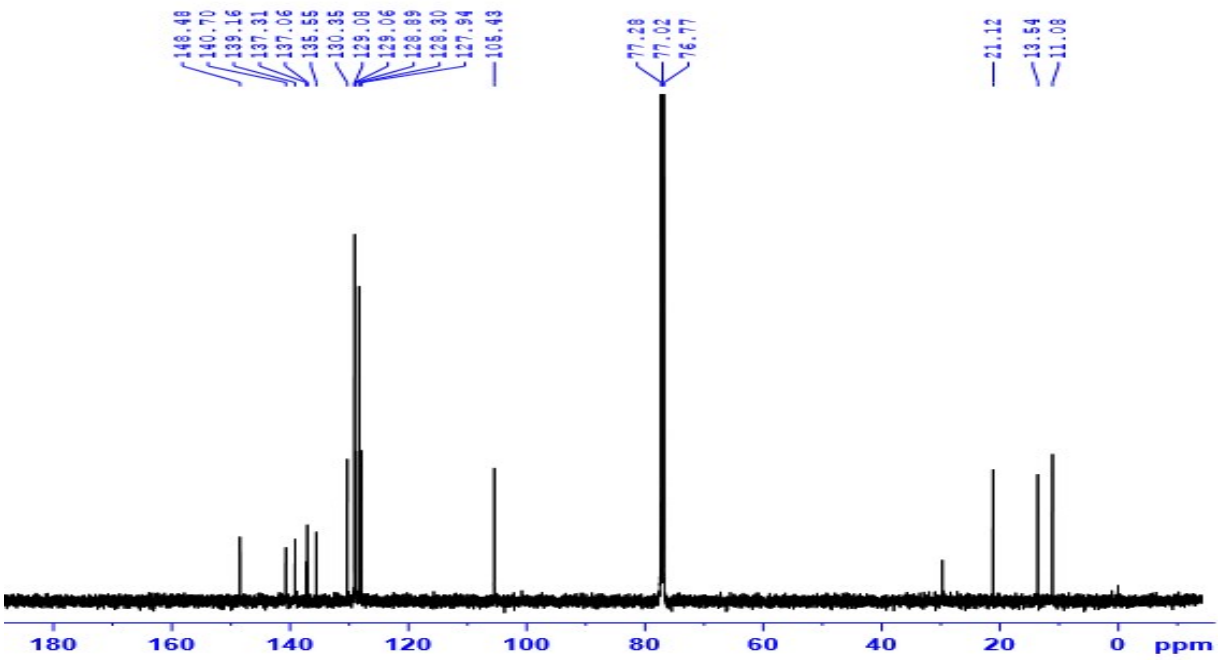


R_f = 0.15 (hexanes/EtOAc 20:1), light-yellow oil. This compound is known.[1]

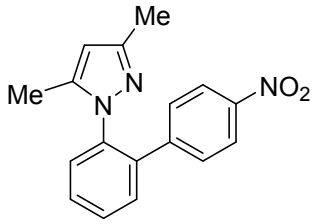
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 – 7.39 (m, 4H), 7.06 (d, *J* = 8.0 Hz, 2H), 7.01 – 6.96 (m, 2H), 5.76 (s, 1H), 2.31 (s, 3H), 2.30 (s, 3H), 1.61 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 148.5, 140.7, 139.2, 137.3, 137.1, 135.6, 130.4, 129.1, 129.1, 128.9, 128.3, 127.9, 105.4, 21.1, 13.5, 11.1.





3,5-Dimethyl-1-(4'-nitro-[1,1'-biphenyl]-2-yl)-1*H*-pyrazole (3ac)

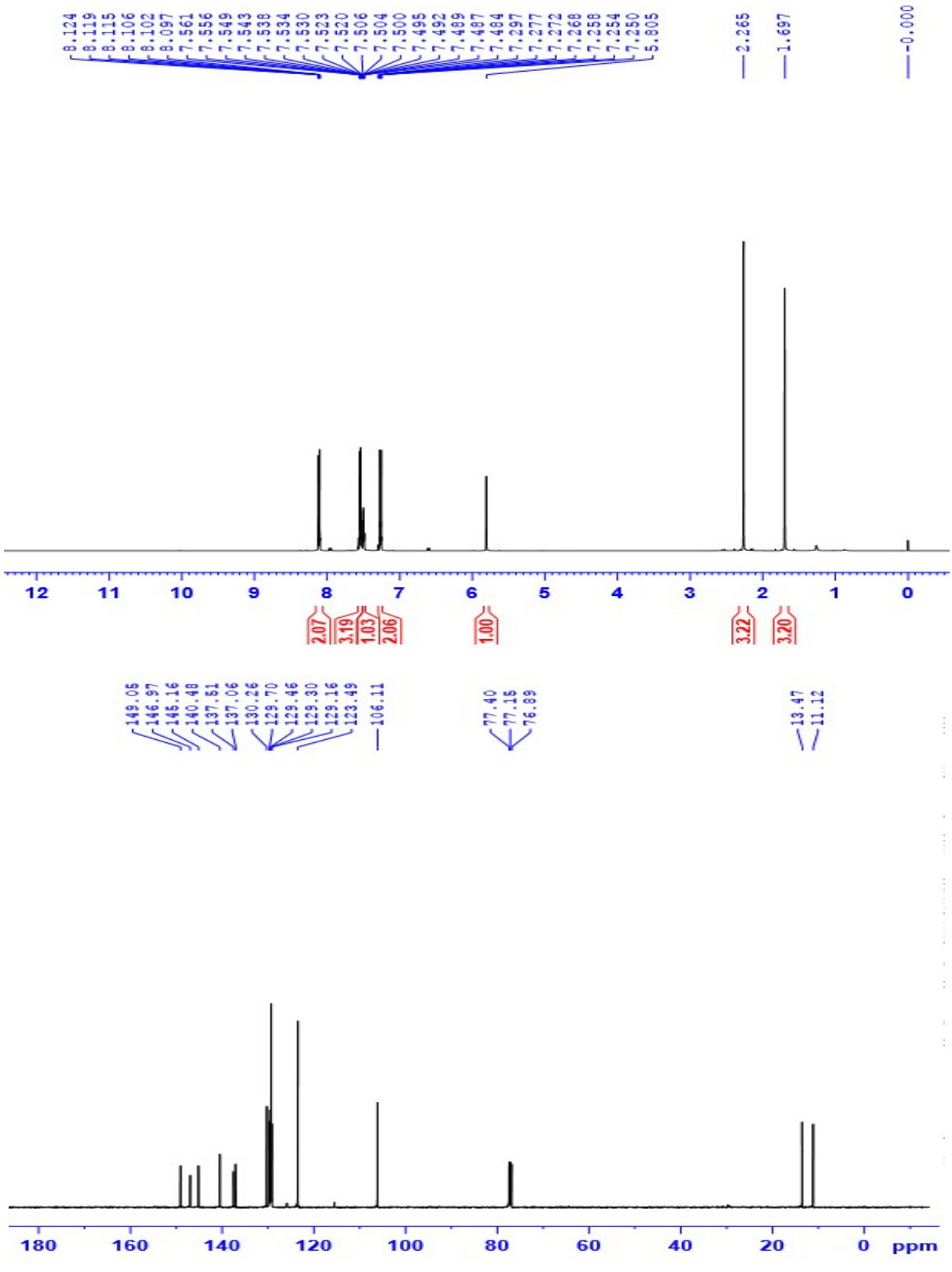


R_f = 0.12 (hexanes/EtOAc 20:1), tan solid, m.p. = 180 – 182 °C.

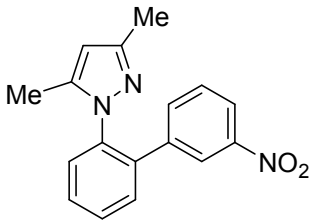
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.14 – 8.08 (m, 2H), 7.59 – 7.47 (m, 4H), 7.30 – 7.23 (m, 2H), 5.81 (s, 1H), 2.26 (s, 3H), 1.70 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 149.1, 147.0, 145.2, 140.5, 137.5, 137.1, 130.3, 129.7, 129.5, 129.3, 129.2, 123.5, 106.1, 13.5, 11.1.

HRMS (ESI) calcd for $C_{17}H_{16}N_3O_2$ $[M + H]^+$ 294.1237, found: 294.1245.


8.124
8.119
8.115
8.106
8.102
8.097
7.561
7.556
7.549
7.543
7.538
7.534
7.530
7.523
7.520
7.506
7.504
7.500
7.495
7.492
7.489
7.487
7.484
7.297
7.277
7.272
7.268
7.258
7.254
7.250
5.805
2.265
1.697
0.000
12 11 10 9 8 7 6 5 4 3 2 1 0
2.07 3.19 1.03 2.06 1.00 3.22 3.20
149.05
146.97
145.16
140.48
137.51
137.06
130.26
129.70
129.46
129.30
129.16
123.49
106.11
77.40
77.15
76.89
13.47
11.12
180 160 140 120 100 80 60 40 20 0 ppm

3,5-Dimethyl-1-(3'-nitro-[1,1'-biphenyl]-2-yl)-1*H*-pyrazole (3ad)

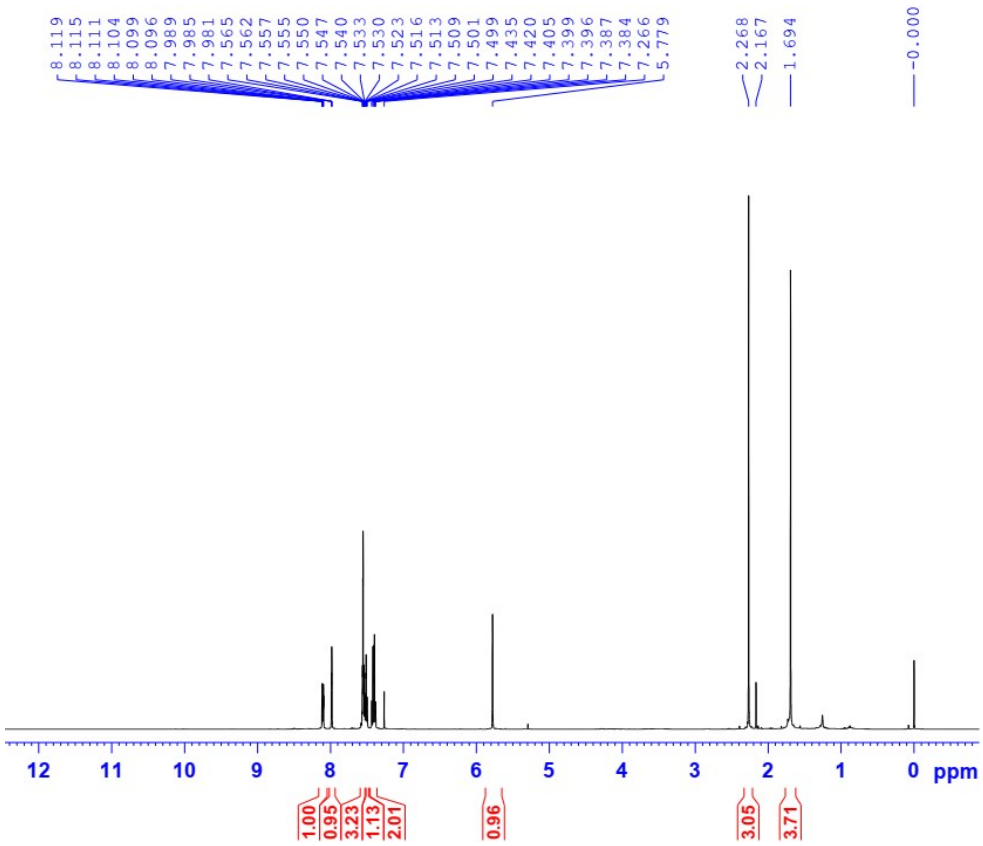


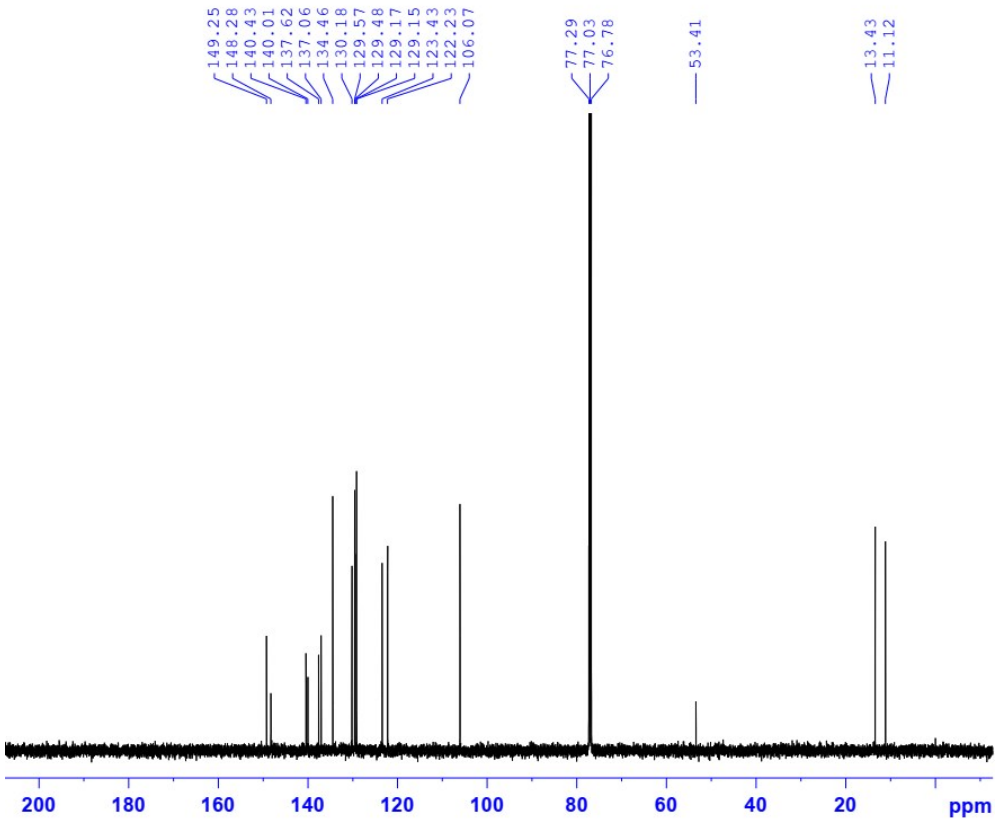
R_f = 0.1 (hexanes/EtOAc 20:1), tan solid, m.p. = 187 – 189 °C.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11 (dt, *J* = 7.7, 2.0 Hz, 1H), 7.98 (t, *J* = 2.0 Hz, 1H), 7.60 – 7.46 (m, 4H), 7.45 – 7.35 (m, 2H), 5.78 (s, 1H), 2.27 (s, 3H), 1.69 (s, 3H).

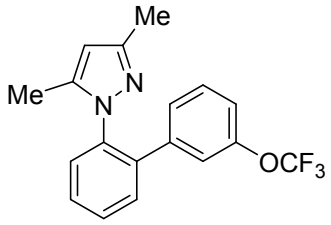
^{13}C NMR (126 MHz, $CDCl_3$) δ 149.3, 148.3, 140.4, 140.0, 137.6. 137.1, 134.5, 130.2, 129.6, 129.5, 129.2, 129.2, 123.4, 122.2, 106.1, 13.4, 11.1.

HRMS (ESI) calcd for $C_{17}H_{16}N_3O_2$ $[M + H]^+$ 294.1237, found: 294.1241.





3,5-Dimethyl-1-(3´-trifluoromethoxy)-[1,1´-biphenyl]-2-yl]-1*H*-pyrazole (3ae)

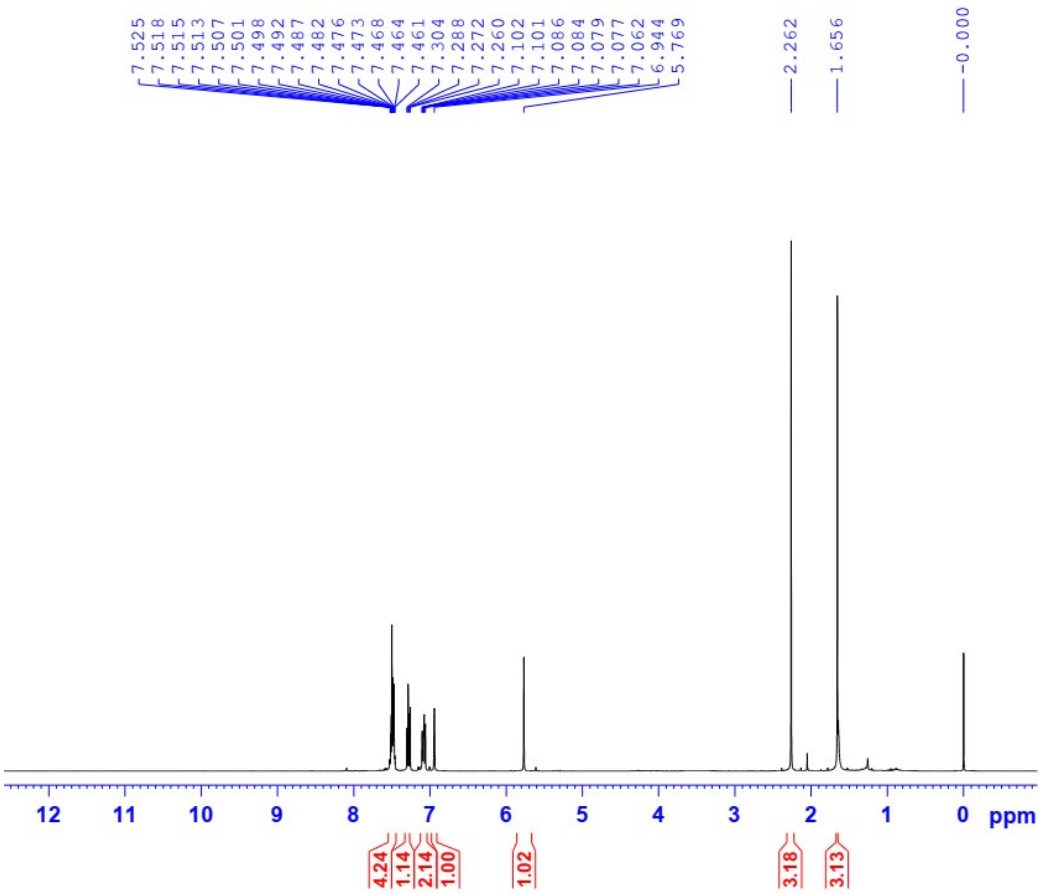


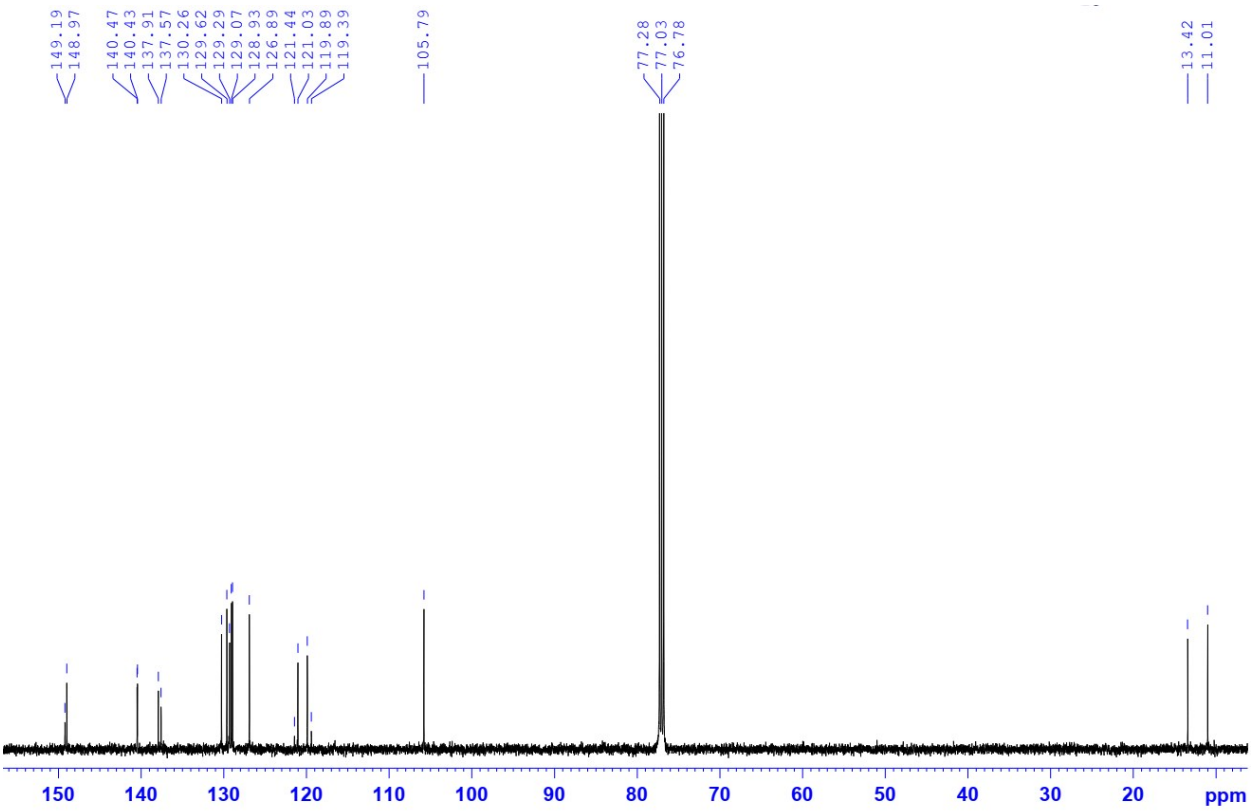
R_f = 0.15 (hexanes/EtOAc 20:1), light-yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 - 7.44 (m, 4H), 7.32 - 7.24 (m, 1H), 7.08 (ddt, *J* = 12.4, 7.8, 1.3 Hz, 2H), 6.94 (s, 1H), 5.77 (s, 1H), 2.26 (s, 3H), 1.66 (s, 3H).

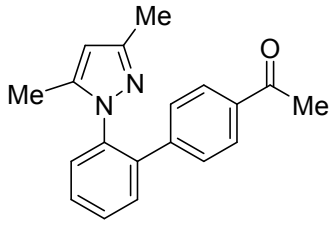
^{13}C NMR (126 MHz, $CDCl_3$, possible peaks are listed) δ 149.2, 149.0, 140.5, 140.4, 137.9, 137.6, 130.3, 129.6, 129.3, 129.1, 128.9, 126.9, 121.4, 121.0, 119.9, 119.4, 105.8, 13.4, 11.0.

HRMS (ESI) calcd for $C_{18}H_{16}F_3N_2O$ $[M + H]^+$ 333.1209, found: 333.1211.


7.525
7.518
7.515
7.513
7.507
7.501
7.498
7.492
7.487
7.482
7.476
7.473
7.468
7.464
7.461
7.304
7.288
7.272
7.260
7.102
7.101
7.086
7.084
7.079
7.077
7.062
6.944
5.769
2.262
1.656
0.000
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
4.24
1.14
2.14
1.00
1.02
3.18
3.13



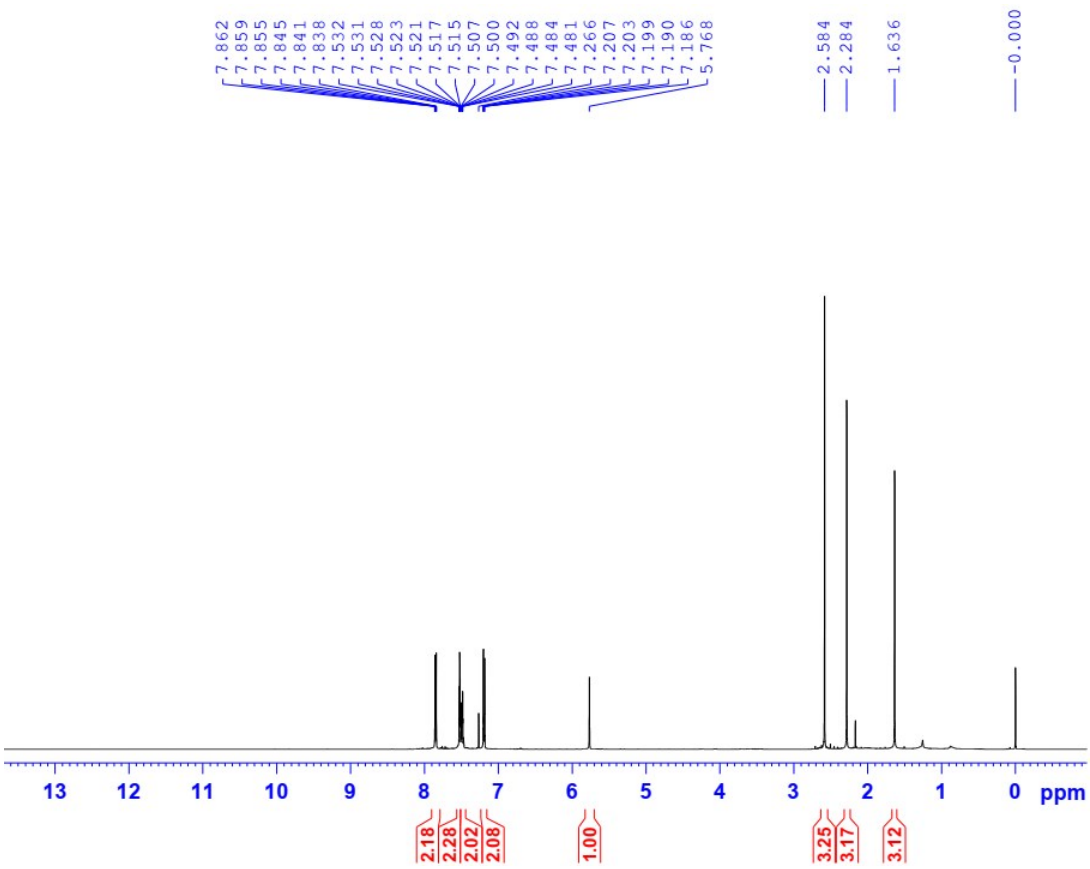
1-(2'-(3,5-Dimethyl-1*H*-pyrazol-1-yl)-[1,1'-biphenyl]-4-yl)ethan-1-one (3af)



R_f = 0.14 (hexanes/EtOAc 5:1), beige solid. This compound is known.[1]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 – 7.82 (m, 2H), 7.55 – 7.51 (m, 2H), 7.51 – 7.46 (m, 2H), 7.23 – 7.17 (m, 2H), 5.77 (s, 1H), 2.58 (s, 3H), 2.28 (s, 3H), 1.64 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 197.8, 148.8, 143.3, 140.6, 138.1, 137.5, 135.8, 130.3, 129.3, 129.1, 129.1, 128.7, 128.4, 105.8, 26.6, 13.5, 11.1.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7.859
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7.838
7.532
7.531
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7.523
7.521
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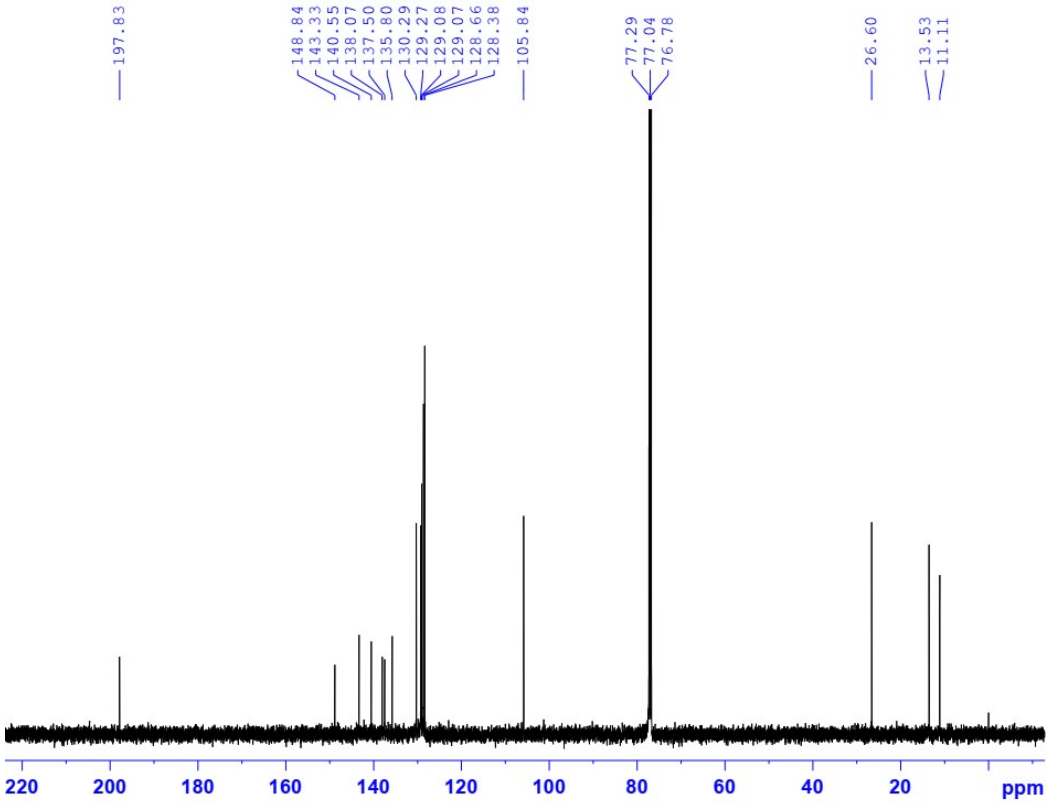
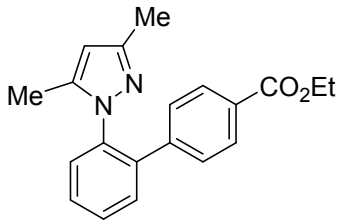
7.515
7.507
7.500
7.492
7.488
7.484
7.481
7.266
7.207
7.203
7.199
7.190
7.186
5.768
2.584
2.284
1.636
0.000
13 12 11 10 9 8 7 6 5 4 3 2 1 0 ppm
2.18
2.28
2.02
2.08
1.00
3.25
3.17
3.12


197.83
148.84
143.33
140.55
138.07
137.50
135.80
130.29
129.27
129.08
129.07
128.66
128.38
105.84
77.29
77.04
76.78
26.60
13.53
11.11
220 200 180 160 140 120 100 80 60 40 20 ppm

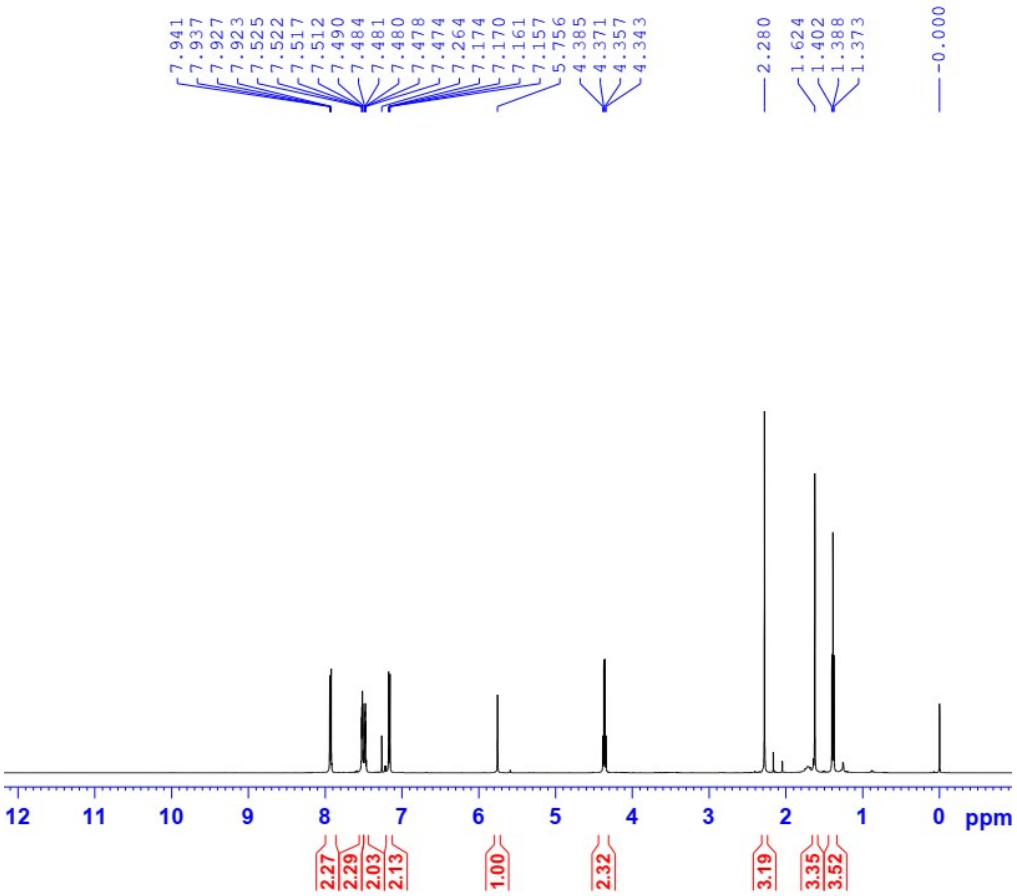
Ethyl 2'-(3,5-dimethyl-1*H*-pyrazol-1-yl)-[1,1'-biphenyl]-4-carboxylate (3ag)



R_f = 0.1 (hexanes/EtOAc 20:1), light-yellow oil. This compound is known.[1]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 - 7.90 (m, 2H), 7.56 – 7.45 (m, 4H), 7.24 – 7.14 (m, 2H), 5.76 (s, 1H), 4.36 (q, *J* = 7.1 Hz, 2H), 2.28 (s, 3H), 1.62 (s, 3H), 1.39 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 166.5, 148.8, 143.1, 140.5, 138.2, 137.6, 130.3, 129.6, 129.3, 129.2, 129.1, 129.0, 128.5, 128.4, 105.8, 61.0, 14.3, 13.6, 11.1.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7.937
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7.923
7.525
7.522
7.517
7.512
7.490
7.484
7.481
7.480
7.478
7.474
7.264
7.174
7.170
7.161
7.157
5.756
4.385
4.371
4.357
4.343
2.280
1.624
1.402
1.388
1.373
0.000
12
11
10
9
8
7
6
5
4
3
2
1
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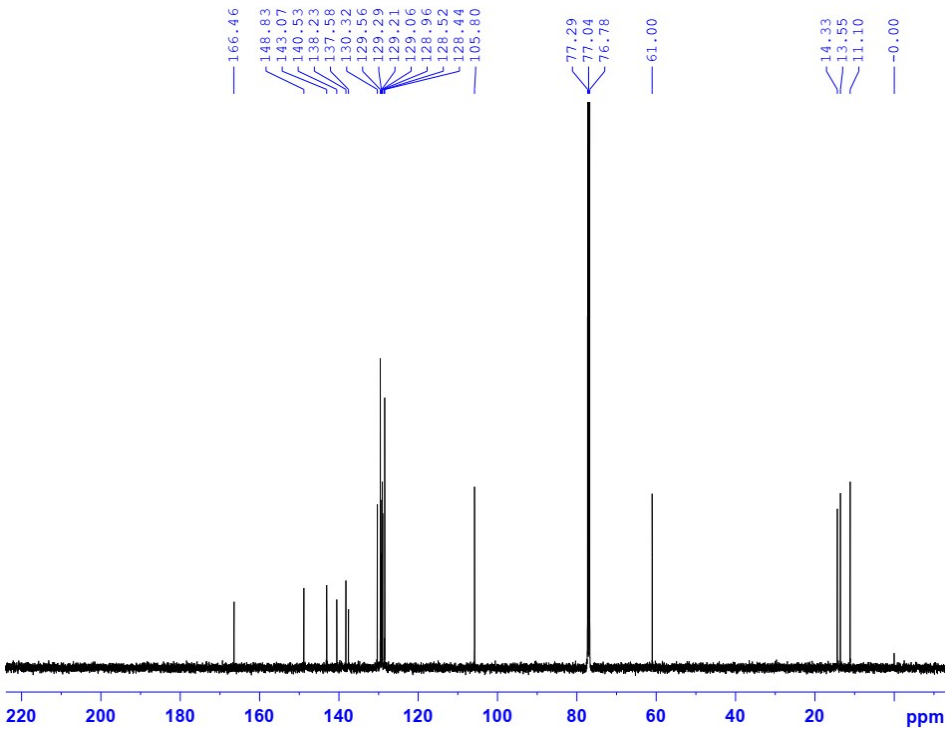
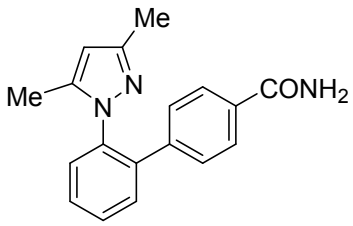
ppm
2.27
2.29
2.03
2.13
1.00
2.32
3.19
3.35
3.52


166.46
148.83
143.07
140.53
138.23
137.58
130.32
129.56
129.29
129.21
129.06
128.96
128.52
128.44
105.80
77.29
77.04
76.78
61.00
14.33
13.55
11.10
0.00
220
200
180
160
140
120
100
80
60
40
20
ppm

2´-(3,5-Dimethyl-1*H*-pyrazol-1-yl)-[1,1´-biphenyl]-4-carboxamide (3ah)

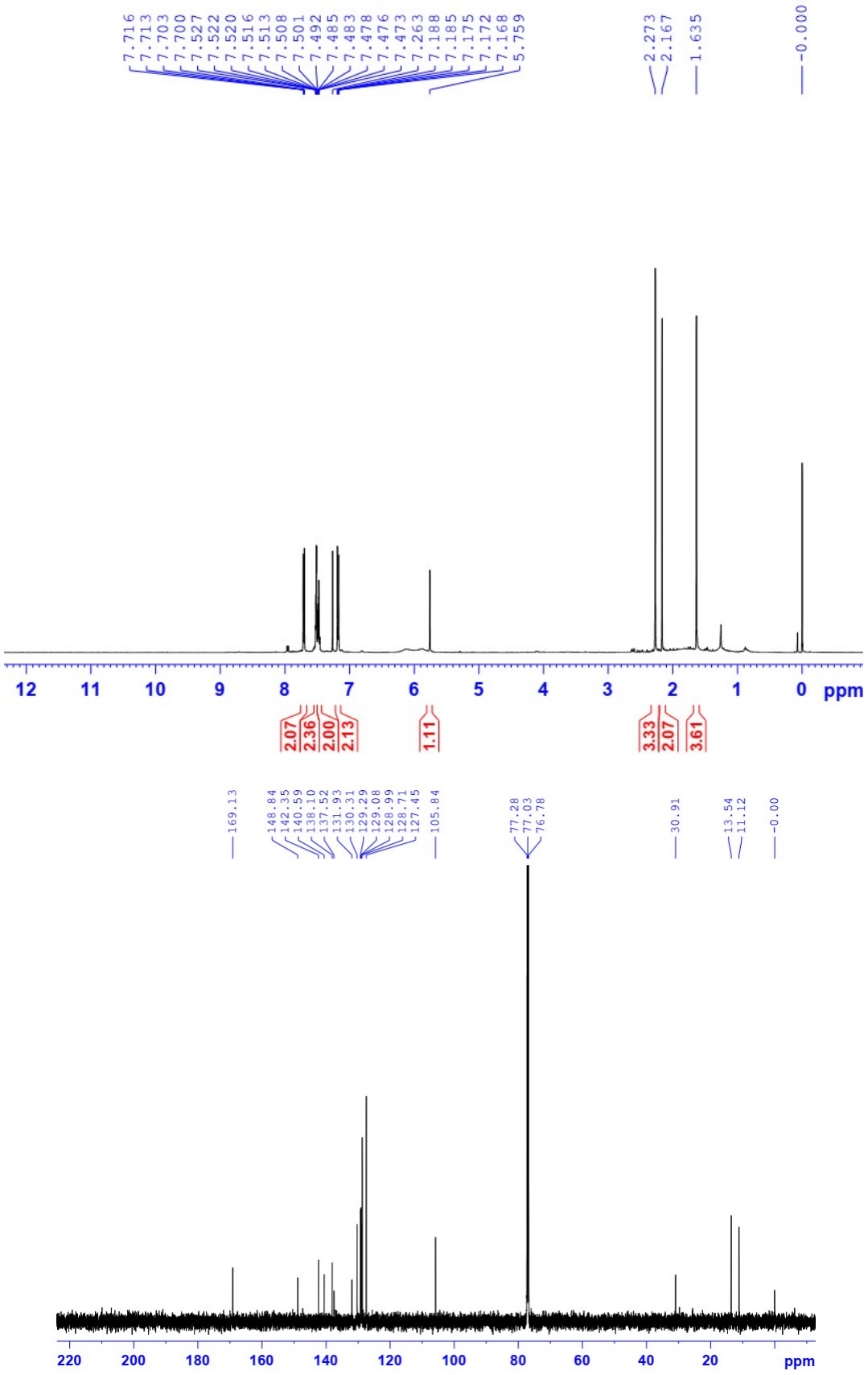


R_f = 0.1 (hexanes/EtOAc 5:1), beige solid, m.p. 113 – 115 °C.

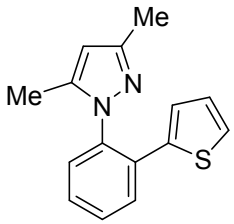
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 – 7.67 (m, 2H), 7.58 – 7.43 (m, 4H), 7.22 – 7.14 (m, 2H), 5.76 (s, 1H), 2.27 (s, 3H), 2.17 (s, 2H), 1.64 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 169.1, 148.8, 142.4, 140.6, 138.1, 137.5, 131.9, 130.3, 129.3, 129.1, 129.0, 128.7, 127.5, 105.8, 13.5, 11.1.

HRMS (ESI) calcd for $C_{18}H_{18}N_3O$ $[M + H]^+$ 292.1444, found: 292.1440.


7.716
7.713
7.703
7.700
7.527
7.522
7.520
7.516
7.513
7.508
7.501
7.492
7.485
7.483
7.478
7.476
7.473
7.263
7.188
7.185
7.175
7.172
7.168
5.759
2.273
2.167
1.635
-0.000
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
2.07
2.36
2.00
2.13
1.11
3.33
2.07
3.61
169.13
148.84
142.35
140.59
138.10
137.52
131.93
130.31
129.29
129.08
128.99
128.71
127.45
105.84
77.28
77.03
76.78
30.91
13.54
11.12
-0.00
220
200
180
160
140
120
100
80
60
40
20
ppm

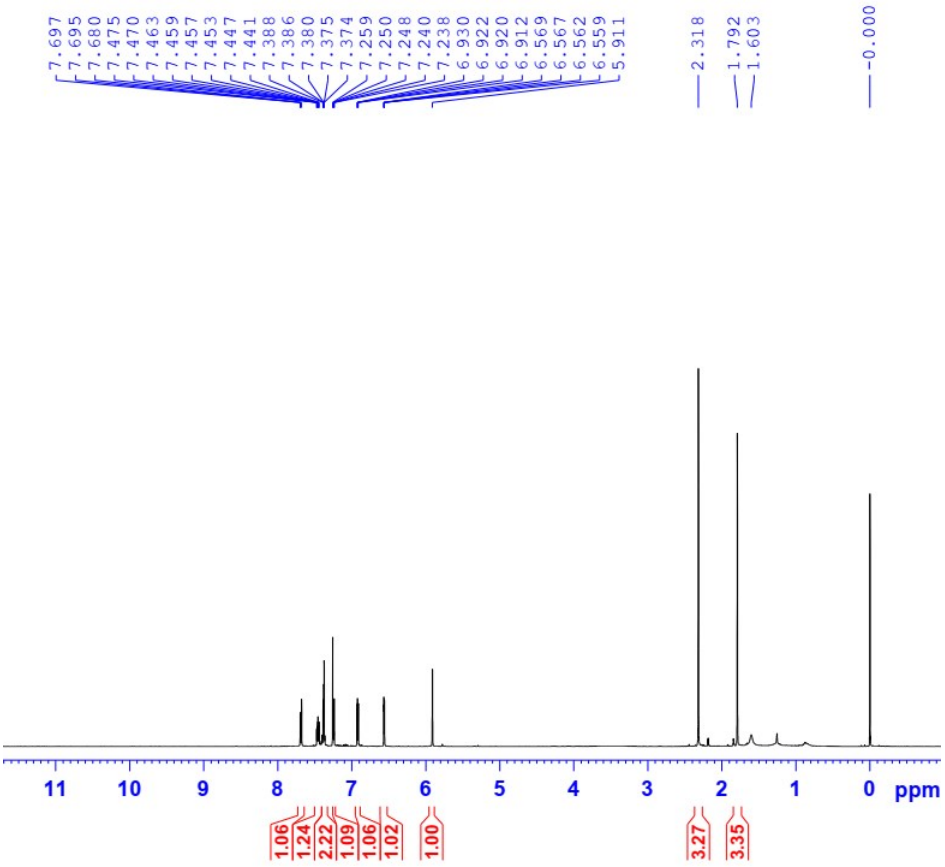
3,5-Dimethyl-1-(2-(thiophen-2-yl)phenyl)-1*H*-pyrazole (3ai)

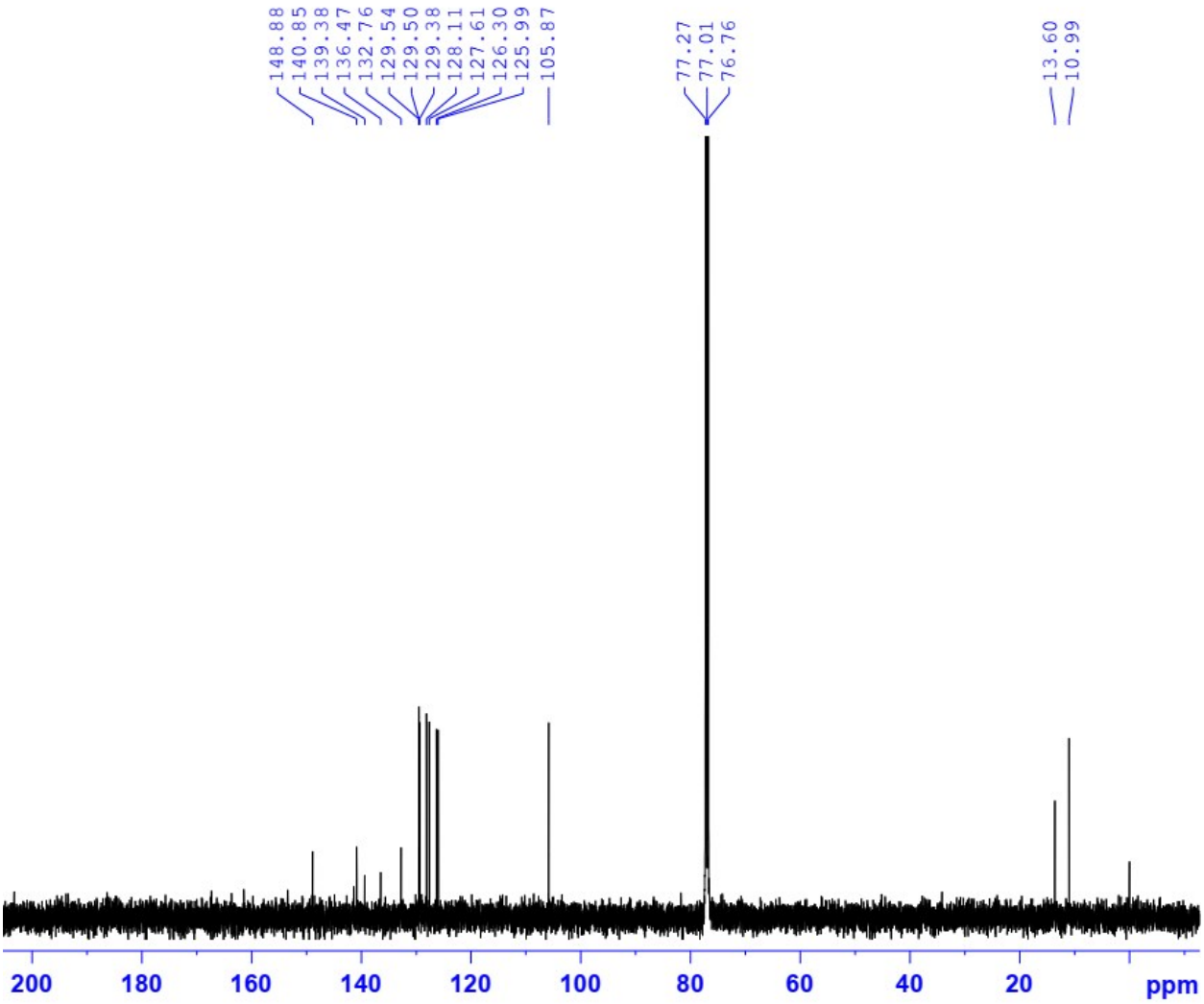


R_f = 0.2 (hexanes/EtOAc 10:1), brown oil. This compound is known.[2]

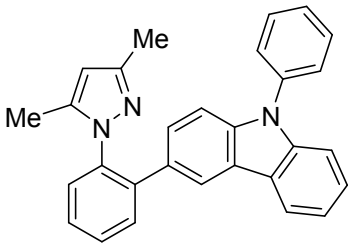
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 – 7.66 (m, 1H), 7.46 (ddd, *J* = 7.8, 6.0, 2.8 Hz, 1H), 7.41 – 7.36 (m, 2H), 7.24 (dd, *J* = 5.1, 1.2 Hz, 1H), 6.92 (dd, *J* = 5.1, 3.6 Hz, 1H), 6.56 (dd, *J* = 3.7, 1.2 Hz, 1H), 5.9 (s, 1H), 2.32 (s, 3H), 1.79 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 148.9, 140.9, 139.4, 136.5, 132.8, 129.5, 129.5, 129.4, 128.1, 127.6, 126.3, 126.0, 105.9, 13.6, 11.0.





3-(2-(3,5-Dimethyl-1*H*-pyrazol-1-yl)phenyl)-9-phenyl-9*H*-carbazole (3aj)



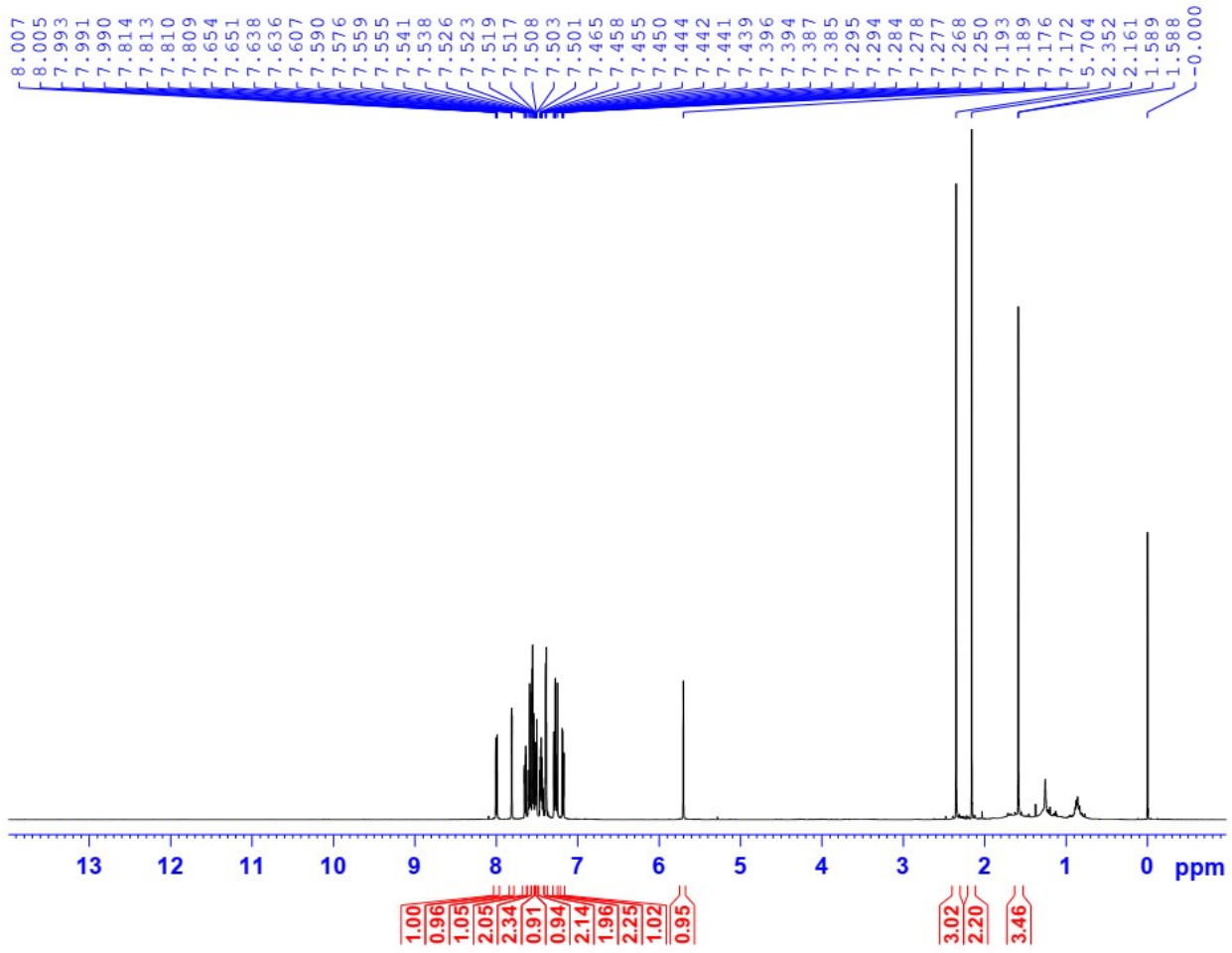
R_f = 0.11 (hexanes/EtOAc 10:1), beige solid, m.p. = 181 – 183 °C.

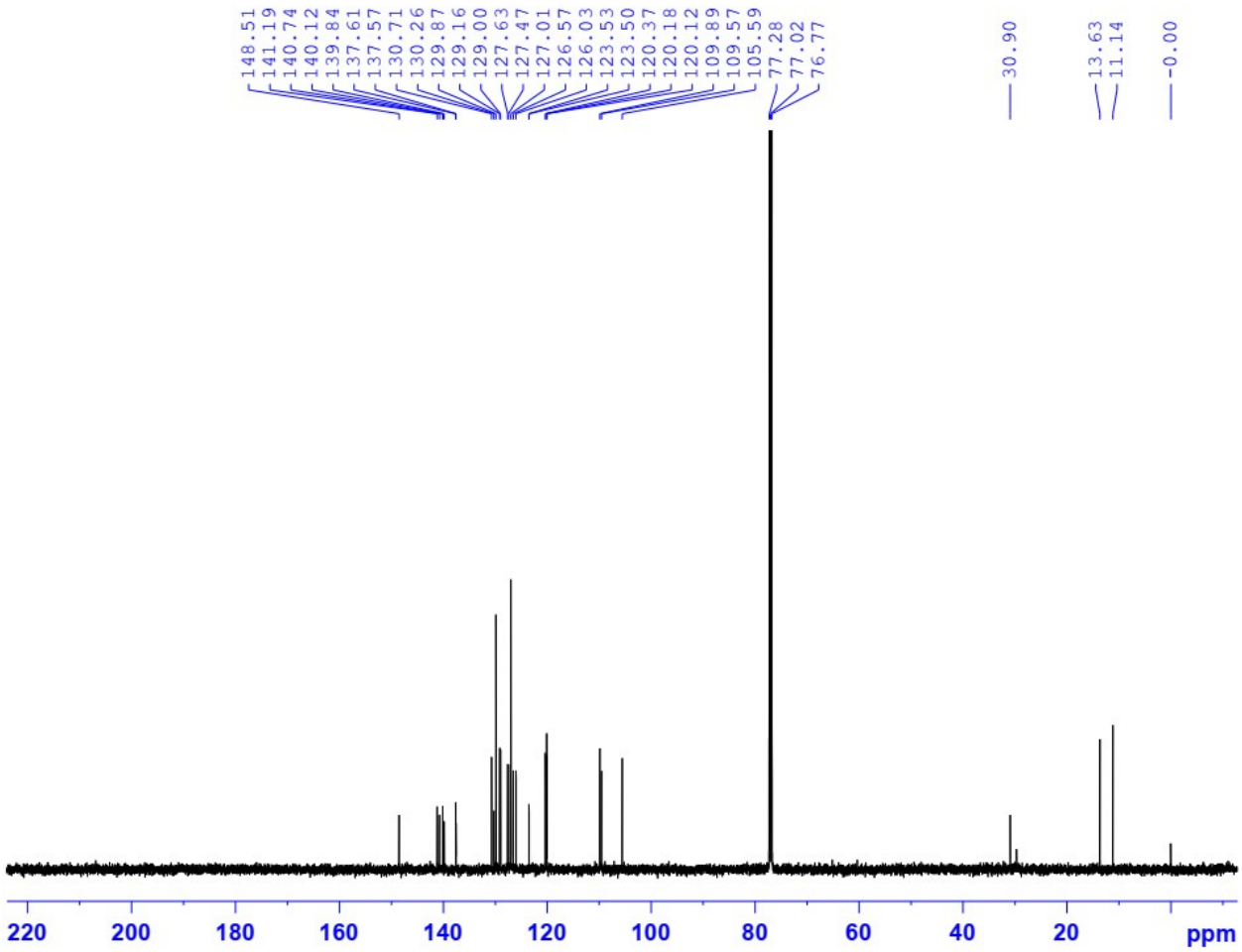
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (dt, J = 7.8, 1.0 Hz, 1H), 7.81 (dd, *J* = 1.8, 0.6 Hz, 1H), 7.67 – 7.63 (m, 1H), 7.62 – 7.57 (m, 2H), 7.57 – 7.53 (m, 2H), 7.53 – 7.49 (m, 2H),

7.45 (dddd, J = 8.0, 7.0, 4.2, 1.5 Hz, 2H), 7.43 – 7.34 (m, 2H), 7.31 – 7.21 (m, 2H), 7.18 (dd, J = 8.5, 1.8 Hz, 1H), 5.70 (s, 1H), 2.35 (s, 3H), 1.59 (s, 3H).

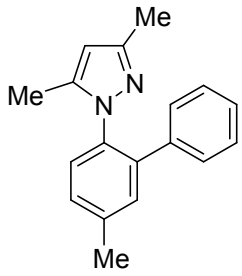
^{13}C NMR (126 MHz, $CDCl_3$) δ 148.5, 141.2, 140.7, 140.1, 139.8, 137.6, 137.6, 130.7, 130.3, 129.9, 129.2, 129.0, 127.6, 127.5, 127.0, 126.6, 126.0, 123.5, 123.5, 120.4, 120.2, 120.1, 109.9, 109.6, 105.6, 13.6, 11.1.

HRMS (ESI) calcd for $C_{29}H_{24}N_3$ $[M + H]^+$ 414.1965, found: 414.1981.





3,5-Dimethyl-1-(5-methyl-[1,1'-biphenyl]-2-yl)-1*H*-pyrazole (3ba)

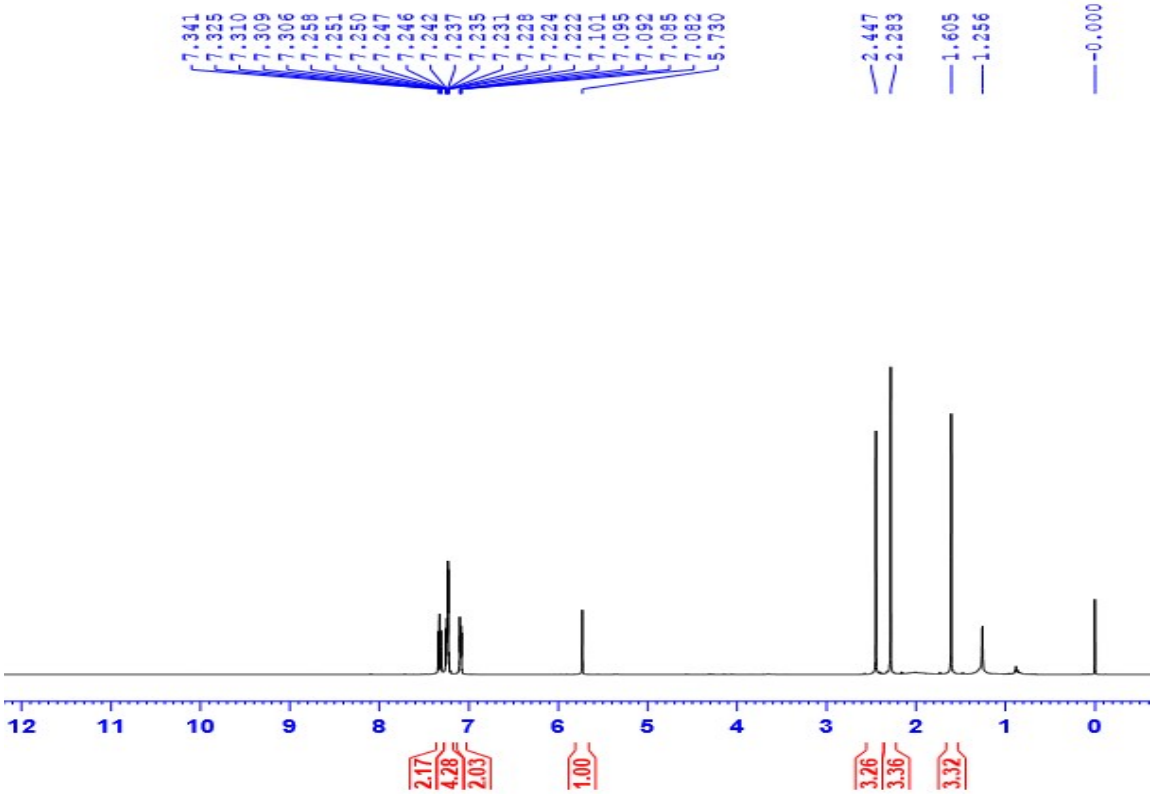


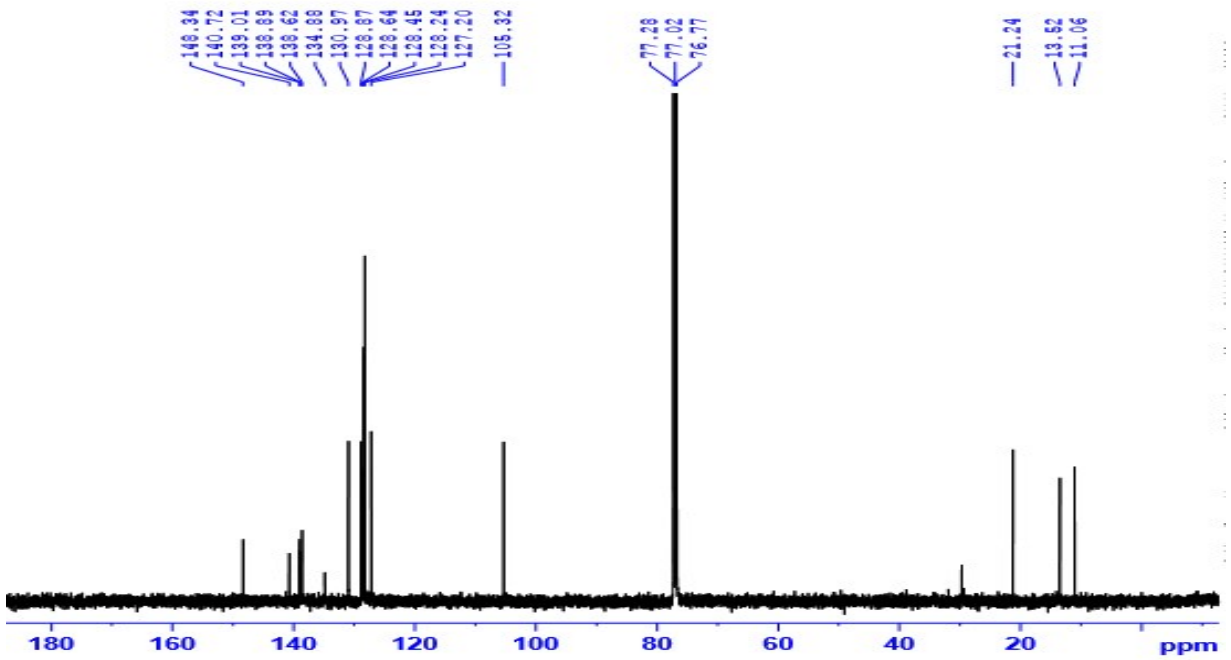
R_f = 0.14 (hexanes/EtOAc 20:1), light-yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 (d, *J* = 8.0 Hz, 1H), 7.31 (d, *J* = 2.0 Hz, 1H), 7.28 – 7.20 (m, 4H), 7.12 – 7.06 (m, 2H), 5.73 (s, 1H), 2.45 (s, 3H), 2.28 (s, 3H), 1.60 (s, 3H).

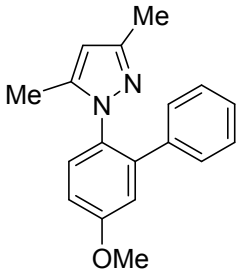
^{13}C NMR (126 MHz, $CDCl_3$) δ 148.4, 140.7, 139.0, 138.9, 138.6, 134.9, 131.0, 128.9, 128.6, 128.5, 128.2, 127.2, 105.3, 21.2, 13.5, 11.1.

HRMS (ESI) calcd for $C_{18}H_{19}N_2$ $[M + H]^+$ 263.1543, found: 263.1538.





1-(5-Methoxy-[1,1'-biphenyl]-2-yl)-3,5-dimethyl-1*H*-pyrazole (3ca)

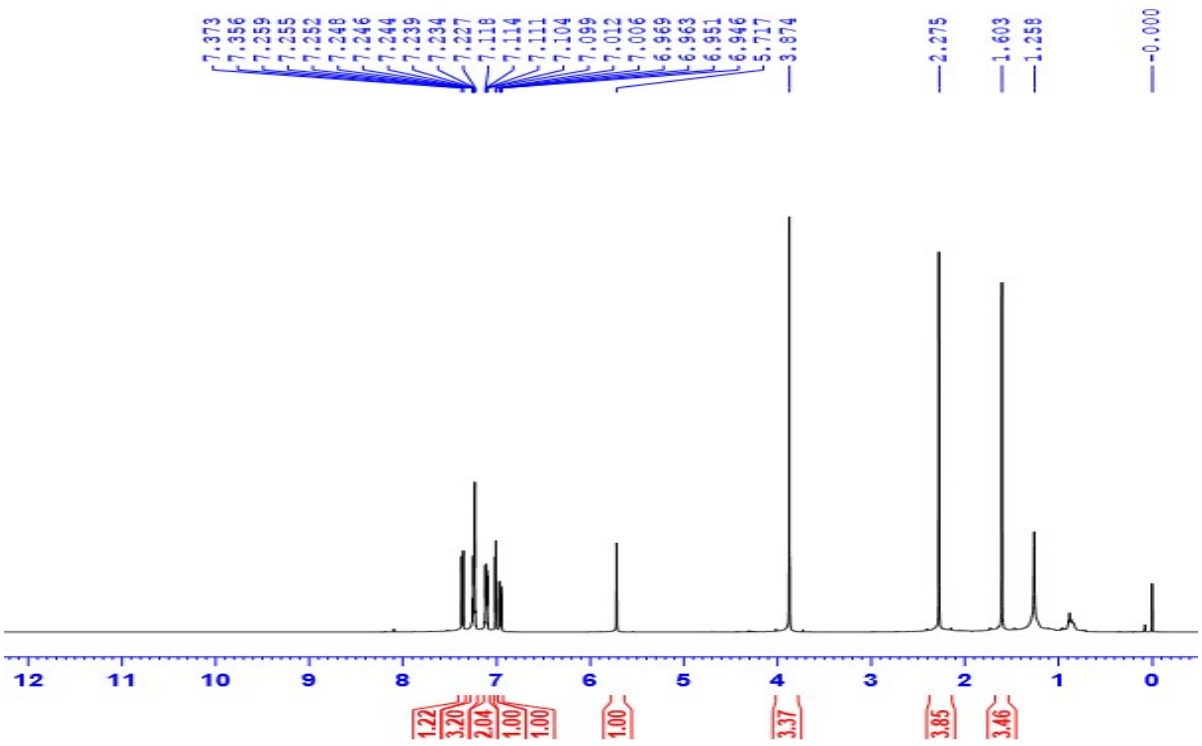


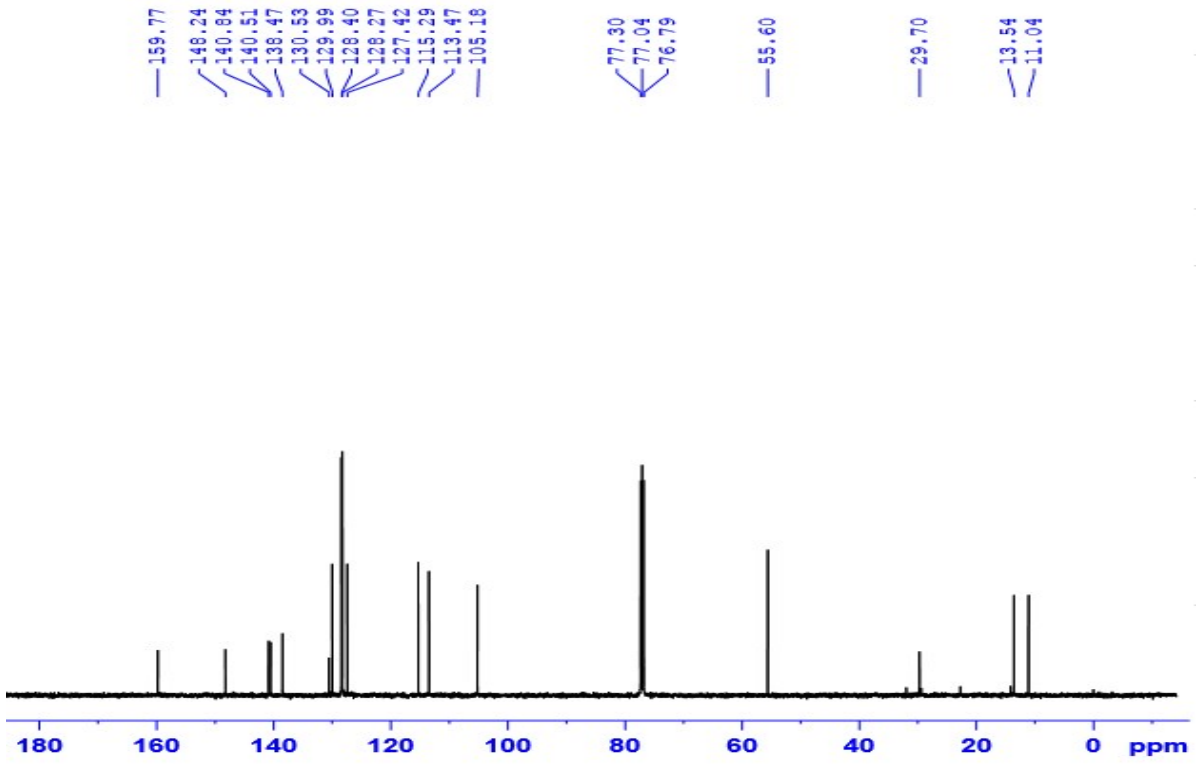
R_f = 0.13 (hexanes/EtOAc 20:1), light-yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 (d, *J* = 8.6 Hz, 1H), 7.28 – 7.22 (m, 3H), 7.14 – 7.08 (m, 2H), 7.01 (d, *J* = 2.9 Hz, 1H), 6.96 (dd, *J* = 8.6, 2.9 Hz, 1H), 5.72 (s, 1H), 3.87 (s, 3H), 2.28 (s, 3H), 1.60 (s, 3H).

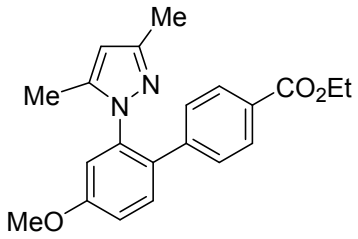
^{13}C NMR (126 MHz, $CDCl_3$) δ 159.8, 148.2, 140.8, 140.5, 138.5, 130.5, 130.0, 128.4, 128.3, 127.4, 115.3, 113.5, 105.2, 55.6, 13.5, 11.0.

HRMS (ESI) calcd for $C_{18}H_{19}N_2O$ $[M + H]^+$ 279.1492, found: 279.1487.


7.373
7.356
7.259
7.255
7.252
7.248
7.246
7.244
7.239
7.234
7.227
7.118
7.114
7.111
7.104
7.099
7.012
7.006
6.969
6.963
6.951
6.946
5.717
3.874
2.275
1.603
1.258
0.000
12
11
10
9
8
7
6
5
4
3
2
1
0
1.22
3.20
2.04
1.00
1.00
1.00
3.37
3.85
3.46


159.77
148.24
140.84
140.51
138.47
130.53
129.99
128.40
128.27
127.42
115.29
113.47
105.18
77.30
77.04
76.79
55.60
29.70
13.54
11.04
180
160
140
120
100
80
60
40
20
0
ppm

Ethyl 2'-(3,5-dimethyl-1*H*-pyrazol-1-yl)-4'-methoxy-[1,1'-biphenyl]-4-carboxylate (3dg)

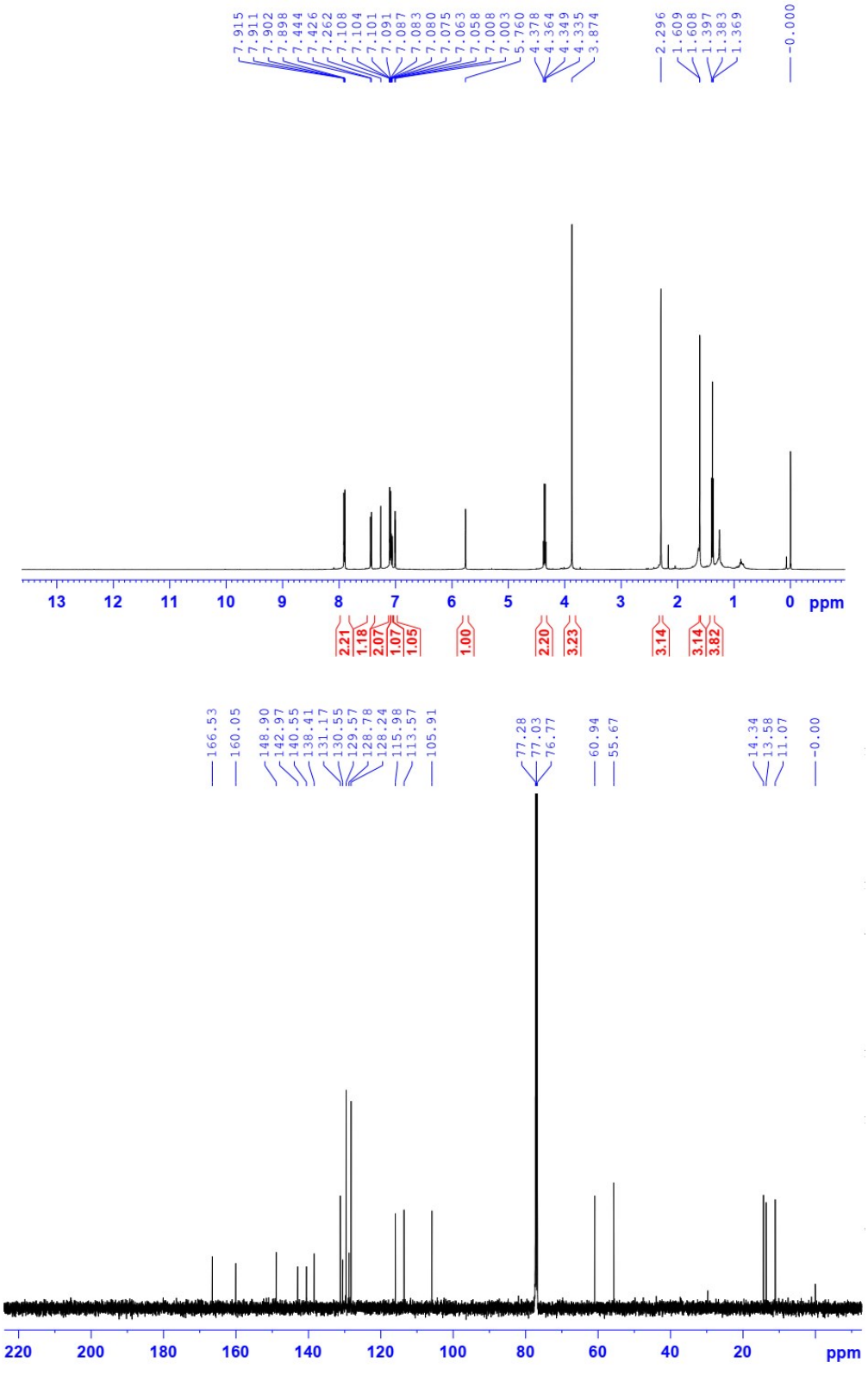


R_f = 0.4 (hexanes/EtOAc 3:1), white solid, m.p. 135 – 137 °C.

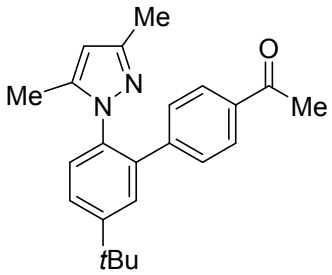
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 – 7.88 (m, 2H), 7.44 (d, J = 8.6 Hz, 1H), 7.1 (d, *J* = 1.9 Hz, 1H), 7.11 – 7.04 (m, 2H), 7.01 (d, *J* = 2.7 Hz, 1H), 5.76 (s, 1H), 4.36 (q, *J* = 7.1 Hz, 2H), 3.87 (s, 3H), 2.30 (s, 3H), 1.61 (s, 3H), 1.38 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 166.5, 160.1, 148.9, 143.0, 140.6, 138.4, 131.2, 130.6, 129.6, 128.8, 128.2, 116.0, 113.6, 105.9, 60.9, 55.7, 14.3, 13.6, 11.1.

HRMS (ESI) calcd for $C_{21}H_{23}N_2O_3$ $[M + H]^+$ 351.1703, found: 351.1697.


7.915
7.911
7.902
7.898
7.444
7.426
7.262
7.108
7.104
7.101
7.091
7.087
7.083
7.080
7.075
7.063
7.058
7.008
7.003
5.760
4.378
4.364
4.349
4.335
3.874
2.296
1.609
1.608
1.397
1.383
1.369
-0.000
13 12 11 10 9 8 7 6 5 4 3 2 1 0 ppm
2.21
1.18
2.07
1.07
1.05
1.00
2.20
3.23
3.14
3.14
3.82
166.53
160.05
148.90
142.97
140.55
138.41
131.17
130.55
129.57
128.78
128.24
115.98
113.57
105.91
77.28
77.03
76.77
60.94
55.67
14.34
13.58
11.07
-0.00
220 200 180 160 140 120 100 80 60 40 20 ppm

1-(5'-(*tert*-butyl)-2'-(3,5-dimethyl-1*H*-pyrazol-1-yl)-[1,1'-biphenyl]-4-yl)ethan-1-one (3ef)

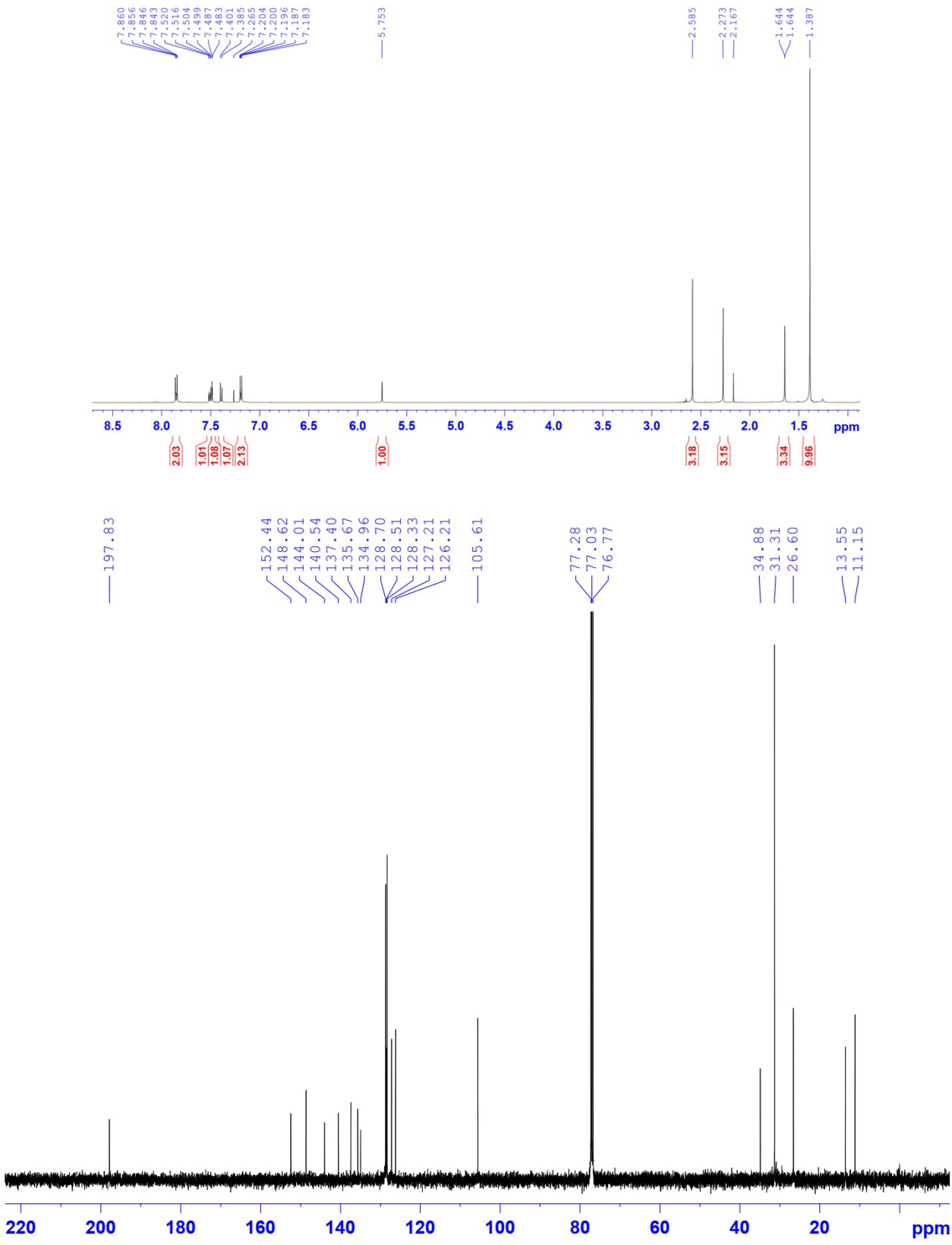


R_f = 0.1 (hexanes/EtOAc 10:1), white solid, m.p. = 113 – 115 °C.

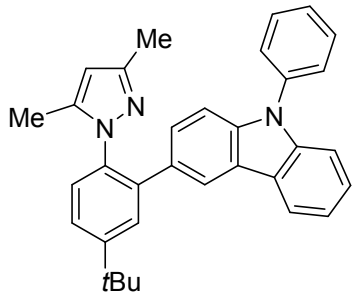
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 – 7.82 (m, 2H), 7.51 (dd, *J* = 8.2, 2.2 Hz, 1H), 7.49 (d, *J* = 2.2 Hz, 1H), 7.39 (d, *J* = 8.2 Hz, 1H), 7.22 – 7.16 (m, 2H), 5.57 (s, 1H), 2.59 (s, 3H), 2.27 (s, 3H), 1.64 (s, 3H), 1.39 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 197.8, 152.4, 148.6, 144.0, 140.6, 137.4, 135.7, 135.0, 128.7, 128.5, 128.3, 127.2, 126.2, 105.6, 34.9, 31.3, 26.6, 13.6, 11.2.

HRMS (ESI) calcd for $C_{23}H_{26}N_2ONa$ $[M + Na]^+$ 369.1937, found: 369.1933.


7.860
7.856
7.846
7.843
7.520
7.516
7.504
7.499
7.487
7.483
7.401
7.385
7.265
7.204
7.200
7.196
7.187
7.183
5.753
2.585
2.273
2.167
1.644
1.644
1.387
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
ppm
2.03
1.01
1.08
1.07
2.13
1.00
3.18
3.15
3.34
9.96
197.83
152.44
148.62
144.01
140.54
137.40
135.67
134.96
128.70
128.51
128.33
127.21
126.21
105.61
77.28
77.03
76.77
34.88
31.31
26.60
13.55
11.15
220
200
180
160
140
120
100
80
60
40
20
ppm

3-(5-(*tert*-Butyl)-2-(3,5-dimethyl-1*H*-pyrazol-1-yl)phenyl)-9-phenyl-9*H*-carbazole (3ej)

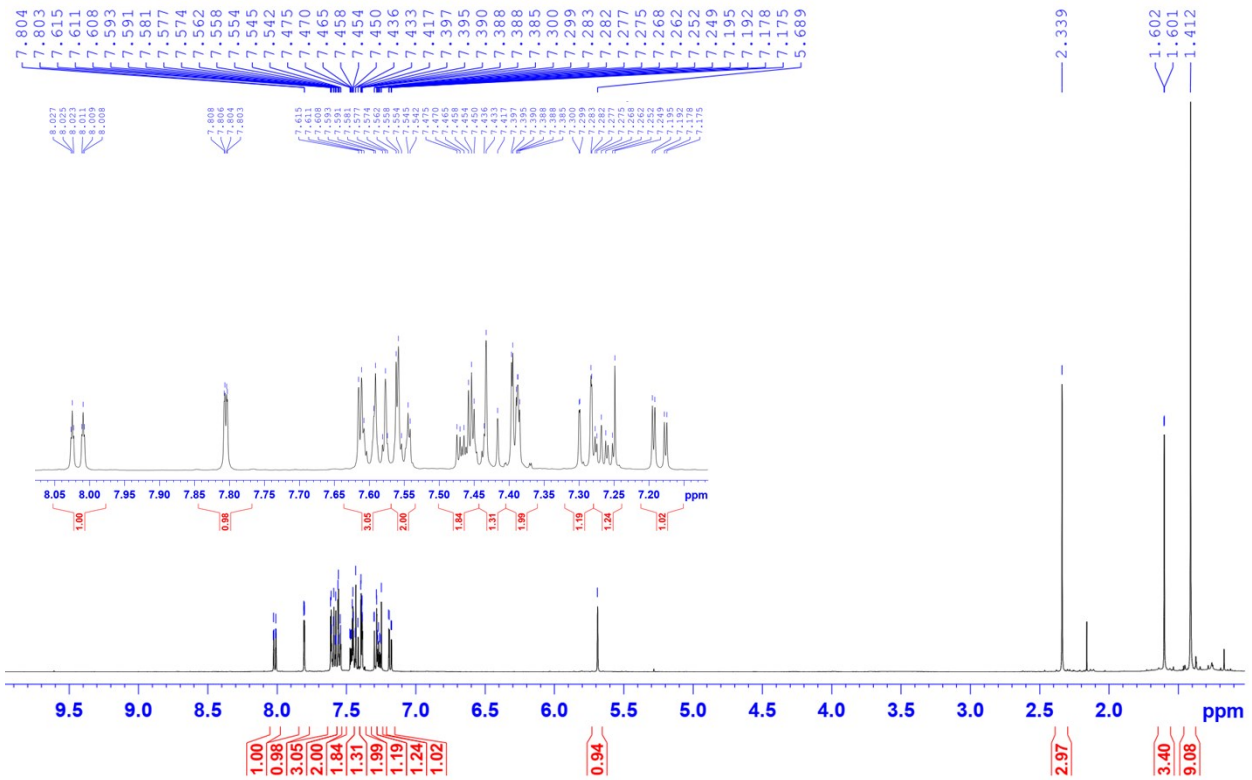


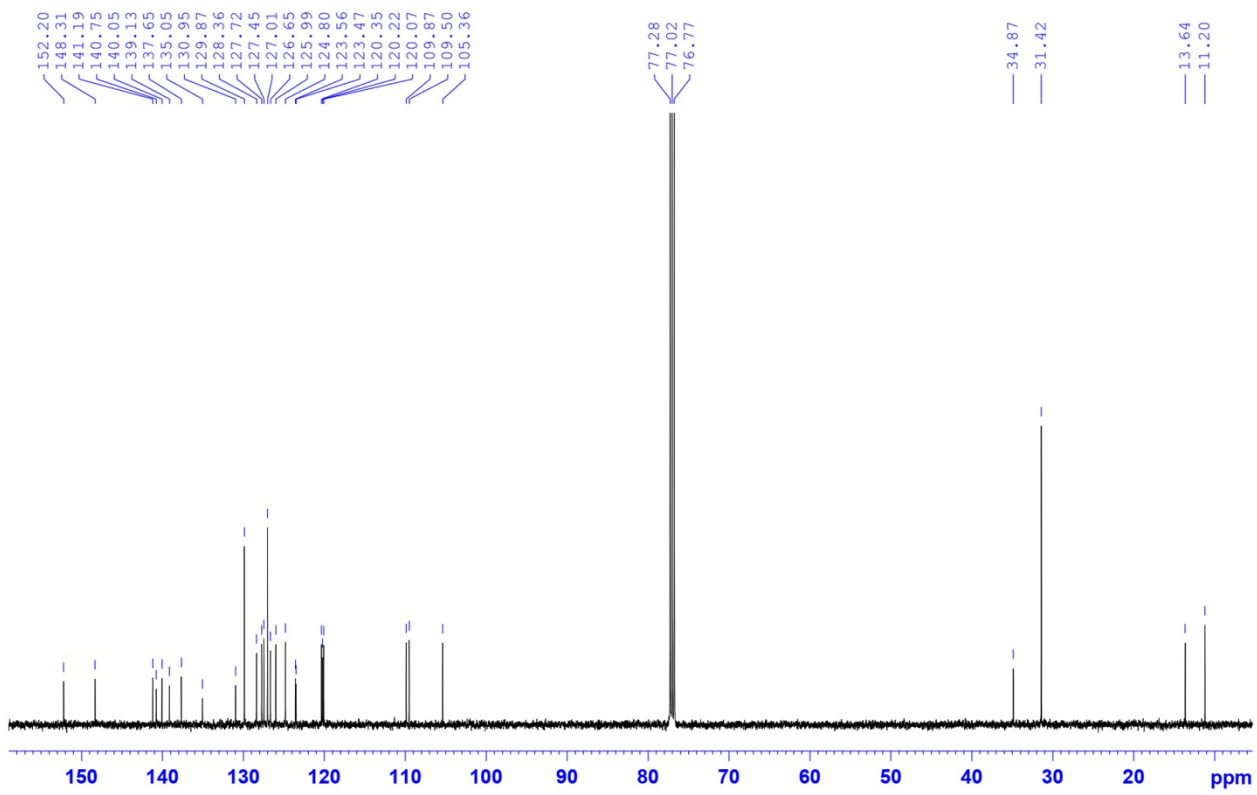
R_f = 0.29 (hexanes/EtOAc 10:1), white solid, m.p. = 188 – 190 °C.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 (dt, *J* = 7.8, 1.0 Hz, 1H), 7.81 (dd, *J* = 1.8, 0.7 Hz, 1H), 7.67 – 7.52 (m, 5H), 7.49 – 7.33 (m, 5H), 7.32 – 7.21 (m, 2H), 7.18 (dd, *J* = 8.5, 1.8 Hz, 1H), 5.71 – 5.67 (m, 1H), 2.34 (s, 3H), 1.60 (s, 3H), 1.41 (s, 9H).

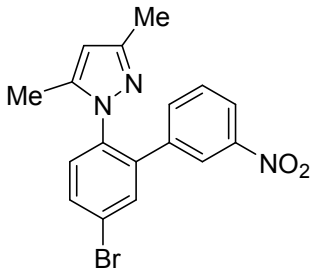
^{13}C NMR (126 MHz, $CDCl_3$) δ 152.2, 148.3, 141.2, 140.8, 140.1, 139.1, 137.7, 135.1, 131.0, 129.9, 128.4, 127.7, 127.5, 127.0, 126.7, 126.0, 124.8, 123.6, 123.5, 120.4, 120.2, 120.1, 109.9, 109.5, 105.4, 34.9, 31.4, 13.6, 11.2.

HRMS (ESI) calcd for $C_{33}H_{32}N_3$ $[M + H]^+$ 470.2591, found: 470.2586.


7.804
7.803
7.615
7.611
7.608
7.593
7.591
7.581
7.577
7.574
7.562
7.558
7.554
7.545
7.542
7.475
7.470
7.465
7.458
7.454
7.450
7.436
7.433
7.417
7.397
7.395
7.390
7.388
7.385
7.300
7.299
7.283
7.282
7.277
7.275
7.268
7.262
7.252
7.249
7.195
7.192
7.178
7.175
5.689
2.339
1.602
1.601
1.412
8.05 8.00 7.95 7.90 7.85 7.80 7.75 7.70 7.65 7.60 7.55 7.50 7.45 7.40 7.35 7.30 7.25 7.20 ppm
1.00 0.98 3.05 2.00 1.84 1.31 1.99 1.19 1.24 1.02
0.94
2.97
3.40 9.08
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 ppm


152.20
148.31
141.19
140.75
140.05
139.13
137.65
135.05
130.95
129.87
128.36
127.72
127.45
127.01
126.65
125.99
124.80
123.56
123.47
120.35
120.22
120.07
109.87
109.50
105.36
77.28
77.02
76.77
34.87
31.42
13.64
11.20
150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

1-(5-Bromo-3'-nitro-[1,1'-biphenyl]-2-yl)-3,5-dimethyl-1*H*-pyrazole (3fd)

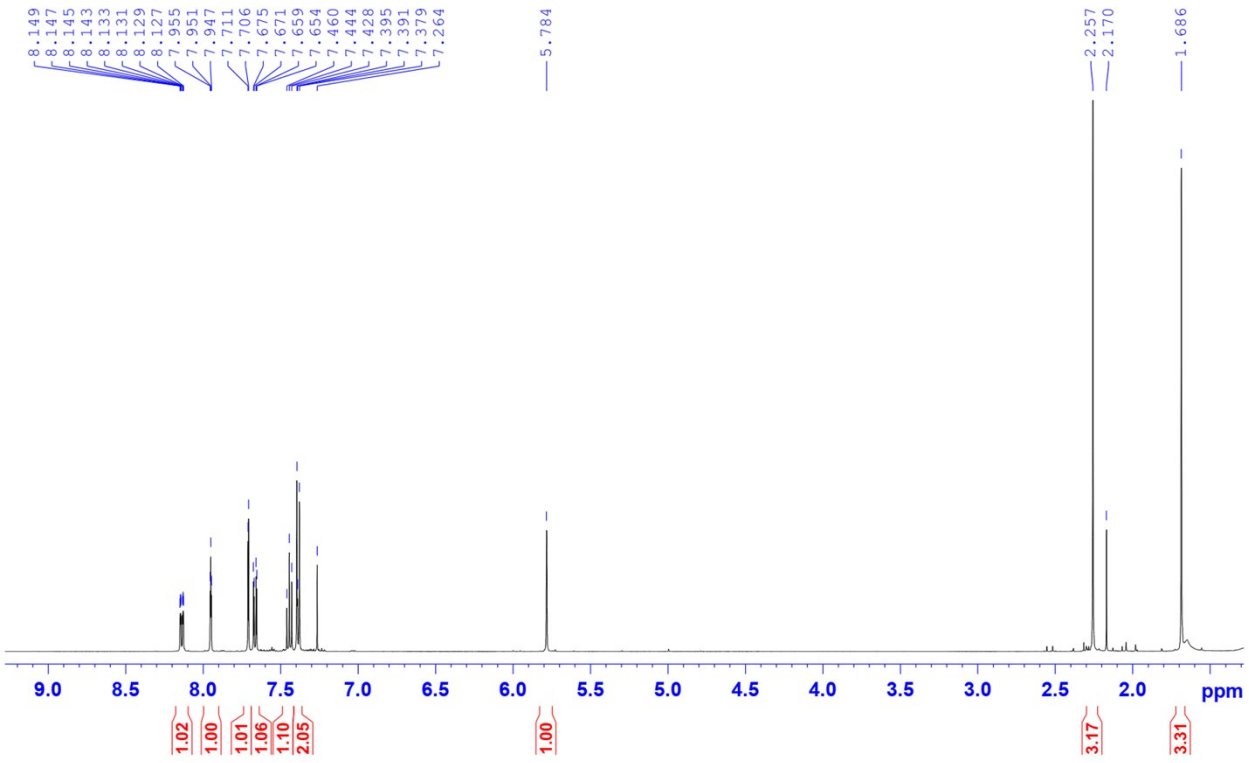


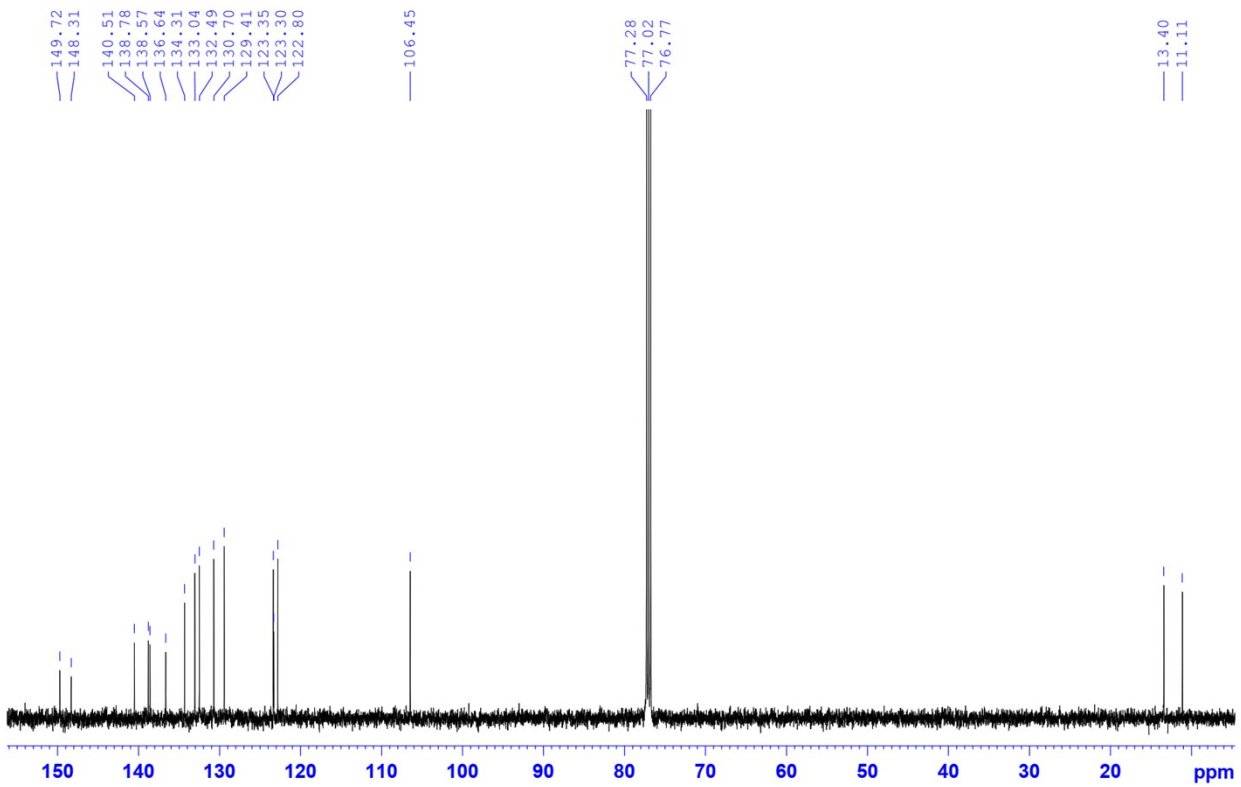
R_f = 0.34 (hexanes/EtOAc 10:1), yellow solid, m.p. = 191 – 193 °C.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.14 (ddd, *J* = 8.1, 2.3, 1.2 Hz, 1H), 7.95 (t, *J* = 2.0 Hz, 1H), 7.71 (d, *J* = 2.2 Hz, 1H), 7.66 (dd, *J* = 8.4, 2.2 Hz, 1H), 7.44 (t, *J* = 7.9 Hz, 1H), 7.41 – 7.34 (m, 2H), 5.78 (s, 1H), 2.26 (s, 3H), 1.69 (s, 3H).

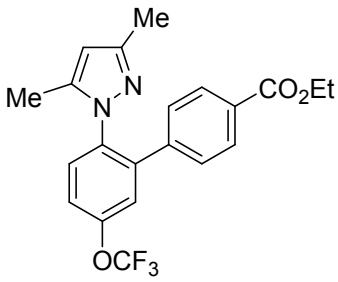
^{13}C NMR (126 MHz, $CDCl_3$) δ 149.7, 148.3, 140.5, 138.8, 138.6, 136.6, 134.3, 133.0, 132.5, 130.7, 129.4, 123.4, 123.3, 122.8, 106.5, 13.4, 11.1.

HRMS (ESI) calcd for $C_{17}H_{15}{}^{79}BrN_3O_2$ $[M + H]^+$ 372.0342, found: 372.0339.





Ethyl 2'-(3,5-dimethyl-1*H*-pyrazol-1-yl)-5'-(trifluoromethoxy)-[1,1'-biphenyl]-4-carboxylate (3gg)

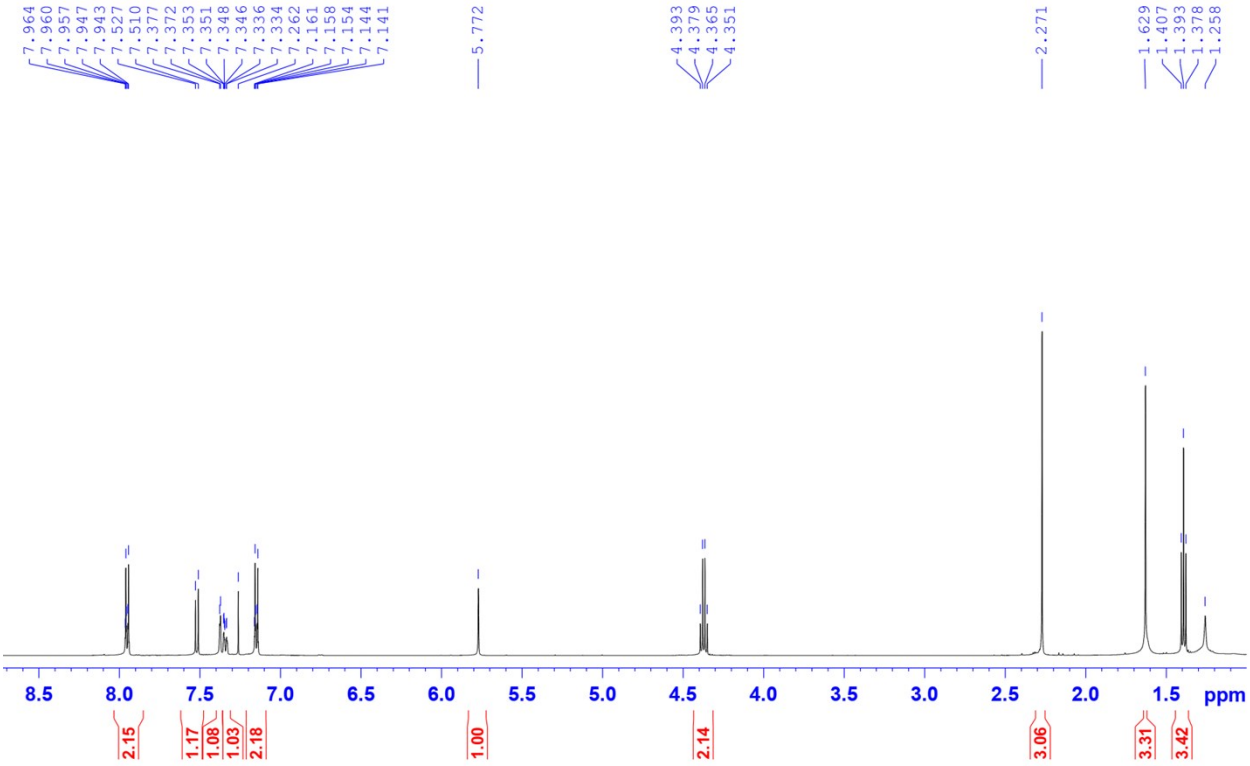


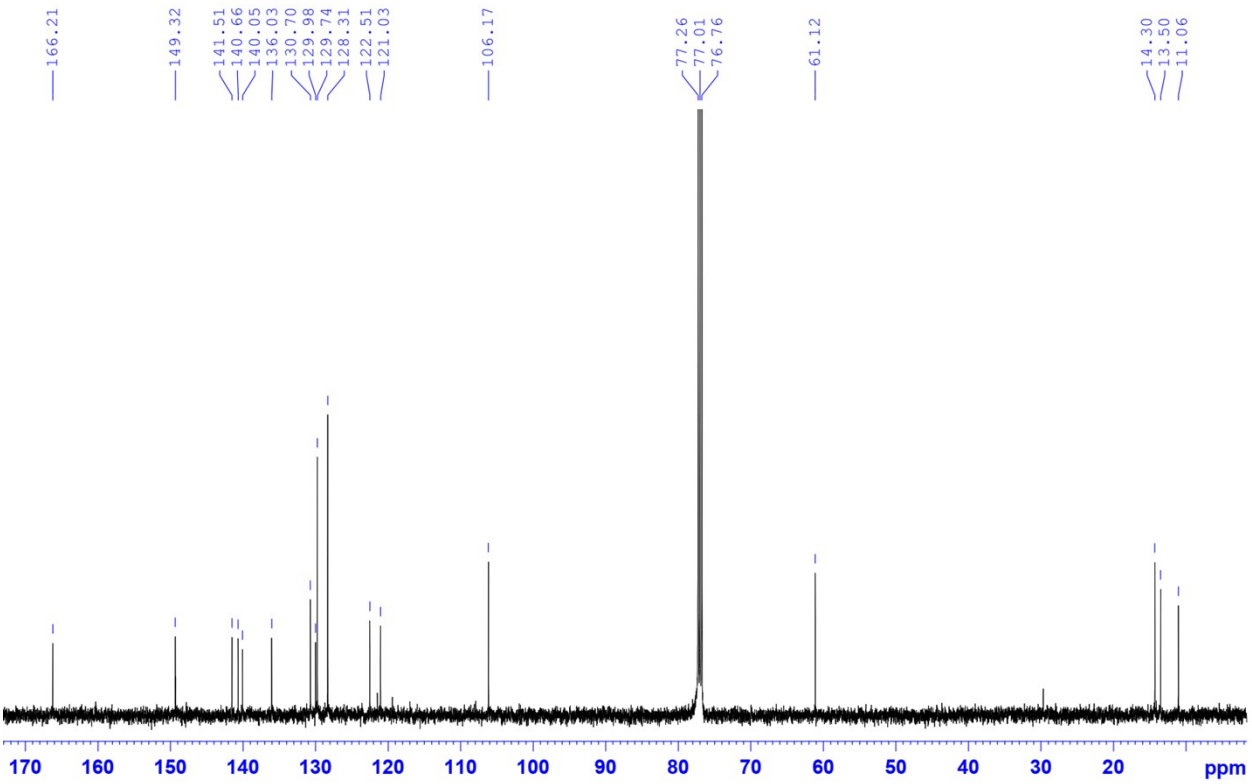
R_f = 0.1 (hexanes/EtOAc 10:1), light-yellow oil which slowly solidified under air.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 – 7.92 (m, 2H), 7.52 (d, *J* = 8.6 Hz, 1H), 7.40 – 7.36 (m, 1H), 7.34 (ddq, *J* = 8.5, 2.2, 1.1 Hz, 1H), 7.19 – 7.12 (m, 2H), 5.77 (s, 1H), 4.37 (q, *J* = 7.1 Hz, 2H), 2.27 (s, 3H), 1.63 (s, 3H), 1.39 (t, *J* = 7.1 Hz, 3H).

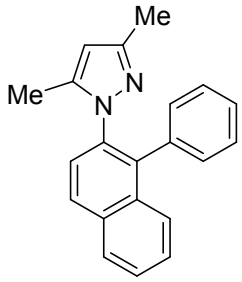
^{13}C NMR (126 MHz, $CDCl_3$) δ 166.2, 149.3, 141.5, 140.7, 140.1, 136.0, 130.7, 130.0, 129.7, 128.3, 122.5, 121.0, 106.2, 61.1, 14.3, 13.5, 11.1.

HRMS (ESI) calcd for $C_{21}H_{20}F_3N_2O_3$ $[M + H]^+$ 405.1421, found: 405.1417.





3,5-Dimethyl-1-(1-phenylnaphthalen-2-yl)-1*H*-pyrazole (3ha)

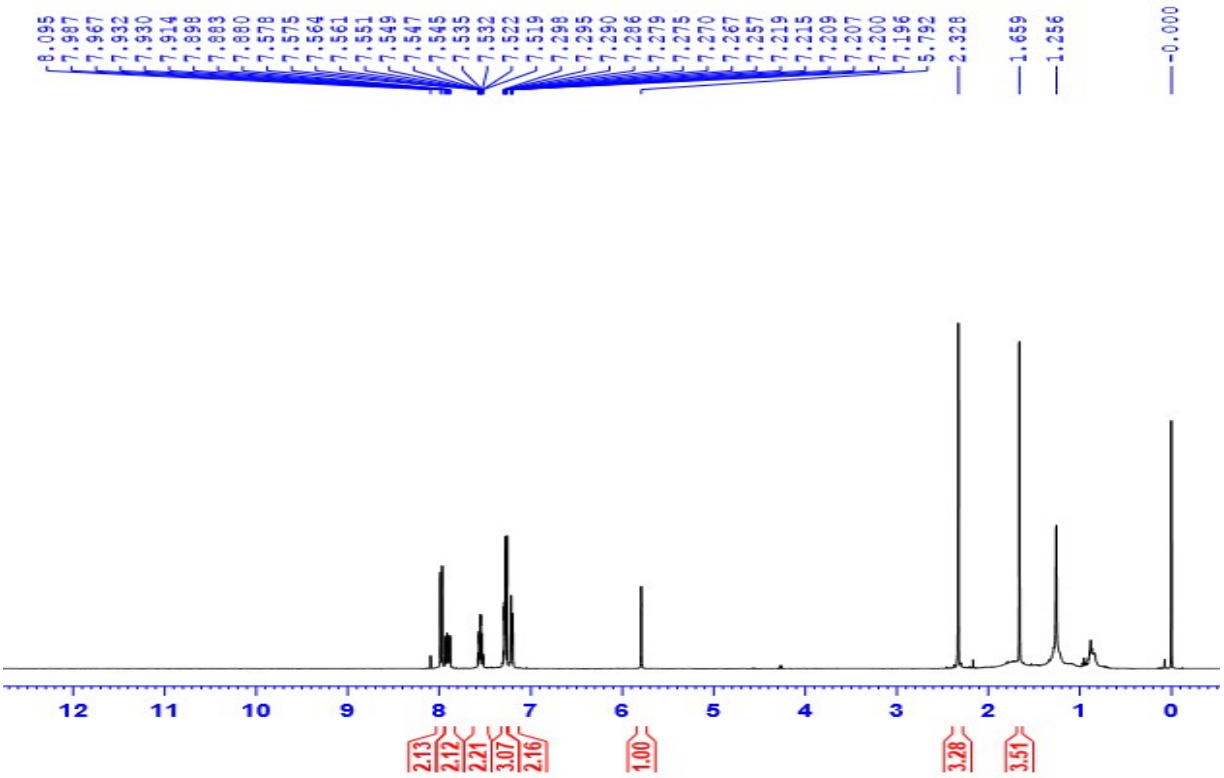


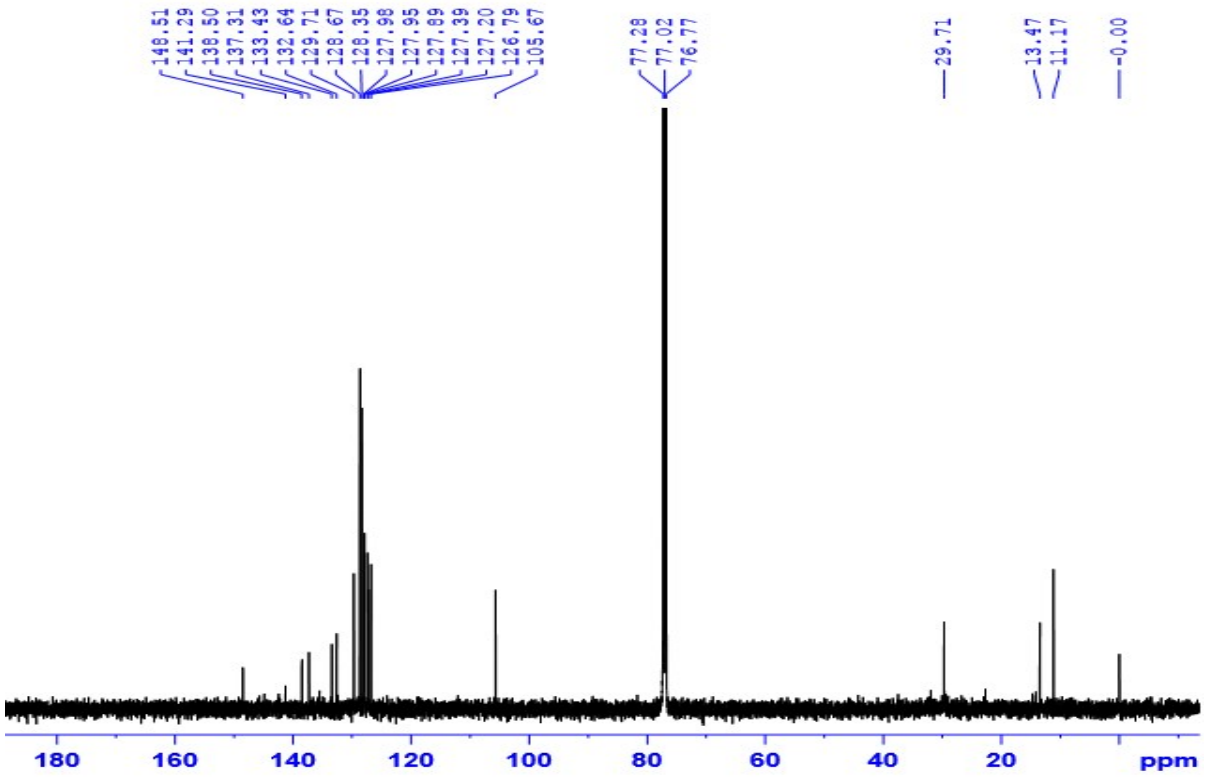
R_f = 0.12 (hexanes/EtOAc 20:1), light-yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 (d, *J* = 9.6 Hz, 2H), 7.95 – 7.86 (m, 2H), 7.60 – 7.50 (m, 2H), 7.29 – 7.25 (m, 3H), 7.20 (dd, *J* = 7.1, 2.7 Hz, 2H), 5.79 (s, 1H), 2.33 (s, 3H), 1.66 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 148.5, 141.3, 138.5, 137.3, 133.4, 132.6, 129.7, 128.7, 128.4, 128.0, 128.0, 128.0, 127.4, 127.2, 126.8, 105.7, 29.7, 13.5, 11.2.

HRMS (ESI) calcd for $C_{21}H_{19}N_2$ $[M + H]^+$ 299.1543, found: 299.1541.




148.51
141.29
138.50
137.31
133.43
132.64
129.71
128.67
128.35
127.98
127.95
127.89
127.39
127.20
126.79
105.67
77.28
77.02
76.77
29.71
13.47
11.17
0.00
180
160
140
120
100
80
60
40
20
ppm