

Synthesis of 4,4'-(4-Formyl-1H-pyrazole-1,3-diyl)dibenzoic Acid Derivatives as Narrow Spectrum Antibiotics for Potential Treatment of *Acinetobacter baumannii* Infections

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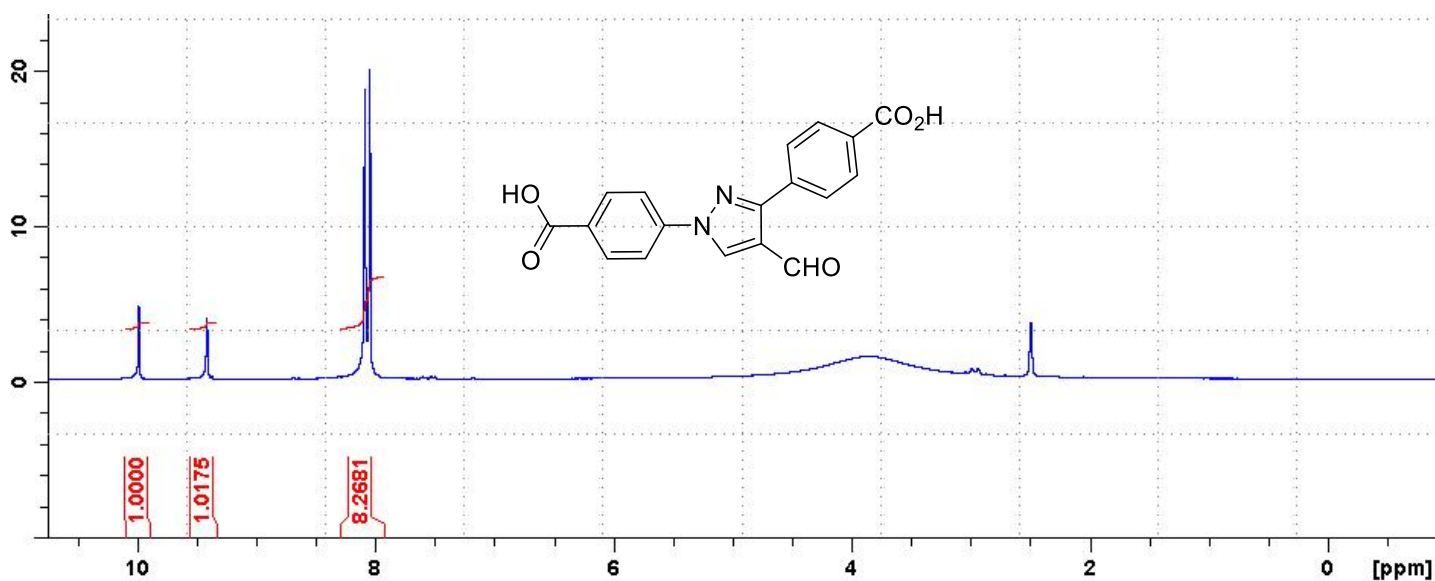
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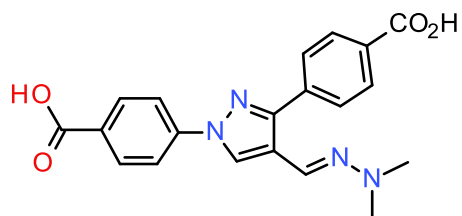
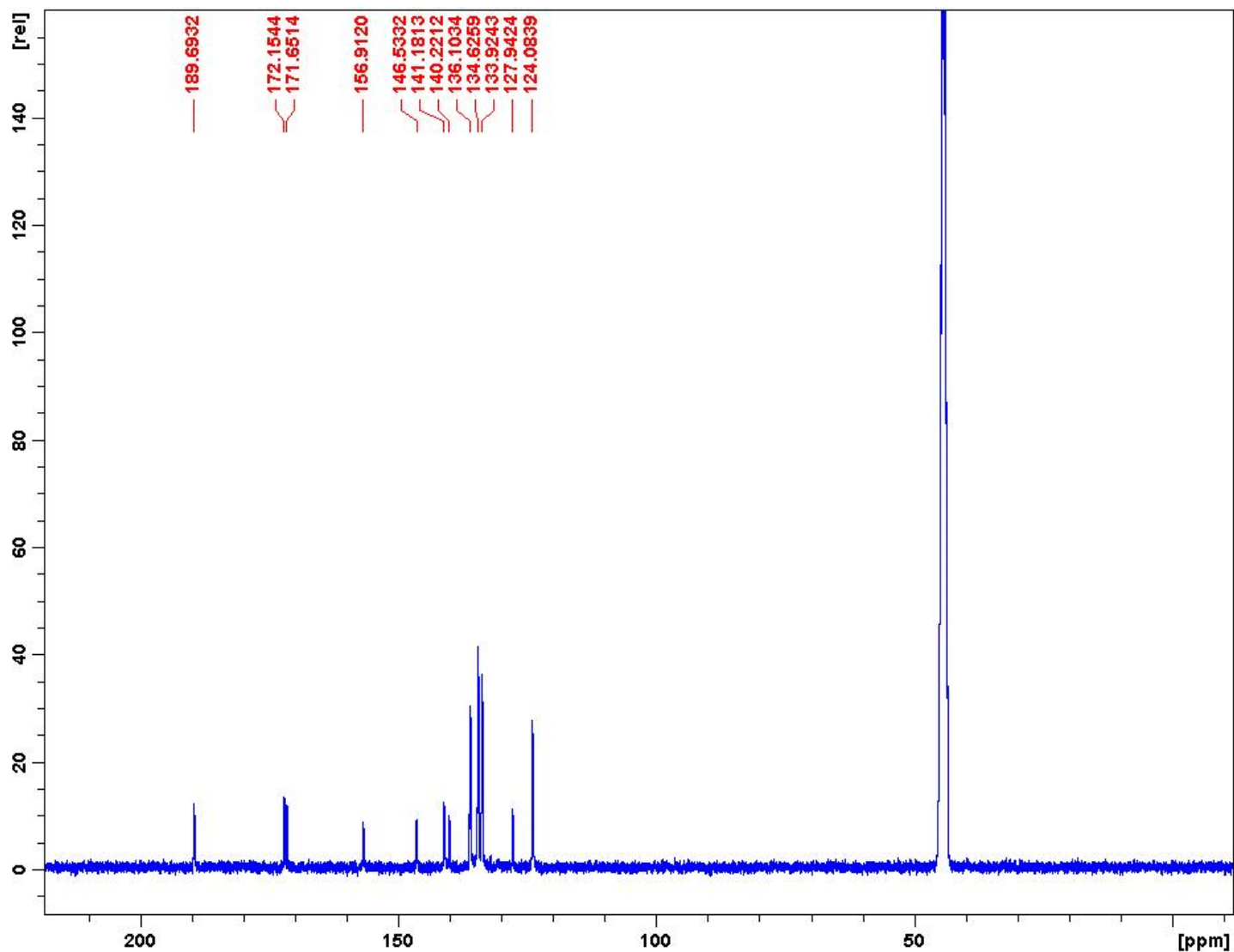
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^d Central Arkansas Veterans Healthcare System, W. 7th St., Little Rock, AR 72205

4,4'-(4-formyl-1H-pyrazole-1,3-diyl)dibenzoic acid (**4**)

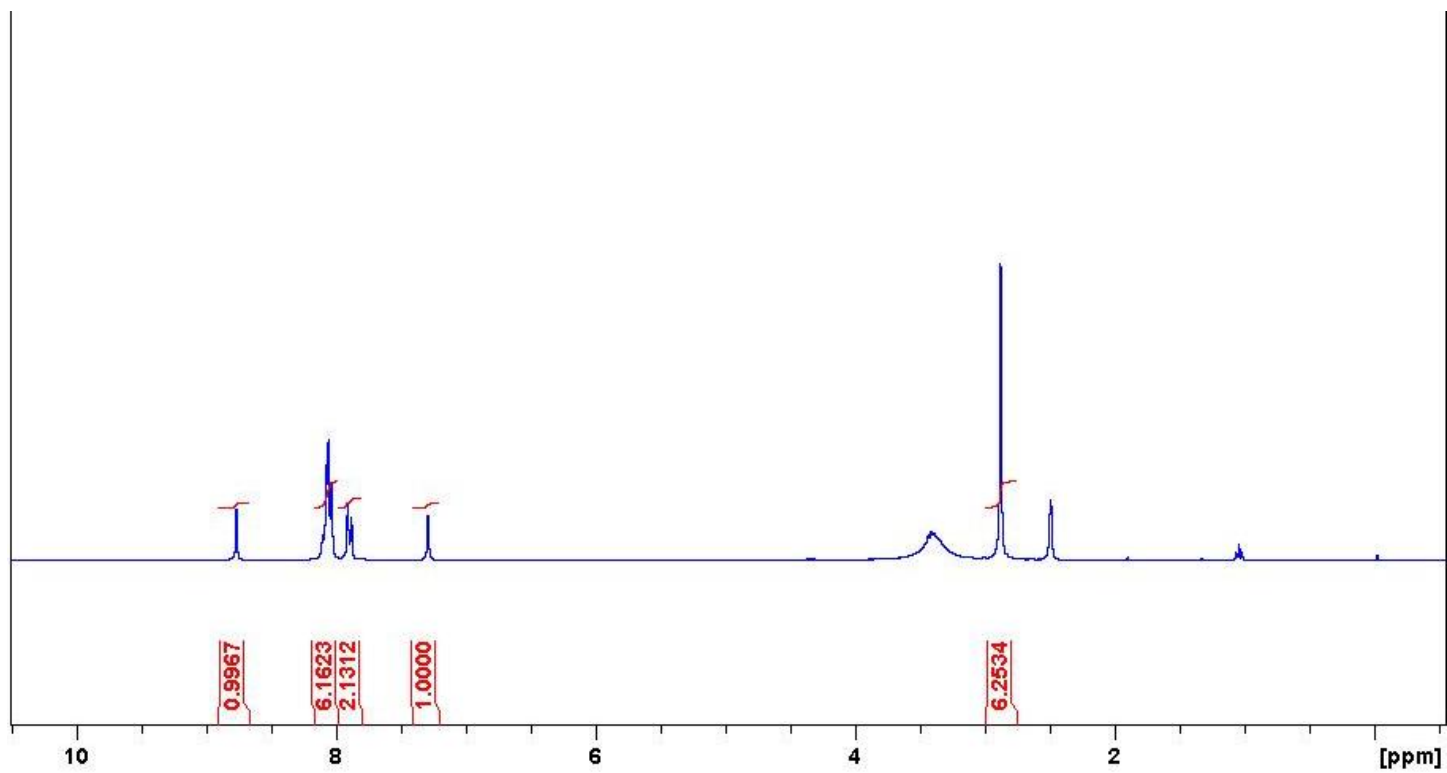
Yellow solid (3.02g 90%). ¹H NMR, 300 MHz (DMSO-d₆): δ 9.99 (s, 1H), 9.41 (s, 1H), 8.09-8.05 (m, 8H); ¹³C NMR (75MHz, DMSO-d₆) δ = 189.6, 172.1, 171.6, 156.9, 146.5, 141.1, 140.2, 136.1, 134.6, 133.9, 127.9, 124.0.

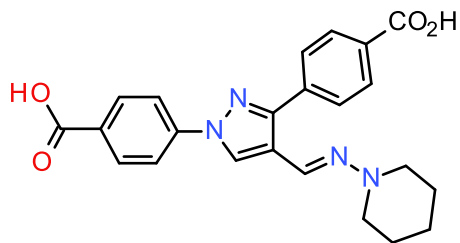
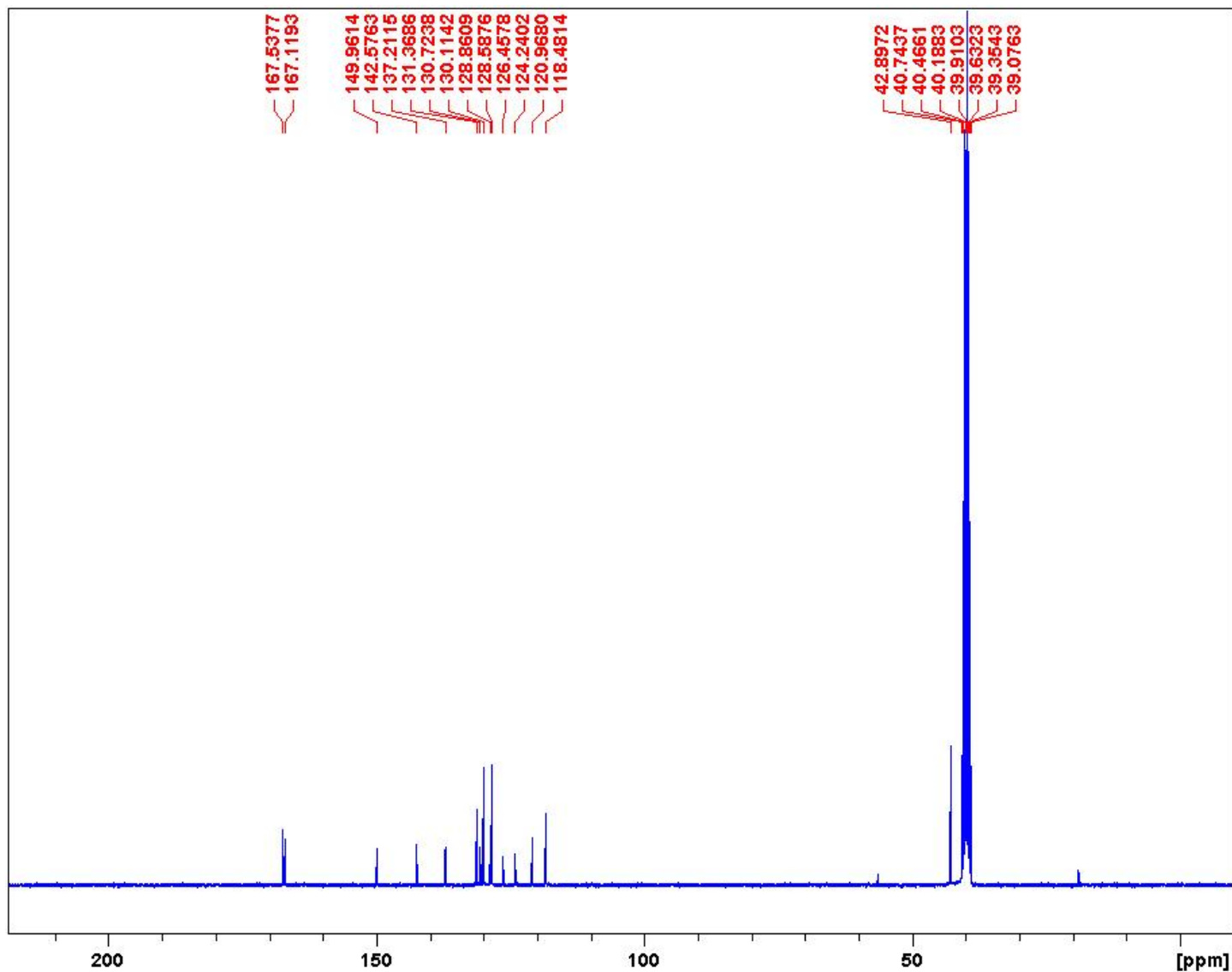




4-[1-(4-carboxyphenyl)-4-[(E)-(dimethylhydrazono)methyl]pyrazol-3-yl]benzoic acid (5)

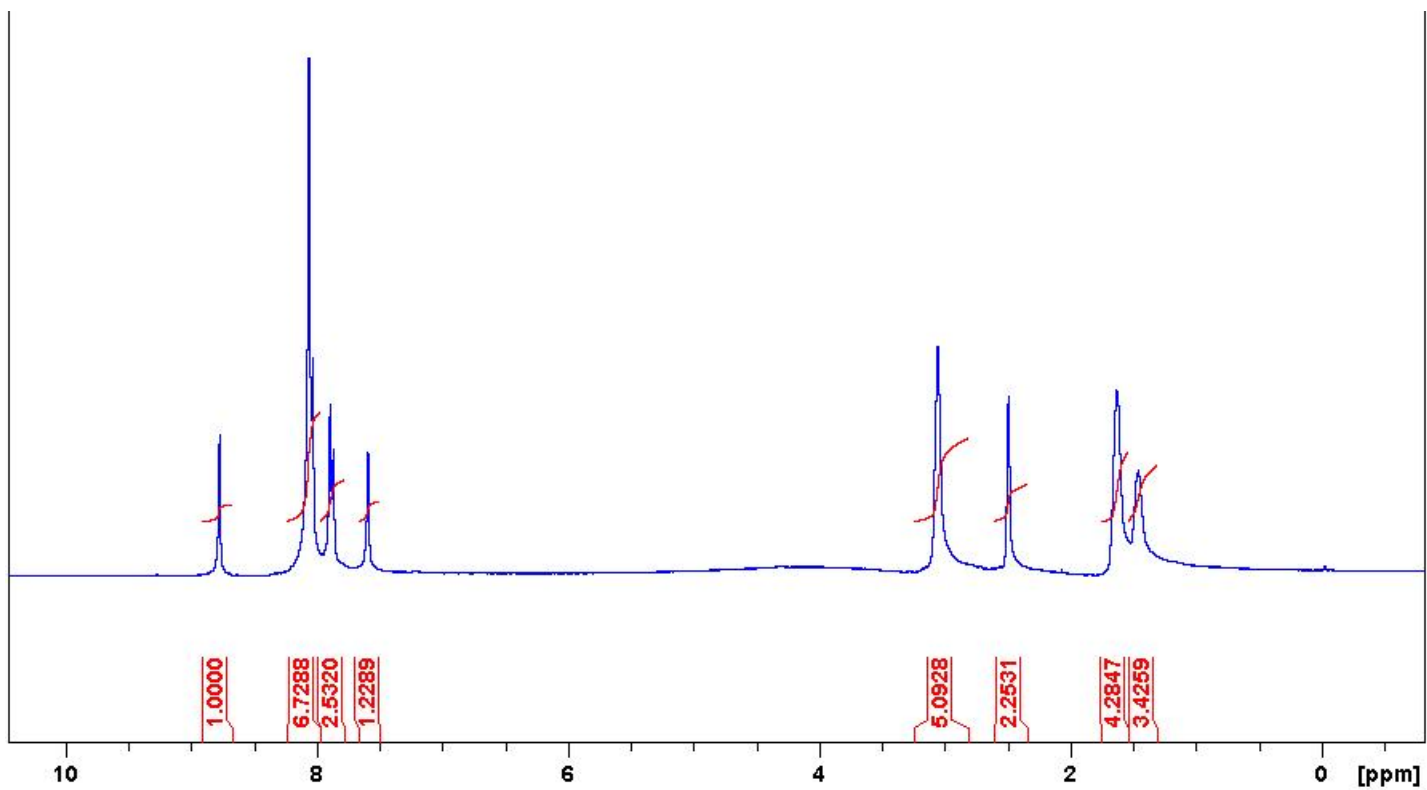
Yellow solid (347 mg, 92%). ¹H NMR (300 MHz DMSO-d₆): 8.77 (s, 1H), 8.11-8.04 (m, 6H), 7.90 (d, J = 8.2 Hz, 2H), 7.29 (s, 1H), 2.88 (s, 6H); ¹³C NMR (75 MHz DMSO-d₆): 167.5, 167.1, 149.9, 142.5, 137.2, 131.3, 130.7, 130.1, 128.8, 128.5, 126.4, 124.2, 120.9, 118.4, 42.8.

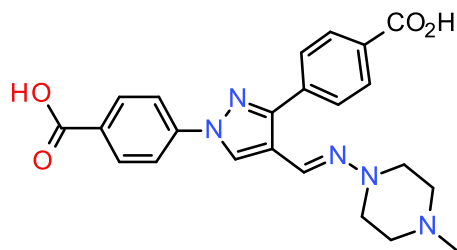
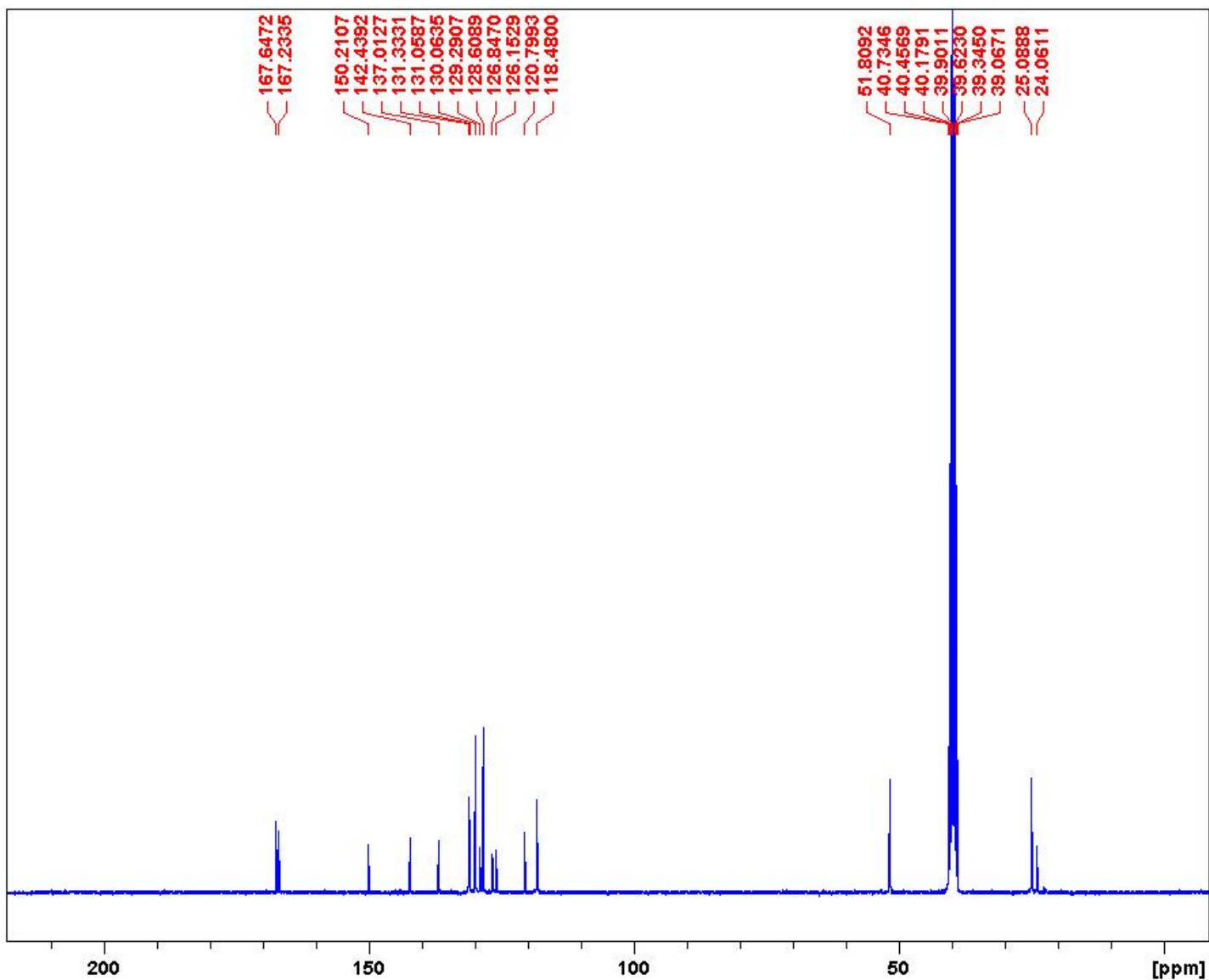




4-[1-(4-carboxyphenyl)-4-[(E)-1-piperidyliminomethyl]pyrazol-3-yl]benzoic acid (6)

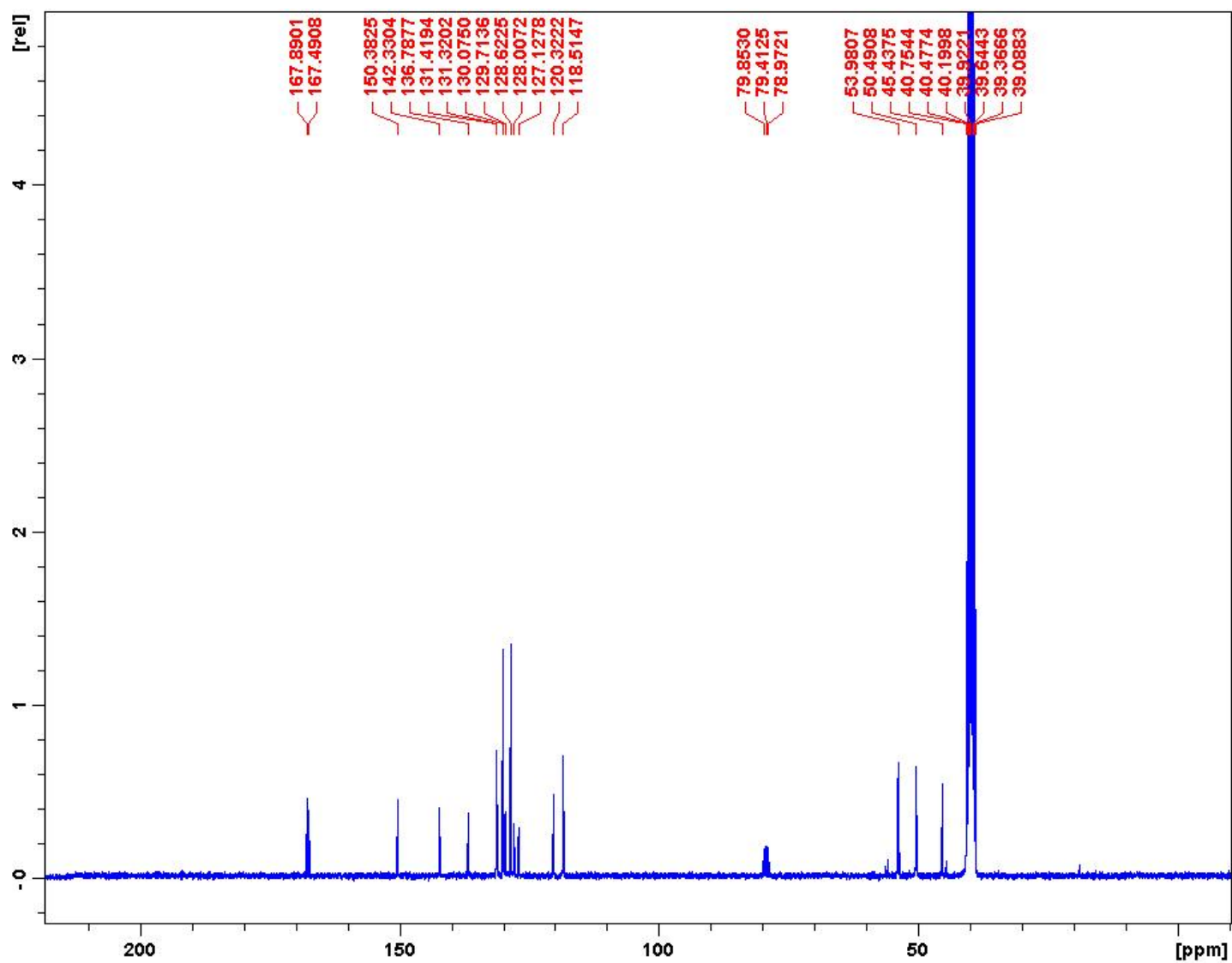
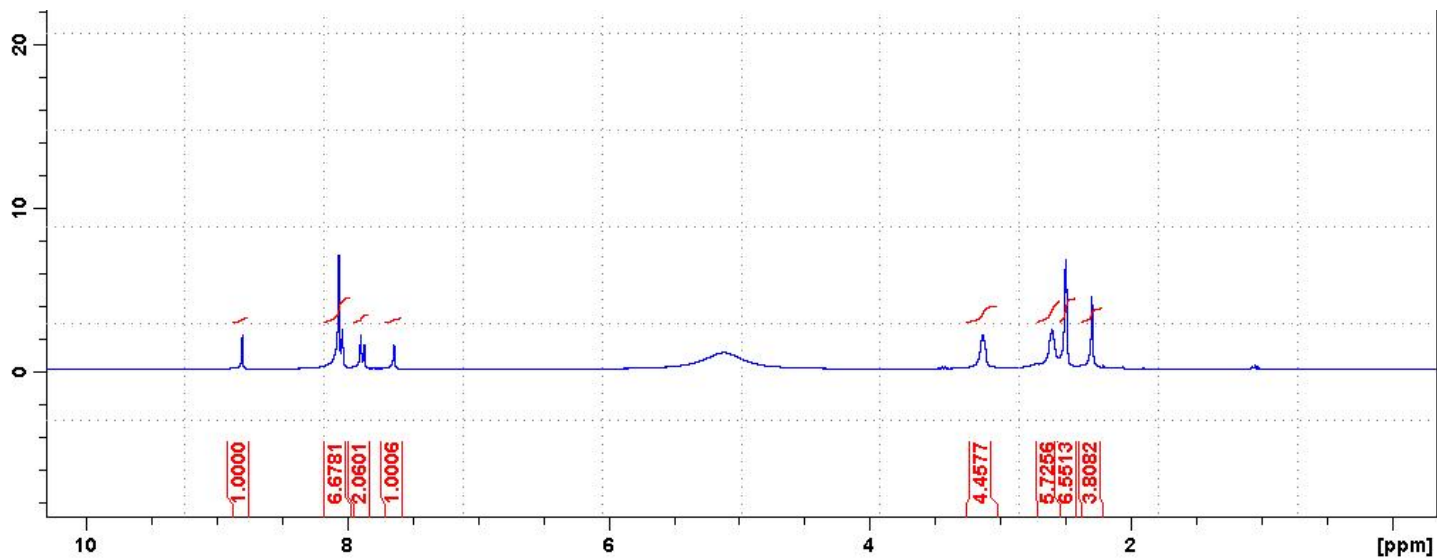
Yellow solid, (376 mg, 91%). ¹H NMR 300 MHz (DMSO-d₆): 8.77 (s, 1H), 8.06-8.03 (m, 6H), 7.88 (d, J = 8.0 Hz, 2H), 7.59 (s, 1H), 3.05 (s, 4H), 1.63 (s, 4H), 1.46 (s, 2H); ¹³C NMR (75MHz, DMSO-d₆) δ = 167.6, 167.2, 150.2, 142.4, 137.0, 131.3, 131.0, 130.0, 129.2, 128.6, 126.8, 126.1, 120.7, 118.4, 51.8, 25.0, 24.0.

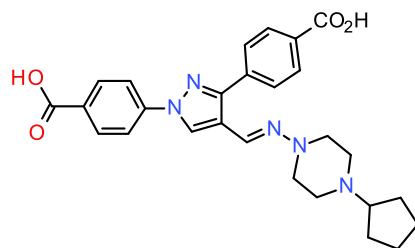




4,4'-{4-[(*E*)-(4-methylpiperazin-1-yl)imino)methyl]-1*H*-pyrazole-1,3-diyl}dibenzoic acid (7)

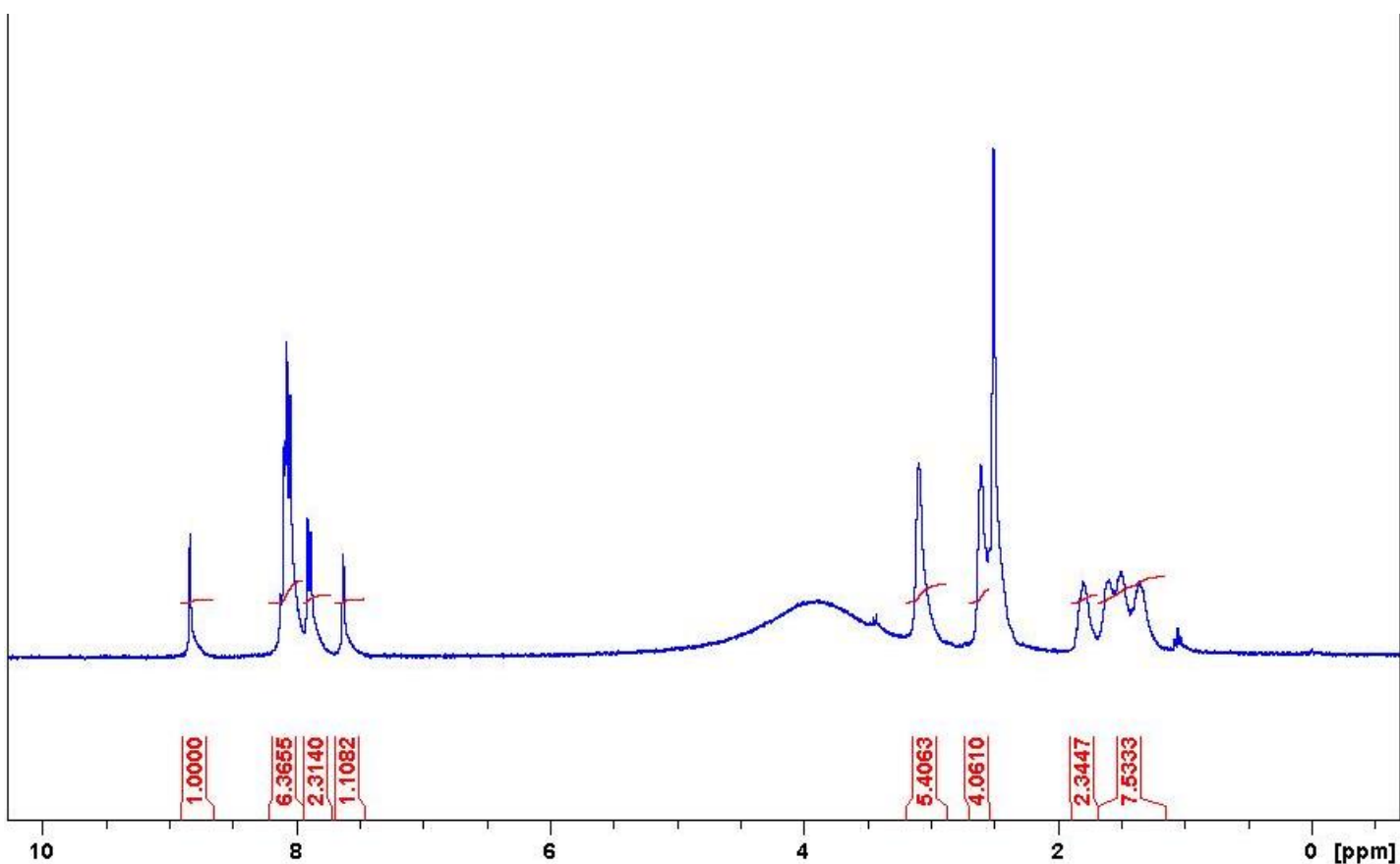
Yellow solid (402 mg, 93%). ¹H NMR 300 MHz (DMSO-*d*₆): δ 8.80 (s, 1H), 8.06 (s, 4H), 8.04 (d, *J* = 8.7 Hz, 2H), 7.88 (d, *J* = 8.3 Hz, 2H), 7.64 (s, 1H), 3.13 (br s, 4H), 2.60 (br s, 4H), 2.29 (s, 3H); ¹³C NMR (75MHz, DMSO-*d*₆ + CDCl₃) δ = 167.8, 167.4, 150.3, 142.3, 136.7, 131.4, 131.3, 130.0, 129.7, 128.6, 128.0, 127.1, 120.3, 118.5, 53.9, 50.4, 45.4.

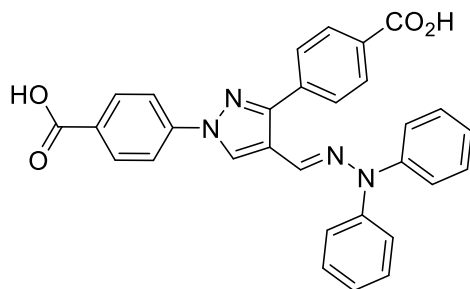
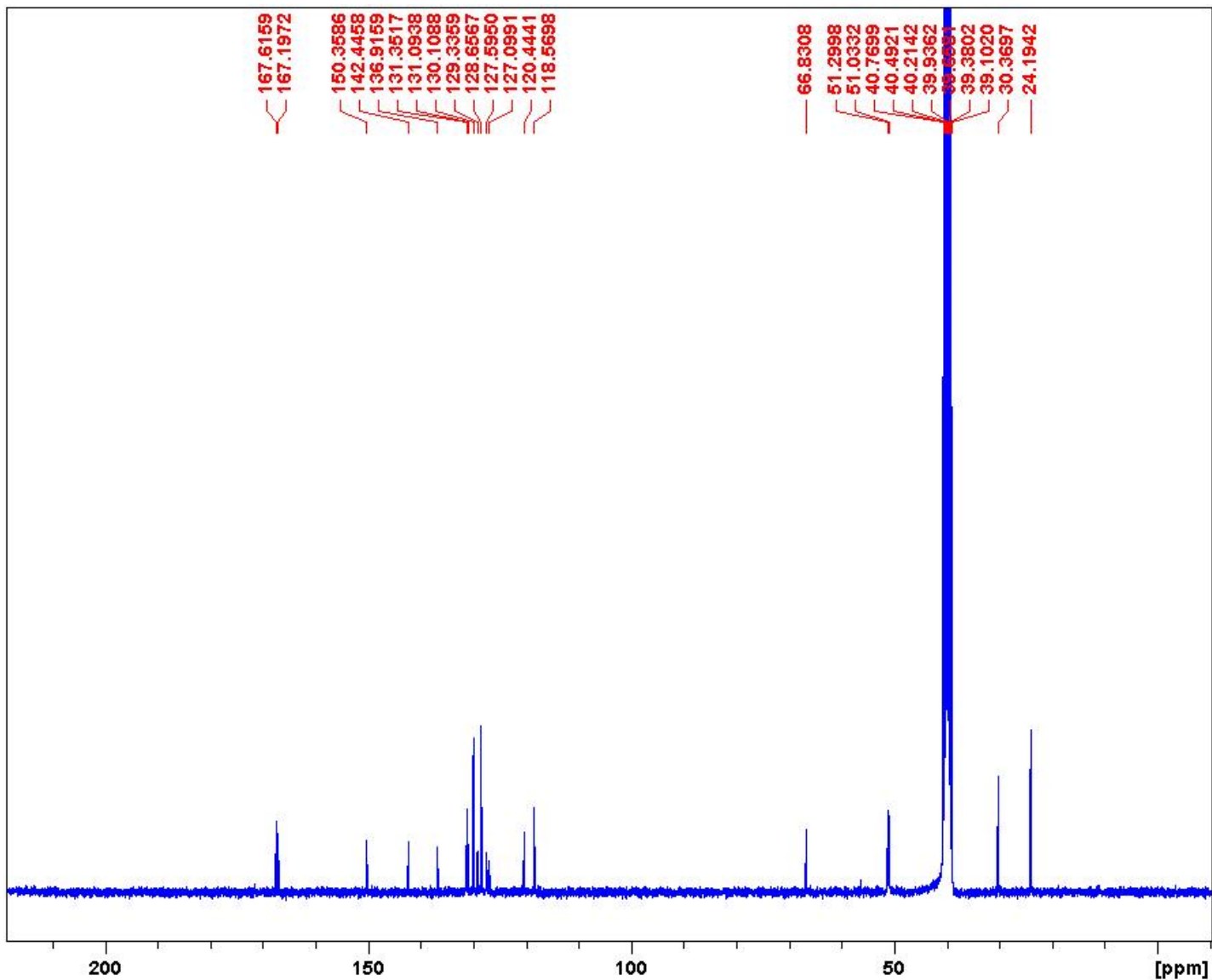




4-[1-(4-carboxyphenyl)-4-[(E)-(4-cyclopentylpiperazin-1-yl)iminomethyl]pyrazol-3-yl]benzoic acid (8)

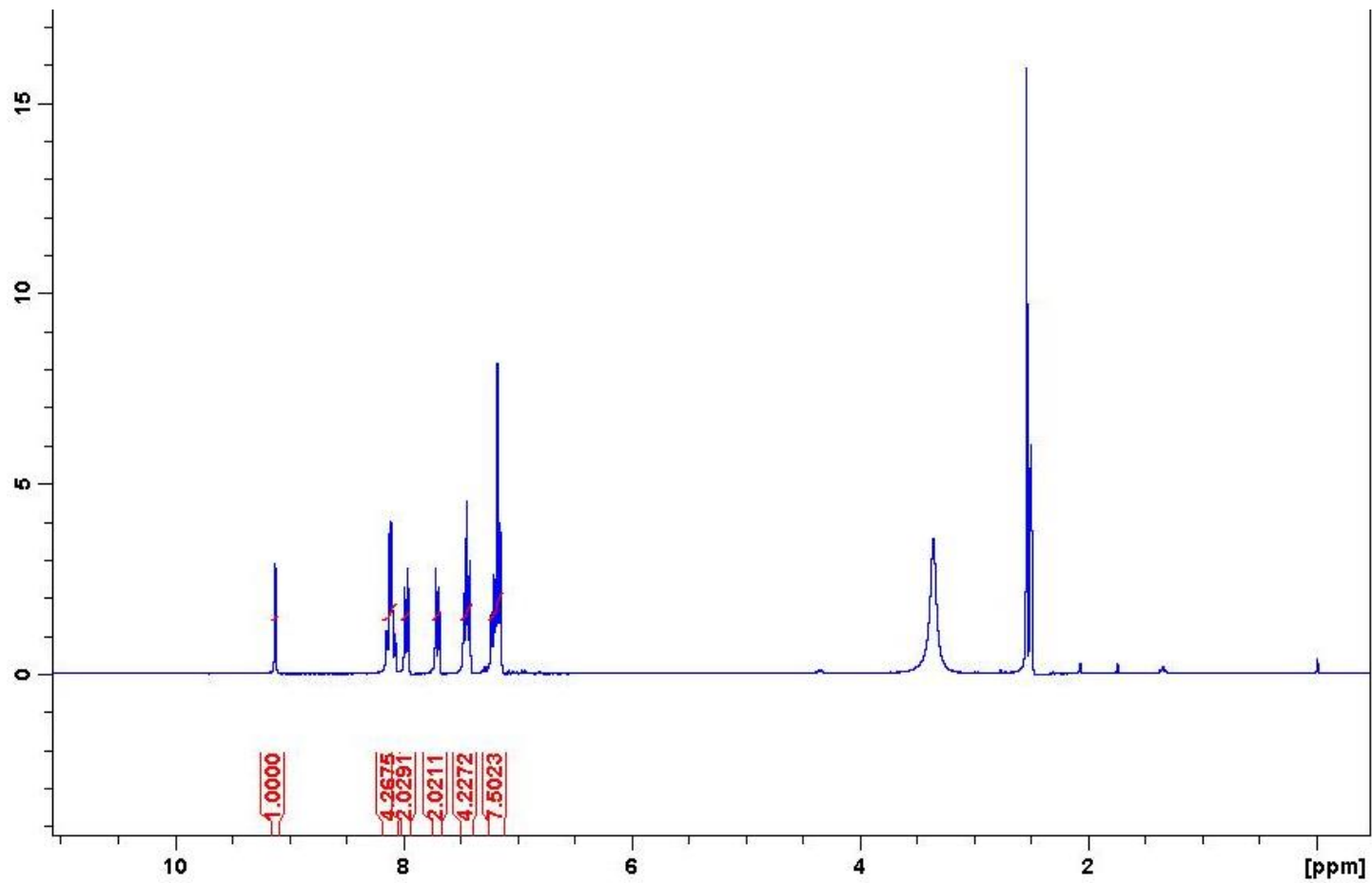
Yellow solid (457 mg, 94%). ^1H NMR, 300 MHz (DMSO- d_6): 8.83 (s, 1H), 8.11-8.04 (m, 6H), 7.89 (d, $J = 8.1$ Hz, 2H), 7.62 (s, 1H), 3.08 (s, 4H), 2.60 (s, 4H), 2.50 (s, 1H), 1.79 (s, 2H), 1.59-1.34 (m, 6H), ^{13}C NMR (75MHz, DMSO- d_6) $\delta = 167.6, 167.1, 150.3, 142.4, 136.9, 131.3, 131.0, 130.1, 129.3, 128.6, 127.5, 127.0, 120.4, 118.5, 66.8, 51.2, 51.0, 30.3, 24.1$.

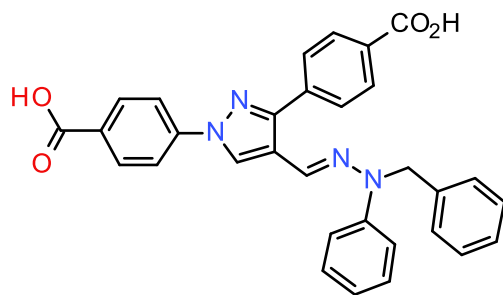
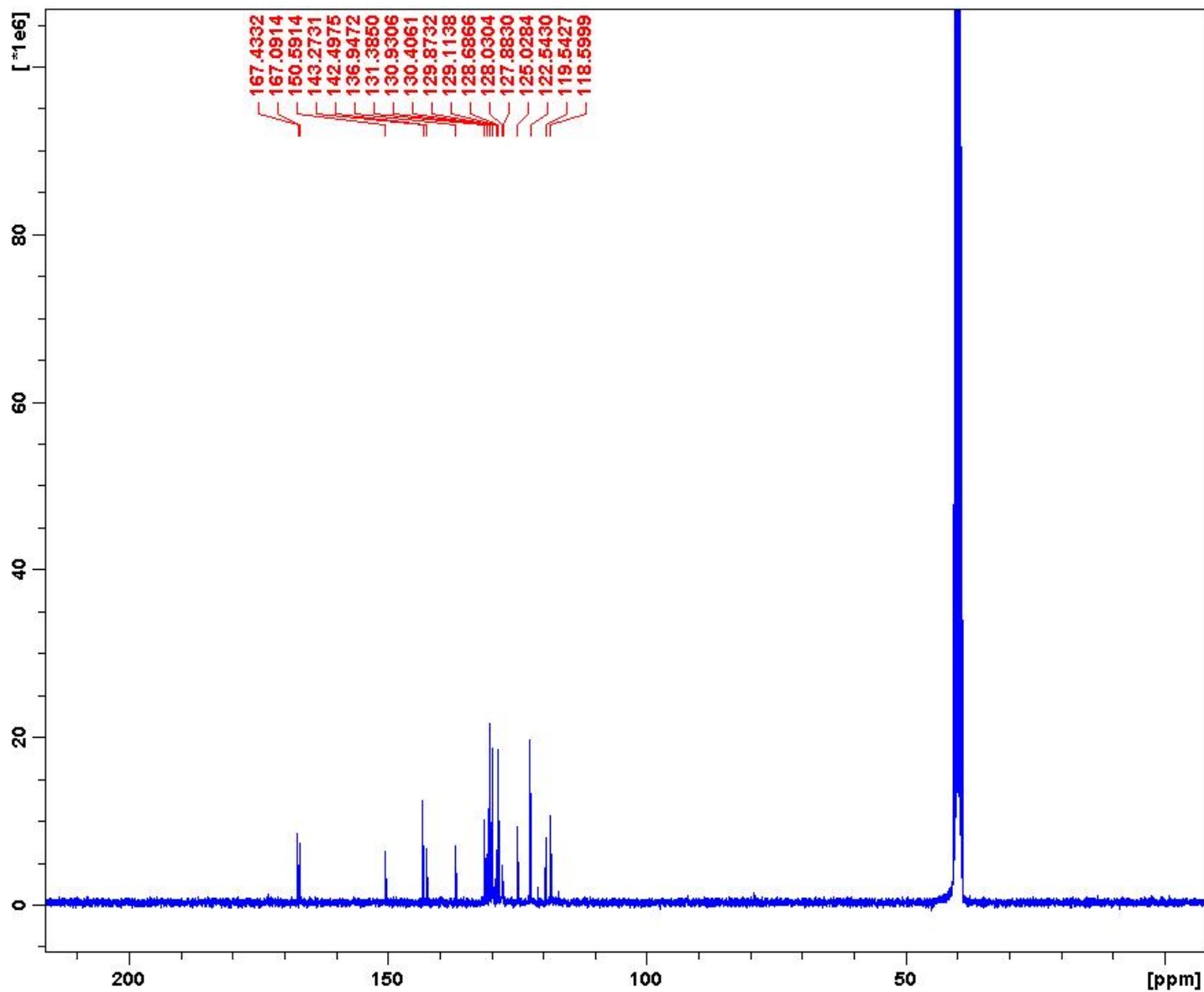




4-[1-(4-carboxyphenyl)-4-[(E)-(diphenylhydrazono)methyl]pyrazol-3-yl]benzoic acid (9)

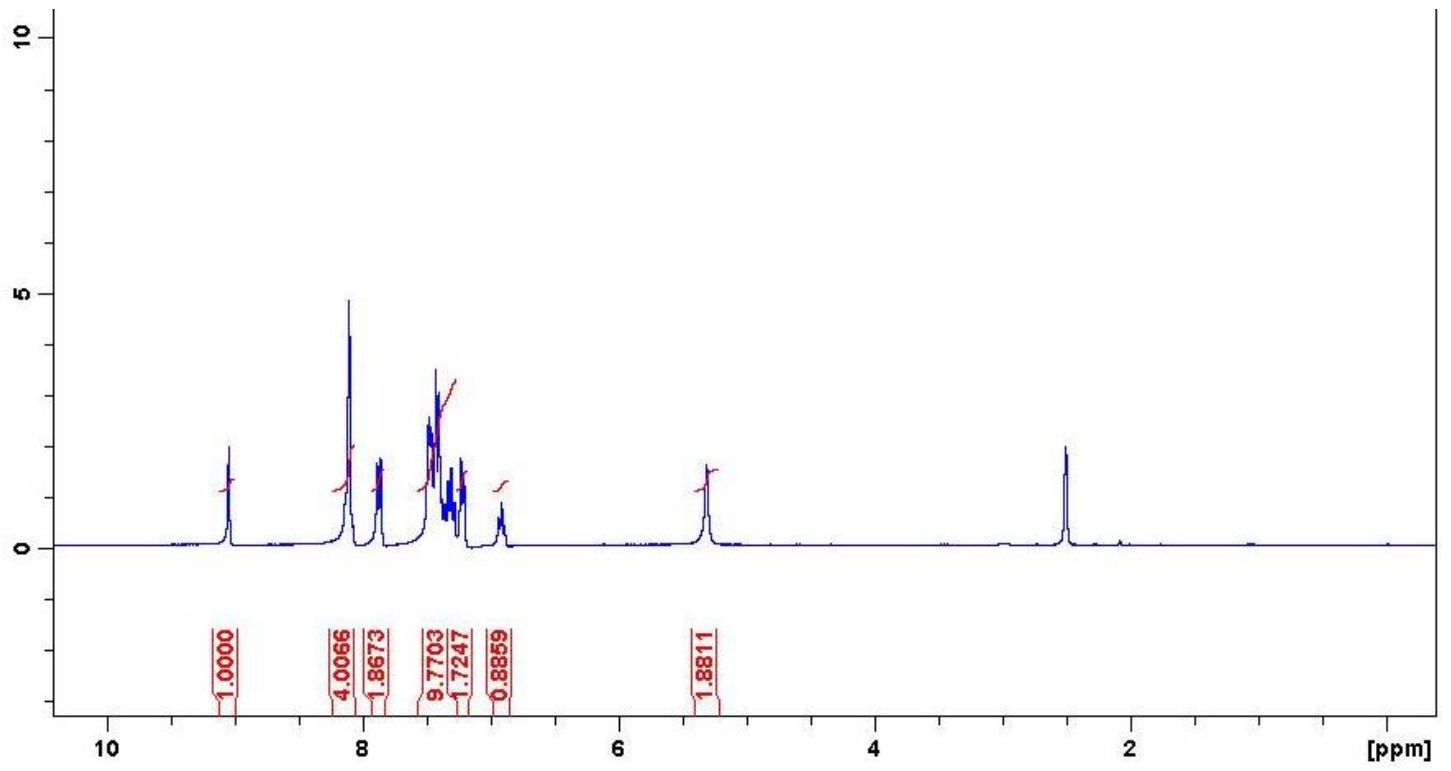
Yellow solid (446 mg, 89%). ¹H NMR, 300 MHz (DMSO-d₆): δ 9.12 (s, 1H), 8.14-8.06 (m, 4H), 7.97 (d, J = 8.1 Hz, 2H), 7.70 (d, J = 8.1 Hz, 2H), 7.44 (t, J = 7.8 Hz, 4H), 7.28-7.14 (m, 7H); ¹³C NMR (75MHz, DMSO-d₆) δ = 167.4, 167.0, 150.5, 143.2, 142.4, 136.9, 131.3, 130.9, 130.4, 129.8, 129.1, 128.6, 128.0, 127.8, 125.0, 122.5, 119.5, 118.5.

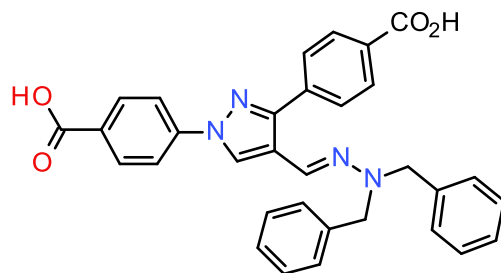
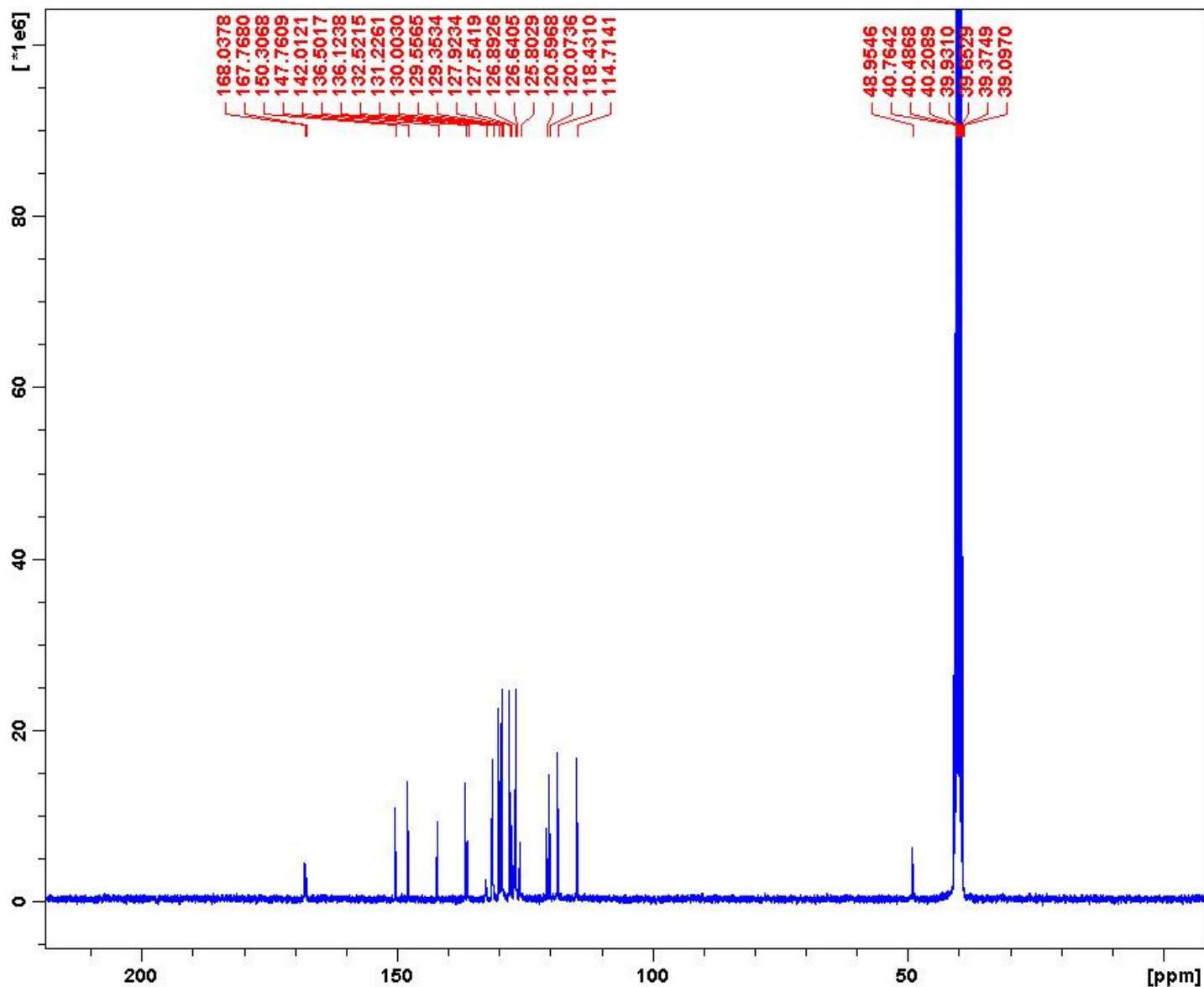




4-[4-[(E)-[benzyl(phenyl)hydrazone]methyl]-1-(4-carboxyphenyl)pyrazol-3-yl]benzoic acid (10)

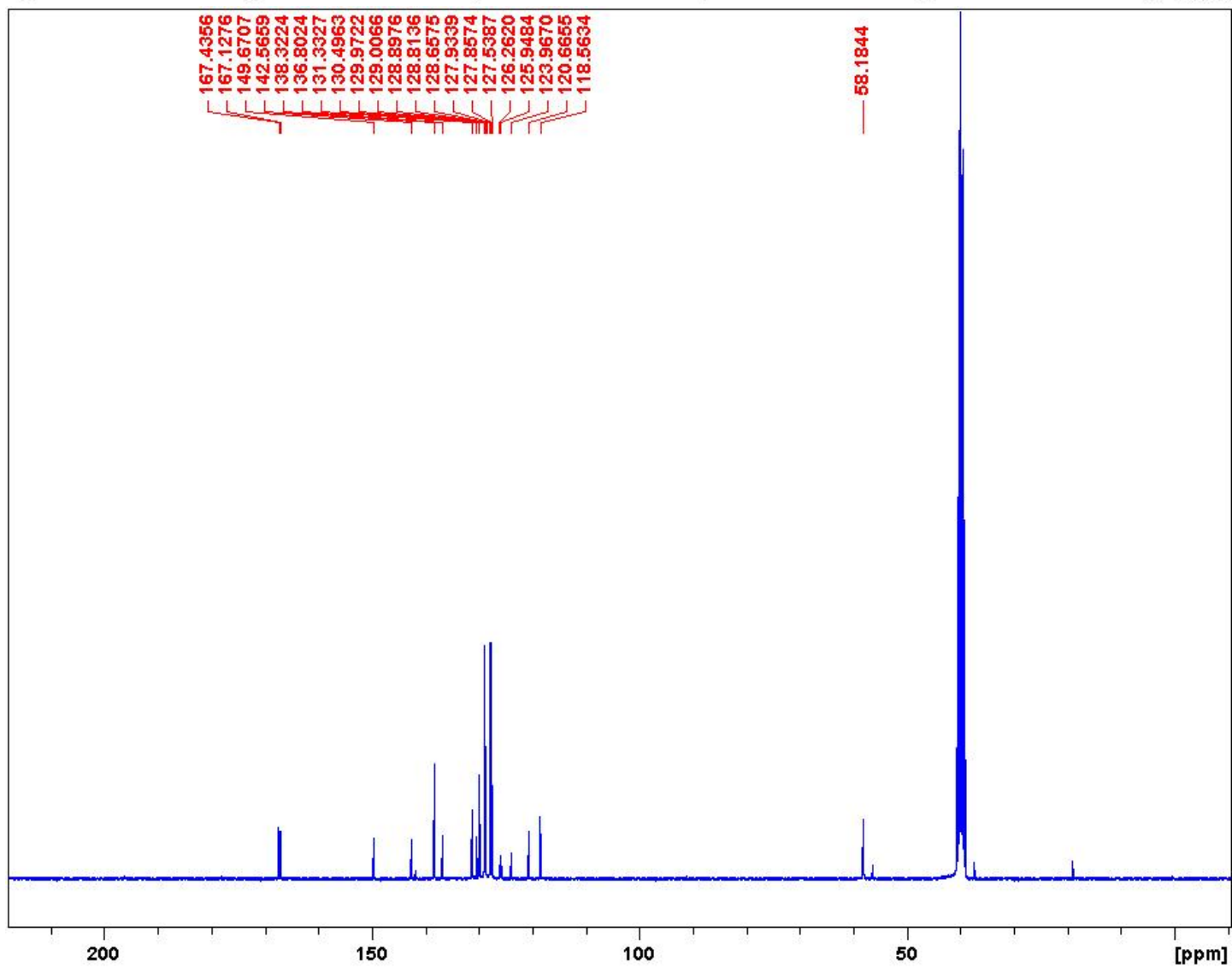
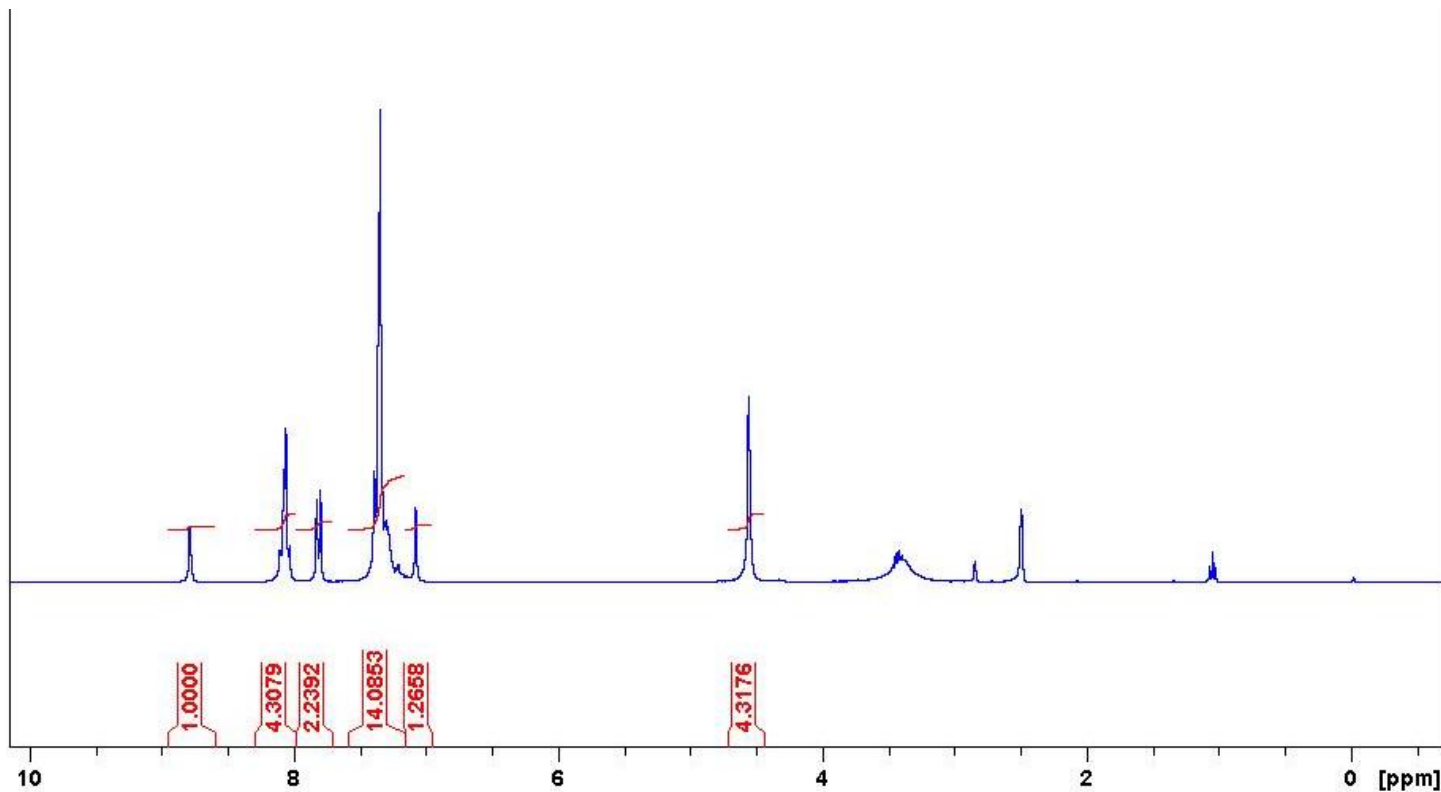
Yellow solid (464 mg, 90%). (¹H NMR, 300 MHz (DMSO-d₆): δ 9.04 (s, 1H), 8.10-8.07 (m, 4H), 7.87 (d, J = 8.0 Hz, 2H), 7.47-7.35 (m, 9H), 7.30 (t, J = 7.9 Hz, 1H), 7.21 (d, J = 7.1 Hz, 2H), 6.91 (t, J = 7.2 Hz, 1H), 5.30 (s, 2H); ¹³C NMR (75MHz, DMSO-d₆) δ = 168.0, 167.7, 150.3, 147.7, 142.0, 136.5, 136.1, 132.5, 131.2, 130.0, 129.5, 129.3, 127.9, 127.5, 126.8, 126.6, 125.8, 120.5, 120.0, 118.4, 114.7, 48.9.

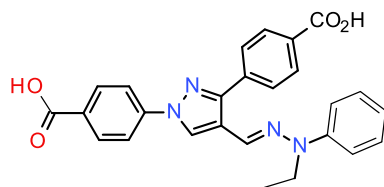




4-[1-(4-carboxyphenyl)-4-[(E)-(dibenzylhydrazono)methyl]pyrazol-3-yl]benzoic acid (11)

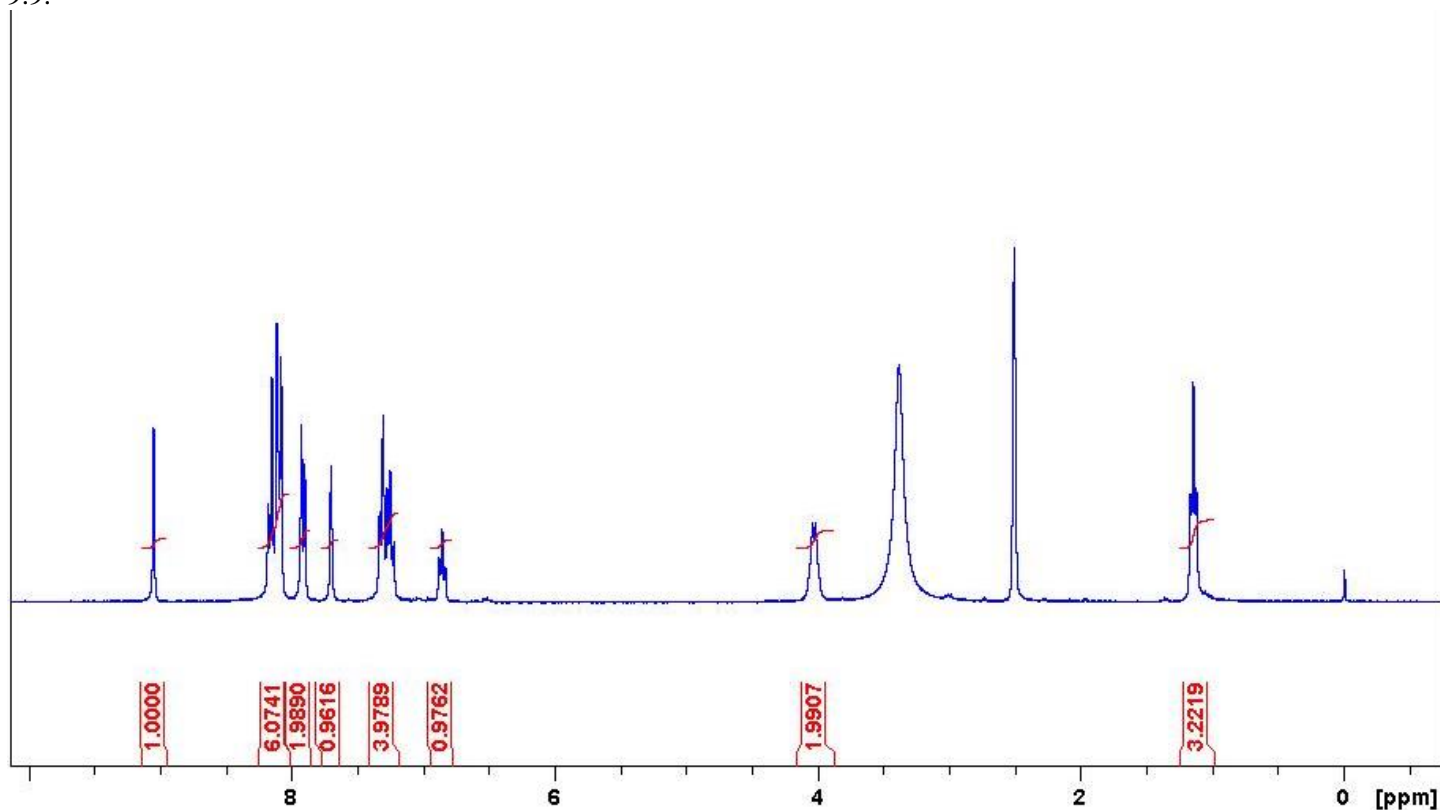
Yellow solid (487 mg, 92%). ¹H NMR, 300 MHz (DMSO-d₆): 8.79 (s, 1H), 8.11-8.03 (m, 4H), 7.82 (d, J = 8.1 Hz, 2H), 7.39-7.21 (m, 12H), 7.08 (s, 1H), 4.56 (s, 4H); ¹³C NMR (75 MHz DMSO-d₆): 167.4, 167.1, 149.6, 142.5, 138.3, 136.8, 131.3, 130.4, 129.9, 129.0, 128.6, 127.9, 127.8, 127.5, 125.9, 123.9, 120.6, 118.5, 58.1.

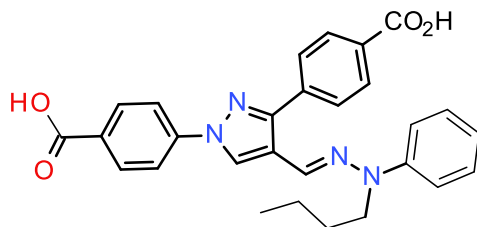
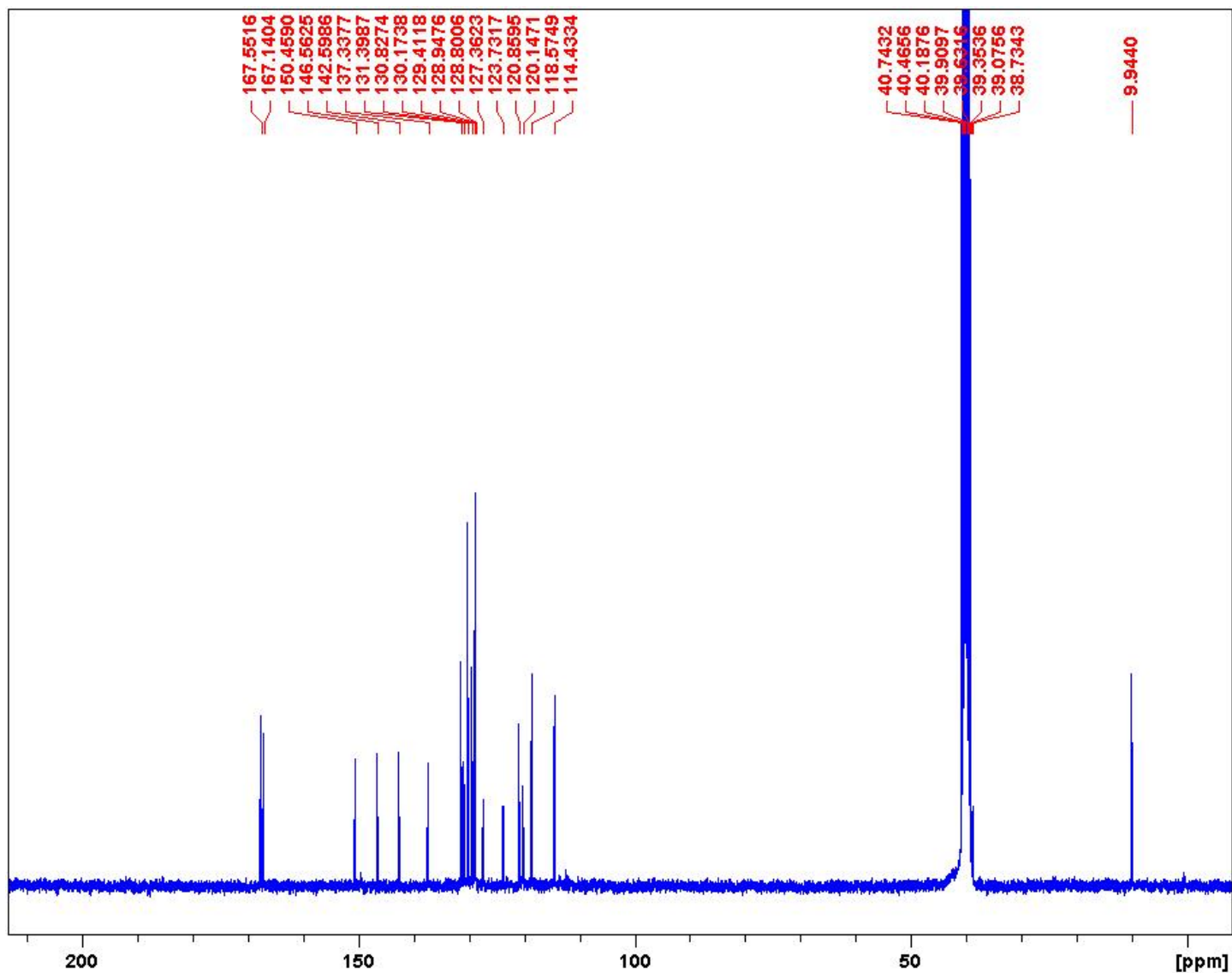




4-[1-(4-carboxyphenyl)-4-[(E)-[ethyl(phenyl)hydrazone]methyl]pyrazol-3-yl]benzoic acid (12)

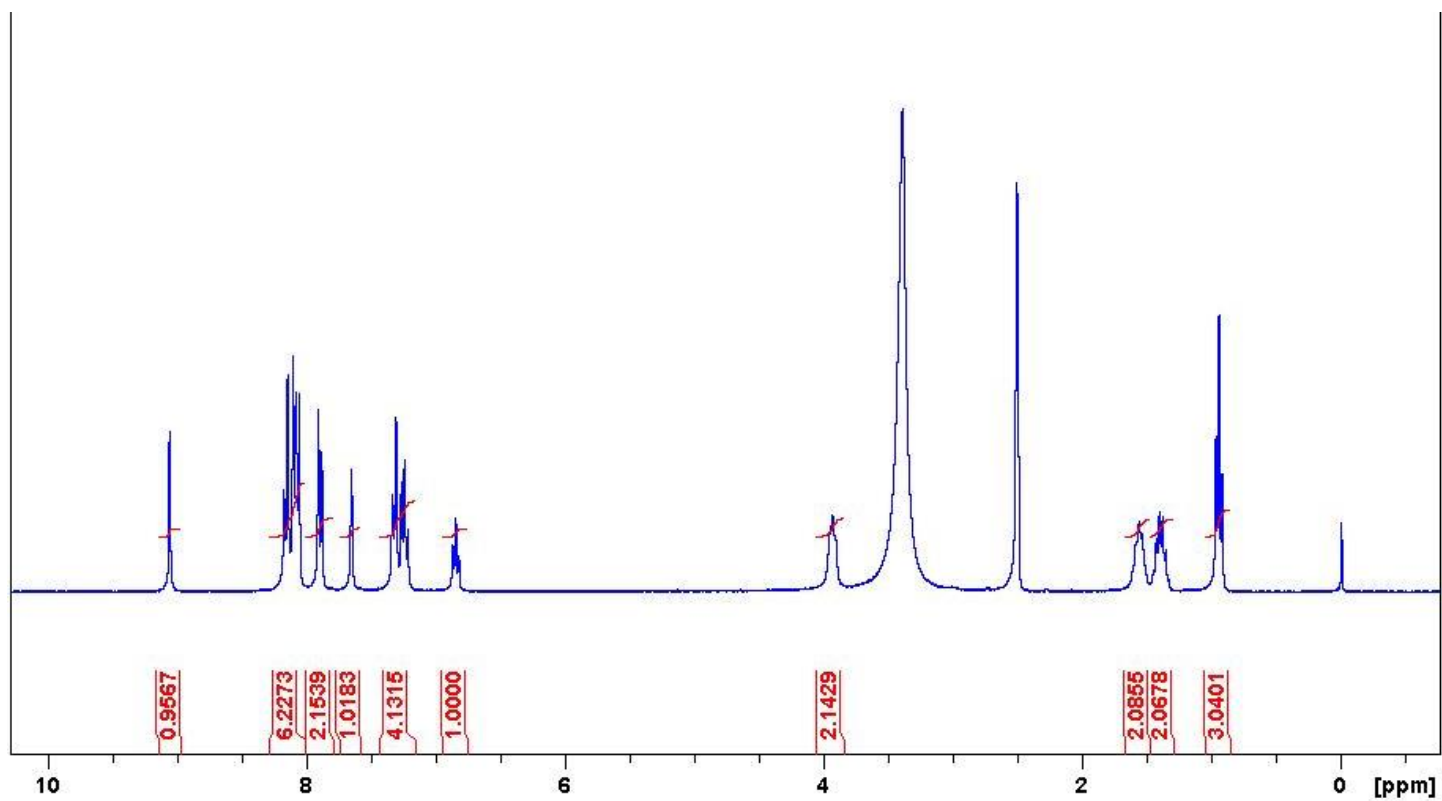
Yellow solid (399 mg, 88%). ^1H NMR, 300 MHz (DMSO- d_6): 9.04 (s, 1H), 8.17-8.07 (m, 6H), 7.91 (m, 2H), 7.69 (s, 1H), 7.32-7.21 (m, 4H), 6.85 (t, 1H), 4.02 (q, $J = 6.5$ Hz, 2H), 1.13 (t, $J = 6.6$ Hz, 3H); ^{13}C NMR (75 MHz DMSO- d_6): 167.5, 167.1, 150.4, 146.5, 142.5, 137.3, 131.3, 130.8, 130.1, 129.4, 128.9, 128.8, 127.3, 123.7, 120.8, 120.1, 118.5, 114.4, 38.7, 9.9.

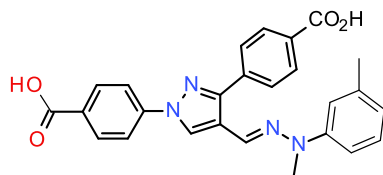
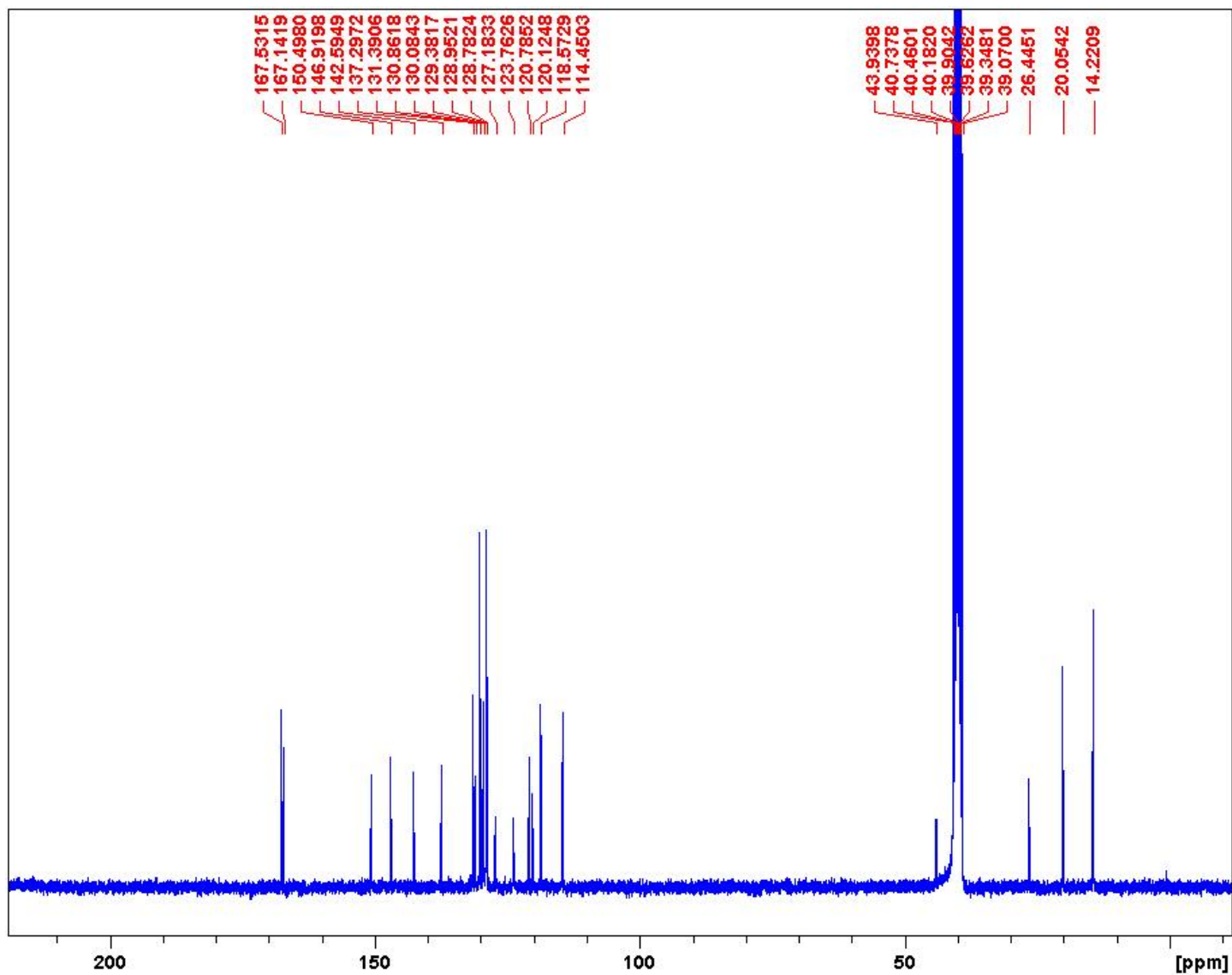




4-[4-[(E)-[butyl(phenyl)hydrazono]methyl]-1-(4-carboxyphenyl)pyrazol-3-yl]benzoic acid (13)

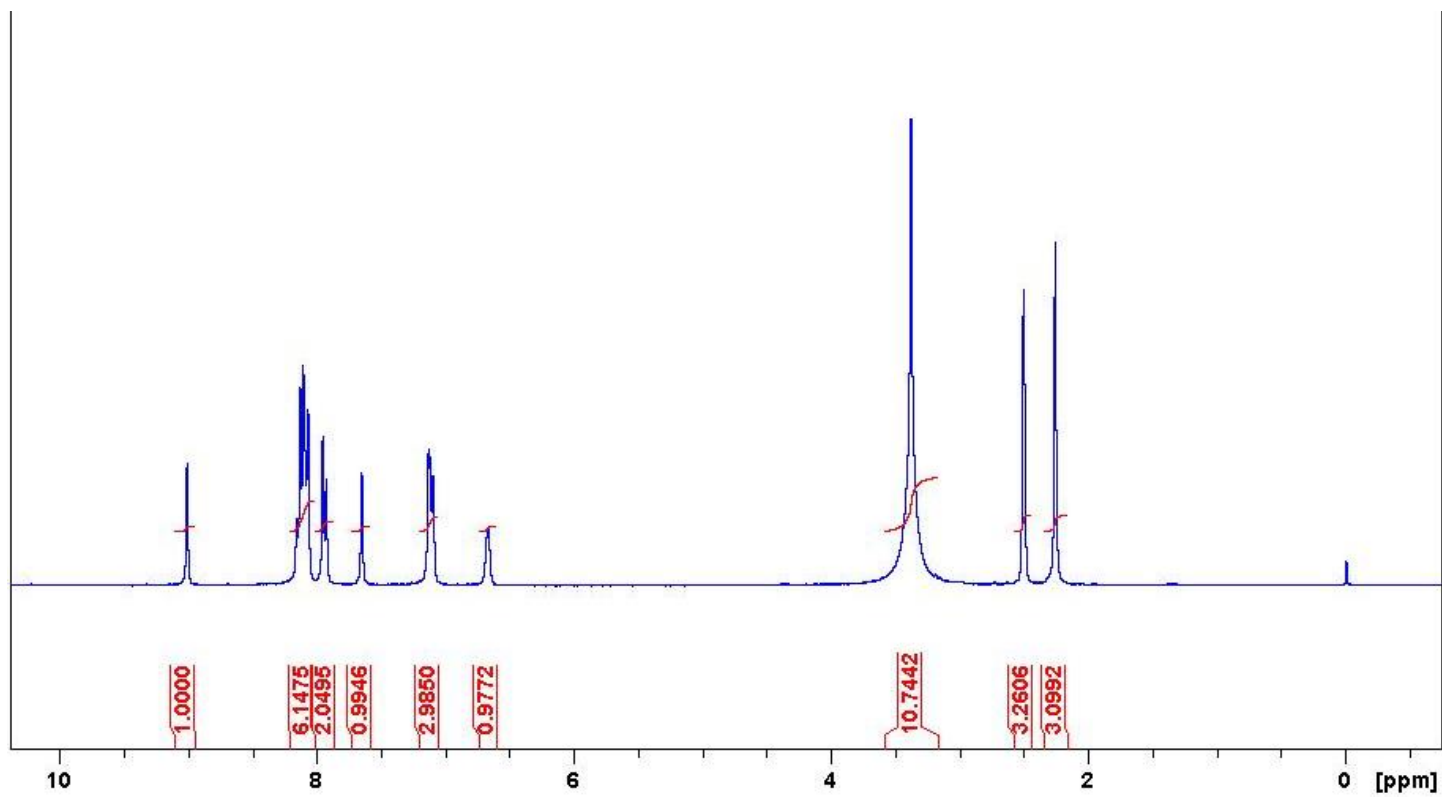
Yellow solid (428 mg, 89%). ¹H NMR, 300 MHz (DMSO-d₆): 9.06 (s, 1H), 8.17-8.05 (m, 6H), 7.89 (d, J = 8.2 Hz, 2H), 7.65 (s, 1H), 7.33-7.21 (m, 4H), 6.84 (t, J = 6.9 Hz, 1H), 3.92 (s, 2H), 1.55-1.53 (m, 2H), 1.42-1.34 (m, 2H), 0.93 (t, J = 7.1 Hz, 3H); ¹³C NMR (75 MHz DMSO-d₆): 167.5, 167.1, 150.4, 146.9, 142.5, 137.2, 131.3, 130.8, 130.0, 129.3, 128.9, 128.7, 127.1, 123.7, 120.7, 120.1, 118.5, 114.4, 43.9, 26.4, 20.0, 14.2.

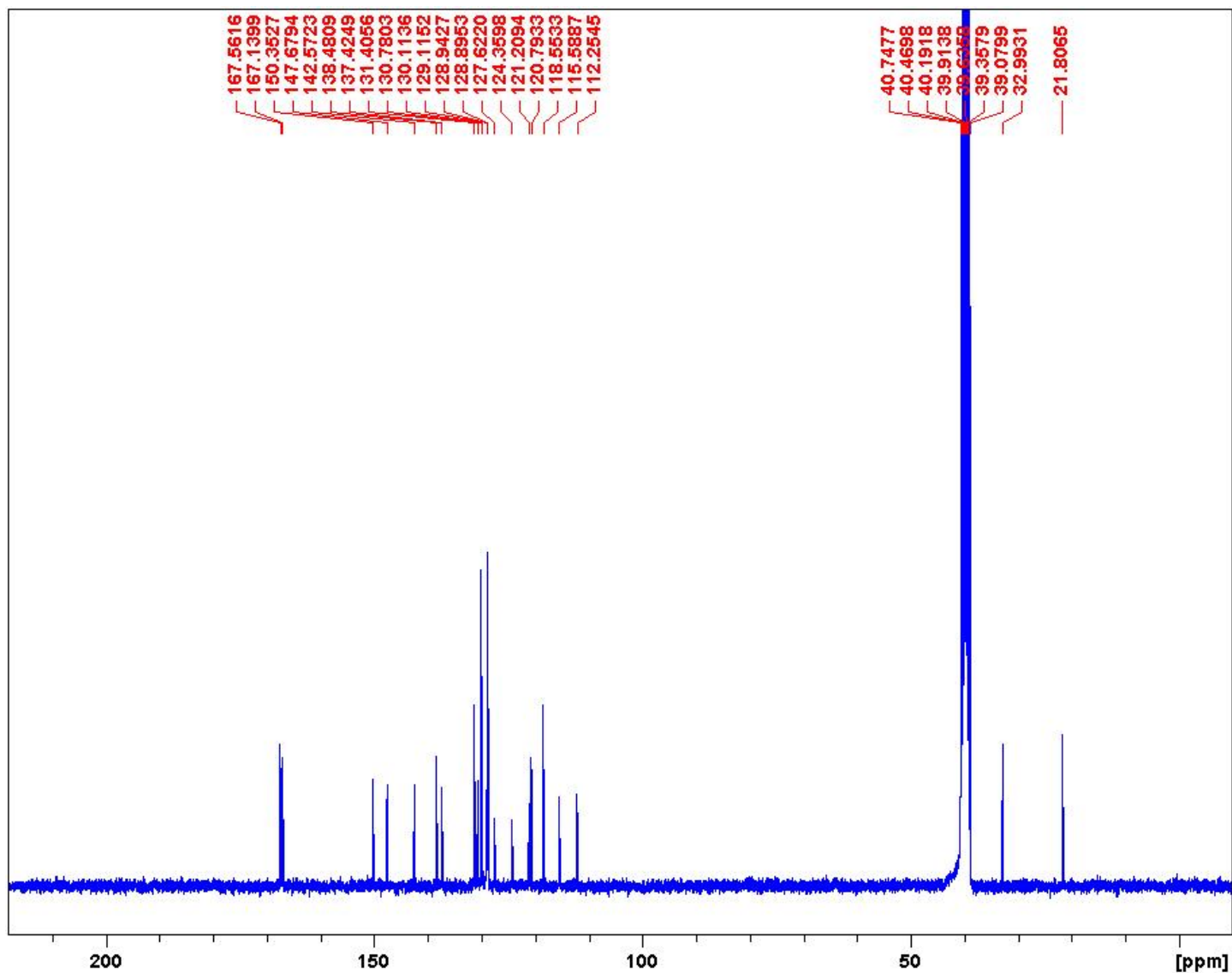




4-[1-(4-carboxyphenyl)-4-[(E)-[methyl(m-tolyl)hydrazono]methyl]pyrazol-3-yl]benzoic acid (14)

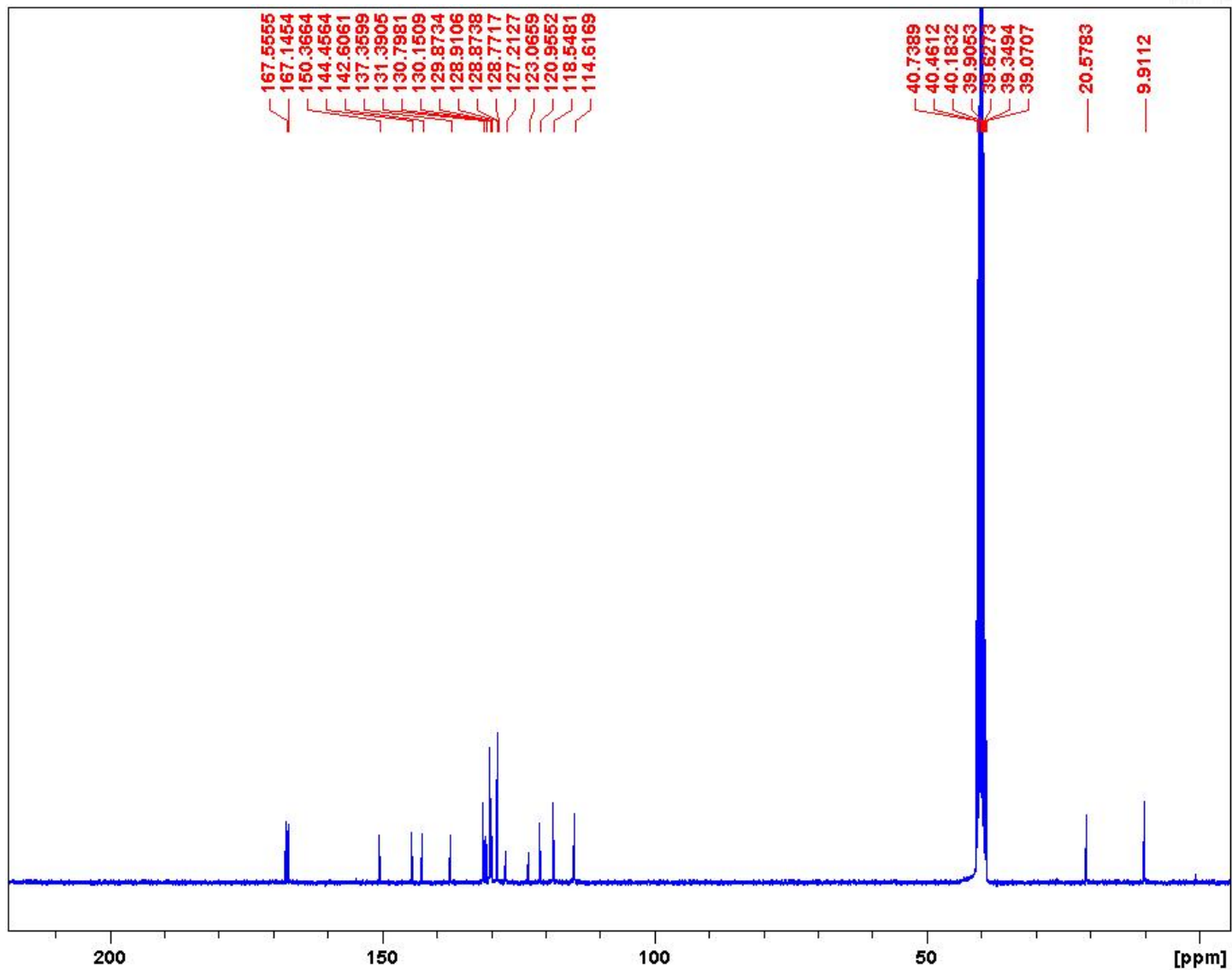
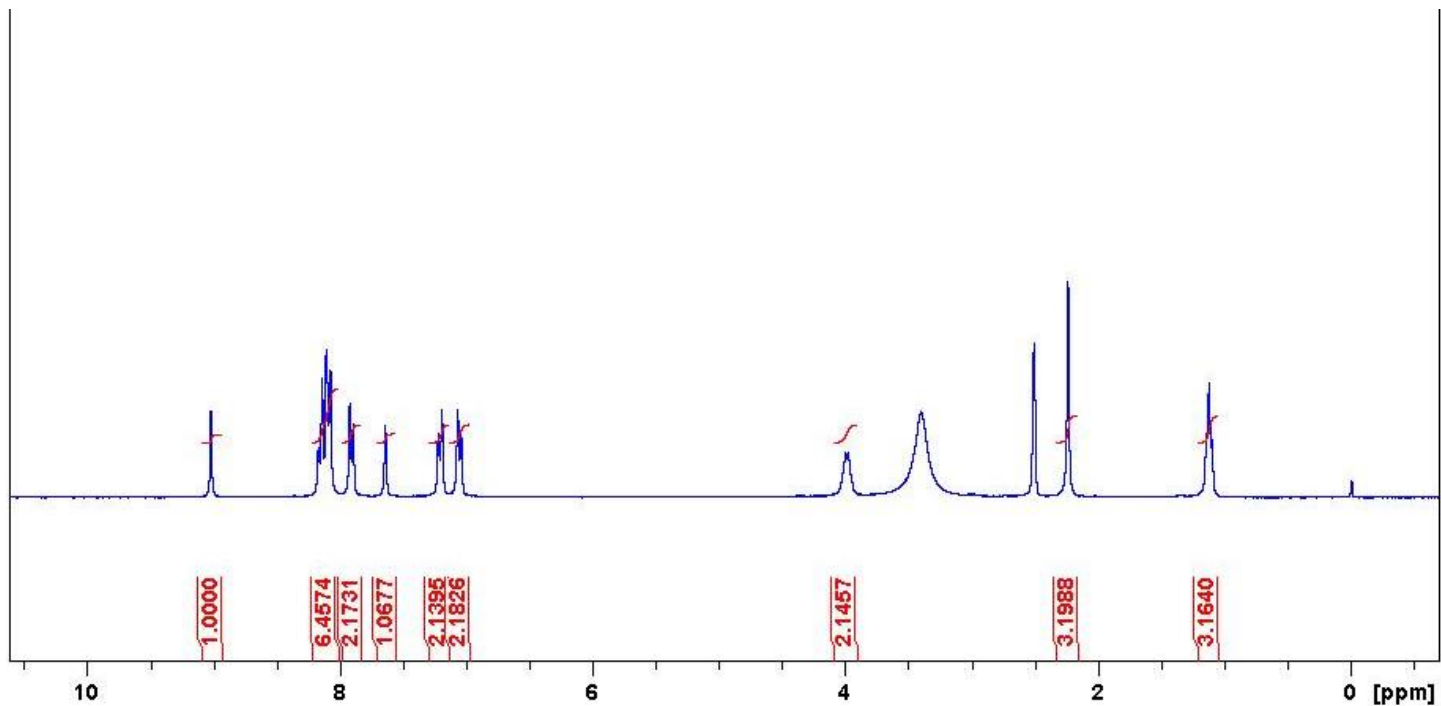
Yellow solid (408 mg, 90%). ¹H NMR (300 MHz DMSO-d₆): δ 9.00 (s, 1H), 8.15-8.06 (m, 6H), 7.94 (d, J = 8.1 Hz, 2H), 7.64 (s, 1H), 7.13-7.09 (m, 3H), 6.66 (s, 1H), 3.37 (s, 3H), 2.25 (s, 3H); ¹³C NMR (75MHz, DMSO-d₆) δ = 167.5, 167.1, 150.3, 147.6, 142.5, 138.4, 137.4, 131.4, 130.7, 130.1, 129.1, 128.9, 128.8, 127.6, 124.3, 121.2, 120.7, 118.5, 115.5, 112.2, 32.9, 21.9.

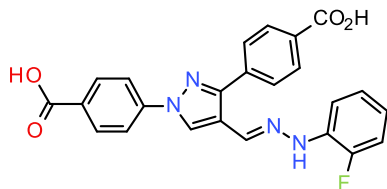




4-[1-(4-carboxyphenyl)-4-[(E)-[ethyl(p-tolyl)hydrazone]methyl]pyrazol-3-yl]benzoic acid (15)

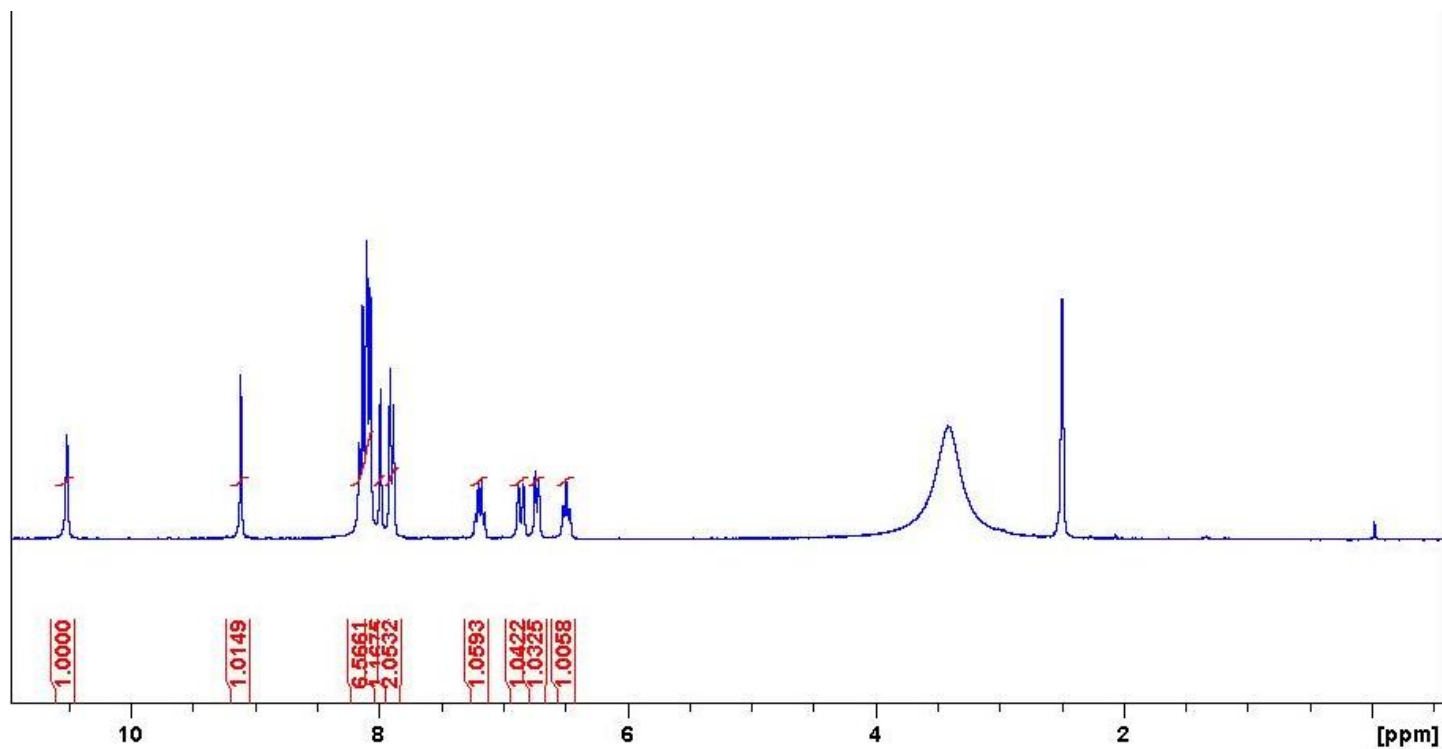
Yellow solid (411 mg, 88%). ¹H NMR, 300 MHz (DMSO-d₆): δ 9.01 (s, 1H), 8.18-8.06 (m, 6H), 7.90 (d, J = 8.1 Hz, 2H), 7.63 (s, 1H), 7.20 (d, J = 8.3 Hz, 2H), 7.05 (d, J = 8.3 Hz, 2H), 3.98 (q, J = 6.4 Hz, 2H), 2.23 (s, 3H), 1.11 (t, J = 6.3 Hz, 3H); ¹³C NMR (75MHz, DMSO-d₆) δ = 167.5, 167.1, 150.3, 144.4, 142.6, 137.3, 131.3, 130.7, 130.1, 129.8, 128.9, 128.8, 128.7, 127.2, 123.0, 120.9, 118.5, 114.6, 20.5, 9.9.

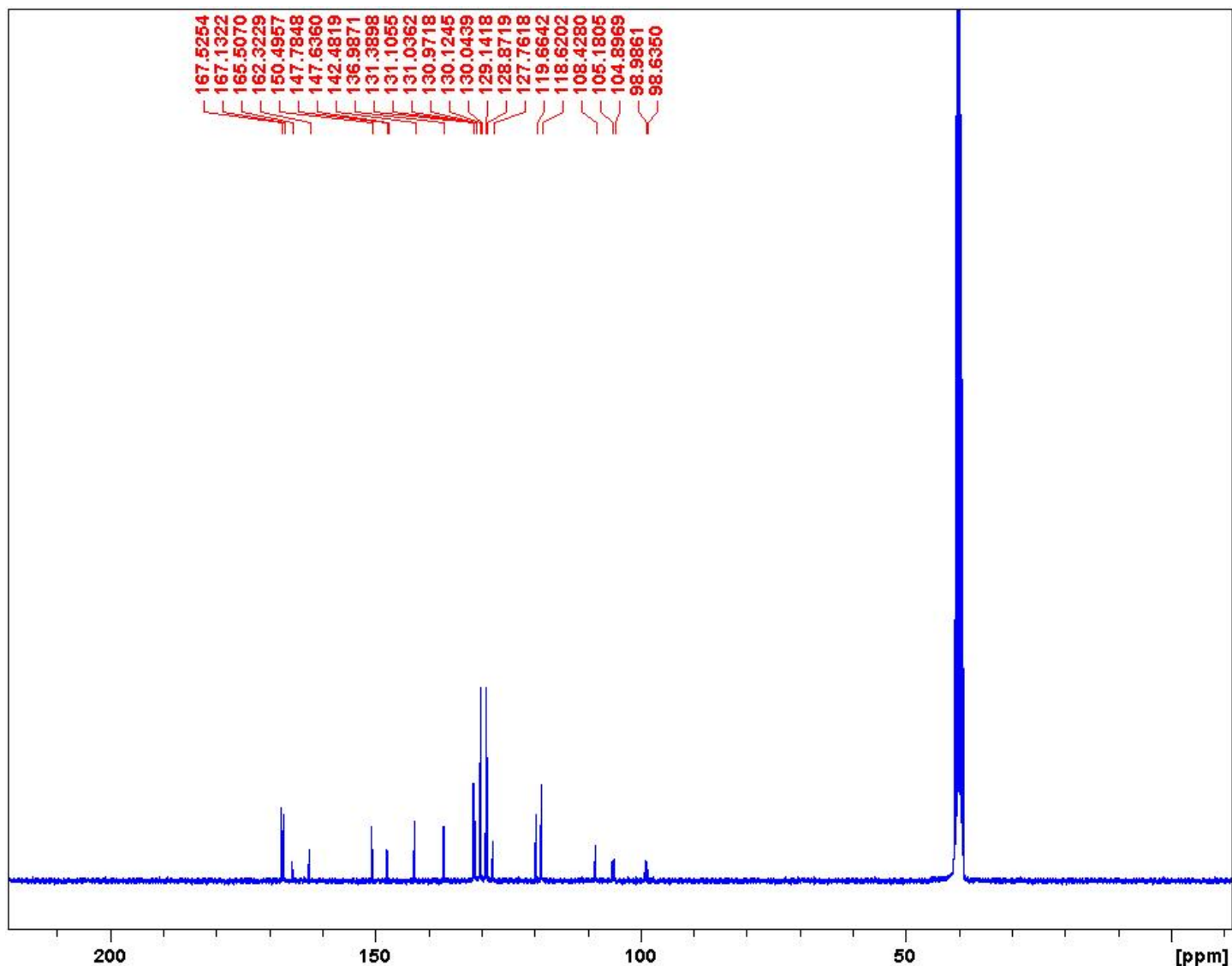




4,4'-(4-{(E)-[2-(2-fluorophenyl)hydrazinylidene]methyl}-1H-pyrazole-1,3-diyl)dibenzoic acid (16)

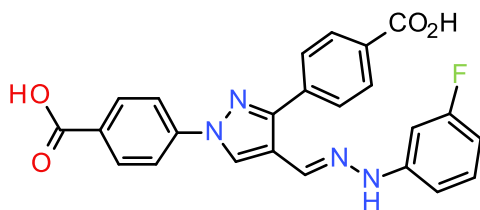
Brownish solid (346 mg, 78%). ^1H NMR, 300 MHz (DMSO- d_6): δ 10.52 (s, 1H), 9.12 (s, 1H), 8.16-8.07 (m, 6H), 7.99 (s, 1H), 7.90 (d, $J = 8.1$ Hz, 2H), 7.22-7.15 (m, 1H), 6.86 (d, $J = 11.7$ Hz, 1H), 6.73 (d, $J = 8.1$ Hz, 1H), 6.49 (t, $J = 6.7$ Hz, 1H); ^{13}C NMR (75MHz, DMSO- d_6) $\delta = 167.5, 167.1, 163.8$ ($^1J_{\text{C-F}} = 238.8$ Hz), 150.4, 147.7 ($^3J_{\text{C-F}} = 11.1$ Hz), 142.4, 136.9, 131.3, 131.03 (d, $^3J_{\text{C-F}} = 10.0$ Hz), 131.0, 130.1, 130.0, 129.1, 128.8, 127.7, 119.6, 118.6, 108.4, 104.5 ($^3J_{\text{C-F}} = 21.2$ Hz), 98.9 ($^3J_{\text{C-F}} = 26.0$ Hz).

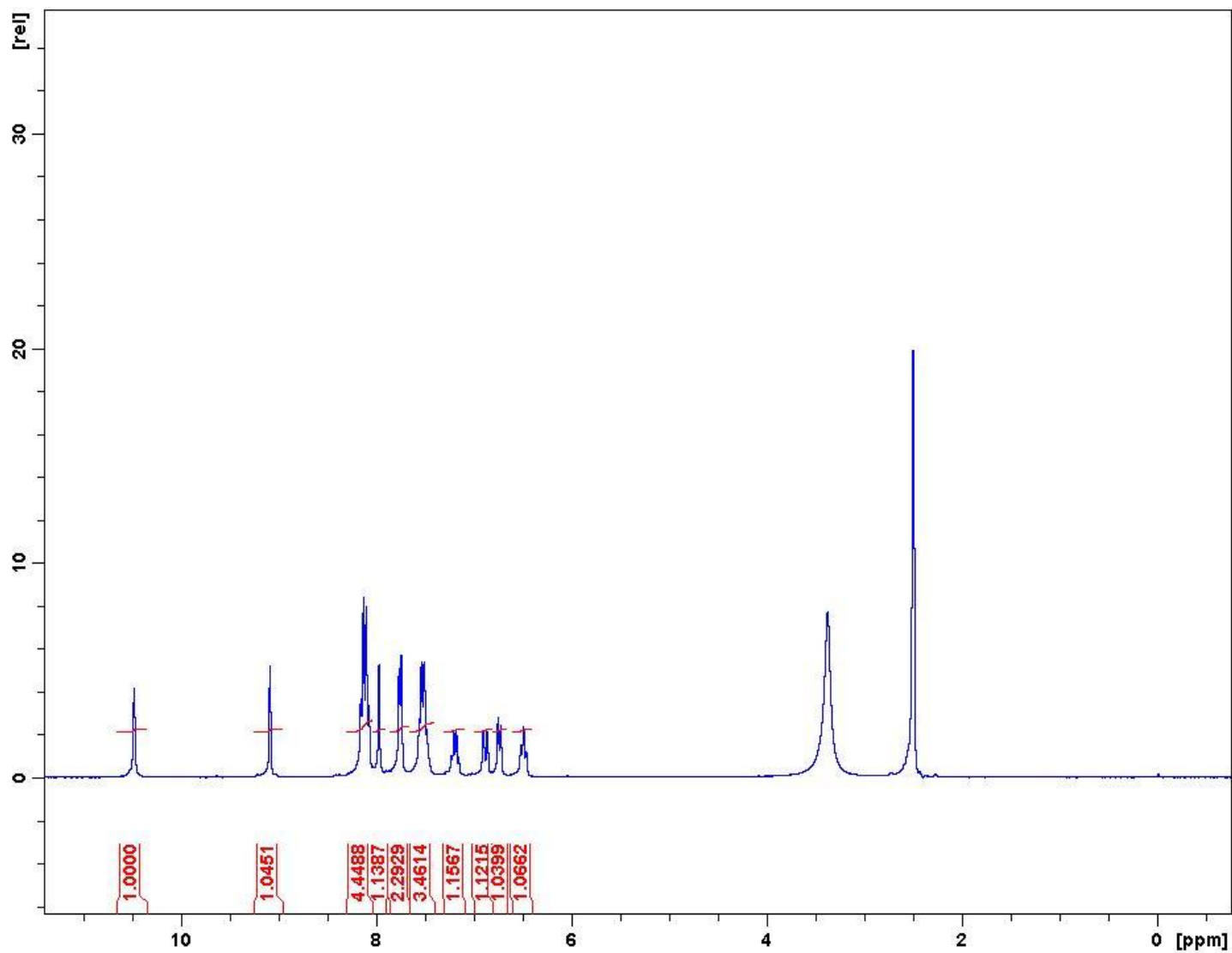


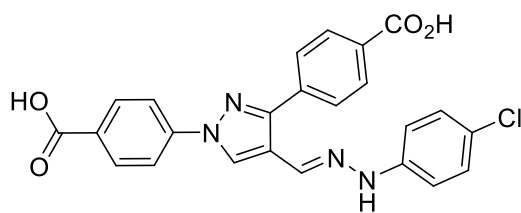
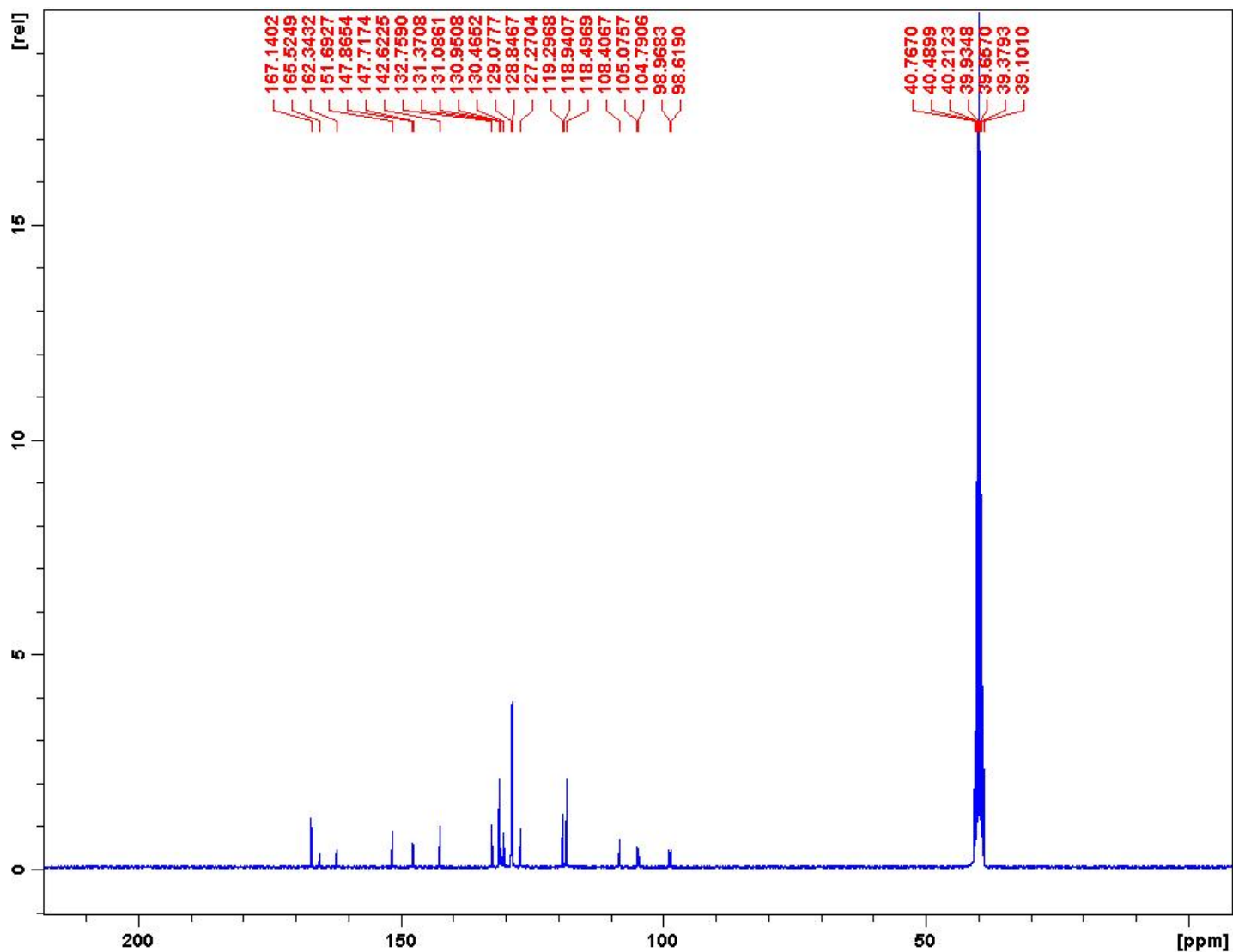


4,4'-(4-{(E)-[2-(3-fluorophenyl)hydrazinylidene]methyl}-1H-pyrazole-1,3-diyl)dibenzoic acid (17)

Brownish solid (346 mg, 78%). ¹H NMR, 300 MHz (DMSO-d₆): δ 10.47 (s, 1H), 9.08 (s, 1H), 8.15-7.90 (m, 4H), 7.97 (s, 1H), 7.75 (d, J = 7.4 Hz, 2H), 7.55-7.48 (m, 2H), 7.19 (q, J = 6.8 Hz, 1H), 6.88 (d, J = 11.7 Hz, 1H), 6.74 (d, J = 8.0 Hz, 1H), 6.49 (t, J = 8.3 Hz, 1H); ¹³C NMR (75MHz, DMSO-d₆) δ = 167.1, 163.9 (d, ¹J = 238.6 Hz), 151.6, 147.8 (d, ³J = 11.1 Hz), 142.6, 132.7, 131.3, 131.0 (d, ³J = 10.1 Hz), 130.4, 129.0, 128.8, 127.2, 119.2, 118.9, 118.4, 108.4, 105.0 (²J = 20.5), 104.7, 98.8 (d, 2J = 26.1 Hz).

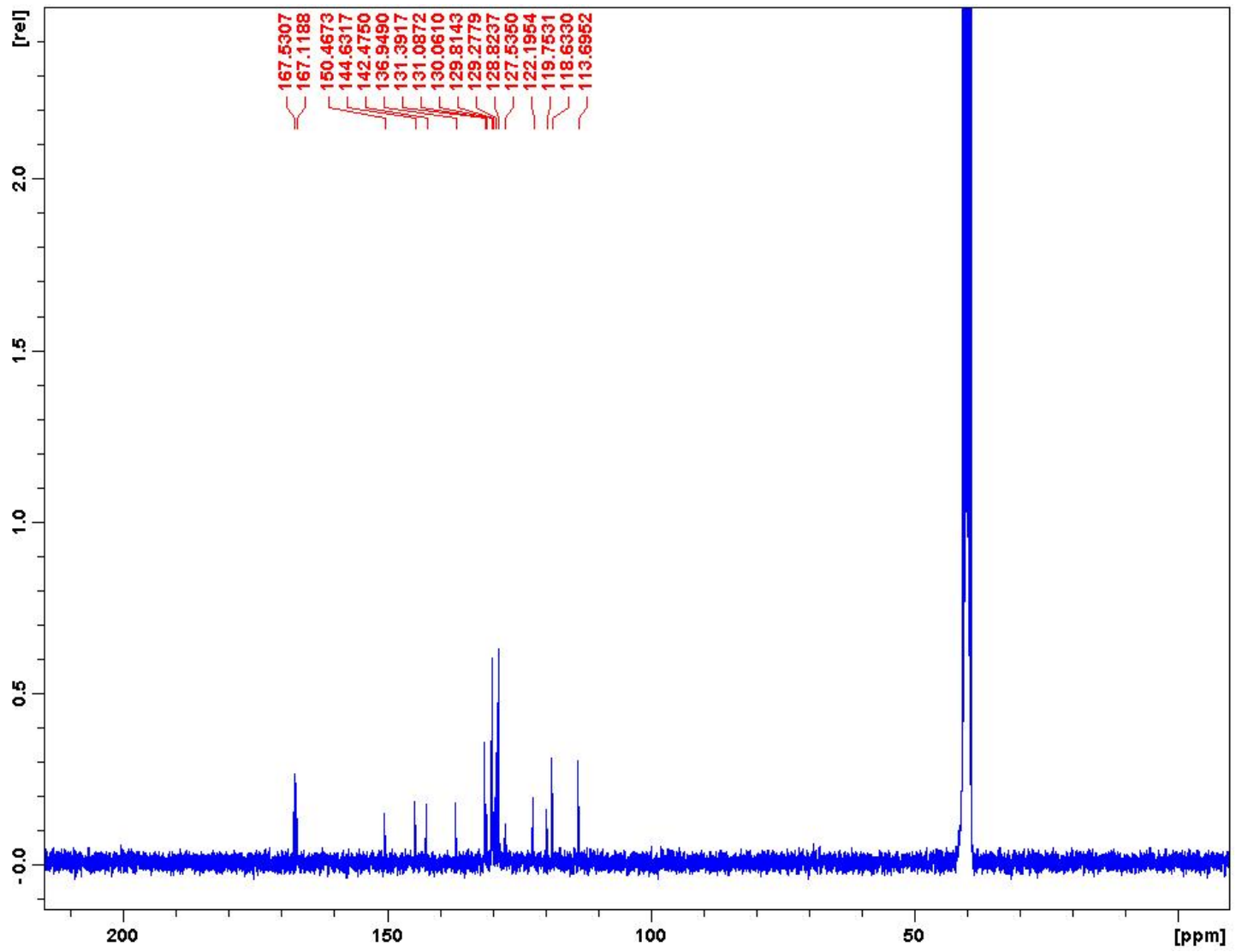
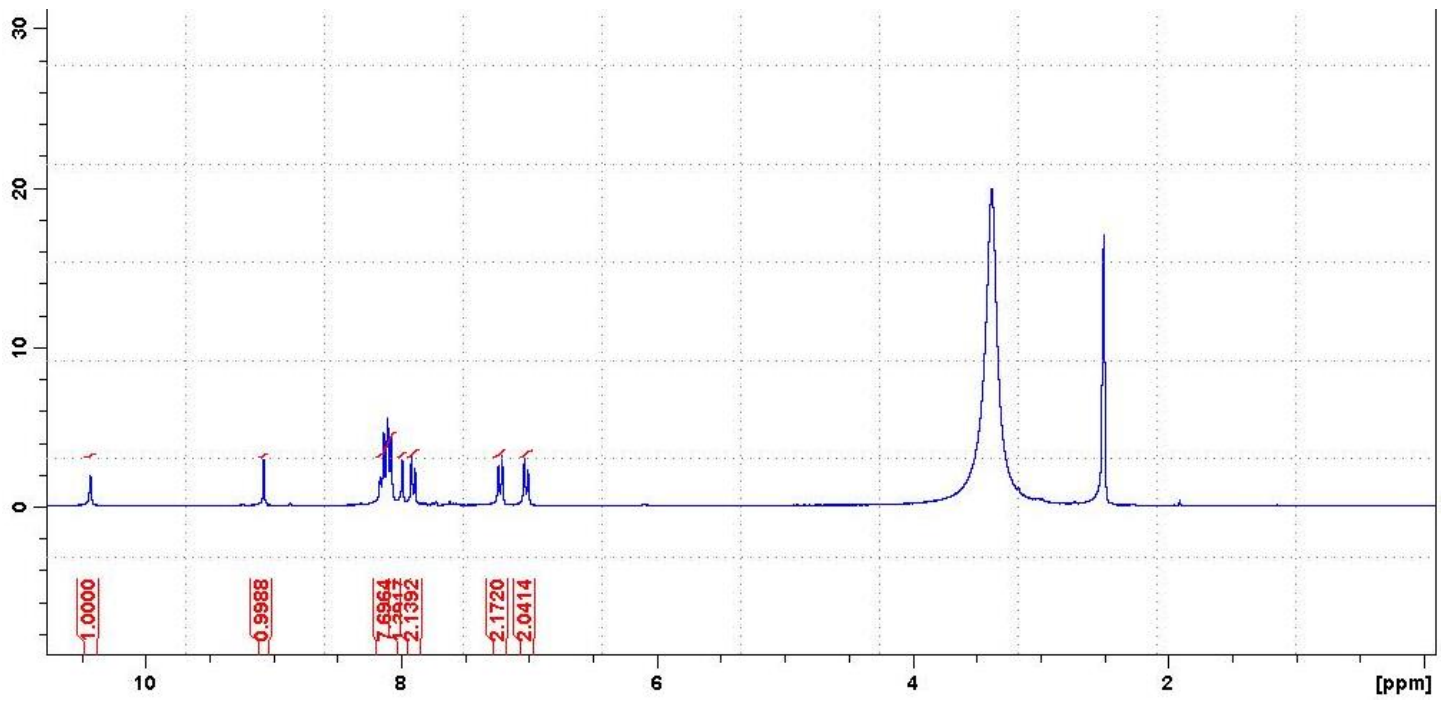


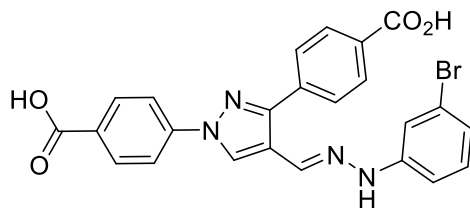




4,4'-(4-((*E*)-[2-(4-chlorophenyl)hydrazinylidene]methyl)-1*H*-pyrazole-1,3-diyl)dibenzoic acid (18)

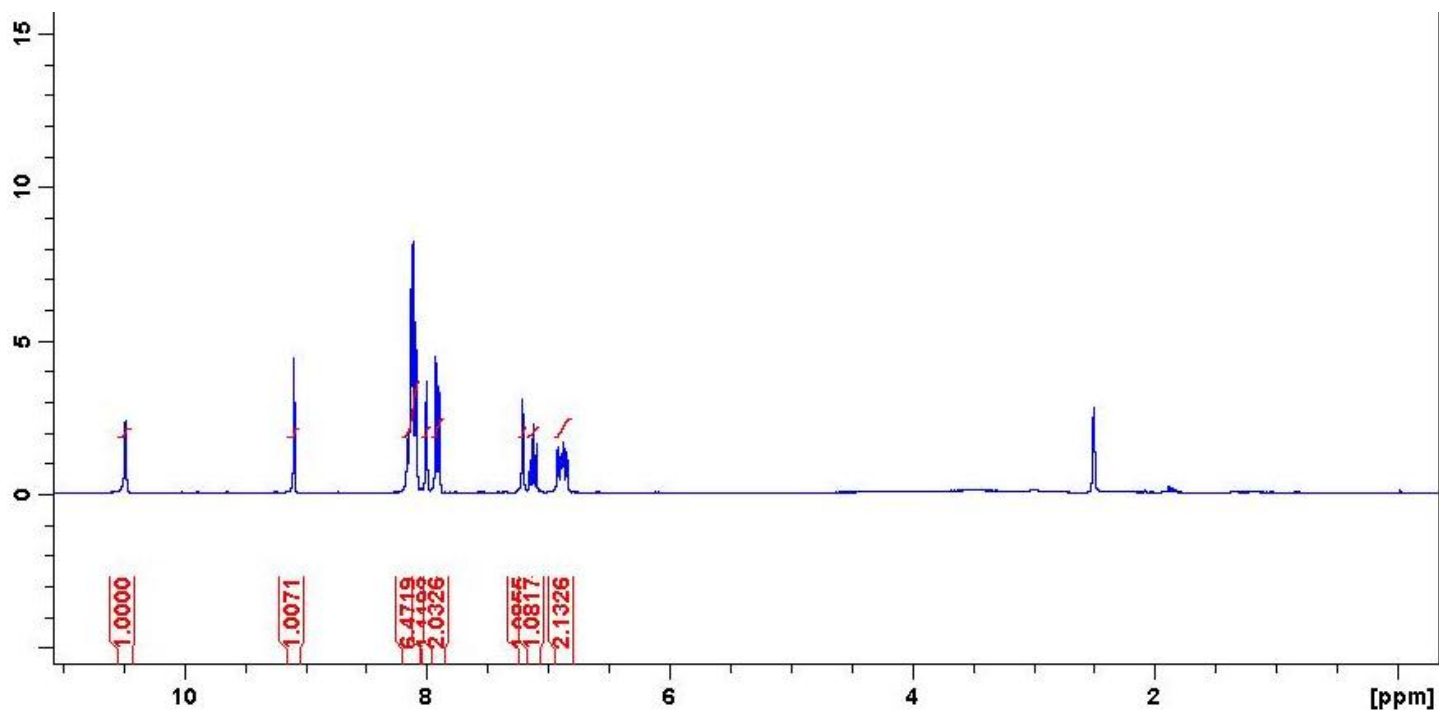
Brownish solid (349 mg, 76%). ¹H NMR, 300 MHz (DMSO-*d*₆): δ 10.42 (s, 1H), 9.07 (s, 1H), 8.16-8.07 (m, 6H), 7.98 (s, 1H), 7.90 (d, *J* = 8.2 Hz, 2H), 7.22 (d, *J* = 8.7 Hz, 2H), 7.02 (d, *J* = 8.7 Hz, 2H); ¹³C NMR (75MHz, DMSO-*d*₆) δ = 167.5, 167.1, 150.4, 144.6, 142.4, 136.9, 131.3, 131.0, 130.0, 129.8, 129.7, 128.8, 127.5, 122.1, 119.7, 118.6, 113.6.

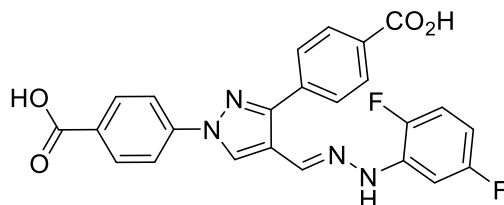
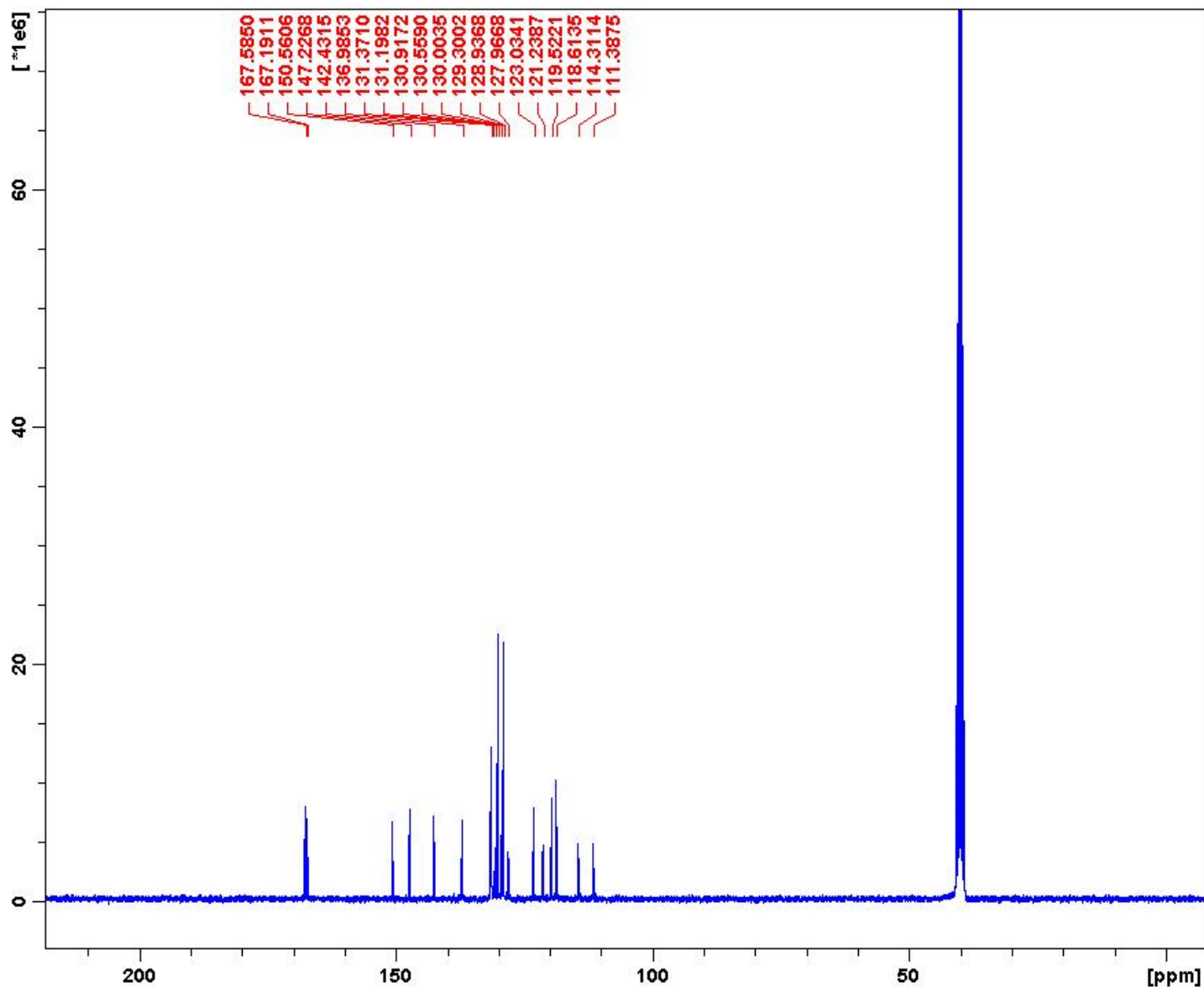




4,4'-(4-((*E*)-[2-(3-bromophenyl)hydrazinylidene]methyl)-1*H*-pyrazole-1,3-diyl)dibenzoic acid (19)

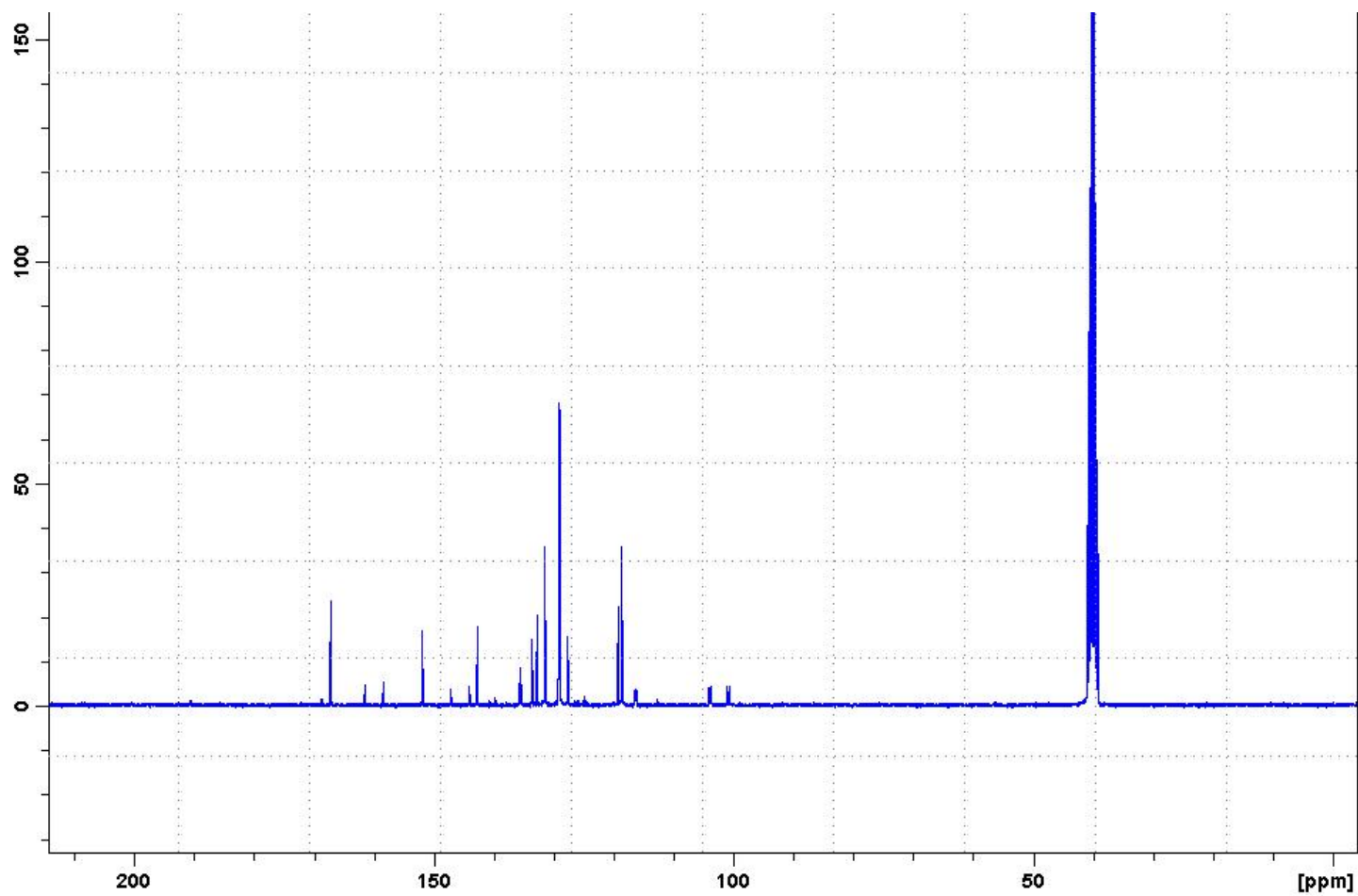
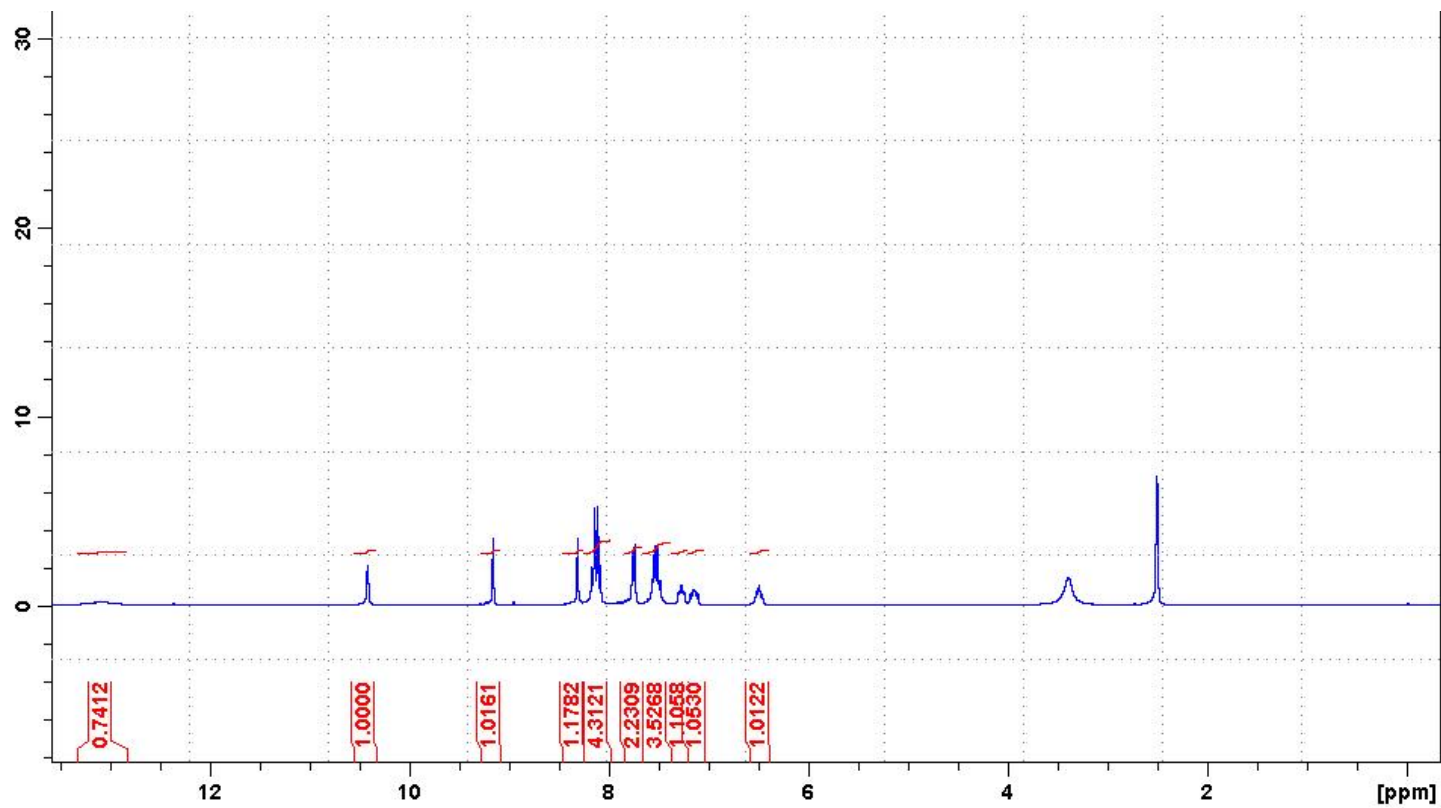
Brownish solid (388 mg, 77%). ¹H NMR, 300 MHz (DMSO-*d*₆): δ 10.47 (s, 1H), 9.22 (s, 1H), 8.15-8.08 (m, 2H), 7.99 (s, 1H), 7.91 (d, *J* = 8.3 Hz, 2H), 7.21-7.20 (m, 1H), 7.11 (t, *J* = 7.9 Hz, 1H), 6.91-6.84 (m, 2H); ¹³C NMR (75MHz, DMSO-*d*₆) δ = 167.5, 167.1, 150.5, 147.2, 142.4, 136.9, 131.3, 131.1, 130.9, 130.5, 130.0, 129.3, 128.9, 127.9, 123.0, 121.2, 119.5, 118.6, 114.3, 111.3.

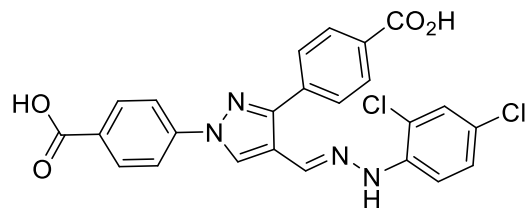




4,4'-(4-((*E*)-[2-(2,5-difluorophenyl)hydrazinylidene]methyl)-1*H*-pyrazole-1,3-diyl)dibenzoic acid (20)

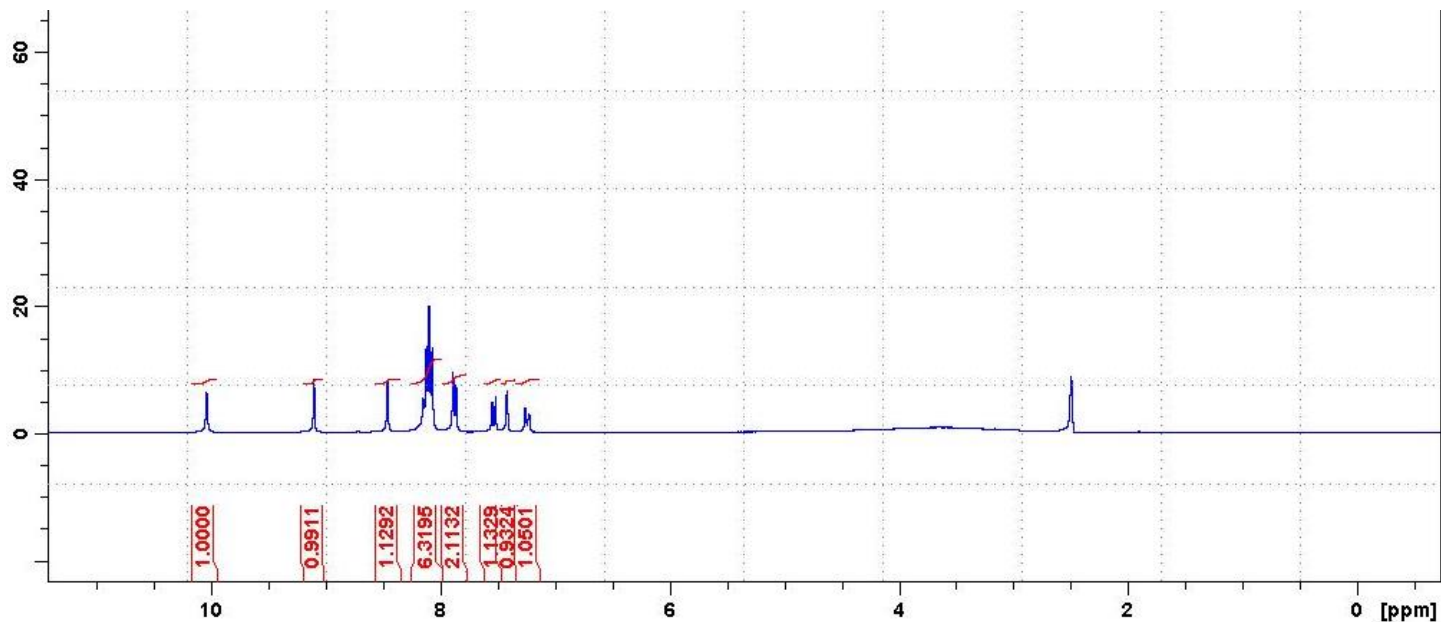
Brownish solid (337 mg, 73%). ^1H NMR, 300 MHz (DMSO- d_6): δ 10.42 (s, 1H), 9.18 (s, 1H), 8.33 (s, 1H), 8.17-8.07 (m, 6H), 7.89 (d, $J = 8.2$ Hz, 2H), 7.25-7.10 (m, 2H), 6.52-6.47 (m, 1H); ^{13}C NMR (75MHz, DMSO- d_6) $\delta = 167.5, 167.1, 160.1$ ($^1J_{\text{C-F}} = 236.4$ Hz), 150.6, 145.5 (d, $J = 234.9$ Hz), 142.4, 136.8, 135.3-135.1 (m), 133.2, 131.3, 131.1, 130.0, 129.3, 128.8, 127.9, 119.4, 118.6, 118.6-116.1 (m), 104.0 ($^{2,3}J_{\text{C-F}} = 25.0, 7.5$ Hz), 100.8 ($^2J_{\text{C-F}} = 30.4$ Hz).

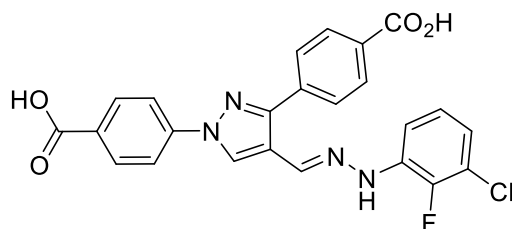
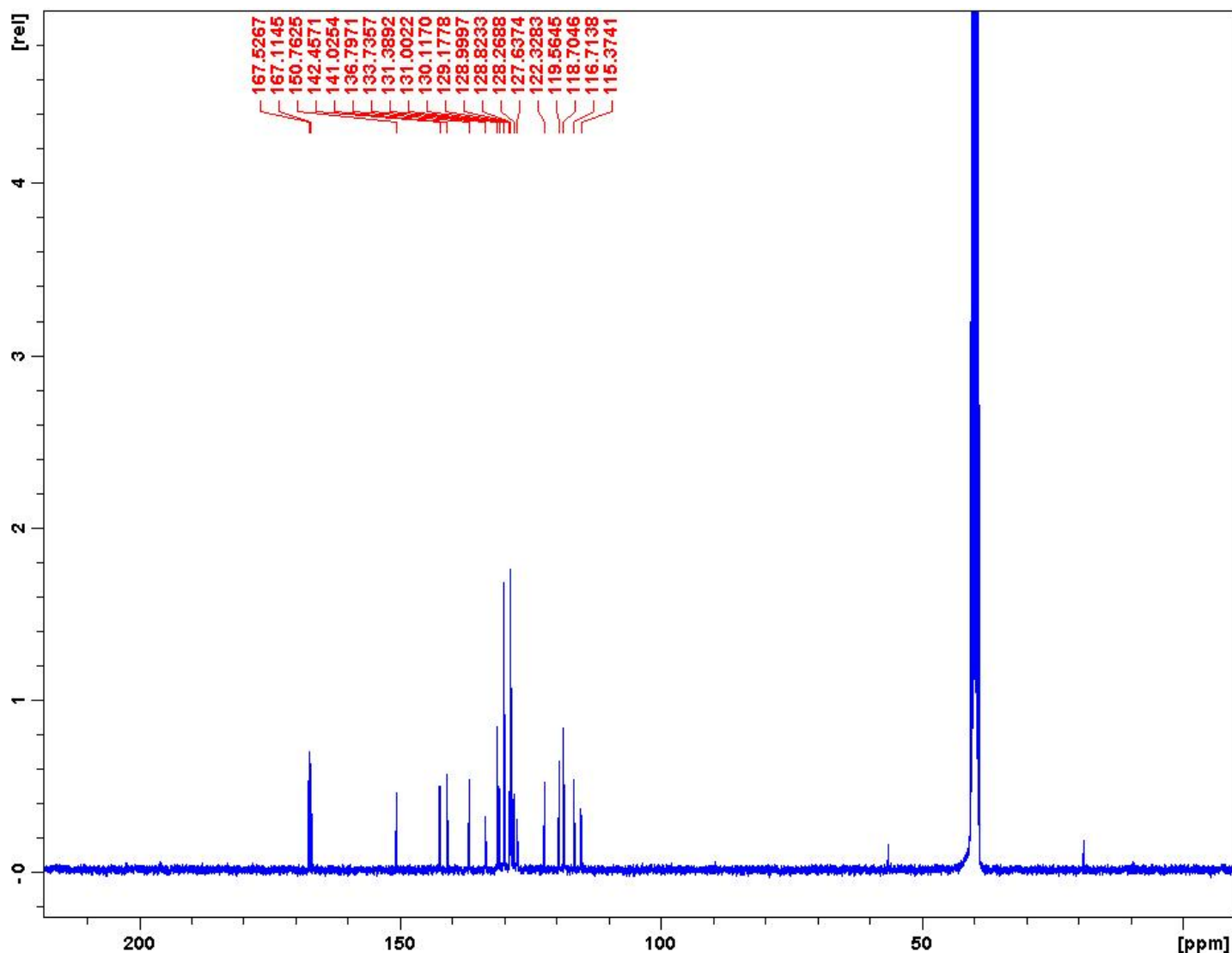




4,4'-(4-((*E*)-[2-(2,4-dichlorophenyl)hydrazinylidene]methyl)-1*H*-pyrazole-1,3-diyl)dibenzoic acid (21)

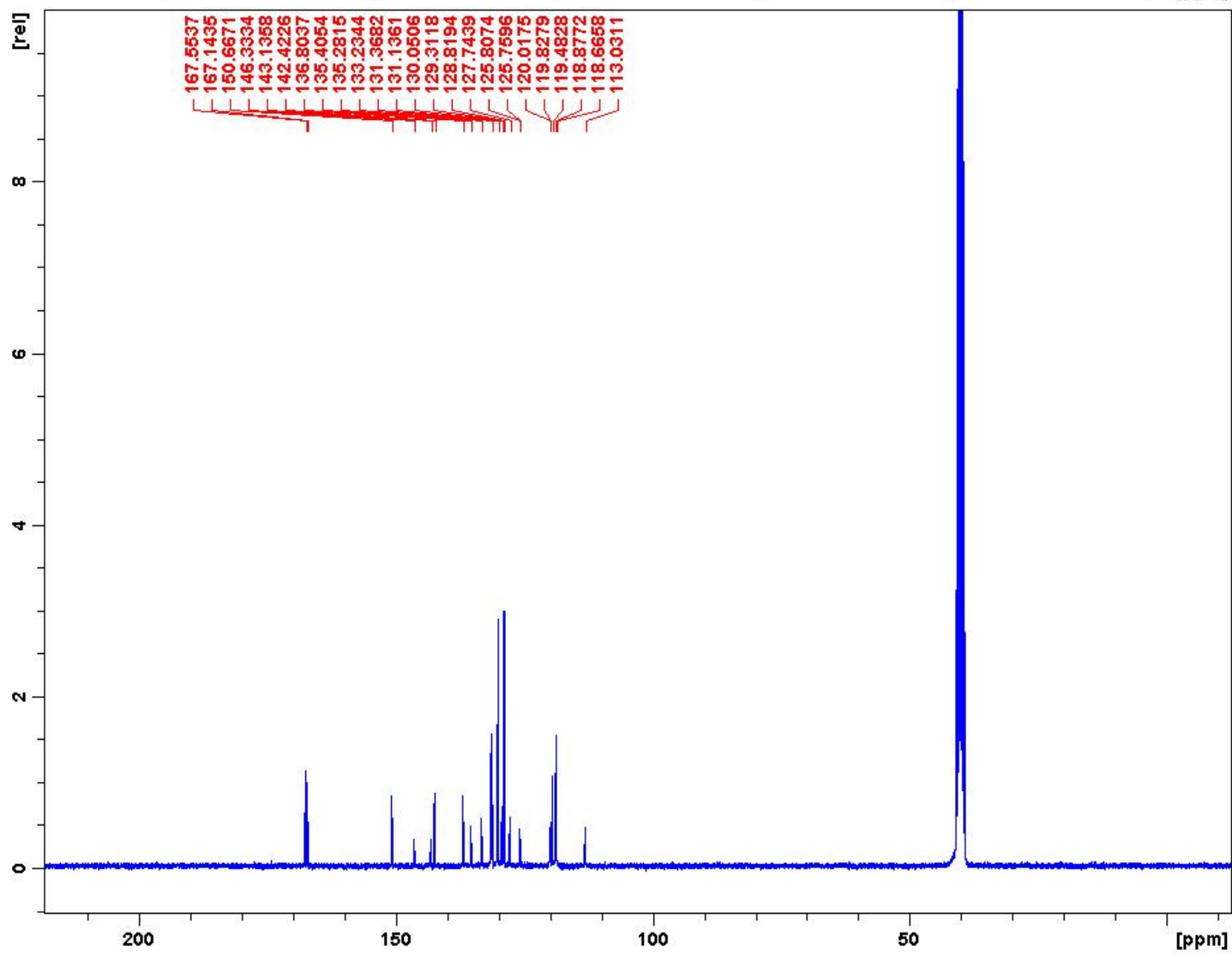
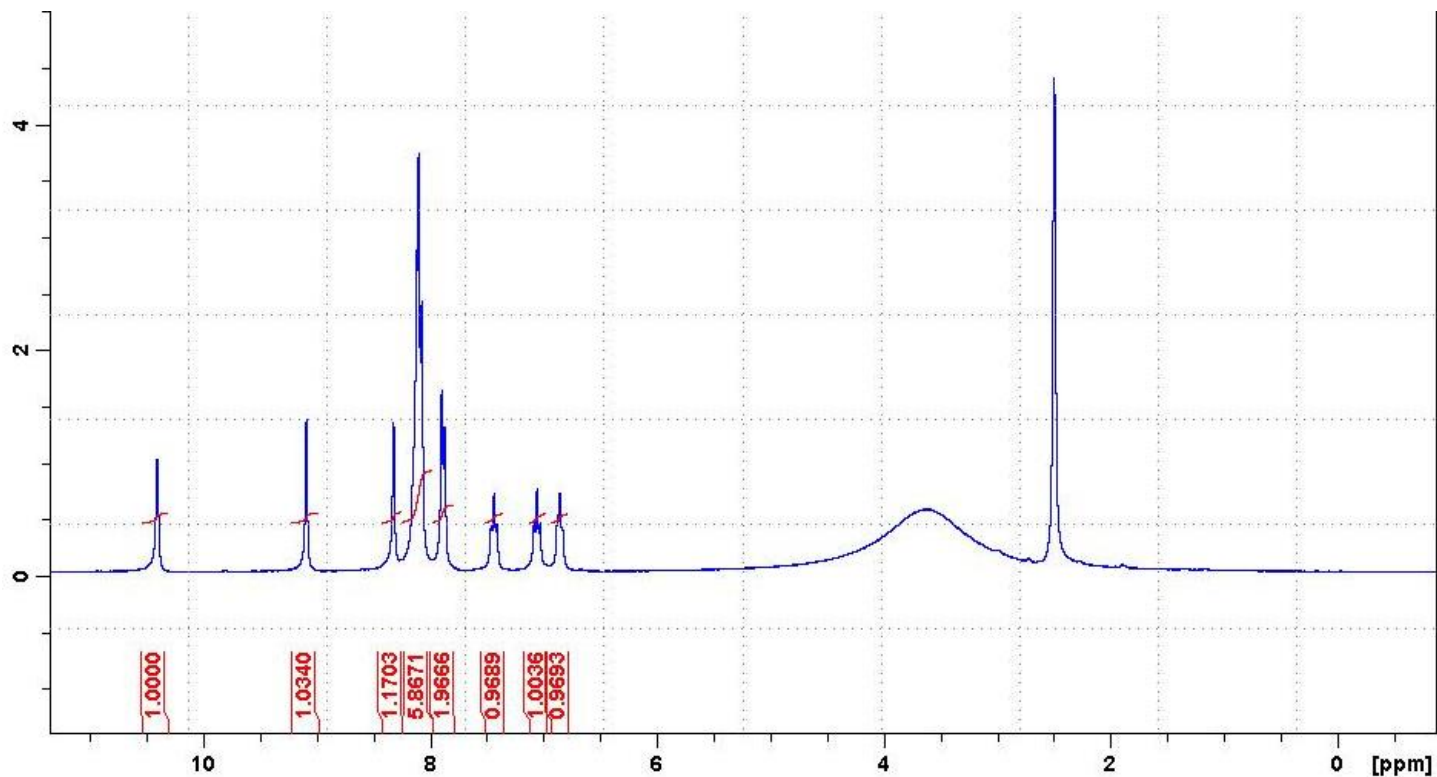
Brownish solid (376 mg, 76%). ¹H NMR, 300 MHz (DMSO-*d*₆): δ 10.04 (s, 1H), 9.11 (s, 1H), 8.47 (s, 1H), 8.16-8.08 (m, 6H), 7.88 (d, *J* = 8.1 Hz, 2H), 7.54 (d, *J* = 8.8 Hz, 1H), 7.43 (d, *J* = 2.0 Hz, 1H), 7.25 (d, *J* = 8.8 Hz, 1H); ¹³C NMR (75MHz, DMSO-*d*₆) δ = 167.5, 167.1, 150.7, 142.4, 141.0, 136.7, 133.7, 131.3, 131.1, 130.0, 129.3, 128.9, 128.7, 128.2, 127.6, 122.3, 119.5, 118.6, 116.7, 115.3.

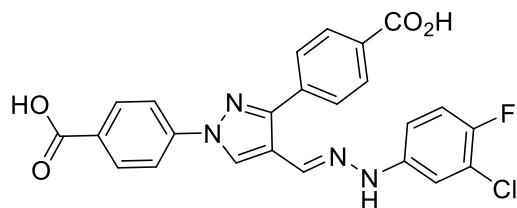




4-[1-(4-carboxyphenyl)-4-[(E)-[(3-chloro-2-fluoro-phenyl)hydrazono]methyl]pyrazol-3-yl]benzoic acid (22)

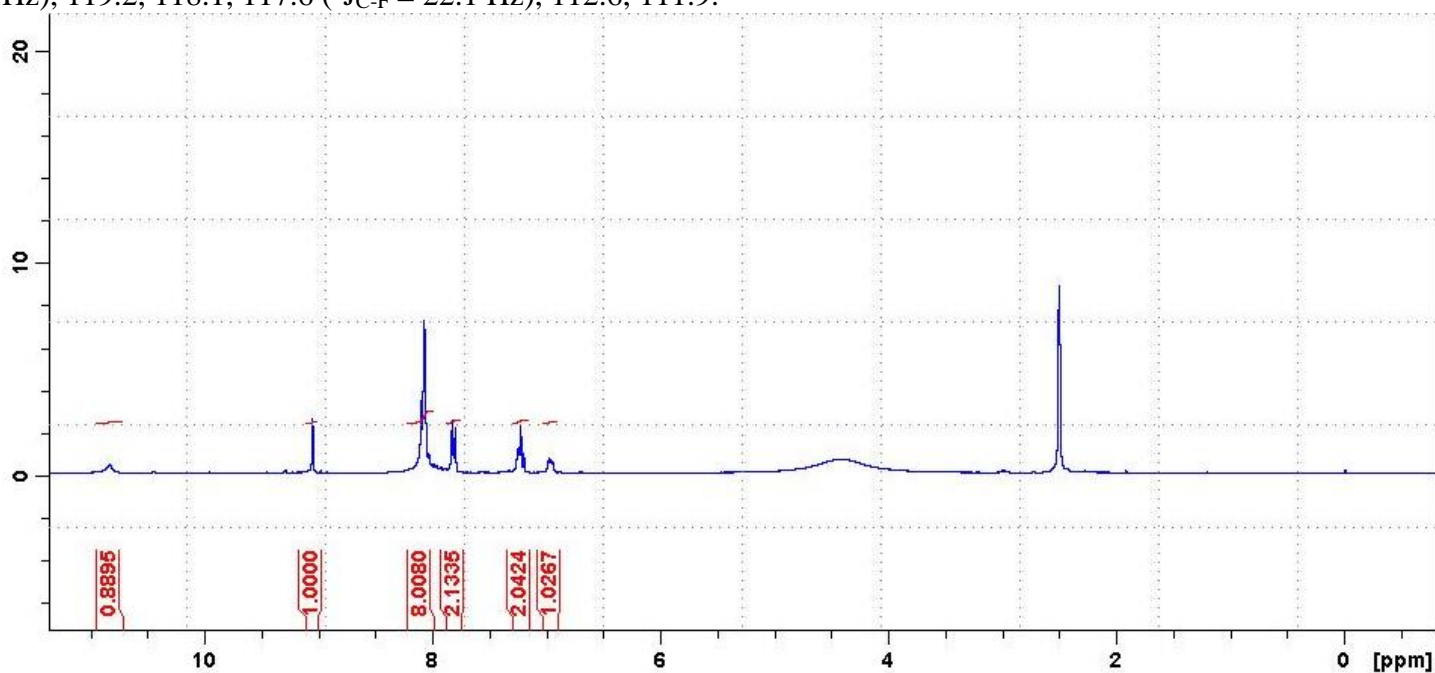
Brownish solid (358 mg, 75%). ^1H NMR, 300 MHz (DMSO- d_6): δ 10.40 (s, 1H), 9.09 (s, 1H), 8.32 (s, 1H), 8.11-8.07 (m, 6H), 7.88 (s, $J = 7.8$ Hz, 2H), 7.43 (t, $J = 7.6$ Hz, 1H), 7.05 (t, $J = 7.7$ Hz, 1H), 6.85 (t, $J = 6.4$ Hz, 1H); ^{13}C NMR (75MHz, DMSO- d_6) $\delta = 167.5, 167.1, 150.6, 144.7$ (d, $^1J = 235.8$ Hz), 142.4, 136.8, 135.3 (d, $^3J = 9.2$), 133.2, 131.3, 131.1, 130.0, 129.3, 128.8, 127.7, 125.8 (d, $J = 3.5$ Hz), 119.9 (d, $^2J = 14.2$ Hz), 119.4, 118.8, 118.6, 113.0.

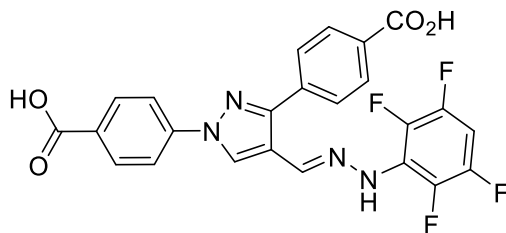
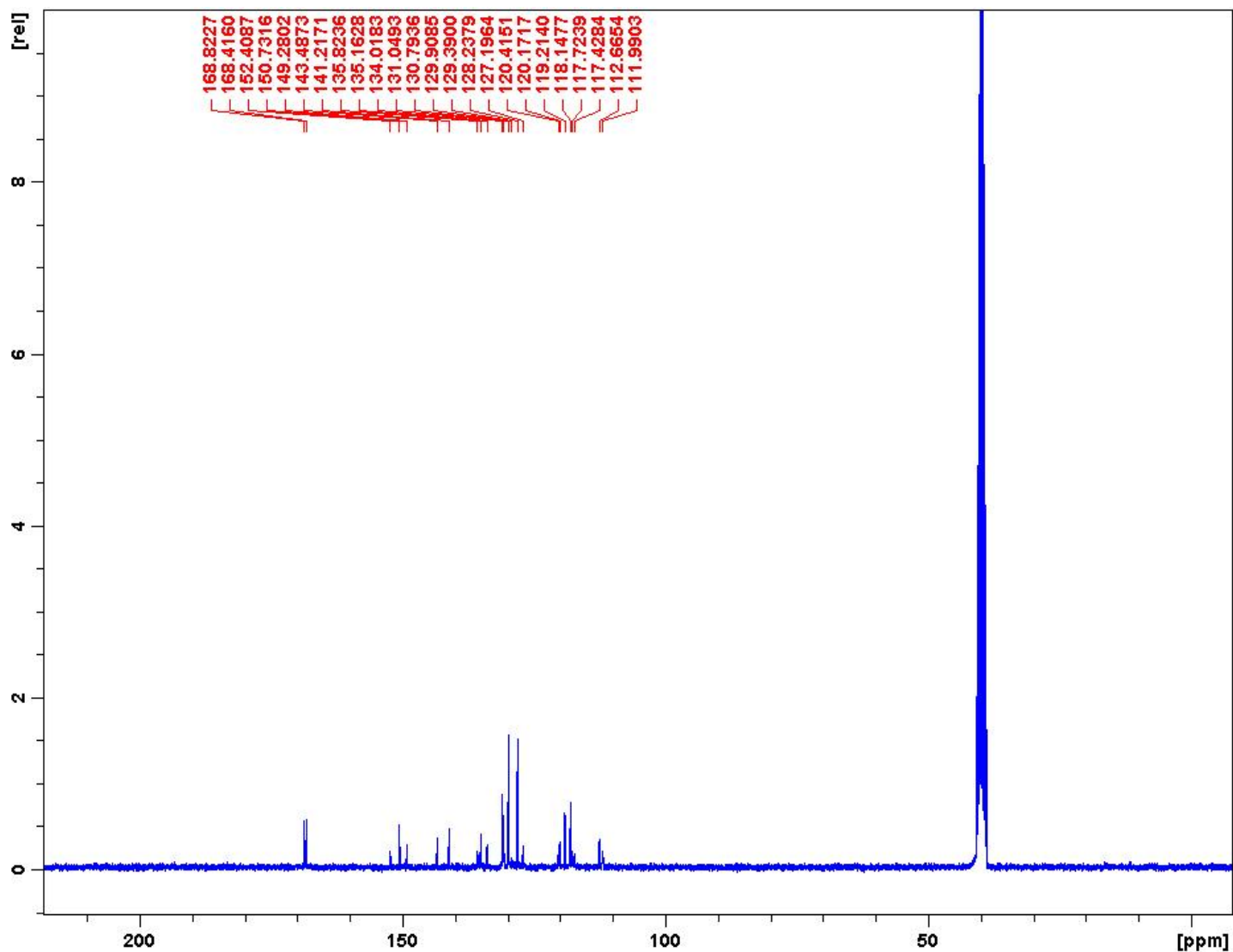




4,4'-(4-((*E*)-[2-(3-chloro-4-fluorophenyl)hydrazinylidene]methyl)-1*H*-pyrazole-1,3-diyl)dibenzoic acid (23)

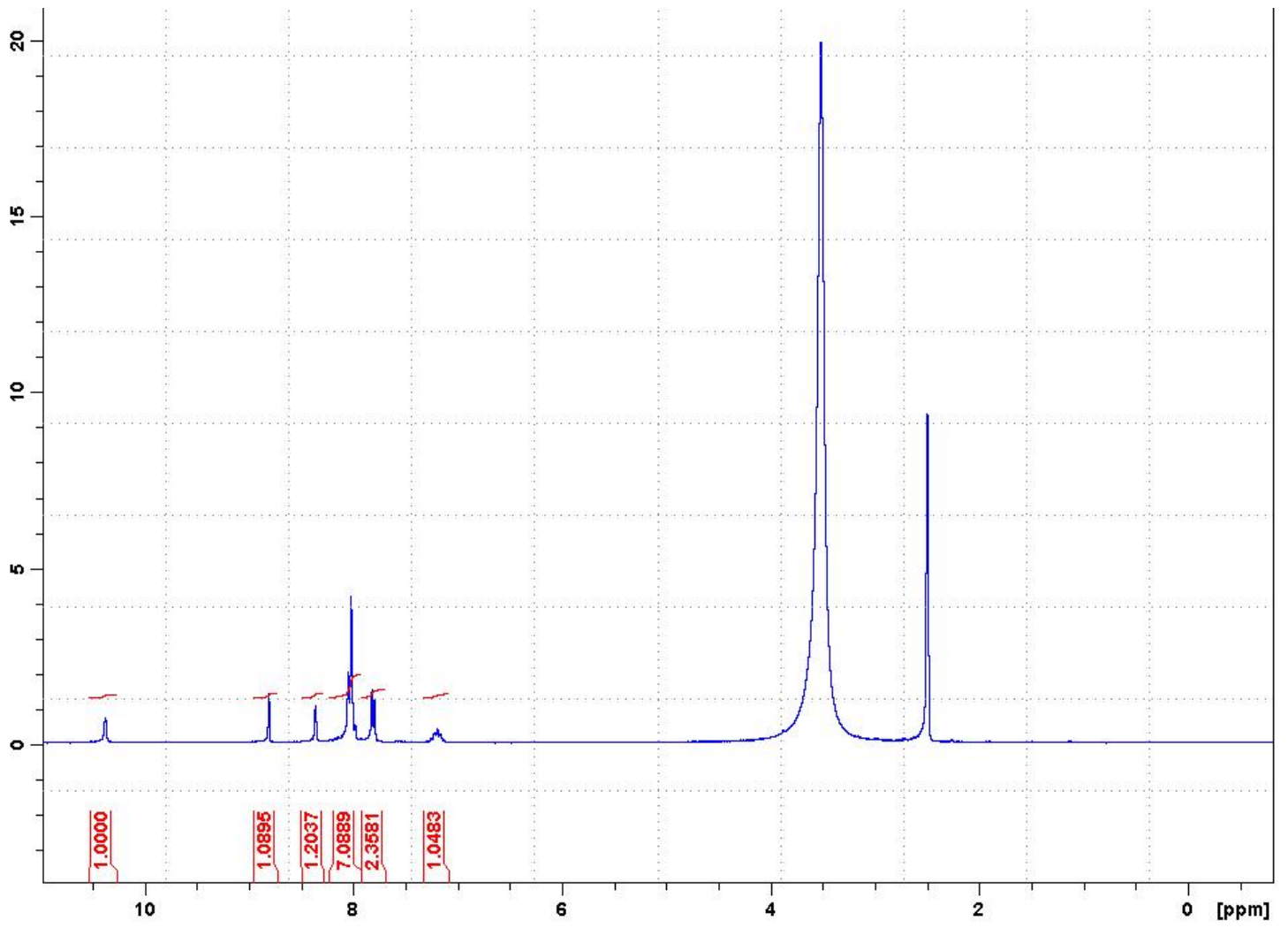
Brownish solid (368 mg, 77%). ^1H NMR, 300 MHz (DMSO- d_6): δ 10.83 (br s, 1H), 9.05 (s, 1H), 8.10-8.98 (m, 7H), 7.81 (d, $J = 8.1$ Hz, 2H), 7.25-7.19 (m, 2H), 6.98-6.94 (m, 1H); ^{13}C NMR (75MHz, DMSO- d_6) $\delta = 168.8, 168.4, 150.7, 151.1$ ($^1J_{\text{C-F}} = 234.6$ Hz), $150.7, 143.4, 141.2, 135.8, 135.1, 134.0, 131.0, 129.9, 128.2, 127.1, 120.3$ ($^2J_{\text{C-F}} = 18.2$ Hz), $119.2, 118.1, 117.6$ ($^2J_{\text{C-F}} = 22.1$ Hz), $112.6, 111.9$.

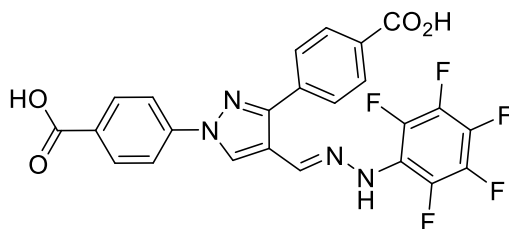
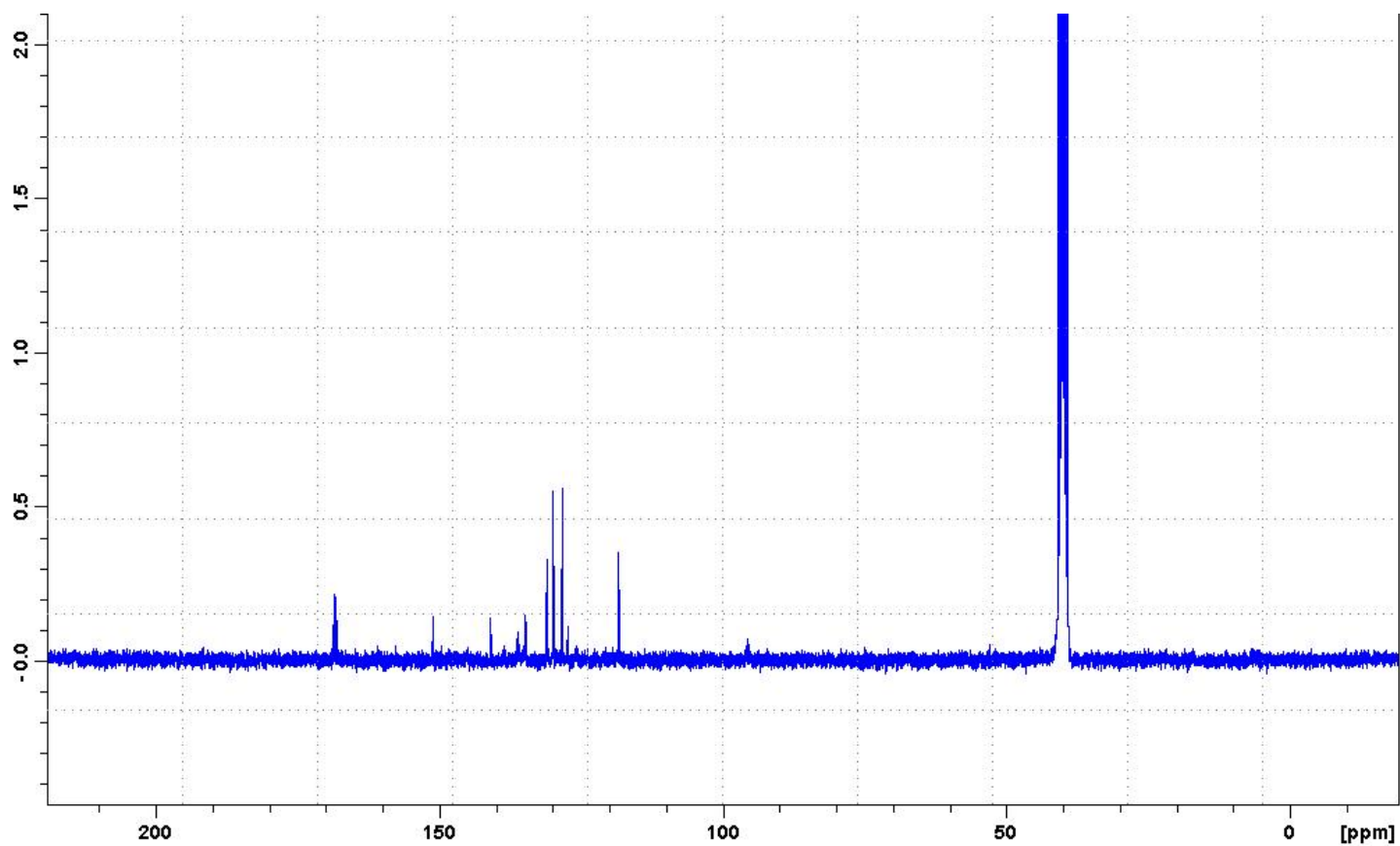




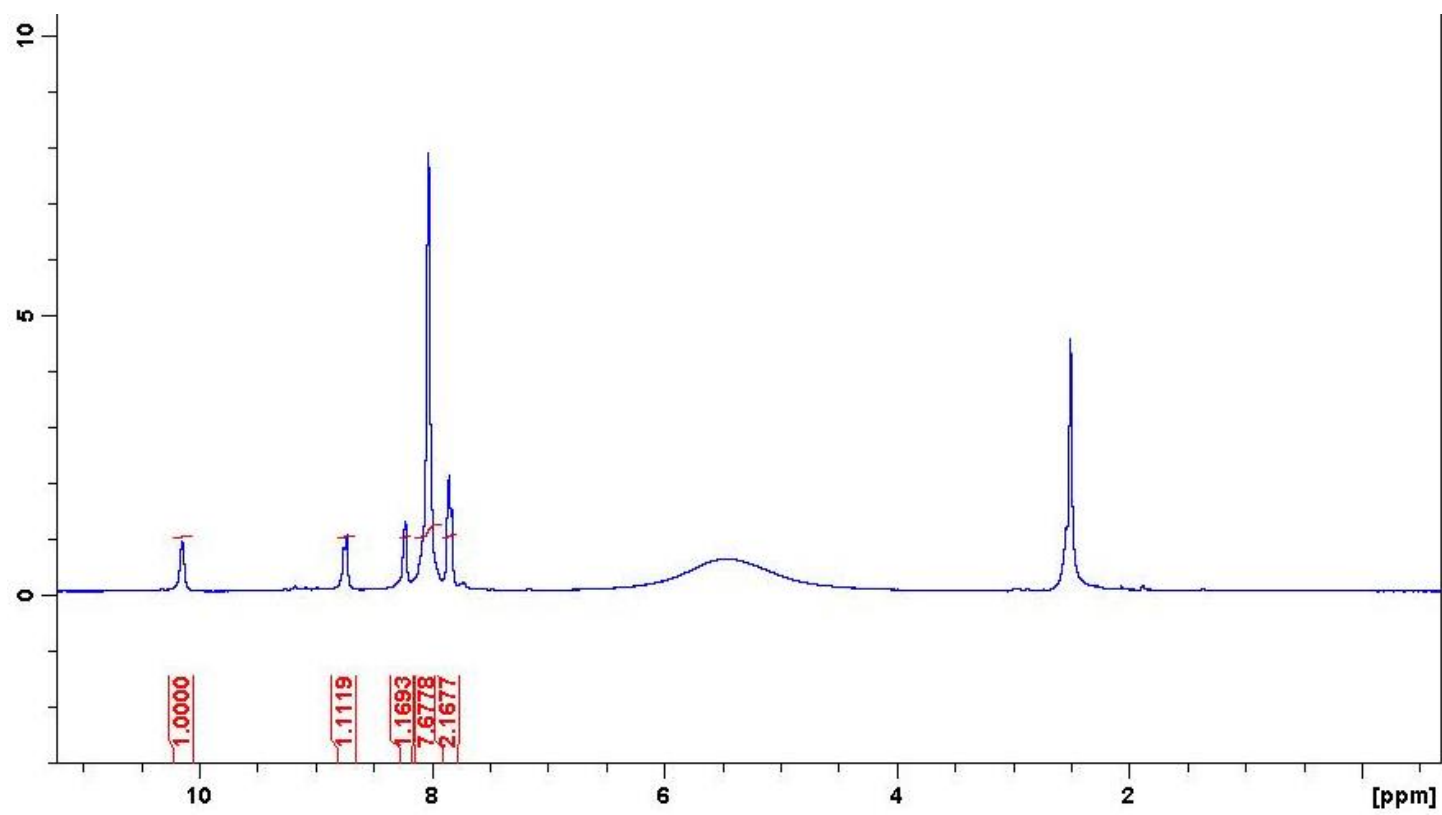
4,4'-(4-{(E)-[2-(2,3,5,6-tetrafluorophenyl)hydrazinylidene]methyl}-1H-pyrazole-1,3-diyl)dibenzoic acid (24)

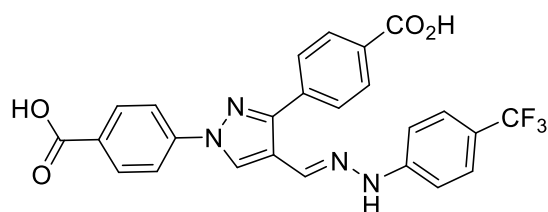
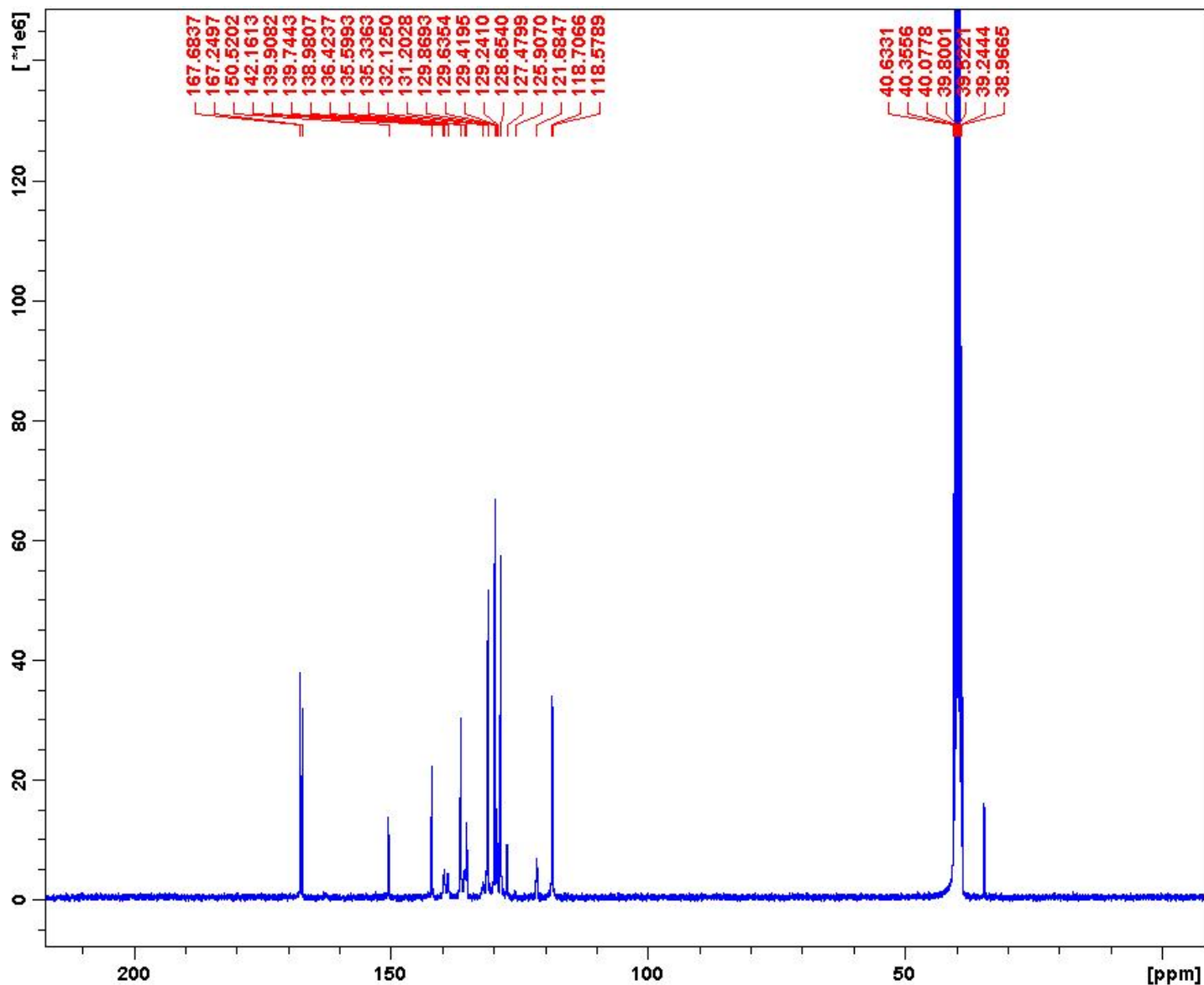
Brownish solid (398 mg, 80%). ^1H NMR, 300 MHz (DMSO- d_6): δ 10.38 (s, 1H), 8.81 (s, 1H), 8.36 (s, 1H), 8.05-7.98 (m, 6H), 7.81 (d, $J = 6.9$ Hz, 2H), 7.25-7.13 (m, 1H); ^{13}C NMR (75MHz, DMSO- d_6) $\delta = 168.4, 168.1, 157.5, 151.0, 140.9, 138.5, 136.1, 135.8, 134.7, 131.0, 129.8, 128.2, 127.2, 118.3, 95.7$ ($^2J_{\text{C-F}} = 25.0$ Hz).





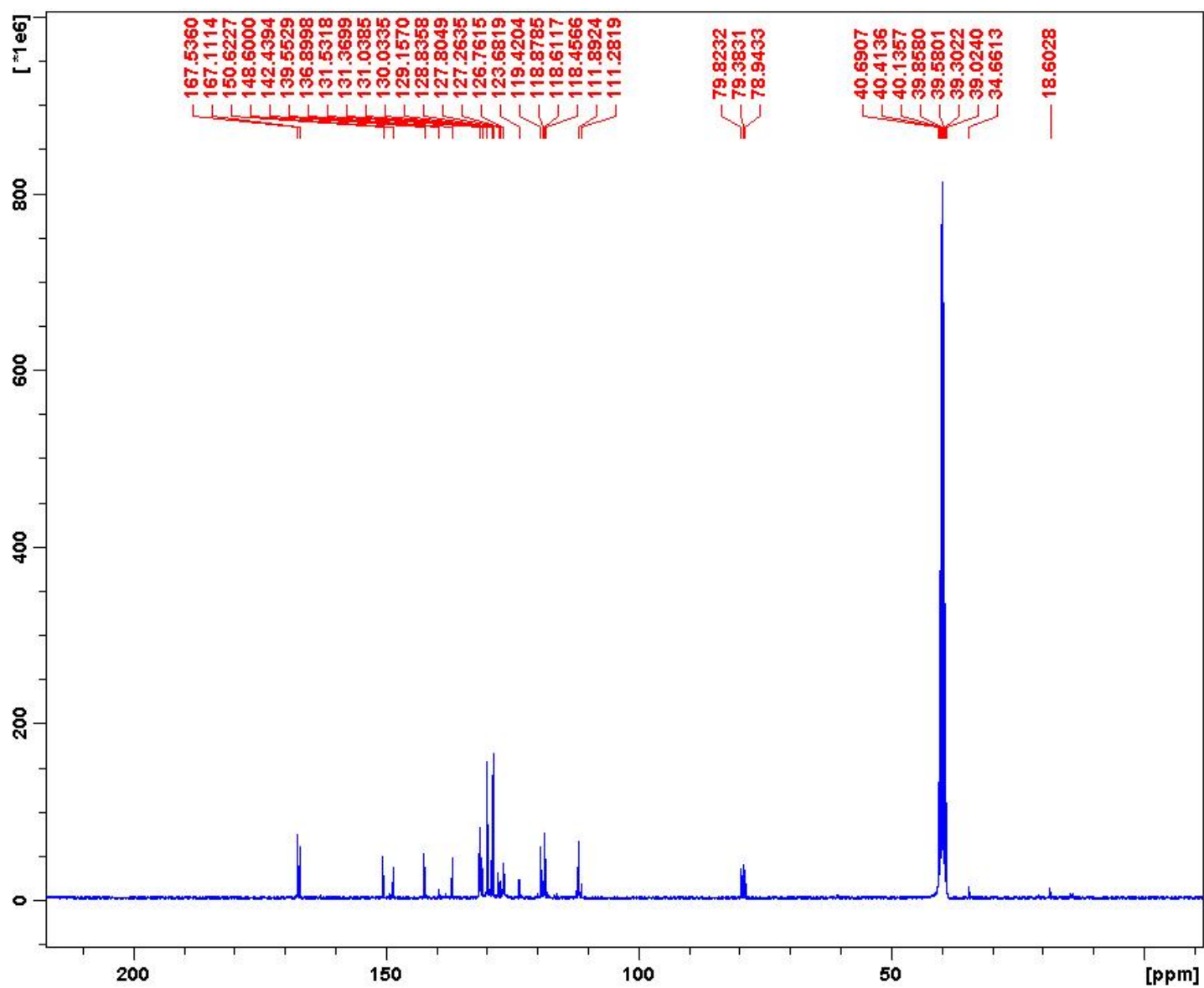
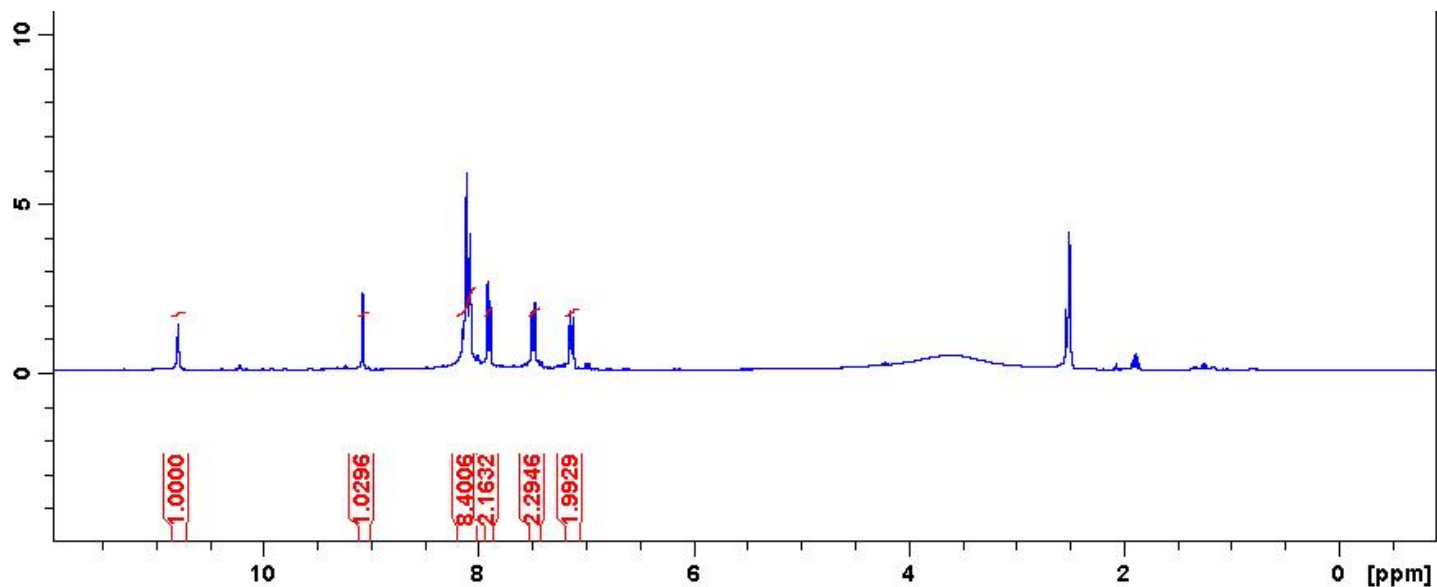
4,4'-(4-((*E*)-[2-(2,3,4,5,6-pentafluorophenyl)hydrazinylidene]methyl)-1*H*-pyrazole-1,3-diyl)dibenzoic acid (25)
 Brownish solid (423 mg, 82%). ¹H NMR, 300 MHz (DMSO-*d*₆): δ 10.13 (br s, 1H), 8.72 (s, 1H), 8.21 (s, 1H), 8.01 (s, 7H), 7.84-7.81 (m, 2H); ¹³C NMR (75 MHz, DMSO-*d*₆) δ = 167.6, 167.2, 150.5, 142.1, 139.9-139.7 (m), 138.9, 136.4, 135.5, 135.3, 131.2, 129.8, 129.6-129.2 (m), 129.4, 128.6, 127.4, 121.6, 118.7, 118.5.

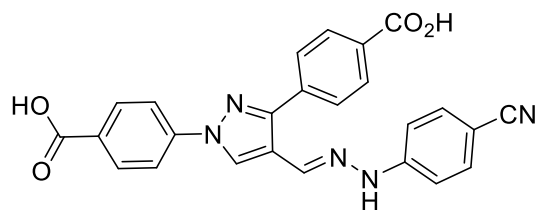




4,4'-(4-{(E)-[2-(4-trifluoromethylphenyl)hydrazinylidene]methyl}-1H-pyrazole-1,3-diyl)dibenzoic acid (26)

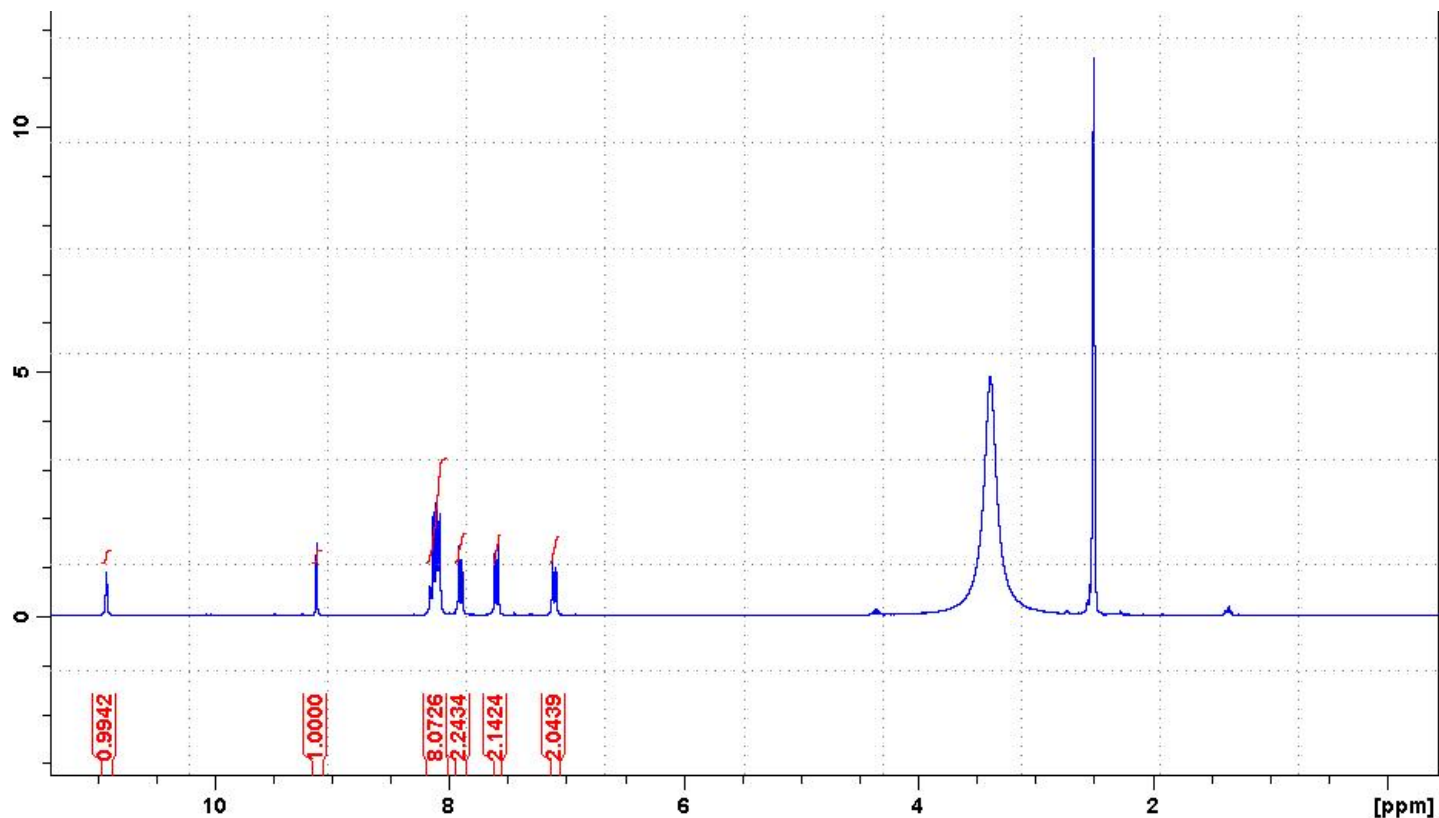
Brownish solid (370 mg, 75%). ^1H NMR, 300 MHz (DMSO- d_6): δ 10.78 (s, 1H), 9.07 (s, 1H), 8.14-8.07 (m, 8H), 7.90 (d, J = 8.3 Hz, 2H), 7.48 (d, J = 8.6 Hz, 2H), 7.13 (d, J = 8.5 Hz, 2H); ^{13}C NMR (75 MHz, DMSO- d_6) δ = 167.5, 167.1, 150.6, 148.6, 142.4, 136.8, 131.5, 131.3, 131.0, 130.0, 129.1, 128.8, 127.8, 126.7, 123.6, 119.4, 118.6, 111.8.

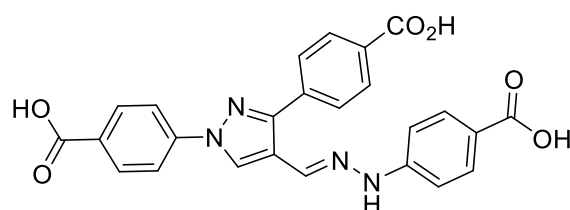
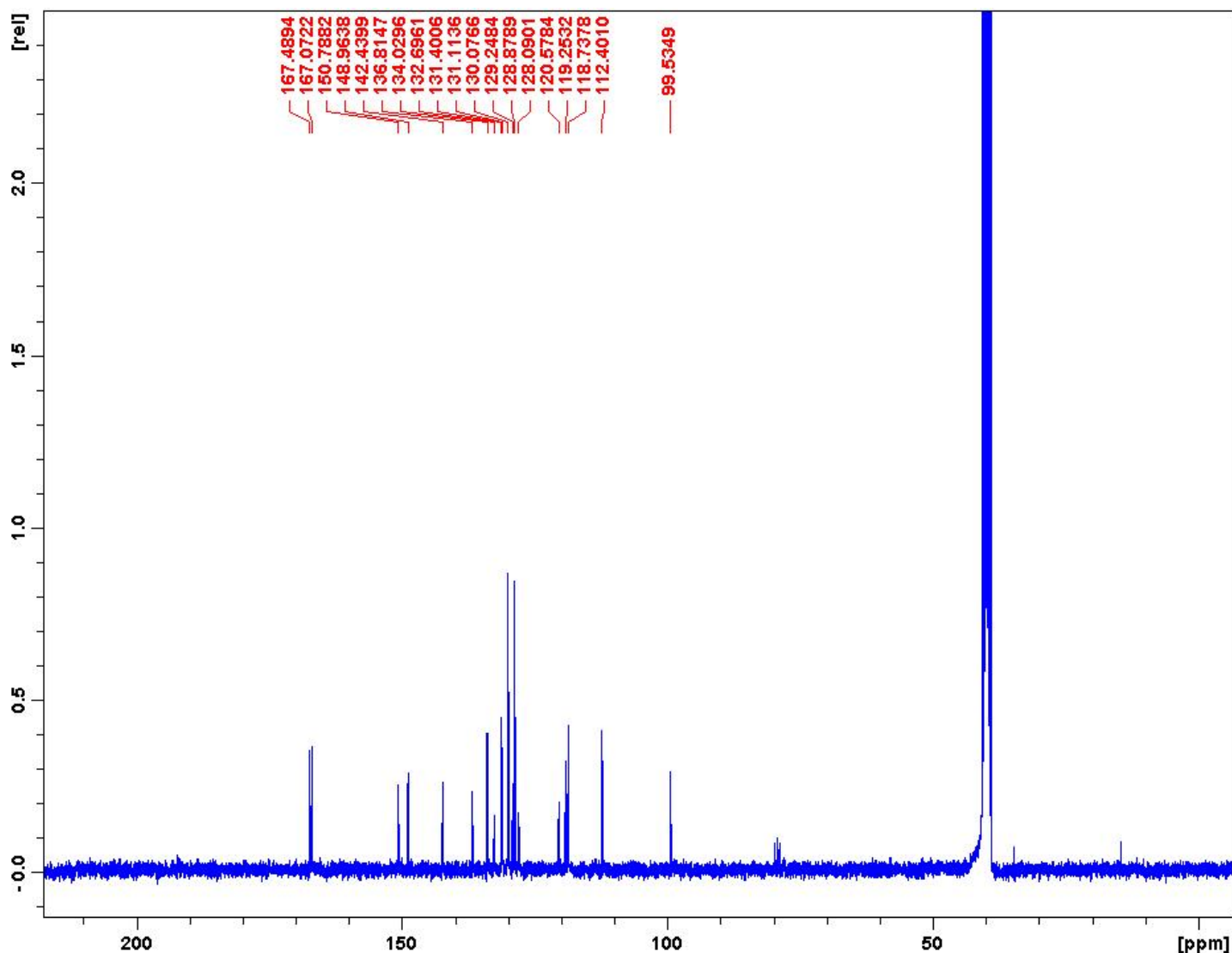




4-[1-(4-carboxyphenyl)-4-[(E)-[(4-cyanophenyl)hydrazono]methyl]pyrazol-3-yl]benzoic acid (27)

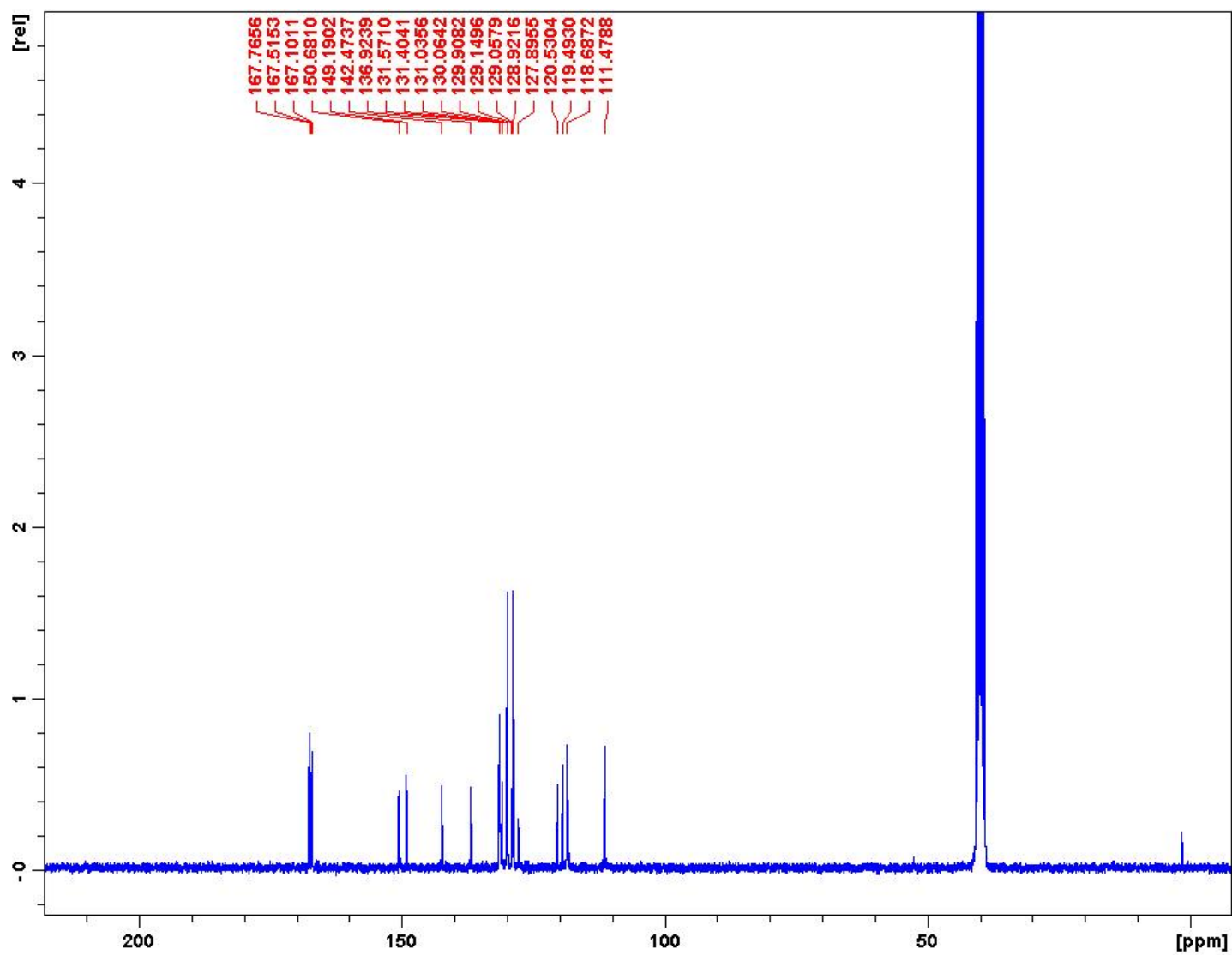
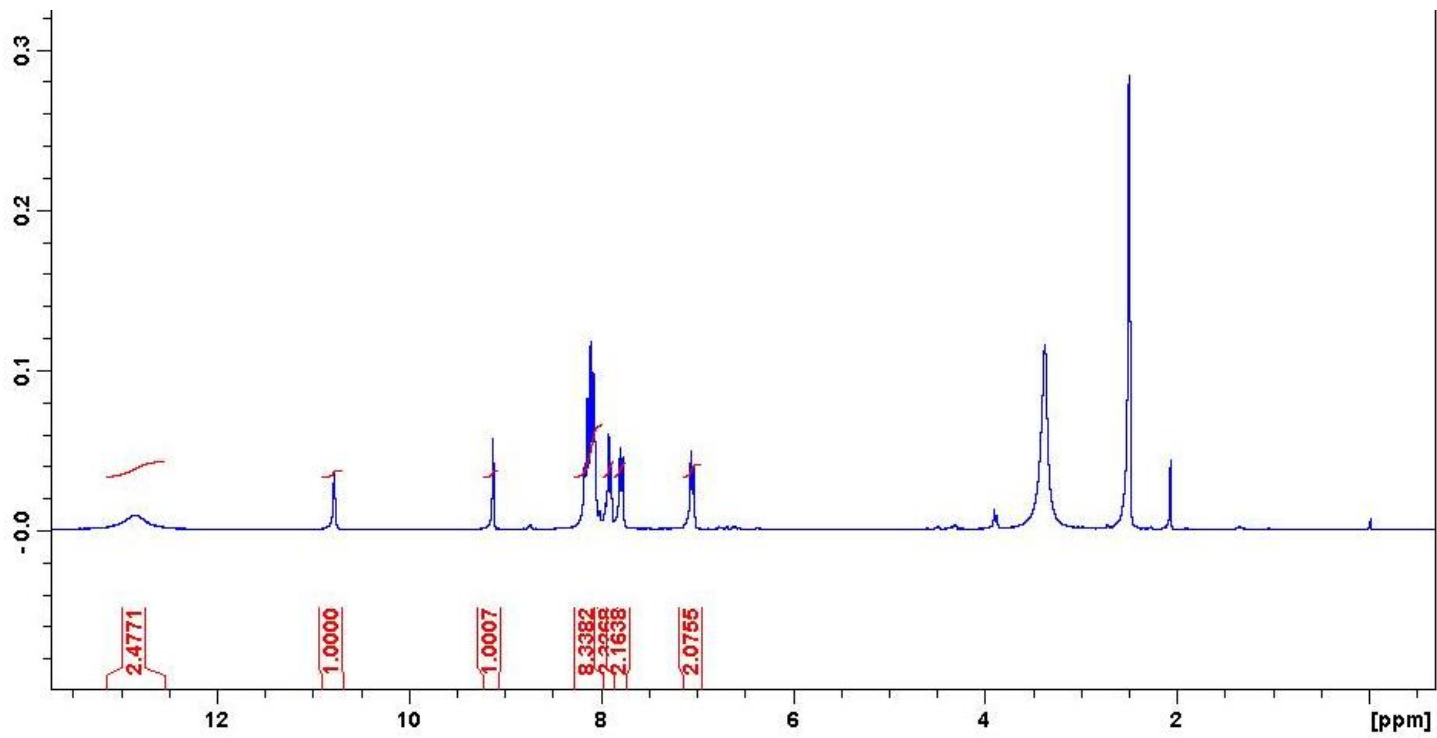
Brownish solid (342 mg, 76%). ^1H NMR, 300 MHz (DMSO- d_6): δ 10.92 (s, 1H), 9.12 (s, 1H), 8.16-8.07 (m, 8H), 7.90 (d, $J = 8.3$ Hz, 2H), 7.59 (d, $J = 8.7$ Hz, 2H), 7.10 (d, $J = 8.6$ Hz, 2H); ^{13}C NMR (75 MHz, DMSO- d_6) $\delta = 167.4, 167.0, 150.7, 148.9, 142.4, 136.8, 134.0, 132.6, 131.4, 131.1, 130.0, 129.2, 128.8, 128.0, 120.5, 119.2, 118.7, 112.4, 99.5$.

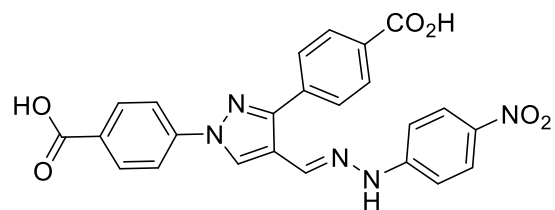




4,4'-(4-((*E*)-[2-(4-carboxyphenyl)hydrazinylidene]methyl)-1*H*-pyrazole-1,3-diyl)dibenzoic acid (28)

Brownish solid (347 mg, 74%). ¹H NMR, 300 MHz (DMSO-*d*₆): δ 12.8 (br s, 3H), 10.77 (s, 1H), 9.12 (s, 1H), 8.17-8.07 (m, 8H), 7.91 (s, 1H), 7.79-7.77 (d, *J* = 8.58 Hz, 2H), 7.05 (d, *J* = 8.4 Hz, 2H); ¹³C NMR (75 MHz, DMSO-*d*₆) δ = 167.7, 167.5, 167.1, 150.6, 149.1, 142.4, 136.9, 131.5, 131.4, 131.0, 130.0, 129.9, 129.1, 129.0, 128.9, 120.5, 119.4, 118.6, 111.4.





4,4'-(4-{(E)-[2-(4-nitrophenyl)hydrazinylidene]methyl}-1H-pyrazole-1,3-diyl)dibenzoic acid (29)

Reddish solid (372 mg, 79%). $^1\text{H NMR}$, 300 MHz (DMSO- d_6): δ 11.31 (s, 1H), 9.17 (s, 1H), 8.15-8.08 (m, 9H), 7.89 (d, J = 8.0 Hz, 2H), 7.10 (d, J = 8.4 Hz, 2H); $^{13}\text{C NMR}$ (75 MHz, DMSO- d_6) δ = 167.7, 167.2, 151.0, 150.9, 142.2, 138.5, 136.5, 134.6, 131.6, 131.3, 130.0, 129.8, 128.8, 128.3, 126.5, 118.9, 118.7, 111.5.

